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Note

Growth of Equilibrium Clusters of Lennard–Jones Molecules

1. INTRODUCTION

The study of materials at the atomic level by computer simulation has received considerable attention since the first attempts at solving the classical N-body problem numerically were undertaken at Los Alamos by Metropolis *et al.* [1]. Such studies become necessary when continuun theories, while adequate to describe macroscopic systems, are incapable of accounting for the mechanics of small N-particle systems. A necessary prerequisite to the study of the dynamics of such systems is a thorough knowledge of their statics.

The purpose of this paper is to describe a method for determining minimum energy configurations that are characteristic of the Lennard–Jones 6–12 potentional function. Little attempt will be made to describe the geometries of the resulting clusters. For an exhaustive description of some of the resulting equilibrium configurations for less than 50 atoms the reader is referred to the landmark papers of Hoare and Pal [2, 7]. Due to the relatively large number of isomers that exist for clusters of more than about 20 atoms and to their high degree of asymmetry, a detailed description of their geometries would not be truly useful. The characteristic that will be used to describe these clusters is the potential energy.

For even a relatively small number of atoms the potential energy is an extremely complicated function of the position coordinates. Since the methods of calculus are, in a practical sense, useless in determining all possible equilibrium configurations for more than two atoms some other method must be implemented in order to determine whether a given minimum is in fact local or absolute in character. For three atoms a combinatorial method may be used to easily enumerate all possible stationary values of the potential function and thus determine the absolute minimum energy configuration (atoms at the vertices of an equilateral triangle). But this method of proof soon becomes unwieldy for as few as four atoms, and unless some other method can be employed, it is unlikely that a given energy minimum can in fact be proven to be absolute.

One must therefore rely on some form of intuition in developing a procedure that can be expected to yield minimum energy configurations. In this investigation the absolute minimum energy configuration for three atoms was used as a starting configuration. Molecules were generated by adding a single atom to the previously static N-cluster at an energetically favorable site (described below) and then cooling the resulting $(N+1)$-cluster to zero degrees Kelvin. This is the same type of

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approach that was used by Hoare and Pal but the manner in which the energetically favorable sites were chosen is much different.

The addition of an atom to a static N-cluster proceeds in the following manner: an atom is chosen (atom $\# n$) and the distances between n and all of the other atoms are calculated. A bubblesort technique is used to sort these distances in order of increasing size. The k and j nearest neighbors are then determined. Two lines are then calculated: one joins n to the point midway between j and k, and the other joins j to the point midway between k and n. The point of intersection of these two lines is then calculated. Two possible tetrahedral sites lie along the line passing through this point normal to the plane formed by n, j, and k. The distance from this plane to each of the proposed sites is set at 0.85 distance units—slightly greather than the distance an atom would lie above the plane formed by the other three in a true Lennard–Jones tetrahedron. The distances between one of the proposed sites and the atoms are calculated and if these distances all exeed a value of 1.0 distance units then the site is not rejected. The kinetic energy of the system is then calculated after one iteration and if the KE exceeds 1.0 energy units then the site is labeled unacceptable and the other site is considered. A value of 1.0 is used because it was found that if the kinetic energy exeeded this value after only one iteration, the resulting cluster would not approach equilibrium quickly enough, if at all. If the second site fails both tests, then another atom $(n+1)$ is chosen. The process is repeated until an acceptable site is located.

After the position coordinates of the new atom have been determined, the resulting cluster must be quenched. A variety of methods exist for cooling N-particle systems including, among others, conjugate gradient techniques [3], individual quenching [4], and simultaneous quenching [5]. These techniques all begin by assuming that the N-cluster under consideration is sufficiently close to equilibrium, and then continuously force it closer to equilibrium. This forcing is accomplished in simultaneous quenching by instantaneously setting the velocity of each particle equal to zero when the cluster passes through a local maximum in its kinetic energy. In individual quenching, the kinetic energy of each particle is monitored separately. The conjugate gradient technique consists of a search through the multidimensional space of atomic position coordinates in directions mutually conjugate, with respect to the matrix of second mixed partial derivatives of the potential function, to previously searched directions. In this investigation the simultaneous quenching technigue was used due to its ease of implementation.

2. ALGORITHM DEVELOPMENT

In order to accurately predict the behavior of an N-particle system, the equations of motion must be integrated. This is most easily accomplished numerically by choosing a time scale that is sufficiently small so that the acceleration a given particle experiences over this period is approximately constant. If this time step is denoted by h and the position vector of particle j at time t is denoted by $r_j(t)$, then

$$r_j(t+h) = r_j(t) + v_j(t) \cdot h + 0.5 \cdot a_j(t) \cdot h^2, \tag{1}$$

where $v_j(t)$ and $a_j(t)$ are the velocity and acceleration, respectively, of particle j at time t. If the substitution

$$v_j(t) = [r_j(t+h) - r_j(t-h)]/(2 \cdot h) \tag{2}$$

is made, then the Verlet algorithm [6]

$$r_j(t+h) = 2 \cdot r_j(t) - r_j(t-h) + a_j(t) \cdot h^2 \tag{3}$$

is obtained. The acceleration is calculated from Newton's second law,

$$a_j(t) = F_j(t)/m_j = \left[\sum (-dV(r_{ij})/dr_{ij}) \cdot e_{ij} \right] \bigg/ m_j, \tag{4}$$

where m_j is the mass of particle j, r_{ij} is the scalar distance between particles i and j, and e_{ij} is a unit vector pointing from i to j. The potential function used was a scaled, non-dimensionalized Lennard–Jones type:

$$V(r_{ij}) = r_{ij}^{-12} - 2r_{ij}^{-6}. \tag{5}$$

Thus,

$$a_j(t) = \left[\sum (12 \cdot r_{ij}^{-13} - 12 \cdot r_{ij}^{-7}) \cdot e_{ij} \right] \bigg/ m_j. \tag{6}$$

A brief description of the algorithm is given below. Readers wishing to examine the results without detailed study of the algorithm may turn directly to the results given in the following section.

The first cluster is generated in a subroutine named STARTS, and an atom is added to the previously static N-cluster by a subroutine named SORTER. The equations of motion are then integrated and simultaneous quenching is implemented until the KE of the cluster falls below 10^{-8} energy units. The number of atoms in the cluster and the corresponding potential energy at equilibrium are then written. An atom is added to the static $N+1$ cluster and the entire process is repeated until the cluster of maximum size has been generated.

3. RESULTS AND DISCUSSION

The results for values of N ranging from 3 to 46 appear in Table I. Values obtained by Hoare and Pal [2, 7] appear in the right-hand columns for com-

TABLE I

The Potential Energies of Equilibrium Clusters of Lennard–Jones Molecules Generated by the Present Algorithm Are Compared with Energies Generated by the Pal–Hoare Procedure

	Reardon Algorithm	Hoare-Pal Procedure	
N	$V_{Algorithm}$	$V_{Maximum}$	$V_{Minimum}$
3	-3.000	-3.000	-3.000
4	-6.000	-6.000	-6.000
5	-9.104	-9.104	-9.104
6	-12.303	-12.303	-12.712
7	-15.593	-15.593	-16.505
8	-19.821	-18.976	-19.822
9	-24.113	-23.172	-24.113
10	-28.423	-26.737	-28.420
11	-32.766	-30.721	-32.765
12	-37.968	-35.215	-37.967
13	-44.327	-37.840	-44.327
14	-47.845	-41.879	-47.845
15	-52.323	-49.664	-52.322
16	-56.816	-54.165	-56.815
17	-61.307	-58.668	-61.307
18	-66.531	-63.897	-66.531
19	-72.660	-69.330	-72.659
20	-77.177	-73.878	-77.177
21	-81.651	-80.147	-81.685
22	-86.810	-85.420	-86.148
23	-92.844	-90.560	-90.647
24	-96.504	-94.997	-96.514
25	-101.878	-100.262	-102.371
26	-106.941	-105.128	-108.313
27	-112.874	-110.416	-112.823
28	-116.653	-115.644	-117.775
29	-122.535	-120.300	-123.585
30	-127.623	-125.670	-128.180
31	-133.294	-131.008	-133.102
32	-137.870	-136.411	-138.820
33	-142.914	-142.440	-143.615
34	-148.603	-148.435	-149.005
35	-153.106	-153.690	-154.085
36	-158.053	-158.732	-158.796
37	-163.760	-163.763	-164.577
38	-168.718	-169.431	-169.593
39	-174.044	-174.230	-174.956
40	-178.768	-179.352	-179.617
41	-182.312	-184.435	-184.895
42	-188.335	-189.256	-190.487
43	-194.971	-194.472	-195.574
44	-200.444	-199.355	-200.972
45	-205.769	-204.649	-206.177
46	-211.943	-210.561	-211.172

Note. Units are non-dimensional and N signifies the number of atoms in the cluster.

parison. The absolute minimum energies found by these authors among the four different growth schemes used (dodecahedral, fcc, pentagonal, and tetrahedral) are listed under the column labeled V_{minimum}, while the highest energies obtained are listed under V_{maximum}. It should be noted that although one of the growth schemes used by Hoare and Pal is labeled tetrahedral, it is not the same procedure that was implemented in this investigation.

The values obtained for the potential energies of the N-clusters fall well within the limits obtained by Hoare and Pal for the majority of the clusters examined.

TABLE II

The Potential Energies of Equilibrium Clusters of Lennard–Jones Molecules Generated by the Current Algorithm Are Presented

N	$V_{\text{Algorithm}}$	N	$V_{\text{Algorithm}}$
47	-215.833	80	-406.559
48	-221.823	81	-413.067
49	-228.211	82	-420.483
50	-233.094	83	-424.386
51	-238.647	84	-430.685
52	-243.431	85	-436.224
53	-249.550	86	-440.774
54	-255.714	87	-446.477
55	-259.921	88	-452.770
56	-265.518	89	-457.738
57	-271.622	90	-469.460
58	-276.576	91	-475.603
59	-280.334	92	-480.526
60	-288.405	93	-489.576
61	-293.439	94	-497.641
62	-302.249	95	-501.755
63	-308.474	96	-506.380
64	-313.380	97	-512.212
65	-318.144	98	-521.283
66	-323.552	99	-527.788
67	-329.644	100	-533.069
68	-337.068	101	-539.422
69	-342.170	102	-546.315
70	-349.737	103	-552.119
71	-355.464	104	-556.269
72	-363.916	105	-561.867
73	-368.976	106	-568.166
74	-373.998	107	-573.341
75	-379.397	108	-581.293
76	-384.394	109	-587.326
77	-388.317	110	-592.290
78	-395.853	111	-596.908
79	-399.782	112	-603.555

Note. Units are non-dimensional and N signifies the number of atoms in the cluster.

There is an apparent transition, however, between the tetrahedral and the pentagonal growth schemes. For $N \leqslant 7$ the molecules follow the tetrahedral growth scheme, but for $N=8$ the arrangement jumps to the minimum energy configuration found for pentagonal growth. For $8 \leqslant N \leqslant 20$ the clusters follow the pentagonal growth scheme. For $N>20$ the clusters assume the forms of isomers whose energies lie in the neighborhood of the above-mentioned growth schemes. It is interesting to note that for $N=23$ the cluster generated by the current algorithm has an energy more than two units lower than the minimum energy cluster found by Hoare and Pal. For $N=66$ the difference is even more pronounced: $V_{\text{algorithm}} = -323.552$, while $V_{\text{Pal-Hoare}} = -308.372$.

Hoare and Pal seem to use growth schemes that minimize the energy of a new atom by carefully placing it into the growing arrangement. The present method, which is less complicated, consistently generates clusters comparable in energy to the lowest energy configurations found by these authors. In some cases, as has been shown, the clusters generated are even lower in energy. Table II lists potential energies for $47 \leqslant N \leqslant 112$. A comparison of energies for each cluster where $N>46$ is not possible due to a lack of data presented by Hoare and Pal.

The current algorithm required approximately 26 h of total run time on an IBM PC/AT enhanced with a DSI-780+/4 board running SVS FORTRAN at 0.2 Mflops to generate the clusters in Tables I and II. This algorithm is well suited for developing starting configurations for molecular dynamics simulations where low energy clusters are needed. Examples include the observation of phase transformations in Lennard–Jones molecules and diffusion in clusters at low temperature. Implementation of the code is neither complicated nor overburdening, since many of the subroutines that are called are an integral part of any such simulation.

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