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Abstract

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ON THE BREAK IN THE SHOCK ADIABAT AT A FIRST-ORDER PHASE TRANSITION

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The shock adiabat of a solid body $P(V)$ (where P is the pressure, V the specific volume), upon intersecting the melting curve, has a break. V. D. Urlin and A. A. Ivanov drew attention to the circumstance that the sign of this break may, generally speaking, be either positive or negative ([1]).

Below we determine the conditions that define the signs of the jumps

$$\Delta = (\partial P/\partial V)_{P_0+0} - (\partial P/\partial V)_{P_0-0}$$

and

$$(\partial T/\partial P)_{P_0+0} - (\partial T/\partial P)_{P_0-0}$$

(where T is the temperature, and the derivatives $\partial P/\partial V$ and $\partial T/\partial P$ are taken along the shock adiabat) in a first-order phase transition at the point with pressure P_0. It will be shown, in particular, that in melting of a solid the sign of Δ coincides with the sign of the difference

$$(\partial T/\partial P)_S - \partial T/\partial P,$$

where $\partial T/\partial P$ is the pressure derivative of the temperature on the melting curve, and $(\partial T/\partial P)_S$ is the isentropic derivative $\partial T/\partial P$ of the solid phase at the point P_0 of intersection of the shock adiabat with the melting curve.

Let us write the equation of continuity of the energy flux in a shock wave propagating through an unperturbed substance with velocity D, in the form

$$H_2 + \frac{D^2}{2}\left(\frac{V_2}{V_1}\right)^2 = H_1 + \frac{D^2}{2}. \tag{1}$$

Here H_1, H_2, V_1, and V_2 are the enthalpy and specific volume of the substance ahead of and behind the shock-wave front, respectively.

In the case where behind the wave front the substance is in a two-phase state, equation (1) can be represented, with the aid of the Clapeyron–Clausius equation, in the form

$$H_I + T\left(V_2 - V_I\right)\frac{dP}{dT} + \frac{D^2}{2}\left(\frac{V_2}{V_1}\right)^2 = H_1 + \frac{D^2}{2}, \qquad (2)$$

where H_I and V_I are the enthalpy and specific volume of phase I at its boundary with the two-phase region I-II at pressure P_2, i.e., at the pressure corresponding to state 2 behind the shock wave. In what follows, the indices I and II everywhere indicate that the quantity marked by them pertains to phase I or to phase II.

Let us next introduce into consideration the metastable state of phase I at a shock-wave intensity slightly exceeding the intensity D_0 corresponding to the onset of melting. (Such a consideration in the case of a first-order phase transition is always thermodynamically possible, including also when the "metastable state" under consideration cannot be realized experimentally.) The slope of the shock adiabat of the metastable state is a continuous function of D at the point P_0. Equation (1) for the metastable state has the form

$$H_3 - \frac{D^2}{2}\left(\frac{V_3}{V_1}\right)^2 = H_1 + \frac{D^2}{2}, \qquad (3)$$

where H_3 and V_3 are the enthalpy and specific volume of phase I in the metastable state behind the shock-wave front.

Subtracting (3) from (2) for one and the same value $D = D_0(1+\varepsilon)$, where ε is a small positive quantity, we find

$$T(S_1 - S_3) + V_2(P_2 - P_3) + \frac{D^2}{V_1^2}V_2(V_2 - V_3) + T(V_2 - V_1)\frac{dP}{dT} = 0, \qquad (4)$$

where S_1 and S_3 are the entropies of phase I at the point with pressure P_2 on the boundary of phase I with the two-phase region I—II and at the point P_3V_3 of the metastable state, respectively.

Taking into account that points 2 and 3 in the PV plane lie on one straight line with point 1 (see Fig. 1), and therefore

$$D^2 = -V_1^2\frac{P_2 - P_3}{V_2 - V_3},$$

after cancellations, instead of (4) we obtain

$$S_1 - S_3 = (V_2 - V_1)\frac{dP}{dT}. \qquad (5)$$

Figure 1: Schematic P-V diagram with points 1, 2, 3, P_0, and Φ.

Figure 1: Figure 1: Schematic P-V diagram with points 1, 2, 3, P_0, and Φ.

Fig. 1. On the study of the kink of the shock adiabat. The dashed line is a smooth continuation of the shock adiabat from the point P_0 into the two-phase region; Φ is the boundary of phase I with the mixture I—II.

Let us express S_1 through the entropy S_2 of the metastable state of phase I at the point P_2V_2, taking into account that S_1 and S_2 refer to the same pressure P_2:

$$S_1 = S_2 + \left(\frac{\partial S}{\partial V}\right)_{P,\mathrm{I}} (V_1 - V_2). \tag{6}$$

Substituting (6) further into (5) and replacing $(\partial S/\partial V)_{P,\mathrm{I}}$ by the identically equal quantity $(\partial P/\partial T)_{S,\mathrm{I}}$, we find:

$$S_3 - S_2 = (V_2 - V_1)\left[\frac{dP}{dT} - \left(\frac{\partial P}{\partial T}\right)_{S,\mathrm{I}}\right]. \tag{7}$$

At the point 3 of intersection of the chord 1—3 with the shock adiabat (Fig. 1), for small differences $V_3 - V_2$ and $S_3 - S_2$, the inequality holds

$$K_1^{-1} \equiv \left(\frac{\partial T}{\partial P}\right)_{S,\mathrm{I}} \frac{S_3 - S_2}{V_3 - V_2} > 0. \tag{8}$$

Indeed, owing to the subsonic character of the motion behind the shock-wave front, the derivative $\partial P/\partial V$ along the chord 1—3 at the point 3 is greater than $(\partial P/\partial V)_{S\,\mathrm{II}}$, and therefore:

$$\left(\frac{\partial P}{\partial S}\right)_V \frac{\partial S}{\partial V} \equiv \frac{\partial P}{\partial V} - \left(\frac{\partial P}{\partial V}\right)_S > 0, \tag{9}$$

where $\partial S/\partial V$ has also been calculated along the chord 1—3. But the sign of $(\partial P/\partial S)_V$, by virtue of the thermodynamic relations $(\partial P/\partial T)_S = -(\partial P/\partial V)_S(\partial S/\partial P)_V$ and $(\partial P/\partial V)_S < 0$, coincides with the sign of $(\partial P/\partial T)_S$; therefore, together with (9), $(\partial P/\partial T)_S(\partial S/\partial V) > 0$ is also valid, which is asserted by inequality (8).

From (7) and (8) it follows that

$$V_3 - V_2 = K_1(V_2 - V_1)\left(\frac{\partial T}{\partial P}\right)_{S,\mathrm{I}}\left[\frac{dP}{dT} - \left(\frac{\partial P}{\partial T}\right)_{S,\mathrm{I}}\right]. \tag{10}$$

Being interested further only in the sign (and not in the magnitude) of $V_3 - V_2$, we replace $V_2 - V_1$ by the quantity $V_{II} - V_I$, which has the same sign, where V_{II} is the specific volume of phase II at pressure P_2 on the boundary of equilibrium of the two-phase region with phase II, and with the aid of the Clapeyron–Clausius equation we obtain instead of (10)

$$V_3 - V_2 = K\left(\frac{\partial T}{\partial P}\right)_{S,\mathrm{I}} \frac{dT}{dP} Q\left[\frac{dP}{dT} - \left(\frac{\partial P}{\partial T}\right)_{S,\mathrm{I}}\right] = KQ\left[\left(\frac{\partial T}{\partial P}\right)_{S,\mathrm{I}} - \frac{dT}{dP}\right], \quad (11)$$

where $Q = T(S_{II} - S_I)$ is the latent heat of the phase transition, S is the entropy, $K > 0$ (K can be expressed explicitly in terms of K_1 and the concentration of phase I in the two-phase mixture).

Expression (11) determines the sign of $V_3 - V_2$, or, what is the same, the sign of Δ at the point where the shock adiabat enters the two-phase region. In an analogous way, the sign of Δ is determined also at the other boundary of the two-phase region, at the point where the phase transition is completed. The only difference is that here, instead of the "superheated" phase I, one must consider the "supercooled" phase II in the neighborhood of the point P_0' where the shock adiabat intersects the boundary of phase II. The expression analogous to (11) in this case has the form

$$(V_3 - V_2)K_2 Q\left[\frac{dT}{dP} - \left(\frac{dT}{dP}\right)_{S_{\mathrm{II}}}\right], \quad (12)$$

where $K_2 > 0$, $(\partial T/\partial P)_{S,\mathrm{II}}$ is the derivative $(\partial T/\partial P)_S$ of phase II at the point P_0'; the points V_2 and V_3 lie respectively on the equilibrium shock adiabat and on the shock adiabat of the metastable phase II at the pressure $P_2 = P_0'(1-\varepsilon)$.

Fig. 2. Line of the phase boundary and arrangement of phases t and zh. *a*—$dT/dP > 0$, *b*—$dT/dP < 0$.

Formula (11), which determines the sign of the kink of the shock adiabat, was obtained under the assumption that the shock adiabat and the melting curve intersect. However, the possibility of such an intersection is in turn associated with certain conditions imposed on Q and dT/dP. Namely, intersection is possible in the case when

$$Q\left[\left(\frac{\partial T}{\partial P}\right)_{\Gamma} - \frac{dT}{dP}\right] > 0, \quad (13)$$

where $(\partial T/\partial P)_\Gamma$ is the derivative along the Hugoniot adiabat of phase I at the point of intersection.

For the proof of (13), let us consider the arrangement of the regions of phases zh and t (phase zh has positive Q relative to phase t) in the PT plane for

$dT/dP > 0$ and $dT/dP < 0$. From Figs. 2a and 2b it is seen that, for any sign of dT/dP, a shock adiabat issuing from phase t can intersect the phase-equilibrium curve only under the condition

Fig. 3

$$\left(\frac{\partial T}{\partial P}\right)_\Gamma > \frac{dT}{dP}. \qquad (14)$$

But since, in the transition from phase t to phase zh, $Q > 0$, (14) is equivalent to (13). In exactly the same way one can verify that if the shock adiabat issues from phase t, then for its intersection with the phase-equilibrium curve the inequality opposite to (14) must be satisfied; but since in this case $Q < 0$, we again arrive at (13). (We note that in the two-phase region $(\partial T/\partial P)_\Gamma = dT/dP$, and therefore (13) determines the sign of the jump of the shock adiabat in the PT plane.) Condition (13) is also satisfied at the point where the shock adiabat exits from the two-phase region into the region of phase II (here $(\partial T/\partial P)_\Gamma$ refers to phase II).

Comparing (13) with (11) and taking into account the inequality

$$\left(\frac{\partial T}{\partial P}\right)_\Gamma - \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial T}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_\Gamma > 0,$$

we find that, at the point where the shock adiabat enters the two-phase region, in the case $Q < 0$ only $\Delta > 0$ is possible, while in the case $Q > 0$ any sign of Δ is possible.

However, even for $Q > 0$, in order for $\Delta < 0$ to occur, dT/dP must satisfy the rather stringent condition

$$\left(\frac{\partial T}{\partial P}\right)_\Gamma > \frac{dT}{dP} > \left(\frac{\partial T}{\partial P}\right)_{S,\mathrm{i}}. \qquad (15)$$

In view of (15), at least for relatively weak shock waves, the case $\Delta < 0$ is unlikely, and it may conventionally be called the case of an anomalous kink of the shock adiabat*.

Everything said about the sign of Δ also holds at the point of completion of the phase transition (see (12)), if Δ is replaced by $-\Delta$. The qualitative picture of the kink of the shock adiabat as it enters and leaves the two-phase region, uniquely possible in the case $Q < 0$ and most probable for $Q > 0$ (for example, on melting), is shown in Fig. 3. Points 1 and 2 correspond to the beginning and completion of the phase transition.

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CITED LITERATURE

1. V. D. Urlin, A. A. Ivanov, DAN, **149**, No. 6, 1303 (1963).

2. L. D. Landau, E. M. Lifshitz, *Mechanics of Continuous Media*, 1953.

* We note that from (15) there follows the impossibility of $\Delta < 0$ for a weak (isentropic) shock wave on melting, in complete agreement with the known inequality $C_\infty > C_0$, where C_∞ and C_0 are the nonequilibrium and equilibrium values of the speed of sound ([2]).

Note: Figure translations are in progress. See original paper for figures.