EOS-FIT V6.0

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INTRODUCTION

EosFit started as a program to fit equations of state (EoS) to P,V data. A number of auxilliary programs were subsequently written to perform functions such as the calculation of P at a given V, to produce P-V data sets, and to fit *P-V-T* data sets. These various programs originally ran on a Vax, and were subsequently ported and further developed in the MS-DOS environment. Version 5.0 was the first integration of these programs into a single package and operates as a command-line interpreter under MS-DOS emulation. It was intended as an intermediate step to a GUI-based system. Version 6.0, and is a number of stand-alone GUI's designed for specific calculations, and these will be later combined into a single package to perform fitting, graphing and subsidiary calculations. Versions 5.x and versions 6.x are being developed in parallel.

Version 6.0 programs available as of March 2001:

> PVCALCULATOR – a GUI that allows calculation of P-V data for various isothermal equations of state. It also provides f-F values and the values of bulk modulus and its pressure derivative at high pressures.

> PVT_CALC – a similar GUI that does P-V-T calculations, for various EoS.

The fitting part of the EOSFIT program in version 4.3 and version 5.x are also both available separately from either http://www.geol.vt.edu/profs/rja/soft/ or http://www.ccp14.ac.uk/

The EosFit programs are distributed on a non-commercial basis and the author would appreciate their use being acknowledged by reference to Angel (2001) in any publications. If you would like to receive program updates (including bug fixes), please register with me as a user by e-mail (rangel@vt.edu). If you discover apparent bugs in the program, please send me the input file, the output file and a full description of the problem by e-mail. Further information will be posted on my web site.

BRIEF USERS GUIDE TO THE GUI

Eos Type: Radio box to enable selection of Eos formulation.

Eos Order: Radio box to enable selection of order of EoS truncation. For lower orders the values of some EoS parameters are fixed by the others (see below).

Eos Parameters: Edit boxes to enable input of parameter values. When parameters are fixed by a choice of EoS order, the values are grayed-out and cannot be edited by the user. See also sub-section on "units" below.

When any of these parameters are changed, the EoS display, the P-V and the f-F displays are all updated and made consistent.

Pressure-Volume group or P-V-T group: Editing any one of these values leads to update of the other values from the existing EoS parameters. In P-V, changes in EoS parameters lead to updates in volume terms based on the pre-existing value of pressure. In P-V-T the updates are based on the T and the V values.

f-F group: Display of appropriate normalised stress (*F*) and normalised strain (*f)* values for the EoS type. Changes in these values leads to an update of the P-V display based upon the pressure.

Elasticity group: Non-editable display of the bulk modulus and its pressure derivative at the pressure displayed in the P-V group. Some of these values are derived through numerical derivatives of the EoS and may not be accurate.

Display Control: Enables number of displayed digits in the P-V, f-F and elasticity groups to be changed by the user.

EQUATIONS OF STATE

Formulations.

The EoS used in EosFit most commonly used for fitting isothermal (i.e. *P-V* datasets) are listed briefly here. Further details of the derivations and limitations can be found in, for example, Anderson (1995) and Angel (2001).

Murnaghan. This can be derived from the assumption that the bulk modulus varies linearly with pressure, $K = K_0 + K_0'P$; K_0' being independent of pressure. Integration yields the *P-V* relationship:

$$V = V_0\left(1 + \frac{K_0'P}{K_0}\right)^{-1/K_0'} \tag{1}$$

This EoS (Murnaghan, 1937) both reproduces *P-V* data and yields correct values of the room pressure bulk modulus for compressions up to about 10% (i.e. $V/V_0 > 0.9$), and has the advantage of algebraic simplicity over other formulations such as the Vinet or Birch-

Murnaghan EoSs (e.g. Anderson 1995, Angel 2001) which should be used if the range of compression is greater than 10%. The Murnaghan EoS can also be re-arranged to provide a direct expression for pressure in terms of compression:

$$P = \frac{K_0}{K_0'}\left[\left(\frac{V_0}{V}\right)^{K_0'} - 1\right]$$

(2)

Birch-Murnaghan. This is a "Finite strain EoS", and is based upon the assumption that the strain energy of a solid undergoing compression can be expressed as a Taylor series in the finite strain, f. The Birch-Murnaghan EoS (Birch 1947) is based upon the Eulerian strain, $f_E = \left[(V_0/V)^{2/3} - 1\right]/2$. Expansion to fourth-order in the strain yields an EoS:

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

If this EoS is truncated at second-order in the energy (see Eos Order on GUI), then the coefficient of f_E must be identical to zero, which requires that K' has the fixed value of 4 (higher-order terms are ignored). The third-order truncation, in which the coefficient of f_E^2 is set to zero yields a three-parameter EoS (with V_0, K_0 and K') with an implied value of K'' given by (Anderson 1995):

$$K'' = \frac{-1}{K_0}\left((3 - K')(4 - K') + \frac{35}{9}\right)$$

(4)

Natural strain. Poirier and Tarantola (1998) developed an EoS based upon the "natural" or "Hencky" measure of linear strain, $f_N = \ln(l/l_0)$ which, for hydrostatic compression, may be written as $f_N = 1/3\ln(V/V_0)$. This yields a pressure-volume relationship expanded to fourth-order in strain of:

$$P = 3K_0\left(\frac{V_0}{V}\right)f_N\left[1 + \frac{3}{2}(K' - 2)f_N + \frac{3}{2}\left(1 + K_0 K'' + (K' - 2) + (K' - 2)^2\right)f_N^2\right] \quad (5)$$

Examination of Equation (5) shows that truncation of this "Natural strain" EoS at second-order in the strain implies a value of $K' = 2$, different from that of the second-order Birch-Murnaghan EoS. For truncation at third-order in the strain, the implied value of K'' is given by:

$$K'' = \frac{-1}{K_0}\left[1 + (K' - 2) + (K' - 2)^2\right]$$

(6)

Vinet. The finite-strain EoS do not accurately represent the volume variation of most solids under very high compression ($\eta < 0.6$), so Vinet et al. (1986, 1987a) derived an

EoS from a general inter-atomic potential. For simple solids under very high compressions the resulting Vinet EoS provides a more accurate representation of the volume variation with pressure:

$$P = 3K_0 \frac{(1 - f_V)}{f_V^2} \exp\left(\frac{3}{2}(K' - 1)(1 - f_V)\right) \tag{7}$$

where $f_V = (V/V_0)^{1/3}$. There is no theoretical basis for truncation of the EoS to lower order, although examination of Equation (7) shows that such truncation yields an implied value for K' of 1. The value of K'' implied by Equation (7) is given by Jeanloz (1988) as:

$$K'' = \frac{-1}{K_0}\left[\left(\frac{K'}{2}\right)^2 + \left(\frac{K'}{2}\right) - \left(\frac{19}{36}\right)\right] \tag{8}$$

Expansions of the Vinet EoS to include a refineable K'' have been proposed but are not required to fit most experimental P-V data of simple solids. Despite being often called a "Universal EoS" (e.g. Vinet et al. 1986, 1987a) it should be noted that the Vinet EoS is not intended for materials with significant degrees of internal structural freedom such as bond-bending (Jeanloz, 1988).

Thermal Equations of State

Within the P-V-T calculator of EosFit, *P-V-T* data is treated with any of the isothermal EoS given above, and by considering the parameters V_0 and K_0 as being the material properties at *P=0* but at elevated temperature *T*. The high-temperature value of the zero-pressure volume is:

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

which is derived by integration of the thermodynamic definition of the thermal expansion coefficient $\alpha(T) = V^{-1}\, \partial V/\partial T$. T_0 is the reference temperature (default value 298 K in the P-V-T calculator, but it can be changed), at which the volume is V_0, and the bulk modulus has the value K_0.

As for the compression of solids, there is no general thermodynamic theory that specifies the form of the function α(T), e.g. Krishnan et al. (1979). At the lowest level of approximation α(T) can be considered a constant, or to vary with linearly with temperature as α(T) = α₀ + α₁T. This second function is used in EosFit, and leads to the expression for the high-temperature volume at zero pressure as:

$$V_0(T) = V_0(T_0) \exp\left(\alpha_0(T - T_0) + \frac{1}{2}\alpha_1\left(T^2 - T_0^2\right)\right) \tag{9}$$

Within the uncertainties of most current experimental measurements, the variation of bulk modulus with temperature can be considered to be linear:

$$K(T) = K_0 + (T - T_0)\left(\frac{\partial K}{\partial T}\right)_P \tag{10}$$

This formulation, combined with use of a variable K' in the associated isothermal EoS, includes all second derivatives of the volume with respect to the intensive variables *P* and *T*, and is usually sufficient to fit most experimental *P-V-T* data sets collected from room temperature up to ~1000 K. The derivations of thermal EoS more applicable to higher-temperature datasets are given by Duffy and Wang (1998). A simplified extension of the Vinet EoS to variable temperature developed by Vinet et al. (1987b) is only applicable above the Debye temperature.

Units

Equations of state for compression are dimensionless – they can all be re-written in terms of the two ratios K_0/P and V/V_0. Therefore EosFit makes no assumptions about the units used for the parameters and variables in the compressional parts of the EoS. That is, you must ensure that your units for K_0 and P are the same (e.g. both kbar or both GPa), and that the units for V_0 and V are the same (e.g. $cm^3.mol^{-1}$, or $Å^3$). The value of K' is then dimensionless, and K'' has the units of inverse pressure.

For the temperature parts of the EoS, again there is no internal use of specific units. You can choose any temperature scale (e.g. K or ^{o}C or ^{o}F). The reference temperature T_0 and the experiment temperature are on this same scale, and the value of the thermal expansion coefficient α is in inverse temperature units. *Important: for ease of display of the small values of α_0 and α_1, they must be entered as, and will be displayed as, multiplied by the factors on the GUI, 10^5 and 10^8 respectively. Thus values of $\alpha(T) = 31 \times 10^{-6} + 2.7 \times 10^{-8}T$ must be entered as $\alpha_0 = 3.1$ and $\alpha_1 = 2.7$.*

Stress-strain (*f-F*)

The f-F display group in the P-V calculator gives the values of normalised stress and the strain appropriate for the EoS type, and corresponding to the P-V values and EoS parameter values displayed on the GUI.

Birch-Murnaghan. Eulerian strain is $f_E = \left[(V_0/V)^{2/3} - 1\right]/2$, normalised stress is defined as $F_E = P/3f_E(1 + 2f_E)^{5/2}$.

Natural Strain EoS. The strain is $f_N = 1/3\ln(V/V_0)$, with a normalised stress $F_N = PV/3f_N V_0 = P\eta/\ln\eta$.

Vinet EoS. The value listed as "f" on the GUI is actually (1-f_V) where $f_V = (V/V_0)^{1/3}$, and the normlised stress is $F_V = \ln(Pf_V/3(1-f_V))$.

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