

Molecular dynamics study of the sintering of two equal sized Cu nanoparticles

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Abstract: Molecular dynamics simulations have been used to investigate the consolidation of two equal-sized nanoparticles of Cu element. Sintering process of two nanoparticles is studied. Two model systems with 4 nm and 10 nm diameter particles are chosen to study the sintering process. Orientation effects on the physical properties of consolidation of two nanoparticles with respect to each other are investigated. Temperature effects on the consolidation of two nanoparticles are also studied. The melting temperatures of the copper nanoparticles are found to decrease as the size of the particle decrease. Simulation results are compatible with the other theoretical calculations.

Keywords: Molecular Dynamics; Coalescence; Sintering Process; Sutto-Chen Potential.

1. INTRODUCTION

Nanostructured materials are of great scientific as they are effectively a bridge between bulk materials and atomic and molecular structures. It is well known that the properties of materials change as their sizes approaches the nanoscale and as the percentage of atoms at the surface and a materials becomes significant. This important area in the material science is obtained by using synthesis of nanostructured materials (1). The interest is due to the novel physical properties that can be induced in a material when synthesized with nanometer dimension (2; 3; 4). Since the nanomaterials possess unique, beneficial chemical, physical and mechanical properties they can be used for a wide varied of applications. These applications include many industrial applications such as next-generation computer chips, longer-lasting medical implants, low-cost flat-panel displays, tougher and harder cutting tools, elimination of pollutants, and high energy density batteries (5). This area attracted to the many researchers to study the coalescence properties of metal clusters points of view theoretically and experimentally. For example, Li *et. al* (6) reviewed the synthesis, properties and environmental applications of nanoscale iron-based materials. The processing of three dimensional nano-materials is still its rudimentary stages although much is known the assembly of nanostructured multilayer thin films. Much work should be done to elucidate the sintering process on the atomic level with experimental studies examining real sintering behavior of powders of nanoparticles. Atomistic simulations are useful tools to understand mechanism of the nanoparticles. They are used by many authors to clarify the phenomenon of sintering process (7; 8; 9; 10; 11; 12; 13; 14).

Molecular dynamic simulations (MD) can, hopefully, provide a fundamental atomistic level understanding of sintering phenomena and competition of different mechanisms in forming nanoparticle products. MD simulation technique also provides important insights and guidance to experimental work. In the past years, many researchers studied the coalescence properties of metal clusters (10; 11; 12; 13; 14). Lewis *et al.* (9) developed a molecular dynamics simulations using the embedded atom method to study the melting, freezing, and coalescence of gold nanoclusters. Qi *et al*(15) investigated the melting and freezing of Ni nanoclusters using molecular dynamics with many-body force field. Zhao *et al.* (16) investigated the coalescence of three identical size nanoclusters by using an analytic embedded-atom potentials. Shim *et al.* (17) also studied the thermal stability of gold nanoparticles, via molecular dynamics technique with the modified embedded-atom method potentials. Bilalbegovic (18) investigated the aggregation of gold clusters by molecular dynamics simulation. Ding *et al.* (19) used molecular dynamics simulations to investigate the coalescence of iron nanoclusters occurring at lower temperatures than the cluster melting point. Arcidiacona *et al.* (20) investigated the coalescence processes of two gold nanoparticles for a host of initial temperatures and starting radii in vacuum with the help of molecular dynamics simulations. Recently times, Fang *et al.* (8) studied the coalescent properties of ZnO clusters through experiment and molecular dynamics simulation in combination with the tight-binding potential and ZnO potential. Hawa *et al.* (21) did a research on coalescence mechanism of unequal sized nanoparticles to understand the coalescence of pairs of silicon nanoparticles of volume ratios between 0.053 and

1 with 10000 silicon atoms using molecular dynamics (MD) simulation under constant temperature.

Main goal of this study is to investigate how to controllably assemble the fundamental nano-particle building blocks. In this work, we apply molecular dynamics (MD) methods using the quantum Sutton-Chen (Q-SC)(22) many body force field to simulate the sintering or coalescence properties of the two equal sized nanoparticles. Each equal sized nanoparticles contain 2844 atoms (4 nm diameter) and 44932 (10 nm diameter) atoms. Two different models of the Cu nanoparticles are studied in this work. One model includes two nanoparticles with diameter of 4 nm particles while other one is 10 nm particles. The results presented in this work are important for understanding of processes and development of new techniques in preparation of copper nanoparticles and nanostructured copper.

2. COMPUTATIONAL METHODS

MD method is very suitable for modeling of large systems on long time scales. Modern ab initio methods are not yet feasible to study large systems on the long time scales. Molecular dynamics simulations (23) are performed via using the MPiSiM software developed at Caltech (24). This program uses the quantum corrected Sutton-Chen (Q-SC) many-body force field (25). The modified Sutton-Chen potential was empirically fitted to data on density, cohesive energy, compressibility, and phonon frequency. Q-SC produces accurate values for surface energy, vacancy energy, and stacking fault energies and has been used in the studies of melting, glass formation and crystallization of pure metals, nanoparticle and alloys (22; 26)

First of all, two model systems of spherical spheres of Cu with diameter 4 nm and 10 nm are generated to start simulation of nanoparticle sintering processes. Fig. ?? shows the initial structures of two nanoparticles with 4 nm diameter to sinter the (100)-(100), (100)-(110) and (100)-(111) planes of them, respectively. The values in the parenthesis corresponds to the orientation of the nanoparticles with respect to each other. That is, they show the interaction planes of the two nanoparticles. As shown in the Figs. ??, each model consists of two identical spherical nanoparticles which are separated by an only small distance in the x direction. In the model system, one particle is fixed and other nanoparticle can be rotated about the any axis. In this study, three different orientation of nanoparticles are considered to match the plane of them. The former case, (100) plane of the first particle is matched to the (100) plane of second particle, that is, there is no rotation about the any axis. In the second case, first particle in the model system is fixed and second one is rotated 45 degrees about z axis to match (100) plane of fixed particle and (110) plane of the rotated particle. In the last one, the plane of (100) of the first nano-particle was considered to match the plane of (111) of the second nano-particle. The models with two spheres are inserted into a rectangular box which has 100 Å, 60Å, 60Å, in the x, y, z directions, respectively. Each model is equilibrated by using MPiSiM program at elevated temperatures ranging from 100 K to 2100 K by increasing temperature of 200 K.

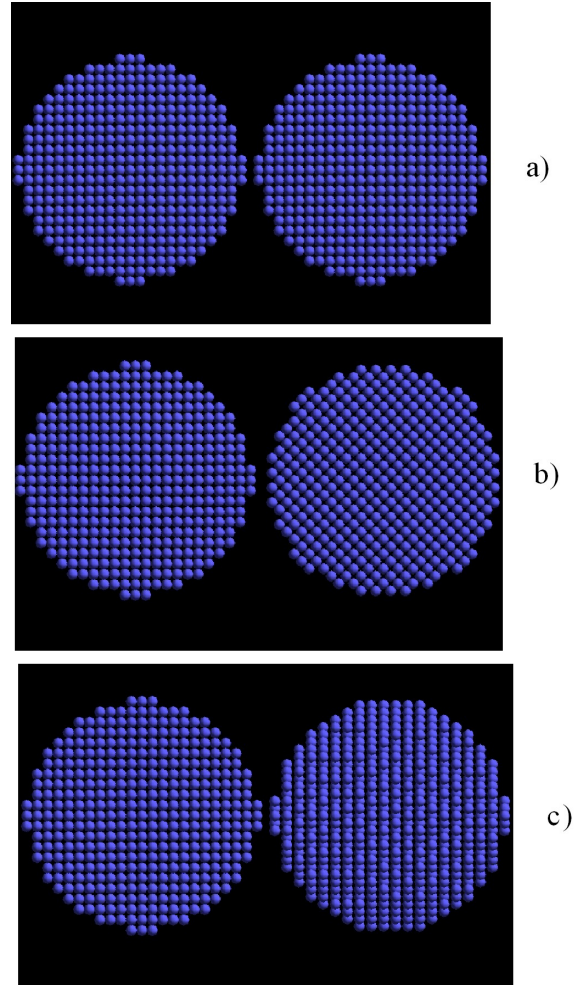


Fig. 1. Initial structures of two nanoparticles with diameter of 4 nm for matching of (100)-(100), (100)-(110) and (100)-(111) planes, respectively, at 0 K. Here, top figure (a) of the page corresponds to the structure of the (100)-(100) planes, middle one (b) is the structure of the (100)-(110) and last one (c) is the (100)-(111) planes.

The system is equilibrated on 50000 time steps in the constant-volume, constant-temperature ensemble (ThN) at the target temperature. Molecular dynamics time step is set as 2 fs. Sutton-Chen potential is used to define the interaction between the atoms.

Total potential energy of the pure metals and alloys in Sutton-Chen formalism for the system of N atoms is given as follows (27; 28);

$$U_{tot} = \sum_i U_i = \sum_i \left[\sum_{j \neq i} \epsilon_{ij} \frac{1}{2} \left(\frac{a_{ij}}{r_{ij}} \right)^{n_{ij}} - c_i \epsilon_{ii} \left(\left(\frac{a_{ij}}{r_{ij}} \right)^{m_{ij}} \right)^{\frac{1}{2}} \right] \quad (1)$$

The first term in Eq. (1) is a two body repulsive interaction between the atoms i and j , separated by a distance r_{ij} . The second term represents the many-body cohesion term associated with atom i . The square root term introduces a many-body component into the energy summation. The popularity of SC potentials is partly due to the computationally tractable form adopted for the many-body forces. It is the relatively simple analytic form of the potential

that enables one to calculate the many physical properties of the materials.

In the Eq. (1), r_{ij} is the distance between atoms i and j , a is a length parameter scaling to the lattice spacing of the crystal, c is a dimensionless parameter scaling the attractive terms, ϵ is an energy parameter determined from experiment, and n, m are integer parameters with $n > m$ which determine the range of the two components of the potential. The interaction length of potential is taken as two lattice parameters for the efficiency of the computer simulation time. The temperature effects in the simulations are considered by giving an additional length of half the lattice parameter.

3. RESULTS

To understand the mechanism of coalescence for two nanoparticles, we present the results of the sintering processes of two equal nanoparticles as shown in Figs.2,3 and 4. Fig. 2 shows the equilibrium structure of the sintering of the (100) plane of left particle and (100) plane of the right particle at the temperatures of 100 K, 700 K, 1300 K and 2100 K, respectively. These temperatures are especially chosen to observe the temperature effects on the sintering of two identical particles at desired temperatures. 100 K and 700 K is less than the melting point of the copper element and temperature of the 1300 K and 2100 is greater than melting point of the copper. we can conclude that the penetration deep of the two particles are strongly dependent on the temperature of the sintering. If we compare the penetrations of the two particles at different temperatures, the least penetration of the two particles takes place at lower temperatures as shown in the Figs. 2, 3 and 4. That is, if gyration radius is considered as distance between the two particles, this gyration radius for high temperature sintering of the two particles are less than the ones of the low temperature sintering processes for two particles. This sintering process takes places as the following way; at the beginning of the simulation, two particles approach at thermal speeds and have an initial contact. Once the collision event has initiated, diffusion processes between the two particles occur and contact area between the two particle increases. Finally, the combined system is equilibrated over the MD steps. At the beginning of the sintering of two particle, the contact area with a neck having a radius is small and it is increased during the simulations and finally the combined system is equilibrated over the MD steps. In the case of the sintering for two particles above the melting temperature of the particles, at the temperatures of the 1300 K and 2100 K, two particles form a one particle by inter-diffusing between the each other. It is obvious that the neck forming between the two particles disappears and only one particle is recognized. The gyration radius in this case is much slower. For the present cases shown in Figs. 2, 3 and 4 for temperatures of 1300 K and 2100 K are not reached into actual sphere. It is difficult to state whether the final configuration will approach to a perfect spherical shape. This event would require a simulation of hundred nanoseconds.

Fig. 5 compares the penetration deeps of the two nanoparticle at temperature of 100 K to observe the effects of orientation of nanoparticles on penetration of them. The

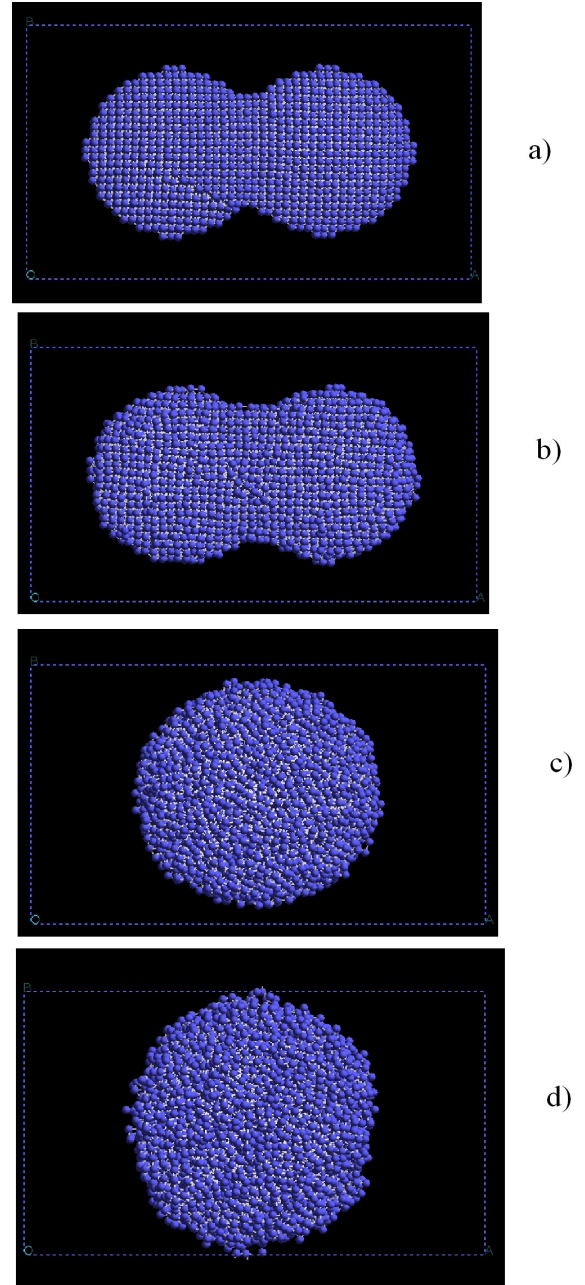
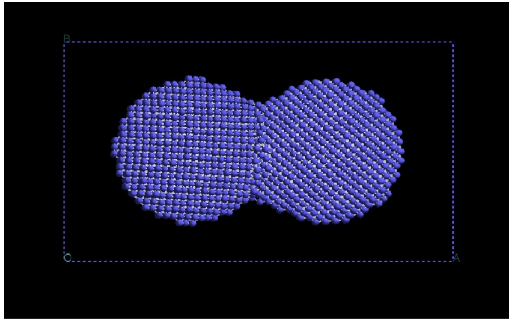
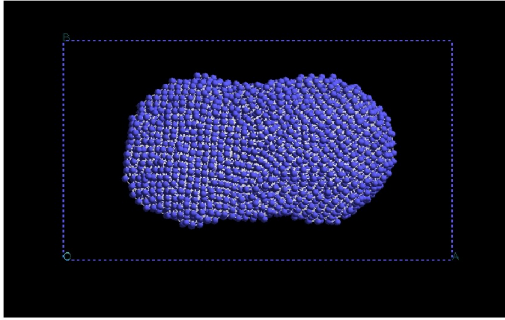


Fig. 2. Sintering of the (100)-(100) planes of the nanoparticles at elevated temperatures of (a) 100 K, (b) 700 K, (c) 1300 K and (d) 2100 K from top to bottom, respectively.

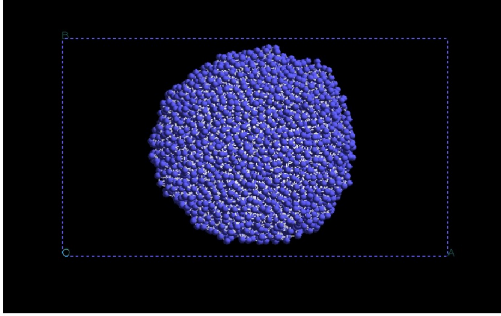
MD results of the matching planes of (100)-(100), (100)-(110) and (100)-(111) of nanoparticles are given in the Fig. 5, respectively. As shown in the Fig.5, the least penetrated case is the matching of the planes of (100)-(111). The most penetration deep is observed in the matching of the nanoparticle planes of the (100)-(110). The middle case is seen in the sintering of the nanoparticle planes of (100)-(100). This results show that the penetration deeps depend strongly on the orientation of the nanoparticles. This is related to the density of atom per square to match the sintered planes considered in this study.



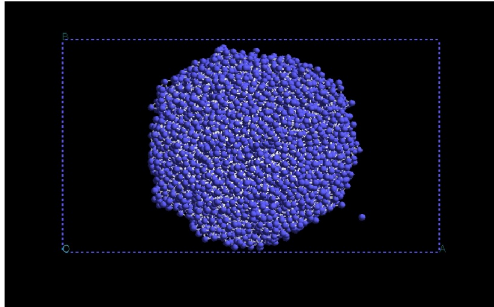
a)



b)



c)

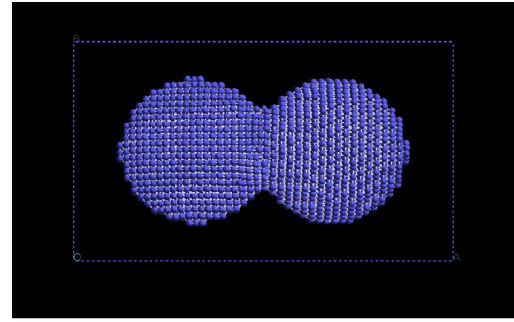


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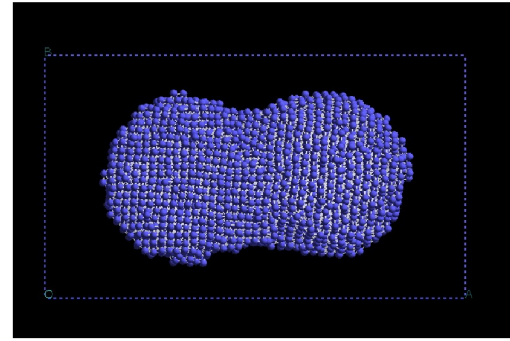
Fig. 3. Sintering of the (100)-(110) planes of the nanoparticles at elevated temperatures of (a) 100 K, (b) 700 K, (c) 1300 K and (d) 2100 K from top to bottom, respectively.

4. CONCLUSION

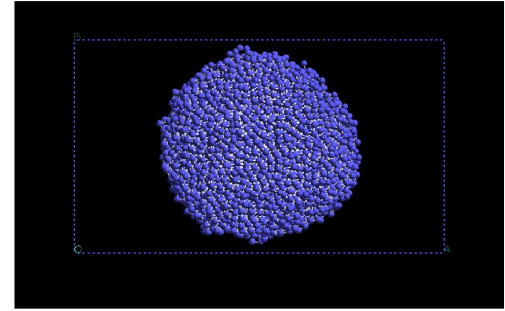
Classical Molecular dynamics simulations using Quantum Sutton-Chen many-body potential have been performed to investigate the coalescence behavior of equal-sized copper nanoparticles. The results of sintering of the equal-sized copper nanoparticles having diameter of 4 nm and 10 nm shows that MD approach is a reliable method to study the physical properties of the coalescence of the nanoparticles. MD results show that the orientation of the nanoparticles with respect to each other is important factor in the sintering processes. Melting temperature of the copper nanoparticle are found to decrease as the size of the particle decreases. It is evident from the



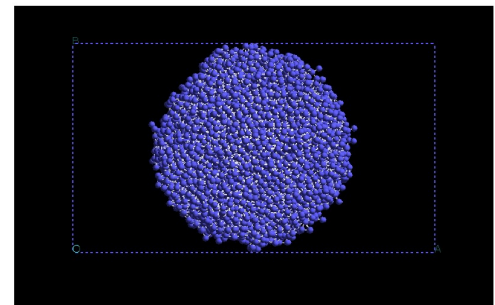
a)



b)



c)



d)

Fig. 4. Sintering of the (100)-(111) planes of the nanoparticles at elevated temperatures of (a) 100 K, (b) 700 K, (c) 1300 K and (d) 2100 K, respectively.

figures that penetration depths of the two nanoparticle at high temperatures are more than the cases for lower temperatures. MD simulations allow ones to synthesize and develop new nanostructured functional materials by controlling nanoparticle size and by increasing the number of nanoparticles to guide the experimentalists. In the next study, the number of nanoparticles in the sintering processes will be increased to design a functional materials.

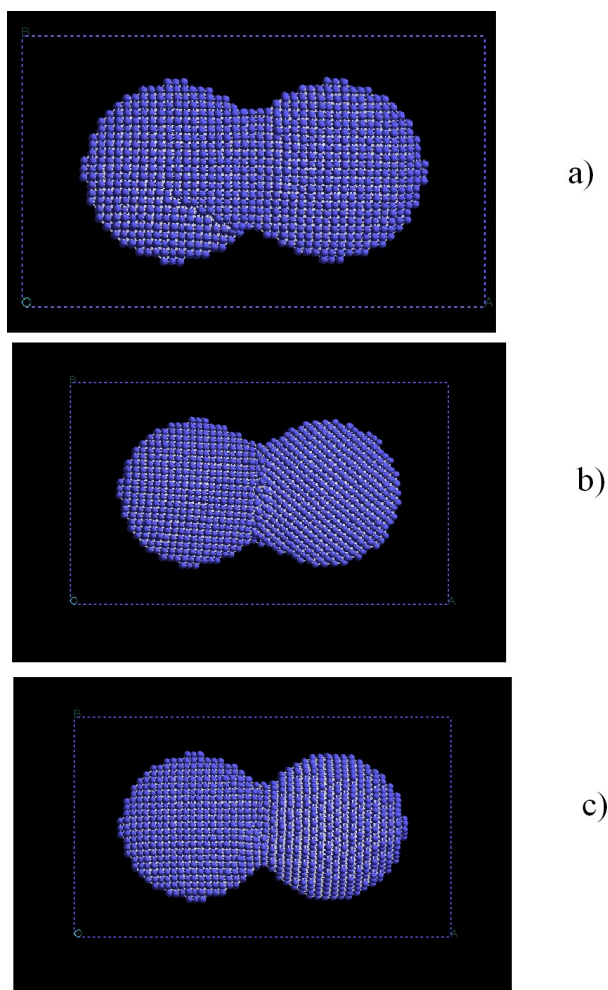


Fig. 5. Comparing the penetration of two nanoparticles at temperature of 100 K for matching planes of (a) (100)-(100), (b) (110)-(110) and (c) (111)-(111), respectively.

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