Vol 11 No 2, February 2002
1009-1963/2002/11(02)/0139-05

Chinese Physics

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A Lennard-Jones embedded-atom potential and its application to the study of melting*

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(Received 17 July 2001; revised manuscript received 28 September 2001)

The nearest-neighbour Lennard-Jones potential from the embedded-atom method is extended to a form that includes more than nearest neighbours. The model has been applied to study melting with molecular dynamics. The calculated melting point, fractional volume change on melting, heat of fusion and linear coefficients of thermal expansion are in good agreement with experimental data. We have found that the second and third neighbours influence the melting point distinctly.

Keywords: many-body effects, melting, molecular dynamics
PACC: 6470D

1. Introduction

The Lennard-Jones (LJ) potential[1] is one of the oldest interatomic potentials in the literature. This potential has been used to model a wide range of materials and phases, ranging from rare gas solids to metallic liquids. A vast amount of results[2] have been acquired using the LJ potential, including homogeneous nucleation from a LJ liquid, the dynamics of diffusion in liquids and solids, and equilibrium structures in supercooled liquids. Certainly, interactions in real materials are more complex than that described by a simple pair interaction. Now it has become well accepted that many-body effects play an important role in real materials, especially in metals and alloys. Also, the embedded-atom method (EAM) developed in the past eighteen years, which can treat metallic systems properly, has achieved great success. To investigate many-body effects, Baskes[2] developed a simple EAM-LJ potential that accommodates both the LJ potential and the EAM. Using the potential, several properties of the potential have been studied. However, this potential is valid only for nearest-neighbour interactions for face-centred cubic (fcc) metals, so its application is limited. For example, its elastic anisotropy is held at a constant 2 and does not agree with the experimental data.

In this paper we present an extended form of the EAM-LJ potential of Baskes for dynamic simulations valid for any choice of cut-off distance. To test the extended potential, we have studied its various properties using molecular dynamics.

2. Theory

The energy of two atoms described by the LJ form is

$$\phi_{\rm LJ} = \frac{1}{r^{12}} - \frac{2}{r^6}, \tag{1}$$

where the energy is measured in units of the well depth, ε, and the atomic separation, r, is measured in units of $r_0 = 2^{1/6}\sigma$, where σ is the LJ diameter. For an equilibrium fcc material with only Z_0=12 nearest-neighbour interactions, the scaled energy is equal to $-Z_0/2$, and the scaled equilibrium nearest-neighbour distance is unity. Using this form and the nearest-neighbour fcc structure as a reference state, Baskes defined a simple EAM model for the total energy of an arbitrary arrangement of atoms as

$$U = \sum_i \left[F(\rho_i) + \frac{1}{2} \sum_{j \neq i} \phi(r_{ij}) \right], \tag{2}$$

where $\phi(r_{ij})$ is a two-body central potential between atoms i and j with the separation distance r_{ij}. $F(\rho_i)$ is the embedding energy of atom i with electron density ρ_i. In the model $F(\rho_i)$ and $\phi(r_{ij})$ have the forms

$$F(\rho_i) = \frac{AZ_0}{2} \rho_i [\ln(\rho_i) - 1], \tag{3}$$

$$\phi(r) = \phi_{\rm LJ}(r) - \frac{2}{Z_0} F(\rho(r)), \tag{4}$$

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where

$$\rho_i = \frac{1}{Z_0}\sum_{j\neq i}\rho(r_{ij}), \tag{5}$$

$$\rho(r) = \exp[-\beta(r-1)]. \tag{6}$$

Note that the dimensionless parameter A is the extent of the many-body bonding, and the parameter β determines the decay of the electron density. For A=0 and any value of β, the potential reduces to a LJ potential which can be reasonably applied to an inert material. The study by Baskes has shown that for certain A (for example $A > 0.5$) and β, the potential can be properly applied to fcc metals. It is easily seen that $F(\rho)$ makes use of the Rose equation;[3] in fact, most EAM potentials do.[4−6] But Baskes took its simple form and let Eq.(3) have the fewest parameters.

With a cut-off distance of 1.4, the above EAM potential does not consider the interactions between atoms over the first nearest-neighbour distances. This may pose a strong limitation to its application. Using the similar method of extending the Johnson potential to the Mei potential,[6] we have extended the above EAM potential to a form for dynamics simulations valid for any choice of cut-off distance. The resultant equations are the same except that Eqs.(5) and (6) are changed respectively into

$$\rho_i = \sum_{j\neq i} f(r_{ij}), \tag{7}$$

$$f(r) = f_{\rm e}\sum_{l=0}^{k} C_l(1/r)^l. \tag{8}$$

It is easy to note that the extension only involves the question of how the electron density is calculated, and r has a longer cut-off distance for all equations. With proper parameters, we found that functions $f(r)$ and $\phi(r)$ have the desirable feature of decaying nearly to zero around the fourth neighbour (less than 1% as compared with that at the first neighbour). In our molecular dynamics (MD) simulations, the long tails of $f(r)$ and $\phi(r)$ were truncated in the following way. By specifying a connecting point $r_{\rm n} < r_{\rm c}$, and introducing the cut-off function

$$g(r) = \begin{cases} 1 & r \le r_{\rm n}; \\ (1-x)^3(1+3x+6x^2) & r_{\rm n} < r < r_{\rm c}; \\ 0 & r \ge r_{\rm c}, \end{cases} \tag{9}$$

where

$$x = (r - r_{\rm n})/(r_{\rm c} - r_{\rm n}), \tag{10}$$

we define new functions $g(r)f(r)$ and $g(r)\phi(r)$. These new functions and their first derivatives go smoothly to zero at $r = r_{\rm c}$. We have taken $r_{\rm n}$=1.75, and $r_{\rm c}$=1.95 in the following calculations.

3. Molecular dynamics simulations of melting

As a useful approach to the study of melting, MD has obtained many results.[7−10] The materials that have been studied by MD are metals and crystals of inert gases, for their centro-symmetric forces can be described by many suitable potentials. Of course, metals and crystals of inert gases are different experimentally.[11−13] On melting, the fractional increase in volume for metals (about 5%) is far smaller than that for inert elements (about 15%). In addition, for inert elements, the melting point is approximately given by $kT_{\rm m}/\varepsilon \approx 0.7$, while for metals the melting point is found to be significantly lower, $kT_{\rm m}/\varepsilon \approx 0.1-0.3$. But previous computer simulations have not shown these differences explicitly, mainly because there was no potential that could accommodate both properly. Based on the EAM-LJ potential developed by Baskes, our potential can be applied to both crystals of inert gases (for small A or A=0) and metals (for larger A).

To test the potential, a group of A and β were chosen to study their influences on melting. We started with a cube of fcc material containing 512 atoms, periodic in three dimensions. The system is simulated at various temperatures and ambient pressure using Nose–Hoover temperature control[14,15] and Anderson pressure control[16] with a time step of 0.001 dimensionless time. At each temperature, the internal energy was monitored until equilibrium was attained. When the temperature was changed, the last configuration of the system was served as the initial configuration for further simulation.

Figure 1 presents the simulation results of the lattice parameter a and the internal energy E as functions of the extent of many-body bonding A and temperature. In the simulation, the decay of the electron density β was held at 4.24. The lattice parameter a has been defined as a=$(4\Omega)^{1/3}$, where Ω is the average atomic volume, both for the solid and liquid phases. As the temperature increases, we see that both the lattice parameters and the internal energies increase. At a certain temperature, an upward jump can be observed for each curve. From the atomic positions of the system (not shown), we see that an order–disorder transition has occurred when the jump takes

place, so the temperature is referred to as its melting point. It is shown in Fig.1 that the melting point of the system decreases with the increase of A, the extent of many-body bonding. The decrease of the melting point may be understood by examining the dependence of the shear elastic constants on A. Such a dependence is also valid for the nearest-neighbour EAM-LJ potential.[2]

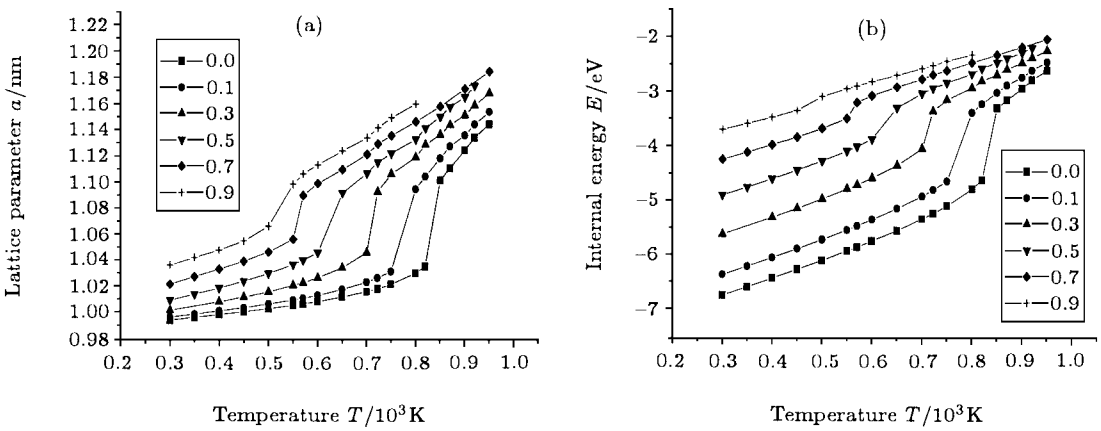


Fig.1. The lattice parameter a and the internal energy E as functions of temperature. The decay of the electron density β was held at 4.24.

Table 1. Comparison of EAM-LJ, experimental properties for fcc materials. All the experimental data are taken from Ref.[2]. The data in row Al (MD) are obtained from MD simulations using the Mei potential.[6]

	$(\Delta a/a)/\%$	$(\Delta V/V)/\%$	α_l/α_s	H_f/ε
A=0.0(LJ)	4.83	14.5	7.13	1.1
A=0.1	3.88	11.6	5.23	0.91
A=0.3	3.23	9.69	3.52	0.47
A=0.5	2.87	8.61	2.45	0.32
A=0.7	2.46	7.38	1.81	0.19
A=0.9	1.59	4.77	1.62	0.11
Ne (exp.)	5.10	15.3	–	–
Ar (exp.)	4.80	14.4	–	–
Cu (exp.)	1.50	4.51	1.27	–
Al (exp.)	2.0	6.0	1.23	–
Al (MD)	1.73	5.19	1.60	–

From Fig.1(a), it can also be seen that, at the melting point, the change of lattice parameter decreases with increasing A. Table 1 shows the estimated lattice parameter change, the corresponding fractional volume change, and various other parameters. We see that our calculated fractional volume is in reasonable agreement with the experimental data for inert materials and metals. Besides, it can be noted from Fig.1(a) that, for a melt with small A, its lattice parameter (and also its volume) increases sharply with increasing temperature. But a melt with larger A shows a less steep increase with temperature. α_l/α_s in Table 1 is the ratio of linear thermal expansion coefficients of liquid to solid. We see that, with increasing A, the ratio α_l/α_s decreases. From Fig.1(b), we see that the heat of fusion decreases with increasing A. These changes are in agreement with experimental data of crystals of inert gases and metals, and can be understood in terms of the many-body effects as follows. The many-body interactions between atoms in a melt with large A are so strong that the melt departs not too far from the solid while the melt with small A approaches gases instead of solids. So, with increasing A, the melt changes from inert gas-like melt to crystal-like melt. When it melts in a gas-like state, its structural change is great, so the heat of fusion is large. While for a system with large A, its structural change is relatively small so the heat of fusion is small. Other changes can be understood similarly.

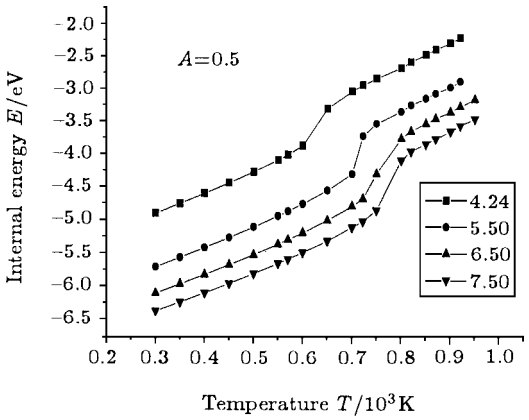


Fig.2. Internal energies for systems with A=0.5.

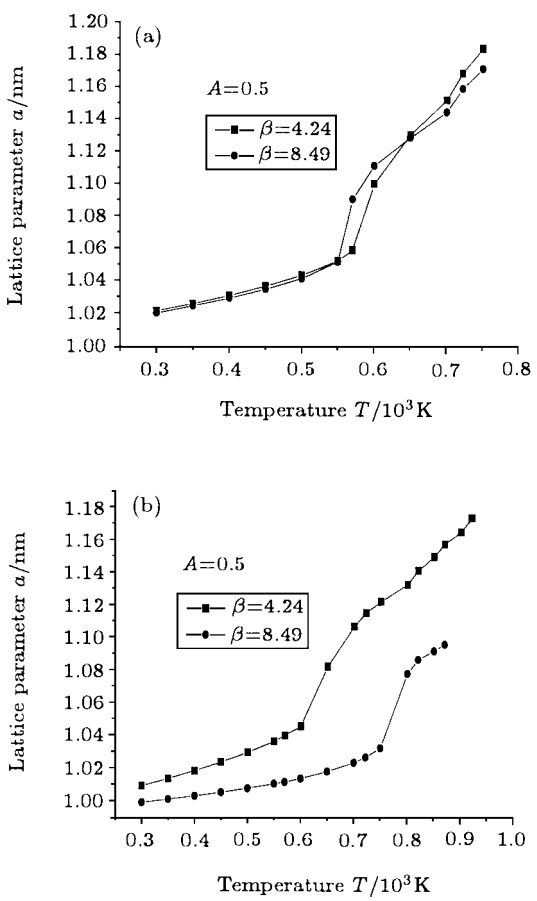


Fig.3. Lattice parameter of nearest-neighbour EAM-LJ potential (a) and our extended EAM-LJ potential (b).

Figure 2 shows the internal energies of systems for A=0.5. We see that with increasing β, the melting point increases. Apparently, this contradicts the result obtained by Baskes[2] which stated that the melting point decreases with increasing β, but in fact it does not. The reason is explained below. According to the shear instability model for melting, a crystal will melt when its shear elastic constant drops to zero. It is generally known that the expansion of the lattice reduces the shear elastic constants. In Fig.3(a), our simulations show that, for the nearest-neighbour EAM-LJ potential, the lattice parameters for crystals almost do not vary with β. So it may be supposed that the shear elastic constants at 0K may determine the order of the melting point of the nearest-neighbour systems, as pointed out by Baskes. However, from Fig.3(b), we see that for our EAM-LJ the lattice parameter of a crystal with small β is significantly larger than that with larger β. The larger lattice parameter of a crystal reduces its shear elastic constant and makes the crystal melt at a lower temperature. So, due to the dependence of the lattice parameter on β, the melting point increases with increasing β with our potential. Certainly, both our results and those of Baskes demonstrate that the shear instability plays a role in melting.

4. Conclusion

In summary, we have extended the nearest-neighbour EAM-LJ potential to a new form for fcc metals, which is valid for any choice of cut-off distance. We believe that our potential may be useful in the study of many-body effects.

We have used the EAM functions to study the melting of a crystal or metal by molecular dynamics simulation. The calculated fractional volume change on melting, heats of fusion and linear coefficients of thermal expansion were found to be in good agreement with the experimental data. The many-body interactions do obviously affect the melting. The second and third nearest neighbours were found to influence various parameters, including the melting point.

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