Molecular Dynamics Calculation for the Clustering Process from Gas and Liquid

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Molecular Dynamics Calculation for the Clustering Process from Gas and Liquid

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Molecular dynamics calculation of two clustering processes for atoms of Lennard-Jones (L-J) potential and water molecules is described. One clustering process is under the adiabatic condition from the gas state by lowering of the temperature. Another is thermal decomposition of liquid droplet. The system consists of 8192 L-J atoms or 512 water molecules. Vibrational, rotational, and translational temperature and potential energy were used to analyze the clustering process. Clear magic number was not observed in any process
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1. Introduction

Clusters are nano-scale particles of atoms or molecules. They are classified between molecule and fine particle. They are being in the fluctuation of their size, structure, temperature, potential energy, electronic, vibrational and rotational states, etc. They are produced under the fluctuation. Final products of the clustering process are distributed in the wide range of these physical parameters, in which some characteristic properties are observed. A typical example is a magic number in the distribution of the cluster size. In order to explain the magic number, many researches have been done after picking up one cluster to calculate the energy states. It may give information which size of the cluster is mostly produced. However, it can not give the size distribution itself, which may be a function of not only the energy states but also activation energy of the production and the decomposition, clustering rate, and interaction to the surroundings during the formation. This clustering process is taking place along the time axe under the interaction with the surroundings. Molecular dynamics (MD) calculation is, therefore, a good tool to know how atoms/molecules gather to produce clusters, what size distribution is observed, what distribution of temperature and energy the clusters have, and so on. These calculations will give us much information to control the clustering process.

In this report, some preliminary results for two kinds of clustering process of symmetrical atom of Lennard-Jones potential and unsymmetrical molecule, water, are given. One process is under the adiabatic condition from the gas state by lowering of the temperature. Another is thermal decomposition of liquid droplets.

2. Calculation

Potential: Lennard-Jones (L-J) potential was combined with a switching function to have a good energy conservation with a large time step.[1] Physical parameters are reduced into non-dimensional values by ε_0 and σ of L-J potential, mass of atom, and Boltzman constant, k_B. In case of water molecule, a simple potential of the rigid model, TIPS2,[2] was used, since it was necessary to calculate for a long period for many molecules. It gives a good structure of liquid water and dynamics.

Adiabatic clustering process: 8192 atoms of L-J potential were at first randomly put in a cubic cell of length 80 (density (ρ) = 1/64) under the periodic boundary condition and annealed at temperature 2.0. After the velocities of all atoms were rescaled to give the temperature of the system to be 0.125, MD calculation was performed under the constant energy with time step equal to 0.01. In case of water system, 512 water molecules were randomly put in a cubic cell of 10 nm with zero velocity under the periodic boundary condition (ρ = 15.3 kg/m^3), being separated by more than 6 nm each other. MD calculation was performed under the constant energy with the time step of 1 fs without annealing process.

Thermal decomposition process: A droplet of 8192 L-J atoms was at first formed in a spherical cell of radius 15.75 at temperature 0.7 (ρ = 0.5). After putting this droplet in a free space and rescaling the velocities to temperature 1.0 - 7.0, MD calculation was performed with time steps from 0.002 to 0.01. In case of the water system, a droplet of 512 water molecules was formed in a spherical cell of radius 1.54 nm (ρ = 1000 kg/m^3) at 298.15 - 900 K. After putting this cluster in a free space, MD calculation was performed with time step 1 fs.

Cluster : Cluster was defined by a group in which potential or distance between two atoms/molecules are less than the certain value. For the L-J system, it was the distance of 2. For the water system, it was the pair potential energy of -5.39×10^{-21} J (cf. the lowest potential energy of the dimmer = -4.31×1^{-20} J).

Temperature : Temperature, T, is defined by the average kinetic energy, E_k, with the freedom, n; $k_BT/2 = E_k/n$. Inner temperature is defined by the inner kinetic energy calculated from the velocity against the center of the mass of the cluster. Rotational temperature, $T_{rotation}$, is defined by rotational energy of the cluster against the center of the mass of the cluster. Vibrational temperature, $T_{vibration}$, is defined by the inner kinetic energy subtracted by the rotational energy. Translational temperature, $T_{translation}$, is defined by the absolute velocity of the cluster.

3. Results and Discussion

3.1 Adiabatic clustering process

Temperature of the system increased with cluster formation because of decreasing of the potential energy in clusters. At the initial stage, inner temperature of clusters is greater than the temperature of the system as shown in Fig. 1 (a), since the translational energy are transferred to the vibrational and rotational motion of the cluster, when it

collides with an atom or another cluster . After many times of the collision, clusters of the big size are formed and potential energy of the clusters decreases as shown in Fig. 1 (b). Since the system becomes near the equilibrium state, inner temperature of the small cluster becomes equal to that of the system. Those new big clusters have the higher temperature than the small clusters, since their states are far from the equilibrium.

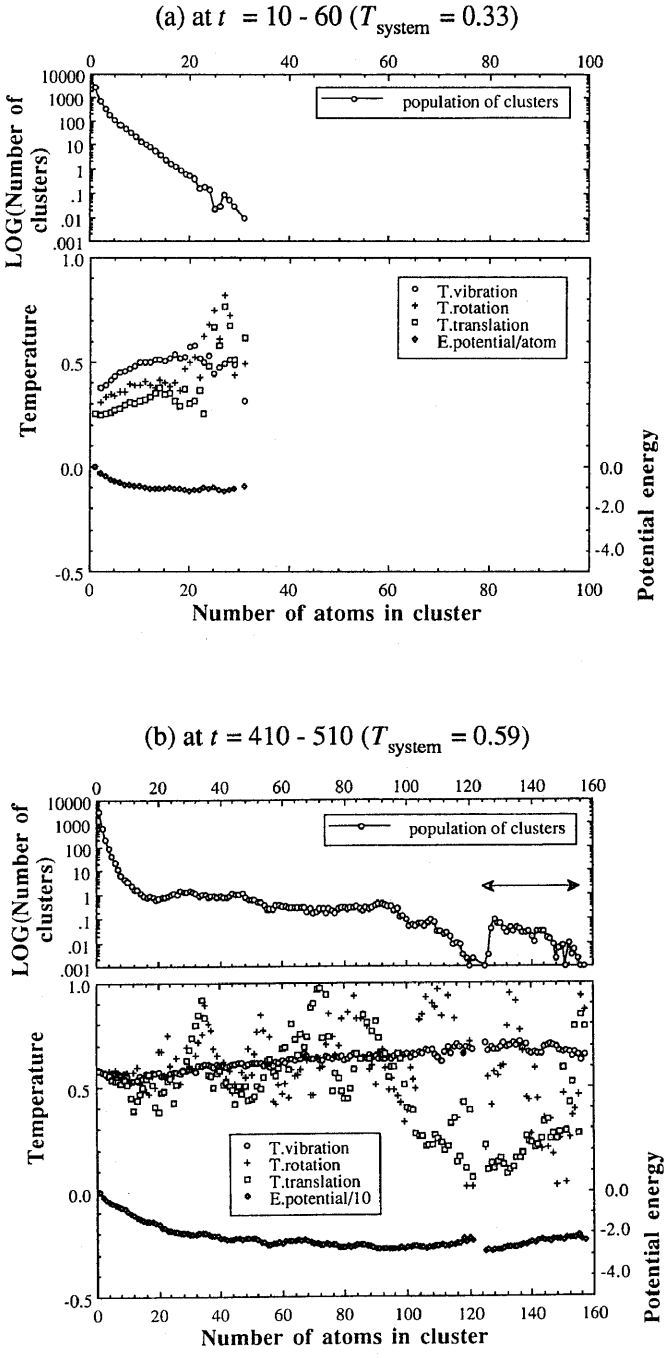

Fig. 1 Size, temperature, and potential energy of L-J atom clusters formed by the adiabatic process.

Trace of the clustering showed that the big clusters were produced by collision of two clusters. It was not by absorption of atoms by the clusters. Because of the high temperature of the cluster after the collision, atoms are evaporated to decrease the potential energy and the temperature. When its temperature and potential energy become sufficiently low , it absorbs atoms to increase the potential energy and the temperature. Size, temperature, potential energy of the biggest cluster in Fig. 1(b) fluctuated in the region shown by the arrow nt. the above scheme. A peak in this size region does not mean a magic number, since such peaks appeared at the different position for the different calculation run.

In case of water cluster, similar behavior was observed as shown in Figs.2. Graphical analysis showed that the water clusters formed at the initial stage are in the planner or one-dimensional structures, which gives higher potential energy. They become sphere with time.

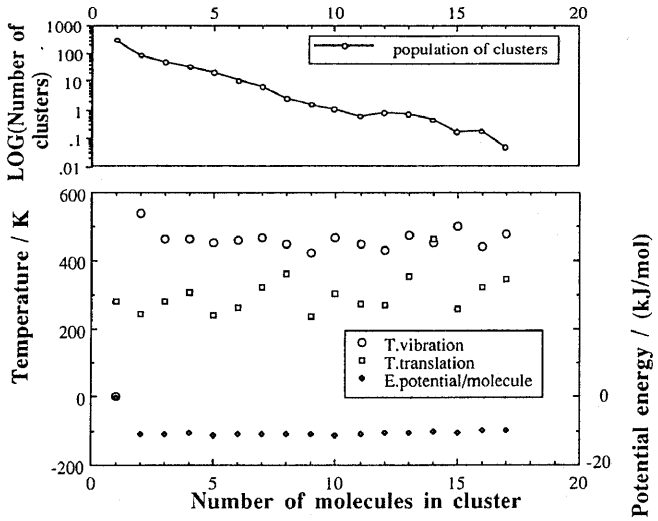

Fig. 2 Size, temperature, and potential energy of water clusters formed by the adiabatic process (t = 11.1 - 16.1 ps, T_{system} = 353 K).

3.2 Thermal decomposition

When a droplet of L-J atoms at T = 0.7 is put in the free space without heating, slow evaporation of atoms was observed as shown in Fig. 3a. The droplet was not decomposed into clusters during the calculation time. It was necessary to heat up to several times of the initial temperature as shown in curves c and d in Fig. 3, in which the changes of the maximum size of clusters are shown for the various initial temperature. When the droplet is heated up to temperature 7.0, it was decomposed into the smaller clusters than heating up to 5.0. For the low initial temperature, evaporation process by atoms or 2- or 3-atom clusters were observed. Inner temperatures of clusters are in range of 0.3 - 0.7 after thermal expansion by T = 5.0 as shown in Fig. 4. Translational temperature is ten times higher than the inner temperature, since thermal energy given at the initial time is transferred to the translational energy. Comparing the configuration of the initial droplet with the final clusters, 70 - 80 % of atoms in the final clusters were found to be closed within distance 2 in the

initial droplet. Size distribution of the final clusters was uniform; no magic number was observed.

In case of water droplet, it was also necessary to heat up to several times of the initial temperature. T emperature and potential energy of clusters formed after the decomposition of the water droplet of 900 K are shown in Fig. 4.

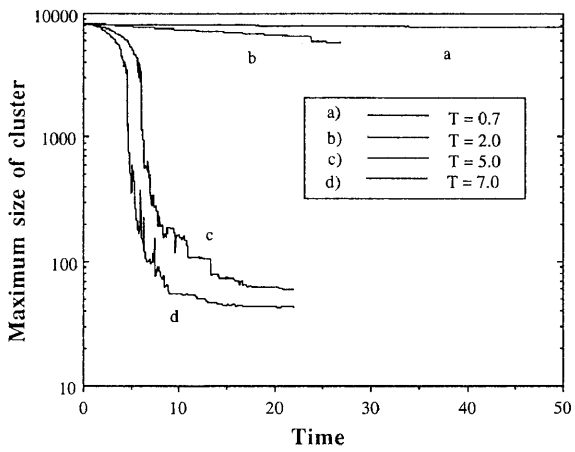

Fig. 3 Change of the maximum cluster size after thermal decomposition of a L-J atom droplet for the various initial temperature .

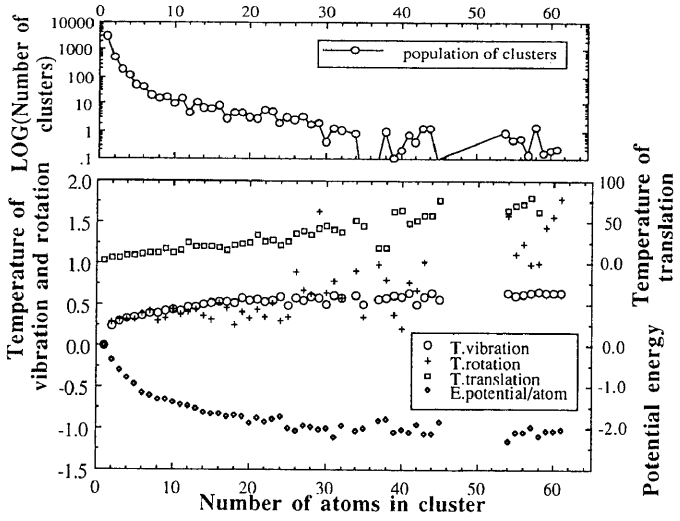

Fig. 4 Size, temperature, and potential energy of a L-J atom cluster at t = 100 - 110 after the thermal decomposition.

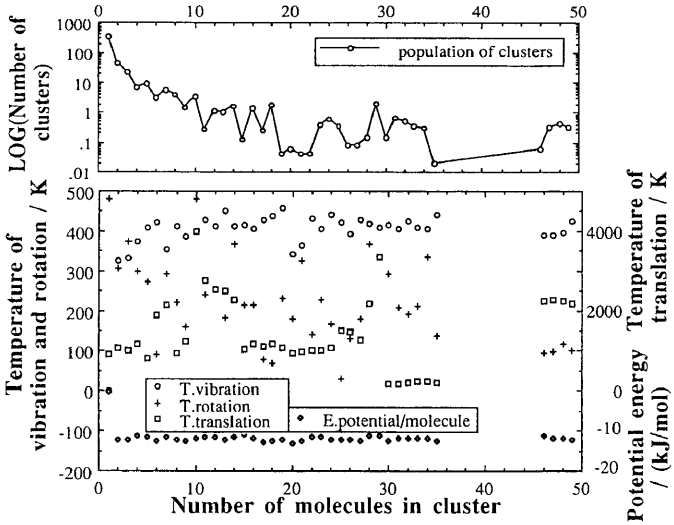

Fig. 5 Size, temperature, and potential energy of water cluster at t = 10 - 11 ps after the thermal decomposition.

3.3 Magic number: Magic number was not clearly observed in any clustering process. A reason is that the system was at so high temperature that the energy was distributed in many states. It may take a long period to relax to the lowest state by the evaporation of atoms/molecules. All experimental results reported for the magic numbers have been obtained for the ions. Ionization process may play an important role to give the certain cluster size.

4. Summary

Adiabatic clustering process showed higher inner temperature of clusters than the system. Thermal decomposition process needed great kinetic energy to initiate clustering. Clear magic number was not observed, since the temperature of the cluster was not so low to keep the cluster at the lowest energy state.

References

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