Discovery of New Global Minima for Lennard – Jones Atomic Clusters Using TRUST Simulations

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Abstract. The preeminent importance of nano-scale materials science is driving the growing interest in discovering the conformation of atomic clusters with lowest energies. Despite its simple formulation, this modeling and simulation problem is extremely hard to solve. The TRUST algorithm, one of the most powerful global optimization (GO) approaches available to date, is applied here for the first time to determining the conformation of *Lennard-Jones* clusters. TRUST identifies lower minima than reported with previous methods and reaches them at considerably lower computational cost.

1. Introduction

In recent years, there has been a growing interest in modeling and simulation of clusters, i.e., of aggregates of atoms or molecules [1-5]. This interest is driven by the realization that the material properties of clusters may be very different from those of discrete molecules or bulk matter. The primary objective of cluster simulations is to determine the atomic (or molecular, or ionic) spatial conformation of lowest potential energy. Bonding models used to describe the interaction between the particles in the cluster may range from simple phenomenological potentials to those derived from *ab initio* molecular orbital calculations or density functional theory.

In this study, we focus on atomic clusters where the interaction is described by the Lennard-Jones (LJ) potential. More precisely, the function to be minimized is the total potential energy of an N atom cluster, given by:

$$E = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \left(\frac{1}{r_{ij}^{12}} - \frac{2}{r_{ij}^{6}}\right) , \qquad (1)$$

where r_{ij} is the distance between atoms i and j in the cluster. Several deterministic and stochastic methods applied to optimizing the LJ clusters have been reported in Refs. [2, 3, 5-14]. These methods have been assessed by various measures of performance such as: (*i*) the number of function iterations needed to attain the (putative) global minimum; (*ii*) the value of the attained minimum: (*iii*) the robustness of the method w.r.t. the initial configuration and seed; (*iv*) dealing with challenging situations (e.g., for N = 75, 98, 102); (*v*) percentage of successful cases; etc. It is interesting to note that, over the years, even minute (less than fractions of a percent) improvements in the value of the global minimum have been considered sufficiently relevant to be reported. [6, 9, 12]

This should indeed be the case, since the GO problem for the LJ clusters is extremely hard. The number of local minima grows at least like $O(e^N)$, which makes the energy surface a very difficult landscape to explore and sort out.

The remainder of this paper is organized as follows. The TRUST method is briefly reviewed in Section 2. In Section 3, we describe the new

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algorithmic and code developments and in Section 4 we present and discuss our results.

2. The TRUST Method

TRUST is a method for solving continuous GO problems [15] that has not only achieved leading edge performance on the standard SIAM benchmarks, but has also shown promising capability for large-scale exploratory seismology problems [16]. It builds on two innovative concepts, namely subenergy tunneling and non-Lipschitzian terminal repellers, to ensure escape from local minima in a fast and computationally efficient manner.

The generic GO problem solved by TRUST can be stated as follows. Determine

$$\mathbf{x}_g = \arg\ \min_{\mathbf{x}\in\mathcal{D}}\{f(\mathbf{x})\}, \tag{2}$$

where $f:\mathcal{D}\subset\mathbb{R}^N\to\mathbb{R}$.

For the considered application, the objective function f is the conformational (potential) model energy, and $\mathcal{D}$ is the domain of the model parameters $\mathbf{x}$, a $3N$-dimensional vector representing the spatial coordinates of the N particles in the cluster. The result of the optimization process produces the optimal (minimum energy) configuration, $\mathbf{x}_g$, and the corresponding global minimum value of the objective function, $f_g = f(\mathbf{x}_g)$.

TRUST solves Eq (2) using an indirect approach. More precisely, rather than minimizing directly $f(\mathbf{x})$, TRUST defines a new (*virtual*) objective function $E(\mathbf{x},\mathbf{x}^*)$. Let $\hat{f}(\mathbf{x}) = f(\mathbf{x}) - f(\mathbf{x}^*)$, and H denote the Heaviside function. Then,

$$E(\mathbf{x},\mathbf{x}^*) = E_{sub}(\mathbf{x},\mathbf{x}^*) + E_{rep}(\mathbf{x},\mathbf{x}^*) \tag{3}$$

$$E_{sub} = \log_e\{\,1/[1+e^{(-\hat{f}(\mathbf{x},\mathbf{x}^*)-a)}]\,\} \tag{4}$$

$$E_{rep} = -\frac{z}{z+1}\rho H(\hat{f}(\mathbf{x},\mathbf{x}^*))\sum_{n=1}^{N}(x_n - x_n^*)^{(z+1)/z} \tag{5}$$

The subenergy tunneling transformation E_{sub} is a nonlinear monotonic transformation that has several useful properties. It has a filter effect:

$$E_{sub}(x,x^*) \cong \begin{cases} 0 & \text{if } f(x)\ge f(x^*) \\ f(x)-f(x^*) & \text{if } f(x)<f(x^*) \end{cases} \tag{6}$$

E_{sub} also has the same critical points as $f(\mathbf{x})$ and the same relative ordering of local minima.

$$\frac{\partial E_{sub}(x,x^*)}{\partial x} = 0 \quad\Leftrightarrow\quad \frac{\partial f(x)}{\partial x} = 0 \tag{7}$$

$$\frac{\partial E_{sub}(x,x^*)}{\partial x} \cong \begin{cases} 0 & f(x)\ge f(x^*) \\ \partial f(x)/\partial x & f(x)<f(x^*) \end{cases} \tag{8}$$

This is illustrated in Fig 1, below for the sample function $f(x) = (\sin[2x] - x - 1)^2$.

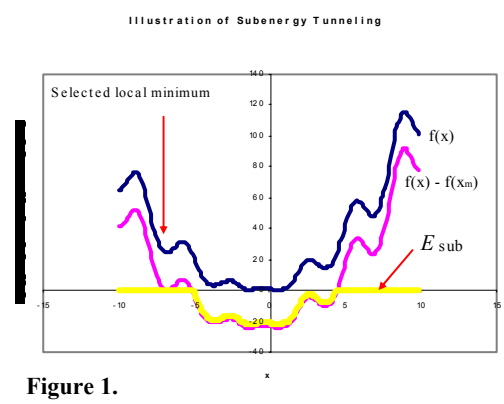

Figure 1.

The virtual objective function (3) is a superposition of two contributing terms. Its effect is to transform the current local minimum of $f(\mathbf{x})$ into a global maximum, while preserving any lower lying local minima. This is illustrated in Fig.2.

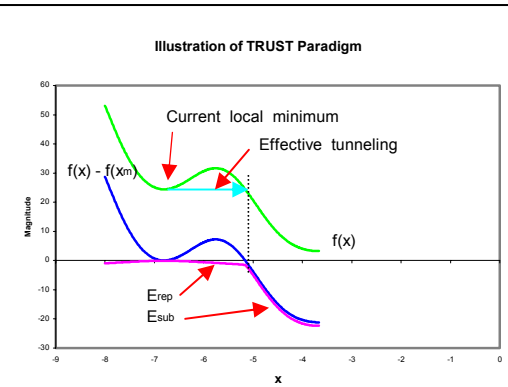

Figure 2.

The actual search for $\mathbf{x}_g$ is carried out in terms of the flow of a system of coupled nonlinear ODEs constructed from the virtual objective function. Specifically,

$$\dot{\mathbf{x}} = -\frac{\partial E(\mathbf{x},\mathbf{x}^*)}{\partial \mathbf{x}} \tag{9}$$

results in

$$\dot{x}_n = -\frac{\partial f(\mathbf{x})}{\partial x_n}\frac{1}{1+e^{f(\mathbf{x})-f(\mathbf{x}^*)+a}} + \rho(x_n - x_n^*)^{1/z}\, H[\, f(\mathbf{x}) - f(\mathbf{x}^*)\,] \quad (10)$$

Each equilibrium state of this equation will be a local minimizer of E, hence a local or global minimizer of f. In Eq (10), the adaptive shift parameter a is recalculated whenever the tunneling solution emerges into a new (lower) basin of attraction. It enables the smooth transition between tunneling and descent to a lower local minimum. The quantity z appearing in the exponent is a positive odd integer called the Zak parameter [17]. As illustrated in Fig 2, gradient descent applied to $f(\mathbf{x})$ and initialized at $\mathbf{x}^*+\varepsilon$ can not escape from the basin of attraction of $\mathbf{x}^*$. However, whenever gradient descent is applied to $E(\mathbf{x}, \mathbf{x}^*)$ and initialized at $\mathbf{x}^*+\varepsilon$, it always escapes the basin. In that sense, TRUST has a global descent property.

3. The TRUST Simulation Code

The modeling and simulations reported herein were carried out using the TRUST code, which is written in Visual FORTRAN 95. The TRUST visualization routines create detailed graphics displays that allow, in real time, to follow the evolution of a simulation.

Figure 3, below, corresponds to a direct screen dump at the conclusion of a simulation. It comprises three regions.

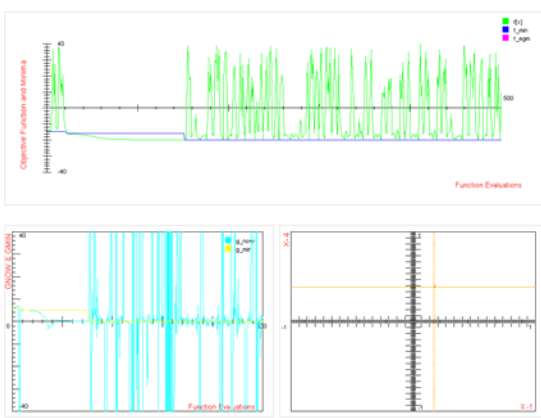

Figure 3.

The upper region displays the successively generated values of the function to be minimized along with the current lowest local minimum. The color-coded magnitudes are plotted versus the number of function evaluations.

The lower left region displays the magnitude of the corresponding largest gradient components. As the simulation progresses, one is able to monitor the convergence status. The lower right region shows the projection on a plane of the solution path in phase space.

The computational kernel at the heart of a TRUST simulation has the following structure. Following appropriate initialization procedures, an iterative search is performed based upon the solution of Eq (10). At each iteration, TRUST first evaluates $f(\mathbf{x})$ and its gradient. The gradient is computed synergistically with $f(\mathbf{x})$. This can be done analytically (in this study), or using an automated differentiation procedure [18]. No finite differences are used. Hence, it entails only a small overhead cost. For each successive point on the energy landscape hypersurface, TRUST then selects the search mode from five currently available options. These include the detection of convergence to a local minimum, the detection of a plateau of $f(\mathbf{x})$, the detection of a well profile, descent into a new basin of attraction, or sub-energy-surface tunneling. When a plateau is detected, a bounded discrete ray tracing algorithm is executed. When a well profile is detected, descent is performed by a new, fast fractional power adaptive switching gradient descent algorithm. Specifically, one uses

$$x_n^{\mu+1} = x_n^{\mu} - \Delta_t \frac{1}{w_n^{\mu}}\left(\frac{\partial f(\mathbf{x}^{\mu})}{\partial x_n}\right)^{1/z} \quad (11)$$

for gradient magnitudes less than one, where $w_n^{\mu} = 2^{g(n,\mu)}$.

The function $g(n,\mu)$ is incremented whenever a gradient component changes sign. The updated information is interfaced to the graphics routines for real-time display. Then, the need for reflections from the domain boundaries is examined, and stopping tests are performed. Finally, key quantities of interest are updated and, if appropriate the next iteration is initiated.

4. Results

Selected results of our simulations are shown in Tables 1 and 2, and in Figure 4. In Table 1, N

denotes the number of atoms in the cluster and *NFGM* is number of function evaluations TRUST needs to reach the global minimum. For the reported results, we used the initial positions given by the Cambridge Table [19].

N	Cambridge Table	TRUST	Difference	*NFGM*
8	-19.821489	-19.821651	0.000162	32
32	-139.635524	-139.63998	0.004456	123
38	-173.928427	-173.93428	0.005853	152
46	-220.680330	-220.68845	0.00812	68010
60	-305.875476	-305.88788	0.012404	176
75	-397.492331	-397.50919	0.016859	855
86	-465.384493	-465.40527	0.020777	62397
98	-543.665361	-543.69189	0.026529	115044
99	-550.666526	-550.69238	0.025854	394

Table 1. Comparison of minimal energies of various clusters as reported in the Cambridge table and obtained by TRUST.

Coordinates from Cambridge table (N=8) (x, y, z)			Coordinates found with TRUST (N=8) (x, y, z)		
0.243304	1.021828	-0.29574	0.24203	1.02189	-0.29396
-0.42129	-0.55447	0.682804	-0.42184	-0.55224	0.68835
-0.86119	-0.2132	-0.15128	-0.86197	-0.21272	-0.14630
0.553196	-0.32323	0.632042	0.55262	-0.32123	0.63672
0.715876	0.146823	-0.23513	0.71485	0.14725	-0.23126
-0.15897	0.214897	-0.71963	-0.15998	0.21393	-0.71584
0.056999	-0.59222	-0.18612	0.05617	-0.59192	-0.18064
-0.12792	0.299569	0.273058	-0.12860	0.30084	0.27670

Table 2. Coordinates of the atoms at the global minimum in a cluster with $N = 8$ atoms.

The results obtained to date show that TRUST discovered global minima that are consistently lower than those determined by previously reported methods. The advances are rather small percentage-wise – which, judging by the existing literature, is quite the norm for this problem – but they are significant, since they identify TRUST as one of the leading engines for discovering conformational structures in computational chemistry and materials science.

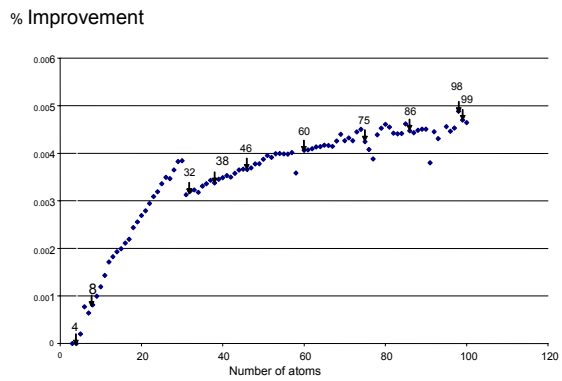

Figure 4. Improvement (percentage-wise) of results obtained with TRUST as a function of *N*. The arrows indicate the clusters reported in Table 1.

This significance is enhanced by the fact that the number of function evaluations required to obtain these minima is, in general, much lower than in other approaches. The improvement curve shown in Fig. 4 indicates clearly two different regimes, corresponding to small and intermediate clusters, respectively. While this feature is not surprising, we intend to investigate it more thoroughly and determine its potential relevance for the GO problem. Substantial effort will also be focused on assessing the robustness of TRUST's performance w.r.t. initial conditions.

ACKNOWLEDGEMENTS. This research was performed at the Center for Engineering Science Advanced Research in the Computer Science and Mathematics Division, Oak Ridge National Laboratory. Funding was provided by the Materials Science and Engineering Program of DOE's Office of Basic Energy Sciences. Additional support (for CR) was received from the Research Alliance for Mathematics and Science, DOE Office of Advanced Scientific Computing Research. ORNL is operated by UT-Battelle LLC, under contract DE-AC05-00OR22725.

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