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DETONATION AND GAS-DYNAMIC DISCONTINUITIES IN PHASE TRANSITIONS OF METASTABLE SUBSTANCES

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The thermodynamic conditions for detonation transition of matter in the metastable phase to a state in thermodynamic equilibrium is determined. Gas-dynamic discontinuities or other phase transition regimes are considered.

RECENT progress in high-pressure physics[1] has led to new possibilities of obtaining different materials (crystalline modifications), including some previously unknown. Some of the materials obtained at high pressures preserve a thermodynamic stability, absolute or relative, even under normal conditions. In connection with the fact that phase transformations of such materials are usually accompanied by a thermal effect and a volume change, it is interesting to elucidate what bearing this can have on the phenomenon of detonation, in other words, whether first-order phase transitions can lead in principle to a detonation and, if this is possible, then, what are the conditions under which it is possible. Ubbelohde[2,3] has pointed both to polymorphic transformations and to the possible source of weak detonation waves. However, the thermodynamic conditions for the realization of detonations in the phase transitions have not been studied. The analysis that follows is devoted to this problem and to the analysis of possible gas-dynamic discontinuities in the transformation of a thermodynamically metastable phase to a stable one.

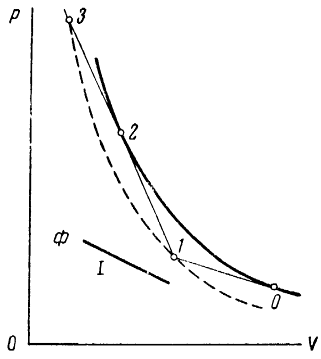

FIG. 1

1. We note first that no detonation is possible in any case if the initial state of the material is in thermodynamic equilibrium. Actually, however, if the phase transitions originate in a shock wave of finite width, they will always be damped, as follows from the general theory of shock waves,[4] as a consequence of the fact that the points 1 and 2, which describe on the PV (pressure, volume) plane the thermodynamical equilibrium states of the material in front of the wave and behind it, lie on the same shock adiabat. Point 2 approaches point 1 as the shock wave is propagated. In this motion along the shock adiabat, the point 2 passes through all the thermodynamical equilibrium phase states lying on its path. The intersection of the shock adiabat and the curves of phase equilibrium lead only to breaks in the shock adiabat and to a splitting of the shock wave in two, which is possible under definite conditions.[5-7] In the latter case, the second wave is damped, followed after its final dissipation by the first. Thus, to realize the detonation regime of phase transition it is necessary that the initial state at the point 1 be metastable.

A substance in a metastable phase state is quite similar to an ordinary explosive. In both cases, the transition along the chord from point 3 to point 2 corresponds to the detonation regime (Fig. 1) in which the substance passes through a series of thermodynamical nonequilibrium states (at least with respect to composition). There is, however, an important difference between the ordinary explosives and metastable phase modifications. In the liberation of the heat of combustion under conditions of thermal isolation, the pressure of the explosion products is always greater than the pressure of the initial explosive materials at the same volume. Therefore, the detonation adiabat on the PV plane is located below the shock adiabat of the initial material. For a phase transition from the metastable phase, both this and the reverse location of the adiabat are possible. The detonation regime of the phase transformation is possible in principle if, in correspondence with the general premises of the theory of detonation, the adiabat of the equilibrium state of the material is located above point 1 (see Fig. 1) and if there is no great loss.[8] (The process of phase transition from state 3 to state 2, Fig. 1, can, however, be so slow that the critical dimensions of the material necessary for development of a detonation turn out to be impossibly large under laboratory conditions.[9,8] For this reason, not all metastable materials characterized by the location of adiabats shown in Fig. 1 can serve in practice as explosives.[1])

Leaving aside the problem of the critical dimensions of the material, let us consider how its thermodynamic properties are associated with some location of shock adiabats relative to the initial point 1. At the pressure P_1, let the enthalpy W of phase I on the curve of equilibrium of phases I and II be equal to W^*, and let the material be in a metastable state of phase I for the same pressure P_1 and for $W_1 = W^* + \delta W$. The volumes V_1 and V^* of phase I at the points P_1, W_1 and P_1, W^* are connected by the relation

$$V_1 = V^* + (\partial V/\partial W)_{P,\mathrm{I}}\,\delta W = V^* + \frac{1}{T}\,(\partial T/\partial P)_{S,\mathrm{I}}\,\delta W \quad (1)$$

(the index I denotes phase I and S the entropy). The volume of the equilibrium state of the material at the same P_1 and for the same increment δW, in accord with the Clapeyron-Clausius equation, is equal to

$$V_p = V^* + \frac{1}{T}\frac{dT}{dP}\delta W, \quad (2)$$

where dT/dP is the derivative along the curve of phase equilibrium at pressure P_1.

It follows from (1) and (2) that for an isobaric and isenthalpic transition from a metastable state to a stable state, the volume change is given by

$$V_p - V_1 = \frac{1}{T}\left[\frac{dT}{dP} - \left(\frac{\partial T}{\partial P}\right)_{S,\mathrm{I}}\right]\delta W. \quad (3)$$

The change in volume, upon simultaneous satisfaction of the condition of constant pressure and constant entropy, is made possible by the change in the phase of the component. Noting that $\delta W = Q\delta\alpha$, where Q is the heat of an equilibrium phase transition I → II at pressure P_1 and α is the relative concentration of phase II, we reach the conclusion that an isenthalpic transition from the metastable state of phase I to a two-phase state in thermodynamical equilibrium at constant pressure is accompanied by a change in volume, the sign of which is identical with the sign of the quantity

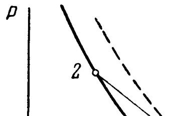

FIG. 2

$$Q[dT/dP - (\partial T/\partial P)_{S,\mathrm{I}}].$$

For example, upon crystallization from a supercooled liquid at W = const, the volume increases if

$$(\partial T/\partial P)_{S,\,\mathrm{liq}} > dT/dP.$$

The equation of the shock adiabat which starts from the point P_1, V_1 of the metastable state, and corresponds to a thermodynamic-equilibrium final state has the form

$$W_{2,p}(P_2, V_2) - W_1 = (P_2 - P_1)(V_2 + V_1)/2. \quad (4)$$

Here $W_{2,p}$ is the enthalpy of the equilibrium state. The change in the volume (3) considered above corresponds to the transition $P_2 = P_1$ and $W_{2,p} = W_1$, which is described by Eq. (4). The point P_1, V_2 of the shock adiabat on the PV plane lies to the right of P_1, V_1 if

$$Q[dT/dP - (\partial T/\partial P)_{S,\mathrm{I}}] > 0, \quad (5)$$

and to the left if

$$Q[dT/dP - (\partial T/\partial P)_{S,\mathrm{I}}] < 0. \quad (6)$$

It is now obvious that the shock (detonation) adiabat location[2] shown in Fig. 1 corresponds to the inequality (5). The difference ΔV between the points P_1, V_1 and P_1, V_2 depends on the degree of superheating (supercooling) of the initial phase. (The line Φ on Fig. 1 denotes the possible location of the boundary of the region of the equilibrium state of phase I with the region of the two-phase mixture.) Upon satisfaction of the inequality (6), the shock adiabat of the metastable phase and the point 1 on it are located above the adiabatic transition into the state of complete thermodynamic equilibrium (Fig. 2). In this case, the amplitude of

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[1] It is possible that one of the reasons for earthquakes is the detonation of rocks[2,4] that are in a metastable state, as the result of their being deformed somehow inside the earth.

[2] Note that (5) and (6) exhibit a natural analogy with the criteria that determine the sign of the break of the shock adiabat which starts out from a certain thermodynamic equilibrium state of phase I, as it crosses the phase equilibrium curve.[7]

the pressure of any shock wave of finite width (for the same reasons as in the case of a stable initial state) falls off to zero monotonically. The derivatives in the square brackets of (6) and their difference can be of any sign. Therefore, the requirement of exothermal character of the process of the phase transformation ($Q < 0$) is nowhere sufficient or necessary for the existence of a detonation, as might appear at first glance (see, for example, [2,3]).

The adiabats of the stable state and the metastable phase can generally cross at some point P, V. At the point of intersection, the pressure, volume, and enthalpy of these states are equal; consequently,

$$Q[dT / dP - (\partial T / \partial P)_{S,\mathrm{I}}] = 0.$$

For this we must have, at the point $P_2 = P$ on the curve of phase equilibrium at a pressure P either

$$dT / dP = (\partial T / \partial P)_{S,\mathrm{I}}, \tag{7}$$

or

$$Q(P) = 0 \tag{8}$$

(the critical point, which is possible if the phases have the same symmetry, or the point where the first-order phase transition degenerates into a second-order phase transition; one can show that at the critical point the condition (7) is also satisfied in addition to (8)). In the case of (7), $Q = 0$ and for $P_2 > P$, that is, for $P_2 > P$, only the adiabat of the stable state has a meaning.

As an example, we shall consider in the light of the inequalities (5) and (6) the so-called condensation discontinuities [10,4] which transform supersaturated vapor into a two-phase mixture (a gas containing a small amount of condensed phase).

On the gas-liquid boundary, far from the critical point,

$$\frac{dT}{dP} = \frac{TV_\mathrm{I}}{|Q|}, \quad \left(\frac{\partial T}{\partial P}\right)_{S,\mathrm{I}} = \frac{\gamma - 1}{\gamma}\frac{V_\mathrm{I}}{R}$$

(V_I is the molar volume of the vapor on the saturation line, R is the gas constant, and γ is the exponent of the Poisson adiabat). Hence

$$Q\left[\frac{dT}{dP} - \left(\frac{\partial T}{\partial P}\right)_{S,\mathrm{I}}\right] = TV_\mathrm{I}\left[\frac{|Q|}{\gamma E} - 1\right]$$

(E is the internal energy of the gas). The value of $[|Q|/\gamma E - 1]$ for any reasonable value of γ far from the critical point is positive, and consequently the shock adiabat is located above the point 1 (Fig. 1), in accord with the initial premise of the theory of condensation discontinuities.

2. In analogy to the two regimes of burning (slow burning and detonation), there are possible two regimes of propagation of the phase transformation along a substance in the metastable phase. In the detonation regime, the shock wave which travels along the metastable phase transforms this phase from the state 1 (Fig. 1) to another metastable state 3, after which a phase transformation takes place, corresponding to the transition from point 3 to point 2 along the chord 1—3 in Fig. 1. The structure of the wave has a form characteristic of a detonation wave ("chemical peak"). Just as in combustion in strong shock waves, a supercompressed detonation is possible here, corresponding to points located under point 2 on the adiabat of equilibrium states.

A surface phase transition (the phase transition on the surface of a metastable phase without the appearance of nuclei in its volume, for example the surface fusion of a superheated crystal or the solidification of a supercooled liquid) is the analog of slow burning. If the superheating (supercooling) is sufficient for the realization of the complete phase transformation without transfer of heat, [11] or if the phase transition on the surface takes place so slowly that the thermal conductivity is not a limiting stage of the process as a whole (for example, in the fusion of materials which possess an enormously high viscosity in the liquid states [12]), then the speed of motion of the phase boundary is determined by the kinetic realignment of the surface and can be constant. In this case, the homogeneous transformation is analogous gas-dynamically to slow burning. In particular, there remains in force here the conclusion [4] that discontinuities corresponding to points of the adiabat located below the point 0 (Fig. 1) are absolutely unstable. In the opposite case, when heat transfer is the limiting process, the motion of the surface of the phase transformation through a metastable phase that has a given constant temperature at infinity has a variable velocity which is characteristic of nonstationary thermal conductivity. [11,13] In this case, to guarantee a stationary and stable 3) regime of slow transformation, it is necessary to satisfy special highly artificial conditions, which are imposed on the state of the material in front of the surface of phase separation. We shall not consider

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3) The plane front of the transformation surface, whose velocity is limited by the thermal conductivity can generally be unstable relative to deformation of its surface (see, for example, the so-called dendritic hardening of supercooled metals[14]).

this question here in further detail. An analog of slow burning under definite conditions is also a phase transformation in which appearance of nuclei of the new phase occurs not on the surface but in the volume. The realization of the stationary volume phase transformation is possible in this case if the material in front of the phase discontinuity is obtained as a result of the propagation through it of some sort of stationary process, for example heating or cooling. This process transforms the material to a state corresponding to the formation, at a rate sufficiently rapid for the scale of the problem, of nuclei of the new phase. An example of such a regime of phase transition with formation of nuclei in the volume are the condensation rarefaction shocks discussed in [4].

3. Finally, we shall consider discontinuities corresponding to the inequality (7). The corresponding location of the shock adiabat relative to the initial point 1 is shown in Fig. 2. The straight lines $P = P_1$ and $V = V_1$, and the tangent to the adiabat of metastable phase at the point 1, divide the shock adiabat into five parts. Two parts—above point 2 and between points 2 and 3—refer to shock waves which differ qualitatively only in structure; in particular, the points of the first parts correspond to strong shock waves and of the second to weak ones according to Zel'dovich.[15] The part 3—4 does not have physical meaning (imaginary flow of matter). The part 4—5 corresponds to the slow surface or volume phase transformations, to which is applicable everything said above concerning such transformations when inequality (6) is satisfied. To the last section of the adiabat correspond absolutely unstable discontinuities, subsonic relative to the material in front of the discontinuity and supersonic relative to the material behind the discontinuity. When shock adiabats of metastable and stable phases merge into one adiabat, the section 4—5 is compressed to the point 1, and the whole region below it reduces to an absolutely unstable discontinuity, in agreement with the well known premises of the theory of shock waves.

In conclusion, I express my gratitude to V. L. Tal'roze and P. A. Yampol'skiĭ who called my attention to a number of problems which became the subject of this investigation.

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