



Analytic Pair Potential Functions for the Calculation of Thermal Expansion Coefficient of Body Centercubic Metals

KEYWORDS

Coefficient of thermal expansion, lattice constants, Pair Potential, Anharmonic Oscillator, Low and High Temperatures.

Abajingin David Dele

Department of Physics and Electronics Adekunle Ajasin University. Akungba- Akoko, Ondo-State. Nigeria.

ABSTRACT

In this study, atoms are considered to be related to one another by inter atomic forces which are considered as a networks of anharmonic oscillators. The corresponding oscillations are here described by a first order polynomial modulated by a simple exponential anharmonic potential function. Using this function, an expression for the coefficient of thermal expansion which depends on the parameters of this function was developed and used to calculate the of some selected body centered cubic, (bcc) at room temperatures. The sensitivity of the calculated values on the cutoff radius of the interatomic radius was equally investigated.

A temperature dependent pair potential function was developed, and validated with some selected bcc metals to generate the functional fit for the variation of () with increase in temperature. The parameters in this pair potential function were fitted to the experimental values of lattice constant, the internal energy and the bulk modulus of the selected cubes. The values of the coefficient of thermal expansion () of cubic metals at room temperature with cutoff interatomic radius showed a good agreement with both experimental values and some theoretical values. The functional fit for the variation of () with increase in temperature equally showed a good agreement with the experimental curve fit.

1. INTRODUCTION

In a cubic metal, the atoms arrange themselves in a regular pattern so that the potential energy of the system is minimal. They are rigidly fixed but vibrate about their respective equilibrium position with amplitude that goes on increasing with rise in temperature which expresses the thermal expansion of metals. This vibrational concept of the atoms has severally being described by anharmonic potentials functions [1]. Many authors have independently used anharmonic potentials functions to calculate some temperature dependent properties of some cubic metals to a high degree of accuracy, [2-6]. Here a modulated first order pair potential function is developed to describe the anharmonicity of vibrating paired atoms for the purpose of calculating the coefficient of thermal expansion (CTE, α) of cubic metals at room temperature.

One of the major problems encountered when a generalized method is developed for (CTE, α) calculation is how to factor in the contributions of phonons to the free energy. This problem was resolved by the molecular-dynamics methods. The first principle model, based on this method developed a model that accounted for the contribution of phonons to the free energy

to estimate the thermal property of cubic metals.[7]. However, as the ionic degrees of freedom are treated classically, these methods are not applicable at a temperature lower than the Debye temperature [8]. The quasi-harmonic approximations model [9], built up from the lattice dynamics theory, have proved to be accurate when used to calculate the (CTE, α) of metals at both temperatures lower than the Debye temperature and at temperature far beyond the melting point of the material [10-14]. One major problem associated with this method is that of its mathematical complexity.

Semi empirical models, void of any mathematical complexity have evolved over the years. Such models include the embedded atom model (EAM), [15] the Finnis and Sinclair model (FS), [16], and method as developed by Moruzzi [17]. These models have been used successively to compute the temperature dependent thermal expansion coefficients (CTE, α) of metals at room temperature but failed to predict the variation of (CTE, α) with temperature variation. The simple-spring-single lattice model (SSSL)[18] evolved with its underlying principle on the molecular dynamics, was used by some author [19] to calculate the (CTE, α) of cubic metals. These authors had a set of results in good standing with the experiments values at room temperature for fcc metals but the results for bcc metals were at variance with those of the experimental values.

Thus, the aim of this study is to examine how the SSSL protocol can be improved upon, using a simple analytic pair potential function, and investigate the effect of cutoff radius on the values of (CTE, α) computed using the SSSL protocol for bcc metals. Since this study is equally aimed at developing a mathematical expression for (CTE, α) based only on the parameters of the pair potential function used in this study, it is necessary to re-define the concept of change in length of a metallic cubic within molecular frame work when there is a change in temperature. The curve variation of (CTE, α) with temperature is thereafter investigated within this virtualized concept.

2. THEORY

A modulated first order polynomial pair potential, of the form

$$\phi(r_{ij}) = \phi_e \left\{ 1 + \beta \left(\frac{r_{ij}}{r_c} - 1 \right) \right\} \exp \left(-\alpha \left(\frac{r_{ij}}{r_c} - 1 \right) \right), \quad \dots\dots\dots (1)$$

is used in this study to represent the interaction between two atoms in metallic cube and equally assumed to describe anharmonic oscillators. In this expression there are three adjustable parameters; (α, β and ϕ_e) and r_{ij} defines the atomic distance between atoms i and j .

The total energy, $E(a)$ in a molecular framework, for of a metallic system is obtained by summing equation (1) over the entire atoms within the system, thus the average energy of the system is given as;

$$E(a) = P \sum_j \left\{ 1 + \beta \left(\frac{M_j a}{r_c} - 1 \right) \right\} \exp \left(-\alpha \left(\frac{M_j a}{r_c} - 1 \right) \right) \dots\dots\dots (2)$$

where $P = -\frac{N\phi_e}{2}$; $r_j = \left[m_j^2 + n_j^2 + l_j^2 \right]^{1/2}$ $a = M_j a$, a is the lattice constant and where N is the Avogadro's number.

The first and the second derivatives of the energy of equation with respect to the lattice constant a are given by

$$\frac{dE(a)}{da} = P \sum_j \left\{ \frac{\beta M_j}{r_c} + \left[1 + \beta \left(\frac{M_j a}{r_c} - 1 \right) \right] \left(\frac{-\alpha M_j}{r_c} \right) \right\} \exp \left(-\alpha \left(\frac{M_j a}{r_c} - 1 \right) \right) \dots\dots\dots (3)$$

$$\frac{d^2 E(a)}{da^2} = P \sum_j \left\{ \frac{-\alpha \beta M_j^2}{r_c^2} + \left[\left[1 + \beta \left(\frac{M_j a}{r_c} - 1 \right) \right] \left(\frac{\alpha^2 M_j^2}{r_c^2} \right) + \frac{\beta \alpha^2 M_j^2}{r_c^2} \right] \right\} \exp \left(-\alpha \left(\frac{M_j a}{r_c} - 1 \right) \right) \dots\dots\dots (4)$$

At absolute zero, $T = 0$, $a = a_0$ the equilibrium lattice constant, equation (3) becomes

$$\left[\frac{dE(a)}{da} \right]_{a_0} = 0, \dots\dots\dots (5)$$

Also

$$B_0 = \frac{a_0}{9V_c} \left[\frac{d^2 E(a)}{da^2} \right]_{a_0} \dots\dots\dots (6)$$

where B_0 is the bulk modulus.

When $r_e = r_c$, equation (2) equally reduces to

$$\phi_e = 2E_c \left/ N \left[1 + \beta \left(\frac{M_j a_0}{r_c} - 1 \right) \right] e^{-\alpha \left(\frac{M_j a_0}{r_c} - 1 \right)} \right. \dots\dots\dots (7)$$

The parameters of our pair potential function are determined by using equations (5) to (7) and the lattice parameter, bulk modulus and the cohesive energy of the selected bcc metals.

3. EXPRESSION FOR THE COEFFICIENTS OF THERMAL EXPANSION AT ROOM TEMPERATURE

Two atoms are here assumed to be bonded together by an atomic pseudo spring with proper potential energy [18, 19]. The atoms are stationary at zero temperature and start to vibrate as the system temperature increases. If the temperature increased by T (K), the associated energy increase $\Delta E = E_2 - E_1$ can be represented by $k_B T / 2$, for a one dimensional diatomic motion, where k_B represents the Boltzmann's constant. The diatom vibrates with their repulsive and attractive vibration amplitude r_1 and r_2 , reaching an average linear displacement $(r_2 - r_1) / 2$. Therefore, the thermal expansion coefficient of the diatomic system is represented by the expression;

$$CTE = \left(\frac{r_2 - r_1}{2} \right) \left/ r_c T \right. \dots\dots\dots (9)$$

In terms of our potential function in equation (2), the energy increase becomes

$$-\phi_e \left[1 + \beta \left(\frac{r_{ij}}{r_c} - 1 \right) \right] e^{-\alpha \left(\frac{r_{ij}}{r_c} - 1 \right)} + \phi_e = \frac{1}{2} k_B T \dots\dots\dots (10)$$

By solving equation (11) the vibration amplitudes r_1 and r_2 are determined as

$$r_2 = \left[-\{\alpha - \beta\} + \sqrt{(\alpha - \beta)^2 + \left(\alpha \beta - \frac{\alpha^2}{2} \right) \left(\frac{k_B T}{2\phi_e} \right)} \right] \left/ 2 \left(\alpha \beta - \frac{\alpha^2}{2} \right) \right] r_c + r_c \dots\dots\dots (11)$$

$$= \left[-\{\alpha - \beta\} - \sqrt{(\alpha - \beta)^2 + \left(\alpha\beta - \frac{\alpha^2}{2}\right)\left(\frac{k_B T}{2\phi_e}\right)} \right] / 2\left(\alpha\beta - \frac{\alpha^2}{2}\right) r_c + r_c \dots\dots\dots (12)$$

The coefficient of thermal expansion can be deduced from r_2 and r_1 as

$$TE = \sqrt{\left\{(\alpha - \beta)^2 + 4\left(\alpha\beta - \frac{\alpha^2}{2}\right)\left(\frac{k_B T}{2\phi_e}\right)\right\}} / T^2\left(\alpha\beta - \frac{\alpha^2}{2}\right)^2 \dots\dots\dots (13)$$

Equation (13) shows that the coefficient of thermal expansion of metals depends solely on the three potential parameters.

4. TEMPERATURE DEPENDENT PAIR POTENTIAL FUNCTIONS

In order to fully describe the variation of CTE with temperature, a temperature related function $A(T)$, expressed as a fourth order polynomial, $a_0 + a_1T + a_2T^2 + a_3T^3 + a_4T^4$, is included in our pair potential function. The values of the constants, a_0, a_1, a_2, a_3 and a_4 , are curve fitted by the experimental data, [20-24]. Thus the pair potential function is now given as

$$\phi_{(r_{ij})} = -\phi_e \left[A(T) + \beta \left(\frac{r_{ij}}{r_c} - 1 \right) \right] e^{-\alpha \left(\frac{r_{ij}}{r_c} - 1 \right)} \dots\dots\dots (14)$$

Solving equation (14), the vibration amplitudes r_1 and r_2 are determined as

$$r_2 = \left[-\{\alpha A(T) - \beta\} + \sqrt{(\alpha A(T) - \beta)^2 + \left(\alpha\beta - \frac{\alpha^2 A(T)}{2}\right)\left(\frac{k_B T}{2\phi_e}\right)} \right] / 2\left(\alpha\beta - \frac{\alpha^2 A(T)}{2}\right) r_c + r_c \dots\dots\dots (15)$$

$$r_1 = \left[-\{\alpha A(T) - \beta\} - \sqrt{(\alpha A(T) - \beta)^2 + \left(\alpha\beta - \frac{\alpha^2 A(T)}{2}\right)\left(\frac{k_B T}{2\phi_e}\right)} \right] / 2\left(\alpha\beta - \frac{\alpha^2 A(T)}{2}\right) r_c + r_c \dots\dots\dots (16)$$

5. RESULTS AND DISCUSSION

Table 1 contains the calculated values of the pair potential parameters (α , β and ϕ_e), put together in columns 2, 3, and 4 and the physical experimental input parameters are put together in columns 6, 7 and 8. These physical inputs are cohesive energy E_c (eV), lattice constant, a (A) are taken from Bozzolo and Ferrante [25], Simmons and Wang [26] and bulk modulus, B ($in 10^{12} \text{ erg/cm}^3$) are taken from Rose, Smith and Ferrant [27], and Kittel [28]. The monovacancy formation energies E_{iv}^F are from Johnson and Oh [29].

The parameters of this pair potential functions are determined through several closed self-consistent form analytical equations, (1) - (6), within the molecular frame work. These values are thereafter used to calculate the coefficient of thermal expansion at room temperature using equation (13) with a cutoff radius r_c . The cut off radius was determined by fitting the first order modulated pair potential function into the total energy equation from the embedded atom model [15] to generate binding energy curves. A series of energy points were calculated around the equilibrium interatomic distance r_e . These energy points are referred to in this study as the cutoff radius r_c , and expressed as

$$r_c = r_e \pm n\% . r_e \dots\dots\dots (17)$$

where n is a certain percentage of r_e .

For bench make purposes, we have investigated the effect of $n = 0.5, 1.0, 1.5$ and 2 , on Mo, W and Na metals. The corresponding values of CTE are reflected in Table 2

Table 1.0. Calculated values for the parameters of pair potential function and the experimental physical inputs

Metals	α	β	ϕ_e (eV)	P (10^{-22})	E_c (eV)	a (Å)	B ($in 10^{12} \text{ erg / cm}^3$)
Cr	15.7479	16.9523	1.0218	-3.07709	4.100	2.880	1.901
Fe	14.4353	16.1642	1.0251	-3.08697	4.290	2.860	1.680
K	10.3134	13.1365	0.1894	-0.57041	0.934	5.225	0.032
Na	10.0026	12.8674	0.2725	-0.66996	1.113	4.225	0.068
Nb	13.3834	15.4807	1.7427	-5.24798	7.570	3.300	1.702
V	13.5071	15.5638	1.2279	-3.69797	5.310	3.030	1.570
W	16.2474	17.2369	2.1902	-6.59594	6.820	3.150	2.725
Mo	16.7503	17.5167	1.7494	-5.2684	8.660	3.160	3.230
Cs	10.9606	13.6782	1.6786	-5.05511	0.804	6.045	0.020
Rb	11.8033	14.3448	0.8844	-5.55260	0.852	5.585	0.031

Table 2 shows the effect of cut off radius on CTE for these three metals calculated from the modified SSSL equation, (13). From Table 2, it can be seen that the value of CTE is sensitive to the cutoff radius. For these three selected metals the variation of n from $\pm (0.5 \text{ to } 2)\%r_e$ leads to large change in CTE. By comparing with experimental values of CTE, we found that the best CTE was obtained with $r_c = r_e \pm 1\%r_e$. Our expectation in the use of cutoff radius was to see a convergence in the calculated values CTE from $rcut_{0.5}$ to $rcut_1$ to $rcut_{1.5}$ to $rcut_{2.0}$ as one fits the potential function through the energy points calculated within the cutoff radius leading to a physically more realistic description of the potential energy surface. However this is apparently not the case. In particular, the values of CTE for Na give a continuous decrease in value.

Table 2. Effect of cutoff radius on CTE ($\alpha, in 10^{-6} K^{-1}$) at room temperature with total energy calculated from the embedded atom model.

r_c	$r_{c0.5}$	r_{c1}	$r_{c1.5}$	$r_{c2.0}$	Expt.
α_{Mo}	24.1(1.51)	8.2(3.03)	4.73(4.57)	22.81(6.12)	9.8
α_w	24.1(1.51)	10.9(3.03)	47.3(4.57)	27.2(6.12)	6.91
α_{Na}	65.3(1.51)	66.73(3.03)	46.68(4.57)	35.16 (6.12)	70.2

Values in the bracket represent the percentage volume change with the cutoff radius r_{cutoff}

The effect of cutoff radius was equally investigated on the volume of the lattice. It has been shown that percentage volume change $\Delta V\%$ is related with the lattice [29] via the following formula

$$\Delta V\% = \left(\frac{r_{cut}}{r_e} \right)^3 - 1 \dots\dots\dots (18)$$

Using this relation, it was found that the percentage volume change $\Delta V\%$ for a cutoff radius $r_{cutoff2}$ for W was 6.12% from equilibrium value. Although there is an increase in the volume of the lattice, this change in volume does not appreciably cause an increase in the density of the solid. This suggests that within this cutoff radius the solid phase of this metal is firmly maintained.

The calculated values of CTE for other bcc metals are presented in Table 3. These values were obtained with $r_c = r_e \pm 1\%r_e$. The results show a better prediction than those of the SSSL method.

Table 3. Comparison of the linear coefficient of thermal expansion, CTE , $(\alpha)10^{-6}/K^{-1}$ at room temperature computed in this study, experimental and SSSL.

Metals	Expt.	This study	SSSL
Cr	9.8 ^b	10.71	10.30
K	82.0 ^a	73.64	142.5
Nb	7.12 ^b	9.73	---
V	7.80 ^a	8.84	---
Cs	87.2 ^b	77.62	184.6
Rb	91.0 ^a	60.62	179.3
Fe	14.7 ^b	14.5	14.3

a from ref. [29], b from ref [5]

The functional fit for equation (14) gives an exponentially decreasing curve when the coefficient of linear expansion CTE is plotted against temperature. For a compatible curve variation of CTE with temperature increase, the repulsive term in the pair potential was modified with a temperature dependent quartic equation $a + bT + cT^2 + dT^3 + eT^4$. The calculated values of the constants of this equation are presented in Table 4 for six bcc metals. In the SSSL method, a quadratic temperature dependent function was used to modify the Morse potential [18]. Calculated values for the constants in the quartic equation for six bcc metals are presented Table 4. The functional fits from this study are compared with the SSSL method and that of experiment for four metals, (V, Fe, Mo and W). These are shown in Figures 1 and 2. The curves obtained from this study show a better fit to the experimental curves than those from the SSSL curves.

Table 4. Calculated values for the constants in the quartic temperature equation.

Metals	a_0	a_1	a_2	a_3	a_4
Cr	0.7501	0.0296	1.3419×10^{-05}	-3.9256×10^{-08}	-5.9251×10^{-11}
Fe	2.2254	0.0243	1.1049×10^{-04}	-1.4568×10^{-07}	-1.5023×10^{-10}
Nb	3.9615	0.0092	3.7868×10^{-05}	-5.2175×10^{-08}	-5.9139×10^{-11}
V	3.8534	0.0068	6.5320×10^{-05}	-7.7130×10^{-08}	-6.4430×10^{-11}
W	1.4159	0.0130	3.4853×10^{-05}	-4.9892×10^{-08}	-6.9587×10^{-11}
Mo	1.2389	0.0130	3.1786×10^{-05}	-4.9892×10^{-08}	-6.9587×10^{-11}

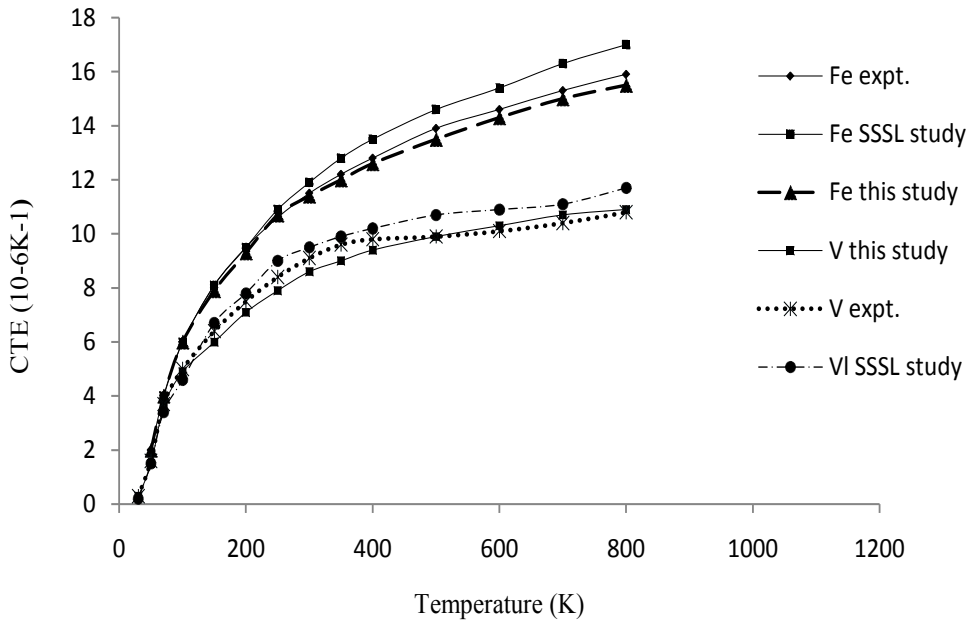


Fig. 1: Temperature dependent CTE with modified pair potential plot compared with experimental CTE plot for Fe and V

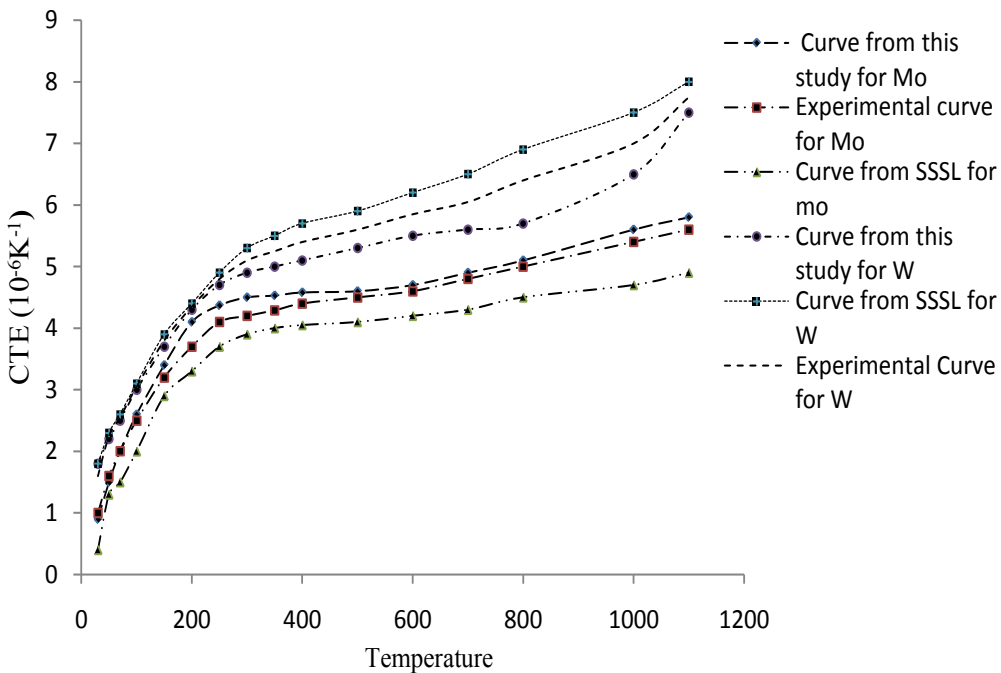


Fig. 2: Temperature dependent CTE with modified pair potential plot compared with experimental CTE plot for W and Mo

CONCLUSION

The study capitalizes on the inability of the atomic-level single-lattice analytical method (SSSL) method to predict the values of coefficient of linear expansion CTE , (α) of bcc metals. This is most reflected in the wide difference between the calculated values from SSSL method and the experimental values of CTE for K, Cs, Rb and Na. In this work the CTE of ten bcc metals were computed by redefining the concept of

the linear increase in length of two vibrating atoms to be the average of the apparent displacement of the two atoms along the repulsive and the attractive arms of total energy of the anharmonic curve. Our results show that in general, our modification to the SSSL method with a cutoff radius of 1% from equilibrium atomic distance r_e yields CTE in excellent agreement with experimental values with a mean absolute deviation of 2% most of the metals.

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