NEW RESULTS FOR MOLECULAR FORMATION UNDER PAIRWISE POTENTIAL MINIMIZATION

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ABSTRACT. We establish new lower bounds on the distance between two points of a minimum energy configuration of N points in $\mathbb{R}^3$ interacting according to a pairwise potential function. For the Lennard-Jones case, this bound is 0.67985 (and 0.7633 in the planar case). A similar argument yields an estimate for the minimal distance in Morse clusters, which improves previously known lower bounds. Moreover, we prove that the optimal configuration cannot be two-dimensional, and establish an upper bound for the distance to the nearest neighbour of every particle, which depends on the position of this particle. On the boundary of the optimal configuration polytope, this is unity while in the interior, this bound depends on the potential function. In the Lennard-Jones case, we get the value $\sqrt[6]{\frac{11}{5}} \approx 1.1404$. Also, denoting by V_N the global minimum in an N point minimum energy configuration, we prove in Lennard-Jones clusters $\frac{V_N}{N} \geq -41.66$ for all $N \geq 2$, while asymptotically $\lim_{N\to\infty} \frac{V_N}{N} \leq -8.611$ holds (as opposed to $\frac{V_N}{N} \geq -8.22$ in the planar case, confirming non-planarity for large N).

INTRODUCTION

In recent years many important advances have been observed in the field of computational methods for the determination of the three–dimensional conformation of clusters of particles interacting via pairwise potential. Many new computational approaches and several very interesting results have been obtained for what concerns in particular Lennard-Jones and Morse potentials, which, by far, are the most extensively studied ones. However, despite a large number of papers devoted to computational aspects of cluster formation, the number of significative research papers dealing with provable theoretical properties of optimal clusters is relatively small and many apparently trivial properties still lack a formal proof. Among the few exceptions in this trend we can find a bunch of papers dealing with the problem of uniformly bounding the minimum inter-particle distance in globally optimal clusters.

In this paper we address some theoretical properties of optimal clusters. First we propose an innovative technique for deriving bounds on the minimum particle separation in globally optimal clusters. The problem of deriving a good lower bound for interparticle distances in globally optimal clusters under a specific pair potential has attracted much research in recent years (see e.g. [12], [5], [1], [10] for some recent

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results). The technique we introduce in this paper yields results that, in the well studied cases of Lennard-Jones and Morse potential, are significantly sharper than all currently published results. Moreover, the proposed general scheme can be quite easily adapted to derive bounds for other pair potential functions.

In the paper we also address some issues which, although probably considered as trivially true by researcher in chemical physics, lacked up to now a formal proof. In particular, we prove that, apart from clusters with no more than three particles, optimal conformations cannot be planar. Although this property seems to be quite evident, its formal proof is far from being trivial. We also provide some characterization of nearest-neighbor pairs, both on the surface and in the interior of optimal clusters and prove that any particle is sufficiently close to another one.

A natural question arises about the usefulness of these results, apart from the fact that any formal proof of a property augments knowledge in the field. It is a fact that the availability of a precise lower and upper bounds on nearest neighbor distances is a crucial requirement in methods used to speed-up the approximate computation of potential for very large clusters: when dealing with clusters with several tens of thousands particles, in order to be able to efficiently compute the potential within reasonable approximation, a particularly effective strategy is to hierarchically cluster particles using specific data structures whose implementation requires knowledge of good bounds for the inter-particle distances; here, the better the bound, the more efficient the algorithm. As an example of the importance of good bounds, we may cite [13] where a fast parallel algorithm is introduced whose sequential version gives an $\mathcal{O}(N)$ bound on the time required to evaluate an N particle interaction, as opposed to the trivial $\mathcal{O}(N^2)$ bound. The constant in the $\mathcal{O}(N)$ term is proportional to $(c_2/c_1)^3$, where it is assumed that the diameter of the cluster is bounded above by $c_2\sqrt[3]{N}$ and c_1 is a lower bound on pairwise distances. We might also recall the fact that any information on specific properties of optimal clusters might be used by stochastic search algorithms which may exploit this knowledge in order to concentrate sampling in those region where it is more likely that optimal clusters will be found.

1. Minimal interparticle distance for pairwise potentials

Borrowing some notation from [6], we let $\mathbf{x}^* = (x_1^*, \ldots, x_N^*) \in \mathbb{R}^{3N}$ be an optimal N-particle configuration, i.e. a solution of the global optimization problem

$$V_N = V(\mathbf{x}^*) = \min\left\{ \sum_{1\le i<j\le N} v(\|x_i - x_j\|) : \mathbf{x} \in \mathbb{R}^{3N} \right\},$$

where $\|\cdot\|$ denotes the Euclidean norm and where v denotes any pairwise potential energy function from the class $\mathcal{V}$ with

$$\mathcal{V} := \left\{ v \in C^2(\mathbb{R}_+) : v(1) = -1, (r-1)\dot{v}(r) > 0 \text{ for } r \neq 1, \int_1^\infty r^2 |v(r)| dr < \infty \right\}$$

(here and in the sequel, $\dot{v}$ denotes derivative w.r.t. a single parameter). Note that any $v \in \mathcal{V}$ has $r = 1$ as its only critical point and global minimizer, and $v(r) \nearrow 0$ as $r \to \infty$, in accordance to Hoare's [2] requirements. Important special cases are the Lennard-Jones pairwise potential energy function

$$v_{\mathrm{LJ}}(r) = r^{-12} - 2r^{-6},$$

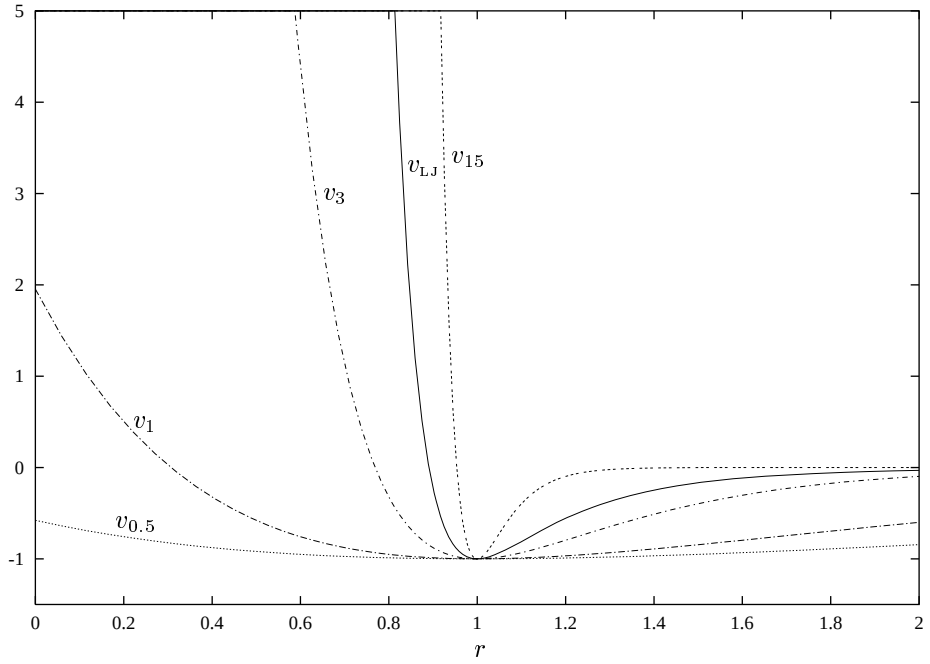

FIGURE 1. The Lennard-Jones pairwise potential energy function v_{LJ}, and the Morse pair potential v_ρ, for various values of ρ.

and the Morse pair potential

$$v_\rho(r) = e^{\rho(1-r)}\big(e^{\rho(1-r)} - 2\big)$$

depending on a positive parameter ρ. Plots of several instances of these functions can be seen in Figure 1.

The idea of the following theorem is that a configuration cannot be optimal, if we can decrease its total energy by moving one member of a pair realizing the closest distance. For two numbers a, b let us abbreviate $a \vee b = \max\{a, b\}$.

Theorem 1. *Fix $v \in \mathcal{V}$ and let $\zeta := \min\{r \geq 0 : v(r) \leq 0\} < 1$ (the zero of v if such exists). Let*

$$U_v(r) := v(r) + \frac{24}{r^3}\int_{\frac{r}{2}\vee(\zeta-\frac{r}{2})}^{\infty}\left(\min_{|s-t|\leq\frac{r}{2}} v(s)\right)t^2dt + 1\,. \tag{1}$$

Assume we know for each $N \geq 2$ a lower bound $\hat{r}_N > 0$ for minimal interatomic distance of an optimal N-particle configuration, and that for $\hat{r} := \inf_{N\geq 2}\hat{r}_N$ we have $\liminf_{r\searrow\hat{r}} U_v(r) \in]0, \infty]$. Then
(a) there exists the smallest solution greater than $\hat{r}$ of

$$U_v(r) = 0\,, \tag{2}$$

which we denote by r_0.
(b) Any optimal N-particle configuration $\mathbf{x}^*$ satisfies

$$\min_{1\leq i<j\leq N}\|x_i^* - x_j^*\| \geq r_0\,. \tag{3}$$

(c) Moreover, we have

$$\lim_{n\to\infty} \frac{V_n}{n} = \inf_{N\geq 2} \frac{V_N}{N} \geq -\frac{v(r_0)+1}{2}. \tag{4}$$

Proof. (a) First note that $\hat{r} \leq \hat{r}_2 \leq 1$. The existence of r_0 now follows from $\liminf_{r\searrow\hat{r}} U_v(r) > 0$, from

$$U_v(1) = v(1) + 24\int_{\frac{1}{2}}^{\infty} \left(\min_{|s-t|\leq\frac{1}{2}} v(s)\right) t^2 dt + 1 \leq 24\int_{\frac{1}{2}}^{\frac{3}{2}} v(1)t^2 dt = -26,$$

and from continuity of U_v. Clearly $r_0 < 1$ holds.
(b) Now if, for some $N \geq 2$, we have $r_0 \leq \hat{r}_N$, then (3) is trivially true.

If $N \geq 2$ is such that $\hat{r}_N < r_0$ holds, we have $U_v(r) > 0$ for $\hat{r}_N \leq r < r_0$. We thus assume that for an optimal N point configuration $\mathbf{x}^*$ we have

$$\sigma := \min_{1\leq i<j\leq N} \|x_i^* - x_j^*\| \in [\hat{r}_N, r_0[, \tag{5}$$

and without loss of generality we let $\sigma = \|x_1^* - x_2^*\|$. We then construct a configuration $\bar{\mathbf{x}}$ with $V(\bar{\mathbf{x}}) < V(\mathbf{x}^*)$ as follows: For $2 \leq i \leq N$ we let $\bar{x}_i = x_i^*$, and $\bar{x}_1$ is chosen (*e.g.* somewhere outside the convex hull of $x_2^*, \ldots, x_N^*$) such that $\min_{2\leq i\leq N} \|x_i^* - \bar{x}_1\| = 1$. Then clearly

$$V(\mathbf{x}^*) - V(\bar{\mathbf{x}}) = \sum_{i=2}^{N} v(\|x_i^* - x_1^*\|) - \sum_{i=2}^{N} v(\|x_i^* - \bar{x}_1\|).$$

We have

$$\sum_{i=2}^{N} v(\|x_i^* - \bar{x}_1\|) \leq -1, \tag{6}$$

by the construction of $\bar{x}_1$. To find a lower bound for $\sum_{i=2}^{N} v(\|x_i^* - x_1^*\|)$ we need some prerequisites:

First of all we let $L_y = \{r \geq 0 : v(r) \leq y\}$ be sublevel sets of v, note that $r \in L_y \Leftrightarrow y \in [v(r), \infty[$, and thus obtain

$$v(r) \geq \min(v(r), 0) = -\int_{-1}^{0} \mathbb{1}_{[v(r),\infty[}(y)dy = -\int_{-1}^{0} \mathbb{1}_{L_y}(r)dy \tag{7}$$

for $r > 0$. Clearly we have $\min(v(r), 0) = v(r)\mathbb{1}_{[\zeta,\infty[}(r)$. Let us remark that by properties of $v \in \mathcal{V}$ the set L_y is a compact interval for any $y \in [-1, 0[$.

Furthermore we let $L_y^a = \{t \geq \frac{a}{2} : \operatorname{dist}(t, L_y) \leq \frac{a}{2}\}$ be the $\frac{a}{2}$-neighborhood of $L_y \setminus [0, a]$. Observing

$$\begin{aligned} L_y^a &= \{t \geq \tfrac{a}{2} : \exists s \text{ such that } |s-t| \leq \tfrac{a}{2} \text{ and } v(s) \leq y\} \\ &= \{t \geq \tfrac{a}{2} : \min_{|s-t|\leq\frac{a}{2}} v(s) \leq y\}, \end{aligned}$$

we note that L_y^a is a sublevel set of the function $\underline{\mathrm{v}}_a : \left[\frac{a}{2}, \infty\right[\to \mathbb{R}$, defined by $\underline{\mathrm{v}}_a(t) := \min_{|s-t|\leq\frac{a}{2}} v(s)$, where $\underline{\mathrm{v}}_a(t) \leq 0 \Leftrightarrow t \geq \zeta - \frac{a}{2}$. We conclude as in (7) that $-\int_{-1}^{0} \mathbb{1}_{L_y^a}(t)dy = \min(\underline{\mathrm{v}}_a(t), 0) = \underline{\mathrm{v}}_a(t)\mathbb{1}_{[\zeta-\frac{a}{2},\infty[}(t)$ holds for $t \geq \frac{a}{2}$, hence

$$-\int_{-1}^{0} \mathbb{1}_{L_y^a}(t)dy = \min_{|s-t|\leq\frac{a}{2}} v(s)\mathbb{1}_{[\frac{a}{2}\vee(\zeta-\frac{a}{2}),\infty[}(t) \tag{8}$$

is true for $t > 0$.

We further let $S_y = \{x \in \mathbb{R}^3 : \|x\| \in L_y\}$ and $S_y^a = \{x \in \mathbb{R}^3 : \|x\| \in L_y^a\}$. Next we define for $A \subset \mathbb{R}^3$

$$\nu_r(A) := \max\Big\{n : \exists \mathbf{x} \in A^n, \min_{1\le i\le n} \|x_i\| \ge r, \min_{1\le i<j\le n} \|x_i - x_j\| \ge r\Big\}, \tag{9}$$

with $r < s$ implying $\nu_r(A) \ge \nu_s(A)$, and observe that an upper bound for $\nu_r(S_y)$ can be obtained by dividing the volume of the spherical shell S_y^r by the volume of a ball of radius $\frac{r}{2}$, more precisely,

$$\nu_r(S_y) \le \frac{24}{r^3} \int_0^\infty t^2 \mathbb{1}_{L_y^r}(t) dt. \tag{10}$$

We are now ready to derive the proposed lower bound for $\sum_{i=2}^N v(\|x_i^* - x_1^*\|)$:

$$\begin{aligned}\sum_{i=2}^N v(\|x_i^* - x_1^*\|) &= v(\sigma) + \sum_{i=3}^N v(\|x_i^* - x_1^*\|) \ge v(\sigma) - \int_{-1}^0 \sum_{i=3}^N \mathbb{1}_{L_y}(\|x_i^* - x_1^*\|) dy \\ &\ge v(\sigma) - \int_{-1}^0 \nu_\sigma(S_y) dy,\end{aligned} \tag{11}$$

where we used (7), and where ν_σ comes into play since, denoting $\xi_i := x_i^* - x_1^*$ for $3 \le i \le N$, we have $\min_i \|\xi_i\| \ge \sigma$ and $\min_{i<j} \|\xi_i - \xi_j\| \ge \sigma$, by (5). Continuing we find by (10), Fubini's Theorem, and (8)

$$\begin{aligned}v(\sigma) - \int_{-1}^0 \nu_\sigma(S_y) dy &\ge v(\sigma) - \frac{24}{\sigma^3} \int_0^\infty t^2 \int_{-1}^0 \mathbb{1}_{L_y^\sigma}(t) dy\, dt \\ &= v(\sigma) + \frac{24}{\sigma^3} \int_{\frac{\sigma}{2} \vee (\zeta - \frac{\sigma}{2})}^\infty \Big(\min_{|s-t| \le \frac{\sigma}{2}} v(s)\Big) t^2 dt = U_v(\sigma) - 1 \\ &> -1,\end{aligned} \tag{12}$$

where the last inequality holds since $\sigma \in [\hat{r}_N, r_0[$ by assumption. Combining (6), (11) and (12) indeed implies $V(\bar{\mathbf{x}}) < V(\mathbf{x}^*)$, and thus contradicts optimality of the configuration $\mathbf{x}^*$. Note that, along similar lines, we derive (replacing σ with r_0 in (12) and thereby loosing strictness of the inequality)

$$v(r_0) - \int_{-1}^0 \nu_{r_0}(S_y) dy \ge -1. \tag{13}$$

(c) We use those ideas that also led to (11) and (12). Assuming that for an optimal configuration $\mathbf{x}^*$ we have $r_1 := \min_{1\le i<j\le N} \|x_i^* - x_j^*\| \ge r_0$, we proceed as follows:

$$\begin{aligned}V_N = V(\mathbf{x}^*) &= \sum_{1\le i<j\le N} v(\|x_i^* - x_j^*\|) = \frac{1}{2} \sum_{1\le i\le N} \sum_{j\ne i} v(\|x_i^* - x_j^*\|) \\ &\ge -\frac{1}{2} \sum_{1\le i\le N} \int_{-1}^0 \nu_{r_1}(S_y) dy = -\frac{N}{2} \int_{-1}^0 \nu_{r_1}(S_y) dy \\ &\ge -\frac{N}{2} \int_{-1}^0 \nu_{r_0}(S_y) dy \ge -N \frac{v(r_0) + 1}{2},\end{aligned}$$

where the last inequality follows from (13). This establishes the inequality in (4).

Next we define $V_0 := 0$, $V_1 := 0$ and note that $(V_n)_{n\ge 0}$ is a subadditive sequence, i.e.,

$$V_{n+m} \le V_n + V_m,$$

holds for all integers $n, m \geq 0$. Indeed, if $V_n = V(\mathbf{x}^*)$ and $V_m = V(\mathbf{y}^*)$, then

$$V_{n+m} \leq V(\mathbf{x}^* \cup (\mathbf{y}^* + \mathbf{z})) \leq V(\mathbf{x}^*) + V(\mathbf{y}^* + \mathbf{z}) = V_n + V_m,$$

where $\mathbf{z} = (z, \ldots, z) \in \mathbb{R}^{3m}$, and $z \in \mathbb{R}^3$ is chosen such that $\operatorname{dist}(\mathbf{x}^*, \mathbf{y}^* + \mathbf{z}) \geq 1$. An application of Fekete's Subadditivity Lemma (*cf.* [9, Theorem 5.1]) now yields the equality in (4). □

Corollary 1. *Assume that for fixed $v \in \mathcal{V}$ we have $\liminf_{r \searrow 0} U_v(r) \in]0, \infty]$, where U_v is defined in (1), and let r_0 be the smallest positive solution of $U_v(r) = 0$. Then any optimal N point configuration $\mathbf{x}^*$ satisfies*

$$\min_{1 \leq i < j \leq N} \|x_i^* - x_j^*\| \geq r_0.$$

Moreover, we have

$$\lim_{n \to \infty} \frac{V_n}{n} = \inf_{N \geq 2} \frac{V_N}{N} \geq -\frac{v(r_0) + 1}{2}.$$

Proof. We will construct lower bounds $\hat{r}_N > 0$ for minimal interatomic distance, which satisfy $\hat{r} = \inf_{N \geq 2} \hat{r}_N = 0$, and can then refer to Theorem 1.

Note that $U_v(r) \leq v(r) - \frac{C}{r^3} + 1$ holds for $r \leq 2$, where $C = -24 \int_1^\infty v(t) t^2 dt > 0$. Thus $\liminf_{r \searrow 0} U_v(r) \in]0, \infty]$ implies $\lim_{r \searrow 0} v(r) = \infty$. This yields a positive lower bound for the interatomic distance in an optimal configuration: We use the same idea as in the previous proof, keeping (6), but replacing (11) and (12) by

$$\sum_{i=2}^{N} v(\|x_i^* - x_1^*\|) \geq v(\sigma) + (N-2) v(1) = v(\sigma) - N + 2.$$

Now $\mathbf{x}^*$ cannot be optimal if $v(\sigma) - N + 2 > -1$, which gives the lower bound $\hat{r}_N := \min\{r \geq 0 : v(r) \leq N - 3\} > 0$, and clearly $\hat{r} = \lim_{N \to \infty} \hat{r}_N = 0$ holds. □

Before turning to specific potential functions, we give an alternative representation of the integral appearing in (1), and of a similar integral showing up in the consideration of 2-dimensional configurations further below.

Lemma 1. *For general $v \in \mathcal{V}$, $r \leq 1$ and $\delta \in \{2, 3\}$ we have*

$$\int_{\frac{r}{2} \vee (\zeta - \frac{r}{2})}^{\infty} \left(\min_{|s-t| \leq \frac{r}{2}} v(s) \right) t^\delta dt = \int_{r \vee \zeta}^{\infty} \left(t + \frac{r}{2} \operatorname{sign}(t-1) \right)^\delta v(t) dt - r - \frac{\delta - 2}{12} r^3. \tag{14}$$

Proof. We just have to split the integral into 3 parts, exploit monotonicity properties of v, then make changes (actually shifts by $\pm \frac{r}{2}$) of the variables of integration in the first and third integral, and finally join first and third integral, and evaluate the second:

$$\begin{aligned} &\int_{\frac{r}{2} \vee (\zeta - \frac{r}{2})}^{\infty} \left(\min_{|s-t| \leq \frac{r}{2}} v(s) \right) t^\delta dt \\ &\quad = \int_{\frac{r}{2} \vee (\zeta - \frac{r}{2})}^{1 - \frac{r}{2}} v(t + \tfrac{r}{2}) t^\delta dt + \int_{1 - \frac{r}{2}}^{1 + \frac{r}{2}} v(1) t^\delta dt + \int_{1 + \frac{r}{2}}^{\infty} v(t - \tfrac{r}{2}) t^\delta dt \qquad (15) \\ &\quad = \int_{r \vee \zeta}^{1} \left(t - \tfrac{r}{2}\right)^\delta v(t) dt - \int_{1 - \frac{r}{2}}^{1 + \frac{r}{2}} t^\delta dt + \int_{1}^{\infty} \left(t + \tfrac{r}{2}\right)^\delta v(t) dt. \end{aligned}$$

□

In the following we use the shorthand notations $U_{\mathrm{LJ}} := U_{v_{\mathrm{LJ}}}$ and $U_\rho := U_{v_\rho}$.

Corollary 2. *For $N \geq 2$, any optimal Lennard-Jones configuration $\mathbf{x}^*$ of N points satisfies*

$$\min_{1\leq i<j\leq N} \|x_i^* - x_j^*\| \geq r_0 = 0.656248,$$

and, for $N \geq 2$,

$$\frac{V_N}{N} \geq -\frac{v(r_0)+1}{2} = -66.3507.$$

Proof. This follows readily from Corollary 1 after verifying $\lim_{r\searrow 0} U_v(r) = \infty$ for $v = v_{\mathrm{LJ}}$, which we do by providing an explicit expression of U_{LJ}. Now employing (14) in the case of the Lennard-Jones potential yields for $r \leq \zeta = 2^{-\frac{1}{6}} = 0.8908987$

$$U_{\mathrm{LJ}}(r) = \left(\frac{1}{r^6} - 1\right)^2 - \frac{64}{3}\frac{\zeta^3}{r^3} - \frac{72}{5}\frac{3-\zeta^2}{r^2} - \frac{144}{55}\frac{\zeta}{r} - 2\,. \tag{16}$$

All numerical results in this paper were obtained with Maple V Release 5. □

We recall here that this estimate is significantly sharper than those reported in [1] (0.6108) and [10] (0.6187).

Corollary 3. *For the Morse pair potential $v_\rho(r)$ and integral $\rho \in [6, 15]$, we obtain*

$$\min_{1\leq i<j\leq N} \|x_i^* - x_j^*\| \geq r_0,$$

for any optimal configuration $\mathbf{x}^*$ of $N \geq 2$ points. The values of $r_0 = r_0(\rho)$ are listed in the following table, together with the lower bounds $\hat{r}$ given by Locatelli and Schoen [5] *(there, our $\hat{r}$ is denoted $r_{\min}$) and those obtained in* [10]*, denoted in Vinko's paper as q.*

ρ	$\hat{r}$ [5]	q [10]	$10^{-3}U_\rho(\hat{r})$	r_0
6	0.11352	0.4985948046	31.8	0.567097
7	0.376	0.6113121449	5.70	0.656752
8	0.468	0.6796501438	4.63	0.713711
9	0.528	0.7268978345	4.61	0.753859
10	0.574	0.7618207355	4.76	0.783890
11	0.613	0.7887781722	4.75	0.807275
12	0.644	0.8102494106	4.91	0.826034
13	0.672	0.8277671751	4.84	0.841431
14	0.695	0.8423362542	4.90	0.854303
15	0.715	0.8546451536	4.96	0.865230

Proof. This follows from Theorem 1 after verifying $U_\rho(\hat{r}) > 0$. Therefore we compute, using (14), for $r \leq \zeta = 1 - \frac{\ln 2}{\rho}$,

$$U_\rho(r) = \left(e^{\rho(1-r)} - 1\right)^2 - \frac{24}{r^3}\left(\frac{7 - 6\ln 2 + 2\ln^2 2}{\rho^3} + \frac{6 - 4\ln 2}{\rho^2} + \frac{2}{\rho}\right)$$
$$- \frac{24}{r^2}\left(\frac{1 + 4\ln 2}{2\rho^2} + \frac{1}{\rho} + 1\right) - \frac{12}{r\rho} - 2.$$

In the range $6 \leq \rho \leq 15$ we always have $\hat{r} < 0.88 < 1 - \frac{\ln 2}{6} \leq \zeta$, and the values $U_\rho(\hat{r})$, which are also listed in the table, are seen to be positive. □

The following corollary provides a lower bound for the minimal interatomic distance (which improves that one given by Blanc [1]) and for the energy in an optimal *2-dimensional* Lennard-Jones cluster.

Corollary 4. *For $N \geq 2$, any optimal 2-dimensional Lennard-Jones configuration $\mathbf{x}^*$ of N points satisfies*

$$\min_{1 \leq i < j \leq N} \|x_i^* - x_j^*\| \geq 0.7575$$

and

$$\frac{V_N}{N} \geq -9.205.$$

Proof. The 2-dimensional setting doesn't differ much from the 3-dimensional. We have to use an updated definition of $\nu_r(A_y)$ for annuli $A_y := \{x \in \mathbb{R}^2 : \|x\| \in L_y\}$, which is now upper estimated by the area of the $\frac{r}{2}$-neighborhood of A_y divided by the area of a circle of radius $\frac{r}{2}$, leading to the definition

$$U_v(r) := v(r) + \frac{8}{r^2} \int_{\frac{r}{2} \vee (\zeta - \frac{r}{2})}^{\infty} \left(\min_{|s-t| \leq \frac{r}{2}} v(s) \right) t \, dt + 1,$$

For the Lennard-Jones potential we thus obtain, using (14), for $r \leq \zeta = 2^{-\frac{1}{6}}$

$$U_{\mathrm{LJ}}(r) = \left(\frac{1}{r^6} - 1 \right)^2 - \frac{24}{5} \frac{\zeta^2}{r^2} - \frac{96}{55} \frac{6 - \zeta}{r}.$$

Clearly we have $\lim_{r \searrow 0} U_{\mathrm{LJ}}(r) = \infty$. The smallest positive solution of $U_{\mathrm{LJ}}(r) = 0$ is $r_0 = 0.7575$, and a lower bound for $\frac{V_N}{N}$ is then given by $-\frac{v(r_0)+1}{2} = -9.205$, which completes the proof. □

Remark 1. Our method of proving Theorem 1 is based on the following observation: A number r is not the minimal distance in an optimal configuration, if for any configuration where, say, x_1 and x_2 are at distance r, it is possible to reduce the energy of the configuration by moving x_1 to some position outside the convex hull of the points $x_2, \ldots, x_N$. Since some crude estimates were used in the proof, it might be interesting to know that, in the Lennard-Jones case, even if full precision is kept by avoiding any estimates, the best lower bound for the minimal distance achievable by our method cannot exceed 0.8, as is shown by Example 1 below.

In contrast, the true minimal distance in an optimal Lennard-Jones configuration might be something like 0.91 as is suggested by looking at the putative global minima listed for $2 \leq N \leq 150$ in [11], among which the shortest minimal distance 0.9165 appears at $N = 71$.

So what about deriving lower bounds for distances based on the following observation? A number r is not the minimal distance in an optimal Lennard-Jones configuration, if for any configuration where, say, x_1 and x_2 are at distance r, it is possible to reduce the energy of the configuration by only moving x_1 to some *arbitrary* position (not necessarily outside the convex hull of the points $x_2, \ldots, x_N$). Now, the best lower bound for the minimal distance achievable that way cannot exceed ≈ 0.865, as is shown by Example 2 below.

Example 1. Let x_1 be the origin and let $x_2', \ldots, x_{13}'$ be the vertices of a regular icosahedron of circumradius 1 and centered in the origin. Now let x_2 by the point on the line segment joining the origin and x_2', at distance 0.8 to the origin, and let $x_i = x_i'$ for $3 \leq i \leq 13$. As one can show (*e.g.* by numerical methods), it is

not possible to improve this configuration by moving x_1 to somewhere outside the convex hull of $x_2, \dots, x_{13}$.

Example 2. Let x_1 be the origin, and let $x_2, \dots, x_{13}$ be $\sqrt{\frac{1}{2}}$ times the points

$$(\pm 1, \pm 1, 0), (\pm a, 0, 1), (\pm 1, 0, -1), (0, \pm 1, 1), (0, \pm a, -1),$$

where $a = 0.705$. Then

$$\min_{2 \le i < j \le 12} \|x_i - x_j\| > \min_{2 \le i \le 12} \|x_i - x_1\| = \sqrt{\frac{1+a^2}{2}} = 0.865166$$

and, denoting $F(x) := \sum_{2 \le i \le 12} v(\|x_i - x\|)$, we have $F(x_1) = \min_{x \in \mathbb{R}^3} F(x)$.

2. Refinements for the Lennard-Jones potential

The bounds given in Corollary 2 can be improved by considering also second-smallest, third-smallest, fourth-smallest distances. For a set $\mathbf{x}$ of N points in $\mathbb{R}^3$, and $x \in \mathbf{x}$, let $0 = d_x^0 \le d_x^1 \le \cdots \le d_x^{N-1}$ be the multiset $\{\|y - x\| : y \in \mathbf{x}\}$ in increasing order, and define for $1 \le k < N$

$$d^k = d^k(\mathbf{x}) := \min_{x \in \mathbf{x}} d_x^k.$$

In particular we have $d^1 = \min_{x,y \in \mathbf{x}, x \ne y} \|y - x\|$, and clearly $d^k \le d^\ell$ for $k < \ell$. For $1 \le k < N$ let $\mathbf{r} = (r_1, \dots, r_k) \in \mathbb{R}^k$, with $0 < r_1 \le r_2 \le \cdots \le r_k$. For $A \subset \mathbb{R}^3$ we generalize (9) as follows:

$$\nu_{\mathbf{r}}(A) := \max \left\{ n : \exists \mathbf{x} \in A^n, \min_{1 \le i \le n} \|x_i\| \ge r_1, d^1(\mathbf{x}) \ge r_1, \dots, d^k(\mathbf{x}) \ge r_k \right\}.$$

For $\mathbf{r}, \mathbf{s} \in \mathbb{R}^k$ we write $\mathbf{r} \le \mathbf{s}$ (or $\mathbf{s} \ge \mathbf{r}$) iff $r_i \le s_i$ for $1 \le i \le k$. Clearly $\mathbf{r} \le \mathbf{s}$ implies $\nu_{\mathbf{r}}(A) \ge \nu_{\mathbf{s}}(A)$.

As in Theorem 1, we have the upper bound $\nu_{\mathbf{r}}(S_y) \le \frac{24}{r_1^3} \int_0^\infty t^2 \mathbb{1}_{L_y^{r_1}}(t) dt$. Another sometimes stricter upper bound can be found as follows: Let a set of N points $\mathbf{x} \subset S_y$ satisfy $\mathbf{d}(\mathbf{x}) \ge \mathbf{r}$, and let for $1 \le i \le N$

$$C_i := \{x \in \mathbb{R}^3 : \|x - x_i\| \le \frac{r_k}{2}, \|x - x_i\| \le \|x - x_j\| \text{ for } 1 \le j \le N\}$$

be the intersection of the ball $B(x_i, \frac{r_k}{2})$ and the Voronoi cell around x_i. Then the interiors of $C_i, 1 \le i \le N$ are disjoint, and we have $\bigcup_{i=1}^N C_i \subset S_y^{r_1} \cup S_y^{r_k}$, which gives rise to the inequality $N \le \mathrm{vol}(S_y^{r_1} \cup S_y^{r_k}) / \min_{1 \le i \le N} \mathrm{vol}(C_i)$. Note that $S_y^{r_1} \cup S_y^{r_k} = S_y^{r_k}$ holds for $r_k \le \zeta$.

We proceed by estimating $\mathrm{vol}(C_i)$. Assuming that $d_{x_i}^\ell$ is attained at x_j, *i.e.*, $d_{x_i}^\ell = \|x_i - x_j\| \ge r_\ell$, we infer that the set $\{x \in \mathbb{R}^3 : \|x - x_i\| \le \|x - x_j\|\}$ contains a halfspace $H_{i,\ell}$ with $\mathrm{dist}(x_i, \mathbb{R}^3 \setminus H_{i,\ell}) = \frac{r_\ell}{2}$. Thus a lower bound (which is independent of i) for the volume of C_i is given by the volume of a ball of radius $\frac{r_k}{2}$, from which $k-1$ caps of height $\frac{r_k - r_\ell}{2}, 1 \le \ell < k$, are missing,

$$\mathrm{vol}(C_i) \ge \frac{4\pi}{3} \left(r_k^3 - \frac{1}{4} \sum_{\ell=1}^{k-1} (r_k - r_\ell)^2 (2r_k + r_\ell) \right).$$

(Actually the removed caps will in general partly overlap, but assuming that they don't, we are on the safe side.) This is of use only if the r.h.s. is positive, but

obviously, $\nu_{\mathbf{r}}(S_y) \leq \mu_{\mathbf{r}}(S_y)$ always holds, where

$$\mu_{\mathbf{r}}(S_y) := \frac{24 \int_0^\infty t^2 \mathbb{1}_{L_y^{r_1} \cup L_y^{r_k}}(t) dt}{\left(r_k^3 - \frac{1}{4}\sum_{i=1}^{k-1}(r_k - r_i)^2(2r_k + r_i)\right) \vee r_1^3}. \tag{17}$$

Lemma 2. *If for some configuration* $\mathbf{x}$ *and some* ℓ, $1 \leq \ell \leq k$ *we have*

$$\ell v(d^\ell(\mathbf{x})) - \int_{-1}^0 \mu_{\mathbf{d}(\mathbf{x})}(S_y) dy + 1 > 0, \tag{18}$$

then neither $\mathbf{x}$*, nor any* $\mathbf{y}$ *satisfying* $\mathbf{d}(\mathbf{y}) \geq \mathbf{d}(\mathbf{x})$ *and* $d^\ell(\mathbf{y}) = d^\ell(\mathbf{x})$*, can be optimal.*

Proof. As in the proof of Theorem 1, we can argue that by moving one of the points which have ℓ neighbors at distance at most $d^\ell(\mathbf{x})$ outside of the convex hull of the remaining points we can decrease the energy of the configuration, thus $\mathbf{x}$ cannot be optimal. The same argument works with μ replaced by ν. Now (18) implies

$$\ell v(d^\ell(\mathbf{x})) - \int_{-1}^0 \nu_{\mathbf{d}(\mathbf{x})}(S_y) dy + 1 > 0,$$

and

$$\ell v(d^\ell(\mathbf{y})) - \int_{-1}^0 \nu_{\mathbf{d}(\mathbf{y})}(S_y) dy + 1 > 0,$$

for any configuration $\mathbf{y}$ with $\mathbf{d}(\mathbf{y}) \geq \mathbf{d}(\mathbf{x})$ and $d^\ell(\mathbf{y}) = d^\ell(\mathbf{x})$. This means that $\mathbf{y}$ cannot be optimal either. □

For fixed $k \geq 1$ we now solve the system of equations

$$\ell v(r_\ell) - \int_{-1}^0 \mu_{\mathbf{r}}(S_y) dy + 1 = 0, \quad 1 \leq \ell \leq k \tag{19}$$

for the vector $\mathbf{r} = (r_1, \ldots, r_k)$.

Theorem 2. *There is a component-wise smallest positive solution* $\mathbf{r}^* = (r_1^*, \ldots, r_k^*)$ *of* (19)*, such that for any optimal Lennard-Jones configuration* $\mathbf{x}^*$ *of* $N > k$ *points, we have* $d^\ell(\mathbf{x}^*) \geq r_\ell^*$ *for* $1 \leq \ell \leq k$*. Moreover* $\frac{V(\mathbf{x}^*)}{N} \geq -\frac{v(r_1^*)+1}{2}$ *holds.*

Proof. Let $\zeta = 2^{-\frac{1}{6}}$ be the unique positive zero of v. For $0 < t \leq \zeta$ and $1 \leq i \leq k$ the equation

$$v(t) = iv(r_i)$$

can be uniquely solved:

$$r_i = r_i(t) = v^{-1}\left(\frac{v(t)}{i}\right) \in]0, \zeta].$$

Let $\mathbf{r}(t) = (r_1(t), r_2(t), \ldots, r_k(t))$ be the vector of solutions, then we have in particular $\mathbf{r}(\zeta) = (\zeta, \zeta, \ldots, \zeta)$, and $\mathbf{r}(t) \leq \mathbf{r}(u)$ for $0 < t \leq u \leq \zeta$. Also note that $r_1(t) = t$. As $t \to 0$, we have $v(t) \sim t^{-12}$, while $\int_{-1}^0 \mu_{\mathbf{r}(t)}(S_y) dy = \mathcal{O}(t^{-3})$. Indeed, the denominator in (17) does not depend on y, and integration of the numerator yields a similar result as in the calculation of (16), replacing r with t. Denoting

$$U(t) := v(t) - \int_{-1}^0 \mu_{\mathbf{r}(t)}(S_y) dy + 1, \tag{20}$$

we thus have $\lim_{t\to 0} U(t) = \infty$ and $U(\zeta) \leq -25$, since $\mu_{\mathbf{r}(\zeta)}(S_y) \geq \mu_{\mathbf{r}(\zeta)}(S_{-1}) = 2 + \frac{24}{\zeta^2} \geq 26$ holds. Since U is continuous, there has to be a smallest positive zero

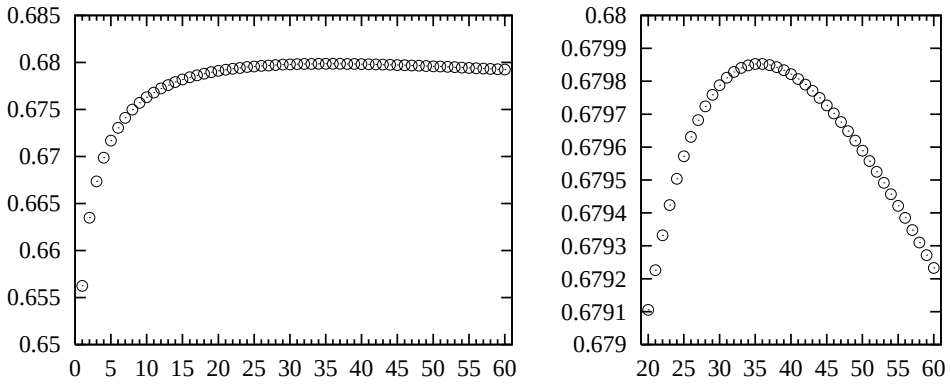

FIGURE 2. The lower bounds $r_1^*(k)$, plotted over $k \in [1, 60]$, and a close up for the range $k \in [20, 60]$.

τ of U in the interval $]0, \zeta]$, which gives rise to a component-wise smallest positive solution $\mathbf{r}^* = \mathbf{r}(\tau)$ of (19). We denote $\mathcal{D} := \{\mathbf{r}(t) : 0 < t \leq \tau\}$. Now assume that for an optimal Lennard-Jones configuration $\mathbf{x}^*$ of at least $k+1$ points the vector $\mathbf{d} = \mathbf{d}(\mathbf{x}^*)$ does not satisfy $\mathbf{d} \geq \mathbf{r}^*$. Then $\mathbf{r}' := \max\{\mathbf{r} \in \mathcal{D} : \mathbf{r} \leq \mathbf{d}\} = \mathbf{r}(t') < \mathbf{r}^*$, for some $t' \in]0, \tau[$, and for some ℓ we have $d^\ell = r'_\ell$. Therefore

$$\ell v(r'_\ell) - \int_{-1}^{0} \mu_{\mathbf{r}'}(S_y)dy + 1 = U(t') > 0,$$

and by the lemma we conclude that $\mathbf{x}^*$ is not optimal, a contradiction. Finally, the proof of the inequality (4) can easily be adapted to furnish a proof of the last assertion of the theorem. □

Theorem 2 readily leads to the following corollary.

Corollary 5. *For $N \geq 2$, any optimal Lennard-Jones configuration $\mathbf{x}^*$ of N points satisfies*

$$\min_{1 \leq i < j \leq N} \|x_i^* - x_j^*\| \geq 0.67985, \tag{21}$$

and, for $N \geq 2$,

$$\frac{V_N}{N} \geq -41.66. \tag{22}$$

Proof. Taking $k = 36$, we compute the smallest positive solution of $U(t) = 0$, with U defined in (20), obtaining $\tau = r_1^* = 0.67985262762$. Theorem 2 then tells us that (21) and (22) hold for $N \geq 37$. (Indeed, numerical evidence suggests that $k = 36$ yields the largest value of r_1^*, *cf.* Figure 2).

For $2 \leq N \leq 36$ we use the lower bounds depending on N (but not on the dimension of the space in which we look for optimal configurations) which we derived in the proof of Corollary 1,

$$\hat{r}_N = \min\{r \geq 0 : v(r) \leq N - 3\}.$$

Luckily we derive

$$\min_{2 \leq N \leq 36} \hat{r}_N = \hat{r}_{36} = 0.72597 > 0.67985,$$

and from the trivial lower bound $V_N \geq -\binom{N}{2}$ we obtain

$$\min_{2\leq N\leq 36} \frac{V_N}{N} \geq -17.5 > -41.66,$$

which completes the proof. □

There is also a refinement of the lower bound for the 2-dimensional setting based on the ideas of this section.

Corollary 6. *For $N \geq 2$, any optimal 2-dimensional Lennard-Jones configuration $\mathbf{x}^*$ of N points satisfies*

$$\min_{1\leq i<j\leq N} \|x_i^* - x_j^*\| \geq 0.76333$$

and

$$\frac{V_N}{N} \geq -8.22.$$

Proof. Lemma 2 and Theorem 2 also hold in the 2-dimensional setting, we only have to redefine $\mu_{\mathbf{r}}$, accounting for circular segments instead of spherical caps: For the annulus $A_y = \{x \in \mathbb{R}^2 : \|x\| \in L_y\}$ we let

$$\mu_{\mathbf{r}}(A_y) := \frac{8\int_0^\infty t \mathbb{1}_{L_y^{r_1}\cup L_y^{r_k}}(t)dt}{\left(r_k^2 - \frac{1}{\pi}\sum_{i=1}^{k-1}(r_k^2 \arccos\frac{r_i}{r_k} - r_i\sqrt{r_k^2 - r_i^2})\right) \vee r_1^2}.$$

Numerical evidence then suggests that $k = 10$ yields the best result, which is $r_1^* = 0.76333698899$. Finally computing $\frac{v(r_1^*)+1}{2} = 8.22$ completes the proof for $N \geq 11$. The cases $2 \leq N \leq 10$ are successfully handled by the same special treatment as the cases $2 \leq N \leq 36$ in the proof of Corollary 5. □

The next lemma will be needed for an upper estimate of the limit of the sequence $\left(\frac{V_N}{N}\right)_{N\geq 1}$. It deals with the potential energy of any one atom when atoms reside in the points of a lattice.

Lemma 3 ([Lennard-]Jones and Ingham, 1925)**.** *Denote by L the face centered cubic (f.c.c.) lattice, let $L' := L \setminus \{o\}$ and define $aL' := \{ax : x \in L'\}$. Furthermore denote $C(a) := \frac{1}{2}\sum_{x\in aL'} v_{\mathrm{LJ}}(\|x\|)$, which is the potential energy per one atom of the lattice aL. Then*

$$C(a^*) := \min_{a>0} C(a) = -\left(\sum_{x\in L'} \frac{1}{\|x\|^6}\right)^2 \Big/ \sum_{x\in L'} \frac{2}{\|x\|^{12}} = -8.610.$$

Proof. With $C(a) = \frac{1}{2a^{12}}\sum_{x\in L'}\frac{1}{\|x\|^{12}} - \frac{1}{a^6}\sum_{x\in L'}\frac{1}{\|x\|^6}$, we have to solve $\dot{C}(a^*) = 0$, yielding $(a^*)^6 = \sum_{x\in L'}\frac{1}{\|x\|^{12}} \Big/ \sum_{x\in L'}\frac{1}{\|x\|^6}$, see [3, §3] for results corresponding to general pairwise potential functions of the form $v(r) = \frac{\lambda_n}{r^n} - \frac{\lambda_m}{r^m}$. Computing the lattice sums to high precision is a nontrivial task due to their poor convergence properties. From the data provided in [3, Table I] we get $8.6101964 < C(a^*) < 8.6102041$, and Maple, appropriately tuned, gives us a bit more, $C(a^*) = 8.6102001567$. □

Remark 2. The lattice sums $\sum_{x\in L'}\frac{1}{\|x\|^k}$, of which the instances $k \in \{6, 12\}$ were needed for the calculation of the constant $C(a^*)$, are given in [3] for integers k in the interval $[4, 30]$, not only for the f.c.c. lattice, but also for the simple cubic and the body centered cubic lattice. Furthermore the f.c.c. lattice and the hexagonal close

packing (h.c.p.) are compared in [4] for potentials of the form $\frac{1}{r^k} - \frac{k}{6r^6}$ for several values of k, and it is found that the potential energy per one atom is smaller for h.c.p., which leads to a constant -8.6110697 in the Lennard-Jones case. Moreover a slight compression of the h.c.p. in the plane-stacking direction further diminishes the potential energy per one atom to -8.6110704, see [8]. Although the h.c.p. and the compressed h.c.p. aren't lattices, they are distance invariant sets (a set P is called distance invariant if for all $d \geq 0$ the numbers $|\{y \in P : \|y - x\| = d\}|$ do not depend on $x \in P$), so that we can justly speak of the potential energy per one atom.

Theorem 3. *For the Lennard-Jones potential the optimal values V_N satisfy*

$$\lim_{N\to\infty} \frac{V_N}{N} \leq -8.611\,.$$

Proof. Denote by H a translate of the compressed h.c.p. mentioned in the previous remark which contains the origin o, let $H' := H\setminus\{o\}$, and denote $C^* := -8.6110704$, the potential energy per one atom in H. Let $\bar{\mathbf{x}}$ consist of N points of H closest to the origin (in general not unique). We will show

$$V(\bar{\mathbf{x}}) = C^*N + \mathcal{O}\left(N^{\frac{2}{3}}\right),$$

which immediately implies the assertion of the theorem. We use the abbreviation $v = v_{\mathrm{LJ}}$. From [4, 8] we know that $\min\{\|x\| : x \in H'\} > 0.971$, and therefore $v(\|x-y\|) < 0$ for any pair (x, y) of distinct points from H. The following estimate will be needed:

$$\sum_{x\in H':\|x\|\geq R} v(\|x\|) = \mathcal{O}\left(\sum_{k\geq R} k^2|v(k)|\right) = \mathcal{O}\left((R+2)^{-3}\right). \tag{23}$$

By the distance invariance of H the sum $\sum_{x\in H\setminus\{\bar{x}_i\}} v(\|x-\bar{x}_i\|) = C^*$ is independent of i, which is used to derive

$$V(\bar{\mathbf{x}}) = \frac{1}{2}\sum_{1\leq i\leq N}\sum_{j\neq i} v(\|\bar{x}_j - \bar{x}_i\|) = C^*N - \frac{1}{2}\sum_{1\leq i\leq N}\sum_{x\in H\setminus\bar{\mathbf{x}}} v(\|x-\bar{x}_i\|).$$

Let $M \in \mathbb{N}$ be such that $\max_{x\in\bar{\mathbf{x}}}\|x\| \leq M$ and $\min_{x\in H\setminus\bar{\mathbf{x}}}\|x\| \geq M-1$. Clearly we have $M = \mathcal{O}\left(N^{\frac{1}{3}}\right)$. Note that $\|x-\bar{x}_i\| < M - 1 - \|\bar{x}_i\|$ for some $x \in H$ implies $\|x\| \leq \|\bar{x}_i\| + \|x-\bar{x}_i\| < M-1$, *i.e.* $x \in \bar{\mathbf{x}}$. Hence for some $c > 0$ we have

$$\begin{aligned} 0 > \sum_{x\in H\setminus\bar{\mathbf{x}}} v(\|x-\bar{x}_i\|) &\geq \sum_{x\in H\setminus\{\bar{x}_i\}:\|x-\bar{x}_i\|\geq M-1-\|\bar{x}_i\|} v(\|x-\bar{x}_i\|) \\ &= \sum_{x\in H':\|x\|\geq M-1-\|\bar{x}_i\|} v(\|x\|) \geq -c(M+1-\|\bar{x}_i\|)^{-3} \end{aligned}$$

by (23), and thus

$$\begin{aligned} \left|\sum_{1\leq i\leq N}\sum_{x\in H\setminus\bar{\mathbf{x}}} v(\|\bar{x}_i - x\|)\right| &\leq \sum_{1\leq i\leq N} c(M+1-\|\bar{x}_i\|)^{-3} \\ &= \mathcal{O}\left(\sum_{k=1}^{M} k^2(M+1-k)^{-3}\right) = \mathcal{O}(M^2) = \mathcal{O}\left(N^{\frac{2}{3}}\right), \end{aligned}$$

which completes the proof. ∎

Remark 3. At least for large N, an optimal Lennard-Jones cluster of N points from $\mathbb{R}^3$ cannot be contained in a plane. This follows from Corollary 6 and Theorem 3. It will be proved in the next section, that optimal Lennard-Jones clusters can be 2-dimensional only if $N \leq 3$.

3. Nearest neighbor results and non-planarity of locally optimal configurations

In the sequel, it will pay to abbreviate $d_{ij}(\mathbf{x}) = \|x_i - x_j\|^2$ the squared Euclidean distances, and $w(d) = v(\sqrt{d})$. Then in terms of w the potential takes the form

$$V(\mathbf{x}) = W(\mathbf{d}(\mathbf{x})) = \frac{1}{2} \sum_i \sum_{j:j\neq i} w(d_{ij}(\mathbf{x}))\,. \tag{24}$$

We start by considering the first and second-order derivatives of V, which we structure into blocks according to the position x_i of the i-th particle.

Lemma 4. *Denote by*

$$\varphi_i(\mathbf{d}) = \sum_{j:j\neq i} \dot{w}(d_{ij})$$

and by

$$A_i = 4 \sum_{j\neq i} \ddot{w}(d_{ij}(\mathbf{x}))(x_i - x_j)(x_i - x_j)^\top \quad \textit{and} \quad B_i = A_i + 2\varphi_i(\mathbf{d}(\mathbf{x}))I_3\,.$$

where I_n denotes the $n \times n$ identity matrix. Then

$$\frac{1}{2}\nabla_{x_i} V(\mathbf{x}) = \sum_{j,j\neq i} \dot{w}(d_{ij})(x_i - x_j) = \varphi_i(\mathbf{d}(\mathbf{x}))x_i - \sum_{j,j\neq i} \dot{w}(d_{ij}(\mathbf{x}))x_j \tag{25}$$

and for the corresponding 3×3 blocks of the Hessian of V we get

$$\nabla^2_{x_i x_i} V(\mathbf{x}) = B_i\,. \tag{26}$$

In a locally optimal configuration $\bar{\mathbf{x}}$, we have

$$\sum_i \varphi_i(\mathbf{d}(\bar{\mathbf{x}})) \leq 0 \tag{27}$$

while

$$-2 \sum_{j:j\neq i} \ddot{w}(d_{ij}(\bar{\mathbf{x}}))d_{ij}(\bar{\mathbf{x}}) \leq 3\varphi_i(\mathbf{d}(\bar{\mathbf{x}})) \quad \textit{for all } i\,. \tag{28}$$

Furthermore, if $N \geq 5$ then there exists a particle i such that

$$\varphi_i(\mathbf{d}(\bar{\mathbf{x}})) < 0\,. \tag{29}$$

Proof. The formulae for the derivatives follow by straightforward calculus. To establish (27), consider the homothety map (i.e., replace x with λx where λ is a scalar close to 1), and calculate the derivative w.r.t. λ:

$$\frac{\mathrm{d}}{\mathrm{d}\lambda}\, V(\lambda\mathbf{x}) = \frac{\mathrm{d}}{\mathrm{d}\lambda}\, W(\lambda^2\mathbf{d}(\mathbf{x})) = \lambda \sum_{i,j} \dot{w}(\lambda^2 d_{ij}(\mathbf{x}))d_{ij}(\mathbf{x})\,.$$

In a local minimizer $\bar{\mathbf{x}}$ of V, the derivative with respect of λ at $\lambda = 1$ must be zero. Hence we obtain

$$\sum_i \sum_{j,j\neq i} \dot{w}(d_{ij}(\bar{\mathbf{x}}))d_{ij}(\bar{\mathbf{x}}) = 0\,.$$

Now, since $v \in \mathcal{V}$, we also get $(d-1)\dot{w}(d) > 0$ for all $d \neq 1$. Hence

$$0 = \sum_i \sum_{j:j\neq i} \dot{w}(d_{ij}(\bar{\mathbf{x}}))d_{ij}(\bar{\mathbf{x}}) \geq \sum_i \sum_{j:j\neq i} \dot{w}(d_{ij}(\bar{\mathbf{x}}))1 = \sum_i \varphi_i(\mathbf{d}(\bar{\mathbf{x}}))\,.$$

Now, if $N \geq 5$, obviously not all distances $d_{ij}(\bar{\mathbf{x}})$ can be equal to unity. Therefore the preceding inequality has to be strict, yielding (29) for at least one i. Furthermore, the trace of the Hessian diagonal block B_i cannot be negative if B_i is positive-semidefinite (which is indeed the case in a local minimizer $\bar{\mathbf{x}}$). This trace equals

$$0 \leq \operatorname{trace} B_i = 4 \sum_{j:j\neq i} \ddot{w}(d_{ij}(\bar{\mathbf{x}}))d_{ij}(\bar{\mathbf{x}}) + 6\varphi_i(\mathbf{d}(\bar{\mathbf{x}}))\,,$$

so that we arrive at (28). □

We continue with a result which seems to be evident. However, this appears to be the first formal proof.

Theorem 4. *Suppose that $\bar{\mathbf{x}}$ is a local minimizer of V of N particles with $N \geq 4$. Then all particle positions $\bar{x}_i$ cannot be contained in the same common plane.*

Proof. Clearly, for $N \leq 3$ the optimal configuration is planar. For $N = 4$, the optimal configuration is a tetrahedron with unity edge length, and therefore non-planar. For $N \geq 5$, we argue by contradiction. Suppose that all $\bar{x}_i$ belong to a two-dimensional subspace. Then the rank of the matrix A_i introduced in Lemma 4 cannot exceed two, whence there exists a vector $v \in \mathbb{R}^3 \setminus \{o\}$ such that $A_i v = o$. On the other hand, B_i must be positive-semidefinite, so that we arrive at

$$0 \leq v^\top B_i v = v^\top A_i v + \varphi_i(\mathbf{d}(\bar{\mathbf{x}}))v^\top v = \varphi_i(\mathbf{d}(\bar{\mathbf{x}}))\|v\|^2 \quad \text{for all } i\,,$$

contradicting (29). Hence the assumption that there is a locally optimal planar configuration $\bar{\mathbf{x}}$ is absurd. □

We close this section by a result on the nearest neighbor distances in a locally optimal configuration.

Theorem 5. *Suppose that $\bar{\mathbf{x}}$ is a local minimizer of V with $N \geq 4$ particles.*
(a) Let $\bar{x}_i$ be a boundary point of the configuration polytope $\operatorname{conv}(\bar{x}_1, \ldots, \bar{x}_N)$. *Then the nearest neighbor particle is not more than unity apart:*

$$\min_{j\neq i} d_{ij}(\bar{\mathbf{x}}) \leq 1\,.$$

(b) Assume that there is a largest zero ξ of the function $d\ddot{w}(d) + \frac{3}{2}\dot{w}(d)$. Then any nearest neighbor particle is not more than $\sqrt{\xi}$ apart:

$$\min_{j\neq i} d_{ij}(\bar{\mathbf{x}}) \leq \xi\,.$$

Proof. To establish (a), assume the contrary: $d_{ij}(\bar{\mathbf{x}}) > 1$ for all $j \neq i$. Then $\dot{w}(d_{ij}(\bar{\mathbf{x}})) > 0$ for all $j \neq i$. Being a boundary point, $\bar{x}_i$ clearly belongs to some facet F of $\operatorname{conv}(\bar{x}_1, \ldots, \bar{x}_N)$. Let v be orthogonal to the supporting hyperplane spanned by F, and oriented such that $\beta_j := v^\top(\bar{x}_i - \bar{x}_j) > 0$ for all $\bar{x}_j \notin F$. By Theorem 4 there is at least one j with that property. Note that in a local minimizer $\bar{\mathbf{x}}$, the gradient must vanish, so that multiplying (25) by $v^\top$ yields $0 = \sum_j \beta_j \dot{w}(d_{ij}(\bar{\mathbf{x}})) > 0$,

which is absurd. Thus, for some $x_j \notin F$ we have $d_{ij}(\bar{\mathbf{x}}) \leq 1$. To prove (b), we show that

$$d\ddot{w}(d) + \frac{3}{2}\dot{w}(d) < 0 \quad \text{for all } d > \xi \vee 1\,. \tag{30}$$

(Since $1\ddot{w}(1) + \frac{3}{2}\dot{w}(1) \geq 0$ this will give us $\xi \geq 1$ as a byproduct.) Indeed, if the opposite sign were the case in (30), from dividing by $d\dot{w}(d) > 0$ we would obtain

$$0 \leq \int_{t_0}^{t} \left(\frac{\ddot{w}(s)}{\dot{w}(s)} + \frac{3}{2s} \right) ds = \left[\ln \left(\dot{w}(s) s^{\frac{3}{2}} \right) \right]_{t_0}^{t} \quad \text{for all } t \geq t_0 := \xi \vee 1\,,$$

which would entail $\dot{w}(t) \geq \dot{w}(t_0) t_0^{\frac{3}{2}} t^{-\frac{3}{2}}$, and hence, after performing another integration, $w(d) = -\int_d^\infty \dot{w}(t)dt \leq -2\dot{w}(t_0) t_0^{\frac{3}{2}} d^{-\frac{1}{2}}$ or $r^2|v(r)| \geq Cr$ with $C > 0$, conflicting with the integrability condition in the definition of $\mathcal{V}$. But now it is immediate that $d_{ij}(\mathbf{x}) > \xi$ cannot hold for all $j \neq i$: else, we would arrive, by (30) at

$$\sum_{j:j\neq i} \ddot{w}(d_{ij}(\bar{\mathbf{x}})) d_{ij}(\bar{\mathbf{x}}) + \frac{3}{2}\varphi_i(\mathbf{d}(\bar{\mathbf{x}})) < 0\,,$$

contradicting (28). □

Corollary 7. *For the Lennard-Jones potential function, the nearest-neighbor distance in a locally optimal configuration is at most* $\sqrt[6]{\frac{11}{5}} \approx 1.1404$. *Also, the Morse potential functions satisfy the condition in Theorem 5(b) and the corresponding nearest neighbor distance bounds* $\sqrt{\xi_\rho}$ *are specified for selected values of* ρ *in the table below.*

ρ	$\sqrt{\xi_\rho}$	ρ	$\sqrt{\xi_\rho}$
6	1.1466	11	1.0719
7	1.1216	12	1.0652
8	1.1037	13	1.0596
9	1.0904	14	1.0549
10	1.0801	15	1.0509

Proof. It is straightforward to show that there is a unique zero $\xi = \sqrt[3]{\frac{11}{5}}$ of $d\ddot{w}_{\mathrm{LJ}}(d) + \frac{3}{2}\dot{w}_{\mathrm{LJ}}(d) = 3d^{-7}\left(11 - 5d^3\right)$ in the Lennard-Jones case. For the Morse potential, we put $u_\rho = \rho(1-r)$ and observe that a zero of $d\ddot{w}_\rho(d) + \frac{3}{2}\dot{w}_\rho(d)$ with $w_\rho(d) = e^{2u_\rho} - 2e^{u_\rho}$ and $d = r^2$ satisfies

$$\frac{\rho}{2}\, r = \frac{1 - e^{u_\rho}}{1 - 2e^{u_\rho}}\,.$$

Since the right-hand side above tends to unity as $r \to \infty$, there must be a largest zero also in this case. □

Remark 4. The following example shows that there are pairwise potential functions in $\mathcal{V}$ which violate the condition in Theorem 5(b): Let

$$w(d) = \frac{2\cos(6\ln d) - 4\sin(6\ln d) - 19}{10d^3} - \frac{5\cos(6\ln d) - 5\sin(6\ln d) - 19}{20d^6} = \mathcal{O}(d^{-3})$$

as $d \to \infty$, with $w(1) = -1$ and derivative $\dot{w}(d) = \dot{w}_{\mathrm{LJ}}(d)\frac{19 - 10\cos(6\ln d)}{20}$ which has the same sign as its counterpart in the Lennard-Jones case $\dot{w}_{\mathrm{LJ}}(d) = 6\left(d^{-4} - d^{-7}\right)$.

Hence $v(r) = w(r^2)$ gives a function $v \in \mathcal{V}$. Taking a further derivative we arrive at

$$\frac{4d^4}{3}\left(d\ddot{w}(d) + \frac{3}{2}\dot{w}(d)\right) = [10\cos(6\ln d) + 24\sin(6\ln d) - 19] + \mathcal{O}(d^{-3}),$$

and the bracketed expression on the right-hand side has an unbounded sequence of zeroes with non-vanishing derivative. By continuity arguments, there also has to be an unbounded sequence of zeroes of $d\ddot{w}(d) + \frac{3}{2}\dot{w}(d)$.

Conclusions

In this paper we introduced a new technique which, under quite mild assumptions, provides quite accurate lower bounds on the minimum inter-particle distance in globally optimal clusters of identical particles interacting via a pairwise potential. Our technique, when applied to the well-known Lennard-Jones and Morse potentials, yields bounds which significantly improve over those previously known in the literature. We also obtained results on the non planarity of optimal configurations, derived bounds on nearest neighbor distances and obtained improved bounds on the ratio V_N/N. Although these results are an improvement over published ones, one quite important property still remains to be proven (as it seems very reasonable to think that it holds true), namely the fact that the diameter of a globally optimal configuration cannot grow faster than $\mathcal{O}(\sqrt[3]{N})$. The proof of non planarity of optimal clusters (of course for $N \geq 4$) is a step in the good direction, but a proof of this bound on the maximum inter-particle distance and, what might be extremely important in applications, a sharp estimate of the constant behind the $\mathcal{O}(\sqrt[3]{N})$ term is still missing and can be considered as a good challenge for researchers in the field.

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