COMPUTER SIMULATION OF GOLD MICROCLUSTERS

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ABSTRACT

We performed a set of computer simulations of clusters of 38, 55 and 79 gold atoms by the constant-energy molecular dynamics method using N-body interactions. Within a finite temperature range of total energy, the cluster exhibited structural fluctuations between solid-like and liquid-like states. Based on our simulations, we propose a scenario in which the thermal expansion of the cluster initiates the structural fluctuations and the fluctuation is accompanied by the breathing of expansion and contraction of the cluster. The change of solid to liquid causes expansion and the change of liquid to solid contraction. The initial kinetic energy for fluctuation is decreased with decreasing the size of cluster.

1. Introduction

The physical and chemical properties of microclusters are quite different from those of bulk size. A crystal of bulk size does not change its outer shape spontaneously. In a crystal of very small size, however, the energy required for a structural reshuffle may be small enough to allow the crystal to change its shape by thermal fluctuations.

Such structural fluctuations were actually observed in microclusters of gold atoms [1]. A high resolution electron microscope images showed that a cluster of about 460 gold atoms transformed itself from a face centered cubic (fcc) structure to an icosahedron or other multiply twinned structure. A cause for these structure transformations was, at first, not clarified because of a relatively high flux of electrons used in the experiment. A later experiment [2], however, with a reduced electron flux, showed similar fluctuations of the cluster shape and led to a conclusion that the origin of these structural changes was thermal fluctuations.

The latest experiment [3] substantiated this conclusion by demonstrating that a gold cluster started changing its shape after it was decoupled from a MgO substrate.

It was concluded that when a cluster was on the substrate, it was trapped in a deep potential energy well, but once it was decoupled from the substrate, it began to migrate over a shallow potential energy surface, whose minima corresponded to different cluster shapes. They called this thermally fluctuating state a "quasi-melting" state, which they had previously predicted [4] to occur below melting point by calculating Gibbs free energy of single crystal as well as multiply twinned structures based on their elastic continuum model.

Prior to these findings, Berry and his coworkers had suggested [5] that there might be a temperature range where a small cluster would show a coexistence of liquid-like and solid-like states [6], and performed a series of computer simulations for clusters of 7 to 33 argon atom clusters using mainly the constant energy molecular dynamics method [7]. We also reported the simulation on argon microclusters [8].

In this paper, based on the computer simulations, we report the structural fluctuations of gold microclusters containing 38, 55 and 79 atoms. And new knowledge about gold microclusters after our previous paper[10] is reported.

2. Simulations

Using the constant-energy molecular dynamics method with Verlet's algorithm [9], we studied behavior of clusters of 79 gold atoms [10]. An embedded function was chosen for an interatomic potential. This potential is different from two body potential in argon. In this scheme the interaction between atom i and atom j is represented by an N-body potential depending on the atomic configuration of surroundings of atoms i and j. Here the potential developed by Oh and Johnson [11] is used. The potential energy of an atom i is written as

$$U_i = f(\rho_i) + (1/2)\sum_j V_{ij} \tag{1}$$

$$\rho_i = \sum_j \phi_{ij} \tag{2}$$

,where V_{ij} is a central pair potential, f is an embedding function and V_{ij} and ϕ_{ij} are functions only of the interatomic distance r_{ij}. A time step Δt was taken to be 5 $\times$ 10^{-15} (sec). We started with fcc structures for 38 and 79 atom clusters and with an icosahedron for 55 atom cluster as depicted in Figure 1, and gradually heated it up by raising its kinetic energy. Figure 2 summarized the present heating process for the 79 atom cluster, in which we performed fairly long runs up to 5 $\times$ 10^6 steps.

Our heating process was up to about 1.6×10^6 steps. Strictly speaking, the fcc structure chosen for the initial configuration is not the lowest energy structure, but structures built around multi-layer icosahedron (N= 55) have the slightly lower potential energy, while the cluster underwent structural fluctuations. It is likely that once structural fluctuations are set in, an initial configuration should be not so important.

In order to make clear the structural fluctuation, we first examine the change of kinetic energy which is converted to temperature. The high kinetic energy which is associated with the low potential energy corresponds to solid-like state as pointed out in ref.[8]. We also enumerated all the octahedra composed of neighboring atoms. By keeping track of the numbers of these octahedra during each simulation, we found that the solid-like states contain more octahedra than the liquid-like states do [8].

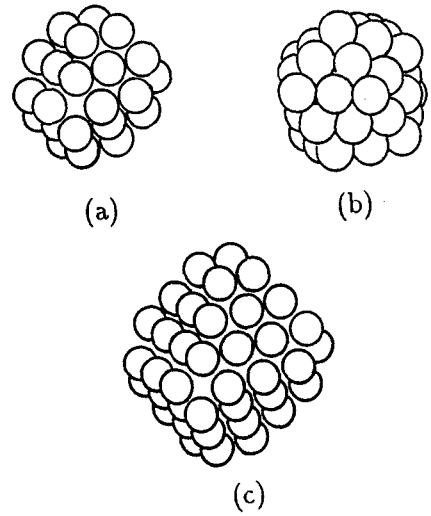

Fig.1 Initial atomic configurations of (a) 38, (b) 55 and (c) 79 atom clusters.

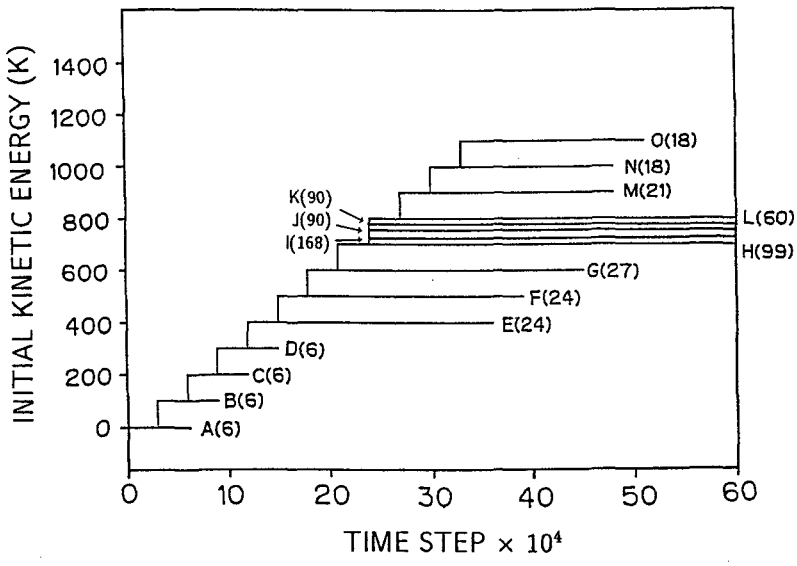

Fig.2 Summary of calculations for the 79 atom cluster in the heating process. The kinetic energy (vertical axis) is converted to temperature.

Furthermore we examine the pair correlation function, the angular distribution function and the mean square displacement together with the loci of movement of atoms. What distinguishes the solid-like states from the liquid-like states are (1) small peaks seen around $\sqrt{2}$ times the first peak distance in the pair correlation functions, (2) peaks observed around 90° in the angular distribution functions, and (3) small constant values for the mean square displacement. (1) and (2) suggest that our cluster, in the solid-like states, contain some octahedra consisting of neighboring atoms, and (3) shows that there is no diffusive movements of atoms in the solid-like states.

3. Results and Discussion

Figure 3 shows the change of temperature which corresponds to kinetic energy of 79 atom cluster at the initial kinetic energy H indicated in Fig.2. At the energy H, no change in temperature is seen even after 1 million steps, where the number of octahedra is not changed and the pair correlation function and the angular distribution function has shown the solid state. These results suggest that the solid state is kept during the steps below the energy H.

On the other hand, at energies I to L, the fluctuation of temperature and the number of octahedron has been observed. Figure 4 shows the synchronism of fluctuations of the temperature and the number of octahedron at energy I. The arrow a in the figure indicates the initial point of the fluctuation and arrows b and c show the typical points for fluctuation we examined. At point b, the temperature is lower and the number of octahedron is smaller than those at point c.

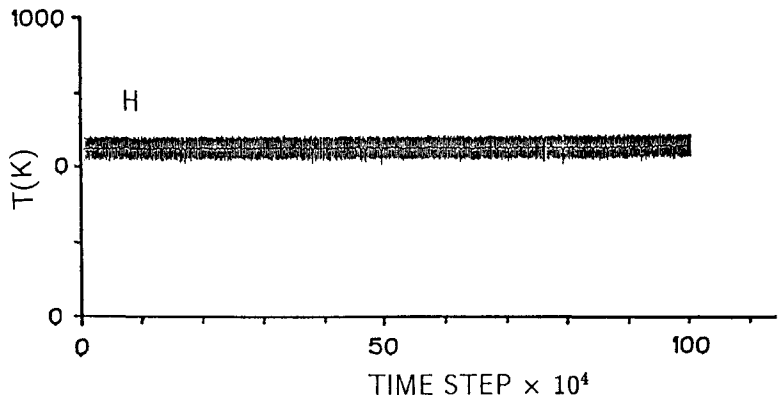

Fig.3 Temperature (kinetic energy) as a function of time step at the initial energy H.

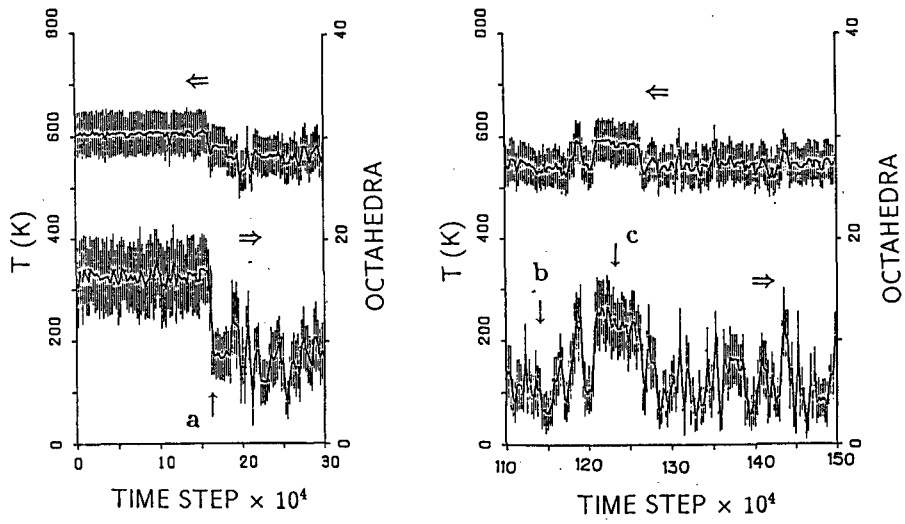

Fig.4 Temperature (kinetic enrrgy) and number of octahedron as a function of time step at the initial energy I.

To make clear the fluctuation more precisely, the mean square displacement of all 79 atoms, $<[R(t)-R(0)]^2>$, for 3×10^4 steps after points b and c are shown in Fig.5, where R(0) is the initial position at each point b or c. Gradual increase of the displacement is observed for point b (Fig.5a), whereas the displacement for point c (Fig.5b) is almost constant. This situation is confirmed by the loci of movement of atoms during the same steps with Fig.5 as shown in Fig.6. The atoms at point c keep their initial position rather rigidly than those at point b. By these calculations, therefore, it is concluded that the structures at points b and c are in liquid-like and solid-like states, respectively. The changes of temperature (kinetic energy) and of number of octahedron as shown in Fig.4 are due to the structural fluctuation between liquid-like and solid-like states. For larger time

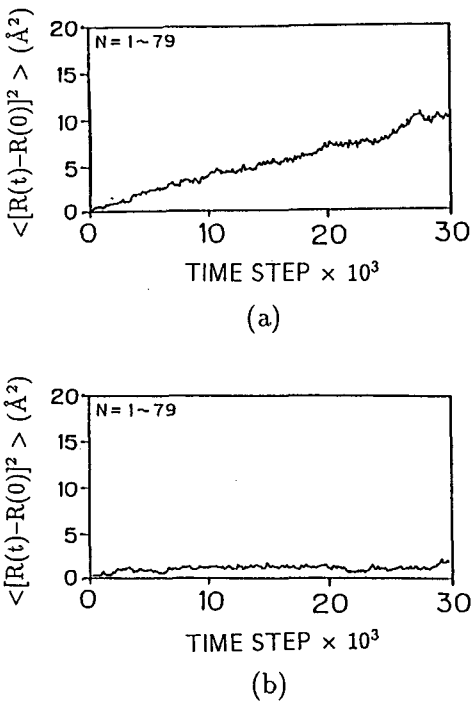

Fig.5 Mean square displacement of all atoms in 79 atom cluster as a function of time steps for 3×10^4 steps after points b (a) and c (b) indicated in Fig.4.

scale, the fluctuation might be the coexistence of liquid-like and solid-like states. We also studied the pair correlation function and the angular distribution function at points b and c. However, very small differences of these functions between points b and c has been observed. It seems that it is difficult for judgment of such structural fluctuations to utilize the heights of peaks of the functions discussed above.

Then, in the coexistence region, the mean distance <R> of atoms from the center of cluster has been calculated. Figure 7 shows the change of <R> as a function of steps at energy I. It is seen in Fig.7 that the expansion of cluster takes place at the starting point a of structural fluctuation indicated in Fig.4. And the mean distances for the solid-like and liquid-like states change from those for the liquid and solid states; the solid-like state transforms to liquid-like state with expansion while the liquid-like state dose with contraction. In other words, the

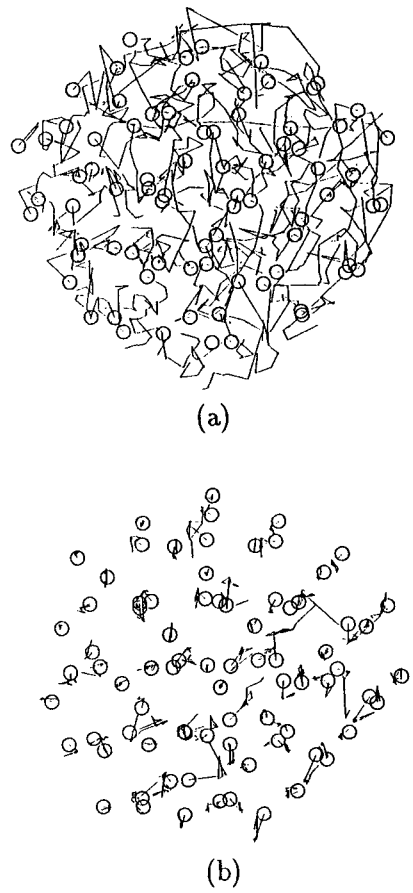

Fig.6 Loci of movement of atoms in 79 atom cluster for 3 × 10^4 steps after points b (a) and c (b) indicated in Fig.4.

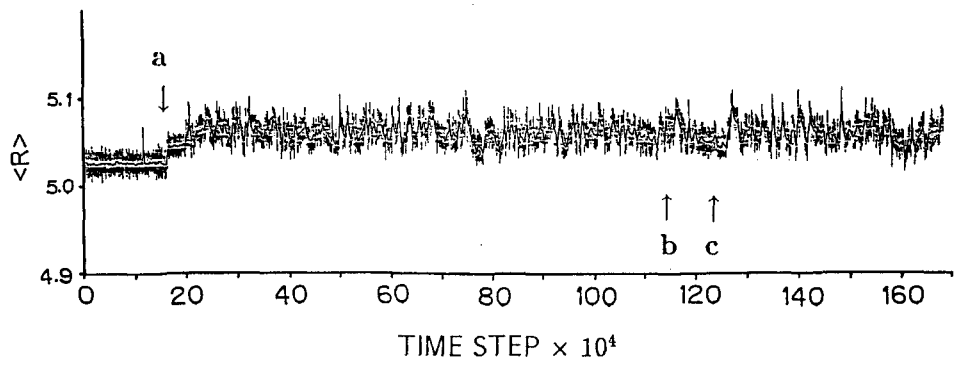

Fig.7 Mean distance <R> of 79 atoms from the center of the cluster as a function of time steps at the initial energy I.

structural fluctuation is always accompanied by the fluctuation of the mean distance corresponding to expansion and contraction. Accordingly it is concluded that the mode of the present structural fluctuation is breathing mode.

At higher initial energies than point M in Fig.2, the cluster has been kept in liquid state. The situation has been distinguished by the number of octahedron, the pair correlation function and the mean square displacement.

Next we calculated the change of kinetic energy and the number of octahedron for 38 and 55 atom clusters as shown in Fig.8. The structural fluctuations take place at the initial energy of 400K and 510K for 38 and 55 atom clusters, respectively.

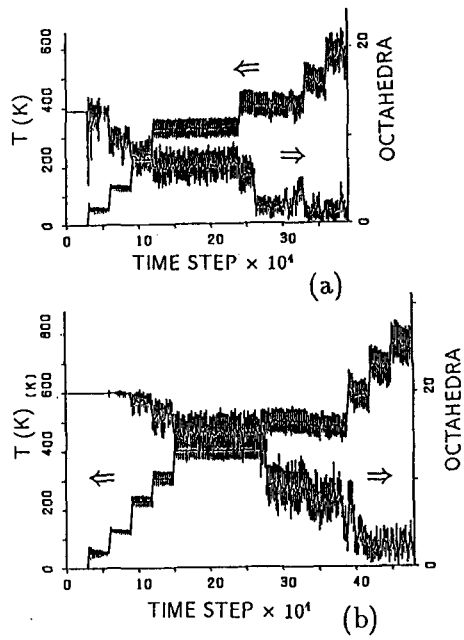

Fig.8 Temperture (kinetic energy) and number of octahedron as a function of time steps; (a) for 38 atom cluster and (b) for 55 atom cluster.

Since the initial temperature of 79 atom cluster is 600K, the initial temperature decreases with decreasing the size of cluster. The temperature decreases with increasing the ratio of number of atoms at surface to total number of atoms of the cluster. In our previous report for an Ar microcluster with 79 atoms, such initial energy for structural fluctuation was 37K[8]. The ratios of the initial energy to the melting point of bulk size are 0.44 and 0.45 for Ar and Au microclusters with same number of atoms, respectively. Accordingly the structural fluctuation takes place when the ratio is about 0.45, which is independent of species of atoms.

In conclusion, the structural fluctuation between solid-like and liquid like states is observed in a finite initial energy range for gold microclusters which may be similar in nature to the spontaneous change of crystal shapes observed in gold clusters. The thermal expansion of the cluster initiates the structural fluctuations. The fluctuation is accompanied by the breathing of expansion and contraction of the cluster. The change of solid to liquid causes expansion and the change of liquid to solid contraction. The initial kinetic energy for fluctuation is decreased with decreasing the size of cluster.

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References

[1] S. Iijima and T. Ichihashi: Phys. Rev. Lett. 56 (1986) 616.

[2] M. Mitome, Y. Tanishiro and K. Takayanagi: Z. Phys. D12 (1989) 45.

[3] P. M. Ajayan and L. D. Marks: Phys. Rev. Lett. 63 (1989) 279.

[4] P. M. Ajayan and L. D. Marks: Phys. Rev. Lett. 60 (1988) 585.

[5] R. S. Berry, J. Jellinek and G. Natanson: Phys. Rev. A30 (1984) 919.

[6] There has been an experiment which suggests the coexistence of solid-like and liquid-like states in argon clusters. See M. Y. Hahn and R. L. Whetten: Phys. Rev. Lett. 61 (1988) 1190.

[7] J. Jellinek, T. L. Beck and R. S. Berry: J. Chem. Phys. 84 (1986) 2783;
F. G. Amar and R. S. Berry: J. Chem. Phys. 85 (1986) 5943;
H. L. Davis, J. Jellinek and R. S. Berry: J. Chem. Phys. 86 (1987) 6456;
T. L. Beck, J. Jellinek and R. S. Berry: J. Chem. Phys. 87 (1987) 545;
T. L. Beck and R. S. Berry: J. Chem. Phys. 88 (1988) 3910.

[8] H. Matsuoka, T. Hirokawa, T. Uchida, M. Matsui and M. Doyama: Proc. of the First Intern. Conf. and Exihib. on Computer Applications to Materials Science and Engineering, Tokyo, 1990, p.365.

[9] L. Verlet: Phys. Rev. 159 (1967) 98.

[10] T. Uchida, H. Matsuoka, M. Matsui and M. Doyama: Proc. of the First Intern. Conf. and Exihib. on Computer Applications to Materials Science and Engineering, Tokyo, 1990, p.371.

[11] D. J. Oh and R. A. Johnson: J. Nucl. Mater. 169 (1989) 5
D. J. Oh and R. A. Johnson: Atomistic Simulation of Materials, Beyond Pair Potentials, ed. by V. Vitek and D. J. Srolovitz, Plenum, New York, 1989, p.233