New bounds for atomic clusters*

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Abstract

This paper introduces a general method for obtaining lower bounds for the total energy and the minimal inter-particle distance in optimal atom cluster problems with pair potential functions under weak general conditions on the pair potential. The bounds obtained are sharper than those previously known for both the Lennard-Jones potential and various Morse potentials. Statistics on the putative optimal structures for Lennard-Jones clusters (taken from sources on the WWW) are also presented.

Keywords: atom clusters, lower bounds, minimal distance, Lennard-Jones clusters, Morse clusters.

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1 Introduction

In computational chemistry, many applications lead to global optimization problems, since typically only the global minimizer of the free energy corresponds to a situation matching reality. In this paper we consider a very simple model describing atom clusters, where only the energy between pairs of atoms are taken into account. These models are known to be reasonably realistic for inert gas clusters.

Given a cluster of n atoms in d-dimensional space ($d > 1$), define the coordinate vectors $x_i \in \mathbb{R}^d$ ($i = 1, \ldots, n$) as the center of the ith atom. The potential energy of the cluster $x = (x_1, \ldots, x_n) \in \mathbb{R}^{dn}$ is then 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

$$r_{ij} = \|x_i - x_j\|_2$$

is the Euclidean distance of x_i and x_j and $V(r)$ is the value of the pair potential for two particles at distance r. We shall assume that V is bounded below, is positive for small r, takes somewhere negative values, and $V(r) \to 0$ for $r \to \infty$, and define, for a global minimizer $s > 0$, the **unimodal hull**

$$v(r) := \begin{cases} \min\{V(r') \mid r' \le r\} & \text{for } r \le s, \\ \min\{V(r') \mid r' \ge r\} & \text{for } r \ge s. \end{cases}$$

$v(r)$ is a continuous, piecewise differentiable function, decreasing for $r \le s$ and increasing for $r \ge s$. Moreover, $v(r) = V(r)$ if V already has this property. The definition implies that

$$v(s) < 0, \quad v(r) \ge v(s) \ \text{ for } r \ne s. \tag{2}$$

The aim of this paper is to obtain lower bounds for the total energy and for the minimal interatomic distance in the optimal structure of (1) assuming only that the pair potential satisfies the additional property

(P) There is some $R \in [0, s]$ such that

$$\int_s^\infty \left\lfloor \left(\frac{2r}{R} + 1\right)^d \right\rfloor v'(r)dr < \min\left\{v(R) + |v(s)|, \frac{1}{2}v(R) + \frac{3}{2}|v(s)|\right\}.$$

Note that this property is automatically satisfied with $R = 0$ if the potential $V(r)$ diverges for $r \to 0$.

Since $v(r) \le V(r)$ in general, the lower bounds generated from $v(r)$ are also bounds for the original. Thus we may take without loss of generality $V(r) = v(r)$, and, for simplicity, we also refer to the function v as pair potential.

Previous results. General results on the topics of the present paper can be found in physics or chemistry books and articles. In particular, the book by Ruelle [12] contains

in Section 2.3 (see also the references given there) related investigations, also under quite general assumptions. Ruelle calls a pair potential function *stable* if the associated total energy of a cluster is bounded from below by a linear function of the cluster size, and proves sufficient conditions for stability (see Proposition 3.2.7 and 3.2.8 in [12]) but without giving explicit formulas for the resulting bounds.

In the field of computer science, a number of papers deal with the topic of the present work. However, they consider only special pair-potential functions. The paper by Xue *et al.* [15] contains the first explicit nonzero lower bound for the minimal distance in Lennard-Jones cluster. They also proved (independently of Ruelle) that the global optimum can be bounded from below and above by an expression linear in the number of atoms. Maranas & Floudas [9] proved other results for the minimal distance in Lennard-Jones clusters. In particular, they established bounds that are functions of the number of atoms, useful for small n. A second paper by Xue [16] contains a lower bound for inter-particle distance in the optimal Lennard-Jones cluster which is independent of the number of atoms in the cluster. Improved lower bounds for the same potential function in two and three dimensions were obtained by Blanc [1]. A preprint of Huang [6] claiming even better bounds for the Lennard-Jones clusters had been available on the Web for some time but was later retracted since it contained a severe error in the proof of the main result.

For Morse clusters, Locatelli & Shoen [8] established lower bounds for the interatomic distance in the optimal structures. In a recent paper of Vinkó [13] a general method was introduced to obtain lower bounds on the minimal distance and linear lower bounds on the total energy for general potential functions satisfying natural asymptotic properties. Better bounds for the Lennard-Jones and Morse clusters were found, but the improved bounds for the Morse clusters depend on the weaker results by Locatelli and Schoen.

In this paper we give a general method which can handle directly a wide class of potential functions. The theoretical results are applied numerically to the Lennard-Jones and Morse clusters. All numerical computations in Section 4 and Section 6 were done both with MuPAD [10] and Mathematica [14], to be sure the correctness of the results we obtained. This was found necessary since earlier computations done using Maple 9 turned out to yield erroneous results, due to a bug in Maple 9 that miscalculates numerical integrals involving the floor function in the integrand. Note that Mathematica provided faster evaluation times than MuPad.

Notation. The following notation will be used. A global minimizer of the function E is any configuration $x^* \in \mathbb{R}^{dn}$ with

$$E^* := E(x^*) = \min_{x \in \mathbb{R}^{dn}} E(x), \tag{3}$$

where $d > 1$ is the dimension of the space containing the cluster. (Of interest are mainly $d = 2$ and $d = 3$.) Let r_{ij} be the Euclidean distance of the points x_i^* and x_j^* $(i, j = 1, \ldots, n)$. The **potential energy** of particle i in an arbitrary configuration x is defined as

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

and we put

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

Clearly, the total energy is

$$E(x) = \frac{1}{2}\sum_{i=1}^{n} E_i(x). \tag{4}$$

If the number of atoms is to be emphasized, the notation $E^*(n)$ and $E_i^*(n)$ is used for the optimal total energy and for the optimal potential energy of particle i, respectively.

We write R_k for the minimum over i of the kth smallest distance of some atom from x_i. Then $R_1 = 0$, and

$$R_2 = r_{\min} := \min_{i,j} r_{ij} \quad (i, j = 1, \ldots, n) \tag{5}$$

is the minimal distance in the optimal configuration. We give some atom (to be determined later) the label 1 and label the remaining atoms such that $r_i := r_{1i}$ satisfies

$$0 = r_1 \le r_2 \le \ldots \le r_n.$$

In the applications to Lennard-Jones clusters and Morse clusters, the unique zero of the potential is denoted by t. Thus $v(t) = 0$.

2 Energy bounds

In this section we prove bounds on the optimal total energy. We first generalize considerations by Maranas & Floudas [9] for the Lennard-Jones potential.

Lemma 1. *An optimal n-atom cluster has total energy bounded by*

$$-\frac{n(n-1)}{2}|v(s)| \le E^*(n) \le -d(n-d+1)|v(s)|. \tag{6}$$

Proof. Since $v(r_{ij}) - v(s) \ge 0$, we have

$$\begin{aligned} E^*(n) &= \sum_{i<j} \Big(v(r_{ij}) - v(s) + v(s)\Big) \\ &= \sum_{i<j} \Big(v(r_{ij}) - v(s)\Big) + \sum_{i<j} v(s) \\ &\ge -\frac{n(n-1)}{2}|v(s)|, \end{aligned}$$

giving the lower bound.

If we construct a cluster containing n atom where $n-d$ particles are in a position that each of them touches (i.e., has minimal distance s to) d others, starting with d particles in such a way that the distances between these points are s (i.e., a line segment in dimension 2, an equilateral triangle in dimension 3, and so on), we get a cluster of total energy $-d|v(s)| - d(n-d)|v(s)| + M \le -d(n-d+1)|v(s)|$ with nonpositive M. Thus this is an upper bound for the total energy of the optimal structure. Since $M < 0$, the upper bound follows. □

Lemma 2. *In the optimal configuration the potential energy of particle i can be bounded by*

$$-(n-1)|v(s)| \le E_i^*(n) < -e_d|v(s)|, \tag{7}$$

where $e_d = 1$.

Proof. To prove the upper bound, 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 $\|z_i - z_l\| \ge s$ for all $l \neq i$. Then place the atom z_i on the line determined by the origin and the coordinates of z_k in such a way that z_i has the maximal r_j value. Thus $E_i(z) < -|v(s)|$. By construction of z,

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

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

$$E^* - E_i^* = E(z) - E_i(z) > E(z) + |v(s)| \ge E^* + |v(s)|,$$

we find the upper bound $E_i^* < -|v(s)|$. The lower bound comes from the fact that $v(r)$ is monotone decreasing in the interval $[0, s]$ and from the definition of $E_i^*(n)$. Indeed, the formula for $E_i^*(n)$ contains $n-1$ terms and all of them have the lower bound $-|v(s)|$. □

Remark. The upper bound in (7) is in fact independent from the dimension and the size of the given optimal cluster. Huang [6] tried to strengthen the above argument (for the Lennard-Jones cluster) to show that $e_d = d$ (for $n > d = 3$) since the optimal structure most likely has d contacts, but showing this rigorously seems to be nontrivial, so that the statement remains open. The results in Section 5 indicate the empirical correctness of the bound with $e_d = d$ at least for $d = 3$ and the Lennard-Jones cluster, and that a much better value cannot be expected.

To get size-independent lower bounds on E_i^* and linear lower bounds on the total energy, we proceed to find upper and lower bounds on sums of the form

$$\Sigma_m := \sum_{k=2}^{m} v(r_k).$$

Let $N_d(r)$ be the maximal number of disjoint open unit balls fitting into a ball of radius r. By a simple volume comparison one can easily find the upper bound

$$N_d(r) \le \lfloor r^d \rfloor, \tag{8}$$

which we shall use in the following. Any improvement in this geometric packing bound would result in corresponding improvements of our estimates depending on it.

Proposition 1. *Let*

$$K(r) := \min_{m \in \mathbb{N}, R_m > 0} (m-1) N_d\Big(\frac{2r}{R_m} + 1\Big).$$

Then K is an increasing function of r, and

$$k \le K(r_k) \quad \textit{for all } k = 1, 2, \ldots. \tag{9}$$

In particular,

$$K(r) \le (m-1)\Big\lfloor \Big(\frac{2r}{R_m} + 1\Big)^d \Big\rfloor \quad \textit{for all } m = 2, 3, \ldots. \tag{10}$$

Proof. Fix $k \geq 1$ and $m \geq 2$. We consider the set S consisting of the k atoms closest to atom 1. We recursively pick an atom from S, starting with atom 1, and remove it and the $m-2$ atoms nearest to it from S, until S is empty. This picks a set of $\kappa = \lceil k/(m-1) \rceil$ atoms at mutual distance at least R_m. Thus the open balls of radius $R_m/2$ around these atoms are disjoint and inside the open ball of radius $r_k + R_m/2 = (2r_k + R_m)/2$ around the atom labelled 1. A scaling argument gives

$$\kappa \leq N_d\Big(\frac{2r_k}{R_m} + 1\Big),$$

hence

$$k \leq (m-1)\kappa \leq (m-1)N_d\Big(\frac{2r_k}{R_m} + 1\Big) \leq (m-1)\Big\lfloor \Big(\frac{2r_k}{R_m} + 1\Big)^d \Big\rfloor.$$

□

Proposition 2. *If $r_m \leq s$ then*

$$\Sigma_m \leq -m|v(s)| + E_1^* + \int_s^\infty K(r)v'(r)dr. \tag{11}$$

Moreover, if $m \geq 2$ and $R_m \leq s$ then

$$(m-1)v(R_m) + (m + e_d)|v(s)| \leq \int_s^\infty K(r)v'(r)dr. \tag{12}$$

Proof. Let first m be the largest integer with $r_m \leq s$. Then

$$K(r) \geq K(r_m) \geq m \quad \text{for } r \geq s$$

by proposition 1, and $r_{m+1} > s$, hence $v(r_{k+1}) - v(r_k) \geq 0$ for $k \geq m+1$. Therefore, with $r_{n+1} = \infty$, $v(\infty) = 0$, we have

$$\begin{aligned}\sum_{k=m+1}^{n} k(v(r_{k+1}) - v(r_k)) &\leq \sum_{k=m+1}^{n} K(r_k)\int_{r_k}^{r_{k+1}} v'(r)dr \\ &\leq \sum_{k=m+1}^{n}\int_{r_k}^{r_{k+1}} K(r)v'(r)dr = \int_{r_{m+1}}^{\infty} K(r)v'(r)dr.\end{aligned}$$

The left hand side equals

$$-mv(r_{m+1}) - \sum_{k=m+1}^{n} v(r_k) = -mv(r_{m+1}) - E_1^* + \Sigma_m,$$

and since $\int_r^\infty v'(r)dr = -v(r)$, we find

$$\begin{aligned}\Sigma_m &\leq E_1^* + \int_{r_{m+1}}^\infty (K(r) - m)v'(r)dr \leq E_1^* + \int_s^\infty (K(r) - m)v'(r)dr \\ &\leq E_1^* + mv(s) + \int_s^\infty K(r)v'(r)dr.\end{aligned}$$

This proves (11) for the maximal allowed value of m. Since

$$\Sigma_m - mv(s) = \sum_{k=2}^{m} (v(r_k) - v(s)) - v(s)$$

is a sum of nonnegative numbers, the left hand side is monotone increasing in m; thus (11) also holds for all smaller values of m.

By definition of R_m, one can label some atom as 1 such that $r_m = R_m$. In this case, we have for $k < m$ the trivial lower bound

$$\Sigma_m \geq (m-1)v(R_m).$$

Combining this inequality with (11) and with $E_1^* < -e_d|v(s)|$ gives (12). □

Theorem 1. *If*

$$B := -|v(s)| + \int_s^\infty K(r)v'(r)dr < \infty \tag{13}$$

then

$$E_i^* \geq -B \quad \textit{for all } i = 1, \ldots, n. \tag{14}$$

Moreover, for any constant B satisfying (14)*,*

$$-\frac{B}{2}n \leq E^*. \tag{15}$$

Proof. The special case $m = 1$ of (11) gives

$$0 = \Sigma_1 \leq -|v(s)| + E_1^* + \int_s^\infty K(r)v'(r)dr = E_1^* + B$$

which leads to (14) for $i = 1$. Since the choice of the label 1 is arbitrary, (14) holds for all i. Finally, (15) follows from (4). □

Corollary 1. *If q is a lower bound on the minimal inter-particle distance $r_{\min}$ then* (14) *holds with*

$$B := -|v(s)| + \int_s^\infty \left\lfloor \left(\frac{2r}{q} + 1\right)^d \right\rfloor v'(r)dr. \tag{16}$$

Proof. Using (10) for $m = 2$ and (5), we can bound B as defined in (13) by

$$B \leq -|v(s)| + \int_s^\infty \left\lfloor \left(\frac{2r}{r_{\min}} + 1\right)^d \right\rfloor v'(r)dr \leq -|v(s)| + \int_s^\infty \left\lfloor \left(\frac{2r}{q} + 1\right)^d \right\rfloor v'(r)dr.$$

□

As mentioned in the introduction, Ruelle [12] calls a potential function **stable** if the energy of the optimal cluster is bounded below by a multiple of the cluster size. We summarize his

sufficient conditions for stability in [12, Section 3.2.6]. We say that a continuous function f is of **positive type** if

$$\sum_{i=1}^{n}\sum_{j=1}^{n} f(x_i - x_j) \geq 0. \tag{17}$$

In general it is not trivial to show that a pair potential function is of positive type, but RUELLE [12] quotes the known result (BOCHNER [2]) that f is of positive type if and only if the Fourier transform of f is of positive type.

Proposition 3. (RUELLE [12]) *If the pair potential v is of positive type and $v(0)$ is finite then it is stable, and*

$$-\frac{n}{2}v(0) \leq E^*. \tag{18}$$

Proof.

$$0 \leq \sum_{i=1}^{n}\sum_{j=1}^{n} v(||x_i^* - x_j^*||) = nv(0) + 2\sum_{i<j} v(||x_i^* - x_j^*||),$$

hence

$$-\frac{v(0)}{2}n \leq \sum_{i<j} v(||x_i^* - x_j^*||).$$

□

3 Bounds on the minimal distance

Theorem 1 depends on a lower bound for the minimal inter-particle distance. This section is devoted to obtain such lower bounds.

Lemma 3. *If $n > 2 + e_d$ then*

$$q(n) = w\Big((n - 2 - e_d)|v(s)|\Big) \tag{19}$$

is a lower bound for the minimal inter-particle distance in the optimal configuration. Here w is the inverse function of v, defined by

$$w(x) = \begin{cases} r & \text{iff } x = v(r) \text{ and } r \geq s, \\ 0 & \text{otherwise.} \end{cases}$$

Proof. Let $E_1^*(n)$ be the term which contains the minimal distance in the optimal structure. Using Lemma 2, we find

$$\begin{aligned} -e_d|v(s)| &> \sum_{j=2}^{n} v(r_j) \\ &= \sum_{j=3}^{n} v(r_j) + v(r_2) \\ &\geq -(n-2)|v(s)| + v(r_2). \end{aligned}$$

Rearranging the inequalities one obtains $v(r_2) < (n-2-e_d)|v(s)|$, which gives (19). □

This result generalizes an argument given by HUANG [6] for the Lennard-Jones potential (with different proof), except that he used the unproved (but heuristically plausible) assumption $e_d = d = 3$.

Lemma 4. *In the optimal configuration the minimal interatomic distance is always less than or equal to the minimizer point of the pair potential function, i.e., $r_{\min} \le s$ holds.*

Proof. Suppose that in the optimal configuration $r_{\min} > s$. We know that function v is increasing for $r \ge s$. Hence, rescaling all of the distances such that $r_{\min} = s$ decreases the total energy. Thus $r_{\min} \le s$. □

Theorem 2. *Let $[\underline{R}, \overline{R}] \subseteq [0, s]$ be such that*

$$\int_s^\infty \left\lfloor \left(\frac{2r}{R}+1\right)^d \right\rfloor v'(r)dr \le v(R) + |v(s)| \quad \text{for all } R \in [\underline{R}, \overline{R}], \tag{20}$$

$$\int_s^\infty \left\lfloor \left(\frac{2r}{\overline{R}}+1\right)^d \right\rfloor v'(r)dr < \min\left\{ v(\underline{R}) + |v(s)|, \frac{1}{2}v(\underline{R}) + (1+\frac{e_d}{2})|v(s)| \right\}. \tag{21}$$

Then the function defined by

$$f(q) := v(q) + (2+e_d)|v(s)| - \int_s^\infty \left\lfloor \left(\frac{2r}{q}+1\right)^d \right\rfloor v'(r)dr \tag{22}$$

has a smallest zero q in $]\overline{R}, \infty[$, and we have then $r_{\min} \ge q$.

Note that property (P) implies the satisfiability of the assumption (take $\underline{R} = \overline{R} = R$.)

Proof. For any integer $m \ge 2$ we find from (10) and (12) that $R = R_m$ satisfies

$$(m-1)v(R) + (m+e_d)|v(s)| \le \int_s^\infty (m-1)\left\lfloor \left(\frac{2r}{R}+1\right)^d \right\rfloor v'(r)dr,$$

hence

$$v(R) + |v(s)| < v(R) + \frac{m+e_d}{m-1}|v(s)| \le \int_s^\infty \left\lfloor \left(\frac{2r}{R}+1\right)^d \right\rfloor v'(r)dr.$$

This contradicts (20) unless

$$R_m < \underline{R} \quad \text{or} \quad R_m > \overline{R}.$$

If the first case can happen for some $m \ge 2$, let m be the largest integer such that $R_m < \underline{R}$. Then $R_{m+1} > \overline{R}$, hence

$$K(r) \le m \left\lfloor \left(\frac{2r}{R_{m+1}}+1\right)^d \right\rfloor \le m \left\lfloor \left(\frac{2r}{\overline{R}}+1\right)^d \right\rfloor,$$

and since $v(\underline{R}) \leq v(R_m)$, we find from (12) that

$$\frac{1}{m}\Big((m-1)v(\underline{R}) + (m+e_d)|v(s)|\Big) \leq \int_s^\infty \left\lfloor \Big(\frac{2r}{\overline{R}} + 1\Big)^d \right\rfloor v'(r)dr.$$

The left hand side is monotone in m, hence extremal at the boundary, and since $m \geq 2$, this contradicts (21). Thus the first case cannot happen. In particular, we find for $m = 2$ that

$$r_{\min} = R_2 > \overline{R}.$$

Since (12) implies for $m = 2$ that $f(r_{\min}) \leq 0$ and (20) implies $f(\overline{R}) > 2|v(s)| > 0$, the intermediate value theorem implies that f has a zero in $]\overline{R}, \infty[$, and that $r_{\min}$ cannot be smaller than the smallest such zero. □

4 Lennard-Jones clusters

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

In general form the Lennard-Jones pair potential function is

$$v_{t,\varepsilon}(r) = 4\varepsilon\Big[\Big(\frac{t}{r}\Big)^{12} - \Big(\frac{t}{r}\Big)^{6}\Big], \tag{23}$$

where t is the zero of the pair potential, ε is the pair well depth and

$$s = 2^{1/6}t$$

is the pair separation at equilibrium. In the literature, one usually considers either the **scaled version** (with $s = 1, \varepsilon = 1$) or **reduced units** (with $t = 1, \varepsilon = 1$). Note that the property (P) required for the application of the general method is trivially satisfied with $R = 0$.

Using (1) and (23), the Lennard-Jones potential function is defined by

$$LJ_{t,\varepsilon}(x) = \sum_{1 \leq i < j \leq n} v_{t,\varepsilon}(\|x_i - x_j\|). \tag{24}$$

Size dependent bound for the minimal distance. Lemma 3 gives $v_{t,\varepsilon} \leq (n-2-e_d)|v(s)|$. From this inequality it follows for the optimal Lennard-Jones atom cluster problem that if $n > 2 + e_d$, then

$$q(n) = s\Big(\frac{\sqrt{\varepsilon^2 + \varepsilon|v_{t,\varepsilon}(s)|(n-2-e_d)} - \varepsilon}{(n-2-e_d)|v_{t,\varepsilon}(s)|}\Big)^{\frac{1}{6}} \tag{25}$$

is a lower bound for the minimal inter-particle distance.

For the case of the scaled version, the bound (25) can be compared with the result by Maranas & Floudas [9] for $d = 3$ and $s = 1$, and turns out to be better than the latter when $n > 6$.

Size independent bounds. Inequality (20) gives the exclusion intervals $[0, 0.653775s]$ and $[0, 0.752915s]$ for $d = 3$ and $d = 2$, respectively. Thus in this case $v_{t,\varepsilon}(\underline{R}) = \infty$. Hence solving equation (22) gives for $d = 3$,

$$q = 0.654673s = 0.734846t \tag{26}$$

and for $d = 2$

$$q = 0.759006s = 0.851955t \tag{27}$$

as lower bounds for $r_{\min}$.

Table 1 compares the new lower bounds obtained here with earlier bounds for the (two and three dimensional) scaled Lennard-Jones potential. The $d = 2$ value for Vinkó was computed from the formulas given in [13], since there an explicit value was not stated.

dimension	Xue [16]	Blanc [1]	Vinkó [13]	present work
2	–	0.7286	(0.7284)	0.7590
3	0.5	0.6108	0.6187	0.6547

Table 1: Lower bounds for the inter-particle distances in optimal scaled Lennard-Jones clusters.

Linear lower bound on the optimal value. Theorem 1 implies the following linear lower bounds the total energy of Lennard-Jones clusters with $d = 3$,

$$-68.9554\varepsilon n \leq LJ^*_{t,\varepsilon},$$

and $d = 2$,

$$-9.4478\varepsilon n \leq LJ^*_{t,\varepsilon}.$$

5 Experimental statistics for Lennard-Jones clusters

As a continuation of the previous section, some empirical statistics are presented for the Lennard-Jones clusters with reduced unit. The data are taken from the Cambridge Cluster Database (CCD) [3] and the Chemoinformatics Laboratory at the University of Science and Technology of China [4]. At the websites cited, one can find for the Lennard-Jones problem with reduced units the best known configurations (in many cases believed to be the global minima) together with the coordinates of the minimizers for $n \leq 1000$.

In this section, $d = 3$, and the notation $E^* = LJ^*_{1,1}$ is used. The global minimum values, bounds for E^*_i and the minimal and maximal interatomic distance are considered as functions of the number of atoms.

Global minimum values. In Figure 1 (a) putative global minimum values are displayed. To see that the energy level of the optimal configurations are bounded linearly we plot the

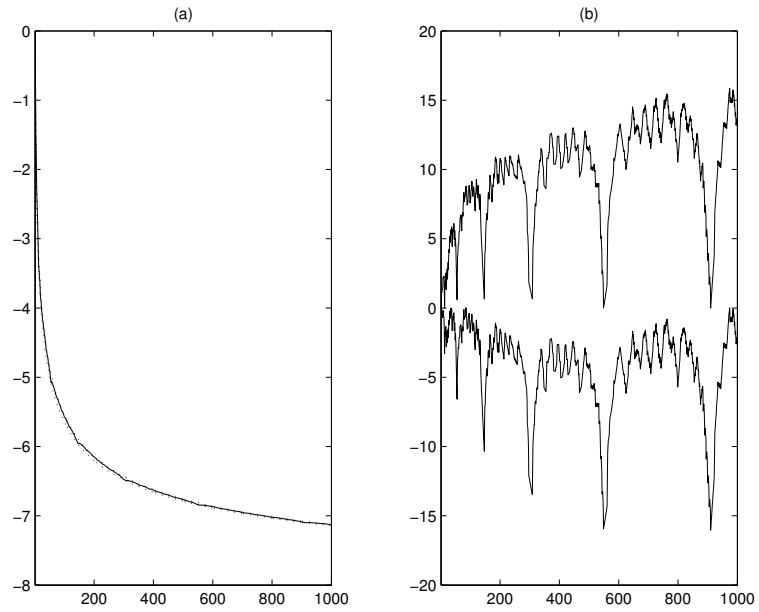

Figure 1: (a) The quotients $E^*/n\varepsilon$ and a cubic fit in $n^{1/3}$, (b) differences to over- and underestimating bounds.

quotients $E^*(n)/n\varepsilon$. The figure shows also results of a cubic fit in $n^{1/3}$. A polynomial lower bound for E^* is

$$-8.6263n - 59.0267n^{2/3} - 66.9958n^{1/3},$$

hence the true asymptotic lower bound for $E^*(n)/n\varepsilon$ as $n \to \infty$ is (empirically) -8.6263, while our proved lower bound is -68.9554. A similar polynomial upper bound also exists; Figure 1 (b) displays the differences to these under- and overestimating bounds.

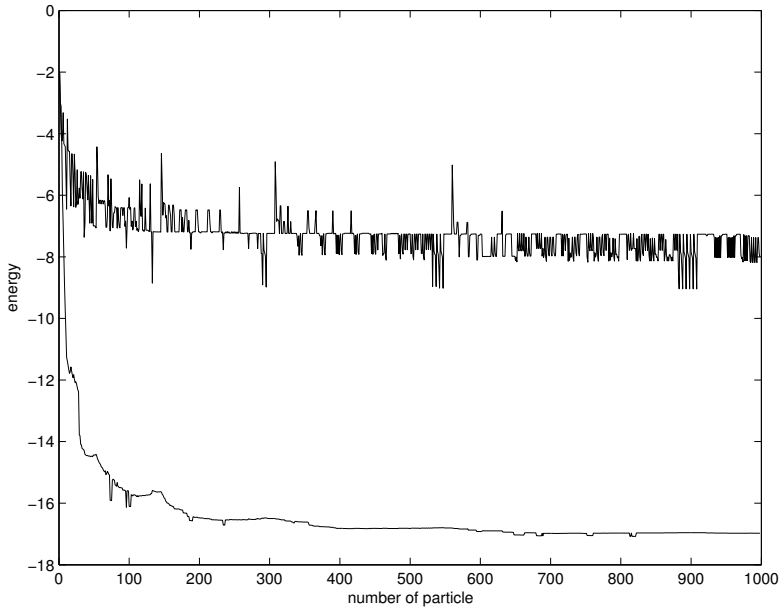

Figure 2: Maximal and minimal E_i^*/ε as a function of cluster size n.

Bounds on particle energies. As we have seen, $E_i^* < -\varepsilon$ ($= -1$ for the scaled and for the reduced version). From the experimental data one can compute the values $\min E_i^*$ and $\max E_i^*$ for every available configuration. In Figure 2 these minimal and the maximal values of E_i^*/ε are shown as function of the number of atoms up to 1000.

Here we can see that Huang's conjecture $\max E_i^* < -3\varepsilon$ (cf. Section 2) holds empirically.

For $n > 30$, the quotient $\min E_i^*/\varepsilon$ oscillates between the values -14 and -17.1 (the exact minimum value is -17.0799 for the case $n = 823$), while our bound from Section 4 is -137.9108.

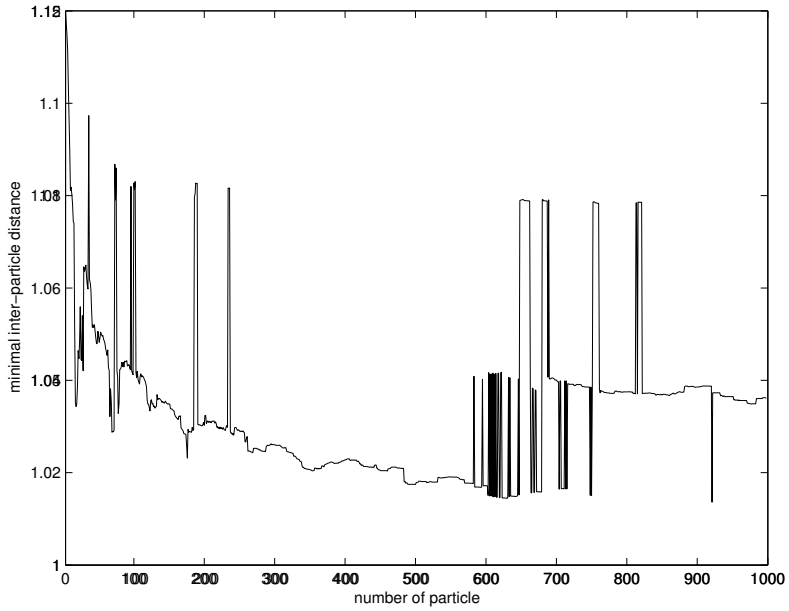

Figure 3: Scaled ($\varepsilon = 1$) minimal inter-particle distances as a function of cluster size n.

Bounds on minimal distances. Figure 3 shows the value of $r_{\min}/t$ for the best configurations known. From these data we can see that the minimal inter-particle distance is always greater than the zero of the Lennard-Jones pair potential function. Figure 3 makes one wonder whether there is a phase transition between around 580 and 700, or whether the strange behavior is due to the unreliability of the present list of putative global minimizers.

Bounds on maximal distances. Xue [16] conjectured that the diameter of the optimal Lennard-Jones cluster (equivalently the maximal distance) is bounded above by $\mathcal{O}(n^{1/3})$. While no theoretical results are known, Figure 4 shows this conjecture to be empirically well-founded. Blanc [1] proved that the maximal distance in the optimal Lennard-Jones cluster is bounded by n.

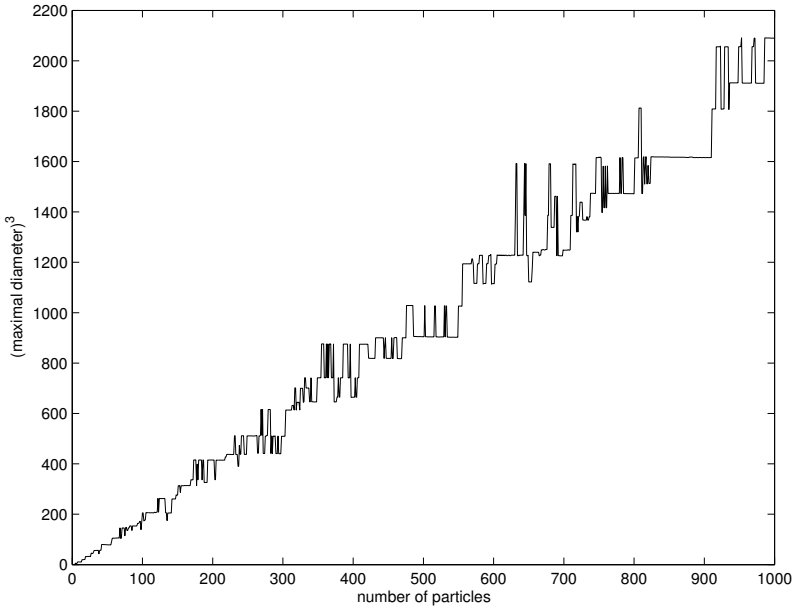

Figure 4: Third power of maximal distance (in reduced units, $t = 1$) as a function of cluster size n.

6 Morse clusters

The pair potential function for Morse clusters is

$$v_\rho(r) = e^{\rho(1-r)}\Big(e^{\rho(1-r)} - 2\Big), \tag{28}$$

where $\rho > 0$ is a parameter. Using (28) and (1), the Morse potential function is defined by

$$M_\rho(x) = \sum_{1\le i<j\le n} v_\rho(\|x_i - x_j\|). \tag{29}$$

The zero t and the minimizer s of the function v_ρ are given by

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

respectively. (Note that our general assumptions require the existence of a positive zero, hence $\rho > \ln 2$.)

For $\rho = 6$, the Morse and the scaled Lennard-Jones pair potential are related; they have the same curvature at the minimum point $r = 1$. In the context of global optimization, the cases $\rho > 6$ are most interesting, since these are more difficult problems than finding the optimal Lennard-Jones structures (see Doye *et al.* [5]). On the other hand, finding minimal interatomic distance in the optimal Morse cluster becomes more difficult as ρ becomes smaller and the pair potential becomes less repulsive at small distances.

Size dependent bound for the minimal distance. Lemma 3 gives $(\exp(\rho(1-r)) - 1)^2 - 1 \le (n - 2 - e_d)|v_\rho(s)|$. From this inequality it follows that

$$q(n) = \max\left\{1 - \rho^{-1}\ln\left(\sqrt{|v_\rho(s)|(n-2-e_d)} + 1\right), 0\right\} \tag{30}$$

is a lower bound for the minimal inter-particle distance of an optimal Morse cluster with $n > 2 + e_d$ particles. This formula yields a strictly positive bound if

$$n \le \left\lfloor (2 + e_d) + \frac{e^\rho(e^\rho - 2)}{|v_\rho(s)|} \right\rfloor .$$

Size independent bound and linear lower bound for the energy. RUELLE [11] proved that if $\rho > \ln 16 \approx 2.7726$, then the Fourier transform of the pair potential v_ρ is of positive type, hence it is stable by Bochner's theorem [2] and Proposition 3. The resulting linear lower bound,

$$-\frac{v_\rho(0)}{2} n \le M_\rho^* \qquad (\rho > \ln 16) \tag{31}$$

is quite poor: For $\rho = 4.967$ (the smallest value for which our property (P) holds) and for $\rho = 15$ formula (31) gives the $-1.0166 \cdot 10^4 n$ and $-5.3432 \cdot 10^{12} n$, respectively.

No bound on the minimal distance is available from Ruelle's argument. The derivation of a size independent bound for the minimal distance of optimal Morse clusters is a nontrivial problem since v_ρ is finite at $r = 0$, i.e., when two particles are in the same position. LOCATELLI & SCHOEN [8] overcame this difficulty and proved (with complicated geometric arguments) that, for $6 \le \rho \le 15$, the minimal distance remains bounded away from zero by a constant independent of the number of particles. Based on their result, VINKÓ [13] further improved these bounds.

ρ	t	$\underline{R}$	$\overline{R}$	q from Theorem 2	q from L&S [8]	q from VINKÓ [13]	new bounds for E_ρ^*
15	0.95379	0.00001	0.86424	0.865683	0.715166	0.854645	$-21.6176n$
14	0.95049	0.00197	0.85320	0.854691	0.694918	0.842336	$-22.5917n$
13	0.94668	0.00039	0.84018	0.841725	0.671606	0.827767	$-23.8037n$
12	0.94224	0.00077	0.82460	0.826193	0.644492	0.810249	$-25.3520n$
11	0.93699	0.00152	0.80559	0.807236	0.612565	0.788778	$-27.3977n$
10	0.93068	0.00302	0.78187	0.783551	0.574381	0.761821	$-30.2230n$
9	0.92298	0.00608	0.75135	0.753054	0.527627	0.726898	$-34.3707n$
8	0.91336	0.01250	0.71045	0.712129	0.467709	0.679650	$-41.0345n$
7	0.90097	0.02663	0.65212	0.653727	0.375988	0.611312	$-53.4416n$
6.353	0.89090	0.04058	0.59809	0.599581	(0.221433)	(0.546518)	$-69.2975n$
6	0.88448	0.06167	0.55928	0.560668	0.113522	0.498595	$-84.4438n$
5	0.86137	0.20982	0.33235	0.333473	–	–	$-365.2798n$
4.967	0.86045	0.23439	0.30471	0.306227	–	–	$-461.7701n$

Table 2: Lower bounds on minimum inter-particle distance and total energy of optimal Morse clusters.

The method presented in this paper provides even sharper results with a simpler proof, valid over a larger range of parameters. Table 2 contains the results of the application of Theorem 2 for Morse clusters, together with the previous results from the literature. Note that the case $\rho = 6.3532$ is the parameter value where the corresponding Morse pair potential has the same zero as the scaled Lennard-Jones pair potential function. The last line ($\rho = 4.967$) shows the smallest ρ where Theorem 2 could be applied. The linear lower bounds for E_ρ obtained from Theorem 1 are also presented.

References

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

[2] S. Bochner. *Lectures on Fourier Integrals*. Princeton University Press, 1959.

[3] The Cambridge Cluster Database, WWW document
`http://brian.ch.cam.ac.uk/CCD.html`

[4] Global minimal energies and coordinates of the LJ clusters, WWW document
`http://chinfo.ustc.edu.cn/chmm/pubmats/LJ/`

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

[6] H.X. Huang. Lower bounds on minimum inter-particle distance at global minima of Lennard-Jones clusters. *Manuscript*, 2004.

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

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

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

[10] MuPAD Research Group. `http://www.mupad.de`

[11] D. Ruelle. Classical statistical mechanics of a system of particles. *Helvetica Physica Acta* 36:183–197, 1963.

[12] D. Ruelle. *Statistical Mechanics – Rigorous Results.* Benjamin, New York. 1969.

[13] T. Vinkó. Minimal inter-particle distance in atom clusters. *Acta Cybernetica* 17:105-119, 2005.
`http://www.inf.u-szeged.hu/~tvinko/mindist_vinko.pdf`

[14] Wolfram Research. Mathematica.
`http://www.wolfram.com/products/mathematica/index.html`

[15] G. L. Xue, R. S. Maier, and J. B. Rosen. Minimizing the Lennard-Jones potential function on a massively parallel computer. *Proc. 6th Int. Conf. Supercomputing.* 409–416, 1992.

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