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# Efficient moves for global geometry optimization methods and their application to binary systems

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We show that molecular dynamics based moves in the minima hopping method are more efficient than saddle point crossing moves. For binary systems we incorporate identity exchange moves in a way that allows one to avoid the generation of high energy configurations. Using this modified minima hopping method, we re-examine the binary Lennard-Jones benchmark system with up to 100 atoms and we find a large number of new putative global minima. © 2011 American Institute of Physics. [doi:10.1063/1.3530590]

## I. INTRODUCTION

In a global geometry optimization one has to search over many local minima of the potential energy surface<sup>1</sup> until one finds the global minimum. Moves are necessary to jump from the catchment basin of the current local minimum into another catchment basin. Various types of moves such as random moves,<sup>2</sup> molecular dynamics (MD) moves,<sup>3</sup> crossover operations,<sup>4</sup> or saddle point based moves<sup>5</sup> are used and they are discussed in various articles.<sup>6</sup> The type of move has a strong influence on the performance of the method.

The number of local minima is increasing exponentially with increasing energy. It is therefore important to search only over an energy interval above (and including) the global minimum which is not too large. Otherwise the number of configurations in this interval is so large that one will most likely miss the global minimum. This means that one should use moves that will never or only rarely lead into high energy structures. If moves with this property are not used, the majority of the configurations has to be discarded in an acceptance/rejection step which can be found in most global optimization algorithms. A large rejection ratio is however also highly inefficient. If one considers moves that lead from one minimum into a neighboring one, it has been shown that molecular dynamics based moves are very efficient.<sup>7</sup>

Since a molecular dynamics trajectory has a fixed and limited kinetic energy, it follows from energy conservation that it cannot go over barriers that are higher than this kinetic energy. Since the Bell–Evans–Polanyi principle<sup>8</sup> tells us that the minima behind low energy barriers are on average also low in energy, molecular dynamics based moves do not lead into high energy structures if their kinetic energy is chosen such that they can only overcome low energy barriers. This is highly advantageous during phases of a global optimization run where one goes down in energy within a funnel. Once the bottom of a funnel has been reached it will be necessary to jump out of this funnel if the present funnel does not contain the global minimum. In such a phase of a global optimization run, high barriers have to be overcome to escape from the funnel.

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In this paper we will first compare two classes of moves that both are able to find low energy escape paths from a current minimum, namely, molecular dynamics based moves with the moves that are saddle point based. In the second part of the paper we will discuss the moves for binary systems. We will, in particular, discuss under which circumstances moves that exchange the identity of two atoms are efficient. In the third part we will apply our resulting global optimization scheme to the benchmark set of binary Lennard-Jones (BLJ) clusters<sup>9</sup> and show that many global minimum structures had been overlooked in previous studies. The Lennard-Jones (LJ) potential poses the same kind of problems for global geometry optimization methods as other more realistic potentials<sup>10</sup> and the efficiency of an algorithm for an LJ system is therefore indicative of the success for other potentials.

## II. SADDLE POINT ESCAPE MOVES VERSUS MOLECULAR DYNAMICS ESCAPE MOVES

We will construct in the following several variants of the minima hopping (MH) method which are, however, based on the same principles, namely:

- We escape over low barriers during a phase where we go down in energy in a funnel. Such a phase will simply be called a downward phase in the following. It has to be noted however that the system will not go down in energy in every step, but it will go down predominantly.
- The method is ergodic, i.e., if a minimum is visited twice, the minima visited afterward will be different.
- Trapping at the bottom of a funnel is excluded by some feedback mechanism. Such a phase where the feedback forces the system to escape from a funnel will be called a escape phase in the following.

We will now compare the efficiency of various moves for downward phases within the minima hopping method. These variants can be generally classified into two categories, namely, molecular dynamic based moves and saddle point based moves.

The original MH method, belonging to the first category, consists of a sequence of short molecular dynamics trajectories followed by local geometry optimizations.<sup>11</sup> The molecular dynamics trajectory allows one to cross barriers to hop from one catchment basin into another and the local geometry optimization will then bring the system to the bottom of the catchment basin. As usual<sup>12</sup> we start our molecular dynamics trajectory in a soft direction, i.e., in a direction with low curvature in order to overcome a low barrier with a small number of molecular dynamics steps. This direction should however not exactly be identical to the direction of the lowest curvature, i.e., the lowest eigenvector of the Hessian matrix, because we would lose ergodicity in this way. We need enough randomness in the initial direction of the velocity vector to be able to jump into different catchment basins when we escape repeatedly from a certain minimum.

The other kind of moves are based on saddle point searches. Starting from a local minimum, the system is propagated toward a saddle point. After reaching such a transition state and barely crossing it, a local geometry optimization brings the system down again to a new minimum. We use the dimer method<sup>13</sup> with a few modifications to search the saddle points (transition states) in this modified version of the MH method. The main change concerned the method for the dimer rotation. We found that using direct inversion in iterative subspace (DIIS) (Ref. 14) is most suitable for our purpose, since it allows us to find much more distinct saddle points around a minimum. To do so, we started several saddle point searches by following all low lying modes at the minimum. Using DIIS for the rotation enables us to stay on the initially selected mode with high reliability and leads, therefore, to many distinct saddle points. We also examined whether a minimization in the tangent space<sup>15</sup> gives any benefit. It turned out that this procedure is only suitable for searches following the lowest mode and not for those searches following higher modes. For those cases, a minimization in the tangent space will in many cases lead to a “switch” to another mode, since only the lowest mode is a stable one; all other modes are stationary points, but no minima with respect to the curvature.

In the present implementation of our saddle point searches we put the focus on reliability and not on speed, since we are only interested in understanding the principle of the various types of moves. Therefore about 1000 force evaluations are required if we want to have a success rate of some 99%. Further tuning might still bring down the number of force evaluations, but it seems unlikely that it can be reduced by 1 order of magnitude, which would be necessary to compete with molecular dynamics based moves. So it is clear that saddle point based moves are only of interest in practice if the global minimum can be found much faster with respect to the number of minima that have to be visited until the global one is found.

With the exception of the moves, whose details will be explained below, the standard MH algorithm was used, i.e., new minima are accepted if they are not higher than  $E_{\text{diff}}$  in energy and the value of  $E_{\text{diff}}$  is adjusted by a feedback mechanism such that on average half of the new configurations are accepted. In addition to the moves, this feedback mechanism is an important difference to the Monte Carlo plus energy

minimization<sup>2</sup> and the similar basin hopping method.<sup>16</sup> Since we do a reset to the local minima positions, our minima hopping method is actually more akin to the Monte Carlo plus energy minimization method than to the basin hopping method. Small values of  $E_{\text{diff}}$  allow one to explore only the lower energy minima and result in higher efficiency. Since the value of  $E_{\text{diff}}$  is not set by hand, but by the feedback mechanism  $E_{\text{diff}}$  is a measure of the quality of the moves.

The second feedback mechanism—namely, that acting on  $E_{\text{kin}}$ —in the minima hopping method<sup>11</sup> is essential to prevent trapping at the bottom of a funnel which is not the global minimum. If some configurations, which are typically those at the bottom of a funnel, are visited more than once the kinetic energy is increased until the MD trajectory has enough energy to escape from this funnel. In order to prevent trapping we have left this part in all the variants of the minima hopping methods that we will now present. In our tests for the saddle point based versions, we switched back to MD based escapes whenever a minimum was visited more than once. In this way, MD moves are mainly used in escape phases, whereas in the standard minima hopping method MD moves are always used. If MD moves are predominantly used for escape phases, the average value of  $E_{\text{kin}}$  is higher than in the standard minima hopping method, where  $E_{\text{kin}}$  is low in downward phases and high in escape phases.

We use the Lennard-Jones clusters LJ<sub>55</sub> and LJ<sub>38</sub> as test systems because they behave very differently. The LJ<sub>55</sub> is a structure seeker for which it is very easy to find the global minimum. LJ<sub>38</sub> on the other hand is a two funnel system<sup>1</sup> for which it is surprisingly difficult to find its global minimum in view of its small size. During a global optimization one typically falls into the funnel which does not contain the global minimum and one has to overcome a high barrier to jump into the funnel which contains the global minimum. One hundred global optimization runs are done in all the cases to get well defined average values.

Let us now discuss the different variants of the MH method in more detail. One possibility to incorporate saddle points into the minima hopping algorithm is to replace the MD based moves of the original method by a saddle point based escape move over the lowest barrier, given we have determined the height of all barriers surrounding our current local minimum. Since such a kind of move requires the calculation of a large number of saddle points, it is of course numerically incredibly expensive. Doing a one sided search for a single saddle point requires typically already a few hundred force evaluations and exploring more or less all the saddle points around a local minimum to find out which is the lowest one is even much more expensive. At this stage we are, however, only interested in understanding the efficiency of a certain type of move and we will for the moment not care about the cost of a single move. We will measure the efficiency of the moves by counting how many local minima will be visited on average before the global minimum is found, ignoring the fact that the CPU time can be very long due to the cost of the moves. For a system with  $N$  atoms we perform saddle point searches along all  $2(3N - 6)$  modes starting from the current local minimum to find the majority of the saddle points.

TABLE I. Comparison of the performance of all four minima hopping moves for both LJ<sub>38</sub> and LJ<sub>55</sub> clusters: “Distinct accepted minima” denotes the number of distinct accepted minima visited before the global minimum was found. “Total number of moves” is the total number of moves necessary to find the global minimum. This later quantity is larger than the first one since the results of half of the moves are rejected and since some minima are visited several times. The acronyms for the different variants of the minima hopping method are described in the text.

	LJ <sub>38</sub>		LJ <sub>55</sub>	
	Total number of moves	Distinct accepted minima	Total number of moves	Distinct accepted minima
MD	1583	297	193	28
LB	1597	251	232	40
RB	1293	312	309	67
LM	1922	388	362	71

The factor 2 comes from the fact that each mode gives two degenerate directions along the positive and negative eigenvector. Out of these we choose the one exhibiting the lowest barrier. Since the saddle point searches sometimes give saddle points which are not connected to the initial minimum (meaning that a local geometry optimization starting at that saddle point would not lead back to the initial minimum), these barriers may be meaningless. However, we do not care about this fact and simply choose the saddle point with the lowest value.

Table I gives an overview over the performance of the various variants. The notation applied here classifies the methods according to their moves in a downward phase. Therefore the version we just discussed, which escapes over the lowest barrier, is denoted by LB, whereas the original version, which is always based on MD, is consequently labeled with MD.

As one sees the best two methods are those which go over the possible LBs in a downward phase and which use MD throughout, i.e., the original minima hopping method. The fact that MD gives about the same performance as LB in spite of the fact that it does not necessarily go over the lowest barrier can be explained by the fact that MD based moves can sometimes cross more than one saddle point and they can in this way faster go down in the steep funnel of a structure seeker such as LJ<sub>55</sub>.

A clear decrease in performance can be seen if the lowest barrier moves are replaced by moves of a randomly chosen barrier (RB) for LJ<sub>55</sub>. In the case of the LJ<sub>38</sub> cluster the performance also decreases when measured by the number of distinct minima but increases based on the total number of moves. This is due to the fact that moves over randomly chosen barriers allow one to escape somewhat faster from the wrong funnel and that the minima in the wrong funnel are sampled less completely in this variant.

As already mentioned all the methods that pick the lowest saddle point in the downward phase are incredibly expensive and we have just implemented them to better understand the principles of global optimization. In spite of the fact that the lowest barrier escape moves already do not give a convincing performance advantage over the original minima hopping method, we present still a second scheme which is more realistic since it does not require to find all the barriers around

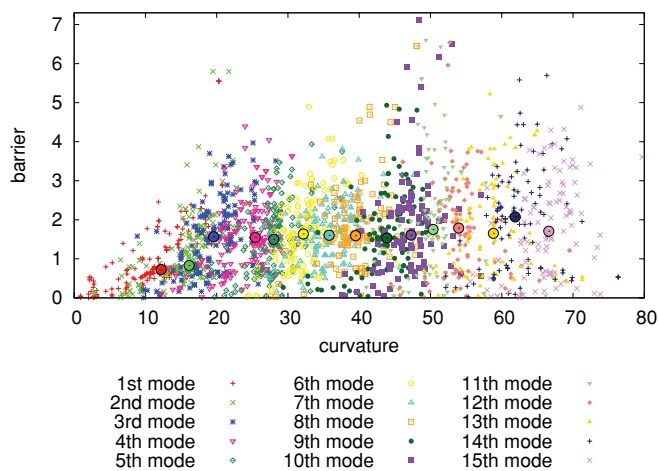


FIG. 1. A plot of the barrier heights as a function of the curvature along the direction in which the saddle point search was started. In addition, the numbers of the modes along which the search was started are distinguished by colors. The median value for each mode (median value of the curvature as well as the median value of the barrier) is plotted with a large dot. One can see that it is very unlikely to find high barriers along the softest (lowest curvature) directions. Along the stiffer (higher curvature) directions one finds increasingly higher barriers, but in addition there exist also low barriers.

a local minimum to make a single move but is nevertheless more elaborate than simply choosing a barrier at random. In this scheme we exploit the fact that there is a correlation between the curvature of the direction into which we start our saddle point search and the height of the saddle point found. This correlation is obtained if the energy along the reaction pathway can be described by a “reasonable” function. One of the simplest choice is polynomials and it has been verified by numerical experiments that this correlation is valid for several systems.<sup>17</sup> A more detailed analysis<sup>17</sup> shows that the barrier height also grows quadratically with respect to the distance between the minimum and saddle points. Since we do not impose any distance constraints on our MD trajectory, we can ignore this dependence. For the case of the LJ<sub>19</sub> cluster, the above discussed correlation is shown in Fig. 1. Exactly the same correlation is also exploited when we start our molecular dynamics trajectories in soft directions. In this scheme, which we denote by lowest mode (LM), we search for the saddle point in the softest direction if the minimum is visited for the first time. Its performance, which is listed as well in Table I, is comparable to the RB scheme. Even if we start our saddle point search in a soft direction we can frequently obtain rather high saddle points, whereas in the molecular dynamics based moves energy conservation will prevent the crossing of such high barriers. The energy of the molecular dynamics trajectory is usually much larger than needed to cross a barrier, and one would therefore not expect that there is a correlation between the energy of the trajectory crossing from one catchment basin into another one and the height of the saddle point that connects the minima of the two catchment basins. However, we found that such a correlation does indeed exist, as shown in Fig. 2. Moving always in the softest direction reduces the randomness and ergodicity of the simulation and is presumably the main reason for the fact that the performance of the LM is not better than of the RB method. A similar loss

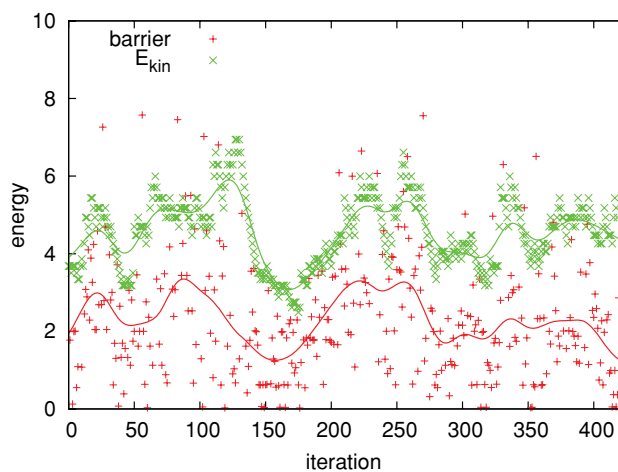


FIG. 2. The correlation between barrier heights and kinetic energy for LJ<sub>55</sub> during a MD minima hopping run. The kinetic energy is scaled down by a factor of 3 for better visualization. The straight lines are convolutions of the data with a Gaussian. There is a clear correlation between the barrier height and the kinetic energy, even if the kinetic energy is much higher than the barriers.

in performance can be observed in the MD variant if the velocities are chosen along too soft directions.

Independent of whether the lowest barrier or just some barrier is chosen for the move, it has to be stressed that all the saddle point barriers are quite low in energy compared to the barriers that have to be overcome when random displacements are used. For this reason random displacements are some 2 orders of magnitude less efficient and we have not even included them in our table.

The results in Table I also show what was to be expected, namely, that the downward phase moves are the essential ones for a structure seeker such as LJ<sub>55</sub>, whereas the speed with which one can escape from a wrong funnel is another important aspect for multifunnel systems such as LJ<sub>38</sub>. Stronger feedback mechanism for LJ<sub>38</sub> can be found which result in improved performance for LJ<sub>38</sub>, but we did not include them in our results since we wanted to treat both LJ<sub>55</sub> and LJ<sub>38</sub> with the same methods as one does not know in general in advance the characteristics of a system.

### III. MOVES FOR BINARY SYSTEMS

In the case of binary systems, one might think that the molecular dynamics based moves are inefficient since atoms of a certain type will only move by some slow diffusive motion to their right place. A process which can bring atoms potentially faster to their right place is an identity exchange where the identity of two atoms that are possibly far apart is exchanged. In a BLJ cluster the identities will be denoted by A and B. On the other hand, we know that the efficiency of the molecular dynamics based moves in minima hopping is due to the fact that high energy configurations are rarely visited which leads to small values of  $E_{\text{diff}}$ . Table II shows these values for several BLJ systems which have different size-mismatch values  $\sigma$ . The  $E_{\text{diff}}$  value is always the value which gives on average an acceptance ratio of 0.5 in the standard MD based version of MH.  $\sigma = \sigma_{BB}/\sigma_{AA}$  is the size of

TABLE II. Acceptance/rejection (acc./rej.) ratio for identity exchange moves with a fixed  $E_{\text{diff}}$  determined by a standard minima hopping run for the same system.

$\sigma$	System	$E_{\text{diff}}$	Acc./rej.
1.05	A <sub>19</sub> B <sub>26</sub>	0.44	1.50
1.15	A <sub>31</sub> B <sub>63</sub>	0.66	0.14
1.20	A <sub>33</sub> B <sub>63</sub>	0.37	0.03
1.25	A <sub>42</sub> B <sub>58</sub>	0.46	0.01

the larger type B atom in a BLJ cluster where the smaller type A atoms are chosen to have size 1. The interaction potential is then given by

$$E = 4 \sum_{i < j} \epsilon_{\alpha\beta} \left[ \left( \frac{\sigma_{\alpha\beta}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{r_{ij}} \right)^6 \right],$$

where  $\alpha$  and  $\beta$  are the types of atoms  $i$  and  $j$ .  $\sqrt[6]{2}\sigma_{\alpha\beta}$  is the equilibrium pair separation and  $\epsilon_{\alpha\beta}$  is the well depth of the pair potential from atoms  $i$  and  $j$ . We set  $\epsilon_{AA} = \epsilon_{BB} = \epsilon_{AB} = \epsilon = 1$  and  $\sigma_{AB} = (\sigma_{AA} + \sigma_{BB})/2$ . With these settings, the only free parameter besides the number of type A atoms  $N_A$  is  $\sigma$  which is chosen to be  $\sigma \in \{1, 1.05, \dots, 1.3\}$ .

Table II also shows the acceptance ratio for identity exchange moves followed by a local geometry optimization, if the  $E_{\text{diff}}$  of the MD move for the same system is used. One can see that these acceptance ratios get smaller and smaller with increasing  $\sigma$ . This means that in most cases exchanging two atom types will lead to rather high energy configurations and is hence less efficient than MD moves. In nature real atoms do not only differ by size (e.g., covalent radius) but also by their electronic properties. Exchange moves are therefore expected to be efficient only if the atoms are very similar in every respect. If the atoms are very different there is actually a strong driving force present in the MD moves to put the different types of atoms at the right positions. If the global minimum structure is, for instance, a core-shell structure, we obtain a core-shell-like structure starting from a random position already after some 100–1000 MD moves (see Fig. 3). Atomic identity exchange moves are therefore not only not necessary, but would even be counterproductive.

For systems with two similar types of atoms (i.e., small  $\sigma$  for BLJ-systems) identity exchange moves can however reduce the average search time for the global minimum. Due to the significantly lower acceptance ratio at constant  $E_{\text{diff}}$ , these exchange moves can not be treated on an equal footing as the MD moves. In particular it would be too expensive to do a local geometry optimization after each exchange move. For this reason we have incorporated exchange moves in the following way in our minima hopping algorithm: after each MD move we do a number of exchange moves which are roughly equal to the number of force evaluations required in the geometry optimization. If the energy of the unrelaxed configuration resulting from this exchange move increases by less than  $E_{\text{relax}}$  with respect to the original configuration it is relaxed and taken as the result of this combined MD/exchange move.  $E_{\text{relax}}$  is the energy that is on average gained by a local geometry optimization starting from a relaxed configuration where the identity of two atoms is exchanged. Hence the

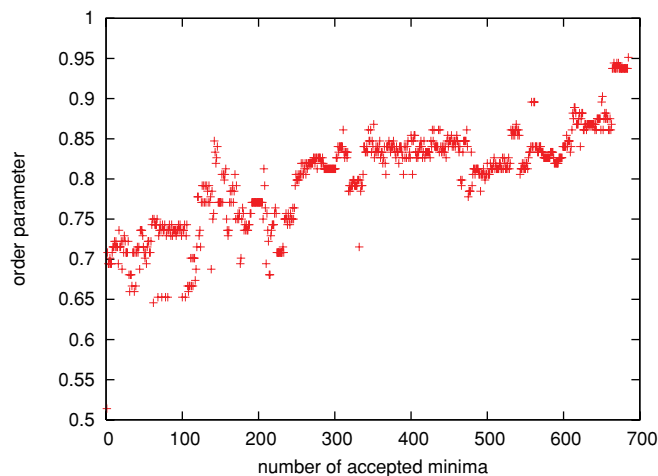


FIG. 3. Figure shows how fast a core shell structure of a BLJ cluster is formed if one starts from a random distribution of atoms of type A and B. The order parameter is defined as the fraction of atoms which are in the core. An order parameter of one corresponds thus to the global minimum structure of a particular system. The evolution toward the core-shell structure is plotted only until the order parameter reaches the value 0.95 where the core-shell structure is already clearly visible. The data is obtained for the system  $A_{39}B_{12}$  with  $\sigma = 1.1$ .

relaxed energy of the exchanged configuration will be on average lower than the energy of the original configuration. In this way the exchange moves can help in finding the global minimum even if their acceptance probability is lower than the acceptance probability of the MD moves by a factor which is roughly equal to the number of force evaluations needed by the MD moves.

#### IV. RESULTS FOR THE BINARY LJ BENCHMARK SYSTEMS

Finding the global minimum for a binary Lennard-Jones cluster is significantly more difficult than for a monoatomic Lennard-Jones cluster. In the limit where the two atoms become identical (but are still slightly different) each configuration becomes degenerate with a degeneracy of  $(N_A + N_B)!/N_A!N_B!$ , where  $N_A$  is the number of BLJ atoms of type A and  $N_B$  is the number BLJ atoms of type B. Such configurations, that can be transformed into each other by identity exchanges of the atom types, are called homotopes.<sup>18</sup>

If the type A and type B atoms have a larger size-mismatch  $\sigma$ , not all  $(N_A + N_B)!/N_A!N_B!$  homotopes are stable but nevertheless a smaller number of homotopes exist. The existence of stable homotopes increases the number of local minima of binary systems compared to the monoatomic case. Depending on the system size and composition this number can thus be significantly larger.

The difficulty of the global optimization of binary Lennard-Jones systems is also reflected in the data of the Cambridge Cluster Database.<sup>9</sup> For monoatomic Lennard-Jones systems the putative global minima up to a cluster size of 1000 atoms are listed but for BLJ systems only for system sizes  $N = 5$  up to  $N = 100$  atoms. Since the putative global minimum structures are given for six different size

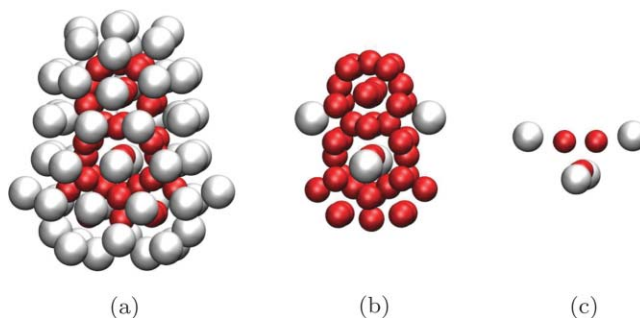


FIG. 4. 4Z14 structure of  $BLJ_{100,\sigma=1.3}$  with  $C_5$  symmetry and the putative ground state energy  $-604.796\ 307$ . (a) Shows the whole cluster. (b) Disclination network embedded into the core. (c) Disclination network.

ratios  $\sigma$ , the database contains 576 structures. A first computation of the putative global minima in this database was done by Doye and Meyer.<sup>19</sup> Cassioli *et al.*<sup>20</sup> re-examined the problem and found nearly 100 new putative global minima for the 600 structures in the database. A few new structures were also found by Pullan.<sup>21</sup> In spite of the fact that several groups have already re-examined the database we were able to find the following 17 structures which are lower in energy than the structures listed in the database (status June 2010):

- $\sigma = 1.30$ :  $BLJ_{100}$ ,  $BLJ_{99}$ ,  $BLJ_{98}$ ,  $BLJ_{97}$ ,  $BLJ_{96}$ ;
- $\sigma = 1.25$ :  $BLJ_{100}$ ,  $BLJ_{99}$ ,  $BLJ_{98}$ ,  $BLJ_{97}$ ,  $BLJ_{96}$ ;
- $\sigma = 1.20$ :  $BLJ_{100}$ ,  $BLJ_{97}$ ,  $BLJ_{96}$ ,  $BLJ_{95}$ ;
- $\sigma = 1.15$ :  $BLJ_{94}$ ,  $BLJ_{93}$ ,  $BLJ_{92}$ .

The global optimization runs for systems with a size-mismatch ratio of  $\sigma \geq 1.2$  were done with the standard MH algorithm.<sup>11</sup> The putative global minima with  $\sigma = 1.15$  have been found by using the above mentioned identity moves.

We did not systematically recalculate the whole Cambridge Cluster Database. However, a visualization of the putative global minimum structures provided by the database revealed that several structures did not fit into the “series” under the same  $\sigma$  due to too much disorder of the clusters or a still incomplete separation of core and shell. These structures were re-examined and new energetically lower structures, that frequently had also different stoichiometric compositions, were found in many cases.

#### A. New putative global minima

We now present the structures corresponding to the new putative global minima. Using the classification criteria of Doye and Meyer,<sup>22</sup> we will assign all cluster structures to their structural type families and their symmetry point groups.

A new class of structures which introduces a new region in the structural phase diagram<sup>19,22</sup> for large system sizes  $N \geq 98$  and  $\sigma \geq 1.25$  is the global minimum structure of  $BLJ_{100,\sigma=1.3}$  (see Fig. 4). The polytetrahedral structure with a disclination network can be classified as the 4Z14 structure with point group symmetry  $C_5$ . Generally, Z14-atoms are part of a single disclination line, whereas Z15 (see Fig. 5) and Z16 atoms act as nodes connecting 3 or 4 disclination lines, respectively. Disclination lines always pass edges with six tetrahedra around them, see Fig. 5.

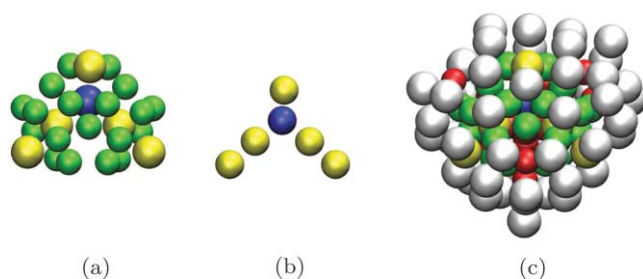


FIG. 5. Putative global minimum structure of  $\text{BLJ}_{97,\sigma=1.25}$  represented by the  $\text{A}_{39}\text{B}_{58}$  composition. (a) Three (single) disclination lines (yellow) passing through six tetrahedra around them (green), connected at the Z15-node (blue). (b) Disclination network colored. (c) The whole cluster in corresponding colors.

The four atoms with coordination number  $Z = 14$  form four pairwise disconnected (single) disclination lines ending at four  $Z = 13$  shell-atoms.<sup>23</sup> The structure of  $\text{BLJ}_{100}$ , shown in Fig. 4, is also the corresponding putative global minimum structure of  $\text{BLJ}_{99,\sigma=1.3}$ ,  $\text{BLJ}_{100,\sigma=1.25}$ ,  $\text{BLJ}_{99,\sigma=1.25}$ , and  $\text{BLJ}_{98,\sigma=1.25}$ . The core of these structures consists of 42 atoms and is completely covered by the shell atoms (pure core-shell). Depending on the cluster size there is only an absence of one or two type B shell atoms. The putative ground state energy of  $\text{BLJ}_{100,\sigma=1.3}$  is  $-604.796\,307$  in common units.

A summary of the structural types and energies corresponding to all other minima we found is given in Table III. Figure 5 shows the  $\text{A}_{39}\text{B}_{58}$  composition of  $\text{BLJ}_{97,\sigma=1.25}$  and how the disclinations are embedded into the whole cluster. It is a polytetrahedral Z15 structure with  $C_1$  symmetry and the typical Z15-disclination network. The putative global minimum energy is  $-578.201\,634$ .

Doye and Meyer<sup>22</sup> describe the structural motives of other common binary Lennard-Jones structures up to a system size  $N = 100$ .

In addition to binary LJ clusters, binary LJ solids are an important benchmark set. Basin hopping,<sup>24</sup> as well as minima

TABLE III. System size  $N$ , energies  $\epsilon$ , compositions, point groups, and structural types of the new putative global minima.

$N$	$\sigma$	$\epsilon$	Stoichiometry	Point group	Structural type
100	1.3	-604.796307	$\text{A}_{42}\text{B}_{58}$	$C_s$	4Z14
99	1.3	-597.592233	$\text{A}_{42}\text{B}_{57}$	$C_s$	4Z14
98	1.3	-590.787413	$\text{A}_{41}\text{B}_{57}$	$C_1$	Z14
97	1.3	-583.871531	$\text{A}_{41}\text{B}_{56}$	$C_1$	Z14
96	1.3	-576.517002	$\text{A}_{41}\text{B}_{55}$	$C_1$	Z14
100	1.25	-599.264624	$\text{A}_{42}\text{B}_{58}$	$C_s$	4Z14
99	1.25	-592.138846	$\text{A}_{42}\text{B}_{57}$	$C_s$	4Z14
98	1.25	-584.930661	$\text{A}_{42}\text{B}_{56}$	$C_s$	4Z14
97	1.25	-578.201634	$\text{A}_{39}\text{B}_{58}$	$C_1$	Z15
96	1.25	-571.389275	$\text{A}_{39}\text{B}_{57}$	$C_1$	Z15
100	1.2	-591.768143	$\text{A}_{35}\text{B}_{65}$	$C_1$	Z16Z15
97	1.2	-571.392434	$\text{A}_{33}\text{B}_{64}$	$C_1$	Z16Z15
96	1.2	-564.674461	$\text{A}_{33}\text{B}_{63}$	$C_1$	Z16Z15
95	1.2	-557.690639	$\text{A}_{33}\text{B}_{62}$	$C_1$	Z16Z15
94	1.15	-542.476905	$\text{A}_{31}\text{B}_{63}$	$C_1$	Z16Z15
93	1.15	-535.594853	$\text{A}_{31}\text{B}_{62}$	$C_1$	Z16Z15
92	1.15	-529.190149	$\text{A}_{28}\text{B}_{64}$	$C_1$	Z16Z15

hopping<sup>25,26</sup> adapted to periodic structures, gave some unexpected putative global minimum structures.

## V. CONCLUSIONS

According to the Bell–Evans–Polanyi principle one should escape over low barriers during downward phases of a global optimization run. We have implemented a scheme which escapes always over the lowest possible saddle point (LB) and it indeed gives very good performance even though its performance is not significantly different from the purely MD based scheme. From the point of view of computing time this scheme is however not competitive at all due to the fact that finding the lowest saddle point is extremely costly since it requires a complete exploration of the potential energy surface around the local minimum from which one wants to escape. Good performance is also obtained in a cheaper scheme where one searches for saddle points in a soft direction, which leads in most cases to low energy saddle points. Even such a single saddle point search is however considerably more costly than an MD based escape. So from the point of view of computing time the original minima hopping escapes moves, which are uniquely based on molecular dynamics, are the most efficient ones.

The value of the parameter  $E_{\text{diff}}$  in the minima hopping method is a good measure of the quality of the moves. If the moves lead on average in other low energy configurations  $E_{\text{diff}}$  will be small and one has to search only over low energy structures. One has, therefore, to search only over a number of local minima which is much smaller than in the case where one has to search in a larger energy window above the global minimum. According to this criterion identity exchange moves are in general worse than MD based moves except for very small values of  $\sigma$ . If identity exchange moves are however added as some kind of post processing step to an MD based move without the need of an additional geometry optimization for each exchange trial, the efficiency of the minima hopping method can be improved. With such an improved version of the minima hopping method we were able to find several new global minima structures for binary Lennard-Jones clusters with up to 100 atoms and size ratios of  $\sigma = 1.15$ . For large values of  $\sigma$  the ordinary minima hopping method without identity exchanges was used and turned out to be powerful enough to find new global minima structures for size ratios of  $\sigma = 1.2, 1.25, \text{ and } 1.3$ .

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