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On the thermodynamic stability of steady-state adiabatic systems

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This paper begins by reviewing Bethe's (1942) work on the subject. He considered the propagation of a normal shock wave in a medium with an arbitrary equation of state. Difficulties arise if one attempts to extend his theory to systems containing plane oblique shocks or the reflection or refraction of such shocks. The object of the present paper is to resolve these difficulties. General conditions for the local thermodynamic equilibrium and thermodynamic stability, of a non-equilibrium system in steady-state, adiabatic, flow are summarized by the *principle of maximum entropy production*, which gives

$$\Delta s \geqslant 0; \quad \mathrm{d}(\Delta s) = 0; \quad \mathrm{d}^2(\Delta s) < 0,$$

for h_t constant, where s is the specific entropy and h_t is the specific total enthalpy; it is deduced from the second law. Conversely the consequences of $\Delta s < 0$, $\mathrm{d}(\Delta s) \neq 0$, $\mathrm{d}^2(\Delta s) = 0$, are discussed and may lead to either an impossibility or to some form of instability such as unsteadiness, or a change in the structure of the system (a catastrophe).

1. Introduction

Many authors have studied the stability of shock waves in adiabatic systems: D'Yakov (1956), Kontorovich (1957), Erpenbeck (1962), Morduchow & Paulley (1971), Swan & Fowles (1975), Fowles (1976, 1981), Griffith, Sandeman & Houwing (1975), Salas & Morgan (1983), Houwing, Fowles & Sandeman (1983), Fowles & Houwing (1984). Typically these theories discuss the interaction of linear acoustic waves with a shock and determine whether the perturbation will grow with time. The disturbance can be produced by a boundary, such as a perturbing downstream piston. These may be regarded as problems in mechanical stability because they deal with the virtual exchange of work with the surroundings but not usually with the exchange of heat. Several types of stability have been studied, for example the effect of transverse disturbances on the shock, or the effects of shock corrugation where a slightly diverging part of the shock might travel slightly faster than a slightly converging part.

Here, we shall follow the approach taken by Bethe (1942) which concentrates on the thermodynamic theory of the problem. We shall be concerned with the adiabatic systems in steady-state flow. We shall assume that the compressible medium is in a single phase, but otherwise as far as possible, there will be no restriction on its equation of state. There are difficulties with the Bethe theory, especially if one tries to extend it to an oblique shock or to multiple-shock systems. The object of this paper is to try and resolve some of these difficulties. It is found that the principle of maximum entropy production emerges naturally from the analysis and is of use in resolving an ambiguity that arises during the transition between regular, and Mach reflection of a plane oblique shock.

2. Bethe's work

2.1. *Thermodynamic irreversibility*

In a remarkable paper, Bethe studied the propagation of a normal shock wave in a medium with an arbitrary equation of state. The medium was in local thermodynamic equilibrium (LTE) upstream and downstream of the shock, and in each of these regions the properties of the medium were independent of position and time, (x, t) say. He assumed that the shock would be thermodynamically stable if the specific entropy of the medium increased as it passed through the shock. Formerly his criterion was (my wording):

(*A*) *A normal shock will be thermodynamically stable if the specific entropy of the medium increases as it passes through the shock.*

If v is the specific volume of the medium and if higher terms of Δv are neglected then by expanding the Hugoniot equation he found that for weak shocks,

$$\Delta s \equiv s_2 - s_1 = -\left(\frac{\partial^2 P}{\partial v^2}\right)_s \frac{(\Delta v)^3}{12T}. \tag{1}$$

where P is the pressure, T the temperature, and the subscripts 1, 2 refer to the state upstream and downstream of the shock respectively. It followed that a necessary condition for a weak compression shock to be stable is that the equation of state of the medium satisfied

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_s > 0, \tag{2}$$

for both

$$\Delta s \equiv s_2 - s_1 > 0, \tag{3}$$

$$\Delta v \equiv v_2 - v_1 < 0. \tag{4}$$

Conversely if the medium satisfied (2) then he proved that a sufficient condition for a compression shock of arbitrary strength to cause an increase in the entropy of the medium was that

$$\left(\frac{\partial P}{\partial e}\right)_v > -2, \tag{5}$$

where e was the internal energy. The proof again depended on the use of the Hugoniot equation. He concluded that (5) 'is valid for all substances in practically all states'.

Strictly speaking $\Delta s > 0$ is not a condition for stability but one for irreversibility. It is of course the Clausius inequality deduced from the second law for an adiabatic system. So it is a necessary condition for the *existence* of the normal shock system (either compressive or expansive) and not for its stability; for it is certainly reasonable that an irreversible adiabatic system cannot exist unless $\Delta s > 0$. On the other hand unstable systems can exist in the steady state with $\Delta s > 0$, for example a stoichiometric mixture of hydrogen and oxygen flowing through a normal shock that is so weak that it does not cause detonation – a metastable system.

We can partly invert the Bethe argument that requires (5), by assuming that an adiabatic *compressive* normal-shock system in the steady state must obey the Clausius inequality, so that we have

$$\Delta s \equiv s_2 - s_1 > 0, \quad \Delta v \equiv v_2 - v_1 < 0.$$

Now if the medium obeys (2), and the shock obeys the Hugoniot equation, then (5) follows without difficulty as a sufficient condition for the existence of a compressive shock of arbitrary strength. Thus we conclude from the fundamental Clausius inequality and the Hugoniot equation that a sufficient condition for the existence of a steady-state, compressive, adiabatic, normal-shock system is that the equation of state of the medium obeys (2) and (5).

If expansion shocks $\Delta v > 0$ are to exist then by (1) the sign of condition (2) must be reversed, and apparently this can happen for some substances near their critical point. Indeed Borisov *et al.* (1983) have detected these shocks in freon 13.

2.2. *Stability against splitting*

Bethe assumed that a shock wave could be unstable if it were to split into partial waves (a structural change or catastrophe) but he concluded that a sufficient condition to prevent this happening was for the medium to obey a third condition,

$$\left(\frac{\partial P}{\partial v}\right)_e < 0, \tag{6}$$

which he obtained by differentiating the Hugoniot equation. He proved that when (6) was fulfilled, the energy increased monotonically with the entropy for compressed states.

Further study lead him to conclude that 'none of the three conditions was required by any general or statistical argument because for each one of the three conditions there exists some substances for which the condition is violated at certain temperatures and densities'.

Bethe also proved the well-known result that a normal shock propagates at supersonic speed relative to the medium ahead if it and at subsonic speed relative to that behind it. From this he deduced the 'subsonic–supersonic' criterion for shock stability, thus:

(*B*) *No shocks can split into 'partial waves' travelling in the same direction whether the partial waves be shock waves or infinitesimal ones.*

This criterion has been mentioned by leading texts, Courant & Friedrichs (1948), Landau & Lifshitz (1959), but it has not been generally accepted; in fact Fowles & Houwing (1984) say that it is neither necessary nor sufficient for stability. According to (*B*) it is still permissible for an unstable shock to split into waves moving in *opposite* directions, but Bethe claims to prove that:

(*C*) *A shock can never split in a material whose equation of state fulfills the three conditions* (2), (5) *and* (6).

In addition to the above we shall use Bethe's 'central theorem' for a normal shock propagating in a single-phase material that satisfies (2), (5) and (6), namely:

(*D*) *If the state in front of the shock* (v_1, s_1) *is given, there is one and only one solution of the shock equations for any given value of the entropy* s_2 *behind the shock* $(s_1 < s_2 < \infty)$.

The Bethe theory has been widely accepted as correct, except for the shock-splitting criteria (*B*) and (*C*). It is natural to try and extend the theory to oblique shocks and to their reflections, but difficulties soon appear. For suppose that a wedge of apex angle δ is placed in a supersonic stream of Mach number M, then if δ is less than the shock detachment angle $\delta < \delta_{\text{det}}$, the Rankine–Hugoniot (RH) theory, Ames (1953) provides two oblique-shock solutions. One solution has supersonic flow downstream of the shock and the other subsonic flow, yet it is the supersonic–supersonic solution that appears and is stable even when the medium satisfies (2), (5) and (6). Thus the 'subsonic–supersonic' criterion which is the basis for (*B*) and (*C*) is apparently violated. Similarly the von Neumann (1943) theory for the regular reflection of oblique shocks also provides two solutions, and again with supersonic and subsonic flow downstream, and once more it is the supersonic solution that appears during an experiment. We shall study these difficulties in an attempt to overcome them.

3. Thermodynamic stability

3.1. *Maximum entropy*

Consider a control mass of a pure substance in a single phase in stable thermodynamic equilibrium contained in a cylinder closed by two pistons, figure 1(*a*). The entire system has adiabatic walls. Initially the substance and the pistons move with the same constant velocity U_{p_1} with respect to a fixed laboratory frame of reference; so the control mass is compatible with its boundaries. The thermodynamic and dynamic state of the system is given the set of parameters σ_1,

$$\sigma_1 \equiv \{e_1, v_1, U_{\mathrm{p}_1}\}, \tag{7}$$

and because the system is in stable equilibrium then by the second law its entropy is a maximum. However this is subject to the constraint that its internal energy e_1 is constant (Guggenheim 1959; Callen 1958): thus

$$\mathrm{d}s_1 = 0, \tag{8}$$

$$\mathrm{d}^2 s_1 < 0, \tag{9}$$

with e_1 constant.

Now suppose that at some time $t = 0$ the velocity of the right-hand piston is impulsively reduced below the velocity of the left-hand piston, $U_{\mathrm{p}_2} < U_{\mathrm{p}_1}$. Instantly a normal shock will appear on the face of the right-hand piston. It will be assumed that the set of system parameters, which is now σ_{12},

$$\sigma_{12} \equiv \{e_1, v_1, U_{\mathrm{p}_1}, U_{\mathrm{p}_2}\}, \tag{10}$$

is such that the shock is stationary in the laboratory frame; the RH equations (Ames 1953), show us how to adjust, say U_{p_2}, to ensure this. A short time later some of the substance will have passed through the shock and arrived at a new stable state (e_2, v_2) with velocity U_{p_2}, figure 1(*b*). The entropy $s_2 > s_1$. At a still later time the left-hand piston will reach the shock and it will be assumed that its velocity is then impulsively reduced to U_{p_2}, figure 1(*c*). The state of the system is now determined by σ_2,

$$\sigma_2 \equiv \{e_2, v_2, U_{\mathrm{p}_2}\}. \tag{11}$$

So we see that each stable homogeneous region moving with a constant velocity U_{p_1} or U_{p_2} has a maximum entropy s_1 or s_2 subject to the constraints that the internal energy e_1 or e_2 of each region is constant. For given σ_{12} the RH equations show that

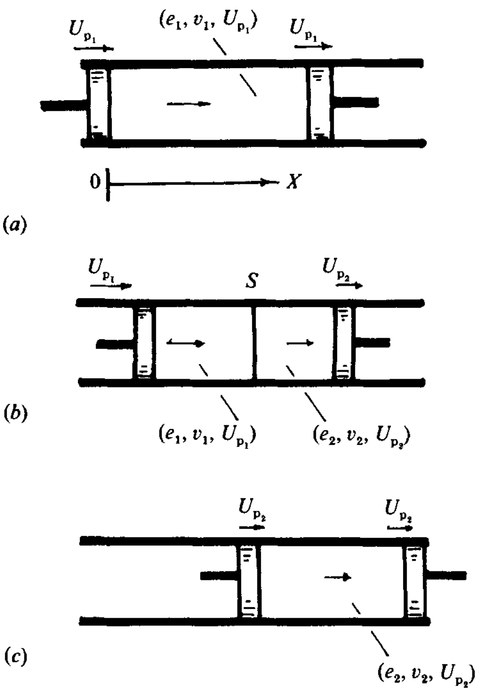

FIGURE 1. The steady state normal shock system. S, shock wave, U_{p_1}, U_{p_2}, velocities of left- and right-hand pistons; e_1, e_2 internal energy; v_1, v_2 specific volumes.

the production of entropy per unit *mass* of the medium $\Delta s \equiv s_2 - s_1$ is determined by $U_{p_1} - U_{p_2}$ and furthermore Bethe's theorem (D) shows that Δs is unique. It will be noticed that when both regions are present at the same time then it is impossible to choose a coordinate system that is simultaneously at rest with respect to every part of the system, so the system is not in thermodynamic equilibrium, it is at most in piecewise local thermodynamic equilibrium.

3.2. *Physical consequences of the maximum-entropy condition*

For coordinates which are at rest with respect to any medium there is Gibb's equation,

$$\mathrm{d}e = T\,\mathrm{d}s - P\,\mathrm{d}v. \tag{12}$$

The fundamental thermodynamic equation for any system is obtained by integrating it,

$$s = s(e, v). \tag{13}$$

If this equation can be expanded in a Taylor series about the equilibrium point, then the first-order terms must vanish by (8) if s is to have a stationary value,

$$\mathrm{d}s = 0 = \frac{\partial s}{\partial e}\mathrm{d}e + \frac{\partial s}{\partial v}\mathrm{d}v. \tag{14}$$

But, from (12),

$$\left(\frac{\partial s}{\partial e}\right)_v = \frac{1}{T}; \quad \left(\frac{\partial s}{\partial v}\right)_e = \frac{P}{T}, \tag{15}$$

and using standard technique, e.g. Guggenheim (1959), Callen (1985), it can be shown that this gives the condition that (P, T) are constant throughout a homogeneous region if the region is to be in equilibrium. In steady-state flow, it is also required that the particle velocity u of a region should everywhere be equal to the piston velocity U_p of the boundary, so (P, T, u) are everywhere constant for a region. We will say that it is then in LTE with, $ds = 0$.

If the equilibrium is to be stable, then $d^2s < 0$ and the second-order terms of the expansion lead to

$$d^2s = \frac{1}{2}\left\{\frac{1}{s_{ee}}\left(d\frac{1}{T}\right)^2 + \frac{s_{ee}\,s_{vv} - (s_{ev})^2}{s_{ee}}(dv)^2\right\} < 0. \tag{16}$$

It is seen that the coefficients in both terms must be independently negative, which gives successively

$$\left(\frac{\partial^2 s}{\partial e^2}\right)_v < 0, \tag{17}$$

$$\frac{s_{ee}\,s_{vv} - (s_{ev})^2}{s_{ee}} < 0, \tag{18}$$

and so

$$\left(\frac{\partial^2 s}{\partial v^2}\right)_e < 0. \tag{19}$$

Once more using (12), one obtains from (17)

$$\left(\frac{\partial^2 s}{\partial e^2}\right)_v = \frac{\partial}{\partial e}\left(\frac{1}{T}\right) = -\frac{1}{T^2}\left(\frac{\partial T}{\partial e}\right)_v = -\frac{1}{T^2 C_v} < 0,$$

therefore

$$C_v > 0, \tag{20}$$

which means that the temperature of a stable system will increase if it is heated at constant volume. The next condition is a little more difficult, but it may be confirmed that

$$\frac{s_{ee}\,s_{vv} - (s_{ev})^2}{s_{ee}} = -\left(\frac{\partial^2 F/T}{\partial v^2}\right)_{1/T} = \left(\frac{\partial P/T}{\partial v}\right)_{1/T} = \frac{1}{T}\left(\frac{\partial P}{\partial v}\right)_T < 0;$$

and because $T > 0$,

$$\left(\frac{\partial P}{\partial v}\right)_T < 0, \tag{21}$$

so if a stable system is compressed isothermally its volume will decrease. Here F is the Helmholtz free energy and F/T the corresponding (Legendre transformed) Massieu function (Callen 1985). The inequalities (17) and (18) also imply that

$$\left(\frac{\partial^2 s}{\partial e^2}\right)\left(\frac{\partial^2 s}{\partial v^2}\right) - \left(\frac{\partial^2 s}{\partial e\,\partial v}\right)^2 > 0,$$

which is a well-known necessary condition for a maximum. The third condition (19) gives,

$$\left(\frac{\partial^2 s}{\partial v^2}\right)_e = \left(\frac{\partial P/T}{\partial v}\right)_e < 0, \tag{22}$$

which is more general than the Bethe condition (6), but here it is a consequence of (20) and (21) taken together. It reduces to (6) for a polytropic substance, $e = e(T)$.

We can extend (20) and (21) by means of the formulas (Landau & Lifshitz 1958)

$$C_p - C_v = -\frac{T(\partial v/\partial T)_p^2}{(\partial v/\partial P)_T}, \tag{23}$$

$$-\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_s + \frac{T}{C_p v}\left(\frac{\partial v}{\partial T}\right)_P^2, \tag{24}$$

so that (20) and (21) become

$$C_v > C_p > 0, \tag{25}$$

$$\left(\frac{\partial P}{\partial T}\right)_T < \left(\frac{\partial P}{\partial v}\right)_s < 0. \tag{26}$$

All known single-phase substances in equilibrium, and above 0 °K, obey (20) and (21), and therefore also (22), (25) and (26). Bethe did not specify (20) as a condition for the stability of the normal-shock system, yet he used it repeatedly, calling C_v 'a positive definite quantity'. We conclude that (20) and (21) are the fundamental necessary conditions required for the thermodynamic stability of any region in LTE. Each region must obey them regardless of whether shocks are present or not. Bethe's condition, (6), is a consequence of these conditions, whereas his conditions (2) and (5) are only required for the special case for the existence of compressive shocks.

4. The principle of maximum entropy production: the steady-state normal shock system

Suppose there are two normal shock systems operating simultaneously (figure 2*a*, *b*). Both are in the steady state and both have a shock that is stationary with respect to the same laboratory frame. As before, it will be assumed that the medium is in a single phase but otherwise has an arbitrary equation of state. The first system (figure 2*a*) has the same parameters σ_{12} as before and because the shock is stationary its Mach number M_s can be found from

$$M_s = \frac{U_{p_1}}{a_1}, \tag{27}$$

where a_1 is the speed of sound, which can in turn be found from

$$a_1^2 = -v_1^2\left(\frac{\partial P_1}{\partial v_1}\right)_{s_1}, \tag{28}$$

and from the equation of state, which is assumed to be known. In the second system (figure 2*b*) the parameters (e_1, v_1) are still the same but the velocity of the left-hand piston is infinitesimally larger, so that its shock Mach number M_s^1 is given by

$$M_s^1 = \frac{U_{p_1} + dU_{p_1}}{a_1}. \tag{29}$$

To keep the shock stationary it is necessary to adjust U_{p_2} slightly. For a compression shock, e_2 will be increased to $e_2 + de_2$, while v_2 will be changed to $v_2 + dv_2$, where $dv_2 < 0$ compared with the first system. The initial entropy s_1 is the same for both systems but there is a difference ds_2 in the final entropy of the two systems which can be found from (12),

$$ds_2 = \frac{de_2}{T_2} + \frac{P_2}{T_2} dv_2, \tag{30}$$

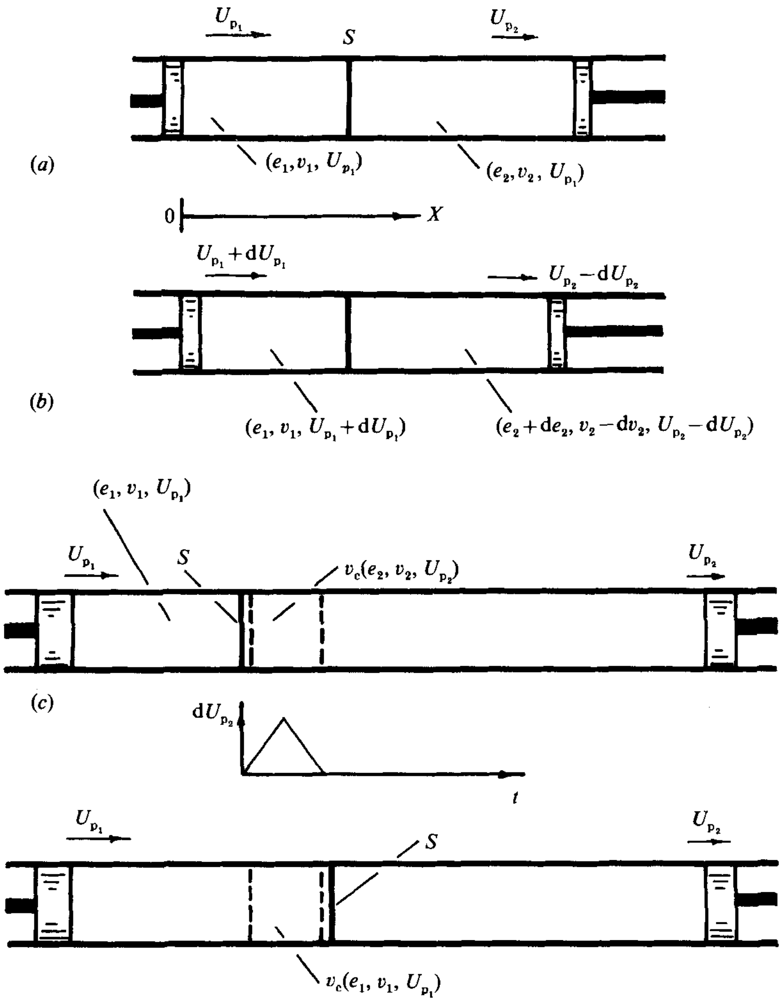

FIGURE 2. Boundary perturbation of the normal shock system. v_c, control volume.

where we have found that for compression shocks $de_2 > 0$, and $dv_2 < 0$. Now suppose that we wait until all the substance has passed through the shock in the second system, and that we then expand the substance so that $v_2 - dv_2$ becomes v_2. This can be done by a reversible exchange of work with surroundings, moving both pistons outwards by the same amount in such a way that $e_2 + de_2$ remains constant. Assuming that the substance obeys (20) and (21) then an infinitesimal quantity of heat per unit mass will have to be added to the system to keep $e_2 + de_2$ constant. The exchange of work has no effect on $s_2 + ds_2$ but the exchange of heat does, and the amount can be found from (30).

$$ds_2 = \frac{P_2}{T_2} dv_2; \tag{31}$$

but we are expanding the substance in this process so that $dv_2 > 0$ whereas $dv_2 < 0$ in (30). Then adding (30), (31), we get

$$ds_2 = (ds_2)_{\text{I}} + (ds_2)_{\text{II}} = \frac{de_2}{T_2} \tag{32}$$

where I, II refer respectively to equations (30) and (31). Equation (32) is the total change in s_2 as a result of the substance passing through the shock with v_2 held constant. We have considered the processes taking place consecutively, but we can also imagine them occurring simultaneously and in the same system. Then, from (32),

$$\left(\frac{\partial s_2}{\partial e_2}\right)_{v_2} = \frac{1}{T_2}, \tag{33}$$

and because T_2 may always be considered positive, we have proved that the entropy increases monotonically with the internal energy when the medium obeys (20) and (21). Bethe proved this along the shock Hugoniot with the help of (6). However our proof uses only the fundamental equation (12) so the conclusion is generally valid for any steady-state system that obeys (20) and (21). Differentiation of (33) leads again to (20), as it should. In a similar way we can keep $v_2 - \mathrm{d}v_2$ constant while $e_2 + \mathrm{d}e_2$ is reduced to e_2; this can be done by exchanging heat reversibly between the medium and the surroundings at constant volume $(v_2 - \mathrm{d}v_2)$, then (30) leads without difficulty to

$$\left(\frac{\partial s_2}{\partial v_2}\right)_{e_2} = \frac{P_2}{T_2}. \tag{34}$$

Thus we have proved generally that the entropy increases monotonically with the volume for any steady-state system that obeys (20) and (21). It was shown by Bethe that along the shock Hugoniot $\partial s/\partial v$ may not be positive definite but then e_2 is *not* constant. Indeed he found that the curve could have volume minima so that $\partial v/\partial s = 0$. However we have proved that this cannot happen when e is constant.

In all of these processes s_1 is held constant, but for a stable system we have, from (8) and (9),

$$\mathrm{d}(\Delta s) \equiv \mathrm{d}(s_2 - s_1) = \mathrm{d}s_2 = 0 \tag{35}$$

and

$$\mathrm{d}^2(\Delta s) \equiv \mathrm{d}^2(s_2 - s_1) = \mathrm{d}^2 s_2 < 0. \tag{36}$$

So we see that in such a system, not only are s_1 and s_2 maximum but *so also is the entropy production per unit mass* Δs. Furthermore, from the energy equation for an adiabatic system the total enthalpy h_t is constant,

$$h_t = h_1 + \tfrac{1}{2}u_1^2 = h_2 + \tfrac{1}{2}u_2^2, \tag{37}$$

where u_1, u_2 are the velocities of the medium; they must equal the corresponding piston velocities U_{p_1}, U_{p_2} if the system is to be compatible with its boundaries. Thus we have both the Clausius inequality for adiabatic irreversibility (or extending it to include reversibility),

$$\Delta s \geqslant 0, \tag{38}$$

and the maximum-entropy-production condition for stability,

$$\mathrm{d}(\Delta s) = 0, \tag{39}$$

$$\mathrm{d}^2(\Delta s) < 0, \tag{40}$$

all subject to the constraints that the total enthalpy of the system is constant and that the system is compatible with its boundaries. Since we are only interested in entropy differences we can take s_1 as the reference point for measuring s_2, even if s_1 is itself changing, that is, we can put $s_1 = 0$. Thus, Δs is a maximum when s_2 is a maximum, so (39) and (40) are consequences of the second law, and so of course is (30). Thus, by combining (38)–(40) we get the general *principle of maximum entropy* *production* as a necessary condition for the existence and stability of steady-state, non-equilibrium, adiabatic systems:

(*E*) *The necessary conditions for the thermodynamic stability of an adiabatic system consisting of a steady-state, non-equilibrium flow of a medium with its upstream and downstream regions in LTE and connected by a process that produces entropy in the medium as it passes from one state to the other are that the entropy production is non-negative and a maximum, but subject to the constraints that the total enthalpy of the flow is constant and that the system is compatible with its boundary conditions.*

The essence of the principle is contained in (38)–(40); it includes the existence conditions for irreversibility and reversibility (38). It also includes those for LTE, which lead to the constancy of the parameters (P, T, u) and finally those for stability, which require $C_v > 0$, and $(\partial P/\partial v)_T < 0$. The principle is not concerned with the time rate of entropy production $\mathrm{d}s/\mathrm{d}t$, but only with the change of entropy per unit mass Δs. Accordingly it is not necessarily incompatible with the *principle of minimum entropy production*, which deals with time rate (Glansdorff & Prigogine 1971). We shall now consider the physical consequences that follow from the violation of (*E*).

5. Violations of the conditions $\mathrm{d}(\Delta s) = 0$ or $\mathrm{d}^2(\Delta s) < 0$

5.1. *The unsteady normal shock system*, $\mathrm{d}(\Delta s) \neq 0$

Refer again to the steady-state normal shock system and imagine that there is a small control volume v_c just downstream of the shock and at rest in the laboratory frame (figure 2*c*). The right-hand piston is assumed to be remote, but suppose that its velocity U_{p_2} receives a perturbation $\mathrm{d}U_{p_2}$ which increases continuously to an infinitesimal maximum and then decreases continuously to zero again. Then, so long as $\mathrm{d}U_{p_2} > 0$, an infinitesimal band of expansion waves will be propagated upstream towards the shock. Later these will be followed by a band of compressions, generated when $\mathrm{d}U_{p_2} < 0$. The arrival of the expansions weakens the shock and causes it to move slowly downstream and pass through the control volume. The system is now unsteady. The passage of the shock will cause a substantial decrease in entropy s_2 to s_1 inside the control volume. Therefore $\mathrm{d}s_2 = \mathrm{d}(\Delta s) \neq 0$ and the condition for equilibrium has been locally violated. This is confirmed by the fact that there are also substantial changes to (P, T, u) inside the control volume. Suppose now that the compressions arrive soon after the shock has passed through it. It is assumed that any secondary waves arising from interaction with the shock are dissipated by the medium or suppressed by the piston. The result is a net displacement in the position of the shock (figure 2*d*). For the control volume we now have that $\mathrm{d}s_1 = 0$, so it is in a new equilibrium state, which is also stable if the material satisfies (20) and (21). By definition, it will be said that a steady-state system becomes unstable if it becomes unsteady, so the normal shock system becomes unstable if the condition for equilibrium $\mathrm{d}s = 0$ is violated in some part of it.

5.2. *Instabilities in velocity profiles*, $d^2(\Delta s) = 0$

It is known from the Rayleigh theory and its subsequent developments (Rosenhead 1963) that a necessary condition for the *instability* of an inviscid, incompressible, constant-temperature, free shear boundary layer is that there should be an inflexion point in the velocity profile, figure 3. For these flows $\mathrm{d}(1/T) = 0 = \mathrm{d}v$ and inequality

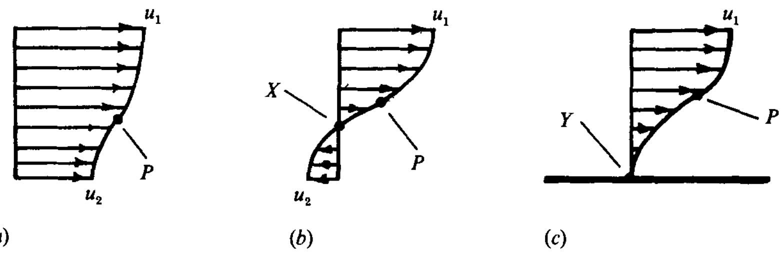

FIGURE 3. Instabilities in velocity profiles (u). (a) Free shear layer with inflection point at P, $\mathrm{d}^2u = 0$; (b) counter-current layer with a zero-velocity point X, ($u = 0$), and an inflection P; (c) boundary-layer profile with an inflection P, and a zero-shear-stress point Y, $u = 0 = \mathrm{d}u$.

(16) gives $\mathrm{d}^2s = \mathrm{d}^2(\Delta s) = 0$ everywhere. However this neglects the kinetic energy of the flow, so consider instead the energy equation, and its differential over the layer,

$$h + \tfrac{1}{2}u^2 = h_t, \tag{41}$$

thus

$$\mathrm{d}h + u\,\mathrm{d}u = 0;$$

but,

$$\mathrm{d}h = T\,\mathrm{d}s + P\,\mathrm{d}v,$$

thus

$$\mathrm{d}h + u\,\mathrm{d}u = T\,\mathrm{d}s + v\,\mathrm{d}P + u\,\mathrm{d}u = 0.$$

Suppose we assume, as is often done, that P is constant over the layer, then

$$T\,\mathrm{d}s + u\,\mathrm{d}u = 0, \tag{42}$$

so $\mathrm{d}s \rightarrow 0$, with $\mathrm{d}u$, in the limit about some point in the layer. Therefore a small neighbourhood of any point can be considered to be in LTE if (P, T, u) are locally well defined. Taking a second differential,

$$T\,\mathrm{d}^2s + \mathrm{d}T\,\mathrm{d}s + u\,\mathrm{d}^2u + (\mathrm{d}u)^2 = 0, \tag{43}$$

where (43) can also be written in terms of $\mathrm{d}(\Delta s) = \mathrm{d}s$. Now $\mathrm{d}T\,\mathrm{d}s$ vanishes for a constant-temperature layer and so does $u\,\mathrm{d}^2u$ at a velocity profile inflexion P, or zero point X, Y, figure 3. Then

$$\mathrm{d}^2(\Delta s) = \mathrm{d}^2s = -\frac{1}{T}(\mathrm{d}u)^2,$$

so $\mathrm{d}^2(\Delta s) = \mathrm{d}^2s$, vanishes quadratically with $\mathrm{d}u$ at these points. Thus the thermodynamic theory is consistent with the Rayleigh theory.

6. The oblique shock system

6.1. *Solution ambiguities*

Consider now a system containing a single wedge of apex angle δ_1 in a steady state, supersonic stream (figure 4a). If δ_1 is less than the detachment angle, $\delta_1 < \delta_{1_{\mathrm{det}}}$, then a straight oblique shock will propagate from its apex. A convenient set of system parameters is σ_{w_1},

$$\sigma_{\mathrm{w}_1} = \{e_1, v_1, U_{\mathrm{p}_1}\}, \tag{44}$$

with

$$\delta_1 < \delta_{1_{\mathrm{det}}}.$$

The RH equations determine two oblique shock solutions (α_1, α_2) on σ_{w_1}, one solution (the weaker α_1) usually has supersonic flow downstream of it $M_2 > 1$, while the other

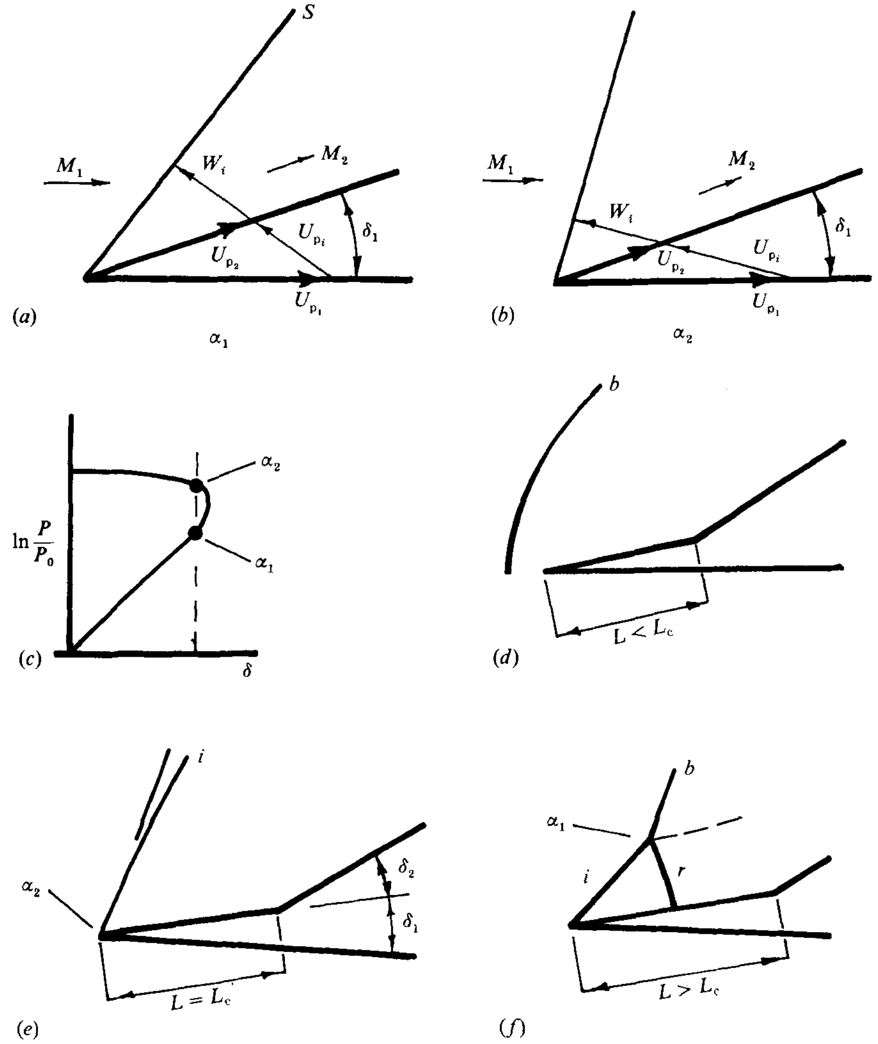

FIGURE 4. The weaker and stronger shock solutions at a wedge apex and the adjacent shock systems. (*a*) Weaker (α_1) solution; (*b*) stronger (α_2) solution; (*c*) polar diagram for the α_1,α_2 solutions; (*d*) detached bow shock system; (*e*) stronger α_2 shock at apex with a Guderley boundary (second wedge); (*f*) three-shock system with weaker (α_1) solution on apex, and with a Guderley boundary. δ_1, δ_2 apex angle of upstream and downstream wedges respectively; L, distance between wedge apexes; L_c, critical distance between apexes which supports the α_2 shock on the apex of the upstream wedge; M_1, M_2, Mach number respectively upstream and downstream of oblique shock; U_{p_i}, piston (particle) velocity of incident shock i; U_{p_1}, piston (particle) velocity of upstream free stream flow; U_{p_2}, resultant piston (particle) velocity of the flow downstream of the oblique shock; W_i, wave velocity of the incident shock.

(the stronger α_2) always has subsonic flow downstream (figure 4*a*–*c*). If we construct the vector diagrams for the wave and particle velocities, we find that the particle (piston) vector U_{p_i} for the oblique shock of both solutions just touches the surface of the wedge. In both cases also, the resultant of U_{p_i} and the free-stream vector U_{p_1} coincides with the wedge surface. So both solutions satisfy the boundary condition δ_1. However, experiment shows that it is invariably the weaker solution (α_1) which appears (Henderson & Lozzi 1975, 1979). The shock is straight for the α_1 solution and the regions upstream and downstream of it are homogeneous. The flow can be resolved into components perpendicular and parallel to the shock and the system can then be treated like the normal shock system but with the same velocity component parallel to the shock superimposed everywhere. This component has no effect on the production of entropy and because the normal shock system is stable so also will be this oblique shock system. The system also obeys Bethe's central theorem (D), which means that its entropy production is unique; but now we have a paradox because there are two solutions (α_1, α_2) defined on σ_{w_1}. We shall consider the stability of the second solution.

6.2. *The stronger solution and set completeness*

Guderley (1962) has discussed the circumstances for which the stronger solution may exist. He found that if a second wedge is placed in the flow such that its apex angle δ_2 exceeds the detachment angle for $M_2, \delta_2 > \delta_{2_{\text{det}}}$, then the stronger solution would appear at the apex of the first wedge, provided that the distance L between the two apexes had a certain critical value $L = L_c$ (figure 4e). This implies that the reason for the ambiguity is that the set of parameters σ_{w_1}, although complete for the weaker solution is incomplete for the stronger one. A complete set for the latter case is σ_{w_2}

$$\sigma_{w_2} \equiv \{e_1, v_1, U_{p_1}, \delta_1, \delta_2, L_c\} \tag{45}$$

with $$\delta_1 < \delta_{1_{\text{det}}}; \quad \delta_2 > \delta_{2_{\text{det}}}.$$

The second wedge will cause the downstream region to be non-uniform and the entropy will vary from streamline to streamline. Therefore, the flow cannot be reduced to that of a normal shock system, nor is Bethe's theorem (D) applicable, but we do now have unique solutions on σ_{w_1} and σ_{w_2}.

Guderley's analysis showed that a detached bow shock appeared when $L < L_c$, and that a three-shock system appeared when $L > L_c$ (figure 4d,f). In the latter case, the oblique shock on the apex of the first wedge corresponded to the weaker solution. Evidently the detached shock system exists for a continuum of values, $0 \leqslant L < L_c$, and so does the three-shock system, $L_c \leqslant L < \infty$, but the stronger oblique shock system only exists at a *single point* $L = L_c$. This means that any fluctuations no matter how small in any of the σ_{w_2} parameters will cause the stronger solution to change discontinuously into one of the adjacent systems; so at most it can exist only momentarily at transition between the other two. Furthermore, because it can only exist at the single point $L = L_c$, and because the entropy changes discontinuously during transition between the systems, we cannot define $\mathrm{d}s$ and d^2s at the point. Thus, the stronger solution is not in equilibrium and it is therefore unsteady and unstable, so it may be discarded. The existence of the entropy discontinuities at the first wedge apex means that there is a singularity or catastrophe associated with the structural changes to the shock.

7. Regular and Mach reflection

7.1. *The von Neumann solutions*

Von Neumann (1943) applied the RH equations to the regular reflection (RR) of a plane oblique shock at a rigid wall in a perfect gas (figure 5a). He imposed the boundary condition that the streamline deflection angle δ of the incident, i, and reflected, r, shock should be equal in magnitude and opposite in sign,

$$\delta_1 + \delta_2 = 0. \tag{46}$$

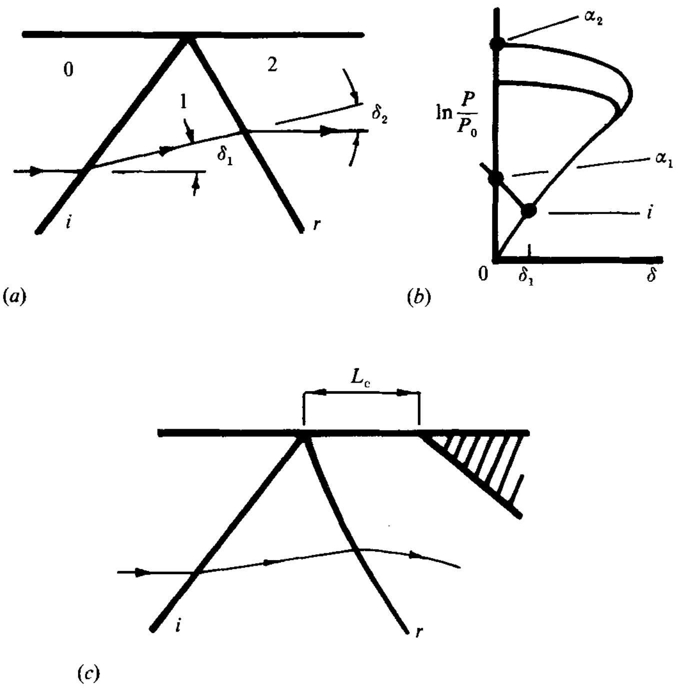

FIGURE 5. Regular reflection of a plane oblique shock i at a rigid wall in a perfect gas. (*a*) Weaker (α_1) solution, (*b*) polar diagram; (*c*) stronger (α_2) solution with a Guderley boundary.

The RR theory shows that a convenient set of parameter σ_r for a given gas is

$$\sigma_r \equiv \{e_0, v_0, U_{p_1}, \delta_1\}. \tag{47}$$

Once more the theory defines two solutions (α_1, α_2) on the set, where the weaker α_1 solution usually has supersonic flow downstream of $r, M_2 > 1$, and the stronger α_2 solution always has subsonic flow (figure 5*a*–*c*). The problem can be reduced to that of the single wedge by noting that the region between i and r is uniform and approaches the surface at the angle δ_1 which is effectively also the wedge apex angle for the plane shock r. It is immediately concluded that the α_1 solution is the stable one and that the α_2 solution is unstable even with a Guderley boundary (figure 4*d*). Experiment verifies the conclusion so the α_2 solution will be discarded (Henderson & Lozzi 1975; Hornung & Robinson 1982).

Von Neumann applied the same methods to the Mach reflection (MR) of the shock i at a rigid wall. He replaced the boundary condition (46) at the wall with a compatibility condition at the shock triple point,

$$\delta_1 + \delta_2 = \delta_b, \tag{48}$$

where δ_b is the streamline deflection by the Mach shock. The same set of parameters σ_r now define up to three solutions, designated $(\beta_1, \beta_2, \beta_3)$ (figure 6). The β_2 and β_3 solutions require extra boundaries to be placed upstream of the shock triple point if they are to exist, for example, as in figure 6(*c*), and because these boundaries are not present we will discard β_2 and β_3. Thus on the set σ_r we are left with an ambiguity consisting of the α_1 solution for RR and the β_1 solution for MR, and to resolve it we must study the boundary conditions in more detail.

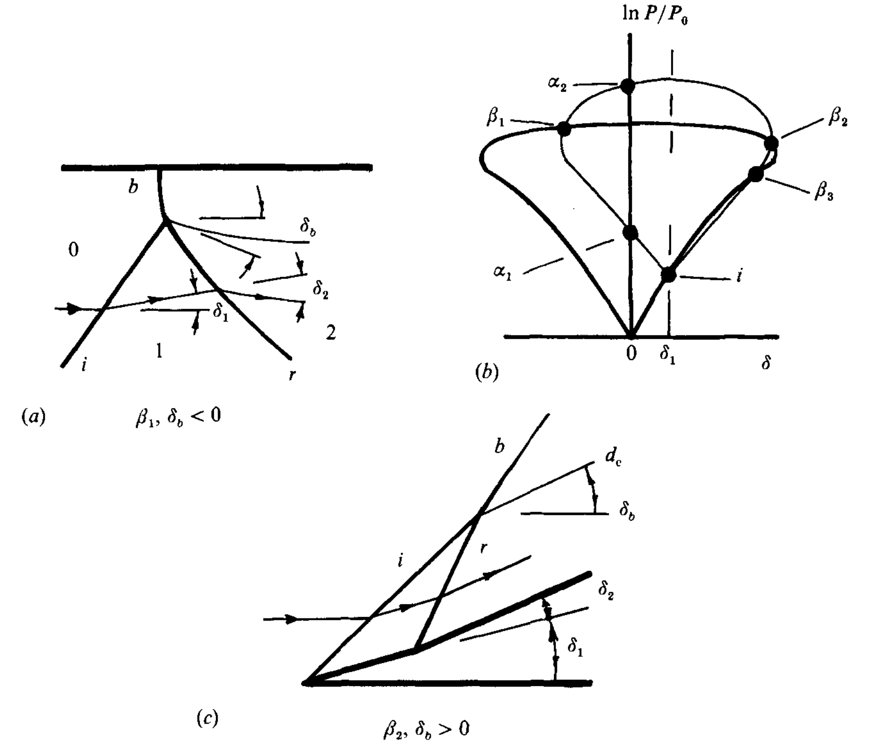

FIGURE 6. Mach reflection of a plane oblique shock i at a rigid wall in a perfect gas. (*a*) β_1 solution with Mach shock b forward of triple point; (*b*) polar diagram for Mach $(\beta_1, \beta_2, \beta_3)$ and regular (α_1, α_2) shock-system solutions; (*c*) β_2 solution with second wedge apex upstream of the shock triple point. d_c, contact discontinuity.

7.2. *The regular–Mach reflection ambiguity*

7.2.1. *The Mach shock forward of the triple point*

Suppose that the values of the σ_r parameters are such that the β_1 solution is in the negative-δ half-plane of the polar diagram, figure 6(*b*). Consequently, $\delta_b < 0$, so the flow is deflected *away* from the walls by the shock system, and the Mach shock is everywhere forward of the triple point, figure 6(*a*). Now, the production of entropy caused by the Mach shock is always greater than the total produced by the incident and reflected shocks near the triple point (this may be inferred from Zel'dovich & Raizer 1966, par 16 and especially their figure 1.31 on p. 59) which is a necessary condition for an MR to be more stable than an RR. In spite of this many experiments show that an RR is present when $\delta_b < 0$ (Pantazapol, Bellet & Soustre 1972; Henderson & Lozzi 1975, 1979; Hornung & Robinson 1982). This suggests that σ_r is complete for the RR system but not for the MR one. To investigate this hypothesis we begin with a detached bow shock b standing off a wedge of apex angle δ_2 (figure 7*a*). Next, we place another wedge in the flow upstream of the initial one and such that its apex angle $\delta_1 < \delta_{1_{\text{det}}}$. It generates a plane shock i arranged to intersect the bow shock b, figure 7(*b*). The parameters σ_{rb} are now

$$\sigma_{rb} \equiv \{e_0, v_0, U_{p_1}, \delta_1, \delta_2\}, \tag{49}$$

with $$\delta_1 < \delta_{1_{\text{det}}}; \quad \delta_2 > \delta_{1_{\text{det}}}.$$

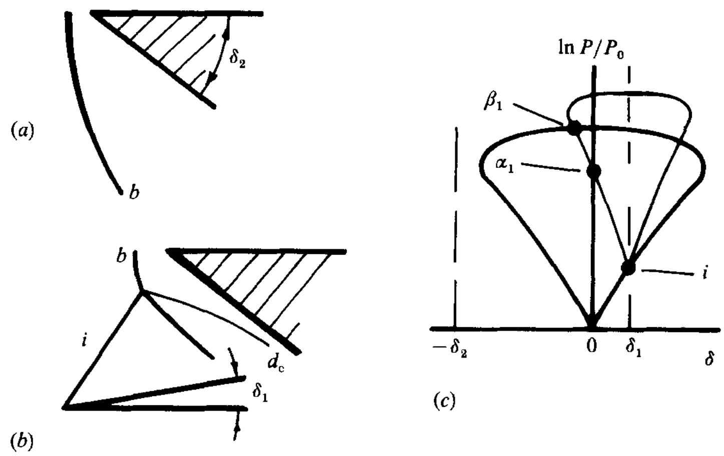

FIGURE 7. Mach reflection with the Mach shock b forward of the triple point.

We now have an MR in which the Mach shock is the remnant of the bow shock, and it is also forward of the triple point. Evidently the MR is generated by three boundary disturbances $(U_{p_1}, \delta_1, \delta_2)$, whereas the RR requires only two (U_{p_1}, δ_1). Henderson & Lozzi (1979) obtained an MR system of this type by replacing the δ_2 wedge with a downstream throat or throttle of variable area. When the throat was well open, an RR was obtained, but when the throttle was sufficiently closed an MR with b forward of the triple point was obtained. So this and the other experiments cited lend some experimental support to the hypothesis. We conclude that for $\delta_b < 0$, the set σ_r is complete for regular reflection, but not for Mach reflection: an MR requires the σ_{rb} set for completeness and without it, it cannot exist.

7.2.2. *The Mach shock backward of the triple point*

Let the values of the σ_r parameters be changed so that the β_1 solution maps into the positive δ half-plane of the polar diagram, figure 8(*b*). The shock system now deflects the flow *towards* the wall, $\delta_b > 0$, and the Mach shock is behind the triple point. Many experiments give the remarkable result that it is the MR (β_1) solution that now appears and not the RR (α_1) one (Mölder 1971; Pantazapol *et al.* 1972; Henderson & Lozzi 1975, 1979; Hornung & Robinson 1982), so the extra boundary in σ_{br} is no longer needed to produce an MR! This suggests that it is the impact of flow deflected towards the wall $(\delta_b > 0)$ which makes enough extra disturbance for the wall to support the MR with its larger entropy production. If this is correct, then it should be possible to suppress the MR by relaxing the boundary condition with a reflex corner at the point where i would intersect the wall; the reflex angle would match δ_b (figure 8*c*). Unfortunately, even infinitesimal variations in any of the σ_r parameters would move the shock reflection point from the corner, so the system is too strict and thus unstable. But there is another way to test the hypothesis, for suppose the wall is a compressible medium of greater shock impedance than the gas; the system could then be regarded as a *refraction* of the shock i as it passed from the gas into the wall material. If we replace the wall by a compliant material such as another gas (with a greater impedance than the original gas), then the boundary between the two gases will be able to deform during the refraction, a reflex corner will be then automatically generated, and it may possibly suppress the MR. Experiments have been done with shocks refracting at gas interfaces (Jahn 1956; Abdel-Fattah,

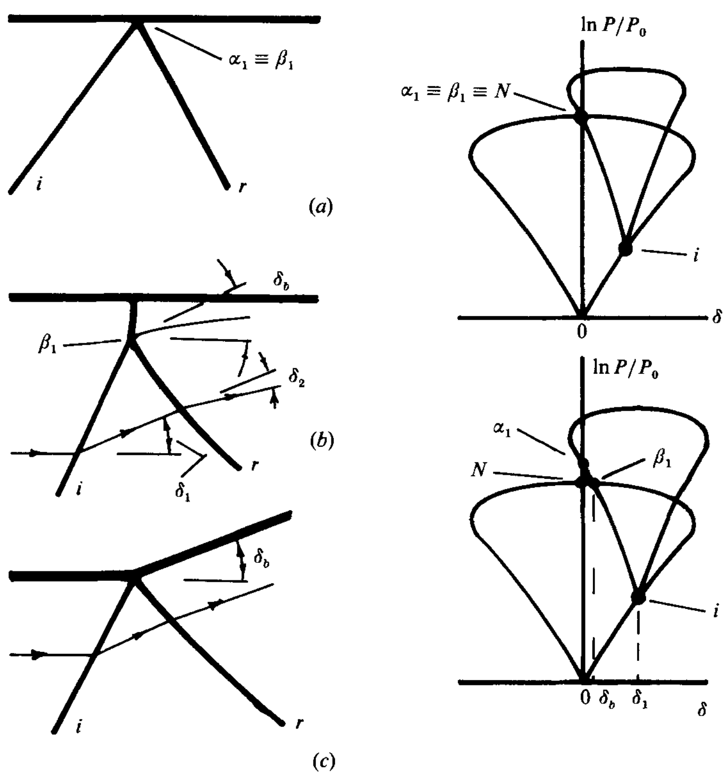

FIGURE 8. Mach reflection with the Mach shock b behind the triple point. (a) The von Neumann-point transition criterion RR$\rightleftarrows$MR, Mach shock is normal to the flow but of zero length; (b) Mach reflection, β_1 solution; (c) suppression of Mach reflection by change of the boundary condition, namely the reflex corner of angle $\pi+\delta_b$.

Henderson & Lozzi 1976; Abdel-Fattah & Henderson 1978*a*, *b*). Abdel-Fattah & Henderson (1978*a*) studied a shock refracting from air into sulphur hexafluoride SF_6. If one takes the acoustic impedance $Z \equiv \rho a$ as an approximate measure of the shock impedance then Z is about 414 kg m^{-2} s^{-1} for air and about 853 kg m^{-2} s^{-1} for SF_6, so the impedance does increase. The polar diagram for the refraction shows that the RR (α_1) solution for a rigid wall is transferred from the $\delta = 0$ axis to the new point A_1 on the intersection of the SF_6 and reflected shock polars, and this point determines the reflex angle $(\pi+\delta_b)$, figure 9(a). The shock system is of a type referred to as regular refraction; it has no Mach shock and can be thought of as a generalization of regular reflection.

The cited paper shows that the theory of the system agrees well with experiment. We conclude that an MR can be suppressed with the help of a reflex corner, and conversely that a rigid flat surface can support an MR when the flow is deflected towards the wall $\delta_b > 0$. Yet a stable regular reflection also appears to be possible for the same set σ_r; after all if the RR were to appear then the flow would not be directed towards the wall (46) and the extra disturbance would *not* exist. The rigid flat surface therefore appears to be associated with the (α_1, β_1) ambiguity. Since the entropy production caused by the Mach shock is larger than that by the incident and reflected shocks there seems no alternative but to conclude that the ambiguity is resolved by the system preferring the higher-entropy-producing solution.

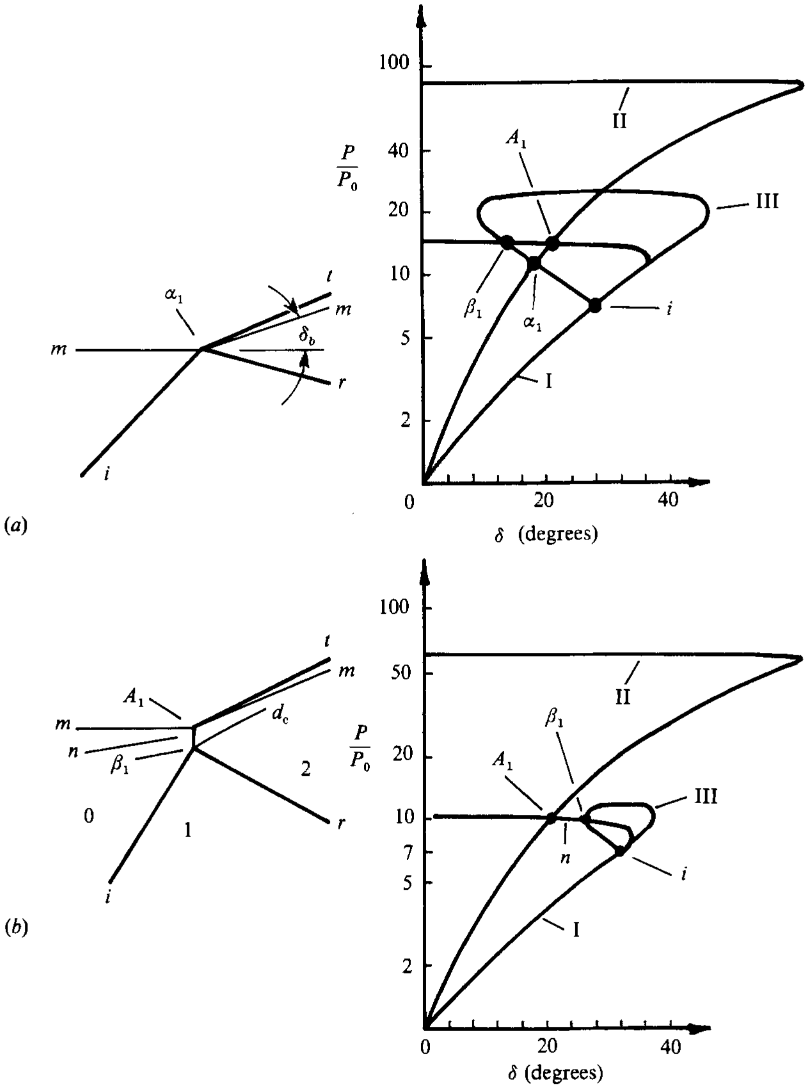

FIGURE 9. Regular and irregular refraction of a plane oblique shock wave at an air–sulphur hexafluoride interface (after Abdel-Fattah & Henderson 1978*a*). Inverse shock strength $P_0/P_1 \equiv \xi_i = 0.143$. (*a*) Regular refraction wave and polar diagram at the angle of incidence of the incident shock i is $\omega_0 = 45°$. (*b*) Irregular refraction wave and polar diagram at $\omega_0 = 56°$; *mm*, gas interface; t, transmitted shock in SF_6; i, r, incident and reflected shocks in air; n, Mach shock in air; A_1, intersection point of the polars for the undisturbed gases, I (air) and II (SF_6); III, reflected shock polar in air.

7.2.3. *Transition between regular and Mach reflection*

The transition point N for RR$\rightleftarrows$MR is on the $\delta = 0$ axis of the polar diagram, figure 8(*a*). At this condition, the Mach shock is of zero length but normal to the flow. It is variously called the normal-shock point, the von Neumann point, or the mechanical-equilibrium point; the last term arises from the fact that the pressure downstream of the reflected shock is continuous through transition. This point only exists for incident shocks which von Neumann called ‘strong’, and our discussion will be confined to this case. Strong Mach reflections have supersonic flow downstream of their reflected shocks near transition, while weak MR's have subsonic flow downstream. The transition point is a singularity or catastrophe on the shocks i and r at their point of reflection where the structure of the shock system changes. A contact discontinuity develops from it as MR appears. We find that the entropy of the flow behind the Mach shock b is larger than that behind the Mach shock r (Zel'dovich & Raizer 1966), so the contact discontinuity is also an entropy discontinuity. The free-stream temperature of the substance and its velocity are also discontinuous across it. We see, therefore, that transition to MR involves the sudden appearance of an entropy, temperature and velocity discontinuity in the flow; the system is thus thermodynamically unstable at transition since it is impossible to define $\mathrm{d}s$, or d^2s in every direction from the transition reflection point.

Because, for strong MR, the flow downstream is supersonic, $M_2 > 1$, the reflected shock r is straight and the flow downstream of r is homogeneous and in LTE. On the other hand, the flow downstream of the Mach shock b is subsonic and inhomogeneous, but it may be considered to be in stable LTE if C_v and $(\partial P/\partial v)_T$ can be defined at each point. At the contact discontinuity d_c which forms the boundary between these two regions, the flow is not in equilibrium because of viscous momentum exchange and thermal conductivity, so $\mathrm{d}s \neq 0$, and the flow is locally unstable. Since it is a free shear layer it would be expected that Kelvin–Helmholtz instability would develop along it as well. However, behind the r shock all of these disturbances are swept downstream at supersonic speed, and even behind the Mach shock experiment suggests that they have little effect on the stability of the flow. It is concluded that the regions downstream of the reflected and Mach shocks are separately stable but that a local instability exists at the boundary between them. But the instability develops so slowly that its effect on the neighbourhood of the triple point is negligible. So the flow downstream of strong Mach reflection can be regarded as being at least meta-stable.

A Mach reflection can also appear in an irregular shock refraction, figure 9(b). Transition between the regular and irregular refraction occurs at the point A_1 which is the intersection of the primary polars for the two gases, figure 9(a, b). The point A_1, or a point very close to it is supported by experiment in the cited references, and it may be regarded as a generalization of the von Neumann point N. The onset of MR in refraction is again a thermodynamic instability.

8. Conclusions

The systems considered here are in steady-state, adiabatic flow but not necessarily in thermodynamic equilibrium, for instance it may be impossible to choose a coordinate system that is simultaneously at rest with respect to every part of the system. However the systems are considered to be in piecewise local thermodynamic equilibrium (LTE). For these systems we conclude that:

(a) By the second law, a necessary condition that a system is in piecewise LTE is that the entropy of any region of the medium should have a stationary value,

$$\mathrm{d}s = 0, \tag{50}$$

under the constraint that the internal energy e is constant and that the region is compatible with the system boundaries. This implies that (P, T, u) are constant for the region.

(b) By the second law, a necessary condition that a region in LTE is stable is that its entropy is a maximum,

$$\mathrm{d}^2 s < 0, \tag{51}$$

which implies both that

$$C_v > 0,$$

$$\left(\frac{\partial P}{\partial v}\right)_T < 0,$$

and consequently (equations (20 and (21)), (22), that

$$\left(\frac{\partial P/T}{\partial v}\right)_e < 0.$$

Equations (20) and (21) may be extended to (25) and (26). According to the second law these conditions are generally valid for stability both for the systems considered here and also those in strict equilibrium.

Bethe's condition (6) follows from (22) when the medium is a polytropic substance. He required (6), as a sufficient condition to prevent the shock becoming unstable by splitting (a structural change, or catastrophe); however (6) is a consequence of the more general conditions (20) and (21).

(*c*) Not only must the systems satisfy the Clausius inequality/equality for irreversibility/reversibility for their existence,

$$\Delta s \geqslant 0, \tag{52}$$

but, by the second law, Δs must also be a maximum if the system is to be stable, that is

$$\mathrm{d}(\Delta s) = 0, \tag{53}$$

$$\mathrm{d}^2(\Delta s) < 0, \tag{54}$$

subject to the constraints that the total enthalpy h_t of the system is everywhere constant and that the system is compatible with its boundaries. This is the principle of *maximum entropy production* (E) in the text. The entropy production is per unit *mass* not per unit *time* so it is not necessarily in conflict with Prigogine's *minimum-entropy-production principle*.

(*d*) The Bethe conditions (2) and (5) are consequences of $\Delta s > 0$, $\Delta v < 0$, and the Hugoniot equation. They were formulated only for the special case of compressive normal shock systems, and they are not generally required for stability, as (20) and (21) are.

(*e*) Violation of the principle of maximum entropy production means the loss of the necessary conditions for the existence and, or, stability of the system. Among the possible violations are the following:

(i) $\mathrm{d}s \neq 0$ and, or $\mathrm{d}(\Delta s) \neq 0$, the system is not then in piecewise LTE so that any, or all, of (P, T, u) may change in time; the system is then unstable because it is unsteady. An example is the non-stationary normal-shock system discussed in the text.

(ii) $\mathrm{d}^2 s = 0$ and, or $\mathrm{d}^2(\Delta s) = 0$, so the entropy, or entropy production may not be a maximum. This may occur for example at an inflection point in the velocity distribution of a free shear layer or boundary layer, or at a point of zero shear stress in a wake, or on a surface in contact with a separating boundary layer.

(iii) Any, or all, of s, $\mathrm{d}s$, $\mathrm{d}^2 s$, $\mathrm{d}(\Delta s)$, or $\mathrm{d}^2(\Delta s)$ are discontinuous at a point, so that s or its differentials cannot be defined in all directions from the point. This may lead for example to the sudden appearance of a contact discontinuity (free shear layer) as in Mach reflection. Such a layer is associated with an entropy, temperature, and velocity discontinuity across it and therefore it is both thermally and dynamically (Kelvin–Helmholtz) unstable.

(iv) $\Delta s < 0$, this is not a violation but an impossibility for adiabatic systems. It is required for example for the existence of expansion shocks in media satisfying (i) and (ii). So they cannot exist in these circumstances.

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