

## Tetrahedral global minimum for the 98-atom Lennard-Jones cluster

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(Received 11 August 1999)

An unusual atomic cluster structure corresponding to the global minimum of the 98-atom Lennard-Jones cluster has been found using a variant of the basin-hopping global optimization algorithm. The structure has tetrahedral symmetry and an energy of  $-543.665\,361\epsilon$ , which is  $0.022\,404\epsilon$  lower than the previous lowest-energy minimum. The  $LJ_{98}$  structure is of particular interest because its tetrahedral symmetry establishes it as one of only three types of exception to the general pattern of icosahedral structural motifs for optimal LJ microclusters. Similar to the other exceptions the global minimum is difficult to find because it is at the bottom of a narrow funnel that only becomes thermodynamically most stable at low temperature.

[S1063-651X(99)51412-8]

PACS number(s): 02.60.Pn, 36.40.Mr, 61.46.+w

The determination of the global minima of Lennard-Jones (LJ) clusters by numerical global optimization techniques has been intensely studied in the size range  $N=13-147$  by both chemical physicists and applied mathematicians [1,2]. The LJ potential, which is given by

$$E = 4\epsilon \sum_{i < j} \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right], \quad (1)$$

where  $\epsilon$  is the pair well depth and  $2^{1/6}\sigma$  is the equilibrium pair separation, is a simple yet reasonably accurate model of the interactions between heavy rare gas atoms. In general, there has been good agreement between physical measurements on rare gas clusters from electron diffractometry [3] and mass spectrometry [4,5] and computational global optimization results regarding magic number sizes and corresponding cluster geometries [6]. Both approaches find that Mackay icosahedra [7] are the dominant structural motif.

The LJ microcluster problem has also become a benchmark for evaluating global optimization algorithms. The number of local minima (excluding permutational isomers) on the potential energy surface (PES) is believed to grow exponentially with  $N$  [8,9] and is estimated to be of the order of  $10^{40}$  for  $N=98$ . From the size of this search space one might presume that global optimization is unfeasible. However, although one would never be able to locate the global minimum using a purely random search, global optimization methods that preferentially sample low energies can succeed for such configurational problems, because the PES is not flat, but often has a topography that directs the system down towards low energy states [10,11]. A wide variety of global optimization techniques have been applied to the LJ problem, including simulated annealing [12], genetic algorithms [13-16], smoothing and hypersurface deformation techniques [17,18], lattice methods [6,19,20], growth sequence analysis [21,22], and tunneling [23]. Unbiased methods that make no assumptions regarding cluster geometry are of the

most interest, since these have the best chance of successful generalization to more complex potentials such as those in the protein folding problem.

Most of the global minima in this size range were first found by Northby in a lattice-based search of icosahedral structures [6]. These structures consist of a core Mackay icosahedron [Fig. 1(b)] surrounded by a partially filled outer shell. More recently, there have been a number of improvements in some of these putative global minima. First, further refinements to Northby's algorithm, particularly the relaxation of the assumption that the core Mackay icosahedron is always complete, has led to a number of new global minima [19,22,24,25]. Second, consideration of particularly stable face-centered-cubic (fcc) and decahedral forms has also led to new global minima [23,26,27]. At  $N=38$  the global minimum is a fcc truncated octahedron [Fig. 1(a)] and at  $N=75-77$  and  $102-104$  the global minima are based on Marks decahedra [Fig. 1(c)]. Third, powerful unbiased global optimization algorithms, particularly the basin-hopping [28] and genetic algorithms [14-16], have recently begun to catch up with those methods that incorporate particular physical insights into the LJ problem, and are now able to find all the known lowest-energy minima.

Given this combined attack on the LJ optimization problem, it might have been imagined that all the global minima for  $N < 150$  had been found. Here, however, we report a different lower-energy structure for  $LJ_{98}$ . It has an energy of

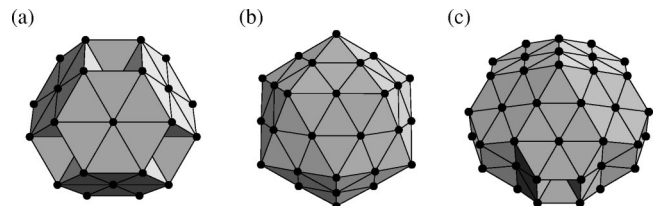


FIG. 1. Three particularly stable examples of the known morphologies for LJ clusters: (a) the 38-atom fcc truncated octahedron, (b) the 55-atom Mackay icosahedron, and (c) the 75-atom Marks decahedron.

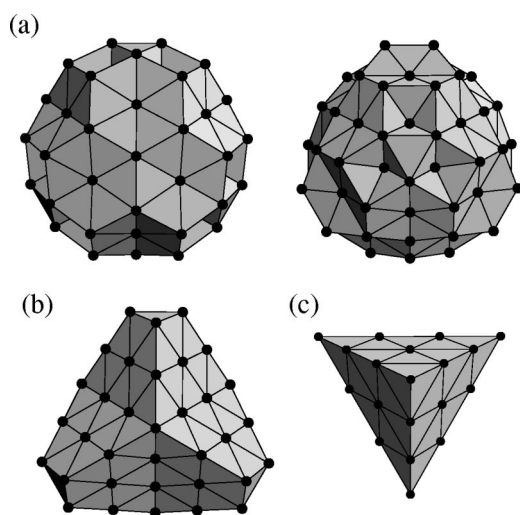


FIG. 2. (a) Front and back views of the new  $LJ_{98}$  global minimum. (b) The 56-atom stellated tetrahedron and (c) the 20-atom tetrahedron that are at the center of this structure.

$-543.665361\epsilon$  and  $T_d$  point group symmetry. This compares to an energy of  $-543.642957\epsilon$  for the previous icosahedral putative global minimum, which was found by Deaven *et al.* [14]. The  $LJ_{98}$  global minimum is organized around a central fcc tetrahedron with four atoms on each edge [Fig. 2(c)]. Four additional fcc tetrahedrons (minus apices) are erected over the faces of the central tetrahedron to form a 56-atom stellated tetrahedron [Fig. 2(b)]. An additional 42 atoms decorate the closed-packed sites on the surface of the stellated tetrahedron to complete the structure [Fig. 2(a)]. The new  $LJ_{98}$  structure is of particular interest because its tetrahedral symmetry establishes it as only the third known type of exception to the general pattern of icosahedral structural motifs for optimal LJ microclusters, and the first to be discovered by an unbiased optimization method.

Given its unusual structure one might wonder why it is so low in energy. For LJ clusters optimizing the energy is a balance between maximizing the number of nearest neighbors and minimizing the strain energy (the energetic penalty for nearest-neighbor distances deviating from the equilibrium pair value) [26]. The spherical shape and high proportion of  $\{111\}$  faces gives the structure a large number of nearest neighbors (432 compared to 437 for the lowest-energy icosahedral minimum and 428 for the lowest-energy decahedral structure), while its strain energy is intermediate between icosahedral and decahedral structures. The lower strain energy allows it to be lower in energy than the icosahedral minima, even though it has fewer nearest neighbors. The strain in the structure is focussed around the six edges of the central fcc tetrahedron. The atoms along these edges have the same local coordination as atoms along the fivefold axis of a decahedron.

It is also natural to ask how general this structure is. First, analogous structures can be formed with smaller and larger tetrahedra at their core. The previous one in this series is at  $N=34$  and the next one is at  $N=195$ . However, these structures are not energetically competitive: the former because it has too high a proportion of  $\{100\}$  faces, and the latter because it is not sufficiently spherical. Second, the structures of the other nonicosahedral LJ global minima have been experi-

mentally observed for gold [29] and nickel [30] clusters, and found to be particularly stable in theoretical calculations of transition metal clusters [31]. Therefore, we performed some optimization calculations for the Sutton-Chen family of potentials [32]. The tetrahedral structure was lowest in energy for silver, but a decahedral minimum was lower in energy for nickel and a fcc minimum for gold. This is consistent with previous results, which indicated that, of these three metals, silver clusters exhibited ordered structures with the most strain [31].

Our  $LJ_{98}$  optimum was found using a variant of the basin-hopping global optimization algorithm [28]. The key idea behind the algorithm is the mapping of the original LJ potential energy function,  $E(\mathbf{x})$ , for each point  $\mathbf{x}$  on the  $3N$ -dimensional Cartesian coordinate space onto a “transformed” energy function,  $T(\mathbf{x})$ .  $T(\mathbf{x})$  takes the value of  $E(\mathbf{x})$  at the local minimum,  $\mathbf{x}_{\min}$ , arrived at by applying a given local optimization procedure, such as the conjugate gradient algorithm, with  $\mathbf{x}$  as the starting point for the algorithm. Thus,  $T(\mathbf{x})$  is a “plateau” function that takes on the constant value  $E(\mathbf{x}_{\min})$  on the catchment basin surrounding each local minimum  $\mathbf{x}_{\min}$ .  $T(\mathbf{x})$  is a lower bound to  $E(\mathbf{x})$  and coincides with  $E(\mathbf{x})$  at all of the latter’s local minima, but all barriers are removed in the  $T(\mathbf{x})$  landscape and transitions between catchment basins can take place all along the basin boundaries.

The original basin-hopping algorithm consists of a Metropolis search of the transformed landscape,  $T(\mathbf{x})$ , using a Monte Carlo sampling procedure to move between local minima. In the variant used in the discovery of  $LJ_{98}$  [33], the Metropolis criterion of accepting uphill moves with a probability that is an exponentially decreasing function of the energy increment is abandoned in favor of only accepting downhill moves. The algorithm is restarted from a fresh random starting local minimum whenever progress stalls for a sufficiently large number of move attempts. The variant was successful in locating the  $LJ_{98}$  global minimum in six of 1000 random starts, with a mean computational time between encounters of about 30 h on a 333 MHz Sun Ultra II processor. This structure has also been subsequently found using the original basin-hopping algorithm [34] and by a method that involves a transformation of the PES that favors compact, spherical clusters [35].

Our results show that the  $LJ_{98}$  global minimum is particularly difficult to find. The origins of this difficulty are probably similar to the other nonicosahedral clusters. Analyses of the PESs of  $LJ_{38}$  and  $LJ_{75}$  using disconnectivity graphs have shown that they consist of a wide icosahedral “funnel” [36,37] and a much narrower funnel leading to the global minimum [38,39]. On relaxation down the PES the cluster is much more likely to enter the icosahedral funnel, where it is then trapped because of the large (free) energy barriers to escape from this funnel into the funnel of the global minimum.

This situation is compounded by the thermodynamics of these clusters [40,41]. The icosahedral funnel has a larger entropy because of the larger number of low-energy minima, and so the funnel of the global minimum is only lowest in free energy at low temperatures. Therefore, at temperatures where the dynamics occur at a reasonable rate there is a thermodynamic driving force to enter the icosahedral funnel.

For LJ<sub>98</sub> there are at least 186 minima that are lower in energy than the second lowest-energy minimum in the tetrahedral funnel, and so the global minimum is only lowest in free energy below  $T=0.0035\epsilon k^{-1}$  (a typical melting temperature for a LJ cluster is  $0.3\epsilon k^{-1}$ ). This transition temperature is markedly lower than for LJ<sub>38</sub> [38] or LJ<sub>75</sub> [28].

The basin-hopping transformation of the PES helps to ameliorate some of these difficulties. The transformation changes the thermodynamics so that the global minimum still has a significant occupation probability at temperatures where the cluster can escape from the icosahedral funnel. However, on relaxation down the PES the system is still

much more likely to enter the icosahedral funnel. For example, our optimization runs were 15 times more likely to terminate at the lowest-energy LJ<sub>98</sub> icosahedral minimum than at the global minimum. (Coordinate files for the new LJ<sub>98</sub> structure, as well as all other putative LJ microcluster global optima, can be found in the Cambridge Cluster Database [42].)

R.H.L. and J.P.K.D. acknowledge financial support from the National Science Foundation under Cooperative Agreement No. ACI 9619020 and from Emmanuel College, Cambridge, respectively.

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