Discovery of Unforeseen Binary Lennard-Jones Clusters Utilizing the Hidden Force Algorithm

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We present a new method for minimizing additive potential energy functions. Utilizing our *hidden force algorithm* in a non-Markovian, parallel Monte Carlo search, we found *17* new putative global minima for binary Lennard-Jones clusters in the size range of *90-100* particles. The method is efficient enough that an unbiased search was possible; no potential energy surface symmetries were exploited. All new minima are comprised of three nested polyicosahedral or polytetrahedral shells when viewed as a nested set of Connolly surfaces (though the shell structure has previously gone unscrutinized, known minima are often qualitatively similar). Unlike known minima, in which the outer and inner shells are comprised of the larger and smaller atoms respectively, in *13* of the new minima, the atoms are not as clearly separated by size. Further, while some known minima have inner shells stabilized by larger atoms, *4* of the new minima have outer shells stabilized by smaller atoms.

Binary Lennard-Jones (BLJ) clusters are practically interesting for modeling properties of binary alloy nanoparticles [1-3] and theoretically interesting for the momentous difficulty required to search their intricate multidimensional configuration-space [4,5]. A BLJ cluster consists of a fixed number of atoms. There are only two atom types and they only differ in size. Minimizing a BLJ cluster requires searching an exceedingly rugged continuous potential energy surface (PES) for each discrete cluster composition. Cluster minimization methods can be split into two categories: biased and unbiased [6]. Biased methods were first used for clusters of a single atom type and conduct a restricted search within an immensely reduced configuration space of some configuration symmetry group assumed *a priori*; unfortunately, BLJ clusters often lack the symmetries required to make biased methods effective. Unbiased methods start with a random configuration and gradually lower the energy by iterative application of geometric perturbations and local minimization, usually with a Monte Carlo scheme. Doye and Meyer's BLJ cluster minimization method [4,5] is based on the very successful basin-hopping method developed by Wales and Doye [7-9] which in turn is based on Li and Scheraga's Monte Carlo-minimization method [10]. Doye and Meyer's method uses Wales and Doye's basin-hopping move-set (random atomic displacements and rotation of low-energy atoms around the center of mass) augmented with swapping two randomly selected atoms' types and changing a single randomly selected atom's type for numerous Monte Carlo searches. Each Monte Carlo

search has a fixed temperature and is periodically restarted using low-energy intermediate configurations discovered by previous searches [5,11]. Our approach is built on a novel move-set we call the *hidden force algorithm (HFA)*. We embed this move-set in a scheme that generalizes Doye and Meyer's Monte Carlo search to exploit parallel computation effectively.

HFA exploits that, for an additive potential, the potential energy gradient is also additive. At local minima, the gradient vanishes $\partial V/\partial x_i = 0, \forall i$ where 'x_i' is the position of atom '*i*' along axis '*x*' (and similarly for the '*y*' and '*z*' axes). Concentrating on pair-wise additive potentials, we have $\partial V/\partial x_i = \sum_j \partial V_{ij}/\partial x_i$ where 'V_{ij}' is the interaction energy between atoms '*i*' and '*j*'. Though the gradient components sum to zero at local minima, each term's magnitude is generally non-zero. Like a multi-team tug-of-war at an impasse, significant opposing forces (the negative of the gradient) may be exerted upon cluster atoms. Disrupting this network of opposing forces will result in the collective rearrangement of cluster atoms. Using the tug-of-war analogy to describe the basic HFA move, one such disruption is for some teams (atoms) to drop simultaneously their ropes (drop their interactions from the potential energy function). The remaining teams then rearrange due to their net non-zero tugging and reach a partial impasse. At this point, the dropouts resume tugging until a new overall impasse is achieved. Specifically, given a local minimum-energy configuration, all of the interactions of a randomly selected subset of the cluster atoms are temporarily dropped and the configuration of the remaining atoms is locally minimized. The original potential energy function is then used to re-minimize the entire cluster. Because the dropped atoms remain at their original positions, they may be brought in close proximity with the remaining atoms. Much like the tug-of-war players cannot occupy the same position on the playing field (whether or not they are tugging), we do not allow dropped atoms to come into close proximity with other atoms via a simple iterative procedure. This avoids huge repulsive forces that can adversely affect the final minimization. There is no guarantee that the resulting cluster configuration will be lower in energy than the starting configuration, but we have found HFA to be an exceptionally successful move-set in a Monte Carlo cluster minimization. Significantly, the HFA trial configuration is highly dependent on the starting configuration since the move is driven by forces already present. Accordingly, the Monte Carlo search will be non-Markovian.

The HFA Monte Carlo search strategy is outlined as follows.

0. Initialize search with a random configuration (and, if applicable, with a random composition) and minimize it. Add the structure to a set of low-energy configurations called the restart pool.

Main iteration loop:

1. If a binary cluster search and a long stretch of iterations with the current composition has not produced a new global minimum configuration, apply single or multiple mutations by flipping the atom type of randomly selected atoms.
2. Apply an HFA move.

3. Accept the trial configuration if the trial energy is less than the minimum of the current configuration energy plus some user defined energy window and the best minimum energy seen plus some other user defined energy window. The second energy window is necessary to prevent accepting a long succession of small uphill energy movements. If rejected, revert to current configuration/composition and go to 6.
4. Make the trial configuration/composition the current configuration and check if it is unique to eliminate homotopes. Uniqueness is tested with a simple hash function including the energy, composition, and cluster radius of gyration. If a unique structure, add to the restart pool.
5. If the current configuration is the best minimum seen, remove restart pool configurations that are outside the new best minimum energy window. (Note that the restart pool typically includes low-energy configurations with different composition.)
6. If after a user-defined number of iterations, there have been no improvements to the best minimum seen, set the current configuration to one selected from the restart pool at random and go to 1. (Since this HFA Monte Carlo algorithm is non-Markovian, the search can get stuck in a limited volume of configuration space from the HFA-interdependence of successive configurations along the search path. We found the periodic restarts very effective in dealing with this problem.)
7. If running in parallel and a user-defined number of iterations have elapsed, copy the restart pool from the search with the overall best minimum seen to the local restart pool, set the current configuration to one selected from the restart pool at random and go to 1. (The HFA Monte Carlo search method is most efficient when using numerous searches run in parallel seeded with different starting configurations. We found a simple winner-takes-all strategy applied to a set of linked searches can often find the global minimum faster than an equal number of independent searches.)
8. If after a user-defined number of iterations the overall best minimum seen energy has not improved to a user-defined energy, return the best minimum energy seen. (We also found that ill-fated searches were likely to get stuck sooner than later and, therefore, searches not showing sufficient progress will be aborted to free up computational resources for new searches started from scratch.)

Search particulars are as follows. The potential is the standard BLJ potential $V_{\mathrm{BLJ}} = 4\sum_{i<j} \epsilon_{\mathrm{AB}}[(\sigma_{\mathrm{AB}}/r_{ij})^{12} - (\sigma_{\mathrm{AB}}/r_{ij})^{6}]$ where *A* and *B* are the atom types, '*i*' and '*j*' are atom indices, $\epsilon_{\mathrm{AB}} \equiv 1$ is the uniform well depth, $\sigma_{\mathrm{AB}} = (\sigma_{\mathrm{AA}} + \sigma_{\mathrm{BB}})/2$ and multiplied by $2^{1/6}$ gives the equilibrium pair separation between atoms '*i*' and '*j*' (with $\sigma_{\mathrm{AA}} \equiv 1$ set to be the unit of length), and r_{ij} is the distance. The size ratio of atom types *A* and *B* $\sigma_{\mathrm{AA}}/\sigma_{\mathrm{BB}} \leq 1$ with A always referring to the smaller atom. The HFA move in 2) above involved 10 to 20% of the cluster atoms. The energy windows in 3) were set to *0.15* $\varepsilon_{\mathrm{AB}}$ and *0.25* $\varepsilon_{\mathrm{AB}}$, respectively, and

the latter window was also used for updating the restart pool in 5). Searches were initiated with an approximately half-and-half A/B composition and run for *1* million iterations unless aborted in 8), which took approximately *6* CPU hours each for clusters in the size range of *90-100* particles on a standard *2.4* GHz Intel processor utilizing SIMD vector acceleration in all force computations and linear algebra operations. The iteration intervals referred to in 1), 6), and 7) were set, respectively, to *10,000*, *1,000* and *100,000*. We wrote a customized version of the LBFGS-preconditioned truncated Newton conjugate gradient method for local minimizations [12] utilizing analytical second derivatives in a sparse Hessian representation. In our preliminary tests we reproduced all global minima previously found for LJ clusters of up to *150* particles [13] including the hard to find tetrahedral global minimum of LJ_{98} [14], and also successfully located the putative global minima of the much larger LJ_{342} and LJ_{347} clusters [15]. The focus of our present work was revisiting the largest BLJ clusters reported in the Cambridge Cluster Database (CCDB) [16] in the size range of *90-100* particles [17,18].

We conducted a total of *66* searches on BLJ_{90} to BLJ_{100} varying the size of the type B atoms σ_{BB} between *1.05* and *1.3* keeping σ_{AA} =1. The energies of the *17* new putative global minima are listed in Table I in ε units, relative to the previous best energies in the CCDB [17] (as of July 2010). The remaining *49* searches furnished the same global minima already found. (An additional *36* unique clusters were found during these searches that had energies lower than these known minima, in most cases with different A/B compositions.) We then used the Maestro molecular modeling environment [19] to analyze the structures as a set of nested shells. We first constructed the convex hull of the entire cluster using the Connolly surface [20] with a *2.5* σ_{AA} probe radius [21]. At this probe radius, atoms on the Connolly surface empirically either occupied a vertex on the convex hull or were positioned just within the convex hull. We removed these atoms and repeated the above until no atoms remained. The first set of atoms removed constituted the outer shell, the second set constituted the middle shell, and so forth.

We found that all *17* new global minima were made of three shells. In some cases the shells were homogenous with the outer shell exclusively made of the larger (type B) atoms and the inner shells made of smaller (type A) atoms (clusters 13, 14, 16, and 17, all with C_S symmetry belong to this class). Fig. 1 shows such a separation; Fig. 1(a) shows the nested shells and (b-d), respectively, the outer/middle/inner shells (type A in maroon and type B in green, color online). The cluster shown in Fig. 1 is the putative global minumum of BLJ_{98}/σ_{BB} =1.25 reported in [11] with E = *-584.930661* in ε units and C_S symmetry, comprised of 42 type A atoms packed inside the shell of 56 type B atoms. Cluster 11 found by our HFA search shown in Fig. 2 has, in fact, slightly lower energy (*-584.953979* ε) and only *39* type A atoms, but more importantly the new putative global minimum configuration of BLJ_{98}/σ_{BB} =1.25 has an entirely different structure with no symmetry. Our unexpected finding demonstrates that, unlike previous BLJ minima in this size range, this cluster has a type A atom in the outer shell [22]. Fig. 2(b) shows a single maroon colored type A atom touching the surface of the outer shell, but not lodged in a vertex position, and Fig. 2(c) shows two explicitly plotted green colored B type atoms in the middle shell; one surfacing in a similar fashion and only the other occupying a lattice point. Fig. 2(d) displays an additional B type atom occupying a vertex of the inner shell.

Similar to cluster 11 every other new minimum with the exception of the aforementioned pure-shell clusters has a few cuckoo's egg atoms alloyed with the dominant atom type of some or all of the three shells. In clusters 1-3, 5, 7, 8, 10, 12, and 15, the B atoms inside the outer shell occupy convex hull vertices of a mixed type middle and/or inner cage. In addition to such B atoms, clusters 4 and 11 have a single A atom, and clusters 6 and 9 have two A atoms lodged in the outer shell. The minimum energy configuration of cluster BLJ_{95}/σ_{BB} =1.2 (with *33* type A atoms and $E = -557.690639\ \varepsilon$) [11] shown in Fig. 3 exemplifies a pure B type outer shell and mixed type middle and inner shells occupying vertices in predominantly A type shells. Our new putative global minimum in Fig. 4 has slightly lower energy ($-557.785217\ \varepsilon$) and its structure is virtually identical to that of Fig. 3 with one additional type A atom, which appears in the middle of a pentagonal pane in the outer convex hull. Figs. 3 and 4 are oriented the same way to highlight the difference in local structure around the maroon type A atom in the outer shell (cf. Figs. 3(b) and 4(b)). Type B atoms inside the outer shell have been previously found in some polytetrahedral clusters and were characterized in the framework of the so-called "disclination" network [4,5]. Our nested shell view reveals that these B atoms are integral to a predominantly A type cage structure. We further conclude that there are two types of "impurities" in BLJ clusters; a common case where a type B atom substitutes for a type A atom vertex in an inner shell (and potentially vice versa, though we have not yet found an example), and an exceptional case in which either atom type appears as a "pockmark" on the shell surface.

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[18] 15 out of our 17 new minima were independently found by Sicher, Mohr, and Goedecker using a significantly different search method [11]. URL http://www-wales.ch.cam.ac.uk/~wales/CCD/NEW_BINARY_LJ_MINIMA/.

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[21] We found the *2.5* σ_{AA} probe radius empirically. A radius much smaller than the equilibrium particle separation, fails to form a shell. A radius much larger asymptotically becomes the convex hull. We found the intermediate value helpful to identify both atoms on the convex hull and atoms interior to but near the convex hull.

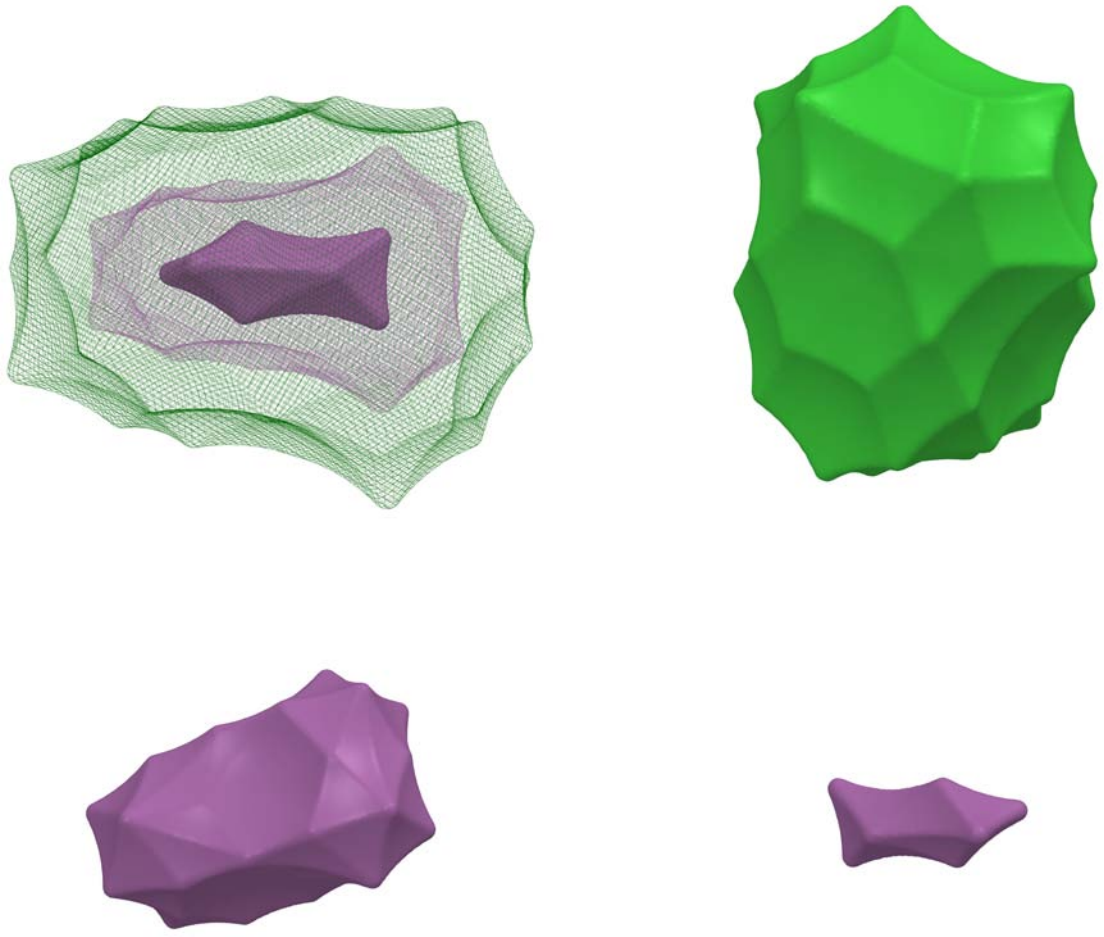
[22] Although to the best of our knowledge we are the first to report such structures, the presence of type A atom(s) in the outer shell has been overlooked. E.g., the previous best BLJ_{99}/σ_{BB} =1.25 minimum seen in the CCDB [17] also features a single type A atom in the outer shell.

Table I. Energies of the 17 new putative global minima listed in ε units, relative to the previous best energies in the CCDB [17]. The numbers in parentheses in the 'Energy' columns show the number of additional unique clusters found with the same number of particles (but in most cases with different A/B compositions) that had energies still lower than the base energy. The 'Cluster' columns identify the clusters and the 'No.' columns list the labels used in the text. Clusters 4 and 11 shown in bold have lower energies than those reported in [11] and their structures are also significantly different (see text). The coordinates of the new putative global minima have been deposited in the CCDB.

No.	Cluster	Energy, [ε]	No.	Cluster	Energy, [ε]
1.	BLJ_{92}, N_A=28, σ_{BB} =1.15	-0.014670 (0)	10.	BLJ_{97}, N_A=41, σ_{BB} =1.30	-1.500728 (3)
2.	BLJ_{93}, N_A=31, σ_{BB} =1.15	-0.156480 (0)	**11.**	**BLJ_{98}, N_A=39, σ_{BB} =1.25**	**-0.295878 (1)**
3.	BLJ_{94}, N_A=31, σ_{BB} =1.15	-0.766377 (3)	12.	BLJ_{98}, N_A=41, σ_{BB} =1.30	-1.428041 (4)
4.	**BLJ_{95}, N_A=34, σ_{BB} =1.20**	**-0.440722 (1)**	13.	BLJ_{99}, N_A=42, σ_{BB} =1.25	-1.082912 (7)
5.	BLJ_{96}, N_A=33, σ_{BB} =1.20	-0.957821 (4)	14.	BLJ_{99}, N_A=42, σ_{BB} =1.30	-1.248290 (2)
6.	BLJ_{96}, N_A=39, σ_{BB} =1.25	-0.203123 (0)	15.	BLJ_{100}, N_A=35, σ_{BB} =1.20	-0.024301 (0)
7.	BLJ_{96}, N_A=41, σ_{BB} =1.30	-0.606835 (1)	16.	BLJ_{100}, N_A=42, σ_{BB} =1.25	-1.202295 (7)
8.	BLJ_{97}, N_A=33, σ_{BB} =1.20	-0.495369 (0)	17.	BLJ_{100}, N_A=42, σ_{BB} =1.30	-1.424056 (3)
9.	BLJ_{97}, N_A=39, σ_{BB} =1.25	-0.252938 (0)			

FIG. 1 (color online). Cluster BLJ_{98}/σ_{BB} =1.25 [11] shown in the nested convex hull representation. (a) Nested shells. (b) Outer shell. (c) Middle shell. (d) Inner shell. Type A atoms in maroon, type B atoms in green. Atoms are located at vertices, they are not shown explicitly.

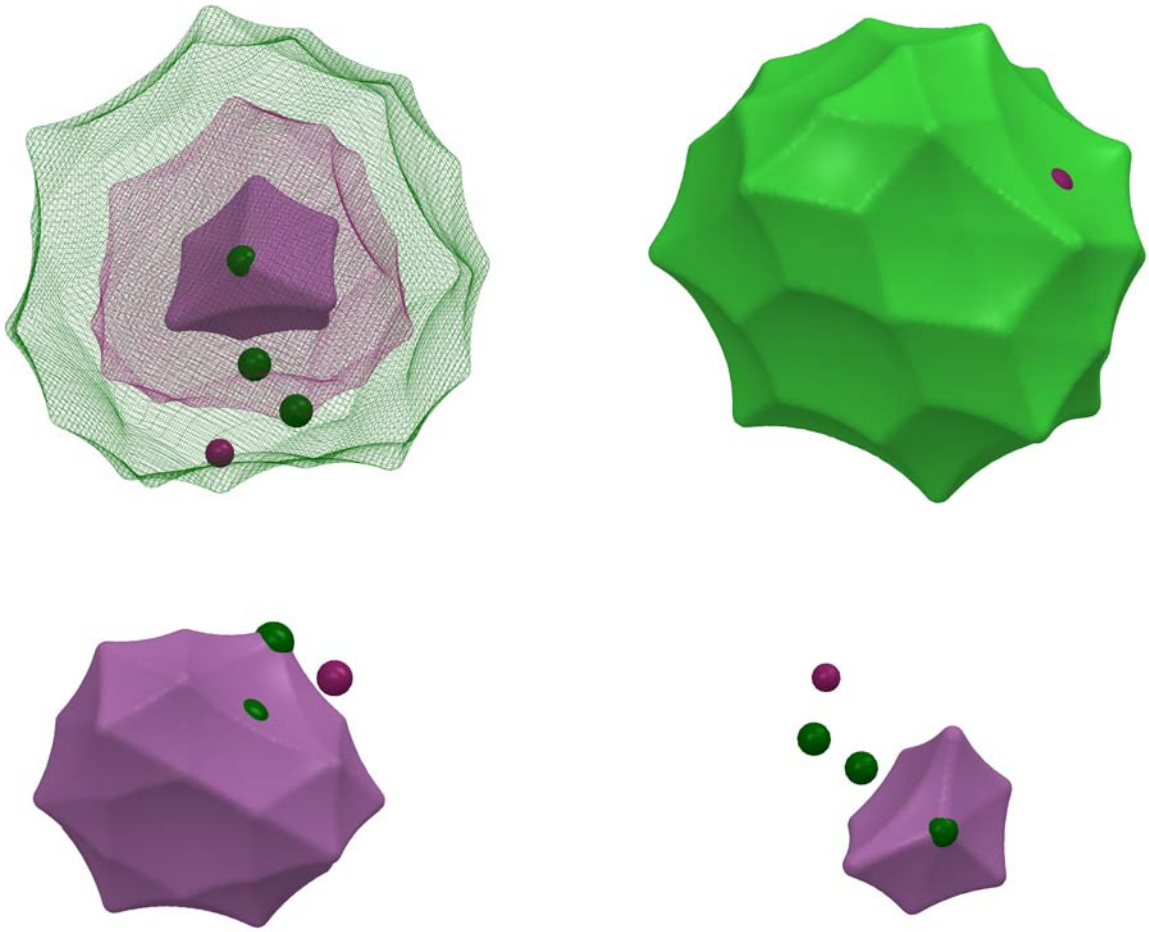
(a) (b)



(c) (d)

FIG. 2 (color online). Our new putative global minimum configuration of cluster BLJ_{98}/σ_{BB} =1.25 (cluster 11) shown in the nested convex hull representation. Atoms not positioned at lattice points of their own type are displayed explicitly (type A maroon, type B green). See text for details.

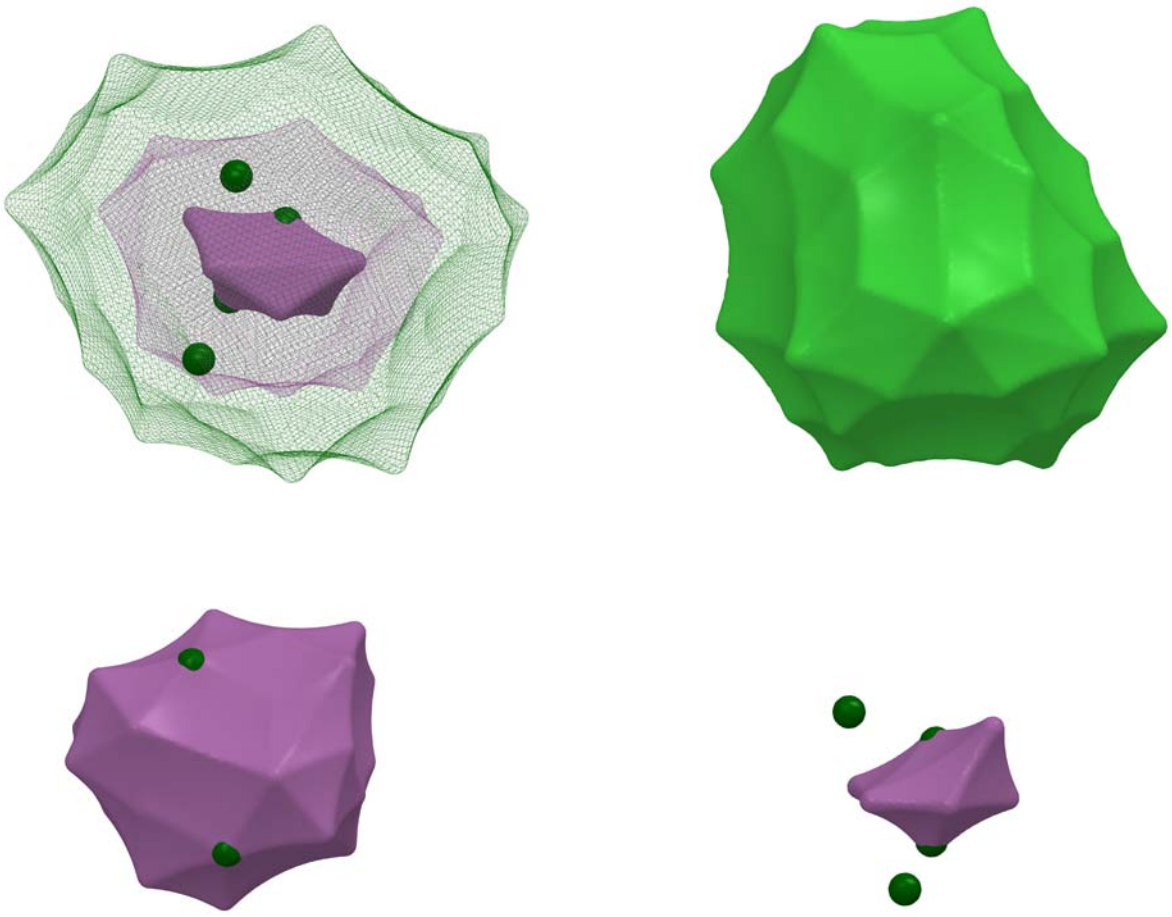
(a) (b)



(c) (d)

FIG. 3 (color online). Cluster BLJ_{95}/σ_{BB} =1.2 [11] shown in the nested convex hull representation. Type B atoms (green) lodged at type A lattice vertices (maroon) are displayed explicitly.

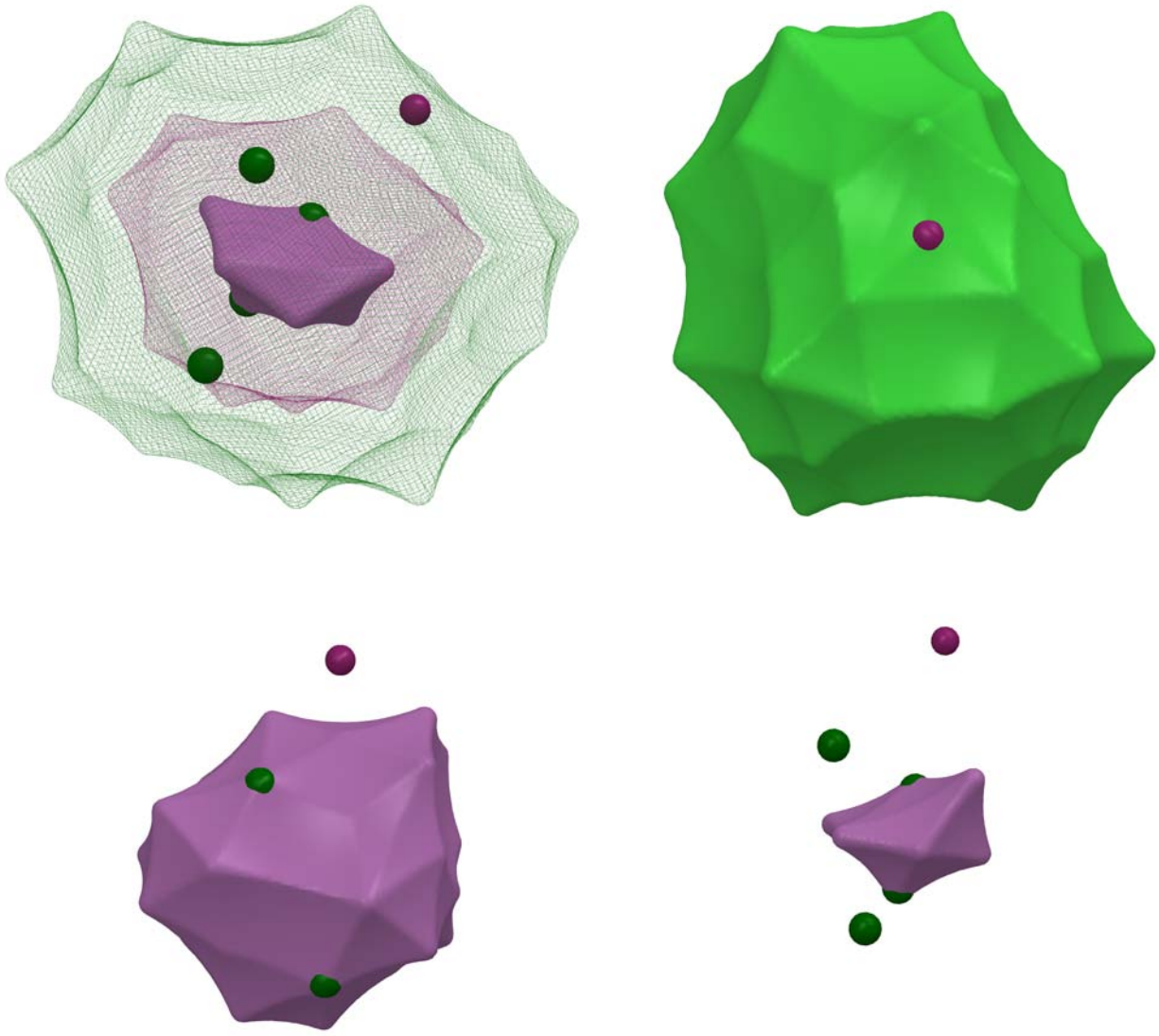
(a) (b)



(c) (d)

FIG. 4 (color online). Our new putative global minimum configuration of cluster BLJ_{95}/σ_{BB} =1.2 (cluster 4) shown in the nested convex hull representation. Atoms not positioned at lattice points of their own type are displayed explicitly (type A maroon, type B green). See text for details.

(a) (b)



(c) (d)