# Gravitational Smoothing as a Global Optimization Strategy

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**Abstract:** An optimization scheme for atomic cluster structures, based on exaggerating the importance of the gravitational force, is introduced. Results are presented for calculations on Lennard-Jones clusters of 13, 38, and 55 atoms, and the 13-atom Morse cluster.

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**Key words:** global optimization; Lennard-Jones; clusters; potential deformation

## Introduction

In molecular simulations of nonionic systems, the longest-ranged contributions to intermolecular pair potentials come from dipole-dipole interactions, which are proportional to the inverse cube of the distance between dipoles. Strictly speaking of course, this is not physically true: there is a gravitational attraction between all pairs of masses, the potential energy of which is proportional to the inverse of the distance between them. Gravitational interactions do not appear in intermolecular pair potentials however, and for good reason. Unless at least one of the particles in the system is very massive, gravitation represents a negligible component of the force acting between pairs of particles.[1]

What would happen if the gravitational force were, in fact, important in molecular simulations? That is, let's imagine the case where the gravitational constant is many orders of magnitude larger than its physical value. Molecular pair potentials would then be written

$$V(r_{ij}) = V_e(r_{ij}) - \frac{\mathcal{G} m_i m_j}{r_{ij}} \quad (1)$$

where $\mathcal{G}$ is a force constant of arbitrary size and $V_e(r_{ij})$ is the typically important potential energy function (including, e.g., bonded, torsional, nonbonded, and charge interactions).

The question arises: how will the inclusion of strong gravitation effect the problem of finding optimal structures for atomic clusters (or even biomolecules)? Previous work on atomic clusters has shown that increasing the length scale of the pair potential reduces the number of distinct minimal structures for atomic clusters.[2–5] Moreover, it has been noted that the structural optimization problem may be easier in clusters of ionic diatomic molecules than in similar-sized neutral atomic clusters,[5,6] and that electrostatic attractions in polypeptides act as "reward" functions in simplifying potential energy surface.[7] That is, longer-ranged pair interactions lead to smoother global potential energy functions.[8]

## Global Optimization

Global optimization of nonlinear functions, which have many local minima, is generally a challenging computational task, and exemplary of an NP-hard problem.[9] Indeed, for this reason, considerable effort has been invested to develop improved techniques for finding solutions to these problems.[10–15] Techniques for global optimization can be divided broadly into two classes (although these are often combined): simulated annealing,[16] possibly with enhanced sampling,[17,18] and potential smoothing.[10,19]

While simulated annealing takes advantage of statistical mechanics to sample the global minimum with greater likelihood as the temperature of the simulation decreases, smoothing methods modify the potential such that the number of local minima is reduced. The smoothing technique presented here works by adjusting a fundamental physical constant; some earlier methods have taken a similar approach, effectively adjusting the ratio of mass to Planck's constant.[20,21]

One successful smoothing strategy for optimizing atomic clusters was proposed a little more than a decade ago by Stillinger and Stillinger.[3] In this method, exemplary of the so-called "antlion strategy,"[7,22] the standard Lennard-Jones 12-6 pair potential is rewritten in parametric form:

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$$V_p(r_{ij}) = 4\left(\frac{1}{r_{ij}^{2p}} - \frac{1}{r_{ij}^{p}}\right) \quad (2)$$

Here, the parameter $p$ may be any integer such that $1 \leq p \leq 6$. Next, the potential energy of the cluster is minimized using a steepest descent or conjugate gradient method.[23] Stillinger and Stillinger found that, for a 13-atom "Lennard-Jones" cluster, the chance of locating the global minimum is dramatically increased as $p$ is reduced. Indeed, for $p = 1$, the probability of finding the global minimum becomes unity.

This parameterization of the Lennard-Jones potential was evidently partly inspired by the findings of Braier et al.,[2] which show that the number of distinct minima in few-atom Morse clusters decreases as the potential becomes softer. This conclusion is also implicit in the early work of Hoare and McInnes,[24] who found fewer minima for small clusters with the softer Morse potential than for corresponding Lennard-Jones clusters.

In the present work, we shall determine how effectively the potential energy modification of eq. (1) reduces the difficulty in identifying the globally optimal structures for 13-atom Lennard-Jones and Morse clusters. We also apply the method to a pair of larger Lennard-Jones clusters, respectively consisting of 38 and 55 atoms.

## Simulations

For both Lennard-Jones and Morse 13-atom clusters, two types of calculations were performed. The first of these involved estimating $S(\mathcal{G})$, the probability of finding the (icosahedral) global minimum structure, for several values of $\mathcal{G}$. The second calculation identified the local minima of the cluster, as a function of $\mathcal{G}$.

Following Stillinger and Stillinger,[3] we employed a Monte Carlo method to evaluate $S(\mathcal{G})$. Ten thousand initial structures were randomly generated, and subsequently minimized for each value of $\mathcal{G}$. These were generated from a uniform distribution, inside a sphere of radius 5. Any initial structures that had contacts of less than 0.75 reduced units ($r \approx 1.08$ being the equilibrium separation for the $\mathcal{G} = 0$ case) were rejected, in order to remove the possibility that these structures would diverge under conjugate gradient minimization.

**Table 1.** Properties of Gravitationally Smoothed 13-Atom Lennard-Jones Clusters.

| $\mathcal{G}$ | $E_{min}(\mathbf{r})$ | Number of local minima | $S(\mathcal{G})$ |
|---|---|---|---|
| 0 | $-4.43268014 \times 10^1$ | 1144 | 0.0273 |
| 1 | $-1.01327213 \times 10^2$ | 634 | 0.1755 |
| 10 | $-6.40277768 \times 10^2$ | 137 | 0.5881 |
| $10^2$ | $-6.77196157 \times 10^3$ | 50 | 0.8309 |
| $10^3$ | $-8.03645285 \times 10^4$ | 38 | 0.8850 |
| $10^4$ | $-9.80531085 \times 10^5$ | 29 | 0.8895 |
| $10^5$ | $-1.20531885 \times 10^7$ | 28 | 0.8875 |
| $10^6$ | $-1.48474238 \times 10^8$ | 23 | 0.8865 |

**Table 2.** Properties of Gravitationally Smoothed 13-Atom Morse Clusters.

| $\mathcal{G}$ | $E_{min}(\mathbf{r})$ | Number of local minima | $S(\mathcal{G})$ |
|---|---|---|---|
| 0 | $-5.17370462 \times 10^1$ | 13 | 0.9896 |
| 1 | $-1.20938686 \times 10^2$ | 4 | 0.9995 |
| 2 | $-1.94440480 \times 10^2$ | 2 | 1 |
| 3 | $-2.71808050 \times 10^2$ | 1 | 1 |

The minimization was performed using a standard Polak-Ribiere conjugate gradient procedure.[23] Minimal structures were determined when the energy difference between iterations was less than $10^{-20}$ and no component of the gradient had a magnitude greater than $2.25 \times 10^{-7}|E_{\min}|$, where $E_{\min}$ is the energy of the global minimum for the appropriate $\mathcal{G}$ (see Tables 1–4).

We were interested in enumerating the local minima of our gravitationally smoothed atomic clusters to get a more complete picture of the potential smoothing (and to compare our calculations with previous work[24,25]). To carry out this enumeration, we discriminated between structures using energies and the principal moments of inertia.[26] A structure was determined to be unique if it had an energy (relative to the ground state) that was different from those of any other minimal structures by at least a single precision amount[27] and had significantly different[28] principal moments of inertia.

## Lennard-Jones Clusters

The potential for the Lennard-Jones clusters, subject to gravitational interactions, as per eq. (1) is

$$V(\mathbf{r}) = \sum_i \sum_{j>i} \left(4\left(\frac{1}{r_{ij}^{12}} - \frac{1}{r_{ij}^{6}}\right) - \frac{\mathcal{G}}{r_{ij}}\right) \quad (3)$$

Table 1 shows the effect that increasing $\mathcal{G}$ has on the potential surface of the 13-atom cluster. Note that the number of local minima is dramatically reduced. The probability of locating the global minimum saturates at about 0.89.

**Table 3.** Global Optimization of Gravitationally Smoothed 38-Atom Lennard-Jones Clusters.

| $\mathcal{G}$ | $E_{min}(\mathbf{r})$ | $S(\mathcal{G})$ |
|---|---|---|
| 0 | $-1.73928426 \times 10^2$ | 0.0001 |
| 1 | $-5.56935783 \times 10^2$ | 0.0018 |
| 10 | $-4.24337847 \times 10^3$ | 0.0117 |
| $10^2$ | $-4.68831557 \times 10^4$ | 0.0186 |
| $10^3$ | $-5.62009977 \times 10^5$ | 0.0174 |
| $10^4$ | $-6.87539944 \times 10^6$ | 0.0164 |
| $10^5$ | $-8.45786449 \times 10^7$ | 0.0158 |
| $10^6$ | $-1.04207998 \times 10^9$ | 0.0165 |

**Table 4.** Global Optimization of Gravitationally Smoothed 55-Atom Lennard-Jones Clusters.

| $\mathcal{G}$ | $E_{min}(\mathbf{r})$ | $S(\mathcal{G})$ |
|---|---|---|
| 0 | $-2.79248470 \times 10^2$ | 0.0009 |
| 1 | $-1.01345933 \times 10^3$ | 0.0036 |
| 10 | $-8.12534807 \times 10^3$ | 0.0110 |
| $10^2$ | $-9.07902106 \times 10^4$ | 0.0079 |
| $10^3$ | $-1.09125683 \times 10^6$ | 0.0078 |
| $10^4$ | $-1.33595454 \times 10^7$ | 0.0039 |
| $10^5$ | $-1.64377124 \times 10^8$ | 0.0039 |
| $10^6$ | $-2.02537913 \times 10^9$ | 0.0058 |

In order to enumerate the local minima of "Lennard-Jones" clusters, we minimized 100,000 randomly generated initial structures. Note that the number of local minima decreases monotonically. Variations in the last three values of $S(\mathcal{G})$ are within the error of our calculations.

### *Morse Clusters*

The potential for Morse clusters, subject to gravitational interactions, becomes

$$V(\mathbf{r}) = \sum_i \sum_{j>i} \left( e^{2\alpha(1-r_{ij})} - 2e^{\alpha(1-r_{ij})} - \frac{\mathcal{G}}{r_{ij}} \right) \quad (4)$$

where, following Hoare and McInnes,[24] we set $\alpha = 3$.

The results of our calculations on Morse clusters are summarized in Table 2. Note that the softer Morse potential makes the global optimization problem almost trivial by comparison with Lennard-Jones clusters, even without the application of any gravitational mutual attraction. Hence, comparatively modest values of $\mathcal{G}$ are required to reduce this system to one with a single global minimum. Because the number of minima for the 13-atom Morse cluster is known to increase rapidly with $\alpha$,[4,5,8] we expect the effect of gravitational smoothing to become more dramatic for larger $\alpha$.

Unlike in our enumeration of "Lennard-Jones" local minima, we did not locate the "Morse" local minima by minimizing randomly generated structures. Instead, we began with the $\mathcal{G} = 0$ Lennard-Jones local minima and minimized them under the potential of eq. (4).

### *Larger Lennard-Jones Clusters*

In addition to the 13-atom cluster, we also applied gravitational smoothing to a pair of larger systems: the 38-atom and 55-atom Lennard-Jones clusters. The 38-atom cluster is noteworthy for its "double-funnel" energy landscape,[29,30] on which the (truncated octahedral) global minimum is located at the bottom of a narrow basin.

Our results for 10,000 minimizations on these larger clusters are summarized in Tables 3 and 4. Gravitational smoothing leads to greater success in globally optimizing both systems, particularly the 38-atom cluster, where we note that $S(\mathcal{G})$ increases by more than two orders of magnitude for larger $\mathcal{G}$.

## Discussion

Our calculations demonstrate the efficacy of gravitational smoothing for the global optimization problem in atomic clusters. The method is more effective with ($\alpha = 3$) Morse clusters than with Lennard-Jones clusters, for which the repulsive part of the interatomic pair potential is relatively hard. This behavior is consistent with the observation that the "inherent structures" of atomic fluids become randomly packed configurations in the hard-sphere limit.[31] With Morse clusters, we expect the effect of gravitational smoothing to be more notable for larger $\alpha$, as the number of local minima increases.

Although we do not find unit success probability with the Lennard-Jones potential, preliminary calculations suggest that with a few annealing steps (in which $\mathcal{G}$ is reduced), gravitational smoothing can reach this limit. It remains to be seen whether this method can effectively simplify the location of global potential minima in biomolecules.

As $\mathcal{G}$ is increased in eqs. (3) and (4), the relative difference in energy between the global minimum and the highest-energy conformer decreases. For example, the highest-energy conformer for the $\mathcal{G} = 0$ 13-atom Lennard-Jones cluster is only 79% as low as the global minimum, while it is 92% in the $\mathcal{G} = 10^6$ case. A more interesting thing to know, however, particularly in the context of possible annealing methods, is the relative energy of transition states (potential energy saddles) as a function of $\mathcal{G}$. We have not explored this here, although we expect the transition states to be of relatively lower energy. In principle, an eigenmode method[32] can answer this question.

Finally, we note that the numbers of local minima found here for the $\mathcal{G} = 0$ case of the 13-atom Lennard-Jones and Morse clusters are different from the results of Hoare and McInnes[24] and the more recent results of Tsai and Jordan[32] and of Doye and Wales.[4,33] This is not necessarily a serious conflict. As the above authors note, along with others,[34] there is no search strategy that guarantees that all the local minima will be enumerated.

## References


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$$V_G(r_{ij}) = -\frac{Gm_im_j}{r_{ij}} = -\frac{G^*m_i^*m_j^*}{r_{ij}^*}$$
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