

SOME PROPERTIES OF COMPRESSIONAL WAVES IN LENNARD-JONES AND DEVONSHIRE LIQUIDS

II. SHOCK WAVE

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Summary

This paper describes some theoretical calculations of the thermodynamic changes which occur when a condensed substance is compressed by a shock wave from an explosion. It is assumed that the material is a simple molecular fluid (or a plastic solid) obeying Lennard-Jones and Devonshire's equation of state.

The calculations have been applied to single and colliding shock waves, to shocks generated in a precompressed material, and to the adiabatic expansion of a material from a shocked state. The results are in good qualitative agreement with the experimental data where these exist. In addition they suggest possible ways of extending the scope and usefulness of shock wave experiments.

I. INTRODUCTION

In Part I of this series (David and Hamann 1961) we computed the speed of sound in liquids obeying Lennard-Jones and Devonshire's (1937) equation of state. The present paper describes similar calculations of the properties of strong shock waves.

The purpose of the work has been to predict the kinds of conditions which may exist in compressional waves launched by explosions. It is known that if a high explosive is detonated in contact with an inert solid or liquid it drives a steep-fronted shock wave into the material and that the pressure behind the shock front may be as great as a million atmospheres for a few millionths of a second. It is possible to measure the pressure, the density, and even some of the chemical properties of shocked materials (see, for instance, Hamann 1960*a*). But no means has yet been devised for measuring the transient temperature. Instead this is estimated by combining a postulated equation of state with the Rankine-Hugoniot shock relations (see, for instance, Hirschfelder, Curtiss, and Bird 1954; Hamann 1960*a*). In the present calculations we have employed Lennard-Jones and Devonshire's (LJD) equation of state in this way. We have used it to calculate (i) the properties of plane shock waves in classical monatomic liquids; (ii) the corresponding properties in a "quantal" liquid; (iii) the conditions after adiabatic expansion from a shocked state; (iv) the conditions

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at the head-on collision of two plane shocks; (v) the initial shock conditions for liquid argon in contact with the explosive 60/40 RDX/TNT; (vi) shock conditions in precompressed liquids.

Since we began this work, Fickett and Wood (1960) have published the results of some LJD calculations of shock properties in liquid argon. Their method was rather more empirical than ours because it made use of the experimental density and energy of unperturbed argon. They employed the LJD theory at high pressures where they believed it right and the experimental data at low pressures where it appeared to be wrong.† For their particular purpose this was a justifiable procedure, but here we have preferred to be consistent and use the theoretical LJD equation throughout.

II. DEFINITIONS OF SYMBOLS USED

Most of the following symbols have been defined more fully in earlier papers (Hamann 1960*b*; David and Hamann 1961).

The subscript zero denotes properties characteristic of the molecules. Asterisks indicate quantities expressed in molecular units.

- N, Avogadro's number,
- k, Boltzmann's constant,
- h, Planck's constant,
- ϵ_0 , depth of the energy well in the Lennard-Jones 12:6 intermolecular potential,
- r_0 , radius of the energy well,
- m , molecular mass,
- M , molar mass ($=Nm$),
- Λ^* , de Boer's (1948) quantal parameter ($=2^{1/6}h/r_0(m\epsilon_0)^{1/2}$),
- C_V , specific heat per mole at constant volume,
- C_V^* , C_V/Nk ,
- E , internal energy per mole,
- \hat{E} , internal energy per unit mass,
- E^* , $E/N\epsilon_0$,
- P , pressure,
- P_0 , $2^{1/2}\epsilon_0/r_0^3$,
- P^* , P/P_0 ,
- S , entropy per mole,
- S^* , S/Nk ,
- T , absolute temperature,
- T_0 , ϵ_0/k ,
- T^* , T/T_0 ,
- u , velocity of sound,
- u_0 , $(\epsilon_0/m)^{1/2}=(N\epsilon_0/M)^{1/2}$,
- u^* , u/u_0 ,

† During the course of our calculations it has become increasingly apparent that the LJD theory is really more appropriate to the solid state than to the liquid. Barker's (1960, 1961*a*) "tunnel" model is a much better one for liquids, and we hope to apply it later in some shock calculations.

- U , shock velocity,
 U^* , U/u_0 ,
 V , volume per mole,
 \hat{V} , volume per unit mass,
 V_0 , $Nr_0^3/2^{3/2}$,
 V^* , V/V_0 ,
 w , flow velocity,
 w^* , w/u_0 .

The following subscripts are applied to shock properties :

- no subscript, indicates the initial conditions ahead of a shock wave,
 subscript 1, denotes the conditions behind a single shock,
 subscript 2, denotes the conditions after the interaction of one shock with another, or with a rarefaction wave.

III. DETAILS OF THE CALCULATIONS

(a) General

A shock wave is a steep-fronted compression wave which causes very abrupt changes in the pressure, density, and temperature of the material through which it passes. The existence of extreme gradients in these properties through the shock front means that the compression is thermodynamically irreversible and non-adiabatic. Nevertheless there exist some rigorous relations between the conditions ahead of and behind the shock front. They are based on the principles of conservation of mass, momentum, and energy, and they are usually known as the Rankine-Hugoniot relations† (Rankine 1870; Hugoniot 1887, 1889). If the fluid ahead of the shock wave is stationary, the relations are

$$U_1 = \hat{V}[(P_1 - P)/(\hat{V} - \hat{V}_1)]^{1/2}, \quad (1)$$

$$w_1 = [(P_1 - P)(\hat{V} - \hat{V}_1)]^{1/2}, \quad (2)$$

$$\hat{E}_1 - \hat{E} = \frac{1}{2}(P_1 + P)(\hat{V} - \hat{V}_1), \quad (3)$$

where P , \hat{V} , and \hat{E} are the pressure, volume per unit mass, and internal energy per unit mass in the initial state, and P_1 , \hat{V}_1 , \hat{E}_1 are the corresponding properties of the shocked fluid. U_1 denotes the velocity of the shock front and w_1 the velocity of flow of the material behind the front. In the limit of low amplitude shock waves $P_1 - P$, $\hat{V} - \hat{V}_1$, w_1 , and $\hat{E}_1 - \hat{E}$ all approach zero and U_1 approaches the normal velocity of sound, $u = \hat{V}(-\partial P/\partial \hat{V})^{1/2}$.

For a Lennard-Jones and Devonshire liquid the Rankine-Hugoniot relations can be rewritten in molecular units (defined in Section II) thus

$$U_1^* = V^*[(P_1^* - P^*)/(V^* - V_1^*)]^{1/2}, \quad (4)$$

$$w_1^* = [(P_1^* - P^*)(V^* - V_1^*)]^{1/2}, \quad (5)$$

$$E_1^* - E^* = \frac{1}{2}(P_1^* + P^*)(V^* - V_1^*). \quad (6)$$

† This title is misleading: formulae equivalent to (1) and (2) were first derived by Stokes (1848).

The last of these formulae is particularly important because it defines all the possible P_1^* , V_1^* points which can be reached in a single shock compression from the initial conditions P^* , V^* . This follows from the fact that $E_1^* - E^*$ is related to P_1^* , V_1^* by the LJD equation of state as well as by the Rankine-Hugoniot relation. It is therefore possible to eliminate $E_1^* - E^*$ and obtain a specific relationship between P_1^* and V_1^* provided that P^* and V^* are specified. The locus of points obtained in this way will be referred to as a "Hugoniot" compression curve, and P^* , V^* will be called the "starting point".

(b) *Single Shock Compression of a Classical Liquid from $P^* \approx 0$*

We shall consider first a set of starting points corresponding to an LJD liquid which is either at atmospheric pressure or under its own vapour pressure. In these circumstances P^* is very small and can be considered to be zero. The LJD theory then gives a unique relationship, which we have already derived (David and Hamann 1961), between V^* and the reduced temperature T^* .

We can trace the Hugoniot curve from any particular starting point in the following way. We first suppose the fluid to be compressed isothermally from V^* to a smaller volume V_1^* . This generally raises its internal energy, although not sufficiently to satisfy equation (6). We then imagine the fluid to be heated at constant volume until it reaches a temperature T_1^* at which the LJD energy *does* equal the Hugoniot energy. This point (P_1^* , V_1^* , T_1^*) must lie on the Hugoniot curve starting at ($P^*=0$, V^* , T^*). By repeating the operation for a range of final volumes we can find the general form of the Hugoniot curve.

In principle the calculations can be performed automatically on a computer, but in our work we have used the existing LJD compilations of Wentorf *et al.* (1950), together with suitable interpolation formulae.† We have calculated Hugoniot curves from seven starting temperatures in the range $T^*=0.7$ to 1.0, and, for comparison, worked out the corresponding isothermal and adiabatic compression curves from the same starting points. We have also estimated some of the thermodynamic properties of the fluid along the Hugoniot curve, again by interpolation in the tables of Wentorf *et al.* (1950).

(c) *Shock Compression of a Quantal Liquid from $P^* \approx 0$*

Lennard-Jones and Devonshire's theory is based on classical statistical mechanics, which are known to be inadequate for light liquids such as helium, hydrogen, and neon. For these it is necessary to use a more general equation of state involving de Boer's (1948) quantal parameter Λ^* . In earlier papers (Hamann 1952, 1957; David and Hamann 1953) we have derived an equation of this kind by applying a quantum correction to the classical theory. We have now used this equation to compute a single Hugoniot curve for a quantal liquid ($\Lambda^*=1$) starting from $P^*=0$, $T^*=0.75$.

† Dr. W. Fickett and Dr. W. W. Wood of the Los Alamos Scientific Laboratory have recently confirmed our results for liquid argon (Fig. 2) by automatic calculations on the IBM 704 computer (personal communication).

(d) Conditions after Adiabatic Expansion from a Shocked State

After the passage of a shock wave through a material the substance expands into its surroundings. This expansion occurs adiabatically because shock waves of rarefaction are forbidden by thermodynamics (Hirschfelder, Curtiss, and Bird 1954, p. 789). We can therefore follow the course of the expansion of a shocked LJD fluid by tracing points of constant entropy starting from a Hugoniot point $(P_1^*, V_1^*, T_1^*, S_1^*)$ and moving to a series of points of lower pressure and larger volume $(P_2^*, V_2^*, T_2^*, S_2^*=S_1^*)$. In this way we have traced adiabats from several points on the Hugoniot based on the starting point $P^*=0, T^*=0.75$.

For reasons to be discussed in the next paragraph, it is sometimes important to know the contribution which the expansion makes to the forward flow velocity of the material. This is given by the Riemann integral

$$w_2^* = \int_{P_1^*}^{P_2^*} \left(-\frac{\partial V^*}{\partial P^*} \right)_{S^*} dP^*, \quad (7)$$

where the integration is carried out along the expansion adiabat (see, for instance, Rice, McQueen, and Walsh 1958). The total flow velocity in the direction of the original shock is then $w_1^* + w_2^*$. In evaluating (7) we have found it convenient to fit the adiabat to an empirical equation of the form used by Tait (1900), and then perform the integration numerically by means of Simpson's rule.

If the material expands into a vacuum, then the final pressure is zero and the corresponding value of $w_1^* + w_2^*$ is the velocity, in molecular units, of the free surface of the material after shock acceleration. If on the other hand the material expands into another substance, say air, it generates a shock wave in the second substance and the boundary conditions require that the absolute pressure P_2 and velocity $w_1 + w_2$ at the interface must lie on the pressure/flow-velocity curve for the second material. If this Hugoniot relation is known, as it is for ideal gases, then the interfacial conditions can be worked out. These conditions are important because they determine whether or not the original material will vaporize after the passage of a shock wave. In the present calculations we have considered the expansion of a shocked LJD fluid into air, which we have assumed to obey the ideal gas relationship

$$w_1 = (P_1 - P) \left(\frac{5\hat{V}}{P + 6P_1} \right)^{\frac{1}{2}}. \quad (8)$$

(e) Conditions at the Head-on Collision of Two Plane Shocks

It is worthwhile to consider the conditions which exist after the head-on collision of two plane shock waves in an LJD fluid. We shall designate these conditions by the subscript 2, and the conditions in one of the initial shocks by the subscript 1. The Rankine-Hugoniot relations (4)–(6) can then be rewritten

$$U_2^* = -V_1^* [(P_2^* - P_1^*) / (V_1^* - V_2^*)]^{\frac{1}{2}}, \quad (9)$$

$$w_2^* = -[(P_2^* - P_1^*)(V_1^* - V_2^*)]^{\frac{1}{2}}, \quad (10)$$

$$E_2^* - E_1^* = \frac{1}{2}(P_2^* + P_1^*)(V_1^* - V_2^*), \quad (11)$$

where U_2^* and w_2^* are velocities *relative to the velocity of flow in the original shock 1*. The *absolute* shock and flow velocities after collision are thus $w_1^* + U_1^*$ and $w_1^* + w_2^*$. Formula (11) can be applied in the same way as (6) to trace the course of the final compression curve from the starting point (P_1^*, V_1^*, T_1^*) . In the present work we have calculated the properties of secondary shocks based on three starting points, all on the primary Hugoniot centred on the unperturbed state $P^*=0$, $V^*=1.0503$, $T^*=0.75$.

An interaction of special interest is the head-on collision of two *equal* shock waves, which is mathematically equivalent to the total reflection of a single shock at a rigid boundary. Such a collision must reduce the absolute flow velocity to zero and the final conditions can be found by imposing the restriction

$$w_2^* = -w_1^*. \quad (12)$$

Interactions of this kind will be discussed in Section IV (d).

(f) *Shock Conditions for Liquid Argon in Contact with the Explosive 60/40 RDX/TNT*

In Section III (c) we considered the transmission of a shock wave from an LJD fluid into another material. We shall now examine the converse process of transmitting a shock from a high explosive into an LJD fluid. Again the boundary conditions require that the pressure and flow velocity be continuous across the interface. These conditions can be satisfied by the reflection of either a compressive shock or a rarefaction wave back into the explosive products.

It is, of course, necessary to match the *absolute* pressures P and flow velocities w at the interface, not the reduced quantities P^* and w^* . This means that we must sacrifice generality and specify the materials of the explosive and the fluid. We have selected the explosive 60/40 RDX/TNT both because it is widely used in experimental work and because Deal (1958) has made a thorough experimental study of the propagation characteristics of shock waves and rarefaction waves in its products of explosion. We have chosen argon as the LJD liquid and transformed our theoretical LJD results into absolute units by means of the following factors derived from the second virial coefficient of gaseous argon (Hamann 1960b).

$$\begin{array}{ll} P = P^* \times P_0 & P_0 = 415 \text{ atm,} \\ V = V^* \times V_0 & V_0 = 24.0 \text{ cm}^3/\text{mole,} \\ T = T^* \times T_0 & T_0 = 120 \text{ }^\circ\text{K,} \\ \left. \begin{array}{l} U = U^* \times u_0 \\ w = w^* \times u_0 \end{array} \right\} & u_0 = 158 \text{ m/sec.} \end{array}$$

The conditions at the interface are given by the point of intersection on a P/w diagram of the Hugoniot curve for forward-going shocks in argon and the curve for backward-going shocks and rarefactions in the explosive products (cf. Fig. 5).

(g) *Shock Conditions in Precompressed Liquids*

It is not difficult to repeat the calculations of Section III (b), starting not from pressures near zero but from quite high pressures. We have made a few calculations of this kind in order to determine the effects of precompression on

the final shock conditions in LJD fluids. In particular, we have estimated the shock properties of precompressed argon in contact with 60/40 RDX/TNT (cf. Section III (f)).

IV. RESULTS AND DISCUSSION

(a) *The Properties of Plane Shock Waves in Classical LJD Liquids*

Figure 1 illustrates the results of some of our calculations of Hugoniot curves for classical LJD liquids. It will be seen that the pressure rises much more rapidly with decreasing volume than it does under isothermal or adiabatic conditions. This is a reflection of the fact that a shock wave always increases the entropy of the material through which it is travelling (Hirschfelder, Curtiss, and Bird 1954, p. 789) and so raises its temperature above the value that would be reached in adiabatic (isentropic) compression over the same volume interval.

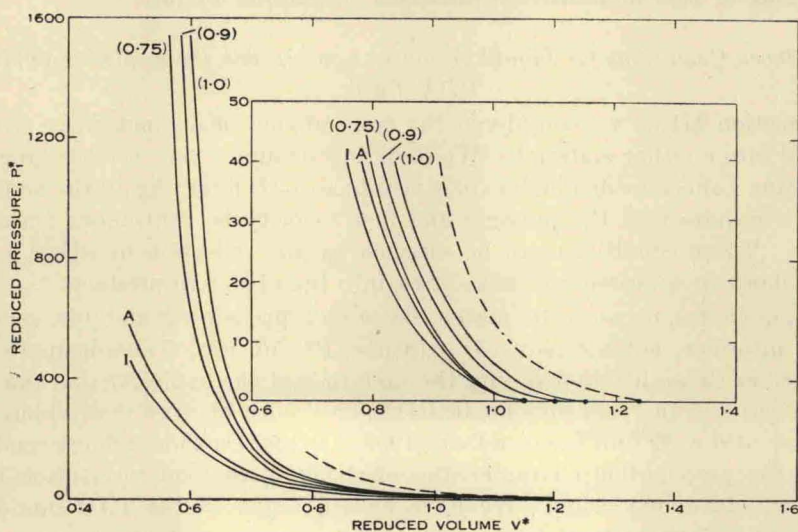


Fig. 1.—Calculated shock Hugoniot curves for LJD fluids. The compressions start at $P^*=0$ and at values of T^* indicated by the numbers in brackets. The curves labelled *I* and *A* are the isotherm and adiabat based on the starting point $P^*=0$, $T^*=0.75$. The dotted curve is the Hugoniot for a quantal liquid ($\Lambda^*=1$) starting from $P^*=0$, $T^*=0.75$.

Table 1 lists some of the thermodynamic properties of an LJD liquid along the Hugoniot based on the starting point $P^*=0$, $T^*=0.75$.

Several points emerge from these results. First, the relationship between the increase in temperature and the shock pressure is accurately described by the simple formula

$$T_1^* - T^* = 0.0198(P_1^*)^{1.21}, \quad (13)$$

which is close to being a linear function. In this connection it is significant that Rice and Walsh (1957) concluded from explosive shock experiments on water that the temperature was "almost linear in pressure". For an ideal gas it would be exactly linear, in the limit of very strong shocks.

TABLE I

THERMODYNAMIC PROPERTIES OF A CLASSICAL LJD FLUID UNDER SHOCK COMPRESSION, STARTING FROM THE LIQUID STATE AT $P^*=0$, $T^*=0.75$, $V^*=1.0503$

The symbols are defined in Section II

Pressure	P_1^*	0	3.007	22.32	123.7	371	1546
Volume	V_1^*	1.0503 (= V^*)	0.9899	0.8485	0.7071	0.6364	0.5657
Temperature	T_1^*	0.750	0.881†	1.605	7.202	26.31	144.9
Energy	E_1^*	-6.063	-5.972	-3.811	+15.16	+70.5	+368
Specific heat	$(C_V)_1$	2.577	2.653	2.710	2.724	2.499	2.248
Entropy	S_1^* ‡	0	0.00	0.50	3.35	5.95	9.33
Shock velocity	U_1^*	6.47	7.41	11.04	19.94	31.44	59.3
Flow velocity	w_1^*	0	0.426	2.122	6.51	12.39	27.4
Velocity of sound	u_1^*	6.47	8.73	11.71	21.8	29.7	58.3

† All the temperatures to the right of this point are above the critical temperature for the liquid state ($T_c^*=1.3$).

‡ The listed values are relative to those at the starting point.

Secondly, there is a nearly linear relationship between the flow velocity and the shock velocity. This agrees with McQueen and Marsh's (1960) conclusions from measurements of these velocities in explosively shocked metals, and with Rice and Walsh's (1957) data for water.† The relationship would be exactly linear for very strong shock waves in a perfect gas.

Thirdly, the speed of sound u always exceeds the flow velocity w , which means that the flow is subsonic over the range of compressions considered. On the other hand, although the speed of sound is slightly greater than the shock velocity U at low pressures, it becomes less than U at high pressures. This is exactly the behaviour which Rice and Walsh (1957) have found in experiments on water and which McQueen and Marsh (1960) have observed in some shocked metals. In an ideal gas u may be either less or greater than w , and it is always less than U .

It seems from these comparisons that the LJD theory gives at least a qualitative description of the properties of shock waves in condensed materials. It is more difficult to test the theory quantitatively because of the paucity of good experimental data for liquids simple enough to conform to the LJD model. The theory assumes that the molecules of the material are non-polar and effectively spherical, and it is thus most appropriate to the condensed inert gases. Of these, only argon has been studied under shock conditions. Dapoigny, Kieffer, and Vodar (1955) have made a few X-ray determinations of the density of argon at shock pressures up to 72 000 atm. There are reasons for believing that their results may be suspect (Rice, McQueen, and Walsh 1958, p. 28) but in the absence of any other data it is worthwhile to compare them with the corresponding

† A plot of U against w from Rice and Walsh's data actually shows *two* straight lines, joined at about 120 000 atm. Altshuler, Bakanov, and Trunin (1958) believe that the discontinuity arises from the partial freezing of water at that pressure.

theoretical LJD Hugoniot curve. This comparison is made in Figure 2, where it will be seen that the agreement between the LJD curve and the experiments is not remarkably good: the LJD model consistently underestimates the specific volume. However, we should emphasize that our entire calculations involve only one experimental quantity, the second virial coefficient of gaseous argon used to derive the molecular units listed in Section II. The comparison in Figure 2 is therefore a very severe test of a long chain of reasoning linking the

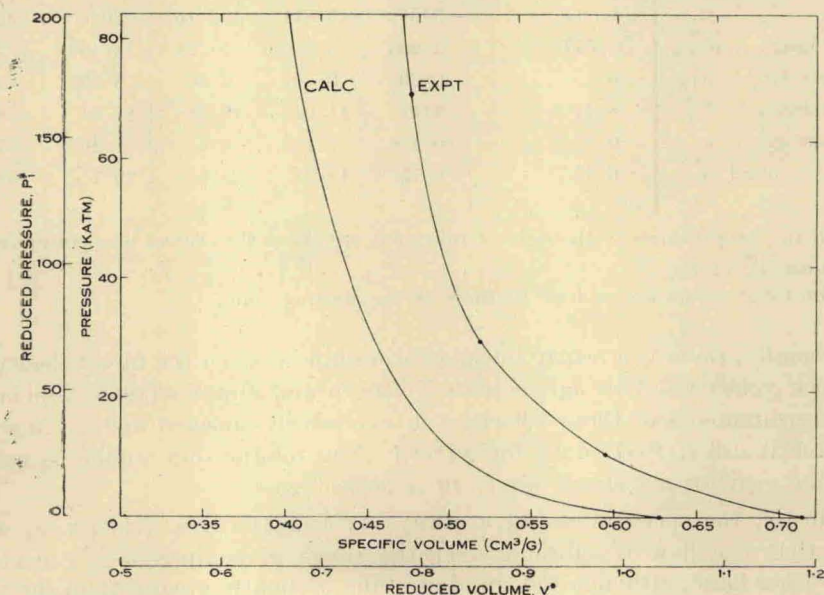


Fig. 2.—A comparison of the calculated LJD Hugoniot curve for liquid argon, initially at 1 atm and 87.2 °K ($P^* \approx 0$, $T^* = 0.727$), with the experimental points of Dapoigny, Kieffer, and Vodar (1955). The calculated (LJD) temperature at the highest experimental point is 1230 °K.

properties of a highly compressed state with those of a dilute gas. We could undoubtedly improve the agreement by incorporating the experimental volume of liquid argon at $P \approx 0$, as was done by Fickett and Wood (1960). But this would be unrealistic, since at that volume the LJD theory predicts a metastable state with a negative pressure of about $P^* = -1.7$. A more justifiable procedure is to calculate the ratio \hat{V}_1/\hat{V} of the volume of the shocked fluid to that of the original liquid. If we do this we find that the LJD values of the ratio are very close to the experimental ones.

(b) The Behaviour of a "Quantal" LJD Liquid

The dotted curve in Figure 1 describes the Hugoniot compression of a quantal liquid ($\Lambda^* = 1$) calculated by the method outlined in Section III (e). It is displaced to volumes larger than those of the classical liquids.

Table 2 lists some thermodynamic properties of the fluid along the Hugoniot curve. Comparing these data with those in Table 1, we find that at any particular

pressure the temperature of the quantal fluid is greater than that of the classical fluid. On the other hand its relative volume V_1^*/V^* is always less, indicating that the compression "squeezes out" some of the quantal inflation of the volume. Unfortunately there are no experimental data to test these conclusions. Some measurements on, say, helium, neon, and argon would be highly desirable.

TABLE 2
THERMODYNAMIC PROPERTIES OF A QUANTAL LJD FLUID ($\Lambda^*=1$) UNDER SHOCK
COMPRESSION, STARTING FROM $P^*=0, T^*=0.75, V^*=1.245$

The symbols are defined in Section II

Pressure	P_1^*	0	2.964	7.023	15.12
Volume	V_1^*	1.245 ($=V^*$)	1.1314	1.0607	0.9899
Temperature	T_1^*	0.75	0.979	1.221	1.671
Energy	E_1^*	-4.115	-3.946	-3.468	-2.185
Specific heat	$(C_V^*)_1$	2.480	2.589	2.650	2.689
Shock velocity	U_1^*	4.58	6.36	7.68	9.58
Flow velocity	w_1^*	0	0.581	1.138	1.964
Velocity of sound	u_1^*	4.58	6.85	8.26	11.51

(c) Conditions after Adiabatic Expansion from a Shocked State

Section III (d) described a method for arriving at conditions during the adiabatic expansion of a shock-compressed material. Our results for LJD fluids are shown as dotted curves in a P^*/V^* plot in Figure 3 and in a P^*/w^* plot in Figure 4. We have worked out a number of thermodynamic properties along the adiabats but there is no need to give the results here. It is sufficient to point out that the adiabats in Figure 3 intersect the zero-pressure line at considerably larger volumes and at higher temperatures than those at which the shock compression began. The highest adiabat only approaches the line at very large volumes, indicating that the liquid is partially vaporized in the final state.

In Figure 4 the adiabats are represented by the right-hand sections of the dotted curves crossing the original Hugoniot. It will be seen that the adiabatic expansion of a shocked fluid from $P_1^*=123.7$ to $P_2^*=0$ increases the flow velocity from $w_1^*=6.51$ to $w_1^*+w_2^*=13.69$.

Of course expansion into a vacuum ($P_2^*=0$) seldom occurs in practice: in most experimental work the shocked material expands into the surrounding air. We can determine the surface conditions here by the method outlined in the last paragraph of Section III (d). If we suppose that the LJD liquid is argon and assume that it is (hypothetically) thermally insulated from air at 25 °C and 1 atm, we find that the conditions of the argon at the starting point in Figure 4 are $P \approx 1$ atm, $\hat{V} = 0.633$ cm³/g, $T = 90$ °K and in the shocked state at the point A are $P_1 = 51\,000$ atm, $\hat{V}_1 = 0.425$ cm³/g, $T_1 = 860$ °K, $w_1 = 1029$ m/sec. The final conditions, given by the point of intersection of the expansion adiabat with the compression Hugoniot for air are $P_2 = 69$ atm, $\hat{V}_2 = 0.926$ cm³/g, $T_2 = 144$ °K,

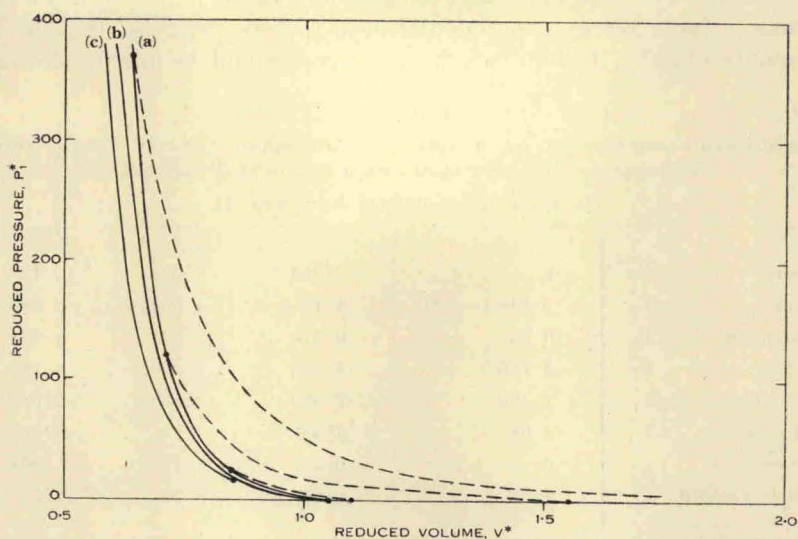


Fig. 3.—Hugoniot curves for normal and precompressed LJD liquids starting from $T^*=0.75$. The starting pressures are (a) $P^*=0$; (b) $P^*=2.041$; (c) $P^*=15.15$. The dotted curves are those for adiabatic expansion from shocked states on the Hugoniot curve (a).

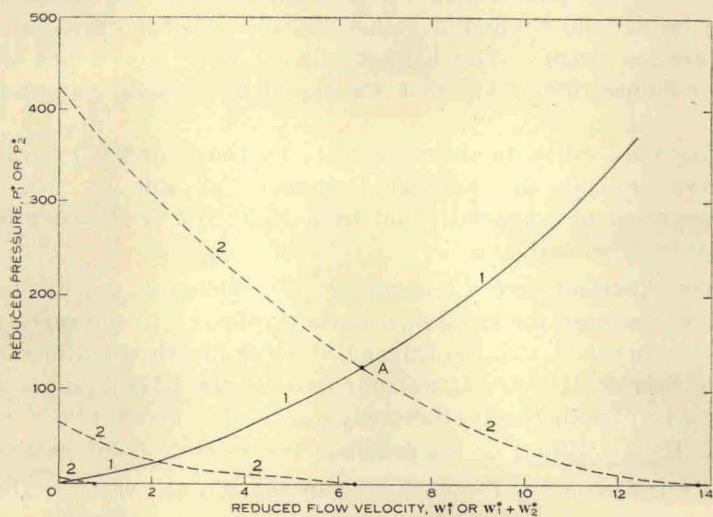


Fig. 4.—A pressure/flow-velocity diagram illustrating the interaction of forward-going shock waves 1 with backward-going shocks or rarefactions 2. The primary shocks 1 are based on the starting point $P^*=0$, $T^*=0.75$.

$w_1 + w_2 = 2160$ m/sec. In this example the final pressure is sufficiently high to prevent the argon from boiling at the interface. The final flow velocity (that is, the "free" surface velocity) is slightly more than twice w_1 , in agreement with some experimental results for water (Rice and Walsh 1957). It would be exactly $2w_1$ in the limit of very weak shocks.

(d) *Conditions at the Head-on Collision of Two Plane Shock Waves*

The left-hand sections of the dotted curves in Figure 4 trace the changes in pressure and flow velocity which occur when secondary shock waves are driven back into the original shock. They were calculated by the method described in Section III (e). It is particularly interesting to consider the conditions which exist after the collision of two equal shocks (which is equivalent to the total reflection of a single shock). Such a collision reduces the absolute flow velocity $w_1 + w_2$ to zero, and the final state is therefore given by the point of intersection of the secondary Hugoniot curve with the pressure axis in Figure 4. The conditions corresponding to three values of the primary shock pressure are given in Table 3.

TABLE 3
CONDITIONS BEFORE AND AFTER THE HEAD-ON COLLISION OF TWO PLANE SHOCK WAVES
Unshocked conditions: $P^* = 0$, $V^* = 1.0503$, $T^* = 0.75$

Before Collision			After Collision		
Pressure P_1^*	Temperature T_1^*	Compression V^*/V_1^*	Pressure P_2^*	Temperature T_2^*	Compression V^*/V_2^*
3.007	0.881	1.061	7.0	0.99	1.115
22.32	1.605	1.238	63.0	2.40	1.431
123.7	7.202	1.485	424	14.88	1.849

It is known that the total reflection of weak (sound) waves doubles the wave pressure at the boundary. But in shock waves the pressure ratio is always greater than this, and in an ideal monatomic gas it approaches the limiting value of 6 in very strong shocks. The LJD results in Table 3 show a similar increase from the low pressure ratio of 2 to a ratio of 3.4 in the strongest shock considered.

It should be noted that the temperature in the doubly-shocked material is considerably lower than it would have been had the liquid been compressed to the same total pressure by a *single* shock wave (cf. Table 1).† This effect could be exploited experimentally as a means of varying the temperature independently of the pressure, which it is impossible to do in a single shock compression from a given starting point.

† The reason for this is that step-wise compression is closer to being adiabatic than is single shock compression. In fact, true adiabatic compression could be imagined to occur by the superposition of an infinite number of infinitesimal shocks.

(e) *Shock Conditions for Liquid Argon in Contact with the Explosive 60/40 RDX/TNT*

By the method outlined in Section III (f) we have estimated that the explosion of a charge of 60/40 RDX/TNT ("Composition B") in contact with argon at 90 °K ($T^*=0.75$) and at atmospheric pressure ($P^*\approx 0$) would launch a shock wave in which the pressure would be 236 000 atm and temperature 5240 °K. These are the conditions at the point of intersection of the Hugoniot curve (a) in Figure 5 with the shock and rarefaction loci for the products of explosion.

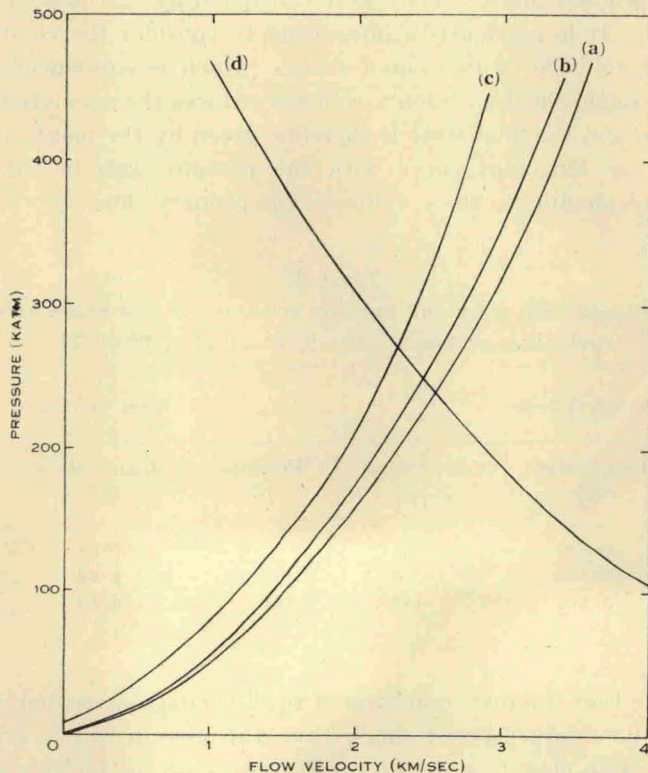


Fig. 5.—A pressure/flow-velocity diagram showing the effects of precompression on the initial shock pressure of liquid argon in contact with the explosive 60/40 RDX/TNT. The curves (a), (b), and (c) are Hugoniot curves based on the starting pressures $P\approx 1$ atm, $P=850$ atm, $P=6300$ atm, respectively, and the starting temperature 90 °K. The curve (d) is the locus of reflected shocks and rarefactions in the explosive products (Deal 1958).

(f) *Shock Conditions in Precompressed Liquids*

We have calculated Hugoniot curves from two finite starting pressures on the isotherm for $T^*=0.75$. The results are listed in Table 4 and plotted in Figure 3. At a given volume the pressure and temperature are always less than for the uncompressed liquid, and at a given pressure the volume and temperature are also less. Precompression therefore provides an additional means of varying

TABLE 4

CALCULATED HUGONIOT COMPRESSIONS FOR NORMAL AND PRECOMPRESSED LJD LIQUIDS, STARTING FROM $T^*=0.75$

The symbols are defined in Section II

Starting Pressure	V_1^*	1.0503	0.9899	0.8485	0.7071	0.6364	0.5657
$P^*=0$	P_1^*	0	3.007	22.32	123.7	371	1546
	T_1^*	0.750	0.881	1.605	7.202	26.31	144.9
	U_1^*	6.47	7.41	11.04	19.94	31.44	59.3
	w_1^*	0	0.426	2.122	6.51	12.39	27.4
$P^*=2.042$	P_1^*		2.042	19.30	101.0	267	964
	T_1^*		0.750	1.238	4.57	14.75	72.0
	U_1^*		7.64	10.93	18.25	27.1	49.5
	w_1^*		0	1.562	5.29	9.68	20.2
$P^*=15.15$	P_1^*			15.15	72.8	167	446
	T_1^*			0.750	1.594	4.07	16.20
	U_1^*			N.D.	17.13	22.7	34.3
	w_1^*			0	2.855	5.67	11.42

the shock temperature independently of the pressure (cf. Section IV (d)). In practice the experiments would be difficult, although not impossible. We have considered it worthwhile to attempt to predict the effects of precompression on the properties of shock waves generated in argon by the explosion of a charge of 60/40 RDX/TNT. Because the behaviour of this explosive is known only under normal conditions, we are forced to consider a hypothetical experiment in which the explosive remains at normal temperature and pressure although it is in

TABLE 5

CALCULATED PROPERTIES OF SHOCK WAVES IN PRECOMPRESSED ARGON IN CONTACT WITH 60/40 RDX/TNT

Initial temperature: 90 °K

Initial Conditions			Shock Conditions		
Pressure, P (atm)	Volume, \hat{V} (cm ³ /g)	Temperature, T (°K)	Pressure, P_1 (atm)	Volume, \hat{V}_1 (cm ³ /g)	Temperature, T_1 (°K)
0	0.633	90	236 000	0.368	5240
850†	0.597	90	247 000	0.356	4150
6300†	0.512	90	270 000	0.331	3300

† Argon is actually solid at these pressures at 90 °K (Robinson 1954). But the results are still significant because the LJD model is a good one for solids (Barker 1961b).

contact with cold argon at a high pressure. However, our calculations should have some bearing on more realistic experiments.

The curves (b) and (c) in Figure 5 are the P/w relations for argon, precompressed to 850 and 6500 atm, respectively, at 90 °K. Their points of intersection with the P/w curve for the explosive products correspond to the conditions listed in Table 5. It will be seen that the precompression has a much greater effect on the shock temperature than on the pressure and volume. It could be a useful way of altering experimental shock conditions and so obtaining more extensive information about the equations of state of real substances.

V. CONCLUSIONS

We regard the results of these calculations as being qualitatively correct. But it is too soon to judge how well they describe the quantitative properties of shock waves in real materials. Perhaps the main value of the calculations lies in the fact that they have enabled us to predict some effects which have not been studied experimentally, and which could be useful in extending the scope of shock-wave techniques.

VI. REFERENCES

- ALTSHULER, L. V., BAKANOV, A. A., and TRUNIN, R. F. (1958).—*Dokl. Akad. Nauk.* **121** : 67.
 BARKER, J. A. (1960).—*Aust. J. Chem.* **13** : 187.
 BARKER, J. A. (1961a).—*Proc. Roy. Soc. A* **259** : 442.
 BARKER, J. A. (1961b).—"Lattice Theories of the Liquid State." (Pergamon Press : London.) (in press).
 BOER, J. DE (1948).—*Physica 'sGrav.* **14** : 139.
 DAPOIGNY, J., KIEFFER, J., and VODAR, B. (1955).—*J. Rech.* **31** : 260.
 DAVID, H. G., and HAMANN, S. D. (1953).—*Trans. Faraday Soc.* **49** : 711.
 DAVID, H. G., and HAMANN, S. D. (1961).—*Aust. J. Chem.* **14** : 1.
 DEAL, W. E. (1958).—*Phys. Fluids* **1** : 523.
 FICKETT, W., and WOOD, W. W. (1960).—*Phys. Fluids* **3** : 204.
 HAMANN, S. D. (1952).—*Trans. Faraday Soc.* **48** : 303.
 HAMANN, S. D. (1957).—*Aust. J. Chem.* **10** : 373.
 HAMANN, S. D. (1960a).—*Rev. Pure Appl. Chem.* **10** : 139.
 HAMANN, S. D. (1960b).—*Aust. J. Chem.* **13** : 325.
 HIRSCHFELDER, J. O., CURTISS, C. F., and BIRD, R. B. (1954).—"Molecular Theory of Gases and Liquids." (John Wiley & Sons : New York.)
 HUGONOT, H. (1887).—*J. Éc. polyt. Paris* **57** : 1.
 HUGONOT, H. (1889).—*J. Éc. polyt. Paris* **58** : 1.
 LENNARD-JONES, J. E., and DEVONSHIRE, A. F. (1937).—*Proc. Roy. Soc. A* **163** : 53.
 MCQUEEN, R. G., and MARSH, S. P. (1960).—*J. Appl. Phys.* **31** : 1253.
 RANKINE, W. J. M. (1870).—*Phil. Trans.* **160** : 277.
 RICE, M. H., MCQUEEN, R. G., and WALSH, J. M. (1958).—"Solid State Physics." Vol. 6. (Academic Press Inc. : New York.)
 RICE, M. H., and WALSH, J. M. (1957).—*J. Chem. Phys.* **26** : 824.
 ROBINSON, D. W. (1954).—*Proc. Roy. Soc. A* **225** : 393.
 STOKES, G. G. (1848).—*Phil. Mag. (Ser. 3)* **33** : 349.
 TAIT, P. G. (1900).—"Scientific Papers." Vol. 2. Nos. 61 and 107. (Cambridge Univ. Press.)
 WENTORF, R. H., BUEHLER, R. J., HIRSCHFELDER, J. O., and CURTISS, C. F. (1950).—*J. Chem. Phys.* **18** : 1484.