Journal of Global Optimization, 11, 83–90 (1997)


# Minimum Inter-Particle Distance at Global Minimizers of Lennard-Jones Clusters

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**Abstract.** In computer simulations of molecular conformation and protein folding, a significant part of computing time is spent in the evaluation of potential energy functions and force fields. Therefore many algorithms for fast evaluation of potential energy functions and force fields are proposed in the literature. However, most of these algorithms assume that the particles are uniformly distributed in order to guarantee good performance. In this paper, we prove that the minimum inter-particle distance at any global minimizer of Lennard-Jones clusters is bounded away from zero by a positive constant which is independent of the number of particles. As a by-product, we also prove that the global minimum of an $n$ particle Lennard-Jones cluster is bounded between two linear functions. Our first result is useful in the design of fast algorithms for potential function and force field evaluation. Our second result can be used to decide how good a local minimizer is.

**Keywords:** Minimum inter-particle distance, global minimizers, Lennard-Jones cluster.

## 1. Introduction

Computer simulation has become a very important tool in the study of molecular conformation and the prediction of the 3D structure of a protein, given the sequence of amino-acid [7]. It is generally believed that the optimal structure of a protein or a cluster of particles corresponds to a global minimizer of a potential energy function associated with the cluster [5, 6].

While these computer simulations require weeks or months CPU time on a modern supercomputer, a significant part of the computing time is spent in the evaluation of potential energy functions and force fields [6]. Therefore many algorithms for fast evaluation of potential energy functions and force fields are proposed in the literature [1, 2, 3, 4]. [9] noticed that the most expensive part of the commonly used potential energy functions is the pair-wise Lennard-Jones potential energy function and therefore concentrated on fast evaluation of Lennard-Jones potential energy functions of a cluster of $n$ particles. However, most of these algorithms assume that the particles are uniformly distributed in order to guarantee good performance.

In this paper, we prove that the minimum inter-particle distance at any global minimizer of a Lennard-Jones cluster is bounded away from zero by a positive con-

*THE RESEARCH OF THIS AUTHOR WAS SUPPORTED IN PART BY NATIONAL SCIENCE FOUNDATION GRANT ASC-9409285.

stant which is independent of the number of particles in the cluster. Although it seems simple from a pure physics point of view, this is the first mathematical proof for the problem model. Based on previous computational results, we believe that the maximum inter-particle distance at any global minimizer of an $n$ particle Lennard-Jones cluster is bounded from above by $O(n^{\frac{1}{3}})$. This essentially says that the particles are almost uniformly distributed near the global minimizer and therefore the algorithms [1, 2, 3, 4, 9] will all have good performance near the global minimizer. Therefore we can concentrate on the design of force field evaluation algorithms that are efficient for almost uniformly distributed clusters. As a by-product, we also prove that the global minimum of an $n$ particle Lennard-Jones cluster is bounded between two linear functions. This is an improvement over a result in [8].

The rest of this paper is organized as follows. In section 2, we define the Lennard-Jones potential energy function and present some of its basic properties. In section 3, we prove the theorem on minimum inter-particle distance. In section 4, we prove the bound on the optimal objective function value. We conclude the paper with some further research directions in section 5.

## 2. The Lennard-Jones Potential Energy Function

**Definition 21** *The Lennard-Jones pair potential function is defined as*

$$v(r) = \frac{1}{r^{12}} - \frac{2}{r^6}, r > 0. \tag{1}$$

This function defines the pair-wise reaction between two particles at a distance of $r$. It can be seen from Figure 1 that the two particles push one another when the distance is smaller than 1 and attract one another when the distance is greater than 1. The reaction becomes extremely strong when $r$ approaches 0 and vanishes when $r$ approaches $\infty$.

A Lennard-Jones cluster of $n$ particles is associated with the following potential energy function.

**Definition 22** *Let $x_1, x_2, \cdots, x_n$ be a cluster of $n$ particles in the 3 dimensional Euclidean space. The Lennard-Jones potential energy function for this cluster is defined as*

$$f(x) = \sum_{1 \le i < j \le n} v(||x_i - x_j||), \tag{2}$$

*where $||\bullet||$ represents the Euclidean norm.*

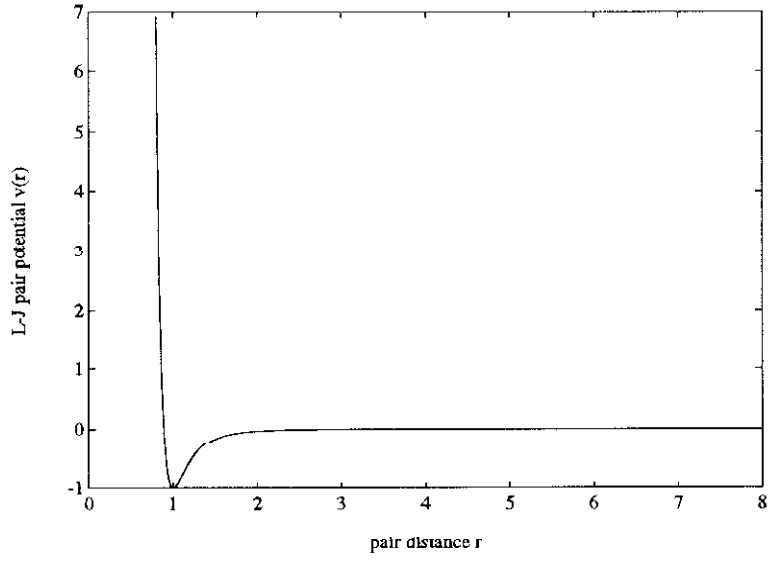


*Figure 1.* The Lennard-Jones pair potential function

**Definition 23** *Let $x_1, x_2, \cdots, x_n$ be a cluster of $n$ particles in the 3 dimensional Euclidean space. The potential energy function due to $x_i$ is*

$$f_i(x) = \sum_{j \neq i} v(||x_i - x_j||). \tag{3}$$

Clearly, the Lennard-Jones potential energy function for a cluster of particles is half of the sum of potentials due to each of the particles.

In molecular conformation and protein folding, people are interested in the global minimizers of the potential energy function. In this paper, we are interested in the minimum inter-particle distance at global minimizers of $f(x)$. In the rest of this paper, we will present some basic properties of the Lennard-Jones potential function.

**Theorem 1** *The following are true for the Lennard-Jones pair potential function.*

- $v(r) \geq -1$ *for* $0 < r < \infty$.
- $v(r) > 0$ *for* $0 < r < (\frac{1}{2})^{\frac{1}{6}}$.
- $v(r) = 0$ *for* $r = (\frac{1}{2})^{\frac{1}{6}}$.

- $v(r) < 0$ *for* $r > (\frac{1}{2})^{\frac{1}{6}}$.
- $v'(r) < 0$ *for* $0 < r < 1$.
- $v'(r) = 0$ *for* $r = 1$.
- $v'(r) > 0$ *for* $r > 1$.
- $v''(r) > 0$ *for* $1 < r < (\frac{13}{7})^{\frac{1}{6}}$.
- $v''(r) = 0$ *for* $r = (\frac{13}{7})^{\frac{1}{6}}$.
- $v''(r) < 0$ *for* $r > (\frac{13}{7})^{\frac{1}{6}}$. □

**Theorem 2** *Let* $f_{min}(n)$ *be the global minimum of the Lennard-Jones function for a cluster of* $n$ *particles. Then*

$$f_{min}(n) \leq -(n-1). \tag{4}$$

**Proof.** Place the particles such that $x_i$ is at $(i, 0, 0)$. The corresponding potential function is

$$\begin{aligned} f(x) &= \sum_{1 \leq i < j \leq n} v(||x_i - x_j||) && (5) \\ &\leq \sum_{i=1}^{n-1} v(||x_i - x_{i+1}||) && (6) \\ &= -(n-1). && (7) \end{aligned}$$

Therefore the glohal minimum of $f(x)$ is no greater than that. □.

**Theorem 3** *Let* $y$ *be a global minimizer of* $f(x)$. *Then* $f_i(y) < 0, (i = 1, 2, \ldots, n)$.

**Proof.** Suppose that $f_i(y) \geq 0$ for some $i$. Let $z$ be defined such that $z_j = y_j$ for all $j \neq i$ and that $||z_i - z_j|| \geq 1$ for all $j \neq i$. Then $f_i(z) < 0$. Therefore we have

$$\begin{aligned} f(z) &= f(y) + f_i(z) - f_i(y) && (8) \\ &\leq f(y) + f_i(z) && (9) \\ &< f(y). && (10) \end{aligned}$$

This is in contradiction with the assumption that $f_i(y) \geq 0$. □.

## 3. Minimum Inter-Particle Distance

**Theorem 4** *The minimum inter-particle distance at any global minimizer of $f(x)$ is greater than or equal to 0.5.*

**Proof.** Let $y$ be a global minimizer for $f(x)$. Let $r$ be the minimum inter-particle distance at this global minimizer. If $r \geq 0.5$, there is nothing to be proved. In the rest, we assume that $r < 0.5$. Without loss of generality, we may assume that $y_1 = 0$ and that

$$r = ||y_2 - y_1|| \leq ||y_3 - y_1|| \leq \cdots \leq ||y_n - y_1||. \tag{11}$$

The proof of this theorem consists of several lemmas. In the following, we will use the notation

$$r_j = ||y_j - y_1||, j = 2, 3, \ldots, n. \tag{12}$$

**Lemma 1** *The number of $r_j$'s that are less than or equal to $1 + kr + \frac{r}{2}$ is bounded by $(\frac{3+k}{r})^3$ for any positive real number $k$.*

**Proof** Since $r$ is the minimum inter-particle distance, we may assume that each particle is a ball of radius $\frac{r}{2}$. The number of $r_j$'s that are less than or equal to $1 + kr + \frac{r}{2}$ can not exceed the number of balls with radius $\frac{r}{2}$ that can he contained in the ball centered at $y_1$ with radius $1 + kr + \frac{r}{2} + \frac{r}{2}$. It follows from a simple volume comparison that this number is bounded by

$$\frac{(1 + kr + \frac{r}{2} + \frac{r}{2})^3}{(\frac{r}{2})^3} = (\frac{2 + 2(k+1)r}{r})^3 \leq (\frac{3+k}{r})^3. \tag{13}$$

This proves the lemma. □

**Lemma 2** *The number of $r_j$'s such that*

$$1 + 2kr + \frac{r}{2} < r_j \leq 1 + 2(k+1)r + \frac{r}{2} \tag{14}$$

*is bounded by $18(\frac{2k+5}{r})^2$ for any positive real number $k$.*

**Proof.** By volume comparison, an upper bound is given by

$$\frac{(1 + 2(k+1)r + \frac{r}{2} + \frac{r}{2})^3 - (1 + 2(k)r + \frac{r}{2} - \frac{r}{2})^3}{(\frac{r}{2})^3} \tag{15}$$

$$= (\frac{2}{r} + 4(k+1) + 2)^3 - (\frac{2}{r} + 4k)^3 \tag{16}$$

$$= 6[(\frac{2}{r} + 4k + 6)^2 + (\frac{2}{r} + 4k + 6)(\frac{2}{r} + 4k) + (\frac{2}{r} + 4k)^2] \tag{17}$$

$$\leq 18(\frac{2}{r} + 4k + 6)^2 \tag{18}$$

$$\leq 18(\frac{2k+5}{r})^2. \tag{19}$$

This proves the lemma. □

**Lemma 3** $\sum_{r_j \le 1+4.5r} v(r_j) \ge v(r_1) - (\frac{7}{r})^3$.

**Proof.** The number of $r_j$'s that are less than or equal to $1+4.5r$ is bounded by $(\frac{7}{r})^3$. One of them is $r_1$. Therefore $\sum_{r_j \le 1+4.5r} v(r_j) \ge v(r_1) - (\frac{7}{r})^3$. □

**Lemma 4** $\sum_{r_j > 1+4.5r} v(r_j) \ge -\frac{36}{r^8} \sum_{k=2}^{\infty} \frac{(2k+5)^2}{(2k+2.5)^6}$.

**Proof.**

$$\sum_{r_j > 1+4.5r} v(r_j) \tag{20}$$

$$\ge -2 \sum_{r_j > 1+4.5r} \frac{1}{{r_j}^6} \tag{21}$$

$$= -2 \sum_{k=2}^{\infty} \sum_{1+2kr+0.5r < r_j \le 1+2(k+1)r+0.5r} \frac{1}{{r_j}^6} \tag{22}$$

$$\ge -2 \sum_{k=2}^{\infty} \sum_{1+2kr+0.5r < r_j \le 1+2(k+1)r+0.5r} (\frac{1}{1+2kr+0.5r})^6 \tag{23}$$

$$\ge -2 \sum_{k=2}^{\infty} (18(\frac{2k+5}{r})^2)(\frac{1}{1+2kr+0.5r})^6 \tag{24}$$

$$= -36 \sum_{k=2}^{\infty} (\frac{2k+5}{r})^2 (\frac{1}{1+2kr+0.5r})^6 \tag{25}$$

$$= -\frac{36}{r^8} \sum_{k=2}^{\infty} \frac{(2k+5)^2}{(\frac{1}{r}+2k+0.5)^6} \tag{26}$$

$$= -\frac{36}{r^8} \sum_{k=2}^{\infty} \frac{(2k+5)^2}{(2k+2.5)^6} \tag{27}$$

$$\tag{28}$$

This proves the lemma. □

Now we can finish the proof of the theorem. From Theorem 2.3 we know that $f_1(y)$ is negative. From the above lemmas, we know that

$$f_1(y) = \sum_{r_j \le 1+4.5r} v(r_j) + \sum_{r_j > 1+4.5r} v(r_j) \tag{29}$$

$$\ge v(r) - (\frac{7}{r})^3 - \frac{0.06}{r^8} \tag{30}$$

$$\ge \frac{1}{r^{12}} - \frac{2}{r^6} - (\frac{7}{r})^3 - \frac{0.06}{r^8}. \tag{31}$$

$$\tag{32}$$

From the above, we know that $r \ge 0.5$. The contradiction proves the theorem. □

## 4. Bound on Optimal Objective Function Value

In molecular conformation, people are interested in finding the global minimizer of the potential energy function [5]. Since the Lennard-Jones potential function has many local minimizers, it is very hard to verify that a local minimizer is a global one. If we know a tight lower bound on the optimal objective function value, we would know how good a local minimizer is.

For the Lennard-Jones cluster, $-O(n^2)$ is a trivial lower bound. In [8], the first non-trivial lower bound of $-O(n^{\frac{19}{13}})$ on the optimal objective function value was prove. They also proved that the optimal objective function value is bounded between two linear functions under the assumption that the minimum inter-particle distance is bounded away from zero. The following theorem is a corollary of Theorem 2.3 in this paper and Theorem 2.2 of [8].

**Theorem 5** *There exist positive constants $\alpha$ and $\beta$ such that*

$$-\alpha n \geq f_{min}(n) \geq -\beta n, n = 2, 3, \cdots; \tag{33}$$

*where $f_{min}(n)$ is the global minimum function value of the Lennard-Jones potential energy function of an $n$ particle cluster.* □

## 5. Conclusions and Further Research

In this paper, we have proved that the minimum inter-particle distance at any global minimizer of a Lennard Jones cluster is bounded away from zero by a positive constant which is independent of the number of particles in the cluster. As a by-product, we also established the first linear lower bound on the optimal objective function value. While these theoretical results are important, further studies are necessary to make them more useful in applications. It would be very important to obtain a linear lower bound for the optimal objective function for the Lennard-Jones cluster that are tight for many values of $n$. Based on previous computational results [5], we make the following conjecture.

**Conjecture 51** *The maximum inter-particle distance at any global minimizer of Lennard-Jones clusters is bounded from above by $O(n^{\frac{1}{3}})$, where $n$ is the number of particles in the cluster.*

Provided that it is true, Conjecture 5.1 and Theorem 3.1 essentially says that the particles are almost uniformly distributed near a global minimizer. Therefore most of the algorithms for fast evaluation of potential energy functions and force fields [1, 2, 4] would have good performance near the global minimizer.

## Acknowledgment

The author would like to thank Jorge Moré and Panos Pardalos for many helpful discussions.

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