Two-Dimensional Lennard-Jones Clusters

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April 1, 2012

ABSTRACT

A growth sequence has been developed to attempt to find the absolutely minimal energy structure for a cluster of n atoms in two dimensions. This sequence produces 62 of the global minima obtained by a random search for $1 \leq n \leq 80$. It also yields energies lower than or equal to the previous best known minima for all but two of 19 sizes reported in MINPACK-2 (B.M. Averick, R. G. Carter, J. J. Moré, and G. L. Xue, "*The MINPACK-2 Test Problem Collection,"* Argonne National Laboratory, Mathematics and Computer Science Division, Technical Memorandum No. 150, June 1992, p. 44).

I. INTRODUCTION

We examine clusters of atoms that interact via the Lennard-Jones (LJ) potential,

$$V_{\mathrm{LJ}} = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} ({r_{ij}}^{-12} - 2{r_{ij}}^{-6}) \qquad (1)$$

where V_{LJ} is the potential in units of the depth of the potential well, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between atom i and atom j in units of the equilibrium distance, and n is the size of the cluster.

We have established a growth sequence for the initial configuration of a cluster of size n in a hexagonal packing system. The resulting energies of these structures prove to be the global minima obtained from our unbiased random search for many cluster sizes.

We conduct an unbiased random search for the absolute or global minimum of (1). We use the Big Bang Algorithm[1], modified for the two-dimensional case, to generate random initial configurations of the clusters and the initial expansion of the clusters. We perform local minimizations starting from the cluster configurations after this initial expansion.

II. METHOD

The construction of clusters by growth sequence greatly facilitates the search for prospective minima. In this approach, also called the "greedy" method, a cluster is simply the preceding size's cluster with one atom appended. The growth sequence approach saves time and effort because it determines from the previous size the positions of all atoms but one. We compared local minimum energies of small clusters and developed the g growth sequence that generates global minima of all sizes from 1 to 33.

We used a hexagonal lattice (See J. C. Yang, "Structure and binding of two-dimensional Lennard-Jones clusters," section 2.2, for comparison of clusters on a hexagonal lattice and other clusters). We

assign the atoms to lattice points, where they remain throughout the sequence. The first atom was placed at the origin, and the subsequent six atoms consecutively around the first, counterclockwise from the positive x-axis. We then proceeded to a new hexagonal "shell." An intuitive approach was used for several larger sizes. One such case is size ten. Figure 2.1 represents two clusters of size ten. The number for each atom is indicated. In figure (a) the tenth atom contributes two nearest-neighbor bonds to the previous cluster in the sequence, whereas it contributes three nearest-neighbor bonds in figure (b). The structure in figure (b) had, indeed, the lowest energy when it and other clusters of the same size were relaxed via local energy minimization. The consideration of nearest-neighbor interactions narrows the pool of prospective minima.

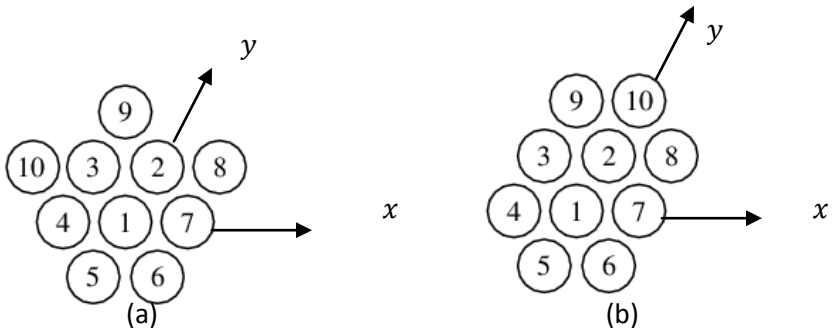

Figure 2.1 Tentative global minimum energy configurations for a cluster of size ten.

GROWTH SEQUENCE

Given the number of atoms n, we find the layer index l, side index s, and atom-on-side index k for atom index i $(i = 1,2, \ldots n)$ in the most closely packed hexagonal structure with the lowest potential energy for the cluster.

Let the central atom $(l = 0)$have $i = 1$ and the first-layer atoms $(l = 1)$ have $i = 2, 3, 4, 5, 6, 7$.

For q completely packed layers, the number of atoms n is

$$n = 3q(q + 1) + 1 = 1, 7, 9, 37, \ldots$$

for

$$q = 0, 1, 2, 3, \ldots$$

Thus

$$3q^2 + 3q + (1 - n) = 0$$

$$q_{\pm}(n) = \frac{-3 \pm \sqrt{3^2 - 4(3)(1-n)}}{6} = \frac{-3 \pm \sqrt{12n - 3}}{6}.$$

Let

$$l(i) = \lceil q_+(i) \rceil,$$

the ceiling function of q_+, or

$$\left\lceil \frac{\sqrt{12i - 3} - 3}{6} \right\rceil \qquad (2)$$

Then

$$l(1) = \left\lceil \frac{\sqrt{12(1) - 3} - 3}{6} \right\rceil = 0,$$

$$l(2) = \left\lceil \frac{\sqrt{12(2) - 3} - 3}{6} \right\rceil = 1, \ldots$$

$$l(7) = \left\lceil \frac{\sqrt{12(7) - 3} - 3}{6} \right\rceil = 1.$$

Let m be the index of the completed layer immediately inside the layer where atom i is located. Then

$$m(i) = l(i) - 1.$$

In addition, the number of atoms c in the core of m completed layers is

$$c = 3m(m + 1) + 1 = 3l(l - 1) + 1.$$

Thus the atom i is the rth atom in the lth layer where

$$r(i) = i - c(i).$$

The side index s for the rth atom in the lth layer is

$$\begin{aligned} \mathrm{s(r)} = \ & 1 \text{ for } r = 1, 2, \dots, l-1 \\ = \ & 2, \qquad l, l+1, \dots, 2l-1 \\ = \ & 3, \qquad 2l, 2l+1, \dots, 3l-1 \\ = \ & 4, \qquad 3l, 3l+1, \dots, 4l-1 \\ = \ & 5, \qquad 4l, 4l+1, \dots, 5l-1 \\ = \ & 6, \qquad 5l, 5l+1, \dots, 6l-1, 6l, \end{aligned}$$

Or

$$s(r) = \begin{cases} \left\lfloor \frac{r}{l} \right\rfloor + 1, \text{if } r < 6l; \\ 6, \qquad \text{if } r = 6l. \end{cases} \qquad (3)$$

The number of atoms in a completed layer l is $6l$:

$$[3l(l+1)+1] - \{3(l-1)[(l-1)+1]+1\} = 3l - (-3l) = 6l.$$

Accumulative number of atoms a in layer l on all sides before side s is

$$\begin{aligned} a(s) = \ & 0 \text{ for } s = 1 \\ & l-1 \qquad 2 \\ & 2l-1 \qquad 3 \\ & 3l-1 \qquad 4 \\ & 4l-1 \qquad 5 \\ & 5l-1 \qquad 6 \end{aligned}$$

or

$$a(s) = \begin{cases} 0, & \text{if } s = 1; \\ (s-1)l - 1 & \text{if } s > 1, \end{cases} \qquad (4)$$

The atom-on side index for the rth atom in layer l is

$$k = r - a[s(r)]$$

Since

$$r = r(i) = i - c(i) = i - \{3l(i)[l(i) - 1] + 1\},$$

thus

$$k = k(i).$$

These, combined with (2),(3), and (4),

$$l(i) = \left\lceil \frac{-3 \pm \sqrt{12i - 3}}{6} \right\rceil,$$

$$s(r) = \begin{cases} \left\lfloor \frac{r}{l} \right\rfloor + 1, \text{if } r < 6l; \\ 6, \qquad \text{if } r = 6l, \end{cases}$$

and

$$a(s) = \begin{cases} 0, & \text{if } s = 1; \\ (s-1)l - 1 & \text{if } s > 1, \end{cases}$$

uniquely define l (≥ 2), s, k for each i.

Assignment of (x, y) coordinates in a nonrectangular coordinate system (See Figure 2.2):

If

$$i = 1, 2, 3, 4, 5, 6, 7$$

$$x = 0, 0, -1, -1, 0, 1, 1$$

$$y = 0, 1, 1, 0, -1, -1, 0$$

For $i \geq 8$,

$s = 1$, $\qquad x = \begin{cases} \frac{l}{2} + (-1)^k \left\lfloor \frac{k}{2} \right\rfloor, l \text{ even} \\ \frac{l+1}{2} - (-1)^k \left\lfloor \frac{k}{2} \right\rfloor, l \text{ odd} \end{cases}, y = l - x$

$s = 2,$ $\quad x = \begin{cases} -\frac{l}{2} + (-1)^k \left\lfloor \frac{k}{2} \right\rfloor, l \text{ even} \\ -\frac{l-1}{2} - (-1)^k \left\lfloor \frac{k}{2} \right\rfloor, l \text{ odd} \end{cases}, y = l$

$s = 3,$ $\quad x = -l, y = \begin{cases} \frac{l}{2} + (-1)^k \left\lfloor \frac{k}{2} \right\rfloor, l \text{ even} \\ \frac{l+1}{2} - (-1)^k \left\lfloor \frac{k}{2} \right\rfloor, l \text{ odd} \end{cases}$

$s = 4,$ $\quad x = \begin{cases} -\frac{l}{2} - (-1)^k \left\lfloor \frac{k}{2} \right\rfloor, l \text{ even} \\ -\frac{l+1}{2} + (-1)^k \left\lfloor \frac{k}{2} \right\rfloor, l \text{ odd} \end{cases}, y = -l - x$

$s = 5,$ $\quad x = \begin{cases} \frac{l}{2} - (-1)^k \left\lfloor \frac{k}{2} \right\rfloor, l \text{ even} \\ \frac{l-1}{2} + (-1)^k \left\lfloor \frac{k}{2} \right\rfloor, l \text{ odd} \end{cases}, y = -l$

$s = 6,$ $\quad x = l, \ y = \begin{cases} -\frac{l}{2} - (-1)^k \left\lfloor \frac{k}{2} \right\rfloor, l \text{ even} \\ -\frac{l+1}{2} + (-1)^k \left\lfloor \frac{k}{2} \right\rfloor, l \text{ odd} \end{cases}.$

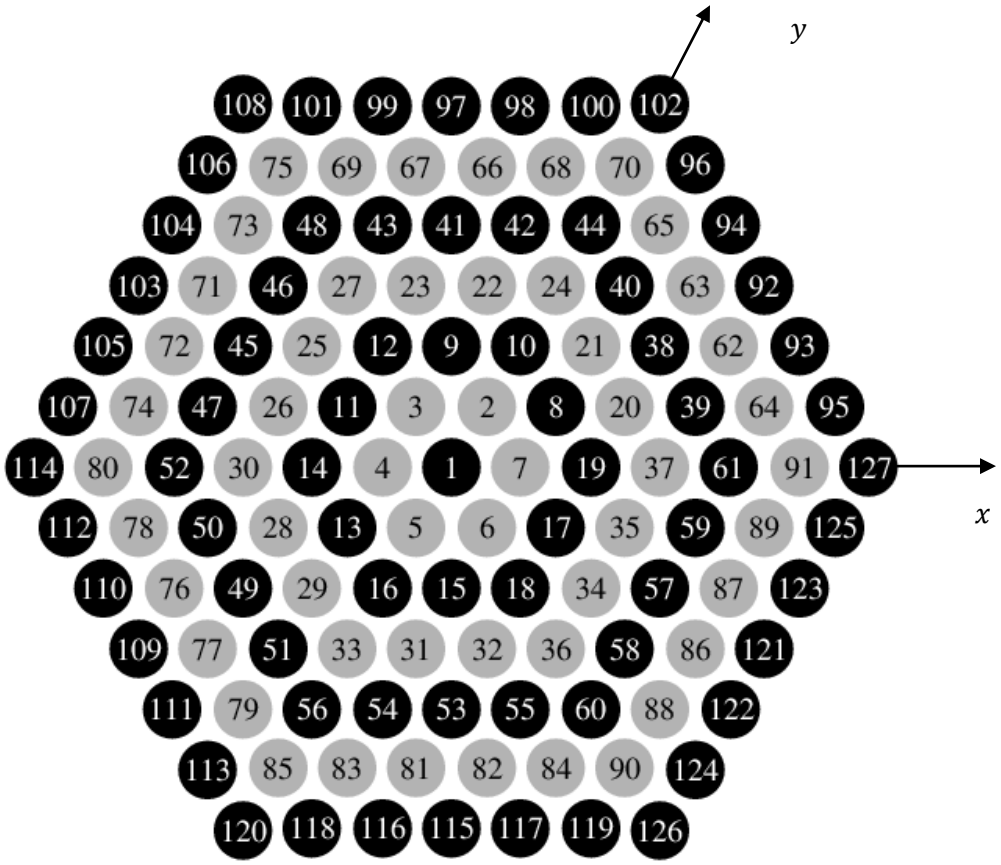

Figure 2.2 Growth sequence configuration for 127, with shells depicted by shading.

GLOBAL MINIMA

We wish to find the absolute or global minimum of (1). We use the Big Bang Algorithm[1], modified for the two-dimensional case, to generate random initial configurations of the clusters and the initial expansion of the clusters. We perform local minimizations starting from the cluster configurations after this initial expansion. (See J. C. Yang, "Structure and binding of two-dimensional Lennard-Jones clusters," for details of the local minimization.) We record the minimum energy obtained from the first local minimization for each cluster size. This is our tentative global minimum on record. We compare subsequent local minimum energies to this tentative global minimum. If a subsequent local minimum energy is lower than the tentative global minimum, that local minimum energy becomes the new tentative global minimum. The tentative global minimum becomes our final global minimum if it is reached 250 times. When a global minimum is reached this many times during an unbiased random search, it is reasonable to terminate the search[2].

III. RESULTS

Table 3.1 shows selected energies obtained through our growth sequence. Table 3.2 shows the growth sequence's results and the difference from the global minima obtained through the random search. Averick et. al[3] have presented their best known minima for selected sizes. The growth sequence's results are lower than or equal to all but two of these minima. Table 3.3 shows these results.

Table 3.1 Energies obtained through growth sequence (V_g) for $n = 100k$, $k = 1,2, \ldots 20$.

n	V_g
100	-293.697155
200	-613.669740
300	-937.703653
400	-1263.246885
500	-1591.147123
600	-1920.310800
700	-2249.524398
800	-2579.787404
900	-2910.362795
1000	-3240.965486
1100	-3572.706159
1200	-3904.281518
1300	-4236.242115
1400	-4568.037413
1500	-4899.806400
1600	-5232.862910
1700	-5565.912918
1800	-5898.852360
1900	-6231.812919
2000	-6565.062394

Table 3.2 Energies obtained through growth sequence (V_g) and their difference from the global minima (V_{min}), $1 \leq n \leq 80$.

Size	(V_g)	(V_{min})- V_g
1	0	0
2	-1	0
3	-3	0
4	-5.073421	0
5	-7.178024	0
6	-9.358274	0
7	-12.534867	0
8	-14.683990	0
9	-16.909315	0
10	-20.101613	0
11	-22.336541	0
12	-25.566704	0
13	-27.804066	0
14	-31.036449	0
15	-33.277828	0
16	-36.511685	0
17	-38.834213	0
18	-42.078075	0
19	-45.351119	0
20	-47.595053	0
21	-50.833597	0
22	-53.158738	0
23	-56.407376	0
24	-59.681547	0
25	-62.008560	0
26	-65.257914	0
27	-68.536250	0
28	-70.863608	0
29	-74.113240	0
30	-77.391824	0
31	-79.719688	0
32	-82.970143	0
33	-86.248911	0
34	-88.584684	-0.0531159
35	-91.919076	0
36	-95.200430	0
37	-98.483470	0
38	-100.812017	0
39	-104.062843	0
40	-107.342522	0

41	-109.678989	-0.0525360
42	-113.013762	0
43	-116.296059	0
44	-119.579281	0
45	-121.916015	-0.0511305
46	-125.251317	0
47	-128.533746	0
48	-131.817784	0
49	-134.154604	-0.0511233
50	-137.489982	0
51	-140.772471	0
52	-144.056559	0
53	-146.393573	-0.0512017
54	-149.729049	0
55	-153.011772	0
56	-156.295899	0
57	-158.640929	-0.1341975
58	-161.977951	-0.0824305
59	-165.345572	-5.5647126E-05
60	-168.630708	0
61	-171.915664	0
62	-174.252839	-0.0506046
63	-177.588544	0
64	-180.871358	0
65	-184.155736	0
66	-186.500932	-0.1342838
67	-189.838184	-0.0825644
68	-193.205900	-0.0003248
69	-196.491298	0
70	-199.776300	0
71	-202.121616	-0.1342229
72	-205.458929	-0.0825639
73	-208.826834	-0.0001217
74	-212.112269	0
75	-215.397494	0
76	-217.742842	-0.1343681
77	-221.080180	-0.0825705
78	-224.448109	-0.0001479
79	-227.733561	0
80	-231.018801	0

Table 3.3 Comparison of energies obtained through growth sequence (V_g) with previous best known minima (min$\{V_2\}$) from Ref. 3.

n	$-\min\{V_2\}$ (Ref. 3)	$-V_g$
100	293.697	293.697155
200	613.700	613.669740
300	937.704	937.703653
400	1263.247	1263.246885
500	1591.147	1591.147123
600	1920.311	1920.310800
700	2249.524	2249.524398
800	2579.787	2579.787404
900	2910.363	2910.362795
1000	3240.966	3240.965486
2000	6565.062	6565.062394
3000	9902.100	9902.102728
4000	13245.562	13245.561388
5000	16595.435	16595.434511
6000	19946.654	19946.653932
7000	23301.707	23301.709632
8000	26658.053	26658.055706
9000	30015.692	30015.692059
10000	33374.616	33374.616004

IV. CONCLUSION

We have developed a growth sequence that predicts the global minimum energy for a cluster of n atoms. After conducting a random search for global minima, we found that the growth sequence produced 62 of the global minima for $1 \leq n \leq 80$. The growth sequence has yielded energies lower than or equal to the previous best known minima for all but two of 19 sizes reported in MINPACK-2. It will serve as a basis for further candidates for global minima.

References

1. R. H. Leary, J. Global Optimization **11**, 50 (1997).
2. J. A. Northby, J. Chem. Phys. **87**, 6166 (1987).
3. B.M. Averick, R. G. Carter, J. J. Moré, and G. L. Xue, "*The MINPACK-2 Test Problem Collection,"* Argonne National Laboratory, Mathematics and Computer Science Division, Technical Memorandum No. 150, June 1992, p. 44.