$j = \rho_0 v_0 = \rho_1 v_1.$

(This relation can be verified by integrating the equations of continuity and motion through a steady shock transition and noting that it is the stress that enters into the equation of motion. Nothing in these two mechanical relations requires an assumption of thermodynamic equilibrium.) This relation allows us to write (18) as

$$\delta = (j^2 + dP/dV)(V - V_r)\dot{V}. \tag{20}$$

Returning to inequality (11), and using the expressions for γ, h, and δ from (14), (17), and (20), we have

$$\dot{V}(V - V_r)[j^2 + dP/dV + (dT/dV)(ds/dV)]_{V_r} \geq 0, \tag{21}$$

where, as previously stated, the derivatives are evaluated on the equilibrium surface along the path representing the projection of the real path.

There are four cases to consider depending on whether the shock is a compression or a rarefaction shock, and depending whether the reference equilibrium state is ahead of or behind the shock.

For compression shocks we have $\dot{V} < 0$, and,

(i) $V_r = V_1, \quad V > V_r$,

(ii) $V_r = V_0, \quad V < V_r$;

while for rarefaction shocks, $\dot{V} > 0$, and,

(iii) $V_r = V_1, \quad V < V_r$,

(iv) $V_r = V_0, \quad V > V_r$.

With respect to the sign of the bracketed quantity in (21) therefore, cases (i) and (iii) referring to the head of either type of shock are equivalent, as are cases (ii) and (iv) referring to the foot of the shock. Thus,

$$j^2 + dP/dV + (dT/dV)(ds/dV) \leq 0 \quad \text{(head)}, \tag{22a}$$

$$\geq 0 \quad \text{(foot)}. \tag{22b}$$

The directional derivatives of relation (21) can be expressed in terms of the derivatives of (3) and hence in terms of properties of the equilibrium surface by the identities,

$$\begin{aligned} ds/dV &= (\partial s/\partial V)_P + (\partial s/\partial P)_V\,(dP/dV) \\ &= (\partial P/\partial T)_s - (\partial V/\partial T)_s\,(dP/dV) \\ &= (\partial V/\partial T)_s\,[(\partial P/\partial V)_s - dP/dV] \end{aligned}$$

and

$$\begin{aligned} dT/dV &= (\partial T/\partial V)_s + (\partial T/\partial s)_V (ds/dV) \\ &= (\partial T/\partial V)_s + (\partial T/\partial s)_V (\partial V/\partial T)_s [(\partial P/\partial V)_s - dP/dV]. \end{aligned}$$

Substituting into (21) gives

$$\dot{V}(V - V_r)\{j^2 + (\partial P/\partial V)_s + (\partial V/\partial T)_s^2 (\partial T/\partial s)_V \\ [(\partial P/\partial V)_s - dP/dV]^2\} \geq 0. \tag{23}$$

Although we make no direct use of it, we note that (23) can be written in a more symmetric way by use of the thermodynamic identity

$$(\partial V/\partial T)_s^2 (\partial T/\partial s)_V = [(\partial P/\partial V)_T - (\partial P/\partial V)_s]^{-1}.$$

Equation (23) then becomes

$$\dot{V}(V - V_r)\{[j^2 + (\partial P/\partial V)_s][(\partial P/\partial V)_T - (\partial P/\partial V)_s] \\ + [(\partial P/\partial V)_s - dP/dV]^2\}_{V_r} \geq 0$$

or

$$\dot{V}(V - V_r)\{[j^2 + (\partial P/\partial V)_s][j^2 + (\partial P/\partial V)_T] - 2[j^2 + (\partial P/\partial V)_s] \\ \times [j^2 + dP/dV] + [j^2 + dP/dV]^2\}_{V_r} \geq 0. \tag{24}$$

This relation is equivalent to (21) and is an expression of the second law, (11), to the first nonvanishing terms.

From (23) it is already clear that at the head of the shock, $\dot{V}(V - V_1) \leq 0$, we must have

$$j^2 + (\partial P/\partial V)_s \leq 0$$

or, in view of (3a),

$$-j^2(\partial V/\partial P)_s \leq 1. \tag{25}$$

It is readily shown, however, that $M^2 = -j^2(\partial V/\partial P)_s$ and therefore, (25) gives

$$M_1^2 \leq 1, \quad M_1 \leq 1 \tag{26}$$

as expected.

Examination of (23) or (24), at the foot of the shock, however, does not lead to the other expected inequality, i.e., $M_0^2 \geq 1$. Moreover, as Truesdell notes, invoking only the inequality (11), admits the possibility that either contribution to the entropy production could by itself be negative if it were compensated for by sufficient entropy production by the other term.[7] This would admit such peculiar circumstances as negative dissipation accompanying a large heat flux. Conversely, sufficiently large dissipation could be accompanied by heat flow in the same direction as the temperature gradient, i.e., heat could flow uphill.

It will now be assumed that each term of the inequality (11) must be positive. This appears justifiable, for example, by noting that according to the usual classical assumption (Fourier conduction law)

$$\mathbf{h} = -k\boldsymbol{\gamma},$$

where k is a positive coefficient. Under this law, the second term of the inequality (11) becomes

$$-\mathbf{h}\cdot\boldsymbol{\gamma} = k(\boldsymbol{\gamma}\cdot\boldsymbol{\gamma}) > 0.$$

Moreover, it is usually assumed, in accordance with the Navier–Stokes equations (Ref. 4, p. 337), that the dissipative stress, $\sigma - P$, is, for one-dimensional flow,

$$\begin{aligned} \sigma - P &= -[(4/3)n + \xi](dv/dx) \\ &= -[(4/3)n + \xi]\rho\dot{V}, \end{aligned}$$

where the viscosity coefficients, n and ξ, are both negative. From Eq. (10), it then follows that under this assumption, the first term of the inequality (11) will be,

$$\rho\delta = [(4/3)n + \xi]\rho^2\dot{V}^2 > 0.$$

These assumptions concerning the constitutive relations can be considered to be empirical laws, or to be simply the first-order terms in a series expansion valid for small temperature or velocity gradients. The principal significance for our purposes is that there are no cross-coupling terms that could cause either term of inequality (11) to make a negative contribution to the entropy production.

In place of inequality (23), we now have two inequalities,

$$\mathring{V}(V-V_r)[j^2+dP/dV]\geqq 0 \tag{27a}$$

and

$$\mathring{V}(V-V_r)[(\partial P/\partial V)_s-dP/dV][(\partial P/\partial V)_T-dP/dV]\geqq 0. \tag{27b}$$

First considering the head of the shock, for which $\mathring{V}(V-V_r)\leqq 0$, we have

$$j^2+dP/dV\leqq 0;\quad dP/dV\leqq -j^2, \tag{28a}$$

$$[(\partial P/\partial V)_s-dP/dV][(\partial P/\partial V)_T-dP/dV]\leqq 0. \tag{28b}$$

The latter inequality requires that the slope, dP/dV, be intermediate between the isentropic and isothermal derivatives, while (28a) requires that it be less than the slope of the Rayleigh line. Consequently, the more restrictive of the inequalities

$$(\partial P/\partial V)_s\leqq dP/dV\leqq\begin{cases}-j^2\\(\partial P/\partial V)_T\end{cases} \tag{29}$$

obtains.

If we consider the foot of the shock, $\mathring{V}(V-V_0)\geqq 0$, we have, in place of (28),

$$j^2+dP/dV\geqq 0 \tag{30}$$

and

$$[(\partial P/\partial V)_s-dP/dV][(\partial P/\partial V)_T-dP/dV]\geqq 0. \tag{31}$$

These have the solutions,

$$dP/dV\geqq -j^2 \tag{32}$$

and either (i)

$$dP/dV\leqq(\partial P/\partial V)_s, \tag{33}$$

$$dP/dV\leqq(\partial P/\partial V)_T,$$

or, (ii)

$$dP/dV\geqq(\partial P/\partial V)_s, \tag{34}$$

$$dP/dV\geqq(\partial P/\partial V)_T.$$

The two solutions, (33) and (34), are seen to exclude the function $P(V)$ from the region between the isentrope and isotherm. If we assume (34) can be correct, however, and compare two hypothetical materials which differ only in the coefficient of thermal conduction, k, then the effect of heat flow would be to *increase* the mechanical dissipation. This is contrary to the Le Chatelier–Braun principle which states that secondary processes induced as a result of a primary process will act in a direction to reduce the primary thermodynamic stress difference.[9] Consequently, we take (33) to be the correct result, and it then follows that

$$-j^2\leqq dP/dV\leqq(\partial P/\partial V)_s \tag{35}$$

and, further,

$$-j^2(\partial V/\partial P)_s=M_0^2\geqq 1,\quad M_0\geqq 1. \tag{36}$$

This is the other result expected.

The restrictions on the slope dP/dV specified by (35) and by (29) are shown in Fig. 2.

It is clear from the diagram that an alternate argument for the exclusion of the solution (34) can be based on the continuity of the curve, $P(V)$. For weak shocks state 1 approaches state 0 and s_1 approaches s_0 (the so-called weak shock approximation.)[10] However, since $P(V)$ is excluded from the region between s_0 and T_0 and is confined between s_1 and T_1, $P(V)$ can be continuous only under the conditions shown, i.e., only if (34) is excluded.

It is interesting to note that the result (29) requires that, whenever the isotherm falls below the Rayleigh line at the head of the shock, i.e.,

$$(\partial P/\partial V)_T<-j^2,$$

then since $dP/dV<(\partial P/\partial V)_T$, it is necessary that some dissipation occur to account for at least the difference in stress between the isotherm and the Rayleigh line. Thus, under these conditions it is not possible to assume strictly nonviscous behavior no matter how conductive the material.[11] The converse is not true, however; there seem to be no restrictions that would rule out nonconducting but viscous behavior as assumed by

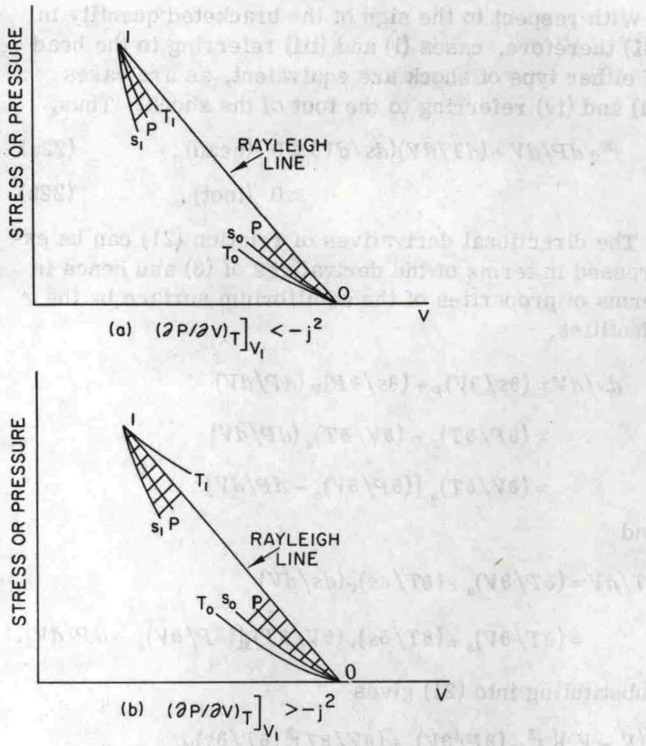

FIG. 2. Allowed regions for the slope dP/dV in the stress–volume plane for a compressive shock. Curves labeled s_0 and T_0 are the isentrope and isotherm through the initial state and those labeled s_1 and T_1 are corresponding curves through the final state. Curves labeled P are the projections of the path on the equilibrium surface traced by a mass element traversing the shock layer. The cross-hatched areas are the permissible bounds for P. (a) $(\partial P/\partial V)_T]_{V_1}<-j^2$; (b) $(\partial P/\partial V)_T]_{V_1}>-j^2$.