Melting of gold nanoparticle: study on structural evolution

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Abstract. We investigate the structural evolution on melting of Gold nanoparticle due to heat treatment from room temperature up to slightly above melting point. The evolution is followed using Molecular Dynamics (MD) simulation. Structure factor and pair distribution function calculation indicated that the system is melted at the end of simulation. Common Neighbour Analysis (CNA) method shows the local lattice structure transformation confirming phase transition.

1. Introduction
Heat treatment in material processing is a significant procedure that will change the behavior of material. In order to justify the change of some properties of materials, structural evolution is needed to ensure that system is already transform from one phase to another.

Difficulties comes when observation of structural change could not be easily performed during material processing. An experimental point of view in the case of structural evolution of a material, Nicoul, et.al. investigated the transformations by means of time-resolved diffuse X-ray scattering for the case of laser induced melting [1]. Another investigation on small-angle scattering and structural transition analysis on laser induced ablation of material are done in MD scheme [2-5]. From theoretical point of view, e.g. by means of MD simulation, structural change can be determined precisely with atomistic detail [5,6].

In this article we explore the structural evolution of Gold nanoparticle due to heat treatment from room temperature up to above melting point. The analysis is based on pair distribution function, structure factor and local crystal structure.

2. Simulation method
The simulation was done based on MD scheme using Large-scale atomic/molecular massively parallel simulator (LAMMPS) [7]. We performed heat treatment from 300 K to 1400 K, which is slightly above melting temperature of Gold (T_m = 1338 K, [8]). The system consists of 28894 atoms arrange as single nanosphere with diameter 9.5 nm. The potential interaction between atoms are based on Foiles, et.al. using cut-off radius 5.55 Å [9]. Before heat treatment started, the system has been relaxed for 20 ps at room temperature and 0.0 GPa pressure.

Atomistic illustration has been carried out using OVITO [10], employing several calculations within the package, e.g. Common Neighbor Analysis (CNA) [11,12]. Thermodynamics properties of the atoms
are considering the virial theorem [13,14]. The structure factor as the reciprocal representation and pair distribution function are calculated employing Debyer package [15] by considering some approach related to the system [5,16,17].

3. Results and discussion
The evolution of the system indicated from temperature changes is shown in Figure 1. The simulation started when the system is in room temperature (a) and heated up step by step up to 1400 K. Temperature of the system uniformly distributed at the beginning, while the inner part suffered from heat due to increased temperature as can be seen until 600 K (b) – (d). The elevation of temperature up to 1000 K (e) – (h), brought the system into uniform heating throughout nanoparticle. Approaching melting temperature of Gold, phase transformation occurred (i) – (k). At T = 1400 K (l), the system already in a melting phase. All the atoms are uniformly possessed with temperature slightly above melting point. In contrast with Aluminum thin film due to heat treatment [6], Gold nanoparticle also completely melted as the temperature already above melting threshold.

![Figure 1](image_url)

Figure 1. Temperature evolution of Gold nanoparticle. Atoms are colored based on local temperature in K (color scale is given). (a) 300 K, (b) 400 K, (c) 500 K, (d) 600 K, (e) 700 K, (f) 800 K, (g) 900 K, (h) 1000 K, (i) 1100 K, (j) 1200 K, (k) 1300 K, (l) 1400 K.

Figure 2 shows the structural change of the system as can be seen through pair distribution function g(r) and structure factor S(Q) profile. At room temperature, the system is in crystalline state indicated by the sharp peaks on S(Q) with several peak points correspond to (1 1 1), (2 0 0), (2 2 0) and (3 1 1). The Gold nanoparticle structure factor peak within this simulation is suppressed by the size of the system which only 9.5 nm, while to have a fine peak the system should be as larger as possible [5]. Hence, for the case of nanoparticle with sub-10-nm size, the broadening of the peak is inevitable [18,19]. The pair
distribution function at 300 K also exhibits fine peaks where the nearest neighbor atoms indicated by the strongest peak at distance $r$ of 2.875 Å with several peaks following the probabilities to find atoms inside nanoparticle.

Figure 2. Pair distribution function (left) and structure factor (right) profile at several temperature points, $T = 300$ K, 700 K, 1000 K and 1400 K. Shifted value of $g(r)$ and $S(Q)$ in order to clarify the transformation of the structure.

Figure 3. Left: Local lattice structure of Gold nanoparticle. The figures are sliced part with view from inside the system. (a) 300 K, (b) 700 K, (c) 1000 K, (d) 1400 K. Right: Local FCC percentage as a function of temperature.

Increasing the temperature up to 1000 K, it was observed that the peak in $S(Q)$ and $g(r)$ suffered broadening and several peaks are merged. The coordination between atoms breaks and local structure cannot be maintained by the system. It indicates that the system started to transform from crystalline
state to liquid state. In non-equilibrium case, such as ultrahigh intensities laser induced melting, the phase transformation also occurred, only with shorter time scale [2-4,20]. At the end of simulation, T = 1400 K, the system is completely melted, and the liquid structure are shown by S(Q) and g(r).

CNA analysis indicated that at the beginning of simulation FCC structure dominated the system since Gold atoms are arrange in FCC as shown in Figure 3. The calculation of CNA will produce unidentified local crystal structure for the surface. Thus, at room temperature, 84.1 % of atoms are arranged in FCC structure, while 15.9% at the surface are recognized as unidentified structure. Continuing to 700 K, the heat already breaks atomic bonds dominantly on near surface regions. The system survived with 63.8 % FCC structure. Following the heat treatment up to 1000 K, it was shown that phase transformation from crystalline state to liquid state are strongly evidenced.

4. Conclusion

We studied the influence of heat treatment from room temperature to slightly above melting point on Gold nanoparticle. The phase transformation from crystalline state to liquid state are strongly evidenced by pair distribution function g(r), structure factor S(Q) and local lattice structure investigation performed by Common Neighbor Analysis (CNA). The percentage of the local lattice structure is inversely related to the temperature. This was supported by the calculation of g(r) and S(Q) where broadening and merging of several peaks indicated that the system is melted at the end of simulation.

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