Article ID: 1000-5773(2007)03-0269-10

Modified Einstein Model to Consider Thermal Effect and Applied to Three Universal Equations of State*

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Abstract: The Einstein model to consider thermal effect in universal equations of state (UEOS) is modified. It is proposed that the zero-point vibration term should be deleted in a thermal UEOS, and the parameters can not be directly taken as experimental data at a reference temperature, V_R, B_R, B'_R and γ_R^G, but their values at absolute zero temperature, V_0, B_0, B'_0 and γ_0^G. An approach is proposed to solve V_0, B_0, B'_0 and γ_0^G from V_R, B_R, B'_R and γ_R^G. The approaches are applied to three typical universal EOSs, including the Baonza, mMNH and Vinet EOSs. The numerical results show that the solved values of parameters are almost identical for different EOSs. And the thermo-physical properties predicted through different EOSs are almost identical at zero and low-pressure conditions, once the same approach and input experimental data are used to solve parameters. It is concluded that the prediction of thermo-physical properties at zero and low-pressure conditions cannot be taken as the criteria to judge the applicability of a universal EOS.

Key words: equation-of-state; high-pressure; thermodynamic properties; thermal expansions

CLC number: O521.2 **Document code**: A

1 Introduction

The equation of state(EOS) of a system describes the relationships among thermodynamic variables such as pressure, temperature, and volume. It provides numerous information of a material at high pressure, and has been widely applied in engineering and other scientific research. Recently, rapid advances in computational capabilities and accurate high-pressure experimental techniques have given a strong impetus to theoretical work. Significant progress has been achieved over the past few years as regards describing the properties of condensed matter in terms of universal relationships involving a small number of parameters. Especially since 1986 Rose et al.[1] proposed that there is a universal EOS (UEOS) valid for all kinds of solids through analyzing the energy-band data; a lot of forms of the UEOSs have been proposed with varying success[2-19].

Holzapfel's et al.[17-18] pointed out that most of present EOS cannot satisfy the Fermi gas (FG) limitation at high pressure[17-21], and thus modified the ER2 EOS to satisfy the FG limitation condition. However, the form of EOSs modified by Holzapfel et al. becomes complicated, and loses some important merits. And recently, we proposed two Murnaghan-type EOSs[19], and compared the preci-

* **Received date**: 2006-09-22; **Revised date**: 2007-03-15

Foundation Item: Program of Sichuan Province of China under Grant(06ZQ026-010); Program of Education Ministration of China under Grant(NCET-05-0799); Program of UESTC under Grant(23601008)

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sion of five EOSs including Baonza and Holzapfel EOSs by fitting the experimental compression data of 50 solids. The results show that EOSs strictly satisfying the FG limitation give the worse results than other EOSs not satisfying. For practical applications, the FG limiting condition is not important for it only operates as volume tends zero.

Among the EOSs, the Baonza EOS has been shown to have fairly high precision[8-14]. The original Baonza EOS is a cold EOS. Recently, Baonza et al.[13-14] have extended their EOS to consider thermal effect by the aid of the Einstein model

$$p = p_c(V) + \frac{\gamma_R^G}{V_R} 3Nk\Theta_E \left(\frac{1}{2} + \frac{1}{e^{\Theta_E/T} - 1} \right) \tag{1}$$

$$p_c = \frac{\beta B_R}{B'_R} \left\{ [1 + B'_R(\beta^{-1} - 1)\ln(V_R/V)]^{1/(1-\beta)} - 1 \right\} \tag{2}$$

where β can be taken as universal constant, $\beta \approx 0.85$, Θ_E is the Einstein characteristic temperature of the solid, it can be taken as experimental values. Baonza et al. directly take other four parameters B_R, B'_R, γ_R^G and V_R as their values at zero pressure and a reference temperature T_R.

The approach of Eq. (1) to dispose thermal effect has an advantage; all parameters can be directly taken as their experimental values. However, it can be easily seen that Eq. (1) has a physically incorrect problem. That is the equation can not satisfy the zero-pressure condition, $p(T_R, V_R) = 0$. In order to overcome this problem, we think two modifications should be taken. At first, we should delete zero-point vibration term from Eq. (1). At second, the parameters B_R, B'_R, γ_R^G and V_R should be replaced by their values at zero pressure and 0 K, B_0, B'_0, γ_0^G and V_0. This does not mean we do not consider zero-point vibration, but alternatively include it in the cold pressure term through consistently solving parameters B_0, B'_0, γ_0^G and V_0. Then Eq. (1) and Eq. (2) change to following form

$$p = p_c(V) + \frac{3\gamma_0^G Nk\Theta_E}{V_0(e^{\Theta_E/T} - 1)} \tag{3}$$

$$p_c = \frac{\beta B_0}{B'_0} \left\{ [1 + B'_0(\beta^{-1} - 1)\ln(V_0/V)]^{1/(1-\beta)} - 1 \right\} \tag{4}$$

Although the difference of physical quantities deduced from Eqs. (1), (2) and that from Eqs. (3), (4) are small, we think the modification to Eqs. (1), (2) is necessary for the physical inconsistence can be avoided in the modified Eqs. (3), (4). Otherwise, the parameters B_0, B'_0, γ_0^G and V_0 at 0 K are interesting for many applications, but their values are difficult to access. So in most cases people avoid using these parameters at 0 K. Our modification provides an approach to obtain their values conveniently. This is meaningful for practical applications.

We notice that different forms of UEOS have different precision to fit the isothermal compression data, although many authors claim that the thermodynamic properties calculated by using different thermal UEOS are in good agreement with experiments. Thus we have three main goals in this paper. The first goal is to modify three typical UEOS to consider thermal effect by using approach related to Eqs. (3) and (4), including the Baonza, mMNH and Vinet EOSs. The second goal is to develop a procedure to solve parameters at zero pressure and 0 K from experimental data at zero pressure and a reference temperature. The third goal is to compare thermo-physical properties of 22 typical materials calculated through the three UEOSs at zero and low-pressure conditions.

In Sec. 2, the volume analytic Baonza EOS with thermal effect taken into account is presented, and analytic expressions for bulk modulus and thermal expansivity are derived. The approach to solve parameters in the zero pressure and 0 K is presented. In Sec. 3, the procedure in Sec. 2 is applied to the mMNH EOS. In Sec. 4, the procedure in Sec. 2 is applied to the Vinet EOS. In Sec. 5, the numerical results are given and compared with experimental data available. At last in Sec. 6, the conclusion is presented.

2 Thermal Baonza Equation of State

The thermal Baonza EOS in Eqs. (3), (4) can be easily converted to following volume analytic form

$$\ln(V_0/V) = [B'_0(\beta^{-1}-1)]^{-1} \cdot (Q^{1-\beta}-1) \tag{5}$$

$$Q = 1 + \frac{B'_0 p}{\beta B_0} - \frac{3B'_0 \gamma_0^{\mathrm{G}} Nk\Theta_{\mathrm{E}}}{\beta B_0 V_0 (\mathrm{e}^{\Theta_{\mathrm{E}}/T}-1)} \tag{6}$$

Here Q is an auxiliary quantity. The bulk modulus can be derived as follows

$$B = B_0[1 + B'_0(\beta^{-1}-1)\ln(V_0/V)]^{\beta/(1-\beta)} \tag{7}$$

The derivative of bulk modulus with respect to pressure can be derived as follows

$$B' = B'_0[1 + B'_0(\beta^{-1}-1)\ln(V_0/V)]^{-1} \tag{8}$$

Substitution of Eq. (5) into Eq. (7) and Eq. (8) yields

$$B = B_0 Q^{\beta} \tag{9}$$

$$B' = B'_0 Q^{\beta-1} \tag{10}$$

The equation for thermal expansion coefficient also can be derived as follows

$$\alpha = \frac{3\gamma_0^{\mathrm{G}} Nk}{Q^{\beta} B_0 V_0} \left(\frac{\Theta_{\mathrm{E}}}{T}\right)^2 \frac{\mathrm{e}^{\Theta_{\mathrm{E}}/T}}{(\mathrm{e}^{\Theta_{\mathrm{E}}/T}-1)^2} \tag{11}$$

By using Eqs. (5)～(11), we can easily calculate the variation of V, B, B' and α versus temperature and pressure relations. Substituting Eq. (9) into Eq. (11), we have

$$\alpha = \frac{3\gamma_0^{\mathrm{G}} Nk}{BV_0} \left(\frac{\Theta_{\mathrm{E}}}{T}\right)^2 \frac{\mathrm{e}^{\Theta_{\mathrm{E}}/T}}{(\mathrm{e}^{\Theta_{\mathrm{E}}/T}-1)^2} \tag{12}$$

Although Eq. (12) has been derived based on the Baonza EOS, it can be applied to other UEOS, provided the same Einstein model to consider thermal effect in Eqs. (3, 4) is used.

Now we give the approach to solve B_0, B'_0, γ_0^{G} and V_0 from B_{R}, B'_{R}, $\gamma_{\mathrm{R}}^{\mathrm{G}}$ and V_{R} at zero pressure and a reference temperature T_{R}. Considering Eqs. (5), (6), (9), (10) can be applied to any temperature, we would apply them to zero pressure and reference temperature T_{R}

$$\ln(V_0/V_{\mathrm{R}}) = [B'_0(\beta^{-1}-1)]^{-1} \cdot (Q_{\mathrm{R}}^{1-\beta}-1) \tag{13}$$

$$Q_{\mathrm{R}} = 1 - \frac{3B'_0 \gamma_0^{\mathrm{G}} Nk\Theta_{\mathrm{E}}}{\beta B_0 V_0 (\mathrm{e}^{\Theta_{\mathrm{E}}/T_{\mathrm{R}}}-1)} \tag{14}$$

$$B_{\mathrm{R}} = B_0 Q_{\mathrm{R}}^{\beta} \tag{15}$$

$$B'_{\mathrm{R}} = B'_0 Q_{\mathrm{R}}^{\beta-1} \tag{16}$$

It can be seen that Eqs. (13)～(15) just can solve three unknown parameters. In order to solve four unknown parameters, we need another equation.

Noting that the Grüneisen parameter γ^{G} should be a function of volume $\gamma^{\mathrm{G}}(V)$. And strictly speaking, the factor $(\gamma_0^{\mathrm{G}}/V_0)$ should be $(\gamma^{\mathrm{G}}(V)/V)$. However, it has been shown that $\gamma^{\mathrm{G}}(V)$ can be taken as linear function of volume for most applications[2], $\gamma^{\mathrm{G}}(V) = \gamma_0^{\mathrm{G}}(V/V_0)$. And the factor $[\gamma^{\mathrm{G}}(V)/V)]$ naturally changes to $(\gamma_0^{\mathrm{G}}/V_0)$. Otherwise, we have $\gamma_{\mathrm{R}}^{\mathrm{G}} \equiv \gamma^{\mathrm{G}}(V_{\mathrm{R}}) = \gamma_0^{\mathrm{G}}(V_{\mathrm{R}}/V_0)$, and

$$\frac{\gamma^{\mathrm{G}}(V)}{V} = \frac{\gamma_0^{\mathrm{G}}}{V_0} = \frac{\gamma_{\mathrm{R}}^{\mathrm{G}}}{V_{\mathrm{R}}} \tag{17}$$

Substituting Eqs. (15)～(17) into Eq. (14), Q_{R} can be solved as follows

$$Q_{\mathrm{R}} = \left[1 + \frac{3B'_{\mathrm{R}} \gamma_{\mathrm{R}}^{\mathrm{G}} Nk\Theta_{\mathrm{E}}}{\beta B_{\mathrm{R}} V_{\mathrm{R}} (\mathrm{e}^{\Theta_{\mathrm{E}}/T_{\mathrm{R}}}-1)}\right]^{-1} \tag{18}$$

Now by using Eq. (18), we can analytically calculate V_0, B_0, B'_0 and γ_0^{G} from Eqs. (13), (15)～(17), respectively.

3 Thermal Modified Murnaghan Equation of State

Substituting the modified Murnaghan EOS[19] (called as mMNH here) into Eq. (3), we obtain the thermal mMNH EOS

$$p=\frac{3B_0}{5\lambda}[(\lambda Y+1)^5-1]+\frac{3\gamma_0^G NK\Theta_E}{V_0(e^{\Theta_E/T}-1)} \tag{19}$$

$$Y=(V_0/V)^{1/3}-1,\quad \lambda=(3B'_0-1)/4 \tag{20}$$

Eq. (19) can be converted to following volume analytic form

$$Y=\lambda^{-1}[(1+Q)^{1/5}-1] \tag{21}$$

$$Q=\frac{5\lambda p}{3B_0}-\frac{5\lambda\gamma_0^G NK\Theta_E}{B_0V_0(e^{\Theta_E/T}-1)} \tag{22}$$

The bulk modulus is

$$B=B_0(Y+1)(\lambda Y+1)^4 \tag{23}$$

The pressure derivative of bulk modulus is

$$B'=(5\lambda Y+4\lambda+1)/3(\lambda Y+1) \tag{24}$$

The equation of thermal expansion coefficient is

$$\alpha=\frac{3\gamma_0^G NK}{B_0V_0}\left(\frac{\Theta_E}{T}\right)^2\frac{e^{\Theta_E/T}}{(e^{\Theta_E/T}-1)^2}(Y+1)^{-1}(\lambda Y+1)^{-4} \tag{25}$$

If substituting Eq. (23) into Eq. (25), Eq. (25) can be changed to Eq. (12). This means Eq. (12) also is valid for the thermal mMNH EOS.

Now we give the approach to solve B_0, B'_0, γ_0^G and V_0 from B_R, B'_R, γ_R^G and V_R at reference temperature T_R. Applying Eqs. (21)～(24) to zero pressure and reference temperature T_R, we have

$$Y_R=\lambda^{-1}[(1+Q_R)^{1/5}-1] \tag{26}$$

$$Q_R=-\frac{5\lambda\gamma_R^G NK\Theta_E}{B_0V_R(e^{\Theta_E/T_R}-1)} \tag{27}$$

$$B_R=B_0(Y_R+1)(\lambda Y_R+1)^4 \tag{28}$$

$$B'_R=(5\lambda Y_R+4\lambda+1)/3(\lambda Y_R+1) \tag{29}$$

Noting that $\lambda=(3B'_0-1)/4$, Eqs. (17), (26)～(29) can solve four parameters B_0, B'_0, γ_0^G and V_0 from experimental data of B_R, B'_R, γ_R^G and V_R. The solving procedure is as follows. At first, we give B_0, B'_0 initiative values, $B_0\approx B_R$, and $B'_0\approx B'_R$. At second, we calculate Y_R from Eq. (26) and Eq. (27). At third, we calculate B_0 and B'_0 from Eq. (28) and Eq. (29). The iteration should be done up to the values of B_0 and B'_0 are consistent within acceptable precision. Our calculations show that the iteration is absolutely convergent, and no multiple solutions exist to the iterative problem. We just need about ten times of iterations to reach the desired precision. At last, we calculate V_0 from Eq. (20) and γ_0^G from Eq. (17).

4 Thermal Vinet Equation of State

Substituting the cold Vinet EOS[2] into Eq. (3), we obtain the thermal Vinet EOS

$$p=3B_0\frac{1-X}{X^2}\exp[\eta(1-X)]+\frac{3\gamma_0^G NK\Theta_E}{V_0(e^{\Theta_E/T}-1)} \tag{30}$$

where

$$X=(V/V_0)^{1/3},\quad \eta=3(B'_0-1)/2 \tag{31}$$

By using following two relationships

$$B=-\frac{1}{3}\left(X\frac{\partial}{\partial X}\right)p \tag{32}$$

$$B' = \frac{\partial B}{\partial p} = \frac{1}{9B}\left(X\ \frac{\partial}{\partial X}\right)^2 p \tag{33}$$

we can derive the expressions for the bulk modulus and its derivative with respect to pressure

$$B = \frac{B_0}{X^2}[2 + (\eta - 1)X - \eta X^2]\exp[\eta(1 - X)] \tag{34}$$

$$B' = \frac{4 + (3\eta - 1)X + \eta(\eta - 1)X^2 - \eta^2 X^3}{3[2 + (\eta - 1)X - \eta X^2]} \tag{35}$$

Applying Eqs. (30), (34), (35) to zero pressure and reference temperature T_R, we have

$$X_R = 1 + \frac{X_R^2 \gamma_0^G N k \Theta_E}{V_0(e^{\Theta_E/T_R} - 1)}\exp[\eta(X_R - 1)] \tag{36}$$

$$B_0 = B_R X_R^2[2 + (\eta - 1)X_R - \eta X_R^2]^{-1}\exp[\eta(X_R - 1)] \tag{37}$$

$$\eta = [X_R(3 - X_R)]^{-1}[3B'_R(2 - X_R + \eta X_R - \eta X_R^2) - 4 + X_R - \eta^2 X_R^2(1 - X_R)] \tag{38}$$

Then using Eqs. (17), (36)～(38), we can solve four parameter V_0, B_0, B'_0 and γ_0^G from experimental data of V_R, B_R, B'_R and γ_R^G. The solving procedure is as follows. At first, we give X_R, B_0, B'_0 initiative values, $X_R \approx 1$, $B_0 \approx B_R$, and $B'_0 \approx B'_R$ (or $\eta \approx (3/2)(B'_R - 1)$). At second, we calculate X_R from Eq. (36). At third, we calculate B_0 and η from Eqs. (37), (38). The iteration should be done up to the values of B_0 and η are consistent within acceptable precision. Our calculations show that the iteration is absolutely convergent, and no multiple solutions exist to the iterative problem. We just need about ten times of iterations to reach the desired precision. At last, we calculate $V_0 = V_R/X_R^3$, $B'_0 = 2\eta/3 + 1$ and γ_0^G from Eq. (17).

5 Numerical Results and Discussion

In this section, we apply above three thermal equations of state to 22 solids. All experimental data used here are taken from Ref. [14] and references cited there. In Table 1, we list the experimental data used to determine the parameters of the solids studied in this work, along with selected reference temperatures and Θ_E. The solved parameters V_0, B_0 and B'_0 at zero temperature for the three EOSs are listed in Table 2. In the table, we do not list the values of γ_0^G, since its values can be easily converted by using Eq. (17), or $\gamma_0^G = (V_0/V_R)\gamma_R^G$.

Table 2 shows that the Baonza and mMNH equations give the almost identical values for all three parameters, the Baonza, mMNH and Vinet equations give the almost identical values for two parameters V_0 and B_0. We conclude from these results that the difference of parameters for different EOSs is negligibly small, once the same procedure and the same input experimental data are used to solve the parameters.

In Fig. 1～Fig. 5, we plotted the variation of volume, thermal expansivity and bulk modulus versus temperature at zero-pressure and low-pressure conditions for five typical materials, including Ar, LiF, KCl, Li and Cu. In Fig. 6, we plotted the variation of bulk modulus versus pressure at three temperatures. The parameters are taken from Table 2. These figures show that the agreement of theoretical results with experimental data is fairly good, this verifies that the approach to consider thermal effect is reasonable. However, these figures also show that the difference of thermo-physical properties of solids calculated through the three different equations are invisible in these figures, and are almost identical at zero-pressure and low-pressure conditions. This situation is in agreement with Table 1 and Table 2. Since the values of V_R and B_R at reference temperature T_R have been used to solve V_0 and B_0 at zero temperature, the three EOSs must give the same value of V and B at T_R. Furthermore, since Table 2 shows that the values of V_0 and B_0 are almost identical, the identity of the predicted variation of V and B versus temperature relations is obviously reasonable.

Table 1 Summary of the four input parameters as well as reference temperatures T_R and Einstein temperatures Θ_E (calculated as $0.75\Theta_D$ from the Θ_D values of the references) for the solids studied in this work (These values are taken from Ref. [14])

Solid	T_R/(K)	V_R/(cm³/mol)	B_R/(GPa)	B'_R	γ_R^G	Θ_E/(K)
Ar	40	23.026	2.35	7.5	2.7	69.0
Kr	60	28.012	2.49	7.3	2.8	53.9
Xe	60	35.54	3.02	7.8	2.8	48
NaCl	298	27.00	23.5	5.35	1.59	241
LiF	300	9.833	66.4	5.23	1.63	551
NaF	300	15.02	46.1	5.28	1.52	367
KCl	300	37.529	17.4	5.45	1.41	176
CsCl	300	42.22	16.8	5.85	2.03	113
Li	294	13.02	11.556	3.51	0.878	258
Na	294	23.743	6.06	4.125	1.24	119
K	297	45.557	2.963	4.208	1.24	68
Rb	295	55.74	2.301	4.15	1.26	42
Cs	270	70.00	1.723	3.87	1.14	29
Al	300	10.00	72.8	5.15	2.16	322.9
Fe	300	7.09	163.0	5.99	1.66	354.3
Cu	300	7.11	133.0	5.65	2.00	258.3
Zn	300	9.16	64.8	4.9	1.90	245
Ag	300	10.27	99.6	6.20	2.35	169.9
Cd	300	13.00	49.8	6.77	2.20	157
Pt	300	9.09	277	5.61	2.63	178.8
Au	300	10.21	166.65	6.5	2.99	121.3
Pb	300	18.26	41.7	5.70	2.60	79

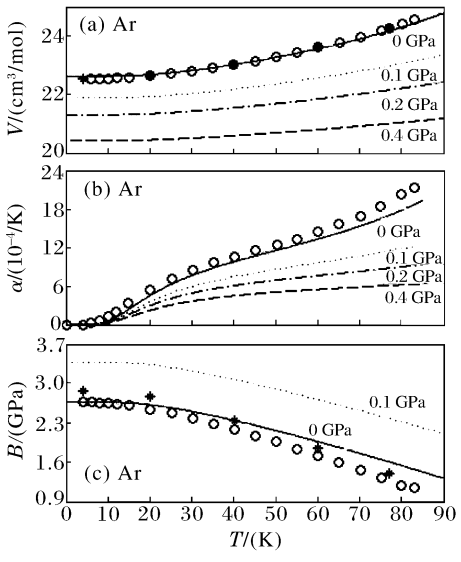


Fig. 1 Temperature dependence of thermodynamic properties for argon at zero and low-pressure conditions (Lines, numerical results calculated in this paper; Symbols, experimental data taken from Ref. [14] and references cited there)

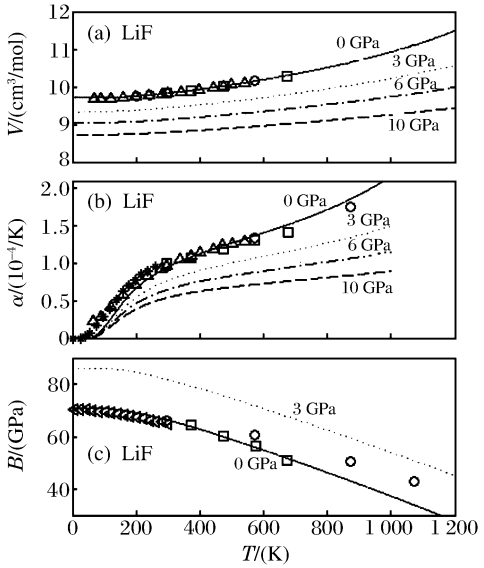


Fig. 2 Temperature dependence of thermodynamic properties for LiF at zero and low-pressure conditions (Lines, numerical results calculated in this paper; Symbols, experimental data taken from Ref. [14] and references cited there)

Table 2　The values of V_0, B_0, B'_0 at zero temperature and zero pressure for 22 solids are calculated from three modified equations of state in this paper

(The experimental data (represented by "Exp") are taken from Ref. [14] and references cited there)

Solid	V_0/(cm³/mol)				B_0/(GPa)				B'_0		
	Exp	Baonza	mMNH	Vinet	Exp	Baonza	mMNH	Vinet	Baonza	mMNH	Vinet
Ar	22.57	22.628 3	22.628 3	22.628 1	2.657	2.674 1	2.673 9	2.670 9	7.330 9	7.322 9	7.197 1
Kr		27.106 9	27.106 9	27.103 0		3.149 1	3.148 5	3.118 7	7.003 7	6.993 6	6.582 0
Xe	34.70	34.723 3	34.723 2	34.721 5	3.647	3.610 2	3.609 6	3.592 3	7.558 1	7.543 9	7.247 4
NaCl	26.32	26.392 8	26.392 8	26.393 4	26.63	26.507 0	26.509 9	26.550 6	5.237 5	5.247 5	5.264 2
LiF	9.684	9.710 1	9.710 1	9.710 3	70.21	70.887 2	70.889 8	71.052 5	5.170 0	5.175 9	5.332 4
NaF		14.780 9	14.780 9	14.781 2		50.144 7	50.147 6	50.261 9	5.202 2	5.209 5	5.317 3
KCl	36.84	36.700 2	36.700 2	36.700 9	19.73	19.626 8	19.628 7	19.656 1	5.335 4	5.344 5	5.355 9
CsCl		40.887 4	40.887 4	40.886 2		20.205 8	20.208 6	20.156 2	5.662 5	5.671 9	5.506 3
Li	12.69	12.691 8	12.691 8	12.692 7	12.65	12.630 7	12.633 5	12.698 7	3.455 4	3.473 2	3.642 9
Na		22.663 7	22.664 0	22.665 7		7.318 7	7.323 6	7.336 6	3.989 9	4.020 4	3.981 9
K		43.163 0	43.163 7	43.165 1		3.702 2	3.705 4	3.703 5	4.045 8	4.080 7	3.978 3
Rb	52.60	52.526 6	52.527 8	52.528 6	2.940	2.928 7	2.931 8	2.927 3	3.977 1	4.015 6	3.888 9
Cs		66.305 6	66.306 7	66.313 5		2.117 2	2.119 2	2.123 4	3.731 8	3.768 4	3.722 9
Al		9.881 0	9.881 0	9.881 2		77.403 6	77.406 3	77.585 6	5.094 6	5.100 4	5.269 7
Fe		7.050 9	7.050 9	7.051 0		168.469 0	168.469 5	168.694 9	5.955 2	5.956 4	6.185 5
Cu	7.026	7.041 4	7.041 4	7.041 4	142.3	140.456 2	140.458 5	140.724 5	5.595 9	5.599 2	5.772 6
Zn		9.024 4	9.024 4	9.024 5		69.682 2	69.686 3	69.871 6	4.837 6	4.845 7	4.995 3
Ag		10.144 5	10.144 5	10.144 6		107.433 2	107.434 4	107.603 4	6.117 7	6.119 6	6.215 8
Cd		12.765 8	12.765 8	12.765 8		56.248 1	56.247 2	56.239 2	6.626 1	6.624 5	6.561 4
Pt		9.039 0	9.039 0	9.039 1		285.851 3	285.852 9	286.257 7	5.578 9	5.580 9	5.820 6
Au		10.105 3	10.105 3	10.105 4		178.129 7	178.129 9	178.389 6	6.424 0	6.424 3	6.537 8
Pb		17.880 3	17.880 3	17.880 6		46.947 9	46.951 2	47.004 0	5.582 0	5.589 0	5.591 6

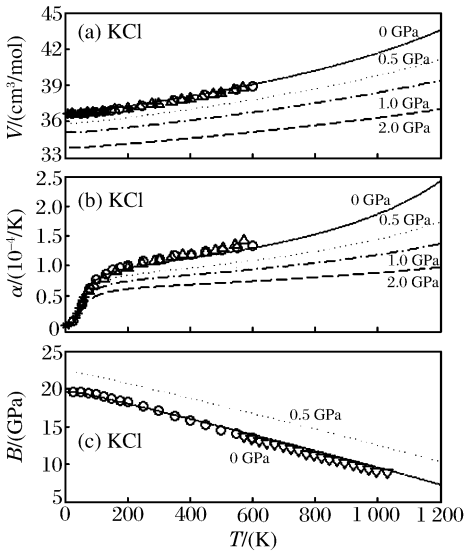


Fig. 3　Temperature dependence of thermodynamic properties for KCl at zero and low-pressure conditions (Lines, numerical results calculated in this paper; Symbols, experimental data taken from Ref. [14] and references cited there)

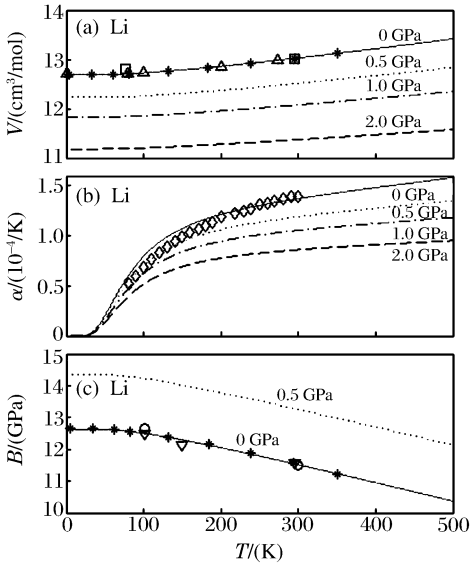


Fig. 4　Temperature dependence of thermodynamic properties for Li at zero and low-pressure conditions (Lines, numerical results calculated in this paper; Symbols, experimental data taken from Ref. [14] and references cited there)

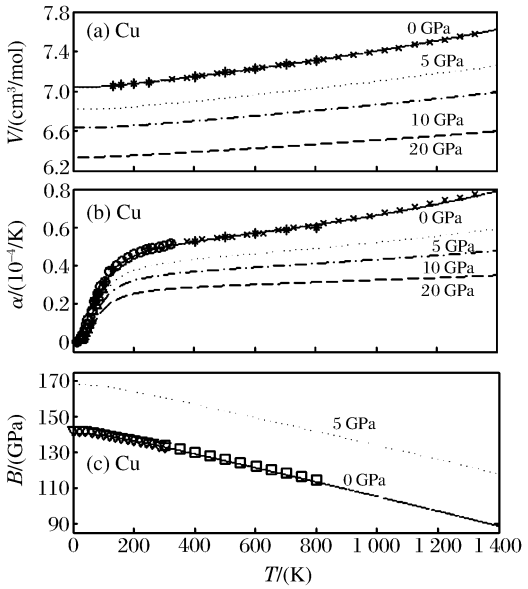


Fig. 5 Temperature dependence of thermodynamic properties for Cu at zero and low-pressure conditions (Lines, numerical results calculated in this paper; Symbols, experimental data taken from Ref. [14] and references cited there)

As for the thermal expansivity, Eq. (12) is the universal expression applicable to all universal EOSs, the predicted variation of thermal expansivity versus temperature relation should be controlled by $V(T)$ and $B(T)$ relationships, and also is identical for different EOSs, since $V(T)$ and $B(T)$ relationships are identical for different EOSs. Otherwise, if we apply Eq. (12) to T_R, we have

$$\alpha(T_R)=\frac{3\gamma_R^G Nk}{B_R V_R}\left(\frac{\Theta_E}{T_R}\right)^2\frac{e^{\Theta_E/T_R}}{(e^{\Theta_E/T_R}-1)^2} \quad (39)$$

thus the values of thermal expansivity should be identical for all EOSs, since V_R and B_R are experimental data being independent to specific EOS forms.

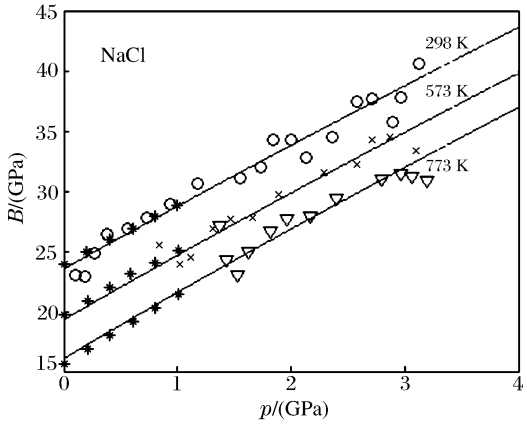


Fig. 6 Pressure dependence of the isothermal bulk modulus for solid NaCl at three temperatures (Lines, numerical results calculated in this paper; Symbols, experimental data taken from Ref. [14] and references cited there)

Baonza et al. have applied their thermal Baonza EOS to research thermo-physical properties of 22 solids. They conclude the thermal Baonza EOS gives fairly good results for thermo-physical properties at zero pressure condition, including the volume, thermal expansivity and isothermal bulk modulus. Here our numerical results show that the conclusion is also valid to the mMNH and Vinet EOSs, not only the Baonza EOS. We also notice that Baonza et al. also conclude that the different EOSs, including Boanza, Vinet and Holzapfel EOSs give almost identical results at moderate pressures. In terms of above results and analysis, we think that the prediction of thermo-physical properties at zero and low-pressure conditions is not appropriate to judge the applicability of a universal EOS.

6 Conclusions

In conclusions, we modified the Einstein model to consider thermal effect in universal EOSs, and proposed an approach to solve the parameters at absolute zero temperature from experiment at a reference temperature. The approaches are applied to three different universal EOSs, the numerical results show that the solved values of parameters are almost identical for different EOSs. Combining above results and analysis, we conclude that the thermo-physical properties predicted through different EOSs are identical, once the same approach and input experimental data are used to solve parameters, and the prediction of thermo-physical properties can not be taken as the criteria to judge the applicability of a universal EOS.

References:

[1] Rose J H, Smith J R, Guinea F. Universal Features of the Equation of State of Metals [J]. Phys Rev B, 1984, 29 (6): 2963-2969.

[2] Vinet P, Smith J R, Ferrante J, et al. Temperature Effects on the Universal Equation of State of Solids [J]. Phys Rev B, 1987, 35(4): 1945-1953.

[3] Dodson B. Universal Scaling Relations in Compressibility of Solids [J]. Phys Rev B, 1987, 35(6): 2619-2625.

[4] Kumari M, Dass N. An Equation of State Applied to Sodium Chloride and Caesium Chloride at High Pressures and High Temperatures [J]. J Phys: Condens Matter, 1990, 2(14): 3219-3229.

[5] Kuchhal P, Kumar R, Dass N. Equation of State of Liquid Metals from Sound-Velocity Measurements [J]. Phys Rev B, 1997, 55(13): 8042-8044.

[6] Parsafar G, Mason E A. Universal Equation of State for Compressed Solids [J]. Phys Rev B, 1994, 49(5): 3049-3060.

[7] Hama J, Suito K. The Search for a Universal Equation of State Correct up to Very High Pressures [J]. J Phys: Condens Matter, 1996, 8(1): 67-81.

[8] Baonza V G, Caceres M, Nunez J. The Spinodal as a Reference Curve for the High-Pressure Volumetric Behavior of Liquids [J]. Chem Phys Lett, 1993, 216(3-6): 579-584.

[9] Baonza V G, Caceres M, Nunez J. High-Pressure Compressibility Behavior of Liquids Referred to a Pseudospinodal Curve [J]. Chem Phys Lett, 1994, 228(1-3): 137-143.

[10] Baonza V G, Caceres M, Nunez J. Experimental Measurement of Quasi-Fermi Levels at an Illuminated Semiconductor/Liquid Contact [J]. J Phys Chem, 1994, 98(19): 4955-4958.

[11] Baonza V G, Caceres M, Nunez J. Universal Compressibility Behavior of Dense Phases [J]. Phys Rev B, 1995, 51(1): 28-37.

[12] Baonza V G, Taravillo M, Caceres M, et al. Universal Features of the Equation of State of Solids from a Pseudospinodal Hypothesis [J]. Phys Rev B, 1996, 53(9): 5252-5258.

[13] Taravillo M, Baonza V G, Caceres M, et al. Simple Equation of State for Solids under Compression [J]. Phys Rev B, 1996, 54(10): 7034-7045.

[14] Taravillo M, Baonza V G, Rubio M, et al. The Temperature Dependence of the Equation of State at High Pressures Revisited: A Universal Model for Solids [J]. J Phys Chem Solids, 2002, 63(9): 1705-1715.

[15] Brosh E, Makov G, Shneck R Z. The Spinodal Constraint on the Equation of State of Expanded Fluids [J]. J Phys: Condens Matter, 2003, 15(19): 2991-3001.

[16] Sushil B R, Papiya B R. An Equation of State Applied to Solid up to 1 TPa [J]. J Phys: Condens Matter, 1999, 11 (50): 10375-10391.

[17] Holzapfel W B. Physics of Solids under Strong Compression [J]. Reports on Progress in Physics, 1996, 59 (1): 29-90.

[18] Holzapfel W B. Equations Comment on "Energy and Pressure versus Volume of State Motivated by the Stabilized Jellium Model" [J]. Phys Rev B, 2003, 67(2): 026102-026104.

[19] Sun J X, Wu Q, Cai L C, et al. Two Universal Equations of State for Solids Satisfying the Limiting Condition at High Pressure [J]. J Phys Chem Solids, 2005, 66(5): 773-782.

[20] Wang Zh Ch. Thermodynamics and Statistical Physics [M]. 3rd ed. Beijing: Higher Education Press, 2003: 309-317. (in Chinese).
汪志诚. 热力学·统计物理 [M]. 第三版. 北京: 高等教育出版社, 2003: 309-317.

[21] Nellis W J. Shock Compression of a Free-Electron Gas [J]. J App Phys, 2003, 94(1): 272-275.

对爱因斯坦模型的修正及考虑热效应的三个通用状态方程

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摘要:对固体考虑热效应的爱因斯坦模型进行了修正。指出考虑热效应的通用状态方程中不应该包含零点振动项,方程参数不应该直接取为参考温度下的实验值 V_R、B_R、B'_R 和 γ_R^G,而应该取为零温下的数值 V_0、B_0、B'_0 和 γ_0^G;提出了一种从 V_R、B_R、B'_R 和 γ_R^G 求解 V_0、B_0、B'_0 和 γ_0^G 的方法。将提出的方法应用于三个典型的通用状态方程,包括 Baonza、mMNH 和 Vinet 方程。数值结果表明,利用相同的实验参数对三个方程解出的参数,以及预测的零压和低压下的热物理性质差异很小,而且都与实验数据符合很好。这些结果表明,在零压和低压下预测热物理性质的精确度不足以用来判断各种通用状态方程的适用性。

关键词:状态方程;高压;热物理性质;热膨胀

中图分类号:O521.2 **文献标识码**:A

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