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To cite this article: Sushil Bose Roy and Papiya Bose Roy 1999 *J. Phys.: Condens. Matter* **11** 10375

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An equation of state applied to solid up to 1 TPa

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Received 10 June 1999

Abstract. In this paper, an isothermal three-parameter equation of state (EOS) of solid is presented in the form $V/V_0 = f(P)$. The proposed EOS uses three parameters expressible in terms of B_0 , B'_0 and B''_0 , denoting bulk modulus and its first and second pressure derivatives at zero pressure. The new EOS is applied to the isotherms of ionic, metallic, quantum and rare-gas solid, with pressures ranging from zero to variable maximum pressures of up to 1 TPa (= 10 Mbar). The fits are uniformly excellent, and equally excellent is the agreement of the fitted parameters B_0 and B'_0 with experimental values. Deviations between data points and fits are computed and compared with the successful EOSs of similar form from the literature, and the drastic superiority of our new model is demonstrated. Further, the proposed model is applied to the isotherms of metals at ultrahigh pressures, with B_0 and B'_0 constrained to experimental values. An inter-comparison of results obtained from different EOSs, including the universal formulations, shows that our new form yields a superior fit.

1. Introduction

The relation between pressure P and relative volume V/V_0 at a given temperature is labelled as an isothermal equation of state (EOS). It provides an extensive body of information on the non-linear compressibility of solids and is widely used in basic and applied science [1]. A lack of precise knowledge of interatomic potential, compounded with procedural constraints to carry through prediction, has compelled workers in this field to resort to simplifying models and approximations, resulting in the formulation of a number of empirical EOSs. Although modern electronic band-structure calculations allow the predictions of the EOSs of solids, these are time consuming and expensive, restricting many such calculations to the ambient-pressure set of lattice parameters, thus precluding the critical comparison with high-pressure experiments [2]. Further, pressure, relative volume and bulk moduli continue to be estimated by fitting the experimental data with an appropriate empirical EOS instead of by numerical differentiation. Since the universal status of two-parameter EOSs is negated [3, 4], the need for the search for a three-parameter empirical EOS, capable of describing the currently available experimental EOSs, with ever-increasing fitting accuracy, continues to exist.

In this paper we shall propose a new isothermal three-parameter EOS and show that it mimics the EOS data quite accurately up to ultrahigh pressures, and that the bulk moduli, B_0 and B'_0 , predicted by it are in excellent agreement with experiment.

2. Empirical equation of state

In this section we will present a new EOS invented by us along with the successful ones, already existing, for the purpose of comparison. Constancy of temperature is assumed throughout

and no special notation is used. V and V_0 denote volume at pressure P and zero pressure respectively, and $x = (V/V_0)^{1/3}$ is the linear compression. Perhaps the best known EOS for solids is credited to Murnaghan [5, 6], and is based on the empirical observation that bulk modulus is a linear function of pressure. The inadequacy of the two-parameter Murnaghan EOS (M2) with implicit $B_0'' = 0$ was realized [7] and the three-parameter Murnaghan EOS (M3) obtained by extending the Taylor expansion of the bulk modulus to second order has been widely used to estimate B_0 , B_0' and B_0'' [8].

A modification and improvement of the Murnaghan EOS by Birch [9, 10] is based on Eulerian finite-strain formalism. The finite-strain expansion for the pressure is, to fourth order in strain

$$P = 3B_0 f(1 + 2f)^{5/2}(1 - 2af + 4bf^2 + \dots) \quad (1)$$

where $a = (3/4)(B_0' - 4)$, $b = (3/8)[B_0 B_0'' + B_0'(B_0' - 7) + (143/9)]$ and $f = (1/2)[x^{-2/3} - 1]$. Equation (1) is the three-parameter Birch–Murnaghan EOS (B3) which reduces to the third order or two-parameter Birch–Murnaghan EOS (B2) by deleting the f^2 -term in equation (1). An EOS of simple form was suggested by Huang and Chow (HC) [11]

$$\frac{V}{V_0} = 1 - a[1 - (1 + bP)^{-c}] \quad (2)$$

with $a = (1 + B_0')/(1 + B_0' + B_0 B_0'')$, $b = (B_0'/B_0) - [B_0''/(B_0' + 1)]$ and $c = (1 + B_0' + B_0 B_0'')/(B_0'^2 + B_0' - B_0 B_0'')$.

The three-parameter EOS proposed by Freund and Ingalls (FI) [12] is a simple modification of the ‘usual’ Tait equation [13]

$$\frac{V}{V_0} = [1 - a \ln(1 + bP)]^c \quad (3)$$

with the parameters $a = [(B_0'^2 - 4B_0 B_0'')^{1/2} - B_0']/[(B_0'^2 - 4B_0 B_0'')^{1/2} + B_0']$, $b = [(B_0'^2 - 4B_0 B_0'')^{1/2} + B_0']/2B_0$ and $c = 2/[(B_0'^2 - 4B_0 B_0'')^{1/2} - B_0']$.

A universal equation of state (U2) for solids proposed by Rose *et al* [14] and strongly promoted by Vinet *et al* [15] is

$$P = [3B_0(1 - x)/x^2] \exp[(3/2)(B_0' - 1)(1 - x)] \quad (4)$$

but universality of U2 falters for materials which have phase transitions or internal degrees of freedom. It also falters for materials which undergo a significant rearrangement of electronic bands under compression, necessitating the inclusion of the higher-order elastic moduli [16, 17]. With the inclusion of B_0'' , the three-parameter universal EOS (U3) is [16]

$$P = 3B_0(x^{-2/3})(1 - x^{1/3})(\exp M). \quad (5)$$

Here, $M = (3/2)(B_0' - 1)(1 - x^{1/3}) + (3/2)(1 - x^{1/3})^2[(1/4)B_0'^2 + (1/2)B_0' + B_0 B_0'' - (19/36)]$. An extension of the Murnaghan equation was given by Kumari and Dass [18, 19] by taking the high-order terms in the Taylor series expansion into account on the assumption that $B_0^{(n+1)}/B_0^n = B_0''/B_0' = -Z$ for $n > 1$, with $B_0^{(n)}$ as the n th-order pressure derivative of the isothermal bulk modulus at zero pressure. The resulting KD equation may be written as

$$\frac{V}{V_0} = [(1 + m) \exp(ZP) - m]^{-(1/n)}. \quad (6)$$

Here, $m = (B_0'/B_0 Z)$, $n = B_0' + B_0 Z$ and Z is a pressure-independent parameter. Our new isothermal three-parameter EOS (designated SP) is

$$\frac{V}{V_0} = 1 - \frac{\ln(1 + aP)}{(b + cP)}. \quad (7)$$

Table 1. Curve-fitting parameters along with root-mean-square deviations in V/V_0 (RMSDs) multiplied by 10^4 for selected solids of different classes. PR is the pressure in kbar and MRV denotes $(V/V_0)_{min}$. $B_0'' = -B_0'Z$ for HC, FI and KD.

EOS	B_0 (kbar)	B_0'	B_0'' (kbar)	$10^3 (Z)$ (kbar)	10^4 (RMSD)	Ref.
NaCl: $T = 25^\circ\text{C}$; PR(0–311.45); MRV = 0.6405						
HC	239.98	4.721		2.872	2.44	[22]
FI	239.19	4.745		3.140	2.15	
KD	240.14	4.54		1.236	1.56	
SP	236.8	4.9	−0.0223		0.32	
	235.6	5.11 ± 0.03	-0.00034 ± 0.00014			[28]
CsCl: $T = 25^\circ\text{C}$; PR(0–416.06); MRV = 0.5759						
HC	170.72	5.283		4.217	5.22	[22]
FI	170.44	5.322		4.660	4.30	
KD	172.51	4.96		1.306	3.79	
SP	167.53	5.55	−0.03688		0.66	
	168.59	5.54	−0.0237			[29]
	167.4 ± 0.9	5.98 ± 0.09	-0.042 ± 0.04			[30]
Cu: $T = 25^\circ\text{C}$; PR(0–4500); MRV = 0.516						
KD	1431.93	4.332		0.1234	5.22	[23]
SP	1389	4.92	−0.00391		3.28	
Cu: $T = 300\text{ K}$; PR(950–10040); MRV = 0.436						
KD	1620	3.79		-1×10^{-5}	14.27	[24]
SP	1420	5.04	−0.00391		7.12	
	1420, 1370	5.25				[31–33]
In: $T = 25^\circ\text{C}$; PR(0–900); MRV = 0.580						
KD	403.52	4.756		0.5059	14.0	[23]
SP	400	5.21	−0.0141		3.59	
	390.77	5.239				[34]
	390	5.26 ^a				[35]
	403 ± 8	6.2 ± 0.1				[36]
Au: $T = 300\text{ K}$; PR(0–2161); MRV = 0.66						
KD	1691.52	5.04		0.1609	1.54	[25]
SP	1667.7	5.43	−0.00348		0.23	
	1666.5 ± 50.0	5.4823 ± 0.5400				[25]
n-H ₂ : $T = 4.2\text{ K}$; PR(0–25.4517); MRV = 0.4165						
KD	1.96	5.22		0.0306	15.93	[26]
SP	1.7	6.78	−4.496		5.61	
	1.70 ± 0.06	7.0 ± 0.3				[26]
n-D ₂ : $T = 4.2\text{ K}$; PR(0–25.2100); MRV = 0.4745						
KD	3.46	5.32		0.02721	10.95	[26]
SP	3.16	6.51	−2.311		3.50	
	3.15 ± 0.06	6.7 ± 0.3				[26]
Xe: $T = 4.2\text{ K}$; PR(0–25.4517); MRV = 0.4165						
SP	36.16	9.29	−0.345		1.15	[27]
	36.3	8.87				[27, 37]
K: $T = 295\text{ K}$; PR(0–19.31); MRV = 0.725						
SP	29.59	4.36	−0.1419		0.75	[8]
	29.71	4.20	−0.0505			[8]

^a An average of literature values.

Table 2. V/V_0 as a function of pressure for sodium chloride at 25 °C.

S No	P (kbar)	V/V_0		S No	P (kbar)	V/V_0	
		Decker's data	Calc. SP			Decker's data	Calc. SP
1	1.44	0.9940	0.9940	36	91.89	0.7992	0.7992
2	2.94	0.9880	0.9880	37	96.04	0.7940	0.7941
3	4.47	0.9821	0.9821	38	100.31	0.7889	0.7889
4	6.06	0.9762	0.9762	39	104.69	0.7838	0.7838
5	7.70	0.9703	0.9703	40	109.21	0.7787	0.7787
6	9.38	0.9644	0.9644	41	113.84	0.7736	0.7737
7	11.12	0.9586	0.9586	42	118.61	0.7686	0.7686
8	12.91	0.9528	0.9527	43	123.52	0.7636	0.7636
9	14.76	0.9470	0.9469	44	128.55	0.7586	0.7586
10	16.67	0.9412	0.9411	45	133.73	0.7536	0.7536
11	18.63	0.9354	0.9354	46	139.06	0.7486	0.7486
12	20.65	0.9297	0.9297	47	144.53	0.7437	0.7437
13	22.74	0.9240	0.9240	48	150.15	0.7388	0.7388
14	24.88	0.9183	0.9183	49	155.93	0.7339	0.7339
15	27.10	0.9127	0.9126	50	161.87	0.7290	0.7290
16	29.37	0.9070	0.9070	51	167.97	0.7242	0.7242
17	31.72	0.9014	0.9014	52	174.25	0.7193	0.7193
18	34.13	0.8958	0.8958	53	180.69	0.7145	0.7145
19	36.62	0.8903	0.8903	54	187.31	0.7097	0.7097
20	39.18	0.8847	0.8847	55	194.12	0.7050	0.7050
21	41.82	0.8792	0.8792	56	201.11	0.7002	0.7002
22	44.53	0.8737	0.8737	57	208.29	0.6955	0.6955
23	47.32	0.8683	0.8683	58	215.67	0.6908	0.6908
24	50.20	0.8628	0.8628	59	223.26	0.6861	0.6861
25	53.16	0.8574	0.8574	60	231.05	0.6815	0.6815
26	56.20	0.8520	0.8520	61	239.05	0.6768	0.6768
27	59.33	0.8466	0.8466	62	247.27	0.6722	0.6722
28	62.55	0.8412	0.8412	63	255.72	0.6676	0.6676
29	65.87	0.8359	0.8359	64	264.39	0.6631	0.6631
30	69.28	0.8306	0.8306	65	273.31	0.6585	0.6585
31	72.79	0.8253	0.8253	66	282.46	0.6540	0.6540
32	76.40	0.8200	0.8201	67	291.87	0.6495	0.6495
33	80.11	0.8148	0.8148	68	301.53	0.6450	0.6450
34	83.93	0.8096	0.8096	69	311.45	0.6405	0.6406
35	87.85	0.8044	0.8044				

Here

$$a = (1/8B_0)[3(B'_0 + 1) + (25B_0'^2 + 18B'_0 - 32B_0B_0'' - 7)^{1/2}]$$

$$b = (1/8)[3(B'_0 + 1) + (25B_0'^2 + 18B'_0 - 32B_0B_0'' - 7)^{1/2}]$$

$$c = [(1/16B_0)[3(B'_0 + 1) + (25B_0'^2 + 18B'_0 - 32B_0B_0'' - 7)^{1/2}][(B'_0 + 1) - (1/8)[3(B'_0 + 1) + (25B_0'^2 + 18B'_0 - 32B_0B_0'' - 7)^{1/2}]].$$

It may be noted that the B2 EOS commanded wide applications until the U2 expression made inroads into the field of equations of state. The U2 expression includes the non-linearity physics more accurately than the B2 equation, and the B2 EOS is in better agreement with the experimental EOS than the M2 model [20]. Freund and Ingalls [12] have shown on the basis of application to the shock wave compression data of Na, In, NaCl and KF, with pressures ranging up to a maximum of 340 kbar, that the three-parameter EOSs, M3, HC and FI, fit the

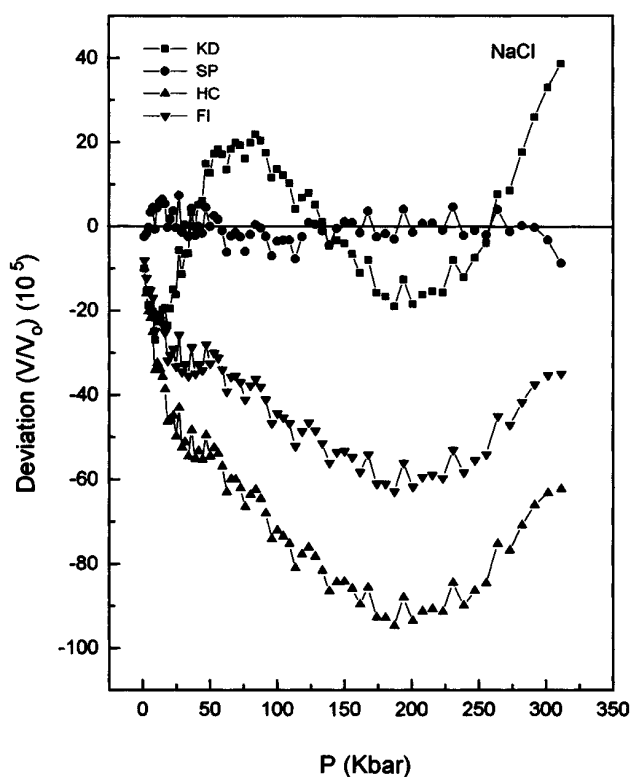


Figure 1. A comparison of deviations in V/V_0 between data and fit with HC, FI, KD and SP equations for the 25 °C isotherm of NaCl [22].

data equally well and better than the two-parameter EOSs of the same form, while Fang and Chen [21] have applied KD and U2 equations to 42 solids and demonstrated that the three-parameter KD expression, which is an improved version of the M3 EOS, generally yields a better fit than the two-parameter U2 equation. Kumari and Dass [18] have shown that their expression is in better agreement with the Decker 25 °C semitheoretical isotherms of NaCl and CsCl [22] than both the HC and FI models.

In section 3.1 we have tested the validity of our new model by applying it to a wide variety of isotherms over a wide pressure range, and compared the results with the successful KD model. The HC and FI equations have been invoked only for the Decker isotherm [22] to examine the nature of the fit. Comparison is restricted, in section 3.1, to the successful EOS in the form $V/V_0 = f(P)$ because such forms are useful for higher-pressure EXAFS work in which one has to express r/r_0 as a function of pressure which is just the third root of V/V_0 . r is the distance between two atoms, e.g., the nearest neighbours.

The regression curve of P on V/V_0 is generally not the same as the regression curve of V/V_0 on P . Due to the complicated nature of the functional form, the B2, B3, U2 and U3 expressions cannot be analytically inverted to the form $V/V_0 = f(P)$. Likewise, the SP equation cannot be changed to the form $P = f(V/V_0)$; however, it is possible to calculate the fit parameter for the regression curve of P on V/V_0 . In section 3.2 we have used the fit parameter for the regression curve of P on V/V_0 for all the EOSs, for the sake of parity in comparison.

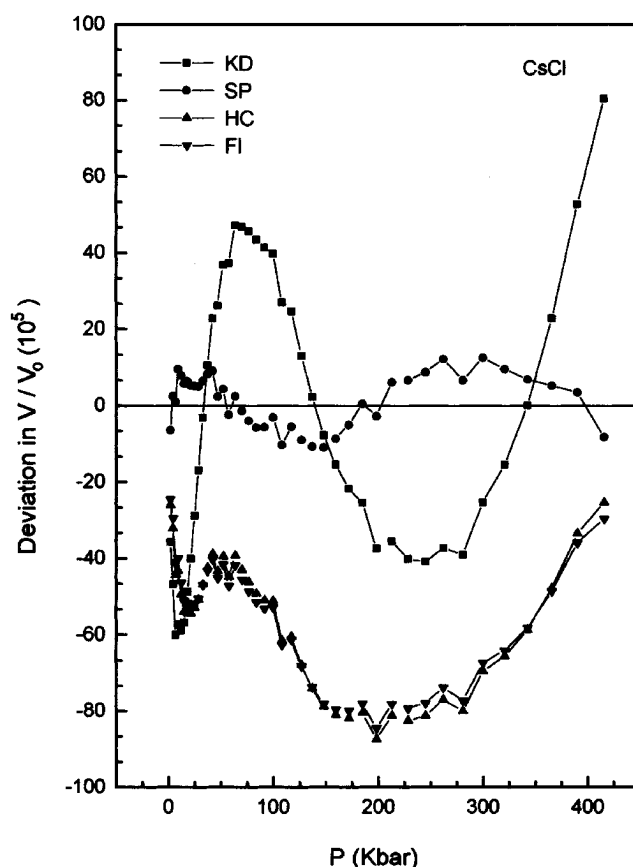


Figure 2. A comparison of deviations in V/V_0 between data and fit with HC, FI, KD and SP equations for the 25°C isotherm of CsCl [22].

3. Test of the new model

3.1.

The new equation SP is applied to the isotherms of NaCl and CsCl [22], In and Cu (shock wave) [23], Cu [24], Au [25], n-H₂ and n-D₂ [26], Xe [27] and K [8]. The curve-fitting bulk moduli parameters along with root-mean-square deviations (RMSDs) between data points and fits are summarized in table 1. Corresponding values for other EOSs are also reported for the purpose of comparison. Experimental values of isothermal bulk moduli of the above solids are presented for easy reference.

3.1.1. NaCl and CsCl. Decker's semitheoretical isotherm of NaCl plays an important role in the study of EOS and NaCl continues to enjoy an esteemed position as a pressure marker in high-precision compression measurements [38].

Using the SP equation and the fit parameters from table 1, the values of V/V_0 as a function of pressure are calculated and presented in table 2. The agreement is extraordinary: at a cursory glance the calculated results might seem to be a replica of Decker's tabulations. The deviations in V/V_0 , between data points and fits, versus pressures are plotted in figures 1 and 2 for NaCl

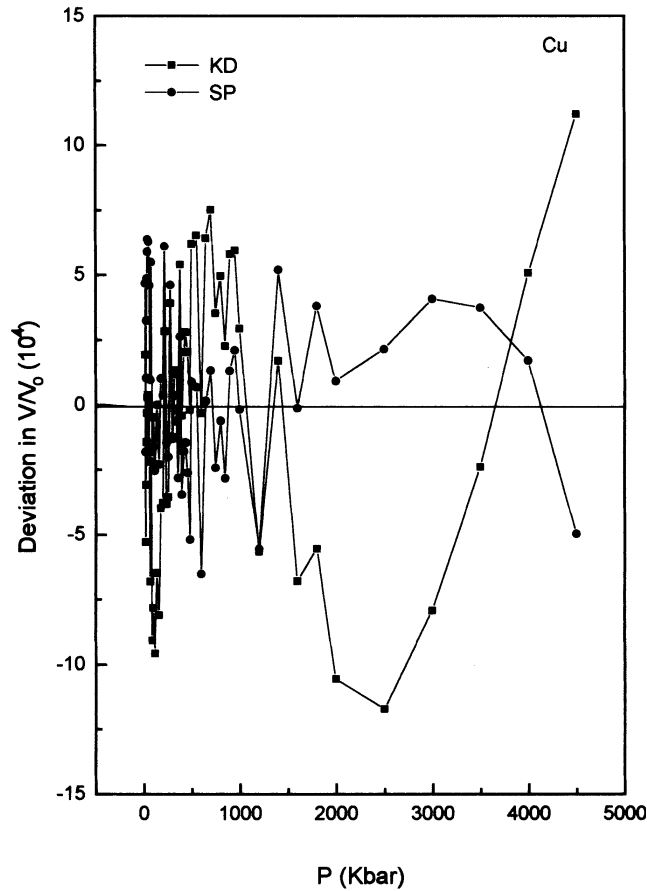


Figure 3. A comparison of deviations in V/V_0 between data and fit with KD and SP equations for the 25 °C shock wave isotherm of Cu [23].

and CsCl respectively. For both NaCl and CsCl, one can notice that deviations with the SP equation are lower and better randomized than with the KD equation. But a systematic bias is quite pronounced with the HC and FI equations, the fit exceeding the data over the entire pressure range. Further, the HC, FI and KD equations lag far behind in fitting capability, with their RMSD values higher than our new form by a factor of about 8, 7 and 5, and 8, 7 and 6 for NaCl and CsCl respectively.

The uncertainty of Decker's semitheoretical isotherm of NaCl is 1% below 50 Kbar, 1.7% below 100 kbar and 2.4% below 200 kbar, and the accuracy of Decker's computation is compatible with the attainable accuracy in experiment. To illustrate the point, the values of V/V_0 are calculated using the fit parameters from table 1 at the pressures used by Liu *et al* [39], and tabulated in table 3. The calculated results are in very good agreement with the measured values judging by the claimed accuracy of $\pm 0.45\%$ in their volume data.

Our fit value of $B'_0 = 4.9$ virtually coincides with the Decker theoretical value of 4.93 [40] and the measured value of 4.92 by Vaidya and Kennedy [29]. It will be interesting to note here that Decker's value is a debated one [30, 40], most of the authors concurring on their objections in that it is much smaller than the ultrasonic values [40]. However, Decker's theoretical value of 4.93 is only 3.5% lower than the latest ultrasonic value of 5.11 [28]. The agreement is

Table 3. V/V_0 as a function of pressure for sodium chloride at 25 °C. The experimental data are taken from Liu *et al* [39].

S No.	P (kbar)	V/V_0	
		Experimental	Calculated
1	40	0.883	0.8830
2	78	0.819	0.8178
3	84	0.810	0.8095
4	95	0.796	0.7953
5	102	0.788	0.7869
6	110	0.778	0.7779
7	137	0.751	0.7505
8	161	0.731	0.7297
9	170	0.722	0.7226
10	183	0.713	0.7128
11	190	0.708	0.7078
12	194	0.705	0.7050
13	200	0.701	0.7010
14	202	0.699	0.6996
15	204	0.698	0.6983
16	222	0.687	0.6869
17	232	0.680	0.6809
18	235	0.679	0.6791
19	247	0.672	0.6724
20	268	0.660	0.6612
21	272	0.658	0.6592
22	288	0.650	0.6513
23	290	0.649	0.6504
24	300	0.645	0.6457

excellent judging by the uncertainties of the measured ultrasonic values [10, 41], and tends to flaw such objections. Measured values of B_0'' vary by as much as two orders of magnitude and our fitted value of lies well within the broad-spectrum experimental values [41].

For CsCl, however, the fitted values are in closer agreement with the static measurements of Vaidya and Kennedy [29] than those of the ultrasonic values [30]. The higher ultrasonic value of B_0' by Barsch and Chang [30] is probably not accurate because the recent compression data [38] yield a small B_0' value.

3.1.2. Cu, In and Au. Shock data of Cu up to 4.5 Mbar from the *AIP Handbook* [23] on fitting with the SP equation yield an RMSD value which is nearly half of that with the KD equation. The SP equation leads to a better randomization of the deviations between data and fits, compared to the KD equation, as can be seen in figure 3.

With regard to shock data of [23], it may be noted that the basic shock Hugoniot data have been reduced to isothermal compressions using the Dugdale–McDonald form of the Gruneisen gamma and it is these 25 °C isothermal ‘data’ which are being fitted. The calculated 25 °C isotherms [23] are probably accurate to $\pm 5\%$ in pressure, and certainly better than $\pm 10\%$.

Nellis *et al* [24] obtained new absolute shock compression data for Al, Cu and Pb in the pressure range 3–10 Mbar. They have combined these data with first principles theory and earlier absolute EOS data to give the first self-consistent description of the thermodynamic states of metals at ultrahigh pressures. An uncertainty of $\pm 10\%$ is claimed in their 300 K isotherm (EOSN) for Al, Cu and Pb. A fit of the SP equation to the EOSN of Cu yields

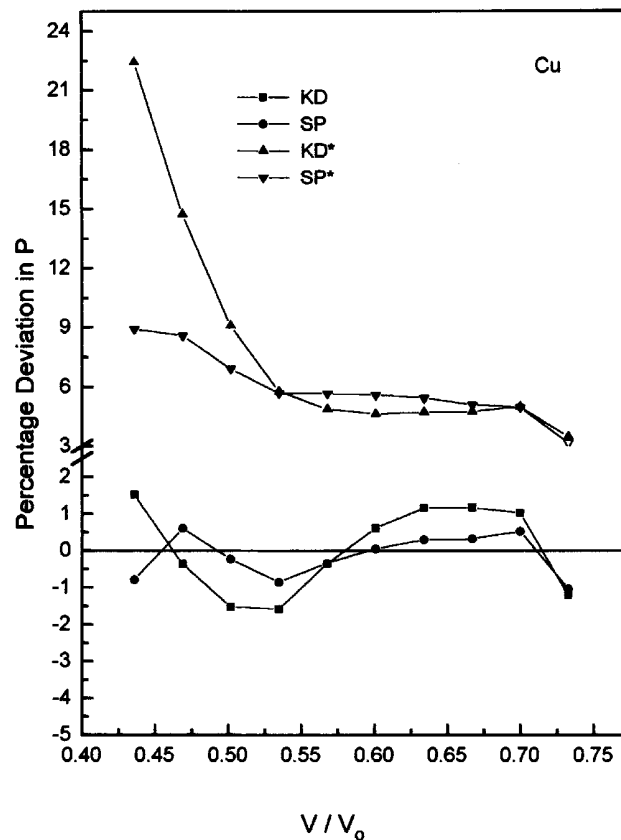


Figure 4. A comparison of percentage deviation in pressure versus relative volume (V/V_0) between KD and SP equations for the 300 K isotherm of Cu [24]. The curves KD* and SP* use the fit parameters as for Cu in figure 3.

an RMSD value which is half of that resulting from the KD form. Fit parameters yielded by the SP equation are in very good agreement with the experimental values, while the fit parameters resulting from the KD EOS disagree widely, e.g., the fitted value of B_0 is higher than the experimental value by about 14%. Using the fit parameters from table 1, pressures are calculated at V/V_0 of the EOSN of Cu. The deviations between data pressures and calculated results are shown by the curves SP and KD in figure 4. The SP EOS agrees with data points within about 1% over the entire compression range up to $V/V_0 = 0.436$, and a pressure of 10 Mbar (figure 4). Further, using the fit parameters from table 1, previously used to fit the lower-pressure *AIP Handbook* shock data of Cu [23], pressures are calculated at V/V_0 of the EOSN of Cu. Deviations between data pressures of the EOSN and calculated results are shown by the curves SP* and KD* in figure 4. It will be interesting to note that while the SP equation agrees with the EOSN well within the error bar of 10%, the KD EOS falters above $V/V_0 = 0.502$, and a pressure of 5.42 Mbar. Thus with a single set of bulk modulus parameters, B_0 and B'_0 of which are in good agreement with experimental values, the SP equation can describe the isotherm of Cu over the entire pressure range from zero to 10 Mbar quite accurately.

It will be interesting to note that since the Nellis EOS fits the basic copper shock Hugoniot data to 4.5 Mbar in addition to the new higher-pressure data, within the 10% uncertainty limit

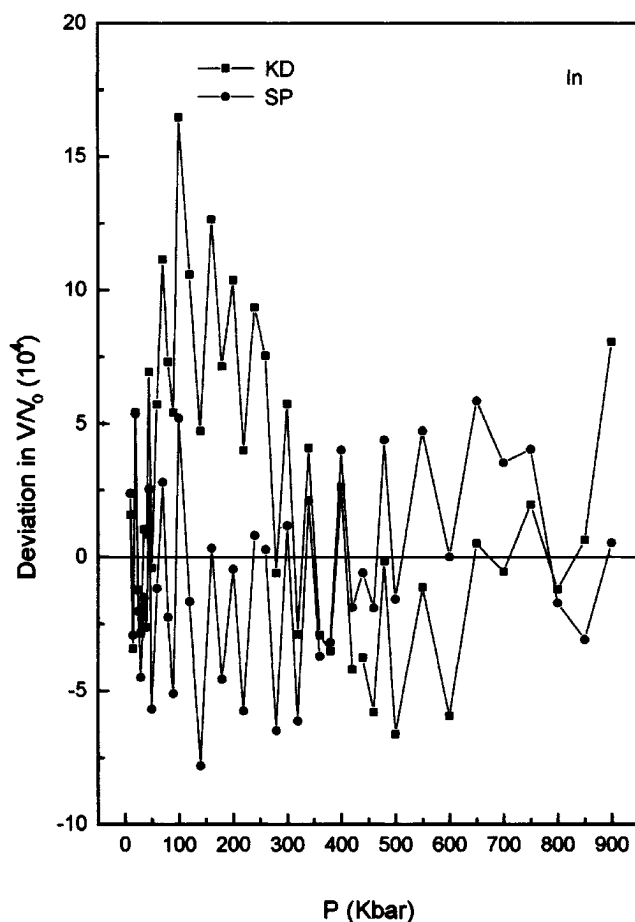


Figure 5. A comparison of deviations in V/V_0 between data and fit with KD and SP equations for the 25 °C shock wave isotherm of In [23].

claimed by Nellis, the apparent differences between the isothermal ‘data’ might be due to the reduction techniques used.

The shock data of In from the *AIP Handbook* [23] on fitting with the SP equation lead to an RMSD value one-quarter of that resulting from the KD EOS. Recently Schulte and Holzapfel [35] accurately studied the crystal structure of In under pressures up to 670 kbar, and observed no structural phase transitions contrary to earlier claims. Further, they noticed a close agreement with the x-ray data by Takemura [35] in the range to 560 kbar as well as with the shock data from the *AIP Handbook* [23]. Schulte *et al* fitted their EOS data with different EOS forms with B_0 fixed at 390 kbar. The average of the fitted values of B'_0 comes to about 5.26. The fitted value of $B'_0 = 5.21$ yielded by our new form is in extraordinary agreement with this average value, and also with the static measurements of Vaidya and Kennedy [34] suggesting a value of 5.239, but much smaller than the ultrasonic value of Voronov and Goncharowa [36]. One can notice in figure 5 that deviations with the SP equation are randomized well about the fit, while the KD equation shows systematic deviations at both low and high pressures.

Due to some inherent problems [25], the range of applicability of NaCl as a pressure marker is restricted in the P - T space. Heinz and Jeanloz [25] measured the compression of

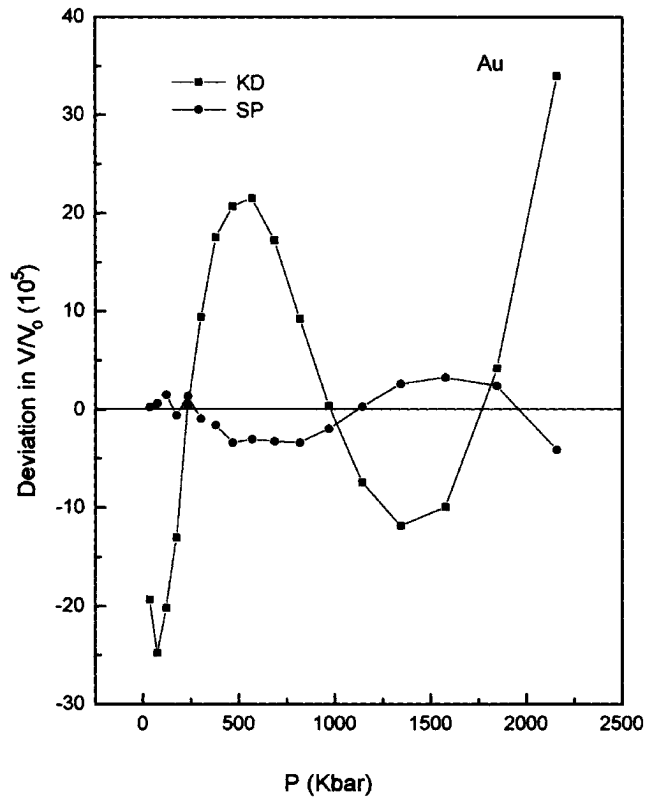


Figure 6. A comparison of deviations in V/V_0 between data and fit with KD and SP equations for the 300 K isotherm of Au [25].

Table 4. Fitted parameter B_0'' (or Z) for the regression curve of P on V/V_0 and error estimates for the Nellis *et al* isotherm of Cu and Al. The asterisked value corresponds to Z . $B_0'' = -B_0'Z$ for KD.

EOS	Cu $B_0 = 1420$ kbar [31]; $B_0' = 5.25$ [33]			Al $B_0 = 721$ kbar [42]; $B_0' = 4.72$ [43]		
	B_0'' (or Z) (kbar ⁻¹) ($\times 10^3$)	Percentage deviation in P		B_0'' (or Z) (kbar ⁻¹) ($\times 10^3$)	Percentage deviation in P	
		Mean	Maximum		Mean	Maximum
SP	-4.15	3.4	4.8	-7.63	3.2	6.3
U2		4.0	16.7		3.8	5.4
U3	-5.14	4.4	6.7	-10.1	4.2	5.8
FI	-3.09	7.0	9.6	-5.66	9.4	12.8
HC	-2.88	7.4	10.2	-5.13	10.4	14.2
KD	0.19*	12.6	17.4	0.318*	21.7	27.8
B2		8.2	12.1		30.2	55.0
B3	-0.316	14.3	22.5	-5.14	15.5	18.6

Au at room temperature to 700 kbar. They derived a thermal EOS of Au by inverting all EOS data simultaneously, and extended the gold pressure-calibration standard to cover a wider P - T space, suggesting an uncertainty in pressure of about 1–2% up to 2000 kbar. The isotherm predicted by the SP expression, with the input data from table 1, is in excellent agreement with

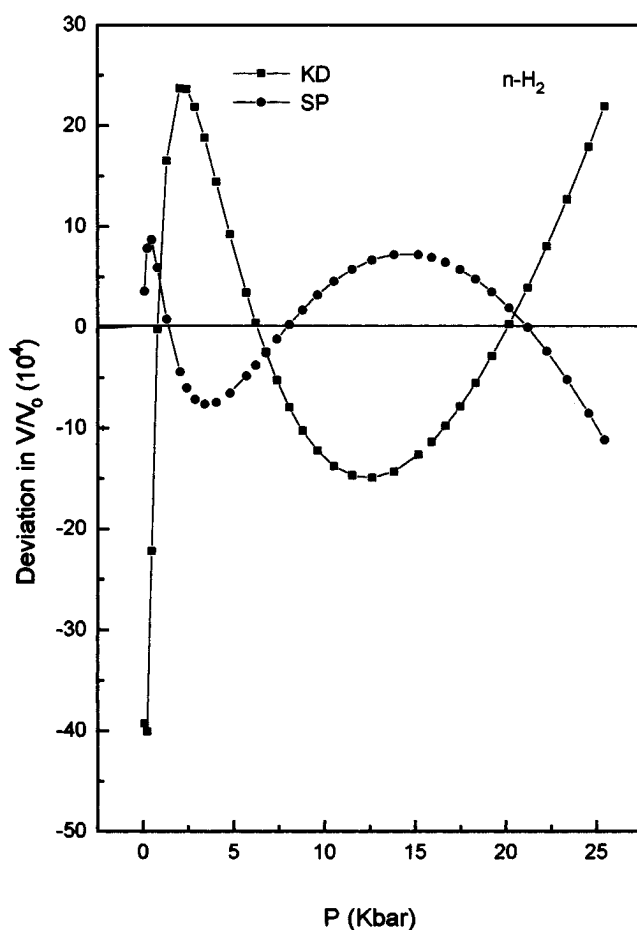


Figure 7. A comparison of deviations in V/V_0 between data and fit with KD and SP equations for the 4.2 K isotherm of n-H₂ [26].

the 300 K isotherm of gold, and our fit parameters B_0 and B'_0 are also in excellent agreement with the bulk modulus parameters used to generate the revised thermal equation of state. The fitting accuracy achieved with our new form is compared with the KD EOS in figure 6.

3.1.3. n-H₂ and n-D₂. The quantum solids n-H₂ and n-D₂ are very compressible because of their zero point energy. The claimed accuracy in V/V_0 , for the measured P - V relations for n-H₂ and n-D₂ by Anderson and Swenson [26], ranges from $\pm 10^{-3}$ at low pressures to 3×10^{-3} at 25 kbar. Table 1 shows that fit parameters B_0 and B'_0 yielded by the SP EOS are in excellent agreement with the measured values. For both n-H₂ and n-D₂, deviations in V/V_0 with the SP equation are well within the error bar (figures 7 and 8), while the KD equation exceeds the limit of experimental uncertainty at low pressures. RMSD values with the KD equation are higher than our new form by a factor of about 3 for both n-H₂ and n-D₂.

3.1.4. Xe and K. To test the validity of our model we have chosen the high-precision piston-displacement EOS for Xe [27] and K [8]. It is not possible to discriminate between EOSs with these low-compression isotherms; the noteworthy point is the excellent agreement of the

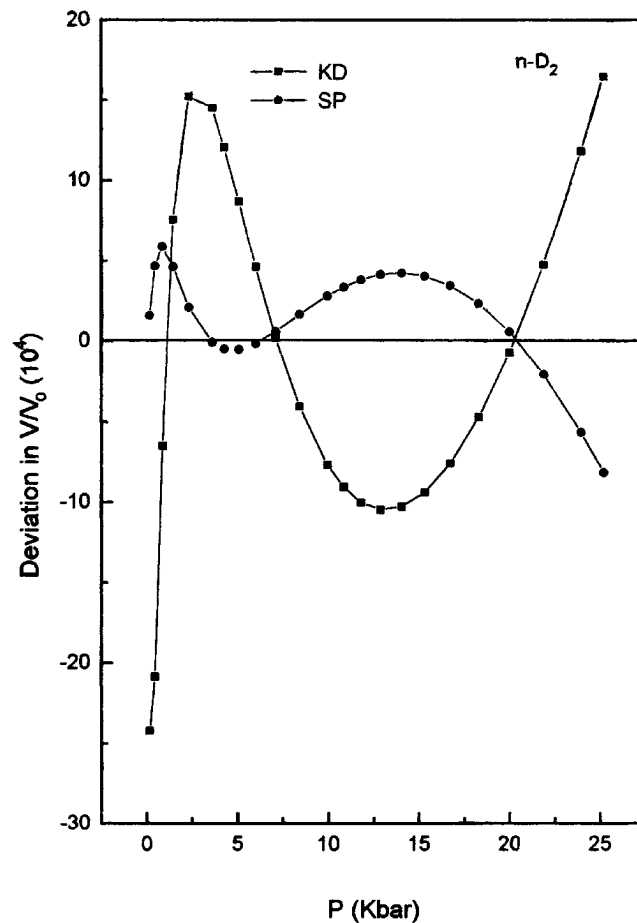


Figure 8. A comparison of deviations in V/V_0 between data and fit with KD and SP equations for the 4.2 K isotherm of n-D₂ [26].

fitted values of B_0 and B'_0 with experimental ones. Excellent fitting accuracy is shown by the very low values of RMSD for both Xe and K. Our fit value of $B'_0 = 9.29$ for Xe might seem to disagree (table 1) with Packard's value of 8.87 [37], but is only about 5% higher than the latter. The agreement is excellent in view of the fact that B'_0 when determined from fitting compression data with EOS has an error of the order of 10%.

3.2. Application at ultrahigh pressures with B_0 and B'_0 constrained

In the true spirit of a universal EOS, it is desirable that B_0 , B'_0 and B''_0 are not adjustable parameters but the real values at zero pressures. However, the problem on the way is the reliability of measured bulk moduli data, especially the B''_0 value. The experimental determination of B''_0 is difficult because it is related to the third pressure derivative of the quantity being measured (volume) and thereby prone to large uncertainties. Further, B''_0 is strongly influenced by the format of the EOS and virtually relegated to a fitting parameter [10, 40, 41]. Therefore, we will constrain B_0 and B'_0 to experimental values, and fit the value of B''_0 only.

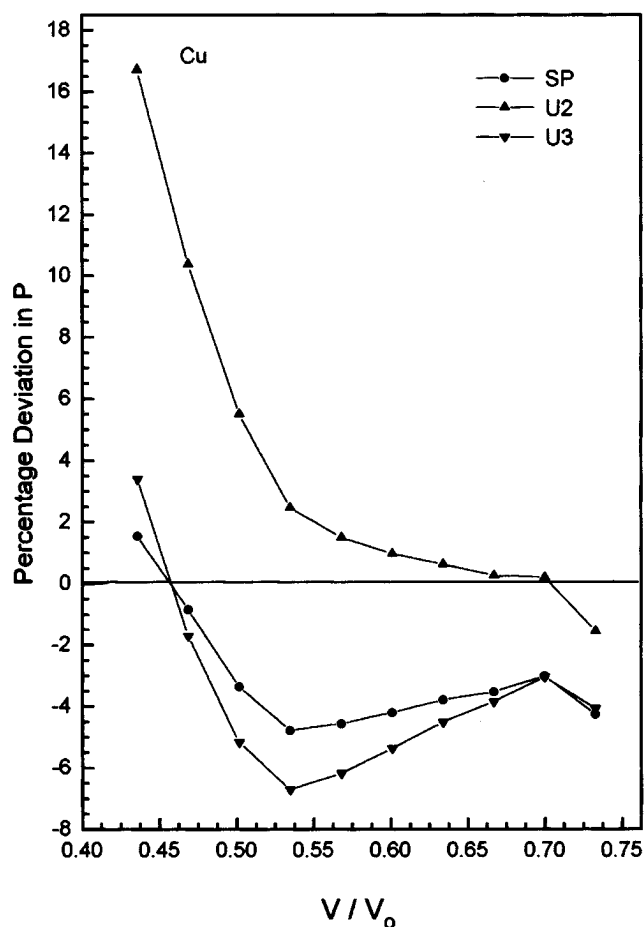


Figure 9. A comparison of percentage deviation in pressure versus relative volume (V/V_0) between U2, U3 and SP equations for the 300 K isotherm of Cu [24].

Divergence in the fitting capability of an EOS becomes conspicuous when pressure ranges high and the compression becomes stronger. Therefore, we have chosen the highly regarded isotherms of Cu and Al by Nellis *et al* (section 3.1.2), where the EOS has been measured to 10 Mbar. The values of B_0 and B'_0 chosen for Cu and Al are from well accepted sources, and are presented in table 4, along with the numerical results for fits of EOS data sets of Cu and Al with different EOS forms. Slightly different values of B_0 and B'_0 confronted in the literature will not alter the conclusions to be reached from the present inter-comparative study. Percentage deviations in pressure versus relative volume (V/V_0) with U2, U3 and SP equations are plotted in figures 9 and 10 for Cu and Al respectively. With regard to agreement between data and fits, the following broad features can be inferred from data, table 4 and figures 9 and 10.

- (i) Only two EOSs, SP and U3, survive the stringent test of successfully describing the EOSN of both Cu and Al.
- (ii) The fact that for Cu, a material undergoing continuous $d \rightarrow s$ electron transfer under compression, the U2 EOS falters above $V/V_0 = 0.502$ and a pressure of 5.42 Mbar, while the U3 EOS agrees with data over the entire compression range, argues strongly in favour of [16] and [17]. However, the mean deviation with the U3 EOS is higher than U2.

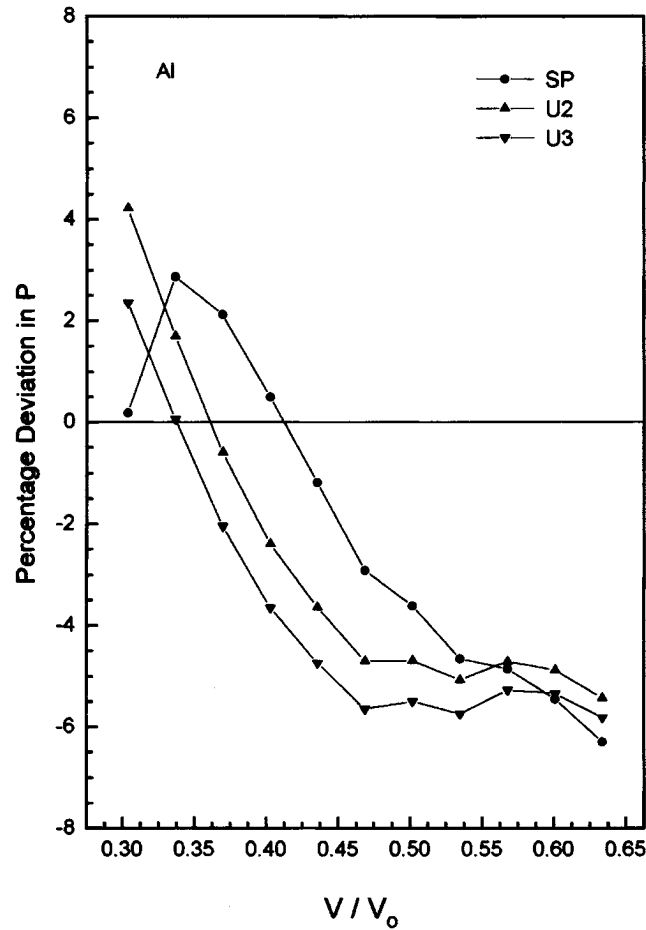


Figure 10. A comparison of percentage deviation in pressure versus relative volume (V/V_0) between U2, U3 and SP equations for the 300 K isotherm of Al [24].

- (iii) For Al, with no significant electronic structure changes under compression [17], the validity of the U2 EOS is upheld at larger compressions. Notably, use of the U3 EOS is counterproductive, with both its mean and maximum deviations higher than the U2 EOS. A similar erratic behaviour can be noticed with the B3 EOS for Cu. The B3 EOS, however, does a poor job for both Cu and Al.
- (iv) For Cu, the U2 EOS shows very good agreement up to $V/V_0 = 0.535$ and a pressure of 4.14 Mbar. Above, agreement with the SP equation is better than U2 up to $V/V_0 = 0.436$ and a pressure of 10.04 Mbar.
- (v) For Al, the SP equation shows better agreement than both U2 and U3 EOSs from $V/V_0 = 0.535$ and a pressure of 1.68 Mbar to $V/V_0 = 0.403$ and a pressure of 4.35 Mbar.
- (vi) The KD equation, in spite of its high fitting capability (table 1), lacks the desired universal characteristics.
- (vii) Overall, the SP model with the lowest mean deviations, and maximum deviations well within the error bar, emerges as the most successful EOS form in describing EOS data of both Cu and Al up to 10 Mbar.

The reported values of B_0 for Pb differ by a wide margin. To illustrate, the B_0 values reported by Simmons and Wang [31] and Vaidya and Kennedy [34] are 488 and 399.8 kbar respectively, differing by about 20%. Thus the high uncertainty of B_0 may cast a serious doubt on a meaningful comparison, and might possibly be the reason for the difficulties faced by Sikka [17] in accounting for the drastic departure of the U2 EOS from the isotherm of Pb.

However, we have fitted SP, KD, U2 and U3 equations to the Nellis EOS for Pb, with B_0 and B'_0 constrained to ultrasonic [31] and static [34] data, to clear up the options about the experimental data on Pb. We observe that none of the equations tested succeeds in reproducing the Nellis EOS for Pb within the claimed 10% uncertainty limit. But using the ultrasonic data, the agreement between data points and fits is decisively better, for all four equations, than what can be achieved with the static data. It is thus inferred that ultrasonic data are a better option for Pb.

4. Conclusion

The proposed model fits a variety of isotherms, at low to ultrahigh pressures, with a significantly high accuracy, and may be of substantial value for smoothing and interpolation of pressure–volume data, and in the extraction of isothermal values of B_0 and B'_0 . Further, the new form might possibly be useful for the analysis of EXAFS data of solids under a wide range of pressures.

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