



MOLECULAR DYNAMICS SIMULATION OF COHESIVE ENERGIES AND ITS CORRESPONDING LATTICE PARAMETER OF SOME NANOCRYSTALS

*¹Yusuf Tajuddeen Batsari, ¹Isaiah Eze Igwe and ²Ahmed Hamisu

¹Department of Physics, Faculty of Physical Science, Federal University Dutisn-Ma, Km 60, Katsina-Kankara Express Way, P.M.B 5001 Dutsin-Ma, Katsina State. Nigeria

²Plot 247, Total House 1, Opposite NNPC Towers, Herbert Macaulay Way, Central Bussiness District, Abuja

*Corresponding authors' email: tyusuf@fudutsinma.edu.ng

ABSTRACT

Bulk solids have a microstructure that differs significantly from nanoscale materials. In modern era, new devices are always produced at nano-scale level and existing ones are quantized to fit the global demand. To achieve this, there is a need to understand the behaviour of materials at atomic level. As a result, examining the properties of nanoparticles can help in understanding the nature of small-scale material behavior. The cohesive energy and lattice constant are essential physical quantities that can be used to predict other material properties. In this research, the equilibrium cohesive energies and its corresponding lattice constants of three nanosized crystals (Al, Cu and Ni), were investigated using molecular dynamics simulation method with a semi-empirical embedded atom model (EAM) potential function. The simulated results reveal that the three nanocrystals' lattice constant match the experimental data. Besides, Al, Cu and Ni have cohesive energies of -3.40 eV, -3.55 eV, -4.44 eV respectively. Cu's cohesive energy differs from experimental data unlike Al and Ni. The findings in the current research are in good agreement with those obtained utilizing the First principle calculation method.

Keywords: cohesive energy, lattice parameter, nanocrystals, molecular dynamics

INTRODUCTION

It is common knowledge that all material qualities are dependent on the structure of the material, therefore it is important to understand the properties before deciding on its technological applications. Under constant temperature and pressure, the majority of bulk material properties, such as optical, electrical, and thermal, remain constant. However, in the case of a nanosized crystal, the size of the material will have a significant effect on these properties (Ouyang et al., 2009; Wang & Yang, 2005; Xia 2003). Finding these properties through experimental techniques is nearly impossible and expensive at the nanoscale, and it is sometimes impossible to predict. The cohesive energy of a solid, which equals the energy required to break all bonds and separate the solid into isolated atoms, is an essential physical quantity that accounts for bond strength. Cohesive energy is also a fundamental quantity in material thermodynamics, from which we can derive almost all thermodynamic properties. As a significant coupling physical quantity, cohesive energy can be utilized to predict other physical qualities such as melting point (Goswami & Nanda, 2010; Safaei et al., 2008), diffusion activation and vacancy formation energies (Safaei, 2010a), evaporation temperature (Safaei, 2010b) and Curie temperature (Yang & Li, 2007). The thermodynamic performance of a substance is determined by its atomic cohesive energy, which changes depending on the environment of atomic coordination. The nanoscopic thermodynamics are determined by the cohesive energy disparity between the core and the shell. Experimentally, the heat of sublimation can be used to determine a solid's cohesive energy. Kim et al., (2002), were able to obtained experimental data of cohesive energies. In the experiments, the cohesive energy of nanostructures was found to be highly dependent on their size. Unlike the bulk solid, the cohesive energy of nanoparticles is difficult to quantify experimentally. As a result, numerous theoretical models concentrating on size dependence to determine the cohesive energy of nanostructures have been developed, such

as the broken bond model (Yang & Li, 2007; Yin, Palmer, & Guo, 2006), the bond-OLS model (Wang, Zhu, & Jiang, 2008), the latent heat model (Verma, Sarkar, & Jindal, 2010), the thermodynamics model (Safaei et al., 2008) and the liquid drop model (Safaei et al., 2008). However, because several parameters used in calculations are not easy to estimate, most theoretical calculations of cohesive energy are inconvenient. Computational modeling of cohesive energy at the nanoscale has received a lot of attention as a result of the foregoing. In order to use nanoparticles in optoelectronic and microelectronic systems, they must sometimes be embedded in a heterogeneous matrix. Although it has been reported that the cohesive energy of a free nanoparticle lowers as its size decreases (Weihong, Wang, 2002), it has not been investigated in experiments whether the cohesive energy of nanoparticles embed in a heterogeneous matrix increases or decreases relative to its bulk material. Meanwhile, just a few theoretical models focus on the effects of the additional material on the nanoparticles embedded in it (Xie et al., 2005; Xie, Wang, & Qi, 2004). The physical mechanism behind the cohesive energy of embedded nanoparticles has not been well understood so far. In this paper, an embedded atom model potential function was used to perform molecular dynamic simulation calculation of equilibrium cohesive energy and its corresponding lattice parameters of some nanocrystal (Al, Cu and Ni). Studying the characteristics of embedded nanoparticles might thus aid in the selection of appropriate materials and the development of integrated devices.

THEORETICAL MODEL

The energy required to divide atoms into discrete atomic species is defined as the cohesive energy of a solid. The cohesive energy is calculated using the overall energy of the solid as well as the isolated atoms. The energy difference between isolated atoms and the solid is equal to the cohesive energy of the solid (Li, 2014):

$$E_{coh} = E_{isolated} - E_{solid} \quad (1)$$

The cohesive energy of bulk material A can be expressed as

$$E_{Bulkcoh} = E_{isolated} - E_{Bulk}^A \quad (2)$$

Similarly, a nanoparticle of material A's cohesive energy is described as

$$E_{NPcoh}^A = E_{isolated} - E_{NP}^A \quad (3)$$

If the number of atoms in equation (2) equals the number in equation (3), then the cohesive energy of a free nanoparticle can be expressed as

$$E_{NPcoh}^A = E_{Bulkcoh}^A - (E_{NP}^A - E_{Bulk}^A) \quad (4)$$

E_{Bulk}^A , the energy of a bulk solid, can be compared to the energy of an ideal nanoparticle squeezed from its host bulk material. As a result, $(E_{NP}^A - E_{Bulk}^A)$ denotes the energy difference between a free nanoparticle and its bulk version, which is formed by disrupting the bonding between the nanoparticle's surface atoms. Atoms on the surface have more energy than those in the bulk substance in solid-state physics. The surplus energy at a material's surface in relation to the main substance is known as surface energy. The surface energy of a nanoparticle should be equal to the excess energy of the nanoparticle as compared to its bulk state.

Potential Function

In this study, Molecular Dynamics (MD) simulations were carried out using the embedded atom method (EAM) potential function. The EAM formalism describes the total potential energy of a system of atoms in the following way (Daw & Baskes, 1983)

$$E_{tot} = \sum_i F_i(\phi) + \frac{1}{2} \sum_i \sum_{j \neq i} \varphi_{ij}(r_{ij}) \quad (5)$$

F_i is a function of the effective electron density at atom i as seen in the equation above. The energy required to embed atom i into an effective electron density as a result of the surrounding atoms is defined by the many-body term i . The term $\varphi_{ij}(r_{ij})$ is a simple pair potential typically attributed to electrostatic interactions. It can be shown that the form of EAM can be deduced using density functional theory (DFT) arguments (Murray, et al., 1992). Furthermore, in order to obtain particular parameters for the embedding energy, effective electron density, and pair potential, these potentials often require experimental data or ab-initio calculations where m_i is mass of particle, F_i is the interatomic force acting on that particle, r_i is its position vector, and is the overall system's interatomic potential energy.

After the potential function is determined, it has been seen that, atoms are always intend to go towards equilibrium position, and the magnitude of molecules force F_{ij} that is pushes them towards its position is given by derivative of the potential energy (Scott, 2018).

$$F_{ij} = - \frac{\partial U(r_{ij})}{\partial r_{ij}} \quad (6)$$

Computational Details

The molecular dynamics technique depicts the atomic motions of material constituents by assuming that classical mechanics concepts still hold true at the atomic scale (Frenkel & Smit, 2002). MD simulations were run in the conventional ensemble with the total number of particles N , volume V , and temperature T set using the velocity Verlet technique in this work. The atomic position and velocity were calculated using the Verlet numerical integration algorithm. The simulation's time steps were set to 1 second. The x, y, and z coordinate axes represent the [100], [010], and [001] lattice directions, respectively. To initialize the simulation, a relaxation state is defined and the atoms are left freely with a random velocity using NVT. To ensure a good statistical averaging result following the equilibrium process, simulations were run for 1106 time steps (500 ps) to ensure credible results for particle properties. The bulk system, with 4000 atoms in the cube, was also simulated and the cohesive energy and lattice constant calculated under constant temperature and constant volume (NVT) conditions with periodic boundary conditions for comparison.

RESULTS AND DISCUSSION

The calculated cohesive energy of the three nanocrystals (Al, Cu and Ni) are as shown in Fig. 1 (a), (b) and (c). The results show that the values of cohesive energy decrease with increase in lattice constant until it reached an equilibrium (a minimum), and then increase with increase in lattice constant for all the nano-metals. The equilibrium values are presented in table 1. A comparison of the simulated results with experimental results showed a discrepancy of 0.99% for the lattice constant of aluminum while there exist discrepancies of -% and -% for the lattice constants of Cu and Ni respectively. Comparing the equilibrium cohesive energies of the simulated results, discrepancies of -%, 1.69% and -% were observed for Al, Cu and Ni respectively. These observations shown that, simulated results are in concurrent with the experiment, since the observed values of discrepancies for both lattice constant and cohesive energy are less than 2% (Fitraina et al., 2019; Qi, 2016). The cohesive energy in the embedded model utilized in this study is controlled not only by the nanoparticle's surface energy, but also by the adhesion energy between the embedded particle and its adjacent atoms.

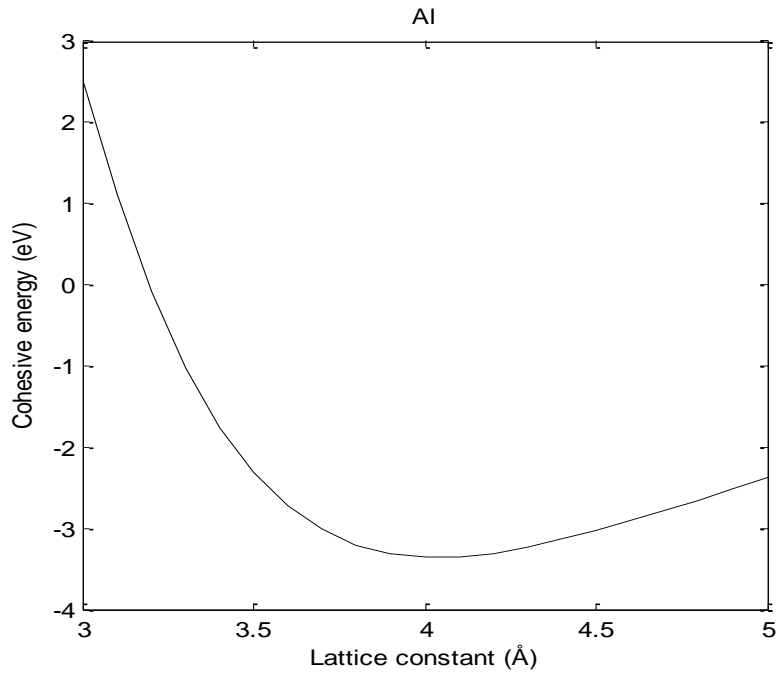


Figure 1 (a): Graph of cohesive energy against lattice constant for Aluminium

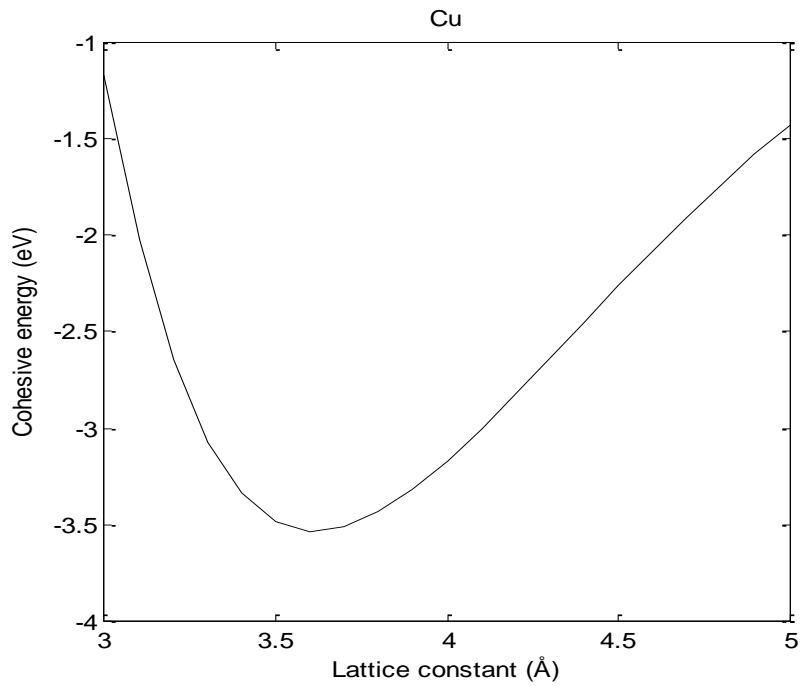


Figure 1 (b): Graph of cohesive energy against lattice constant for Copper

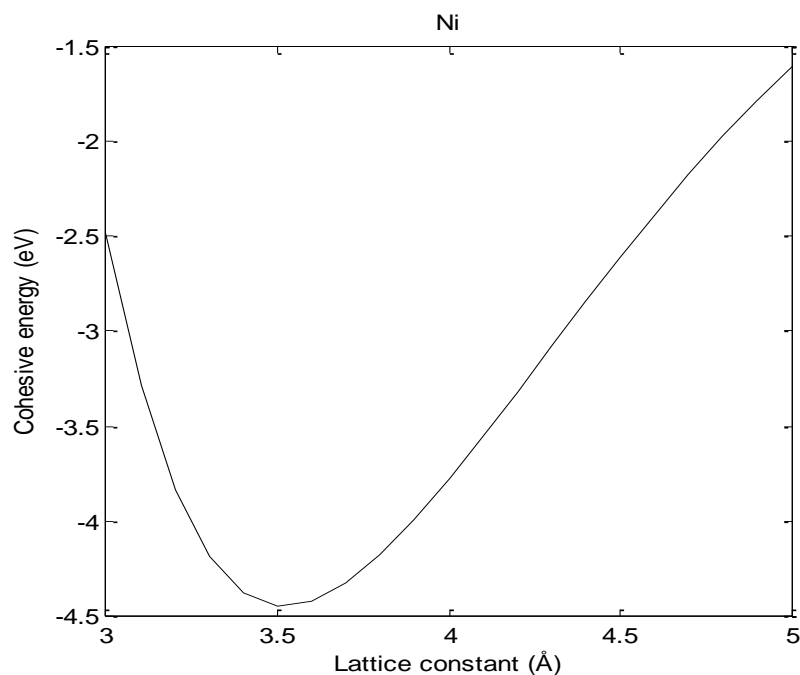


Figure 1 (C): Graph of cohesive energy against lattice constant for Nickel

Element	Equilibrium lattice constant (Å)		Equilibrium cohesive energy (eV)	
	Calculated	experiment	calculated	Experiment
Aluminum	4.00	4.04	-3.40	-3.40
Copper	3.62	3.62	-3.55	-3.49
Nickel	3.50	3.52	-4.44	-4.44

CONCLUSION

Molecular dynamics has been used successfully to calculate the cohesive energy of nano-crystalline aluminum, copper and nickel. The embedded atom model (EAM) potential function was used to optimize cohesive energy as a function of lattice constant. It is found that the cohesive energy decreases with increase in lattice constant until it reached an equilibrium (a minimum), and then increase as lattice constant increase. The calculated results show a discrepancy of 0.1% for aluminum with no difference for Cu and Ni. The present modeling results are reasonably consistent with the corresponding experimental values and other existing theoretical models.

REFERENCES

- Daw, M. S., & Baskes, M. I. (1983). Semiempirical, Quantum Mechanical Calculation of Hydrogen Embrittlement in Metals. *Phys Rev Lett*, 50(17), 1285-1288. doi:10.1103/PhysRevLett.50.1285
- Frenkel, D., & Smit, B. (2002). Chapter 6 - Molecular Dynamics in Various Ensembles. In D. Frenkel & B. Smit (Eds.), *Understanding Molecular Simulation (Second Edition)* (pp. 139-163). San Diego: Academic Press.
- Fitriana Faizatu Zahroh, Iwan Sugihartono and Ernuk D. Safitri (2019) Young's Modulus Calculation of Some Metals Using Molecular Dynamics Method Based on the Morse Potential
- Goswami, G. K., & Nanda, K. K. (2010). Size-Dependent Melting of Finite-Length Nanowires. *The Journal of Physical Chemistry C*, 114(34), 14327-14331. doi:10.1021/jp100820c

Kim, H. K., Huh, S. H., Park, J. W., Jeong, J. W., & Lee, G. H. (2002). The cluster size dependence of thermal stabilities of both molybdenum and tungsten nanoclusters. *Chemical Physics Letters*, 354(1), 165-172. [https://doi.org/10.1016/S0009-2614\(02\)00146-X](https://doi.org/10.1016/S0009-2614(02)00146-X)

Li, X. (2014). Modeling the size- and shape-dependent cohesive energy of nanomaterials and its applications in heterogeneous systems. *Nanotechnology*, 25(18), 185702. doi:10.1088/0957-4484/25/18/185702

Murray S. Daw, A. Stephen, M. Foiles A. and Michael I. Baskes (1992) the embedded-atom method: a review of theory and applications

Ouyang, G., Wang, C. X., & Yang, G. W. (2009). Surface Energy of Nanostructural Materials with Negative Curvature and Related Size Effects. *Chemical Reviews*, 109(9), 4221-4247. doi:10.1021/cr900055f

Qi, W. (2016). Nanoscopic Thermodynamics. *Acc Chem Res*, 49(9), 1587-1595. doi:10.1021/acs.accounts.6b00205

Safaei, A. (2010a). The effect of the averaged structural and energetic features on the cohesive energy of nanocrystals. *Journal of Nanoparticle Research*, 12(3), 759-776.

Safaei, A. (2010b). Shape, structural, and energetic effects on the cohesive energy and melting point of nanocrystals. *The Journal of Physical Chemistry C*, 114(32), 13482-13496.

Safaei, A., Shandiz, M. A., Sanjabi, S., & Barber, Z. H. (2008). Modeling the Melting Temperature of Nanoparticles

- by an Analytical Approach. *The Journal of Physical Chemistry C*, 112(1), 99-105. doi:10.1021/jp0744681
- Scott A. Hollingsworth and Ron O. Dror (2018). Molecular Dynamics Simulation for All <https://doi.org/10.1016/j.neuron.2018.08.011>
- Verma, A. S., Sarkar, B. K., & Jindal, V. K. (2010). Cohesive energy of zincblende (AIIIBV and AIBVI) structured solids. *Pramana*, 74(5), 851-855. doi:10.1007/s12043-010-0105-9
- Wang, C. X., & Yang, G. W. (2005). Thermodynamics of metastable phase nucleation at the nanoscale. *Materials Science and Engineering: R: Reports*, 49(6), 157-202. doi:<https://doi.org/10.1016/j.mser.2005.06.002>
- Wang, T., Zhu, Y., & Jiang, Q. (2008). Size effect on evaporation temperature of nanocrystals. *Materials Chemistry and Physics*, 111(2-3), 293-295.
- Weihong Qi - Wang M. P. (2002). Size effect on the cohesive energy of nanoparticle. *Journal of Material Science Letter* 21(22):1743-1745. <http://doi.org/10.1023/A:1020904317133>
- Xia, Y., Yang, P., Sun, Y., Wu, Y., Mayers, B., Gates, B., . . . Yan, H. (2003). One-Dimensional Nanostructures: Synthesis, Characterization, and Applications. *Advanced Materials*, 15(5), 353-389. doi:<https://doi.org/10.1002/adma.200390087>
- Xie, D., Wang, M. P., & Cao, L. F. (2005). Comment on "Size effect on the cohesive energy of nanoparticle"—Extending the model available for embedded nanoparticle. *Journal of Materials Science*, 40(13), 3567-3568. doi:10.1007/s10853-005-2886-7
- Xie, D., Wang, M. P., & Qi, W. H. (2004). A simplified model to calculate the surface-to-volume atomic ratio dependent cohesive energy of nanocrystals. *Journal of Physics: Condensed Matter*, 16(36), L401-L405. doi:10.1088/0953-8984/16/36/101
- Yang, C. C., & Li, S. (2007). Investigation of cohesive energy effects on size-dependent physical and chemical properties of nanocrystals. *Physical Review B*, 75(16), 165413.
- Yin, F., Palmer, R., & Guo, Q. (2006). Nanoscale surface recrystallization driven by localized electric field. *Physical Review B*, 73(7), 073405. doi:10.1103/PhysRevB.73.073405



©2022 This is an Open Access article distributed under the terms of the Creative Commons Attribution 4.0 International license viewed via <https://creativecommons.org/licenses/by/4.0/> which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is cited appropriately.