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NEW NANOSTRUCTURES OF MINIMUM POTENTIAL BY LENNARD JONES AND MORSE

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Abstract: Molecular design and the study of nanostructures by Computational Chemistry, for example, under a minimum Van Der Waals type potential, such as Morse and Lennard Jones potentials, is a way of modeling and predicting new structures of nanomolecules. of particles complementary to expensive experimental investigations. This work presents novel nanostructures stable to small potential changes, called nanovehicles that can possibly be created experimentally. The predicted nanovehicles are stable because they are potential minimum and consist of an envelope of layers of particles capable of containing different, focused and separated nuclei of few particles in their center of mass. Stability to potential variations is checked by a novel comparison between Morse potentials similar to the Lennard Jones potential. The results show the novel geometric shapes that are obtained between different layers of shells and different types of core.
Keywords: Materials chemistry, Nanochemistry, Molecular dynamics.

INTRODUCTION

There is extensive literature on Morse and Lennard Jones potentials and their minimum potential clusters (Hartke, 2002; Morse, 1929; Hoare and McInnes, 1983; Northby, 1987; Gómez and Barrón, 1991; Maier et al., 1992; Maranas and Floudas, 1994, Deaven and Ho, 1995, Barrón et al., 1997, Leary, 1997, Wales and Doye, 1997, Doye, 1998, Doye, et al., 1999, Wolf & Landman, 1998, Leary, 1999; Hartke, 1999; Barrón et al., 1999; Wille, 1999; Solov'yov et al., 2003; Jiang et al., 2003; Huang et al., 2002; Cai et al., 2002a; Cai et al., 2002b; Jiang et al., 2003; Shao et al., 2004a; Xiang et al., 2004b; Xiang et al., 2004a; Shao et al., 2004b; Barrón, 2005; Shao et al., 2005; Doye, 2006; Dittner & Hartke, 2016; Barron, 2022a, 2022b). These single potentials have been shown to have great predictive power to aid experimental investigations in the creation of new geometric shapes of nanomaterials. Clusters of Lennard Jones and Morse potentials have been used as predictive models (see Cambridge Cluster Database (CCD), Wales et al., 1995). For example, icosahedral nuclei with no central particle (here named N12IC) are found in gold nanomaterials (Saho, et al., 2004b), sodium clusters matching the magic number sequence (Haberland et al. , 2005), design of icosahedral quasi-crystals (Noya et al., 2021).

METHODOLOGY

The numerical experimentation in this work uses two Van Der Waals potential functions that satisfy the properties of a potential well (Pardalos et al., 1994):

$$\mathrm{LJ}(d) = \frac{1}{d^{12}} - \frac{2}{d^{6}} \quad \text{y}$$
$$\mathrm{Morse}\,(\delta, d) = e^{\delta(1-d)}\left(e^{\delta(1-d)} - 2\right)$$

where d is the distance between particles. The selection of the Morse parameter is to have two close approximations to the Lennard Jones potential, MR(d)=Morse (6, d) and MO(d) = Morse (5.3554, d) (see Barrón, 2022b).

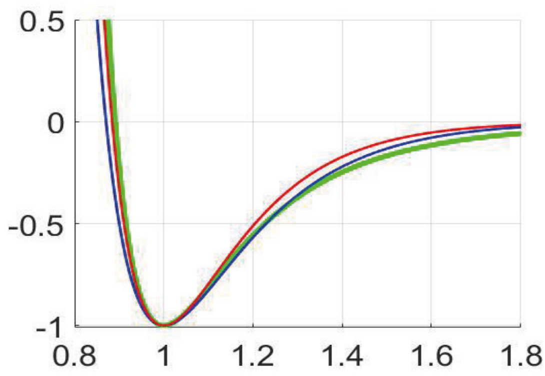

Figure 1. MR (red), LJ (green) and MO (blue) potentials.

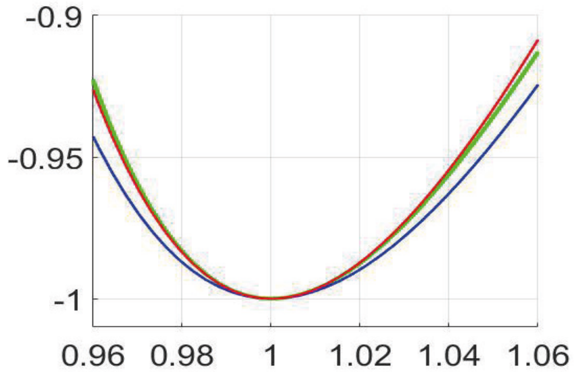

Figure 2. Valley of attraction of the MR (red, narrow), LJ (green, reference) and MO (blue, wide) potentials.

By means of a second order Taylor expansion around the optimal distance 1, the potential functions of LJ, MR and MO satisfy:

$$LJ(1+h) \approx -1+36h^2,\ MR(1+h) \approx -1+36h^2 \text{ y } MO(1+h) \approx -1+\frac{57.361}{2}h^2$$

where h is a small value. This property indicates that the particles are strongly bound around the optimal distance 1 and together with the low strength of the interactions in the asymptotic zone (d>1.4) the existence of groups of particles at distance 1 and together with the asymptotic zone is predicted. (d∈[1.4,∞)), envelopes can be created, that is, they are convex layers with an empty center. In this work, various types of envelopes of at least two levels were created, that is, on two different and close radii to the center of mass, with an empty center or capable of maintaining a small nucleus or cluster inside.

The determination that the clusters form a stable nanovehicle is when the conditions are met (stability with potential variation): 1) They correspond to local minima of potential and 2) They do not change their structure with the variations of the potentials of LJ, MR and MO (see figure 7). For local minimization, the limited memory algorithm (L-BFGS-B) of the free distribution in FORTRAN language offered (Morales and Nocedal, 2011) is used. Item 1) refers to keeping the experimental conditions, such as constant refrigeration and pressure, so that the potential function remains constant during refrigeration to search for a state of minimum potential (Haberland et al., 2005), for example: minimization without changing the potential function. While item 2) refers to the change of the experimental conditions, for example, for transport under different conditions of experimentation, pressure temperature of its corresponding refrigeration process to verify that the structure of a cluster of minimum potential does not change due to the variation of the potential function, i.e., corresponds to minimizing changing from one potential function to another potential function (see figure 7). This point is very relevant for the study of the stability of nanostructures, under similar potential changes.

DESIGN OF THE EXPDESIGN OF THE EXPERIMENTS

The simulations to determine nanovehicles in this work are based on a selection of cores and envelopes constructed from latices.

NUCLEI

The selected nuclei are a central particle, the minimized tetrahedron (oLJ4_N4T is the largest global minimum cluster by classical first and second order optimality conditions), a minimized cube (N8CB), the icosahedron with central particle (oLJ13_n13IC, see Barrón, 2022a), pentagonal prism with pentagonal pyramid caps (N13IR), 20-particle pentagonal ball is a local minimum (N20BallP), 32-particle pentagonal star is a local minimum (N32StarP), face-centered cubic truncated octahedron of 38 particles (Doye et al. 1999) is a global optimum for LJ and MO, for MR it is a local minimum cluster (here we call it oLJ38_N6OC) and the possible global minimum cluster of pentagonal dipyramid nucleus (we call it oLJ39_N7PBP). Figure 3 shows the nuclei. Figure 3. I. shows the possible global minimum cluster of 39 particles that has been colored with spheres of half the minimum interaction radius. Such coloring gives off the property that this nucleus is orientable, it distinguishes two directions, upper and lower in the orientation shown.

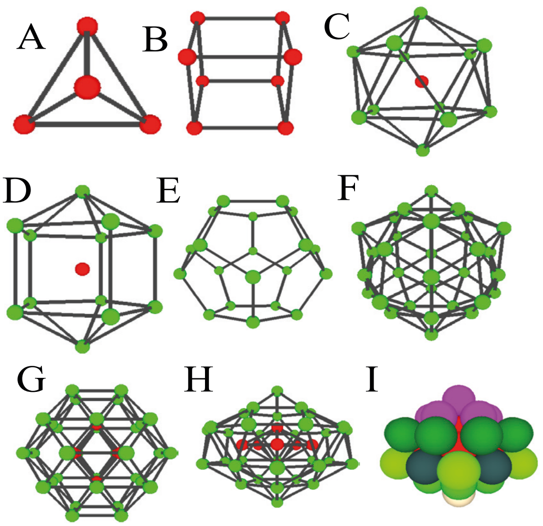

Figure 3. Nuclei **A**. oLJ4 (oLJ4__N4T), **B**. N8CB, **C**. oLJ13 (oLJ13_N13IC), **D**. N13IR, **E**. N20BalP (N20 Pentagonal Ball), F. N32EstP (N32 Pentagonal Star), **G**. oLJ38 (oLJ38_N6OC) , **H**. oLJ39 (oLJ39_N7PBP), **I**. OLj39_N7PBP with spheres of minimum interaction radius for orientation.

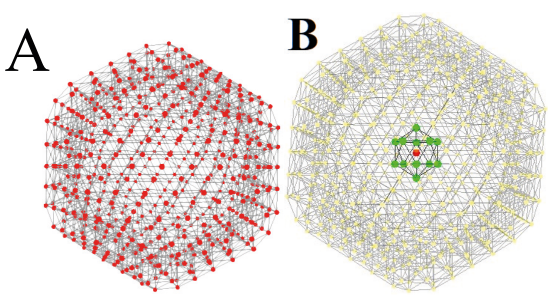

Figure 4. A. Rounded shell of 614 IC lattice particles, **B. N**ano-vehicle of 627 particles with oLJ13_N13IC in the center.

WRAPPERS

Convex regions of the latices, crystalline type networks with optimized minimum distance. Figure 9 shows the IC lattice envelopes of 614, 2654, and 3656 particles used in this work. The envelopes are layers of the latices IC (which is built from an icosahedron with a core particle, Fig. 3.C), IR (in this case it starts from the pentagonal prism with pentagonal cap pyramids, Fig. 3. D), N4T (the zero layer is the minimized tetrahedron oLJ4_N4T), N6OC (starts from the minimized octahedron) and N7PBP (starts from the minimized pentagonal dipyramid). In this work all the reported clusters are minimized by the L-BFGS-B algorithm. That is, they are constructed geometrically as Bravais crystal lattices and selecting a large number from an appropriate center is minimized. Subsequently, the inner layers are removed and outer layers are selected, which can be rounded, i.e., the particles are selected from the center by means of a sphere of an appropriate radius (see figure 4.A.) or scaled.

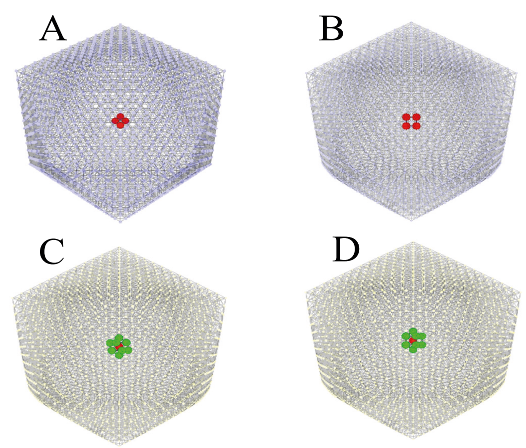

Figure 5. A. Nano carrier 2658, oLJ4 in 2654 particle IC envelope, B. **N**ano carrier 3664, N8CB in 3656 particle IC shell, C. **N**ano carrier 2667, oLJ13 in 2654 particle IC shell, D. **N**ano carrier 3669 , N13IR in 3656-particle IC envelope.

RESULTS AND DISCUSSION

Experiments have been carried out with a variety of envelopes, for this work those derived from the IC lattice are presented.

The results tables show the value of the potential in the first row of each nucleus when it was possible to construct it by fixing the potential, i.e., the experimental conditions are fixed and correspond to one of the potentials LJ, MO or MR. Below the value of the potential in each column the transition from one potential to another is indicated, i.e., starting from a local minimum structure of the conditions of a potential, it is changed to the laboratory conditions of another potential and it is expected that it will stabilize and not the initial structure is altered (success is indicated by ü and failure by X). For the N13IR nucleus, failure is indicated when it changes to oLJ13 (indicated with X oLJ13), in the other cases X, failure means that the nucleus has lost its shape. When the structure does not change with the potential changes indicated in figure 7, the nanovehicle is considered stable, otherwise it is unstable.

Table 1. shows the results of the wrapping of figure 4.A, which is clearly insufficient to obtain stable nanocarriers for some large nuclei.

The figures of the results only show the cores and the first shells that allow to create stable nanovehicles, i.e., the unstable cases are omitted.

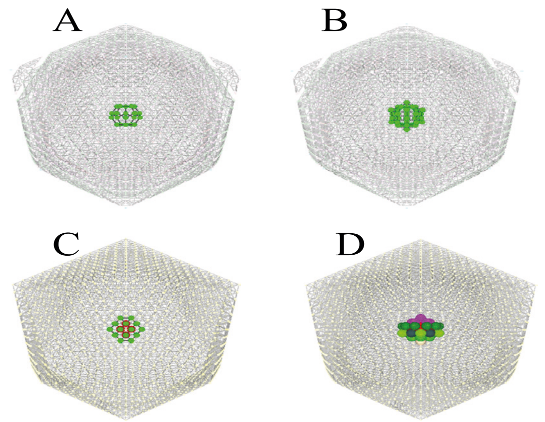

Figure 6. A. **N**ano vehicle 3676, N20BalP in 3656-particle IC envelope, B. **N**ano vehicle 3688, N32EstP in 3656-particle IC envelope, C. **N**ano vehicle 652, oLJ38 in 614-particle IC envelope, D. Nano vehicle 3695 , steerable oLJ39 in 3656-particle IC envelope.

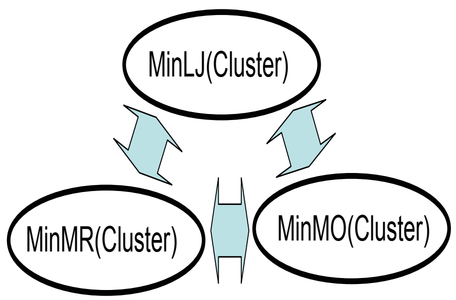

Figure 7. Stability to potential changes means minimizing a cluster with different potentials without changing its shape.

Table 2 corresponds to the IC envelope of layers 11 and 12 of an IC region centered on an icosahedron with a central particle, the central particle being the zero layer. The envelope of 3656 particles from layers 10, 11 and 12 of IC was built and table 3 shows results similar to those of table 2. Of the nuclei proposed in figure 3, the nuclei N13IR, N20BalP and N32EstP are unstable under potential changes because its structure breaks or collapses because the bonds between pairs of particles do not have the rigidity of the tetrahedron or the icosahedron.

The last experiment presented consists of a design with a nucleus different from those selected, it is an octahedron rhombus of 24 particles. Figure 8 shows the stable nanovehicle of 3459 particles that was structured with an octahedron rhombus of 24 particles with a central particle, its envelope comes from the IC lattice, it is round and its radius was expanded from 10.55 to 11.9 to achieve stability, the minimum potentials are LJ = -8259.2572, MO= -7286.5215, MR= -6230.2296.

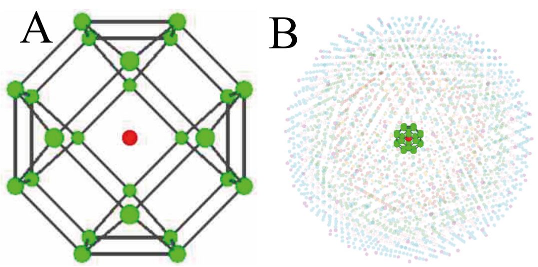

Figure 8. A. 24-particle octahedron rhombus with central particle, B. Nano vehicle 3459, with a 25-particle octahedron rhombus as core within a special shell (rounded and scaled to radius 11.9) of 3434-particle IC latice.

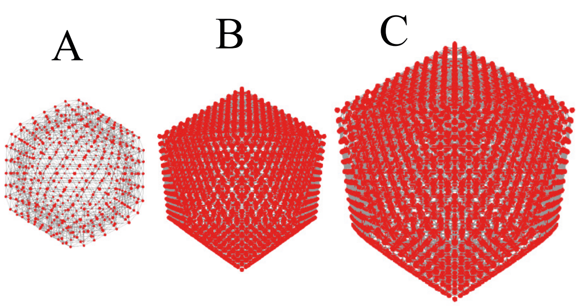

Figure 9. Latice envelopes IC of A) 614, B) 2654 and C) 3656 particles.

CONCLUSIONS AND FUTURE WORK

Numerical simulations open a path for the creation of this type of structure experimentally. Achieving stability for the minimization and variation of potentials is shown in table 3 and in the design of the nano vehicle 3459 in figure 6. It is very likely that for the design of the nanovehicle cores only fixed and controlled the experimental conditions (local minimization under a given potential function). The N13IR nucleus showed instability within the envelopes, when the potential function is changed in the minimization, it changes its structure to that of the oJL13_N13IC nucleus (which recently went from putative to being the global minimum for 13 particles for the LJ potential , Barron, 2022a). The nuclei N20BalP (N20 Pentagonal Ball) and 32EstP (N32 Pentagonal Star) are not stable in the chosen shells. The results show novel geometric shapes that are obtained between different layers of shells and different types of core that open a range of possibilities for the experimental design of stable nanostructures.

Nucleus	LJ LJ→MO LJ→MR	MO MO→LJ MO→MR Stability	MR MR→LJ MR→MO
oLJ4	-3464.5573 ✓ ✓	-3161.5262 ✓ ✓ Stable	-3026.9701 ✓ ✓
N8CB	X	-3170.4340 X X Unstable	-3035.1504 X X
oLJ13	-3505.5432 ✓ ✓	-3198.8640 ✓ ✓ Stable	-3063.4143 ✓ ✓
N13IR	X	-3195.8978 X X Unstable	-3060.3357 X X
N20BalP	X	X Unstable	X
N32EstP	X	X Unstable	X
oLJ38	-3647.0086 ✓ ✓	-3319.5074 ✓ ✓ Stable	-3178.5605 ✓ ✓
oLJ39	X	X Unstable	X

Table 1. Rounded shell of 614-particle IC latice, layers 5 and 6. No interior space for large nuclei or to maintain the structure of some small nuclei.

Nucleus	LJ LJ→MO LJ→MR	MO MO→LJ MO→MR	MR MR→LJ MR→MO
		Estabilidad bajo variación del potencial	
oLJ4	-14897.4997	-13621.0961	-13073.2003
	✓	✓	✓
	✓	✓	✓
		Stable	
N8CB	-14906.8185	-13629.9967	-13081.3791
	X	X	X
	X	X	✓
		Unstable	
oLJ13	-14935.9207	-13658.4138	-13109.6402
	✓	✓	✓
	✓	✓	✓
		Stable	
N13IR	-14933.1494	-13655.4457	-13106.5610
	X oLJ13	X oLJ13	X oLJ13
	X oLJ13	X oLJ13	X oLJ13
		Unstable	
N20BalP	-23906.0392	-21424.2778	-20383.1031
	X		X
	X	X	X
		Unstable	
N32EstP	X	X	X
	X	X	X
		Unstable	
oLJ38	✓	✓	✓
	✓	✓	✓
		Stable	
oLJ39	✓	✓	✓
	✓	✓	✓
		Stable	

Table 2. 2654 particle IC latice shell, layers 11 and 12. Some cores do not hold.

Nucleus	LJ LJ→MO LJ→MR	MO MO→LJ MO→MR	MR MR→LJ MR→MO
		Stability low variation of the potential	
oLJ4	-23873.6788	-21395.3864	-20355.9404
	✓	✓	✓
	✓	✓	✓
		Stable	
N8CB	-23883.0357	-21404.2870	-20364.1192
	X	✓	X
	X	✓	✓
		Unstable	
oLJ13	-23912.1856	-21432.7041	-20392.3802
	✓	✓	✓
	✓	✓	✓
		Stable	
N13IR	-23909.4148	-21429.7360	-20389.3011
	X oLJ13	X oLJ13	X oLJ13
	X oLJ13	X oLJ13	X oLJ13
		Unstable	
N20BalP	-23906.0392	-21424.2778	-20383.1031
	X	X	X
	X	X	X
		Unstable	
N32EstP	-23971.9812	-21486.4488	-20444.3553
	X	X	X
	X	X	X
		Unstable	
oLJ38	-24042.3418	-21552.7954	-20507.3473
	✓	✓	✓
	✓	✓	✓
		Stable	
oLJ39	-24048.4744	-21559.1035	-20513.4224
	✓	✓	✓
	✓	✓	✓
		Stable	

Table 3. IC lattice envelope of 3656 particles, layers 10, 11 and 12. Stability by minimization and potential variation in almost all proposed nuclei.

THANKS

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REFERENCES

Barrón-Romero, C. (2022a). The oLJ13_N13IC cluster is the global minimum cluster of Lennard Jones potential for 13 particles, 2022 IEEE 3rd International Conference on Electronics, Control, Optimization and Computer Science (ICECOCS), Fez, Morocco, 2022, pp. 1-6.

Barrón-Romero, C. (2022b). Estudio de sensibilidad y crecimiento de Nanoestructuras bajo los potenciales de Morse y Lennard Jones, Revista Tendencias en Docencia e Investigación Química 2022, 508-515.

Barrón-Romero, C. (2005). Minimum search space and efficient methods for structural cluster optimization. arXiv, http://arxiv.org/abs/math-ph/0504030. *To honor the CIMAT's XXV Anniversary*.

Barrón-Romero, C., Gómez, S., y Romero, D. (1997). Lower Energy Icosahedral Atomic Cluster with Incomplete Core. Applied Mathematics Letters, 10(5):25-28.

Barrón-Romero, C., Gómez, S., Romero, D., y Saavedra, A. (1999). A Genetic Algorithm for Lennard-Jones Atomic clusters. Applied Mathematics Letters, 12:85-90.

Beale, E. M. L. (1972). A derivation of conjugate-gradients. In Lootsma, F., editor, Numerical methods for nonlinear optimization. Academic Press.

Byrd, R. H., Lu, P., Nocedal, J., y Zhu, C. (1995). A limited memory algorithm for bound constrained optimization. SIAM Journal on Scientific Computing, 16(5):1190-1208.

Cai, W., Feng, Y., Shao, X., y Pan, Z. (2002a). Optimization of Lennard-Jones atomic clusters. THEOCHEM, 579:229-34.

Cai, W., Jiang, H., y Shao, X. (2002b). Global optimization of Lennard-Jones clusters by a parallel fast annealing evolutionary algorithm. Journal of Chemical Information and Computer Sciences, 42(5):1099-1103.

Deaven, D. M. y Ho, K. M. (1995). Molecular Geometry Optimization with a Genetic Algorithm. Physical Review Letters, 75(2):288-291.

Dittner, M. y Hartke, B. (2016). Conquering the hard cases of Lennard-Jones clusters with simple recipes. Computational and Theoretical Chemistry.

Doye, J. P. K. (1998). Thermodynamics and the global optimization of Lennard-Jones clusters. Journal of Chemical Physics, 109(19):8143-8153.

Doye, J. P. K. (2006). Physical Perspectives on the Global Optimization of Atomic Clusters, pages 103{139. Springer US, Boston, MA.

Doye, J. P. K. y Wales, D. J. (1995). Magic numbers and growth sequences of small face-centered-cubic and decahedral clusters. Chemical Physics Letters, 247:339-347.

Doye, J. P. K, Miller, M.A. y Wales, D. J. (1999). The double-funnel energy landscape of the 38-atom Lennard-Jones cluster. The Journal of Chemical Physics, 110(14): 6896--6906.

Echt, O. , Sattler, K. y Recknagel, E. Magic Numbers for Sphere Packings: Experimental Verification in Free Xenon Clusters. Phys. Rev. Letters, 47:1121, October 1981.

Gómez, S. y Barrón-Romero, C. (1991). The Exponential Tunneling Method. Technical Report Research Report 3(1), IIMAS-UNAM.

Haberland, H., Hippler, T., Donges, J., Kostko, O., Schmidt, M., y Issendorff, B. V. (2005). Melting of Sodium Clusters: Where Do the Magic Numbers Come from? Physical Review Letters, 94:035701-4.

Hartke, B. (1999). Global Cluster geometry Optimization by a Phenotype Algorithm with Niches: Location of Elusive Minima, and Low-Order Scaling with Cluster Size. Journal of Computational Chemistry, 20(16):1752-1759.

Hartke, B. (2002). Structural transitions in clusters. Angewandte Chemie International Edition, 41(9):1468-1487.

Hoare, M. R. y McInnes, J. A. (1983). Morphology and statistical statics of simple microclusters. Advances in Physics, 32(5):791-821.

Huang, H. X., Pardalos, P. M., y Shen, Z. J. (2002). Equivalent formulations and necessary optimality conditions for the Lennard-Jones problem. Journal of Global Optimization, 22(1-4):97-118.

Jiang, H., Cai, W., y Shao, X. (2003). New lowest energy sequence of marks' decahedral Lennard-Jones clusters containing up to 10,000 atoms. Journal of Physical Chemistry A, 107(21):4238-4243.

Leary, R. H. (1997). Global Optima of Lennard-Jones Clusters. Journal of Global Optimization, 11(1):35-53.

Leary, R. H. (1999). Tetrahedral global minimum for the 98-atom Lennard-Jones cluster. Physical Review E, 60(6):6320-6322.

Maier, R., Rosen, J., y Xue, G. (1992). A discrete-continuous algorithm for molecular energy minimization. In Proceedings. Supercomputing '92. (Cat. No.92CH3216-9), 16-20 Nov. 1992, Proceedings. Supercomputing '92. (Cat. No.92CH3216-9), 778-786.

Maranas, C. D. y Floudas, C. A. (1994). Global minimum Potential Energy Conformations of Small Molecules. Journal of Global Optimization, 4(2):135-170.

Morales, J. L. y Nocedal, J. (2011). Remark on .algorithm 778: L-BFGS-B: Fortran subroutines for large-scale bound constrained optimization". ACM Transactions on Mathematical Software, (7).

Morse, P. M. (1929). Diatomic Molecules According to the Wave Mechanics. II. Vibrational Levels. Phys. Rev., 34:57-64.

Northby, J. A. (1987). Structure and binding of Lennard-Jones clusters: $13 \leq n \leq 147$. Journal of Chemical Physics, 87(10):6166-6177.

Noya, E. G., Wong, Ch. K., Llombart, P y Doye, J. P. K. How to design an icosahedral quasicrystal through directional bonding, Nature, 596, Augost, 2021.

Pardalos, P. M., Shalloway, D., y Xue, G. L. (1994). Optimization methods for computing global minima of nonconvex potential-energy functions. Journal of Global Optimization, 4(2):117-133.

Shao, X., Jiang, H., y Cai, W. (2004a). Parallel random tunneling algorithm for structural optimization of Lennard-Jones clusters up to n = 330. Journal of Chemical Information and Computer Sciences, 44(1):193-199.

Shao, X., Xiang, Y., y Cai, W. (2004b). Formation of the central vacancy in icosahedral Lennard-Jones clusters. Chemical Physics, 305(1-3):69-75.

Shao, X., Xiang, Y., y Cai, W. (2005). Structural Transition from Icosahedra to Decahedra of Large Lennard-Jones Clusters. Personal Communication.

Solov'yov, I. A., Solov'yov, A. V., y Greiner, W. (2003). Fusion process of Lennard-Jones clusters: global minima and magic numbers formation. ArXiv Physics e-prints, pages 1-47.

Wales, D. J. y Doye, J. P. K. (1997). Global Optimization by Basin-Hopping and the Lowest Energy Structures of Lennard-Jones Clusters Containing up to 110 Atoms. J. Phys. Chem. A., 101(28):5111-5116.

Wales, D. J., Doye, J. P. K., Dullweber, A., Hodges, M. P., Naumkin, F. Y., Calvo, F., Hernández-Rojas, J., y Middleton, T. F. The Cambridge Cluster Database, Lennard-Jones clusters, https://www-wales.ch.cam.ac.uk/CCD.html.

Wille, L. T. (1999). Lennard-Jones Clusters and the Multiple-Minima Problem. Annual Reviews of Computational Physics, VII:25-60.

Wolf, M. y Landman, U. (1998). Genetic Algorithms for Structural Cluster Optimization. Journal of Physical Chemistry A, 102(30):6129-6137.

Xiang, Y., Cheng, L., Cai, W., y Shao, X. (2004a). Structural distribution of Lennard-Jones clusters containing 562 to 1000 atoms. Journal of Physical Chemistry A, 108(44):9516-9520.

Xiang, Y., Jiang, H., Cai, W., y Shao, X. (2004b). An Efficient Method Based on Lattice Construction and the Genetic Algorithm for Optimization of Large Lennard-Jones Clusters. Journal of Physical Chemistry A, 108(16):3586-92.