

Two-parameter equations of state for the NaCl crystal

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Abstract

An isothermal equation of state (EOS) for ionic crystal solids is derived by starting from the theory of interionic potential and the simple Born - Mayer potential model. A critical analysis of the two-parameter equations of state: Birch Murnaghan EOS, Kumar EOS, Vinet EOS, Shanker EOS, and the one derived here, EOS, is presented by investigating the pressure volume and isothermal bulk modulus data for the NaCl crystal. The results show that the EOS is in good agreement with the other EOSs and with experimental data up to very high pressures.

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Accessed Date:
26 March 2018

INTRODUCTION

The isothermal equation of state (EOS) gives us valuable information about the change in volume under the effect of pressure at a fixed temperature. EOS studies are of wide importance in physics as well as in chemistry and geosciences. The EOS is fundamentally important for the study and prediction of high-pressure properties of solids, and can provide extensive information on nonlinear compressibility of solids; it is therefore widely used in basic and applied sciences. Though present-day calculations from first principles may predict the EOSs of solids accurately, they are time-consuming because they have to be done individually for a number of volumes. Therefore many workers have been compelled to resort to simplifying models and approximations, and have endeavored to search for simple semi-empirical and phenomenological forms of EOSs of solids, which have a small number of parameters and predict correctly high-pressure behaviors, irrespective of the material. Among

these EOSs, the two-parameter EOSs are very important and successful up to high pressures. The Birch - Murnaghan EOS, based on Eulerian strain, is known to be extremely successful in matching finite-compression data with low-pressure elasticity measurements obtained by ultrasonic methods (Birch 1978, 1986; Heinz and Jeanloz 1984; Jeanloz 1988; Knittle *et al* 1985). The semi-empirical Kumar EOS used to study different types of solids is a good EOS up to the transition pressures of solids (Kumar 1995a, 1995b). The Shanker EOS (Shanker *et al* 1997) is derived from the lattice potential theory by using the concept of the short-range force constant as introduced by Born and Huang (1954). Though this EOS has been derived for ionic solids, its validity and usefulness have been demonstrated for other types of solids too (Shanker *et al* 1999). The Vinet EOS is derived from the reduced bonding energy of metals (Rose *et al* 1983) and is widely applicable for different types of materials (Schlosser and Ferrante 1988; Vinet *et al* 1986, 1987a, 1987b, 1989). In this paper, we derive a phenomenological equation of state (EOS) within the framework of the theory of lattice potential for ionic crystals, starting from the Born - Mayer exponential potential model (Tosi 1964) and using the method developed by Shanker *et al* (1997, 1999). At the same time, we use it to study the compression behavior and properties of the NaCl ionic crystal. The method of analysis is given in section 2. Numerical analysis for the NaCl crystal along with the results and discussion are presented in next section.

MATERIAL AND METHODS

We start from the basic thermodynamic relationship

$$P = -\frac{dW}{dV} \quad (1)$$

and

$$B_T = -V \frac{dP}{dV} = V \frac{d^2W}{dV^2}, \quad (2)$$

$$B_T' = \frac{dB_T}{dP}, \quad (3)$$

Where, B_T and B_{OT} denote the isothermal bulk modulus and its first-order pressure derivative, respectively. The volume and pressure derivatives are taken at constant temperature. Here W is crystal lattice potential energy, which can be expressed as a function of unit-cell volume V . In this paper, we use the Born-Mayer potential model (Tosi 1964) as repulsive potential, f , for ionic crystal solids expressed as follows:

$$W = -\alpha_M \frac{e^2}{V^{1/3}} + \phi(r) = -\alpha_M \frac{e^2}{V^{1/3}} + \beta \exp\left(-\eta_0 \frac{r}{r_0}\right), \quad (4)$$

where the first term on the right represents the long-range electrostatic Madelung potential energy with the Madelung constant α_M , and the second term denotes the short range overlap repulsive potential energy, f , expressed in the Born-Mayer exponential form (Tosi 1964) with parameters b and Z_0 as the repulsive strength and hardness, respectively; e is the charge of the electron. Here these parameters are independent of T and P . Finally, r is the nearest-neighbor interionic separation, and the relationship between r and V can be written as follows: $V = kr^3$, where k is a geometrical factor dependent of the type of crystal structure; $k = 2$ for NaCl-type structure. Using the standard definition of the short-range force constant, A , as given by Born and Huang (1954):

$$A = \frac{1}{3} \left[\frac{d^2\phi}{dr^2} + \frac{2}{r} \frac{d\phi}{dr} \right], \quad (5)$$

and inserting the Born-Mayer exponential potential model into equation (5), we derive the short-range force constant, A , of the nearest-neighbour interionic separation r :

$$A = \frac{\beta\eta_0}{3r_0^2} \left(\eta_0 - 2 \frac{r_0}{r} \right) \exp\left(-\eta_0 \frac{r}{r_0}\right), \quad (6)$$

$$A = A_0 \left[\eta_0 - 2 \left(\frac{V}{V_0} \right)^{-1/3} \right] \exp\left[-\eta_0 \left(\frac{V}{V_0} \right)^{1/3} \right], \quad (7)$$

where $A_0 \equiv \beta\eta_0/3r_0^2$ is a constant to be determined. Let the function

$$f\left(\frac{V}{V_0}\right) \equiv \left[\eta_0 - 2 \left(\frac{V}{V_0} \right)^{-1/3} \right] \exp\left[-\eta_0 \left(\frac{V}{V_0} \right)^{1/3} \right]. \quad (8)$$

We can then rewrite equation (7):

$$A = A_0 f\left(\frac{V}{V_0}\right). \quad (9)$$

According to the definition of the short-range force constant, A , and using basic thermodynamic relationships, we have obtained the following relationships as given by X-Q Deng, Z-T YanShanker *et al* (1997):

$$B_T = \frac{A}{3k^{2/3}V^{1/3}} + \frac{4}{3}P, \quad (10)$$

$$B'_T = \frac{dB_T}{dP} = -\frac{V}{B_T} \frac{dB_T}{dV} = \left(\frac{4}{3} \frac{P}{B_T} - 1\right) \left(\frac{V}{A} \frac{dA}{dV} - \frac{5}{3}\right) + \frac{16}{9} \frac{P}{B_T}, \quad (11)$$

$$P \left(\frac{V}{V_0}\right)^{4/3} = -B_0 \left\{ f_0 \left[\int f \left(\frac{V}{V_0}\right) d\left(\frac{V}{V_0}\right) + C \right] \right\}^1, \quad (12)$$

where B_0 is the value of B_T at $P = 0$ and $V = V_0$. The value of C is determined by applying the condition that $V = V_0$ at $P = 0$. Equations (10)–(12) can be used to predict the isothermal bulk modulus and its pressure derivative, and pressure as a function of the relative change in volume (V/V_0), provided we know the short-range force constant, A , and its volume derivative dA/dV at different pressures. With the help of the Born–Mayer potential model and taking the first volume derivative of equation (9), we get the following expressions:

$$\frac{V}{A} \frac{dA}{dV} = -\frac{1}{3} \left[\eta_0 \left(\frac{V}{V_0}\right)^{1/3} + 1 \right]. \quad (13)$$

The constant η_0 is determined by substituting equation (13) in equation (11) and using the condition that $dB_T/dP = B'_0$ at $P = 0$ and $V = V_0$. Here we find the value of η_0 as being equal to $3(B'_0 - 2)$. The constant A_0 is determined by inserting equation (9) into equation (10) and applying the condition that $B_T = B_0$ at $P = 0$ and $V = V_0$. A_0 is equal to $3k^{2/3}V_0B_0/f_0$, and f_0 is equal to $(3B'_0 - 8) \exp[3(B'_0 - 2)V/V_0]$. Substituting the values of η_0 , A_0 , and equation (13) into equations (10)–(12), and putting $x \equiv (V/V_0)^{1/3}$, we obtain:

$$B_T = \frac{B_0}{3B'_0 - 8} \left(3 \frac{B'_0 - 2}{x} - \frac{2}{x^2} \right) \exp[3(B'_0 - 2)(1 - x)] + \frac{4}{3}P, \quad (14)$$

$$B'_T = (B'_0 - 2)x \left(1 - \frac{4P}{3B_T} \right) - \frac{8P}{9B_T} + 2. \quad (15)$$

Equations (14) and (15) can be used to predict the values of B_T and B'_T as a function of compression only, with the use of input data on B_0 and B'_0 for ionic solids. Then substituting equation (8) in equation (12), and using the condition that $V = V_0$ at $P = 0$, we finally derive the following expression:

$$P = \frac{3B_0}{3B'_0 - 8} \frac{1}{x^4} \{ x^2 \exp[3(B'_0 - 2)(1 - x)] - 1 \}. \quad (16)$$

Equation (16) is the isothermal equation of state (D–Y EOS) derived here, based on the Born–Mayer potential model, representing the relationship between pressure and relative change in volume in terms of B_0 and B'_0 only. It can be used to predict the compression behaviour of ionic crystal solids. Using it to investigate the properties of ionic solids we can test the validity of the Born–Mayer potential model for ionic crystals from a different angle.

For the sake of convenient comparison and numerical analysis, we list below some two-parameter EOSs:

$$P_{\text{BM}} = \frac{3}{2}B_0 \left(\frac{1}{x^7} - \frac{1}{x^5} \right) \left[1 + \frac{3}{4} (B'_0 - 4) \left(\frac{1}{x^2} - 1 \right) \right], \quad (17)$$

$$P_{\text{K}} = \frac{B_0}{B'_0 + 1} \exp \left[(B'_0 + 1) \left(1 - \frac{V}{V_0} \right) \right], \quad (18)$$

Table 1. Calculated values of pressure, bulk modulus and its first-order pressure derivative corresponding to different values of V/V_0 . Relative pressure percentage errors and relative bulk modulus percentage errors, calculated from the respective equations, are listed in parentheses ($\Delta\%$). The experimental data (exp) are from Birch (1986).

| $\frac{V}{V_0}$ | P/GPa | | | | | |
|-----------------|------------------|-----------------|-----------------|-----------------|-----------------|------|
| | eqn (17) | eqn (18) | eqn (19) | eqn (20) | eqn (16) | exp |
| 0.9627 | 1.00 (0.0) | 1.00 (0.0) | 1.00 (0.0) | 1.00 (0.0) | 1.00 (0.0) | 1 |
| 0.9324 | 2.01 (0.5) | 2.01 (0.5) | 2.01 (0.5) | 2.01 (0.5) | 1.98 (1.0) | 2 |
| 0.9067 | 3.03 (1.0) | 3.03 (1.0) | 3.02 (0.7) | 3.03 (1.0) | 2.97 (1.0) | 3 |
| 0.8845 | 4.06 (1.5) | 4.06 (1.5) | 4.04 (1.0) | 4.05 (1.0) | 3.96 (1.0) | 4 |
| 0.8649 | 5.10 (2.0) | 5.10 (2.0) | 5.06 (1.2) | 5.08 (1.6) | 4.95 (1.0) | 5 |
| 0.7910 | 10.5 (5.0) | 10.4 (4.0) | 10.3 (3.0) | 10.3 (3.0) | 10.0 (0.0) | 10 |
| 0.7397 | 16.1 (7.3) | 15.9 (6.0) | 15.6 (4.0) | 15.7 (4.7) | 15.1 (0.7) | 15 |
| 0.7004 | 22.1 (10.5) | 21.4 (7.0) | 21.1 (5.5) | 21.2 (6.0) | 20.4 (2.0) | 20 |
| 0.6685 | 28.3 (13.2) | 27.1 (8.4) | 26.7 (6.8) | 26.9 (7.6) | 25.9 (3.6) | 25 |
| 0.6416 | 34.8 (16.0) | 32.8 (9.3) | 32.4 (8.0) | 32.7 (9.0) | 31.5 (5.0) | 30 |
| $\frac{V}{V_0}$ | B_T/GPa | | | | | |
| | eqn (21) | eqn (22) | eqn (23) | eqn (24) | eqn (14) | exp |
| 0.9627 | 29.1 (0.7) | 29.1 (0.7) | 29.0 (0.4) | 29.1 (0.7) | 28.6 (1.0) | 28.9 |
| 0.9324 | 34.1 (1.5) | 34.2 (1.8) | 34.0 (1.2) | 34.1 (1.5) | 33.2 (1.2) | 33.6 |
| 0.9067 | 39.1 (2.6) | 39.1 (2.6) | 38.8 (1.8) | 38.9 (2.1) | 37.8 (0.8) | 38.1 |
| 0.8845 | 44.0 (3.5) | 43.9 (3.3) | 43.4 (2.1) | 43.7 (2.8) | 42.1 (0.9) | 42.5 |
| 0.8649 | 48.8 (4.5) | 48.6 (4.1) | 47.9 (2.6) | 48.3 (3.4) | 46.3 (0.9) | 46.7 |
| 0.7910 | 72.8 (10.1) | 71.1 (7.6) | 69.6 (5.3) | 70.8 (7.1) | 67.1 (1.5) | 66.1 |
| 0.7397 | 96.8 (15.8) | 92.1 (10.2) | 90.3 (8.0) | 92.6 (10.8) | 87.3 (4.4) | 83.6 |
| 0.7004 | 121.2 (21.4) | 111.9 (12.1) | 110.5 (10.7) | 114.0 (14.2) | 107.3 (7.5) | 99.8 |
| 0.6685 | 146.2 (27.1) | 138.8 (20.7) | 130.4 (13.4) | 135.0 (17.4) | 127.4 (10.8) | 115 |
| 0.6416 | 171.9 (33.3) | 148.9 (15.4) | 150.3 (16.5) | 156.1 (21.0) | 147.7 (14.5) | 129 |

Table 1 (contd.)

| $\frac{V}{V_0}$ | B'_T | | | | |
|-----------------|----------|----------|----------|----------|----------|
| | eqn (25) | eqn (26) | eqn (27) | eqn (28) | eqn (15) |
| 0.9627 | 5.11 | 5.11 | 5.03 | 5.07 | 5.12 |
| 0.9324 | 4.93 | 4.92 | 4.80 | 4.87 | 4.96 |
| 0.9067 | 4.80 | 4.76 | 4.63 | 4.71 | 4.83 |
| 0.8845 | 4.70 | 4.61 | 4.49 | 4.58 | 4.73 |
| 0.8649 | 4.61 | 4.49 | 4.00 | 4.48 | 4.64 |
| 0.7910 | 4.34 | 4.02 | 3.86 | 4.12 | 4.35 |
| 0.7397 | 4.17 | 3.70 | 3.77 | 3.90 | 4.18 |
| 0.7004 | 4.07 | 3.45 | 3.62 | 3.75 | 4.05 |
| 0.6685 | 3.99 | 3.25 | 3.50 | 3.64 | 3.96 |
| 0.6416 | 3.92 | 3.01 | 3.40 | 3.54 | 3.88 |

and

$$P_V = \frac{3B_0}{x^2} (1-x) \exp \left[\frac{3}{2} (B_0 - 1)(1-x) \right], \quad (19)$$

$$P_S = B_0 \left(\frac{V}{V_0} \right)^{4/3} \left\{ \left(1 - \frac{1}{t} + \frac{2}{t^2} \right) [\exp(ty) - 1] + y \left(1 + y - \frac{2}{t} \right) \exp(ty) \right\}, \quad (20)$$

where $x = (V/V_0)^{1/3}$, $y = 1 - V/V_0$, and t is a constant for a given solid, equal to $B'_0 - \frac{8}{3}$. From the definitions of the isothermal bulk modulus and its first-order pressure derivative: $B_T = -V(dP/dV)$ and $B'_T = dB_T/dP$, we obtained the corresponding expressions for B_T and B'_T from the above equations of state (17)–(20):

$$B_T = \left(\frac{1}{2} B_0 \right) (7x^{-7} - 5x^{-5}) + \left(\frac{3}{8} B_0 \right) (B'_0 - 4)(9x^{-9} - 14x^{-7} + 5x^{-5}), \quad (21)$$

$$B_T = B_0 \frac{V}{V_0} \exp(B'_0 + 1) \left(1 - \frac{V}{V_0} \right), \quad (22)$$

$$B_T = \frac{B_0}{x^2} [1 + (\eta x + 1)(1-x)] [\exp[\eta(1-x)]], \quad (23)$$

$$B_T = \frac{B_0}{x} (1 + y + y^2) \exp(ty) + \frac{4}{3} P, \quad (24)$$

and

$$B'_T = \frac{B_0}{8B_T} [(B'_0 - 4)(81x^{-9} - 98x^{-7} + 25x^{-5}) + \frac{4}{3}(49x^{-7} - 25x^{-5})], \quad (25)$$

$$B'_T = (B'_0 + 1) \frac{V}{V_0} - 1, \quad (26)$$

$$B'_T = \frac{1}{3} \left[2 + \eta x + \frac{x(1-\eta) + 2\eta x^2}{1 + (\eta x + 1)(1-x)} \right], \quad (27)$$

$$B'_T = \frac{4}{3} + \left(1 - \frac{4P}{3B_T} \right) \left[\frac{1}{3} + \frac{V}{V_0} \frac{t + (1+2y)}{1 + y + y^2} \right], \quad (28)$$

where $\eta = \frac{3}{2}(B'_0 - 1)$, and other parameters are as defined earlier.

RESULTS AND DISCUSSION

In order to test the validity of the EOS and equations (14) and (15), we choose the NaCl ionic crystal and studied its compression behavior and the relationship between bulk modulus and pressure. We inserted the ultrasonic experimental values of the input parameters $B_0 = 23.84 \text{ GPa}$, $B_0' = 5.35$, reported by Spetzler and Sammis (1972) for the NaCl crystal, into the above EOSs. The P-V and B-T -V data for this solid are available up to a pressure of 30 GPa (Birch 1986). The values of pressure, isothermal bulk modulus, and its first-order derivative with respect to pressure calculated by these equations are listed in table 1, along with the corresponding experimental data. From table 1, we see that all the two-parameter equations under study are in good agreement with the experimental data over the entire range of pressures. We also find that P vs V/V_0 and B_T vs V/V_0 calculated by the D-YEOS and equation (14), respectively, are in a remarkably close agreement with the experimental data in the high-pressure range. We also calculated relative pressure errors and relative bulk-modulus errors yielded by different EOSs, and these are also listed in table 1. We find that the errors of values calculated by equations (16) and (14), respectively, are smaller than those yielded by other equations at pressures above 15 GPa. Then equations of state derived in this paper are very useful and valid for the NaCl crystal up to very high pressures. Moreover, because we have derived the new equations of state [equations (14) - (16)] within the framework of theory of the lattice potential for ionic crystals, we can use them to investigate the compression behavior and its other bulk modulus for the ionic crystal solids, provided the parameters B_0 and B_0' are known. We have not investigated here variations of the inter ionic potential

with pressure or Compression; we have only used the form of the inter ionic potential to derive the new EOS. Investigation of the EOS and the corresponding new relationships provides further confirmation that the Born-Mayer exponential potential model is a good repulsive potential model for the NaCl crystal. At the same time, we can extend the application of the EOS to other ionic crystal solids.

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Source of Support: None Declared
Conflict of Interest: None Declared