NONUNIQUENESS AND STABILITY OF DETONATION MODES

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Submitted to JETP editor August 11, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) 52, 309–317 (January, 1967)

It is shown that the detonation mode in an unbounded medium may become nonunique in the case of nonmonotonic heat release. The stability of detonation modes with respect to their transformations into one another is investigated. Under some minor restrictions, the number of stable modes is larger by unity than the number of unstable ones. A simple model of nonmonotonic heat release is considered by way of an illustration.

THE Chapman-Jouguet rule, formulated as the condition that the equilibrium detonation adiabat be tangent on the pressure-volume plane to the straight line 1-2 joining the initial and final states on the discontinuity, determines the minimum velocity D^* of the discontinuity corresponding to the transition to the equilibrium state. The velocity determined in this manner is a thermodynamic quantity in the sense that it does not depend on the concrete kinetic mechanism of detonation combustion. It is known [1] that this quantity is not always to the velocity D of a plane detonation wave in an unbounded medium, but only provided the irreversible chemical process occurring behind the shock-wave front is exothermal in all its stages.[1)]

If the transition to the equilibrium state corresponds to a heat release q^*, and if during the combustion process there is first released the maximum heat $q_{max} > q^*$ (we shall call such a heat-release process nonmonotonic), then the speed of the detonation wave in an unbounded medium is determined by the condition that the straight line 1-2 be tangent to the adiabat of the intermediate states [1], which corresponds to a heat release q_{max}, so that $D > D^*$. (We bear in mind the fact that a larger heat release usually corresponds on the pressure-volume plane to a higher-lying adiabat.)

We show in this paper that in the case of nonmonotonic heat release the detonation mode in an unbounded medium can become nonunique under certain conditions. In this connection, we consider also the question of the stability of the mode against a transition into another possible mode, and the question of the number of modes. We analyze the general qualitative aspect of the question, which we illustrate with a numerical calculation of a simple heat-release model.

1. Unlike q^*, the quantity q_{max} is a kinetic characteristic of the process and depends itself on the concrete path followed by the transition to the equilibrium state. Indeed, q_{max} is determined by the relation between the characteristic times τ_i of two or several physico-chemical processes (chemical reactions, vibrational relaxation, thermal conductivity in the case of an inhomogeneous medium, etc.) governing the irreversible process as a whole. But since τ_i usually depends strongly on the conditions under which the reaction takes place, for example on the temperature distribution, q_{max} is likewise generally speaking dependent on the same conditions.

Let us consider first the particular case when the character of the heat release behind the front of the shock wave is determined by the intensity of that wave, independently (or practically independently) of the possible variations of the picture of the flow behind the front. This makes it possible to trace in the simplest manner the main qualitative laws of the phenomenon. It will be shown in Sec. 3 that they remain in force also in the general case of heat release.

We represent the dependence of q_{max} on the velocity of the shock wave in the form

$$q_{max} = \varphi(D). \tag{1}$$

However, independently of (1), for the normal detonation mode it is necessary also to satisfy the

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[1)]It has been shown in recent years that the front of a detonation wave is not always plane [2], and this may lead to a change in D. However, if the energy of the related "turbulent" pulsations [3,4] is small compared with the energy of the detonation wave, then D does not change noticeably. Moreover, the role of the pulsation is in general insignificant [5] if the value of the Gruneisen coefficient for the explosion products is larger larger than or equal to 2/3.

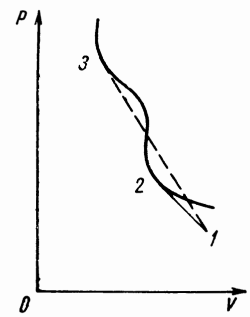

FIG. 1.

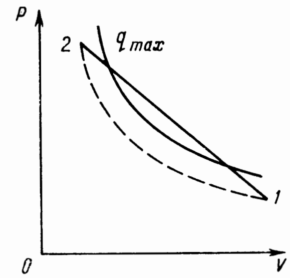

FIG. 2.

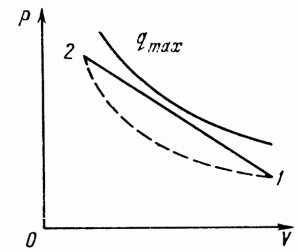

FIG. 3.

tangency condition, which can be represented in the form[2)]

$$q_{max} = \psi(D). \tag{2}$$

The equation

$$\varphi(D) = \psi(D) \tag{3}$$

determines in general not necessarily one value, but a certain discrete set of values of D for normal detonation modes. We note that if the heat release can be only monotonic, then $q_{max} = q^*$ and the equation

$$\psi(D) = q^* \tag{4}$$

has a unique solution under the condition that on the detonation adiabat we have for the second derivative of the pressure with respect to volume $d^2P/dV^2 > 0$. In the opposite case the solution of (4) can also be nonunique, and if this is the case, then only the one mode with the smallest D is stable. All the modes (3) satisfying the tangency conditions with larger D are unstable against perturbations that decrease D. Figure 1 shows an equilibrium detonation adiabat which does not satisfy the condition $d^2P/dV^2 > 0$, and two tangents to it passing through the initial point 1 and respectively through the tangency points 2 and 3.

If the solution of (3) for nonmonotonic heat release is not unique, then the question arises of the stability of the detonation mode against transition to another mode which is possible in accord with (3). We shall henceforth define "stability" in just this sense. The stability of the detonation front against a bending of its front and against propagation of a second detonation wave through shock-compressed matter was investigated in [6-9] and is not considered here.

We assume that the intensity of a shock wave of velocity satisfying (3) has become altered for some accidental reason, so that

$$D = D_1 + \delta D, \quad 0 < \delta D \ll D_1. \tag{5}$$

A chemical transformation process behind the wave front leads under the new condition to another heat release:

$$q_1 + \delta q = q_1 + \varphi'(D)\,\delta D,$$

to which, in accord with the tangency condition (2), corresponds a new value of D:

$$D = D_1 + \delta q \,/\, \psi'(D). \tag{6}$$

(φ' and ψ' are the derivatives of φ and ψ with respect to D. In accordance with the physical meaning, it is assumed that the functions φ and ψ are single-valued, continuous, and have first derivatives[3)].)

If the shock-wave velocity (5) is larger than given by (6), then the perturbed motion under consideration is an overcompressed detonation wave (Fig. 2, dashed shock adiabat), which, as is well known, attenuates and goes over into a detonation wave that satisfies (3). The reciprocal relation between velocities (5) and (6) denotes that the velocity of the shock wave is smaller than that of the detonation wave (Fig. 3). The shock wave will in this case become intensified by the chemical reaction (is always the case when a weak initiating shock wave toes out into the stationary detonation mode [2,10-12]). In other words, the perturbation will grow.

We analyze in similar form the development of a small perturbation that weakens the wave:

$$D = D_1 - |\delta D|.$$

The considered stability condition is expressed in more compact form as follows: The detonation wave propagating with velocity D_1 is stable (in the sense defined above) against small perturbations if

$$\psi'(D) > \varphi'(D), \quad D = D_1, \tag{7}$$

[2)]For a strong detonation wave in a gas with a constant adiabatic exponent γ, Eq. (2) has, as is well known, the form $q_{max} = D^2 / 2(\gamma^2 - 1)$.

[3)]In the case when the detonation adiabat has kinks that are connected, say, with phase transitions, it is necessary to consider the derivatives on both sides of the kink, and this does not involve any fundamental difficulties. This case, however, is rarely encountered and is not considered here.

and unstable[4)] when the inequality sign in (7) is reversed. If the first derivatives of φ and ψ are equal at the point D_1, i.e., $d\varphi/d\psi = 1$, then it is necessary to investigate derivatives of higher order. However, the relative probability of realizing such an equality simultaneously with (3) is equal to zero.

Let us prove two premises characterizing the properties of the solutions (3).

1) Assume that there are no kinks on the detonation adiabat, and that at the points D_i satisfying (3) we have

$$d\psi / d\varphi \neq 1. \quad (8)$$

It is stated that the maximum (D_{max}) and minimum (D_{min}) roots of Eq. (3) describes modes that are stable with respect to transitions into one another or into any other modes (3). (The quantities D_{max} and D_{min} exist, since q is bounded from above by energy considerations and $q \geq q^*$.)

We shall prove the stability of the solution D_{max} by contradiction. We assume that the solution D_{max} is unstable, i.e., an inequality inverse to (7) is satisfied at the point D_{max}. This means that at small positive increments δD we should have

$$\varphi > \psi|_{D=D_{max}+|\delta D|}. \quad (9)$$

But when D increases without limit the function ψ becomes infinite, whereas φ is bounded because the heat release is limited. It follows therefore that when the excess $D > D_{max}$ is sufficient, the inequality sign in (9) is reversed. This proves, by virtue of the continuity of φ and ψ, the existence of a solution of (3) when $D > D_{max}$, contradicting the initial condition and thereby proving the stability of D_{max}. The stability of D_{min} is proved in a similar manner.

2) Two neighboring values of the roots of Eq. (3), D_i and D_{i+1}, correspond under the restriction (8) to opposite characters of the stability, i.e., if the mode at point D_i is unstable (stable), then it is stable (unstable) at the point D_{i+1}. This property of the solutions of (3) follows directly from the stability criterion (7), and from the continuity and uniqueness of the functions φ and ψ (Fig. 4).

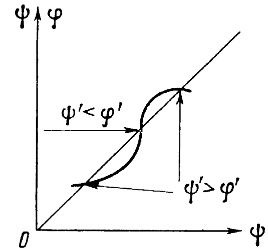

FIG. 4.

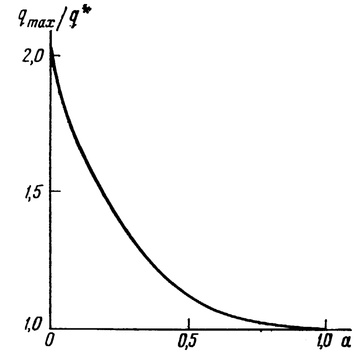

FIG. 5.

From properties 1) and 2) there follows, under the same minor restriction (8), that: a) Eq. (3) has an odd number of solutions; b) if the solution of (3) is unique, then it is stable; c) if Eq. (3) has three solutions, then the solutions with the maximum and minimum D_i are stable, and the third unstable.

2. Let us consider one simple model of nonmonotonic heat release. Let the transition to the equilibrium state behind the shock wave in an unbounded medium be characterized by heat release x and heat absorption y, so that the total heat released by the instant of time t is equal to $q = x - y$.

We denote the equilibrium values of q, x, and y by q^*. x^*, and y^* ($x^* > y^*$, since $q^* > 0$) and assume that the kinetics of the process is described by the equations

$$dx / dt = (x^* - x) / \tau_1, \quad dy / dt = (y^* - y) / \tau_2,$$
$$x = y = 0|_{t=0}, \quad x^* = \text{const}, \quad y^* = \text{const}, \quad x^* > y^*; \quad (10)$$

here τ_1 and τ_2 are the relaxation times, which in this model depend only on the shock-wave intensities, i.e., on the thermodynamic parameters directly behind the shock-wave discontinuity. The value of q_{max} depends on the ratio $a \equiv \tau_1/\tau_2$. After integrating (10) and carrying out simple calculations, we obtain for the extremum point

$$\frac{q_{ex}}{q^*} = 1 + \frac{b}{b-1}\left(\frac{b}{a}\right)^{1/(a-1)}\left(\frac{1}{a} - 1\right), \quad b \equiv \frac{x^*}{y^*}. \quad (11)$$

Analyzing the solution of Eqs. (10) together with (11), we can show that if a decreases in the region $1 < a < 0$, then $q_{max} = q_{ex}$ and increases monotonically from q^* to x^* with decreasing a. For all $a \geq 1$ the maximum heat release is attained in

[4)] A condition similar to (7) was used by Schall [13] in his analysis of the stability of a detonation in an unbounded medium. Schall defines a function similar to φ as having the meaning of the heat released in the region between the discontinuity and the tangency point. But in the investigation of the stability of the stationary mode it is necessary to consider perturbed motion, for which a tangency point does not necessarily exist, and the analog of φ which is defined verbally in [12] has no concrete meaning. In addition, even for the stationary mode in a bounded medium φ should be defined not as the heat release, but as the difference between the heat release and the losses at that instant when their time derivatives are equal [10]. We shall not deal here with other papers touching to one degree or another upon the question of stability of detonation with losses in bounded media.

the limit as $t \to \infty$ and is equal to q^*. (When $a > b$ the extremum determined by (11) corresponds to a minimum. The solutions (11) in the region $1 < a < b$ pertain to negative t and have no physical meaning.) The dependence of q_{max}/q^* on a when $b = 2$ is shown in Fig. 5.

For convenience in the calculations we shall characterize the intensity of the shock wave not by its velocity, but by the temperature T of its front[5], and assume that the dependence of a on T is determined by the Arrhenius law

$$a = A \exp [\mu E / RT] \qquad (12)$$

(μ—molecular weight of the initial material, R—gas constant, A - constant factor preceding the exponential). If $\tau_2 \approx$ const, then E has the meaning of the specific activation energy for an exothermal reaction. The model under consideration describes approximately the heat-release kinetics in the detonation of a mechanical mixture of an active substance with inert matter having a small coefficient of thermal expansion (or a large specific heat). An exothermal reaction (for example, monomolecular disintegration of the active substance) can then be described by a relation such as (12), and an endothermal reaction (decrease in pressure as a result of transfer of heat to an inert medium) is characterized by the temperature equalization time τ_2. This time is determined by the geometry of the system and by the thermal conductivity coefficient, and depends little on T.

Equations (11) and (12) express a connection of type (1) between the shock-wave intensity and the heat release.

The tangency condition establishes a second connection between T and q_{max}. In gases with a constant adiabatic exponent γ, the dependence of T on q_{max} for strong detonation waves is linear and is of the form

$$T = \mu q_{max}(\gamma - 1)(\gamma^2 - 1) / \gamma R.$$

This formula is obtained from the relation between T and the square of the velocity of a strong shock wave, and from the tangency conditions $D^2 = 2(\gamma^2 - 1) q_{max}$.

In the general case T and q_{max} are connected in a more complicated manner, but in first approximation, which certainly is sufficient for the model in question), we can assume

$$T = cq_{max} \equiv c\psi, \quad c = \text{const}. \qquad (13)$$

[5]The temperature and velocity of the front are connected by a unique relation, at any rate if $(\partial P/\partial T)_V > 0$.

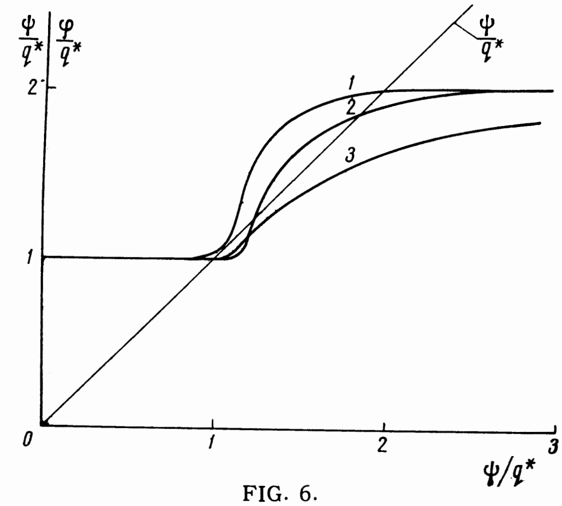

FIG. 6.

It assumed that the initial matter has a temperature $T_1 \ll T$.

Relation (13) constitutes, for the model in question, the concrete form of an equation of type (2), and together with (11) and (12) it makes up one equation (3) determining the values of q_i and the corresponding T_i and D_i for the detonation modes.

The solutions of (11)—(13) depend on the parameters A, b, and $K \equiv \mu E/Rcq^*$. The physical meaning of b is clear from the foregoing. The values of A and K are determined by the concrete mechanisms of the exothermal and endothermal reactions. For the discussed effect of nonuniqueness of the solution of (3), the most interesting variants are $A \ll 1$ and $K > 1$. When these inequalities are satisfied, there exist sufficiently broad ranges of shock-wave intensity at which $q_{max}/q^* > 1$ and $q_{max}/q^* = 1$.

Figure 6 shows plots of φ/q^* and ψ/q^* against the values of ψ/q^* determined by Eqs. (11)—(13) at certain values of A, b, and K. Curve 1 corresponds to $A = 3.2 \times 10^{-5}$, $b = 2$ and $K = 10$; curve 2 to $A = 9 \times 10^{-5}$, $b = 2$, and $K = 10$; and curve 3 to $A = 7 \times 10^{-3}$, $b = 2$, and $K = 10$. Solutions of Eq. (3) correspond to the points of intersection of the φ/q^* and ψ/q^* curves. It is seen from Fig. 6 that one stable solution with $q_{max}/q^* = 2$ and $q_{max}/q^* \approx 1$ is realized in variants 1 and 3. In variant 2 there are three solutions, two of which (with maximum and minimum q_{max}/q^*) are stable and the third unstable.

3. The properties of the number of detonation modes and their stability, established in Sec. 1, are actually valid also in the general case, i.e., when q_{max} depends not only on the shock-wave intensity, but also on the field of the gas dynamic quantities behind the shock-wave discontinuity. This statement will be proven if we succeed in

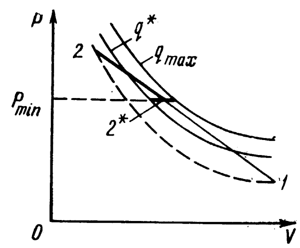

FIG. 7.

proving that in the general case there exists a certain single-valued function f(D) which coincides with φ(D) at all points D_i where (3) is stationary (the function $\varphi(D_i)$ has the same meaning as before also in the general case considered here, since the structure of the wave and q_{max} are determined uniquely by the wave velocity at the stationary points) and which characterizes, in full analogy with (7), the stable mode when the following inequality is satisfied

$$\psi'(D) > f'(D), \quad D = D_i \tag{14}$$

and the unstable mode when the opposite inequality holds.

Such a function exists and can be constructed in the following manner. If a continuous transition from the point 2 on the shock adiabat to the equilibrium state (Fig. 2) along the line 2—1, which characterizes the shock-wave velocity, is possible (overcompressed detonation wave or one satisfying the condition of tangency with q_{max}), the f(D) is equal to the maximum heat released in this process. But if such a transition is impossible, then f(D) is equal to the maximum heat released during the course of an irreversible chemical transformation from the point 2 along the line 2-1 to the point with the minimum value P_{min} (the point where the course of the irreversible reaction becomes incompatible with the requirement for the variation of P and V along the line 2-1) and further along the isobar P_{min} through the adiabat with heat release f(D) to the equilibrium state 2* (Fig. 7, thick line). Motion along the isobar proceeds either with a monotonic increase of volume, or with an increase followed by a decrease, depending on whether f(D) = q* or f(D) > q*. The function constructed in this manner is a single-valued function of the shock-wave velocity D, and coincides by definition with $\varphi(D_i)$ at all the points where (3) is stationary, i.e., at all the stationary points

$$f(D_i) = \psi(D_i). \tag{15}$$

To clarify the connection between (14) and the stability of the detonation wave, we assume (as in Sec. 1) that the intensity of the shock wave whose velocity D_i satisfies (15) and whose width from the front to the point of tangency is equal to l has increased accidentally by a small amount δD, with a corresponding small change in the gas dynamic quantities in the entire interval l, so that the resultant wave motion is quasistationary (stationary during the time $t > l/D$). The fact that we are considering a small perturbation of a special type does not limit the generality of the proof that follows. If the mode is stable against the given "broad" perturbation, it will be stable also with respect a narrower perturbation having the same amplitude. On the other hand, to prove the instability of a mode it is sufficient to prove instability against an arbitrary small perturbation.

If we have for the considered perturbed motion

$$f(D) > \psi(D), \tag{16}$$

then this means that not all the heat is released in the new quasistationary discontinuity. A certain part of the heat is released in the nonstationary wave (the total heat release will exceed ψ(D) but will not necessarily equal f(D)), leading to an increase of pressure in the rarefaction wave[6] and, in final analysis, to a new intensification of the wave. The detail picture of the buildup of the perturbation can be quite complicated, but does not differ in essence from what occurs when a weak initiating shock wave goes over into the normal detonation mode with monotonic heat release, a situation investigated in sufficient detail both experimentally and theoretically ([2,10,11] and others).

It is also easy to verify that if

$$f(D) < \psi(D), \tag{17}$$

then the resultant perturbation is an overcompressed detonation wave, i.e., the perturbation attenuates. We can prove similarly stability against a small decrease of the wave intensity. With this, unlike the case $\delta D > 0$, a stable mode corresponds to the inequality (16) and an unstable one to (17). The stability of the D_i mode against small perturbations of arbitrary sign is expressed in unified fashion in the form of the inequality (14), q.e.d. The restriction (8), with which the results of Sec. 1 were obtained, is formulated for the general case in analogy with (8) except that φ is replaced by f.

[6]The stationarity requirement leads in this case to a velocity discontinuity and to the occurrence at the point P_{min} of a shock wave moving in the direction of the detonation wave front.

DISCUSSION OF RESULTS AND CONCLUSIONS

In the case of nonmonotonic heat release, even in an unbounded medium, there can be not one but several detonation modes. Subject to the minor restriction (8), the total number of modes is odd. Among them are modes that are stable and unstable against transformation into one another under small perturbations. The number of stable modes exceeds by unity the number of unstable ones.

The model considered in Sec. 2 should be regarded only as an illustration of the general laws developed above. For concrete detonation processes, the form of the dependences of f and ψ will be other, but the qualitative features of the phenomenon remain the same.

If the equations of state of the initial matter and of the products are known, as well as the kinetics of the exothermal and endothermal reactions, then the problem can always be solved quantitatively. On the other hand, we can hope that an analysis of the corresponding experimental data, with allowance for the foregoing, will yield new information on the kinetics of physico-chemical processes in detonation waves.

Nonmonotonic heat release in a detonation wave is a relatively rare phenomenon. It must be noted, however, that the foregoing analysis of the number and stability of the detonation modes is relevant also for a bounded medium with monotonic heat release, in which the analog of heat absorption is lateral dispersion of the detonation products [10]. This problem will be considered separately.

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Translated by J. G. Adashko
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