Sci. Rep. RITU A43 (1997) pp. 43-46
No. 1, March 1997

Molecular Dynamics Simulation for the (Magic Number) Size Effect in Nucleation and Evaporation of Clusters

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(Received December 28, 1996)

Cluster formation of Lennard-Jones particles (65,536 atoms in a unit cell with overall number density equal to 0.0149) was simulated by molecular dynamics. The temperature was controlled to decrease linearly with time by various thermostats, starting from a gas state temperature and ending at zero temperature. Nucleation (aggregation) and evaporation processes of clusters are separately analyzed. No particular size dependence in the former process was found. Evaporation process made the clusters into the stable structure of the particular sizes (13, 19, 23, *etc.*) in cooperate with cooling the clusters.

KEYWORDS: molecular dynamics, cluster, nucleation, size effect, magic number.

1. Introduction

Term "cluster" is used in many fields with the different meanings. In case of molecular and atomic clusters, they are defined as aggregates of atoms or molecules [1]. Even though they are not in a stable phase, they are in many cases stable in vacuum. Such clusters are experimentally produced through a nucleation process from the gas state by rapid cooling with supersonic jet, inert gas flow, *etc.*, and typically observed by a mass spectrometer A lot of different size clusters are formed by these methods, but they are not produced in the uniform distribution. Some predominantly strong peaks are observed in the mass spectra of the clusters. These "magic" number peaks are generally explained as formation of clusters of geometrically ordered structures [2] or electronic shell ones [3]. Size distribution is, however, not completely reflected by the stability of clusters, *i.e.* free energy of clusters. In some cases, size distribution is dependent on the formation process. Therefore, there might be a kinetic effect in the cluster formation process.

In order to see how clusters are formed, molecular dynamics (MD) calculation for Lennard-Jones (L-J) particles was performed using the various thermostats which would make it possible to simulate the various cooling methods. The results were already presented elsewhere that the rapid cooling by the inert gas give the smooth size distribution and that a long time evaporation makes the clusters be more stable structures, resulting higher peaks at the magic numbers in the size distribution [4,5]. In this report, detail analysis of size dependence in the cluster formation by rapid cooling and graphical observation of the magic number cluster formation by evaporation.

2. Calculation

The L-J potential, U_{ij}, between atoms i and j was combined with a switching function, F_{switch}, [6] centered at 5.5σ:

$$U_{ij} = 4\varepsilon \{(r_{ij}/\sigma)^{-12} - (r_{ij}/\sigma)^{-6}\}F_{switch}$$

$$F_{switch} = 1/\{1 + (r_{ij}/5.5\sigma)^{24}\}$$

Physical parameters such as energy and distance are given in the usual L-J units of ε, σ, m (mass of the atom), and k_B (the Boltzmann constant). The unit of length ($r^*=r/\sigma$) corresponds to 0.34 nm, the unit of energy ($E^*=E/\varepsilon$) to 0.99 kJ/mol, the unit of temperature ($T^*=Tk_B/\varepsilon$) to 120 K, and the unit of time ($t^*=t(\varepsilon/m)^{1/2}/\sigma$) to 2.2 ps in case of argon. MD calculations were done using a timestep of $\delta t^*=0.01$ with the velocity Verlet algorithm. 65,536 L-J atoms (N) were at first placed randomly in a unit cell of volume V with periodic boundary conditions at a number density of $n^*=N\sigma^3/V=0.0149$, and the system was annealed at $T^*=1.0$. The temperature was then decreased linearly to 0 at time $t^*=1000$ with a thermostat. All clusters produced with the translational temperature thermostat [4,5] were taken out of the system and subject to subsequent constant-energy MD calculations under free boundary conditions with no interaction between clusters and between clusters and free atoms. The time for the constant-energy MD is represented by $t^*_{evaporate}$. A cluster was defined as a group in which each atom had at least one neighbor within a distance 2σ. Several series of such MD calculations were performed, starting from different initial configurations.

With the Andersen thermostat [7], 256 atoms were selected randomly every timestep and assigned new velocities drawn from the Boltzmann distribution at the desired temperature. The Nosé thermostat [8] with thermal inertia parameter equal to 200 was used. In the translational temperature thermostat, the barycentric velocities of all clusters were rescaled every 10 timesteps to set the translational temperature of the system as desired.

3. Results and Discussion

3.1 Cluster size changes during thermostatting

Size distributions during linear cooling from T^*=1.0 to 0 by three thermostats are shown in Figs. 1a-c. In the early stage of cluster formation ($t^* \leq 200$), the size distribution decays exponentially with cluster size by any thermostats as experimentally observed in the small cluster size region in the supersonic jet [9] and a Knudsen cell [10]. In this time region, the system temperature is higher than the condensation temperature of the L-J gas. Therefore, this exponential relationship shows that the system was in the equilibrium with the constant free energy difference between any M_n and M_{n+1} clusters. These clusters are very short lived. Lowering the temperature, the number of large clusters increased and the number of small clusters decreased. The system is no more under the equilibrium. Cluster-cluster aggregation became dominant at T^*<0.5, resulting in the high noises in the size distribution.

In Fig2. 2 and 3, how clusters change their size during cooling by the Andersen's thermostat are shown. At time t^*=600-700, almost all clusters increased their sizes more than 5 atoms as shown in Fig. 2. There is no particular size effect in the increase of the sizes, since the clusters in this temperature range (T^*=0.4) are in the liquid-like state. Decreasing the temperature, aggregation rate becomes lower since less free atoms and lower translational speed of clusters, which decreases the rate for clusters to meet atoms or clusters. Then, single atom addition becomes a main process for increasing the size at t^*=900-1000 as shown in Fig. 3. An important feature which can be understood from these figures is that there is no size effect in the increase of the sizes of the clusters even in the solid like state (T^*=0.1-0). Magic number clusters of 13 atoms, most of which were in icosahedron (confirmed by graphics view), might be expected to have lower reactivity than others. However, there is no big difference in size change between 12 and 13 atom clusters (Fig. 3), in which clusters are in a solid-like state. This means small difference in the reactivity among the different size clusters within the accuracy in this simulation. (There might be a possibility to observe such a small difference with more sampling.)

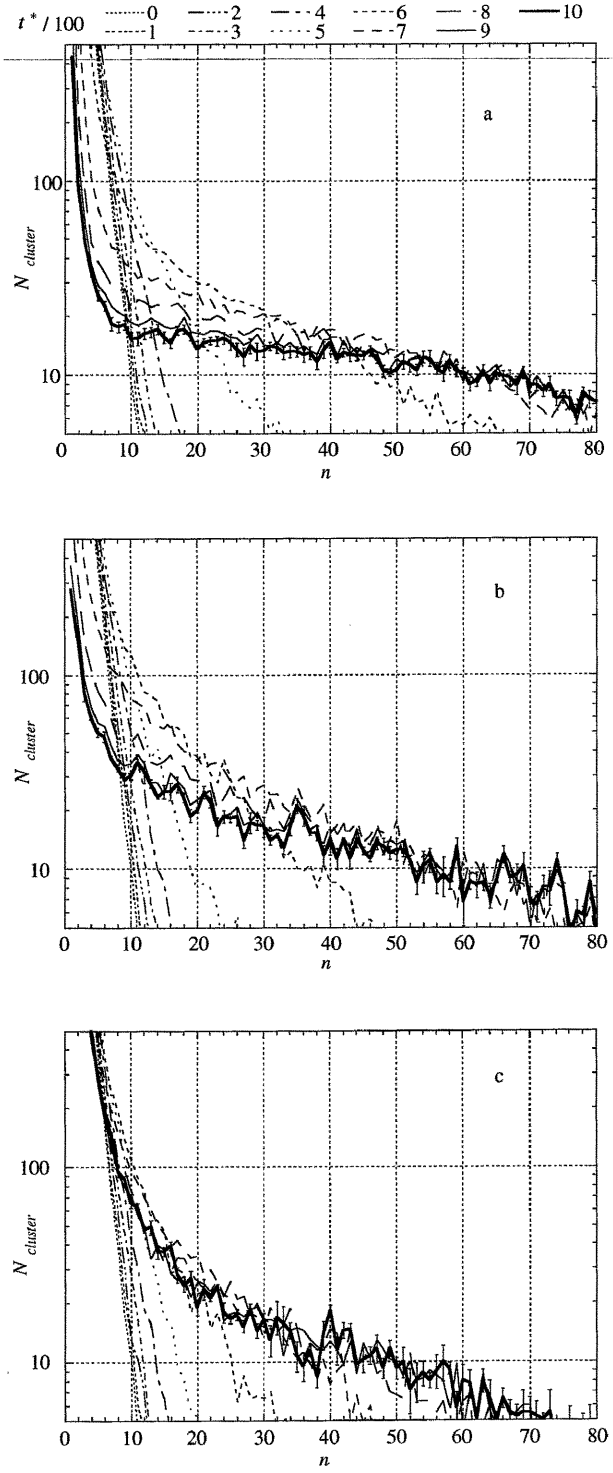

FIG. 1 Cluster size distributions at various times during linear decrease of temperature. (The y axis shows the average number of clusters of size n in the unit cell. Error bars show the standard error from 14, 6 and 4 independent runs for a, b and c respectively.)
a, by the Andersen thermostat; b, by the Nosé thermostat; c, by the translational temperature thermostat.

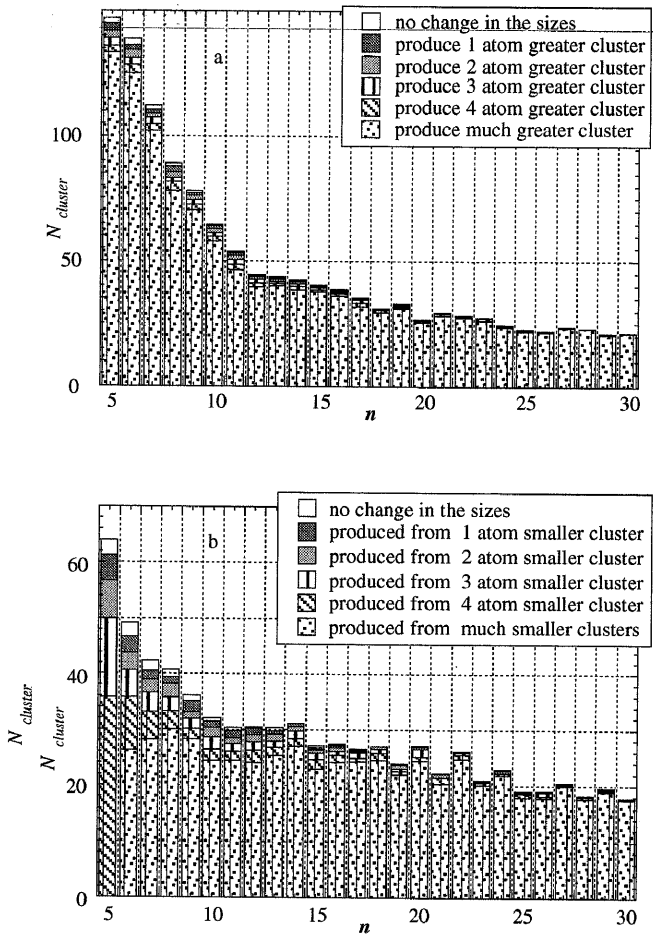

FIG. 2 Cluster size change from t^*=600 to 700.
a, to which size clusters each cluster at t^*=600 changes;
b, from which size clusters the cluster of size n at t^*=700 is formed.

3.2 Evaporation Process

The translational thermostat gave the smooth size distribution as shown in Fig. 1c. It simulates the supersonic jet cooling in which only the relative velocities are cooled. Since the clusters formed by this thermostat have still higher temperature of the internal motion, they will be cooled by evaporation under the constant energy calculation after isolating them from the system. This could simulate free flying after supersonic expansion. Fig. 4 shows a trace of such a cluster at $t^*_{evaporate}$=1000-2000 under the constant energy molecular dynamics with no interaction between clusters and between clusters and free atoms. The cluster was obtained by the separate calculation using a small system (N=8192, n^*=0.0149, 30,000 steps) with the translational thermostat at T^*=0.4-0.5. It flied from left to right and 11 snapshots are overlapped. Several atoms were evaporated during flying from the first position to the second one, and it was kicked to change its trace ($t^*_{evaporate}$=1000-1100). Evaporation of an atom between the third and second positions from the right ($t^*_{evaporate}$=1800-1900) made the cluster icosahedron and slightly changed the trace.

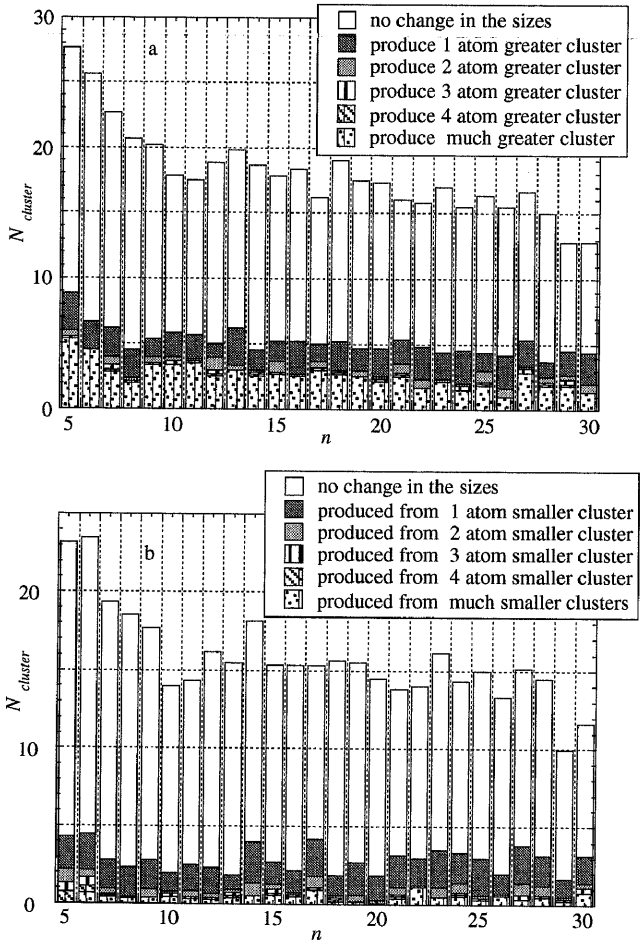

FIG. 3 Cluster size change from t^*=900 to 1000.
a, to which size clusters each cluster at t^*=900 changes;
b, from which size clusters the cluster of size n at t^*=1000 is formed.

Magic number peaks, 13, 19, 23, (and 26), were really observed by the molecular dynamics calculation under the constant energy for the clusters which were obtained by the translational thermostat. The details of magic number peaks and the structures were already presented [4, 5].

4. Conclusion

Detail analysis on how clusters grow during cooling showed no magic number like effect on growing rate was observed. Graphical view could clearly show magic number clusters are formed through the evaporation process.

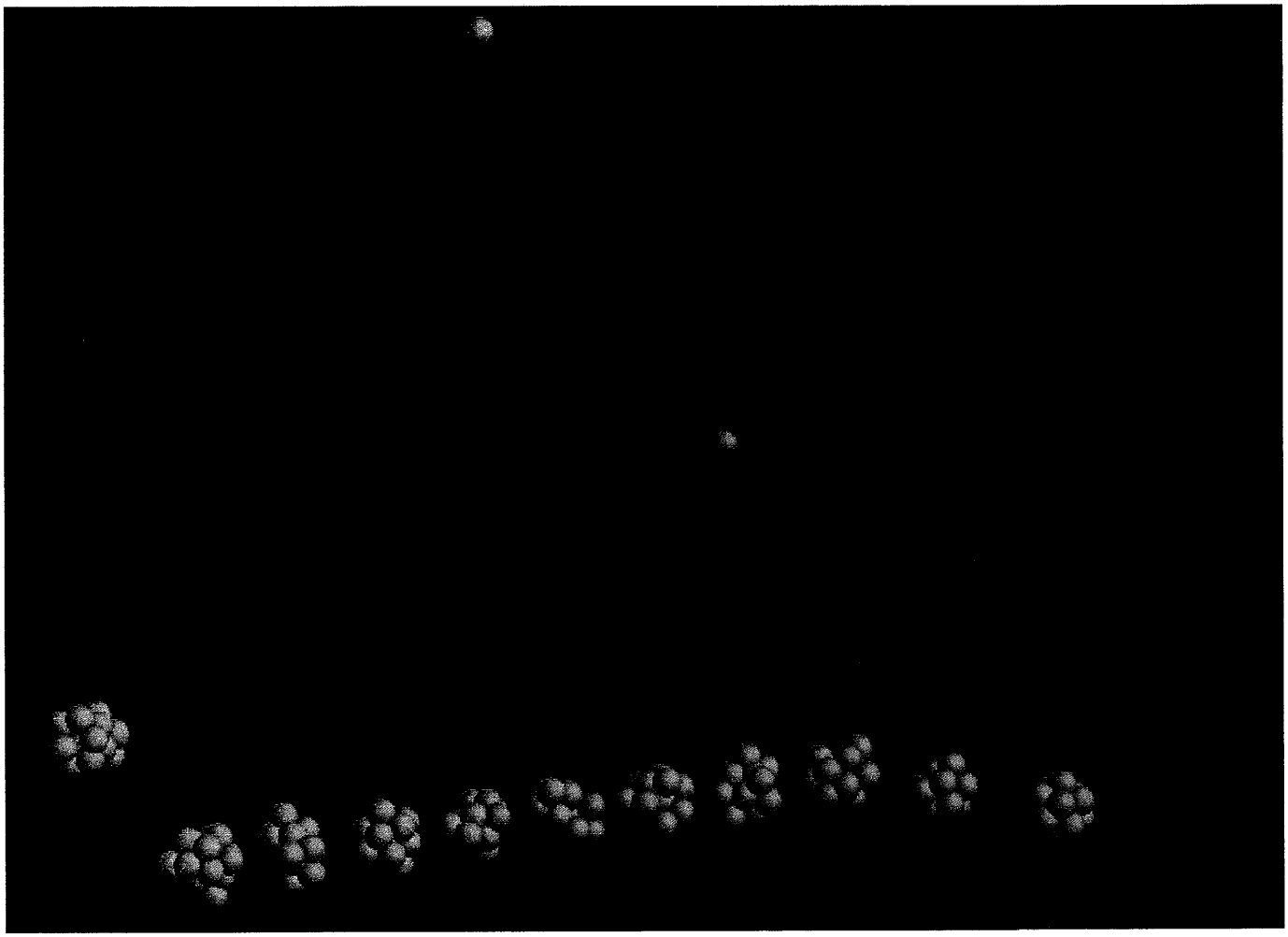

FIG. 4 Trace of a cluster with the constant energy MD with no interaction from another clusters/atoms. (Eleven snapshots of the cluster flying from left to right at $t^*_{evaporate}/1000$=100-200 are overlapped.)

Acknowledgement

The author acknowledges Prof. B. Hafskjold, Dr. Y. Hashi, and Prof. Y. Kawazoe for their discussion and helps for this work. Two supercomputers, the CRAY C916 at the Research Information Processing Center, AIST and the HITAC S-3800/380 at the Institute for Materials Research, Tohoku University, were used.

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