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On the possibility of complete condensation shock waves in retrograde fluids

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Shock discontinuities for which the upstream state is vapour and the downstream state is liquid are considered. The possibility of such shock waves is associated with a large number of molecular degrees of freedom: it is necessary that the ideal-gas specific heat $c_v \geqslant 24R$ at the critical temperature, a condition which is met by several common fluids. Shock properties are found from a corresponding-states thermodynamic model and from several calculations based on data for particular fluids. Condensation shock waves satisfy the usual stability conditions and should be found in laboratory experiments.

1. Introduction

We define a condensation shock wave to be a compression discontinuity for which the upstream state is vapour and the downstream state is liquid. It is like an ordinary shock wave in which the compression leads to complete condensation of the vapour.

Condensation shocks of this kind are distinct from the classical 'moisture' condensation shocks often found in steam and moist air. The moisture shock is in fact a partial condensation resulting from an adiabatic *expansion* to a state of supersaturation (Stever 1958). The shocks discussed in the present article are associated with an adiabatic *compression* and we henceforth use the term condensation shock only in this sense.

We emphasize complete condensation shocks, in which the vapour–liquid transition across the shock is complete and the upstream vapour state is dry.

The behaviour of compression shock waves in the presence of phase transition has been studied by Bethe (1942) and especially by Zel'dovich & Raizer (1967). In addition, Saltanov, Tsiklauri & Shanin (1970) discussed incomplete condensation shocks in very wet steam and reported some experimental results. These problems are similar in many ways to that considered here. To our knowledge, however, neither an experimental demonstration nor the theoretical basis of the complete condensation shock has been reported. We believe that such shocks will be found in relatively simple experiments.

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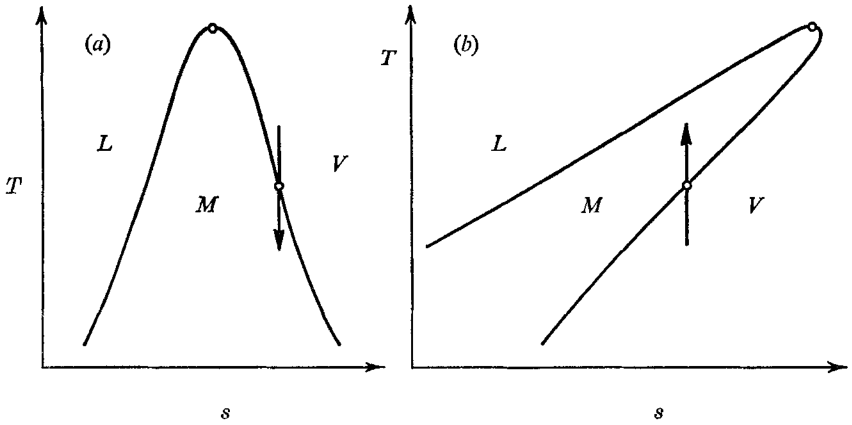

FIGURE 1. Isentropic condensation of regular and retrograde fluids, shown on a temperature–entropy diagram. (*a*) Regular fluid, such as water, in which isentropic expansion leads to condensation. (*b*) Retrograde fluid, such as octane, in which isentropic compression leads to condensation. The liquid, mixture and vapour regions are indicated by L, M and V respectively.

2. Physical plausibility of condensation shocks

It has been suggested that condensation shocks are impossible (Landau & Lifshitz 1959). They do, in fact, appear to be impossible in ordinary fluids such as air, water or carbon dioxide; their probable existence in fluids of somewhat higher molecular complexity (e.g. at the level of the constituents of gasoline) can, however, be demonstrated. We first remark that the idea of a strong compression leading to condensation is intuitively reasonable; the properties of the fluid only set certain limits on the conditions under which such a condensation is possible. We discuss below requirements for the existence of condensation shocks.

Adiabatic condensation. In order that a vapour be condensed by the compression process in a shock wave, it is necessary that it should tend to condense on isentropic compression (like ordinary shocks, condensation shock waves tend toward isentropicity in the small amplitude limit). Fluids having this property are said to be *retrograde* and were already known to Planck (1903) and van der Waals. For example, all the fluids in the paraffin hydrocarbon series above the complexity level of propane are retrograde. The isentropic condensation of regular and retrograde fluids is shown in figure 1.

Energy. Suppose that a condensation shock takes the fluid from the saturated-vapour to the saturated-liquid state. Then the increase Δt in the temperature of the liquid over that of the vapour must account for the latent heat of condensation h_{LV} and the upstream kinetic energy $\frac{1}{2}u_1^2$ (because the density ratio is large, the downstream kinetic energy is negligible). This leads to the (approximate) energy balance

$$c_p \Delta t \approx h_{LV} + \tfrac{1}{2}u_1^2, \tag{1}$$

where c_p is the liquid specific heat. We can roughly estimate the terms on the right-hand side and thus get an idea of the specific heat required. At temperatures not too near the critical value, $h_{LV} \sim 10RT_c$, where R is the gas constant and T_c is the critical temperature. If the upstream flow is supersonic, $\frac{1}{2}u_1^2 \sim c_1^2 \sim RT_c$. Then (1) yields $\Delta t \sim 11RT_c/c_p$. But Δt must be less than about $\frac{1}{2}T_c$ in order for the transition to be in the vapour–liquid range. Then (1) yields the *estimate*

$$c_p > 22R. \tag{2}$$

Fluids with specific heats in this range are invariably retrograde.

Stability. A condensation shock is expected to be stable if the upstream Mach number M_1 and downstream Mach number M_2 satisfy

$$M_1 \geqslant 1 \geqslant M_2. \tag{3}$$

Detailed calculations will show that these conditions are indeed satisfied by complete condensation shocks. A related condition on the entropy jump $[s]$,

$$[s] \geqslant 0, \tag{4}$$

is also satisfied.

Approach to equilibrium. The shock can have a small thickness only if the condensed downstream state is reached in a relatively short time, that is, if the 'relaxation time' for condensation is short. In the case of an equilibrium downstream state of low moisture content, e.g. in a moisture shock, rather long condensation times are associated with the kinetic problem of molecular capture by condensation nuclei, i.e. the cross-section for condensation is small. In the case of a complete condensation shock, almost all the vapour molecules would be moving towards the downstream liquid surface and capture would thus be very likely. On this account we expect that such a shock would be thin.

This cursory discussion hardly resolves the difficult question of shock structure, which would be especially troublesome if both the upstream and downstream states were in the mixture region (Saltanov *et al.* 1970).

3. Thermodynamic model

The shock thermodynamics are described by the Rankine–Hugoniot equation

$$[h] = \tfrac{1}{2}(v_1+v_2)[P], \tag{5}$$

where h, v and P are respectively enthalpy, volume and pressure. Together with suitable equation-of-state information, this fixes the shock adiabat in any desired set of thermodynamic co-ordinates.

We first consider the case where the upstream state (subscript 1) lies on the saturated-vapour boundary. Then (5) yields for the downstream-state quality x_2

$$1-x_2 = \frac{h_{2V}-h_{1V}-\frac{1}{2}(v_{2V}+v_{1V})[P]}{h_{2LV}-\frac{1}{2}v_{2LV}[P]}, \tag{6}$$

where the subscripts V and LV refer respectively to the saturated-vapour state and the difference between the saturated-vapour and the saturated-liquid states (e.g. h_{2LV} is the latent heat at the pressure P_2). This allows the construction of the shock adiabat through the mixture region to the saturated-liquid boundary, where $x_2 = 0$.

To evaluate the terms in (6) we have used various basic and approximate empirical relations, all expressed in reduced form, denoted by a caret (e.g. $\hat{v}$ is the reduced specific volume). The saturated-liquid volume was taken from the Rackett (1970) equation

$$\hat{v}_L = Z_c^{(1-\hat{T})^{\frac{2}{7}}}, \tag{7}$$

where Z_c is the critical compressibility factor. The vapour pressure $\hat{P}(\hat{T})$ was taken from the equation of Riedel (1954) and the Clausius–Clapeyron equation was used to relate h_{LV} and v_{LV} to the vapour-pressure derivative. Properties in the vapour region were found from a six-term polynomial which has the form of a truncated virial equation of state,

$$Z = 1 + \frac{B}{\hat{v}} + \frac{C}{\hat{v}^2} + \frac{D}{\hat{v}^3} + \frac{E}{\hat{v}^4} + \frac{F}{\hat{v}^5}, \tag{8}$$

and is constrained to satisfy the classical conditions at the critical point. The value of B was taken from a modified version of the Pitzer correlation (Tsonopoulos 1974). The temperature dependence of C was that of Zellner, Claitor & Prausnitz (1970) and that of D was taken from the calculations of Barker, Leonard & Pompe (1966); E and F were taken to be linear functions. The temperature dependence of the specific heat $\hat{c}_v^0 = c_v^0/R$ was described by

$$\hat{c}_v^0 = \tilde{c}_v(1 + n \ln \hat{T}), \tag{9}$$

where the characteristic specific heat $\tilde{c}_v = \hat{c}_v^0(1)$ is a measure of the molecular degrees of freedom or molecular complexity and n is a constant for each substance. The values of the Riedel parameter α_c, critical compressibility Z_c and the coefficient n were empirically correlated with $\tilde{c}_v$, covering the entire range of non-polar substances:

$$\alpha_c = 5{\cdot}7 + 0{\cdot}34(\tilde{c}_v - \tfrac{3}{2})^{\frac{1}{2}}, \quad Z_c = 0{\cdot}296 - 0{\cdot}0056\tilde{c}_v^{\frac{1}{2}}, \qquad (10), (11)$$

$$n = 1{\cdot}2[1 - \exp\{-0{\cdot}2(\tilde{c}_v - \tfrac{3}{2})\}] - 0{\cdot}6[1 - \exp\{-0{\cdot}06(\tilde{c}_v - \tfrac{3}{2})\}]. \tag{12}$$

In this way, the reduced properties of any fluid may be approximately characterized by $\hat{v}$, $\hat{T}$ and $\tilde{c}_v$.

In order to confirm the applicability of this model, we have compared its results with those obtained from detailed calculations tailored to individual substances (Canjar & Manning 1967; Das & Kuloor 1967; Starling 1973; Imperial Smelting 1970†). In addition, we have used the data of Keenan *et al.* (1969) for water, a polar fluid.

4. Behaviour with increasing molecular complexity

A condensation shock with an upstream state in the mixture region and a downstream state in the liquid region is possible even for fluids of low molecular complexity, e.g. water. With increasing complexity, the possible upstream states for fully condensed downstream states will move upwards in quality, i.e. the

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† *Tables of Thermodynamic Properties for Flutec.* Imperial Smelting Corp. Ltd, Avonmouth, Bristol.

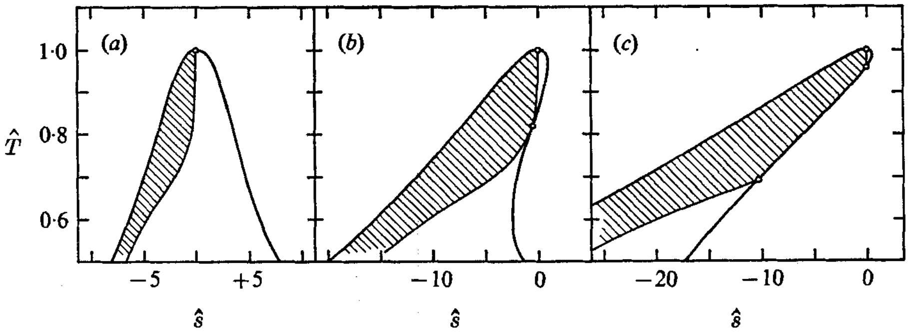

FIGURE 2. Envelopes of maximum quality for inverse adiabats with a downstream state on the saturated-liquid boundary, shown on a temperature–entropy diagram for fluids of increasing complexity. Possible upstream states for shocks with a fully condensed downstream state lie within the hatched regions. (*a*) Water, $\tilde{c}_v = 3{\cdot}46$. (*b*) Fluid of minimum complexity for a complete condensation shock, $\tilde{c}_v = 24{\cdot}1$. (*c*) Fluid with $\tilde{c}_v = 51{\cdot}6$.

mixture becomes less wet, until finally a dry upstream state on the saturated-vapour boundary is found.

To determine the regions for which a fully condensed downstream state is possible, we have calculated the *inverse* adiabat from a fixed downstream state on the saturated-liquid boundary: from (5) one obtains for the quality x_1

$$x_1 = \frac{h_{2L} - h_{1L} - \frac{1}{2}(v_{2L} + v_{1L})\,[P]}{h_{1LV} + \frac{1}{2}v_{1LV}[P]}. \tag{13}$$

This represents all the possible upstream states (subscript 1) in the mixture region leading to a fixed downstream liquid state (subscript 2). The resulting regions are shown in figure 2. For $\tilde{c}_v \geqslant 24{\cdot}1$ (according to our thermodynamic model) complete condensation shocks are possible.

5. Results for complete condensation shocks

In this section we give explicit results for complete condensation shocks for which the upstream state is saturated vapour and the downstream state is saturated liquid. This basic version of a condensation shock corresponds to physically realizable processes and can be extended to cases in which both end states lie within the single-phase regions.

For upstream states at low reduced temperatures $\hat{T}_1 \sim 0{\cdot}6$, there are no condensation-shock solutions to (5). There are, however, solutions in which the downstream state lies on the saturated-*vapour* boundary. For a range of somewhat higher upstream temperatures, proper condensation-shock solutions are found. Nearer the critical temperature, $\hat{T}_1 \sim 1$, there is an interval $s \gtrsim s_c$ in which the downstream state is again on the saturated-vapour boundary. This progression from vapour → vapour to vapour → liquid to vapour → vapour solutions is illustrated in figure 3.

Confining our attention to condensation shocks, we see in figure 3(*a*) that $\hat{T}_1(\hat{T}_2)$ is a double-valued function. The two branches $\hat{T}_1 > \hat{T}_{1E}$ and $\hat{T}_1 < \hat{T}_{1E}$ are

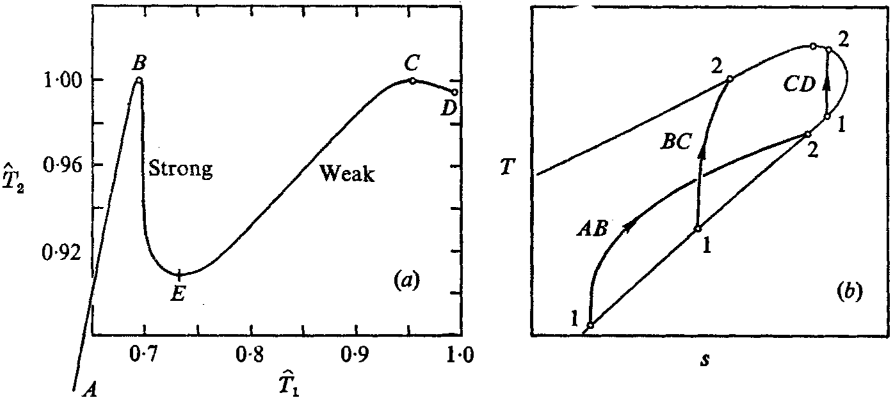

FIGURE 3. Vapour → vapour and vapour → liquid solutions for upstream states on the saturated-vapour boundary and downstream states on either saturation boundary. (*a*) Downstream temperature $\hat{T}_2$ *vs.* upstream temperature $\hat{T}_1$ for perfluoro-dimethylcyclohexane, $\tilde{c}_v = 51{\cdot}6$; vapour → liquid solutions lie between *B* and *C*. (*b*) Temperature–entropy diagram showing shock adiabats corresponding to the three intervals *AB*, *BC* and *CD*. (Not to scale.)

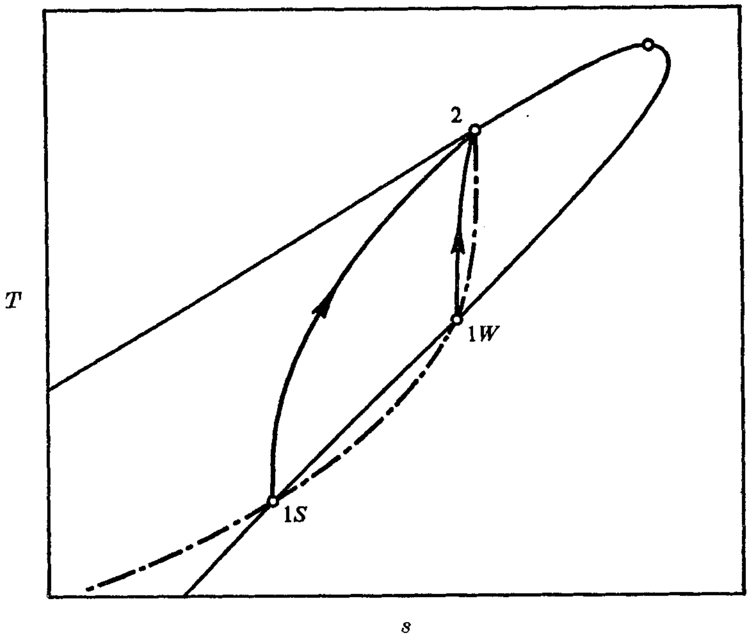

FIGURE 4. Shock adiabats for the weak (*W*) and strong (*S*) solutions leading to a common downstream state 2. The conventional adiabats are shown solid and the inverse adiabat is dashed.

labelled respectively *weak* and *strong*, corresponding to the usual measures of shock strength, such as the entropy jump. Representative adiabats for the weak and strong solutions are shown in figure 4.

Additional calculated results are shown in figures 5–7. Figure 5 includes a comparison between results from our thermodynamic model and those obtained

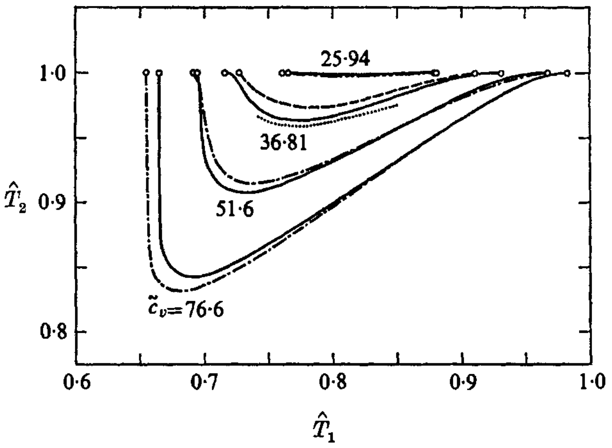

FIGURE 5. Downstream temperature $\hat{T}_2$ *vs.* upstream temperature $\hat{T}_1$ for condensation shocks with saturated end states, compared with results from various thermodynamic models. — · —, Imperial Smelting; — - - —, Canjar & Manning; – – – –, Das & Kuloor; ······, Starling; ——, empirical corresponding states. The substances corresponding to the various values of $\tilde{c}_v$ on the figure are *n*-hexane (25·94), *n*-octane (36·81), perfluoro-dimethylcyclohexane (51·6) and perfluoro-methyldecalin (76·6).

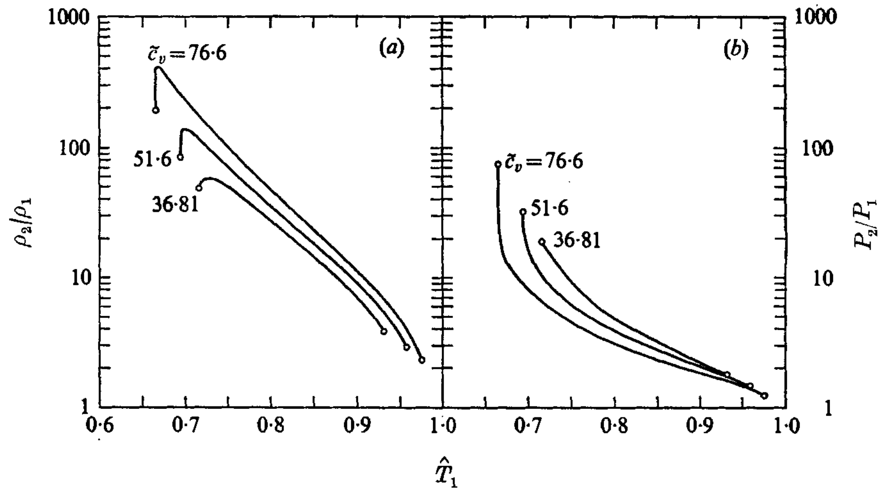

FIGURE 6. Properties of condensation shocks with saturated end states. The numerical values of $\tilde{c}_v$ labelling the curves correspond to the substances given in figure 5. (*a*) Density ratio ρ_2/ρ_1 *vs.* temperature $\hat{T}_1$. (*b*) Pressure ratio P_2/P_1 *vs.* temperature $\hat{T}_1$.

from equations of state tailored to individual substances. The shocks are all well behaved in that $[s] \geqslant 0$ and $M_1 \geqslant 1$ (we have not calculated downstream Mach numbers M_2: they are typically of order 10^{-2}). It is interesting that, as the minimum $\tilde{c}_v$ permitting condensation shocks is approached, the downstream states become focused near the critical temperature, even over a fairly wide range of possible upstream states.

To give an example of how these results translate into palpable quantities, we

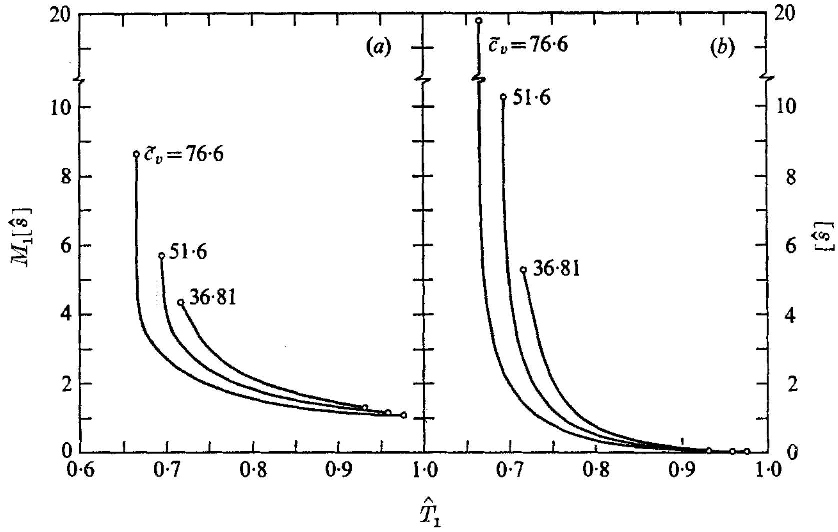

FIGURE 7. Further properties of condensation shocks with saturated end states. The numerical values of $\tilde{c}_v$ labelling the figures correspond to the substances given in figure 5. (a) Shock Mach number M_1 vs. temperature $\hat{T}_1$. (b) Non-dimensional entropy jump $[\hat{s}] \equiv [s]/R$ vs. temperature $\hat{T}_1$.

t_1 (°C)	t_2 (°C)	P_1 (atm)	P_2 (atm)	v_1 (cm^3/g)	v_2 (cm^3/g)	w_1 (m/s)
120	200	1·7	9·5	43·7	0·80	187
140	208	2·8	10·8	26·5	0·83	149
160	218	4·4	13·0	16·8	0·89	124
180	227	6·6	14·9	10·9	0·95	100

TABLE 1. Representative solutions with saturated end states for perfluoro-dimethylcyclohexane ($\tilde{c}_v$ = 51·6, T_c = 514·7 °K, P_c = 18·6 atm, v_c = 1·52 cm^3/g)

list in table 1 some dimensional upstream and downstream values for representative condensation shocks in perfluoro-dimethylcyclohexane, for which $\tilde{c}_v = 51{\cdot}6$. This corresponds to a complexity level characteristic of the higher fractions in gasoline.

6. Related forms of condensation shock

The case in which the end states are saturated can be extended to the case of a complete condensation shock in which the upstream state is in the superheated-vapour region and the downstream state is in the compressed-liquid region.

Extension of the adiabat into the liquid region requires a liquid equation of state adaptable to a corresponding-states form. We have been unable to find an adequate equation and shall use instead the simple incompressible model

$$v = v_L = \text{constant}, \tag{14}$$

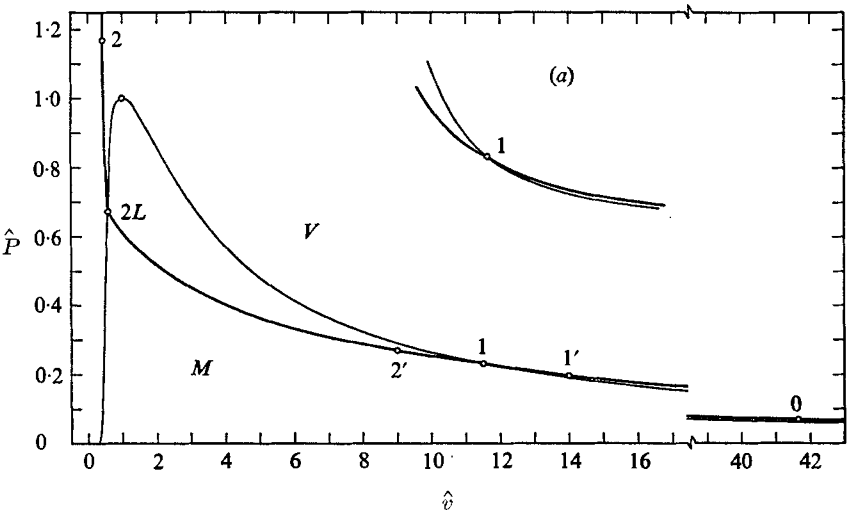

FIGURE 8. Normal and inverse shock adiabats drawn from an upstream state 1 on the saturated-vapour boundary, shown on a pressure–volume diagram. The case shown corresponds to $t_1 = 160\,^{\circ}\mathrm{C}$ in table 1. Point 0 represents the initial state for production of the shock $1 \rightarrow 2L$ as a reflected shock. Inset (*a*) shows the vicinity of point 1, with the horizontal scale contracted by a factor of four, to show more clearly the discontinuity in the slope of the adiabat.

where $v_L(T)$ is the volume of the saturated liquid. Thus the adiabat becomes a vertical line in the P, v plane. For a complete condensation shock with a fixed upstream state the volume jump $[v]$ is then fixed. It follows from the shock conditions that

$$[P] \propto w_1^2, \tag{15}$$

where $w_1 = M_1 c_1$ is the upstream velocity relative to the shock front.

The shock adiabat can also be extended, as an inverse adiabat, into the vapour region from the saturation boundary, as shown in figure 8. The significance is somewhat different, since points on this adiabat represent possible upstream states for a downstream state at point 1. For example, a shock from point 0 to point 1 would be reflected from a rigid boundary as a complete condensation shock from point 1 to point $2L$.

The discontinuity in slope at point 1 results in a formal prediction of shock *splitting*, e.g. of one (unstable) shock $1 \rightarrow 2'$ into two distinct shocks $1' \rightarrow 1$ and $1 \rightarrow 2'$, as discussed by Bethe and especially by Zel'dovich & Raizer. This will not occur for any of the complete condensation shocks considered, as shown by the result $M_1 > 1$. As a matter of interest, the discontinuity in the slope of the isentrope at point 1 can be related to retrograde behaviour: thermodynamic manipulation yields

$$\frac{(\partial P/\partial v)_{sf}}{(\partial P/\partial v)_{sm}} - 1 = -\frac{T}{Z_c \hat{c}_{vf}} \left(\frac{\partial \hat{P}}{\partial \hat{v}}\right)_{Tf} \left(\frac{d\hat{s}}{d\hat{P}}\right)_{\mathrm{sat}} \geqslant 0, \tag{16}$$

where $\hat{s} \equiv s/R$, a subscript f denotes the single-phase (vapour) region and m denotes the mixture region. This is usually a fairly small number, having a maximum value of 0·3 for $\hat{c}_v = 51{\cdot}6$, for example.

Because the density change across a condensation shock is large, quite large turning angles can be achieved across an *oblique shock*, even for shock angles fairly close to 90°, as was pointed out by Saltanov *et al.* In general, the downstream Cartesian velocity components U_{2x} and U_{2y} are related by

$$U_{2y}^2 = (U_1 - U_{2x})(U_{2x} - U_1/r), \tag{17}$$

where $r \equiv \rho_2/\rho_1$ and the velocities can be considered to be normalized with respect to any desired characteristic velocity, e.g. the upstream sound speed c_1. This is the equation for a conventional shock-polar diagram. In our case r = constant and the equation is that of a circle centred at $U_{2x} = [(r+1)/2r]\,U_1$. As a numerical example, a shock with $U_1 = M_1 = 2$ and $r = 20$ yields a turning angle of 51° for a shock angle of 86°.

7. Concluding remarks

We have investigated the properties of true condensation shock waves and find that they should occur over a wide range of conditions. It has been possible to say very little about the structure of such a shock.

Laboratory production of a condensation shock should be feasible in a shock tube. The large density ratio typical of such shocks indicates that the amount of liquid produced will be small. An attractive technique would be to produce the condensation shock as a reflected shock from the rigid end wall of the tube, which should have the effect of stabilizing the liquid region.

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