Structural optimization of Lennard-Jones clusters by a genetic algorithm

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We use a newly-developed genetic algorithm to determine the lowest energy atomic configurations of 2 – 100 atoms in the Lennard-Jones potential. Our method, which contains no bias to specific symmetries, yields structures which are identical to or are lower in energy than all previously published structures.

The task of minimizing the energy of complicated atomic structures is notoriously difficult. Because the number of locally stable structures tends to grow exponentially in the number of atoms N, searches for the global minimum become impossible for large enough values of N. Depending upon the potential, "large enough" may actually be quite small. For example, the relatively simple Lennard-Jones clusters addressed here exhibit sufficiently many local minima to make optimization by various sophisticated techniques unreliable even for $N < 100$.

In this letter we describe the application of a new technique which extends the range in N accessible to unbiased structural optimizations.[1] The approach is based on the genetic algorithm, an optimization strategy inspired by the Darwinian evolution process.[2,3] Starting with a population of candidate structures, we relax these candidates to the nearest local minimum. Using the relaxed energies as the criteria of fitness, a fraction of the population is selected as "parents." The next generation of candidate structures is produced by "mating" these parents. The process is repeated until several generations go by with no further reduction in energy, indicating that the ground state structure has been located. Genetic algorithms have been used quite successfully for general purpose optimizations in many fields outside of the physical sciences.[3]

We consider clusters of atoms interacting with each other via the the Lennard-Jones pair potential

$$v(r) = \frac{1}{r^{12}} - \frac{2}{r^6} \tag{1}$$

where r is the distance between two atoms. The ith atom has energy $E_i = (1/2)\sum_{j\neq i} v(r_{ij})$, and the total energy for N atoms is $E = \sum_i E_i$. This system has been studied intensely[4] and is known to have an exponentially increasing number of local minima, growing roughly as $\exp(0.36N + 0.03N^2)$ near $N = 13$, at which point there are already at least 988 minima.[4] If this scaling continues, more than 10^{140} local minima exist when N approaches 100. Nevertheless, sophisticated search techniques and the increased accessibility of modern computer simulations have helped to produce a rich literature, much of whose discussion centers on candidate configurations for global energy minima. Such candidates have been published for N as large as 147, using searches concentrated around hypothetical growth patterns,[5] and larger values of N have been studied to compare trends in binding energy for simple growth models such as icosahedral versus face-centered cubic clusters.[6] The potential energy landscapes which generically appear in cluster systems have been heavily investigated,[7] and search methods based on deformations of the potential to remove local minima have been applied.[8] Finally, more sophisticated search algorithms[9–11] have yielded a few candidate configurations for up to $N = 75$ atoms.

This letter is organized as follows. In the next section, we describe some of the details of our approach.[1] We then discuss the new results we can contribute to the catalog of global energy minimum candidates for Lennard-Jones clusters containing up to 100 atoms. Finally, we discuss the interesting cases where our technique has beaten others, for as few as 38 atoms, and also explore the prospects of extending our technique to even larger values of N.

Method – As we have described previously,[1] we maintain a population consisting of p clusters, with p chosen to be small, though typically no smaller than 4. These clusters are "mated" to form new child clusters by choosing a random plane passing through the center of mass of each "parent" cluster, then cutting the parent clusters in this plane, and assembling the "child" from the two halves. Each child produced in this way is then relaxed to the nearest local minimum using a conjugate-gradient minimization.

Clusters may be chosen to be parents by a variety of schemes. In this work we found it most effective to per-

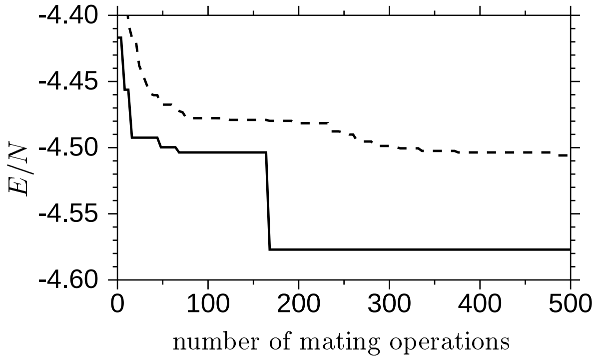

FIG. 1. Energies of the members of a population of Lennard-Jones clusters containing $N = 38$ atoms, during a typical run of the genetic algorithm, using a population containing $p = 8$ members. The lowest (highest) energy members are represented by the solid (dashed) line.

form all possible mating pairings within a population, then allow the children produced by these operations to replace members of the population which are higher in energy than the children. This selection step is performed sequentially; each child is either accepted into the population or discarded before the next child is considered. During the selection process, we also enforce a minimum energy difference δE between the members of the population, preserving the population's diversity. We do this by checking to see if a member of the population is within δE of a child that has been accepted. If so, either the child or the existing member is discarded. As a result, configurations within a range of energies δE are represented by at most one member of the population.

Finally, we occasionally admit mutated candidates into the population (regardless of their energy), using one of two mutation schemes. The first scheme scrambles the atoms by applying a series of randomly chosen atomic displacements followed by the restoration of a minimum nearest neighbor separation. The second mutation scheme uses a simple search for an adjacent local minimum in configuration space. This search is performed by taking a number of steps along a local direction which is mainly parallel to the gradient but can be rotated away from the gradient by an angle. This angle and the direction of rotation away from the gradient are varied as the search progresses using a heuristic algorithm which avoids large peaks in the energy (such as when two atoms approach each other closely). Usually, a small number of steps (typically 30) is sufficient to move the configuration into the attraction basin of a different local minimum. The details of this procedure do not affect the effectiveness of the mutation; almost any scheme that significantly alters the configuration serves equally well as a mutation. We apply mutations at a rate of a few percent of the mating operation rate, and found them to be more effective when applied to children immediately after the parenting operation than when directly applied to relaxed members of the population.

Initially, the population is filled with configurations chosen completely at random, subject only to the constraint that atoms do not lie on top of each other and that groups of atoms are close enough to each other to interact within the potential.[12]

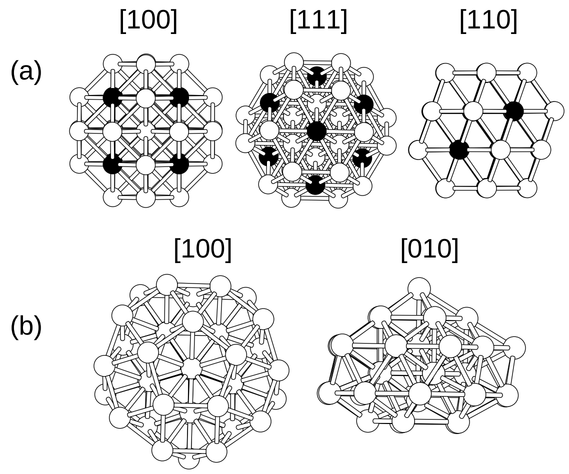

FIG. 2. (a) Optimal structure of the $N = 38$ Lennard-Jones cluster, with energy $E/N = -4.577063$. The atoms colored black are those whose energy falls in the large peak near $E = -5$ visible in figure 4. Each of the three views is characterized by the view direction $[xyz]$ in (arbitrary) cartesian coordinates. (b) Alternate $N = 38$ structure with energy $E/N = -4.559273$.

Results – We were able to reproduce all of the results found in references 5 and 9, and in addition we found some lower energy configurations. In one case, for $N = 38$, our algorithm discovered two distinct configurations with lower energies than previously reported in the literature.

Figure 1 illustrates the behavior of our algorithm for $N = 38$. The solid line in figure 1 shows the lowest energy of a cluster in the population versus the number of genetic mating operations that have been performed for a genetic algorithm with $p = 8$ members in the population, and a minimum energy difference $\delta E = 5 \times 10^{-4}$. In this case, the candidate ground state (figure 2a) is discovered after only 170 mating operations, though depending upon the particular values of p and δE, the algorithm can require up to a thousand mating operations to find this candidate. If no mutation is used, the algorithm can get trapped in a class of structure (figure 2b) with a dramatically different symmetry than the lowest energy structure. This alternate structure also has a lower energy than can be found in the literature.

Referring to figure 2a, the $N = 38$ ground-state structure is strikingly different from the other clusters in the range $N = 20$ to 50. It is an fcc tetrakaidecahedron crystallite, similar to structures predicted for much larger Lennard-Jones clusters.[13] Referring to the [111] view of the $N = 38$ cluster in figure 2a, the ABCABC stacking of an fcc lattice can easily be seen. We find it remarkable that studies have predicted a cross-over from icosahedral structures to fcc structures near $N = 1600$, while our results suggest that for particular small values of N as low

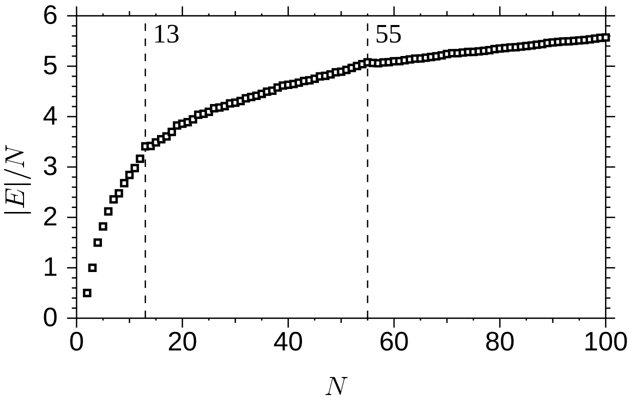

FIG. 3. Binding energy of the lowest energy configurations in the Lennard Jones potential for clusters containing $N = 2$ through $N = 100$ atoms. The vertical dashed lines indicate several special values of N at which the Mackay shells are closed (see text).

as $N = 38$ the ground state is an fcc structure.

Figure 3 shows the binding energies of the lowest energy configurations we found for clusters containing 2–100 atoms. The growth of these small clusters is known to occur in icosahedral shells,[4] filling complete shells at $N = 13, 55, \ldots$ and so forth. The binding energy versus N shows mild discontinuities near these values (refer to the vertical dashed lines in figure 3). A much better illustration of the global structural changes that are taking place in this series of clusters is shown in figure 4, where we plot the distribution of atomic energies for each value of N. That is, each cluster is associated with one trace in figure 4 which shows how many atoms in the cluster are at a particular energy.

Several trends are immediately obvious in figure 4. The lowest energy for a single atom steadily drops as the cluster size increases. These atoms are at the core of the growing cluster. The highest energy atoms, which are being added to the outermost shell of the cluster, also indicate structural changes. The "closed shell" structures at $N = 13$ and $N = 55$ (the Mackay icosahedra) show up clearly in figure 4. In addition, a dramatic change occurs at $N = 31$, midway through the growth of the second shell of atoms: the lowest atomic energy drops suddenly due to a subtle change in the cluster geometry. From $14 \leq N \leq 17$, atoms are added to the outside of a 13-atom icosahedron. At $N = 19$, a barrel-shaped double icosahedron can be formed (Note for $N = 19$ the absence of exposed outer atoms with energy $E_i > -3$ in figure 4). When $20 \leq N \leq 30$, the lowest energy structure is constructed by adding atoms to the outside of this double icosahedron. At $N = 31$, a different arrangement becomes favorable: building 13-atom icosahedral units around one central icosahedron. This arrangement, which lowers the core atom energy as shown in figure 4, can be accomplished throughout the course of completing the second shell at $N = 55$. The peak near $E_i = -6.5$ which persists past $N = 31$ is due to atoms in the overlapping regions between icosahedral units which are also 12-fold coordinated.

For $N \geq 31$, the lowest atomic energy drops slowly as more outer shell atoms are added. As the third shell is begun at $N = 56$, figure 4 clearly shows the lowest atomic energy crossing over the second shell minimum, as the core atoms interact with those in the third shell.

Table I gives our results for the lowest E/N for those clusters where we found a lower number than those previously published. The largest reduction in energy over previously published estimates is at $N = 38$. The other new results in table I arise from subtle ways of arranging atoms in the third shell, sometimes with an incomplete second shell. For example, referring to figure 5, the best $N = 98$ structure we found has a second shell minus one atom (figure 5(a)) partially covered by third-shell atoms. The main conclusion we can draw from these new results is that the genetic algorithm is capable of exploring the large space of possible configurations very efficiently.

TABLE I. Newly discovered lowest-energy configurations.

	lowest E/N	
N	present work	previously published[(a)]
38	-4.577063	-4.556166
65	-5.153407	-5.152534
69	-5.215152	-5.213424
76	-5.294323	-5.291803
88	-5.443553	-5.442443
98	-5.547377	-5.546400

[(a)] reference 5.

Discussion – We have presented a very general method for performing unbiased structural optimization within a theoretical model potential. We expect this method to be an efficient, practical means of performing such optimizations in a wide variety of chemical systems.

The present calculation can be applied to study larger clusters than we have presented in this letter. At $N = 100$, we found the ground state in roughly four hours of computer time on an IBM RS/6000 workstation. Our algorithm is implemented on several parallel supercomputer platforms, which should allow us to extend the calculations to larger N in a straightforward way. Also, by enforcing symmetry upon the solutions, we could investigate even larger clusters which are constrained to possess an n-fold rotation axis, e.g. with $n = 2$ or $n = 5$. This reduces the number of degrees of freedom that the genetic algorithm must manipulate, which should lead to increased efficiency. Of course, only special values of N can be expected to have perfect rotational symmetry.

Our technique has several strengths, most notably the fact that the search is unbiased towards particular structures. In particular, we note that the structure of the $N = 38$ cluster would always be missed by approaches which "build-up" large structures using smaller structures as a starting point.[5,9,10] This is a strong advantage of our approach: we make no assumptions about any cluster's structure, treating each new cluster as a new problem instead. For this reason, our approach is the first that has matched or improved upon the known energies of all Lennard-Jones structures for $N < 75$. (Previous

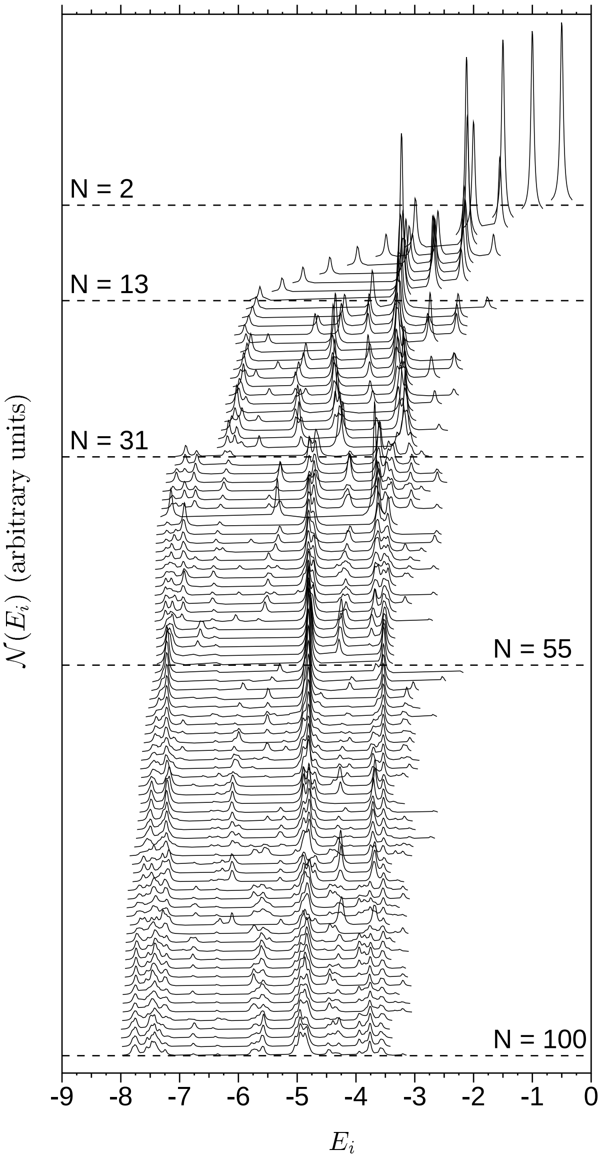

FIG. 4. Fraction of atoms with a given binding energy for the lowest energy Lennard-Jones clusters containing from $N = 2$ (uppermost line) to $N = 100$ (lowermost line) atoms. All of the traces are in the same arbitrary units. The histograms have been broadened slightly to make the plot easier to read. The horizontal dashed lines point out results for several specific values of N.

results have been obtained by a variety of methods, with no single method proving to be reliable for all structures.) While our approach is not infallible, it appears to be the most generally reliable.

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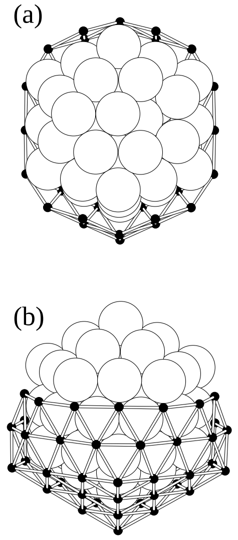

FIG. 5. Optimal structure for $N = 98$. The atoms colored black and drawn smaller form part of the third shell of atoms surrounding a roughly spherical inner core (large white atoms). In (a), the view is from the direction opposite the partially completed shell, while in (b) the view is rotated roughly 30° about a horizontal axis in the plane of the paper with respect to that in (a). Note that in (a), the atom missing from the inner core is visible.

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