EXTRAPOLATION OF AN ISENTROPE OF A SOLID IN THE REGION OF HIGH PRESSURES

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The behavior of a material under compression is determined by its equation of state, which relates three (or more) thermodynamic parameters; for example, the pressure p, the temperature T, and the specific volume v. We consider barotropic processes for which the pressure is a single-valued function of the volume. In the general case of compression, the stress tensor is nonspherical; we shall, however, consider only states of isotropic (hydrostatic) compression in which the stresses are characterized only by the scalar p. Information concerning the behavior of a material under compression is gained from experiments involving isothermal (static) compression as well as from shock-wave measurements. At the present time, an isotherm for most materials is determined experimentally over a fairly narrow interval, $\Delta v/v_0 = 0.2$ to 0.1, of compression. For many material the shock adiabat $p_S(v)$ is known for v_0/v in a range from two to three. In an interval of large compressions the equation for an isotherm or for the cold pressure (the zero isotherm) is obtained in a variety of ways: 1) The cold pressure is deduced from the shock adiabat upon making certain loosely justified assumptions concerning the behavior of the equation of state [1-3]; 2) the isotherms of Birch and Keene [4] are obtained from various model representations; 3) the cold pressure is obtained theoretically with the aid of the method of the pseudopotential (up to the present time this technique has been successful only for the alkali metals [5-7]); 4) an equation for the pressure is obtained by extrapolating experimental data without drawing on additional physical assumptions concerning the behavior of the equation of state of the material.

We consider the last method. As the basic parameter defining the compressibility of a material, we have the modulus of compression

$$K_v(v) = -v(\partial p/\partial v)_v$$

(v is the index of barotropicity), the initial value for which is known for many materials. As the simplest extrapolation of a barotrope we have the expression

$$p = (K_{0v}/v_0)(v_0 - v), \; p(v_0) = 0, \; K_{0v} = K_v(v_0),$$

which represents the first term in the Taylor-series expansion for the pressure in terms of the volume. A more exact extrapolation can be had if one knows an experimental value for the derivative of the modulus of compression:

$$K_p = (\partial K_v/\partial p)_v.$$

Then, putting $K_p = \text{const}$ [4, 8], we obtain the equation

$$p = (K_{0v}/K_p)\left[(v_0/v)^{K_p} - 1\right], \tag{1}$$

which in the isothermal case is referred to as Murnaghan's equation. For a more exact extrapolation of a barotrope, experimental data are currently augmented by means of certain model representations, for example, by a functional form of the interatomic interaction potential [4]. A number of ways exist for describing barotropic equations. However, for practical use (for example, to numerically solve gasdynamic problems), it is desirable to have a uniform form for the equation of a barotrope. In order to obtain uniform expressions for the barotrope of various materials, extrapolating them more exactly than does (1), we introduce the auxiliary function

$$B_v(v) = (K_p + 1)/4 = -(v/4)p''/p' \tag{2}$$

(the primes indicate differentiation with respect to volume). In terms of the function B_v, we define the zero isotherm B_c, the isotherm B_T, the isentrope B_S, and the shock adiabat B_s. We calculate the pressure from (2) as follows:

$$p(v) = p_0 + \frac{K_{0v}}{v_0} \int\limits_v^{v_0} \exp\left(4 \int\limits_w^{v_0} B_v(x)/x\,dx\right) dw. \tag{3}$$

We now establish some properties of the various barotropes B_v. For qualitative estimates we use the Mie–Grüneisen equation of state,

$$p(v) = p_c(v) + (\gamma(v)/v)(E - E_c), \tag{4}$$

where E is the specific internal energy; E_c is the elastic energy; p_c is the cold (elastic) pressure; and $\gamma(v) \simeq 2$ is the Grüneisen coefficient, assumed to be a weakly varying quantity [9]. For $\tau = (p - p_c)/K_{0c} \ll 1$, from (4) we obtain

$$B_S(v) = B_c(v) + A_S(v)\tau, \tag{5}$$

where A_S can be obtained when the function $\gamma(v)$ is known. We write the equation of an isotherm in the form

$$p_T = p_c + \frac{\gamma(v)}{v} \int\limits_0^T C_V dT,$$

from whence we obtain

$$B_T(v) = B_c(v) + A_T(v)\tau, \tag{6}$$

where $A_T(v)$ depends on $\gamma(v)$ and the heat capacity $C_V(v)$.

The function $B_S(v)$ has a fairly simple physical interpretation [8], namely, the following: At the initial point of the shock adiabat

$$B_S(v_0) = B_s(v_0) = dU/du, \tag{7}$$

where U is the shock-wave velocity and u is the particle velocity. The use of the functions $B_S(v)$ makes it possible to write the equations of one-dimensional isentropic gasdynamics in the form of the characteristics and the relationships on them in the following way:

$$dx/dt = u \pm c, \quad d(u \pm c)/du = 2B_S(v) + 1,$$
$$c = c_0 \exp\left(2 \int\limits_v^{v_0} B_S(w)/w\,dw\right), \tag{8}$$

where x is a coordinate, t is the time, and c is the sound velocity. The empirical relationship

$$U = a + bu, \tag{9}$$

which approximates well the results of shock-wave measurements [10] (a and b are constants), allows us to estimate the initial value of an isentrope through use of (7); thus,

$$B_S(v_0) \simeq b = 1\text{--}2.$$

The sign of approximate equality reflects the fact that the relationship (9) applies for high pressures (high yield strength) when the compression can be considered to be isotropic.

In the limiting case $v \to 0$, a material can be considered to be a degenerate Fermi gas [11],

$$p(v) \sim v^{-5/3},$$

from which we have

$$\lim_{v \to 0} B_{c,T,S} = 2/3.$$

The properties of the functions $B_v(v)$, considered here, enable us to assume that in the absence of phase transitions (jumps in p' and p''), this function is bounded, $B \sim 1$. It is therefore convenient to obtain the barotrope equation from (3), where B(v) is approximated by the Taylor series

$$B(v) = B_0 + B_1(v - v_0) + B_2(v - v_0)^2 + \cdots \tag{10}$$

It is desirable to know how errors made in determining B(v) affect the determination of p(v).

The expression (3) allows us to find the relationship between the variations δB and δp. Thus, we have

$$|\delta p|/p(v) \leqslant \left| \exp\left(4 \int_v^{v_0} (\delta B/w)\, dw \right) - 1 \right|;$$

for $(v_0 - v)/v_0 \ll 1$ and $\delta B = \Delta = \mathrm{const}$, we obtain

$$|\delta p|/p \leqslant 4|\Delta|(v_0 - v)/v_0,$$

while for the variation $|\delta B| = H_n(v - v_0)^n$, by which we can estimate the remainder of the series (10) with n first terms, we obtain the expression

$$|\delta p|/p = [4H_n/(n+1)]((v_0 - v)/v_0)^{n+1}.$$

We use experimental data to determine the coefficients of the series (10). Using data for an isothermal compression [12-15], we write the function $B_T(v)$ in the form $B_T = B_0 + B_1(v - v_0)$. We select the coefficients B_0 and B_1 from the condition of best approximation to the experimental data:

$$\sigma^2 = [\min(B_0, B_1)] \frac{1}{q} \sum_{i=1}^q (1 - p(v_i, B_0, B_1)/p_e(v_i))^2,$$

where $p_e(v)$ is the pressure, obtained experimentally; $p(v, B_0, B_1)$ is the pressure calculated from (3). Results from the calculations are presented in Table 1.

We note that for Na the values of B_0, calculated with the aid of the data of the various authors, are close to one another. At the same time, the values of B_1 differ sharply from one another (see Table 1), which forces one to doubt the possibility of calculating B_1 in the remaining cases also. Consequently, to approximate the data from an isothermal compression, it is sufficient in (10) to take into account the first term; i.e., for the pressure we obtain an equation of the form (1). Taking the second term into account does improve the approximation to the experimental data but it does not add to our knowledge concerning the true behavior of $p(v)$. We return now to the results of the shock-wave measurements and we attempt to obtain from them the successive coefficients in (10). To do this, we establish relationships for the derivatives of p_s and p_S with respect to the volume at the initial point of the shock adiabat, $v = v_0$, $p_s = p_S = p_0$, $E_s = E_S = E_0$ (E is the specific energy).

We write the energy-balance equation upon passage through the shock. Thus, we have

$$E_s - E_0 = (p_s + p_0)(v_0 - v)/2. \tag{11}$$

We write the difference between p_s and p_S in the series form

$$p_s - p_S = \alpha(E_s - E_S) + \beta(E_s - E_S)^2 + \ldots, \tag{12}$$

where

$$\alpha(v) = (\partial p/\partial E)_v; \quad \beta(v) = (\partial^2 p/\partial E^2)_v/2.$$

The first term of the series corresponds to the Mie-Grüneisen equation of state (2), where $\alpha(v) = \gamma(v)/v$. Differentiating (11) and (12), we obtain the first five derivatives, which do not contain β:

$$p_s' = p_S', \quad p_s'' = p_S'', \quad p_s''' = p_S''' - (\alpha/2)\, p_S'',$$

$$p_s^{(IV)} = p_S^{(IV)} + (\alpha^2/2 - 2\alpha')\, p_S'' - \alpha p_S''', \tag{13}$$

$$p_s^{(V)} = p_S^{(V)} - (3/2)\,\alpha p_S^{(IV)} + [(3/2)\,\alpha^2 - 5\alpha']\, p_S''' - [5\alpha'' + \alpha\alpha'/2 + (3/4)\,\alpha^3]\, p_S'.$$

The first two equations are trivial and yield the known result (7),

$$B_s = B_S.$$

For the first derivative of B_S we obtain

$$B_s' = B_1 = B_S' + (\gamma/2v)\, B_S, \tag{14}$$

where the value of α is replaced by γ/v. The relation (14) allows us to obtain B_1 from the experimentally known adiabat $p_S(v)$; for this it is sufficient to know the initial value of the Grüneisen coefficient, which for the majority of materials is determined experimentally [3].

TABLE 1.

Case	Material investigated	T, °K	v_0, cm^3/gm	K_0, kbar	B_0	$v_0 B_1$	Calc. value	Exptl. value
							σ, %	
1	Na [12]	400	1,086	60,82	1,21	0*	1,2	0,2
2		400	1,086	60,82	1,28	0,67	0,1	0,2
3	[13]	201	1,010	64,56	1,16	—0,13	1,3	0,2
4		20	0,986	74,91	1,09	—0,13	2,0	0,2
5	K [14]	0	1,108	37,00	1,22	0*	0,7	0,5
6		0	1,108	37,00	1,25	—0,31	0,4	0,5
7	Ca [15]	0	0,645	182,63	0,99	0,43	0,5	—
8	Ba [15]	0	0,265	94,62	0,78	0,13	1,0	—

*The minimization of σ in (13) was carried out only with respect to B_0; the value of B_1 was set equal to zero.

We can obtain the function $B_S(v)$ through use of the empirical relation (9), from which we get an expression for the pressure all over again [8], and then we have

$$B_s(v) = bvy[1 + (3/2)b(v_0 - v)y]/[1 + 2b(v_0 - v)y], \qquad (15)$$

where $y = [v_0 - b(v_0 - v)]^{-1}$. The expression (15) describes $B_S(v)$ for $v < v^* < v_0$; i.e., both it and (9) are suitable expressions over this interval. In Fig. 1 we show the function $B_S(v/v_0)$ for Na (curve 1), where the solid curve corresponds to (15) for $b = 1.26$ (see [10]) and the dashed curve represents the assumed behavior in a neighborhood of $v/v_0 = 1$ ($v_0 = 1.086$ cm^3/g, $B_0 = 1.2$). From Fig. 1 it is evident that $B_S' \ll 1$, and, therefore, upon neglecting this quantity, we obtain

$$v_0 B_1 = \gamma B_0/2 \simeq 1$$

($\gamma = 1.8$ from [8]). The line segment 2 in Fig. 1 corresponds to a linear approximation for B_S; the line segments 3, 4, and 5 correspond to a linear approximation for B_T in accordance with the tabular data (data in rows 2, 3, and 4). We conclude, therefore, that the available experimental data is sufficient for extrapolating B_S linearly with respect to the volume.

To improve the extrapolation of $B_S(v)$, it is desirable to know the following terms of the series (10). Using (13), we can obtain B_S' and B_S'', independently of $\beta(v)$. Thus, for B_S'' we obtain an expression which contains γ_0':

$$B_S' = 2B_2 = B_s'' + \alpha B_s' - 2\alpha' B + 2\alpha B^2/v.$$

An analogous expression can be obtained for B_S''', but involving γ_0''. At the present time, experimental data [10] do not permit even a crude determination of γ_0' and γ_0''.

Approximate theoretical expressions are available which relate $\gamma(v)$ and the cold pressure $p_c(v)$. These expressions, obtained by various authors, can be subsumed in a common form (see [3]), namely,

$$\gamma(v) = -(v/2)(p_x v^n)''/(p_x v^n)' + \mu, \qquad (16)$$

where n and μ are constants; in particular, the values $n = 0$ and $n = 2/3$ yield, respectively, the formulas due to Landau–Slater and to Dugdale–MacDonald. Expressions for the cold pressure $p_c(v)$ of certain materials, obtained with the use of (16) and Eq. (4), have appeared in [1-3].

Differentiating (16), we have

$$v_0 \gamma_0' = n(2B - 5/2 - n/2) + 2B_s' v_0. \qquad (17)$$

A similar procedure yields an expression for γ_0''. Factors such as the thermal pressure of the electrons, the heat capacity, the anharmonicity of the lattice vibrations, and others enter into the second term of (12) and the fifth term of (10).
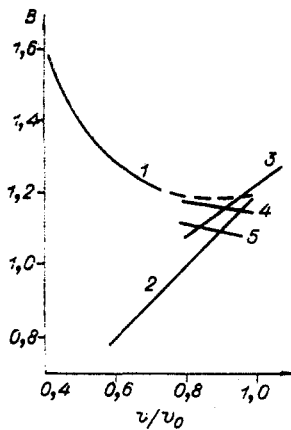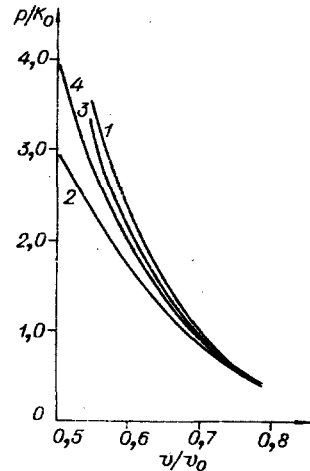
Fig. 1   Fig. 2

At the present time, the approximate formula (16), wherein differing n values yield differing values of the initial derivative γ_0', [see the relation (17)], exhausts our knowledge of how the Grüneisen coefficient depends on the volume. Inaccuracy in the determination of $\gamma(v)$ begins to manifest itself in the third term of (10); therefore, to take into account a fifth term hardly leads to any refinement in the function $B_S(v)$. To obtain the zero isentrope (cold pressure) by means of our method, it is necessary to know the shock adiabat of the material starting from a temperature close to absolute zero. For moderate temperatures we can neglect differences among B_S, B_T, and B_c [see the relations (5) and (6)] and use the resulting B_S to calculate the isothermal and the cold pressure in accordance with (3). To illustrate our method, in Fig. 2 we display $p_S(v)$ for Cu, wherein the curves 1, 2, and 3 correspond, respectively, to taking into account one, two, and three terms of the series (10); curve 4 corresponds to the cold pressure $p_c(v)$ from [2].

Uniformity of the barotrope equation is understood here in the sense of uniformity in the representation of $B_v(v)$ by means of the power series (10). From the latter we can obtain the function $p(v)$ in the necessary form and with the necessary accuracy. For example, using two terms of (10), $B(v) = B_0 + B_1(v - v_0)$, we can, with accuracy to $O(v - v_0)^3$, put

$$B(v)/v = B_0^2/(B_0 + (B_0 - v_0 B_1)(v - v_0)),$$

from which we get

$$p(v) = [K_0'/(4\beta - 1)][((\omega + v/\rho)/(\omega + v_0/\rho))^{4\rho - 1} - 1],$$

where

$$\omega = v_0^2 B_1/B_0^2; \quad \rho = B_0^2/(B_0 - B_1 v_0).$$

In the general case, $B(v)$ may be extrapolated by means of several terms of the series (10). The accuracy of such an extrapolation depends on the accuracy of the experimental data used and also on the magnitude of the remainder of the series (10). The extrapolation of $B(v)$ can be improved if experimental values of $B(v)$ are available for several values of v. To acquire such values, we can suggest two types of experiments:

1. Measurement of the shock-wave velocity U and the particle velocity u in a precompressed (statically or dynamically) material. Then $B_S(v) = dU/du$ [see the relation (7)].

2. Realization of a simple wave experimentally (the wave being one of either compression or rarefaction). For an isentropic one-dimensional flow we obtain, from the relation along the characteristics (8), the result

$$\frac{\partial}{\partial t}(\partial x/\partial u)_t = \pm (2B_s + 1). \tag{18}$$

By measuring u(x) at two different times, we obtain $B_S(u)$ from (18). For determining v(u) we have the differential equation

$$d^2 v/du^2 = \pm (2B_s(u) + 1)(dv/du)/v,$$

which can be solved numerically for arbitrary $B_S(u)$.

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Questions as to the feasibility of such measurements call for a separate study.

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