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TOWARD AN EQUATION OF STATE FOR FINITE-
DIFFERENCE COMPUTER PROGRAMS

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December 3, 1974

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TOWARD AN EQUATION OF STATE FOR FINITE-DIFFERENCE COMPUTER PROGRAMS

ABSTRACT

This report first reviews equation-of-state properties, then discusses the relationship between the shock Hugoniot locus for a shock-compressed porous material and that for the corresponding solid material. From this relationship a procedure is developed for determining the approximate shock Hugoniot locus for the material at any porosity. Experimental data for various materials with different porosities are compared with predictions of the model.

1. EQUATION-OF-STATE (EOS) PROPERTIES

Introduction

The formalism provided by this report is intended as a general approach which can be taken as the starting point for theoretical or quantitative development. The various equations presented are considered adequate first approximations. They can in general be improved by further development or by provision of additional material parameters. Our approach here is to provide an analytical approximation with the least number of material constants consistent with a reasonable approximation for the P, V, E surface.

Symbol Definitions

C	sound speed
D	shock velocity
E	specific internal energy
F_i	function of volume (reference)
G_i	function of volume (thermal)
P	pressure
T	temperature
u	particle velocity
V	specific volume
V_0	initial specific volume (solid)
V_p	initial specific volume (porous)
x	relative volume decrement (solid) ($x = -\Delta V/V_0$)
ρ_0	initial specific density ($\rho_0 = 1/V_0$)
σ	stress

EOS Surfaces

In this report we will be concerned with a P, V, E surface; however, we may use P, V, and T data in the development since it is more readily available than P, V, E data. In Fig. 1a we show the P, V, T diagram for H_2O ,¹ and in Figs. 1b and 1c we show the corresponding P, V curves and the energy-pressure-density diagram.²⁻⁵ Figure 1a will be referred to as an aid in discussing several features of EOS surfaces in general. The most prominent features in Fig. 1a (neglecting the portion at low temperatures and pressures) are the melting region (liquid-solid coincident state) and the crystalline phase-change regions (see the ice VI and ice VII coincident state). The second important consideration is the difference between any given isotherm and the shock Hugoniot locus. If we consider the 20°C isotherm, we see that at about 9 kbar* the liquid "freezes" under increasing isothermal compression. However, the 20°C shock Hugoniot adiabat does not cross the melting curve on this figure.⁵ At about 22 kbar the 20°C isotherm has a second phase separation. H_2O belongs to a somewhat special class of materials (bismuth, etc.), which expand across the low-pressure liquid-solid phase path. Figures 2a and 2b show hypothetical pictures of EOS surfaces for two distinct types of materials. Materials such as water and bismuth have a low-pressure EOS surface of the type shown in Fig. 2a, and more common materials have an EOS surface of the type shown in Fig. 2b. There are six general features associated with the EOS surface for any material which are important in finite difference programs:

1. Polymorphic phase changes.
2. The melting curve.
3. The vaporization curve.
4. The critical curve.
5. The triple line.
6. The sublimation curve and tensile properties.

The polymorphic phase changes for some materials are very numerous and complex; they may include atomic or molecular realignments as in H_2O , iron, quartz, etc., or they may also occur when electronic shell configurations are altered under pressure (see the P, T diagram for cesium⁶ shown in Fig. 4).

The melting curves for the elements have been widely investigated up to about 50 kbar, and for most materials the melting temperature increases rapidly with increasing pressure. Figures 3a and 3b, which show the experimental melting data for the element rubidium⁷ and for a basalt rock,⁸ are typical of the melting characteristics for many materials. The melting curve is not monotonically increasing; in fact, several materials show a distinct peak and dip when the melting temperature is plotted as a function of static pressure.⁹ In cesium¹⁰ the anomalous dip in the

* 1 kbar = 0.1 GPa $\approx 10^9$ dynes/cm².

Fig. 1a. The P, V, T surface for water, showing all the triple points. Constructed by Verwiebe¹ on the basis of measurements by Bridgman with shock loci by Rice and Walsh.²

Fig. 1b. P, V curves for water: 25°C isotherm³ and 20°C Hugoniot.²

Fig. 1c. Equilibrium equation of state for H_2O .⁴ IEEOS and HUG refer to computer programs; the shock melting point is from Ref. 5.

Fig. 2. P, V, T surfaces for (a) a substance that expands upon freezing, (b) a substance that contracts upon freezing.

Fig. 3a. Phase diagram for rubidium from resistance measurements of Bundy.⁷
Hugoniot point: $2M = 39 \text{ kbar}$.

Fig. 3b. Phase relations within the basalt and eclogite melting regions.
Experimental results.

melting behavior as seen in Fig. 4 has been shown to be associated with an electronic phase change.¹¹ Some investigators have hypothesized that all materials have a peak in the melting curve,¹² but this is not a widely accepted opinion. The phase diagram of the basalt in Fig. 3b shows a typical crystalline (molecular) change across the indicated transition zone.

Referring back to Fig. 1 we see that the melting region has associated with it a change in volume. The well-known Clapeyron equation¹ relates the change in volume across the phase change to the heat of fusion through the dP/dT slope. The change in volume and heat of fusion both decrease along the fusion curve as the pressure increases. But the change in volume is not well documented for most materials. The Clapeyron equation depends on the P , T slope along the melting curve and hence does not by itself define the variables across the phase change. Kawai and Inokuti¹² suggested that the peak in the melting curve coincided with the point on the melting curve where the volume change was zero. The importance of all these observations is that single-valued equations such as Lindemann's law, Simon's law, etc.,^{13, 14} do not describe the entire melting behavior of some materials. In Ref. 6 we derive a first approximation for the P , V , E point at which the shock Hugoniot curve for an initially condensed (nonporous) material crosses the melting curve. Hence, the low-pressure melting curves combined with the high-pressure shock melting point can give a first approximation for the melting curve up to the Hugoniot value.

In Ref. 6 we also divide materials into three categories depending upon their compressibility before and after melting. This classification is demonstrated in Fig. 5a and 5b. Although we do not stress the point, the evidence suggests that the categories are related to the position of the shock melting point with respect to the melting curve peak. Our type I materials cross the melting curve at a pressure below the melting curve peak, and the type III materials cross the melting curve at a pressure above the melting curve peak. Type II materials appear to cross the melting curve near the peak (e.g., rubidium in Fig. 3).

The critical isotherm is a quantity which has not been extensively investigated at very high pressures¹⁵ (see Figs. 2 and 3 for the critical isotherm, T_c). However, we show in Ref. 6 that the shock melting energy is closely correlated to the cohesive (sublimation) energy at 1 atm — particularly if the molecular weight of the vapor is taken into account (Rodean¹⁶). This suggests that in the compression part of the EOS surface the vaporization energy is indeed approximately constant and correlates with the shock melting value.

The critical phenomena are the topic of countless studies. The order-disorder theory of Lennard-Jones¹⁷ and the significant structure theory of Eyring¹⁸ are two well-known examples, with the latter being the more modern approach. The critical point is the value at which the liquid, gas, and liquid-vapor states coincide. The calculations to compute critical phenomena are extensive and for that reason are unsuited for a finite-difference code EOS. The triple line is the line along which the solid-vapor and liquid-vapor states coincide, and is approximately an isotherm as shown in Fig. 2.

Fig. 4. Pressure-temperature stability diagram for cesium in the range 30-55 kbar and 25-225°C. The insert shows the fusion curve and phase fields to 50 kbar, modified from Kennedy et al.¹¹

Fig. 5. Schematics of the three types of Hugoniot melting. (a) Shock velocity vs particle velocity. (b) Pressure vs relative volume decrement.

The tensile considerations are linked to the material strength of matter, and in general negative stresses cannot exceed relatively small values. Confusion exists at times about sublimation and tensile behavior of materials. Essentially, all changes in thermodynamics are considered to be quasi-static. In finite difference codes the changes are, in general, rapid. The EOS surface and the sublimation curve discussed in thermodynamics are different from the EOS and material behavior when material strength is considered. In the latter case spall can occur and the material can experience a negative stress before spalling — a situation which does not exist for hydrodynamic quasi-static changes, where the material sublimates when the pressure and energy are reduced to sufficiently low values, and the solid and vapor coexist. Expressed in another way, quasi-static thermodynamics does not consider material strength, i. e., the shear stress in hydrodynamics is due to the material viscosity.

The EOS Surface of a Porous Material

A familiar approach to elastic-plastic flow in finite difference programs is the decomposition of the stress-strain relationship into a volumetric part plus a deviator part, where the latter defines the contribution due to distortion.¹⁹⁻²¹ In this approach the pressure is explicit in the conservation laws, and the functional dependence of pressure on volume and energy is the basis on which the EOS definition supplies the volumetric behavior. A transition from the elastic to the plastic state according to ad hoc assumptions about how materials "fail" provides the necessary link between the elastic and hydrodynamic behavior.

Usually materials do not go from the elastic state to the plastic state in a discontinuous manner. Even brittle failure has associated with it a nonzero relaxation time. In any case the approach to the thermodynamic plastic state can be described by the failure model. That is, the thermodynamic surface is fixed for a given initially solid (nonporous) material, and is not dependent on the material's time history. The constitutive equations describing the transition from the elastic to the plastic state can (at least in principle) embody the material behavior due to ductility, work hardening, and other rate-dependent or hysteretic effects.

Now we come to the consideration of the EOS surface of an initially distended (porous) material. We can picture the EOS surface of a porous material in two different but equivalent ways.

Case 1. The EOS surface of an initially porous material is identical to the EOS surface of the corresponding solid material, and the effect of porosity is completely described by the constitutive equations modeling the elastic-plastic relationship. In this case the compression of the constitutive material which makes up the porous matrix would refer to the EOS surface of the corresponding solid for the volumetric behavior of the matrix material. The rate-dependent and pore-failure effects would be described by ad hoc equations of elastic-plastic flow (failure).

Case 2. The EOS surface for the porous material is different for every value of porosity, and the constitutive equations modeling the elastic-plastic transition change

not only in their initial conditions, but also in relationship to the decrease in the number and/or size and shape of the void spaces (i. e., the material behaves differently when some of the voids are removed, and when some of the voids change shape).

In case 1 life is simple in the sense that if the EOS surface of the solid material is known and a porous constitutive theory is given, the material behavior for any porosity is obtainable. This is the "ultimate" in the sense that the burden is shifted to the constitutive model for the details of how material strength affects the finite difference calculations.

In case 2 we are confronted by the limitations of the current constitutive theories, and the EOS surface for all porosities must be supplied as well as constitutive laws of elastic-plastic behavior. This case is exemplified in some current computer programs which model porous behavior primarily on the basis of the shear stress properties of the material, where a loading and unloading P, V curve must be supplied for every porosity.

Note that to a first approximation the EOS surface differs in the porous and solid cases only in the region where the solid material is slightly compressed or is in the solid-vapor mixed state. This follows from the requirement that the void spaces do not alter the melting or vaporization properties of the porous material's constituent matrix. That is, the porous material must melt at less than or the same temperature as the normal nondistended solid, with the melting accompanied by a volume change in which the voids all collapse (the gas in the pores is not considered here). In Fig. 6 we have sketched this characteristic of a hypothetical EOS surface, and its corresponding P, V curve.

This same dichotomy exists in the case of a porous sample in a state of tension. One can assume that the EOS surface of the nondistended solid supports a pressure nearly zero, where the tensile properties are defined strictly by the elastic and failure theories. Or one can define the stress and strain in such a way that the EOS surface has a negative pressure region which is terminated by the failure theory.

The Shock Hugoniot Loci

In Fig. 1 the calculated shock locus for water at an initial temperature of 20°C is shown² with the approximate -10°C shock locus for ice. In Fig. 7 we show the hypothetical shock adiabats for two different porosities of a single hypothetical material.²² When a porous material is shock-compressed, the work required to collapse the voids is partially "stored" in the material in the form of heat. Hence the shock compression states corresponding to increasing initial porosity lie at higher and higher relative energies (temperatures). For each increase in initial void space, the internal energy required to reach the normal density increases, as does the pressure. The locus of shock Hugoniot states does not span the space of thermodynamic compressed states. However, a large portion of the EOS surface can be reached by porous shock loci; in particular, all states below the ambient nonporous shock adiabat can be (in principle) reached.

Fig. 6. Hypothetical EOS surface and its corresponding P, V curve. V_p is the initial porous volume, V_0 the initial solid volume. Solid lines denote the nondistended surface, and dashed lines show a porous superposition on the original surface.

Fig. 7. A typical P, V, T thermodynamic surface.²²

Constructing an EOS Surface

It would be highly desirable for finite difference programs to have a simple analytic approximation for the portion of the EOS surface used in the calculation. There are currently a number of different EOS approximations being used in finite difference codes. They range in accuracy, complexity, and sophistication from a tabulated P, V curve which is interpolated, to the GRAY²³ or CHARTD²⁴ type calculations which are extensive semiempirical calculations. A first approximation for essentially all materials of interest with a relatively simple calculation for pressures and energies in the EOS surface where the energy dependence is linear is the desired type of initial approach.

We assume that the EOS surface is independent of the time history of the material, since pore collapse, work hardening, and other rate-dependent phenomena will be considered to be defined in the constitutive model²⁵⁻²⁷ of the material used in the finite difference program. On the other hand, the thermodynamic behavior of the material — melting, vaporization, crystalline phase changes, etc. — is a characteristic which the EOS surface (once it is defined) can provide to the finite difference calculation, since the thermodynamic information is assumed to be independent of the material's time history. Once the EOS surface is defined, all hydrodynamic loading and unloading paths are known, and the EOS and strength of the material combine to give the elastic-plastic behavior.

The Available EOS Data and Theories

The 0°C isotherm has been calculated for many materials.²⁸⁻³⁰ The Thomas-Fermi²⁹ and higher order quantum approximations^{31, 32} for a degenerate electron gas have been derived for very-high-pressure, high-temperature asymptotic values. It is questionable how important the zero-degree isotherm is to finite difference calculations. The reason for this is that in computer calculations the states reached by the calculation seldom correspond to pressures above the shock Hugoniot locus, except in some cases of reflected shock waves. Also, care must be taken in considering extreme states. For example, one finds that the limiting shock compression (ρ/ρ_0) is a factor of 4, because this is the value obtained by deriving the limiting compression for an ideal gas in terms of the ratios of specific heats (γ). However, Gross³³ points out the limiting compression is 9 when radiation is considered. Of all the elements, only lithium has a limiting shock compression greater than 9 (~ 9.25) when the experimental data is extrapolated. Johnson and Teller³⁴ derived the limiting compression from relativistic considerations. Their results show that in the rest frame the compression is proportional to the internal energy behind the shock and increases indefinitely.

For many materials, isothermal static P, V measurements have been made. Almost always these static measurements are the ambient isotherm. High-pressure shock data is available for many materials in addition to the static P, V data. For

many rocks, and for a few elements and compounds, both P, V data and shock data are available for different initial porosities. In Fig. 8 we show where these different measurements lie in a hypothetical EOS surface. It seems obvious that this wide variety of information should be used to obtain at least a first approximation to the required portion of the EOS surface. When the surface is approximated, all hydrostatic loading and unloading paths are defined. This is in contrast to isothermal loading and unloading curves, or isentropic or adiabatic curves which define specific paths along the surface. In Ref. 6 we showed that for solids, the low-pressure ambient isotherm and the shock Hugoniot P, V projection agree to a first approximation for almost all initially solid elements. The high-pressure energy dependence can be derived in part from the additional information available to us in the form of porous shock data.

When the P, V data and shock data are combined with an adequate gas description for the expansion portion of the EOS surface, the essential aspects of the EOS problem are solved. Clearly the gas description must match previously tabulated values such as those of Butkovich⁴ or steam tables. Adding approximations for the melting curve and phase changes complete the important gross features of the surface.

Functions Defining the Required Portion of the EOS Surface

We assume that a Grüneisen-like equation will describe the EOS surface adequately.^{35, 36} This assumption will define the limits of validity of the formalism. Note that the linear energy dependence does not imply a linear temperature dependence, since the specific heat function which relates the energy and temperature is at least linear in temperature, and is a complicated function near phase changes. If we also assume that one major polymorphic phase change provides an adequate approximation to the EOS surface, then the equations defining the EOS surface can be approximated as follows:

The first solid phase,

$$P = F_1 + G_1 E. \quad (1.1)$$

The second solid phase,

$$P = F_2 + G_2 E. \quad (1.2)$$

The liquid phase,

$$P = F_3 + G_3 E. \quad (1.3)$$

Fig. 8. A hypothetical EOS surface showing the six regions and their bounding reference curves, some Hugoniot reference curves, and the linear energy dependence.

The gas phase,

$$P = F_4 + G_3 E. \quad (1.4)$$

The liquid-vapor mixed phase,

$$P = F_5 + G_4 E. \quad (1.5)$$

The solid-vapor mixed phase,

$$P \approx 0. \quad (1.6)$$

The functions F_1 , F_2 , F_3 , F_4 , and F_5 are reference functions which define the surface; they are functions of volume. The functions G_1 , G_2 , G_3 , and G_4 are the thermal functions which determine the surface between the reference functions. Figure 8 shows the numbered regions in which these functions apply.

In a finite difference program the EOS routine is supplied the specific, or relative, volume and the specific internal energy. The routine then determines which phase the volume and energy correspond to on the EOS surface, and the pressure is then calculated from one of the equations (1.1)-(1.6). Equation (1.6) implies that the negative stress is given by the constitutive theory.

The reference functions can be further defined as follows. For the solid phases,

$$F_1 = P_{H1} - G_1 E_{H1}, \quad (1.7)$$

$$F_2 = P_{H2} - G_2 E_{H2}, \quad (1.8)$$

where P_{Hi} and E_{Hi} are the shock pressure and energy for the ith phase.

In Sec. 2 of this report we present approximations for the shock adiabats for arbitrary porosity. For finite difference programs which are primarily applied to transient wave problems, the stress state usually lies on or near the shock Hugoniot locus except for expansions or reflections. In Fig. 7 we show a hypothetical release (unloading) curve from a shock state. The pressures above the shock Hugoniot locus can only be reached by precooling; e.g., in multiple reflections, or by isothermally compressing a material. We assume that the thermal functions (G_i) are adequate to determine "cool" P , V , E states above the shock Hugoniot, and therefore we will not require a very-high-pressure "cold" compression curve to be explicitly calculated.

The liquid reference function is

$$F_3 = P_f - G_3 E_f, \quad (1.9)$$

where P_f and E_f are the pressure and energy functions defining the fusion (melting) curve.

The gas-phase reference function is defined similarly:

$$F_4 = P_{CE} - G_3 E_{CE}, \quad (1.10)$$

where P_{CE} and E_{CE} are the pressure and energy defining the vaporization curve.

The mixed-phase reference function (liquid, liquid-vapor) is given by

$$F_5 = P_T - G_4 E_T, \quad (1.11)$$

where P_T and E_T are the triple point values and G_4 can be approximated by

$$G_4 = \frac{P_{LVG} - P_T}{E_{LVG} - E_T}; \quad (1.12)$$

the pressures and energies in (1.11) and (1.12) remain to be defined. The melting and vaporization pressures and energies are the values at which melting or vaporization begin. Adding the heat of fusion and the heat of vaporization respectively defines the energies at which complete melting and vaporization take place respectively. In keeping with the theory of first-order phase changes^{1, 28} the temperature and pressure are constant across the phase change for crystalline changes, melting, and vaporization. The changes in entropy and volume provide the necessary conservation requirements.

Care must be taken in finite difference programs using this type of EOS description to prevent division by zero in the case where the pressure might be constant ($\Delta P = 0$). First order phase changes are reversible, and the heat of fusion (or vaporization) is recovered upon solidification (or condensation), i. e., during the calculation some energy can be "stored" in the material when phase changes occur.

Recapitulating, we can see that if a constitutive model for material strength is given, and if the thermodynamic surface is taken to be independent of the time history of the material, then the surface can be defined analytically by providing functional approximations for:

1. The shock Hugoniot curve for arbitrary porosity.
2. The melting curve.
3. The vaporization curve.
4. The critical curve.
5. The triple line.
6. The thermal functions, G_i , $i = 1, 5$.

In Sec. 2 we provide the first of these requirements.

2. THE SHOCK HUGONIOT CURVE FOR ARBITRARY POROSITY

Introduction

Symbol Definitions

B	bulk modulus
C	sound speed
D	shock velocity (solid)
D'	shock velocity (porous)
E_H	specific internal shock energy (solid)
E_H'	specific internal shock energy (porous)
$f(R)$	the porous scaling function
M	shock modulus
R	porous ratio ($R = \rho_p / \rho_0 = V_0 / V_p$)
S	slope of D, u line
Sample S	the normal condensed solid material
Sample P	the corresponding porous material
u	particle velocity (solid)
v	particle velocity (porous)
V	specific volume
x	relative volume decrement (solid) ($x = -\Delta V / V_0 = 1 - V / V_0$)
μ	volumetric strain ($\mu = \Delta V / V = V_0 / V - 1$)
ξ	relative volume decrement (porous) ($\xi = -\Delta V / V_p = 1 - V / V_p$)
ξ_s	value of ξ at $V = V_0$ (solid) ($\xi_s = 1 - R$)
ρ	specific density ($\rho = 1 / V$)
ρ_0	initial specific density (solid) ($\rho_0 = 1 / V_0$)
ρ_p	initial specific density (porous) ($\rho_p = 1 / V_p$)
σ_H	uniaxial shock stress (solid)
σ_H'	uniaxial shock stress (porous)
ϕ	potential energy

Our aim is to derive a first-order approximation for the shock Hugoniot locus for a material having an arbitrary porosity. To be most useful as the basis for an equation of state the equation for the shock locus should require a minimum of material

constants and should not require empirical information for different initial porosities. Finally, the model should not be merely a curve-fitting procedure, but should have some heuristic value.

In Ref. 6 we derive the relationship between elementary potential theory and shock theory. We show how potential theory can be used to predict the shock melting point. These results are summarized below.

The Rankine-Hugoniot relationships can be written as^{28, 37, 38}

$$\sigma_H = \rho_0 u D, \quad (2.1)$$

$$x = -\frac{\Delta V}{V_0} = \frac{u}{D}, \quad (2.2)$$

$$E_H = \frac{1}{2} \frac{\sigma_H}{\rho_0} x. \quad (2.3)$$

The variables u and D are the particle and shock velocities, σ_H is the uniaxial shock stress, $V = 1/\rho$ is the specific volume, and E_H is the specific internal energy. A zero subscript denotes the initial undisturbed state, and nonsubscripted quantities are the compressed states. For shock amplitudes well above the Hugoniot elastic limit (HEL), i.e., amplitudes at which the material behaves hydrodynamically, σ_H is approximately the shock adiabat value. That is, multiple wave phenomena are neglected in Eqs. (2.1)-(2.3).

Empirical evidence has shown that for a given phase state of a condensed solid, the shock and particle velocities are linearly related^{28, 37}:

$$D = C + Su, \quad (2.4)$$

For the elastic wave, $C = C_L$ (the longitudinal sound speed). Along the shock hydrostat, $C = C_0$ (the bulk sound speed). Equations (2.1) through (2.4) can be combined to give σ_H and E_H in terms of the volume decrement:

$$\sigma_H = M \frac{Sx}{(1 - Sx)^2}, \quad (2.5)$$

$$E_H = \frac{M}{2\rho_0 S} \left(\frac{Sx}{1 - Sx} \right)^2. \quad (2.6)$$

To a first approximation the parameters are related by⁶

$$MS = \rho_0 C_0^2 \approx B_0, \quad (2.7)$$

$$\frac{M}{2\rho_0 S} = \frac{1}{2} \left(\frac{C_0}{S} \right)^2 \approx \frac{B_0 V_0}{nm} = \phi_0, \quad (2.8)$$

where M and S are the plastic wave values, B_0 is the bulk modulus evaluated at $V = V_0$, and ϕ_0 is the cohesive energy. If ϕ is the approximate magnitude of the interatomic potential well, we can write³⁹

$$\phi = \phi_0 \frac{nm}{n-m} \left[\frac{1}{n} \left(\frac{V_0}{V} \right)^n - \frac{1}{m} \left(\frac{V_0}{V} \right)^m \right]. \quad (2.9)$$

For $V \approx V_0$,⁶

$$n = 2S, \quad (2.10)$$

$$m = S. \quad (2.11)$$

From the adiabatic nature of shock compression it follows that shock melting occurs at a particle velocity⁶

$$u_{\text{melt}} = C_0/S, \quad (2.12)$$

and substitution gives the point on the Hugoniot curve at which a material melts under shock loading.

$$\sigma_{\text{melt}} = 2M, \quad (2.13)$$

$$x_{\text{melt}} = \frac{1}{2S} = \left(\frac{-\Delta V}{V_0} \right)_{\text{melt}}. \quad (2.14)$$

Equations (2.12)-(2.14) define to a first approximation the values at which any particle can escape the potential well under shock loading. In Refs. 5 and 6 we compare the calculated point $(x_{\text{melt}}, \sigma_{\text{melt}})$ with other computed⁴⁰ and experimental⁴¹ values and find good agreement. This completes our summary of the previously derived equations for nonporous materials.

Hugoniot Theory for Porous Materials.

The behavior of porous materials under shock compression has been widely studied, and the multiple wave phenomenon is well known.^{28, 38, 42, 43} We will assume that the reader is familiar with porous phenomena and proceed to the theory. Our objective is to obtain a shock locus for a material of arbitrary porosity in terms of the shock Hugoniot curve for the corresponding condensed solid material. Herrmann's P- α model is a well-known approach⁴⁴ to porous compression, but requires an empirical parameter for every material in addition to the Hugoniot curve for the condensed solid. Butkovich's PMUGEN program⁴⁵ calculates the compression curves for rocks, and is based upon curve fitting using some empirical scaling laws. The P- α

model attempts to relate the porous Hugoniot state to the Hugoniot state of the condensed solid by assuming equal pressures in the two cases and subsequently finding a volume relationship. We will show that the volume relationship can be derived directly. To complete the porous model the energy (temperature) dependence must be established (recall that porous compression results in an increase in the internal energy of the material above that associated with the nonporous shock state). The difference in internal energy for the initially porous and initially normal condensed shock states is approximated by making the material constants of the condensed solid a function of the initial porosity to obtain the porous values.

To simplify the terminology we will consistently refer to the properties of an initially porous material as sample P properties. We will refer to the corresponding initial condensed solid as sample S. Let ρ_p be the initial in situ (dry) porous density (sample P) and we will continue to use ρ_0 as the initial condensed solid density (sample S).

If v and D' are the particle and shock velocities in sample P, then the Rankine-Hugoniot relationships can be written

$$\sigma_H' \approx \rho_p v D',$$

$$\xi = -\frac{\Delta V}{V_p} \approx v/D', \quad (2.15)$$

$$E_H' \approx \frac{1}{2} \frac{\sigma_H'}{\rho_p} \xi,$$

where first wave velocities (zero-subscripted) have been neglected.

The initial porosity of sample P is defined by the ratio

$$R = \rho_p / \rho_0, \quad (2.16)$$

where $0 < R \leq 1$. If both sample P and sample S are shock-compressed to the same final volume V , the relative volume decrement in the two samples will be

$$\xi = 1 - V/V_p = 1 - \rho_p / \rho \quad (\text{sample P}) \quad (2.17)$$

and

$$x = 1 - V/V_0 = 1 - \rho_0 / \rho \quad (\text{sample S}). \quad (2.18)$$

If we define

$$\xi_s = 1 - R \quad (2.19)$$

to be the volume decrement at which sample P reaches the sample S density (ρ_0), then Eqs. (2.16)-(2.19) can be used to give the volume relationship between samples P and S for the same constituent material when the two samples have been compressed to volume V. That is,

$$x = \frac{\xi - \xi_s}{R}. \quad (2.20)$$

We refer to ξ_s as the "solid point."

No assumptions have been made at this point about shock stress, and Eq. (2.20) is subject to no restrictions other than $\xi > \xi_s$ ($x > 0$).

Equation (2.20) has been presented in an entirely different form by Krupnikov et al.⁴⁶ and other Soviet authors.⁴⁷ From Eqs. (2.15) through (2.20) the following derivation gives the Soviet equation. Define

$$m = \frac{1}{R} \quad (2.21)$$

and

$$\sigma = \rho/\rho_0. \quad (2.22)$$

Then since

$$\frac{V}{V_0} = \frac{\rho_0}{\rho} = 1 - x \quad (2.23)$$

and Eqs. (2.15) give

$$\frac{\rho_0 v^2}{\rho_H^1} = \frac{\xi}{R}, \quad (2.24)$$

we have by substitution in (2.20) the Russian equation

$$m = \frac{1}{\sigma} + \rho_0 \frac{v^2}{\sigma_H^1}, \quad (2.25)$$

where precursors have been neglected. The implications of this relationship with regard to the sample S and sample P relative volume decrements apparently have been overlooked up to now.

The volume transformation from sample S to sample P is given by Eq. (2.20), but the corresponding change in internal energy must now be considered. If the shock heating in sample S and sample P were the same upon being compressed to volume V, we would substitute Eq. (2.20) into (2.5) to obtain the porous Hugoniot locus, using the parameters M and S from the sample S Hugoniot curve. But when a shock wave is driven into an initially porous material a portion of the shock energy is deposited in

the material in the form of random motion (heat) as the void spaces are crushed out. If samples P and S are shock-compressed to the same density, the sample P shock state will correspond to a higher temperature and pressure than the sample S shock state. A higher temperature in sample P as compared to sample S corresponds to a larger value of the repulsive potential at volume V for sample P as compared to sample S. Since the initial porosity is defined by the ratio R, and the final shock state depends only on the initial state of the sample, it follows that the repulsive potential exponent should depend on R in some way (we showed that the potential exponent was related to the shock parameter S in Eqs. (2.10) and (2.11)). Let the parameter S have the porous value S', where

$$S' = \frac{S}{f(R)}. \quad (2.26)$$

We have found empirically that the function f(R) is approximately exponential in behavior, and we have fitted a functional form which gives good agreement for porous shock data. That is, we use the empirical form

$$f(R) = \max(R^2, -1.5 + 4.5R - 2R^2). \quad (2.27)$$

This function is shown in Fig. 9 as the heavy line, where the dashed line is R^2 .

The sample S model is linear (two parameters, M and S), and the sample P model is linear for a given porosity with parameters M' and S'. Equations (2.26) and (2.27) give the dependence of S' on the porosity ratio R. Now the dependence of the porous shock modulus, M', on R must be determined.

Let sample S be shock-compressed to volume decrement x (stress σ , internal energy E). Let sample P of the same material be shock-compressed to the same stress, and let its volume decrement be x'. From Eq. (2.5) we have

$$M \frac{Sx}{(1 - Sx)^2} = M' \frac{S'x'}{(1 - S'x')^2}, \quad (2.28)$$

where $x' = \frac{\xi' - \xi_s}{R}$.

M' and S' are the sample P material parameters, which are related to M and S. In Fig. 10 we show the relationship between x' and x. For void space of 30% or less the data has relatively little scatter and obeys the relationship given by

$$x' = f(R)x, \quad (2.29)$$

where f(R) is given by Eq. (2.27). As the porosity increases beyond 30% the scatter in the data increases considerably, making a fair comparison very difficult. There are several reasons for the large scatter as the initial porosity increases. One is the

Fig. 9. The function $f(R) = \max(R^2, -1.5 + 4.5R - 2R^2)$.

(a) Aluminum 2024, $\rho_0 = 2.79$

(b) Aluminum, $\rho_0 = 2.7$

(c) Tungsten, $\rho_0 = 19.17$

(d) Copper, $\rho_0 = 8.93$

Fig. 10. The empirical relationship between $x'/f(R)$ and x for (a) aluminum 2024, (b) aluminum, (c) tungsten, (d, e) copper, (f) uranium, (g) limestone, and (h) alluvium. The dashed lines suggest that the porous ratio, R , is in error; i. e., either ρ_0 or ρ_p is incorrect and the linear relationship is displaced from zero approximately 5%.

(e) Copper, $\rho_0 = 8.93$

(f) Uranium, $\rho_0 = 19.07$

(g) Limestone, $\rho_0 = 2.70$

(h) Alluvium

Fig. 10 (Continued).

difficulty in obtaining reproducible samples (each point is a shock experiment) when the void space approaches or exceeds the volume of the constituent material. Additional problems include impurities and effects of machining the samples. We have included data for elements of all atomic weights and also data for limestone and SiO_2 to show that the relationship is a general one for compounds as well as elements. Equations (2.28) and (2.29) give the desired relationship. That is, if

$$S' = S/f(R) \quad (2.30)$$

then

$$M' = M. \quad (2.31)$$

We can now rewrite the equations that have been derived for the sample P shock adiabat in the region where precursors are not important.

$$\xi = 1 - V/V_p,$$

$$R = \rho_p/\rho_0,$$

$$\xi_s = 1 - R,$$

$$x = \frac{\xi - \xi_s}{R},$$

$$f(R) = \max(R^2, -1.5 + 4.5R - 2R^2),$$

(2.32)

$$\sigma_H = M \frac{\frac{Sx}{f(R)}}{\left[1 - \frac{Sx}{f(R)}\right]^2},$$

$$E_H = \frac{M}{2\rho_p S/f(R)} \left[\frac{\frac{Sx}{f(R)}}{1 - \frac{Sx}{f(R)}} \right]^2 \frac{f(R)\xi}{Sx},$$

$$\text{for } \xi > \xi_s.$$

The porous shock stress can be derived explicitly in terms of ξ as

$$\sigma_H = M \bar{S}_p \frac{\xi - \xi_s}{(1 - \bar{S}_p \xi)^2}, \quad (2.33)$$

where

$$M_p = \frac{M}{1 + \bar{S}_p \xi_s},$$

$$\bar{S}_p = \frac{S_p}{1 + \bar{S}_p \xi_s}, \quad (2.34)$$

$$S_p = \frac{S}{Rf(R)}.$$

Comparison of (2.32) with (2.5) shows that in the sample S coordinates (x, σ) the shock Hugoniot curve is universal (has the same shape) for all materials. The universal curve has the form

$$Y = \frac{X}{(1 - X)^2}, \quad (2.35)$$

where $Y = \sigma/M$ and $X = Sx$ for each distinct phase. In the coordinate system of sample P (ξ, σ') the curve is not universal but has the same shape for any given value of R and $\bar{S}$ and has the form

$$Z = \frac{W - \bar{S}_p \xi_s}{(1 - W)^2}, \quad (2.36)$$

where $Z = \sigma'/M_p$ and $W = \bar{S}_p \xi$.

Manipulation of the above equations for $\xi > \xi_s$ gives the relationship between shock velocity and particle velocity for sample P:

$$D' = \frac{v}{g(v)}, \quad (2.37)$$

where

$$g(v) = \frac{\beta}{2} \pm \sqrt{\left(\frac{\beta}{2}\right)^2 - \alpha}, \quad (2.38)$$

and

$$\alpha = \frac{r}{(\bar{S}_p r)^2 - 1}$$

$$\beta = \frac{2\bar{S}_p r^2 - \xi_s}{(\bar{S}_p r)^2 - 1},$$

$$r = v/C_p, \quad (2.39)$$

$$C_p = \sqrt{\frac{M_p \bar{S}_p}{\rho_p}}.$$

Equation (2.37) has a singularity at $v = C_p/\bar{S}_p$. The plus sign must be used for $v < C_p/\bar{S}_p$, and the minus sign for $v > C_p/\bar{S}_p$. The limiting values of (2.37) are

$$D' \approx \frac{v}{\xi_s} \text{ for } \xi \approx \xi_s \quad (2.40)$$

and

$$D' \approx C_p + \bar{S}_p v \text{ for } \xi \approx \frac{1}{\bar{S}_p}. \quad (2.41)$$

Equation (2.40) is simply the snowplow approximation near the solid point, and (2.41) is the analog of the sample S linear relationship, Eq. (2.4). The snowplow approximation is derived by assuming that the shock wave compacts the porous material in the manner of a snowplow. Ahrens⁴⁸ has pointed out that the slope of the Hugoniot locus is undefined when the slope of the D', v curve is D'/v . The quantity $g(v)$ in (2.37) is approximately independent of v when ξ approaches ξ_s — i.e., v approaches zero.

This completes the description of the Hugoniot curve for sample P in terms of the Hugoniot curve for sample S for $\xi > \xi_s$. In the Appendix we will present the empirical scaling equations used to approximate the Hugoniot stress curves in the elastic and pore-crushing regimes.

The equations for crushing do not correspond to a satisfactory physical model, and do not address the problem in terms of the constitutive equations of elastic-plastic theory. Our primary reason for providing them is completeness.

Comparison of Experimental Data with the Derived Theory

In Fig. 11 we show the computerized plots of sample S aluminum data. A small plus (+) is an experimental shock data point. The asterisks (*) are experimental hydrostatic values. An x denotes experimental hydrostatic measurements using the x-ray technique.⁴⁹ The large plus denotes the shock melting point computed from

$$x = \frac{1}{2S},$$

$$\sigma = 2M,$$

$$u = \frac{C_0}{S}, \quad (2.42)$$

$$D = 2C_0.$$

EOS 13
ALUMINUM

M 580.00
S 1.340
CL 6.086
C0 5.365
MS 777.20

RH00 2.700
P1 4.10
CSII 0.0041

Fig. 11a. Computer plots of D vs u for solid aluminum, $\rho_0 = 2.700$.

Fig. 11b. Computer plots of P vs ξ for solid aluminum, $\rho_0 = 2.700$.

In the log-log plot of pressure versus x (note: $x = \xi$ for sample S) the elastic portion terminates at approximately the Hugoniot elastic limit.^{28, 50} The quantities printed are:

EOS	our EOS number (=Z, the atomic number for elements),
M	the shock modulus (kbar),
S	the D, u slope,
C0	the bulk sound speed (km/sec),
CL	the longitudinal sound speed (km/sec),
MS	the bulk modulus (kbar),
RHO0	the sample S initial density, ρ_0 (g/cm ³),
P1	the porous Hugoniot elastic limit (kbar),
CSII*	the HEL volume decrement, ξ_{HEL} .

The static data has been transformed using the shock relationships to show the relative location of the static and shock data in the D, u plane, but the transformation has no physical significance.

The sound speed C_L and the Hugoniot elastic limit parameters are assumed to be related by

$$C_L = \frac{P1}{RHO0 \times CSII} \cdot \quad (2.43)$$

The parameters P1 and CSII are chosen to satisfy experimental data for the HEL (P1) and the sound speed (C_L).

Figures 12, 13, and 14 show additional type II melting materials, i.e., copper, sodium chloride, and limestone. Figures 15, 16, and 17 show type I melting materials: iron, silicon, and germanium. Finally, in Figs. 18 and 19 we show the type III melting elements calcium and europium. In Ref. 2 we discussed three melting types, but a fourth type must be added to accommodate the elements carbon (graphite) and possibly iodine. The plots for graphite are shown in Fig. 20. The type IV melting characteristic is the large volume change at the melting point. In Fig. 21 the phase diagram for carbon is given.^{51,55} From the phase diagram and our shock melting pressure (~ 320 kbar) the shock melting temperature is $\sim 3900^\circ\text{K}$ (note the unusual decreasing melting curve for carbon). We have not found any evidence that type IV geological materials exist.

In Figs. 22 through 25 we show the computer plots of experimental data for samples of porous aluminum alloy. The data is presented in the sample P coordinate, ξ , and care must be taken in comparing that data with the data presented previously in the sample S coordinate, x . In Figs. 26-31 we show examples of porous copper, porous tungsten, and porous limestone. In Figs. 32-38 we show porous iron and porous carbon. All of these porous shock curves have been generated by using the values of M, S, and ρ_0 for the solid, with the porous density ρ_p being used to define the porous ratio R. No other information (except the Hugoniot elastic limits for the solid) is required to calculate these curves.

*Phonetic representation of ξ_1 .

EOS 29
COPPER

M 953.00
S 1.470
CL 4.618
CO 3.961
MS 1400.91

RH00 8.930
P1 4.00
CS1 0.0021

Fig. 12a. Computer plots of D vs u for solid copper, $\rho_0 = 8.930$.

Fig. 12b. Computer plots of P vs ξ for solid copper, $\rho_0 = 8.930$.

EOS 105 MELTING TYPE 2
SODIUM CHLORIDE

M 187.00
S 1.350
CL 4.111
CO 3.411
MS 252.45

RH00 2.170
P1 2.20
CSI1 0.0060

Fig. 13a. Computer plots of D vs u for solid sodium chloride, $\rho_0 = 2.170$.

Fig. 13b. Computer plots of P vs ξ for solid sodium chloride, $\rho_0 = 2.170$.

EOS 157
LIMESTONE

MELTING TYPE 2

M 260.00
S 1.490
CL 6.592
CO 3.781
MS 387.40

RH00 2.710
P1 27.00
CSII 0.0230

Fig. 14a. Computer plots of D vs u for solid limestone, $\rho_0 = 2.710$.

Fig. 14b. Computer plots of P vs ξ for solid limestone, $\rho_0 = 2.710$.

EOS 26 MELTING TYPE 1
IRON

	PHASE I	PHASE II
M	1319.00	660.00
S	1.370	1.650
CL	5.945	
CO	4.795	
MS	1807.03	

RH00 7.860
P1 15.00
CSII 0.0054

PHASE	CHANGE	PRESSURES
128.7	145.5	2704.8

Fig. 15a. Computer plots of D vs u for solid iron, $\rho_0 = 7.860$.

Fig. 15b. Computer plots of P vs ξ for solid iron, $\rho_0 = 7.860$.

EOS 14 MELTING TYPE 1
SILICON

	PHASE I	PHASE II
M	925.00	66.00
S	1.092	1.700
CL	9.320	
CO	6.584	
MS	1010.10	

RH00 2.330
P1 85.00
CSII 0.0420

PHASE CHANGE PRESSURES
127.3 320.2 2003.7

Fig. 16a. Computer plots of D vs u for solid silicon, $\rho_0 = 2.330$.

Fig. 16b. Computer plots of P vs ξ for solid silicon, $\rho_0 = 2.330$.

ECS 32 MELTING TYPE 1
GERMANIUM

	PHASE I	PHASE II
M	660.00	110.00
S	1.150	1.670
CL	4.689	
CO	3.767	
MS	759.00	

RHO 5.350
P1 100.00
CSI 0.0850

PHASE	CHANGE	PRESSURES
256.0	271.2	1320.2

Fig. 17a. Computer plots of D vs u for solid germanium, $\rho_0 = 5.350$.

Fig. 17b. Computer plots of P vs ξ for solid germanium, $\rho_0 = 5.350$.

EOS 20 MELTING TYPE 3
CALCIUM

	PHASE I	PHASE II
M	200.00	65.00
S	0.940	1.265

CO 3.517
MS 188.00

RHO0 1.520
P1 0.49
CSII 0.0020

PHASE CHANGE PRESSURE
 400.2

Fig. 18a. Computer plots of D vs u for solid calcium, $\rho_0 = 1.520$.

Fig. 18b. Computer plots of P vs ξ for solid calcium, $\rho_0 = 1.520$.

EOS 63 MELTING TYPE 3
EUROPIUM

	PHASE I	PHASE II
M	152.00	11.50
S	0.900	1.470
CL	2.260	
CO	1.592	
MS	136.80	

RH00 5.400
P1 1.93
CSII 0.0070

PHASE CHANGE PRESSURE
 304.7

Fig. 19a. Computer plots of D vs u for solid europium, $\rho_0 = 5.400$.

Fig. 19b. Computer plots of P vs ξ for solid europium, $\rho_0 = 5.400$.

EOS 6 MELTING TYPE 4
CARBON (GRAPHITE)

PHASE I PHASE II
M 160.00 1100.00
S 2.100 1.010

CO 3.864 CL 4.472
MS 336.00

RH00 2.250
P1 1.80 CS11 0.0040

PHASE CHANGE PRESSURES
320. 700.

Fig. 20a. Computer plots of D vs u for solid carbon (graphite), $\rho_0 = 2.250$.

Fig. 20b. Computer plots of P vs ξ for solid carbon (graphite), $\rho_0 = 2.250$.

Fig. 21. P, T phase diagram for carbon.⁵² Stars denote the triple points reported in Ref. 53. Circles denote the coordinates of the volume discontinuities obtained using shock waves.⁵⁴ Dash-dot lines show the phase boundaries and the triangle gives the triple point coordinates, all reported in Ref. 55. (Figure reproduced from Sov. Phys. Usp.⁵¹)

EOS 127 MELTING TYPE 2
ALUMINUM 2024

M 590.00
S 1.355

CO 5.358	CL 6.285
MS 799.45	CP 5.317
F(R) 0.939	SPB 1.388
MP 516.19	R 0.910
RH00 2.785	RHOP 2.534
P1 3.43	CSII 0.0050

Fig. 22a. Computer plots of D vs u for porous aluminum 2024, $\rho_p = 2.534$.

Fig. 22b. Computer plots of P vs ξ for porous aluminum 2024, $\rho_p = 2.534$.

EOS 127
ALUMINUM 2024

MELTING TYPE 2

M 590.00
S 1.355

CO	5.358	CL	6.285
MS	799.45	CP	5.234
F(R)	0.820	SPB	1.462
MP	417.52	R	0.800
RH00	2.785	RHOP	2.228
P1	1.80	CS11	0.0050

Fig. 23a. Computer plots of D vs u for porous aluminum 2024, $\rho_p = 2.228$.

Fig. 23b. Computer plots of P vs ξ for porous aluminum 2024, $\rho_p = 2.228$.

EOS 127
ALUMINUM 2024

MELTING TYPE 2

M 590.00
S 1.355

CO	5.358	CL	6.285
MS	799.45	CP	5.010
F(R)	0.670	SPB	1.548
MP	316.25	R	0.700
RHOC	2.785	RHOP	1.950
P1	0.93	CS11	0.0050

Fig. 24a. Computer plots of D vs u for porous aluminum 2024, $\rho_p = 1.950$.

Fig. 24b. Computer plots of P vs ξ for porous aluminum 2024, $\rho_p = 1.950$.

EOS 127 MELTING TYPE 2
ALUMINUM 2024

M 590.00
S 1.355

CO	5.358	CL	6.285
MS	799.45	CP	4.392
F(R)	0.459	SPB	1.640
MP	193.23	R	0.590
RH00	2.765	RHOP	1.643
P1	0.39	CS11	0.0050

Fig. 25a. Computer plots of D vs u for porous aluminum, $\rho_p = 1.643$.

Fig. 25b. Computer plots of P vs ξ for porous aluminum, $\rho_p = 1.643$.

EOS 29
COPPER

MELTING TYPE 2

M 953.00
S 1.470

CO	3.961	CL	4.618
MS	1400.91	CP	3.865
F(R)	0.911	SPB	1.503
MP	781.42	R	0.880
RHOC	8.930	RHOP	7.860
P1	2.11	CS11	0.0021

Fig. 26a. Computer plots of D vs u for porous copper, $\rho_p = 7.860$.

Fig. 26b. Computer plots of P vs ξ for porous copper, $\rho_p = 7.860$.

EOS 29
COPPER

MELTING TYPE 2

M 953.00
S 1.470

CO	3.961	CL	4.618
MS	1400.91	CP	3.810
F(R)	0.853	SPB	1.531
MP	699.73	R	0.826
RH00	8.930	RHOP	7.380
P1	1.54	CS11	0.0021

Fig. 27a. Computer plots of D vs u for porous copper, $\rho_p = 7.380$.

Fig. 27b. Computer plots of P vs ξ for porous copper, $\rho_p = 7.380$.

EOS 29
COPPER

MELTING TYPE 2

M 953.00
S 1.470

CO	3.961	CL	4.618
MS	1400.91	CP	3.591
F(R)	0.687	SPB	1.608
MP	508.42	R	0.710
RH00	8.930	RHOP	6.340
P1	0.72	CS11	0.0021

Fig. 28a. Computer plots of D vs u for porous copper, $\rho_p = 6.340$.

Fig. 28b. Computer plots of P vs ξ for porous copper, $\rho_p = 6.340$.

EOS 74
TUNGSTEN

MELTING TYPE 2

M 2495.00
S 1.250

CO	4.033	CL	5.672
MS	3118.75	CP	2.793
F(R)	0.271	SPB	1.662
MP	457.77	R	0.509
RH00	19.170	RHOP	9.750
P1	1.26	CS11	0.0060

Fig. 29a. Computer plots of D vs u for porous tungsten, $\rho_p = 9.750$.

Fig. 29b. Computer plots of P vs ξ for porous tungsten, $\rho_p = 9.750$.

EOS 157 MELTING TYPE 2
LIMESTONE SOLENHOFEN

M 260.00
S 1.490

CO	3.781	CL	6.582
MS	387.40	CP	3.739
F(R)	0.970	SPB	1.496
MP	240.62	R	0.950
RH00	2.710	RHOP	2.575
P1	20.91	CS11	0.0230

Fig. 30a. Computer plots of D vs u for porous Solenhofen limestone, $\rho_p = 2.575$.

Fig. 30b. Computer plots of P vs ξ for porous Solenhofen limestone, $\rho_p = 2.575$.

EOS 157 MELTING TYPE 2
LIMESTONE (CALCIUM CARBONATE)

M 260.00
S 1.490

CO	3.781	CL	6.582
MS	387.40	CP	3.187
F(R)	0.572	SPB	1.661
MP	107.03	R	0.646
RH00	2.710	RHOP	1.750
PJ	3.03	CSII	0.0230

Fig. 31a. Computer plots of D vs u for porous limestone (calcium carbonate),
 $\rho_p = 1.750$.

Fig. 31b. Computer plots of P vs ξ for porous limestone (calcium carbonate), $\rho_p = 1.750$.

EOS 26 MELTING TYPE 1
IRON

M 1319.00 660.00
S 1.370 1.650

CO	4.795	CL	5.945
MS	1807.03	CP	4.742
F(R)	0.921	SPB	1.412
MP	1114.03	R	0.890
RH00	7.860	RHOP	6.995
P1	8.37	CSII	0.0054

PHASE TWO CHANGES
128.7 145.5 2704.8

Fig. 32a. Computer plots of D vs u for porous iron, $\rho_p = 6.995$.

Fig. 32b. Computer plots of P vs ξ for porous iron, $\rho_p = 6.995$.

EOS 26 MELTING TYPE 1
IRON

M 1319.00 660.00
S 1.370 1.650

CO 4.795	CL 5.945
MS 1807.03	CP 4.608
F(R) 0.765	SPB 1.505
MP 842.56	R 0.760
RH00 7.860	RHOP 5.974
P1 3.80	CS11 0.0054

PHASE TWO CHANGES
128.7 145.5 2704.8

Fig. 33a. Computer plots of D vs u for porous iron, $\rho_p = 5.974$.

Fig. 33b. Computer plots of P vs ξ for porous iron, $\rho_p = 5.974$.

EOS 26 MELTING TYPE 1
IRON

M 1319.00 660.00
S 1.370 1.650

CO 4.795	CL 5.945
MS 1807.03	CP 3.974
F(R) 0.480	SPB 1.639
MP 454.39	R 0.600
RH00 7.860	RHOP 4.716
P1 1.17	CS11 0.0054

PHASE TWO CHANGES
128.7 145.5 2704.8

Fig. 34a. Computer plots of D vs u for porous iron, $\rho_p = 4.716$.

Fig. 34b. Computer plots of P vs ξ for porous iron, $\rho_p = 4.716$.

EOS 26 MELTING TYPE 1
IRON

M 1319.00 660.00
S 1.370 1.650

CO 4.795	CL 5.945
MS 1807.03	CP 3.697
F(R) 0.404	SPB 1.662
MP 365.03	R 0.565
RH00 7.860	RHOP 4.440
PI 0.86	CSII 0.0054

PHASE CHANGE PRESSURES
128.7 145.5 1528.2

Fig. 35a. Computer plots of D vs u for porous iron, $\rho_p = 4.440$.

Fig. 35b. Computer plots of P vs ξ for porous iron, $\rho_p = 4.440$.

EOS 6 MELTING TYPE 4
CARBON

M 160.00 1100.00
S 2.100 1.010

CO	3.864	CL	4.472
MS	336.00	CP	3.296
F(R)	0.937	SPB	1.958
MP	101.53	R	0.813
RH00	2.250	RHOP	1.830
P1	0.64	CSII	0.0040

PHASE CHANGE PRESSURES
207.6 410.

Fig. 36a. Computer plots of D vs u for porous carbon, $\rho_p = 1.830$.

Fig. 36b. Computer plots of P vs ξ for porous carbon, $\rho_p = 1.830$.

EOS 6 MELTING TYPE 4
CARBON

M 160.00 1100.00
S 2.100 1.010

CO	3.864	CL	4.472
MS	336.00	CP	3.146
F(R)	0.778	SPB	1.939
MP	88.31	R	0.709
RH00	2.250	RHOP	1.730
P1	0.48	CS11	0.0040

Fig. 37a. Computer plots of D vs u for porous carbon, $\rho_p = 1.730$.

Fig. 37b. Computer plots of P vs ξ for porous carbon, $\rho_p = 1.730$.

EOS 6 MELTING TYPE 4
CARBON

M 160.00 1100.00
S 2.100 1.010

CO	3.864	CL	4.472
KS	336.00	CP	2.663
F(R)	0.566	SPB	1.090
MP	55.16	R	0.653
RH00	2.250	RHOP	1.470
P1	0.21	CS11	0.0040

PHASE CHANGE PRESSURES
166.77 310.

Fig. 38a. Computer plots of D vs u for porous carbon, $\rho_p = 1.470$.

Fig. 38b. Computer plots of P vs ξ for porous carbon, $\rho_p = 1.470$.

The melting point for porous materials has been scaled according to the equations

$$x_{\text{melt}}(\text{porous}) = R f(R) x_{\text{melt}}(\text{solid}), \quad (2.44)$$

$$\sigma'_{\text{melt}}(\text{porous}) = \frac{\frac{MS}{f(R)} x_{\text{melt}}(\text{porous})}{\left[1 - \frac{S}{f(R)} x_{\text{melt}}(\text{porous}) \right]^2}, \quad (2.45)$$

where $f(R)$ is given by Eq. (2.27).

3. CALCULATIONS USING THE POROUS THEORY

A series of calculations was run with the one-dimensional computer program UKO.⁵⁶ The equation-of-state subroutine incorporated the porous theory derived in Sec. 2. The melting and vaporization was treated in the manner described in Sec. 1. The data presented in this section are from gas-gun and high-explosive plane wave calculations. Plane wave impact calculations were modeled with UKO, and the resulting Hugoniot plateau value was plotted for comparison with the experimental values. The data references have not been cited, since there were a large number.

Figures 39 and 40 show sample calculated waveforms and the resulting Hugoniot plateau values. In Fig. 41 the calculated Hugoniot plateau values and the experimental shock data for initially solid aluminum are plotted. Figure 42 gives the comparison between theory and experiment for initially solid SiO_2 (the data includes quartz, quartzite, granite, and gneiss). Figures 43-49 give the comparison for initially porous copper and SiO_2 -type materials.

In the comparisons a small dot or plus (+) is the experimental value and the circled dot is the computer experiment. The asterisk in the copper comparison is hydrostatic data.⁵⁷ The uniaxial granite data is from Brace.⁵⁸

Fig. 39. Calculated waveforms and Hugoniot plateau values for aluminum, showing stress vs radius.

Fig. 40. Calculated waveforms and Hugoniot plateau values for aluminum showing stress vs time.

Fig. 41. Calculated Hugoniot plateau values and experimental shock data for initially solid aluminum.

Fig. 42. Comparison between experiment and theory for initially solid SiO_2 (including quartz, quartzite, granite, and gneiss).

Fig. 43. Computer plots of P vs ξ for porous copper, $\rho_p = 7.86$.

Fig. 44. Computer plots of P vs ξ for porous copper, $\rho_p = 6.05$.

Fig. 45. Comparison between experiment and theory for porous SiO_2 (alluvium), $\rho_p = 2.0$ to 1.94 ,

Fig. 46. Comparison between experiment and theory for porous SiO_2 (alluvium), $\rho_p = 1.7$.

γ

Fig. 47. Comparison between experiment and theory for porous SiO_2 (alluvium), $\rho_p = 1.53$ to 1.59 .

Fig. 48. Comparison between experiment and theory for porous SiO₂ (playa), $\rho_p = 1.41$ to 1.47 .

Fig. 49. Comparison between experiment and theory for porous SiO_2 (tuff and SiO_3).

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APPENDIX

EQUATIONS FOR COMPUTING SHOCK STATES AND HYDROSTATS IN POROUS MATERIALS BELOW THE SOLID POINT

The equations used to compute the shock states and the hydrostats below the Hugoniot elastic limit are outlined below. The sample P states for $\xi > \xi_s$ are given in terms of the two sample S parameters and the porosity ratio, i.e., M, S, and R.

Sample S

The approximate elastic equations for a uniaxial strain are

$$K_0 = \rho_0 C_L^2, \quad (A-1)$$

where C_L is the longitudinal sound speed;

$$\sigma = K_0 \frac{x}{1-x}, \quad (A-2)$$

where $\frac{x}{1-x} = -\frac{\Delta V}{V}$, the volumetric strain, and

$$x = 1 - V/V_0;$$

and

$$E = \frac{1}{2} \frac{\sigma}{\rho_0} x. \quad (A-3)$$

The Hugoniot elastic limit is given by

$$\sigma_{HEL} = K_0 \frac{x_{HEL}}{(1-x_{HEL})}, \quad (A-4)$$

where x_{HEL} is the volume decrement at the elastic limit.

The hydrostat equations for a plane shock wave are

$$B = MS = \rho_0 C_0^2 = \rho_0 C_B^2, \quad (A-5)$$

where C_B is the bulk sound speed and C_0 is the shock velocity intercept. Also

$$\sigma_H = M \frac{Sx}{(1-Sx)^2}$$

and

$$E_H = \frac{1}{2} \frac{\sigma_H}{\rho_0} x. \quad (A-6)$$

From Eq. (A-6) the limiting compression for sample S is $x - 1/S$.

Sample P

If r_0 is the distance between nearest neighbor atoms, then $r_0/R^{1/3}$ is proportional to the distance in the corresponding porous sample whose porosity is defined by the porous ratio $R = \rho_p/\rho_0$. The bulk modulus in the porous sample differs from the sample S bulk modulus by R^5 . This is an empirical observation, and is equivalent to assuming that $C_p = RC_0$.

The elastic equations for sample P are assumed to be

$$K_0' = \rho_p C_{pL}^2 = R^5 K_0, \quad (A-7)$$

where K_0 is the sample S elastic modulus,

$$\sigma' \approx K_0' \frac{\xi}{1 - \xi}, \quad (A-8)$$

where $\xi = 1 - V/V_p$, and

$$E' = \frac{1}{2} \frac{\sigma'}{\rho_p} \xi. \quad (A-9)$$

The Hugoniot elastic limit is

$$\sigma_{HEL}' \approx K_0' \frac{\xi_{HEL}}{1 - \xi_{HEL}}. \quad (A-10)$$

The pore collapse equation for a plane wave shock for $\xi_{HEL} < \xi < \xi_s = 1 - R$ is approximated by a quadratic curve

$$\sigma' \approx \sigma_{HEL}' + R^5 M (\xi - \xi_{HEL})^2. \quad (A-11)$$

The solid point stress σ_s at $\xi = \xi_s$ is then

$$\sigma_s' = R^5 M (\xi_s - \xi_{HEL})^2 + \sigma_{HEL}'. \quad (A-12)$$

For $\xi > \xi_s$

$$\sigma'' = M \frac{\frac{S}{f(R)} x}{\left[1 - \frac{S}{f(R)} x\right]^2}, \quad (\text{A-13})$$

where

$$x = \frac{\xi - \xi_s}{R}$$

and $f(R)$ is as defined by Eq. (2.27). In this region the stress is defined to be

$$\text{stress} = \max(\sigma', \sigma'') \quad (\text{A-14})$$

for a plane wave shock, and

$$E' = \frac{1}{2} \frac{(\text{stress} + \sigma'_{\text{HEL}})}{\rho_p} \xi. \quad (\text{A-15})$$

The Porous Hydrostat

The values of the porous hydrostat outside the pore crushing region are known from the development up to this point. For example, the hydrostat for $\xi < \xi_0$ (ξ_0 is the volume decrement at the static elastic limit) is

$$P = R^5 M \frac{S\xi}{(1 - S\xi)^2}; \quad (\text{A-16})$$

for any value of $R < 1$ and $\xi > \xi_s$, the hydrostat is

$$\begin{aligned} P &= M \frac{\frac{S}{f} x}{\left(1 - \frac{S}{f} x\right)^2} \\ &= M \frac{\frac{S}{f} \frac{\xi - \xi_s}{R}}{\left(1 - \frac{S}{f} \frac{\xi - \xi_s}{R}\right)^2}, \end{aligned} \quad (\text{A-17})$$

where $f = f(R)$ from Eq. (2.27). Let the form of P in the pore-crushing region be given by

$$P = C \frac{\frac{S\xi - a}{b}}{\left(1 - \frac{S\xi - a}{b}\right)^2}, \quad (A-18)$$

where a , b , and c will vary with ξ and R to give the limiting forms in (A-16) and (A-17).

The following inequalities define the limits of a , b , and c which give the correct values in A-16 and A-17.

$$\begin{aligned} 0 &\leq a \leq S \xi_s, \\ 1 &\leq b \leq Rf(R), \\ R^5 &\leq C \leq 1. \end{aligned} \quad (A-19)$$

The left-hand limit corresponds to $\xi \leq \xi_0$ and the right-hand limit corresponds to $\xi \leq \xi_s$. The following linear functions satisfy the limiting requirements.

$$\begin{aligned} a &= S \xi_s Z, \\ b &= 1 - (1 - Rf)Z, \\ c &= R^5 + (1 - R^5)Z, \end{aligned} \quad (A-20)$$

where

$$Z = \frac{\xi - \xi_0}{\xi_s + \xi_2} \quad (A-21)$$

and Z is defined to be zero for $\xi < \xi_0$ and unity for $\xi \geq \xi_s + \xi_2 + \xi_0$. The parameter ξ_2 can be determined by requiring that the static hydrostat and shock hydrostat be approximately equal at the solid point P_s defined by Eq. (A-12). That is,

$$C \frac{\frac{S\xi - a}{b}}{\left(1 - \frac{S\xi - a}{b}\right)^2} = P_s,$$

and solving for $\frac{S\xi - a}{b}$ we have

$$\frac{S\xi - a}{b} \equiv \eta = \left(1 + \frac{R^5 M}{2P_s}\right) - \sqrt{\left(1 + \frac{R^5 M}{2P_s}\right)^2 - 1}. \quad (A-22)$$

Solving for ξ_2 gives

$$\xi_2 = \frac{R f(R) \eta}{S} \xi_0 \quad (A-23)$$

and

$$Z = \frac{\xi - \xi_0}{\xi_s - \xi_0 + \frac{R f(R) \eta}{S}} \quad (A-24)$$

This completes the sample P approximation in the elastic and pore-crushing regimes.

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