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A Theoretical Study of the Compression Curves for NaCl

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ABSTRACT

The compression curves for NaCl have been calculated using Birch-Murnaghan, Vinet, Misra-Goyal, Bardeen, Brennan-Stacey and the modified Lennard-Jones equations of state. The curves result from these equations of state have been compared with the results calculated from other theoretical methods based on Kumar equation. The variation of V/V_o with T at different pressures are calculated using Kumar equation to show the effect of P and T at the same time on V/V_o. The compression curves resulted from the used equations of state and Kumar equation at room temperature are plotted together with the experimental data of NaCl for the sake of comparison.

Keywords: compression curves, NaCl, Kumar equation.

دراسة نظرية لمنحنيات الانضغاط لكلوريد الصوديوم

الملخص

تم في هذا البحث حساب منحنيات الانضغاط لكلوريد الصوديوم باستخدام معادلات حالة مختلفة (برخ- مرنكهان، ميسرا- كويال، فينت، باردين، برينان- ستاسي ولينارد- جونس المحورة). وتمت مقارنة النتائج المحصلة من معادلات الحالة أعلاه مع نتائج تم حسابها بطريقة نظرية أخرى مستندة إلى معادلة كومار. تم حساب تغير النسبة (V/V_o) مع درجة الحرارة T عند ضغوط مختلفة باستخدام معادلة كومار لتوضيح تأثير الضغط ودرجة الحرارة في الوقت نفسه على النسبة (V/V_o). إن منحنيات الانضغاط الناتجة من معادلات الحالة المستخدمة في هذا البحث والنتائج المحصلة من معادلة كومار عند درجة حرارة الغرفة رسمت معاً مع نتائج عملية لكلوريد الصوديوم لغرض المقارنة.

الكلمات الدالة: منحنيات الانضغاط، كلوريد الصوديوم، معادلة كومار.

INTRODUCTION

The equation of state (EOS) of a system describes the relationships among thermodynamic variables such as pressure, temperature and volume. It provides numerous pieces of information relating to the non-linear compression of a material at high pressure, and has been widely applied in engineering and other scientific researches. The study that is based on the EOS at high pressure and high temperature is of fundamental interest because they permit interpolation and extrapolation into the regions in which the experimental data are not available adequately.

Among these EOSs, the Vinet EOS (Vinet *et al.*, 1987) has been shown to have fairly high precision. The most currently used EOS, especially in the treatment of experimental compression data of minerals, is the Eulerian finite strain Birch-Murnaghan EOS (Poirier, 2000; Tripathi *et al*., 2006; Birch, 1947). The modified Lennard-Jones EOS (Jiuxun, 2005) is just two parameter EOS which has almost all of the merits of ideal universal EOS. The merits are mentioned in the reference (Jiuxun, 2005). From first-principles calculations, the Misra-Goyal EOS (Tripathi *et al.*, 2006) was generated using ab initio pseudopotential framework, no experimental data are used in the generation of this EOS other than atomic variables such as the Wigner-Seitz radius. Due to this the Misra-Goyal EOS is one of the superior EOSs.

The validity of any theoretical method should be done by comparing its results with experimental data. Sometimes the results of these methods agree with experimental data as in (Kushwah and Bhardwaj, 2009).

THEORETICAL DETAILS

The EOSs used in this work are:

The modified Lennard-Jones EOS which is based on the generalized Lennard-Jones potential is (Jiuxun, 2005) :

$$P_{LJ} = \frac{B_o}{n}\left(\frac{V_o}{V}\right)^n \left[\left(\frac{V_o}{V}\right)^n - 1\right] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where $n = \frac{1}{3}B_o'$

B_o is the bulk modulus at zero pressure.

B_o' is the first-order pressure derivative of bulk modulus at zero pressure.

V_o is the volume at zero pressure. V is the volume at pressure P.

Misra-Goyal EOS which is generated using the ab initio pseudopotential formalism is (Tripathi *et al.*, 2006) :

$$P_{MG} = \frac{B_o}{20}\left[\alpha\left\{6\eta^{-2} - 15\eta^{-5/3} + 10\eta^{-4/3} - \eta^{-1/3}\right\} + \beta\left\{3\eta^{-2} - 5\eta^{-4/3} + 2\eta^{-1/3}\right\} + \gamma\left\{\eta^{-2} - \eta^{-1/3}\right\}\right] \ldots(2)$$

with

$\alpha = 6 + 9B_oB_o'' + (3B_o' - 4)(3B_o' - 7)$, $\beta = 2(3B_o' - 7)$, $\gamma = 12$.

B_o'' is the second pressure derivative of B_o.

$\eta = V/V_o$ is the compression.

Birch-Murnaghan EOS which is based on finite strain theory is (Tripathi *et al.*, 2006; Birch, 1947) :

$$P_{BM}=\frac{3B_o}{2}\left[\eta^{-7/3}-\eta^{-5/3}\right]\left[1+\frac{3}{4}\left(B_o'-4\right)\left(\eta^{-2/3}-1\right)\ \right] \qquad \text{……………………….. (3)}$$

The Vinet EOS which is based on interatomic potential is (Vinet *et al.*, 1987) :

$$P_V=3B_o\eta^{-2/3}\left(1-\eta^{1/3}\right)\exp\left[\left\{\frac{3}{2}\left(B_o'-1\right)\right\}\left\{1-\eta^{1/3}\right\}\ \right] \qquad \text{…………………….(4)}$$

The Bardeen EOS is based on interatomic potentials (Bardeen J., 1938) :

$$P_B=3B_o\left[\eta^{-5/3}-\eta^{-4/3}\right]\left[1+\frac{3}{2}\left(B_o'-3\right)\left(\eta^{-1/3}-1\right)\right] \qquad \text{………………………(5)}$$

The Brennan-Stacey EOS is based on assumed relationships between the variables within the EOS (Brennan and Stacey , 1979) :

$$P_{BS}=\frac{3B_o}{\left(3B_o'-5\right)}\eta^{-4/3}\left[\exp\left\{\left(\frac{3B_o'-5}{3}\right)\left(1-\eta\right)\right\}-1\right] \qquad \text{……………………….. (6)}$$

It has been the usual practice to propose a new EOS for solids and to demonstrate its validity by fitting the experimental data . However , the fitting of experimental data corresponding to a limited range of pressures does not provide any support for the validity of the proposed EOS beyond the range of fitting (Digpratap *et al.*, 2005). The above equations (1-6) are isothermal EOSs at room temperature.

In addition to the above EOSs, the following equation is used in this work (Nand and Kumar, 2010; Kumar, 1995)

$$\frac{V}{V_o}=1-\frac{1}{A}\ln\left[1+\frac{A}{B_o}\left\{P-\alpha_o B_o\left(T-T_o\right)\right\}\right] \qquad \text{………………………….. (7)}$$

which is proposed by Kumar for high pressure and high temperature conditions.
Where $A=\left(\delta_T+1\right)$, δ_T the Anderson-Gruneisen parameter, α the coefficient of the volume thermal expansion and ($_o$) refers to the initial value of that quantity.

The existence of T in Eq.(7) enables to plot the variation of V/V_o with temperature at different pressures. δ_T is temperature dependant parameter (Vinet *et al.*,1989) this dependence is given by the following empirical relationship (Chandra *et al.*, 2008)

$$\delta_T=\delta_T^o\left(\frac{T}{T_o}\right)^k \qquad \text{…………………………..(8)}$$

where T_o is the room temperature and δ_T^o is the value of Anderson-Gruneisen parameter at $T=T_o$. k is a dimensionless thermo elastic parameter.

RESULS AND DISCUSSION

The compression curves for NaCl are plotted in Fig. 1 using the EOSs (1-6) in addition to Eq.(7) at room temperature. This equation can be used to plot V/V_o versus T at different pressures taking into account the variation of δ_T with temperature by using Eq. (8). The values of B_o = 24 GPa, B'_o = 5.5 for NaCl have been taken from reference (Digpratap *et al.*, 2005) and B''_o = -0.223 $(\text{Gpa})^{-1}$ based on experimental ultrasonic data (Hart and Greenwood, 1983). The values of α_o= 11.8×10^{-5} K^{-1}, δ_T^o=6.56 and the parameter k in Eq.(8) is -0.79 for NaCl (Chandra *et al.*, 2009).

Fig. 1 shows that, at pressures (0-20 GPa), all compression curves coincide. Beyond this, the curves diverge more or less, and this divergence increases significantly at higher pressures. The reason for this behavior is that each equation of the EOSs used in this work is derived from different theoretical bases. It is seen that Birch-Murnaghan EOS yields results which are consistent with the results obtained from Misra-Goyal EOS even at relatively high pressures.

In Fig.1 we see that the curve results from Eq.(7) at T=300K is closer to the curve obtained from the modified Lennard-Jones EOS than the other EOSs and coincides with it at the range (250-300 GPa). However, we can say that the curves result from Eq.(7) have the same behavior of the compression curves of the EOSs, i.e. the same non-linear variation. It is seen from Fig. 2 by plotting the volume ratio V/V_o with temperature T at different pressures [P= (0, 6, 50, 100, 150) GPa] that the increase in temperature at (P=0) causes an increase in V/V_o , this behavior is inverted at (P=6 GPa). At this point the effect of temperature balanced by the effect of (6 GPa) pressure according to Eq. (7). Beyond this point the effect of pressure on V/V_o ratio dominates the effect of temperature. The reason of this behavior is that at P=0 the increase in temperature causes an expansion in volume i.e. increase in V/V_o while at (P>6 GPa) the effect of pressure is greater than that of temperature and causes compression in volume.

The variation of V/V_o with pressure using Eq.(7) at (T=300 K) and the modified Lennard-Jones EOS with pressures not more than (30~34 GPa) are shown in Fig. 3 , together with available experimental data of NaCl (Vaidya and Kennedy, 1971; Sorensen, 1983) for the sake of comparison of the results. We chose the modified Lennard-Jones EOS to be plotted in Fig. 3 because the results of this EOS -shown in Fig. 1- is closer to the results of Eq.(7) at 300 K than the result of the other EOSs. It is found that there is a good agreement between the results of Eq.(7) and experimental data in the range (0-4 GPa), beyond that this curve diverges from the experimental data. The compression curve of the modified Lennard-Jones EOS has a good agreement with the experimental data.

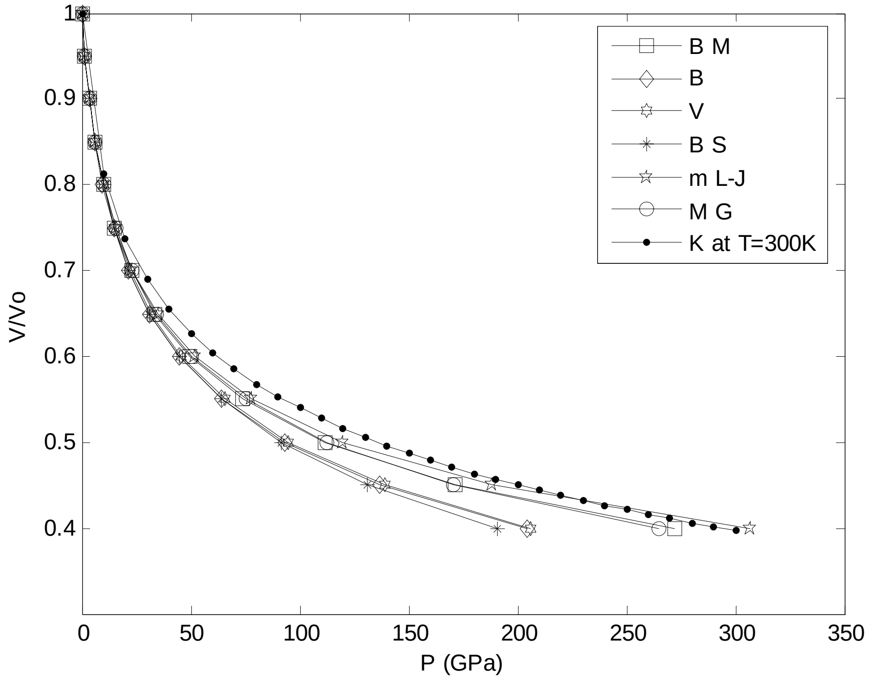

Fig. 1: Isothermal compression curves for NaCl using different EOSs.

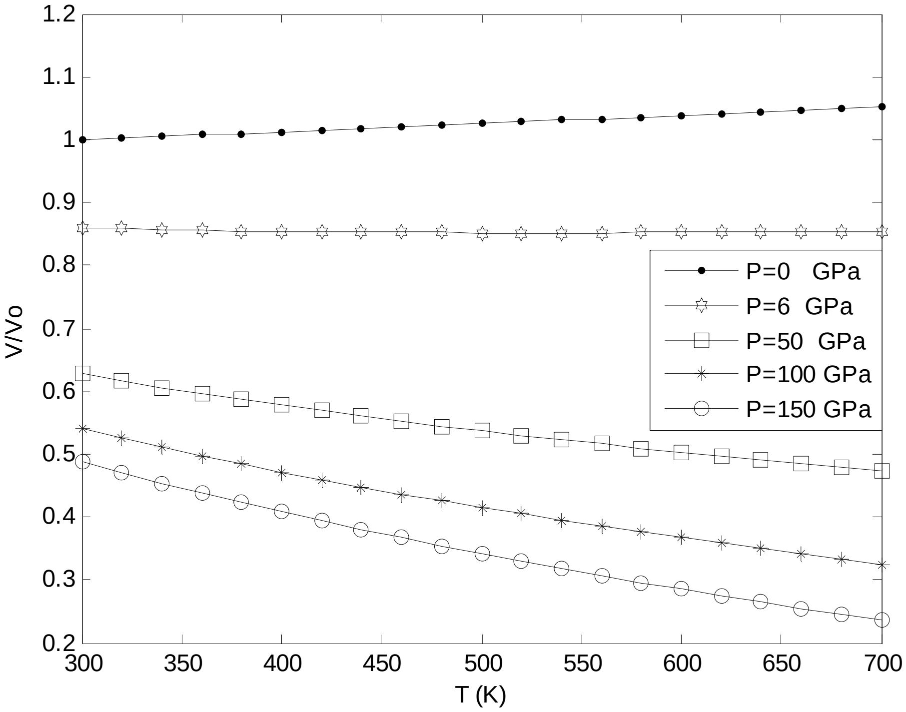

Fig. 2: Variation of V/V_o with temperature at different pressures for NaCl using Eq.(7).

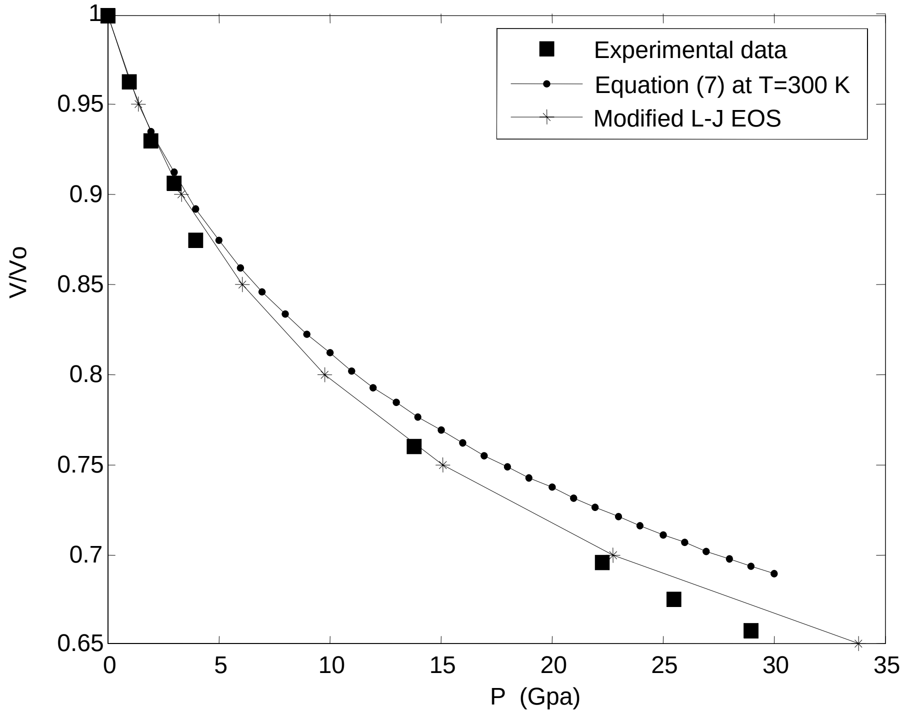

Fig. 3: Variation of V/V_o with pressure at room temperature using experimental data (Vaidya and Kennedy, 1971; Sorensen, 1983), Eq. (7) and the modified Lennard-Jones EOS for NaCl.

CONCLUSIONS

The compression curves which result from the EOSs used in this work coincide at (P=0-20 GPa) as shown in Fig. 1 . The compression curves of Birch-Murnaghan and Misra-Goyal EOSs have good agreement with each other in the case of NaCl. The results from Eq.(7) at T=300K is much closer to the curve obtained from the modified Lennard-Jones EOS than the other EOSs. According to Eq.(7), the increase in temperature causes an increase in V/V_o for the same value of P at (P<6 GPa) and a decrease in V/V_o at (P>6 GPa) as shown in Fig. 2 i.e. by increasing pressure and temperature at the same time, the effect of pressure (compression) is greater than the effect of temperature (expansion) when the pressure is more than (6 GPa). The results of the modified Lennard-Jones EOS have better agreement with the experimental data than the results obtained from Eq.(7).

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