

Calculation of the Parameters of the Lennard-Jones Potential for Pairs of Identical Atoms Based on the Properties of Solid Substances

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Abstract—On the basis of the parameters of the crystal structure and evaporation heat of pure substances, the Lennard-Jones potentials for pairs of identical metal atoms are calculated using the developed algorithm. The algorithm considers the preliminary correction of the parameter values in accordance with the required cutoff radius of the potential. The initial data and calculation results for α -Fe, Cr, V, Mo, α -W, Al, Ni, and Cu are given. Using the obtained values of the potential, values of the energy of formation of a vacancy for the simulated equilibrium crystal structures of pure substances are calculated that comply with the published data.

Keywords: potential of pair interaction, computer simulation, crystal structure, defects, thermodynamic characteristics

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INTRODUCTION

Many computer models applied in physics of materials are based on first principles, i.e., on the interatomic interaction parameters called potentials. Various physical phenomena such as phase and structural transformations, diffusion, and adsorption are described using these parameters. The parameters of the function of potentials are determined from the thermodynamic properties, crystal structure, and other characteristics of substances by solving the inverse problem, namely, simulation of any physical properties by means of the specified potential. The explicit form of the function of potentials and its parameters are chosen in such a way that the macroscopic characteristics of a substance that are calculated by its means agree with the experimental data. The larger the number of parameters of the potential, the larger the number of independent experiments required for their determination; at the same time, the difficulties connected with consistency of the experimental data obtained by different methods increase. Considering the last circumstance and the fact that the use of the same type of potentials for comparing the contributions of the atoms of different types to subsequently simulated processes is more correct, the potentials with a smaller number of parameters often should be applied. Potentials of pair interactions are the simplest ones. The relevancy of the chosen forms of potentials and their parameters is evaluated from the results of simulation of the real physical phenomena with their use.

The interatomic interaction in the pair approximation is given in the form of the function $v(r_{ij})$, which

describes the energy change depending on the distance between the centers of atoms. Redistribution of the electron density and other effects of the interatomic interaction are not considered in this case; however, they are taken into account indirectly, since the potentials are constructed on the basis of the real properties of substances. Thus, despite the limitations described above for the potentials of pair interactions, they are often used in simulations of various physical phenomena or as the zero approximation upon constructing more complicated potentials.

The aim of the present work was the development and implementation of an algorithm for determining the parameters of the Lennard-Jones potential for pairs of identical atoms that comprise elements which are the main alloying components forming substitutional solid solutions in iron alloys under certain conditions.

CALCULATION TECHNIQUES

The Lennard-Jones potential has the shape shown schematically in Fig. 1 and described by the following expression:

$$v(r) = 4\varepsilon \left[\left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right], \quad (1)$$

where ε and r_0 are the parameters of the specified potential, and r is the distance between the centers of the atoms. In addition, the so-called cutoff radius r_c , determining the distance at which the interaction between the atoms can be considered as equal to zero,

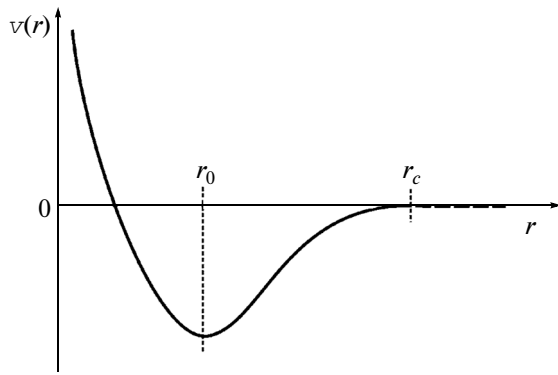


Fig. 1. The Lennard-Jones interatomic pair interaction potential.

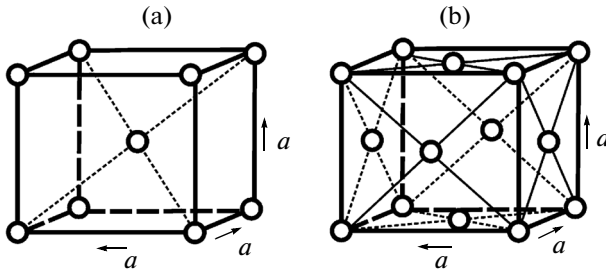


Fig. 2. Unit cells of the (a) BCC and (b) FCC crystal structures.

should be included in the computer models in order to reduce the calculation time upon using the potentials.

The method suggested in [1] for face-centered cubic (FCC) crystals, which also has been extended to the body-centered cubic (BCC) crystal structure, is used upon calculation of the parameters of the potential (1), as shown below.

The total energy of the crystal is determined by summing up the bond energies of all the atomic pairs as follows:

$$V(r) = \frac{1}{2} N \sum_r v(r) \quad (2)$$

The summation in (2) is carried out over all the lattice vectors, where N is the number of atoms.

As shown in [1], the distances between the atoms in a crystal lattice can generally be expressed via the lengths a , b , and c of the basis vectors \vec{a} , \vec{b} , and \vec{c} and the angles α , β , and γ between them as follows:

$$r = (a^2 k^2 + b^2 l^2 + c^2 m^2 + 2abkl \cos \alpha + 2bclm \cos \beta + 2akcm \cos \gamma)^{1/2}; \quad (3)$$

$$k, l, m = 0, \pm 1, \pm 2, \dots$$

where $k, l, m = 0, \pm 1, \pm 2, \dots$

Thus, the interatomic distances for the FCC and BCC crystals, the unit cells of which are shown in Figs. 2a and 2b, can be expressed as follows:

$$\text{FCC: } r = \frac{\sqrt{2}}{2} a (k^2 + l^2 + m^2 + kl + km + lm)^{1/2}; \quad (4)$$

$$k, l, m = 0, \pm 1, \pm 2, \dots,$$

and

$$\text{BCC: } r = \frac{1}{2} a (k^2 + l^2 + m^2)^{1/2}; \quad k, l, m = 2n; \quad (5)$$

$$k, l, m = 2n + 1, \quad n = 0, \pm 1, \pm 2, \dots$$

On the basis of the above equations, the total crystal energy can be expressed as follows:

$$V(a) = \frac{1}{2} N 4\epsilon \left[\left(\frac{A_0 r_0}{a} \right)^{1/2} A_{12} - \left(\frac{A_0 r_0}{a} \right)^6 A_6 \right], \quad (6)$$

where A_0 is the constant corresponding to the lattice symmetry, a is the lattice period, and A_{12} and A_6 are the results of summation over all the crystal cells:

$$A_{12}^{\text{FCC}} = \sum_{k, l, m} (k^2 + l^2 + m^2 + kl + km + lm)^{-12/2}, \quad (7)$$

$$A_6^{\text{FCC}} = \sum_{k, l, m} (k^2 + l^2 + m^2 + kl + km + lm)^{-6/2},$$

$$A_{12}^{\text{BCC}} = \sum_{k, l, m} (k^2 + l^2 + m^2)^{-12/2}, \quad (8)$$

$$A_6^{\text{BCC}} = \sum_{k, l, m} (k^2 + l^2 + m^2)^{-6/2}.$$

The A_{12} and A_6 values for other crystal structures are calculated in a similar way. The numbers k , l , and m in Eqs. (7) and (8) take integer values specified for each lattice type.

The equilibrium lattice period is obtained from the following prerequisite for the total crystal energy minimum: $\partial V(a)/\partial a = 0$. Accordingly, the first equation for determination of the parameters of the pair interaction potential can be obtained:

$$a = r_0 A_0 (2A_{12}/A_6)^{1/6}. \quad (9)$$

After substituting Eq. (9) into Eq. (6) and equating the total energy of the crystal to the sublimation heat H of the corresponding pure substance, taken with the opposite sign, one can obtain the second equation for determination of the parameters of the pair potential:

$$H = 1/2 N \epsilon A_6^2 / A_{12}. \quad (10)$$

RESULTS AND DISCUSSION

From solution of the set of Eqs. (9) and (10) with respect to r_0 and ϵ , the parameters of the interaction potentials for the corresponding pairs of identical atoms are obtained.

The A_{12} and A_6 values depending on k , l , and m decrease upon an increase in these parameters. At the same time, more and more distant interatomic inter-

Table 1. Parameters of the Lennard-Jones potential of pairs of identical atoms calculated on the basis of the thermodynamic and crystallographic characteristics of pure substances

Element	Structure type	Lattice period, nm	Heat of sublimation, kJ/mol ($T = 298$ K, $p = 0.1$ MPa)	Potential parameters		
				ε , eV/at ¹	r_0 , nm	r_c/a
α -Fe	BCC	0.28664	417.60	0.70641	0.226738	1.3
Mo	BCC	0.31468	657.41	1.11195	0.248919	1.3
V	BCC	0.30231	515.37	0.87173	0.239134	1.3
α -W	BCC	0.31652	858.11	1.45142	0.250374	1.3
Cr	BCC	0.28840	398.05	0.67322	0.228130	1.3
Cu	FCC	0.36147 0.36153	338.07	0.52031	0.229726	0.85
Ni	FCC	0.35238	429.42	0.66092	0.223949	0.85
Al	FCC	0.40496	329.60	0.50722	0.257366	0.85

¹ 1 eV/at = 96.5 kJ/mol.

actions in the crystal lattice are taken into account upon determining the ε and r_0 values. The r_c value in the suggested approach can be easily adjusted to the maximum k , l , and m values, since they are directly connected with the interatomic distances in a crystal lattice through the period a . The ε and r_0 values obtained in such a way for large and the small r_c values will differ from each other, and r_c plays the role of an additional (in this case the third) parameter of the potential function.

The H and a values are determined from the experimental properties of pure substances. The averaged room-temperature data on the sublimation heat and lattice period from [2–5] are used in the present studies.

Solving the set of Eqs. (9) and (10), we calculate the r_0 and ε parameters of the interaction potentials for the relevant pairs of identical atoms of different elements at the r_c/a ratio corresponding to the cutoff potential between the first and second coordination spheres of an atom in the crystal lattice. The obtained calculation results for the ε , r_0 , and r_c/a parameters are given in Table 1.

The energy of formation of point vacancies in pure metals are calculated to check the reliability of the potentials obtained in the present studies.

Simulation of the equilibrium atomic configuration of a vacancy in the present studies is based on the computer model in which the quasidynamic method of constructing the equilibrium atomic configuration in a particular defect is implemented as suggested by Gibson et al. and described in detail in [4], where it was used for the calculation of the equilibrium configurations of elongated defects.

The scheme of constructing the equilibrium configuration of atoms consists in the following. On the

basis of the structures of a defect-free crystal and similar crystal with the specified defect (vacancy), the initial positions of atoms are stipulated. Next the total energy of the system as the sum of pair interactions of all the atoms is evaluated separately for each case. After that, each atom is successively moved in small steps until the resulting force acting on it from the side of other atoms becomes equal to zero. The amount of motion in a single step is determined from the laws of Newtonian mechanics by taking into account the mass of the atom and the force acting on it. The components of the force are calculated as derivatives of the energy with respect to corresponding coordinates taken with the opposite sign. Upon completion of the entire cycle of motions, the total energy of the system is calculated and compared to the calculation result in the previous cycle. Such a procedure is applied to the atoms until the moment when changes in the total energy of the system approach zero within a specified accuracy level, which corresponds to an equilibrium state. The calculation schemes of motions and interatomic interaction forces for the computer simulation of the equilibrium structure of a crystal defect can be found in [5, 6].

The vacancy formation energy given in Table 2 is calculated in the present study as the difference $E = E_1 - E_0$ using the approach from [6], where E_1 is the energy of the crystal containing one vacancy and E_0 is the energy of the defectless crystal containing the same number of atoms. It should be noted that the energy E_0 is calculated for the defectless crystal consisting of 60 atoms in the relaxed condition, and the energy E_1 is determined in the same manner for the crystal consisting of 61 atoms, the central atom of which is replaced by a vacancy.

Table 2. Energy of formation (E , kJ/mol) of a vacancy in pure substances according to different experimental data and calculation results based on the pair interaction potentials

Element	Structure type	Calculation results based on pair interaction potentials		Experimental data from [5, 7]
		Lennard-Jones from Table 1	others [5–9]	
α -Fe	BCC	130	132	135–145
Mo	BCC	276	—	290–313
V	BCC	197	—	203
α -W	BCC	383	—	303–386
Cr	BCC	150	—	162–219
Cu	FCC	82	39–124	95–126
Ni	FCC	142	135	—
Al	FCC	76	38–284	62–76

As follows from Table 2, the calculation results agree well with the experimental and theoretical data reported in [5–9].

CONCLUSIONS

Using the developed algorithm, the parameters of the Lennard-Jones potential of pairs of identical metal atoms are calculated on the basis of the characteristics of the crystal structure and the heat of evaporation of pure substances. The algorithm takes into account the necessary corrections of the parameter values according to the required cutoff radius of the potential. The parameters of the Lennard-Jones potential of the interatomic interaction between pairs of identical atoms of the following metals having the BCC and FCC structure are obtained: α -Fe, Cr, V, Mo, α -W, Al, Ni, and Cu. The vacancy formation energies in the above-specified metals are calculated in good agreement with the published data. These results can be

used for computer simulation of the transformations of the crystal structure and defects in pure metals upon plastic deformation and also in connection with phase segregations and separations.

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