A New Isothermal Equation of State for Solids

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Z. Naturforsch. **64a,** 54 – 58 (2009); received July 30, 2008

A new isothermal equation of state (EOS) for solids is derived by starting from the theory of lattice potential and using an analytical function for the volume dependence of the short-range force constant. A critical analysis of the isothermal EOSs: Murnaghan EOS, Vinet EOS, and the new EOS derived here, is presented by investigating the pressure-volume data for rare gas solids, metals and minerals. It is found that the results obtained from the new EOS are in good accordance with the corresponding values obtained from the Vinet EOS and with experimental data for all the solids up to very large compressions. On the other hand, the Murnaghan EOS is less successful at high pressure in most cases.

Key words: Equation of State; Rare Gas Solids; Metals; Minerals.
PACS numbers: 64.10; 64.30

1. Introduction

The isothermal equation of state (EOS) provides an extensive body of information on the nonlinear compressibility of solids and is fundamentally important in basic and applied science [1]. The study of the forces between atoms and molecules is essential explaining an EOS as well as the thermodynamic properties of a substance. The exact evaluation of these forces by the atomic theory is one of the most difficult problems of quantum theory and wave mechanics. Hence, due to lack of precise knowledge of the inter-atomic forces, a theoretical EOS cannot be easily obtained [2]. Therefore, different simplified models and approximations have been used to obtain an EOS, and due to this reason semi-empirical EOSs have been developed [3 – 6].

Here, we develop a method, within the framework of the theory of lattice potential, to obtain a new two-parameter phenomenological isothermal equation of state. The method is based on a simple relationship between the short-range force constant A and the lattice volume V.

In order to test the validity of the isothermal EOS presented here, we have selected some solids and investigated their behaviour during compression. The method of formulation and analysis is given in Section 2. Numerical analyses, results and discussion are presented in Section 3.

2. Method of Analysis

Starting from the basic thermodynamic relationships, the pressure P and the isothermal bulk modulus B_T are expressed as [2]

$$P = \frac{\mathrm{d}W}{\mathrm{d}V} \tag{1}$$

and

$$B_T = -V\frac{\mathrm{d}P}{\mathrm{d}V} = V\frac{\mathrm{d}^2W}{\mathrm{d}V^2}, \tag{2}$$

where the volume derivatives are taken at constant temperature. Here W is the crystal lattice potential energy, which can be expressed as a function of the unit-cell volume V. The derivatives of W with respect to V can be expressed in terms of the derivatives of W with respect to the interatomic separation r by using the relationship

$$V = kr^3, \tag{3}$$

where k is the geometrical factor depending on the structure of the solid. With the help of (3) we can rewrite (1) and (2) as

$$\frac{\mathrm{d}W}{\mathrm{d}V} = \frac{\mathrm{d}W}{\mathrm{d}r} \times \frac{\mathrm{d}r}{\mathrm{d}V} = \frac{1}{3kr^2} \times \frac{\mathrm{d}W}{\mathrm{d}r} \tag{4}$$

and

$$V\frac{\mathrm{d}^2W}{\mathrm{d}V^2} = \frac{1}{9kr}\left(\frac{\mathrm{d}^2W}{\mathrm{d}r^2} - \frac{2}{r}\frac{\mathrm{d}W}{\mathrm{d}r}\right). \tag{5}$$

0932–0784 / 09 / 0100–0054 $ 06.00

Substituting (4) and (5) into (1) and (2), we get the following expression:

$$V\frac{\mathrm{d}^2W}{\mathrm{d}V^2}=\frac{1}{9kr}\left(\frac{\mathrm{d}^2W}{\mathrm{d}r^2}+\frac{2}{r}\frac{\mathrm{d}W}{\mathrm{d}r}\right)+\frac{4P}{3}. \tag{6}$$

Using the standard definition of the short-range force constant A in terms of the Laplacian operator as given by Born and Huang [7],

$$A=\frac{1}{3}\left(\frac{\mathrm{d}^2W}{\mathrm{d}r^2}+\frac{2}{r}\frac{\mathrm{d}W}{\mathrm{d}r}\right), \tag{7}$$

we can rewrite (6) as

$$V\frac{\partial^2W}{\partial V^2}=\frac{A}{3kr}+\frac{4P}{3}. \tag{8}$$

It has been found that the short-range force constant can be expressed as a function of the interatomic separation and lattice volume, and the volume derivatives of A have been used in studies on the pressure dependence of the dielectric properties of solids [8]. With the help of (3) and (8), (2) can be rewritten in the following form:

$$B_T=\frac{A}{3k^{2/3}V^{1/3}}+\frac{4P}{3}. \tag{9}$$

Taking the pressure derivative of (9), we get an expression for the pressure derivative of the isothermal bulk modulus at constant temperature:

$$B_t'=\frac{\mathrm{d}B_T}{\mathrm{d}P}=\left(\frac{4P}{3B_T}-1\right)\left(\frac{V\mathrm{d}A}{A\mathrm{d}V}-\frac{5}{3}\right)+\frac{16P}{9B_T}. \tag{10}$$

Here, we consider the square effect of interatomic separation on the short-range force constant under compression and take the specific function for the interatomic separation dependence on the short-range force constant:

$$A=A_0f\left(\frac{V}{V_0}\right)=A_0\frac{1}{r^2}\exp\left[-\beta\left(\frac{r}{r_0}\right)^2\right], \tag{11}$$

where A_0 and β are constants for a given solid independent of P and V, V_0 is the volume and r_0 the interatomic separation at $P=0$. $f(V/V_0)$ is a function of linear compression (r/r_0) or compression (V/V_0). Using the condition of equality: $B_T=B_0$, when $P=0$, $V=V_0$, we obtain the following relationship from (8) and (11):

$$A_0=3B_0V_0\exp\beta. \tag{11a}$$

Here B_0 is the isothermal bulk modulus at $P=0$, and f_0 is the function $f(V/V_0)$ at $P=0$, $V=V_0$, which equals to $r_0^{-2}\exp(-\beta)$. Substituting (3), (11) and (11a) into (9), we get the relationship

$$B_T=B_0\left(\frac{r}{r_0}\right)^{-3}\exp\left[\beta\left(1-\left(\frac{r}{r_0}\right)^2\right)\right]+\frac{4P}{3}. \tag{12}$$

Taking the volume derivative of (11), we derive the volume dependence on the volume derivative of A:

$$\frac{V}{A}\frac{\mathrm{d}A}{\mathrm{d}V}=-\frac{2}{3}\left(1+\beta\left(\frac{r}{r_0}\right)^2\right). \tag{13}$$

Substituting (13) into (10), we get the expression

$$B_T'=\frac{1}{3}\left(1-\frac{4P}{3B_T}\right)\left(7+\beta\left(\frac{r}{r_0}\right)^2\right)+\frac{16P}{9B_T} \tag{14}$$

for the pressure derivative of the isothermal bulk modulus B_T.

Taking use of the condition: $B_T'=B_0'$, when $P=0$, $V=V_0$, $B_T=B_0$, we obtain an important relationship between β and B_0':

$$\beta=\frac{3B_0'-7}{2}. \tag{14a}$$

Using this relationship one can determine the value of β from the value of B_0'. Equations (12) and (14) are isothermal relationships between the bulk modulus and compression, and the pressure derivative of the bulk modulus and compression, respectively, with the information about the isothermal EOS (P-V relationship) given. They can describe the second-order elastic properties of compression of solids. We will obtain the isothermal EOS in the following. Integrating (9) and (12) we get the EOS

$$P=-\left(\frac{V_0}{V}\right)^{\frac{4}{3}}\frac{B_0}{f_0}\int_{V_0}^{V}f\left(\frac{V}{V_0}\right)\mathrm{d}\left(\frac{V}{V_0}\right). \tag{15a}$$

Substituting the value of f_0 and (3) and (11) into the (15a), we rewrite (15a) as follows:

$$P=-3B_0\left(\frac{r}{r_0}\right)^{-4}\cdot\int_1^{r/r_0}\exp\left[\beta\left(1-\left(\frac{r}{r_0}\right)^2\right)\right]\mathrm{d}\left(\frac{r}{r_0}\right). \tag{15b}$$

Table 1. Input data of B_0 and B_0' based on experimental data [1, 9] at $T = 298$ K and $P = 0$.

Material	B_0 (kbar)	B_0'
Cu	1309.2	5.65
Mo	2660.0	3.99
Pd	1803.3	5.42
K	31.77	3.98
Xe	36.5	8.87
NaF	465	5.28
NaCl	238.4	5.35
MgO	162	4.13

Table 2. Cu: Values of pressure P at different compressions calculated according to the corresponding equations of state. The last column denotes experimental data [10].

V/V_0	P (kbar)			
	MEOS	VEOS	New EOS	Exp. [10]
1.0	0.0	0.0	0.0	0
0.993	9.4	9.4	9.4	10
0.985	20.7	20.7	20.6	20
0.979	29.5	29.6	29.5	30
0.9527	73.0	72.8	72.7	73
0.9380	101.0	100.5	100.4	101
0.9257	126.7	125.8	125.7	127
0.9107	161.4	159.7	159.5	160
0.9028	181.2	179.6	179.4	180
0.8905	214.5	210.9	210.6	209

Table 3. Mo: Values of pressure P at different compressions calculated according to the corresponding equations of state. The last column denotes experimental data [10].

V/V_0	P (kbar)			
	$\mathrm{M_1}$EOS	VEOS	New EOS	Exp. [10]
1.0	0.0	0.0	0.0	0
0.9741	73.6	73.5	73.5	74
0.9656	99.9	99.8	99.8	100
0.9576	125.8	125.6	126.3	126
0.9426	177.3	176.8	176.9	177
0.9357	202.4	201.6	201.7	201
0.9178	272.1	270.3	270.5	270
0.8917	386.6	382.0	382.7	382
0.8555	576.0	563.5	565.3	563
0.8211	797.0	769.7	773.5	769
0.8093	884.1	849.3	854.1	847
0.7950	998.4	952.4	958.8	950

Table 4. Pd: Values of pressure P at different compressions calculated according to the corresponding equations of state. The last column denotes experimental data [10].

V/V_0	P (kbar)			
	MEOS	VEOS	New EOS	Exp. [10]
1.0	0.0	0.0	0.0	0
0.9679	64.4	64.3	64.3	65
0.9330	151.8	150.7	150.9	155
0.8941	277.6	272.2	273.3	275
0.8130	689.1	644.4	652.8	659

Here the integral cannot be evaluated exactly. However, we can use an approximate method for evaluating this integral. Let $y = 1 - r/r_0$ and using the truncated function $\mathrm{e}^t = 1 + t + t^2/2$ (if $t \ll 1$), the integral is reduced to

$$P = 3B_0 \left(\frac{r}{r_0}\right)^{-4} \int_0^{1-r/r_0} \left[1 - \beta y^2 + \beta^2 y^4\right] \cdot \exp(2\beta y)\mathrm{d}y. \tag{15c}$$

Let $x = (V/V_0)^{1/3}$, (15b) and (15c) yield the relationship

$$\begin{aligned} P = \frac{3}{2}\frac{B_0}{\beta}\frac{1}{x^4}\Bigg[&\left(1 - \frac{1}{2\beta} + \frac{3}{4\beta^2}\right) + \left(\frac{3}{2} - \beta\right)(1-x)^2 - \beta(1-x)^3 \\ &+ \beta^2(1-x)^4\Bigg] \exp[2\beta(1-x)] \\ &- \frac{3}{2}\frac{B_0}{\beta}\left(1 - \frac{1}{2\beta} + \frac{3}{4\beta^2}\right). \end{aligned} \tag{15}$$

In obtaining (15) we have neglected the high-order terms which are relatively small. It is possible to obtain a better approximation than that given by (15), but it is convenient to use a simpler equation.

For the sake of convenient comparison and numerical analysis, we write out the Vinet EOS [4] and Murnaghan EOS [3]:

$$P_{\mathrm{V}} = 3B_0 \frac{1}{x^2}(1-x)\exp\left[\frac{3}{2}(B_0' - 1)(1-x)\right], \tag{16}$$

$$P_{\mathrm{M}} = \frac{B_0}{B_0'}[\exp(-B_0' \ln x^3) - 1]. \tag{17}$$

The expressions given above for P are based on the different EOSs and have been used in the present study to obtain the results discussed in the following section.

3. Results and Discussion

According to the spirit of a universal EOS, it is desirable that B_0 and B_0' are not adjusted by a fitting method, but their real values at zero pressure are used [1]. So, we have used the zero-pressure experimental values for the input parameters [1, 9] without any adjustment or fitting (Table 1). We have calculated the pressure P isothermal for Cu, Mo, Pd, K, Xe, NaF,

Table 5. K: Values of pressure P at different compressions calculated according to the corresponding equations of state. The last column denotes experimental data [10].

V/V_0	P (kbar)			
	MEOS	VEOS	New EOS	Exp. [10]
1.0	0.0	0.0	0.0	0
0.8809	5.2	5.2	5.2	5
0.8073	10.7	10.3	10.4	10
0.7550	16.4	15.3	15.5	15
0.7132	22.7	20.5	20.8	20

Table 6. Xe: Values of pressure P at different compressions calculated according to the corresponding equations of state. The last column denotes experimental data [10].

V/V_0	P (kbar)			
	MEOS	VEOS	New EOS	Exp. [10]
1.0	0.0	0.0	0.0	0
0.956	2.0	2.0	2.0	2
0.926	4.0	3.9	4.0	4
0.903	6.1	5.8	5.9	6
0.884	8.2	7.7	7.9	8
0.868	10.3	9.6	9.8	10
0.854	12.6	11.4	11.8	12
0.842	14.8	13.2	13.7	14
0.831	17.1	15.0	15.7	16

Table 7. NaF: Values of pressure P at different compressions calculated according to the corresponding equations of state. The last column denotes experimental data [11].

V/V_0	P (kbar)			
	MEOS	VEOS	New EOS	Exp. [11]
1.0	0.0	0.0	0.0	0
0.9803	9.8	9.8	9.8	10
0.9623	19.8	19.8	19.8	20
0.9462	29.9	29.8	29.8	30
0.9319	39.7	39.5	39.5	40
0.868	97.9	95.6	95.5	94
0.832	144.5	138.6	138.7	140
0.804	190.6	179.5	179.9	180
0.782	234.5	217.1	218.0	210
0.778	243.4	224.5	225.5	224

Table 8. NaCl: Values of pressure P at different compressions calculated according to the corresponding equations of state. The last column denotes experimental data [11].

V/V_0	P (kbar)			
	MEOS	VEOS	New EOS	Exp. [11]
1.0	0.0	0.0	0.0	0
0.9627	10.0	10.0	10.0	10
0.9325	20.2	20.1	20.1	20
0.9067	30.7	30.2	30.3	30
0.8828	42.3	41.3	41.4	40
0.760	148.9	132.8	135.7	135
0.702	251.3	208.2	205.5	200
0.697	262.8	216.1	223.9	220
0.675	320.3	254.3	255.2	250
0.658	373.7	287.9	296.9	290

Table 9. MgO: Values of pressure P at different compressions calculated according to the corresponding equations of state. The last column denotes experimental data [12].

V/V_0	P (GPa)			
	MEOS	VEOS	New EOS	Exp. [12]
1.0	0.00	0.00	0.00	0
0.9788	3.63	3.63	3.63	3.52
0.9606	7.08	7.07	7.07	7.54
0.9400	11.42	11.38	11.38	12.00
0.9196	16.22	16.12	16.13	16.25
0.8955	22.65	22.39	21.32	21.88
0.8798	27.34	26.91	26.96	27.45
0.8603	33.80	33.07	33.15	34.25
0.8398	41.44	40.25	40.38	41.55
0.7999	59.41	56.65	56.91	58.55
0.7600	82.61	76.90	77.40	81.56
0.7204	112.76	101.83	105.66	109.00

NaCl and MgO using the Murnaghan EOS (MEOS) [3], the Vinet EOS (VEOS) [4] and the new EOS under very large compressions.

A crucial test for making a judgment regarding the adequacy of different EOS is possible when comparing the results obtained in the present study with the experimental data [10 – 12]. Such a comparison is presented in Tables 2 – 9. The following conclusions can be drawn from a comparison between the results obtained in the present study and the experimental data.

(1) The New EOS yields very similar results to those obtained from the Vinet EOS [4] up to large compressions for the solids considered here. These results are in good agreement with experimental data [10 – 12]. It is pertinent to mention that the Vinet EOS [4] derived from the binding energy of metals is widely applicable in different types of materials. Hama and Suito [13] found that the Vinet EOS [4] is in good agreement with the theoretical results for all the solids obtained from the APW method [14] and the QSM [15] for the P-V relationship up to very large compressions.

(2) The Murnaghan EOS [3] is not as desirable as the Vinet EOS [4] and the new EOS. The results based on the Murnaghan EOS [3] deviate much from the experimental data at high compressions in most cases. Here it should be mentioned that Dass and Kumari [16] pointed out that the Murnaghan EOS is the best among all the EOSs from the utility and practical point of view. Moreover, they considered pressures only up to 32 kbar. Actually, the decision whether a given EOS is best or not will depend upon whether the results of P versus V/V_0 predicted by the EOS are in good agreement with the experimental values at high pressures.

(3) Semi-empirical EOSs are based on some initial assumptions. For example, the Murnaghan EOS [3] considers the isothermal bulk modulus as a linear function of pressure. Another example is the Vinet EOS [4] which is based on the universal relation between binding energy of the solids and intermolecular distance. On the other hand, the new EOS is based on the empirical relationship between the short range interatomic force constant and the volume [cf. (11)]. Investigation of the new EOS provides further confirmation that the empirical relationship is a good assumption for solids.

In summary, we presented new and applicable phenomenological EOSs from another angle. Considering the most effective one of repulsive force in the compression, we introduce the square effective of the interatomic separation in the analytical function of the short-range force constant rather than the structure of solids. So, this new EOS is also applicable for other solids at sufficiently high pressures, provided the experimental input data is available.

Acknowledgements

This work has been financially supported by Key Laboratory of Opto-electronic Information Acquisition and Manipulation of Ministry of Education of China (No. 9603) and by the Natural Science Foundation of the Education Department of Anhui Province, China (No. KJ2008B014).

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