Structure of transition metal clusters: A force-biased Monte Carlo approach

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Abstract. We present a force-biased Monte Carlo (FMC) method for structural modeling of transition metal clusters of Fe, Ni, and Cu with 5 to 60 atoms. By employing the Finnis-Sinclair potential for Fe and the Sutton-Chen potential for Ni and Cu, the total energy of the clusters is minimized using a method that utilizes atomic forces in Monte Carlo simulations. The structural configurations of the clusters obtained from this biased Monte Carlo approach are analyzed and compared with the same from the Cambridge Cluster Database (CCD). The results show that the total-energy of the FMC clusters is very close to the corresponding value of the CCD clusters as listed in the Cambridge Cluster Database. A comparison of the FMC and CCD clusters is presented by computing the pair-correlation function, the bond-angle distribution, and the distribution of atomic-coordination numbers in the first-coordination shell, which provide information about the two-body and three-body correlation functions, the local atomic structure, and the bonding environment of the atoms in the clusters.

1. Introduction
In recent years there has been a rapid development in the global optimization techniques, which include state-of-the-art evolutionary search strategies to the population-based swarm intelligence and differential-evolution approaches [1]. In spite of this development, the Monte Carlo (MC) methods–based on the Metropolis or related algorithms–continue to play a major role in addressing difficult optimization problems in science and engineering. Since the calculation of local gradients of a potential is computationally more complex than the evaluation of the total energy of a system, the MC methods are often preferred in many optimization problems where local gradients are either not available or computationally too expensive to compute. However, the advantage of the MC methods is often outweighed by their slow convergence behavior, which require a longer simulation time to produce results with the desired accuracy when compared to the Newton-like and Conjugate-Direction methods. The main purpose of the paper is to explore the usefulness of employing atomic forces in Monte Carlo simulations. In particular, we study here the application of a simple gradient-based Monte Carlo method, originally introduced by Rossky et al. [2, 3], to optimize the transition metal clusters of Fe, Ni, and Cu and compare the results with the putative global minimum of these clusters reported in recent literature [4, 5].

Transition metal clusters (TMCs) have been studied extensively from computational and experimental points of view [4–8]. Theoretical efforts to study TMCs include empirical Monte Carlo and molecular-dynamics simulations to semi-empirical tight-binding and full ab initio calculations. Among numerous studies, the structure of Fe clusters obtained from the Finnis-Sinclair potential [9, 10] and that of Ni
and Cu clusters bound by the Sutton-Chen potential [11] are of particular interest. The putative global minima of Ni and Cu clusters of varying sizes have been studied systematically by Doye and Wales [5] using the Sutton-Chen potential. Likewise, Elliott et al. [4] have recently addressed the computation of the global minima of several Fe clusters using the Finnis-Sinclair potential. In both the cases, the authors have employed an improved version of the basin-hopping algorithm of Li and Scheraga [12] using Monte Carlo simulations coupled with the Conjugate-Gradient optimization [13]. The total energy and structures of these clusters are available from the Cambridge Cluster Database (CCD). In the following, we refer these clusters as the CCD clusters and use them as a benchmark for the comparison of the total energy and structure of Fe, Ni, and Cu clusters obtained from the force-biased Monte Carlo (FMC) simulations presented here.

2. Computational Method

We began by generating a random configuration consisting of N atoms and computing the total energy of the configuration using an appropriate interatomic potential. Here, we chose to employ the Finnis-Sinclair potential [9] for Fe clusters and the Sutton-Chen potential [11] for Ni and Cu clusters. The initial configuration was equilibrated at temperature \( T = 3000 \) K for \( 10^5 \) Monte Carlo steps (MCS). Thereafter, the temperature was decreased by a factor of 0.99 and the system was equilibrated for \( 10^5 \) MCS at each temperature until the final temperature of the system was reduced to 1 K. The total-energy relaxation was achieved in two steps: a) first, we computed the total force on each atom in the initial state and displaced a randomly selected atom at site \( i \) from an initial state \( n \) to a proposed state \( m \) by \[ \Delta r_{mn} = \alpha \delta r_{mn} + \beta A f^n_i. \] Here, \( \beta = \frac{1}{k_B T} \) and, \( \alpha \) and \( A \) are parameters that determine the length of the random displacement \( \alpha \delta r_{mn} \) and the contribution from the potential gradient \( -f^n_i \) at site \( i \) in generating a proposed configuration \( m \), respectively. The displacement \( \delta r_{mn} \) is generally, but not necessarily, drawn from a Gaussian distribution with a zero mean and a variance \( 2A \); b) second, the proposed configuration obtained in step (a) was either accepted or rejected. Following Rossky et al. [2], and Allen and Tildesley [3], one can show that the proposed move in Eq. (1) can be accepted with the probability \[ P_{mn} = \min[1, \exp(-\beta \Delta E_{mn})], \] where \begin{equation}
\Delta E_{mn} = \Delta E_{mn} + \left[ \frac{1}{2}(f^n_i + f^m_i) \cdot \Delta r_{mn} + \frac{\beta A}{4}((\delta f^n_{mn})^2 + 2f^n_i \cdot \delta f_{mn}^i) \right],
\end{equation}

\[ \delta E_{mn} = E^m - E^n, \quad \delta f_{mn}^i = f^m_i - f^n_i. \]

In Eq. (2) above, \( E^n \) and \( E^m \) are the total energy of the system in the initial state and the proposed state, respectively. Likewise, \( f^n_i \) and \( f^m_i \) are the total force on an atom at site \( i \) before and after the displacement, respectively. In this work, we moved one atom at a time but it is straightforward to move a group of atoms simultaneously by ensuring that the change of total energy, \( \Delta E_{mn} \), associated with multi-atom moves, is properly evaluated. To improve the acceptance rate, we adjusted the step length by restricting \( \alpha \) between 0.001 Å at 1 K and 0.05 Å at 3000 K. The value of \( A \) was chosen in such a way that \( \beta A \approx 4-5 \times 10^{-3} \) and \( \delta r_{mn} \) was a random number drawn from a uniform distribution between -1 and +1. In this preliminary study, we made no attempts to optimize the values of \( \alpha \) and \( A \), which can be adjusted during simulations to improve the efficiency of the method.

3. Results and Discussions

3.1. Total energy of Fe, Ni, and Cu clusters

In this section, we present the results from our simulations with an emphasis on the structural properties of the clusters. Following a comparison of the total-energy values of the FMC clusters with the same from the Cambridge Cluster Database [4, 5], we analyze the two- and three-body correlation functions.
Table 1. Total energy of Fe, Ni, and Cu clusters from the FMC and CCD simulations.

| N   | Fe (eV) FMC (CCD) | Ni (eV) FMC (CCD) | Cu (eV) FMC (CCD) |
|-----|------------------|------------------|------------------|
| 5   | -11.8598 (-11.8598) | -14.6033 (-14.6033) | -11.5120 (-11.5120) |
| 10  | -28.5357 (-28.5357) | -32.5487 (-32.5487) | -25.6584 (-25.6585) |
| 15  | -46.6371 (-46.6375) | -51.3230 (-51.3231) | -40.4584 (-40.4586) |
| 20  | -64.8373 (-64.8385) | -69.9806 (-69.9833) | -55.1663 (-55.1686) |
| 25  | -82.9394 (-82.9402) | -89.0701 (-89.0708) | -70.2151 (-70.2155) |
| 30  | -101.4469 (-101.4513) | -108.4284 (-108.4296) | -85.4753 (-85.4762) |
| 35  | -119.5937 (-119.5971) | -127.9645 (-127.9657) | -100.8758 (-100.8767) |
| 40  | -138.5100 (-138.5112) | -147.5979 (-147.6000) | -116.3534 (-116.3547) |
| 45  | -156.6982 (-156.6997) | -167.1068 (-167.1649) | -131.7262 (-131.7780) |
| 50  | -175.4342 (-175.4720) | -187.0454 (-187.2391) | -147.6007 (-147.6026) |
| 55  | -194.6847 (-194.6868) | -207.6107 (-207.6135) | -163.6617 (-163.6640) |
| 60  | -214.4256 (-214.4278) | -226.8486 (-226.9008) | -178.8274 (-178.8684) |

and show that the three-dimensional distribution of atoms in the FMC and CCD clusters are very close to each other as far as these correlation functions are concerned. We then address the distribution of the coordination numbers of the atoms in order to obtain further information about the atomic arrangement in the first-coordination shell of atoms. Table 1 lists the total energy of Fe, Ni, and Cu clusters from the FMC simulations. The corresponding total energy of the CCD clusters is also indicated in Table 1. A comparison of the total-energy values suggests that the maximum absolute deviation of the total energy (between the FMC and CCD structures) is less than 0.2 eV, which translates a percentage deviation of 0.1% (see Ni50). Figure 1 presents the total-energy difference, $\Delta E = E_{\text{FMC}} - E_{\text{CCD}}$, between the FMC and CCD clusters. For Fe clusters of up to 45 atoms, the FMC and CCD structures have practically the same energy, whereas the energy of the remaining few clusters with $N > 45$ shows a minor deviation of up to 0.05 eV from the CCD configuration. A similar observation applies for Cu clusters in Fig. 1(c) and Ni clusters in Fig. 1(b) with the exception of Ni50, as mentioned earlier. It is evident from Table 1 that the optimized FMC clusters are as stable as the corresponding CCD clusters as far as the total energy of the clusters is concerned.

Figure 1. Total-energy difference ($\Delta E$) as a function of the cluster size ($N$) for a) Fe, b) Ni, and c) Cu clusters.

3.2. Local structure and atomic environment

We now discuss the two- and three-body correlation functions in order to examine the three-dimensional distribution of atoms in the clusters. Toward that end, the pair-correlation functions for Fe, Ni, and
Cu clusters are plotted in Fig. 2 along with the corresponding pair-correlation functions for the CCD clusters. The bond-angle distributions for these clusters are also plotted in Fig. 3 for comparison. The results indicate that the two-body and three-body correlation functions from the FMC structures match very closely with their CCD counterparts reflecting structural similarities from the point of view of radial and bond-angle distribution functions.

**Figure 2.** The pair-correlation functions for a) Fe, b) Ni, and c) Cu clusters from the FMC simulations. The corresponding pair-correlation functions for the CCD clusters are also shown for comparison.

**Figure 3.** Bond-angle distributions for a) Fe, b) Ni, and c) Cu clusters from the FMC and CCD structures.

**Figure 4.** The atomic-coordination numbers in a representative 40-atom a) Fe, b) Ni, and c) Cu cluster.

While the pair-correlation function and the bond-angle distribution of a cluster provide considerable information about the local atomic structure and the bonding geometry of the atoms, these distributions cannot uniquely characterize a three-dimensional distribution of atoms in real space. Reverse Monte Carlo simulations of amorphous materials [15–17] – and the recent work on amorphous silicon and amorphous silica [18–21], using hybrid simulation strategies, which employed both the total energy and the atomic forces in structural determination of complex non-crystalline materials – indicate that one
needs to include structural information beyond three-body atomic correlations in order to generate a unique atomic arrangement from a given set of structural data from experiments. For this purpose, we have computed the distribution of the atomic-coordination numbers in the first-coordination shell of the atoms and their bonding environment in order to obtain additional information on the atomic arrangement of the clusters beyond the two-body and the reduced three-body correlation functions. In Fig. 4, we have shown the distributions of the atomic-coordination numbers for Fe, Ni, and Cu clusters. The results indicate that not only the average-coordination number of an FMC cluster and a CCD cluster matches with each other, which is evident from the area under the first peak of the pair-correlation function in Fig. 2, but also the full distribution of the atomic-coordination numbers as shown in Fig. 4.

4. Conclusion
In this paper, we have presented a Monte Carlo study of total-energy optimization and structural properties of transition metal clusters of Fe, Ni, and Cu. Using a force-biased Monte Carlo method, we have optimized the total energy of the clusters by employing the Finnis-Sinclair potential for Fe and the Sutton-Chen potentials for Ni and Cu. Unlike conventional Monte Carlo simulations, where the acceptance probability of a random displacement of an atom is governed by the energy difference between the final and initial states only, the present method employs both the total-energy difference and atomic forces in determining the acceptance probability associated with the Monte Carlo moves. The total energy of the clusters obtained from the FMC simulations is compared with the data listed in the Cambridge Cluster Database (CCD). The results suggest that the FMC method can produce structural configurations, which are essentially identical to that of the CCD configurations as far as the total energy, the pair-correlation function, the bond-angle distribution, and the atomic-coordination numbers are concerned. The method can be applied to model bulk amorphous solids where one is primarily interested in obtaining a set of atomic configurations that correspond to a few low-lying local minima on the potential energy surface. In a future communication, we shall address this problem using an optimized version of the FMC algorithm.

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