New algorithm in the basin hopping Monte Carlo to find the global minimum structure of unary and binary metallic nanoclusters

Hyoung Gyu Kim, Si Kyung Choi, and Hyuck Mo Lee

Department of Materials Science and Engineering, KAIST, Gusung-dong 373-1, Yusung-gu, Daejeon 305-701, South Korea

(Received 22 January 2008; accepted 28 February 2008; published online 9 April 2008)

The basin-hopping Monte Carlo algorithm was modified to more effectively determine a global minimum structure in pure and binary metallic nanoclusters. For a pure metallic Ag55 nanocluster, the newly developed quadratic basin-hopping Monte Carlo algorithm is 3.8 times more efficient than the standard basin-hopping Monte Carlo algorithm. For a bimetallic Ag42Pd13 nanocluster, the new algorithm succeeds in finding the global minimum structure by 18.3% even though the standard basin-hopping Monte Carlo algorithm fails to achieve it. © 2008 American Institute of Physics. [DOI: 10.1063/1.2900644]

I. INTRODUCTION

Nanoclusters that consist of at least several tens to several thousands of atoms have recently attracted considerable attention, first because of their unusual thermodynamic properties, such as a lower melting point and surface melting, and second, because of their unique structures, such as icosahedrons, decahedrons, truncated octahedrons, and even core-shell structures. These properties are sensitively dependent on the size and composition of the nanoclusters; thus, the optical and catalytic properties can be tuned by controlling the size and composition, and, in turn, the structures. It is important therefore to determine the exact structure in terms of size and composition.

The basin-hopping Monte Carlo (BHMC) method is one of the widely used methods of determining the global minimum structure. The BHMC method has been thoroughly investigated by Doye and Wales using the Lennard-Jones (LJ) and Sutton–Chen potentials, and it predicts successfully the global minimum structure of pure metallic clusters. However, the search space of the BHMC method increases exponentially with the size of the system, and, when the LJ potential is used, the number of minima of a cluster composed of even 55 atoms is at least 1010 plateaus. Thus, when an empirical potential is used to determine the global minimum structure in a system of pure metallic clusters, the maximum size of the system is reported to be not more than 200 atoms, even if recently developed methods are applied. In a bimetallic cluster, the number of minimum conditions increases sharply with the composition; thus, even the recent studies that reported on methods of determining the global minimum were limited to a system size of less than 60 atoms. One study has reported on a global minimum structure for a bimetallic cluster with 98 atoms at most; however, this achievement was only made possible by means of a newly developed method that combines a genetic algorithm, the BHMC algorithm, and a shell optimization approach, all of which require a very long calculation time. We therefore propose to modify and test the BHMC algorithm, which is simpler and more efficient, for determining the global minimum structure, especially for a bimetallic cluster.

II. COMPUTATIONAL DETAILS

We consider a small nanocluster system. The system is described by the potential energy $E(r)$, where $r$ is a multidimensional vector of the internal coordinates. We then search for the global energy minimum of $E(r)$. According to the standard BHMC algorithm, the choice of preserving a current coordination or accepting a new coordination is based on the Metropolis algorithm. The difference from the standard MC algorithm is that the energy should be minimized with respect to the local minimum before the Metropolis acceptance rule is applied. Reported that the use of a minimization procedure before the application of the acceptance criterion is equivalent to searching for a transformed potential energy surface defined by

$$\tilde{E}(r) = \min\{E(r)\},$$

where $r$ represents the vector of coordinates and $\min$ represents the energy minimization that is performed starting from $r$.

In the standard BHMC algorithm, the new coordinate $r_{\text{new}}$ is generated by summing $r$ and the random perturbation. The maximum value of the random perturbation at each atom is constant, which means that the total energy is minimized whenever the system is assumed to be a bulk material. In a nanocluster, however, the diffusion coefficient of atoms in the core differs from that of atoms in the surface; thus, the atoms in the surface area move much faster than the atoms in the core. Our modification of the standard BHMC algorithm is based on this idea. The detailed procedures are as follows:

1. Find the geometrical center of the system.
2. Calculate the distance $D_i$ from the geometrical center to an $i$th atom.

4$^{a}$Author to whom correspondence should be addressed. Electronic mail: hmlee@kaist.ac.kr. Telephone: +82-42-869-3334. Fax: +82-42-869-3310.
(3) Set the maximum displacement in proportion to $D_i$ (a linear BHMC algorithm) or $D_i^2$ (a quadratic BHMC algorithm). The standard BHMC algorithm refers to a constant maximum displacement.

(4) Allow every atom to move by random perturbation. The value of the random perturbation is selected within the maximum displacement of each atom.

(5) Apply the conjugated gradient method to a new configuration made by random perturbation. We use the adaptive conjugated gradient method.\textsuperscript{23}

(6) Accept or refuse a new tentative configuration by the Metropolis rule.

The simplest method of considering the realistic diffusion behavior of the nanocluster is to apply different displacements of atoms at the core and in the surface. However, the method of dividing a certain atom into the core or surface takes $O(N^2)$ as a computational complex theory. We therefore use a linear (or quadratic) BHMC algorithm because it takes $O[N]$. The calculation time with a quantum Sutton–Chen (QSC) potential takes $O[N^2]$: thus, the increased consuming time of the modified algorithm is negligible in comparison with the standard BHMC algorithm especially when the nanocluster size is large.

The details of the simulation conditions are as follows. In both the Ag$_{55}$ cluster and the Ag$_{42}$Pd$_{13}$ cluster, the simulation starts from a completely random structure that satisfies only one condition, namely, that every atom should hold at least one neighbor atom between $0.8r_{nn}$ and $1.3r_{nn}$, where $r_{nn}$ stands for the distance to the nearest neighbor.\textsuperscript{24} The maximum displacement is given a constant value of 0.8 Å in the standard BHMC algorithm and the maximum displacement is set to 1.2 Å according to a linear or quadratic BHMC algorithm. The modified BHMC algorithm is performed for 5000 MC step (MCS) with respect to the Ag$_{55}$ and for 9500 MCS for the Ag$_{42}$Pd$_{13}$ at 1000 K, which means that the acceptance rate in the Metropolis rule is about 11.4% at the energy barrier of 0.3 eV. The high temperature guarantees a high probability of overcoming the energy barrier; however, it also induces a high probability of explosion. Before observing the morphology of the nanoclusters, we perform additional 500 MCS at 0 K with the maximum displacement of 0.3 Å to find the more detailed configuration with the minimum energy.

The modified BHMC algorithm is tested in relation to a pure metallic cluster of Ag$_{55}$ and a bimetallic cluster of Ag$_{42}$Pd$_{13}$. Note that we selected Ag$_{55}$ and Ag$_{42}$Pd$_{13}$ as model systems because of their widely known global minimum structures.\textsuperscript{13,20} The QSC potential was used in all the simulations.\textsuperscript{25} The relevant potential parameters of Ag and Pd are reported in our previous studies.\textsuperscript{26,27}

III. RESULTS AND DISCUSSION

Figure 1 shows a typical example of a potential energy versus MCS curve as well as the corresponding snapshots of the system for the Ag$_{55}$. We used a quadratic BHMC algorithm, which, as mentioned, starts from a random structure and goes through a rough morphology at 71 MCS. At 171 MCS, a cluster appeared where the crystalline behavior was observed. At 363 MCS, only one atom was not in the correct position of an icosahedron, and that atom is indicated by an arrow. This structure at the local minimum is one of the slightly excited and deviated structures from the global minimum. Finally, Ag$_{55}$ shows a complete icosahedron structure at 1718 MCS. After 5000 MCS, the potential energy drops abruptly and the final minimum energy is $-136.89$ eV.

Figure 2 shows similar behavior for the bimetallic cluster Ag$_{42}$Pd$_{13}$ as simulated with a quadratic BHMC algorithm. The Ag atoms are colored red (dark contrast) and the Pd atoms are blue (bright contrast). The structure also started from a disordered one where several Pd atoms are located on the surface. From the beginning, the surface rearrangement occurred simultaneously with the movement of the Ag atoms.
from the core to the surface. The active migration process is almost over at 1720 MCS. Furthermore, the continued migration of excited atoms in the short range enabled the slightly excited local minimum structure to be attained at 2253 MCS. The arrow indicates an atom that has deviated from the core-shell structure. After 6077 MCS, we finally obtained a perfect core-shell structure with an icosahedron, and the final energy calculated with the QSC potential is −150.41 eV.

To confirm the improved efficiency with the quadratic BHMC algorithm, we performed simulations in more than a hundred trials to determine the global minimum structure. The results, which are shown in Table I, were obtained by three different BHMC algorithms along with optimized parameters. The standard BHMC algorithm had a success rate of 34.6% in determining the global minimum, and the average convergence speed among the successful cases was 2852 MCS. The success rate of the linear BHMC algorithm almost doubled that of the standard one, though the convergence speed was not increased significantly. In the case of the quadratic BHMC algorithm, the success rate and the convergence speed were both significantly improved.

When the modified BHMC algorithms were tested in a bimetallic system the results were more dramatic. After 104 trials with the standard BHMC algorithm, we failed to obtain a core-shell type of icosahedron structure and the lowest energy was greater than −147.60 eV. In contrast, the energy of the global minimum structure was −150.41 eV (see Fig. 3). With respect to the linear BHMC algorithm, eight of 116 trials succeeded in forming a core-shell structure with a perfect icosahedron. Ultimately, the quadratic BHMC algorithm yielded an impressive success rate of 18.3% with a reasonable converging time and an average value of 5829 MCS.

We considered and tested two other possibilities as an alternative to the quadratic BHMC algorithm (the best of three algorithms in Table I), namely, an exponential BHMC algorithm [the maximum displacement in proportion to \( \exp(D/1) \)] and a two-staged BHMC algorithm (in which the diffusion coefficient is 0.3 Å if \( r < 0.8r_{\text{max}} \) or 1.2 Å if \( r > 0.8r_{\text{max}} \), where \( r \) is the distance from the geometrical center to an \( i \)th atom and \( r_{\text{max}} \) is the largest distance). Neither alternative, however, achieved better efficiency than the quadratic BHMC algorithm, at least in the case of Ag\(_{42}\)Pd\(_{13}\).

It is harder to determine the exact global minimum structure in a bimetallic cluster than in a pure metallic cluster mainly because of the increased possible number of local minimum structures to be considered. Figures 3(a) and 3(b) show typical examples of local minimum structures attained in a bimetallic system and Fig. 3(c) is for the global minimum structure. In Fig. 3(a), only one atom, indicated by an arrow, is out of the correct position of a core-shell icosahedron.
While the structure of Fig. 3(b) shows that two atoms (one Pd atom indicated by an arrow and one Ag atom inside the core) are exchanged from a core-shell icosahedron. The structure of Fig. 3(a) would have been the second lowest energy configuration if the system was a pure metallic. In a bimetallic nanocluster, however, the atomic configuration in Fig. 3(b) is more stable than in Fig. 3(a). Therefore, the atom-exchange process, the most efficient way of transition from Fig. 3(b) to Fig. 3(c), is a key role to achieve the global minimum structure in a bimetallic nanocluster. In our experience of repeated trials, the atom-exchange process occurred more frequently in the quadratic BHMC algorithm than in the standard BHMC algorithm, which seems to be probably caused by the more realistic atomic displacement value.

The merit of the quadratic BHMC algorithm lies in its great adaptability with other BHMC algorithms, such as a multicanonical basin-hopping method,\textsuperscript{16,17} a basin-hopping method mixed with other optimization methods,\textsuperscript{21} and a basin-hopping method based on the density functional theory.\textsuperscript{28-30} Our modified algorithm focuses on a method of generating a new tentative configuration of nanoclusters in the BHMC algorithm. As such, it can be easily applied to any other MC techniques and it reduces the computation time for a metallic cluster, especially for a bimetallic cluster.

IV. SUMMARY

We have discussed the development of a modified BHMC algorithm for determining the global minimum structure in unary and binary metallic nanoclusters. This idea originated from the natural diffusion properties of a nanocluster, where the atoms in the surface area move faster than those at the core. A quadratic BHMC algorithm performs better than several candidate algorithms. For a pure metallic nanocluster of Ag\textsubscript{55}, the efficiency of the new algorithm is 3.8 times better than that of the standard BHMC algorithm. For a bimetallic nanocluster of Ag\textsubscript{42}Pd\textsubscript{13}, the success rate of the new algorithm is increased remarkably by up to 18.3\%, and the system is converged within a reasonable time. In contrast to it, the standard BHMC algorithm fails to find the global minimum structure under the same conditions. Because this algorithm can be applied simultaneously to other recently developed algorithms, it is a useful tool for determining the global minimum structure of a large number of atoms in unary and binary metallic clusters.

ACKNOWLEDGMENTS

One of the authors (S.K.C.) acknowledges support by the Korea Science and Engineering Foundation (KOSEF) through the National Research Laboratory Program funded by the Ministry of Science and Technology (M1040000024-04J0000-02410).