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

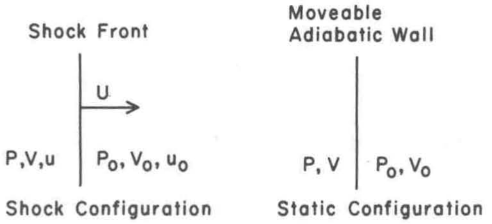

FIG. 13. Shock and static configurations with same thermodynamic states.

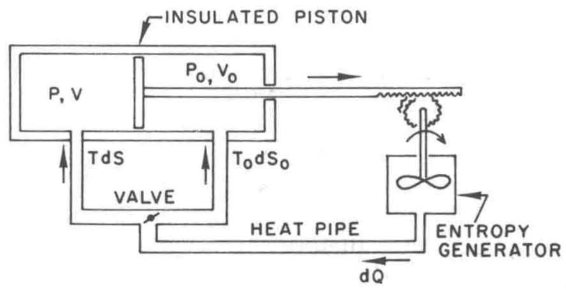

FIG. 14. Equilibration machine. Static configuration of Fig. 13 approaches equilibrium while each subsystem remains in internal equilibrium.

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

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

$$dE' = dE + P_0dV, \quad dE_0' = dE_0 + PdV_0 \; .$$

Invoking the requirement that each subsystem be in internal equilibrium implies

$$dE = TdS - PdV$$

and

$$dE_0 = T_0dS_0 - P_0dV_0 \; .$$

Hence,

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

and

$$dE_0' = T_0dS_0 - (P-P_0)dV \; .$$

Finally, energy conservation requires

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

or

$$TdS + T_0dS_0 - (P-P_0)dV = 0 \; ,$$

so that

$$dE' = -T_0dS_0 \; ,$$

and

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

Moreover,

$$TdS = (P-P_0)dV - T_0dS_0 \; ,$$

and

$$T_0dS_0 = (P-P_0)dV - TdS \; . \tag{25}$$

We now note that both conditions $TdS \geq 0$ and $T_0dS_0 \geq 0$, 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

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

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

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

and

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

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).