Computer simulation of Au clusters properties[①]

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Abstract: An alternate approach to parametrizing the expression for the total energy of Au clusters within the second-moment approximation (SMA) of the tight-binding (TB) theory has been described. A type of many-body interatomic potential for Au from first-principle's calculations has been constructed. The key of the approach is adjusting the total-energy expression of the TB-SMA method to augmented-plane-wave (APW) total-energy results. The lattice constant, melting temperature, and the bulk modulus are in agreement with available experimental values. The method and results of Au cluster properties are shown to be very useful and suitable in describing the clusters and bulk metals.

Key words: computer simulation; Au cluster properties; tight-binding theory   **Document code:** A

1 INTRODUCTION

With the development of nanometer electronics, nanometer particles have been used to compound the nanodevices. Among them, gold nanoclusters are a fundamental part of recently synthesized nanocrystalline materials[1,2]. This is one of the reasons why theoretical and experimental studies on structure, electronic, and other physical and chemical properties of isolated and passivated gold clusters, as well as their size dependence, are at the front of cluster and nanoelectronic science.

Cluster computer modeling has been developed over the last twenty years in condensed-matter and material research[3,4]. Crucial to the success of any simulation is the interatomic potential. One of the approaches is the first-principle molecular dynamics (MD) introduced in Ref. [5]. This scheme provides an accurate description of atomic interactions, but requires enormous computational time. Another one deals with empirical potentials, which reproduces very fast with enough accuracy of the thermodynamics and structure properties of materials in many cases.

In this paper, some MD simulation results on the properties of gold clusters are presented. A many-body interatomic potential to describe gold clusters has been put forward[6,7]. The class of many-body potentials is based on local density approximation (LDA) calculations and the second moment approximation (SMA).

The SMA expression of the total energy is based on a small set of empirical parameters that are usually determined by matching with experimental elastic constants. First-principle's calculations within the local density approximation of the total energy and electronic bands were performed using an augmented-plane-wave(APW) method[8]. The total energy was computed from Janak's expression by using the resulting self-consistent crystal potential, charge density and the eigen value sum[9,10]. The total energy was calculated for at least five different lattice constants. By a parabolic fitting, the equilibrium lattice constant and the total-energy curve were determined. The total energy for six different lattice parameters for fcc structure of Au was also calculated.

2 METHODS AND RESULTS

The total potential energy within the tight binding (TB)-SMA mode[11] could be written as

$$U_{coh} = \sum_i \varepsilon_0 \sum_{j \neq i} \exp[- p(r_{ij}/r_0 - 1)] - \sum_i \{ \sum_{j \neq i} \xi_0^2 \exp[- 2q(r_{ij}/r_0 - 1)] \}^{1/2}$$

(1)

where the first sum corresponds to the pair-potential repulsive term of Born-Mayer type and the second sum to the band structure term, which has a many-body character due to its square root form. In expression (1), r_{ij} is the interatomic distance; r_0 is usually fixed to the value of the first-neighbor distance, in this case, r_0 is an additional free parameter, as suggested in Ref. [7]. Sums were taken over neighbors within 12 coordination shells in a crystal and over all atoms in clusters. Thus the above potential has five parameters. The parameters of the above potential were fitted to a LDA database that consists of the to-

tal energy as a function of the lattice constant. Therefore, these potentials are based on rigorous first-principle's LDA results. The five parameters ξ_0, ε_0, q, p and r_0, which have been determined from expression (1) by fitting to the APW total-energy, are functions of lattice constant for Au fcc structures and they are, respectively, $\xi = 10.925\,eV$, $\varepsilon_0 = 13.5959$ eV, $q = 2.7381$, $p = 6.3469$, $r_0 = 0.17517\,nm$.

In order to study the binding energy of gold clusters, an electronic term to the potential energy was added to describe subshell closing in a semi-classical description[12]:

$$E_N = \frac{U_{coh}}{N} - \frac{0.2}{N} \sum_K N_K^{1/3} \delta(N - N_K) \qquad (2)$$

where U_{coh} represents the structural contribution to the binding energy per atom, K is the subshell index, and N_K is the number of electrons closed in the K subshell. The last term is a sum of delta functions peaked at each subshell index and weighted by a dependence on $N_K^{1/3}$, to reflect the contribution of the surface curvature to the cluster binding energy per atom. Using the above interatomic potential, MD simulations were performed in the microcanonical ensemble in order to validate the model at various temperatures. Fig. 1 shows the binding energy for Au. The potential gives satisfactory binding energies and excellent agreement with experiment[13].
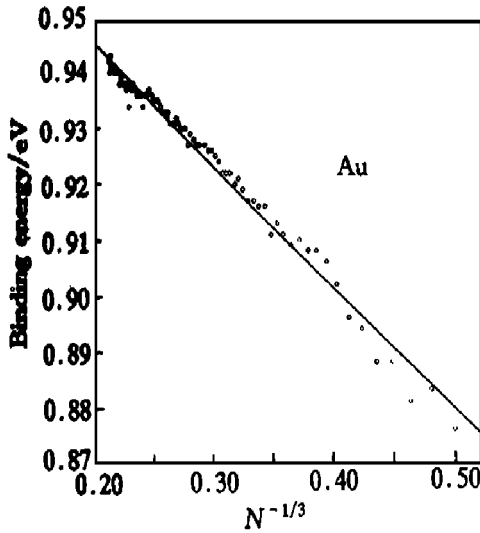

Fig. 1 Cluster binding energy per atom vs $N^{-1/3}$

The melting temperature T_m for Au fcc crystals calculated from Lindemann's criterion is

$$T_m = \frac{N \cdot m(0.15d)^2/k}{\sum_{i=1}^{3N}\sum_{j=1}^{3N-6} e(i,i)^2/\omega_j^2} \qquad (3)$$

where $d = \sqrt{3}a/2$, m is the atomic mass, a is the lattice constant for the fcc crystal symmetry, $e(i,j)$ is matrix showing the contribution of the normal mode ξ with frequency ω_j to the particle displacement u_i, and k is Boltzmann's constant. For Au crystals, the computation result is $T_m = 1322.7$ K

and the experimental result is $T_m = 1337.6$ K.

Using our model potential, the normal modes of clusters and crystals could be found. The $(3N - 6)$ normal mode frequencies for every cluster size N are also obtained. For crystals, a number of symmetrical k-mesh points in the Brilloun zone, whose average are taken up with the corresponding weights, are chosen. From the normal modes, the bulk modulus which can be compared with experiments are calculated. For the bulk modulus B of Au, the calculated result is $K = 164\,GPa$, and the experimental result is $K = 169\,GPa$. For the lattice constant a of Au, the calculated result is $a = 0.406\,nm$, and the experimental result is $a = 0.407\,nm$. In addition, the elastic constants were calculated with the experimental lattice constant at room temperature by evaluating the total energy using an orthorhombic and a monoclinic strain on the lattices and then determining the difference between total energies of the distorted and undistorted lattices. For the elastic constant of Au, the calculated results are $C_{11} = 226\,GPa$, $C_{12} = 193\,GPa$, $C_{44} = 47.5\,GPa$, the experimental results are $C_{11} = 189\,GPa$, $C_{12} = 159\,GPa$, $C_{44} = 42\,GPa$.

Fig. 2 illustrates the trend of the zero point energy as a function of cluster size. The zero point energy is not negligible and presents a strong dependence on cluster size up to about $N = 50$. This zero point energy has been systematically neglected in the studies of energy balance at zero temperature where clusters are assumed to be structureless. Additionally, the cluster Helmholtz free energy in the harmonic approximation could be written as

$$F = -\sum_{i=1}^{3N-6} kT \cdot \ln\left[\frac{\exp(-\hbar\omega_i/2kT)}{1-\exp(-\hbar\omega_i/kT)}\right] + E_N N \qquad (4)$$

where ω_i is the normal mode frequencies for a cluster of size N; E_N is the binding energy for the cluster
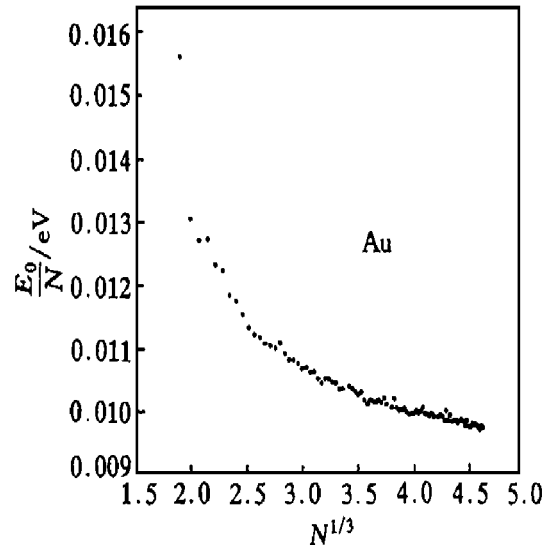

Fig. 2 Zero point energy per atom vs N for gold cluster

size N. Results of the free energy per particle at three low temperatures for sizes N from 6 to 99 are shown in Fig. 3. It is apparent that as clusters grow larger they become more stable and their free energy slowly tends toward the bulk value.
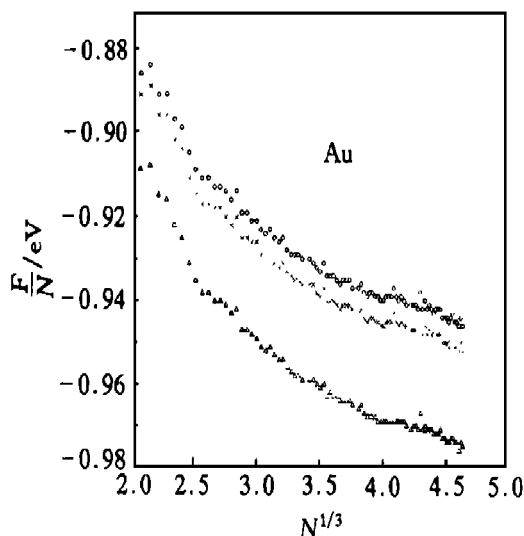

Fig. 3 Free energy per atom vs cluster size $N^{1/3}$ at three different temperatures 55 K(triangles), 200 K(circles), and 500 K(crosses)

The free energy are also calculated at the melting temperature of each cluster size. This potrait was given in Fig. 4, where each point indicates the free energy per particle at T_m for every given size. Solid lines are drawn to guide eye. Below the line clusters are liquidlike and above the line cluster are solidlike. This phase portrait clearly shows that the solidlike phase increases its stability as the cluster grows larger.
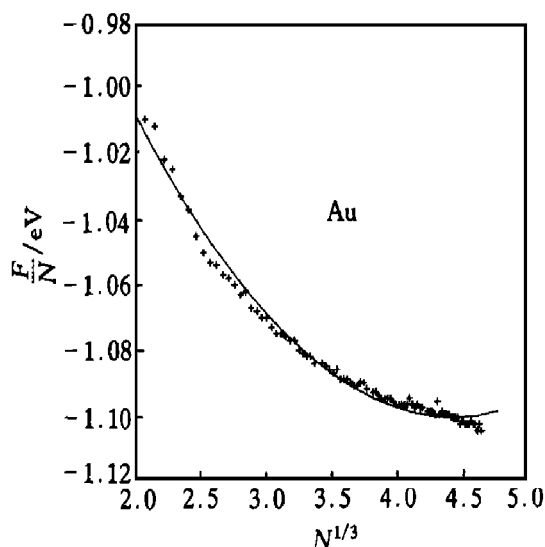

Fig. 4 Portrait in plane of free energy vs cluster size $N^{1/3}$

3   CONCLUSIONS

In order to validate the quality of our parameters, a potential for Au cluster from first-principle's

calculations have been constructed. A modified method for determining the parameters of tight-binding second-moment approximation interatomic potentials were presented by adjusting the corresponding expressions to first-principle's total-energy calculations. The potentials are shown to be very good in describing the properties of clusters and bulk metals. The lattice constant, melting temperature, the vibration mode and the bulk modulus are in agreement with available experimental values. The binding energy, zero point energy, and free energy at various temperatures and clusters sizes have been obtained. The results have shown that the multi-body potential provides a good and quick description of the bonding and energetics of the Au cluster system.

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