

Second-moment interatomic potential for aluminum derived from total-energy calculations and molecular dynamics application

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Abstract

We have obtained an interatomic potential for Al within the second-moment approximation of the tight-binding theory by fitting to the volume dependence of the total energy of the metal, computed by first-principles APW calculations. This scheme was applied to calculate the bulk modulus, elastic constants, vacancy formation and surface energies of Al. The predicted values are in good agreement with the measurements. We also have used this potential to perform molecular-dynamic simulations and determine the temperature dependence of the lattice constant and atomic mean-square displacements (MSDs), as well as the phonon spectra and surface related thermodynamic properties. A satisfactory accuracy has been obtained, denoting the success of the method. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Recently, atomistic simulations have been potentially developed in the area of condensed matter and materials research [1–3]. The choice of interatomic potential is very important to reproduce the thermodynamic and structural properties of materials with good accuracy. It is recognized that the *ab initio* molecular-dynamics (MD) [4] is one of the more accurate techniques to approach the physical properties of solids, but requires enormous computational time. On the other hand, the

empirical potentials [5], while simple, in many cases provide an acceptable and quick description of these properties. One of these methods is the second-moment approximation (SMA) to the tight-binding (TB) model [6–9], which is based on a small set of adjustable parameters and incorporates the essential band character of the metallic bond.

In previous works [5,10], we have presented results of evaluation of interatomic potentials of noble metals and their alloys in the framework of the TB-SMA, by fitting to the volume dependence of the total energy of these materials, computed by first-principles augmented-plane wave (APW) calculations, without using experimental data [11]. This approach provided satisfactory agreement with experimental results of elastic and structural

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properties along with a finite temperature physical quantities.

The motivation of this work is to check the validity of this interatomic potential for Al, which has free-electron-like character and has always been considered difficult to treat by a TB formalism. Recent calculations by Yang et al. [12] have demonstrated the applicability of TB in the case of Al.

2. Computational details

The electronic structure calculations of Al were performed self-consistently by the APW band-structure method within the muffin-tin approximation [13]. The calculations were scalar relativistic and used the Hedin–Lundqvist exchange correlation functional [14]. The total energy of both the fcc and bcc structures of metal were calculated at six different lattice constants from Janak’s expression [15], which requires the crystal potential, charge density and the eigenvalue sum. The resulting volume dependence of the energy was fitted to a parabolic function [16]. The Brillouin zone mesh contained 89 and 55 k-points in the irreducible wedge for the fcc and bcc structures, respectively.

The total energy of the system within the TB-SMA scheme [7,8] is written as

$$E = \sum_i \left(A \sum_{j \neq i} e^{-p(r_{ij}/r_0-1)} - \zeta \sqrt{\sum_{j \neq i} e^{-2q(r_{ij}/r_0-1)}} \right), \quad (1)$$

where the first sum represents a pair potential repulsive term of Born–Mayer type and the second sum corresponds to the band-energy term. In the above expression r_{ij} is the distance between atoms i and j and the sums over j are extended up to fifth neighbors. In this scheme there are five adjustable parameters A , ζ , p , q and r_0 , which have been determined from the expression (1) by simultaneous fitting to the APW total-energy curves as a function of volume for both the fcc and bcc structures. It should be noted that before the fitting procedure, we subtracted from both the fcc and bcc

APW total-energies the energy of isolated Al atom, calculated in the local-density-approximation (LDA), i.e. we constructed the cohesive energy curves. Furthermore, we shifted the computed cohesive energies uniformly, so that the absolute minimum of the fcc structure gives the experimental cohesive energy of Al, given that the total-energy of isolated atoms is poorly described within the LDA approach.

As a test of the quality of our parameters, we have calculated the bulk modulus of Al by the method proposed in [16], as well as the elastic constants at the experimental lattice parameter, at room temperature, by evaluating the difference in total energies of the distorted and undistorted lattices [17].

Furthermore, using the above interatomic potential (1) we performed MD simulations in the microcanonical ensemble aiming to validate the model at various temperatures. The system was made of 4000 particles arranged on fcc lattice. The simulation box contained 40 atomic layers with 100 atoms each with periodic boundary conditions in space. For the integration of the equations of motion, we used a time-step of 5 fs and the Verlet algorithm. Thermodynamic averages were taken over 50 ps trajectories after equilibration of the system. The vacancy formation and surface energies were calculated at $T = 0$ K by a quasidynamic minimization method integrated in the MD code. The MSDs were deduced from averages of the atomic density profiles, while the phonon DOS and phonon dispersion curves were calculated by Fourier transforming the velocity autocorrelation function. Details of these computational procedures are reported elsewhere [5].

3. Results and discussion

In Table 1 we give the calculated equilibrium lattice constant and cohesive energy of Al using the APW method, as well as the corresponding experimental values [18,19]. We find that the computed lattice parameter is within 0.5% of the experimental value. Concerning the cohesive energy, there is an overestimation of 25%, due to the

Table 1

Calculated and experimental lattice constant [18], a , along with the cohesive energy [19], E_c , of Al

Element	a (Å)		E_c (eV)	
	Calculated	Experimental	Calculated	Experimental
Al	4.00	4.02	4.19	3.34

well-known inaccuracy of the LDA for atoms. To correct for this effect, we uniformly shifted our energies to match the experimental value of the cohesive energy. This adjustment does not affect the validity of our elastic constant calculations and phonon spectra results, because we maintain the same volume variation of the energy.

In Fig. 1 we present the first-principles cohesive energy of Al (with opposite sign) as a function of the volume in the fcc and bcc structures (solid lines) after the uniform energy shift as described in Section 2. The filled symbols in the same graph show the results of the fit using the expression (1). We note that the fitting is almost excellent for both structures. From this procedure, we have obtained the potential parameters of the expression (1) listed in Table 2.

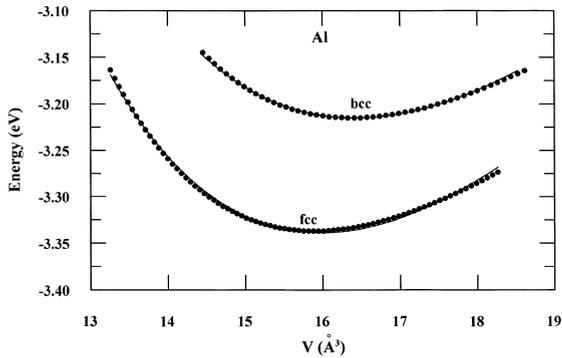


Fig. 1. Volume dependence of the calculated cohesive energies of Al (with opposite sign). Solid lines and filled symbols correspond to the APW calculations and to the results of fit (expression (1)), respectively.

Table 2

Potential Parameters of expression (1) deduced by fitting to the APW calculated cohesive energy as a function of volume

Element	ζ (eV)	A (eV)	q	p	r_0 (Å)
Al	0.7981	0.0334	1.1120	14.6147	2.8119

These parameters have been used to calculate the bulk modulus and elastic constants of Al. In Table 3 we report these calculated values, and the corresponding experimental values [20]. The calculated values of the bulk modulus and the elastic constants C_{11} and C_{12} are in very good agreement with the measurements, with first-principles calculations [21] and the elaborate TB method [12], while the elastic constant C_{44} shows a rather large discrepancy.

We also have determined the vacancy formation energy to be 1.45 eV, compared to the experimental value of 0.66 eV [22], while the TB approach of [12] gives good agreement with experiment (0.40 eV). In addition, the relaxed surface energy of (100) face is found to be 1.56 J/m², which is close to the reported measured value of 1.20 J/m² [23,24].

Furthermore, using the above-described interatomic potential, we have performed MD simulations at various temperatures. In Fig. 2 we present the computed temperature dependence of the lattice constant of Al, along with available measurements [25]. We see that the maximum lattice constant deviation between simulation and experiment is about 0.6% at room temperature, while the differences are smaller with increasing temperature. The linear expansion coefficient is found to be $3.5 \times 10^{-5} \text{ K}^{-1}$, compared to the experimental value of $2.4 \times 10^{-5} \text{ K}^{-1}$ [19].

In Fig. 3 we plot the computed atomic MSDs as a function of temperature for bulk atoms (dashed line), (100) surface atoms (empty triangles) and single adatoms (filled squares). In the same figure,

Table 3

Bulk modulus B and elastic constants of Al in (GPa). The calculations were performed within the SMA method and the experimental values were taken from [20]

Element	Al			
	B	C_{11}	C_{12}	C_{44}
Calculated (GPa)	73	116	52	48
Experimental (GPa)	76	107	61	29

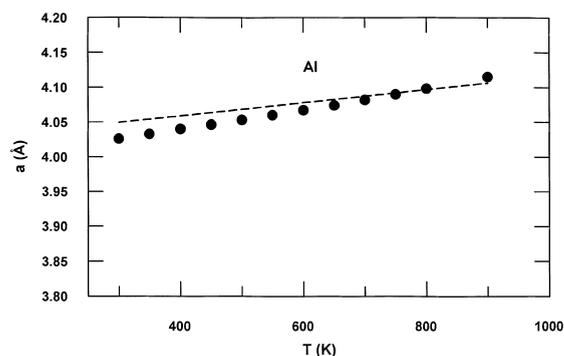


Fig. 2. Lattice constant of Al as a function of temperature. The filled circles correspond to the results of simulation, while the dashed line to the experimental data from [25].

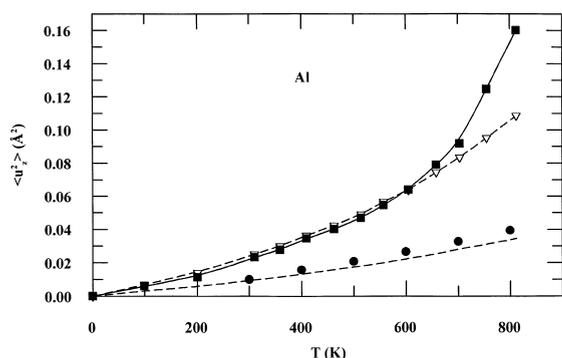


Fig. 3. Mean-square displacements of Al as a function of temperature. The dashed line, triangles and squares correspond to the results of our simulation for the bulk, surface atoms and adatoms, respectively, while the filled circles are the experimental data from [26].

we also show the experimental data for bulk atoms from neutron or X-ray scattering measurements [26] (filled circles). We note an excellent agreement between the predicted MSDs and measurements. Following Lindemann's criterion [27], we deduce

an approximate melting temperature of 1050 ± 100 K, estimated by the bulk MSDs values, close to the experimental value of 933 K [28]. From Fig. 3 we also note that the vibrations of surface atoms and adatoms present strong anharmonic behavior at temperatures above 500 K. In addition, the vibrational amplitudes of the adatoms and the surface atoms are roughly the same up to 600 K and differ above this temperature.

In Fig. 4 we present the calculated phonon DOS of Al at room temperature and in the inset we show the measured spectrum [29]. Comparing the shape of our theoretical DOS with that deduced from neutron scattering [29], we note that our model reproduces well the main features of the experimental spectrum at the correct frequencies. Nevertheless, the computed phonon spectrum is smooth and without the experimental sharp discontinuities, a fact that is related to the method of its calculation (Fourier transform of the velocity autocorrelation function).

Finally, in Fig. 5 we give the phonon-dispersion curves for Al at 300 K, along with the corresponding measurements using neutron spectrometry [30]. We observe a remarkable accuracy of our model for all the high-symmetry branches and the cutoff frequency, except for a slight overestimation of about 1 THz for the transverse mode along $[100]$ and T_1 and L along $[110]$ direction, in the

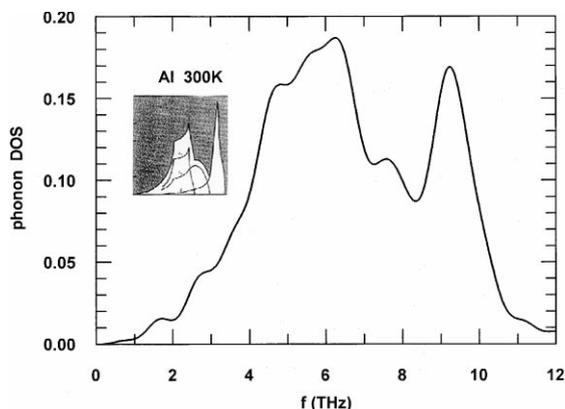


Fig. 4. Phonon DOS of Al at 300 K deduced from the present MD simulation; in the inset we show the measured spectrum [29].

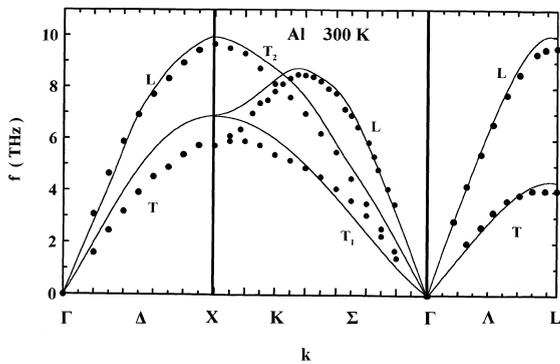


Fig. 5. Phonon dispersion curves of Al at 300 K along high symmetry directions. Solid lines correspond to MD simulations after a cubic spline interpolation; filled circles refer to the measured data from [30].

vicinity of point X. This is compatible with the inaccuracy found in our calculated value of C_{44} .

4. Conclusions

We have presented a method of evaluating the parameters of interatomic potential for Al in the framework of the second-moment approximation of the tight-binding theory by fitting it to the volume dependence of the total energy, computed by first-principles APW calculations. This method was applied to calculate the bulk modulus, elastic constants, vacancy formation and surface energies of Al. Our theoretical results achieved good accuracy, except for the vacancy formation energy and the elastic constant C_{44} . The more elaborate TB model of [12] is in better agreement with experiment. However, the present SMA scheme is much more computationally efficient for MD simulations.

Our molecular-dynamics simulations deduced the temperature dependence of the lattice parameter and atomic mean-square displacements, along with the phonon spectrum at room temperature. A comparison of the computed properties with the corresponding experimental values shows that the agreement is very good, despite the simplicity of the present model and denotes that this interatomic potential can be useful to provide reliable results in long-scale simulations.

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