Molecular Dynamics Simulation for the Formation of Magic Number Clusters with a Lennard-Jones Potential

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The formation of clusters from a gas state of particles interacting with a Lennard-Jones potential was simulated by a large-scale molecular dynamics calculation with a new temperature-control scheme. Decreasing the translational temperature of atoms and clusters followed by a long-term evaporation produced several peaks in a cluster-size distribution. The peak positions obtained correspond to sizes 13, 19, 23, and 26, which are the magic numbers expected from polyicosahedra.

The appearance of magic numbers, which are observed as high-intensity peaks in mass spectra, is one of the characteristic features of atomic and molecular clusters. There are two well-known series of magic numbers, depending on the substance. The van der Waals clusters show relatively high stability for the closed geometrical shell structures together with various combinations of icosahedra, which give the series of 13, 55, 147, etc. (multilayer icosahedra) and 19, 23, 26, etc. (polyicosahedra), respectively [1]. Another series of 8, 20, 40, etc. observed for metal clusters is due to the closed electronic shell structures of the free electrons [2]. The way these magic-number clusters are formed is still not clear, partly due to the complexity of the process from formation to detection. Clusters are formed by cooling a gas, evaporated, ionized, and detected using mass spectroscopy. In experiments, these steps are coupled, and it is not known in which step the magic numbers appear. Experiments with laser irradiation after cluster formation have shown that evaporation plays an important role in producing magic-number clusters [3]. Evaporation due to excess ionization energy also seems to be important. Ionization may also have an influence on the size distribution, since the structure of the ionized clusters that are observed in mass spectroscopy is somewhat different from the neutral clusters of the same size [4]. There is no direct evidence that magic numbers of the neutral clusters will appear, since there is currently no experimental method to detect neutral clusters as accurately as ionized clusters by mass spectroscopy. This Letter deals with molecular dynamics (MD) simulation on how the magic-number peaks of the neutral clusters appear.

Computer simulation by classical MD, Monte Carlo, or *ab initio* calculation at 0 K can explain why magic-number clusters are stable [5]. Simulation studies of the formation process and cluster size distributions, including magic-number peaks, have not been made according to our knowledge. In reality, clusters are not formed at 0 K for studies on cluster stability. At higher temperatures,

where clusters are formed, computer simulations have yet to show any magic numbers. For instance, recent MD calculations of evaporation dynamics for the neutral clusters of Lennard-Jones (LJ) particles have shown a size distribution which is smooth up to 30-atom clusters [6]. Although MD simulations for a cluster formation by nucleation from vapor have been carried out since the 1970s, no significant peaks have been reported [7–9]. Fragmentation of a big liquid droplet to small clusters has also been a subject of MD simulation, but no magic numbers were able to be observed [8,10]. In most of these simulations, the objects were liquidlike clusters, which are not expected to have any magic numbers, and only the initial stage of a cluster formation was able to be simulated. Previous simulations for a cluster formation have been of the small-scale and short-run type. The kinetic approach for condensation and evaporation of LJ particles could show higher populations of 13-atom and 19-atom clusters at the steady state [11], but the approach contains a lot of assumptions, and long-time evaporation makes those peaks disappear [12]. We show here that MD simulations can provide the expected cluster-size distribution for van der Waals clusters with a large enough system which is allowed to develop over a long enough time under appropriate conditions. By "large enough," we mean a system with enough particles to give a signal-to-noise ratio that distinguishes magic-number peaks from statistical noise. By "long enough," we mean that the evaporation process is simulated during a time domain when the clusters of the magic numbers are formed. By "appropriate conditions," we mean that the irreversible process to form clusters is temperature controlled in a way that closely mimics the experimental situation under which magic numbers are observed. We take a typical cluster formation technique, supersonic jet, for the present simulation study.

In the supersonic jet, the velocities of the atoms in the gas injected into a vacuum chamber are equalized due to the gas atoms colliding against each other. Relative

velocities of the atoms become small, even though the absolute velocities in the laboratory-fixed frame are high. The system then becomes cold, and the clusters are formed because of the condensation. To simulate this highly nonequilibrium cooling process, we allow the translational velocities of the free atoms and the center of the mass of each cluster (the translational temperature) to develop independently from the inner (vibrational and rotational) temperature of the clusters. The translational velocities are simply rescaled to give a certain temperature at every time step. The underlying assumption is that the coupling between the translational and vibrational modes is too weak. The translational and inner temperatures, T_{trans} and T_{inn}, respectively, of a cluster are defined as

$$T_{\text{trans}} = (nm/3)\left(\sum_{i}^{n} v_i/n\right)^2 \bigg/ k_B, \qquad (1)$$

$$T_{\text{inn}} = [m/3(n-1)]\sum_{i}^{n}\left(v_i - \sum_{i}^{n} v_i/n\right)^2 \bigg/ k_B, \quad (2)$$

where n is the number of atoms in the cluster, v_i the velocity of atom i with respect to the laboratory fixed frame, and k_B the Boltzmann constant.

Even after decreasing the translational temperature completely to zero using this method, the inner temperature of the clusters is still high. They are liquidlike with no magic numbers. Evaporation can thus be simulated for this smooth distribution. During supersonic expansion, the distance between the clusters increases so that evaporation takes place with essentially no interaction with other clusters or free atoms. In the simulations reported here, clusters were picked up from the system after decreasing the translational temperature, and a microcanonical simulation was performed for each cluster to avoid any interaction with the surrounding particles.

In these simulations, the LJ potential between atoms i and j at distance r_{ij}, $U_{ij} = 4\varepsilon\{(r_{ij}/\sigma)^{-12} - (r_{ij}/\sigma)^{-6}\}$, was combined with a switching function to truncate the potential energy to zero at a cutoff length of 6σ. Physical parameters such as energy and distance are given in units of ε and σ, respectively, and we took m (mass of atom) and k_B to be equal to unity in these adopted units. A unit of time ($t = 1$) corresponds to 2.2 ps and a unit of temperature ($T = 1$) to 120 K in case of argon. 65 536 LJ atoms were at first placed randomly in a unit cell with periodic boundary conditions at a number density of 0.0149, and the system was annealed at $T = 1.0$. The translational temperature was then decreased linearly to 0 at time $t_{\text{cool}} = 1000$ using a time step of $\delta t = 0.01$. This will be referred to as the cooling process in the supersonic jet. After the clusters were taken out of the system, constant-energy MD calculations for all clusters were performed under free boundary conditions with no interaction between the clusters. This is referred to as the evaporation process. After $t_{\text{evap}} = 12\,000$ (from the start of the evaporation

period), clusters having sizes from 8 to 32 atoms were simulated. A cluster was defined as a group in which the distance between two atoms was less than 2σ [8]. Four series of such MD calculations were performed, starting from different initial configurations. One run needed about 100 CPU hours and 500 Mbyte of memory in our supercomputers.

During the cooling period, the inner temperature of the clusters decreased linearly at first, but it remained constant after T_{inn} reached ca. 0.5. At the end of the cooling period ($t_{\text{cool}} = 1000$, i.e., $t_{\text{evap}} = 0$), 80% of the atoms were involved in the clusters, and the size distribution was very smooth as seen in Fig. 1. This was the starting situation for the evaporation period. Since there was no constraint for the inner motion in these clusters during the cooling period, the inner temperature was given by the balance between the growth processes such as atom-cluster and cluster-cluster fusions and the decomposition processes such as evaporation and fission. The former processes increased the inner temperature and the latter decreased it. Since evaporation was effective in cooling down the small clusters, they had lower temperatures than the larger clusters as shown in Fig. 2 ($t_{\text{cool}} = 1000$). In this temperature range, the clusters were liquidlike [13]. The smooth size distribution shown in Fig. 1 ($t_{\text{cool}} = 1000$) is considered to be due to this liquidlike state of the clusters, in which the potential energy was a smooth function of the cluster size.

After separating the clusters from the system, the cluster sizes only decreased due to the evaporation. This made the inner temperatures decrease with the clusters becoming solidlike, and the potential energy was no longer a smooth function of the cluster size. Magic-number peak 13 then
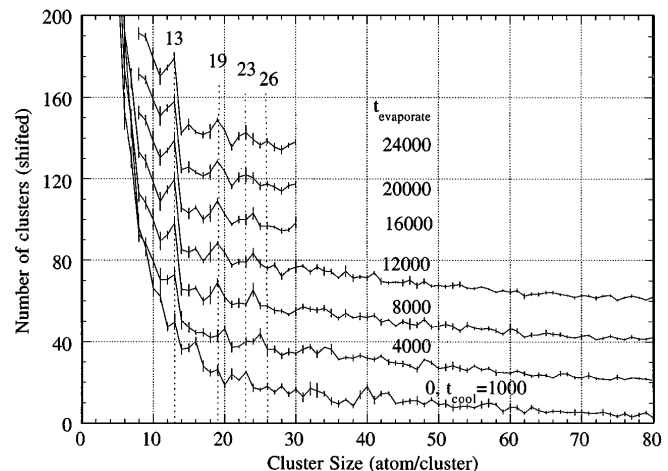

FIG. 1. Cluster-size distributions during evaporation. The number of clusters are those in a unit cell and averaged from four independent runs. Error bars show standard errors from these four runs. Each line is shifted vertically by 20. (At $t_{\text{evap}} = 12\,000$, clusters from $n = 8$ to 32 were detected and further MD calculations were carried out only for these clusters.)
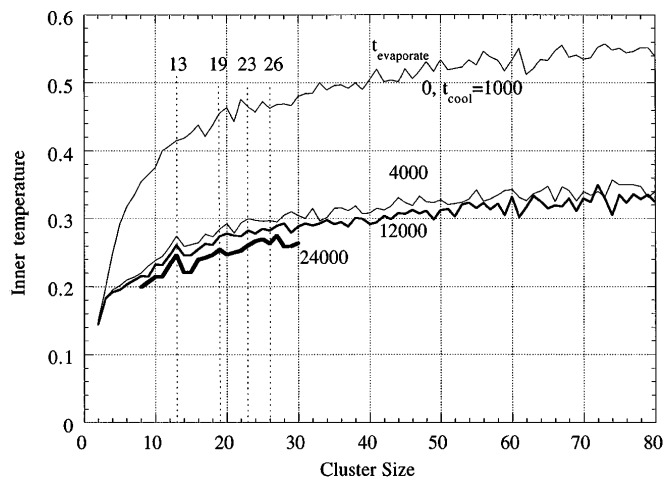
FIG. 2. Temperature profile during evaporation.

appeared clearly at $t_{evap} = 4000$, and it increased with time. The peak at $n = 20$ appearing at $t_{evap} = 4000$ moved to $n = 19$ after $t_{evap} = 8000$. This size is a magic number due to double icosahedra sharing some atoms [1]. The peak at $n = 25$ appearing at $t_{evap} = 4000$ moved to $n = 24$ and finally to $n = 23$, which is also a magic number due to triple icosahedra sharing some atoms [1]. At $t_{evap} = 24\,000$, a weak peak at $n = 26$ could be observed. This size is also a magic number due to quadruple icosahedra sharing some atoms [1]. However, this peak is too weak (similar to the peak at $n = 15$, which shifted from $n = 16$), and the present simulation could therefore not provide any statistically significant evidence for $n = 26$ as a magic number. These peaks were assigned not only by the signal-to-noise ratio in Fig. 1 but also by how these peaks lasted and systematically moved. From these points, the peaks at $n = 13$ and 19 are quite clearly assigned and the peak at $n = 23$ is not so strongly assigned. As a result of this simulation, it appeared that clusters were trapped by evaporation at these magic-number sizes, in which these isomers in polyicosahedra with the highest symmetry and the lowest potential energy had higher evaporation energy than the other isomers and clusters. In these trapped clusters, evaporation did not take place sufficiently enough to decrease the size even at higher temperatures. This higher temperature can be clearly seen for the 13-atom clusters and possibly also for the 19-atom clusters in Fig. 2 ($t_{evap} = 24\,000$). Not all the clusters obtained by evaporation for $t_{evap} = 24\,000$ had the lowest energy structures; 85%, 44%, 34%, and 23% for the 13-, 19-, 23-, and 26-atom clusters, respectively, were in such a polyicosahedra structure. Because of this effect and the smaller difference in the evaporation energy for the larger clusters, the clusters of 23 and 26 did not have higher temperatures. The peak height of the magic numbers in the size distribution (Fig. 1) became small for the larger clusters for the same reasons.

It will take much more time to obtain magic-number structures for the larger clusters. In this simulation, it took 4.4×10^{-8} s in simulated time for the Ar clusters to obtain magic numbers up to 23. Since the cooling process using the supersonic jet takes $10^{-7}-10^{-6}$ s and the traveling time to the detector may be $10^{-4}-10^{-3}$ s under experimental conditions, magic-number clusters are expected to be formed within a short time after expansion. The nucleation process during cooling in this simulation took place under a constant number density higher than the experimentally used injection gas density, with the nucleation rate being much higher than the evaporation rate. Therefore high temperature clusters could be obtained but no magic-number peaks could be seen during nucleation. Since, in a real supersonic jet, the density suddenly decreases after expansion, evaporation may take place and give magic-number peaks during expansion as calculated by the kinetic approach [11]. The magic numbers obtained here for the neutral LJ potential particles are similar to those of Xe_n^+ [14] and Ar_n^+ [15] except for the relative intensities. They are, however, completely different from those of Kr_n^+ and Ar_n^+ under the strong influence of the ionic processes [16].

In this paper, we have applied a large-scale computer simulation to reveal that magic numbers can be realized with the LJ potential. Magic numbers at 13, 19, 23, and (26) as expected from the polyicosahedra structure appear, and those of 13 and 19 have higher temperatures than the other size clusters.

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