EQUATIONS OF STATE AND THEIR APPLICATIONS IN GEOSCIENCES

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Abstract. This lecture is an attempt to give an overview of the equations of state (EoS) commonly used to fit *P-V* data in Geosciences and to discuss their assumptions. It is limited to static data (i.e. data obtained by squeezing a sample between pistons or anvils and measuring the associated change in volume). The various details of how to determine the parameters of an EoS from experimental data and of the best fitting procedure are discussed extensively in *Angel* (2000) and will be the subject of a workshop.

1. Equations of State

An EoS describes a physical system with a relation between its thermodynamic quantities, such as pressure, temperature, density, entropy, specific heat, *etc.* The best known EoS is of course the one for ideal gases:

$$PV = nRT \qquad (1)$$

which is considered the beginning of thermodynamics and statistical mechanics. Especially at high pressures and at low temperatures, however, real gases deviate from the perfect gas law and equation (1) has been modified according to different assumptions in order to better describe the real gas behaviour. For solids and liquids, temperature has a minor effect on the *P-V* relationship and it is normally introduced as a thermal expansion correction to a chosen isothermal equation of state. There are several excellent reviews of the various EoS that have been proposed and used to describe the behaviour of condensed matter, see for example *Stacey et al.* (1981); *Anderson* (1995); *Holzapfel* (2001).

At low pressures the *P-V* relationship of a solid may be represented in terms of Hooke's law where the applied stress is the change in hydrostatic pressure ΔP and the resulting strain is the fractional volume change $\Delta V/V$.

The bulk modulus or incompressibility is the coefficient that scales strain to stress:

$$\Delta P = -K \frac{\Delta V}{V} \qquad (2)$$

This relationship is valid only for pressure ranges much smaller than K, since due to inter-atomic repulsions a solid becomes stiffer with increasing pressure and, hence, large compressions require an expression for which the bulk modulus increases with pressure.

The simplest relationship satisfying the requirement of increasing stiffness with pressure is given by:

$$K = K_0 + K_0' P \qquad (3)$$

where K_0 is the bulk modulus at room pressure and $K_0' = (\mathrm{d}K/\mathrm{d}P)_{P=0}$ is the pressure derivative of K and is assumed to be independent of pressure. This is referred by *Murnaghan* (1951) as the "integrated linear theory". For pressures in the range $0 < P < K_0/2$ this approximation is reasonable for many materials.

These simple relationships illustrate an important point, *i.e.* that *P-V* data are usually represented by "parametric" EoS forms which use temperature dependent parameters V_0, K_0, K_0' and K_0'', etc. for the volume, bulk modulus and its pressure derivatives, respectively (the index 0 indicates that these values refer to room pressure).

1.1. EQUATION OF STATE BASED ON THE FINITE STRAIN THEORY

The classical theory of infinitesimal elasticity is based on two assumptions: 1) the strains are uniquely determined by the stresses and are reversible, and 2) the strains are so small that their squares and products are negligible. In finite strain theory, the first assumption is retained, but the restriction to small strains is removed (*Birch* 1938). A theoretical treatment of finite strains was given first by *Love* (1927), but practical expressions for finite strain were developed by *Murnhagan* (1951) and applied to the Earth by *Birch* (1952). Since the finite strain is defined by the change in distance between two neighboring points during deformation, a reference state needs to be defined. In the Lagrangian formulation the strain is defined relative to the unstrained state (*i.e.* the volume at room pressure), whereas in the Eulerian formulation the strained state (*i.e.* the volume at the final compression) is used as reference state. The two schemes yield definitions of strain that are equivalent for infinitesimal strain but different for finite strains. Other formulations are of course possible as we will see in section 1.1.2. It is worth stressing that all finite strain theories are empirical in the

sense of having plausible analytical forms that appear to follow the trend of observation once the EoS parameters (V_0, K_0 and its pressure derivatives) are properly adjusted to suit the behaviour of different materials. Any analytical form will of course fit a given set of *P-V* data if sufficient adjustable parameters are allowed. However, as it is the case of any fit procedure, the EoS which use the fewest parameters to achieve a particular precision of fit will be favored.

1.1.1. *Birch-Murnaghan EoS*

The most widely used isothermal EoS in Geoscience is the Birch-Murnaghan EoS, because it satisfies the criteria outlined above. In spite of the fact that (and I cite directly from *Anderson,* 1995) "the long use and wide application of this EoS has engendered for it a certain authority in the literature, nevertheless, like all other isothermal EoS's, it is based on an unproven assumption. In this case, the EoS rests on the assumption of Eulerian strain". The derivation of such equation from the finite strain theory is given not only in the original papers (see for example *Birch* 1947) but also in several other texts (*i.e. Stacey et al.*, 1981; *Poirier,* 2000) and it will not be repeated here. It is based upon the assumption that the Helmholtz free energy of a solid can be expressed as a Taylor expansion of the Eulerian finite strain ε, or better of a quantity f which is the negative of ε in order to deal with positive strain in compression:

$$f = -\varepsilon = \frac{1}{2}\left[\left(\frac{V}{V_0}\right)^{-2/3} - 1\right] \tag{4}$$

The choice of Eulerian strain has been ascribed by *Birch* (1952) to the fact that the expansion of the free energy was more strongly convergent than that obtained from an expansion of the Lagrangian finite strain. The fourth-order EoS has the form:

$$P = 3K_0 f\left(1+2f\right)^{5/2}\left(1+\frac{3}{2}\left(K_0{}'{-}4\right)f + \frac{3}{2}\left(K_0 K_0{}''{+}\left(K_0{}'{-}4\right)\left(K_0{}'{-}3\right)+\frac{35}{9}\right)f^2\right) \tag{5}$$

By substituting f and doing successive differentiation (Stacey et al. 1981) we obtain:

$$P = \frac{3}{2}K_0\left(\left(V/V_0\right)^{-7/3} - \left(V/V_0\right)^{-5/3}\right)$$

$$\left\{1+\frac{3}{4}\left(K_0{}'{-}4\right)\left(\left(V/V_0\right)^{-2/3}-1\right)+\frac{3}{8}\left(K_0 K_0{}''{+}\left(K_0{}'{-}4\right)\left(K_0{}'{-}3\right)+\frac{35}{9}\right)\left(\left(V/V_0\right)^{-2/3}-1\right)^2\right\}$$

$$\tag{6}$$

$$K = K_0 \left(V/V_0\right)^{-5/3}$$

$$\left\{1+\left(\frac{3}{2}K_0'-\frac{5}{2}\right)\left(\left(V/V_0\right)^{-2/3}-1\right)+\frac{9}{8}\left(K_0K_0''+K_0'\left(K_0'-4\right)+\frac{35}{9}\right)\left(\left(V/V_0\right)^{-2/3}-1\right)^2\right\}$$

$$(7)$$

$$K' = K_0'+\frac{3}{2}K_0K_0''\left(\left(V/V_0\right)^{-2/3}-1\right) \tag{8}$$

The derivation of these equations involves a number of implicit assumptions (a part from the fundamental assumption of Eulerian strain) about the properties of solids under compression. First of all it is strictly valid for isotropic or cubic materials (*Birch,* 1947), second it implies that the solid under compression is homogeneously strained *i.e.* that all part of its structure compress at the same rate. This is clearly far from reality in the case of those materials which contain different type of bonds between atoms as is the case of many silicates (*Angel and Ross,* 1996) or even worse for molecular crystals which have groups of atoms strongly bonded kept together by very weak interactions. Moreover, it is assumed that the EoS parameters are continuously differentiable with respect to pressure (an assumption made for all finite strain EoS) which means that the EoS cannot describe the behaviour of a material through a high-pressure phase transformation. Finally, the free energy Taylor expansion of the BM-EoS is very often truncated either at the second (K_0' has an implied value of 4) or at the third order (with an implied negative value of K_0'') depending on the accuracy of the data and this implicitly assumes that higher order terms are considerably small compared to the lowest-order terms.

1.1.2. *Logarithmic equation of state*

If, instead of choosing as reference state either the undeformed or the deformed state, one chooses to define an increment of strain $d\varepsilon$ corresponding to the increase or decrease by dl of the length l of a sample experiencing extension or compression, the total finite strain or Hencky strain experienced by a material which changes its length from l_0 to l is:

$$\varepsilon_H = \int_{l_0}^{l} d\varepsilon_H = \ln\frac{l}{l_0} \tag{9}$$

A logarithmic EoS can be derived from a Taylor expansion of the free energy in terms of the Hencky strain whose third-order form is (*Poirier,* 2000):

$$P = K_0 \frac{\rho}{\rho_0} \ln \frac{\rho}{\rho_0} \left[1 + \left(\frac{K_0{}'-2}{2} \right) \ln \frac{\rho}{\rho_0} \right] \tag{10}$$

which for K0' = 2 reduces to the simple second-order expression (*Poirier and Tarantola,* 1998):

$$P = K_0 \frac{\rho}{\rho_0} \ln \frac{\rho}{\rho_0} \tag{11}$$

1.2. EQUATIONS OF STATE BASED ON INTERATOMIC POTENTIAL

An alternative approach of deriving EoS is to propose a form of inter-atomic potential which defines the mutual forces between atoms in the crystal so that density can be calculated as a function of pressure. The atomic potentials used, however, are just as empirical as the strain equations described above. *Stacey et al.*, (1981) and *Anderson* (1995) give an extensive review of EoS derived from several different atomic potential. Here, I will describe two of the commonly used.

1.2.1. *Born-Mie potential*

The potential function studied first by G. Mie has the form:

$$E(r) = -\frac{a}{r^m} + \frac{b}{r^n} \tag{12}$$

where the interatomic potential $E(r)$ is expressed in terms of long-range attractive and short-range repulsive forces, i.e. $n > m$. Adjusting a and b to obtain $r = r_0$ and $K = K_0$ at $P = 0$, the following free energy expression is obtained (*Poirier,* 2000):

$$F(V) = \frac{9K_0 V_0}{n-m} \left[-\frac{1}{m} \left(\frac{V_0}{V} \right)^{-m/3} + \frac{1}{n} \left(\frac{V_0}{V} \right)^{-n/3} \right] \tag{13}$$

and:

$$P = \frac{3K_0}{n-m} \left[\left(\frac{V_0}{V} \right)^{1+n/3} - \left(\frac{V_0}{V} \right)^{1+m/3} \right] \tag{14}$$

with

$$K_0{}' = \frac{1}{3}(m+n+6) \tag{15}$$

$$K_0 K_0'' = -\frac{1}{9}(m+3)(n+3) \qquad (16)$$

which is negative as required.

Specific values of m and n have been used by different authors (*Stacey et al.*, 1981). In the simple case of ionic crystals (Born potential) $m = 1$ and the potential curve is asymmetric resulting in anharmonic oscillations. In the special case of $m = 2$ and $n = 4$ expression (14) coincides with the second order BM-EoS.

1.2.2. *Vinet EoS*

This equation:

$$P = 3K_0 \left(\frac{V}{V_0}\right)^{-2/3} \left[1 - \left(\frac{V_0}{V}\right)^{1/3}\right] \exp\left\{\frac{3}{2}(K_0'-1)\left[1-\left(\frac{V_0}{V}\right)^{1/3}\right]\right\} \qquad (17)$$

(see derivation in *Vinet et al.*, 1987; 1989 and in *Poirier,* 2000) has a special interest because it gives good results for very compressible solids and at very large pressure. It is derived from a Morse potential and has the implied value for K_0'' of:

$$K_0 K_0'' = -\left[\left(\frac{K_0'}{2}\right)^2 + \frac{K_0'}{2} - \frac{19}{36}\right] \qquad (18)$$

Note however that such EoS is not intended for material with significant degree of structural freedom such as bond-bending.

1.3. THERMAL EQUATIONS OF STATE

There is a number of EoS which can be used to treat high-temperature and high-pressure data. Details of their derivations and their limits can be found in *Duffy and Wang* (1998) and *Poirier* (2000). Here we limit the discussion to consider the high-temperature Birch-Murnaghan EoS which is a relatively simple approach but is sufficient for fitting most of the *P-V-T* data collected up to 1000 K. The zero pressure parameters are (as in the case of expression (6)) V_{T0}, K_{T0} and K_{T0}' and refer to an initial high-temperature state, *i.e.* the compression curve is considered as isotherms at a given high-temperature and different isotherms (one for every T data set) are considered in the fitting procedure. The high-temperature values of the volume and bulk modulus are given by:

$$V(T) = V_0(T_0) \exp \int_{T_0}^{T} \alpha(T) dT \tag{19}$$

$$K(T) = K_0(T_0) + \left(\frac{\partial K}{\partial T}\right)_P (T - T_0) \tag{20}$$

where T_0 is the reference temperature (usually 298 K) and both thermal expansion $\alpha(T) = a + bT$ and bulk modulus are considered to vary linearly with T. Given the uncertainties on most of the P-V-T data, it is usually assumed that K' does not vary with T and its value is fixed to 4; however, if the data are particularly accurate, it is possible to use a variable K' associated with each isothermal EoS.

2. Comparison between EoS

In spite of its number of assumptions, the most widely used EoS in the Geoscience community is the BM-EoS (second or third order depending on the accuracy of the data). *Poirier* (2000) has shown that the third-order BM-EoS gives practically the same result as the logharitmic and the Vinet EoS at relatively low pressures or at any pressure for $K_0' = 3.5$.

As a practical example I have refitted single-crystal *P-V* data of an MgSiO$_3$ perovskite containing a small amount of Al and Fe (*Saikia et al.*, 2008) using a second and a third-order BM, a third-order logarithmic and a third-order Vinet EoS. The resulting EoS parameters from the fitting of the *P-V* data using the three different EoS are reported in Table 1. As expected all three third-order EoS give the same results given that the *P-V* data represent a small compression, the only difference being the implied value of K_0''. The requirements of having few adjustable parameters and of following the trend of the experimental data appear therefore fulfilled by all three EoS and the choice of using a BM-Eos instead of any of the other two as done by Saikia et al. (1998) is a matter of common use.

Table 1. EoS parameters resulting from the fitting of the P-V data of sample $Fe^{3+}_{0.03}$-$Al_{0.05}$ from Saikia et al. 2008

EoS	V_0	K_0	K_0'	K_0'' (implied)
BM II order	163.673 (7)	247.4 (7)	4 (impied)	-0.0157
BM III order	163.681 (9)	243 (3)	5.0 (7)	-0.0247
Logarithmic	163.681 (9)	243 (3)	5.1 (7)	-0.0579
Vinet	163.681 (9)	243 (3)	5.1 (7)	-0.0351
Ono et al. 2004	164.24 (fixed)	272 (8)	4 (fixed)	

If these EoS parameters, however, are used to extrapolate the compressibility behaviour of perovskite to pressures far beyond the experimental range studied (*i.e.* to the Earth's lower mantle conditions), a significant difference among the three predictions is visible (Fig. 1) and the third-order BM-EoS suggests the smallest compressibility of perovskite.
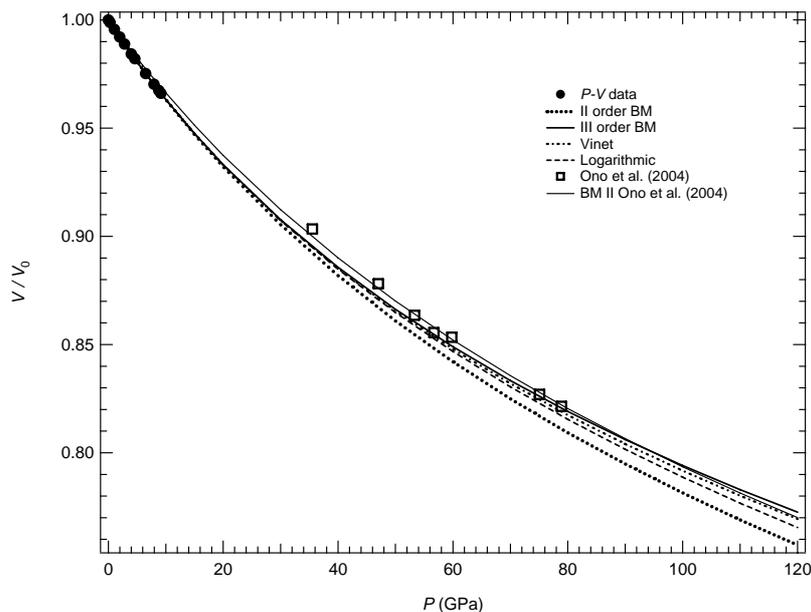
Fig. 1. Comparison of different EoS fitting of *P-V* data of $Fe^{3+}_{0.03}$-$Al_{0.05}$ $MgSiO_3$ perovskite (*Saikia et al.,* 2008). At high pressures the different Eos define different trends in spite of resulting in the same EoS parameters at room pressure.

Note that none of the extrapolation fits the high-pressure data collected for a perovskite of similar composition (*Ono et al.* 2004), although, at least for the highest-pressures data points the third-order BM-EoS seems the best solution. Few points need to be stressed here. Single-crystal x-ray diffraction data are usually collected using *in-house* facilities and are limited to low pressures (< 10 GPa). The precision and accuracy of the data collected is such that not only K_0 and K_0' can be refined, but also subtle changes in compression behaviour can be detected. However, as we have seen above, extrapolations at pressures of the Earth's interior depend on the chosen EoS formalism. In the other hand, powder diffraction data can be collected at megabar pressures using synchrotron facilities, but their scatter is such that very often only a second-order BM Eos can be used. As a result very often the room pressure bulk modulus values reported in the two

different types of studies may differ quite significantly. In situations where compression data are available only at very high-pressure it is advisable to employ EoS parameters for which the reference is not at zero pressure but at the pressure of the first volume measurement.

3. Pressure determination

Not only will the uncertainties in the volume measurements but also those in the pressure determination influence the accuracy and precision of the EoS parameters. For single-crystal X-ray diffraction experiments up to 10 GPa, *Angel et al.*, (1997) suggest to use as pressure internal standard an oriented single-crystal of quartz for which they have determined an accurate BM-EoS. This results in a precision of the pressure determination of 0.009 GPa at 9 GPa, which is a considerable improvement with respect to the pressure determination by means of the ruby fluorescence technique. However, for room *T* high-pressure experiments which exceed 10 GPa, the pressure-induced wavelength shift of the ruby fluorescence spectrum is at the moment the easiest solution. Note, however, that the wavelength shift depends not only on the absolute pressure, but also on the pressure medium used, and therefore the correct calibration of the ruby shift need to be used. Three calibration are available, one for non-hydrostatic media as NaCl or LiF (*Mao et al.*, 1978), one for quasi-hydrostatic media as Ar (*Mao et al.*, 1986) and recently one for He pressure medium (*Jacobsen et al.,* 2008). As an alternative to ruby, MgO is sometime used as internal standard in high-pressure powder diffraction experiment since its EoS has been better and better refined over the years.

In high-pressure high-temperature experiments, unfortunately, the precision of pressure determination is limited. The ruby fluorescence shift has been calibrated up to 15 GPa and 600 °C by *Rekhi et al.* (1999) and its extrapolation at higher pressures and temperatures is commonly used in spectroscopic experiments. In diffraction experiments the unit-cell lattice parameters of a metal (for example gold) are used to determine the pressure at temperatures. However, in both cases the uncertainties can be up to 1-2 GPa at very high-pressures and moderate temperatures.

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