Simple energy minimization for huge Lennard-Jones clusters by dramatic parameter reduction

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Abstract

We have designed several schemes to reduce the number of parameters in the problem of minimizing the total energy of Lennard-Jones clusters. We will discuss our schemes development in three dimensions. The value of our work lies in the simplicity with which it provides a new approach to problems involving huge Lennard-Jones clusters.

Key words: Optimization, Lennard-Jones clusters, asymptotic values

1 Introduction

Numerical minimization of the so-called Lennard-Jones clusters, a system consisting of particles interacting under the Lennard-Jones potential

$$U(a) = \frac{1}{a^{12}} - \frac{2}{a^6},$$

is of considerable interest to the researchers [1, 2, 3, 4, 5, 6, 7, 8] in chemistry, physics, biology, materials science as well as optimization. We have tested six variations of our methods which render the energy as a function of a single parameter, making it much more effective to minimize arbitrarily large clusters than most existing numerical methods. We present results for up to 55,000 particles by calculations on spheres and on lattices, for both 3D and 2D cases. We show plots of per-particle energy versus number of particles of the clusters, as well as asymptotic values for the average per-particle energy and average inter-particle distance. Our approximate results not only help understand the system's asymptotic behavior but also provides the most efficient initialization for further numerical minimization which usually requires huge computer resources.

2 The schemes

The derivation of formulae for interactions for all cases in 1D, 2D and 3D, on spheres and on lattices, follows a similar procedure. We design a method to locate the particles in a systematic way. A general expression for the distance between two particles is then obtained and summing over all particles we can get an expression for the total energy requiring only one parameter.

We now introduce the general method by doing the simple 1-d case and then present our work for the case of the 3D shells.

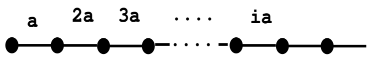

Figure 1: One dimensional lattice. The only parameter is a, the inter-particle distance.

The position of an arbitrary particle is $a_i = ia$ where a is the distance between two consecutive particles and i ranges from 1 to N, N being the total number of particles. The distance between a pair (i,j) is $a_{ij} = (i-j)a$ and the total energy of N particles is then

$$E(a) = \frac{1}{2}\left(\frac{1}{a^{12}}\sum_{i\neq j=1}^{N}\frac{1}{(i-j)^{12}} - \frac{1}{a^{6}}\sum_{i\neq j=1}^{N}\frac{2}{(i-j)^{6}}\right).$$

Define two functions $F(N)$ and $G(N)$

$$F(N) = \sum_{i\neq j=1}^{N}\frac{1}{(i-j)^{12}},$$

$$G(N) = \sum_{i\neq j=1}^{N}\frac{1}{(i-j)^{6}}.$$

E can now be written as

$$E(a) = \frac{1}{2}\left(\frac{1}{a^{12}}F(N) - \frac{2}{a^{6}}G(N)\right). \tag{1}$$

Although we only derived this expression in this 1D case, it turns out to be valid for all the other cases that we consider. The specific form of $F(N)$ and $G(N)$ depends on the dimension and on the configuration of the problem.

The value of parameter a at which E is minimal is

$$a_0 = \left(\frac{F(N)}{G(N)}\right)^{1/6}, \tag{2}$$

and the associated minimal energy per particle is

$$\mathcal{E} = -\frac{G^2(N)}{2NF(N)}. \tag{3}$$

Therefore, the problem lies in finding the analytical forms for $F(N)$ and $G(N)$. These functions are usually very complicated sum whose indexes are implicit functions of N and of previous indexes. It is however straightforward to use a computer to evaluate $F(N)$ and $G(N)$.

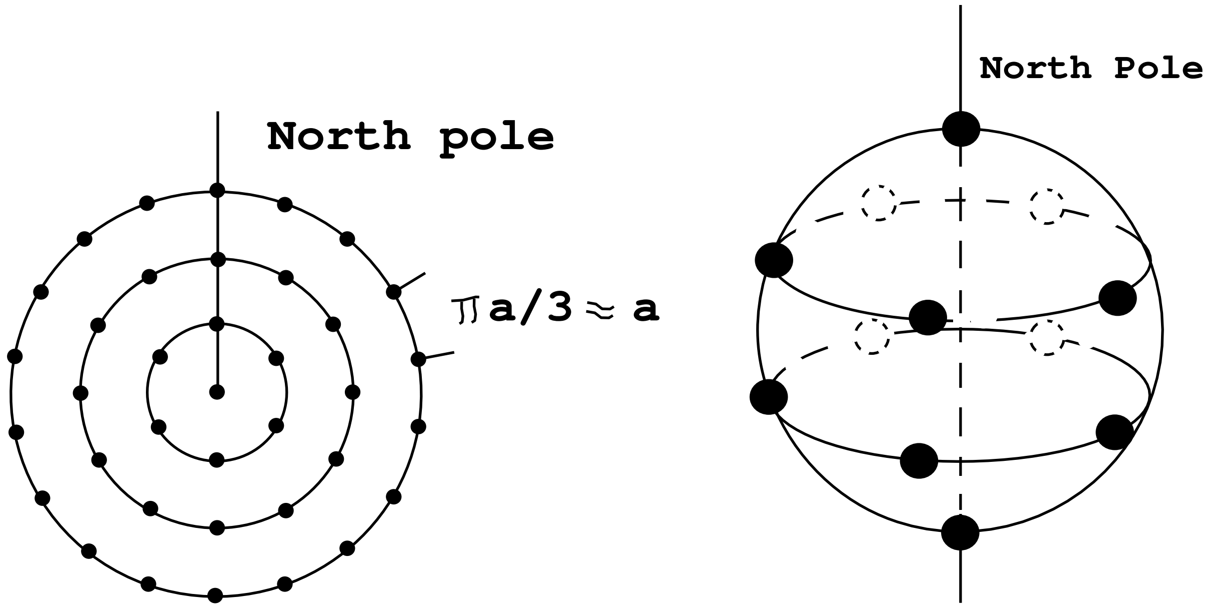

Figure 2: Figure on left: Particles on concentric rings. The parameter is a, the radial distance between two consecutive rings and the approximate nearest neighbor distance for any particle. Figure on right: 3D perspective of the first shell.

We now describe the arrangement in shells and find the expressions for $F(N)$ and $G(N)$. The configuration consists of concentric shells, identified by an index i. The radius of shell i equals ia. The smallest, most interior, shell corresponds to $i = 1$ and has radius a.

We fix a north pole, the shells are then cut into rings perpendicular to this south-north line, (Figure 2). The spacing of the rings as measured along the arc of a geodesic parallel to the north pole is fixed and equals $(\pi/3)a$. The number of these rings depends on the radius of the shell, for a shell of radius ia there are $3i + 1$ rings (including the top and bottom rings which shrink to a dot and which will include one particle each.) Along the arc-length of each of these rings we then distribute particles such that the distance along the arc between any two adjacent particles is the same, $(\pi/3)r$, where r is the radius of the ring. The two special particles are placed at the top and bottom rings, with radius $r = 0$.

We next introduce two new parameters α and β. For a given shell i, α indicates which ring we are treating starting from north pole where $\alpha = 0$ and going down to the south pole where $\alpha = 3i$. For a given shell i and a given ring α, β indicates the position of the particle along the arc-length of the ring.

The distance along the arc between adjacent particles in ring α, shell i is

$$\frac{2\pi ia \mid \sin\left(\frac{\pi\alpha}{3i}\right) \mid}{\left[6i\sin\left(\frac{\pi\alpha}{3i}\right)\right]}$$

where $[a]$ indicates rounding to the nearest integer and taking absolute value of a. A particle is then localized completely by its shell number i, its ring number α, and its position on the ring that we label β. In spherical coordinates we have

$$a_{i\alpha\beta} = \left(ia, \frac{\alpha\pi}{3i}, \frac{2\pi\beta}{\left[6i\sin\left(\frac{\pi\alpha}{3i}\right)\right]}\right)$$

where i=1...I; α=0...3i; β=0... $[6i\sin\left(\frac{\pi\alpha}{3i}\right)]$-1; and where I is an implicit function of N. Further, we define $\theta_{i\alpha} = \frac{\alpha\pi}{3i}$ and $\phi_{i\alpha\beta} = \frac{2\pi\beta}{\left[6i\sin\left(\frac{\pi\alpha}{3i}\right)\right]}$. The distance between two points $a_{i\alpha\beta}$ and $a_{j\gamma\sigma}$ is then

$$\begin{aligned} a_{i\alpha\beta j\gamma\sigma} &= ((ia\sin\theta_{i\alpha}\cos\phi_{i\alpha\beta} - ja\sin\theta_{j\gamma}\cos\phi_{j\gamma\sigma})^2 + (ia\sin\theta_{i\alpha}\sin\phi_{i\alpha\beta} - \\ &\qquad ja\sin\theta_{j\gamma}\sin\phi_{j\gamma\sigma})^2 + (ia\cos\theta_{i\alpha} - ja\cos\theta_{j\gamma})^2)^{1/2} \\ = a_{i\alpha\beta j\gamma\sigma} &= a\sqrt{i^2 + j^2 - 2ij[\sin\theta_{i\alpha}\sin\theta_{j\gamma}\cos(\phi_{i,\alpha\beta} - \phi_{j,\gamma\sigma}) + \cos\theta_{i\alpha}\cos\theta_{j\gamma}]} \end{aligned}$$

Define $f_{i\alpha\beta j\gamma\sigma} = a_{i\alpha\beta j\gamma\sigma}/a$ and the corresponding $F(N)$ and $G(N)$, including now a particle in the center of the shells become,

$$F(N) = \sum_{i,j=1}^{I} \sum_{\alpha,\gamma=0}^{\alpha=3i,\gamma=3j} \sum_{\beta,\rho} \frac{1}{f_{i\alpha\beta j\gamma\sigma}^{12}} + 2\sum_{i=1}^{I}\sum_{\alpha=0}^{3i}\sum_{\beta}\frac{1}{i^{12}}$$

$$G(N) = \sum_{i,j=1}^{I} \sum_{\alpha,\gamma=0}^{\alpha=3i,\gamma=3j} \sum_{\beta,\rho} \frac{1}{f_{i\alpha\beta j\gamma\sigma}^{6}} + 2\sum_{i=1}^{I}\sum_{\alpha=0}^{3i}\sum_{\beta}\frac{1}{i^{6}}$$

3 Numerical results

We have performed calculations for as many as 55,000 particles. Figure 3A shows the average per-particle energy as a function of the number of particles for 3D lattice and sphere, and the published numerical results from [9]. Figure 3B shows the inter-particle distance for 3D lattice and sphere. Figure 3C shows the average per-particle energy for the 2D case while 3D the inter-particle distance.

Through least-square fittings we have found the large-N asymptotic average per-particle energy $\mathcal{E}_\infty$ and average inter-particle distance a_∞. For the energy, we fit to $\mathcal{E}_I$ (for 2D lattices and rings) and and $\mathcal{E}_{II}$ (for 3D lattices and rings). The purpose of fitting specific case by a special formula is to reduce fitting error. Formulae are : $\mathcal{E}_I(N) = \mathcal{E}_\infty + \frac{\mathcal{E}_\alpha}{N^\alpha} + \frac{\mathcal{E}_\beta}{N^\beta}$ and $\mathcal{E}_{II}(N) = \mathcal{E}_N e^{-\alpha N^\beta} + \mathcal{E}_\infty$. In these formulae, α and β are fitting parameters. While for the inter-particle distance, perform similar fits. Fitting results are shown in Table 1.

	$\mathcal{E}_\infty$	a_∞
2D lattice	-2.66592	0.977509
2D rings	-2.85726	0.937327
3D lattice	-5.54535	0.951598
3D sphere	-6.50053	0.888979

Table 1: The asymptotic values for the average per-particle energy $\mathcal{E}_\infty$ and average inter-particle distance a_∞.

4 Remarks

We have designed several schemes to place particles on lattices, spheres, and icosahedron to minimize the energy of the large Lennard-Jones clusters, approximately, by analytical approaches. Using our methods, we have obtained the asymptotic values for the average per-particle energy and average inter-particle distance. The spherical scheme produces the most accurate results among the cases we consider, which suggests the clusters tend to form spherical structures. The value of our work is the drastic reduction of parameters for the energy minimization of the Lennard-Jones Clusters. Our methods can provide efficient initialization for more accurate numerical calculations on small clusters with 1000s of particles. Moreover, our methods can produce estimates for large clusters that no other numerical means can do currently.

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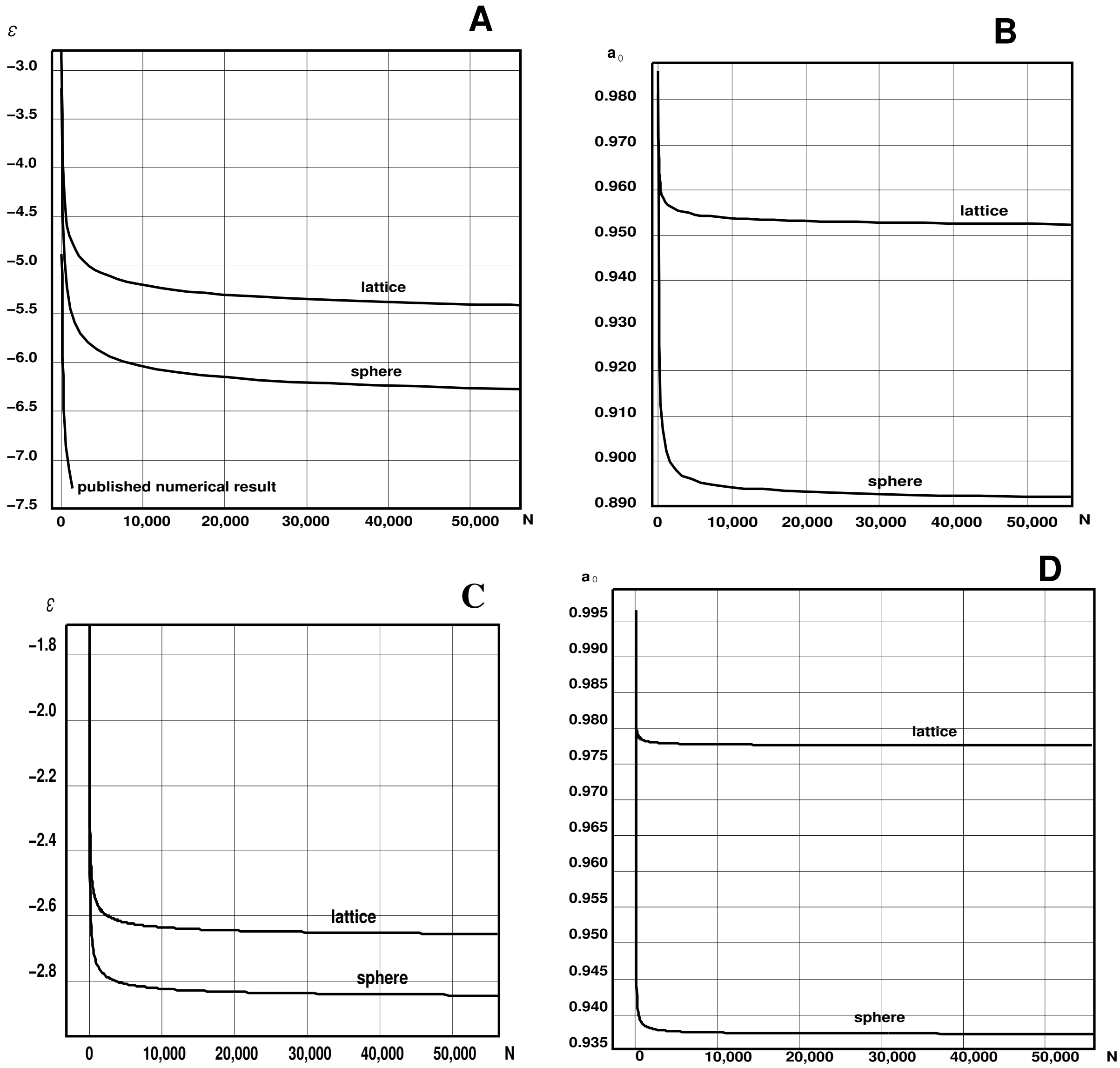

Figure 3: Results, Figure A: shows the average per-particle energy for 3D lattice, sphere and for published numerical result from [9]. Figure B: shows the average inter-particle distance for 3D lattice and sphere. Figure C: shows average per-particle energy for the 2D cases. Figure D: shows average inter-particle distance for 2D cases.