A Global Optimization Approach for Lennard–Jones Microclusters

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June 1992

Abstract

A global optimization approach is proposed for finding the global minimum energy configuration of Lennard–Jones microclusters. First, the original nonconvex total potential energy function, composed by rational polynomials, is transformed to the difference of two convex functions **(DC transformation)** via a novel procedure performed for each pair potential that constitute the total potential energy function. Then, a decomposition strategy based on the **GOP** algorithm [1, 2, 3, 4] is designed to provide tight bounds on the global minimum through the solutions of a sequence of relaxed dual subproblems. A number of theoretical results are included which expedite the computational effort by exploiting the special mathematical structure of the problem. The proposed approach attains ϵ–convergence to the global minimum in a finite number of iterations. Based on this procedure global optimum solutions are generated for small microclusters $n \leq 7$. For larger clusters $8 \leq N \leq 24$ tight lower and upper bounds on the global solution are provided serving as excellent initial points for local optimization approaches. Finally, improved lower bounds on the minimum interparticle distance at the global minimum are provided.

1 Introduction

Microclusters are [5] aggregates of atoms, ions, or molecules, sufficiently small that a significant proportion of these units is present on their surfaces. Typically, they consist of two to several hundred atoms. In microclusters, we are faced with systems that are neither single entities nor continua composed by a large number of units, but lie somewhere in between, providing the link between single atoms or molecules and bulk matter. The importance of microclusters ranges from the area of catalysis to astrophysics and crosses the boundaries of subjects such as nucleation, crystal growth and surface physics. The remarkable increase of interest in microcluster physics in the last few years has been catalyzed by the emergence of several fields of direct application in the study of cluster properties.

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The study of the topography of the potential energy function of a microcluster in the internal configurational space was and still remains a central problem in this area of research [5, 6]. Even under simplifying assumptions about the interaction energy, the minimization of the total potential energy is very difficult to solve because it corresponds to a non–convex optimization problem involving numerous local minima. It has been reported [5] that the number of local minima of an n–atom microcluster grows as ($exp[n^2]$). In fact, it has been shown [7], that the complexity of determining the global minimum energy of a cluster of particles interacting via two-body forces belongs to the class NP. In other words, there is no known algorithm that can solve this problem in non-exponential time [8]. A geometrical, possibly topological proof that a local minimum is both unique and global is not likely to be found because there still exist unsolved problems in the theory of sphere packings where difficulties are undoubtably less acute [9, 10, 11, 12], than those in the minimization problem at hand.

Faced with these difficulties, current methods use physical intuition, approximation procedures, mimicking of physical phenomena, random searches, lattice optimization/relaxation, or local optimization approaches. Hoare in a series of papers [13, 14, 15, 16, 6] proposed a method of finding minima of the total potential function of an $5 \leq N \leq 66$ particle LJ cluster based on a *growth scheme* involving the repetitive placement of an extra atom at all packing vertices of an initial compact cluster. The resulting structures are then relaxed and the obtained local minima are recorded. However, solutions of low–symmetry are not likely to be found with this method [17]. Another method [18] is based on the simple idea of smoothly deforming the potential energy hypersurface [19], by using the diffusion equation, so that local minima disappear gradually, while the global one grows at their expense. One then eventually ends up with a single minimum which is conjectured to correspond to the global minimum. However, it has been observed that when the global minimum corresponds to a narrow potential well of large depth it might disappear faster than a wider, originally shallower, potential well.

Molecular dynamics (MD), Monte Carlo (MC) simulations, and simulated annealing (SA) correspond to the most widespread methods in the study of clusters. Simulation calculations using the molecular dynamics technique were carried out [20, 21, 22, 23, 24] in an attempt to investigate the energetics and the structural stability of microclusters. Monte Carlo techniques based on the Metropolis procedure [25], were employed [26, 27, 28] for studying the structure size and configuration, thermodynamic properties, and melting behavior of Lennard–Jones microclusters. The simulated annealing method, which can be viewed as a method for stochastically tracing the annealing process by Monte Carlo simulation, has been widely used either alone [17, 29, 30, 31, 32, 33] or in conjuction with some other method(s) [34, 35, 36] for solving the potential energy minimization problem of various microclusters of atoms involving different body interaction terms. Furthermore, a deterministic method [37, 38] for annealing the potential energy function by tracing the evolution of a multiple–Gaussian–packet approximation and using notions of renormalization group theory has been applied to microcluster conformation problems.

It appears that lattice optimization techniques are the most efficient in generating structures involving the lowest known potential energy. It has been proposed [39] that the most energetically favored microclusters in the range $20 \leq N \leq 50$ are the ones involving interpenetrating icosahedra (polyicosahedra) or **(PIC)**. For $N \leq 55$ a double icosahedral **(DIC)** growth scheme was introduced [40] and for $55 \leq N \leq 147$ [41] a third layer icosahedral structure using two different surface arrangements was presented. Using these notions [42] optimal configurations for LJ microclusters were derived in the range $13 \leq N \leq 147$ based on a lattice optimization/relaxation algorithm. First, a heuristic procedure is employed for finding a set of lattice local minimizers assuming icosahedral **IC** or face–centered **FC** arrangements. Then, the currently *best* lattice minimizers are relaxed by using a local optimization algorithm. Later, this method was improved [43] by reducing the time complexity and by relaxing *every* lattice local minimizer yielding a number of better optimal configurations. A parallel implementation [44] allowed results on minimum energies for clusters of up to $N = 1,000$ atoms and by employing a parallel version of a two–level simulated annealing algorithm, solutions for cluster sizes as large as $N = 100,000$ have been reported [45].

2 Problem Definition

The problem which is to be addressed in this work can be simply stated as follows:

> *Given N interacting particles, find their configuration(s) in the three-dimensional Eucledian space involving the global minimum potential energy.*

The main assumptions in this work are the following:

1. Many–body interactions are not taken into account.
2. Quantum effects are not taken into consideration.
3. All particles are considered to be spherical and of the same size.
4. The scaled Lennard–Jones pair potential is employed: $\left(\frac{1}{r^{12}} - \frac{2}{r^6}\right)$.

Assumption (1) restricts the applicability of the global optimization approach as developed to systems of particles interacting with central two–body forces. Conceptually, however, the proposed approach can be extended to systems of particles interacting with many–body forces if an analytic expresssion for the total potential energy is given. Assumption (2) implies that the total potential energy is a continuously varying quantity, in other words it is not quantized. Any formulation of the problem that takes into account quantum effects must involve a number of discrete variables which further increase the already high complexity of the problem. Thus, quantum aspects are not the focus of current work, instead they are left as a future target. Assumption (3) implies that all particles are identical and are of the same size. This assumption has been introduced for the sake of simplicity and can easily be relaxed. Assumption (4) is made initially for computational convenience, and is by no means restrictive since the developed framework is general enough to conceptually incorporate different expressions for the total potential energy.

In this work the scaled Lennard–Jones potential is chosen due to its simplicity and wide acceptance in the study of microclusters. With this scaling we define a universal Lennard–Jones potential that is applicable to different atoms such as He, Ar, Kr, etc., because of the corresponding states property that we have implicitly imposed. Given N particles whose interactions are described with Lennard–Jones pair potentials, the problem of finding the structure with the absolute minimum energy can be formulated in the (x_i, y_i, z_i) coordinate space as follows:

$$
\begin{aligned}
\min V &= \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} v_{ij} \\
&= \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \\
&\quad \left\{ \frac{1}{[(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^6} \right. \\
&- \left. \frac{2}{[(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^3} \right\} \qquad (1)
\end{aligned}
$$

Note that by selecting a cartesian coordinate system where the first particle is fixed at the intersection of all three axes, the second one lies on the x–axis, and the the third one stays on the xy–plane, we have $x_1 = y_1 = z_1 = y_2 = z_2 = z_3 = 0$. In this way, we eliminate all translational and rotational degrees of freedom for the microcluster.

The main difficulty in solving this problem arises from the fact that the objective is a non–convex function of many variables which has been reported [5] to involve numerous local minima. In the next section a procedure is introduced for transforming the initial non–convex objective function to a difference of two convex functions (**DC** transformation). Then, by exploiting the acquired **DC** structure of the problem a global optimization algorithm is proposed.

3 Transformation to a DC programming problem

The main difficulty in solving the minimization problem as it has been presented in the previous section arises from non–convexities in the objective function. In fact, even the expression for a single pair potential interaction v_{ij} is a non–convex function.

Let us pose the problem in the (x,y,z) coordinate space and consider a single pair potential interaction $v_{1,2}$. Note that $v_{1,2}$ is a function of six variables $x_1, y_1, z_1, x_2, y_2, z_2$.

$$\begin{aligned} v_{1,2} &= \left\{ \frac{1}{[(x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2]^6} \right. \\ &- \left. \frac{2}{[(x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2]^3} \right\} \end{aligned} \tag{2}$$

The eigenvalues of the Hessian matrix of $v_{1,2}$, which can be calculated by using symbolic computation [46], are:

$$\lambda_1 = \lambda_2 = \lambda_3 = 0 \tag{3}$$

$$\lambda_4 = \lambda_5 = 24 \left(\frac{1}{r_{1,2}^8} - \frac{1}{r_{1,2}^{14}} \right) \tag{4}$$

$$\lambda_6 = 24 \left(\frac{13}{r_{1,2}^{14}} - \frac{7}{r_{1,2}^8} \right) \tag{5}$$

where $r_{1,2} = [(x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2]^{\frac{1}{2}}$ is the eucledian distance between particles (1) and (2). Note that λ_4 and λ_5 become zero at $r_{1,2} = 1$, are positive for $r_{1,2} > 1$, and are negative for $r_{1,2} < 1$. Also, λ_6 is zero at $r_{1,2} = (13/7)^{1/6} \approx 1.108683$, positive for $r_{1,2} < 1.108683$, and negative for $r_{1,2} > 1.108683$. *Therefore, only when $r_{1,2} \in (1, 1.108683)$, all eigenvalues are non–negative which implies that $v_{1,2}$ is convex.* The convexity of $v_{1,2}$, however, can be maintained by adding a "strongly" convex term to $v_{1,2}$. This term may have the form $\alpha(x_1^2+y_1^2+z_1^2+x_2^2+y_2^2+z_2^2)$, where α is an arbitrarily large positive number. Note that the effect of this extra term in the Hessian matrix is to add the term 2α to all the diagonal elements of the matrix which, given a sufficiently large α, forces all the eigenvalues to become non-negative by overpowering the convexity characteristics of $v_{1,2}$. Let F1 be the summation of $v_{1,2}$ and the extra term $\alpha(x_1^2+y_1^2+z_1^2+x_2^2+y_2^2+z_2^2)$.

$$
\begin{aligned}
F1 &= \frac{1}{[(x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2]^6} \\
&- \frac{2}{[(x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2]^3} \\
&+ \alpha(x_1^2+y_1^2+z_1^2+x_2^2+y_2^2+z_2^2) \qquad (6)
\end{aligned}
$$

It can easily be derived that the eigenvalues of the Hessian matrix corresponding to F1 are:

$$\lambda_1 = \lambda_2 = \lambda_3 = 2\alpha \qquad (7)$$

$$\lambda_4 = \lambda_5 = 24\left(\frac{1}{r_{1,2}^8} - \frac{1}{r_{1,2}^{14}}\right) + 2\alpha \qquad (8)$$

$$\lambda_6 = 24\left(\frac{13}{r_{1,2}^{14}} - \frac{7}{r_{1,2}^8}\right) + 2\alpha \qquad (9)$$

Since we want all the eigenvalues to be non–negative, we have the following inequality constraints for α.

$$
\begin{aligned}
\alpha &\geq 0 && (10) \\
\alpha &\geq 12\left(\frac{1}{r_{1,2}^{14}} - \frac{1}{r_{1,2}^8}\right) && (11) \\
\alpha &\geq 12\left(\frac{7}{r_{1,2}^8} - \frac{13}{r_{1,2}^{14}}\right) && (12)
\end{aligned}
$$

The minimum value of α that will maintain all eigenvalues of F1 non–negative for *all values of* $r_{1,2}$ can then be derived as the solution of the following optimization problem over $r_{1,2}$:

$$
\alpha = \max_{r_{1,2}} \begin{cases} 12\left(\frac{1}{r_{1,2}^{14}} - \frac{1}{r_{1,2}^8}\right) & \text{if } r_{min} \leq r_{1,2} \leq 1 \\ 0 & \text{if } 1 \leq r_{1,2} \leq 1.108683 \\ 12\left(\frac{7}{r_{1,2}^8} - \frac{13}{r_{1,2}^{14}}\right) & \text{if } r_{1,2} \geq 1.108683 \end{cases}
$$

where r_{min} is a lower bound on $r_{1,2}$. Note that at the global minimum all interparticle distances are never significantly less than one, because otherwise the corresponding pair potential resumes a large positive value which cannot occur at the global minimum. In Appendix A rigorous lower bounds on the minimum interparticle distances are given for different cluster sizes. A sufficient value of r_{min} for all practical purposes is about 0.8–0.99. If we define F2 as

$$F2 = \alpha(x_1^2 + y_1^2 + z_1^2 + x_2^2 + y_2^2 + z_2^2) \tag{13}$$

then the initial non–convex expression for the pair potential has been transformed to the difference of two convex functions, more specifically $v_{1,2} = F1 - F2$. By applying the same analysis to every pair potential interaction the total potential energy expression can be then written as the difference of two convex functions (**DC** structure). It should be noted that this analysis is by no means restricted to the specifics of the problem at hand. It can be applied to any non–convex objective function as long as the eigenvalues do not diverge to $-\infty$ and analytical expressions for them can be derived.

The transformation of every pair potential term to the difference of two convex functions results in values of α's which are much larger than the ones required to maintain the entire expression for the total potential energy a difference of only two convex functions. In fact, even at the global minimum not all pair potential expressions are convex. It would have been ideal if the above procedure could have been applied to the entire total potential energy function. Unfortunately, this cannot be performed since it is a complicated function of $3N-6$ variables, and hence no closed form expression for the eigenvalues of the Hessian matrix can be obtained. In Appendix B a procedure for assigning an α to each variable rather than to each pair potential is briefly discussed. This approach involves the following extra term:

$$\sum_{i=1}^{N}(a_{xi}x_i^2 + a_{yi}y_i^2 + a_{zi}z_i^2) \tag{14}$$

The initial non–convex objective function can be rewritten as the difference of two convex functions by assigning appropriate values to a_{xi}, a_{yi}, a_{zi}. It should be noted that both ways of transforming the initial objective function to a difference of two convex functions are equivalent since by combining/expanding terms, one collapses to the other. Only the values of the α parameters are different. In the next section a global optimization procedure is introduced which employs the initial transformation without loss of generality.

4 Problem Formulation

The problem of finding the global minimum energy of N particles interacting with central Lennard–Jones forces can be formulated as the following non–linear optimization problem **NLP**.

$$
\begin{aligned}
\min V &= \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \\
&\quad \left\{ \frac{1}{[(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^6} \right. \\
&- \left. \frac{2}{[(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^3} \right\} \\
\text{st} &\quad x_i^L \le x_i \le x_i^U, \qquad i = 2, \ldots, N \\
&\quad y_i^L \le y_i \le y_i^U, \qquad i = 3, \ldots, N \\
&\quad z_i^L \le z_i \le z_i^U, \qquad i = 4, \ldots, N \\
&\quad x_1 = y_1 = z_1 = y_2 = z_2 = z_3 = 0
\end{aligned}
\tag{\textbf{P1}}
$$

where $x_i^L, y_i^L, z_i^L, x_i^U, y_i^U, z_i^U$ define the box constraints for the x_i, y_i, z_i variables. In formulation **(P1)** the objective function is non–convex so no guarantee for convergence to the global minimum can be made. In view of the transformation presented in the previous section **(P1)** can be reformulated as the following **(DC)** programming problem.

$$
\begin{aligned}
\min V &= \left\{ \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \right. \\
&\quad \frac{1}{[(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^6} \\
&- \frac{2}{[(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^3} \\
&+ \left. \alpha_{ij}(x_i^2 + y_i^2 + z_i^2 + x_j^2 + y_j^2 + z_j^2) \right\} \\
&- \left\{ \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \alpha_{ij}(x_i^2 + y_i^2 + z_i^2 + x_j^2 + y_j^2 + z_j^2) \right\} \\
\text{st} &\quad x_i^L \le x_i \le x_i^U, \qquad i = 2, \ldots, N \\
&\quad y_i^L \le y_i \le y_i^U, \qquad i = 3, \ldots, N \\
&\quad z_i^L \le z_i \le z_i^U, \qquad i = 4, \ldots, N \\
&\quad x_1 = y_1 = z_1 = y_2 = z_2 = z_3 = 0
\end{aligned}
\tag{\textbf{P2}}
$$

$$\text{where} \quad \alpha_{ij} = \max_{r_{ij}} \begin{cases} 12\left(\frac{1}{r_{ij}^{14}} - \frac{1}{r_{ij}^{8}}\right) & \text{if } r_{min} \leq r_{ij} \leq 1 \\ 0 & \text{if } 1 \leq r_{ij} \leq 1.108683 \\ 12\left(\frac{7}{r_{ij}^{8}} - \frac{13}{r_{ij}^{14}}\right) & \text{if } r_{ij} \geq 1.108683 \end{cases}$$

$$\text{and} \quad r_{ij} = \left[(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2\right]^{\frac{1}{2}} \tag{15}$$

In this work an approach for finding the global minimum based on the global optimization algorithm **GOP** developed by Floudas and Visweswaran [1, 2, 3, 4] is presented. The **GOP** algorithm can be applied to optimization problems that have or can be transformed to the following form, and it guarantees ϵ–convergence to the global minimum in a finite number of steps:

$$\begin{aligned} & \min f(x,y) \\ \text{st} \quad & g(x,y) \leq 0 \\ & h(x,y) = 0 \\ & x \in \mathbf{X},\ y \in \mathbf{Y} \end{aligned}$$

(P3)

Here $\mathbf{X}$,$\mathbf{Y}$ are non–empty, compact, convex sets and $f(x,y), g(x,y)$ and $h(x,y)$ are continuous, piecewise differentiable, and analytical functions over $\mathbf{X} \times \mathbf{Y}$. The initial variable set is partitioned to the sets $\mathbf{X}$ and $\mathbf{Y}$ in such a way that the following conditions are satisfied.

- $f(x,y)$ and $g(x,y)$ are convex in x for every fixed y, and convex in y for every fixed x.
- $h(x,y)$ is linear in x for every fixed y, and linear in y for every fixed x.

If these conditions cannot be satisfied with only partitioning of variables, transformation of variables can be employed. The **GOP** algorithm has been applied to optimization problems involving bilinear, quadratic, polynomial, or rational polynomial terms in the objective function and/or constraints [1, 2, 3, 4].

In view of the **GOP** requirements for convergence to the global minimum the following transformation of variables is performed on formulation **(P2)**. The coordinate set of variables x_i, y_i, z_i **(x–type)** is "mirrored" to X_i, Y_i, Z_i **(y–type)** so $x_i = X_i,\ y_i = Y_i,\ z_i = Z_i,\ \forall\, i = 1, \ldots, N$. Then, for each pair–potential we add the term $\alpha(X_i^2 + Y_i^2 + Z_i^2 + X_j^2 + Y_j^2 + Z_j^2)$ to the total potential energy function. The purpose of these added terms is to "convexify" each pair potential by transfering the non–convexities to the terms that we subtract from each pair–potential contribution. These terms have the following form; $\alpha_{ij}(x_iX_i + y_iY_i + z_iZ_i + x_jX_j + y_jY_j + z_jZ_j)$. Note that they are linear in x_i, y_i, z_i for fixed X_i, Y_i, Z_i and vice–versa. The values of α_{ij}'s are selected so that they are the minimum ones that guarantee convexification of each pair–potential term with the addition of the extra terms. Based on the above **(P2)** can be reformulated as follows:

$$
\begin{aligned}
\min V \quad &= \quad \Bigg\{ \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \\
& \quad \frac{1}{[(X_i - X_j)^2 + (Y_i - Y_j)^2 + (Z_i - Z_j)^2]^6} \\
&- \quad \frac{2}{[(X_i - X_j)^2 + (Y_i - Y_j)^2 + (Z_i - Z_j)^2]^3} \\
&+ \quad \alpha_{ij}(X_i^2 + Y_i^2 + Z_i^2 + X_j^2 + Y_j^2 + Z_j^2) \Bigg\} \\
&- \quad \left\{ \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \alpha_{ij}(x_iX_i + y_iY_i + z_iZ_i + x_jX_j + y_jY_j + z_jZ_j) \right\} \\
\text{st} \quad & \quad x_i = X_i, \qquad i = 2, \ldots, N \\
& \quad y_i = Y_i, \qquad i = 3, \ldots, N \\
& \quad z_i = Z_i, \qquad i = 4, \ldots, N \\
& \quad x_i^L \le x_i \le x_i^U, \qquad i = 2, \ldots, N \\
& \quad y_i^L \le y_i \le y_i^U, \qquad i = 3, \ldots, N \\
& \quad z_i^L \le z_i \le z_i^U, \qquad i = 4, \ldots, N \\
& \quad x_1 = y_1 = z_1 = y_2 = z_2 = z_3 = 0
\end{aligned}
\qquad \textbf{(P4)}
$$

Note that if we fix X_i, Y_i, Z_i and let x_i, y_i, z_i vary, formulation **(P4)** corresponds to a linear programming problem. If now we fix x_i, y_i, z_i and let X_i, Y_i, Z_i vary **(P4)** becomes a convex **NLP** programming problem. Thus, all **GOP** requirements are satisfied. Let now consider a more restrictive version of **(P4)** where all y–type variables are fixed, namely $X_i = X_i^K, Y_i = Y_i^K, Z_i = Z_i^K$.

$$
\min V \quad = \quad \Bigg\{ \sum_{i=1}^{N-1} \sum_{j=i+1}^{N}
$$

$$
\begin{aligned}
& \frac{1}{[(X_i^K - X_j^K)^2 + (Y_i^K - Y_j^K)^2 + (Z_i^K - Z_j^K)^2]^6} \\
- \quad & \frac{2}{[(X_i^K - X_j^K)^2 + (Y_i^K - Y_j^K)^2 + (Z_i^K - Z_j^K)^2]^3} \\
+ \quad & \alpha_{ij}[(X_i^K)^2 + (Y_i^K)^2 + (Z_i^K)^2 + (X_j^K)^2 + (Y_j^K)^2 + (Z_j^K)^2]\Big\} \\
- \quad & \left\{ \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \alpha_{ij}(x_i X_i^K + y_i Y_i^K + z_i Z_i^K + x_j X_j^K + y_j Y_j^K + z_j Z_j^K) \right\}
\end{aligned} \qquad (\mathbf{P5})
$$

$$
\begin{aligned}
\text{st} \quad & x_i = X_i^K, \qquad i = 2, \ldots, N \\
& y_i = Y_i^K, \qquad i = 3, \ldots, N \\
& z_i = Z_i^K, \qquad i = 4, \ldots, N \\
& x_i^L \leq x_i \leq x_i^U, \qquad i = 2, \ldots, N \\
& y_i^L \leq y_i \leq y_i^U, \qquad i = 3, \ldots, N \\
& z_i^L \leq z_i \leq z_i^U, \qquad i = 4, \ldots, N \\
& x_1 = y_1 = z_1 = y_2 = z_2 = z_3 = 0
\end{aligned}
$$

Problem **(P5)** is called the *primal problem* and its solution provides an upper bound to the solution of **(P4)** since it corresponds to a more restricted form of **(P4)**. It is clear that **(P5)** is always feasible and its solution corresponds to a single function evaluation. By applying the **KKT** conditions [47] we obtain for the Lagrange multipliers $\lambda_{xi}, \lambda_{yi}, \lambda_{zi}$ associated with the equality constraints in **(P4)**:

$$
\lambda_{xi} = (\sum_{j=2}^{N} \alpha_{ij}) X_i^K, \qquad i = 2, \ldots, N \tag{16}
$$

$$
\lambda_{yi} = (\sum_{j=3}^{N} \alpha_{ij}) Y_i^K, \qquad i = 3, \ldots, N \tag{17}
$$

$$
\lambda_{zi} = (\sum_{j=4}^{N} \alpha_{ij}) Z_i^K, \qquad i = 4, \ldots, N \tag{18}
$$

By applying the strong duality theorem [48], and substituting the values for $\lambda_{xi}, \lambda_{yi}, \lambda_{zi}$ we obtain the relaxed dual **(RD)** formulation **(P6)**. The solution of this problem provides a lower bound to the solution of **(P2)** since it corresponds to its relaxation.

$$
\min_{X_i, Y_i, Z_i, \mu_B} \mu_B
$$

$$
\begin{aligned}
\text{subject to} \quad \mu_B \quad & \geq \quad L(x_i, y_i, z_i, X_i, Y_i, Z_i) = \min_{x_i, y_i, z_i} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \\
& \quad \frac{1}{[(X_i - X_j)^2 + (Y_i - Y_j)^2 + (Z_i - Z_j)^2]^6} \\
& - \quad \frac{2}{[(X_i - X_j)^2 + (Y_i - Y_j)^2 + (Z_i - Z_j)^2]^3} \\
& + \quad \sum_{i=2}^{N} (\sum_{j=1}^{N} \alpha_{ij})(X_i^K - X_i)(x_i - X_i) \\
& + \quad \sum_{i=3}^{N} (\sum_{j=1}^{N} \alpha_{ij})(Y_i^K - Y_i)(y_i - Y_i) \\
& + \quad \sum_{i=4}^{N} (\sum_{j=1}^{N} \alpha_{ij})(Z_i^K - Z_i)(z_i - Z_i) \\
& \quad x_i^L \leq x_i \leq x_i^U, \qquad i = 2, \ldots, N \\
& \quad y_i^L \leq y_i \leq y_i^U, \qquad i = 3, \ldots, N \\
& \quad z_i^L \leq z_i \leq z_i^U, \qquad i = 4, \ldots, N \\
& \quad x_1 = y_1 = z_1 = y_2 = z_2 = z_3 = 0 \\
& \quad x_i^L \leq X_i \leq x_i^U, \qquad i = 2, \ldots, N \\
& \quad y_i^L \leq Y_i \leq y_i^U, \qquad i = 3, \ldots, N \\
& \quad z_i^L \leq Z_i \leq z_i^U, \qquad i = 4, \ldots, N \\
& \quad X_1 = Y_1 = Z_1 = Y_2 = Z_2 = Z_3 = 0
\end{aligned}
\qquad (\mathbf{P6})
$$

Problem **(P6)** is linear in x_i, y_i, z_i so at the minimum point, x_i, y_i, z_i will be at an upper or lower bound depending on whether their coefficient is negative or positive respectively. These variables x_i, y_i, z_i are called *connected variables* and the gradients of the Lagrange function in terms of the connected variables are called *qualifying constraints* which in problem **(P6)** have the following form:

$$X_i^K - X_i \tag{19}$$

$$Y_i^K - Y_i \tag{20}$$

$$Z_i^K - Z_i \tag{21}$$

This suggests that instead of minimizing explicitly in terms of the connected variables

x_i, y_i, z_i, it is sufficient to solve **(P6)** once for each combination of their bounds and select the infinum over the calculated minima in all iterations. We have shown that the solution of **(P5)** provides an upper bound and the solution of **(P6)** a lower bound on the actual solution of the problem. This calls for an iterative scheme between **(P5)** and **(P6)** to determine the global solution of **(P2)**.

Based on the above analysis, the solution of the initial non–convex problem **(P2)** has been transformed to the solution of a series of convex non–linear relaxed dual problems which can efficiently be solved with existing algorithms. The solution of the primal problem, which corresponds to a single function evaluation, provides an upper bound to the global minimum whereas the relaxed dual problems yield lower bounds. It has been proved [1, 4] that by iterating between the primal problem and the relaxed dual problems ϵ–convergence to the global minimum is achieved in a finite number of steps.

The main limitation with this approach is that for n connected variables, up to 2^n relaxed dual problems must be solved per iteration. Furthermore, a large number of these relaxed dual problems do not contribute to the bounding of the solution because they are infeasible. These early observations motivated the development of a number of computational properties. First, if a qualifying constraint always maintains constant sign, then the relaxed dual problems involving the reverse qualifying constraint do not need to be solved [3]. Furthermore, if a qualifying constraint is rigorously equal to zero for some iteration k, then the corresponding connected variable can be set to either its lower or upper bound [3]. In this work the bounds of the variables are updated because this results in tighter lower bounding of the objective function. More specifically, the bounds of the variables for the current iteration coincide with the bounds of the variables of the relaxed dual problem whose solution is the current point. Based on this we can define a 2^n–tree with nodes corresponding to relaxed dual problems and levels corresponding to iterations. In the current iteration, only the Lagrange functions of relaxed dual problems which correspond to predecessor nodes for the node of the current relaxed dual problem are incorporated. It is interesting to note that their number is very small typically of the order $\log_2(K)$. The bounds for the current iteration are provided by the relaxed dual problem corresponding to the parent node of the current relaxed duals. Note also that no qualifying constraints are needed in the formulation. The application of this property greatly reduces the required number of iterations for convergence as well as improves the solution time for each relaxed dual problem by including only a small number of previous Lagrange functions and by excluding all qualifying constraints from the current relaxed dual problem.

Based on the presented problem formulation and the properties mentioned above, an algorithmic procedure has been developed for the location of the global minimum which is outlined in the following section.

5 Algorithmic Procedure

The basic steps of this procedure are as follows:

STEP 1 - *Initialization*

An initial point X_i^o, Y_i^o, Z_i^o is selected, the iteration counter K is set to zero, and a convergence tolerance ϵ is decided. Appropriate box constraints x_i^L,y_i^L,z_i^L,x_i^U,y_i^U,z_i^U for each variable x_i,y_i,z_i,X_i,Y_i,Z_i are selected. P^{UBD},R^{LBD} are defined as the minimum solution of the primal problems and the maximum solution of the relaxed dual problems so far respectively.

STEP 2 - *Primal problem*

The primal problem **(P6)** is solved at X_i^K, Y_i^K, Z_i^K for the variables x_i, y_i, z_i and the Lagrange multipliers $\lambda_{xi}, \lambda_{yi}, \lambda_{zi}$. If the solution of the primal is less than P^{UBD} then P^{UBD} is equal to the solution of the primal problem.

STEP 3 - *Selection of previous Lagrange functions and update of bounds*

The Lagrange functions from relaxed dual problems in previous iterations ($k = 1, 2, \ldots, K - 1$) corresponding to predecessor nodes for the current iteration are included to be constraints in the current iteration's relaxed dual problems. The box constraints of the current iteration are the ones of the relaxed dual problem corresponding to the parent node for the current tree level (iteration).

STEP 4 - *Update of α_{ij} parameters*

The convexification parameters α_{ij} are updated in every iteration as follows:

$$\alpha_{ij} = \max_{r_{ij}} \begin{cases} 12\left(\frac{1}{r_{ij}^{14}} - \frac{1}{r_{ij}^{8}}\right) & \text{if } r_{min} \leq r_{ij} \leq 1 \\ 0 & \text{if } 1 \leq r_{ij} \leq 1.108683 \\ 12\left(\frac{7}{r_{ij}^{8}} - \frac{13}{r_{ij}^{14}}\right) & \text{if } r_{ij} \geq 1.108683 \end{cases}$$

$$\begin{aligned} r_{ij} &= \left[(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2\right]^{\frac{1}{2}} \\ x_i^l \leq x_i \leq x_i^u, & \qquad i = 2, \ldots, N \\ y_i^l \leq y_i \leq y_i^u, & \qquad i = 3, \ldots, N \\ z_i^l \leq z_i \leq z_i^u, & \qquad i = 4, \ldots, N \\ x_1 = y_1 = z_1 &= y_2 = z_2 = z_3 = 0 \end{aligned}$$

Here $x_i^l, y_i^l, z_i^l, x_i^u, y_i^u, z_i^u$ are the current bounds on x_i, y_i, z_i.

STEP 5 - *Non–interior current point* (X_i^K, Y_i^K, Z_i^K)

If any of the X_i^K, Y_i^K, Z_i^K is at its bound (lower/upper) then the appropriate relaxed dual problems are eliminated.

STEP 6 - *Current Lagrange function completely above* P^{UBD}

If the current Lagrange function is completely above P^{UBD} within the box constraints of the current relaxed dual problem, then the global minimum is not contained inside the current box constraints and the corresponding relaxed dual problem does not have to be solved. If so the algorithm proceeds with **STEP 9**.

STEP 7 - *Solution of relaxed dual problems*

For every combination of bounds $B_{xi}^K, B_{yi}^K, B_{zi}^K$ of the connected variables x_i, y_i, z_i respectively, that has not been found to activate any checks in **STEPS 5,6** the following relaxed dual problem is solved.

$$\min_{X_i, Y_i, Z_i, \mu_B} \mu_B$$

subject to

$$\mu_B \geq L_k(x_i^{B_{xi}^k}, y_i^{B_{yi}^k}, z_i^{B_{zi}^k}, X_i, Y_i, Z_i), \quad \forall \quad k = 1, 2, \ldots, K-1$$

$$\mu_B \geq L_K(x_i^{B_{xi}^K}, y_i^{B_{yi}^K}, z_i^{B_{zi}^K}, X_i, Y_i, Z_i) \qquad \textbf{(P7)}$$

$$\begin{aligned} x_i^{K,l} \leq X_i \leq x_i^{K,u}, &\qquad i = 2, \ldots, N \\ y_i^{K,l} \leq Y_i \leq y_i^{K,u}, &\qquad i = 3, \ldots, N \\ z_i^{K,l} \leq Z_i \leq z_i^{K,u}, &\qquad i = 4, \ldots, N \\ X_1 = Y_1 = Z_1 = Y_2 = Z_2 = Z_3 = 0 & \end{aligned}$$

Here L_k, L_K are the Lagrange functions from the previous iterations and the current one respectively, $B_{xi}^k, B_{yi}^k, B_{zi}^k$ are the set of values of the connected variables x_i, y_i, z_i in the Lagrange function from the k^{th} iteration and $x_i^{K,l}, y_i^{K,l}, z_i^{K,l}, x_i^{K,u}, y_i^{K,u}, z_i^{K,u}$ are the bounds on X_i, Y_i, Z_i in the current iteration K.

STEP 8 - *Update* $R^{LBD}, X_i^K, Y_i^K, Z_i^K$

After all relaxed dual problems have been solved, a new lower bound R^{LBD} for the global minimum is selected which corresponds to the lowest value of the stored solutions of all relaxed dual problems from all iterations so far. At the same time, the values of X_i, Y_i, Z_i of the minimum stored solution are selected for the next current point $X_i^{K+1}, Y_i^{K+1}, Z_i^{K+1}$.

Once selected, the stored solution is deleted from the list. This ensures that no relaxed dual problem will return to the same solution during successive iterations.

STEP 9 - *Check for convergence*

If $P^{UBD} - R^{LBD} < \epsilon$, then ϵ–convergence has been achieved and the algorithm is stopped. Otherwise, we set $K = K + 1$ and we return to **STEP 2**.

This global optimization algorithmic procedure has been applied to a number of problems which are presented in the next section.

6 Examples for $N \leq 7$

By using the global optimization procedure presented earlier along with the transformation presented in Appendix B the global minimum potential energy configurations of small microclusters $2 \leq N \leq 7$ are generated. The global minimum structure for $N = 2,\ E^*(2) = -1$ corresponds to two particles "touching" each other. For $N = 3,\ E^*(3) = -3$ three particles form a unit equilateral triangle at the global minimum. For $N = 4,\ E^*(4) = -6$ the four particles are placed at the vertices of a regular tetrahedron. For $N = 5,\ E^*(5) = -9.104$ (rounded to the third decimal place), a trigonal bipyramid slightly contractred along the symmetry axis and distended in the symmetry plane corresponds to the global minimum energy structure. For $N = 6,\ E^*(6) = -12.712$ a regular octahedron with slightly contracted sides yields the global optimum configuration. Finally, for $N = 7,\ E^*(7) = -15.593$ the regular icosahedron (pentagonal bi–pyramid) with slightly distended edges and contracted axial distances is the structure involving the global minimum total potential energy.

For larger N the complexity of the problem limits the use of the general global optimization procedure. In the next section a "relaxation" of the global optimization procedure is presented which for larger microclusters yields tight lower and upper bounds on the global minimum total potential energy as well as excellent initial points for a possible local optimization approach.

7 A Relaxation of the Global Optimization Approach

As it has been mentioned earlier, the time bottleneck of the employed global optimization approach is the large number of connected variables of the problem which potentially gives rise to a very high number of relaxed dual problems per iteration. This motivates a relaxation of the global optimization approach which stems from the fact that usually the global minimum potential energy configuration of an N–particle cluster is composed by the slightly perturbed global minimum configuration for $N - 1$ particles plus an extra particle.

This means that when solving for the global minimum structure of N particles and the global minimum configuration for $N-1$ particles is known, tight bounds for the coordinate variables of the first $N-1$ particles can be used around the global minimum positions of an $(N-1)$–particle microcluster and only for the N^{th} particle "loose" bounds are required. Based on this, the global minimum potential energy problem in **(P1)** can be reformulated as:

$$
\begin{aligned}
\min V \quad = \quad & \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \\
& \left\{ \frac{1}{[(x_i-x_j)^2+(y_i-y_j)^2+(z_i-z_j)^2]^6} \right. \\
- \quad & \left. \frac{2}{[(x_i-x_j)^2+(y_i-y_j)^2+(z_i-z_j)^2]^3} \right\} \\
\text{st} \quad & x_i^* - e \le x_i \le x_i^* + e, \qquad i = 2, \ldots, N-1 \\
& y_i^* - e \le y_i \le y_i^* + e, \qquad i = 3, \ldots, N-1 \\
& z_i^* - e \le z_i \le z_i^* + e, \qquad i = 4, \ldots, N-1 \\
& \\
& -E \le x_N \le E \\
& -E \le y_N \le E \\
& -E \le z_N \le E \\
& \\
& x_1 = y_1 = z_1 = y_2 = z_2 = z_3 = 0
\end{aligned}
\qquad \textbf{(P8)}
$$

Here $e = 0.01 - 0.05$ accounts for the perturbation around the nominal point x_i^*, y_i^*, z_i^* which corresponds to the global minimum potential energy configuration of an $N-1$ microcluster. Also, $E = 2.0 - 4.0$ defines a cube where the N^{th} particle is expected to be. Since x_i^*, y_i^*, z_i^* corresponds to the global minimum potential energy point of an $N-1$ microcluster, V in formulation **(P8)** must be convex in terms of $x_i, y_i, z_i, \quad i = 1, \ldots, N-1$ in a neighborhood of x_i^*, y_i^*, z_i^*. By assuming that e in formulation **(P8)** is sufficiently small, then in order to transform V to the difference of two convex functions only the term $(a_{xN} x_N^2 + a_{yN} y_N^2 + a_{zN} z_N^2)$ is required. Thus, the Lagrange function resumes the following form:

$$
\begin{aligned}
L(x_i, y_i, z_i, X_i, Y_i, Z_i) &= \min_{x_i, y_i, z_i} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \\
& \frac{1}{[(X_i - X_j)^2 + (Y_i - Y_j)^2 + (Z_i - Z_j)^2]^6} \\
&- \frac{2}{[(X_i - X_j)^2 + (Y_i - Y_j)^2 + (Z_i - Z_j)^2]^3} \\
&+ a_{xN}(X_N^K - X_N)(x_N - X_N) \\
&+ a_{yN}(Y_N^K - Y_N)(y_N - Y_N) \\
&+ a_{zN}(Z_N^K - Z_N)(z_N - Z_N)
\end{aligned}
\qquad \textbf{(P9)}
$$

Note that formulation **(P9)** involves only three connected variables x_N, y_N, z_N which means that irrespective of how large N is, only up to $2^3 = 8$ relaxed dual problems must be solved per iteration. By combining the Lagrange function in formulation **(P9)** with the presented global optimization procedure a number of examples $8 \leq N \leq 24$ has been considered. Tight lower and upper bounds on the global minimum solutions were first established by selecting the tolerance to be between $0.01 - 0.05$. Then, by switching to a local optimization algorithm the global minimum potential energy structures were found. All these results are summarized in Table 1 where E^L, E^U correspond to the lower and upper bounds on the global minimum energy E^* and Iter is the total number of iterations for obtaining the bounds. It should be noted that the provided lower and upper bounds include the best reported solutions for $8 \leq N \leq 24$.

Although this simplification cannot guarantee convergence to the global minimum it appears that it behaves very well for small microclusters $N \leq 24$. This approach can be extended to larger microclusters by allowing more than one particle to have "loose" coordinate bounds. In this case, if M particles involve "loose" coordinate bounds then up to 2^{3M} relaxed dual problems must be solved per iteration.

8 Discussion on the structures

For $N \leq 7$ by applying the developed global optimization procedure, the cartesian coordinates of all particles in the three Eucledian space along with the total potential energy corresponding to the global minimum potential energy configuration of the microcluster are obtained. It should be noted that the geometry of the global optimum structures changes considerably as N increases. The mere addition of an extra atom does not always result in the global optimum configuration without restructuring of the initial one.

For $8 \leq N \leq 24$ the developed relaxation procedure provides bounds on the global minimum configurations by generating a number of structures whose coordinates are very close to the coordinates of the structure involving the global minimum total potential energy. It should be emphasized that for $8 \leq N \leq 24$ the global minimum configurations are not unrelated, instead it seems that they follow a certain pattern. More specifically, they correspond to the relaxation of icosahedral structures with one central particle, an initial IC layer involving 13 particles and an incomplete second FC sublayer. Furthermore, the particles occupying the second sublayer tend to aggregate together.

An important feature of the proposed approach is that it generates a sequence of lower and upper bounds on the global optimum configuration. Each upper bound corresponds to a different configuration of the particles in the three dimensional space, and hence the upper bounds generated in the last iterations represent excellent candidates for "low energy" structures that are very close to the global optimum configuration. At the same time, the lower bounds exclude most of the local optimum structures and concentrate the search in the domain of the best structures. As it can be seen from Table 1 within a few iterations excellent lower bounds are generated that eliminate almost all the sub–optimal configurations.

9 Conclusions

In this work a global optimization approach was introduced for finding the global minimum potential energy configuration of small Lennard–Jones microclusters. It involved the transformation of the initial non–convex total potential energy expression to the difference of two convex functions (**DC** transformation) and the application of a Primal–Relaxed Dual global optimization approach guarranteed to converge to the global optimum in a finite number of iterations. For larger microclusters a relaxation of this methodology yielded tight lower and upper bounds on the global minimum and initial points very close to the global optimum.

It should be emphasized that the developed **DC** transformation as well as the employed global optimization procedure are not restricted to the specifics of the problem at hand. They can conceptually be applied to system of many different particles interacting with complex many–body forces. Extensions in this direction are currently under way.

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Appendix A: Lower Bounds for r_{min}

It is essential for the presented **DC** transformation that all the eigenvalues of the Hessian matrix remain greater than $-\infty$. This is achieved only if all eucledian distances between the particles are strictly greater than zero at the global minimum. Furthermore, the larger r_{min} is the better the lower bounding of the objective function becomes. This motivates not only the proof of existence of an $r_{min} > 0$ but also the identification of the tightest possible one.

Theorem 1 *The minimum eucledian distance r_{min} over all particle pairs remains strictly greater than zero at the global minimum potential energy microcluster configuration.*

Proof: Let $E^*(n)$ be the global minimum potential energy of an n–particle Lennard–Jones microcluster and $E^L(n)$, $E^U(n)$ lower and upper bounds respectively of $E^*(n)$. By assuming that all particles are "touching" each other the following second order in n lower bound on $E^*(n)$ can be obtained:

$$E^L(n) = -\frac{n(n-1)}{2} \tag{22}$$

A n-particle microcluster can be constructed by placing $n-3$ particles so that each of them touches three others, starting with three particles forming a equilateral triangle. This provides the following linear in n upper bound on $E^U(n)$:

$$E^U(n) = -3 - 3(n-3) = -3n + 6 \tag{23}$$

Let $r_{n-1,n}$ be the minimum interparticle distance of an n–particle microcluster at its global minimum potential energy configuration.

$$\begin{aligned}
-3n+6 &= E^U(n) \\
&\geq E^*(n) \\
&= \sum_{i=1}^{n-2} \sum_{j=i+1}^{n-1} v_{i,j} + \sum_{i=1}^{n-1} v_{i,n} \\
&\geq E^*(n-1) + \sum_{i=1}^{n-1} v_{i,n} \\
&= E^*(n-1) + \sum_{i=1}^{n-2} v_{i,n} + v_{n-1,n} \\
&\geq E^L(n-1) - (n-2) + v_{n-1,n}
\end{aligned}$$

Solving for $v_{n-1,n}$ we get:

$$\begin{aligned} v_{n-1,n} = \frac{1}{r_{min}^{12}} - \frac{2}{r_{min}^{6}} &\leq E^U(n) - E^L(n-1) + (n-2) \\ &= -3n + 6 + \frac{(n-1)(n-2)}{2} + (n-2) \\ &= \left(\frac{1}{2}n^2 - \frac{7}{2}n + 5\right) \end{aligned}$$

Thus, for the minimum interparticle distance $r_{min}^{(I)}(n)$ of an n–particle microcluster we have:

$$r_{min}^{(I)}(n) = \left[\frac{-1 + \sqrt{\frac{1}{2}n^2 - \frac{7}{2}n + 6}}{\frac{1}{2}n^2 - \frac{7}{2}n + 5}\right]^{\frac{1}{6}}$$

Tighter lower bounds for $r_{n-1,n}$ can be obtained if instead of $E^U(n) = -3n + 6$ we use the best reported solution in the literature as an upper bound of the global optimum solution $E^{opt}(n) \geq E^*(n)$.

$$\frac{1}{r_{min}^{12}} - \frac{2}{r_{min}^{6}} \leq E^{opt}(n) + \frac{(n-1)(n-2)}{2} + (n-2) = E^{opt}(n) + \frac{1}{2}n^2 - \frac{1}{2}n - 1$$

After solving for $r_{min}^{(II)}(n)$ we get:

$$r_{min}^{(II)}(n) = \left[\frac{-1 + \sqrt{E^{opt}(n) + \frac{1}{2}n^2 - \frac{1}{2}n}}{\frac{1}{2}n^2 - \frac{1}{2}n - 1}\right]^{\frac{1}{6}}$$

Table 2 summarizes the results for $r_{min}^{(I)}(n), r_{min}^{(II)}(n)$ and $3 \leq n \leq 24$. These bounds appear to be much tighter than the ones reported by Xue *et al.*, [49] $\Box$.

Appendix B: Alternative DC Transformation

As presented earlier, instead of transforming each and every pair potential expression to a difference of two convex functions by adding and subtracting the following term:

$$\alpha_{ij}\left(x_i^2+y_i^2+z_i^2+x_j^2+y_j^2+z_j^2\right) \tag{24}$$

it is quite advantageous to rewrite the total potential energy expression as the difference of two convex functions by adding and subtracting the following single term:

$$\sum_{i=1}^{N}\left(a_{xi}x_i^2+a_{yi}y_i^2+a_{zi}z_i^2\right) \tag{25}$$

This is because it results in tighter bounding of the objective function when the afformentioned global optimization is applied. Let F be the summation of the original total potential energy function plus the above extra term.

$$\begin{aligned} F(x_i,y_i,z_i) &= \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} \\ & \left\{\frac{1}{[(x_i-x_j)^2+(y_i-y_j)^2+(z_i-z_j)^2]^6}\right. \\ &- \left.\frac{2}{[(x_i-x_j)^2+(y_i-y_j)^2+(z_i-z_j)^2]^3}\right\} \\ &+ \sum_{i=1}^{N}\left(a_{xi}x_i^2+a_{yi}y_i^2+a_{zi}z_i^2\right) \end{aligned} \tag{26}$$

Note that F is a non–separable function in terms of x_i, y_i, z_i of $3N-6$ variables. Thus, no closed form analytical expressions for the eigenvalues of the Hessian matrix of F can be derived. However, for convexifying F the actual expressions for all eigenvalues are not required to be known. In fact, only the minimum value of the minimum eigenvalue over a prespecified domain is needed in order to conclude whether or not F is convex in a particular domain. If this value is non-negative then for the current set of a_{xi}, a_{yi}, a_{zi} and for the specified variable range F is convex. This can be formulated as the following non–convex optimization problem:

$$\min \lambda$$

subject to

$$\det\left(He-\lambda I\right)=0$$

(P10)

$$
\begin{aligned}
x_i^L \leq x_i \leq x_i^U, & \qquad i = 2, \ldots, N \\
y_i^L \leq y_i \leq y_i^U, & \qquad i = 3, \ldots, N \\
z_i^L \leq z_i \leq z_i^U, & \qquad i = 4, \ldots, N
\end{aligned}
$$

Here λ is the minimum eigenvalue of the Hessian matrix He of F and I is the identity matrix. Problem **(P9)** was solved for $N = 2, 3$ using local optimization techniques. Although no guarantee for global optimality can be made, by performing multiple runs from different initial points it appeared that a_{xi}, a_{yi}, a_{zi} of value ≈ 6 are sufficient for maintaining λ non-negative and consequently F convex. By assuming that the required values of a_{xi}, a_{yi}, a_{zi} remain more or less unchanged with N, a number of examples have been solved $3 \leq N \leq 24$ by employing the later transformation. By emloying the later transformation the Lagrange function of the problem resumes the following form:

$$
\begin{aligned}
L(x_i, y_i, z_i, X_i, Y_i, Z_i) \quad = & \quad \min_{x_i, y_i, z_i} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \\
& \quad \frac{1}{[(X_i - X_j)^2 + (Y_i - Y_j)^2 + (Z_i - Z_j)^2]^6} \\
- & \quad \frac{2}{[(X_i - X_j)^2 + (Y_i - Y_j)^2 + (Z_i - Z_j)^2]^3} \\
+ & \quad \sum_{i=2}^{N} a_{xi} (X_i^K - X_i)(x_i - X_i) \\
+ & \quad \sum_{i=3}^{N} a_{yi} (Y_i^K - Y_i)(y_i - Y_i) \\
+ & \quad \sum_{i=4}^{N} a_{zi} (Z_i^K - Z_i)(z_i - Z_i)
\end{aligned}
$$

It should be noted that the selection process of a_{xi}, a_{yi}, a_{zi} is very important so as the minimum possible values for these parameters are selected. Furthermore, the possibility of eliminating some of these parameters for certain variable ranges is worth exploring.

N	E^L	E^U	e	E	Iter	E^*
8	-20.633	-19.683	0.01	1.0	12	-19.822
9	-28.321	-24.111	0.01	1.0	21	-24.113
10	-29.783	-28.326	0.01	1.5	26	-28.423
11	-34.233	-32.559	0.02	1.5	31	-32.766
12	-39.522	-37.557	0.02	1.5	29	-37.968
13	-44.487	-42.290	0.02	1.5	15	-44.327
14	-49.469	-47.218	0.02	1.5	10	-47.845
15	-52.655	-52.083	0.02	1.5	11	-52.323
16	-57.612	-56.601	0.02	1.5	21	-56.816
17	-62.463	-61.222	0.05	1.5	32	-61.318
18	-67.591	-65.615	0.05	1.5	20	-66.531
19	-73.567	-72.117	0.10	1.5	22	-72.660
20	-78.485	-76.972	0.10	1.5	21	-77.177
21	-83.265	-81.427	0.10	1.5	14	-81.685
22	-87.754	-86.116	0.10	1.5	16	-86.810
23	-92.949	-91.276	0.10	1.5	8	-92.844
24	-98.920	-96.997	0.10	1.5	19	-97.349

Table 1: Bounds and global minimum potential energies $8 \leq N \leq 24$

n	$r_{min}^{(I)}$	$r_{min}^{(II)}$
3	1	1
4	1	1
5	0.8909	0.8949
6	0.8458	0.8505
7	0.8135	0.8272
8	0.7885	0.7984
9	0.7680	0.7798
10	0.7508	0.7626
11	0.7360	0.7479
12	0.7230	0.7359
13	0.7115	0.7265
14	0.7011	0.7137
15	0.6918	0.7033
16	0.6832	0.6940
17	0.6753	0.6854
18	0.6681	0.6780
19	0.6613	0.6714
20	0.6550	0.6640
21	0.6491	0.6579
22	0.6435	0.6518
23	0.6383	0.6468
24	0.6334	0.6414

Table 2: Lower bounds on r_{min}

Response to the Reviewer's Comments

Our responses to the received comments have as follows:

Comment 1. The value of the parameter α is defined as the maximum of three mutually exclusive possibilities over the region in which $r_{1,2}$ is expected to vary. Thus, there is an one to one correspondence between the region in which $r_{1,2}$ is defined and the parameter α, but not an one to one correspondence between $r_{1,2}$ and α. Corrective action has been taken in the text in order to strengthen and emphasize this point.

Comment 2. The afformentioned typographical errors have been detected and corrected.

Comment 3. An extra section named " Discussion on the structures" has been added where a disscusion on the global minimum structures is presented.