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Minimal interatomic distance in Morse clusters

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Abstract. In this paper we derive a lower bound, independent from the number of atoms N, for the minimal interatomic distances between atoms in a cluster whose total energy is modelled by means of the so called Morse potential. A similar result was previously proven for Lennard–Jones clusters but the proof can not be extended to Morse clusters. Besides the theoretical interest, the derivation of this lower bound is important for the definition of efficient procedures for the computation of the total energy of clusters with a large number of atoms.

Key words: Morse clusters, Lennard–Jones clusters, Global optimization, Interatomic distances

1. Introduction

The investigation of molecular conformation is one of the most active fields in computational chemistry and molecular biology; given an appropriate model for the potential energy of a molecule or of a cluster of atoms, many approaches have been developed to find the global optimum configuration, i.e., the relative position of atoms which corresponds to the global minimum of the potential energy. The problem itself can be considered as an essentially unconstrained high dimensional global optimization problem in which the decision variables are the three–dimensional coordinates of the center of each atom. Given the positions $x_i, i = 1, ..., N$ of N atoms, or particles, a potential energy $\text{Energy}(x_1, ..., x_N)$ is defined which expresses the contribution to the total energy due to different kinds of interactions between particles. Then the molecular conformation problem can be stated as the global optimization problem

$$\min_{x_1,...,x_N \in I\!R^3} \text{Energy}(x_1, ..., x_N).$$

In the literature many different models have been considered for the accurate definition of the potential energy; many of these include pairwise interactions, as well as more complex interactions due, e.g., to the torsion angles in the cluster. However, it is widely recognized that even very simple models which take into account only pairwise interactions between atoms deserve much interest, both in theory and in practice.

A well known and widely explored model is represented by the Lennard–Jones (LJ) potential

$$LJ(x_1, \ldots, x_N) = \sum_{1 \leqslant i < j \leqslant N} \left[\frac{1}{\|x_i - x_j\|^{12}} - \frac{2}{\|x_i - x_j\|^6} \right].$$

The search for globally optimal solutions of this potential energy model is still very active. Many putative global optimum solutions were detected in (Northby, 1987) through a method based on a search over an icosahedral lattice. Some icosahedral solutions have been improved, e.g., in Coleman et al. (1994), Deaven et al. (1996), Xue (1994), but a remarkable step was the detection of lower energy configurations for some values of N which do not have an icosahedral structure. In Doye et al. (1995), Gomez and Romero (1994) and Pillardy and Piela (1995) a face centered cubic (FCC) solution has been detected for $N = 38$. Decahedral structures were detected in Doye et al. (1995) and Doye and Wales (1995) for N=75–77,102–104. Very recently in Leary and Doye (1999) a tetrahedral structure has been detected for $N = 98$. In Locatelli and Schoen (2001) a compression technique (further analyzed in (Doye, 2000)) has been proposed which considerably reduces the effort needed for detecting the nonicosahedral best known solutions mentioned above. Best known solutions up to $N = 147$ are reported at the web site *http://brian.ch.cam.ac.uk/∼jon/structures/LJ.html*, while best known solutions for $N = 148$–309 are reported at the web site *http://www.vetl.uh.edu/∼cbarron/LJ_cluster/LJpottable.html* (see also Barron et al. (1999)).

Another widely studied energy model is the so called Morse potential. The Morse pair potential is defined as follows

$$E(r; \rho) = e^{\rho(1-r)}[e^{\rho(1-r)} - 2],$$

where $\rho > 0$ is a parameter. The Morse pair potential is employed to define the Morse potential energy for a cluster of N atoms

$$\text{MORSE}(x_1, \ldots, x_N; \rho) = \sum_{i<j} E(\|x_i - x_j\|; \rho).$$

For $\rho = 6$ the Morse pair potential and the LJ pair potential are strictly related. Indeed, they have the same curvature at the minimum point $r = 1$. However, the Morse function introduces a higher degree of flexibility, allowing to model those situations in which the curvature is smaller (for $\rho < 6$) or greater (for $\rho > 6$). For instance, physically meaningful values for sodium and potassium are $\rho = 3.15$ and $\rho = 3.17$, while for C_{60} molecules it is $\rho = 13.62$.

Best known solutions for the Morse potential for different values of N and ρ are reported at the web site *http://brian.ch.cam.ac.uk/∼ jon/structures/Morse.html* (see also Doye and Wales (1997)).

In this paper we wish to find a lower bound, independent from N but dependent on ρ, for the minimal interatomic distance at a globally optimal solution $(x_1^*, \ldots, x_N^*)$ of the Morse potential energy, i.e., a lower bound for

$$r_{\min} = \min_{i \neq j} \|x_i^* - x_j^*\|.$$

The lower bound will be derived in the next section. It must be pointed out that this problem is not only of theoretical interest but has also relevant practical consequences. In Xue (1998) it has been shown that knowledge of a strictly positive lower bound on the minimum interatomic distance is an essential assumption in order to be able to compute the total energy in $O(N)$ time through a special purpose data structure, while direct methods which need to compute the distance between each pair of atoms require $O(N^2)$ time.

2. A lower bound for the minimal interatomic distance

In Xue (1997) an analogous lower bound for $r_{\min}$ is given for the optimal solutions of the LJ potential energy. In this case it is shown that a lower bound for $r_{\min}$ is 0.5. The proof of the result in Xue (1997) is based on an observation which can be easily extended to the Morse potential for any value $\rho > 0$. Let us define the contribution to the total Morse potential energy of the i-th atom of the optimal solution $(x_1^*, \ldots, x_N^*)$ as follows

$$C^N(i; \rho) = \sum_{j \neq i} E(\|x_j^* - x_i^*\|; \rho),$$

which is simply the sum of all the terms in the Morse potential energy in which the i-th atom appears. We note that

$$\text{MORSE}(x_1^*, \ldots, x_N^*; \rho) = \frac{1}{2} \sum_{i=1}^{N} C^N(i; \rho).$$

The proof of the existence of a strictly positive lower bound on the inter-atomic distance for globally optimal Morse cluster will proceed as follows: first it will be shown that the contribution of each single particle to the overall energy, in a global optimum, is negative. This is the simplest part of the proof and the only one in which the assumption of a global optimal cluster is used; then it will be shown that the negative contribution can be split into the sum of a positive and a negative contribution and that the positive one is due to the pairwise interactions between close atoms. Then it will be shown that, given a covering of $\mathbb{R}^3$ with cubes of a prescribed edge length, there exists at least a cube which contains sufficiently many atoms; based on this result, a bound for the positive contribution to the energy is found, from which, based upon the observation that the contribution to the total energy given by the minimum distance pair of atoms cannot be greater than this positive contribution, the final result is found.

Let us start with a simple, but fundamental, property enjoyed by globally optimal Morse clusters.

THEOREM 1. *For a globally optimal Morse cluster, it holds that*

$$C^N(i;\rho) < 0 \qquad 1 \leqslant i \leqslant N, \forall \rho > 0.$$

Proof. The proof is completely analogous to that of a similar result in Xue (1997) for Lennard–Jones clusters: if an atom i in the optimal solution has $C^N(i;\rho) \geqslant 0$ it is possible to move it at a distance greater than 1 from any other atom. In this way $C^N(i;\rho)$ becomes negative and the total energy is reduced, thus contradicting the optimality of the solution.

The result in Xue (1997) starts from this observation and proceeds as follows. Let k be an atom whose minimal distance from the other atoms is equal to $r_{\min}$. If we decrease $r_{\min}$ we have two opposite effects.

Effect 1 The potential energy between atom k and the atom whose distance from atom k is equal to $r_{\min}$ increases.

Effect 2 The number of atoms whose distance from atom k is as close as possible to 1 is allowed to increase so that the sum of the potential energies between these atoms and atom k decreases.

It is shown in Xue (1997) that for Lennard–Jones clusters, if $r_{\min}$ is small enough (in particular for $r_{\min} \leqslant 0.5$) the first effect overcomes the second one and makes it impossible to bring the total contribution of atom k below 0, thus contradicting the result of Theorem 1. This approach works for the Lennard–Jones potential basically because the Lennard–Jones pair potential increases to $+\infty$ as the distance between two atoms decreases to 0. The same is not true for the Morse potential, for which two atoms in the same position, i.e., with distance equal to 0, have a finite pair potential energy. Therefore, the proof for Lennard–Jones clusters can not be directly extended to Morse clusters. As a proof of this fact let us consider the following example. Let us assume that an atom is in the same position of atom k, or, equivalently, that $r_{\min} = 0$. Can we discard this situation by the same argumentation employed above? The answer is no. Indeed, let us place the remaining $N-2$ atoms in the same position at distance 1 from atom k. Then the contribution of atom k is equal to

$$-(N-2) + E(0;\rho),$$

and there exists $\overline{N} = \overline{N}(\rho)$ such that $\forall\, N \geqslant \overline{N}$, $C(k;\rho) < 0$. Therefore, situations such as the one just described can not be simply excluded by the previous argumentation. We need some other way to ensure that such situations can not hold at an optimal solution of the Morse potential energy and to find a lower bound for the minimal interatomic distance in Morse clusters. First we need to introduce some

notation. We denote by $\lambda(\rho) = 1 - \ln 2/\rho$ the unique solution of the equation $E(r; \rho) = 0$ and we assume that $\rho \geqslant \ln 2$. We note that

$$E(r; \rho) > 0 \quad \forall\, r < \lambda(\rho),$$

and

$$E(r; \rho) < 0 \quad \forall\, r > \lambda(\rho).$$

The contribution $C^N(i; \rho)$ of the i-th atom can be split into two terms:

$$L^N(i; \rho) = \sum_{j \neq i:\ \|x_j^* - x_i^*\| < \lambda(\rho)} E(\|x_j^* - x_i^*\|; \rho) > 0$$

and

$$U^N(i; \rho) = \sum_{j \neq i:\ \|x_j^* - x_i^*\| \geqslant \lambda(\rho)} E(\|x_j^* - x_i^*\|; \rho) \leqslant 0.$$

Obviously it holds that

$$C^N(i; \rho) = L^N(i; \rho) + U^N(i; \rho) \qquad \forall\, i.$$

Now we consider an atom k for which the value of L^N is maximum, i.e.

$$k \in \arg\max_i L^N(i; \rho),$$

and we set

$$L^N(\rho) = L^N(k; \rho).$$

Without any loss of generality we can assume that $x_k^* = 0$, i.e. that atom k is in the origin. The following property holds trivially.

THEOREM 2. *It holds that*

$$L^N(\rho) \geqslant E(r_{\min}; \rho).$$

Proof. Let $v_1, v_2 \in \{1, \ldots, N\}$ be such that

$$\|x_{v_1}^* - x_{v_2}^*\| = r_{\min}.$$

Then

$$L^N(v_1; \rho) \geqslant E(r_{\min}; \rho).$$

Since $L^N(\rho) \geqslant L^N(v_1; \rho)$, the observation is proven. □

Now let us consider the spheres S_j, $j = 1, \ldots$ with center $x_k^* = 0$ and radius $2j$, i.e.

$$S_j = \{x :\ \|x\| \leqslant 2j\}.$$

We note that

$$\mathrm{vol}(S_j) = j^3 \mathrm{vol}(S_1). \tag{1}$$

We consider the values

$$d_j = \frac{|\{i : x_i^* \in S_j\}|}{\mathrm{vol}(S_j)},$$

defining the densities of atoms in the optimal solution belonging to the spheres S_j. If we denote with

$$d^* = \max_{j \geqslant 1} d_j,$$

the maximal density of atoms of the optimal solution in the spheres S_j, then we will be able to obtain a lower bound on d^*. First however we need a technical result:

LEMMA 3. *For any* $a > 13 + \sqrt{149}/2$

$$\sum_{j=2}^{\infty} j^3 a^{-j} \leqslant \frac{9}{(a-1)^2} \tag{2}$$

Proof. From classical results on the summation of series, we have

$$\begin{aligned}\sum_{j=0}^{\infty} j^3 a^{-j} &= \frac{a}{(a-1)^2}\left(1 + \frac{6}{(a-1)} + \frac{6}{(a-1)^2}\right) \\ &= a\frac{1+4a+a^2}{(a-1)^4}\end{aligned}$$

for $a > 1$. From this we obtain

$$\begin{aligned}\sum_{j=2}^{\infty} j^3 a^{-j} &= \sum_{j=0}^{\infty} j^3 a^{-j} - a^{-1} \\ &= \frac{a\left(1+4a+a^2\right)}{(a-1)^4} - \frac{1}{a} \\ &= \frac{8a^3 - 5a^2 + 4a - 1}{(a-1)^4 a} \\ &\leqslant \frac{8a^3 - 5a^2 + 4a}{(a-1)^4 a} \\ &= \frac{8a^2 - 5a + 4}{(a-1)^4} \\ &\leqslant \frac{9}{(a-1)^2}\end{aligned}$$

which holds for a sufficiently large. In particular it can be easily seen that the inequality holds for $a > (13 + \sqrt{149})/2$. □

Now we are ready to prove the result on the density of atoms.

LEMMA 4. *The maximal density of atoms in the spheres S_j, $j = 1, \ldots,$ satisfies the following inequality*

$$d^* \geqslant \frac{\mu(\rho) L^N(\rho)}{vol(S_1)},$$

where

$$\mu(\rho) = 1 - 18\frac{e^{3\rho}}{(e^{2\rho} - 1)^2}$$

The inequality is non-trivial only when $\mu(\rho) \geqslant 0$, i.e. only for ρ sufficiently large. In particular it is sufficient that $\rho \geqslant 3.2$.

Proof. First we recall that, in view of Theorem 1 it must hold that

$$C^N(k; \rho) = L^N(\rho) + U^N(k; \rho) < 0,$$

or, equivalently, that

$$U^N(k; \rho) < -L^N(\rho). \tag{3}$$

Let, for any $j \geqslant 1$,

$$Sol_j = \{x_i^* : \ x_i^* \in S_j \setminus S_{j-1}\},$$

denote the set of atoms in the optimal solution belonging to the set $S_j \setminus S_{j-1}$ (the set S_0 is defined as the empty set). Then,

$$U^N(k; \rho) \geqslant - \mid \mathrm{Sol}_1 \mid + \sum_{j=2}^{\infty} E(2j - 2; \rho) \mid \mathrm{Sol}_j \mid .$$

Now, let us assume that

$$\exists \bar{\jmath} \geqslant 2 : \ \mid Sol_{\bar{\jmath}} \mid \geqslant \bar{\jmath}^3 L^N(\rho). \tag{4}$$

Then, recalling also (1)

$$d_{\bar{\jmath}} = \frac{\mid \cup_{i=1}^{\bar{\jmath}} \mathrm{Sol}_i \mid}{\mathrm{vol}(S_{\bar{\jmath}})} \geqslant \frac{\mid \mathrm{Sol}_{\bar{\jmath}} \mid}{\bar{\jmath}^3 \mathrm{vol}(S_1)} \geqslant \frac{L^N(\rho)}{\mathrm{vol}(S_1)}.$$

Since $d^* \geqslant d_{\bar{\jmath}}$ and $\mu(\rho) < 1$ the result of the lemma immediately follows.
Therefore, we only need to prove the result when (4) does not hold, i.e. when

$$\mid \mathrm{Sol}_j \mid < j^3 L^N(\rho) \qquad \forall\, j \geqslant 2.$$

In this case it follows that

$$U(k;\rho) \geqslant -\mid \mathrm{Sol}_1 \mid + L^N(\rho) \sum_{j=2}^{\infty} j^3 E(2j-2;\rho).$$

From Lemma 3, we obtain

$$\begin{aligned} \sum_{j=2}^{\infty} j^3 E(2j-2;\rho) &= \sum_{j=2}^{\infty} j^3 e^{\rho(3-2j)}(e^{\rho(3-2j)}-2) \\ &\geqslant -2e^{3\rho} \sum_{j=2}^{\infty} j^3 e^{-2\rho j} \\ &\geqslant -2e^{3\rho} \frac{9}{(e^{2\rho}-1)^2} \end{aligned}$$

Thus

$$U(k;\rho) \geqslant -\mid \mathrm{Sol}_1 \mid -18 L^N(\rho) \frac{e^{3\rho}}{(e^{2\rho}-1)^2}$$

Recalling (3), it must also hold that

$$-\mid \mathrm{Sol}_1 \mid -18 L^N(\rho) \frac{e^{3\rho}}{(e^{2\rho}-1)^2} < -L^N(\rho),$$

i.e.,

$$\mid \mathrm{Sol}_1 \mid > \left(1 - 18 \frac{e^{3\rho}}{(e^{2\rho}-1)^2}\right) L^N(\rho)$$

and the result of the lemma immediately follows. □

Now let us consider, for any sphere S_j a cover of this sphere with $\Omega_j(\ell)$ cubes whose edge length is $\ell > 0$, with $\ell < \lambda(\rho)$. An upper bound on the number of cubes necessary to cover S_j is given by $\lceil (4/\ell) \rceil^3 j^3$, but, through complete enumeration, it is possible to obtain better bounds by eliminating cubes whose intersection with S_j is empty. As an example, the following lemma gives an upper bound for the minimal number $\Omega_j(1/3)$ of cubes with edge length $1/3$ which are necessary to cover S_j.

LEMMA 5. *It holds that*

$$\Omega_j(1/3) \leqslant 1256 j^3.$$

Proof. We first derive an upper bound for Ω_1. An obvious bound is obtained by considering the cube

$$C = \{(x, y, z) \,:\, -2 \leqslant x, y, z \leqslant 2\},$$

which contains S_1, and partitioning it into $4^3 * 3^3 = 1728$ subcubes with edge length $\frac{1}{3}$. Obviously, these subcubes also form a cover of S_1, so that $\Omega_1 \leqslant 1728$. But some of these subcubes have an empty intersection with S_1 and they can be eliminated. Now we want to derive the number of subcubes which can be eliminated. By symmetry we can restrict our attention to the subcubes in

$$C' = \{(x, y, z) \ : \ 0 \leqslant x, y, z \leqslant 2\}.$$

Each subcube in C' is identified by the coordinates

$$\left(\frac{i_1}{3}, \frac{i_2}{3}, \frac{i_3}{3}\right) \quad i_1, i_2, i_3 \in \{0, \ldots, 5\}, \tag{5}$$

of its vertex closest to the origin (which is also the center of S_1). For this reason the subcube is indicated as $C(i_1, i_2, i_3)$. A subcube $C(i_1, i_2, i_3)$ can be eliminated if its vertex (5) has distance from the origin not lower than 2, the radius of S_1, i.e., if

$$\frac{i_1^2}{9} + \frac{i_2^2}{9} + \frac{i_3^2}{9} \geqslant 4.$$

Through complete enumeration, we can easily see that the total number of subcubes in C' which can be eliminated is 59. By symmetry this number is multiplied by 8 to give the total number of subcubes which can be eliminated in cube C. Therefore,

$$\Omega_1(1/3) \leqslant 1728 - 59 * 8 = 1256.$$

What has been proven above for S_1 can be immediately extended to S_j to give the upper bound $1256 * j^3$ for $\Omega_j(1/3)$. □

The following lemma gives a lower bound for the number of atoms contained in at least one subcube with edge length ℓ.

LEMMA 6. *There exists at least one cube with edge length ℓ containing at least*

$$\beta = \left\lceil \frac{\mu(\rho) L^N(\rho)}{\Omega_1(\ell)} \right\rceil$$

atoms of the optimal solution.

Proof. Given the density d_j, $j \geqslant 1$, of atoms belonging to the optimal solution and contained in the sphere S_j, it holds, in view of (1) that

$$\text{vol}(S_j) d_j = j^3 \text{vol}(S_1) d_j$$

It follows that at least one of the $j^3 \Omega_1(\ell)$ cubes with edge length ℓ which cover S_j, contains, in its intersection with S_j, at least

$$\left\lceil \frac{j^3 \text{vol}(S_1) d_j}{\Omega_1(\ell) j^3} \right\rceil = \left\lceil \frac{\text{vol}(S_1) d_j}{\Omega_1(\ell)} \right\rceil$$

atoms of the optimal solution. In view of Lemma 4, for some $\bar{\jmath} \geqslant 1$ it holds that

$$\left\lceil \frac{\mathrm{vol}(S_1) d_{\bar{\jmath}}}{\Omega_1(\ell)} \right\rceil \geqslant \left\lceil \frac{\mu(\rho) L^N(\rho)}{\Omega_1(\ell)} \right\rceil,$$

as we wanted to prove. □

Now we can proceed towards finding a lower bound on the minimal interatomic distance, which is the main aim of this paper. Before proceeding, we still need another technical result. Let C be the unit cube in $\mathbb{R}^3$, $[0, 1]^3$, and let us assume that it has been subdivided into eight equal cubes of edge length $1/2$. Let us assume that two points, X and Y are chosen in the unit cube such that $X \in [0, 1/2]^3$ and $Y \in [1/2, 1]^3$. Then the following result holds.

LEMMA 7. *The minimal distance between any point in the cube and the points X and Y is at most $\sqrt{6}/2$, i.e.*

$$\max_{Z \in C} \min\{\|Z - X\|, \|Z - Y\|\} \leqslant \frac{\sqrt{6}}{2};$$

this bound cannot be improved.

Proof. Any point Z in the unit cube belongs to one of the eight cubes of edge length $1/2$ in which the unit cube has been subdivided. If Z belongs to the cube containing either X or Y, the thesis is obviously satisfied. Otherwise, Z belongs to one of the remaining six cubes. Any such cube has a two-dimensional face in common with either $[0, 1/2]^3$ or $[1/2, 1]^3$. Thus Z belongs to a parallelepiped containing either X or Y, whose edges measure 1, $1/2$ and $1/2$ respectively and whose diameter is thus $\sqrt{6}/2$. The bound cannot be improved, as it is immediately seen choosing for example $X = (0, 0, 0)$, $Y = (1, 1/2, 1/2)$, $Z = (0, 1, 1)$. □

Next lemma gives a lower bound for the value $L^N(h; \rho)$ of at least one atom h of the optimal solution.

LEMMA 8. *If ρ is sufficiently large and ℓ and ρ are such that*

$$\sqrt{3}\ell + \frac{\ln 2}{\rho} < 1$$

then

$$L^N(\rho) \leqslant L^*(\ell, \rho) = \max \left\{ \frac{E\left(\frac{\sqrt{6}}{2}\ell; \rho\right)}{\frac{\mu(\rho)}{2\Omega_1(\ell)}\left(E\left(\frac{\sqrt{6}}{2}\ell; \rho\right) + E\left(\sqrt{3}\ell; \rho\right)\right) - 1}, \right. \tag{6}$$
$$\left. \frac{E\left(\frac{\sqrt{3}}{2}\ell; \rho\right)}{\frac{\mu(\rho)}{4\Omega_1(\ell)}\left(E\left(\frac{\sqrt{3}}{2}\ell; \rho\right) + 3E\left(\frac{3}{2}\ell; \rho\right)\right) - 1} \right\}$$

Proof. In view of Lemma 6 there exists at least one cube $\mathcal{C}$ with edge length ℓ containing at least β atoms of the optimal solution. Let us subdivide this cube into eight equal cubes, each one with edge length $\ell/2$. Let us call 'opposite' any two such subcubes which have only a vertex in common. There are only two possibilities:

1. there exist at least two opposite cubes each of which contains at least an atom;
2. in any pair of opposite cubes at least one of the cubes contains no atom. Thus all atoms are contained in at most 4 subcubes.

Let us first consider the first situation; thanks to Lemma 7, two spheres of radius $\ell\sqrt{6}/2$ centered in such two atoms cover the cube and, thus, contain all the atoms in the cube. Then, by symmetry, there exists at least an atom x_h^* in one of these two subcubes such that at least $\beta_1 \geqslant \beta/2$ of the atoms of the cube $\mathcal{C}$ are within a distance of $\ell\sqrt{6}/2$ from x_h^*; let us denote by $\mathcal{S}$ the sphere centered in x_h^* with radius $\ell\sqrt{6}/2$. Then

$$\left|\left|x_h^* - x_j^*\right|\right| \leqslant \begin{cases} \frac{\sqrt{6}}{2}\ell & \text{if } x_j^* \in \mathcal{C} \cap \mathcal{S} \\ \\ \sqrt{3}\ell & \text{otherwise} \end{cases}.$$

From the hypothesis, it holds that $\sqrt{3}\ell < \lambda(\rho)$; thus

$$\begin{aligned} L^N(h;\rho) &= \sum_{j\neq h:\ \|x_h^* - x_j^*\| < \lambda(\rho)} E(\|x_h^* - x_j^*\|;\rho) \\ &\geqslant (\beta_1 - 1)\, E\left(\frac{\sqrt{6}}{2}\ell;\rho\right) + (\beta - \beta_1)\, E\left(\sqrt{3}\ell;\rho\right) \end{aligned}$$

and, recalling that $E\left(\frac{\sqrt{6}}{2}\ell;\rho\right) > E\left(\sqrt{3}\ell;\rho\right)$, we further obtain

$$L^N(h;\rho) \geqslant \left(\frac{\beta}{2} - 1\right) E\left(\frac{\sqrt{6}}{2}\ell;\rho\right) + \frac{\beta}{2} E\left(\sqrt{3}\ell;\rho\right);$$

as $L^N(\rho) \geqslant L^N(h;\rho)$, it follows immediately that

$$L^N(\rho) \geqslant \frac{\beta}{2}\left(E\left(\frac{\sqrt{6}}{2}\ell;\rho\right) + E\left(\sqrt{3}\ell;\rho\right)\right) - E\left(\frac{\sqrt{6}}{2}\ell;\rho\right).$$

Now, recalling the definition of β,

$$L^N(\rho) \geqslant \frac{L^N(\rho)\mu(\rho)}{2\Omega_1(\ell)}\left(E\left(\frac{\sqrt{6}}{2}\ell;\rho\right) + E\left(\sqrt{3}\ell;\rho\right)\right) - E\left(\frac{\sqrt{6}}{2}\ell;\rho\right).$$

from which

$$L^N(\rho)\left(\frac{\mu(\rho)}{2\Omega_1(\ell)}\left(E\left(\frac{\sqrt{6}}{2}\ell;\rho\right) + E\left(\sqrt{3}\ell;\rho\right)\right) - 1\right) \leqslant E\left(\frac{\sqrt{6}}{2}\ell;\rho\right).$$

Noticing that, if $\rho \to \infty$, $\mu(\rho) \to 1$ and

$$E\left(\frac{\sqrt{6}}{2}\ell; \rho\right) + E\left(\sqrt{3}\ell; \rho\right) \to +\infty,$$

the coefficient of $L^N(\rho)$ will be positive for ρ big enough, the thesis immediately follows.

If on the other hand in every pair of opposite cubes there always exists an empty cube, it is immediately seen that all the atoms must lie inside four of the eight subcubes, so that there must exist a cube of edge length $\ell/2$ containing at least $\beta/4$ atoms. Chosen any atom x_h^* in such a cube it is immediately seen that $\beta/4-1$ atoms are within $\ell\sqrt{3}/2$ distance from it; recalling that no atom is placed in the subcube of edge length $\ell/2$ having only a vertex in common with the one containing x_h^*, each of the remaining $3\beta/4$ atoms lies in a parallelepiped with edge lengths $\ell, \ell, \ell/2$ and, thus, they are within a maximum distance of

$$\sqrt{2\ell^2 + \frac{\ell^2}{4}} = \frac{3}{2}\ell$$

from x_h^*. Thus, following a similar proof as given above, it is readily seen that, in this case,

$$L^N(\rho)\left(\frac{\mu(\rho)}{\Omega_1(\ell)}\,\frac{1}{4}\left(E(\frac{\sqrt{3}}{2}\ell; \rho) + 3E(\frac{3}{2}\ell; \rho)\right) - 1\right) \leqslant E\left(\frac{\sqrt{3}}{2}\ell; \rho\right).$$

From this the thesis follows. □

Now we are ready for the final theorem.

THEOREM 9. *If ρ is large enough and ℓ is such that $\sqrt{3}\ell + \frac{\ln 2}{\rho} < 1$, then the minimal interatomic distance r_{min} between two atoms of an optimal solution of the Morse potential satisfies the following condition:*

$$E(r_{min}; \rho) \leqslant L^*(\ell, \rho). \tag{7}$$

Proof. Recalling Theorem 2:

$$E(r_{\min}; \rho) \leqslant L^N(\rho);$$

the thesis immediately follows. □

Condition (7) can now be applied to derive lower bounds for some values of ρ. For instance, choosing $\ell = 1/3$ it holds $\Omega_1(\ell) \leqslant 1256$ and it can be seen that Theorem 7 holds provided that $\rho \geqslant 6.3$ approximately. For instance, if $\rho = 7$ the following results hold:

$$\mu(7) \approx 0.98359 \quad E\left(\frac{\sqrt{6}}{6}; 7\right) \approx 3836.2 \quad E\left(\frac{\sqrt{3}}{3}; 7\right) \approx 332.79$$

and

$$E\left(\frac{\sqrt{3}}{6};7\right)\approx 20841.35 \quad E\,(1;7)\approx 1030.40$$

so that condition (7) becomes

$$E(r_{\min};7)\leqslant \max\left\{\begin{array}{c}\dfrac{3836.2}{\frac{0.98359}{2512}(3836.2+332.79)-1}\approx 6066.1\\ \dfrac{20841.35}{\frac{0.98359}{1256}\frac{1}{4}(20841.35+3\times 1030.40)-1}\approx 5655.0\end{array}\right\}$$

and, numerically solving the equation $E(r_{\min},7)=6066.1$ the bound

$$r_{\min}\geqslant 0.37599$$

is obtained. The table below reports some results on the minimal interatomic distance for different values of ρ:

ρ	$r_{\min}$
7	0.376
8	0.468
9	0.528
10	0.574
11	0.613
12	0.644
13	0.672
14	0.695
15	0.715

We also observe that, when $\rho\to\infty$,

$$\frac{E\left(\frac{\sqrt{6}}{6};\rho\right)}{\frac{\mu(\rho)}{2512}\left(E\left(\frac{\sqrt{6}}{6};\rho\right)+E\left(\frac{\sqrt{3}}{3};\rho\right)\right)-1}\to 2512$$

and

$$\frac{E\left(\frac{\sqrt{3}}{6};\rho\right)}{\frac{\mu(\rho)}{4\times 1256}\left(E\left(\frac{\sqrt{3}}{6};\rho\right)+3E\left(\frac{1}{2};\rho\right)\right)-1}\to 5024$$

However we also have that, if $\ell<1$, $E(\ell,\rho)\to\infty$ as $\rho\to\infty$, so that $r_{\min}$ must converge to 1, as expected.

2.1. THE CASE $\rho = 6$

We would also like to be able to find a lower bound for the minimal interatomic distance when $\rho = 6$, a case in which the resulting clusters have a structure which is almost identical to that of Lennard-Jones ones; however, the reasoning which led us to discover lower bounds for $\rho \geqslant 7$ does not hold for the case $\rho = 6$ as the denominator in the first term in (6) becomes negative; the second term can be evaluated as 33 264. In order to be able to find a lower bound, further refinements are necessary. A possibility is to iterate the reasoning which led to Lemma 8 with a finer subdivision of the cube. Let us assume that the cube with edge length $1/3$ is subdivided into eight subcubes, each of edge length $1/6$; the subcube $\mathcal{C}'$ with the highest number of atoms will contain at least $\frac{\beta}{8}$ atoms; let us assume that this subcube is further subdivided into eight subcubes of edge length $\frac{1}{12}$. There are two possibilities: either two of these subcubes with only a vertex in common both contain an atom of the global optimum, or the $\frac{\beta}{8}$ atoms belong to only four of the eight subcubes. We can thus follow a reasoning similar to that which led us to Lemma 8; however, we can take also into account the fact that the $\frac{7}{8}\beta$ remaining atoms cannot be concentrated in few subcubes. It is easy to show that a valid bound can be obtained by observing that no more than $\frac{3}{8}\beta$ atoms may belong to the three subcubes of edge length $\frac{1}{6}$ which have a planar face in common with $\mathcal{C}'$, no more than $\frac{3}{8}\beta$ can be placed in the three subcubes which have only an edge in common with $\mathcal{C}'$, while at most $\frac{1}{8}\beta$ belong to the subcube which is opposite to $\mathcal{C}'$. These two cases correspond respectively to

$$\frac{E(\frac{1}{12}\sqrt{6}, 6)}{\frac{\mu(6)}{1256}(\frac{1}{16}E(\frac{1}{12}\sqrt{6}, 6) + \frac{1}{16}E(\frac{\sqrt{3}}{6}, 6) + \frac{3}{8}E(\frac{1}{6}\sqrt{6}, 6) + \frac{3}{8}E(\frac{1}{2}, 6) + \frac{1}{8}E(\frac{1}{3}\sqrt{3}, 6)) - 1},$$

(approximately equal to 41 270), and

$$\frac{E(\frac{1}{12}\sqrt{3}, 6)}{\frac{\mu(6)}{1256}(\frac{1}{32}E(\frac{1}{12}\sqrt{3}, 6) + \frac{3}{32}E(\frac{3}{12}, 6) + \frac{3}{8}E(\frac{1}{6}\sqrt{6}, 6) + \frac{3}{8}E(\frac{1}{2}, 6) + \frac{1}{8}E(\frac{1}{3}\sqrt{3}, 6)) - 1}$$

($\approx$ 41 203). It is then readily obtained that $L^N(6)$ is bounded by the maximum between 41 270, 41 203 and 33 264, from which

$$E(r_{\min}, 6) \leqslant 41270.,$$

which leads to the lower bound

$$r_{\min} \geqslant 0.11352$$

valid for $\rho = 6$. It is still unclear what is the minimum value of ρ for which it is possible to derive positive lower bounds on the minimum interparticle distance.

3. Conclusion

In this paper a lower bound for the minimum interatomic distance between atoms in Morse clusters has been derived. A similar result, but with a different proof technique, was proven in Xue (1997) for Lennard-Jones clusters. In the proof proposed here first a lower bound for the energy due to the interactions of a single atom with other atoms close to it has been derived in Lemma 8, and then, by combining the bound with the result in Theorem 2, it is shown that the minimal interatomic distance can not fall below a threshold depending on ρ but not on N. Besides the theoretical interest of the result, it was shown in Xue (1998) that the lower bound can be employed to build data structures which enable to define fast procedures for the computation of the energy of clusters with very large number of atoms.

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