

RICHTMYER [7] in which time is advanced in increments of ΔT , and at each new time the positions, velocities, pressures, densities and energies of all the mass elements are computed. With this procedure in mind, we suppose that at a given point in the mixed phase region all the thermodynamic quantities are known and we then advance specific volume by a small amount dV and compute the other thermodynamic variables anew.

In an equilibrium phase change we assume that p and T are common to both phases and that extensive variables are given by a mass-weighted average over the two phases; *i.e.*, for example:

$$(54) \quad V = V_1(1-f) + V_2f,$$

$$(55) \quad E = E_1(1-f) + E_2f, \text{ etc.},$$

where f is the mass fraction of material in phase 2. We now suppose that $V \rightarrow V + \Delta V$ and consequently $p \rightarrow p + \Delta p$, $f \rightarrow f + \Delta f$, $E \rightarrow E + \Delta E$, $T \rightarrow T + \Delta T$, etc., and proceed to calculate Δp , ΔT , ΔE and Δf . We must first of all assume that the equation of state is known for each phase individually, and it is most convenient to assume equations of state in the form

$$(56a) \quad V_i = V_i(p, T), \quad i = 1, 2,$$

$$(56b) \quad E_i = E_i(p, T).$$

Equations (54)-(56) are now differentiated with the intent of expressing dV and dE in terms of dp , dT , and df with coefficients that depend on p , T , f . The result is

$$(57) \quad dV = l_1 dp + m_1 dT + n_1 df,$$

$$(58) \quad dE = l_2 dp + m_2 dT + n_2 df,$$

where

$$(59a) \quad l_1 = (1-f)V_{1,p} + fV_{2,p},$$

$$(59b) \quad l_2 = -(1-f)(TV_{1,T} + pV_{1,p}) - f(TV_{2,T} + pV_{2,p}),$$

$$(59c) \quad m_1 = (1-f)V_{1,T} + fV_{2,T},$$

$$(59d) \quad m_2 = (1-f)(C_{p1} - pV_{1,T}) + f(C_{p2} - pV_{2,T}),$$

$$n_1 = V_2 - V_1,$$

$$n_2 = E_2 - E_1,$$

$$V_{1,T} \equiv (\partial V_1 / \partial T)_p, \quad V_{2,p} \equiv (\partial V_2 / \partial p)_T, \text{ etc.},$$

$$C_{p1} = \text{specific heat at constant pressure for phase 1, etc.}$$

There is an additional relation between dE and dV , *viz.* the first law. If there is no heat transfer,

$$(60) \quad dE = -(p + q)dV,$$

where q represents any irreversible forces in the compression process. Equations (57), (58) and (60) can now be solved for dp and dT :

$$(61) \quad dp = a_1 dV + a_2 df,$$

$$(62) \quad dT = b_1 dV + b_2 df,$$

where

$$(63a) \quad a_1 = [m_2 + m_1(p + q)]/D,$$

$$(63b) \quad a_2 = (m_1 n_2 - m_2 n_1)/D,$$

$$(63c) \quad b_1 = -[l_2 + l_1(p + q)]/D,$$

$$(63d) \quad b_2 = (l_2 n_1 - l_1 n_2)/D,$$

$$(63e) \quad D = l_1 m_2 - l_2 m_1.$$

It's clear from eqs. (61) and (62) that, since only dV is given, one more relation is required before dp and dT can be computed. For reversible transitions this is the Clausius-Clapeyron relation:

$$(64) \quad dp/dT = \Delta S/\Delta V = \text{fcn. of } p \text{ or } T.$$

Combining eqs. (61), (62) and (64) yields

$$(65) \quad df = \chi(p, T, V, f) dV.$$

This equation, together with eqs. (61) and (62), makes it possible to determine dp and dT . When that is accomplished, another increment, dV , is taken and the process is continued until the mass element enters the single phase region.

The above relations are also useful for computing the Hugoniot directly. To do this, replace eq. (60) by the differential form of the Rankine-Hugoniot equation and continue as before. To determine an isentrope, set $q = 0$ in eq. (60).

We have seen in Sect. 4 how the cusp in the (p, V) compression curve gives rise to a double wave: the elastic precursor followed by a plastic shock. The cusp at the phase boundary, shown in Fig. 17, is also a point of instability