Universality in the Compressive Behavior of Solids

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We have discovered that the isothermal equation of state for solids in compression is of a simple, universal form. This single form accurately describes the pressure and bulk modulus as a function of volume for ionic, metallic, covalent, and rare gas solids.

THEORETICAL ASPECTS

The various classes of solids - covalent, metallic, ionic, and rare gas - can be distinguished by their rather different types of interatomic interactions. These differences would appear to preclude a common description of the energetics of these systems.

We have found, however, that equations of state (P, V, T, relations) for these classes of solids in compression are of a universal nature. In the following we will first discuss reasons why one might expect to find a universal form for the equation of state (EOS) of solids. Next we will propose a universal expression. Finally, the considerable EOS data available will be used to test our proposed universal form.

EOS are valuable not only for prediction of thermodynamical properties but also to obtain insight into the nature of solid state and molecular theories (refs. 1 and 2). In reference 3 a general zero temperature EOS was reported which describes well the compression of metals (in the absence of phase transitions). This was derived from a cohesive energy which was found essentially to depend exponentially on the interatomic spacing. That is, it depends on the deviation of the Wigner-Seitz radius from the equilibrium value, \( r_{\text{WS}} = r_{\text{WSe}} \). (Here \( r_{\text{WS}} \) is defined in terms of the volume \( V \) per atom as \( V = 4\pi r_{\text{WS}}^3/3 \).)
Wave-function-overlap interactions such as those occurring in metals are also found in varying degrees in covalent, ionic, and rare gas solids under high pressures. There are additional types of interactions important in determining the EOS of ionic and rare gas solids, however. Attractive coulombic interactions and attractive fluctuating dipole interactions are also present. In addition, if we now consider nonzero temperatures, there is a contribution to the pressure due to the variation of entropy. It is of the form $T(\partial S/\partial V)_T$ for the isothermal EOS.

The pressure contribution due to electron overlap varies essentially exponentially with $r_{WS} - r_{WSe}$. All other contributions to the pressure for solids on compression vary much less rapidly as a function of $r_{WS}$. For example, the entropy pressure is $T(\partial S/\partial V)_T = aBT$, where $\alpha$ is the thermal expansion coefficient and $B$ is the isothermal bulk modulus. The product $aB$ is known (ref. 4) to be essentially independent of $V$ for $T > \Theta_0$, where $\Theta_0$ is the Debye temperature. Thus, the entropy contribution to the pressure is expected to be nearly independent of $r_{WS}$, at least for $T > \Theta_0$. Also the ionic or fluctuating dipole interactions depend only on powers of $r_{WS}$. Thus, these ionic or fluctuating dipole interactions provide a pressure component which is also relatively slowly varying with $r_{WS}$ compared to electron overlap interactions.

Consequently, one may expect the shape of the EOS in compression to be determined essentially by the exponential wave function overlap. Note this is not true in expansion. For example, as the interatomic separation becomes significantly larger than the equilibrium separation for ionic solids, the wave-function overlap becomes small and the electrostatic interaction between the ions becomes dominant. This is quite different from metals, where it has been demonstrated (ref. 3) that the exponential interaction remains dominant well into the attractive region.

A NEW EQUATION OF STATE FOR SOLIDS

From the foregoing discussion, we propose that an exponential expression similar to that found (ref. 3) for metals applies to all classes of solids in compression over a range of temperatures excluding phase transitions. This expression has the form

$$P(X, T) = 3B_T[(1 - X)/X^2]\exp[\eta_T(1 - X)]$$  \hspace{1cm} (1)

where $B_T$ is the isothermal bulk modulus at zero pressure, $X = (V/V_0)^{1/3}$ ($V_0 = 4\pi r_{WSe}^3/3$ is the equilibrium atomic volume), and

$$\eta_T = 3[(aB/\partial P)_T - 1]/2$$  \hspace{1cm} (2)

Equation (2) follows from equation (1), where $(aB/\partial P)_T$ is evaluated at zero pressure. To test this, we first rearrange terms:

$$H(X, T) = \ln[PX^2/(1 - X)] = \ln B_T + \eta_T(1 - X)$$  \hspace{1cm} (3)

If our expression were universal, then one would expect isothermal plots of experimental $H(X, T)$ to be linear in $1 - X$, with intercept and slope yielding
By and \((\partial B/\partial P)_T\), respectively. The effects of entropy and forces other than those due to wave-function overlap enter only through these two parameters and \(V_0\).

We have tested equation (3) against high pressure data from all classes of solids, excluding materials which have phase transitions within the experimental pressure range. We found it to be remarkably successful. In figure 1 we have examples from each class of solid at a variety of temperatures: solid hydrogen (4.2 K data, ref. 5), solid xenon (150 K, ref. 6), cesium (295 K, ref. 7), molybdenum (293 K, ref. 8), sodium chloride (298 K, ref. 9, see also ref. 10), and magnesium oxide (293 K, ref. 8).

Despite the fact that all classes of solids are represented from a variety of experimental methods, the data are linear in \(1 - X\) as predicted by equation (3). This graphically illustrates that EOS are, in fact, universal in form, our primary result.

One may also find this way of plotting the data convenient for analyzing it. The values of \(B_T\) and \((\partial B/\partial P)_T\) obtained from intercept and slope of these plots as listed in the caption of figure 1 are in very good agreement with experimental values available in the literature (see, e.g., refs. 1, 5, and 11).

One need only know two zero pressure equilibrium numbers, \(B_T\) and \((\partial B/\partial P)_T\), at each temperature to obtain the pressure-volume curve through equation (3). Many of these equilibrium values are available in the literature. For example, one can use ultrasonic values of \(B_T\) and \((\partial B/\partial P)_T\) to predict \(P(V)\) through equation (1) and compare it with independent high pressure experimental results. This is shown in figure 2 for NaCl. NaCl was chosen because of the large amount of experimental data available which allows it to be used as a high pressure reference scale (refs. 1 and 10). Values of \(B_T = 2.34 \times 10^{10}\) Pa and \((\partial B/\partial P)_T = 5.35\) were taken from ultrasonic experiments (ref. 1). The agreement between the predicted pressures (eq. (1), solid curve), and the experimental data is very good over a broad range of \(V/V_0\).

Another gauge of the accuracy of equation (1) is found from a comparison with the Murnaghan EOS:

\[
P(X,T) = \left[ B_T/(\partial B/\partial P)_T \right] \left[ -3(\partial B/\partial P)_T - 1 \right] X
\]

Equation (4) is obtained by integrating the linear approximation

\[
B(P,T) = B_T + (\partial B/\partial P)_T P
\]

so that equation (4) has increasing accuracy as \(P \rightarrow 0\). The Murnaghan EOS is perhaps the most extensively used EOS for solids and has been argued (refs. 1 and 2) to be one of the "best" two-parameter EOS available. The dashed curve in figure 2 is a plot of the Murnaghan EOS (eq. (4)). While good agreement with the data and equation (1) is obtained at low pressures, the Murnaghan expression deviates from both at larger pressures. This is a critical test of the universal expression equation (1), because it shows that the exponential form correctly describes the nonlinear pressure contributions which are not included in equation (5).
A more severe test of nonlinear pressure effects is shown in figure 3, where hydrogen data is plotted for relative compressions of over 50 percent in volume. The data are due to Anderson and Swenson (ref. 5). The predicted pressures from the universal expression, (eq. (1)), are shown in figure 3(a) as the solid curve while the Murnaghan prediction, (eq. (4)), is the dashed curve. The input values used in both predictions are $B_T = 1.7 \times 10^8$ Pa and $(\partial B/\partial P)_T = 7.0$, as listed in reference 5. Note these input values are quite close to those obtained from the intercept and slope, respectively, in figure 1. Again, the agreement between equation (1) and experiment is good, while at the higher pressures the Murnaghan prediction deviates significantly. Bulk modulus data are also given in reference 5, which provides another test. From equation (1) we have

$$B(X,T) = \frac{(B_T/X^2)[2 + (\eta_T - 1) X - \eta_T X^2]}{\eta_T X^2} \exp[\eta_T(1 - X)] \tag{6}$$

Figure 3(b) compares the experimental data (circles) with the predictions of equation (6) (solid curve) and of Murnaghan (eq. (5), dashed curve). Again, the prediction from the universal expression, (eq. (6)), agrees well with the data, while the linear (Murnaghan) prediction deviates at high pressures.

We conclude that the EOS of all classes of solids in compression is, to a good approximation, a universal function. It can be represented by a simple exponential form which yields at each temperature accurate predictions of pressure and bulk modulus versus volume.

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**REFERENCES**


Figure 1. - Experimental values of $H(X,T) = \ln \left( \frac{P X^2}{\theta (1 - X)} \right)$ versus $1 - X$, where $x = \frac{(v/v_0)^{1/3}}{v_0}$ and $v_0$ is the equilibrium volume per atom. The source of the data and values of $B_T$ and $(\partial B_T/\partial P)_T$ as obtained from the intercept and slope of the plots of figure 1 are respectively: hydrogen, ref. 5, $1.66 \times 10^8$ Pa, 7.33; xenon, ref. 6, $1.63 \times 10^8$ Pa, 8.87; cesium, ref. 7, $1.68 \times 10^8$ Pa, 4.07; molybdenum, ref. 8, $2.66 \times 10^{11}$ Pa, 3.99; sodium chloride, ref. 9, $2.35 \times 10^{10}$ Pa, 5.15; and magnesium oxide, ref. 8, $1.52 \times 10^{11}$ Pa, 4.81.
Figure 2. Pressure versus reduced volume for NaCl. Solid curve, Eq. (1). Dashed curve, Murnaghan expression, Eq. (4).
Figure 3. - Pressure (3a) and isothermal bulk modulus (3b) versus reduced volume for solid hydrogen. Experimental data is from ref. 5. Present model is Eqs. (1) and (6). Murnaghan expressions are Eqs. (4) and (5).
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- Bulk modulus
- Compressibility

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