Clustering Evolution from Ultrafast Laser Irradiation of Gold Nanoparticle: A Molecular Dynamics Study

Riser Fahdiran$^{1,3}$, Iwan Sugihartono$^1$, Erfan Handoko$^1$, Setia Budi$^2$ and Herbert M. Urbassek$^{3,#}$

$^1$Department of Physics, State University of Jakarta, Jalan Rawamangun Muka, Jakarta Timur, 13220, Indonesia
$^2$Department of Chemistry, State University of Jakarta, Jalan Rawamangun Muka, Jakarta Timur, 13220, Indonesia
$^3$Physics Department and Research Center OPTIMAS, University of Kaiserslautern, Erwin-Schrödinger-Straße 67663 Kaiserslautern, Germany

E-mail: *) riser-fahdiran@unj.ac.id ; #) urbassek@rhrk.uni-kl.de

Abstract. We study the evolution of clusters from ultrafast laser induced ablation of Gold nanoparticle by means of Molecular Dynamics (MD) simulation. The energy given to the system are varied from 2 eV/atom, with increment 1 eV/atom, up to 8 eV/atom which already above ablation threshold. The nanoparticle is considered to absorb energy from laser irradiation instantaneously and homogenously throughout the system and MD follow trajectories up to 20 ps. The case for the lowest energy breaks up the system and forming hollow structure. While starting from 3 eV/atom, the system tears up and evaporate with final temperature above 2500 K. Clusters formation for all energies indicated that number of monomers increases following the increasing of energy while the sizes of overall cluster is decreases.

1. Introduction

Intense laser pulses with ultrashort and ultrafast irradiation gives insight in such a way it interact with materials where the mechanism which is heterogeneous and non-equilibrium [1–5]. The mechanism includes the laser energy absorb by the system followed by temperature increase and compressive pressure in the beginning. Following this compressive state, the system started to expand while rarefaction produce tensile pressure, which depends on energy, where it creates voids and for higher energies it will produce spallation or even more an evaporation over the entire system.

In the context of materials, the study on metal thin film confirm the mechanism by means of molecular dynamics simulation [1,6]. As an approach to nanoparticle (NP), Fahdiran and Urbassek [7] performed a study where NP is considered to have atomic interactions using Lennard-Jones (LJ) potential. It is found that for lower energy, the system will create hollow structure with smaller clusters filled in the system. While for higher energy, it will evaporate where small clusters dominate the system of NP.
Within this paper, we performed simulation using Molecular Dynamics (MD) scheme to illustrate the interaction of ultrafast laser irradiation of Gold NP. Simplification is used in modeling the laser absorption energy where it is homogeneous and instantaneous at the beginning of simulation. Such a condition is possible for the case of ultrashort intense laser pulses where the energy transfer is possible in sub-ps scale and experimentally performed by ultrafast X-ray pulses such as FLASH [2].

2. Simulation Method
Large-scale atomic/molecular massively parallel simulator (LAMMPS) is used to continuously follow the trajectories of the atoms in this MD simulation [8]. Visualization of the atomic representation is using OVITO [9]. The Gold NP system are composed of atoms in FCC structure based on sphere geometry with radius 9.8 nm which consists of 28870 atoms where it has been relaxed at 0 K temperature and 0 GPa pressure for 20 ps as initial state for all simulation. The interatomic potential describing the interaction between atoms inside the system is obtained from Zhakovskii, et.al. with cut-off radius 6.875 Å with cohesive energy $E_{coh} = 3.81$ eV/atom [10].

The simulation started by providing absorption energies ($E_0$) to the system varied from 2 eV/atom, with increment 1 eV/atom, up to 8 eV/atom. Compared to cohesive energy, this will be called energization with range of $\varepsilon = E_0/E_{coh} = 0.52 – 2.1$. These energies are given homogenously and instantaneously throughout all atoms. We followed the trajectories of the atoms up to 20 ps. The thermodynamics properties, i.e. temperature and pressure, are calculated by considering virial theorem [11]. The detection of clusters is based on algorithm by Stoddard [12].

3. Results and Discussion
Figure 1 shows the atomic local temperature of initial state for all simulation and final state for $E_0 = 2$ eV/atom up to $E_0 = 8$ eV/atom. The comparison of these final states indicates significance information on how the system fragmented into clusters. For the lowest energy, the system formed hollow structure which indicate spallation mechanism, while start from 3 eV/atom, the system tears up as smaller cluster [7,13].

![Figure 1. Atomic local temperature of Gold NP (color scale is given). Sizes are not to scale. (a) Initial state at T = 0 K. End of simulation for (b) $E_0 = 2$ eV/atom, (c) $E_0 = 3$ eV/atom, (d) $E_0 = 4$ eV/atom, (e) $E_0 = 5$ eV/atom, (f) $E_0 = 6$ eV/atom, (g) $E_0 = 7$ eV/atom, (h) $E_0 = 8$ eV/atom.](image-url)
The final state from 3 eV/atom up to 8 eV/atom indicates evaporation as the mechanism on how the system fragmented. The higher energies boiled up the system where it starts to evaporate at t ~ 4.1 ps for 3 eV/atom and become earlier for 8 eV/atom at t ~ 1.2 ps. It can be seen from Figure 1, that final state for higher energies indicated that the system is composed by majority of small clusters.

The evolution of temperature and pressure for the two selected energies (2 eV/atom and 8 eV/atom) is shown in Figure 2. For the case of 2 eV/atom, as the absorption energy heated up the system with temperature of 15263 K, it expands the system from inside and void start to form at t ~ 3 ps. When the expansion continues to extend the system radially, voids develop, and spallation occurred. Following the trajectories until the end of simulation, the fragmentation turns the system into big clusters with different sizes constructing hollow structure filled with small clusters.

Temperature profile for 8 eV/atom of the system becomes smaller than 2 eV/atom at the end of simulation. This is caused by the formation of small clusters that occupied the entire system at the end of simulation. As it can be seen from the way temperature is calculated, it is explained that smaller cluster will have smaller temperature [11].

**Figure 2.** Temperature and Pressure evolution of $E_0 = 2$ eV/atom and $E_0 = 8$ eV/atom. Inset part are shown up to t = 0.1 ps.

The pressure evolution indicates strong compressive pressure since the beginning of simulation. For 2 eV/atom and 8 eV/atom, the maximum compression reaches 0.74 GPa at t ~ 0.042 ps and 1.69 GPa at t ~ 0.030 ps, respectively. When compressive pressure at its maximum, the temperature become minimum due to suppression of the system into the center as it shown in inset part of Figure 2. The atoms are compressed so the movement becomes slower that produce smaller temperature due to decreasing of kinetic energy, while the potential energy becomes stronger it enhanced the pressure to highest value.

After this state, rarefaction start to expand Gold NP from the center of its system [1,6]. Due to this rarefaction, tensile pressure starts to grow at t ~ 0.75 ps for 2 eV/atom and t ~ 1 ps for 8 eV/atom. The tensile pressure for lowest energy grows at strongest value compare to the others, this cause the system at lowest energy become spallated. For higher energies, since the systems are evaporated, tensile pressure is not as strong as lowest one. After t ~ 3 ps, all systems are relaxed with pressure oscillating near 0 GPa while it expands. One of significance finding in the study of this Gold NP simulation, the tensile pressure exists for all case, while in metal thin film for higher energies the system evaporates with compressive pressure all the time [7]. For metal thin film, the expansion of the system is considered only in the direction of the thickness while lateral is set to be periodic. While for this study, the expansion occurred radially, so the tensile pressure was built up in all direction.
The final temperature of the system and number of monomers (i.e. cluster with single atom, Y(1)) normalized to total number of atoms, both as a function of energy, is shown in Figure 3. For energy of 8 eV/atom, the number of monomers occupied 19.2 % of the system, in contrast to 2 eV/atom which occupied only 0.6 %. This can be correlated to the final temperature of each energies. For 2 eV/atom, since monomers is not dominant, the overall temperature is $T_{\text{final}} = 3961.8$ K. While for 8 eV/atom, monomers are dominant together with small clusters with $T_{\text{final}} = 2552.4$ K. Consequently, by increasing energies from 2 eV/atom up to 8 eV/atom, number of monomers is increasing while final temperature as a function of energies is decreasing.

Figure 3. Final temperature (left) and number of monomers (right) at the end of simulation. Both figures are as a function of energy.

We calculated the cluster properties using the definition given by Upadhyay dan Urbassek [13]. The $Y_{\text{cl}}$, $Y_{\text{bound}}$, $f_{cl}$ and $<m>$ are cluster yield, number of atoms bound in cluster, cluster fraction and average cluster size, respectively. These properties at the end of simulation are shown in Figure 4.

Since the number of monomers ($Y(1)/N$) increases correspond to energy, the bound atoms normalized to the total number of atoms ($Y_{\text{bound}}/N$) is decreases. It confirmed the consistency of number of atoms that bound in a clusters is inversely related with number of monomers, since $Y_{\text{bound}}/N = 1 - Y(1)/N$. The summation between $Y_{\text{bound}}$ and number of monomers will give total number of atoms which can be seen in this study. Furthermore, the normalized cluster yield ($Y_{\text{cl}}/N$) which gives number of clusters without monomers is increasing and indicated that the energies produce more clusters at higher value. Cluster fraction shows that more or less 50 % of the fragment for all energies is actually a cluster.

Increasing the absorption energies also gives inverse relation with average cluster sizes, $<m>$. The size of clusters depends on number of atoms bound in cut-off radius from each detected atom. The average cluster size does not include monomers, hence it gives the representation of clusters over the entire system. It is shown that at 2 eV/atom, $<m> = 182$ and significantly decrease to $<m> = 29$ at energy 3 eV/atom. Comparing to the analysis on temperature, it is coherent with the mechanism itself where evaporation started from 3 eV/atom up to 8 eV/atom where $<m> = 4$.

Cumulative cluster distribution, $C(m)$, is given in Figure 5. For 2 eV/atom, big clusters (m ≥ 1000) contribute 63.9 % to the overall system. While for 8 eV/atom, small clusters (m ≤ 10) occupied 87.8 % of the system. This percentage contribute to the final temperature of each system, where it decreases due to number of small clusters increases which possesses low temperature at each clusters [7,13].
Figure 4. (a) Cluster yield, $Y_{cl}$; (b) Number of atoms bound in cluster, $Y_{\text{bound}}$; (c) Cluster fraction, $f_{cl}$; (d) Average cluster size, $<m>$. All figures are for $t = 20$ ps.

Figure 5. Cumulative cluster distribution, at $t = 20$ ps, for $E_0 = 2$ eV/atom and $E_0 = 8$ eV/atom.
4. Conclusion
We investigate the clusters evolution from Gold NP as a function of increasing absorption energy which can be performed in ultrafast laser irradiation. For energy 2 eV/atom, we found that the system expands with voids formed inside and constructing hollow structure at the end of simulation. In contrast to this, from 3 eV/atom up to 8 eV atom, the systems are evaporated, and small clusters formed dominantly. With increasing energy, it is found that number of small clusters increases following the increasing of energy while average cluster sizes is decreases.

References
[1] A. K. Upadhyay, N. A. Inogamov, B. Rethfeld, and H. M. Urbassek, Phys. Rev. B 78, 1 (2008).
[2] M. Nicoul, F. Quirin, a. M. Lindenberg, a. Barty, D. M. Fritz, D. Zhu, H. Lemke, M. Chollet, D. a. Reis, J. Chen, S. Ghimire, M. Trigo, M. Fuchs, K. J. Gaffney, J. Larsson, T. Becker, S. Meyer, T. Payer, F. Meyer zu Heringdorf, M. Horn von Hoegen, M. Jerman, and K. Sokolowski-Tinten, EPJ Web Conf. 41, 04013 (2013).
[3] D. Zhang, B. Gökke, and S. Barcikowski, Chem. Rev. 117, 3990 (2017).
[4] K. Sokolowski-Tinten, J. Bialkowski, A. Cavalleri, D. Von der Linde, A. Oparin, J. Meyer-Ter-Vehn, and S. I. Anisimov, Phys. Rev. Lett. 81, 224 (1998).
[5] D. S. Ivanov and L. V. Zhigilei, Phys. Rev. Lett. 98, 1 (2007).
[6] D. Ivanov and L. Zhigilei, Phys. Rev. B 68, 1 (2003).
[7] R. Fahdiran and H. M. Urbassek, Eur. Phys. J. D 69, 35 (2015).
[8] S. Plimpton, J. Comput. Phys. 117, 1 (1995).
[9] A. Stukowski, Model. Simul. Mater. Sci. Eng. 18, 015012 (2010).
[10] V. V. Zhakhovskii, N. A. Inogamov, Y. V. Petrov, S. I. Ashitkov, and K. Nishihara, Appl. Surf. Sci. 255, 9592 (2009).
[11] T. J. Colla and H. M. Urbassek, Comput. Mater. Sci. 6, 7 (1996).
[12] S. D. Stoddard, J. Comput. Phys. 27, 291 (1978).
[13] A. K. Upadhyay and H. M. Urbassek, Phys. Rev. B 73, 1 (2006).

Acknowledgments
We acknowledged financial support from Hibah Penelitian Unggulan Universitas BLU Universitas Negeri Jakarta under contract Nr: 19/KOMP-UNJ/LPPM-UNJ/2019.