Universal equation of state

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The "universal" equation of state recently proposed by Vinet, Ferrante, Rose, and Smith is numerically equivalent, to leading order in finite strain, to several well-established two-parameter equations of state. Notably, it is in accord with the Birch-Murnaghan equation that is derived from Eulerian finite-strain theory, and hence is applicable to condensed matter involving any bonding type. It is well established that the Eulerian finite-strain formalism is exceptionally successful in describing the compressional behavior of materials at high pressures. This argues strongly in favor of the conclusion of Vinet and co-workers that their equation of state is universal in the sense of successfully reproducing the pressure-volume relations of a wide variety of materials. It appears, however, that no existing two-parameter equation of state is fully in accord with all measurements of high-order elastic moduli. In detail, published values of compressional moduli imply that deviations from the "universal" and Birch-Murnaghan equations of state exist, but these can be accounted for with higher-order terms.

It has recently been proposed[1] that the isothermal pressure-volume $(P\text{-}V)$ relations for a wide variety of materials can be accurately described by the "universal" equation of state

$$P(x) = 3K_0(1-x)x^{-2}\exp[\tfrac{3}{2}(K_0'-1)(1-x)] . \quad (1)$$

Here, $x = (V/V_0)^{1/3}$ is the linear compression, K is the bulk modulus, prime indicates differentiation with respect to pressure, and subscript zero indicates zero-pressure conditions. The form of (1) is based on an expression for the cohesive energy of a condensed system that is assumed to vary only as a function of a normalized interparticle separation (a^*). Specifically, the energy is given in normalized form as $E^*(a^*) = -(1+a^*+\cdots)\exp(-a^*)$, in which higher-order terms in the Taylor expansion are ignored in deriving (1). The presence of the exponential term in the energy has been explained in a general way as reflecting the typical form of interatomic repulsions,[1,2] and the success of (1) has been shown empirically by way of comparing the $P(x)$ relation derived from ultrasonic measurements of K_0 and K_0' with the pressure-volume relations obtained by finite-compression measurements (e.g., static compression or shock-wave Hugoniot data). Good agreement is found for a wide variety of metallic, covalent, ionic, and van der Waals crystals, thus supporting the view that (1) is universal in the sense that its applicability is independent of bonding character. Additionally, the success of (1) is remarkable in that the original derivation of the expression for $E^*(a^*)$ was motivated by an interest in modeling cohesive, surface and vacancy energies; that is, in reproducing the cohesive energy curve in the regime of "negative" pressures.[1,2] It should be noted, however, that this equation of state is not intended for materials with significant internal degrees of freedom, e.g., with bond bending (molecular rotation) or crystallographic transformation accommodating the compression under pressure.

An alternative approach to the equation of state of solids, developed by Murnaghan[3] and Birch[4] is based on finite-strain theory. This also leads to an equation of state that is independent of bonding character in that the derivation is obtained entirely from continuum mechanics. A connection with interatomic potentials can be made,[4,5] but this is not necessary. The main ambiguity is in using the appropriate frame of reference in defining the finite strain. However, it is now widely recognized that Birch's development based on the Eulerian strain measure $f = [(V_0/V)^{2/3} - 1]/2$ is empirically the best.[4,6-8]

A Taylor expansion of the strain energy in terms of f yields the following equation of state:

$$P(f) = 3K_0 f(1+2f)^{5/2}[1+a_1 f + \cdots] . \quad (2)$$

This Birch-Murnaghan relation, truncated at the third-order term of energy in strain $[a_1 = \tfrac{3}{2}(K_0'-4)]$, is known to be extremely successful in matching finite-compression data with low-pressure elasticity measurements obtained by ultrasonic techniques.[7,8] Even the second-order form (Birch equation, with $K_0'=4$) has long been known to yield a very good approximation to the equation of state of solids.[6] Although the enormous success of the Eulerian finite-strain formulation is not fully understood, a recent analysis by Grover[9] provides at least a partial explanation at the microscopic scale. It is also worth noting that the generalization to a complete thermal equation of state is well established.[10]

As with (1), (2) is found to apply to a wide variety of compression data for metallic, ionic, covalent, and van der Waals systems, including structurally complex compounds and melts[4,8] [again, internal degrees of freedom are ignored, with SiO_2 glass being a good counterexample: Ref. 10(a)]. Furthermore, it has recently been shown that (2) is identical, to leading order in finite strain, to the linear relation between shock velocity (U_s) and particle velocity (u_p) which describes most Hugoniot data on single phases.[11] This is significant because although the linear $U_s\text{-}u_p$ equation of state is purely empirical, it is probably the most abundantly documented by high-pressure measurements on condensed systems.[12] Also, the linear $U_s\text{-}u_p$

relation appears to successfully describe the cohesive energies of metals and their behavior under negative pressure.[13]

Both (1) and (2) are two-parameter (K_0, K_0') equations of state which can therefore be directly compared. It is clear from Fig. 1 that for the most common range of values for K_0' $(3 \lesssim K_0' \lesssim 6)$ the two equations of state agree in pressure to better than 7% down to a volume compression $V/V_0 = 0.6$. As only a few materials have been compressed to $V/V_0 = 0.6$ without undergoing a phase transition, this in practice represents a close agreement between the equations of state. Algebraically, the near identity of the "universal" equation of state with the Birch-Murnaghan form can be seen by recasting (1) in terms of f to yield

$$P = 3K_0 f(1+2f)^{5/2}$$

$$\times [1 + a_1 f + \tfrac{1}{2}(a_1^2 - 3a_1 - \tfrac{19}{4})f^2 + \cdots] . \quad (3)$$

Recognizing that $a_1 \sim 0$ (i.e., $K_0' \sim 4$ for most materials[4,6-8,11]) shows that (1) and (2) deviate by a term of only $\sim 1 - 2.4f^2$ in the ratio of the universal to the Birch-Murnaghan pressure. This difference is small because of the small magnitude of f (<0.203 for $0.6 < V/V_0 \le 1.0$).

At compressions of $V/V_0 = 0.6$, uncertainties of 5-10% in the equation of state are common either due to experimental uncertainties or because higher-order elastic moduli begin to contribute significantly to the equation of state. Thus, Fig. 1 can be taken as an indication of the good agreement between (1) and the form (2) derived from Eulerian finite-strain theory. All of the data that have been shown to be in accord with the Birch-Murnaghan equation of state, including all of the Hugoniot data which follow a linear U_s-u_p relation, are compatible with the universal form (1). Conversely, (1) can be viewed as an excellent algebraic approximation to the third-order Eulerian equation of state. As has been pointed out by Birch, the Grover-Getting-Kennedy (GGK)
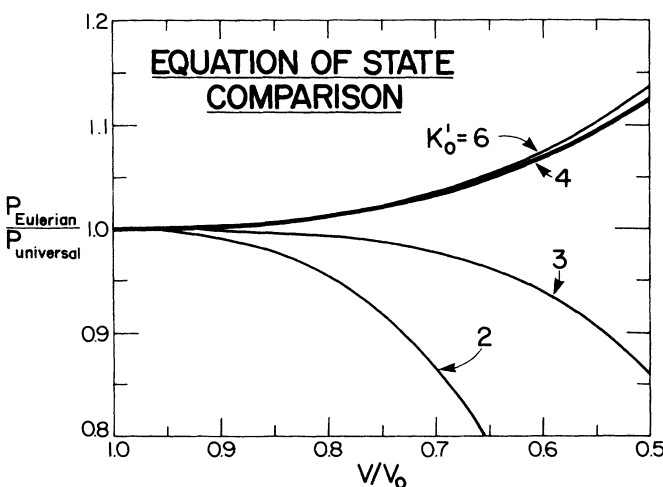
equation of state, which was obtained completely empirically, is also numerically almost equivalent to (2).[14(a)]

The agreement between (1) and (2) goes even further in that each of these two-parameter forms imply specific values for the higher-order elastic moduli. Continued differentiation of (1) with respect to pressure yields $-K_0 K_0'' = (K_0'/2)^2 + (K_0'/2) - (19/36)$, whereas truncation of (2) at third order (i.e., $a_2 = 0$) requires $-K_0 K_0'' = (K_0')^2 - 7K_0' + (143/9)$. Correspondingly, differentiation of the GGK equation of state results in $-K_0 K_0'' = K_0'$. These relations are compared with existing ultrasonic measurements to show that all three equations of state imply a similar tradeoff between K_0' and $K_0 K_0''$ over the common range $3 \lesssim K_0' \lesssim 6$ (Fig. 2). Given the scatter and uncertainty in the data, it is impossible to choose one equation of state as being empirically better than the other two.

What is also shown by Fig. 2, however, is that none of these two-parameter equations of state fully agrees with the existing data. If one accepts the published estimates of uncertainties in the compressional moduli, measurable deviations from the predicted relation between K_0' and $-K_0 K_0''$ are found in several instances and (1) is no more universally successful in reproducing the data than either (2) or the GGK equation. Analogously, the two-parameter linear U_s-u_p equation of state is considered to be only approximately valid in detail.[12] It is for this reason that higher-order elastic moduli (e.g., $K_0 K_0''$) seem to be required for describing the equations of state of materials that have been carefully studied to high compression.[14(b)] In the Eulerian finite-strain formulation, this is readily accomplished by adding the fourth-order term $a_2 f^2$ to the bracketed expansion of (2) {here, $a_2 = 3[K_0 K_0'' + K_0'(K_0' - 7) + (143/9)]/2\}$. Similarly, the universal and GGK equations of state can be extended to incorporate the higher-order terms that appear to be required by the existing elasticity and compression measurements.
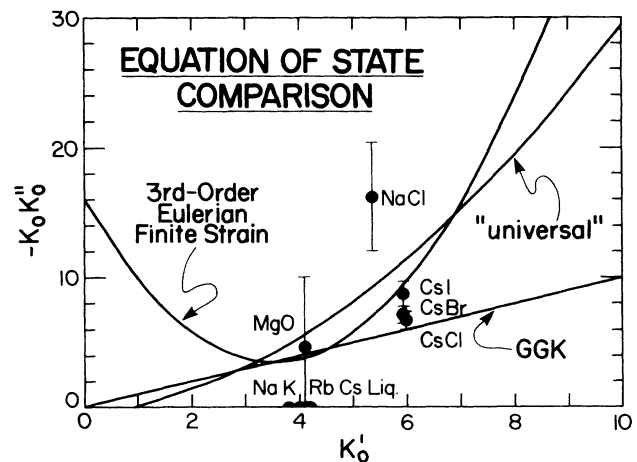

FIG. 1. Ratio of pressures derived from (2) (P_{Eulerian}) and (1) ($P_{\text{universal}}$) given as a function of volume compression for several values of K_0'. The common value $K_0' = 4$ is highlighted by the bold curve.

FIG. 2. Tradeoff between the compressional moduli $-K_0 K_0''$ and K_0' predicted by the third-order Eulerian finite-strain (Birch-Murnaghan), universal, and GGK equations of state as described in the text. Ultrasonic measurements on several crystalline compounds and liquid metals are shown for comparison (Refs. 7 and 15).

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