Building clusters atom by atom: from local order to global order.

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Abstract

We have carried out extensive density functional calculations for series of sodium clusters \(Na_N\) ranging from \(N=10\) to 147 and have obtained \(\approx 13000\) distinct isomers. We unravel a number of striking features of the growth characteristics. The growth shows order-disorder-order pattern of cyclic nature. Between two ordered clusters the growth proceeds via disordered clusters having multi-centered icosahedral local order. The Global order emerges suddenly with the addition of one or two atoms only. The clusters around \(N=92\), the electronically closed shell system, behave completely differently and do not show the favored icosahedral local order. It is the absence of icosahedral local order which is responsible for rather low melting temperatures observed in the experiments.

Clusters are a focus of considerable attention due to their importance as building blocks for nano materials as well as due to intrinsic properties arising out of their finite size. It is now well...
established that in the small size regime, typically below few 100 atoms, clusters show individu-
ality. Specifically, they show size dependent features in their geometries, energy gaps and binding
energies, stability, polarizability, melting temperatures, and shapes of the heat capacity
curves. In spite of a large number of studies a clear evolutionary pattern of the growth over a
wide range of size has not been developed. There is no clear answer to a rather simple question of
interest namely how does a cluster grow atom by atom? Most of the systematic theoretical studies
at ab initio level are limited to sizes below 40 atoms or so and describe geometries of individual
clusters and energetics. An interesting work explaining shape transition in Si_N (N=20-27) has been
reported by Jackson et al. 

Clusters of sodium atoms are perhaps the most intensively studied both experimentally as well
as theoretically. Although features like stability can be understood on the basis of
simple jellium models, ab initio methods are required for determining the geometries and other
properties. Even for these simple metal atom systems there is no understanding of the evolutionary
behavior. These clusters also show very peculiar irregular behavior in some of the properties like
melting temperature. Most of the early work on these clusters is restricted to N < 20. For example
Röthlisberger et al. have discussed the nature of individual geometries and possible occurrence
of some motifs as atoms are added one by one.

In the present work the focus is on understanding the systematics of structural evolution of Na_N
over a wide size range: N=10-147. We examine the basic question; how do sodium clusters grow
when a single atom is added starting from N=10? We have carried out extensive density functional
calculations and have obtained at least 200 distinct isomers for all the clusters for N ≤ 80 and
at least 100 isomers for all the clusters having even number of atoms with 80 < N ≤ 147. All
the calculations have been performed within unified framework using plane wave basis, ultrasoft
pseudopotential, local density exchange correlation potential of Ceperley-Alder, and the same box
length (36 Å). Our results are based on the analysis of about 13000 equilibrium structures for
105 clusters. These equilibrium structures were obtained by minimizing a few hundred (100-
200) initial configurations per cluster. These configurations were chosen from ab initio constant
temperature molecular dynamical runs carried out at 2 different temperatures for the period of 50 to 90 ps. All the lowest energy structures are subjected to vibrational analysis. For many of the large clusters nearly degenerate levels near Fermi level were handled by redistributing the occupancies by assigning appropriate low temperature to the electrons.

We have analyzed the ground-states structures mainly focusing on the nature of their geometries. We examine their shapes by using shape deformation parameter ($\epsilon_{\text{def}}$) defined below, the geometric shell structure as viewed from the Center Of Mass (COM) and the distribution of all the relevant bond length in the system. $\epsilon_{\text{def}}$ is defined as: $\epsilon_{\text{def}} = \frac{2Q_y}{Q_x+Q_z}$, where $Q_x \geq Q_y \geq Q_z$ are the eigenvalues of the quadrupole tensor $Q_{ij} = \sum I R_{II} R_{Ij}$. Here $R_{II}$ is the $i$th coordinate of ion $I$ relative to the COM. We also examine the coordination numbers for all the atoms to locate possible existence of any local order. Then we examine the motifs formed by $\approx 12$ nearest neighbors for all the atoms having 11-13 nearest neighbors. We also calculate the surface energy $S$ through the following relationship: $S = E_{\text{tot}}(N) - \epsilon_{\infty}N$ where $E_{\text{tot}}(N)$ is the total energy of the cluster and $\epsilon_{\infty}$ is the energy per atom of the bulk sodium. The surface area of a given cluster is calculated by approximating the shape as ellipsoidal.\(^{19}\)

It is fruitful to begin by noting some characteristic features in the geometries seen over the entire series. The series has two distinctive clusters $Na_{55}$ and $Na_{147}$ which are complete McKay icosahedra displaying geometric shell closing and a full five fold rotational symmetry. $Na_{13}$, a possible icosahedral structure is seriously distorted due to Jahn-Teller distortion. We call the two above clusters as completely ordered. Apart from these two spherically symmetric clusters, the clusters with $N=20, 40, 58, 92,$ and 138 are electronically closed shell systems and are also spherical. We also note that among these, $Na_{92}$ is very special in the sense that its location is far from complete icosahedral clusters namely $Na_{55}$ and $Na_{147}$. As we shall see the atomic arrangement in the clusters around $N=92$ will turn out to be dramatically different than the growth pattern observed after $N > 55$.

Although the general principle determining the shapes of these clusters is the total energy minimization its manifestation on the growth pattern is due to a delicate balance between two
competing energies: the surface energy which will tend to make the cluster spherical and the nature of the binding which would like to place the atoms so as to have optimum coordination number to maximize the binding energy locally. The interesting issues we address are: (1) how do cluster grow from one ordered cluster to another ordered cluster? (2) How do the competing interactions noted above influence the growth pattern locally as well as globally? (3) Is there a characteristic difference between the atomic arrangements of geometrically closed shell clusters and electronically closed shell clusters?

Our analysis uncovers a number of striking features of the growth characteristics. Firstly, the growth shows order-disorder-order pattern of cyclic nature. Secondly, we observe firm local order, in this case icosahedral local order as the growth proceeds between the two ordered structures. Thirdly, we also observe a peculiar atomic arrangement in the clusters around \( N=92 \). In fact it turns out that these clusters do not exhibit the favored icosahedral local order.

We begin the discussion by presenting in Figure 1, the surface energy per unit area and the distance of the nearest atom from the COM for the entire series. There are a number of interesting features that are seen in the figure. The shape changes cyclically from spherical (\( \varepsilon_{\text{def}} \approx 1 \)) to the non spherical (\( \varepsilon_{\text{def}} \approx 1.8 \)) and back to spherical structure. Thus, clusters with \( N=20,40,55,70,92 \) and within the range of 134-147 are spherical. The change of the shape from non spherical to spherical is rather abrupt as indicated by sharp drops in \( \varepsilon_{\text{def}} \), normally by addition of two to three atoms, \( N=92 \) being an exception. The minima and the maxima in the shape parameter correlates extremely well with the behavior of surface energy, it being minimum for spherical systems. Interestingly for \( N \leq 70 \) the spherical clusters also have an atom very near or on the COM. However from \( N=71-108 \) i.e over a wide range of sizes, the nearest atom from the COM is away at about 1.5 Å. This happens to be true even for \( Na_{92} \), a spherical cluster. We have carefully examined the detailed arrangement of atoms in the GS of all the clusters by calculating the distance of all the atoms from the COM. In Figure 2 we show the distance from the COM, ordered in increasing fashion, for all the atoms. Such a plot shows characteristic step like structure if the cluster contains a well defined shell structure. For example \( Na_{147} \) shows characteristic steps containing 13,30,12,20,60, and 12
number of atoms corresponding to complete icosahedron. The representative samples shown in
Figure 2 is large enough to show the formation and destruction of these shells as the clusters grow.
It can be seen that for the clusters in the range $N=19-37$ there is hardly any shell formation (except
at $Na_{34}$). Although shell formation is seen around $N=40$, it gets destroyed at $N=44$ and seen again
at $N=53$ onwards. Again clusters in the range of $67 \leq N < 134$ have no obvious shell structure
except at $N=92$. All the clusters having high value of $\varepsilon_{\text{def}}$ do not show any shell structure, have
higher surface energy per unit area and also do not have an atom at or near the COM. A detailed
examination of the atomic arrangements reveals that there is no particular rotational symmetries
present in these clusters. Thus, these clusters are disordered.

It turns out that the clusters grow from one ordered geometry to another one via a disordered
growth. These disordered clusters show large deviations from the sphericity. The exception is
$N=92$ the electronically driven system which we shall discuss separately. We have carefully ex-
amined the coordination numbers of all the atoms in each of the cluster. Then we focused on the
atomic arrangements around all the atoms in a given clusters having 12 nearest neighbors. Strik-
ingly, the thirteen atom motif thus formed turns out to be that of icosahedron. In fact there is a
pattern in the formation of such centers of local order in these disordered clusters. As the clusters
grow atom by atom, the number of such centers grow forming interpenetrating icosahedra. The
first appearance of icosahedron occurs at $N=19$. Figure 3 shows some representative geometries
between $N=19$ and $N=134$ where we have highlighted at least one such icosahedron. The number
of such centers grow to about 8 at $N=40$ and to about 10 at $N=52$. The emergence of the global
order out of such multi-centers of local order can best be illustrated by examining the growth from
$N=45$ to $N=55$. Let us recall that the ordered cluster $Na_{55}$ consist of one central 13 atom icosa-
hedron and has 12 peripheral decahedra. As the clusters grow from $N=40$ they become progressively
disordered, their shell structure is destroyed, and $\varepsilon_{\text{def}}$ grows to $\approx 2$ till $N=52$. With the addition of
one atom this cluster completely reorganizes into nearly spherical, well-ordered icosahedron with
2 atoms missing from the last shell. This transformation is sharp and is driven by surface energy.
Thus the global order emerges out of locally ordered but globally disordered clusters rather sud-
denly. A similar pattern is observed as the clusters grow after \( N=55 \). We observe one icosahedral center having 55 atoms between \( N=56-70 \). At \( N=71 \) two interpenetrating icosahedral motifs appear. This is accompanied by a sharp increase in \( \epsilon_{\text{def}} \), accompanied by displacement of the atom on the COM by about 1.5\( \text{Å} \) and the cluster becomes prolate.

A third such center appears at \( N=80 \) making the cluster(\( Na_{80} \)) more spherical. This pattern of forming local icosahedral order with 55 atoms is interrupted around \( N=88 \) and is established again at \( N=108 \). It may be noted that \( Na_{92} \) is an electronically closed shell system, having spherically symmetric charge density, forcing the ionic geometry to be spherical. The shell structure evident in Figure 2 is not that of icosahedron. There is no rotational symmetry in the system. However there is a peculiar local order that can be discerned. In Figure 4(a), Figure 4(b) we show all the atoms in the first 2 shells and in the first and third shell respectively. The rotational symmetry in the motifs shown is evident. Thus, this globally disordered cluster shows strong local order although not icosahedral. All the atoms in the first three shells have 12 nearest neighbors. Interestingly within each of the shells the 12 atom motif formed by these nearest neighbors is unique and is identical(up to 2 decimal places) for all the atoms in that shell. There are no icosahedral motif seen in the cluster but we do see around third shell atoms decahedral motif. A typical one seen around the second shell atoms is shown in Figure 4(c). The motif around the third shell atom is slightly distorted decahedron(not shown). The expected growth pattern for \( N>88 \) should have given rise to interpenetrating multi-centers of 55 atoms icosahedra. Instead, this electronically driven spherically symmetric cluster develops a peculiar local order which is not icosahedral. The 55 atom icosahedron reappears at \( N=108 \) but is not centered on COM. Evidently the icosahedral shell structure as seen from the COM is completely recovered at \( Na_{134} \). A careful examination of Figure 1(c) and Figure 2 for clusters in the range \( N=130 \) to 134 clearly bring out the sharp effect of adding one or two atoms. All the atoms after \( N>134 \) just fill in the last shell without destroying the shape.

Recently Kostco et al.\(^{12}\) reported ground state structures of sodium clusters using photoelectron spectroscopy. They conclude that the structures at intermediate sizes between closed shell
Icosahedra ($N=55-147$) are formed by growth of layers on icosahedral motifs. Our geometries for $Na_{71}$ and $138 \leq N \leq 147$ are consistent with this. However the clusters around $Na_{92}$ (especially $86 < N < 108$) do not show any icosahedral motif.

Finally we offer a clear physical explanation for the most important experimentally observed feature namely rather low values of melting temperature ($210$ K) around $N=92$. Quite clearly the clusters in this region are characterized by absence of local icosahedral order. In fact the bond length of the 12 nearest neighbors atoms from the central one forming the motif discussed above differ by as much as $0.5$ Å. This is in sharp contrast to the other clusters in the series. It is precisely the absence of local icosahedral order which is responsible for rather low melting points. The sharp rise in the melting temperature seen around $N=134$ coincides with the establishment of central icosahedron consisting of well-formed 5 icosahedral shells.

In conclusion the growth of sodium clusters $Na_N$ ($N=10-147$) shows an order-disorder-order pattern. We observe formation of multi-centers having strong icosahedral local order specially in the disordered clusters. The establishment of global order is sudden, accompanied by a sharp change in the shape parameter. Clusters around $N=92$ (electronically closed shell system) show no local icosahedral order. We attribute observed low melting temperatures to the absence of favored icosahedral order.

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(19) The surface area $s$ is calculated via $s \approx 4\pi \left( \frac{a^p b^p + a^p c^p + b^p c^p}{3} \right)^{\frac{1}{p}}$ where $a$, $b$, and $c$ are elliptic radii and $p \approx 1.6075$. 
Captions for Figures

fig.1. (a) The shape deformation parameter, (b) surface energy per unit area, (c) distance of the nearest atom from the COM as a function of size for the \( Na_N \) \( N=13-147 \).

fig.2. The distance from the COM for each atom ordered in the increasing fashion for the ground-states of selected clusters. The sharp steps indicate formation of geometric shells.

fig.3. (Color online). The ground-state geometries of some clusters. Motifs formed by dark spheres (blue online) show icosahedral local order.

fig.4. (Color online). (a) and (b) Atomic arrangement for the first two and the first and third shells in \( Na_{92} \). (c)The unique motif seen around all the atoms in the second shell of \( Na_{92} \).

fig.5. (Color online). Ground state geometry of \( Na_{108} \) depicting formation of icosahedra. (Blue spheres)
Figure 1:
Figure 2:
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Figure 3:
Figure 4:
Figure 5: