# A Tight-Binding Molecular-Dynamics Study of Copper Clusters

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# A Tight-Binding Molecular-Dynamics Study of Copper Clusters

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Using a tight-binding molecular-dynamics method, optimized structures of icosahedral and cuboctahedral $Cu_N$ ($N$=55, 147, and 309) are obtained. By comparing the total-energies of these optimized copper clusters, it is shown that icosahedral copper clsuters are more stable. The cluster size dependence of the interatomic distances agrees well with the results of EXAFS experiments. 3*d*-band evolution from $Cu_{55}$ to fcc bulk copper is also discussed in the light of previously reported ultraviolet photoelectron spectra.

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## I. Introduction

Metal clusters reveal characteristic and interesting physical and chemical properties different from the bulk. Many researchers have intensively studied their properties in the last decade[2]. Especially, valence s-electrons in simple metals show 'free-electron like' properties and their properties have been discussed in terms of the electronic shell model[3]. Copper clusters also have one valence 4s electron per atom, and this causes copper clusters to show magic numbers in their physical quantities, *e.g.*, time-of-flight spectra, electron-affinity, and HOMO-LUMO gap.

In the field of cluster science, 'How large a cluster can show bulk properties?' is one of the most intriguing questions. The cluster size dependence of the interatomic distances shows a transition from cluster to bulk, and it is known that in general the average nearest-neighbor distances decrease with decreasing cluster sizes. Montano *et al.* have measured the average nearest-neighbor distances of copper clusters going from the dimer to one with 1.5 nm diameter using EXAFS[6]. They observed contraction of nearest-neighbor distances compared to the bulk value in all cluster sizes they measured. By using effective-medium theory, Hansen *et al.* tried to reproduce the results of EXAFS by Montano *et al.* In the model potential calculation of Hansen *et al.*, however, interatomic distances of copper clusters showed increase as cluster size decrease[7]. D'Agostino also performed similar calculation by many-body tight-binding potential of Tomaneck *et al.*[12] Results of D'Agostino show better agreement with the experimets of Montano *et al.*, but the difference between experiments and theory is still large.

As a cluster-bulk transition seen in electronic structures, cluster size dependence of UPS spectra have been reported by Cheshnovsky *et al.* and Taylor *et al.*[4][5] Cheshnovsky *et al.* and Taylor *et al.* observed the UPS spectra of $Cu_2^-$–$Cu_{410}^-$, and it was confirmed that the 3*d*-band of copper clusters emerges at the $Cu_9^-$, and it evolves toward that of the bulk at larger clusters. We could not find out theoretical study on the evolution of 3*d*-band of copper clusters in literature.

So far, the stable structures of copper clusters have been extensively investigated. A number of theoretical tools have been developed and applied to determine the stable structures of copper clusters. The first-principles calculation is the most accurate and reliable one among them. Owing to its high computational cost, however, this method has been applied to only very small clusters up to 10 atoms[9][10]. Many-body potentials[12] and effective-medium theory[13][14] have also been used to study copper clusters. These methods are computationally faster than the first-principles methods and applied to a larger cluster which consists of about 8000 atoms, but they have less quantum mechanical characteristics.

Tight-binding molecular-dynamics (TBMD) method, which is a quantum mechanical calculation and computationally more efficient than the first-principles methods, has been successfully applied to covalent systems, *e.g.*, carbon and silicon systems. Since this method is suitable to deal with dynamics of low symmetry systems, many applications to atomic clusters, surfaces and interfaces have been done[15][16]. Recently, new TB parameters for transition metals have been proposed by Mehl and Papaconstantopoulos[1]. Mehl and Papaconstantopoulos showed that the new TB parameters can well reproduce bulk and surface properties computed by the first-principles methods, such as lattice constants, bulk moduli and surface energies. So far, no application of these new TB parameters to clusters have been reported. We have firstly applied the TB parameters to study ground state structures of copper clusters and investigated the cluster-bulk transition in the geometric and electronic properties of copper clusters.

In the following chapters, we first describe details of the computational tools we used. In Section 3, the structure stability of $Cu_{55}$–$Cu_{309}$ and cluster size dependence of the nearest-neighbor distances and the electronic density of states (DOS) are presented. Section 4 is

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devoted to a brief summary.

## II. Computational Model

In the present study, we use a TB parameter proposed by Mehl and Papaconstantopoulos[1], which has spd non-orthogonal basis. Diagonal elements of our Hamiltonian matrix have an environment-dependent form;

$$h_{i,\alpha}=a_{i,\alpha}+b_{i,\alpha}\rho_i^{2/3}+c_{i,\alpha}\rho_i^{4/3}+d_{i,\alpha}\rho_i^2 \quad (1)$$

where, $i$ is atom index and $\alpha=3d$, $4s$, $4p$. $\rho_i$ is an environment-dependent parameter, representing a 'density' around atom $i$,

$$\rho_i=\sum_{j\neq i}\exp\left[-\lambda_{ji}^2 R_{ij}\right]F_c(R_{ij}), \quad (2)$$

where $\lambda_{ji}$ is atom-type dependent parameter, $R_{ij}$ is interatomic distance between atoms $i$ and $j$. $F_c(R)$ is a cut-off function,

$$F_c(R)=\frac{1}{1+e^{(R-R_0)/l}}, \quad (3)$$

where $R_0$ and $l$ are cutoff parameters. Off-diagonal elements of our Hamiltonian and overlap matrices have a standard two-center form, and they depend on an interatomic distance only. The total-energy is computed by taking the sum of eigenvalues over occupied eigenstates. For the force calculation, Hellmann-Feynman theorem is used[16].

For structure relaxation, steepest-descent (SD) algorithm are adopted. When the maximum force on a particle goes below the assumed convergence criterion (here $1.0\times10^{-3}$ Hartree/Bohr†), the calculation is stopped. In the present simulation, 1 molecular-dynamics step is 5 fs and the Verlet algorithm is used to update the atomic coordinates.

## III. Results and Discussion

We have relaxed structures of $Cu_N$ ($N=55$, 147, and 309) with icosahedral and cuboctahedral symmetries. In **Table 1**, the total-energies of these optimized clusters are shown. As one can see from Table 1, icosahedral clusters are more stable than the cuboctahedral (fcc) ones in this size region. The stable structures of copper clusters is associated to their size, and there is a critical size where a transition from icosahedral to fcc structures takes place. Reinhard *et al.* experimentally studied the size dependence of structures of free copper clusters using electron diffraction, and it was found that the icosahedral structure is more stable than the fcc structure up to about 2500 atoms[8]. Valkeakahti *et al.*[11] performed computer simulation on the stability of copper clusters and obtained the results in agreement with the experiments by Reinhard *et al.* The present result is consistent with these previous studies.

Table 1 Geometry and total-energy of the structure optimized copper clusters. The origin of total-energy is shifted by Mehl and Papaconstantopoulos owing to the special functional form of their tight-binding parameters.

| Number of atoms | Geometry | Total-energy (eV/atom) |
|---|---|---|
| 55 | Icosahedral | −2.9350 |
| 55 | Cuboctahedral | −2.8477 |
| 147 | Icosahedral | −3.2219 |
| 147 | Cuboctahedral | −3.1663 |
| 309 | Icosahedral | −3.4291 |
| 309 | Cuboctahedral | −3.3496 |
| bulk | fcc | −3.99 |

† 1 Hartree ≈ 27.2 eV, 1 eV ≈ $1.6\times10^{-19}$ J, 1 Bohr ≈ 0.0529 nm.

Cluster size dependence of the averaged nearest-neighbor distance for icosahedral $Cu_N$ ($N=55$, 147, and 309) is shown in **Fig. 1**. The average nearest-neighbor distances in these clusters are lower than that of bulk fcc copper. The reason could be that in the crystalline fcc phase, each copper atom has 12 nearest-neighbors, whereas in all the studied clusters the averaged number of nearest-neighbors is smaller than 12 due to surface atoms. Therefore, atoms gather closer to each other, and the nearest-neighbor distance becomes smallest at dimer. The experimental EXAFS results by Montano *et al.*[6] are also shown in Fig. 1. In the figure, the results of effective medium theory of Hansen *et al.*[7] and a many-body potential of D'Agostino[12] are plotted. At the larger clusters, agreement between experimental and these two and the present computational results is similar. At smaller cluster size (these clusters corresponds to right hand side of the Fig. 1), agreement between the present simulation and the EXAFS results are much better compared to the result of effective-medium theory of Hansen *et al.*, where the nearest-neighbor distances of copper clusters show increment as cluster size decreases. Although the results of many-body potential of D'Agostino at the smaller clusters is better agreement with the EXAFS data compared to that of effective medium theory, the agreement is still poor. These disagreement between experiment and calssical model potentials is mainly due to lack of quantum mechanical characters in the classical potentials. Importance of quantum mechanical characters in smaller cluster size will be disscused in the following section in terms of the electronic structure of copper clusters.

The electronic DOS of the structure optimized copper clusters are shown in **Fig. 2**. These DOS curves are generated by using Gaussian broadening which has width of 0.3 eV. In the figure, the DOS for bulk fcc copper is also plotted. As can be seen in Fig. 2, except for small sharp peaks in the 3*d*-band, which comes from $e_g$ and $t_{2g}$ symmetry of bulk fcc, the DOS curve for $Cu_{309}$ and bulk copper have almost similar 3*d*-band width and low energy tail part.

Cheshnovsky *et al.*[4] have measured the 3*d*-band by ultraviolet photoelectron spectroscopy up to $Cu_{410}^-$, and found out that 3*d*-band emerges at $Cu_9^-$, and the 3*d*-band evolve toward that of bulk as cluster size increase. Indeed, the present result for DOS of $Cu_{55}$ has broad 3*d*-

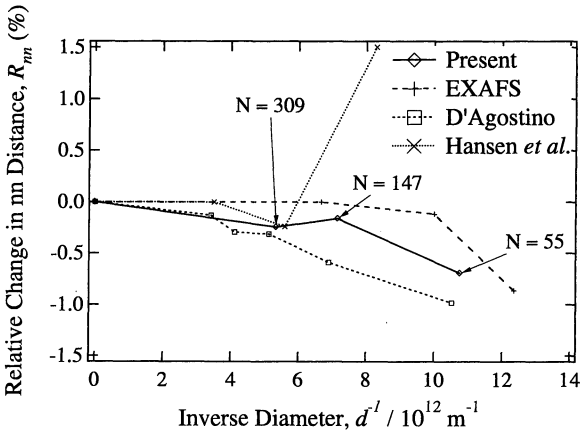


Fig. 1 Cluster size dependence of nearest-neighbor (nn) distance for relaxed icosahedral $Cu_N$ ($N$=55, 147, and 309). Inverse of the diameter of a cluster is denoted as $d^{-1}$. Longitudinal axis corresponds to relative change in nn distance compared to bulk value.

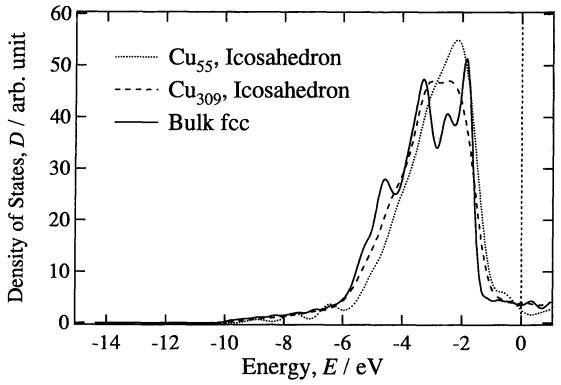


Fig. 2 Electronic DOS for icosahedral $Cu_{55}$, $Cu_{309}$, and bulk copper. The Fermi energy is shifted to zero and all DOS curves are scaled for comparison.

band. However, the 3*d*-band of $Cu_{55}$ is still narrower and sharper than that of bulk. This is ascribed to the large number of surface atoms in $Cu_{55}$ (in $Cu_{55}$, 76.4% of the total atoms belong to surface). By using discrete variational method, Delley *et al.*[17] have implied that the partial-DOS of the surface part of $Cu_{79}$ has a narrower 3*d*-band compared to the central 19 atoms. This indicates that the surface atoms makes the width of DOS narrower. In the present study, the ratio between the number of surface and non-surface atoms in $Cu_{309}$ is almost 1:1 ($Cu_{309}$ has 52.4% surface atoms).

From Fig. 2, it can be seen that $Cu_{55}$ and $Cu_{309}$ have different low energy tail part of DOS curves. The DOS of $Cu_{55}$ has an oscillating curve with comparatively large amplitude at the low energy tail, and $Cu_{309}$ has non-oscillating low energy part. This oscillation is due to the discreteness of the electronic energy levels. The low energy tail of DOS for copper clusters consist of mainly s electrons, and the bonding electrons in copper are also mainly s electrons. As we can see from Fig. 1, the present results for $Cu_{55}$ show much better agreement with EXAFS compared to classical potentials. This better agreement is mainly due to explicit treatment of quantum mechanical characters. Some quantum mechanical corrections, such as one-electron correction in effective medium theory[13][14], will improve the results of classical potentials in the cluster size with atoms less than fifty-five.

## IV. Summary

Icosahedral and cuboctahedral $Cu_N$, ($N$=55, 147, and 309) are studied using TBMD and SD. Icosahedral structures are energetically preferred in the size region. Cluster size dependence of the nearest-neighbor distance agree well with EXAFS results. The overall shape of 3*d*-band for $Cu_{309}$ is similar to that of bulk. It is pointed out that importance of quantum mechanical characters in smaller copper clusters, at least for the clusters consist of less than fifty-five atoms.

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REFERENCES

(1) M. J. Mehl and D. A. Papaconstantopoulos: Phys. Rev., **B54** (1996), 4519-4530.
(2) R. F. Service: Science, **271** (1996), 920-945.
(3) W. A. de Heer: Rev. Mod. Phys., **65** (1993), 611-676.
(4) O. Cheshnovsky, K. J. Taylor, J. Conceicao and R. E. Smalley: Phys. Rev. Lett., **64** (1990), 1785-1788.
(5) K. J. Taylor, C. L. Pettiette-Hall, O. Cheshnovsky and R. E. Smalley: J. Chem. Phys., **96** (1992), 3319-3329.
(6) P. A. Montano, G. K. Shenoy and E. E. Alp: Phys. Rev. Lett., **56** (1986), 2076-2079.
(7) L. B. Hansen, P. Stoltze, J. K. Norskov, B. S. Clausen and W. Niemann: Phys. Rev. Lett., **64** (1990), 3155-3158.
(8) D. Reinhard, B. D. Hall, P. Berthoud, S. Valkealahti and R. Monot: Phys. Rev. Lett., **79** (1997), 1459-1462.
(9) K. A. Jackson: Phys. Rev., **B47** (1993), 9715-9722.
(10) C. Massobrio, A. Pasquarello and R. Car: Chem. Phys. Lett., **238** (1995), 215-221.
(11) S. Valkeakahti and M. Manninen: Phys. Rev., **B45** (1992), 9459-9462.
(12) G. D'Agostino: Phil. Mag., **B68** (1993), 903-911.
(13) O. B. Christensen, K. W. Jacobsen, J. K. Norskov and M. Manninen: Phys. Rev. Lett., **66** (1991), 2219-2222.
(14) O. B. Christensen: Phys. Rev., **B50** (1994), 1844-1847.
(15) M. Sternberg, W. R. L. Lambrecht and Th. Frauenheim: Phys. Rev., **B56** (1997), 1568-11492.
(16) M. Menon and K. R. Subbaswamy: Phys. Rev., **B47** (1993), 12754-12759.
(17) B. Delley, D. E. Ellis, A. J. Freeman, E. J. Baerends and D. Post: Phys. Rev., **B27** (1983), 2132-2144.