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THE HUGONIOT OF A SOLID DETERMINED BY MEANS OF A VARIATIONAL PRINCIPLE

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FOREWORD

The work reported herein, performed by the University of Dayton Research Institute, Dayton, Ohio, was partially supported by Air Force Contract F33615-70-C-1228, "Response of Materials to Impulsive Loading," Project 7360, Chemical, Physical, and Thermodynamic Properties of Aircraft, Missile and Spacecraft Materials, Task 736006, Impact Damage and Weapons Effects on Aerospace System Materials. This contract is administered by Mr. Gordon H. Griffith, Project Engineer, AFML.

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THE HUGONIOT OF A SOLID DETERMINED BY MEANS OF A VARIATIONAL PRINCIPLE

I. INTRODUCTION

A much used form of an equation of state for solids is the so-called Mie-Grüneisen relation,

$$p - p_c(v) = \frac{\Gamma(v)}{v}\left(E - E_c(v)\right) ,$$

where p_c and E_c are the pressure and specific internal energy at 0 °K, and Γ, the Grüneisen coefficient, is a function of volume only. One way of implementing this relation for arbitrary (p, v, E) states involves taking p, E to be known Hugoniot states p_H, E_H, noting that $p_c = -E_c'(v)$, and taking for Γ one of the several formulas available from the theory of lattice dynamics (Slater[1], Dugdale-MacDonald[2], Zubarev-Vashchenko[3]), which express Γ in terms of E_c and its derivatives. The resulting nonlinear differential equation is then solved for E_c. With p_c, E_c and Γ then known functions of v, the Mie-Grüneisen relation can be used to describe off-Hugoniot states.

The shortcomings and inconsistencies of these lattice-dynamical formulas for the Grüneisen coefficient, and an account of what this implies in geophysical calculations relating to the internal structure of the earth, have been given by Shapiro and Knopoff[4]. Considerable interest therefore attends the possibility of determining the Grüneisen coefficient by an independent approach. In the work reported here, based on a variational principle, an equation is derived which relates the cold energy function E_c and the Hugoniot, so that knowledge of one yields the other and hence the Grüneisen coefficient. This result is illustrated in the case of aluminum, where an analytic formulation for E_c due to McKenna and Pastine[5] is used to derive the Hugoniot function. The latter function is found to agree with available experimental data very closely up to 340 kb. An interesting by-product in this regard is a quadratic expansion in the particle velocity, which approximates the shock velocity; the coefficients of this expansion are simple formulas involving physically meaningful quantities.

II. ANALYSIS

As was shown recently by Heyda[6] the temperature-independent Grüneisen coefficient of a solid, $\Gamma(u)$, may be expressed in the form

$$\Gamma(u) = \Gamma^*(u)\, G \quad , \tag{1}$$

where $\Gamma^*(u)$ is the form which Γ takes on the basis of the approximate doubling of the particle velocity u behind a planar shock wave moving through the solid with speed D and arriving at a free surface parallel to the shock front. The function $\Gamma^*(u)$ was found to be

$$\Gamma^*(u) = \frac{(D - u)(D + uD')\, D'}{D^2} \quad , \tag{2}$$

where the prime indicates differentiation with respect to u. The function G, which can be regarded as a normalized Grüneisen coefficient,

$$G = \Gamma(u) \;/\; \Gamma^*(u) \quad , \tag{3}$$

was shown in turn to be given by

$$G = \left(\frac{D}{uD'}\right)^2 \left[1 - \frac{1}{u_r'^{\,2}}\right] + \frac{1}{u_r'^{\,2}} \quad , \tag{4}$$

where $u_r = u_{fs} - u$ and u_{fs} is the free surface velocity.

Solving Eq. (4) for u'_r and integrating with respect to u, we may write

$$u_r = \int_0^u \sqrt{\frac{1 - \epsilon^2}{1 - \epsilon^2 G}}\; du \quad , \tag{5}$$

where

$$\epsilon = uD' \;/\; D \quad . \tag{6}$$

It is convenient to change the independent variable from u to ε and to regard u, G, u_r and D as functions of ε. If ε should be known from an independent source as a function of u, the relation (6) may be looked upon as a differential equation for the determination of the Hugoniot function D(u). Making this change we can rewrite Eq. (5) in the form

$$u_r = \int_0^{\varepsilon} u'(\tilde{\varepsilon}) \sqrt{\frac{1 - \tilde{\varepsilon}^2}{1 - \tilde{\varepsilon}^2 G(\tilde{\varepsilon})}}\, d\tilde{\varepsilon} \quad , \tag{7}$$

where now the prime indicates differentiation with respect to ε.

For ε arbitrary but fixed it is natural to regard $u_r \equiv u_r[G, u]$ as a functional defined on the set of functions G and u and to consider extremizing $u_r[G, u]$ over a family of curves $G = G(\varepsilon)$, $u = u(\varepsilon)$ lying on some constraint surface $g \equiv g(\varepsilon, G, u) = 0$.

To obtain a suitable function g we refer to the Mie-Grüneisen form of the equation of state of a solid, namely,

$$p - p_c(v) = \frac{\Gamma(v)}{v} \left[E - E_c(v) \right] \quad , \tag{8}$$

where v is specific volume and p, E denote pressure and specific energy, respectively; the subscript c indicates pressure and specific energy at 0°K. Taking p, E along the Hugoniot of the solid centered at the normal conditions

$$p_H = 0, \; E_{H_o} = E_c(v_o) + E_o \quad , \tag{9}$$

where v_o is the specific volume of the solid at $T = T_o$, $p = 0$, and E_o is the specific thermal energy of the solid at these same conditions, (in our calculations of the aluminum hydrostat we shall take $T_o = 300\,°K$), we may write

$$\frac{\Gamma}{v} \left[E_c - E_H \right] - p_c + p_H = 0 \quad . \tag{10}$$

Since

$$p_c = - E'_c(v) \tag{11}$$

and

$$E_H = E_{H_o} + \frac{p_H}{2}(v_o - v) \quad , \tag{12}$$

we can, upon making the definition

$$E^*_c(v) = E_c(v) - E_c(v_o) - E_o \quad , \tag{13}$$

rewrite Eq. (10) as

$$\frac{\Gamma}{v}\left[E^*_c - \frac{p_H}{2}(v_o - v)\right] + E'_c(v) + p_H = 0 \quad . \tag{14}$$

From the Hugoniot relation (for a derivation of the Pankine-Hugoniot relations, see Ref. (7))

$$v = v_o\left(1 - \frac{u}{D}\right) \tag{15}$$

we obtain

$$\frac{dv}{du} = - \frac{v_o(1 - \epsilon)}{D} \quad , \tag{16}$$

so that

$$\frac{dE_c}{dv} = - \frac{D}{v_o(1 - \epsilon)} \frac{dE_c}{du} \quad ,$$

or, in a less accurate but more convenient notation,

$$E'_c(v) = - \frac{D}{v_o(1 - \epsilon)} E'_c(u) \quad . \tag{17}$$

Recalling that

$$p_H = \rho_o Du, \quad p_H(v_o - v) = u^2, \quad \rho_o = 1/v_o \quad , \tag{18}$$

we find, upon substituting from Eqs. (15), (17), (18) into Eq. (14), that

$$\frac{\Gamma}{D-u}\left(E_c^* - \frac{1}{2}u^2\right) - \frac{E_c'(u)}{1-\epsilon} + u = 0 \quad . \tag{19}$$

From Eqs. (1) and (2), however, it follows that

$$\frac{\Gamma}{D-u} = \epsilon(1+\epsilon)G(\epsilon) \Big/ u \quad , \tag{20}$$

which, substituted into Eq. (19), yields the desired form of the constraint surface g = 0, namely,

$$g(\epsilon, G, u) = \epsilon(1+\epsilon)G(\epsilon) - H(u, \epsilon) = 0 \quad , \tag{21}$$

where the function H is defined by

$$H(u, \epsilon) = \left[\frac{uE_c'(u)}{1-\epsilon} - u^2\right] \Big/ \left[E_c^* - \frac{1}{2}u^2\right] \quad . \tag{22}$$

In the space of the variables ϵ, G, u the equation (21) constitutes a surface passing through the curve $G = G(\epsilon)$, $u = u(\epsilon)$. For each choice of the function G, there is determined a corresponding function $u(\epsilon)$. Assume then that the functional $u_r[G, u]$ has an extremum for the curve

$$G = G(\epsilon), \quad u = u(\epsilon) \quad . \tag{23}$$

Then since g_G and g_u do not vanish simultaneously at any point of the surface (21), there exists (see Theorem 2, p. 46 of reference (8)) a function $\lambda(\epsilon)$ such that the curve (23) is an extremal of the function

$$\int_o^\epsilon \left[F + \lambda(\bar{\epsilon})g\right] d\bar{\epsilon} \quad ,$$

where F is defined by

$$F \equiv u'(\epsilon)\sqrt{\frac{1-\epsilon^2}{1-\epsilon^2 G(\epsilon)}} \quad , \tag{24}$$

the necessary conditions for which are given by

$$F_G + \lambda g_G = 0, \quad \lambda g_u = \frac{d}{d\epsilon} F_{u'} \quad . \tag{25}$$

Eliminating λ in Eqs. (25) and, for convenience, letting

$$P \equiv \sqrt{\frac{1-\epsilon^2}{1-\epsilon^2 G}} \quad , \tag{26}$$

we obtain the single equation

$$u' P_G H_u = \epsilon(1+\epsilon)\left[P_\epsilon + G' P_G\right] \quad . \tag{27}$$

However, from Eq. (21) we have

$$\epsilon(1+\epsilon)G' + (1+2\epsilon)G = H_u u' + H_\epsilon \quad , \tag{28}$$

so that u' and G' can be eliminated simultaneously from Eqs. (27), (28) and no differential equation need be solved to obtain $G(\epsilon)$ and $u(\epsilon)$. The result is

$$\left[(1+2\epsilon)G - H_\epsilon\right] P_G = \epsilon(1+\epsilon)P_\epsilon \quad . \tag{29}$$

When Eq. (26) is taken into account in Eq. (29) and the resulting differentiations carried out, we find the result

$$G(\epsilon) = \frac{2-(1-\epsilon)H_\epsilon}{1-\epsilon+2\epsilon^2} \quad . \tag{30}$$

From Eq. (22) we note that

$$(1 - \epsilon) H_\epsilon = H + \frac{u^2}{E_c^* - \frac{1}{2} u^2}$$

$$= \epsilon (1 + \epsilon) G + \frac{u^2}{E_c^* - \frac{1}{2} u^2} \quad ,$$

so that Eq. (30) assumes the final form

$$G(\epsilon) = \frac{2}{1 + 3\epsilon^2} \cdot \left(\frac{u^2 - E_c^*}{\frac{1}{2} u^2 - E_c^*} \right) , \qquad (31)$$

where the function $u = u(\epsilon)$ is obtained by eliminating $G(\epsilon)$ between the Eqs. (21), (31), the function E_c^* being assumed to be known. Actually, it is easier to obtain the function $\epsilon = \epsilon(u)$. We find that it satisfies the equation

$$\epsilon^3 \left[2E_c^* + u^2 \right] + 3\epsilon^2 u \left[E_c'(u) - u \right] + \epsilon \left[3u^2 - 2E_c^* \right] + u \left[E_c'(u) - u \right] = 0. \qquad (32)$$

From the relation (17) we may readily show that

$$u E_c'(u) = (1 - \epsilon)(x - x_o) E_c'(x) \quad , \qquad (33)$$

where $x = v/v_{oK}$ and v_{oK} is the specific volume at $T = 0\,°K$ and $p = 0$.

With the relation (33) we may then recast the cubic equation (32) in the form

$$(u^2 - E_c^*)(1 - \epsilon)^2 = (1 + 3\epsilon^2) \left[(x - x_o) E_c'(x) - E_c^* \right] \quad , \qquad (34)$$

where a factor $(1 - \epsilon)$ has been divided out. Equation (34) can now be solved for ϵ, and hence for D', to get

$$D' = \frac{D}{u}\left\{\frac{1 \pm \sqrt{4Q - 3Q^2}}{1 - 3Q}\right\} , \qquad (35)$$

where

$$Q = \frac{(x - x_o)\,E_c'(x) - E_c^*}{u^2 - E_c^*} .$$

Since

$$E_c'(x) = -v_{oK}\,p_c$$

and

$$x = x_o\left(1 - \frac{u}{D}\right) , \quad x_o = v_o/v_{oK} \qquad (36)$$

we may rewrite Q as

$$Q = \frac{\dfrac{v_o u p_c}{D} - E_c + E_{H_o}}{u^2 - E_c + E_{H_o}} ,$$

upon using the relations (13) and (9).

We note that $Q \to 1$ as $u \to 0$. Hence the minus sign in Eq. (35) must be chosen in order that D' remain finite. The indeterminacy in the right member of Eq. (35) at $u = 0$ may be resolved by rewriting it in the form

$$\frac{D}{u}\left[\frac{1 - Q}{1 + \sqrt{4Q - 3Q^2}}\right]$$

and noting that

$$\frac{1 - Q}{u} = \frac{u - \dfrac{v_o p_c}{D}}{u^2 - E_c + E_{H_o}} .$$

Since E_c and p_c are generally known as functions of x, and x in turn may be expressed in terms of u and D by means of relation (36), we see that the Hugoniot function D = D (u) may be obtained by solving the first order nonlinear differential equation

$$D' = f(u, D) \quad , \tag{37}$$

where

$$f(u, D) = \frac{R(u, D)}{1 + \sqrt{4Q(u, D) - 3Q^2(u, D)}} \tag{38}$$

and

$$Q = \frac{\frac{v_o u p_c}{D} - E_c + E_{H_o}}{u^2 - E_c + E_{H_o}} \quad , \qquad R = \frac{uD - v_o p_c}{u^2 - E_c + E_{H_o}} \quad , \tag{39}$$

subject to the initial condition

$$u = 0 \quad , \qquad D = D(0) \equiv c_o \quad . \tag{40}$$

Since a closed form solution of Eq. (37) appears unlikely, the solution D (u) must be obtained either through numerical integration or expansion in series. If we denote the expansion for D through the quadratic term by

$$D = c_o + su + bu^2 \quad , \tag{41}$$

we find by putting u = 0 in Eq. (38) that s is given by the simple formula

$$s = -\frac{v_o p_c (v_o)}{2E_o} \quad , \tag{42}$$

or equivalently,

$$s = \frac{x_o E'_c(x_o)}{2E_o} \quad . \tag{43}$$

Continuing, we find upon differentiating (37) with respect to u and then putting u = 0 that

$$b = \frac{D''(0)}{2} = \frac{c_o^2 - x_o^2 E''_c(x_o) - 6s^2 E_o}{4E_o c_o} \quad . \tag{44}$$

It might be noted that the value of s given by formula (43) will normally differ from tabulated values of the slope of the "linear" shock velocity-particle velocity relation since the latter represents an empirical fit to experimental data over a range of particle velocities well beyond u = 0. The Hugoniot formulation (38) will in addition reflect passage through a minimum point on the curve $E_c = E_c(v)$ at $v = v_{oK}$ as v decreases from v_o, i.e. as u increases from u = 0.

Additional coefficients beyond $D''(0)/2$ may be calculated by the same procedure. However existing analytical formulations for $E_c^*(x)$ do not offer sufficient accuracy in the values of $E_c^{*(n)}(x_o)$ beyond n = 2. Anticipating that such formulations may become more accurate in the future we have calculated one additional coefficient:

$$h = \frac{D'''(0)}{6} = \frac{x_o^3 E'''_c(x_o) - 24sE_o c_o D''(0) - 8E_o s^3 + 2sc_o^2}{12E_o c_o^2} \quad . \tag{45}$$

The Grüneisen coefficient $\Gamma(u)$ is now readily available from Eqs. (2), (3), and (31). We find

$$\Gamma(u) = \frac{2\left[D'(u) - \varepsilon\right](1+\varepsilon)}{1 + 3\varepsilon^2} \left\{ \frac{E_o + u^2 - \left[E_c - E_c(v_o)\right]}{E_o + \frac{1}{2}u^2 - \left[E_c - E_c(v_o)\right]} \right\} , \tag{46}$$

or, equivalently,

$$\Gamma(u) = (D - u)\left[\frac{\dfrac{E_c'(u)}{1-\varepsilon} - u}{E_c^* - \dfrac{1}{2}u^2}\right] . \qquad (47)$$

The initial value of Γ turns out to be $\Gamma(0) = 2s$, whence from Eq. (43) we obtain

$$\Gamma(0) = 2s = \frac{x_o E_c'(x_o)}{E_o} , \qquad \left(G(0) = 2\right) , \qquad (48)$$

a result which follows directly from the Mie-Grüneisen relation (14) by putting $v = v_o$.

That the extremal (23), where $G(\varepsilon)$ and $u(\varepsilon)$ are defined by the relations (31) and (32), maximizes the functional $u_r[G, u]$ is evident from the fact that for the choice $G \equiv 1$ (which corresponds to taking Γ in accordance with the velocity doubling approximation) we obtain $u_r = u$, whereas a three term expansion of the integral in Eq. (5) yields the result

$$u_r = u + \frac{s[\Gamma(0) - s]}{6c_o^2} u^3 , \qquad (49)$$

which in view of the result (48) shows that $u_r > u$. Indeed, with c_o assumed to be known and with $D \approx c_o + su$, the D function (or, equivalently, the G function) which maximizes u_r is that for which $s[\Gamma(0) - s]$, considered as a function of s, is a maximum. This occurs evidently for $\Gamma(0) = 2s$, in agreement with relation (48).

The approximate relation (49) is of interest in its own right as it gives good agreement with tabulated values of u_r/u for many of the metals studied by Rice, McQueen, and Walsh[7]. Using the Γ_o and s values listed there, we find the comparisons for copper, 24 ST aluminum, silver, and zinc shown in Table I.

TABLE I

COMPARISON OF VALUES FROM EQ. (49) WITH THOSE GIVEN IN REF. 7

Copper

p (kb)	u (cm/μsec)	u_r/u [Eq. (49)]	u_r/u [Ref. 7]
100	0.0263	1.001	1.001
300	0.0681	1.004	1.005
500	0.1025	1.010	1.012

24 ST Aluminum

p (kb)	u (cm/μsec)	u_r/u [Eq. (49)]	u_r/u [Ref. 7]
100	0.0580	1.002	1.003
300	0.1465	1.013	1.015
500	0.2145	1.028	1.030

Silver

p (kb)	u (cm/μsec)	u_r/u [Eq. (49)]	u_r/u [Ref. 7]
100	0.0256	1.002	1.001
300	0.0658	1.011	1.010
500	0.0992	1.024	1.022

Zinc

p (kb)	u (cm/μsec)	u_r/u [Eq. (49)]	u_r/u [Ref. 7]
100	0.0378	1.003	1.004
300	0.0925	1.019	1.022
500	0.1373	1.043	1.042

III. EXAMPLE FOR ALUMINUM

For aluminum we employ the analytical formulation given by McKenna and Pastine in Ref. 5,

$$E_c(x) = v_{oK}\left(\frac{3A}{2\beta}\right)\left[e^{2\beta(1-x^{1/3})} - 2e^{\beta(1-x^{1/3})}\right] , \qquad (50)$$

where

$v_{oK} = 0.366$ cc/gm, $v_o = 0.371$ cc/gm,

$A = 0.6271$ Mb, $\beta = 3.772$

$E_o = .00164$ Mb cc/gm, $c_o = .5404$ cm/μsec, $T_o = 300\,°K$.

Substituting into formulas (43), (44), and (48) we obtain

$s = 1.171$, $b = 1.303$ μsec/cm, $\Gamma_o = 2.342$,

so that the Hugoniot function D is approximated by the three term expansion

$$D = 0.5404 + 1.171\,u + 1.303\,u^2 \quad . \qquad (51)$$

This function is plotted in Figure 1 and agrees with the experimental data for 24 ST aluminum, given by Walsh and Christian in Ref. (9) and Walsh, Rice, McQueen and Yarger in Ref. (10), remarkably well up to $u = 0.165$ cm/μsec, which corresponds to a pressure of approximately 340 kb. Byond this point the curve diverges slowly from the data taken from Ref. (10). An additional term in Eq. (51) would remedy this if derivatives of $E_c(x)$ of the third and higher orders were known at $x = x_o$ with sufficient accuracy. This, however, puts too great a strain on the empirical form (50).

IV. CONCLUSION

The tentative conclusion is that the aluminum hydrostat is determinable from the variational principle proposed here and that the same may well be true for other solids. Accepted as a general principle, the procedure may be reversed and the cold energy may be obtained by solving the linear differential equation (32) for E_c with an accurate experimentally determined Hugoniot as input. Calculation of the Grüneisen coefficient can then be made directly from the Mie-Grüneisen relation (8), thereby avoiding any use of formulas based on the theory of lattice dynamics.

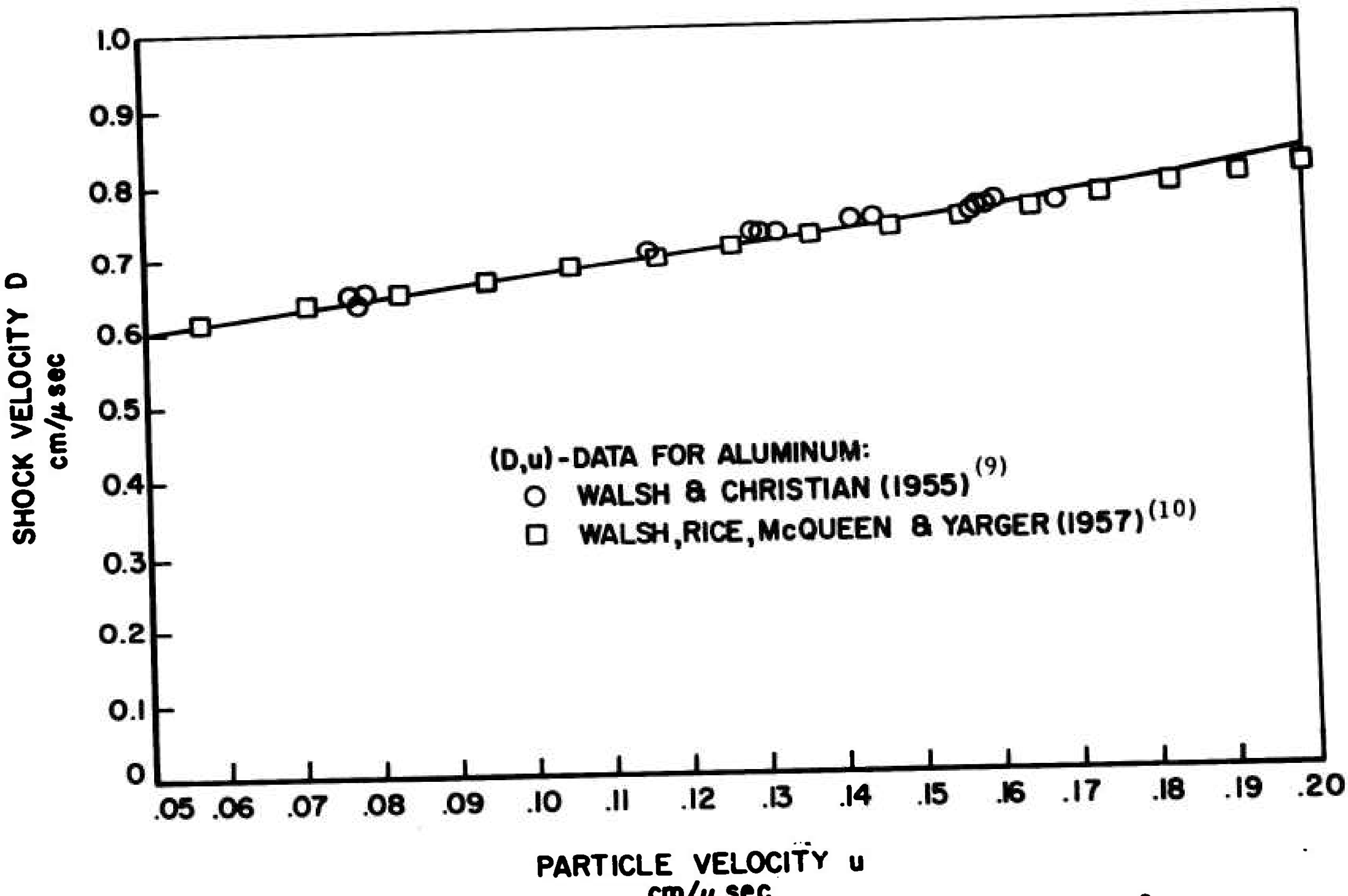

Figure 1. Curve represents the theoretical Hugoniot $D = 0.5404 + 1.171u + 1.303u^2$ cm/μsec determined by maximizing the free surface velocity subject to a Mie-Gruneisen constraint condition over the class of all possible Hugoniots.

REFERENCES

1. Slater, J. C., Introduction to Chemical Physics, Chapter XIII, McGraw-Hill, New York (1939).

2. Dugdale, J. S. and D. K. C. MacDonald, "The Thermal Expansion of Solids," Phys. Rev., 89, 832 (1953).

3. Vashchenko, V. Ya. and V. N. Zubarev, "Concerning the Grüneisen Constant," Soviet Physics - Solid State, 5, No. 3, 653 (1963).

4. Shapiro, J. N. and L. Knopoff, "Comments on the Interrelationships between Grüneisen's Parameter and Shock and Isothermal Equations of State," J. Geophys. Res., 74, No. 6, 1439 (1969).

5. McKenna, P. and D. J. Pastine, "Volume Dependence of the Grüneisen Parameter for Aluminum, " J. Appl. Phys. 39, 6104 (1968).

6. Heyda, J. F., "The Grüneisen Coefficient Implied by the Velocity Doubling Rule," J. Appl. Math. and Phys. (ZAMP), 22, Fasc. 2, 350 (1971).

7. Rice, M. H., R. G. McQueen and J. M. Walsh, "Compression of Solids by Strong Shock Waves, in Solid State Physics, Vol. 6, Academic Press, New York (1958).

8. Gelfand, I. M. and S. V. Fomin, Calculus of Variations, Prentice-Hall, Englewood Cliffs, New Jersey (1963).

9. Walsh, J. M. and R. H. Christian, "Equations of State of Metals from Shock Wave Measurements," Phys. Rev., 97, 1544 (1955).

10. Walsh, J. M., M. H. Rice, R. G. McQueen and F. L. Yarger, "Shock-Wave Compression of Twenty-Seven Metals. Equations of State of Metals," Phys. Rev., 108, No. 2, 196 (1957).

11. Pastine, D. J., "Equation of State for Sodium Metal," Phys. Rev., 166, No. 3, 703 (1968).

APPENDIX

We list here some additional formulas of interest which are derivable from those obtained in Section II.

First of all we may readily show that Eq. (32) may be converted to the form

$$p_c = \left[\frac{1 - \varepsilon + 2\varepsilon^2 - \dfrac{2}{G(\varepsilon)}}{1 + 3\varepsilon^2 - \dfrac{2}{G(\varepsilon)}} \right] p_H , \tag{A-1}$$

which relates the Hugoniot and the cold pressure in an interesting way.

Next by requiring this relation to hold in the limit as $\varepsilon \to 0$, we obtain

$$G'(\varepsilon)\Big|_{\varepsilon=0} = 0 , \qquad G''(\varepsilon)\Big|_{\varepsilon=0} = -12 + \frac{2c_o^2}{E_o s^2} , \tag{A-2}$$

and the limiting result

$$p_c(v_o) = - \frac{4\rho_o c_o^2}{s\left[12 + G''(\varepsilon)\Big|_{\varepsilon=0}\right]} = -2\rho_o E_o s . \tag{A-3}$$

From Eq. (4), however, we find that

$$G'(0) = \frac{1}{3}\left(\frac{c_o}{s}\right)^3 u_r^{(4)}(0) - \frac{2(\Gamma_o - s)\left[c_o D''(0) - s^2\right]}{s^3} ,$$

so that in conjunction with relation (A-2) we obtain an additional term for the series (49), namely,

$$\frac{\left(\Gamma_o - s\right)}{4c_o^3}\left[c_o D''(0) - s^2\right] u^4 \quad . \qquad \text{(A-4)}$$

Finally, by differentiating Eq. (3), taking note of Eq. (2), and again employing relation (A-2), we find

$$\Gamma'(v_o) = \frac{2}{v_o}\left[c_o D''(0) + s(s-1)\right] \quad . \qquad \text{(A-5)}$$

Close to $x = x_o$, then, we have

$$\Gamma(x) \doteq \Gamma(x_o) + \Gamma'(x_o) \cdot (x - x_o) \quad , \quad x = v_o / v_{oK} \quad .$$

Thus for aluminum,

$$\Gamma(1) = \Gamma(1.01366) + 3.714(1 - 1.01366)$$
$$= 2.300$$

This compares favorably with McKenna and Pastine[11], who find $\Gamma(1) = 2.301$.

A final example is the evaluation of $\Gamma_o = 2s$ for metallic sodium. From Eq. (43) we have

$$\Gamma_o = \frac{x_o E'_c(x_o)}{E_o} = \frac{(1.0299)(0.00314)}{0.002784} = 1.16 \quad ,$$

which compares well with the value of 1.15 obtained by Pastine in Ref. 11, in which he evaluated the role of anharmonic contributions in determining Γ by a lattice dynamical approach. In this calculation we obtained $p_c = -.00314$ Mb by interpolating in Table I of Ref. (11). The value of E_o was obtained from the Debye expression

$$E_o = \frac{3RT_o}{A} D_1\left(\frac{\theta(x_o)}{T_o}\right) \quad ,$$

where $R = 8.314 \times 10^{-5}$ Mb cm^3/deg, $T_o = 300\,^\circ K$, $A = 22.997$ gm, and D_1 is the Debye function with argument $\theta(x_o) = 140\,^\circ K$ obtained from an approximate formula given by Pastine(11). The value of $D_1(\frac{140}{300})$ turns out to be 0.85578.