Acta Cybernetica **17** (2005) 107–121.

# Minimal inter-particle distance in atom clusters*

Tamás Vinkó†

**Abstract**

A general method for obtaining minimal interatomic distance in molecule conformation problems is introduced. The method can be applied to a wide family of potential energy functions having reasonable properties. Using this method new lower bounds for the minimal inter-particle distance for the optimal Lennard-Jones and Morse potential functions are derived which are independent from the number of atoms. Improved linear lower bounds for the optimal function values for Lennard-Jones and Morse potentials are also given.

## 1 Introduction

Given a cluster of $n$ atoms, define $x_i \in \mathbb{R}^3$ $(i = 1, \ldots, n)$ as the center of the $i$th atom. The potential energy of the cluster $x = (x_1, \ldots, x_n) \in \mathbb{R}^{3n}$ is defined as the sum of the two-body inter-particle pair potentials over all of the pairs, i.e.,

$$E(x) = \sum_{i<j} v(r_{ij}), \tag{1}$$

where $r_{ij} = \|x_i - x_j\|$ and $v(r)$ is the value of a pair potential of distance $r$. For the pair potential $v(r)$ we set the following requirements to be satisfied:

(P1) The function $v$ is continuous.

(P2) There exists a unique $s$ with $v(s) < 0$ and if $r \neq s$ then $v(r) > v(s)$ (single stable state property).

(P3) If $r \leq s$ then $v$ is strictly decreasing and $v(r) \geq r^{-4}$.

(P4) If $r > s$ then $v$ is strictly increasing and $v(r) \geq -r^{-4}$.

The properties (P3) and (P4) come from sphere packing arguments used in the paper. We should use here $Cr^{-3}$ bounds instead, but the *a priori* determination of the constant $C$ is quite difficult.

*This work has been supported by the grants OTKA T 048377 and AÖU 60oü6.

†Research Group on Artificial Intelligence of the Hungarian Academy of Sciences and University of Szeged, H-6720 Szeged, Aradi vértanúk tere 1., Hungary email: tvinko@inf.u-szeged.hu

The aim of the paper is to obtain lower bounds for the minimal interatomic distance in the optimal structure of (1), independent of the number of atoms and assuming only that the pair potential minimally satisfies properties (P1)–(P4). Many papers deal with this topic, however, they specialized the pair potential function.

## 1.1 Previous results

The first paper is by Xue *et al.* [9], where a poor lower bound for the minimal distance in Lennard-Jones cluster is established. They also proved that the global optimum can be bounded from below and above by linear (in the number of atoms) functions. In a paper of Maranas and Floudas [7] results for the minimal distance can be found. They established bounds as functions of the number of atoms. That value is useful only for small $n$ since it goes to zero as the number of atoms grows. In another work of Xue [11], a lower bound for inter-particle distance in the optimal Lennard-Jones cluster is given which is independent of the number of atoms in the cluster. Improved lower bound is obtained by Blanc [1]. For Morse clusters (for which property (P3) does not hold) Locatelli and Shoen [5] establish lower bound for the interatomic distance in the optimal structures. In this paper, better lower bounds for the Lennard-Jones and the Morse cluster (where we use the results from [5]) are derived as applications of the introduced general method.

Apart from the theoretical interest, this kind of results can be used efficiently in the construction of global optimization methods, especially in branch-and-bound type methods. As shown by Locatelli and Schoen in [4], information about the minimal interatomic distance can be used efficiently in starting point generator algorithm for (stochastic) optimization methods. Such a lower bound can also be applied to construct special data structures for fast procedures to compute potential functions with large number of atoms, see [12].

## 1.2 Notation

In the rest of the paper the following notation will be used. The set of real numbers, positive real number and nonnegative integers are denoted by $\mathbb{R}, \mathbb{R}_+$ and $\mathbb{N}_0$, respectively. $V$ denotes the set of functions $v : \mathbb{R}_+ \to \mathbb{R}$ satisfying properties (P1)–(P4) Using this notation $v \in V$ is supposed in this paper. The global minimizer of the function $E$ is the configuration $x^* \in \mathbb{R}^{3n}$ with

$$E(x^*) = \min_{x \in \mathbb{R}^{3n}} E(x). \tag{2}$$

The global minimum will be denoted by

$$E^* = E(x^*).$$

Let $r_{ij}$ be the Euclidean distance of the points $x_i^*$ and $x_j^*$ $(i, j = 1, \ldots, n)$. Define the potential energy of particle $i$ as

$$E_i(x) = \sum_{i \neq j} v(\|x_i - x_j\|) \quad (i = 1, \ldots, n)$$

and $E_i^* = E_i(x^*)$. It is obvious that

$$E(x) = \frac{1}{2}\sum_{i=1}^{n} E_i(x) \tag{3}$$

holds. The minimal inter-particle distance in the optimal structure is

$$r^* = \min_{i,j} r_{ij} \quad (i,j = 1,\ldots,n). \tag{4}$$

Lower bound for the minimal distance is denoted by $q$, i.e., our task is to find a good underestimation

$$q \le r^*.$$

In order to obtain good lower bound $q$ we assume that in the configuration taken into account the minimal distance between the particles equal to $q$.

The positive root of $v$ is denoted by $t$. Properties (P1)–(P4) imply that that $t$ is unique and $t < s$. Note that with the general method only such a lower bound can be obtained which satisfies $q < t$.

Without loss of generality let us suppose that $x_1 = 0$ and $0 = r_1 < r_2 \le \ldots \le r_n$, where

$$r_j = \|x_j - x_1\| = \|x_j\| \quad (j = 1,\ldots,n).$$

In the rest of the paper we consider only the cases $n > 2$.

# 2 Lower bound on the minimal inter-particle distance

To give a good lower bound for the minimal inter-particle distance we generalize the arguments given by Xue in [11] and Blanc in [1]. To do that, first we establish an upper bound for $E_i^*$ $(i = 1,\ldots,n)$. Suppose that $p \in \mathbb{R}_+$ is a parameter such that

$$pq \ge s. \tag{5}$$

Then we use the partition

$$E_1^* = \sum_{q \le r_j < pq} v(r_j) + \sum_{r_j \ge pq} v(r_j) \tag{6}$$

and give underestimations for the two terms. With suitable chosen parameters we show that if the minimal distance is too small, then we get a contradiction with the upper bound for $E_1^*$.

## 2.1 The auxiliary bounds

**Lemma 1.** *In the optimal configuration the potential energy of particle $i$ is always less than the global minimum of $v$, i.e. the inequality $E_i^* < v(s)$ holds for all $i = 1,\ldots,n$.*

*Proof.* Let $k = n$ if $i \neq n$ and $k = n-1$ if $i = n$, and define the configuration $z = (z_1, \ldots, z_n)$ in such a way that $z_j = x_j^*$ for all $j \neq i$, $\|z_i - z_k\| = s$ and $\|z_i - z_l\| \geq s$ for all $l \neq i$. Then put the atom $z_i$ to the line determined by the origin point and the coordinates of $z_k$ in such a way that then $z_i$ has the maximal $r_j$ value. Thus $E_i(z) < v(s)$. By construction of $z$,

$$E^* - E_i^* \quad = \quad E(z) - E_i(z).$$

Since $E_i(z) < v(s)$ and

$$E^* - E_i^* = E(z) - E_i(z) > E(z) - v(s),$$

we find $E_i^* < v(s)$. □

**Lemma 2.** *For $\frac{q}{2} < a < b$, the index set $\mathcal{J}_{ab} = \{j \mid a \leq r_j < b\}$ has size*

$$|\mathcal{J}_{ab}| \leq \left(\frac{2b+q}{q}\right)^3 - \left(\frac{2a-q}{q}\right)^3.$$

*Proof.* We may assume that the particles are centers of disjoint open balls of radius $q/2$. The cardinality of the set $\mathcal{J}_{ab}$ can not exceed the number of balls with radius $q/2$ that can be contained in the ball centered at the origin with radius $b + q/2$. With volume comparison this gives the upper bound

$$|\mathcal{J}_{ab}| \leq \left(\frac{b+\frac{q}{2}}{\frac{q}{2}}\right)^3.$$

On the other hand, since $r_j \geq a$, we can drop out all the balls with radius $q/2$ from the ball centered in the origin and having radius $a - q/2$. □

**Lemma 3.** *If $pq \geq s$, then the first term of* (6) *can be underestimated with*

$$\sum_{q \leq r_j < pq} v(r_j) \geq v(q) + v(s)\left((2p+1)^3 - 1)\right). \tag{7}$$

*Proof.* Suppose that $r_2 = r_3 = \ldots = r_{m+1} = q$, (i.e. there are $m \geq 1$ distances equal to $q$). Since they give positive contributions we can cancel all of them but one (about what we supposed that exists, see Section 1.2) and this one can be taken out from the sum. Thus

$$\sum_{q \leq r_j < pq} v(r_j) \geq v(q) + \sum_{q < r_j < pq} v(r_j) \tag{8}$$

holds. Moreover, using Lemma 2 and the monotonicity property of the pair potential $v$ we get

$$\begin{aligned} v(q) + \sum_{q < r_j < pq} v(r_j) \quad &\geq \quad v(q) + v(s)\left(\left(\frac{2pq+q}{q}\right)^3 - \left(\frac{2q-q}{q}\right)^3\right) && (9) \\ &= \quad v(q) + v(s)\left((2p+1)^3 - 1)\right). && (10) \end{aligned}$$

□

**Lemma 4.** *Let $s \le pq = R_0 < R_1 < R_2 < \dots$ be an infinite strictly increasing sequence and define the index set $\mathcal{I}_k = \{j \mid 2 \le j \le n, R_k \le r_j < R_{k+1}\}$ $(k = 0, 1, 2, \dots)$. If $pq \ge s$, then the second term of (6) can be underestimated with*

$$\sum_{r_j \ge pq} v(r_j) \ge \frac{1}{q^3} \sum_{k=0}^{\infty} v(R_k) \left( (2R_{k+1} + q)^3 - (2R_k - q)^3 \right). \tag{11}$$

*Proof.* Again, we can use the monotonicity property of $v$ and Lemma 2 with the index set $\mathcal{I}_k$:

$$\begin{aligned} \sum_{r_j \ge pq} v(r_j) &= \sum_{k=0}^{\infty} \sum_{r_j \in \mathcal{I}_k} v(r_j) && (12) \\ &\ge \sum_{k=0}^{\infty} \sum_{r_j \in \mathcal{I}_k} v(R_k) && (13) \\ &\ge \frac{1}{q^3} \sum_{k=0}^{\infty} v(R_k) \left( (2R_{k+1} + q)^3 - (2R_k - q)^3 \right), && (14) \end{aligned}$$

which completes the proof. □

## 2.2 The general method

Using the above lemmas the following method can be introduced to obtain the minimal interatomic distance in the optimal potential energy function $E$. Recall that $t$ and $s$ are the zero and the minimizer of the pair potential $v$, respectively. Suppose that $v \in V$. In Lemma 4 we use an increasing sequence $R_k$ which represents an infinite sequence of spherical shells. Instead of this sequence one can use function $R : \mathbb{R}_+ \times \mathbb{N}_0 \to \mathbb{R}_+$ having the properties

$$R(Q, k) < R(Q, k+1) \text{ and } R(Q, 0) = c,$$

where $c \in \mathbb{R}_+$ is a constant (in the proof of Lemma 4 this constant is $pq$, the staring point of the infinite sequence). For technical reasons we use the notation $R_k^Q$ for the functions $R(Q, k)$. Moreover, we write

$$U_c^Q := \{R_k^Q \mid R_k^Q < R_{k+1}^Q \text{ and } R_k^Q = c \text{ and } k = 0, 1, \dots\}.$$

Let us define now

$$\begin{aligned} F(q, p) &:= v(q) + v(s) \left( (2p+1)^3 - 1 \right), && (15) \\ S(q, p, R) &:= \frac{1}{q^3} \sum_{k=0}^{\infty} v(R_k^Q) \left( \left( 2R_{k+1}^Q + q \right)^3 - \left( 2R_k^Q - q \right)^3 \right), && (16) \\ G(q, p, R) &:= F(q, p) + S(q, p, R). && (17) \end{aligned}$$

Using these functions and Lemma 3 and 4, we have the lower bound:

$$\begin{aligned} E_1^* &= \sum_{q \le r_j < pq} v(r_j) + \sum_{r_j \ge pq} v(r_j) \\ &\ge G(q,p,R) \end{aligned} \tag{18}$$

where $p \in \mathbb{R}_+$ such that $pq \ge s$ and $R \in U_{pq}^Q$.

**Theorem 1.** *Define the function $g_v(q,p,Q) := G(q,p,R)$. If $g_v(q,p,Q) > -\infty$ then in the optimal atom cluster problem (2) the minimal inter-particle distance is greater than or equal to the solution $q$ of the nonlinear system of equations*

$$\frac{\partial g_v(q,p,Q)}{\partial p} = 0, \tag{19}$$

$$\frac{\partial g_v(q,p,Q)}{\partial Q} = 0, \tag{20}$$

$$g_v(q,p,Q) - v(s) = 0. \tag{21}$$

*Proof.* The finiteness of $g_v$ comes from properties (P3) and (P4). These properties also guarantee that $g_v$ is monotone in $q$ on the interval $[0,s]$. Thus (21) has exactly one solution.

From Lemma 1 we know $E_1^* < v(s)$. Moreover, $g_v \le E_1^*$ comes from (18). We are looking for the largest $q$ for which the underestimation $g_v < v(s)$ does not hold. Now let us consider the optimization problem

$$\begin{array}{ll} \max & q \\ \text{s.t.} & g_v(q,p,Q) \ge \quad v(s) \end{array} \tag{22}$$

Thus (19) and (20) are the first order optimality conditions for $p$ and $Q$, respectively, in the optimization problem (22). Finally, (21) guarantees the largest possible $q$ for which the the inequality $g_v < v(s)$ does not hold. In this manner the minimal inter-particle distance in (2) is at least $q$. □

One can improve the result can be achieved with Theorem 1. If we substitute the first $m$ term of the sequence $R_k$ with variables $p_1, \ldots, p_m$ then we have a function $G$ with $m+2$ variables. Namely,

$$\begin{aligned} G(q,p_1,\ldots,p_m,R) \;:=\; & F(q,p) + \sum_{i=1}^{m-1} v(p_i q)\left((2p_{i+1}+1)^3 - (2p_i-1)^3\right) \\ & + \frac{1}{q^3}\sum_{k=0}^{\infty} v(R_k^Q)\left(\left(2R_{k+1}^Q + q\right)^3 - \left(2R_k^Q - q\right)^3\right), \end{aligned}$$

where $F(q,p)$ is defined in (15), $p_1 q \ge s$, and $R_k^Q \in U_{p_m q}^Q$.

**Corollary 1.** *Define the function* $g_v(q, p_1, \ldots, p_m, Q) := G(q, p_1, \ldots, p_m, R)$. *If* $g_v > -\infty$ *then in the optimal atom cluster problem* (2) *the minimal inter-particle distance is greater than or equal to the solution* $q$ *of the nonlinear system of equations*

$$\begin{aligned}
\frac{\partial g_v(q, p_1, \ldots, p_m, Q)}{\partial p_1} &= 0, \\
&\vdots \\
\frac{\partial g_v(q, p_1, \ldots, p_m, Q)}{\partial p_m} &= 0, \\
\frac{\partial g_v(q, p_1, \ldots, p_m, Q)}{\partial Q} &= 0, \\
g_v(q, p_1, \ldots, p_m, Q) - v(s) &= 0.
\end{aligned}$$

# 3 Linear lower bounds on the optimal values

Using the results of the previous section we can establish linear lower bounds for the optimal objective function value. These bounds are valid for arbitrary large clusters.

## 3.1 The general method

**Theorem 2.** *If* $q$ *is a lower bound obtained by the usage of Corollary 1 for the minimal inter-particle distance in the problem* (2)*, then there exists a constant* $K$ *such that*

$$-\frac{K}{2}n \le E^*.$$

*Moreover,* $K$ *can be computed using the value of* $q$.

*Proof.* Let $i \in \{1, \ldots, n\}$ arbitrary but fixed. Recall from Section 1.2 that $s$ is the minimizer and $t$ is the positive root of $v$, respectively. Let us define the interval $M = [t, pq)$, where $pq \ge s$. Then one can make the underestimation

$$\sum_{\substack{j=1 \\ j \ne i}}^{n} v(r_{ij}) \ge \sum_{\substack{j=1 \\ j \ne i, r_{ij} \in M}}^{n} v(r_{ij}) + \sum_{\substack{j=1 \\ j \ne i, r_{ij} \ge pq}}^{n} v(r_{ij}).$$

Using Lemma 2, an underestimation of the first term is

$$\sum_{\substack{j=1 \\ j \ne i, r_{ij} \in M}}^{n} v(r_{ij}) \quad \ge \quad v(s)\left((2p+1)^3 - \left(\frac{2t-q}{q}\right)^3\right). \tag{23}$$

From Lemma 2 and 4 we have a lower bound for the second term:

$$\sum_{\substack{j=1\\ j\neq i, r_{ij}\geq pq}}^{n} v(r_{ij}) \quad \geq \quad \frac{1}{q^3}\sum_{k=0}^{\infty} v(R_k^Q)\left((2R_{k+1}^Q+q)^3-(2R_k^Q-q)^3\right), \qquad (24)$$

where $R_k^Q \in U_{pr^*}^Q$ (see section 2.2). Moreover, as in Corollary 1 we can extend these considerations with introducing more variables in (24). This leads to the underestimation

$$\begin{aligned}\sum_{\substack{j=1\\ j\neq i}}^{n} v(r_{ij}) \quad &\geq \quad v(s)\left((2p+1)^3-\left(\frac{2t-q}{q}\right)^3\right)+\\ &\quad +\sum_{l=1}^{m-1} v(p_l r^*)\left((2p_{l+1}+1)^3-(2p_l-1)^3\right)+\\ &\quad +\frac{1}{q^3}\sum_{k=0}^{\infty} v(R_k^Q)\left(\left(2R_{k+1}^Q+q\right)^3-\left(2R_k^Q-q\right)^3\right)\\ &=: \quad -K,\end{aligned}$$

where $p_1 q \geq s$ and $R_k^Q \in U_{p_m q}^Q$. If $g_v$ is finite (see Corollary 1) then the substitution of the solution vector from Corollary 1 guarantees the finiteness of $K$. Finally, equation (3) yields a linear lower bound for the optimal potential function:

$$-\frac{K}{2}n \leq E^*.$$

□

# 4 Lennard-Jones clusters

In this section the generalized method introduced in the previous section is applied to the Lennard-Jones function.

In general form the Lennard-Jones pair potential function is

$$v_{\sigma,\epsilon}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right], \qquad (25)$$

where $\epsilon$ is the pair well depth and $2^{1/6}\sigma$ is the pair separation at equilibrium. In the global optimization literature the function (25) with reduced units, i.e. $\epsilon = \sigma = 1$ and $s = 2^{1/6}$,

$$v_{1,1}(r) = \frac{4}{r^{12}} - \frac{4}{r^6},$$

or the so-called scaled Lennard-Jones pair potential ($\epsilon = 1$, $\sigma = 2^{-1/6}$, $s = 1$)

$$v_{2^{-1/6},1}(r) = \frac{1}{r^{12}} - \frac{2}{r^6} \qquad (26)$$

is investigated. Note that the properties (P1)–(P4) required for the application of the general method are satisfied by (25). The scaled version is plotted in Figure 1.

Using (1) and (25), the Lennard-Jones potential function is defined by

$$E_{\sigma,\epsilon}(x) = \sum_{1 \le i < j \le n} v_{\sigma,\epsilon}(\|x_i - x_j\|). \tag{27}$$

In the following minimal distance in the optimal Lennard-Jones cluster is given.

## 4.1 Minimal distance

**Theorem 3.** *In the optimal Lennard-Jones atom cluster problem the minimal inter-particle distance is greater than or equal to* $2^{1/6}\sigma \cdot 0.6187356774$.

*Proof.* The translation between the general and the scaled Lennard-Jones pair potential is

$$v_{\sigma,\epsilon}(r) = \epsilon v_{2^{-1/6},1}(r/s), \tag{28}$$

thus the minimal distance scales with $s$ and the potential scales with $\epsilon$. We give a proof for the scaled version; then the result for the general case is straightforward.

For the sake of simplicity, in the proof we use the notation

$$v(r) = v_{2^{-1/6},1}(r) \quad \text{and} \quad E = E_{2^{-1/6},1}.$$

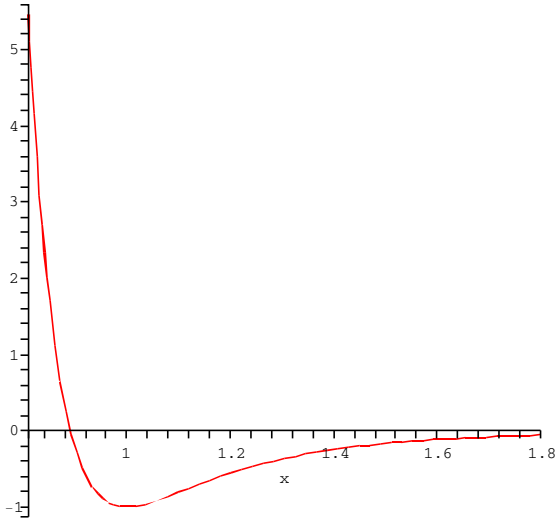


Figure 1: The scaled Lennard-Jones pair potential function.

One can easily see that the zero point and the minimizer point of the function $v$ is

$$t = 2^{-1/6} \quad \text{and} \quad s = 1,$$

respectively.

From Lemma 1 we have $E_1^* < -1$. The lower bound for $E_1^*$ can be established with the usage of Lemma 3 and 4. To prove the theorem by contradiction we should choose a suitable function $R(Q,k)$ to keep that lower bound greater than or equal to $-1$.

Define the function $R(Q,k) = pqQ^k$ $(pq \geq 1, Q > 1, k = 0,1,2,\ldots)$. Since property (P4) is satisfied by $v$, it is easy to see that

$$S_{LJ}(q,p,Q) := \sum_{k=0}^{\infty} \left( \frac{1}{pqQ^{12k}} - \frac{2}{pqQ^{6k}} \right) \left( \left(2pQ^{k+1}+1\right)^3 - \left(2pQ^k - 1\right)^3 \right) > -\infty \tag{29}$$

holds. Indeed, because $Q > 1$ holds, as $k$ goes to infinity the first term in the sum (i.e. $v(pqQ^k)$) tends to 0 faster than the second term goes to infinity. Thus the function

$$g_v(q,p,Q) := v(q) + 1 - (2p+1)^3 + S_{LJ}(q,p,Q) \tag{30}$$

is well defined. Figure 2 shows the graph of this function, where the variable $q = 0.618$ is fixed. Note that the function $g_v$ is monotone decreasing in variable $q$.

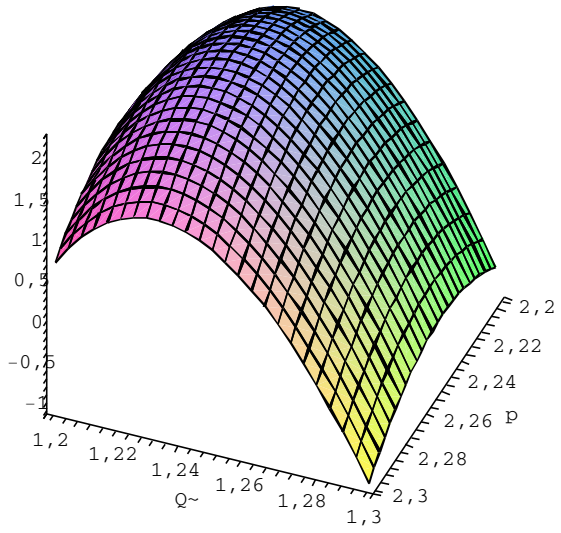


Figure 2: The graph of function $g_v(0.618, p, Q)$.

To obtain a lower bound one has to solve the nonlinear system of equations with three variables:

$$\begin{aligned} \frac{\partial g_v}{\partial p}(q,p,Q) &= 0, \\ \frac{\partial g_v}{\partial Q}(q,p,Q) &= 0, \\ g_v(q,p,Q)+1 &= 0. \end{aligned}$$

The closed formula of the convergent series (29) and the partial derivative in the nonlinear system of equation above can be calculated with the usage of a symbolic-algebraic system. For this task we used MAPLE 9 [6]. The solution of the nonlinear system is

$$Q = 1.234749976, \quad p = 2.24086158005346, \quad q = 0.61845034503861, \tag{31}$$

which gives a lower bound on the minimal interatomic distance for the optimal scaled Lennard-Jones problem.

As it is stated in Corollary 1, we can improve this bound with introducing more parameters. Using 5 variables instead of 3, one obtains:

$$q = 0.6187356774, \tag{32}$$

which gives a slightly better underestimation for the minimal distance. □

Note that we do not have significantly better bound with Corollary 1 using more and more variables, but more complicated calculations have to done.

As it is mentioned in the introduction, there are papers about the minimal distance in optimal scaled Lennard-Jones clusters. These results are compared in the following table including the minimal distance obtained in this paper.

| Xue [11] | Blanc [1] | general method |
|---|---|---|
| 0.5 | 0.6108 | 0.6187 |

Note that all these results are independent of the number of particles in the configuration.

The next corollary specializes the previous result for the case of reduced unit.

**Corollary 2.** *The minimal inter-particle distance in the optimal Lennard-Jones clusters with reduced units is greater than or equal to* 0.6945073156.

## 4.2 Linear lower bound on the optimal value

**Theorem 4.** *The optimal Lennard-Jones potential function has the linear lower bound*

$$-138.6775911n \cdot \epsilon \leq E^*_{\sigma,\epsilon} \quad (n = 2, 3, \ldots).$$

*Proof.* One can use the values from the numerical result of Theorem 3 and equation (28) then the statement of the theorem is straightforward from the considerations in section 3.1, thus the proof is omitted. □

# 5 Morse clusters

The pair potential function in Morse cluster is

$$v_\rho(r) = e^{\rho(1-r)}\left(e^{\rho(1-r)} - 2\right), \tag{33}$$

where $\rho > 0$ is a parameter. For $\rho = 6$ the Morse and the scaled Lennard-Jones pair potential are related, they have similar curvature at the minimum point $r = 1$.

Using (33) and (1) the Morse potential function is defined by

$$M_\rho(x) = \sum_{1 \le i < j \le n} v_\rho(\|x_i - x_j\|). \tag{34}$$

The zero point and the minimizer point of the function $v_\rho$ is

$$t = 1 - \frac{\ln 2}{\rho} \quad \text{and} \quad s = 1,$$

respectively. Note that if $\rho < \ln 2$ then $v_\rho$ has no positive root. In the context of global optimization, the cases $\rho > 6$ are interesting, since these are more difficult problems than finding the optimal Lennard-Jones structures [2].

## 5.1 Minimal distance

We must emphasize that property (P3) is not satisfied by the Morse potential. The reason is that the pair potential function $v_\rho$ is defined even in the case $r = 0$, i.e., when two particles are in the same position. In other words the function $G$ from (15) has two roots, i.e. becomes negative for small $q$ values. Thus the general method cannot be applied directly to $M_\rho$. In this case, information on the minimal inter-particle distances can be helpful. In [5] the minimal inter-particle distance in optimal Morse clusters is investigated. The proposed technique differs from the method introduced by Xue in [11] and from the general method introduced in this paper. In [5] it has been proved that there are positive minimal distances in the optimal Morse clusters for $\rho \ge 6$. Using this information these bounds can be improved by the application of the general method.

In the rest of this subsection we use the notation $M := M_\rho$ for a given $\rho > 0$. From Lemma 1 we know that $M_i^* < -1$ for all $i = 1, \ldots, n$ and $\rho > 0$. As for the Lennard-Jones potential, define the function $R(Q, k) := pqQ^k$ ($pq > 1, Q > 1, k = 0, 1, \ldots$). The infinite series

$$S_M(q, p, Q) := \sum_{k=0}^{\infty} \left( \left(e^{\rho(1-pqQ^k)} - 1\right)^2 - 1 \right) \left( \left(2pQ^{k+1} + 1\right)^3 - \left(2pQ^k - 1\right)^3 \right) \tag{35}$$

is convergent –the first term of the sum (i.e. $v_\rho(pqQ^k)$) goes to zero faster than the second term goes to infinity–, thus the function

$$g_v(q, p, Q) := v_\rho(q) + 1 - (2p + 1)^3 + S_M(q, p, Q) \tag{36}$$

is well defined.

In Table 1 the results from [5] are collected and compared with the results can be achieved with the usage of the general technique introduced in this paper. Note that the new results are achieved using the results from [5], i.e. using that $q$ must be greater than the second column in Table 1. One can see that the new method produces much better lower bounds, especially for the case $\rho = 6$.

The present method works for $\rho \geq 6$. For $\rho = 5$, the corresponding nonlinear system of equation has no non-negative solution. The technique used in [5] also gives no results for the cases $\rho \leq 6$ (at least without further non-trivial refinements).

## 5.2 Linear lower bounds on the optimal values

**Theorem 5.** *The optimal Morse potential function has the linear lower bound for different $\rho$ values:*

$$\begin{aligned}
-177.6190601n &\leq M_6^* \\
-97.52208250n &\leq M_7^* \\
-69.76159670n &\leq M_8^* \\
-55.71197450n &\leq M_9^* \\
-47.25499588n &\leq M_{10}^* \\
-41.61681210n &\leq M_{11}^* \\
-37.59385566n &\leq M_{12}^* \\
-34.58070042n &\leq M_{13}^* \\
-32.24012281n &\leq M_{14}^* \\
-30.36965466n &\leq M_{15}^*
\end{aligned}$$

*Proof.* The values in the statement can be derived by the considerations from section 3.1 and from the numerical result of section 5.1, thus the proof is omitted. □

| $\rho$ | $q$ from [5] | $q$ by the general method |
|---|---|---|
| 6 | 0.114 | 0.4985948046 |
| 7 | 0.376 | 0.6113121449 |
| 8 | 0.468 | 0.6796501438 |
| 9 | 0.528 | 0.7268978345 |
| 10 | 0.574 | 0.7618207355 |
| 11 | 0.613 | 0.7887781722 |
| 12 | 0.644 | 0.8102494106 |
| 13 | 0.672 | 0.8277671751 |
| 14 | 0.695 | 0.8423362542 |
| 15 | 0.715 | 0.8546451536 |

Table 1: Lower bounds for the minimal distances in optimal Morse clusters for different $\rho$.

# 6 Summary

The method introduced in this paper can be used to obtain minimal inter-particle distance in optimal atom clusters. For the usage, only natural requirements are supposed for the pair potential function. Linear lower bounds on the optimal potential energy is also established. As application, new results for the Lennard-Jones and Morse clusters are derived. These theoretical results can be used for accelerating global optimization methods.

# Acknowledgment

The author would like to thank Prof. Arnold Neumaier (University of Vienna) for the introduction to this topic and his valuable suggestions and ideas. The author is grateful to the two anonymous referees for the valuable comments and suggestions which have led to better quality in the explanations.

# References

[1] X. Blanc. Lower bounds for the interatomic distance in Lennard-Jones clusters. *Computational Optimization and Applications*, 29:5-12, 2004.

[2] J.P.K. Doye, R.H. Leary, M. Locatelli and F. Schoen. The global optimization of Morse clusters by potential energy transformations. *INFORMS Journal On Computing*, 16:371-379, 2004.

[3] H.X. Huang, P. Pardalos and Z.J. Shen. Equivalent formulations and necessary optimality conditions for the Lennard-Jones problem. *Journal of Global Optimization*, 22:97-118, 2002.

[4] M. Locatelli and F. Schoen. Fast global optimization of difficult Lennard-Jones clusters *Computational Optimization and Applications*, 21:55-70, 2002.

[5] M. Locatelli and F. Schoen. Minimal interatomic distance in Morse-clusters. *Journal of Global Optimization*, 22:175-190, 2002.

[6] The Maplesoft Product Site, `http://www.maplesoft.com`

[7] C. Maranas and C. Floudas. A global optimization approach for Lennard-Jones microclusters. *Journal of Chemical Physics*, 97:7667-7678, 1992.

[8] J.A. Northby. Structure and binding of Lennard-Jones clusters: $13 \leq n \leq 147$. *Journal of Chemical Physics*, 87:6166-6178, 1987.

[9] G. L. Xue, R. S. Maier, and J. B. Rosen. Minimizing the Lennard-Jones potential function on a massively parallel computer. *Proceedings of the 6th international conference on Supercomputing*, 409-416, 1992.

[10] G.L. Xue. Improvements on the Northby algorithm for molecular conformation: better solutions. *Journal of Global Optimization*, 4:425-440, 1994.

[11] G.L. Xue. Minimum inter-particle distance at global minimizers of Lennard-Jones clusters. *Journal of Global Optimization*, 11:83-90, 1997.

[12] G.L. Xue. An $O(n)$ time hierarchical tree algorithm for computing force field in $n$-body simulations. *Theoretical Computer Science*, 197:157-169, 1998.

*Received July, 2004*