Theoretical
Equations of State

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The primary objective of theoretical equation-of-state work in geophysics has been to provide a framework with which the ultrasonic, X-ray compression, and shock data can be used in interpreting the seismic velocity and density profiles in the earth. Each of these experimental techniques falls short of the ultimate experiment of reproducing the temperature-pressure conditions at any depth in the earth and measuring $V_P$, $V_S$, and $\rho$ of mantle-candidate mineral assemblages for direct comparison with the seismic profiles. The ultrasonic data give $V_P$, $V_S$, and $\rho$ as a function of $T$ and $P$, but the pressure range has been limited to ~10 kbar. This limit necessitates a large extrapolation for comparison of even the upper mantle. The X-ray static compression measurements have a pressure range to 300 kbar, but are limited to room temperature and to only the pure compression properties $K_T$ and $\rho$. Finally, although the shock-wave techniques can generate pressures comparable to those found throughout the earth's mantle and core, the shock-produced states are characterized by pressure and internal energy. Thus an $E(T, P)$ equation of state is required before the data can effectively be used. Further, like static compression experiments, the shock technique now yields only $K$ and $\rho$.

Both the refinement of the seismic velocity profiles and the accumulation of laboratory data for oxides and silicates during the past 4 years have led to an increased amount of work on theoretical equations of state.

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Systematics

The systematics approach to the use of laboratory data is empirical in nature; the objective is to formulate some relationship between elastic-wave velocities and density with mean atomic weight, ionic radii, packing index, or some other property of the solid as a parameter. It is then hoped that the observed trends in the laboratory data will allow one to predict the properties of unmeasured mantle-candidate minerals (usually high-pressure polymorphs).

Systematics is an empirical substitute for a theoretical equation of state; its rather extensive development and use in geophysics over the past 4 years reflect our lack of a more theoretically sound relation between velocity and density. It is hoped that the finite strain and atomistic theories recently introduced into the geophysical literature and discussed in later sections will eventually eliminate the need for this approach.

Although the development of systematics over the last 4 years is covered in the accompanying review of the elastic properties of minerals by Liebermann and Schreiber, the key papers on the subject will be discussed here because there have been many attempts either to theoretically suggest the form a systematic should take or to theoretically justify the observed trends.

In the spirit of Birch's [1961] empirical relation between compressional velocity $V_p$, mean atomic weight $M$, and density $\rho$, $\rho = A(M) + BV_p$ D. L. Anderson [1967] suggested the 'seismic equation of state' relating the seismic parameter $\Phi = V_p^2 - (4/3)V_T^2 = K/\rho$ to the density according to the equation $\rho = A(M) + BV_p$. Using the relation $\Phi = (dP/d\rho)_H$, Anderson was able to show that the seismic equation of state is consistent with the functional form of a wide variety of theoretical equations of state. Hence the observation that compositional and pressure effects on $\Phi$ are similar was given some theoretical foundation. He also pointed out that one
should expect temperature to have a predictably different effect:

\[
\frac{\delta \ln \Phi}{\delta \ln V_p} = \left( \frac{\delta \ln \Phi}{\delta \ln V} \right)_T - \epsilon
\]

D. L. Anderson [1969] empirically investigated the effect of coordination, ionic radii, FeO content, and CaO content on the parameter \( A \).

It is also possible to relate other velocities such as the bulk sound speed, \( C = (K/\rho)^{1/2} \), to the density [Wang, 1968a] in direct analogy to Birch's \( V_p - p \) relation; such trends have not been shown to have any theoretical basis. The parameters \( C = \Phi^2 = A + B \rho, \Phi = C^2 = A + B \rho \), and \( \rho = A \Phi^2 \) were found from ultrasonic data for a number of rocks and minerals by D. L. Anderson [1970]. Anderson and Kanamori [1968], Ahrens et al. [1969], and Wang [1968a] used such constraints at \( P = 0 \) to interpret shock-wave results on high-pressure polymorphs of geophysically interesting rocks and minerals.

In an attempt to explain the empirically observed relation \( K_s V_0 \) = constant, where \( K_s \) is the ambient bulk modulus and \( V_0 \) is the specific volume, Anderson and Anderson [1970] expressed \( K_s V_0 \) in terms of the parameters of a simple Born-Mayer two-body interatomic potential model. They found that for a series of isostructural compounds of isomorphic electronic structure one would expect \( K_s V_0 \approx \) constant, the value of the constant depending on the valence product and the ionicity.

It should be pointed out that the only systematics that has been shown to have a theoretical basis involves the compressional properties \( K \) and \( \rho \). Because seismology gives both \( V_p \) and \( V_s \), the desirability of using the shear information has led to the recent work on finite strain theory and interatomic potential models, which will now be discussed.

**Finite Strain**

The finite strain approach to the formulation of an equation of state involves the expansion of the internal energy of a solid as a series in some tensor measure of the strain. Because the choice of the strain tensor is quite arbitrary and because all such expansions must be truncated to allow the coefficients to be evaluated in terms of the available data, the key question in this approach becomes the convergence of the series; i.e., at what compression do the higher-order terms neglected in the truncation make a large enough contribution to introduce an unacceptable error in the truncated expression.

First consider recent work on isotropic finite strain theory of which the Murnaghan and Birch-Murnaghan equations are the best known. Anderson and Kanamori [1968] and Chung et al. [1970] have emphasized the difference between the two equations by showing that the Murnaghan equation, which is based on the assumption that \( d(K/K_0)/dp = \) constant, and the Birch-Murnaghan equation, which follows from a second-order truncation of the free energy expansion in terms of the Eulerian strain invariants, give different curves for the seismic parameter \( \Phi = dP/dp \) as a function of pressure. Fritz and Thurston [1970] have suggested the addition of two parameters to the Murnaghan equation to allow \( dK/dp \) to change smoothly from its zero pressure value to some predetermined realistic value as \( P \rightarrow \infty \). This proposal was a follow-up to a suggestion by O. L. Anderson [1968a], who proposed the use of Keane's equation to constrain the high-pressure behavior. Sammis et al. [1970] have extended Birch's [1938] expressions for \( V_p(P) \) and \( V_s(P) \) to one higher order in the strain; thus they could discuss the derivatives \( (dV_p/dP)_0 \) and \( (dV_s/dP)_0 \). The resultant expressions are consistent with the Birch-Murnaghan equation of state, Jordan et al. [1970] fit these equations to \( V_p(z), V_s(z), \) and \( \rho(z) \) (\( z \) is depth in the earth) and obtained the zero-pressure elastic parameters of presumed homogeneous adiabatic regions of the mantle. By fitting the next higher-order equations, they found that, although the parameters \( (V_p)_0, (V_s)_0, \) and \( p_0 \) were not affected, the higher-order parameters \( (dV_p/dP)_0 \) and \( (dV_s/dP)_0 \) were sensitive to the order of the fit and were thus poorly determined.

As pointed out by Thomsen and Anderson [1969], the equations are strictly isotothermal (or adiabatic depending on the constants used) and are not consistent with either the Mie-Grüneisen or Hühnebrand equations, which are usually used in conjunction for calculations along thermodynamic paths that are neither adiabatic nor isothermal. Thomsen [1970a, b] introduced Leibfried and Ludwig's [1961] formulation into the geophysical literature. Naming it the 'fourth-order anharmonic theory,' he showed that (1) expansions of the free energy to the same order in the Eulerian and Lagrangian strain tensor lead to significant differences in the extrapolations; (2) the Eulerian expansion can be shown to be consistent with the Mie-Grüneisen equation of state and is therefore to be preferred in a self-consistent scheme; and (3) the temperature and pressure dependence of the individual elastic constants can be discussed free from the usual central-force two-body approximations inherent in the atomistic approaches. The success of the fourth-order Lagrangian expansion in predicting the observed \( C_{44} = 0 \) shear instability in NaCl is taken by Thomsen as further evidence for the preference of this expansion. It should be emphasized, however, that, even though the fourth-order anharmonic theory in the Lagrangian formulation is in many ways superior to the isothermal-adiabatic isotropic formulations, the usual problems of convergence still exist. Fifth-order terms have been measured in the laboratory, and the temperatures and pressures at which these higher-order terms become important in a geophysical context have yet to be determined.

**Atomistic Theories**

In the atomistic approach the free energy is written in terms of the interatomic potential, which is then differentiated to yield the pressure and elastic constants as a function of volume. Because all expressions are in
closed form, the convergence problems facing the finite strain approaches do not arise; they are replaced, however, by problems arising from our incomplete knowledge of the interatomic potential. It is usually assumed that the free energy can be expressed as the sum of two-body interactions consisting of a coulombic attraction and a two-parameter empirical repulsion. The two repulsive parameters are fixed by laboratory data, usually the bulk modulus and density of the static lattice. This procedure was pioneered by Born and his co-workers between 1918 and 1950 and is called the Born model.

The first use of the Born model in geophysical arguments was O. L. Anderson's [1968b] use of Blackman's results for the ZnS lattice to explain the observed negative $du/dP$ for ZnO. He pointed out that, although $dK/dP$ does not seem to be related to crystal structure, $du/dP$ is extremely sensitive to the details of the structure, particularly the coordination. Anderson and Liebermann [1970] explored this dependence in detail by comparing the Born model predictions for the ZnS, CaC1, and CaCl2 structures. O. L. Anderson [1970] cast the results in a form that is common to the exponential and power law form of the repulsion, discussed the limitations of the central force model, and interpreted the discrepancies between Born model predictions and experiment as being due to noncentral forces. Anderson and Demarest [1971] emphasized the shear instabilities ($C_{44} = 0$) predicted by the lattice models and their effect on the properties of a polycrystalline aggregate. Gaffney and Ahrens [1969, 1970] used the Born model to investigate the relative stability of several possible high-pressure polymorphs of mantle-candidate minerals by comparing their theoretical internal energies. Sammis [1970] showed how the Born model can be applied to more complex structures. He emphasized the importance of retaining the identity of the various bonds and suggested that, to first order, the repulsive parameters of a bond may depend only on the interacting species and are independent of the particular crystal. If this interpretation proves correct, the elastic behavior of unmeasured polymorphs may be predicted.

The atomistic approach has the advantage over finite strain that it can be tested, because only a very small amount of the ultrasonic data is used as input. As more high-precision ultrasonic data are collected, the functional form assumed for the potentials can be tested. It should be pointed out that much theoretical work toward a better understanding of the noncentral, many-body terms in the potential, the effects of ionic polarizability, and the nature, extent, and effect of covalent bonding are required before predicted elastic properties of the various high-pressure polymorphs can be given any measure of confidence. The primary hope in the atomistic approaches is that the details of the interatomic potential play a less important role than the crystal structure in the calculation of elastic properties.

Grüneisen's Constant

It has been conventional to express the thermal part of almost every equation of state in terms of Grüneisen's constant $\gamma$, where $\gamma$ represents some average of the volume derivatives of the normal modes. The approximation $\gamma = \text{constant}$ is not sufficient, and, because knowledge of $\gamma$ at high temperatures and pressures is essential in the reduction of shock data to an adiabat or isotherm, a great deal of theoretical effort has gone into predicting the temperature and volume dependence of $\gamma$.

Starting with the thermodynamic definition $\gamma = \alpha T V/C_p$, Basset et al. [1968] used a purely thermodynamic development to express $\gamma$ in $\gamma = \gamma_0 (V/V_0)^4$ as a function of measurable quantities. They found $0.68 < \gamma < 1.7$ for a number of oxides and alkalide halides.

O. L. Anderson [1968c] investigated the volume dependence of the Dugdale McDonal $\gamma$ by using several theoretical equations of state to calculate the required volume derivatives of the pressure. He found that for all cases, except the Murnaghan, $\gamma < 1/2$ at $P = 0$ and decreased to zero at high pressure. He also stressed the importance of the pressure dependence of the shear constants in any calculation of $\gamma(T)$.

Ahrens et al. [1970] suggested $6 < \gamma < 10$ may be necessary to interpret the shock data for stishovite.

Knopoff and Shapiro [1969] compared the various conventional methods of computing the Grüneisen constant $\gamma$ and showed that the methods (1) lead to different isotherms when used in shock reduction, (2) ignore the contribution of shear modes which may be ten times as important as the compressional modes, and (3) ignore dispersion of high-frequency elastic waves. They further point out that lattice models may be of little use in shock-wave reduction because the high temperatures associated with the shock probably cause the solid to melt or surpass its elastic limit. The 'pseudo-Grüneisen' parameter of liquids was further investigated by Knopoff and Shapiro [1970], Shapiro [1970] and Shapiro and Knopoff [1970] investigated the Lindeman melting law and the Grüneisen parameter of some cubic metals in the framework of Born-von Kármán lattice models. The Grüneisen constant is found to be most heavily dependent on the shear constant $C_{44}$ and its pressure derivative.

Closely related to the problem of the volume dependence of $\gamma$ is the volume dependence of the coefficient of thermal expansion $\alpha$, as discussed by O. L. Anderson [1967], Birch [1968], and Clark [1969]. The controversy pursued in these papers gives one a true grasp of the problems involved. Like $\gamma$, the volume dependence of $\alpha$ at large pressure requires knowledge of the volume dependence of the entire vibrational spectrum, which will probably require lattice calculations in the spirit of those of Shapiro and Knopoff [1970].

Aggregate Properties

With the exception of the paragraphs on isotropic finite strain, the theories discussed have dealt mostly with single crystals. Any application to the earth requires the calculation of isotropic elastic constants from the single crystal values. Kumazawa [1969] discusses the various averaging techniques, pointing out that the Reuss average gives the isotropic bulk modulus of a single crystal whereas the Hill average is appropriate
to polycrystalline aggregates and shows that the difference between the Reuss and Hill values is related to the nonelastic properties of the aggregate. Simons [1967] gives the Hashin-Strickman bounds for a large number of cubic crystals, showing that they are much tighter than the Voigt-Reuss bounds. Thomsen [1970c] shows that for a perfectly random aggregate, Kröner's [1967] theory gives the isotropic constants, rather than upper and lower bounds. He shows that Kröner's theory is in agreement with the Hill average and thus presents the first theoretical 'justification' for the Voigt-Reuss-Hill scheme.

In a different vein, Walsh [1968, 1969] has investigated the effect of composite mediums by calculating the elastic and anelastic behavior of a medium with ellipsoidal inclusions. Walsh [1969] and Anderson and Spetzler [1970] applied the theory to the partial melt problem.

As the seismic profiles in the earth are further refined and more high-precision ultrasonic data become available for a wider variety of structures to high pressures and temperatures, further refinements in the theoretical treatments outlined above will certainly be forthcoming.

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Rock Mechanics and Dynamic Processes in the Crust

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During the past four years experimental and theoretical studies of the fracture and flow of rock have provided important new insights into the dynamics of geologic processes in the crust and upper mantle. In addition, intensive new observational studies, particularly along the San Andreas Fault in California, have yielded new information on the mechanism of earthquakes and faulting. Of particular interest are: (1) work on the friction characteristics of rock under crustal temperature and pressure conditions and its application to the mechanism of faulting; (2) use of laboratory experiments as scale models of seismicity with applications to earthquake statistics; (3) recognition and measurement of fault creep over extensive portions of the San Andreas fault system; (4) use of geologic, geodetic, and seismic data for the determination of rates of movement and strain accumulation on the San Andreas Fault; (5) observations and experiments with earthquake triggering; (6) studies of the creep of rock at high temperatures and pressures.

Brace and Byerlee [1966] noticed that frictional sliding of rock under moderate confining pressure was often accomplished by rapid jerks with significant displacements and stress drops. They proposed that this behavior, termed stick-slip, was the mechanism of shallow earthquakes. Stick-slip was found to occur in a wide variety of rock types over a considerable range of pressure, temperature, and strain rate [Byerlee and Brace, 1968; Brace and Byerlee, 1970].

In addition, stable sliding, i.e., slow frictional sliding unaccompanied by measurable stress drops, is often observed [Byerlee, 1967a; Scholz, 1968a]. This type of frictional sliding was in turn proposed as the mechanism of fault creep [Byerlee and Brace, 1968; Scholz et al., 1969]. The series of studies by Byerlee and Brace delineated the conditions under which stick-slip occurs. They found that for a wide variety of rocks stick-slip does not occur when the applied normal stress across the fault is less than one kilobar. Many altered rocks, however, do not show stick-slip at any normal stress. Stick-slip was also found to disappear at elevated temperatures, the critical temperature increasing linearly with the normal stress. Outside the field of stick-slip occurrence, stable sliding occurs, but it also often occurs within the stick-slip field as well. These results may explain why earthquakes do not occur below 10–20 km on faults such as the San Andreas, why large earthquakes are not often generated at depths less than a few kilometers, and why creep is restricted to certain sections of faults like the San Andreas.

Studies of microfracturing during deformation and fracture of brittle rock have revealed features of the mechanics of those processes in considerable detail [Brown and Singh, 1967; Scholz, 1968a–e; Chugh et al., 1968; Hardy, 1969]. It was shown that, regardless of the type of loading, microfracturing activity begins at stress differences that are low with respect to the fracture stress difference and increases rapidly as the fracture stress is approached. This was explained as a general consequence of the inhomogeneity of rock [Scholz, 1968a] and was used as a scale model of seismicity. The microfracturing obeys a frequency-magnitude relation identical to that of earthquakes, where the Gutenberg and Richter parameter b decreases with stress [Scholz, 1968b]. Under constant stress conditions the frequency of microfracturing decreases hyperbolically with time. This was explained by static fatigue of individual grains and was proposed as the mechanism of creep in brittle rock [Scholz, 1968c; Hardy et al., 1969] and, on a larger scale, of earthquake aftershock sequences [Scholz, 1968d]. Theoretical work on these topics has also been done by Brady [1969, 1970] and by Ranalli and Scheidegger [1969]; detailed statistical studies of aftershock sequences have been done by Page [1968] and Ranalli [1969].

Laboratory-scale models of seismicity using networks of frictional elements have also pointed to physical interpretations of earthquake statistics [Burridge and Knopoff, 1967; King and Knopoff, 1968]. Intensive studies have been made of fault initiation in laboratory specimens [Wawersik, 1968; Scholz, 1968a; Friedman et al., 1970; Wawersik and Brace, 1970] and of crack growth under compression [Bomblakis, 1968; Byerlee and Pesslennick, 1970].

Fault creep has been recognized as a widespread process along many parts of the San Andreas fault system. This process, which serves as an alternative to earthquakes for releasing tectonic strain, has been measured precisely by displacement transducers and small scale geodetic networks at many points along the major faults in Central California [Raleigh and Burbard, 1969; Nason, 1969; Nason and Tcherer, 1970; Miller, 1967; Miller, 1968; Meade, 1968]. The measurements showed that

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