VOLUME 90, NUMBER 5 PHYSICAL REVIEW LETTERS week ending 7 FEBRUARY 2003

Cluster Growing Process and a Sequence of Magic Numbers

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(Received 22 July 2002; published 5 February 2003)

We present a new theoretical framework for modeling the cluster growing process. Starting from the initial tetrahedral cluster configuration, adding new atoms to the system, and absorbing its energy at each step, we find cluster growing paths up to the cluster sizes of more than 100 atoms. We demonstrate that in this way all known global minimum structures of the Lennard-Jones (LJ) clusters can be found. Our method provides an efficient tool for the calculation and analysis of atomic cluster structure. With its use we justify the magic number sequence for the clusters of noble gas atoms and compare it with experimental observations.

DOI: 10.1103/PhysRevLett.90.053401 PACS numbers: 36.40.Qv, 36.40.Mr, 61.46.+w

It is well known that the sequence of cluster magic numbers carries essential information about the electronic and ionic structure of the cluster [1]. Understanding of the the cluster magic numbers is often equivalent or nearly equivalent to the understanding of cluster electronic and ionic structure. A good example of this kind is the observation of the magic numbers in the mass spectrum of sodium clusters [2]. In this case, the magic numbers were explained by the delocalized electron shell closings (see [3] and references therein). Another example is the discovery of fullerenes, and, in particular, the C_{60} molecule [4], which was made by means of the carbon clusters mass spectroscopy.

The formation of a sequence of cluster magic numbers should be closely connected to the mechanisms of cluster formation and growing. It is natural to expect that one can explain the magic number sequence and find the most stable cluster isomers by modeling mechanisms of cluster assembling and growing. On the other hand, these mechanisms are of interest on their own, and the correct sequence of the magic numbers found in such a simulation can be considered as a proof of validity of the cluster formation model.

The problem of magic clusters is closely connected to the problem of searching for global minima on the cluster multidimensional potential energy surface. The number of local minima on the potential energy surface increases exponentially with the growth cluster size and is estimated to be of the order of 10^{43} for $N = 100$ [1]. Thus, searching for global minima becomes an increasingly difficult problem for large clusters. There are different algorithms and methods of the global minimization, which have been employed for the global minimization of atomic cluster systems (see [1] and references therein). These techniques are often based on the Monte Carlo simulations.

The algorithm that we describe in this Letter is based on the dynamic searching for the most stable cluster isomers in the cluster growing process. Our calculations demonstrate that our approach is an efficient alternative to the known techniques of the cluster global minimization. The big advantage of our approach consists in the fact that it allows one to study not just the optimized cluster geometries, but also their formation mechanisms.

In the present work we approach the formulated problem in a simple, but general, form. In our simplest scenario, we assume that atoms in a cluster are bound by Lennard-Jones potentials and the cluster growing takes place atom by atom. In this process, new atoms are placed on the cluster surface in the middle of the cluster faces. Then, all atoms in the system are allowed to move, while the energy of the system is decreased. The motion of the atoms is stopped when the energy minimum is reached. The geometries and energies of all cluster isomers found in this way are stored and analyzed. The most stable cluster configuration (cluster isomer) is then used as a starting configuration for the next step of the cluster growing process.

Starting from the initial tetrahedral cluster configuration and using the strategy described above, we have analyzed cluster growing paths up to the cluster sizes of more than 100 atoms. We have found that in this way practically all known global minimum structures of the Lennard-Jones clusters (see [1] and references therein) can be determined, which proves that our method is indeed an efficient alternative to other cluster global optimization techniques such as the basin hopping algorithm [1].

In our model we consider an atomic cluster as a group of atoms that interact with each other by pairing forces. The interaction potential between two atoms in the cluster can, in principle, be arbitrary. In this work, we use the

Lennard-Jones (LJ) potential,

$$U(r) = 4\varepsilon\{(\sigma/r)^{12} - (\sigma/r)^{6}\}, \tag{1}$$

where r is the interatomic distance, ε is the depth of the potential well ($\varepsilon > 0$), and $2^{1/6}\sigma$ is the pair bonding length.

The constants in the potentials allow one to model various types of clusters for which LJ pairing force approximation is reasonable. The most natural systems of this kind are the clusters consisting of noble gas atoms Ne, Ar, Kr, Xe. The constants in the LJ potential appropriate for the noble gas atoms one can find in [5]; thus, for Ne, Ar, Kr, and Xe, $\varepsilon = 3.6$, 12.3, 17.2, and 24.3 meV, respectively. The LJ forces are also appropriate for modeling nuclear clusters consisting of alpha particles [6]. Note that for the LJ clusters it is always possible to choose the coordinate scale so that $\sigma = 1$. It makes all LJ cluster systems scalable. They differ only by the choice of the energy parameter ε and the mass of a single constituent (atom).

In our approach the atomic motion in the cluster is described by the Newton equations with the LJ pairing forces. The system of coupled equations for all atoms in the cluster are solved numerically using the 4th order Runge-Kutta method. The primary goal in this simulation was to find the solutions of the equations that lead to the stable cluster configurations and then to choose energetically the most favorable one. The choice of initial conditions for the simulation and the algorithm for the solution of this problem are described below.

Our cluster searching algorithm is constructed on the idea that each minimum on the cluster potential energy surface corresponds to the situation, when all the atoms are located in their equilibrium positions. A minimum can be found by allowing atoms to move, starting from a certain initial cluster configuration, and by absorbing all their kinetic energy in the most efficient way. If the starting cluster configuration for $N + 1$ atoms has been chosen on the basis of the global minimum structure for N atoms, then it is natural to assume, and we prove this in the present work, that the global minimum structure for $N + 1$ atoms can be easily found. The success of this procedure reflects the fact that in nature clusters in their global minima often emerge, namely, in the cluster growing process, which we simulate in such calculation.

We have employed the following algorithm for the kinetic energy absorption. At each step of the calculation we consider the motion of one atom only, which undergoes the action of the maximum force. At the point in which the kinetic energy of the selected atom is maximum, we set the absolute value of its velocity to zero. This point corresponds to the minimum of the potential well at which the selected atom moves. When the selected atom is brought to the equilibrium position, the next atom is selected to move and the procedure of the kinetic energy absorption repeats. The calculation stops when all the atoms are in equilibrium.

We have considered a number of scenarios of the cluster growing on the basis of the developed algorithm for finding the stable cluster configurations.

In the simplest scenario clusters of $N + 1$ atoms are generated from the N-atomic clusters by adding one atom to the system. In this case the initial conditions for the simulation of $(N + 1)$-atomic clusters are obtained on the basis of the chosen N-atomic cluster configuration by calculating the coordinates of an extra atom added to the system on a certain rule. We have probed the following paths: the new atom can be added either ($A1$) to the centers of mass of all the faces of the cluster (here the cluster is considered as a polyhedron) or ($A2$) to the points that are close to the centers of all the faces of the cluster, located from both sides of the face on the perpendicular to it, ($A3$) to the centers of mass of the faces laying on the cluster surface.

The choice of the method of how to add atoms to the system depends on the problem to be solved. The $A1$ and $A2$ methods can be used for searching the most stable, i.e., energetically favorable, cluster configurations or for finding cluster isomers with some other specific properties. The $A2$ method leads to finding more cluster isomers than the $A1$ one, but it takes more CPU time. The $A3$ method is especially convenient for modeling the cluster growing process which we focus on in this paper. Using this method one can generate the cluster growing paths for the most stable cluster isomers.

When considering the cluster growing process, new atoms should be added to the system starting from the initially chosen cluster configuration step by step until the desired cluster size is reached. Each new step of the cluster growing should be made with the use of the methods $A1$–$A3$. The criteria for the cluster selection in this process can be as follows: at every step ($SE1$) one of the clusters with the minimum number of atoms is selected, or ($SE2$) the cluster with the minimum energy among the already found stable clusters of the maximum size is selected, or ($SE3$) the cluster with the maximum energy among the already found stable clusters of the maximum size is selected.

Calculations performed with the use of the methods described above show that often clusters of a higher symmetry group possess relatively low energy. Thus, the symmetric cluster configurations are often of particular interest. The process of searching the symmetric cluster configurations can be sped up significantly, if one performs the cluster growing process with the imposed symmetry constraints. This means that for obtaining a symmetric N atomic cluster isomer from the initially chosen symmetric $(N - M)$-atomic configuration one should add M atoms to the surface of this isomer symmetrically.

Using our algorithms we have examined various paths of the cluster growing process and determined the most stable isomers up to the cluster sizes of more than 100 atoms. The binding energies per atom as a function of cluster size for the calculated cluster chains are shown in Fig. 1. In the inset of Fig. 1 we present the experimentally measured abundance mass spectrum for the Ar clusters at 77 K [7].

We have generated the chains of clusters based on the icosahedral, octahedral, tetrahedral, and decahedral symmetries with the use of the $A1$–$A3$ and $SE1$–$SE3$ methods. In a few particular cases for $N > 70$, we have also used manual modifications of the starting cluster geometries. In all our calculations we have used the dimensionless form of the LJ potential, i.e., put $\sigma = 1$. Such a choice is the most universal. The potential constant has been chosen as $\varepsilon = 1/12$.

Figure 1 shows that the most stable clusters are obtained on the basis of the icosahedral symmetry configurations with exceptions for $N = 38$, $75 \leq N \leq 77$, and $N = 98$. In these cases the octahedral, decahedral, and tetrahedral cluster symmetry becomes more favorable, respectively.

The main trend of the energy curves plotted in Fig. 1 can be understood on the basis of the liquid drop model, according to which the cluster energy is the sum of the volume and the surface energy contributions:

$$E_N = -\lambda_V N + \lambda_S N^{2/3} - \lambda_R N^{1/3}. \qquad (2)$$

Here the first and the second terms describe the volume and the surface cluster energy correspondingly. The third term is the cluster energy arising due to the curvature of the cluster surface. Choosing constants in (2) as $\lambda_V = 0.717\,03$, $\lambda_S = 1.293\,02$, and $\lambda_R = 0.567\,57$, one can fit the global energy minimum curve plotted in Fig. 1 with the accuracy less than 1%. The deviations of the energy curves calculated for various chains of cluster isomers from the liquid drop model (2) are plotted in Fig. 2. The curves for the icosahedral and the global energy minimum cluster chains go very close with each other, and the peaks on these dependences indicate the increased stability of the corresponding magic clusters. The ratio between the volume and surface energies in (2) can be characterized by the dimensionless parameter $\delta = \lambda_V/\lambda_S$, being equal in our case to $\delta = 0.5545$.

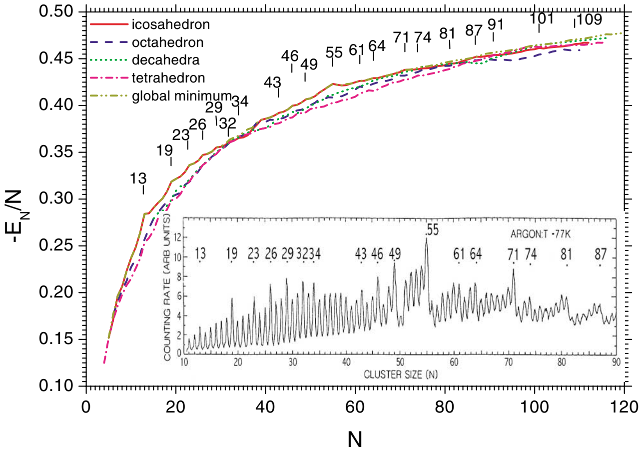

FIG. 1 (color online). Binding energy per atom for LJ clusters as a function of cluster size calculated for the cluster chains based on the icosahedral, octahedral, tetrahedral, and decahedral symmetry. In the inset we present the experimentally measured abundance mass spectrum for the Ar clusters at 77 K [7]

The dependence of the binding energies per atom for the most stable cluster configurations on N allows one to generate the sequence of the cluster magic numbers. In the inset of Fig. 2 we plot the second derivatives ΔE_n^2 for the chain of icosahedral isomers. We compare the obtained dependence with the experimentally measured abundance mass spectrum for the Ar clusters at 77 K [7] (see inset of Fig. 1) and establish the striking correspondence of the peaks in the measured mass spectrum with those in the ΔE_n^2 dependence. Indeed, the magic numbers determined from $\Delta^2 E_N$ are in a very good agreement with the numbers experimentally measured for the Ar and Xe clusters: 13, 19, 23, 26, 29, 32, 34, 43, 46, 49, 55, 61, 64, 71, 74, 81, 87, 91, 101, 109, 116, 119, 124, 131, 136, 147 [7]. The most prominent peaks in this sequence 13, 55, and 147 correspond to the closed icosahedral shells, while other numbers correspond to the filling of various parts of the isosahedral shell.

The connection between the second derivatives $\Delta^2 E_N$ and the peaks in the abundance mass spectrum of clusters one can understand using the following simple model. Let us assume that the mass spectrum of clusters is formed in the evaporation process. This means that changing the number of clusters, n_N, of the size N in the cluster ensemble takes place due to the evaporation of an atom

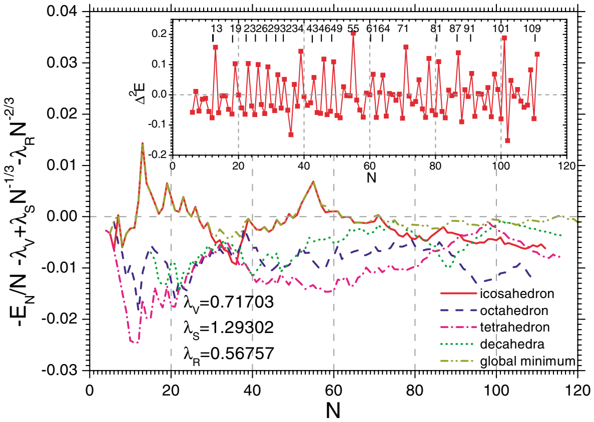

FIG. 2 (color online). Energy curve deviations from the liquid drop model (2) calculated for various cluster isomer chains. In the inset we plot the second derivative $\Delta^2 E_N$ calculated for the icosahedral cluster isomer chain.

by the clusters of the size N and $N+1$, i.e., $\Delta n_N \sim n_{N+1}W_{N+1\to N} - n_N W_{N\to N-1}$, where the evaporation probabilities are proportional to $W_{N+1\to N} \sim e^{-(E_N+E_1-E_{N+1})/kT}$ and $W_{N\to N-1} \sim e^{-(E_{N-1}+E_1-E_N)/kT}$. Here T is the cluster temperature, and k is the Boltzmann constant. In our model $E_1 = 0$, so after simple transformations the equation for Δn_N reads as $\Delta n_N \sim n_{N+1}e^{-(E_N-E_{N+1})/kT}(1 - \frac{n_N}{n_{N+1}} e^{-(E_{N-1}-2E_N+E_{N+1})/kT})$. Let us now estimate the relative abundances in the mass spectrum for argon clusters for temperatures about 100 K. The exponent, $e^{-(E_N-E_{N+1})/kT}$, influences the absolute value of Δn_N. This factor becomes exponentially small at $kT \ll E_N - E_{N+1}$, which for the Ar clusters means $T \ll 800$ K, because $\langle \Delta E_N^{\mathrm{Ar}} \rangle = 0.071$ eV ~ 800 K. The small value of this factor results in the growth of the characteristic period of the evolution of n_N with time. The factor in the brackets determines the relative cluster abundances. Indeed, its positive value for certain N leads to the growth of the corresponding clusters in the system, while the negative value of the factor leads to the opposite behavior. The factor in the brackets is characterized by $\Delta_N^2 E_N = E_{N-1} - 2E_N + E_{N+1}$, which is for the Ar clusters $\langle |\Delta_N^2| \rangle = 0.008$ eV ~ 90 K. Thus, for temperatures $T \gtrsim 90$ K the exponent in the brackets can be expanded. In this case one derives $\Delta n_N \sim n_N e^{-(E_N-E_{N+1})/kT}\frac{\Delta^2 E_N}{kT}$. Here we assumed that $n_{N+1} \sim n_N$. This equation demonstrates that positive values of $\Delta^2 E_N$ lead to the enhanced abundance of the corresponding clusters.

In Fig. 3, we plot images of the magic clusters up to $N = 71$. For $N = 32$ and $N = 34$, we present the icosahedral isomer and the one possessing the global energy minimum. We also plot the image of the octahedral $N = 38$ cluster, which is found to be more stable than the clusters from the icosahedral chain. Experimentally $N = 38$ is not found to be the magic cluster, although it is the global minimum cluster, being magic for the octahedral cluster chain (see Figs. 1 and 2). This fact can be understood if one takes into account that different symmetry cluster chains are formed independently and the transition of clusters from one chain to another at certain N is not possible. It is clear from the binding energy analysis that the icosahedral chain of clusters should be dominating. In experiments, clusters of the icosahedral chain mask clusters of other symmetry chains even in the situations when these other clusters are energetically more favorable, like it occurs for $N = 38$.

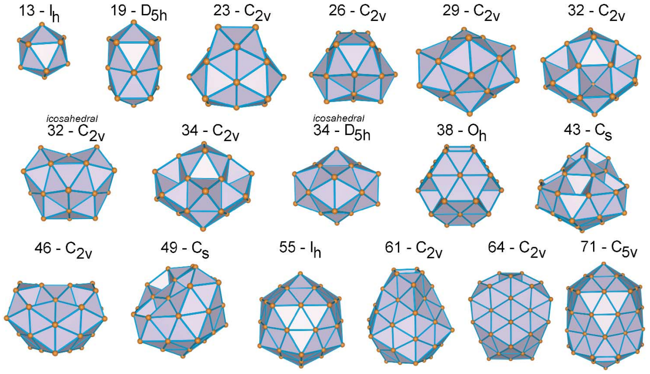

FIG. 3 (color online). Geometries of the magic LJ clusters. The labels indicate the cluster size and the cluster point symmetry group.

In this paper we have discussed the classical models for the cluster growing process, but our ideas can easily be generalized on the quantum case and be applied to the cluster systems with different than LJ type of the interatomic interaction. It would be interesting to see to what extent the parameters of interatomic interaction can influence the cluster growing process and the corresponding sequence of magic numbers or whether the crystallization in the nuclear matter consisting of alpha particles and/or nucleons is possible. Studying cluster thermodynamic characteristics with the use of the developed technique is another interesting problem which is left opened for future considerations.

The authors acknowledge support from the the Alexander von Humboldt Foundation and DAAD.

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