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Analysis of high pressure equation of state for NaCl

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Abstract : A simple theoretical model is developed to study the high pressure behavior of solids and then applied to evaluate the pressure for compression below 0.65 in case of NaCl. Some other well known equation of states reported in the literature has also been included in the study. The comparison of calculated values from all these equation of state with experimental values reveals that the present model yields the best agreement. The present study also shows that it is a good approximation to consider the pressure to be quadratic in the density.

Keywords : Equation of state; Volume compression; High pressure.

INTRODUCTION

The behavior of solids under the effect of high pressure has truly developed into an interdisciplinary area which has important implications for an application in the area of physics, biology, engineering and technology apart from the discovery of various novel and unexpected phenomenon, high pressure research has provided new insight into the behavior of matter[1]. Strength and elastic properties of a solid depend on the strength of its interatomic forces. Therefore, the application of pressure which changes the interatomic distance of the substances changes its physical properties. The EOS gives us valuable information about the relationship between the change in thermodynamic variable viz. pressure, volume and temperature. Every thermodynamic system has its own EOS, independent of others. An EOS expresses the peculiar behavior of one individual system which distinguishes it from the others. In order to determine the EOS of a system, the thermodynamic variables of the system, are accurately measured and a relation is expressed between them. The EOS of a solid can be used as pressure gauge in high pressure measurements. Attempts have been made to derive a compressibility equation from molecular theory, but none of them has resulted in convenient equation expressing the results of experiments with adequate accuracy. To meet this need some empirical equations have been proposed, the sole justification of which is that it works. In spite of impressive advances on the theoretical front over the past decades, the need for the search of an EOS continues to exist. Although, Modern electronic band structure calculations allow the prediction of EOS for solids but these are time taking and expansive. In literature, there are number of equation of states, and these arises from an unchecked and improvable assumption concerning an assumed interatomic potential, an assumed strain function, or an assumed boundary condition that is not testable[2]. NaCl is an important material and a typical ionic solid used as a pressure gauge in laboratory measurement of compression data. This is one of the most widely used internal pressure standard in high pressure diffraction experiments due to the availability of the large body of experimental data. NaCl has a stable structure (B1) up to a pressure of about 30 GPa and its melting temperature is nearly 1074K. Thus we have a wide range of pressures and temperatures for studying the equation of state and thermo elastic properties of NaCl. Numerous attempts[3-8] have been made to understand the high pressure behavior of NaCl but an adequate analysis is still lacking.

Since NaCl Crystal is used as a pressure Gauge device in high pressure physics experiments[9,10] it becomes more useful to study volume compression of NaCl crystal. On the basis of a careful analysis of the experimental measurements reported by Boechler and kennedy[11] and by Fritz[12], Birch[13] have obtained the values of volume compression (V/V_0) where V_0 is the values of volume *V* at zero pressure, for NaCl crystal. In the present study to check the validity and superiority of out recently formulated EOS[14] we have compared our results with eight equation of state, viz (i) Born Mie equation[15] (ii) Born-Mayer equation[16] (iii) Murnaghan's equation[17] (iv) Tait equation[18] (vi)Brennan-Stacey equation[19] (v)Birch equation[20], (vii)Vinet et al. equation[20] and (viii) Shanker et al. equation[21]

METHOD OF ANALYSIS

On the basis of the finding that the repulsive branch of binding energy curves can be represented by a simple function of density Parsafar and Mason[22] have considered an EOS as:

$$\mathbf{P}\left(\frac{\mathbf{V}}{\mathbf{V}_0}\right)^2 = \mathbf{A}_0 + \mathbf{A}_1\left(\frac{\mathbf{V}}{\mathbf{V}_0}\right)^{-1} + \mathbf{A}_2\left(\frac{\mathbf{V}}{\mathbf{V}_0}\right)^{-2} \qquad (1)$$

Where, $V/V_0 = \rho_0/\rho$, and V_0, ρ_0 are the zero pressure values of volume V and density ρ, respectively and A_0, A_1 and A_2 are constants at a particular temperature. On the basis of the first-principles calculations, using the augmented-plane-wave (APW) method and quantum statistical model Hama and Suito[23] revealed that the Parsafar–Mason EOS becomes less successful at high compressions (V/V_0 <0.65). Recently, to study the high pressure elastic properties of nano materials Kholiya[24] has expended pressure in powers of density up to the quadratic term and achieved the EOS as:

$$\mathbf{P}(\mathbf{V},\mathbf{T}_0) = \frac{\mathbf{B}_0}{2}\left[(\mathbf{B}_0' - 3) - 2(\mathbf{B}_0' - 2)\left(\frac{\mathbf{V}}{\mathbf{V}_0}\right)^{-1} + (\mathbf{B}_0' - 1)\left(\frac{\mathbf{V}}{\mathbf{V}_0}\right)^{-2}\right] \qquad (2)$$

Equation hear B_0 and B_0' are the bulk modulus and its first order pressure derivative at $P = 0$ and $T = T_0$ respectively.

An equation of state cab be derived from the volume derivative of lattice potential energy[15,16] using the relationship $P = -\left(\frac{dW}{dV}\right)_T$, Where W for an ionic crystal can be written as the sum of electrostatic energy and short range overlap energy $\phi(V)$, $W = -\alpha_M \frac{Z^2e^2}{V^{\frac{1}{3}}} + \varphi(V)$

When we use an inverse power form of $\phi(V)$ such as (aV^{-n}) we get the Born –Mie equation of state[15] after eliminating the parameter a and n in terms of Bo and B_0'

$$\mathbf{p} = \frac{\mathbf{3B_0}}{(\mathbf{3B'_0} - \mathbf{8})}\left[\left(\frac{\mathbf{V}}{\mathbf{V_0}}\right)^{4/3} - \mathbf{B'_0} - \left(\frac{\mathbf{V}}{\mathbf{V_0}}\right)^{-4/3}\right] \qquad (3)$$

When we use an exponential function for $\phi(V)$, we get the Born Mayer equation of state[16]

$$\mathbf{p} = \frac{\mathbf{3B_0}}{(\sigma - 2)}\left[\left(\frac{\mathbf{V}}{\mathbf{V_0}}\right)^{-2/3} \mathbf{exp}\left\{\sigma\left[\mathbf{1} - \left(\frac{\mathbf{V}}{\mathbf{V_0}}\right)^{1/3}\right]\right\} - \left(\frac{\mathbf{V}}{\mathbf{V_0}}\right)^{-4/3}\right] \qquad (4)$$

Where $\sigma = \frac{3}{2}(B'_0 - 1) + \left[\frac{9}{4}(B'_0 - 1)^2 - 6B'_0 + 12\right]^{1/2}$

The most widely used and simple equation is that given by Murnaghan equation of state[17] which can be expressed as follows

$$\mathbf{p} = \frac{\mathbf{B_0}}{\mathbf{B_0'}}\left[\left(\frac{\mathbf{V}}{\mathbf{V_0}}\right)^{-B_0'} - \mathbf{1}\right] \qquad (5)$$

Eq (5) is based on an assumption, according to which the isothermal bulk modulus B_T depends linearly on pressure, i.e.

$$B_T = Bo + B'_0$$

A slightly modified form is that known as the Tait equation[18,25] given as

$$p = \frac{B_0}{(B_0' + 1)}\left[\{\exp(B_0' + 1)(1 - V/V_0)\} - 1\right] \quad (6)$$

Eq (6) has been frequently used for studying the P-V relationship, in case of different types of materials[26,27]. Kumar[28] has presented a derivation of the UTE on the basis of the Chopelas-Boechler approximation[28,30]. Eq (6) is based on the assumption, according to which the pressure derivative of BT varies with compression (V/Vo) as follows

$$\frac{dB_T}{dP} = (B_0' + 1)\frac{V}{V_0} - 1$$

The Birch equation[9] is based on the finite strain theory[31], in which the expansion of Helmholtz free energy is considered as a polynomial series in eulerian strain. By considering the third order approximation, Birch obtained the following equation state[20]

$$p = \frac{3}{2}B_0\left[\left(\frac{V}{V_0}\right)^{-7/3} - \left(\frac{V}{V_0}\right)^{-5/3}\right]\left[1 - \frac{3}{4}(4 - B_0')\left\{\left(\frac{V}{V_0}\right)^{-2/3} - 1\right\}\right] \quad (7)$$

Brennan and Stacey[19] obtained an equation of state using free volume formula[32] for the Gruneisen parameter γ and the assumption that is proportional to volume. This equation can be expressed as follows-

$$p = \left[\frac{3B_0\left(\frac{V}{V_0}\right)^{-4/3}}{(3B_0' - 5)}\right]\left[\exp\left\{\left(\frac{3B_0' - 5}{3}\right)\left(1 - \frac{V}{V_0}\right)\right\} - 1\right] \quad (8)$$

Using a relationship between binding energy and interatomic distance. Vinet proposed the following equation of state[20]

$$p = \frac{3(1 - X)B_0}{X^2}\exp\{\eta(1 - X)\} \quad (9)$$

$$X = (V/V_0)^{1/3}$$

Where $\eta = \frac{3}{2}(B_0' - 1)$

Eq (9) has been used by several investigations[33-35].

Shanker have obtained an equation of state using Born lattice theory[36]. Taking the volume derivative of short range force constant, they have drive the following equation[21]

$$p = \frac{B_0\left(\frac{V}{V_0}\right)^{-4/3}}{t}\left[\left(1 - \frac{1}{t} + \frac{2}{t^2}\right)(\exp(ty) - 1) + y\left(1 + y - \frac{2}{t}\right)\exp(ty)\right] \quad (10)$$

Where $t = B_0' - (8/3)$, $y = 1 - (V/V_0)$

RESULTS AND DISCUSSION

To evaluate the pressure at different volume compression (V/Vo), we have used Eq. (2) to (10). All Equation of state needs only two parameters bulk modulus (Bo) and its first order pressure derivative at zero pressure.

We have used experimental values Bo =23.84GPa and B_0'=5.35 for NaCl measured ultrasonically by Spetzler et al.[37]. For making a meaningful test of the results obtained from various equations, we have used the same value of input parameters without making any adjustments. A comparison of the results obtained from all the equations of state along with the experimental results are presented in TABLE 1. In the low pressure range (up to 5 GPa) all the equation of state yield almost same results. As compression or pressure increases the EOS's starts deviating from each other. The largest deviations from the experimental results are shown by Murnaghan Equation of state (eq.5) this demonstrates that the assumption which is made to obtain MEOS is not adequate. The Second largest deviation is found in case of the Born-Mie equation (eq.4). The Birch equation (7) and the Born Mayer equation (4) yield results which are close to each other. The deviations at the maximum compression are about 15 percent for both the equations (7 and 4). At the highest compression, it is found that the Taits equation (7), the Brennm- Stacy equation (8), the Vinet equation (9), the Shanker equation (10) and present formulation (eq (2)) yield the results which are in agreement with the experimental data within 10 percent. The equation obtained from the present approach eq (2) gives the best agreement and deviates only by 1.7 percent with experimental results at the highest compression. These results show that a simple assumption can provide an EOS which gives the result better than most of the EOSs based on potential model approach. From the overall discussion it may be concluded that the present formulation developed by expending pressure in powers of density up to the quadratic term not only reproduces the experimental results regarding compression but also satisfy the criteria based on the basic thermodynamic relations and hence may be quite useful for studying the high pressure elastic behavior of solids. However the similar equation having different form can also be achieved by Davis-Gordon in the literature using different approach[38].

TABLE 1 : Values of pressure (GPa) as a function of V/Vo calculated from different equation of state. Experimental values are taken from[9]

V/Vo	Born-Mie eq.(3)	Born-Mayer Eq.(4)	Murnqaghan Eq.(5)	Usual Tait Eq.(6)	Birch Eq.(7)	Brennan-Stacy Eq.(8)	Vinet Eq.(9)	Shanker eq.(10)	Kholiya Eq (2)	Exp[9]
0.9627	1.01	1	1.01	1	1	1	1	1	1	1
0.9324	2.02	2.01	2.02	2.01	2.01	2.01	2.01	2.01	2	2
0.9067	3.04	3.04	3.07	3.04	3.04	3.03	3.03	3.03	3	3
0.8845	4.08	4.07	4.14	4.06	4.06	4.04	4.04	4.05	4	4
0.8649	5.13	5.11	5.23	5.1	5.1	5.06	5.06	5.08	4.99	5
0.791	10.6	10.5	11.2	10.4	10.5	10.3	10.3	10.3	9.92	10
0.7397	16.6	16.2	17.9	15.9	16.1	15.6	15.6	15.7	14.81	15
0.7004	22.9	22.1	25.5	21.4	22.1	21	21.1	21.2	19.69	20
0.6685	29.6	28.4	34	27.1	28.3	26.7	26.7	26.9	24.57	25
0.6416	36.8	34.9	43.4	32.8	34.8	32.1	32.5	32.7	29.50	30

REFERENCES

[1] R.Chidambaram, S.M.Sharma; Current Sci.(India), **60**, 397 **(1991)**.
[2] O.L.Anderson; Equations of State of Solids for Geophysics and Ceramic Science. Oxford University Press, Oxford, **(1994)**.
[3] L.M.Thomas, J.Shanker; High Temp.High Pressure, **27/28**, 171 **(1995/1996)**.
[4] S.S.Kushwah, J.Shanker; High Temp.High Pressure, **27/28**, 177 **(1995/1996)**.
[5] L.M.Thomas, J.Shanker; Phys.Stat.Sol.(b), **195**, 67 **(1996)**.
[6] J.Shanker, S.S.Kushwah; J.Phys.Chem.Solids, **59**, 197 **(1998)**.
[7] J.Shanker, S.S.Kushwah; Physica B, **254**, 45 **(1998)**.
[8] Z.H.Fang; High Temp.High Pressure, **31**, 507 **(1999)**.
[9] T.Yagi; J.Phys.Chem.Solids, **39**, 563 **(1978)**.
[10] Y.Wang, D.J.Weidner, F.Guyot; J.Geophysics Res., **101**, 661 **(1996)**.
[11] R.Boehler, G.C.Kennedy; J.Phys.Chem.Solids, **41**, 517 **(1980)**.
[12] J.N.Fritz, S.P.Marsh, W.J.Carter, R.G.McQueen; Accurate characterization of the high pressure environment, E.C.Lloyd, (Ed); NBS Spec.Publ., **326**, 201 **(1971)**.
[13] F.Birch; J.Geophysics Res., **91**, 4949 **(1986)**.
[14] K.Kholiya; Indian J.Phys., **(2013)**.
[15] O.L.Anderson; J.Geophysics Res., **75**, 2719 **(1970)**.
[16] R.W.Roberts, C.S.Smith; J.Phys.Chem.Solids, **31**, 619 **(1970)**.
[17] F.D.Mumaghan; Proc.Natl.Acad.Sci.(USA), **30**, 244 **(1944)**.
[18] J.Freund, R.Ingalls; J.Phys.Chem.Solids, **50**, 263 **(1989)**.
[19] B.J.Brennan, F.D.Stacey; J.Geophysics Res., **84**, 5535 **(1979)**.
[20] P.Vinet, J.Ferrante, J.H.Rose, J.R.Smith; J.Geophys.Res., **92**, 9319 **(1987)**.
[21] J.Shanker, S.S.Kushwah, P.Kumar; Physica B, **239**, 33 **(1997)**.
[22] G.Parsafar, E.A.Mason; Phys.Rev.B, **49**, 3049 **(1994)**.
[23] J.Hama, K.Suito; J.Phys.Condens.Matter, **8**, 67 **(1996)**.
[24] K.Kholiya, J.Chandra; Applied Physics A.
[25] R.Grover, I.C.Getting, G.C.Kennedy; Phy.Rev.B7, 567 **(1973)**.
[26] **(a)** J.R.MacDonald; Rev.Zmod.Phys., **38**, 669 **(1966)**; **(b) 41**, 316 **(1969)**.
[27] H.Schlosser, J.Ferrante; Phys.Rev.B, **40**, 6405 **(1980)**.
[28] **(a)** M.Kumar; Physica B, **212**, 391 **(1995)**; **(b) 217**, 143 **(1996)**.
[29] A.Chopelas, R.Boehler; Geophys.Res.Lett., **19**, 1983 **(1992)**.

[30] J.Shanker, B.Singh, S.S.Kushwah; Physica B, **229**, 419 **(1997)**.
[31] **(a)** F.Birch; Phys.Rev., **71**, 809 **(1947)**; **(b)** J.Geophys.Res., **57**, 227 **(1952)**.
[32] V.Ya.Vashchenko, V.N.Zubarev; Sov.Phys.Solid State, **5**, 653 **(1963)**.
[33] **(a)** S.K.Sikka; Phys.Rev.B, **38**, 8463 **(1988)**; **(b)** Phys.Lett.A, **135**, 129 **(1989)**.
[34] F.E.Prieto, C.Renero; J.Phys.Chem.Solids, **53**, 485 **(1992)**.
[35] M.Kumar, S.P.Upadhyaya; High Temp.High Pressure, **26**, 627 **(1994)**.
[36] M.Born, K.Huang; Dynamical theory of crystal lattices, Clarendon Press, Oxford, **(1954)**.
[37] H.Spetzler, C.G.Sammis, R.J.O'Connell; J.Phys.Chem.Solids, **33**, 1727 **(1972)**.
[38] Davis, Gordon; J.Chem.Phys., **46**, 2650 **(1967)**.