

RELATIONSHIP OF LENNARD-JONES POTENTIAL AND MORSE POTENTIAL WITH $W_z(r)$ POTENTIAL^①

Xie, Youqing

*Department of Materials Science and Engineering,
Central South University of Technology, Changsha 410083*

ABSTRACT

It was proved that Lennard-Jones potential can be transferred to $W_z(r)$ potential according to relationship of their parameters established in this paper. The empirical $W_1(r)$ potential has been developed into semi-empirical $W_z(r)$ potential related to electronic structure of crystals. Relationships of parameters between Morse potential and $W_z(r)$ potential have been also obtained, but if Morse potential equals $W_z(r)$ potential, the parameter a_m in Morse potential can not be constant. Comparing it with other two potentials, the $W_z(r)$ potential is the most perfect.

Key words: potential function cohesive energy thermal expansion elastic modulus

1 INTRODUCTION

The study of H_2 molecule ushered in a new way of establishing microtheory of correlating potential energy with electronic structure of atoms in solids. But the microtheory of metals and alloys has made slow progress, because there are a lot of difficulties in description of electronic structure of atoms in solids, design of potential function with the many-atom interaction and solution of Schrodinger's equation due to complexity of many-body problem. For this reason another way has been developed for studying relations between interaction potential energy and properties of atoms in solids using potential function. The well-known potentials are, respectively, Lennard-Jones potential (referred as $W_1(r)$)^[1]:

$$W_1(r) = A_1/r_{n_1} - B_1/r_{m_1} \quad (1)$$

and Morse potential (referred as $W_m(r)$)

$$W_m(r) = \frac{E_c}{n_m - 1} (e^{-a_m(r-r_0)^{n_m}} - n_m e^{-a_m(r-r_0)}) \quad (2)$$

where r_0 and r are, respectively, distances of interatoms in crystals at equilibrium and unequilibrium; E_c is cohesive energy of crystals; and all of pa-

rameters, A_1 , B_1 , n_1 , m_1 , n_m and a_m are constants.

Recently, a new potential function with many-atom interactions in solids has been proposed by the author for studying relations of crystalline structure, electronic structure and properties of metals and alloys (referred as $W_z(r)$)^[2]:

$$W_z(r) = E_c \left[(n_z - 1) \left(\frac{r_0}{r} \right)^{n_z m_z / (n_z - 1)} - n_z \left(\frac{r_0}{r} \right)^{m_z} \right] \quad (3)$$

It possesses the following characters: (1) It is established on the basis of many-atom interaction model. (2) In the $W_z(r)$ potential, the variable is the reduced distance or bond length of interatoms, so the form of the $W_z(r)$ potential does not become complex due to considering many-atom interactions. (3) The $W_z(r)$ potential is a semi-empirical equation, because the potential energy and bond length of the crystal in equilibrium state may be calculated from the electronic structure of crystals.

(4) The relations of parameters n_z and m_z with microquantities have been established, and only n_z is independent. (5) A series of equations for calculating various elastic moduli have been derived from the $W_z(r)$ potential. (6) It is unnecessary to know

① Project supported by the National Natural Science Foundation of China; Manuscript received June 25, 1993

the bulk modulus for calculating the thermal expansion coefficient as a function of temperature. The purposes of this paper are establishing relations of $W_1(r)$ and $W_m(r)$ potentials with $W_z(r)$ potential, obtaining transfer equations of their parameters and making the best selection from these potentials in practical applications.

2 RELATION BETWEEN $W_1(r)$ AND $W_z(r)$ POTENTIALS

It is necessary to establish transfer equations from A_1 , B_1 , n_1 and m_1 parameters in W_1 potential to m_z and n_z parameters in $W_z(r)$ potential in order to study relation between $W_1(r)$ and $W_z(r)$ potentials. For this purpose it is supposed that $W_1(r)$ and $W_z(r)$ potentials have identical characters, namely, the same $W(r) \sim r$ curve for an identical crystal.

It has been proved that only one parameter n_z in $W_z(r)$ potential is a constant awaiting determined and can be obtained according to one experimental value of thermal expansion coefficient. The relation between m_z and n_z parameters has been derived according to the principle of mechanics and Debye's theory^[3]:

$$m_z = \frac{2\theta K_B r_0}{h j} \sqrt{m/E_c \cdot (n_z - 1)/n_z} \quad (4)$$

and

$$j = \bar{\lambda}/(\lambda_D/2) = (\bar{\lambda}/\pi) \cdot (6\pi^2 N/V_0)^{1/3} \quad (5)$$

where θ is Debye temperature; K_B , Boltzmann's constant; h , Planck's constant; m , atomic mass; λ , average wave length of elastic wave; λ_D , Debye wave length; and j is the multiple of the half Debye wave length.

In order to establish the relationship between $W_1(r)$ and $W_z(r)$, the W_z can be rewritten as

$$W_z(r) = E_c \left[\frac{(n_z - 1)r_0^{n_z m_z/(n_z - 1)}}{r^{n_z m_z/(n_z - 1)}} - n_z \frac{r_0^{n_z}}{r^{n_z}} \right] \quad (6)$$

Comparing Eq. (1) with Eq. (6), the following equations can be obtained:

$$E_c = -A_1/r_0^3 + B_1/r_0^{n_1} \quad (7)$$

$$A_1 = E_c(n_z - 1)r_0^{n_z m_z/(n_z - 1)} \quad (8)$$

$$B_1 = E_c(n_z - 1)r_0^{n_z m_z/(n_z - 1)} \quad (9)$$

$$n_1 = n_z m_z/(n_z - 1) \quad (10)$$

$$m_1 = m_z \quad (11)$$

some knowledges can be drawn from Eqs. (7) ~ (11):

(1) The parameters A_1 , B_1 , n_1 and m_1 in $W_1(r)$ potential are functions of E_c , r_0 , m_z and n_z in $W_z(r)$ potential. The four parameters in the $W_1(r)$ potential are interrelated and interdependent and can not arbitrarily take values, because the cohesive energy E_c and the shortest bond length are determined by electronic structure of crystals^[7, 8], and parameters m_z and n_z are interrelated and interdependent.

(2) If the values of parameters in $W_1(r)$ potential are taken from Eqs. (8) ~ (11), the $W_1(r)$ can be changed into $W_z(r)$ potential. It shows that the $W_z(r)$ potential is developed from the $W_1(r)$ potential. The advances of $W_z(r)$ potential are on both that the completely empirical $W_1(r)$ potential has changed into a semi-empirical potential, and the implications of parameters in $W_1(r)$ are very clear, because relationships of these parameters with micro-quantities have been established.

(3) Because $W_1(r)$ potential can change into $W_z(r)$ potential we can derive not only theoretical equations of bulk modulus, Young's modulus, shear modulus and Poisson's ratio, but also equation of thermal expansion coefficient^[8, 9]:

$$\alpha_T = C_v/3Q[1 - K(U/Q)]^2 \quad (12)$$

where C_v is the molar heat capacity at constant volume, U is the energy of lattice vibrations. If the potential function of the crystal is described by $W_1(r)$ or $W_z(r)$, the parameters Q and K , and Grüneisen constant γ can be calculated by the following equations:

$$Q = V_0 B/\gamma \quad (13)$$

$$K = (m_z + n_z + 3)/6 \quad (14)$$

$$\gamma = (n_z + 2)/6 \quad (15)$$

$$\text{or } Q = \frac{4\theta^2 K_B^2 r_0^2 m}{9h^2 j^2} / \frac{1}{3} \left(\frac{\theta K_B r_0}{h j} \times \sqrt{m/E_c \cdot n_z/(n_z - 1)} + 1 \right) \quad (16)$$

$$K = \frac{\theta K_B r_0 (2n_z - 1)}{3h j} \sqrt{\frac{m}{n_z(n_z - 1)E_c}} + \frac{1}{2} \quad (17)$$

$$r = \frac{\theta K_B r_0}{3h j} \sqrt{m/E_c \cdot n_z/(n_z - 1)} + \frac{1}{3} \quad (18)$$

where V_0 is the volume of one mole of the solid; B is the bulk modulus; other quantities can be known from Eq. (4).

It should be pointed out that it is unnecessary

to know the bulk modulus for calculating the thermal expansion coefficient as a function of temperature, if the potential of the crystal is described by $W_r(r)$ potential. The bulk modulus, Young's modulus and shear modulus can be calculated if the parameters n_r and j have been obtained according to experimental values of thermal expansion coefficients at two temperatures. The high accuracy of results have been confirmed^[3].

3 RELATION BETWEEN $W_m(r)$ AND $W_r(r)$ POTENTIALS

According to the same promise pointed out in the section 2, the relation between $W_m(r)$ and $W_r(r)$ potentials will be discussed in two situations.

(1) At the situation of $r = r_0$;

(a) The differences between attractive and repellant potentials in both $W_m(r)$ and $W_r(r)$ potentials should be equal to negative value of cohesive energy which is determined by electronic structure of crystals:

$$\begin{aligned} & -[n_r E_C]_{rA} + [(n_r - 1)E_C]_{rR} = \\ & -[n_m E_C/(n_m - 1)]_{mA} + [E_C/(n_m - 1)]_{mR} \\ & = -E_C \end{aligned} \quad (19)$$

It means that the interaction potential function of atoms in the crystal with a certain electronic structure can be described by both $W_m(r)$ and $W_r(r)$ potentials.

(b) If $n_m = n_r/(n_r - 1)$, not only the ratios between attractive and repellant potentials in $W_m(r)$ and $W_r(r)$ are equal, but also their absolute values are equal. The correctness of this conclusion can be proved in two aspects.

Supposing the ratios between attractive and repellant potentials in $W_m(r)$ and $W_r(r)$ are equal,

$$\frac{[-n_m E_C/(n_m - 1)]_{mR}}{[E_C/(n_m - 1)]_{mR}} = \frac{[-n_r E_C]_{rR}}{[(n_r - 1)E_C]_{rR}} \quad (20)$$

From Eq. (20) it can be obtained

$$n_m = n_r/(n_r - 1) \quad (21)$$

Supposing attractive and repellant potentials in $W_m(r)$ potential are, respectively, equal to ones in $W_r(r)$ potential:

$$-[n_r E_C]_{rA} = -\left[\frac{n_m E_C}{n_m - 1}\right]_{mA} \quad (22)$$

$$[(n_r - 1)E_C]_{rR} = \left[\frac{E_C}{n_m - 1}\right]_{mR} \quad (23)$$

From both Es. (22) and (23), it can be obtained

$$n_r = n_m/(n_m - 1)$$

From this equation, it can be obtained that

$$n_m = n_r/(n_r - 1)$$

so the suppositions above prove to be correct. The analysis above shows that at the $r = r_0$, the coincident condition of potential curves described by $W_m(r)$ and $W_r(r)$ potentials are dependent on having relation described by Eqs. (21) or (24) between n_m and n_r , and independent on parameters a_m and m_r .

(2) In the situation of $r \neq r_0$

The completely coincident conditions of potential curves described by $W_m(r)$ and $W_r(r)$ potentials are that the parameter a_m in $W_m(r)$ potential is a variable as a function of distance, r , of interatoms, besides $n_m = n_r/(n_r - 1)$. It can be proved following:

The form of potential curves is determined by ratio between attractive and repellant potentials. From $W_m(r)$ potential we can obtain

$$\frac{[W_m(r)]_A}{[W_m(r)]_R} = -n_m e^{a_m(1-a_m)(r-r_0)} \quad (25)$$

From $W_r(r)$ potential we can be obtain

$$\frac{[W_r(r)]_A}{[W_r(r)]_R} = -\frac{n_r}{n_r - 1} \left(\frac{r_0}{r}\right)^{(m_r - a_r n_r / (n_r - 1))} \quad (26)$$

From Eqs. (25) and (26) it can be known that the condition of having the identical potential curves for $W_m(r)$ and $W_r(r)$ potentials is

$$\begin{cases} n_m = n_r/(n_r - 1) \\ a_m = m_r(r - r_0)\ln(r - r_0)/n_r \end{cases} \quad (27)$$

Because $(r - r_0)\ln(r - r_0)$ is not constant, the parameter a_m can not be constant. If the parameter a_m is a constant, $W_m(r)$ and $W_r(r)$ potentials can not have an identical potential curve.

4 CONCLUSIONS

(1) The relationships of parameters A_1 , B_1 , n_1 and m_1 in $W_1(r)$ potential with parameters m_r and n_r in $W_r(r)$ potential have been established, and it shows that A_1 , B_1 , n_1 and m_1 are interrelated and independent constant, and can not arbitrarily take values.

(2) According to established relationships of parameters in $W_1(r)$ potential with ones in $W_r(r)$ potential, the $W_1(r)$ potential can be changed into $W_r(r)$ potential, but the $W_r(r)$ potential has made

great advances; The completely empirical $W_1(r)$ potential related to electronic structure of crystals; The $W_1(r)$ potential with two atoms interaction has been developed into $W_x(r)$ potential with many-atoms interaction; The relationships of parameters in $W_x(r)$ potential, various elastic moduli and thermal expansion coefficient as a function of temperature with microquantities have been derived, so the natures of these parameters and properties of crystals have been more clear.

(3) The relationships of parameters n_m and α_m in $W_m(r)$ potential with parameters m_x and n_x in $W_x(r)$ potential have been established:

$$\begin{cases} n_m = n_x / (n_x - 1) \\ \alpha_m = m_x (r - r_0) \ln(r - r_0) / n_x \end{cases}$$

when $W_m(r)$ potential is used to study interaction of atoms of crystals, the parameter α_m generally is a constant, but $(r - r_0) \ln(r - r_0)$ is not constant, so $W_m(r)$ and $W_x(r)$ potentials can not transfer each other, and can not be able to have identical po-

tential curve.

REFERENCES

- 1 Lennard-Jones, J E. *Physica*, 1937, (10): 941.
 - 2 Milstein, F. *J Appl Phys.* 1937, (44): 3825.
 - 3 Xie, Y Q. *Science in China, Series A*, 1993, (1): 90.
 - 4 Xie, Y Q *et al.* *Transactions of NFsoc*, 1992, (2): 56.
 - 5 Xie, Y Q *et al.* *Science in China, series A*, 1993, (4): 487.
 - 6 Xie, Y Q *et al.* *Science in China, series A*, 1993, (4): 495.
 - 7 Xie, Y Q; Ma, L Y. *Journal of Central-South Institute of Mining and Metallurgy*, 1985, (1): 1.
 - 8 Xie, Y Q *et al.* *Chinese Science Bulletin*, 1992, (16): 1529.
 - 9 Gray, E E. *American Institute of Physics Handbook*. 3rd edition. New York, Toronto, London: McGraw-Hill Book Company, Inc. 1972. 4—119.
-
- (From page 62)
- of small amount of La_2O_3 , whereas the La-Mo wires doped with higher content of La_2O_3 show very good toughness at room temperature when annealed at higher temperatures and have excellent thermionic electron emissive capacity.
- ## REFERENCES
- 1 Lee, K S. *Journal of the Less-common Metals*, 1984, 99: 215—244.
 - 2 Endo, M. In: 12th Inter Plansee Seminal, 1989, 1. 37—52.
 - 3 Eck, R. In: 12th Inter Plansee Seminal, 1989, 1. 483—491.
 - 4 Zhou, Meiling *et al.* *Materials Science and Engineering of Rare Metals*, 1989, (6): 11—15.
 - 5 Bachmann, R; Busbau, C; Gessinger G. US 4083811. 1978.
 - 6 Zuo, Tieyong *et al.* *J of Central-South Institute of Mining and Metallurgy*, 1982, (1): 47—53.
 - 7 Herring, C. *J Appl Phys*, 1950, 21: 437.
 - 8 Coble, B L. *J Appl Phys*, 1963, 34: 1979.
 - 9 Zhou, M; Cheng, Z; Zhang, J; Li, J; Zuo, T. In: 13th Inter Plansee Seminal, 1993, 1: RM70.