SOLUTION AND APPLICATION OF FIRST ORDER POLYNOMIAL MODULATED BY A SIMPLE EXPONENTIAL FUNCTION PAIR POTENTIAL FOR BODY CENTERED CUBES

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ABSTRACT

A first order polynomial modulated by a simple exponential function pair potential function was modeled and used to calculate the physical properties of body center cubes. The parameters of this potential function were calculated using the experimental values for the elastic constants, bulk modulus and the lattice constant of the metallic cubes. The equation of state and the elastic constants which were computed using this pair potential function agreed well with the experimental values for all the selected body center cubes.

INTRODUCTION

In solid metallic materials, the atoms vibrate about a mean position; it is then desirable to obtain a functional form of the pair potential function that describes adequately both the repulsive and the attractive energies that exist between any paired atoms as a result of this existing vibration.

A set of anharmonic pair potential functions were developed to describe the vibrational properties of two atoms from different theoretical models and semi empirical models, ab-initio [1], tight-binding [2], First principle [3], density function theory[4]. In some cases, a simple exponential function has been used, Johnson [5], Cai and Yee [6], equivalent crystal theory [7]. These models have been extensively used to calculate the bulk properties of metals to a very great success due to the simple procedure involved in fitting the experimental data of the selected crystals. If this potential, denoted by $\phi(r)$, duely represents the energy of interaction of two atoms, a distance r apart, then, the following conditions must be satisfied; (1)The force $-\partial\phi(r)/\partial r$ must be attractive at large r and repulsive at small r; therefore, $\phi(r)$ have a minimum at some point $r = r_e$, (2) The magnitude of $\phi(r)$ must decrease more rapidly with r than r^3. (3) All elastic constants are positive. (4) $C_{11} - C_{12} > 0$, where C_{11} and C_{12} are elastic constants, [8].

In this study, anharmonic pair potential function of the form of a simple first order polynomial modulated by a simple exponential function is proposed. The purpose of this study is then to find out if the proposed pair potential function will satisfy the conditions above and investigate applicability of this potential in describing the properties of cubic metals.

MODEL

A modulated first order polynomial pair potential of the form

$$\phi(r_{ij}) = -\phi_e \left\{ 1 + \chi \left(\frac{r_{ij}}{r_e} - 1 \right) \right\} \exp\left(-\eta \left(\frac{r_{ij}}{r_e} - 1 \right) \right) \dots\dots\dots\dots\dots \quad (1)$$

is proposed in this study.

There are three unknown parameters, ϕ_e, χ and η in this model whose values are numerically determined by fitting the experimental values of the lattice constant, the elastic constants, bulk modulus and equilibrium internal energy of the bcc metals.

In order to obtain the potential energy, $U(r)$, of the whole crystal whose atoms are at rest, it is necessary sum equation (1) over the entire crystal. This is most easily done by choosing one atom in the lattice as an origin, calculating its interaction with all the others in the crystal, and then multiply by $N/2$. Thus the total energy $U(r)$ is given by

$$U(r) = -\frac{N\phi_e}{2} \sum_j \left\{ 1 + \chi \left(\frac{r_j}{r_e} - 1 \right) \right\} \exp\left(-\eta \left(\frac{r_j}{r_e} - 1 \right) \right) \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where N is the atomic number. The Equation (3) requires a summation over a number of nearest neighbour atoms.

Here r_{ij} is the distance from the origin to the jth atom. It is convenient to define the following quantities:

$$P = \frac{-N\phi_e}{2}; \quad T = e^{\alpha}; \quad r_j = \left[m_j^2 + n_j^2 + l_j^2 \right]^{1/2} a = M_j a \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where m_j, n_j, l_j are position coordinates of any of the atom in the lattice. Using equation (3), the energy Eq. (2) can be written as:

$$U(a) = PT \sum \left(1 + \chi M_j / r_e - \beta M_j \right) e^{-\eta M_j a / r_e} \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

The first and the second derivatives of Eq. (4) with respect to a are;

$$\frac{dU(a)}{da} = -\frac{PT\eta}{r_e} \left(1 + \chi M_j / r_e - \chi M_j \right) e^{-\eta M_j a / r_e} \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

$$\frac{d^2U(a)}{da^2} = \frac{PT\eta^2}{r_e^2} \left(1 + \chi M_j / r_e - \beta \chi M_j \right) e^{-\eta M_j a / r_e} \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

At absolute zero $T = 0$, a_0 is value of a for which the lattice is in equilibrium, then $U(a_0)$ gives the energy of cohesion, $\left[dU(a)/da \right]_{a=a_0}$ is related to the compressibility. Thus

$$U(a_0) = U_0(a_0) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

where $U_0(a_0)$ is the energy of sublimation at zero at zero pressure and temperature.

Also
$$\left. \frac{dU(a)}{da} \right|_{a=a_0} = 0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

And the compressibility is given by

$$1/k_{00} = V_0 \left(d^2U_0 / dV^2 \right)_{a=a_0} = V_0 \left(d^2U(a) / dV^2 \right)_{a=a_0} \ldots\ldots\ldots\ldots \quad (9)$$

where V_0 is volume at absolute temperature and k_{00} is the compressibility at zero temperature. The volume per atom V/N is related to the lattice constant a by

$$V/N = ca^3 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

Substitute Eq. (10) in Eq. (9), the compressibility is expressed by

$$1/k_{00} = B_0 = 1/9cNa_0 \left(d^2U(a) / da^2 \right) \ldots\ldots\ldots\ldots\ldots\ldots.. (11)$$

The values of the parameters in the pair potential function can be obtained from self-consistent equations (4-11).

APPLICATIONS TO CALCULATION OF PHYSICAL QUANTITIES
EQUATION OF STATE

The equation of state can be computed from the energy equation. Here the thermal part of the free energy can be adequately represented by Debye model. The Helmholtz free energy obtained from this procedure, [12], is given by;

$$A = E(r) + 3NkT \ln(1 - e^{-\theta/T}) - NkTD(\theta/T) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (12)$$

where k is the Boltzmann's constant, T is the absolute temperature, θ is the Debye temperature and

$$D(\theta/T) = 3(\theta/T)^3 \int_O^{\theta/T} x^3 / (e^x - 1)dx \dots\dots\dots\dots\dots\dots\dots (13)$$

The thermodynamic expression for pressure is

$$P = -\left(\frac{\partial A}{\partial V}\right)_T \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (14)$$

Therefore the equation of state is given as

$$P = (1/3Ncr^2)dE(r)/dr + (3\gamma NkT/V)D(\theta/T) \dots\dots\dots\dots\dots\dots\dots (15)$$

where γ is the Gruneisen constant and V is the volume.

Equation (11) can be expressed as a direct relationship between the applied pressure P and the fractional change in volume $\Delta V/V$, by using $V = Ncr^3$ and the relation $r = r_e\left(1 + \Delta V/V_0\right)^{1/3}$. After some transformations, the equation of state (13) becomes

$$P = \frac{1}{6cr_e^2(1-x)^{2/3}}\left\{ P\sum_j \left\{ \frac{\alpha\beta}{r_e} + \frac{\beta}{r_e} - \frac{\alpha}{r_e} - \frac{\alpha\beta(1-x)^{1/3}}{r_e}\right\} \exp\left(-\alpha\left((1-x)^{1/3} - 1\right)\right)\right\} + \frac{3\gamma kT}{cr_e^3(1-x)}D\left(\frac{\theta}{T}\right)\dots..$$

(16)

where $x = -(V - V_0)/V_0 = -\Delta V/V_0$.

The state equation (16) contains mainly the parameters, (α, β and ϕ_e) of the proposed pair potential function.

Calculation of the elastic constants

The Universal energy function proposed for all materials has been used to obtain the embedded energy function. This energy function is given as

$$E(r) = -E_c\left[1 + \alpha\left(\frac{r}{r_e} - 1\right)\right]\exp\left(-\alpha\left(\frac{r}{r_e} - 1\right)\right)\dots\dots\dots\dots\dots\dots (17)$$

where $\alpha = \sqrt{9\Omega_e B_0/E_c}$, Ω_e is the equilibrium volume, B_0 is the bulk modulus.

The electron density function is given as $\rho(r) = \rho_e \exp\left(-\tau\left(\frac{r}{r_e} - 1\right)\right)\dots\dots\dots\dots\dots\dots$

(18)

Using the embedded atom method equation [9], we have that

$$F(\rho) = -(E_c - 4\phi_e)\left\{1 - \upsilon\ln\left(\frac{\rho}{\rho_e}\right)\right\}\left(\frac{\rho}{\rho_e}\right)^{\upsilon} \dots \dots\dots\dots\dots\dots (19)$$

where $\upsilon = \alpha / \tau$. Equation (18) can be made to closely follow the embedding energy equation of Finnis-Sinclair by setting $\upsilon = \sqrt{1/2}$. With this the values of τ can be obtained for the selected bcc metals.

The values of the elastic constants C_{11}, C_{12} and C_{44} for the selected bcc metals are obtained using the equations derived for these parameters by Iyad and Young [10].

$$C_{11} = \frac{1}{\Omega_e}\left\{ F^{//}(\rho_e)\left[\sum_i \frac{(r_{i1})^2}{r_i}\rho^/(r_i)\right]^2 + F^/(\rho_e)\sum_i \frac{(r_{i1})^2}{(r_i)^2}\left(\rho^{//}(r_i) - \frac{\rho^/(r_i)}{r_i}\right) + \right.$$

$$\left. F^/(\rho_e)\left[\sum_i \frac{(r_{i1})^2}{r_i}\rho^/(r_i)\right]\right\} + \frac{1}{2\Omega_e}\left\{\sum_i \frac{(r_{i1})^4}{(r_i)^2}\left(\phi^{//}(r_i) - \frac{\phi^/(r_i)}{r_i}\right) + \sum_i \frac{(r_{i1})^2}{r_i}\phi^/(r_i).\right\}............(20)$$

$$C_{12} = \frac{1}{\Omega_e}\left\{ F^{//}(\rho_e)\left[\sum_i \frac{(r_{i1})^2}{r}\rho^/(r_e)\right]\left[\sum_i \frac{(r_{i2})^2}{r_i}\rho^/(r_i)\right] + F^/(\rho_e)\sum_i \frac{(r_{i1})^2(r_{i2})^2}{(r_i)^2}\left(\rho^{//}(r_i) - \frac{\rho^/(r_i)}{r_i}\right) + \right.$$

$$\left. \frac{1}{2\Omega_e}\sum_i \frac{(r_{i1})^4}{(r_i)^2}\left(\phi^{//}(r_i) - \frac{\phi^/(r_i)}{r_i}\right)\right\}..(21)$$

$$C_{44} = \frac{1}{\Omega_e}\sum_i\left\{ F^{//}(\rho_e)\sum_i \frac{(r_{i2})^2(r_{i3})^2}{(r_i)^2}\left(\rho^{//}(r_i) - \frac{\rho^/(r_i)}{r_i}\right) + \frac{1}{2\Omega_e}\sum_i \frac{(r_{i2})^2(r_{i3})^2}{(r_i)^2}\left(\phi^{//}(r_i) - \frac{\phi^/(r_i)}{r_i}\right)\right\}....(22)$$

PHYSICAL EXPERIMENTAL INPUTS

The parameters of this potential function were calculated using the experimental values for the elastic constants, bulk modulus and the lattice constant of the metallic cubes. These experimental physical inputs used in the various fittings carried out in this study are put together in Table 1.

Table1. Experimental physical input for the BCC metals. The experimental inputs are the Lattice constants, a and Cohesive energies, Ec and are from Ferrant [11], Bulk modulus, B_0 are from Kittel [12], and Rose, Smith and Ferrant [11]; monovacancy formation energies, E_{iv}^F are from Johnson and Oh [13] and Elastic constants, C_{11}, C_{12} and C_{44} are from Simmons and Wang [14].

Metals	Cohesive Energy ΔE (eV)	Lattice Constant a(A)	Vacancy Formation Energy E_{iv}^F (eV)	Elastic Constants $(in\,10^{12}\,erg/cm^3)$			Bulk Modulus B $(in\,10^{12}\,erg/cm^3)$
				C_{11}	C_{12}	C_{44}	
V	5.310	3.3000	2.20	2.2900	1.2100	0.4440	1.5700
Nb	7.570	3.3000	2.60	2.4650	1.3450	0.2873	1.7020
Ta	8.100	3.3000	2.80	2.6680	1.6110	0.8249	2.0000
Mo	6.820	3.1500	3.00	4.6480	1.6160	1.0890	2.7250
W	8.660	3.1600	4.00	5.2270	2.0450	1.6060	3.2300
Fe	4.290	2.8600	1.60	2.3310	1.3544	1.1783	1.6800

RESULTS

Calculated values of elastic constants c_{11}, c_{12} and c_{44} from equations (21) – (23), are put together in table 3.0. The first row in each of the column on the table contains the values of the elastic constants obtained from this study, followed by the experimental values. The elastic constants are expressed in eV/m^3. These values are good agreement with the experimental values.

Table 2.0 Calculated values of elastic constants and their respective experimental values.

Metals	C_{11}	C_{12}	C_{44}
V	1.2008372	0.9140063	0.5214851
	1.4292937	0.7552163	0.2771206
Nb	1.1965481	1.003126	0.6586538
	1.5385192	0.8394759	0.1793170
Ta	1.5935739	0.9573755	0.8795332
	1.6652207	1.0054987	0.7969466
Mo	1.7843521	0.9655368	0.6795332
	2.901092	1.0086195	0.7969466
W	3.7002133	2.3014341	1.7011671
	3.2624096	1.2763779	1.0023779
Fe	2.2510173	1.3453429	0.9122272
	1.4548836	0.8453429	0.7048564

The values of the parameters of the modulated first order pair potential generated from the fittings in equations (5), (6) and (9) are put together in Table 3.

TABLE 3. Calculated values of the parameters of the modulated first order pair potential.

Metal	β	α	$\phi_e(eV)$	$P(eV)x10^{-22}$
V	5.2667	5.2894	1.7635	5.31
Nb	4.6239	4.6245	2.5141	7.57
Ta	4.6930	4.7088	2.6901	8.10
Mo	5.7923	5.7941	2.2650	6.82
W	5.5359	5.5501	2.8761	8.66
Fe	4.6324	4.6585	1.4247	4.29

DISCUSSION

The applicability of the potentials in this present model was tested by applying the model to predict relationship between the pressure and fractional decrease in the volume of the metals. This relationship is expressed in equation of state (15), which represents the equation of state for the selected bcc metals. The plots for the equation of state of the different metals are shown in Figure 3 for (Nb, W, V and Ta). The curves obtained from this study for metals W and V show a better match with those of the experimental curves than for Ta and Nb. At low values of fractional decrease in volume, all the curves match very well with the experimental curves.

The calculated values for the elastic constants C_{11}, C_{12} *and* C_{44} give the expected trend of magnitude of the elastic constants ($C_{11} > C_{12} > C_{44}$) for each of the selected metal and their values are in good agreement with those of the experimental values taken from Kittel and Handbook of Chemistry and Physics, ed., R. C Weast, CRC, Boca Raton. F. L [15], and the values predicted for the three elastic constants were consistently positive.
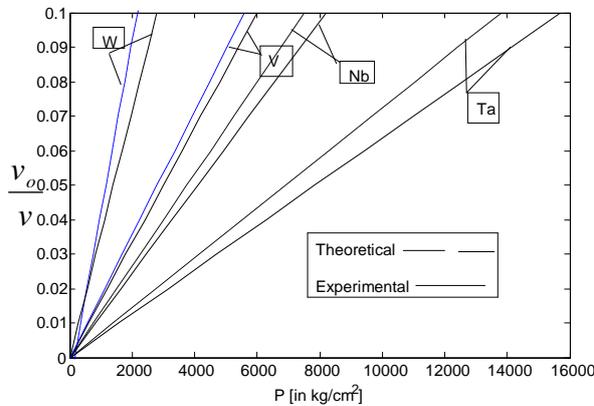

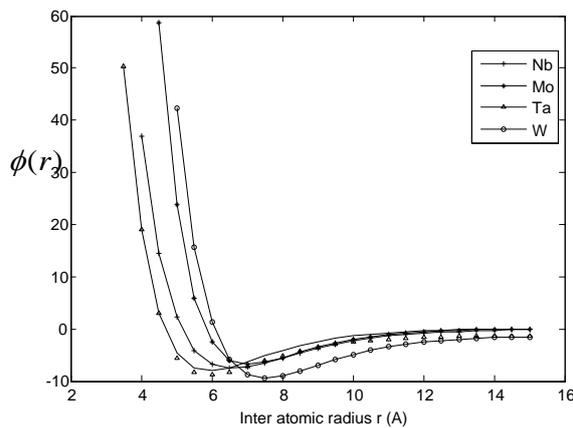Fig. 1. Equation of state curves for W, V, Nb, and Ta

Fig. 2 Functional fits for the pair potential equations (1)

These meet with the conditions (3 and 4) as set by Girifalco and Weizer [8].

The first derivative $-\partial\phi(r)/\partial r$ of the pair potential function is given

$$-(PT\eta/r_e)\left(1 + \chi(r_j - r_e)/r_e - \chi M_j\right)e^{-\eta(r_j - r_e)/r_e}$$

whose functional plot is shown in fig 5 shows that the values of $\phi^{/}(r)$ are attractive at large r and repulsive at small r; therefore, $\phi(r)$ have a minimum at some point $r = r_e$. This again satisfies the second condition as stated by Girifalco and Weizer [8].

CONCLUSION

This paper proffers an alternative process for solving a pair potential function written in form of a polynomial, in this, case a first order polynomial modulated by a simple exponential function. The new potential model has a simple functional form with three unknown parameters and is easy to be used in a computer simulation. The potential parameters were determined by fitting the pure metal bulk properties of the selected bcc metals: equilibrium

lattice constants, a, the elastic constants, (C_{11}, C_{12} and C_{44}) and the cohesive energy, E_c. The fitting procedure has been applied to six selected bcc metals; Nb, V, Mo, W, Ta and Fe. The validity test on the pair potential function showed that this function does not only predict the energetic of a vibrating atom about their mean position but it also satisfies the conformable conditions (1-4) by Girifalco and Weizer. It can be concluded here that simple structured pair potential function which describes anharmonic form of vibrating atom is sufficient and can be more easily adapted to calculate energetics of bcc metals.

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