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January 2019

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ISSN 1358-6254

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A revised equation of state for *in situ* pressure determination using fcc-Pb ($0 < P < 13$ GPa, $T > 100$ K)

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Abstract

A pressure- and temperature-dependent equation of state (PVT EoS) parameterisation for the low-pressure face-centred-cubic polymorph of Pb metal has been derived from literature data. This PVT EoS enables the use of Pb as a pressure marker in high-pressure neutron diffraction studies on the PEARL beamline at ISIS, for example. The new equation of state supersedes the previously used version [Fortes *et al.*, 2007: *High Press. Res.*, **27**, 201-212], being developed from a wider range of experimental data and with a more explicit description of how the final model was arrived at.

1. Introduction

Pb metal is an ideal pressure marker for high-pressure measurements, being used routinely with the Paris-Edinburgh opposed-anvil press on the PEARL beam-line at ISIS (Bull *et al.*, 2016). The face-centred-cubic (FCC) polymorph of Pb is stable up to ~ 13 GPa at room temperature (Kuznetsov *et al.*, 2002), where it melts at ~ 1200 K (Errandonea, 2010). Pb has an isothermal bulk modulus, $K_0 \approx 41$ GPa at 300 K, which is within a factor of 2 – 4 of the bulk moduli of many molecular solids studied on PEARL; moreover, it exhibits a large volume compression across the range of studies done typically with the Paris-Edinburgh (P-E) press, ~ 15 % over 0–10 GPa. The Debye temperature is low, $\theta_D \approx 90$ K, such that there are no large gradients in thermophysical properties over the temperature range of typical P-E cell studies (> 100 K). Lastly, the neutron absorption cross section is very small (Sears, 1992). Contrast these properties with those of many other pressure markers, such as Au or Ag, which have bulk moduli 3 to 4 times larger, and neutron absorption cross sections approximately three orders of magnitude greater than Pb. Sodium chloride, a soft material commonly used for pressure calibration, is soluble in methanol-based pressure media as well as in many of the water- or ammonia-based materials studied on PEARL (Pinho & Macedo, 2005), whereas Pb is chemically inert.

Common practice is thus to introduce a small pellet of rolled Pb foil, with a mass of 50 – 100 mg, in the centre of a powder sample when it is loaded into the encapsulated TiZr gaskets (*cf.*, Marshall & Francis, 2002). In circumstances where liquid loadings are being carried out, a ball of silica wall may be used to support the Pb pellet in the middle of the samples, whilst also aiding nucleation of a polycrystalline powder, or else a coil or pigtail of Pb wire may be stood in the gaskets.

A pressure-volume-temperature (PVT) parameterisation of the Pb equation of state (EoS) was generated from literature data in 2003 for the analysis of measurements I made on ammonia hydrates at high pressure using PEARL (Fortes, 2004). This implementation of the Pb EoS was later published (Fortes *et al.*, 2007) and has been employed by many other PEARL users subsequently (e.g., Goodwin *et al.*, 2008; Lindsay-Scott *et al.*, 2011; Fortes *et al.*, 2009, 2012; Bull *et al.*, 2015, 2017a, 2017b, 2017c). However, this EoS had two main shortcomings:

- (1) The 3rd-order Birch-Murnaghan EoS was parameterised against a very limited range of experimental data, based principally upon the initial need for an EoS in the range 0 – 5 GPa and below 300 K.
- (2) The implementation of error propagation in the original model was not correct.

Both of these shortcomings were addressed in a re-parameterised model in 2012. Thus far, the application of the revised EoS model has been limited due to the lack of a written description, which this report seeks to correct.

2. The re-parameterised Pb equation of state

The pressure as a function of volume is parameterised by a 4th-order Birch-Murnaghan equation of state (BMEOS4) as follows (Murnaghan, 1944; Birch, 1952):

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

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

where V_0 is the zero-pressure unit-cell volume (\AA^3) or the molar volume ($\text{cm}^3 \text{mol}^{-1}$), K_0 is the zero-pressure bulk modulus (GPa), K' is the first pressure derivative of the bulk modulus, $\partial K / \partial P$ (dimensionless) and K'' is the second pressure derivative, $\partial^2 K / \partial P^2$ (GPa^{-1}).

The temperature dependence of these quantities is described with good accuracy by simple first- or second-order polynomials; since I am restricting the application of the EoS to a minimum temperature of 100 K, one avoids the large variations in thermodynamic quantities that occur below 100 K. Only K'' is assumed to be temperature invariant.

$$V_0(T) = V_0(300) + a(T - 300) + b(T - 300)^2 \quad (3)$$

$$K_0(T) = K_0(300) + c(T - 300) + d(T - 300)^2 \quad (4)$$

$$K'(T) = K'(300) + e(T - 300) \quad (5)$$

where $V_0(300)$, $K_0(300)$ and $K'(300)$ are the zero-pressure values of the volume, bulk modulus and its first derivative at a reference temperature of 300 K; a , b , c , d , and e are fit parameters derived in the following sections.

2.1 Thermal expansion

Many datasets describing the temperature dependence of the lattice parameter, the volume expansivity or the linear expansivity of Pb have been published, which cover the range from 10 K up to the melting point, $T_m = 600.6$ K (Dorsey, 1908: Uffelman, 1930: Hidnert & Sweeney, 1932: Dheer & Surange, 1941: Stokes & Wilson, 1941: Nix & McNair, 1942: Richards, 1942: Klug, 1946: Van Duijn & Van Galen, 1957: Feder & Nowick, 1958: Rubin *et al.*, 1962: D'Heurle *et al.*, 1962: White, 1962: Pautomo, 1963: Channing & Weintroub, 1965: Asay *et al.*, 1968: Andres, 1961, 1962, 1964: Balasundaram & Sinha, 1971). The data are piecemeal; several datasets exist from room-T to low-T, and several other datasets exist from room-T upwards – *no single dataset covers the whole range*. These were all transformed to molar volume and parameterised using a Debye model of the internal energy to second order:

$$V(T) = V_0 \left(1 + \frac{U(T)}{Q - bU(T)} \right) \quad (6)$$

where $Q = V_0 K_0 / \gamma$ and $b = \frac{1}{2}(K' - 1)$, with the assumption that K_0 and γ (the Grüneisen parameter) are both independent of temperature. The internal energy of the crystal, $U(T)$ is obtained from a Debye approximation of the vibrational density of states (Cochran, 1973):

$$U(T) = 9Nk_B T \left(\frac{T}{\theta_D} \right)^3 \int_0^{\frac{\theta_D}{T}} \frac{x^3}{e^x - 1} dx \quad (7)$$

N is the number of atoms in the unit cell, k_B is Boltzmann's constant, θ_D is the characteristic Debye temperature, and $x = \hbar\omega/k_B T$.

Fitting to the Pb experimental data yields $V_0 = 17.8850(2) \text{ cm}^3 \text{ mol}^{-1} = 118.795(2)$, $\theta_D = 92.6(14) \text{ K}$, $Q = 32.50(13) \times 10^4 \text{ J cm}^{-3}$, and $b = 3.60(15)$. From this, assuming $\gamma \approx 2.2 - 2.6$

(Asay *et al.*, 1968; Ramakrishnan *et al.*, 1978), one finds $K_0 = 40 - 47$ GPa and $K' = 8.2(3)$, with the caveats outlined above.

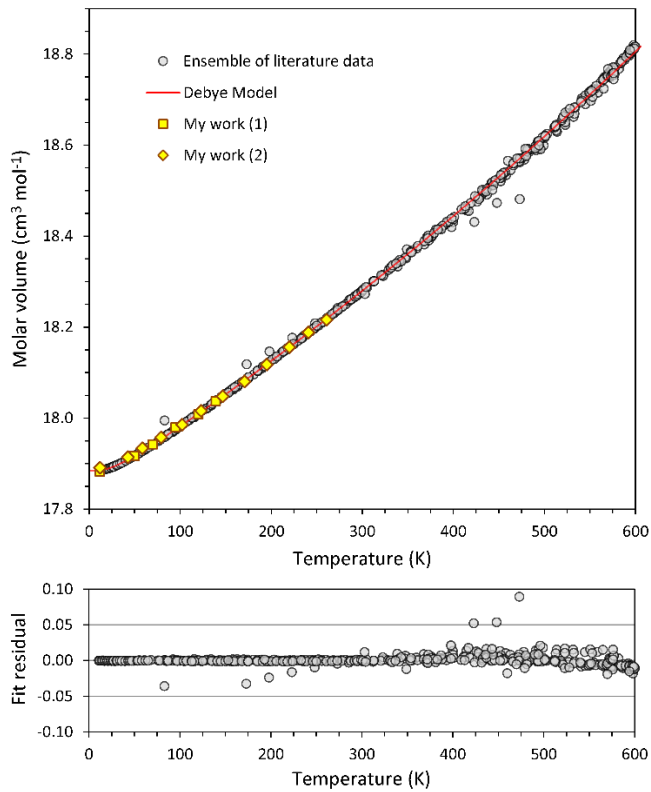


Figure 1:

Debye model fit to the complete ensemble of literature data describing the thermal expansion of Pb. The yellow symbols indicate values obtained by me during a study of Pb-encapsulated ice measured on Osiris at the ISIS neutron spallation source. It is clear by examination of the residuals (bottom) that there is a substantial difference in the scatter of datasets measured below room temperature when compared with those measured above room temperature. There is a clear need for a single coherent set of measurements to be made, on the same sample in the same sample holder, from base temperature up to the melting point.

This description of the thermal expansion was used for the transformation of other quantities (see below) and as the basis for determining $V_0(T)$ (*cf.*, Eq 3). Since we require only the region of slowly-varying volume above 100 K, and since the Debye model is needlessly complex for our stated purpose, the region above 100 K is fitted with a 2nd order polynomial. The parameter values were obtained by fitting to the exact Debye-model result and the uncertainty on the parameters was estimated by fitting the same polynomial model directly to the raw experimental data (Table 1).

2.2 Isothermal incompressibility

Elastic stiffness constants, c_{ij} , have been measured as a function of temperature up to the melting point (Goens & Weerts, 1936; Goens, 1940; Swift & Tyndall, 1942; Prasad & Wooster, 1956; Waldorf & Alers, 1962; Pautomo, 1963; Miller & Schuele, 1969; Vold *et al.*, 1977); like the thermal expansion, the data are split into series measured above and below room

temperature by different groups, there being no single set of measurements spanning the entire range. The *adiabatic* bulk modulus, $K_S = (c_{11} + 2c_{12})/3$.

Using thermodynamic identities, the *isothermal* bulk modulus, K_T , is derived as follows:

$$K_T = K_S / [(\alpha_V^2 V K_S T / C_P) + 1] \quad (8)$$

where K_S is the adiabatic bulk modulus ($\text{Pa} = \text{J m}^{-3}$), α_V is the volume thermal expansion (K^{-1}), V is the molar volume ($\text{m}^3 \text{mol}^{-1}$), T is the temperature (K), and C_P is the isobaric specific heat ($\text{J mol}^{-1} \text{K}^{-1}$).

I use the parameterisation of V (and the concomitant values of α_V) found in Section 2.1, and complement these with a 3rd order polynomial fit to measured specific heats (Figure 2).

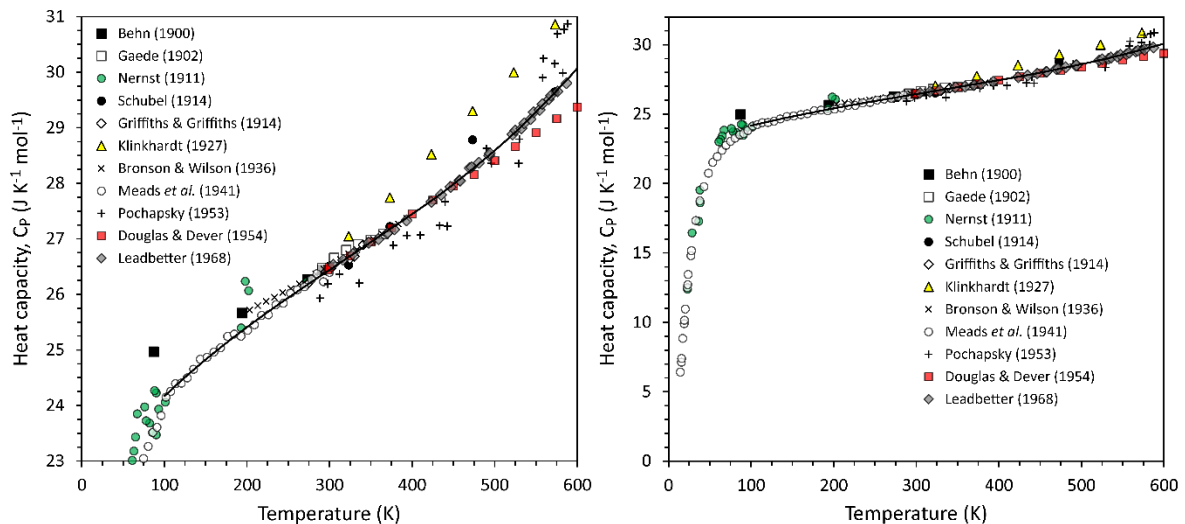


Figure 2:

Literature sources of isobaric specific heat data for Pb, and the polynomial expression fitted to a selected set of data above 100 K (solid line). For context, the range of C_P down to low temperatures is shown on the right, illustrating the dramatic change in thermophysical properties below the Debye temperature.

Again, there are disparate datasets extending above and below room temperature, but no one series that covers the entire range (Behn, 1900: Gaede, 1902: Magnus, 1910: Nernst, 1911: Griffiths & Griffiths, 1913, 1914: Schübel, 1914: Klinkhardt, 1927: Keesom & Andrew, 1927: Keesom & van den Ende, 1934: Bronson & Wilson, 1936: Meads *et al.*, 1941: Pochapsky, 1953: Douglas & Dever, 1954: Leadbetter, 1968a, 1968b: Cordoba & Brooks, 1971, 1972). In particular, the higher temperature datasets exhibit a considerable degree of scatter. A choice was made to fit only the data of Meads *et al.* (1941) below room-temperature and Leadbetter

(1968a,b) above room-temperature. The solid line in Figure 2 illustrates the fitted 3rd-order polynomial.

The values of K_T derived from K_S using the fitted V , α_V and C_P are shown in Figure 3, with a fitted 2nd order polynomial. The temperature dependence of K_T employed in the original 2004 Pb equation of state is shown as a dashed line; the deviations of the new model from the old one are small and mainly restricted to the higher-temperature region close to the melting point. Parameters from this fit are reported in Table 1.

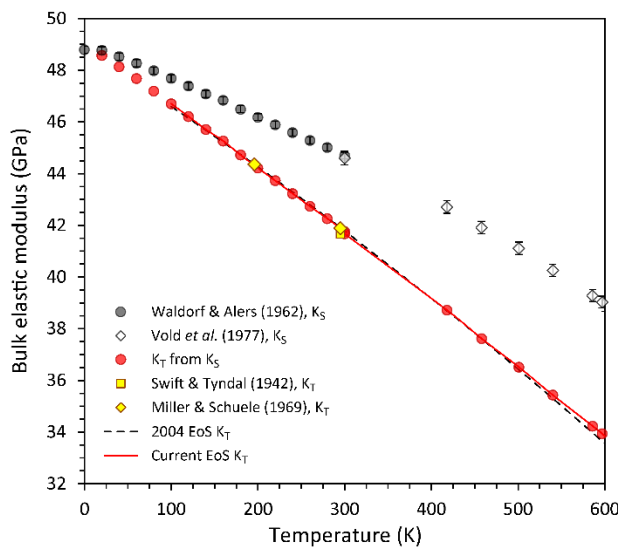


Figure 3:

Adiabatic bulk moduli calculated from c_{ij} data (upper curve) and isothermal bulk moduli obtained using Eq. 8 (lower curve). Yellow symbols indicate where workers reported isothermal values, which provide a useful check of the accuracy with which the conversion from K_S to K_T is achieved.

Differences between my original 2004 Pb EoS parameterisation of K_T and the current version are indicated by the solid and dashed lines.

2.3 PVT data

There have been numerous high-pressure studies of Pb; however, there is a dearth of compression data at low temperatures. The most accurate $V(P)$ measurements were made by Bridgman to 10 GPa (Bridgman, 1922, 1923, 1938, 1945a, 1945b), building on some earlier work by Theodore Richards (Richards, 1907, 1915). These studies were carried out mostly at room-T, although Bridgman reports a fit to some data collected at +75°C (Bridgman, 1923) and refers in passing to unpublished data collected up to 5 GPa at +150°C and -100°C (Bridgman, 1938). I have attempted to locate these measurements in Bridgman's archived laboratory notes without success. There are numerous subsequent room-T compression studies (both static and shock), employing a range of pressure scales, including ruby, NaCl, Au, and α -Fe (Al'tschuler *et al.*, 1960, 1962; Munson & Barker, 1968; Trunin *et al.*, 1969; Vaida & Kennedy, 1970; Mao & Bell, 1978; Anderson & Swenson, 1984; Mao *et al.*, 1990; Rothman

et al., 2005), and one study at high temperature (Kuznetsov *et al.*, 2002), using a NaCl pressure marker, covered the whole range of fcc-Pb stability (0—13 GPa) from room-T up to ~ 800 K. *There are no published compression measurements below room temperature.*

Keeping the parameters obtained previously to describe the temperature dependence of V_0 and K_0 , the pressure derivatives of K_0 were varied by least-squares minimisation against experimental compression data in the range $295 < T < 788$ K to yield the final set of EoS parameters listed in Table 1.

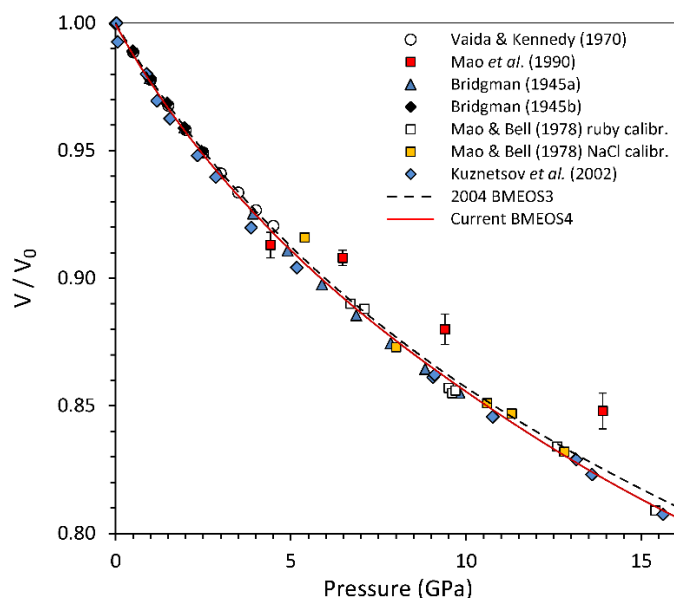
Table 1:

Final set of fitted parameters for the temperature-dependent 4th order Birch-Murnaghan equation of state.

$V_0(0)$	121.418(5) Å ³
a	$1.058(4) \times 10^{-2}$ Å ³ K ⁻¹
b	$3.5(2) \times 10^{-6}$ Å ³ K ⁻²
$K_0(0)$	41.73(1) GPa
c	$-2.544(4) \times 10^{-5}$ GPa K ⁻¹
d	$-2.8(2) \times 10^{-6}$ GPa K ⁻²
$K'(0)$	5.39(25)
e	0.0011(1) K ⁻¹
K''	$-0.33(2)$ GPa ⁻¹

Figure 4:

Comparison of the previous EoS model and the current version (defined by the parameters on the left) at 300 K, along with a selection of room-temperature compression data from the literature.



The absolute differences between the new model parameterisation and the preceding 2004 EoS are quite small (and really within the experimental uncertainty). At room temperature, as shown in Figure 4, the differences are greatest at higher pressures; below 10 GPa the difference in calculated P at any given V is ~ 0.06 GPa at 300 K, falling to ~ 0.02 GPa at 100 K. This largely reflects the use of more high-T and higher-P experimental data in the fit parameterisation. Figure 4 suggests that the new model is marginally more accurate at the highest pressures; in the absence of any published below-room-T compression data it is not possible to assess the accuracy of the new model in the 100 – 300 K range.

By way of a final comparison, Table 2 provides a compilation of previously published values for the isothermal compressibility of Pb, the first pressure derivative and the temperature derivative (where reported or where it may be determined from other quantities). Unless otherwise stated, all values correspond (within 5 – 10 K) with 300 K.

Table 2:

	K_0 (GPa)	K'	$\partial K_0/\partial T$ (GPa K ⁻¹)
Richards (1915)	42.9	–	–
Bridgman (1922)	42.14	6.15	-2.36×10^{-2}
Al'tschuler <i>et al.</i> (1960)	41.4	–	–
Munson & Barker (1966): static	41.3	–	–
Munson & Barker (1966): dynamic	39.4	–	–
Miller & Schuele (1969): 296 K	41.89	5.72	–
Miller & Schuele (1969): 195 K	44.36	5.61	-2.45×10^{-2}
Vaida & Kennedy (1970): polynomial	42.35	3.74	–
Vaida & Kennedy (1970): Murnaghan	39.98	6.76	–
Nellis <i>et al.</i> (1988)	38.98	5.04	–
Mao <i>et al.</i> (1990)	39.9(2)	6.1(1)	–
Vohra & Ruoff (1990)	43.20	4.87	–
Schulte & Holzapfel (1995)	42(5)	5(1)	–
This work	41.7	5.4	-2.5×10^{-2}

3. Implementation of the model

The Pb PVT BMEOS4 model is implemented in a Microsoft Excel spreadsheet hosted on the PEARL analysis PC, and is available to any user on request. The spreadsheet calculates the pressure for a given pair of inputs, temperature and some parameter from which the Pb molar volume may be determined. The latter is permitted to be any one of the following: (i) the unit-cell volume (Å³); (ii), the lattice parameter (Å); (iii) the d-spacing of several strong Bragg reflections from Pb in the diffraction pattern (Å), being either (111) or (200). The relevant input

box uses a range-detection algorithm to automatically identify the type of input being used amongst these three possibilities and writes this out with the pressure result by way of confirmation. Thus one has the option to read off a peak position from a display of the raw data for easy on-the-fly pressure determination, or else to enter a lattice parameter or cell volume from a profile refinement.

The spreadsheet computes partial derivatives of all model parameters with respect to the EoS function and uses these to estimate a minimum value of the uncertainty in the pressure based on manually-entered uncertainties in the cell volume and the temperature. It is worth reminding seasoned users of profile-refinement software that the uncertainty obtained on lattice parameters is questionable (*cf.*, Tian & Billinge, 2011), typically being underestimated by a factor of ‘a few’ and it is up to the user to judge whether the accuracy of the error bars on P propagated in this way by careful evaluation (for example) of the scatter in their data.

Concluding Remarks

Examination of the literature concerning the thermo-elastic properties of Pb reveals two aspects that require action. Firstly, there is not a single temperature-dependent measurement that extends from liquid-helium temperatures up to the melting point of Pb in one unbroken sequence; there are measurements below room temperature by one set of workers, and another set above room temperature by a different set of workers. The higher-T studies typically exhibit more scatter, perhaps because of poorer temperature control or thermal equilibration of the sample. Since it is very straightforward to do so, a high-precision series of measurements of the unit-cell volume from 10 – 600 K is warranted.

Secondly, there are no compression data for Pb below room temperature. Bridgman refers to a measurement made at -150°C , from which he may have derived his value for $\partial K/\partial T$, but the data were not published and I have not been able to find any archived notes. There is scope to carry out a low-temperature study of Pb using a gas-pressure cell with He as the pressure-transmitting medium to reach pressures of ~ 0.8 GPa down to ~ 50 K. Although this range of pressures is small, the pressure can be determined with good accuracy and it would allow some indication of the equation of state’s accuracy to be obtained and perhaps improved.

Acknowledgments

The author thanks Dr Alexei Kuznetsov for sharing his tabulated high P/T data.

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