Size dependencies on melting of Gold nanoparticle: A Molecular Dynamics study

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Abstract. We study the size dependencies on melting of Gold nanoparticle. The nanoparticles are built with different sizes and heated up with same temperature gradient from room temperature up to 1400 K. The trajectories of the atoms are investigated based on Molecular Dynamics (MD) simulation. Pressure evolution as a function of time shows the oscillation pattern as in the case of thermal induced melting. Analysis based on structure factor combined with Common Neighbour Analysis (CNA) indicated the properties of melting depends on nanoparticle sizes.

1. Introduction
Melting of Gold nanoparticle could be affected by the size of the system [1,2]. It can be melt below the melting temperature of bulk Gold, \( T_m = 1338 \) K [3]. The size of the system allowed the pressure to oscillate inside the system with different responses. This pressure evolution could give benefit on understanding the process of phase transformation.

In order to investigate the phase transition during melting dynamics, Fahdiran et al has performed a simulation using MD scheme on Aluminum thin film [4]. It explores the possibilities to study the phase transition in atomistic point of view and calculation of structural evolution and Common Neighbor Analysis (CNA). The analysis confirmed the phase transition due to heat treatment of the system.

This article studies the size dependencies of melting dynamics of Gold nanoparticle when it is heated up from room temperature until melting condition with equally heating rate. The systems are followed using MD simulations and analyzed by structure factor profile supported by local lattice structure analysis using CNA.

2. Simulation method
Gold nanoparticle with different sizes are built and performed in simulation using Large-scale atomic/molecular massively parallel simulator (LAMMPS) [5]. The diameters are 5 nm, 8 nm and 10 nm correspond to 3586 atoms, 16754 atoms and 28894 atoms, respectively. The system is heated in the same temperature gradient from 300 K to 1400 K within 20 ps. The interatomic potential is based on Foiles, et.al. using cut-off radius 5.55 Å [6]. Before the simulation started, the system is relaxed at 300 K and 0.0 GPa for 20 ps. To visualize the atomic representation, OVITO is employed and CNA calculations is used as bundling of the software [7–9]. The calculation of thermodynamics properties in MD scheme is including the virial theorem [10,11]. Structure factor calculation is using Debyer package [12] with several theorems and definition are included [13–15].
3. Results and discussion
Thermodynamics analysis on nanoparticle melting could indicated the behavior of the dynamics of the process itself. The systems are heated with same temperature gradient from 300 K to 1400 K (Figure 1, right), allowing the analysis in the same manner for each case. The size of nanoparticle is not clearly given the effect for the temperature in the beginning while at approaching melting temperature (end of simulation) the temperature is varied clearly for each different diameter of nanoparticle. The inset figure in temperature profile shows the dynamics where size of the nanoparticle gives influence. Smaller diameter suffered higher temperature since it can not hold up the transfer of heat that breaks the bonds between atoms. For the later diameters, the system is maintaining shape while the structure already melted.

The pressure evolution of the system shows the oscillation pattern which is typical for the case of thermal induced melting. It can be seen from Figure 1 (left), smaller diameter possessed higher pressure oscillation compare to larger system. The oscillation pattern ranging from compressive pressure to tensile pressure in the range from -28 to 20 MPa. The tensile pressure (negative pressure) is capable for destructing the material and even for higher value could give ablation [16,17]. In the beginning of simulation, the system is suffering from high pressure oscillation in compressive and tensile value until 12 ps. These pressures are responsible in breaking the bonds between atoms which lead to melting. The oscillation continues until the end of simulation which ranging in the tensile pressure from -22 to -2 MPa. The later case indicated that the system is relaxed while melting continues and transform it into liquid state.

The case for larger diameters, 8 nm and 10 nm, indicated the same pattern oscillation only with suppression of pressure value compare to smallest diameter in the beginning of simulation. The suppression to the compressive pressure continues and in the most of entire simulation, the pressure is tensile. The effect of nanoparticle size is maintaining the shape of the system while tensile pressure is continuing in breaking the system and transform it into liquid state.

The connection between temperature and pressure are clearly seen as the temperature rise approaching melting temperature, the tensile pressure dominates the system. Therefore, the nanoparticle is easily transformed from solid into liquid state at the end of simulation.

Figure 1. Pressure (left) and Temperature (right) evolution of Gold nanoparticle with diameter 5 nm, 8 nm and 10 nm. The oscillation pattern on pressure indicated the thermal induced melting profile. The case at higher temperature indicated that the system evolves as a function diameter size.
Common Neighbor Analysis (CNA) confirming the melting state of system at the end of simulation. For nanoparticle case, the surface will be detected as undefined local lattice structure while for the case of thin film with periodic boundary conditions applied, it will be read as definitive structure [17]. The nanoparticles are arranged in FCC structure in the beginning, and as the system is heated up, the atomic bonds break while unidentified lattice structure is increasing. Figure 2 shows 95% of melting, some local lattice structure is clearly seen, while at the end of simulation, the system is already transformed into liquid state.

The smaller diameter is suppressed by the pressure which ripped out the system earlier than larger diameter, Figure 3 shows the structure factor of the system. For the case of smaller diameter, at $T = 1144$ K, the system already 95% melted. Compared to the calculation by Font and Myers [2], where for diameter 5 nm the system will be melted at around 1050 K, our simulations shows a good agreement with small differences. For the latter diameter, at $T = 1180$ K for 8 nm and $T = 1245$ K for 10 nm, the system already 95% melted. The peaks on 95% melting of smaller scattering vector $(2.7 - 3.2 \, \text{Å}^{-1})$ at 5 nm are almost merged as it is the consequences of the size itself for calculation, while for larger diameter the peaks are still separated. These also indicated that the shape of the system is maintained but the local lattice structure is compromised. At the end of simulation, all nanoparticles are already in liquid state.
Figure 3. Structure Factor: (a) 5 nm, (b) 8 nm and (c) 10 nm. Blue line: 95 % melting. Red line: 100 % melting.

4. Conclusion
Melting of Gold nanoparticles are affected by the size of the system. The size compromised the melting temperature, where for smaller diameter melting occurred earlier compare to the larger system. CNA analysis indicated that at 95 % melting state some local crystal structure survived which is confirmed by the sharp peaks at smaller scattering vector on structure factor profile. Liquid state at the end of simulation shows that the system is completely melted.

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