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Building Clusters Atom-by-Atom: From Local Order to Global Order

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We have carried out extensive density functional calculations for series of sodium clusters Na_N ranging from $N = 10$ to 147 and have obtained ≈13 000 distinct isomers. We unravel a number of striking features of the growth characteristics. The growth shows an order−disorder−order pattern of cyclic nature. Between two ordered clusters, the growth proceeds via disordered clusters having multicentered 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 that is responsible for the 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 a few hundred atoms, clusters show individuality. Specifically, they show size-dependent features in their geometries, energy gaps and binding energies, stability, polarizability,[1−6] melting temperatures, and shapes of the heat capacity curves.[7−10] Despite a large number of studies, a clear evolutionary pattern of the growth over a wide range of sizes 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.[11]

Clusters of sodium atoms are perhaps the most intensively studied, both experimentally and theoretically.[7,12−17] Although features such as 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, such as melting temperature.[7] Most of the early work on these clusters is restricted to $N < 20$. For example, Röthlisberger et al.[16] 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 $N \leq 80$ and at least 100 isomers for all the clusters having even numbers of atoms with $80 < N \leq 147$. All the calculations have been performed within a unified framework using a plane wave basis, ultrasoft pseudopotential, local density exchange correlation potential of Ceperley−Alder, and the same box length (36 Å).[18] Our results are based on the analysis of about 13 000 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 two different temperatures for the period of 50−90 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 an appropriate low temperature to the electrons.

We have analyzed the ground-state structures, focusing mainly on the nature of their geometries. We examine their shapes by using a shape deformation parameter (ε_{def}) defined below, the geometric shell structure as viewed from the center of mass (COM), and the distribution of all the relevant bond lengths in the system. ε_{def} is defined as: $\varepsilon_{def} = (2Q_x)/(Q_y + Q_z)$, 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 ith coordinate of ion I relative to the COM. We also examine the coordination numbers for all the atoms to locate the possible existence of any local order, then we examine the motifs formed by ≈12 nearest neighbors for all the atoms having 11−13 nearest neighbors. We also calculate the surface energy, S, through the following relationship: $S = E_{tot}(N) - \varepsilon_\infty N$ where $E_{tot}(N)$ is the total energy of the cluster and ε_∞ 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 5-fold rotational symmetry. Na_{13}, a possible icosahedral structure, is seriously distorted due to Jahn−Teller distortion. We

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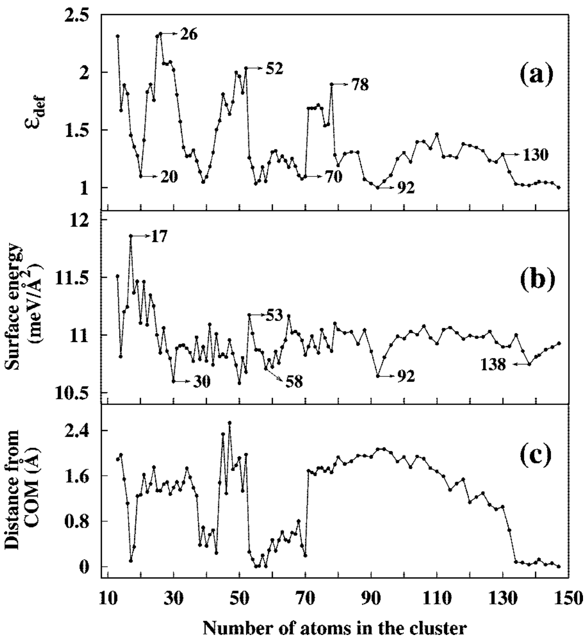

Figure 1. (a) The shape deformation parameter, (b) surface energy per unit area, and (c) distance of the nearest atom from the COM as a function of size for the Na_N, $N = 13-147$.

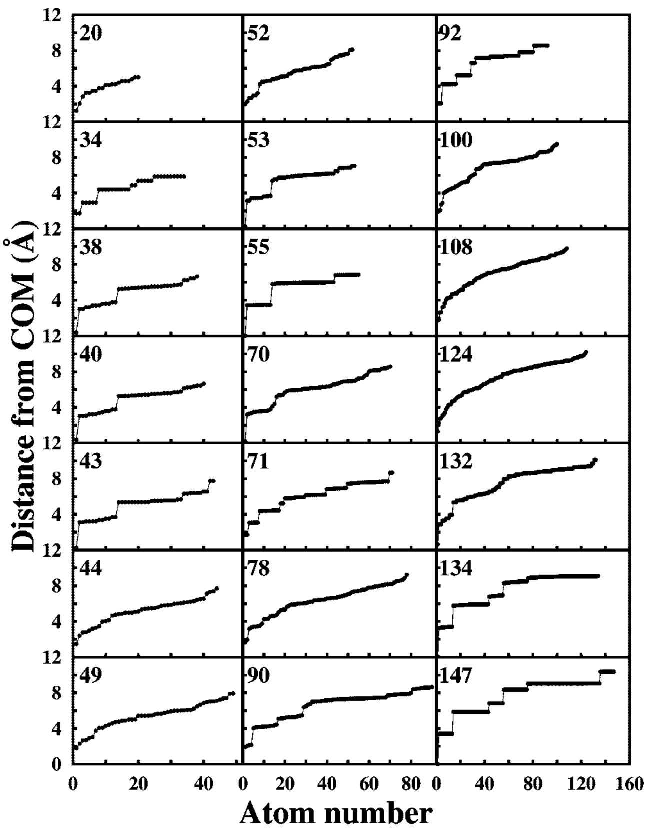

Figure 2. The distance from the COM for each atom ordered in the increasing fashion for the ground states of selected clusters. The sharp steps indicate formation of geometric shells.

label 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 from 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 an optimum coordination number to maximize the binding energy locally. The interesting issues we address are (1) how do clusters 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. First, the growth shows order–disorder–order pattern of cyclic nature. Second, we observe firm local order (in this case, icosahedral local order) as the growth proceeds between the two ordered structures. Third, 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 ε_{def}, 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 ($\varepsilon_{def} \approx 1$) to the nonspherical ($\varepsilon_{def} \approx 1.8$) 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 nonspherical to spherical is rather abrupt, as indicated by sharp drops in ε_{def}, normally by addition of two to three atoms, $N = 92$ being an exception. The minima and the maxima in the shape parameter correlate 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 ~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 steplike 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 numbers 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 is seen again at $N = 53$ onward. Again, clusters in the range of $67 \leq N < 134$ have no obvious shell structure except at $N = 92$. All the clusters having a high value of ε_{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 symmetry 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

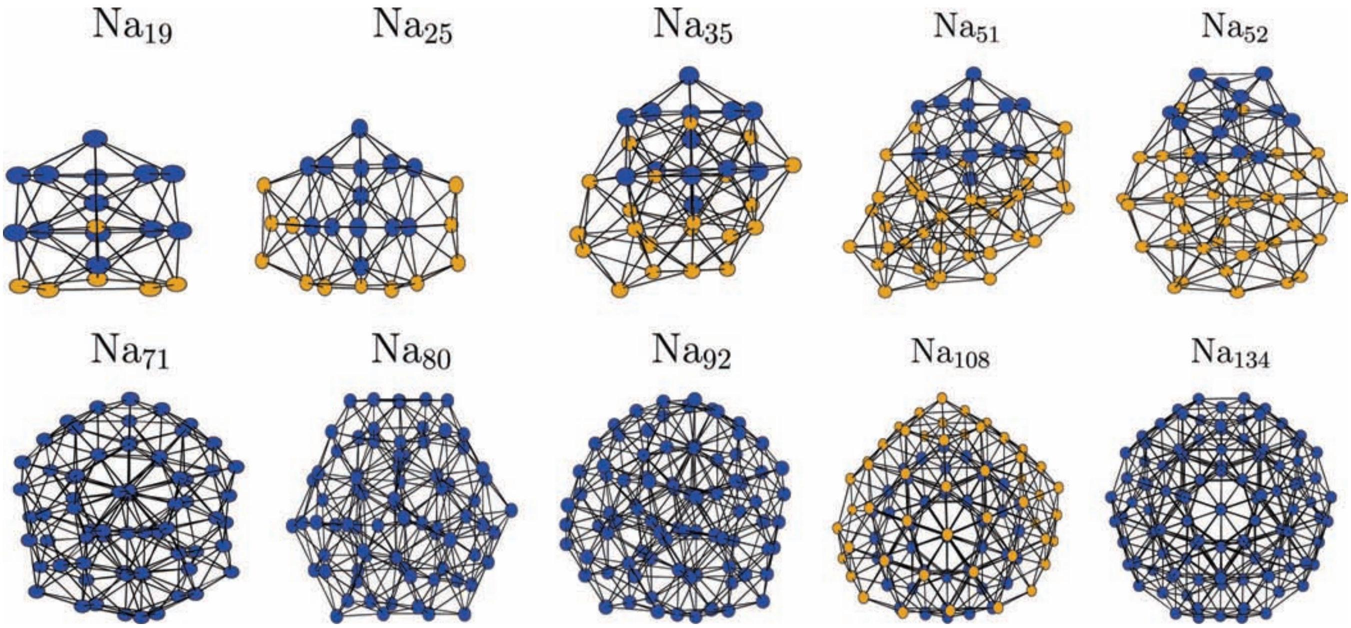

Figure 3. The ground-state geometries of some clusters. Motifs formed by dark spheres show icosahedral local order.

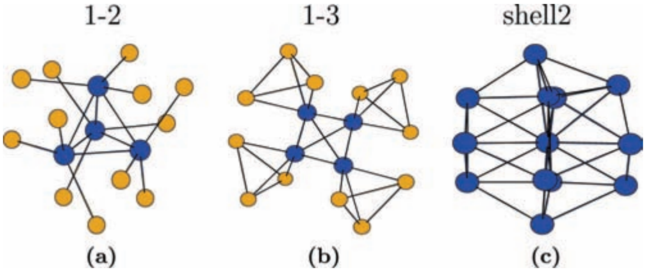

Figure 4. (a, b) Atomic arrangement for the first two and the first and third shells in Na_{92}. (c) The unique motif seen around all the atoms in the second shell of Na_{92}.

show large deviations from sphericity. The exception is $N = 92$, the electronically driven system that we shall discuss separately. We have carefully examined the coordination numbers of all the atoms in each of the clusters.

We then focused on the atomic arrangements around all the atoms in given clusters having 12 nearest neighbors. Strikingly, the 13-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 grows, 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 grows to about 8 at $N = 40$ and to about 10 at $N = 52$. The emergence of the global order out of such multicenters 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} consists of one central, 13-atom icosahedron and has 12 peripheral decahedra. As the clusters grow from $N = 40$, they become progressively disordered, their shell structure is destroyed, and $\varepsilon_{\mathrm{def}}$ grows to ≈ 2 until $N = 52$. With the addition of one atom, this cluster completely reorganizes into a nearly spherical, well-ordered icosahedron with two 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 suddenly.

A similar pattern is observed as the clusters grow after $N = 55$. We observe one icosahedral center having 55 atoms between $N = 56$ and 70. At $N = 71$, two interpenetrating icosahedral motifs appear. This is accompanied by a sharp increase in $\varepsilon_{\mathrm{def}}$, accompanied by displacement of the atom on the COM by about 1.5 Å, and the cluster's becoming 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 an icosahedron. There is no rotational symmetry in the system. However, there is a peculiar local order that can be discerned. In Figure 4a and b, we show all the atoms in the first two shells and in the first and third shells, 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 two decimal places) for all the atoms in that shell. There is no icosahedral motif seen in the cluster, but we do see around third shell atoms a decahedral motif. A typical one seen around the second shell atoms is shown in Figure 4c. The motif around the third shell atom is a slightly distorted decahedron (not shown).

The expected growth pattern for $N > 88$ should have given rise to interpenetrating multicenters of 55-atom icosahedra. Instead, this electronically driven, spherically symmetric cluster develops a peculiar local order that is not icosahedral. The 55-atom icosahedron reappears at $N = 108$ but is not centered on COM. Evidently (Figure 2), the icosahedral shell structure, as seen from the COM, is completely recovered at Na_{134}. A careful examination of Figures 1c and 2 for clusters in the range $N = 130-134$ clearly brings 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 for the melting temperature (210 K) around $N = 92$.[7] Quite clearly, the clusters in this region are characterized by an absence of local icosahedral order. In fact, the bond lengths of the 12 nearest neighbor 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 that is responsible for the rather low melting points. The sharp rise in the melting temperature seen around $N = 134$ coincides with the establishment of a central icosahedron consisting of well-formed five icosahedral shells.

In conclusion, the growth of sodium clusters Na_N ($N = 10-147$) shows an order−disorder−order pattern. We observe formation of multicenters having strong icosahedral local order, especially 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 the observed low melting temperatures to the absence of favored icosahedral order.

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

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