

EQUATION OF STATE AND THERMODYNAMIC PROPERTIES OF BCC METALS

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ABSTRACT

The moment method in statistical dynamics is used to study the equation of state and thermodynamic properties of the bcc metals taking into account the anharmonicity effects of the lattice vibrations and hydrostatic pressures. The explicit expressions of the lattice constant, thermal expansion coefficient, and the specific heats C_V, C_P of the bcc metals are derived within the fourth order moment approximation. The thermodynamic quantities of W, Nb, Fe, and Ta metals are calculated as a function of the pressure, and they are in good agreement with the corresponding results obtained from the first principles calculations and experimental results. The effective pair potentials work well for the calculations of bcc metals.

1. INTRODUCTION

The study of high pressure behaviour of materials has become quite interesting in recent years since the discovery of new crystal structures and due to many geophysical and technological applications. A lot of theoretical models have been proposed in order to predict the P - V - T equation of state (EQS) at the high pressure domain. Using the input data as the volume V_0 , the bulk modulus B_{T0} , etc., at the available low-pressure, these EQS models predict the high-pressure behaviours of materials. However, the results obtained from these semi-empirical models depend on the input data and the kinds of model.

So far, most path integral Monte Carlo (PIMC) [1, 2] and path integral molecular dynamic (PIMD) [3, 4] have been restricted to the calculation of structural and thermal properties of quantum solids or to the calculation of equations of state of condensed rare gases. Within the framework of the density-functional theory (DFT) [5], the thermodynamic properties of solids under a constant pressure can be calculated from the first-principles calculations. For ordered solids, the free energy at finite temperature has contributions from both the lattice vibrations and the thermal excitation of electrons. In the quasiharmonic approximation, the free energy is calculated by adding a *dynamical* contribution which is approximated by the free energy of a system of harmonic oscillators corresponding to the crystal vibrational modes (phonons)- to a *static* contribution- which is accessible to standard DFT calculations [6]. Vibrational modes are treated quantum mechanically, but the full Hamiltonian is approximated by a harmonic expansion about the equilibrium atomic

positions. Anharmonic effects are included through the explicit volume dependence of the vibrational frequencies. The *static* high pressure properties of the transition metals (for example tantalum with the body centred cubic (bcc) structure) obtained from the first principles by using the linearizing augmented plane wave (LAPW) method [7, 8]. Calculations based on various semi-empirical models [9 - 12] as well as on the first-principles methods [13 - 16] demonstrate that the quasiharmonic approximation provides a reasonable description of the dynamic properties of many bulk materials below the melting point.

In the present study, we use the moment method in statistical dynamic [17 - 20] to investigate the equation of state and thermodynamic properties of bcc metals. We will calculate the temperature and pressure dependence of the nearest neighbour distance and the thermodynamic properties of bcc metals.

The format of the present paper is as follows: In Sec. 2, the equation of state and the temperature and pressure dependence of thermodynamic properties of bcc metals are given. The calculation results of thermodynamic properties of W, Nb, Fe and Ta metals at various pressures are presented and discussed in Sec. 3 .

2. EQUATION OF STATE OF BCC METALS

2.1. Pressure versus volume relation

The pressure versus volume relation of the lattice is [17]

$$Pv = -a \left[\frac{1}{6} \frac{\partial U_o}{\partial a} + \theta x \coth x \frac{1}{2k} \frac{\partial k}{\partial a} \right] \quad (1)$$

where $x = \frac{\hbar\omega}{2\theta}$, $\theta = k_B T$, and P denotes the hydrostatic pressure and v is the atomic volume $v =$

V/N of the crystal, being $v = \frac{4}{3\sqrt{3}} a^3$ for the bcc lattice. Using eq.(1), one can find the nearest

neighbour distance a at pressure P and temperature T . However, for numerical calculations, it is convenient to determine firstly the nearest neighbour distance $a(P,0)$ at pressure P and at absolute zero temperature $T = 0$. For $T = 0$ temperature, eq. (1) is reduced to

$$Pv = -a \left[\frac{1}{6} \frac{\partial U_o}{\partial a} + \frac{\hbar\omega_o}{4k} \frac{\partial k}{\partial a} \right]. \quad (2)$$

For simplicity, we take the effective pair interaction energy in metal systems as the power law, similar to the Lennard-Jones

$$\varphi(r) = \frac{D}{(n-m)} \left[m \left(\frac{r_o}{r} \right)^n - n \left(\frac{r_o}{r} \right)^m \right] \quad (3)$$

where D, r_o are determined to fit to the experimental data (e.g., cohesive energy and elastic modulus). For bcc metals we take into account the first nearest, second, third, fourth and fifth nearest neighbour interactions.

Using the effective pair potentials of Eq.(3), it is straightforward to get the interaction energy U_o and the parameter k in the crystal as

$$U_o = \frac{D}{(n-m)} \left[mA_n \left(\frac{r_o}{a} \right)^n - nA_m \left(\frac{r_o}{a} \right)^m \right], \quad (4)$$

$$\begin{aligned}
k &= \frac{1}{2} \sum_i \left(\frac{\partial^2 \varphi}{\partial u_{i\beta}^2} \right)_{eq} \\
&= \frac{Dnm}{2a^2(n-m)} \left\{ \left[(n+2)A_{n+4}^{a_{ix}^2} - A_{n+2} \left(\frac{r_o}{a} \right)^n \right] - \left[(m+2)A_{m+4}^{a_{ix}^2} - A_{m+2} \left(\frac{r_o}{a} \right)^m \right] \right\} \\
&= m_0 \omega_0^2,
\end{aligned} \tag{5}$$

where m_0 is the mass of particle, ω_0 is the frequency of lattice vibration, and $A_n, A_m, \dots$ are the structural sums for the given crystal and defined by

$$\begin{aligned}
A_n &= \sum_i \frac{Z_i}{v_i^n}; \quad A_m = \sum_i \frac{Z_i}{v_i^m} \\
A_n^{a_{ix}^2} &= \frac{1}{a^2} \sum_i \frac{Z_{i,x} a_{ix}^2}{v_i^n}
\end{aligned} \tag{6}$$

here Z_i is the coordination number of i -th nearest neighbour atoms with radius r_i (for bcc lattice $r_k = v_k a_0$)

$$\begin{aligned}
v_1 &= 1, \quad Z_1 = 8; \quad v_2 = \sqrt{\frac{4}{3}}, \quad Z_2 = 6 \\
v_3 &= \sqrt{\frac{8}{3}}, \quad Z_3 = 12; \quad v_4 = \sqrt{\frac{11}{3}}, \quad Z_4 = 24 \\
v_5 &= 2, \quad Z_5 = 24, \dots
\end{aligned}$$

For bcc crystals, structural sums equal to

$$\begin{aligned}
A_n &= 8 + \frac{6}{\left(\sqrt{\frac{4}{3}} \right)^n} + \frac{12}{\left(\sqrt{\frac{8}{3}} \right)^n} + \frac{24}{\left(\sqrt{\frac{11}{3}} \right)^n} + \frac{8}{2^n}, \\
A_n^{a_{ix}^2} &= \frac{8}{3} + \frac{8}{3 \left(\sqrt{\frac{4}{3}} \right)^n} + \frac{32}{3 \left(\sqrt{\frac{8}{3}} \right)^n} + \frac{88}{3 \left(\sqrt{\frac{11}{3}} \right)^n} + \frac{22}{3 \cdot 2^n}.
\end{aligned} \tag{7}$$

From eqs. (2), (4), and (6) we obtain equation of state of bcc crystal at zero temperature

$$\begin{aligned}
Pv &= \frac{Dnm}{6(n-m)} \left[A_n \left(\frac{r_o}{a} \right)^n - A_m \left(\frac{r_o}{a} \right)^m \right] + \\
&\frac{1}{a} \frac{\hbar}{4\sqrt{m}} \sqrt{\frac{Dnm}{2(n-m)}} \frac{\left\{ (n+2) \left[(n+2)A_{n+4}^{a_{ix}^2} - A_{n+2} \left(\frac{r_o}{a} \right)^n \right] - (m+2) \left[(m+2)A_{m+4}^{a_{ix}^2} - A_{m+2} \left(\frac{r_o}{a} \right)^m \right] \right\}}{\sqrt{\left[(n+2)A_{n+4}^{a_{ix}^2} - A_{n+2} \left(\frac{r_o}{a} \right)^n \right] - \left[(m+2)A_{m+4}^{a_{ix}^2} - A_{m+2} \left(\frac{r_o}{a} \right)^m \right]}}.
\end{aligned} \tag{8}$$

Equation (8) can be transformed to the form

$$P \cdot \frac{4}{3\sqrt{3}} r_o^3 = c_1 y^{n+3} - c_2 y^{m+3} + \frac{c_3 y^{n+4} - c_4 y^{m+4}}{\sqrt{c_5 y^n - c_6 y^m}}, \quad (9)$$

where $y = \frac{r_o}{a}$,

$$\begin{aligned} c_1 &= A_n \cdot \frac{Dnm}{6(n-m)} \\ c_2 &= A_m \cdot \frac{Dnm}{6(n-m)} \\ c_3 &= \frac{\hbar}{4\sqrt{m_o}} \sqrt{\frac{Dnm}{2(n-m)}} (n+2) \left[(n+2) A_{n+4}^{a_{ix}^2} - A_{n+2} \right] \frac{1}{r_o} \\ c_4 &= \frac{\hbar}{4\sqrt{m_o}} \sqrt{\frac{Dnm}{2(n-m)}} (m+2) \left[(m+2) A_{m+4}^{a_{ix}^2} - A_{m+2} \right] \frac{1}{r_o} \\ c_5 &= (n+2) A_{n+4}^{a_{ix}^2} - A_{n+2} \\ c_6 &= (m+2) A_{m+4}^{a_{ix}^2} - A_{m+2}. \end{aligned} \quad (10)$$

In principle Eq. (9) permits to find the nearest neighbour distance $a(P,0)$ at zero temperature and pressure P . Using the MAPLE V program and the values of parameters D and r_o determined by the experimental data [21] (Table 1), Eq. (9) can be solved, we find the values of the nearest neighbour distance $a(P,0)$ at temperature $T = 0$ and pressure P . Calculated results for the nearest neighbour distance $a(P,0)$ of W, Nb, Ta and Fe metals at zero temperature and pressure P are presented in the Table 2.

2.2 Thermodynamic quantities of bcc metals at high pressure

For the calculation of the lattice spacing of the crystal at finite temperature and pressure P , we now need fourth order vibrational constants γ and k at pressure P and $T = 0$ K defined by

$$\gamma = \frac{1}{12} \sum_i \left[\left(\frac{\partial^4 \phi_{io}}{\partial u_{ix}^4} \right)_{eq} + 6 \left(\frac{\partial^4 \phi_{io}}{\partial u_{ix}^2 \partial u_{iy}^2} \right)_{eq} \right] \equiv 4(\gamma_1 + \gamma_2), \quad (11)$$

$$\gamma_1 = \frac{1}{48} \sum_i \left[\left(\frac{\partial^4 \phi_{io}}{\partial u_{ix}^4} \right)_{eq} \right]; \quad \gamma_2 = \frac{1}{48} \sum_i \left[6 \left(\frac{\partial^4 \phi_{io}}{\partial u_{ix}^2 \partial u_{iy}^2} \right)_{eq} \right]. \quad (12)$$

Using the effective pair potentials of Eq. (3), the parameter γ of the bcc crystal has the form

$$\gamma = \frac{Dnm}{12a^4(n-m)} \left\{ (n+2)(n+4)(n+6) \left(A_{n+8}^{a_{ix}^4} + 6A_{n+8}^{a_{ix}^2 a_{iy}^2} \right) - 18(n+2)(n+4) A_{n+6}^{a_{ix}^2} \right\}$$

$$\begin{aligned}
& +9(n+2)A_{n+4}\left[\frac{r_o}{a}\right]^n - \left[(m+2)(m+4)(m+6)\left(A_{m+8}^{a_{ix}^4} + 6A_{m+8}^{a_{ix}^2 a_{iy}^2}\right)\right. \\
& \left. - 18(m+2)(m+4)A_{m+6}^{a_{ix}^2} + 9(m+2)A_{m+4}\left[\frac{r_o}{a}\right]^m\right], \quad (13)
\end{aligned}$$

where the structural sums equal to

$$\begin{aligned}
A_n^{a_{ix}^4} &= \frac{1}{a^4} \sum_i \frac{Z_{i,x} a_{ix}^4}{v_i^n}; \quad A_n^{a_{ix}^2 a_{iy}^2} = \frac{1}{a^4} \sum_i \frac{Z_{i,xy} a_{ix}^2 a_{iy}^2}{v_i^n}, \\
A_n^{a_{ix}^4} &= \frac{8}{9} + \frac{32}{9\left(\sqrt{\frac{4}{3}}\right)^n} + \frac{128}{9\left(\sqrt{\frac{8}{3}}\right)^n} + \frac{664}{9\left(\sqrt{\frac{11}{3}}\right)^n} + \frac{128}{9.2^n}, \\
A_n^{a_{ix}^2 a_{iy}^2} &= \frac{8}{9} + \frac{64}{9\left(\sqrt{\frac{8}{3}}\right)^n} + \frac{152}{9\left(\sqrt{\frac{11}{3}}\right)^n} + \frac{128}{9.2^n}. \quad (14)
\end{aligned}$$

Using the obtained results of nearest neighbour distance $a(P,0)$ (Table 2) and Eqs. (5), (7), (13) and (14), we find the values of parameters $k(P,0)$, and $\gamma(P,0)$ at pressure P and T = 0K.

The thermally induced lattice expansion $y_o(P,T)$ at pressure P and temperature T is given in a closed formula using the force balance criterion of the fourth order moment approximation as [17, 18]

$$y_o^2(P,T) = \frac{2\gamma(P,0)\theta^2}{3k^3(P,0)} A(P,T) \quad (15)$$

where

$$\begin{aligned}
A(P,T) &= a_1 + \frac{\gamma(P,0)^2 \theta^2}{k(P,0)^4} a_2 + \frac{\gamma(P,0)^3 \theta^3}{k(P,0)^6} a_3 + \frac{\gamma(P,0)^4 \theta^4}{k(P,0)^8} a_4, \quad (16) \\
a_1 &= 1 + \frac{x \coth x}{2}, \\
a_2 &= \frac{13}{3} + \frac{47}{6} x \coth x + \frac{23}{6} x^2 \coth^2 x + \frac{1}{2} x^3 \coth^3 x, \\
a_3 &= -\left(\frac{25}{3} + \frac{121}{6} x \coth x + \frac{50}{3} x^2 \coth^2 x + \frac{16}{3} x^3 \coth^3 x + \frac{1}{2} x^4 \coth^4 x\right), \\
a_4 &= \frac{43}{3} + \frac{93}{2} x \coth x + \frac{169}{3} x^2 \coth^2 x + \frac{83}{3} x^3 \coth^3 x + \frac{22}{3} x^4 \coth^4 x + \frac{1}{2} x^5 \coth^5 x, \\
x &= \frac{\hbar \omega(P,0)}{2\theta}, \omega(P,0) = \sqrt{\frac{k(P,0)}{m_0}}. \quad (17)
\end{aligned}$$

Then, one can find the nearest neighbour distance $a(P,T)$ at pressure P and temperature T as

$$a(P,T) = a(P,0) + y_o(P,T). \quad (18)$$

Using the above formula of distance $a(P, T)$, we can find the change of the crystal volume at temperature T as

$$\frac{\Delta V}{V} = \frac{a^3(P, T) - a^3(P, 0)}{a^3(P, 0)}. \quad (19)$$

Let us now consider the compressibility of the solid phase (bcc metals). The isothermal compressibility can be given as

$$\chi_T = \frac{3 \left(\frac{a(P, T)}{a(P, 0)} \right)^3}{2P + \frac{\sqrt{3}}{4a(P, T)N} \left(\frac{\partial^2 \Psi}{\partial a^2} \right)_T} \quad (20)$$

Furthermore, from the definition of the linear thermal expansion coefficient, one obtains the following formula

$$\alpha = \frac{k_B \chi_T}{3} \left(\frac{\partial P}{\partial \theta} \right)_V = - \frac{\sqrt{3} k_B \chi_T}{4a^2} \frac{1}{3N} \frac{\partial^2 \Psi}{\partial \theta \partial a}. \quad (21)$$

We find the free energy Ψ of the crystal using the statistical moment method as [17, 19]

$$\begin{aligned} \Psi \approx 3N & \left\{ \frac{1}{6} U_0 + \theta [x + \ln(1 - e^{-2x})] \right\} + \\ & + \frac{3N\theta^2}{k^2} \left\{ \gamma_2 x^2 \coth^2 x - \frac{2\gamma_1}{3} \left(2 + \frac{x \coth x}{2} \right) + \frac{2\theta}{k^2} \left[\frac{4}{3} \gamma_2 x \coth x \left(1 + \frac{x \coth x}{2} \right) \right. \right. \\ & \left. \left. - 2(\gamma_1^2 + 2\gamma_1 \gamma_2) \left(1 + \frac{x \coth x}{2} \right) (1 + x \coth x) \right] \right\}. \end{aligned} \quad (22)$$

Then, the energy of the crystal equal to

$$E \approx 3N \left\{ \frac{1}{6} U_0 + \theta x \coth x \right\} + \frac{3N\theta^2}{k^2} \left\{ \gamma_2 x^2 \coth^2 x + \frac{\gamma_1}{3} \left(2 + \frac{x^2}{\sinh^2 x} \right) - 2\gamma_2 \frac{x^3 \coth x}{\sinh^2 x} \right\}, \quad (23)$$

where U_0 represents the sum of effective pair interaction energies and the second term in the above Eq. (23) given the contribution from the anharmonicity of thermal lattice vibrations and the fourth order vibrational constants γ_1, γ_2 defined by Eq. (12). Then, the specific heat at constant volume C_V is given by

$$C_V = 3Nk_B \left\{ \frac{x^2}{\sinh^2 x} + \frac{2\theta}{k^2} \left[\left(2\gamma_2 + \frac{\gamma_1}{3} \right) \frac{x^3 \coth x}{\sinh^2 x} + \frac{\gamma_1}{3} \left(1 + \frac{x^2}{\sinh^2 x} \right) - \gamma_2 \left(\frac{x^4}{\sinh^4 x} + \frac{2x^4 \coth^2 x}{\sinh^2 x} \right) \right] \right\} \quad (24)$$

The specific heat at constant pressure C_P , the adiabatic compressibility χ_S , and isothermal bulk moduli B_T are determined from the well known thermodynamic relations

$$C_P = C_V + \frac{9TV\alpha^2}{\chi_T}, \quad \chi_S = \frac{C_V}{C_P} \chi_T, \quad \text{and} \quad B_T = \frac{1}{\chi_T}. \quad (25)$$

One can now apply the above formulae to study the thermodynamic properties of bcc metals under hydrostatic pressures. The pressure dependences of the crystal volume, isothermal compressibility, specific heats and the linear thermal expansion coefficient are calculated self-consistently with the lattice spacing of the given bcc crystals.

3. RESULTS AND DISCUSSION

In order to check the validity of the present moment method for the study of the thermodynamic properties of the metallic systems described herein, we performed calculations for pure metals W, Ta, Fe and Nb. Using the experimental data of the parameters D and r_0 (Table 1), and the MAPLE V program, Eq.(9) can be solved, we find the values of the nearest neighbour distance $a(P, 0)$ at temperature $T = 0$ and pressure P for W, Ta, Fe, and Nb metals. Using the obtained results of the nearest neighbor distance $a(P, 0)$ (Tables 2) and Eqs. (5), (13), we find the values of parameters $k(P, 0)$, and $\gamma(P, 0)$ at pressure P and temperature $T = 0$ K.

Table 1: Parameter D and r_0 determined by the experimental data [21]

metal	n	m	$D/k_B(K)$	$r_0(\text{\AA})$
W	11	4	11278.8	2.7365
Ta	12	4	8508.1	2.8648
Fe	10	4,5	4649.6	2.4775
Nb	9	4	8307.3	2.8648

Table 2: Calculated results for the nearest neighbour distance $a(P, 0)$ at zero temperature and pressure P

$P(\text{GPa})$	0	25	50	100	150	200	250	300
W	2.65810	2.60516	2.56788	2.51506	2.47719	2.44756	2.42318	2.40245
Ta	2.78708	2.71489	2.66884	2.60737	2.56511	2.53277	2.50656	2.48451
Fe	2.40855	2.33255	2.28627	2.22589	2.17497	2.15390	2.12882	2.10778
Nb	2.77483	2.68292	2.62648	2.55262	2.50249	2.46439	2.43363	2.40784

With the use of the expressions obtained in Sec. 2, we calculate the values of the lattice constant, a , the bulk modulus, B_T , the specific heats at constant volume and constant pressure, C_V and C_P , and the linear thermal expansion coefficient, α for W, Ta, Fe and Nb metals. The calculated results are presented in Tables 3 - 8 and Figs. 1- 4.

Table 3 shows the lattice constants and bulk moduli for all of the bcc metal studied here, comparing them to first-principles LDA calculations, the tight-binding (TB) results [23], and to experiment [24, 25]. The lattice constant and bulk modulus at temperature $T = 300$ K and zero pressure calculated by the present theory are in good agreement with the first-principles results and experimental data. The lattice constant is within 2% of the SMM values for all of the bcc metals. Similarly, the bulk moduli are in excellent agreement with the experimental results, within < 1% for W, Fe, and Nb metals except tantalum, where the error is 9%. We note that for the bulk moduli of W, Fe and Nb metals, the present calculations give much better results

compared to those by previous theoretical calculations.

Table 3: Calculated results for the lattice constant, a , and bulk modulus, B_T , at $T = 300$ K and $P = 0$, comparing the results of tight-binding parametrization (TB), first-principles local density approximation (LDA) [23] results and experiment (Expt.) (Refs. 24 and 25)

	a (Å)				B_T (GPa)			
	SMM	TB	LDA	Expt.	SMM	TB	LDA	Expt.
W	3.0754	3.14	3.14	3.16	320.034	319	333	323
Ta	3.2298	3.30	3.24	3.30	218.626	185	224	200
Fe	2.7924	2.71	----	2.87	170.088	281	---	168
Nb	3.2130	3.25	3.25	3.30	169.125	187	193	170

In Table 4 we compare with the first-principles calculations and experiment the zero pressure volume, V_0 , and the bulk moduli, B_T for Ta and W metals. We show in Table 4 the results obtained by A. Strachan *et al.* [26] using the linearized augmented plane wave method with the GGA (denoted as LAPW-GGA) and the Embedded Atom Model force fields (named qEAM FF), and zero temperature calculations using full potential linear muffintin orbital method within the GGA approximation and with spin orbit interactions (denoted as FP LMTO GGA SC) by S Ö derlind and Moriarty [27]. The results obtained by Y. Wang *et al.* [29] using the density-functional theory (denoted as DFT), and room temperature experimental values by Cynn, Yoo [28] and A Dewaele *et al.* [30] are also presented in Table 4. The present SMM calculations of the bulk modulus and zero pressure volume at absolute zero and room temperatures agree well with the experimental values and previous theoretical calculations. The zero pressure volume, V_0 , is in excellent agreement with the experimental results, within $\sim 0.5\%$ for W metal except tantalum, where the error is $\sim 6\%$.

Table 4: Comparison between *ab initio*, present study (SMM) and experimental results for Ta and W metals

		T(K)	V_0 (Å ³)	B_T (GPa)	Ref.
Ta	LAPW-GGA	0	18.33	188.27	26
	qEAM FF	0	18.36	183.04	26
	FP LMTO GGA SC	0	17.68	203	27
	SMM	0	16.67	---	present
	qEAM FF	300	18.40	176	
	Expt.	300	18.04	194.7 ± 4.8	28
	SMM	300	16.81	218.626	present
W	DFT		16.26		29
	SMM		15.775		present
	Expt.		15.862		30

The Figs. 1 and 2 show the ratio $V/V_0 = \frac{V}{V_0} = \left(\frac{a(P,T)}{a(0,T)} \right)^3$, and bulk moduli for W, Nb and Ta metals as the functions of the pressure P . The present SMM calculations for the ratio V/V_0 are in good agreement with experimental results which taken from McQueen *et al* [31] for Nb and Ta; and from McQueen and Marsh [32] for W. The lattice constants decrease due to the effect of increasing pressure, therefore the bulk modulus becomes larger. The Fig. 3 shows the bulk modulus B_T of the W, Nb and Ta metals as a function of the temperature T at various pressures P . We have found that the bulk modulus, B_T depends strongly both on the temperature and the pressure. The decrease of B_T with increasing temperature arises from the thermal lattice expansion and the effects of the vibration entropy.

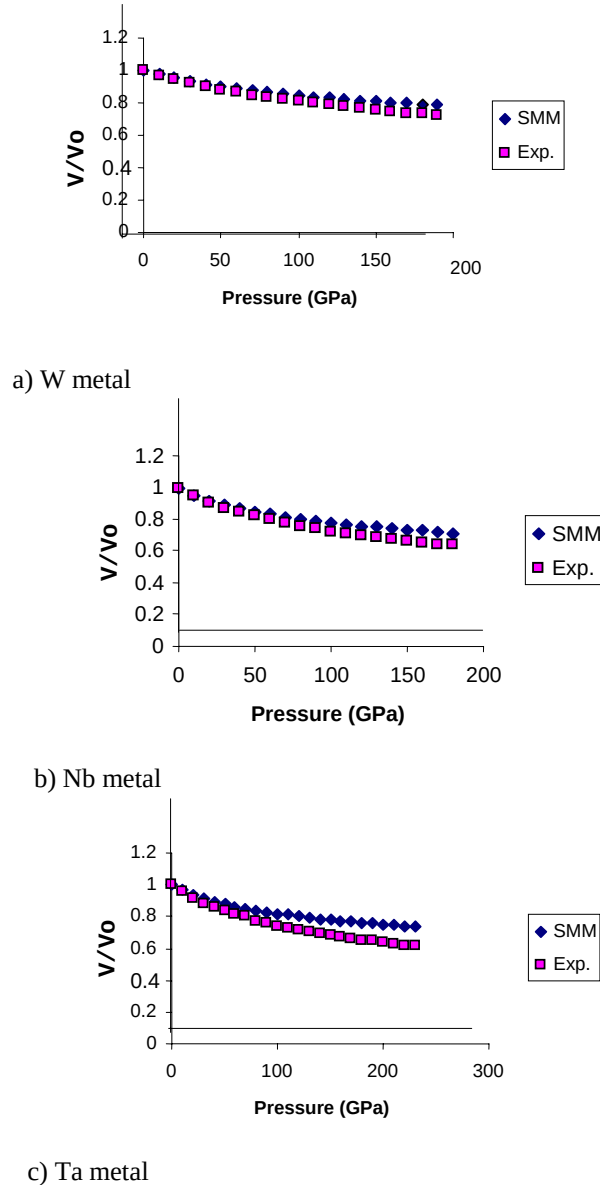
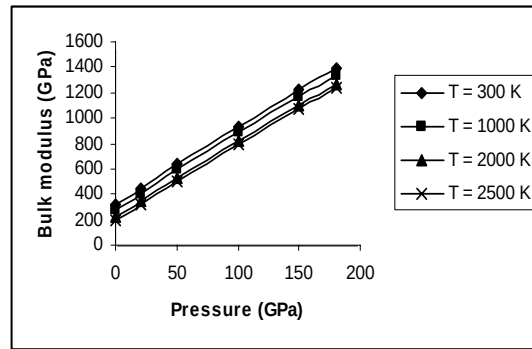
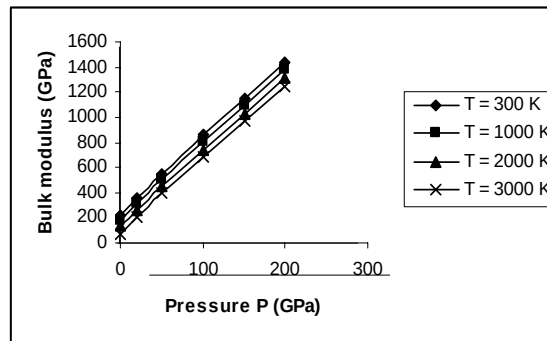


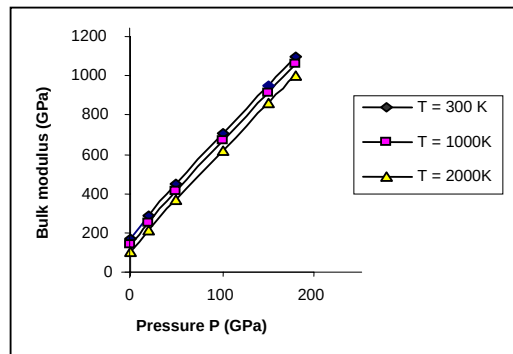
Fig. 1: Pressure dependence of the ratio of V/V_0 for W, Nb and Ta metals



a) W



b) Ta

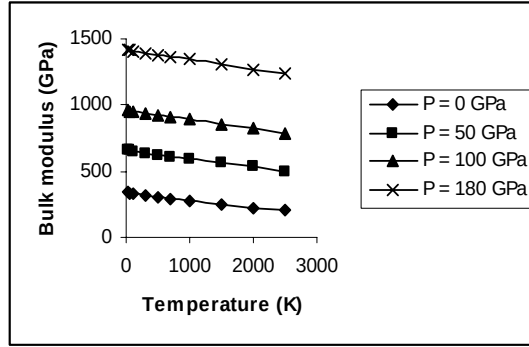


c) Nb

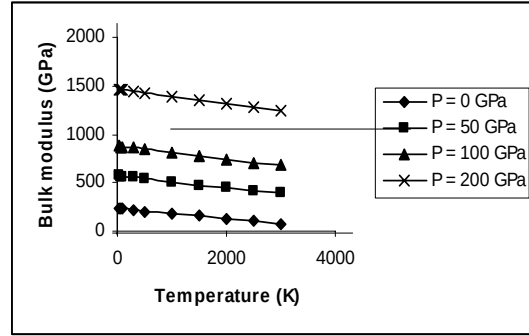
Fig. 2: Pressure dependence of the bulk modulus for W, Nb and Ta metals at various temperatures T

Table 5 shows the specific heats at constant volume and constant pressure, C_V, C_P , calculated by the present SMM calculations for the W, Nb and Ta metals, comparing them to experiment [22]. The present SMM calculations for C_P are in good agreement with the experimental results. The lattice specific heats C_V and C_P at constant volume and at constant pressure are calculated

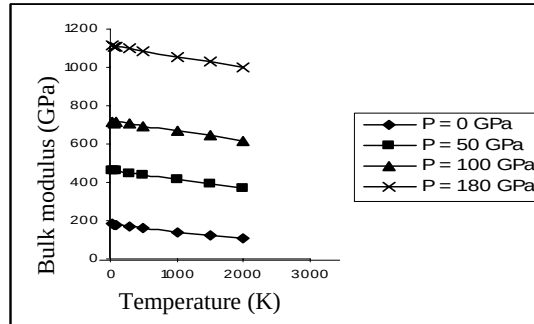
using Eqs. (24) and (25), respectively. However, the evaluations by Eqs. (24) and (25) are the lattice contributions, and we do not include the contributions of lattice vacancies and electronic parts of the specific heats C_V . The calculated values of the lattice specific heats C_V and C_p by the present SMM may not be directly compared with the corresponding experimental values for high temperature region near the melting temperature, but the temperature dependence (curvature) of C_p for the W, Nb and Ta metals is in agreement with the experimental results.



a) W



b) Ta



c) Nb

Fig. 3: Temperature dependence of the bulk modulus for W, Nb and Ta metals at various pressures P

Table 5: Thermodynamic quantities of W, Nb, and Ta metals at pressure $P = 0$ and temperature T

T(K)	200	300	500	600	800	1200	1500	2000	2500	3000
W										
$C_V(\text{cal/mol.K})$	5.45	5.67	5.75	5.76	5.73	5.65	5.59	5.48	5.36	5.24
$C_P(\text{cal/mol.K})$	5.54	5.82	6.01	6.07	6.15	6.29	6.39	6.56	6.72	6.92
Expt.[22]	---	---	6.09	---	6.34	---	6.91	7.33	7.74	8.15
Nb										
$C_V(\text{cal/mol.K})$	5.39	5.63	5.72	5.71	5.68	5.57	5.49	5.34		
$C_P(\text{cal/mol.K})$	5.52	5.85	6.10	6.18	6.32	6.55	6.72	7.02		
Expt.[22]	---	5.95	---	6.24	6.43	6.81	---	7.58		
Ta										
$C_V(\text{cal/mol.K})$	5.54	5.69	5.73	5.71	5.67	5.55	5.46	5.30	5.14	4.98
$C_P(\text{cal/mol.K})$	5.66	5.89	6.07	6.12	6.22	6.39	6.51	6.73	7.06	8.05
Expt.[22]	5.75	6.08	6.38	6.46	6.57	6.76	6.90	7.11		

The variations in temperature of the specific heat at constant pressure, C_p , reported in Table 6, show that the specific heat C_p depends strongly on the temperature. Table 7 shows indeed that the specific heat at constant pressure, C_p , is a strong function of pressure for W, Nb and Ta metals.

Table 6: Temperature dependence of the specific heat C_p for Ta, W, and Nb metals at various pressures P .

Metal s	T(K) P(GPa)	100	300	500	700	1000	1500	2000	2500
Ta	50	3.6173	5.6529	5.8903	5.9758	6.0485	6.1442	6.2475	6.3684
	100	2.9697	5.5122	5.8290	5.9348	6.0127	6.0951	6.1701	6.2518
W	50	3.3908	5.5978	5.8545	5.9398	6.0030	6.0717	6.1368	6.2096
	100	2.8305	5.4718	5.8033	5.9098	5.9825	6.0504	6.1057	6.1625
Nb	50	2.7711	5.4573	5.7972	5.9060	5.9797	6.0495	6.1095	6.1741
	100	2.0821	5.2584	5.7173	5.8618	5.9539	6.0290	6.0829	6.1346

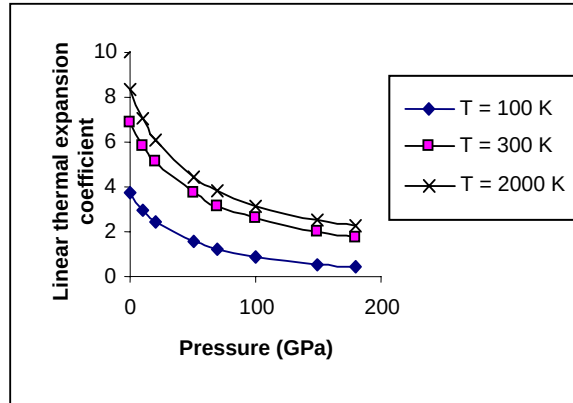
Table 7: Pressure dependence of the specific heat C_p for W, Nb and Ta metals at various temperatures T

Metals	T(K)	P(GPa)				
		0	25	50	100	150
W	300	5.8200	5.6672	5.5978	5.4718	5.3577
	1000	6.2201	6.1123	6.0030	5.9825	5.9638
	2500	6.7203	6.3409	6.2096	6.1625	6.1317
Nb	300	5.8504	5.5705	5.4573	5.2584	5.0833
	1000	6.4340	6.1893	5.9797	5.9539	5.9292
	2000	7.0207	6.4209	6.1095	6.0829	6.0621
Ta	300	5.8905	5.7318	5.6529	5.5122	5.3861
	1000	6.3043	6.1721	6.0485	6.0127	5.9857
	2500	7.0602	6.5743	6.3684	6.2518	6.1912

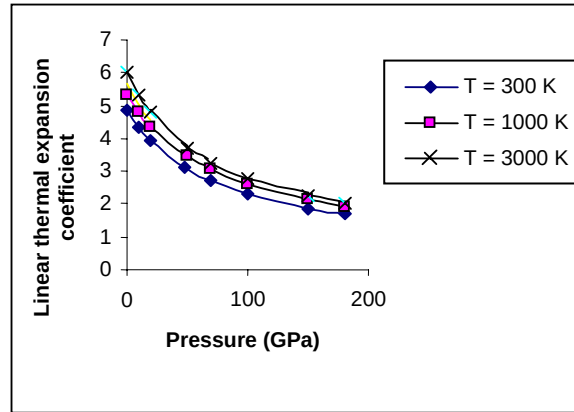
In Table 8, we show the linear thermal expansion coefficient for Nb and Ta metals at various pressure a function of temperature, T , obtained from our calculations, as well as the experimental values at zero pressure [22]. The present SMM calculations for the linear thermal expansion coefficient are in good agreement with the experimental results. The present formalism takes into account the quantum-mechanical zero-point vibrations as well as the higher-order anharmonic terms in the atomic displacements and it enables us to derive the thermodynamic quantities of the bcc metals for a wide temperature range. Fig. 4 shows that the thermal expansivity as a function of pressure. Theory predicts the thermal expansivity to drop rapidly with pressure, and the temperature dependence to decrease. These results are in good agreement with the first-principles calculations reported by R. E. Cohen and O. Gulsenren [16].

Table 8: Temperature dependence of the linear thermal expansion coefficient for Nb and Ta metals at various pressures P (in $10^{-6} K^{-1}$)

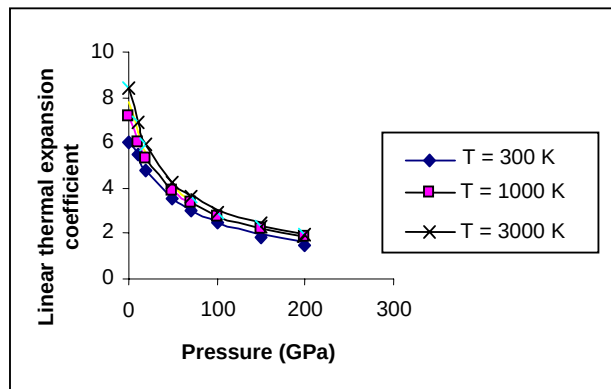
Metals	P(GPa)	T(K)										
		100	300	500	600	800	1000	1200	1600	1900	2000	2500
Nb	0	3.85	7.01	7.41	7.65	7.78	7.85	8.05	8.27	8.55	8.60	8.93
	Expt.[22]	4.30	7.00	---	7.90	8.30	---	8.90	9.90	10.0	---	---
	50	1.50	3.80	4.00	4.05	4.10	4.15	4.20	4.35	4.42	4.45	4.55
	100	0.92	2.83	2.95	3.00	3.05	3.10	3.15	3.22	3.25	3.27	3.32
	150	0.65	2.45	2.55	2.60	2.65	2.70	2.75	2.82	2.85	2.87	2.92
Ta	0	4.43	6.15	6.80	7.05	7.18	7.28	7.42	7.58	7.69	7.82	8.18
	Expt.[22]	---	---	6.80	---	7.10	7.30	---	---	---	8.40	---
	50	2.01	3.65	3.85	3.86	3.88	3.90	3.93	3.96	3.99	4.00	4.04
	100	1.05	2.42	2.66	2.68	2.70	2.71	2.74	2.77	2.78	2.79	2.83



a) Nb



b) W



c) Ta

Fig. 4: Pressure dependence of the linear thermal expansion coefficient for Nb, W and Ta metals at various temperatures T (in $10^{-6} K^{-1}$)

4. CONCLUSION

The SMM calculations are performed by using the effective pair potential for the W, Fe, Nb and Ta metals. The use of the simple potentials is due to the fact that the purpose of the present study is to gain a general understanding of the effects of the anharmonicity of the lattice vibration and pressure on the thermodynamic properties for the bcc metals.

In the present study, we have used effective pair potentials for metal atoms to demonstrate the utility of the present theoretical scheme based on the moment method in the statistical dynamics. The method is simple and physically transparent, and thermodynamic quantities of metals with bcc structures can be expressed in closed forms within the fourth order moment approximation of the atomic displacements. The present formalism is not restricted to the applications of the effective pair potentials, but it is also incorporated with the energetics based on the ab initio electronic theory. In general, we have obtained good agreement in the thermodynamic quantities between our theoretical calculations and first-principles results, and experimental values.

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