Packing Transitions in Nanosized Li Clusters

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The change in cluster properties such as structure as size increases is a problem of considerable interest \[1\]. Recently, the abundance spectra of alkali clusters have been measured \[2,3\] up to very large sizes. The jellium model \[4\] for sizes \(N < 1500\) and structural stabilities based on icosahedral or cuboctahedral (FCC) packing for large clusters \((1500 < N < 22000)\) were successfully used to explain the observed intensity maxima. However, these measurements give no direct structural information. Electron microscope measurements of atomic positions have been reported for gold clusters for sizes above \(400\) atoms \[5\]. Cuboctahedral and icosahedral geometries were observed supporting high density packing for large metal clusters. In the bulk limit, Li and Na undergo a martensitic transformation from BCC to a close-packed crystal at low temperatures \[6,7\].

On the other hand, \textit{ab initio} calculations of geometric and electronic properties of Li clusters within the Hartree-Fock (HF) \[8\], the SCF-CI method \[9,10\] and the generalized valence bond methods \[11\] and spectroscopic measurements \[12\] find that small Li clusters have open structures rather than dense packing. Similar results have been found for other simple metals \[10,13\].

In this article we report optimal structures for Li clusters from the small to large particle regime. An unbiased search, simulated annealing, was used to obtain lowest energy configurations. The Car-Parrinello molecular dynamics which combines dynamics and the local density approximation \[14\] has been successfully used in cluster calculations \[15,16\]. However, the artificial heating of the electron wavefunction makes application of this method to metal clusters difficult. The calculations reported here use an \textit{ab initio} molecular dynamics (AIMD) simulation based on a conjugate gradient algorithm \[17\] to update the electronic structure following each step of atomic motion. With this method we can take much larger time steps, limited only by the time scale of classical motion of the atoms. Except for this modification, the method is the same as in previous AIMD simulations \[13,18,19\].

The calculations were performed within the pseudopotential local spin density (LSD) method \[20,21\]. A simple cubic supercell with lattice constant \(a = 30.0 – 45.0\) a.u. and a cutoff energy of 11.2 Ry provided adequate convergence. Predictions for structure, energies and vibrational frequencies for Li\(_2\) and Li\(_3\) were close to experimental data \[22\], e.g., for Li\(_2\), \(D_e=0.93\) eV (LSD) and 1.07 eV(Exp.); \(\omega = 341 \text{ cm}^{-1}\) (LSD) and 351 cm\(^{-1}\) (Exp.). Annealing was started from a randomly generated initial geometry and the system was allowed to equilibrate at a temperature about twice the bulk melting temperature \((700 – 800\) K) for about 10 picoseconds. After this initial equilibration the cluster was cooled as slowly as possible \((10^{14} – 10^{15} \text{ K/sec})\) until solid-like dynamics appeared. At this point the system was quenched to the nearest minimum energy structure. For clusters of sizes less than 55, repeated annealing led to the same or very similar degenerate structures. Above this size selected geometries were optimized by steepest descent or conjugate gradient minimization.

The electronic shell structures and the large HOMOLUMO gap at the magic numbers \(N=8, 20\) and 40 are in good agreement with the jellium model as in the Na and Be systems \[13,16\]. As in prior alkali metal calculations, the orbital energies are fairly insensitive to the detailed atomic positions \[15\].

However, Li and the other first row elements have large \(sp\) interactions due to the lack of \(p\) orbitals in the core \[23\]. The pseudopotential for the Li \(2p\) state is deeper and less repulsive at the origin than for other group I elements. This results in more participation of \(p\) orbitals in bonding. For example, the \(sp\) promotion for Li clusters is much larger and increases more quickly with size than in Na and K.
For the Li system, the increased \( sp \) promotion results in optimal structures with increased polarization and charge transfer between interior and surface atoms and very different geometries when compared with the Na and K systems. For example, at the LSD level, a three-dimensional structure has the lowest energy at \( N=5 \) [22] for Li, whereas heavier alkali elements remain planar till \( N=6 \) [13].

More remarkably, the enhanced charge transfer in Li\(_8\) leads to the unusual centered trigonal prism (CTP) structure with a capping atom illustrated in Fig. 1a. This structure is very different from the dicapped octahedral (dodecahedron) structure (Fig. 1b) previously found for Na [13] and also for K [24]. The central atom is negatively charged by nearly \( -e \) (the charge is estimated by population analysis [20]). The extra electron on the central atom occupies \( p \) type orbitals. The balance of positive charge is distributed almost equally among surface atoms. Because of this charge distribution, the surface atoms are attracted to the center atom, whereas the attraction between the surface atoms is reduced. The structure is similar to that of ionic solvation and resembles that of the ionic molecule TaF\(_8^+\) [25]. It has not been identified in other calculations [10].

The charge density in the Li\(_8\) CTP structure is largest near the interior atom in contrast to the high charge density between surface atoms in the dicapped octahedral structure of Na and K. In order for such a structure to be stable, the pseudopotential of the central atom must be able to accommodate the increased density and the nodal property of the cluster orbitals at the central atom. Since the additional charge on the central atom occupies atomic \( p \) orbitals, the \( p \) component of the pseudopotential is responsible for the difference between Li and other group I elements. In the Li system the \( sp \) interaction is enhanced by the deep minimum in the \( p \) component of the pseudopotential, whereas the relatively shallow \( p \) potential of the other group I elements suppresses the \( sp \) promotion. Therefore, for the Na and K systems, the CTP structure is not stable and spontaneously distorts to a dicapped triangular prism [22], which has no central atom and very little charge transfer. When the \( p \) component of the Li pseudopotential is artificially made more repulsive, the CTP structure distorts in a way similar to Na and K.

For the Li systems with large charge transfer and short bonds (because of the relatively small core sizes of the first row elements) there is also stability from the Coulomb interactions. While the geometric structures of the Na and Li systems are qualitatively different, the nodal structures of the cluster orbitals and the overall cluster distortions for both systems are well described by the jellium model [3], which focuses on the kinetic energy and shape of the uniform positive background charge.

The CTP structure of Fig. 1a is remarkable not only for its ionic character but also because it initiates a pattern of growth which continues with particle addition. In Figs. 3a-3d we illustrate this pattern schematically. Fig. 3a is a representation of the CTP structure (Fig. 1a) of Li\(_8\). Li\(_9\) forms a structure similar to Li\(_8\) with one more atom in the “solvation shell” (Fig. 3b). The eight surface atoms surrounding the central atom form two squares in staggered positions as in TaF\(_8^+\) [25]. All these molecules minimize the repulsion between charged surface atoms. At \( N=14 \) (Fig. 3c), a second internal atom appears with face sharing CTP structures. The Li\(_{13}\) structure is similar to that of Li\(_{14}\) with one capping atom removed. The 13-atom icosahedral structure (IC13) is 0.035 eV/atom higher in energy. The local coordination around the two internal atoms in Li\(_{11-13}\) [20] is identical to that of Li\(_{14}\).

At \( N=16 \), another atom is in the first shell, increasing the coordination around the interior atoms by one. Above this size, the third solvation shell is gradually developed and a fully solvated structure is produced at \( N=19 \) (Fig. 3d). However, while the total charge transfer per atom is relatively constant, as the system size increases the localization of the charge on the second shell decreases, decreasing the Coulombic stabilization per atom due to charge separation and thus the relative stability of the CTP pattern.

Between \( N=22 \) and 25, simulated annealing produces a new packing pattern. The highest coordination number jumps to 12, indicating a close-packed structure is established. This dense packing is based on interpenetrating 13-atom local icosahedra (LIC) formed by an interior atom and its 12 nearest neighbors. These structures may be constructed from an IC13 core by placing additional surface atoms either on the top of vertex atoms (12 sites) or above the center of triangular faces (20 sites) (Fig. 4 LIC). Structures based on CTP packing were optimized as possible candidates for the optimal structure for clusters larger than 20. These structures distort to higher coordinated capped pentagon structures with somewhat higher energies than the optimal structures. At this point the structures for the Li, Na and K systems are all similarly based on the LIC packing [24]. For the Na and K systems, the CTP structure was never stable so the LIC structure begins at a lower particle number [13] [24].

In order to make a quantitative structural characterization of the minimum energy clusters, a Blaisten-Farojas (BF) analysis [27] was carried out. In this analysis the local geometry around a pair of atoms is characterized by four indices. If the atoms are within a certain distance (\( R_c = 6.0 - 6.5 a_0 \)), an index 1 is assigned. Otherwise, the first index is 0. Next, the number of the nearest neighbors that the two atoms have in common is counted. This number is assigned as the second index. The third index specifies the number of bonds between the nearest neighbors. A fourth index is added to provide a unique correspondence in case different geometries lead to the same indices. For example, choosing the capping atoms in the pentagonal bipyramid that is an important ele-
ment of the icosahedral structure, the BF index is 1551. The BF index for the nearest neighbors of FCC crystal is 1421.

The relative abundance of these indices as a function of cluster size is illustrated in Fig. 3. The index 1551 is very rare for the size \( N < 25 \), showing the lack of pentagonal structures. It suddenly becomes abundant at \( N = 25 \) due to the appearance of LIC packing. For \( N = 55 \), it decreases due to the appearance of a new structure based on Mackay icosahedron (MIC, discussed in more detail below). On the other hand, the index 1421 is prevalent for \( N < 20 \) but completely disappears between \( N = 25 \) and 45. It appears again at \( N = 55 \) due to the appearance of MIC which has a packing similar to that of FCC.

The LIC packing pattern continues at least up to Li\(_{45}\) at which point all the triangular faces and vertex faces may be occupied, producing a highly symmetrical \( I_d \) structure. For the systems \( N = 25, 30 \) and 40, perfect LIC structures were obtained directly from annealing calculations. However, simulated annealing of Li\(_{45}\) converged to a slightly disordered structure which was slightly more stable than the perfect LIC. For \( N = 45 \) and above, there are significant problems with LIC packing which lead to a new packing paradigm. In the perfect Li\(_{45}\) structure, the distance between surface atoms in the optimized perfect structure is large (\( \approx 6.0 \, a_0 \)) relative to the bulk (\( \approx 5.88 \, a_0 \)). More importantly, the center to first shell and the intershell bonds have become very short (\( \approx 5.1 \, a_0 \) and 5.3 \( a_0 \)). The effect of this strain on the system is apparent in the spherically averaged density which for Li\(_{45}\) is much larger in the center of the cluster than the bulk value. The low surface atomic density of the LIC pattern produces high local energy density in the center. However, if bond lengths in the surface are to be kept near those of the bulk, compression of the interior bonds must occur. At some point this compression will become so unfavorable that a new packing pattern will be optimal.

A packing that eases these difficulties and that can extend to larger sizes can be achieved by placing atoms on the 30 bridge sites of the IC\(_{13}\) core cluster instead of on the triangle faces, as illustrated in Fig. 3. MIC. Occupying all these sites on a IC\(_{13}\) core will form a 55-atom Mackay icosahedron (MIC) (13 core + 12 vertex + 30 bridge atoms).

For \( N = 45 \), an incomplete MIC structure is somewhat higher in energy than the perfect LIC structure (\( \Delta E = 0.022 \) eV/atom). However, for \( N = 55 \) the perfect MIC structure is lower in energy than the optimized LIC structures we obtained from simulated annealing.

Another possible structure for the 55 atom system is a fragment of an FCC crystal terminated mostly by (111) facets (a cuboctahedron). We found that the “perfect” FCC structure is higher in energy than the “perfect” MIC structure and distorts with a small activation barrier to the optimized MIC structure. Presumably this is because of the larger number of nearest neighbor interactions in the MIC pattern; 234 for MIC vs. 216 for FCC.

Similar structural transitions have been predicted for Lennard-Jones (LJ) clusters by Northby [28]. However for these systems, the transition from face capping to bridging (LIC to MIC) takes place at a smaller particle number, \( N = 31 \). In order to provide additional support for the stability of the LIC structure for Li above \( N = 31 \) (preference for face capping), we calculated the energy of Li\(_{25}\), Li\(_{30}\), Li\(_{40}\), and Li\(_{45}\) quenched from the Northby structures. In all cases the highly ordered LIC patterns found from simulated annealing gave lower energies.

As the system grows further, our results suggest that the MIC structure forms a core and further growth proceeds as atoms are added to the surface in either bridged sites or face capping sites. However, calculations of Li\(_{45}\) show that growth immediately after \( N = 55 \) is based on face capping. At \( N = 147 \) both MIC and FCC have “perfect” (geometrically spherical) structures. However, for 147 the MIC has a slightly lower energy (\( \Delta E = 0.022 \) eV/atom). There is a suggestion in the electron density and the interior bond lengths (5.38 au for MIC vs. 5.72 au for FCC) that a transition to FCC is imminent. Calculations show that such a transition results in a decrease in the internal electron density. The near degeneracy of the MIC and FCC structures is consistent with the observation of both structures in electron microscope studies for silver clusters [4].

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FIG. 1. The lowest energy structures of (a) Li$_8$ and (b) Na$_8$ (a dodecahedron).

FIG. 2. Schematic representations of (a) Li$_8$, (b) Li$_9$, (c) Li$_{14}$, and (d) Li$_{19}$. Shaded circles indicate vertex atoms of trigonal prisms and solid circles are center atoms in the prisms. Open circles represent atoms capping the sides of the prisms. The shaded and open circles form a solvation shell around the solid circle.

FIG. 3. Blaisten-Farojas analysis. The upper and lower curves indicate the abundance of pentagonal bipyramids and rectangular bipyramids in the lowest energy structure, respectively. $\Delta$ and $\Box$ indicate the LIC at N=55 and the bulk FCC, respectively.

FIG. 4. (a) 45-atom LIC structure. LIC axes passing through the center of IC13 have been drawn. (b) Successive MIC models with complete outer layers are constructed by growing each of the 20 tetrahedra constituting the primitive IC13.