GENERALIZED SHOCK HUGONIOT OF CONDENSED SUBSTANCES

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It is shown that in order to predict the shock Hugoniot of any substance up to a compression ratio equal to two it is sufficient to know the initial density and the initial compressibility. The possibility of finding a priori the equations of state of nonporous mixtures of two substances, porous samples, and solutions is discussed.

1. Individual substances. A knowledge of the shock Hugoniots of condensed substances is required in order to solve a whole series of scientific and technical problems of high-pressure physics. The experimental determination of the curves is so laborious and the ratio of the number of compounds studied to those that remain to be investigated is so small that any attempt to find a method of constructing shock Hugoniots a priori, using as little information as possible about the initial state of the substance, would be welcome. One such method follows from a consideration of the compression of the substance in weak shocks, which in the first approximation are assumed to be isentropic.

The expression for the propagation velocity of a weak shock can be written in the form

$$D = V_0\left(\frac{p-p_0}{V_0-V}\right)^{1/2} \approx \left[\left(\frac{\partial p}{\partial \rho}\right)_S + \frac{1}{2}\left(\frac{\partial^2 p}{\partial \rho^2}\right)_S \Delta\rho\right]^{1/2} \approx c_0 + Bu, \qquad c = \left[\left(\frac{\partial p}{\partial \rho}\right)_S\right]^{1/2}$$

Here, D is the shock wave velocity; u is the particle velocity behind the wave front; c is the volume speed of sound; p, ρ, and s are the pressure, density, and entropy respectively (the ubscript 0 relates to the initial state). The coefficient B is defined as

$$B = \frac{1}{4}\left[2 + \rho\left(\frac{\partial^2 p}{\partial \rho^2}\right)_S\left(\frac{\partial p}{\partial \rho}\right)_S^{-1}\right] = \frac{1}{2}\left[1 + \left(\frac{\partial \ln c}{\partial \ln \rho}\right)_S\right] \tag{1.2}$$

An analysis made by the authors on the basis of the data of ultrasonic experiments has shown that as $V \to V_0$ for most metals, excluding the alkali metals, and salts the value of the coefficient B is close to 1.5, and for organic liquids to 2.0.

Thus, for all substances belonging to a given group the initial sections of the shock Hugoniots in the dimensionless coordinates $\theta = D/c_0$, $\mu = u/c_0$ should coincide. The formal construction of the actual shock Hugoniots in θ, μ coordinates [1, 2] has shown that this law (correspondence of the curves for substances belonging to a particular group) is is satisfied over almost the entire range of pressures investigated.*

The θ (μ) relations obtained in [1, 2] can be represented analytically in the form

$$\theta = 1 + 1.5\mu - 0.05\mu^2 \quad \text{or} \quad D = c_0 + 1.5u - 0.05\ u^2/c_0 \tag{1.3}$$

for inorganic salts and metals (except alkali metals) and

$$\theta = 1 + 2.0\mu - 0.1\mu^2 \quad \text{or} \quad D = c_0 + 2.0u - 0.1\ u^2/c_0 \tag{1.4}$$

for organic liquids.

A similar analysis of the experimental data for alkali metals [3, 4] leads to the expression

$$\theta = 1 + 1.1\mu + 0.04\mu^2 \quad \text{or} \quad D = c_0 + 1.1u + 0.04u^2/c_0 \tag{1.5}$$

Thus, if the speed of sound c_0 in the substance is known, the shock Hugoniot can be constructed a priori from relations (1.2–1.5). As an example, the solid lines in Fig. 1 represent the calculated D(u) relations for copper (Cu,

*For most substances the compression ratio $\sigma = \rho/\rho_0$ does not exceed two at the pressures reached. Substances that experience phase transitions during shock compression were not considered.

c_0 = 3.98 km/sec [5]), tin (Sn, c_0 = 2.76 km/sec [5]), carbon tetrachloride (CCl_4, c_0 = 0.938 km/sec [6]), and benzene (C_6H_6, c_0 = 1.326 km/sec [6]), together with the experimental data from the following sources:

1	2	3	4	5	6	7	8	9	10	11	12	13
[7]	[8]	[5]	[9]	[8]	[10]	[5]	[11]	[12]	[13]	[10]	[12]	[13]

It is clear from the graphs that the experimental data of different authors are closely grouped around the calculated curves for each substance.

The speed of sound c_0 for solids can be determined from the data on the isothermal compressibility of the substance or in terms of the elastic and shear moduli. For most organic liquids and single crystals the value of c_0 can be calculated from Rao's rule [14, 2] (simply on the basis of a knowledge of the structural formula of the compound and its initial density).

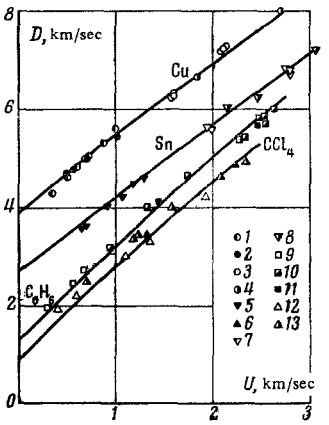

Fig. 1

In practical calculations it is often necessary to construct the shock Hugoniots of mixtures of two or more substances. Consider the following cases.

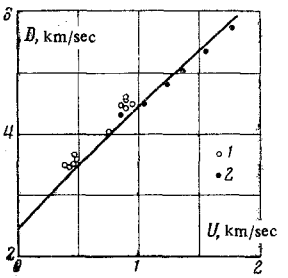

Fig. 2

2. Mixture of two condensed substances. The shock Hugoniot of a nonporous mixture of two solid substances (or a liquid and a solid) can be constructed under the following assumptions: a) the pressure in both components at the wave front is the same; b) at a given pressure the specific volume of each component satisfies the equation of its shock Hugoniot [15]. The latter assumption is associated with the assumption of the absence of heat transfer between the components. Then the expression for the specific volume of the mixture V_{12} can be written in the form

$$V_{012} = \alpha V_{01} + (1 - \alpha) V_{02} \tag{2.1}$$

in the initial state and

$$V_{12} = \alpha V_1 + (1 - \alpha) V_2 \tag{2.2}$$

at the shock front, where the subscript 1 relates to the first component, and the subscript 2 to the second, while α is the mass fraction of the first component. Equality of the pressures implies

$$p_{12} = p_1 = p_2$$

Applying the known relation of shock wave theory

$$u^2 = p\,(V_0 - V) \tag{2.4}$$

to the mixture and to each component individually, using Eqs. (2.1) and (2.2) we obtain

$$V_{012} - V_{12} = \frac{u_{12}^2}{p} = \alpha\,(V_{01} - V_1) + (1-\alpha)(V_{02} - V_2) = \alpha\,\frac{u_1^2}{p} + (1-\alpha)\,\frac{u_2^2}{p} \tag{2.5}$$

or

$$u_{12}^2 = \alpha u_1^2 + (1-\alpha)u_2^2$$

Knowing the shock Hugoniots of the components, using the latter expression we can construct that of the mixture. An example, the solid curve in Fig. 2 represents the calculated shock Hugoniot of a mixture of TNT and RDX in proportions of 40:60 by weight (ρ_0 = 1.72 g/cm^3) together with the experimental data of [16] and [17] (points 1 and 2, respectively).

The shock Hugoniots of TNT with ρ_0 = 1.65 g/cm^3 and RDX with ρ_0 = 1.80 g/cm^3 were written (from (1.4)) in the respective form

$$D = 2.2 + 2u - 0.046u^2, \qquad D = 2.64 + 2u - 0.038u^2 \tag{2.6}$$

The values of the speeds of sound in TNT and RDX (2.2 and 2.64 km/sec) were calculated in accordance with Rao's rule. They are in good agreement with the values of c_0 obtained from data on the isothermal compressibility of these substances at near-maximum density (for TNT, c_0 = 2.2 km/sec at ρ_0 = 1.63 g/cm^3; for RDX c_0 = 2.65 km/sec at ρ_0 = 1.8 g/cm^3 [2]).

Clearly, the agreement between the calculated and the experimental results is fairly good.

3. Porous substances. The experimental data on the shock compression of porous substances can be described on the assumption that the continuous skeleton of the porous sample is compressed as in the monolithic material, while the volume of the cavities behind the shock front is reduced by a factor of seven. The formula for the effective mass velocity behind the wave front (u_*) in a porous material has the forms

$$u_*^2 = u_1^2\left[1 + 0.857\left(\frac{\rho_{01}}{\rho_{0*}} - 1\right)\frac{P_1}{\rho_0 u_1^2}\right] \tag{3.1}$$

Here, $p_1 = p_*$, the subscript 1 relates to the monolithic substance, the asterisk subscript refers to the porous substance. A comparison of the calculated and experimental results in the case of sodium chloride of varying initial density is presented in Fig. 3. Curves a, b, c, and d correspond to initial sample densities of 2.16 (single crystal), 1.43, 1.23, and 1.0 g/cm^3. The experimental data were taken from [18].

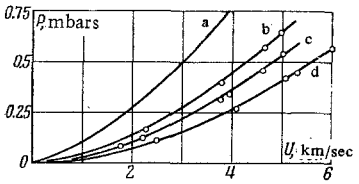

Fig. 3

The experimentally observed propagation velocities of the wave disturbance in the porous sample can also be calculated from the formula

$$\frac{\rho_0}{D_*} = \frac{\rho_0 - \rho_{0*}}{D_1} + \frac{\rho_{0*}}{2u_1} \tag{3.2}$$

proposed in [19].

4. Solutions. Whereas a mixture of two solids is a heterogeneous system, in which each component is present in the form of small particles of the order of 10 μ (occasionally 1 μ) and above, a mixture of two mutually soluble liquids is a homogeneous system with molecular mixing of the components. Accordingly, a solution is always regarded as a certain new liquid. It is natural to assume that the dynamic compressibility of a solution will be described by the generalized shock Hugoniot for liquids (Eq. (1.4)). Then in order to construct the shock Hugoniot of a solution it is sufficient to know the speed of sound in it. If experimental data are not available, the value of c_0 in a solution can be calculated from a number of empirical relations. For example, when the speeds of sound are known for the individual components, it is possible to use the equation recommended in [20],

$$c_{012} = c_{01}c_{02}\frac{\alpha\rho_{02} + (1-\alpha)\rho_{01}}{\alpha\rho_{02}c_{02} + (1-\alpha)\rho_{01}c_{01}} \tag{4.1}$$

where α is the mass fraction of the first component.

If the speeds of sound of the components are not known, the value of c_0 in the solution (i.e., c_{012}) can be calculated from Rao's rule, which in the case of a mixture of two liquids is written in the form [21]

$$c_{012}^{1/3} = (n_1R_1 + n_2R_2)\left(\frac{n_1M_1}{\rho_{01}} + \frac{n_2M_2}{\rho_{02}}\right)^{-1} \tag{4.2}$$

Here, n_1 and n_2, M_1 and M_2, R_1 and R_2 are the mole fractions, molecular weights, and so-called molecular speeds of sound of the first and second components, respectively. The value of R for each component is calculated from the formula $R = \sum_i a_i k_i$, where k_i is the number of chemical bonds of a given type in the substance, and a_i the corresponding bond increment. Values of a_i have been tabulated for most chemical bonds [2, 6]. The difference between the calculated and experimental values of the speeds of sound for binary solutions of normal or weakly associated liquids is not more than 1%, and in the case of strongly associated liquids (for example, aqueous solutions) not more than 10%.

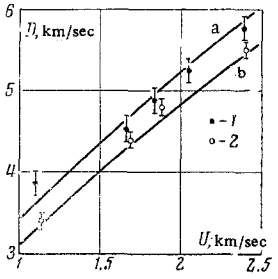

Fig. 4

In order to verify the correctness of using the generalized shock Hugoniot for liquids to construct the shock Hugoniots of solutions, we experimentally determined the Hugoniots of two mixtures: water and acetone 50:50 (ρ_0 = = 0.876 g/cm^3) and benzene and carbon tetrachloride 60:40 (ρ_0 = 1.07 g/cm^3). To record the Hugoniots we used the reflection method described in detail in [5, 8, 9, etc.]. In Fig. 4 the results of the experiments are compared with the shock Hugoniots of the investigated mixtures calculated from Eq. (1.4). Curve a and points 1 relate to the water-acetate solution, curve b and points 2 to the benzene-carbon tetrachloride solution. Each point is the mean of five experiments: the deviation from the mean does not exceed 150 m/sec. The speed of sound in the acetone-water mixture is 1.5 km/sec [22], and in the benzene-carbon tetrachloride mixture 1.16 km/sec [23], so that their shock Hugoniots have the form

$$D = 1.5 + 2u - 0.07u^2, \qquad D = 1.16 + 2u - 0.085u^2 \tag{4.3}$$

Clearly, in this case, too, the calculated and experimental results are in good agreement. In the case of nitromethane-acetone solutions the agreement between experiment [24] and calculation is not quite so good, but still perfectly satisfactory.

Thus, for individual solids and liquids, for mixtures of two solids or two liquids, and for porous substances that do not experience phase transformations during shock compression the shock Hugoniot can be constructed a priori from the generalized curve without performing experiments. For this it is sufficient to know the initial value of the volume

speed of sound in the monolithic substance.

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