Unconstrained Gradient Based Optimisation of Morse Atomic Clusters

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***Abstract* – This research presents the results obtained using a Limited-Memory Broyden–Fletcher–Goldfarb–Shanno (L-BFGS) gradient based algorithm for optimising Morse atomic clusters. This algorithm was able to locate the global minima for $5 \leq N \leq 25$, $N = 27$, $\rho = 6$ as reported in the University of Cambridge database. This research uses an optimiser sourced from the internet to investigate the techniques used to evaluate global minimum configurations for randomised atomic clusters.**

***Keywords* – Clusters, Morse, Gradient based optimisation, Lennard-Jones**

I. INTRODUCTION

Atomic clusters is the interaction of each atom through a central force. The goal of optimisation is to identify the structure which corresponds to the global minimum potential energy for that cluster. It is conjectured that the number of local minima for this problem increases exponentially with the number of atoms. This makes finding local minima trivial, we are instead interested with the global minimum which is a much harder problem that has been extensively studied and has many applications.

The Lennard-Jones (LJ) cluster is a commonly studied optimisation problem where the optimal structures are strictly uniform [1]. Much harder optimisation problems are that of atomic clusters where the potential energy arising from interactions is given by the Morse pair-potentials:

$$v_\rho(r) = (e^{\rho(1-r)} - 1)^2 - 1 \tag{1}$$

Figure 1 shows the form of $v_\rho(r)$ where the minima for all values of ρ occur at $r = 1$.

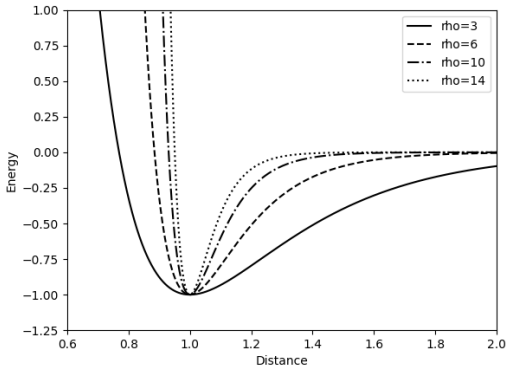

Fig. 1. Morse pair-potentials for $\rho = 3, 6, 10, 14$

The single parameter ρ controls the range of the potential and allows for a wide range of interactions to be modelled. As stated by [2], when $\rho = 6$ the Morse potential is similar to the LJ potential and results in similar optimal structures.

This paper uses the gradient based optimiser created by [3] to investigate the Morse potential for atomic clusters $2 \leq N \leq 32$ and $\rho = 3, 6, 10, 14$ and is structured as follows: Section II presents previous LJ and Morse optimisation methods. Section III describes the approach used for this papers research followed by the results and conclusions drawn in sections IV and V respectively.

II. PREVIOUS WORKS

A. Lennard-Jones Clusters

[4] introduced a technique for finding global minimum over an icosahedral lattice which was later implemented by [5]. Using this technique many punitive global minima were found for the first time. Subsequent lattice search methods have produced global minima for $148 \leq N \leq 309$ [6], $310 \leq N \leq 561$ [7] and $562 \leq N \leq 1000$ [8]. It was proven that lattice techniques are restricted to only a portion of the domain and are therefore bias. They do not explore regions which could contain energy clusters with a non-icosahedral structure. In 2005, [9] introduced an unbiased population-based search algorithm which managed to find punitive global minima for atoms $2 \leq N \leq 372$.

B. Morse Clusters

Compared to Lennard-Jones clusters Morse clusters have a much wider range of potential structures, subsequently far less research has been introduced for unbiased global optimisation. [2] introduced a population-based algorithm which found all punitive global minima as outlined in [10] in the range of $81 \leq N \leq 146$ with $\rho = 14$. This algorithm, much like their work in LJ clusters [9], is a two-phase algorithm which uses an initial population creation phase similar to the Basin-Hopping technique [11] that randomly generates starting clusters. This phase aims to initialise a starting population of eight members whose energies are close to the global minima. The second phase of the algorithm updates the population ranked of closeness to a better solution by performing mutation operations followed by local searches.

A genetic approach laid out by [12] proved successful for small and medium sized atom clusters $N \leq 50$. A potential energy transformation algorithm [13] was successful in finding all clusters described by [10]. This algorithm is gradient-based and sets solid groundwork for the investigation of this paper.

III. TECHNICAL APPROACH

All technical details and inner workings of the optimiser can be found from the documentation [3]. Being a gradient based optimiser, the first step was to create a cost function. This function firstly works out the distance between two atoms based on their positions (x, y, z). From here, the derivative of the Morse potential function and atom distances can be calculated. Lastly, the gradients for each atom can be updated and passed back into the optimiser.

Upon each experiment, atom locations are initialised randomly in three-dimensional space. These locations are then given to the optimiser which uses the cost function previously mentioned to calculate distances and gradients. Upon each iteration the optimiser updates the new atom locations and repeats the process until some minima is found.

The initial location of each atom is box-bounded by N. It was observed that when a bounding box too large was given the optimiser would fail to find any meaningful results in the search space. Similarly, if the bounding box was too small atom placement would be on top of each other, yielding unimportant results. Through experimentation a bounding box size of $\sqrt[3]{N}$ was identified as near optimal.

IV. EXPERIMENTAL RESULTS

As can be seen in Figure 1 the minima of the Morse pair-potentials for values of $\rho = 3,6,10,14$ is -1. To confirm this visualisation, a gradient based optimiser [3] was used to evaluate the minimum of the Morse potential. This optimiser returned a value of -1 for all values of ρ at $N = 2$.

Custer sizes of $2 \leq N \leq 32$ were evaluated using the Morse potential with $\rho = 3,6,10,14$. Each cluster size was iterated $100,000$ times for each value of ρ in search for distinct minima. To classify minima found as distinct a comparison value of $\varepsilon = -1 \times 10^{-6}$ was used.

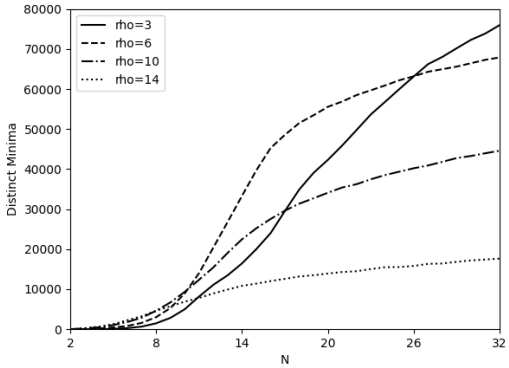

Fig. 2. Distinct minima count for $2 \leq N \leq 32$ at each $\rho = 3,6,10,14$ over 100,000 iterations

Figure 2 and Table 1 dictate that the count of distinct minima do in fact grow at an exponential rate as a function of N and ρ. Initially, the count of distinct minima increases as ρ increases whereas at approximately $N = 15$ the amount of minima decreases as ρ increases. The data stipulates that at $N = 32, \rho = 3$ there is a 75.9% chance of finding a new minima on the next iteration. At $25 \leq N \leq 32$ it can be seen that the count of distinct minima for $\rho = 10,14$ begin cool in terms of exponential growth, whereas the distinct minima found for $rho = 3,6$ still increases exponentially. This indicates that in order to achieve an accurate distinct minima count for $\rho = 3,6$ the iterations should also exponentially increase.

TABLE I

Individual distinct minima count for all $2 \leq N \leq 32$ at each at each $\rho = 3,6,10,14$ over 100,000 iterations

N	$\rho = 3$	$\rho = 6$	$\rho = 10$	$\rho = 14$
2	1	1	1	2
3	2	34	220	259
4	11	171	479	635
5	86	450	1033	1286
6	284	829	1819	2265
7	661	1599	2886	3253
8	1483	3020	4626	4592
9	2841	5293	6706	5773
10	4994	8945	9334	6883
11	8170	14010	12364	7820
12	11096	20404	15448	8947
13	13484	26818	19074	9912
14	16439	33307	22468	10831
15	20003	39675	25214	11384
16	24009	45256	27537	12031
17	29524	48556	29611	12589
18	34892	51495	31358	13176
19	39052	53446	32701	13490
20	42299	55551	34093	13908
21	45881	56866	35395	14292
22	49734	58475	36226	14490
23	53633	59672	37447	15029
24	56803	60888	38503	15496
25	59997	62194	39364	15539
26	63136	63169	40206	15804
27	66201	64307	40903	16332
28	68014	64951	41807	16419
29	70178	65594	42752	16839
30	72274	66435	43274	17197
31	73852	67285	43953	17407
32	75949	67887	44583	17640

An estimation of global minima and its resulting atomic configuration was recorded upon each iteration of N and ρ as described above. It was found that for $5 \leq N \leq 25, N = 27, \rho = 6$ the global minima and configuration was identical to the results reported by [10]. For $N = 26,28 \leq N \leq 32, \rho = 6$ the global minima and resulting atomic configuration was within 0.1% of the minima recorded by [10]. At this size of N and *rho*, Table 1 indicates that there is a 63% chance of finding a new minima at the next iteration. As such, it is hypothesised that with an increase in iterations the global minima would be found.

The following tabular results outline the global minima and resulting atomic configuration for $2 \leq N \leq 10, N = 32, \rho = 6$.

TABLE II

Global atomic configurations and resulting minima for $2 \leq N \leq 10, N = 32, \rho = 6$.

Atom	x	y	z	Global Minima
1	-0.265051	0.0763904	0.616948	
2	-0.652382	-0.581297	-0.0291346	-1
1	0.393083	-0.271477	0.326459	
2	0.42322	0.460999	-0.353666	
3	-0.335995	0.412245	0.295345	-3
1	0.279937	-0.740138	0.132146	
2	-0.668773	-0.426785	0.174084	
3	-0.0775921	-0.132083	-0.576686	
4	0.0779778	0.215151	0.348098	-6
1	-0.291939	0.164777	-0.931577	
2	-0.330342	-0.0710789	0.0378942	
3	0.255463	-0.595065	-0.577937	
4	0.49409	0.347346	-0.339212	
5	0.635418	0.0157846	-1.27038	-9.04493
1	-0.810437	-0.0290642	-1.37233	
2	-0.142627	-0.430407	-0.752632	
3	-0.582875	0.431542	-0.519612	
4	-1.47576	0.00604049	-0.632615	
5	-0.807954	-0.395302	-0.0129158	
6	-1.03552	-0.855909	-0.865635	-12.4878
1	0.457846	-0.0493416	-0.199426	
2	0.0750536	-0.925421	0.0724612	
3	0.953319	0.347387	0.565479	
4	-0.507972	-0.110362	0.0273788	
5	0.155518	-0.212512	0.760396	
6	0.978181	-0.642516	0.405025	
7	0.034826	0.676277	0.33208	-16.2076
1	-0.130997	0.249467	-0.267255	
2	-0.937017	0.374185	0.318353	
3	-0.107498	0.892985	0.490278	
4	-0.615125	0.517927	1.2585	
5	0.75216	-0.399033	0.990384	
6	0.386453	0.491442	1.25159	
7	-0.139126	-0.110525	0.656813	
8	0.685872	0.325408	0.307957	-19.3274
1	-0.0551391	-0.621003	-0.562499	
2	-0.114778	0.155122	-1.18852	
3	-1.6022	-0.120427	-0.592708	
4	-0.669349	0.120894	-0.358394	
5	-0.0115944	-0.78257	-1.53992	
6	-0.976174	-0.821252	-0.231702	
7	-0.549371	-1.39213	-0.942569	
8	-1.06442	0.489133	-1.19006	
9	-0.869272	-0.479755	-1.1513	-23.4172
1	-0.274942	0.184989	-0.491883	
2	-0.681666	-0.34249	0.255598	
3	0.530167	0.681946	-0.118065	
4	0.767087	-0.615789	0.951336	
5	-0.0469608	-1.06378	0.537164	
6	-0.178661	-0.826582	-0.443295	
7	-0.26829	0.537258	0.445266	
8	0.315648	-0.234331	0.1659	
9	-0.130122	-0.219559	1.06892	
10	0.635119	0.387827	0.850121	-27.4733
1	1.45418	0.145831	0.540385	
2	0.0825999	-0.629989	0.708293	
3	0.545684	0.121731	1.99448	
4	-0.996221	0.48145	0.977085	
5	-0.746965	-0.461713	1.13069	
6	1.55938	0.114817	1.57604	
7	1.10703	-0.753858	1.89282	
8	-0.30625	-1.4208	1.04237	
9	0.91745	-0.639288	0.308822	
10	-1.28516	-1.22321	0.911101	
11	-0.523978	-0.068152	2.00532	
12	1.33707	-1.49113	0.304926	
13	0.109441	-0.723294	1.66278	
14	-1.05372	0.638746	-0.0395308	
15	-0.799242	-1.09181	1.85267	
16	-0.0888451	0.467669	-0.424459	
17	0.799058	-0.246704	1.15257	
18	0.306715	-1.39921	0.1733	
19	-0.8263	-0.246589	-0.506973	
20	-0.21218	0.925253	0.497169	
21	1.61484	-0.750682	0.981893	
22	-0.047827	0.226417	1.19995	
23	0.963734	-1.04815	-0.545068	
24	1.02792	-0.0295732	-0.421755	
25	0.482301	0.232268	0.355121	
26	0.736095	-1.24426	1.08025	
27	-0.457154	0.00797361	0.333209	
28	-1.36882	-0.286437	0.376902	
29	0.137703	-0.500049	-0.269948	
30	0.825358	0.710137	1.16085	
31	-0.647127	-0.959661	0.192125	
32	1.79242	-0.632083	-0.0455568	-126.557

It can be seen by the data in Table 2 that as N increases the global minima decreases exponentially. Interestingly, the atomic configuration for each N atom cluster is in the approximate range of (-2, 2) at their respective positions (x, y, z). This is due to each atom being drawn to to each other atoms Morse pair-potential (-1 as seen in Figure 1).

V. CONCLUSION

This paper presented the results obtained using a Limited-Memory Broyden–Fletcher–Goldfarb–Shanno gradient based algorithm for optimising Morse atomic clusters. This research was able to obtain all optimal configurations in the range $5 \leq N \leq 25, N = 27, \rho = 6$ as reported in [10]. The optimiser was sourced from [3] and was used to investigate the techniques used to evaluate global minimum configurations for randomised atomic clusters.

Although promising results were achieved for the configurations tested, further research should be conducted into gradient based optimisers to assess whether they are an accurate tool for finding minima of $26 \leq N \leq 144$ sized atomic clusters. It is worth noting that this type of optimiser may not be the most suited for finding Morse potential. As such, other types of algorithms such as population-based should be considered as well.

Although Morse clusters are a harder problem than Lennard-Jones clusters far less research has gone into them comparatively. The increased coverage of the Morse potential highlight interesting ideologies for future works which should consider gradient based algorithms as well as alternatives.

VI. REFERENCES

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