Development, comparison and application of global optimization methods and investigation of atomic cluster problems

abstract of the dissertation

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1 Introduction

The investigated optimization problems. *Bound constrained global optimization problems* have the form

$$\min_{x \in S} f(x), \tag{1}$$

where $f : \mathbb{R}^n \to \mathbb{R}$ is the *objective function* and $S \subseteq \mathbb{R}^n$ is the *search space*.

Constrained global optimization problems are formalized as

$$\begin{array}{rl} \min & f(x) \\ \text{subject to} & g_i(x) \leq \ 0 \quad (i = 1, \ldots, l) \\ & x \in S, \end{array} \tag{2}$$

where $g_i : \mathbb{R}^n \to \mathbb{R}$ for all $i \in \{1, \ldots, l\}$.

Constraint satisfaction problem are of the form (2) without the objective function.

The set of points that satisfy problem (2) or a constraint satisfaction problem is called the set of *feasible* solutions. The points that are not satisfying the constraints are called *infeasible* solutions.

The topic of the thesis belongs to the field of complete global optimization. *Complete* methods are in exact arithmetic guaranteed to find the global minimizer (with some tolerances) with a predictable amount of work. Here predictable only means relative to known problem characterestic such as Lipschitz constant or other global information needed for the convergence proof. A subclass of the complete methods consists of the rigorous methods. A *rigorous method* reaches a global minimum with certainty and within given tolerances even in the presence of rounding errors. The interval arithmetic based branch-and-bound type global optimization methods belong to this class.

2 Accelerating interval global optimization methods

In this chapter real numbers are denoted by small letters while intervals are denoted by capital letters.

Interval arithmetic. The *interval* X is generally indentified with the (nonempty) set of points between its lower and upper bound: $X = [\underline{X}, \overline{X}] = \{x \in \mathbb{R} \mid \underline{X} \leq x \leq \overline{X}\}$, so that $x \in \mathbb{R}$ is *contained* in interval X, i.e., $x \in X$ iff $\underline{X} \leq x \leq \overline{X}$. We write $\underline{X}$ for the *lower bound* and $\overline{X}$ for the *upper bound* of X. In case of an n dimensional *interval vector* $X = (X_1, \ldots, X_n)^T$ denotes the *components* $X_k = [\underline{X}_k, \overline{X}_k]$ $(k = 1, \ldots, n)$.

The set of all n dimensional intervals is denoted by $\mathbb{I}^n$. If $D \subseteq \mathbb{R}^n$ then $\mathbb{I}(D) := \{X \mid X \in \mathbb{I}, X \subseteq D\}$. The *width* of $X \in \mathbb{I}$ is $\mathrm{wid}\,(X) = \overline{X} - \underline{X} \geq 0$, while the width of $X \in \mathbb{I}^n$ is defined by $\mathrm{wid}\,(X) = \max_{i=1,\ldots,n} \mathrm{wid}\,(X_i)$.

Interval operations. The real type *elementary arithmetic operations* are extended to interval arguments by $X \circ Y := \{x \circ y \mid x \in X, y \in Y\} \in \mathbb{I}$, where $\circ \in \{+, -, \cdot, /\}$. Since the elementary operations are continous these operations can be done easily.

Interval inclusion functions. We call a function $F : \mathbb{I}(X) \to \mathbb{I}$ an *inclusion function* of f in X if $x \in Y$ implies $f(x) \in F(Y)$ for all $Y \in \mathbb{I}(X)$. The *range* of the function f on X is denoted by $f(X)$. Moreover, $\underline{f}(X)$ denotes the lower bound of the range, while $\underline{F}(X)$ and $\overline{F}(X)$ denote the lower and the upper bound of the interval inclusion of the range, respectively.

In the following the derivative (vector) of function f is denoted by f' and its interval inclusion by F'.

Properties of inclusion functions. We call F an *inclusion isotone function* over X, if for all $Y, Z \in \mathbb{I}(X)$ $Y \subseteq Z$ implies $F(Y) \subseteq F(Z)$.

We call the inclusion function F an *α-convergent inclusion function* over X if for all $Y \in \mathbb{I}(X)$ $\operatorname{wid}(F(Y)) - \operatorname{wid}(f(Y)) \leq k(\operatorname{wid}(Y))^\alpha$ holds, where α and k are positive constants.

The function $F : \mathbb{I}^n \to \mathbb{I}$ is said to be *Lipschitz continous* on the interval $X \in \mathbb{I}^n$ if there exists such a $k \in \mathbb{R}$ that $\operatorname{wid}(F(Y)) \leq k \operatorname{wid}(Y)$ holds for all $Y \subseteq X$.

Centered forms

For the sake of simplicity the endpoints of the considered subinterval Y are denoted by a and b. The elements of the gradient vector are denoted by $[\ell_i, u_i]$ $i = 1, \ldots, n$, where the indices are simply neglected in the one dimensional case.

In the following we assume that $\ell_i < 0 < u_i$ holds for all $i = 1, \ldots, n$. If $u_i \leq 0$ or $\ell_i \geq 0$ for some i then f is monotonic, thus the range can easily be calculated.

The one dimensional case is considered first.

Optimal centered forms. The centered form is defined as

$$f(x) \in F_{CF}(Y, c) := f(c) + F'(Y)(Y - c).$$

Here, by the argument of Baumann, c can be chosen to be optimal in the sense that the lower bound of the range inclusion would be maximal (using centered forms).

Linear boundary value form. Following the idea of Neumaier the *linear boundary value form* (lbvf) gives a lower bound for the range as

$$\underline{F}_{LBVF}(Y) = y_s = \frac{uf(a) - \ell f(b)}{u - \ell} + (b - a)\frac{\ell u}{u - \ell}.$$

This is stated in Theorem 4 in the thesis.

Kite inclusion function – one dimensional case

Based on the results of Vinkó, Lagouanelle & Csendes [3] one can see that the simultaneus use of the two methods above leads to a considerably better bound for the range inclusion.

Define the function $\underline{F}_K(Y, c) := \min\{y_r(c), y_t(c)\}$, where

$$y_r(c) := \frac{uf(a) - \ell f(c) + \ell u(c - a)}{u - \ell}, \quad \text{and} \quad y_t(c) := \frac{uf(c) - \ell f(b) + \ell u(b - c)}{u - \ell}.$$

The value $\underline{F}_K(Y,c)$ is called the *lower bound of the kite.*

Using a similar argument, the upper bound $\overline{F}_K(Y,c')$ can also be defined. This can be found in the thesis too.

Theorem 5 [3] *The inequalities* $\max\{\underline{F}_{LBVF}(Y), \underline{F}_{CF}(Y,c)\} \leq \underline{F}_K(Y,c) \leq \underline{f}(Y)$ *hold.*

Optimal center. Consider now the optimal choice of the center of the kite. This is such a point c^* that

$$\underline{F}_K(Y,c^*) = \max_{c\in[a,b]} \underline{F}_K(Y,c) = \max_{c\in[a,b]} \min\{y_r(c), y_t(c)\}$$

holds. The next theorem summarizes some properties of the optimal center.

Theorem 6 [3] *There is a unique* $c^* \in [a,b]$ *such that* $y_R(c^*) = y_T(c^*)$*, and* c^* *is a maximizer of* $\underline{F}_K(Y,c)$*.*

Properties of the kite inclusion. Theorem 7 of the thesis says that if the inclusion F' is isotone then also $F(Y) = [\underline{F}_K(Y,c^*), \overline{F}_K(Y,c')]$ is isotone for all $Y \in \mathbb{I}(X)$ intervals. By Theorem 8 the kite inclusion is quadratically convergent. The pruning effect is explained as follows.

Theorem 9 [3] *Let* $Y = [a,b] \subseteq X$ *be the current considered subinterval,* $c^* \in [a,b]$ *be a maximizer of* $\underline{F}_K(Y,\cdot)$*, and* $\tilde{f}$ *be the current guaranteed upper bound for the global minimum value of* f*. Let us define the following values:*

$$p = a + \frac{\tilde{f} - f(a)}{\ell}, \qquad q = c^* + \frac{\tilde{f} - f(c^*)}{u},$$
$$r = c^* + \frac{\tilde{f} - f(c^*)}{\ell}, \qquad s = b + \frac{\tilde{f} - f(b)}{u}.$$

If $\ell < 0 < u$*, then a pruning technique based on the kite algorithm can be used in the sense that*

(a) If $\tilde{f} < \min\{f(a), f(b), f(c^*)\}$ *then all the global minimizer points of* Y *are contained in the intervals* $[p,q]$ *and* $[r,s]$*.*

(b) If $f(b) \leq \tilde{f} < \min\{f(a), f(c^*)\}$ *then all the global minimizer points of* Y *are contained in the intervals* $[p,q]$ *and* $[r,b]$*.*

(c) If $f(a) \leq \tilde{f} < \min\{f(b), f(c^*)\}$ *then all the global minimizer points of* Y *are contained in the intervals* $[a,q]$ *and* $[r,s]$*.*

(d) If $f(c^*) \leq \tilde{f} < \min\{f(a), f(b)\}$ *then all the global minimizer points of* Y *are contained in the interval* $[p,s]$*.*

(e) If $\max\{f(b), f(c^*)\} \leq \tilde{f} < f(a)$ *then all the global minimizer points of* Y *are contained in the interval* $[p,b]$*.*

(f) If $\max\{f(a), f(c^*)\} \leq \tilde{f} < f(b)$ *then all the global minimizer points of* Y *are contained in the interval* $[a, s]$.

(g) If $\max\{f(a), f(b)\} \leq \tilde{f} < f(c^*)$ *then all the global minimizer points of* Y *are contained in the intervals* $[a, q]$ *and* $[r, b]$.

Numerical results. The numerical computation was done and reported in section 2.4.5 of the thesis to show the performance improvement. We tested 40 one dimensional functions. Two implementations were studied. The first was based on the usage of the first derivative, while the other one used second derivative to made a Newton step. It was shown that the test functions can be solved with less computational effort compared to the traditional algorithm. Another comparison with two recently published methods (one which uses lbvf inclusion and a pruning method and the other one uses the optimal centered form with a pruning) was made as well. The kite method performs better (at least on the used test functions) than those two algorithms.

Kite inclusion – multidimensional case

In this section a possible extension of the kite inclusion function is given based on Vinkó & Ratz [5].

For the remaining of this chapter an inclusion of the gradient vector $f'(y)$ is denoted by $F'(Y)$, while the ith component of this vector we use the notation $F_i'(Y) = [\ell_i, u_i]$. We assume that $\ell_i u_i < 0$ holds for all $i = 1, \ldots, n$.

Componentwise extension of the kite. Let $f : D \subseteq \mathbb{R}^n \to \mathbb{R}$ and $Y = Y_1 \times \ldots \times Y_n \subseteq D$. Let us define $g_i : Y_i \subseteq \mathbb{R} \to \mathbb{I}$ $(i \in \{1, \ldots, n\})$ by

$$g_i(w) := f(Y_1, \ldots Y_{i-1}, w, Y_{i+1}, \ldots, Y_n), w \in Y_i.$$

Using this one dimensional interval valued function we are able to use the one dimensional version of the kite enclosure method. If we have $V \supseteq g_i(\underline{Y}_i), W \supseteq g_i(\overline{Y_i})$ and $Z \supseteq g_i(c_i)$ where $(c_i \in Y_i)$, then the componentwise kite enclosure can be built up with the usage of the componentwise centered form, i.e.

$$\underline{F}_{CF}(Y, c, i) = \underline{Z} + F_i'(Y)(Y_i - c_i), \quad (c_i \in Y_i),$$

and the componentwise linear boundary value form

$$\underline{F}_{LBVF}(Y, i) = \frac{u_i \underline{V} - \ell_i \underline{W}}{u_i - \ell_i} + (\overline{Y_i} - \underline{Y}_i)\frac{\ell_i u_i}{u_i - \ell_i}.$$

This leads to the following result.

Theorem 10 *Let* $\underline{F}_K(Y, c, i) = \min\{y_R(c, i), y_T(c, i)\}$, *where* $c \in Y$,

$$\begin{aligned} y_R(c, i) &= \frac{u_i \underline{V} - \ell_i \underline{Z} + u_i \ell_i (c_i - \underline{Y}_i)}{u_i - \ell_i}, \\ y_T(c, i) &= \frac{u_i \underline{Z} - \ell_i \underline{W} + u_i \ell_i (\overline{Y_i} - c_i)}{u_i - \ell_i}, \end{aligned}$$

$Z \supseteq g_i(c_i)$, $V \supseteq g_i(\underline{Y}_i)$ and $W \supseteq g_i(\overline{Y_i})$, and $i = 1, \ldots, n$. Then

$$\max\{\underline{F}_{LBVF}(Y,i), \underline{F}_{CF}(Y,c,i)\} \leq \underline{F}_K(Y,c,i) \leq \underline{f}(Y)$$

hold for every $i = 1, \ldots n$.

In the inequality above the parameter c can be set to be optimal. That is we can find the point c^* such that

$$\underline{F}_K(Y,c^*,i) = \max_{c \in Y} \underline{F}_K(Y,c,i) = \max_{c \in Y} \min\{y_R(c,i), y_T(c,i)\}.$$

To obtain this optimal c^* Theorem 6 can be used for every coordinate direction.

Theorem 11 [5] *For all $i = 1, \ldots, n$ there is a unique $c^* \in Y$ such that $y_R(c^*,i) = y_T(c^*,i)$, and c^* is a maximizer of $\underline{F}_K(Y,c,i)$.*

Since the computational cost of the componentwise extension is high, it is not recommended to be used in the interval global optimization algorithms as an inclusion function. This approach is used better in the construction of a new accelerating tool.

Componentwise pruning. Using the computed value needed for the construction of the componentwise kite inclusion function, a pruning method can be developed. The following theorem gives the necessary formulas.

Theorem 12 [5] *Let $Y \subseteq X \subseteq \mathbb{I}^n$ be the current considered subinterval, $c \in Y$, $F'(Y)$ be an enclosure of the gradient of $f(Y)$, and $\tilde{f}$ be the current guaranteed upper bound for the global minimum value. If we have $Z \supseteq g_i(c_i)$, $V \supseteq g_i(\underline{Y}_i)$ and $W \supseteq g_i(\overline{Y_i})$,*

$$p_i = \underline{Y}_i + \frac{\tilde{f} - \underline{V}}{\ell_i}, \qquad q_i = c_i + \frac{\tilde{f} - \underline{Z}}{u_i},$$
$$r_i = c_i + \frac{\tilde{f} - \underline{Z}}{\ell_i}, \qquad s_i = \overline{Y_i} + \frac{\tilde{f} - \underline{W}}{u_i},$$

then for every $i \in \{1, \ldots, n\}$ the following statements hold.

(a) If $\tilde{f} < \min\{\underline{V}, \underline{W}, \underline{Z}\}$ then all the global minimizer points of Y are contained in the intervals $Y_1 \times \ldots \times Y_{i-1} \times [p_i, q_i] \times Y_{i+1} \times \ldots \times Y_n$ and $Y_1 \times \ldots \times Y_{i-1} \times [r_i, s_i] \times Y_{i+1} \times \ldots \times Y_n$.

(b) If $\underline{W} \leq \tilde{f} < \min\{\underline{V}, \underline{Z}\}$ then all the global minimizer points of Y are contained in the intervals $Y_1 \times \ldots \times Y_{i-1} \times [p_i, q_i] \times Y_{i+1} \times \ldots \times Y_n$ and $Y_1 \times \ldots \times Y_{i-1} \times [r_i, \overline{Y_i}] \times Y_{i+1} \times \ldots \times Y_n$.

(c) If $\underline{V} \leq \tilde{f} < \min\{\underline{Z}, \underline{W}\}$ then all the global minimizer points of Y are contained in the intervals $Y_1 \times \ldots \times Y_{i-1} \times [\underline{Y}_i, q_i] \times Y_{i+1} \times \ldots \times Y_n$ and $Y_1 \times \ldots \times Y_{i-1} \times [r_i, s_i] \times Y_{i+1} \times \ldots \times Y_n$.

(d) If $\underline{Z} \leq \tilde{f} < \min\{\underline{V}, \underline{W}\}$ then all the global minimizer points of Y are contained in the interval $Y_1 \times \ldots \times Y_{i-1} \times [p_i, s_i] \times Y_{i+1} \times \ldots \times Y_n$.

(e) *If* $\max\{\underline{W}, \underline{Z}\} \leq \tilde{f} < \underline{V}$ *then all the global minimizer points of* Y *are contained in the interval* $Y_1 \times \ldots \times Y_{i-1} \times [p_i, \overline{Y_i}] \times Y_{i+1} \times \ldots \times Y_n$.

(f) *If* $\max\{\underline{V}, \underline{Z}\} \leq \tilde{f} < \underline{W}$ *then all the global minimizer points of* Y *are contained in the intervals* $Y_1 \times \ldots \times Y_{i-1} \times [\underline{Y_i}, s_i] \times Y_{i+1} \times \ldots \times Y_n$.

(g) *If* $\max\{\underline{V}, \underline{W}\} \leq \tilde{f} < \underline{Z}$ *then all the global minimizer points of* Y *are contained in the intervals* $Y_1 \times \ldots \times Y_{i-1} \times [\underline{Y_i}, q_i] \times Y_{i+1} \times \ldots \times Y_n$ *and* $Y_1 \times \ldots \times Y_{i-1} \times [r_i, \overline{Y_i}] \times Y_{i+1} \times \ldots \times Y_n$.

A javasolt algoritmus. Based on the above result a new branch-and-bound type inteval global optimization algorithm was proposed in subsection 2.5.3. Corollary 3 of the thesis states that using this algorithm we cannot loose global minimizer points which are in the starting interval X.

Numerical results. In this section the discussion of the implementation of the proposed algorithm and the numerical comparison with the traditional one is given. Summarizing the numerical results we can conclude that the new algorithm using the pruning technique proved to be better than the traditional one on the test problems. The improvements are larger on the harder to solve problems. A comparison was made with two recently proposed technique (namely AMIGO and MIAG). The kite method was better in general, the performance improvement was 15% and 35% compared to AMIGO and MIAG, respectively. However, calculating the average of the percentages for each of the test problems we obtained worse results. This shows that the other two techniques are a little bit better on the harder to solve problems.

3 A methodology for benchmarking global optimization solvers

In this chapter an algorithmical procedure is introduced to compare and benchmark complete global optimization solvers. Neumaier *et al.* [1] gives the results of a benchmark we performed. In this thesis the underlying methodology is described.

Arrangements

The test set. The test set consists of 1322 models varying in dimension (number of variables, this is the COCONUT Benchmarking Set). The problems are divided into 3 libraries. In each library the problems are sorted with respect to their sizes (number of variables) as size1 ($n \leq 10$), size2 ($10 < n \leq 100$), and size3 ($100 < n \leq 1000$).

Timing. Because of the large number of models to be solved, we performed our tests on a number of different computers. There are many proposition to measure the computational time. After some considerations we decided to norm with the CPU frequency in MHz.

Uniform input. A good benchmark set must be one that can be interfaced with all existing solvers, in a way that a sufficient number of comparative results can be

obtained. Our test sets are coded in the AMPL language. Converters are provided which are able to produce different input formats.

Converters. We provided several converters that mediate between different input formats for the same model. For a correct solution of the models, and for reliable comparisons between different solvers based on different input formats, it is very important that these converters behave correctly. To check the correctness of the converters we used the following general working scheme: From a collection of models in AMPL, make several converted formats. Solve each models with different solvers and then compare the results. Note that in the last Step the differences between the results could also have been caused by the solvers.

Performance criteria. Since the testing was made on different computers the time limits must be normalized to compare the results. Different time limits were set for the problem sizes: $\frac{\text{limit} \times 1000}{\text{CPU MHz}}$ The reliability of the claimed results is the most poorly documented aspect of current global optimization softwares. We proposed categories to describe the quality claimed. These made easier to compare the success of the different solvers.

Cheking for best function value. In the first step all the output of the solvers were uniformed. Then the program `solcheck` form the COCONUT Environment checks the feasibility of putative solutions of solver results. The feasible results were taken into account, and the best function value was chosen from the minimum of the (nearly) feasible solutions by any solver.

The making of the hitlist consists of the following steps. We take all the benchmarking results and choose the best function values. If there are more than one such a candidate then the one for which the maximal infeasibility is minimal. This value is the best solution. If there was no feasible solution for a given model the (local) solution with the minimal residual was chosen (but the result marked as infeasible).

The hitlist is available online from a website.

Notation in tables

The testing environment produces tables about the performance of the solvers.

Summary statistics: how often the solution was in fact global, how often it was in fact not global and how many models are in fact infeasible.

Detailed tables: one can consider the behaviour of a solver based on the introduced output classification.

Comparison of running times: two or more solvers can be compared with respect to their speed and success.

Reliability analysis: gives a summary of the reliability of the solvers.

Short review on the bechmarking results. Among the tested global solvers, BARON is the fastest and most robust one, with LINGO and OQNLP being close.

None of the current global solvers is fully reliable, with one exception: for pure constraint satisfaction problems, ICOS, while slower than BARON, has excellent reliability properties when it is able to finish the complete search.

The benchmarking was helpful for the developers of the solvers. The authors of BARON and ICOS were able to improve the performance and the reliability of their solvers on this basis.

4 Atom cluster problems

In this chapter atom cluster problems are investigated. The results are based on the articles VINKÓ [2] and a VINKÓ & NEUMAIER [4].

Definitions. Given a cluster of n atoms in a 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 thesis deals with potential energy functions that contain only pair potential functions, i.e.,

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

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. The introduced methods are general in the sense that only some properties are fixed to be satisfied by the pair potential functions.

Notation. The following notation will be used. A global minimizer of the function E is any configuration $x^* \in \mathbb{R}^{dn}$ with $E^* := E(x^*) = \min_{x \in \mathbb{R}^{dn}} E(x)$, 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 $E_i(x) = \sum_{i \neq j} v(\|x_i - x_j\|)$ $(i = 1, \ldots, n)$ and we set $E_i^* = E_i(x^*)$. Clearly, the total energy is $E(x) = \dfrac{1}{2} \sum_{i=1}^{n} E_i(x)$. The *minimal inter-particle distance* in the optimal structure is $r^* = \min_{i,j} r_{ij}$ $(i, j = 1, \ldots, n)$. The lower bound for the minimal distance is denoted by q, i.e., our task is to find a good underestimation $q \leq r^*$. The only positive root of the pair potential function is denoted by t, if any.

Without loss of generality let us suppose that $x_1 = 0$ and $0 = r_1 < r_2 \leq \ldots \leq r_n$, where $r_j = \|x_j - x_1\| = \|x_j\|$ $(j = 1, \ldots, n)$.

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

Requirements to be satisfied by the pair potential. For the pair potential $v(r)$ we set the following requirements to be satisfied:

(P1) v is continous.

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

(P3) $v(r) \to 0$ $(r \to \infty)$.

(P4) $v(r)$ is strictly decreasing if $r < s$ and strictly increasing if $r \geq s$.

Size dependent bounds

In this section we suppose that the pair potential function v satisfies the properties (P1)–(P4).

Lemma 1 [4] *An optimal n-atom cluster has total energy bounded by*

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

Lemma 2 [4] *In the optimal configuration the potential energy of particle i can be bounded by $-(n-1)|v(s)| \le E_i^*(n) < -e_d|v(s)|$, where $e_d = 1$.*

The upper bound in Lemma 2 is in fact independent from the dimension and the size of the given optimal cluster. The optimal structure most likely has d contacts, but showing this rigorously seems to be nontrivial, so that the statement remains open. In the following the upper bound of E_i^* will be denoted by $-e_d|v(s)|$.

Lemma 3 [4] *If $n > 2 + e_d$ then*

$$q(n) = w\Big((n-2-e_d)|v(s)|\Big)$$

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

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

Size independent bounds – first version

The following results are based on Vinkó [2].

Requirements to be satisfied by the pair potential. For the usage of the method the restriction of properties (P1)–(P4) are needed. Namely, let us suppose that the pair potential v satisfies properties (P1) and (P2) and

(P3') if $r \le s$ then v is strictly decreasing and $v(r) \ge r^{-4}$,

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

The auxiliary bounds. It is easy to see that $r_{\min} \le s$ holds for the optimal structure. This is stated in Lemma 4. Moreover, the following statements hold.

Lemma 5 [2] *For $\frac{q}{2} < a < b$, the index set $\mathcal{J}_{ab} = \{j \mid a \le r_j < b\}$ has size*

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

Lemma 6 [2] *If $pq \geq s$, then* $\sum_{q \leq r_j < pq} v(r_j) \geq v(q) - \left((2p+1)^d - 1)\right) |v(s)|$.

Lemma 7 [2] *Let $s \leq pq = R_0 < R_1 < R_2 < \ldots$ be an infinite strictly increasing sequence and define the index set $\mathcal{I}_k = \{j \mid 2 \leq j \leq n, R_k \leq r_j < R_{k+1}\}$ $(k = 0, 1, 2, \ldots)$. If $pq \geq s$, then* $\sum_{r_j \geq pq} v(r_j) \geq \frac{1}{q^d} \sum_{k=0}^{\infty} v(R_k) \left((2R_{k+1} + +q)^d - (2R_k - q)^d\right)$.

Minimal inter-particle distance. Using the above lemmas the following method can be introduced to obtain the minimal interatomic distance in the optimal potential energy function E. In Lemma 7 we use an increasing sequence R_k which represents an infinite sequence of spherical shells. Instead of this sequence one can use the function $R : \mathbb{R}_+ \times \mathbb{N}_0 \to \mathbb{R}_+$ having the properties $R(Q,k) < R(Q,k+1)$ and $R(Q,0) = c$, where $c \in \mathbb{R}_+$ is a constant (in the proof of Lemma 7 this constant is pq, the staring point of the infinite sequence). For technical reasons we use the notation R_k^Q for the functions $R(Q,k)$. Moreover, we write $U_c^Q := \{R_k^Q \mid R_k^Q < R_{k+1}^Q$ and $R_k^Q = c$ and $k = 0, 1, \ldots\}$.

Let us define now

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

Theorem 13 [2] *Define the function $g_v(q,p,Q) := G(q,p,R)$. If $g_v(q,p,Q) > -\infty$ then in the optimal atom cluster problem the minimal inter-particle distance is greater than or equal to the solution q of the nonlinear system of equations*

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

One can improve the result that can be achieved with Theorem 13. If we substitute the first m term of the sequence R_k with variables $p_1, \ldots, p_m$ then we have a function G with $m+2$ variables. Namely,

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

where $F(q,p)$ is defined in (3), $p_1 q \geq s$, and $R_k^Q \in U_{p_m q}^Q$.

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

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

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

Theorem 14 [2] *If* q *is a lower bound obtained by the usage of Corollary 1 for the minimal inter-particle distance, then there exists a constant* B_1 *such that* $-\frac{B_1}{2}n \leq E^*$. *Moreover,* B_1 *can be computed using the value of* q.

Size independent bounds – improved version

The motivation for the improved version was the fact that the above method cannot be used directly if the pair potential function diverges as the distance between the atoms taken into account is decreasing. The following results are from Vinkó & Neumaier [4].

Requirements to be satisfied by the pair potential. For the usage of the improvement method we assume that the pair potential function satisfies properties (P1) and (P2) and

(P3") 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 if the potential $v(r)$ diverges for $r \to 0$.

The auxiliary bounds. 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

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

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

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 $N_d(r) \le \lfloor r^d \rfloor$, which we shall use in the following.

Assertion 1 [4] *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 $k \le K(r_k)$ for all $k = 1, 2, \ldots$. In particular,

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

Assertion 2 [4] *If $r_m \le s$ then $\Sigma_m \le -m|v(s)| + E_1^* + \int_s^\infty K(r)v'(r)dr$. Moreover, if $m \ge 2$ and $R_m \le s$ then*

$$(m-1)v(R_m) + (m + e_d)|v(s)| \le \int_s^\infty K(r)v'(r)dr.$$

Minimal inter-particle distance.

Theorem 15 [4] *Let $[\underline{R}, \overline{R}] \subseteq [0, s]$ be such that*

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

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

Then the function defined by

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

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

Note that property (P3") implies the satisfiability of the assumption (take $\underline{R} = \overline{R} = R$.)

Linear lower bound for the optimal energy.

Theorem 16 [4] *If* $B_2 := -|v(s)| + \int_s^\infty K(r)v'(r)dr < \infty$ *then* $E_i^* \geq -B_2$ *for all* $i = 1, \ldots, n$. *Moreover, for any such constant* B_2 $-\frac{B_2}{2}n \leq E^*$ *holds.*

Corollary 2 [4] *If* q *is a lower bound on the minimal inter-particle distance* $r_{\min}$ *then* $E_i^* \geq B := -|v(s)| + \int_s^\infty \left\lfloor \left(\frac{2r}{q} + 1\right)^d \right\rfloor v'(r)dr$.

Lennard-Jones clusters

In general form the Lennard-Jones pair potential function is

$$v_{t,\varepsilon}(r) = 4\varepsilon\left(\left(\frac{t}{r}\right)^{12} - \left(\frac{t}{r}\right)^{6}\right), \tag{3}$$

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 $t = 1, \varepsilon = 1$). The Lennard-Jones potential function is defined by

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

Size dependent bound for the minimal inter-particle 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

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

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

Size independent bounds for the minimal inter-particle distance. The translation between the general and the scaled Lennard-Jones pair potential is

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

thus the minimal distance scales with s and the potential scales with ε. We give the calculation for the scaled version; then the result for the general case is straightforward. Using Theorem 13 one obtains $r_{\min} \geq 0.6187$, while Theorem 15 gives $r_{\min} \geq 0.6547$ for $d = 3$.

Linear lower bounds for the optimal energy. The values from the numerical result of Theorem 13 give $-138.6775911n \cdot \varepsilon \leq LJ_{\sigma,\varepsilon}^*$ $(n = 2, 3, \ldots)$ for $d = 3$. From Theorem 15 and Corollary 2 it follows that $-68.9554\varepsilon n \leq LJ_{t,\varepsilon}^*$ for $d = 3$ and $-9.4478\varepsilon n \leq LJ_{t,\varepsilon}^*$ for $d = 2$.

Morse clusters

Another famous model cluster is the *Morse cluster*, for which the pair potential function is $v_\rho(r) = e^{\rho(1-r)}\left(e^{\rho(1-r)} - 2\right)$. Here, $\rho > 0$ is a parameter. The *Morse potential* is defined as

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

Size dependent bounds for the minimal inter-particle 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

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

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

Size independent bounds for the minimal inter-particle distance. The general method from subection 4.3.1 is not applicable directly here since the Morse potential does not satisfy property (P3'). The reason for it is that function v_ρ is defined even in the case when $r = 0$ (i.e., when two particles are in the same position). In this case information on the minimal interatomic distance could help. Locatelli & Schoen considered such a property of the Morse clusters and proved that if $6 \le \rho \le 15$, then the minimal distance remains strictly positive. This can substitute property (P3').

The following table contains the calculations obtained by the above methods. The results obtained by the first method are in the column three. The improved method was able to establish lower bounds for $\rho \ge 4.967$. It is important to note that in this case no previous information about the value of $r_{\min}$ is needed.

ρ	lower bound for M_ρ by Theorem 14	value of q by Theorem 13	lower bound for M_ρ by Corollary 2	value of q by Theorem 15
15	$-30.370n$	0.854645	$-21.6176n$	0.865683
14	$-32.240n$	0.842336	$-22.5917n$	0.854691
13	$-34.581n$	0.827767	$-23.8037n$	0.841725
12	$-37.594n$	0.810249	$-25.3520n$	0.826193
11	$-41.617n$	0.788778	$-27.3977n$	0.807236
10	$-47.255n$	0.761821	$-30.2230n$	0.783551
9	$-55.712n$	0.726898	$-34.3707n$	0.753054
8	$-69.762n$	0.679650	$-41.0345n$	0.712129
7	$-97.522n$	0.611312	$-53.4416n$	0.653727
6	$-177.619n$	0.498595	$-84.4438n$	0.560668
5	–	–	$-365.2798n$	0.333473
4.967	–	–	$-461.7701n$	0.306227

Linear lower bounds for the optimal energy. The table above contains the results obtained by the introduced methods. The second column gives the lower bounds calculated with the first method, while those provided by the improved version are in column four.

References

[1] A. Neumaier, O. Shcherbina, W. Huyer, and T. Vinkó. A comparison of complete global optimization solvers. *Mathematical Programming*, 103:335–356, 2005.

[2] T. Vinkó. Minimal inter-particle distance in atom clusters. *Acta Cybernetica*, 17:105–119, 2005.

[3] T. Vinkó, J.-L. Lagouanelle, and T. Csendes. A new inclusion function for optimization: Kite – the one dimensional case. *Journal of Global Optimization*, 30:435–456, 2004.

[4] T. Vinkó and A. Neumaier. New bounds for atomic clusters. *Submitted*, 2005.

[5] T. Vinkó and D. Ratz. A multidimensional branch-and-prune method for interval global optimization. *Numerical Algorithms*, 37:391–399, 2004.