Molecular dynamics study of neck growth in laser sintering of hollow silver nanoparticles with different heating rates

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Abstract
Engineered hollow nanoparticles have exhibited their potential in nanotechnology applications, but so far the investigation of the deformation mechanisms for these hollow particles during the sintering process has rarely been reported. Hence, a comparative study of both solid and hollow spherical silver nanoparticles with different sizes under different heating rates of laser sintering is conducted systematically in this paper, based on molecular dynamics simulations. An interesting phenomenon is observed where the temperature for fast neck growth shows an inverse trend in all the hollow nanoparticle pairs at an ultrahigh heating rate, which is quite different from that known in the solid particle cases. This finding implies that besides the size and heating rate, the nanoparticle geometry could also play an important role in the sintering process. At a low heating rate, the plastic deformation combined with structural reconfigurations induced by the lattice sliding in the hollow shells is found to be an important mechanism during the heating process. At an ultrahigh heating rate, the transition from fcc crystal directly to disordered structure from both outside and inside surfaces becomes more dominant than the structural reconfiguration with lattice defects, which is facilitated by the introduction of the inner free surfaces in hollow nanoparticles. The entire hollow particle pairs thus show an obvious tendency to coalesce and melt at a lower temperature level than with a low heating rate.

1. Introduction
Nanoparticles are of growing interest to academia and modern industry, as fundamental building blocks with many potential applications in nanotechnology [1–4]. The use of laser radiation to selectively sinter nanoparticles has shown many advantages from the aspects of meeting performance and cost requirements [5, 6]. Since the late 1980s when it was initially developed, selective laser sintering (SLS) [7, 8] technology has been gaining great improvements, and proved to be a very promising tool for rapid manufacturing, which allows building functional nanostructures from a wide range of commercially available powdered materials. However, strong size effect on the physical and chemical properties of the nanoparticles [9, 10] makes this research topic more complicated, due to high surface-area-to-volume ratios and the possible phenomena of melting and evaporation under high laser intensity [11, 12].

Besides extensive experimental research [5, 6, 13, 14] on the sintering of nanoparticles, many theoretical and computational efforts have been made to model and evaluate the sintering process over the past decades. When the particle size is much smaller than the laser beam radius, the sintering
problem could be solved by a continuum-based model \[15, 16\] with the assumption that the powder bed is uniform and isotropic. However, a single particle level model \[17, 18\] should be considered if the particle size is comparable to the laser beam size. Molecular dynamics (MD) method, as another suitable and effective approach, has been widely employed to study the fundamental physics. It could reveal more details such as neck growth \[19\], gyration radius \[19, 20\], densification and dislocation \[21\] from the molecular level of the particle sintering. By comparing the simulation-predicted neck growth with the empirical-theoretical formulations, the reliability of MD simulations has been proved for the sintering of metallic nanoparticles \[22\]. Different elements, e.g. the nanoparticles of Au \[19, 12, 23\], Ag \[14\], Cu \[21\], Fe \[24\], Ni \[20\] and metal oxide \[25\] (among others), have been considered in both previous experiments and simulations, and most of these studied nanoparticles are spherical in shapes with solid spheres.

With the development of experimental technology, more and more functional nanoparticles with novel hollow structures are synthesized \[26, 27\]. As mentioned by Yin et al \[28\], the ability to manipulate the morphology and structures of porous solids in nanoscale would enable greater control of the local chemical environment. They successfully demonstrated the formation of hollow nanoparticles with a mechanism analogous to void formation in the nanoscale Kirkendall effect. Schwartzberg et al \[29\] reported synthesis, characterization, and tunable optical properties of hollow gold nanoparticles, which have shown great potential for chemical and biological sensing applications. Chen et al \[30\] reported the preparation of ordered arrays of hollow silver nanoparticles by colloidal crystal templating. Anumol et al \[31\] also reported a general method for the synthesis of hollow structures of various functional inorganics by partial sintering of mesoporous nanoparticle aggregates, which is attractive for many applications, such as catalysis, drug delivery and biosensing.

Although much progress has been made on the experiments of both solid and hollow nanoparticles, the existing analytical and computational investigations of nanoparticle sintering are mainly focused on solid spheres, and the study of hollow spheres is rarely reported, as can be found from the open literature. A basic question is therefore raised: will there be any fundamental difference between the solid and hollow nanoparticles in the sintering process? If so, how will the heating rates influence the properties such as neck growths, gyration radii and melting of the hollow nanoparticles during the laser sintering? These questions have not been answered yet. In this paper, the sintering of two hollow silver (Ag) nanoparticles by laser heating is modelled using MD simulations. Since the sizes of two particles are rarely identical in a real sintering process, a series of simulations with different sizes and heating rates are performed. For the purpose of comparison, solid nanoparticles corresponding to hollow sphere cases are also considered. The effects of particle size as well as the laser heating rates on the neck growth are systematically investigated. Other key properties for both solid and hollow nanoparticles during the sintering process are also discussed.

**2. Methodology**

**2.1. Atomic model preparation**

The system geometries studied are depicted schematically in figure 1. The 3D atomic models of nanoparticles are created through a top-down method. First, a solid sphere (shown in figure 1(a)) is extracted from a bulk face-centred cubic (fcc) Ag crystal with the [100], [010] and [001] crystallographic directions, which coincide with the x-, y- and z-axes, respectively. Then, removing atoms from the centre of the nanoparticle leaves a hollow spherical space inside and thus forms a hollow nanoparticle. The shell thickness for all the hollow nanoparticles in the current study is set as 3a.

![Figure 1. Sketches of (a) solid and (b) hollow nanoparticles. The sectional views are taken from the planes cut from the middle. The particle sizes are determined by \(d_1\) and \(d_2\) and the initial distance between the two particles is 5 Å. The shell thickness for all the hollow particles in the current study is set as 3a.](image)

The two-nanoparticle-model is characterized by two parameters \(d_1\) and \(d_2\), which are the diameters of the two spheres (or the outer diameters of the hollow spheres). To study the particle size effects on the neck growth during sintering, \(d_1\) and \(d_2\) can be varied, as 10a, 16a and 24a, respectively. Thus, there are twelve combinations in total for the solid and hollow models, as listed in table 1. The centroids of both particles have the same x and y coordinates and the initial gap between two nanoparticles in the z-direction is 5 Å. In each simulation case, two solid/hollow nanoparticles in one pair are thermally equilibrated separately at 298 K for 1 ns, which is performed to reduce the initial stresses resulting from the introduction of free surfaces cut from the bulk. Then two equilibrated solid or hollow nanoparticles are assembled...
The system temperature is computed and monitored every 10 steps during the simulations of the heating process. If the difference between the computed and desired temperatures is greater than 1 K, the atomic velocities are rescaled in order to make sure that the system temperature is reset to the desired value. For all simulations, a time step of 2 fs is used. No heat loss to the environment is considered.

2.3. Auxiliary computations and analysis

Common neighbour analysis (CNA) [38] was used to study the local crystal structure in the nanoparticles; this analysis can facilitate the visualization of the evolution of the deformation configurations and has been widely used in previous research [39]. During the sintering simulation, at each desired time step, different colours with corresponding colour numbers will be assigned to each atom based on CNA. For instance, a series of numbers 1, 2, 3, 4 and 5 represents the colours of grey, blue, green, red and gold, respectively. These numbers are output along with the three coordinate values for the atoms, so that the crystalline structure evolution can be tracked by plotting the entire atomic configurations with a certain colour distribution. In the results discussed below,fcc atoms are shown as grey, hexagonal close-packed (hcp) atoms blue and other twofold-coordinated atoms green, and the remaining atoms which are not in any typical ordered crystalline structure are classified as disordered atoms and shown as gold. A local crystalline structure is classified as an intrinsic stacking fault if it contains two adjacent layers of atoms in the local hcp structure, an extrinsic stacking fault if it contains two hcp layers separated by a single fcc layer, and a twin boundary if it consists of a single hcp layer. Disordered or non-structured atoms are typically located at surfaces or dislocation cores [40, 41].

A post-processing computer program was developed, which can collect all the atoms in the same type of lattice structure based on the same colour number and thus obtain the total number of atoms in the specific lattice structure. The number density shown in the figures of this paper is defined as the ratio of the number of atoms in the specific lattice structure to the total number of atoms in the system. For a clear illustration, all the atomic configuration profiles in this paper are extracted from the middle cross-section on the y – z plane with a thickness of one unit cell length along the x-axis.

Gyration radius, as an important characteristic of a sintering process, is defined as the root mean square distance of atoms of two spheres measured from their mass centre:

\[ R_g^2 = \frac{1}{M} \sum_{i=1}^{N} m_i (r_i - r_{cm})^2, \]

where \(M\) is the total mass of the group, \(r_i\) is the position of each atom, and \(r_{cm}\) is the centre-of-mass position of the group, and the subscript \(i\) runs over all atoms in the system. The mean square displacement (MSD), as another important calculation, is a measure of the average distance

### Table 1. Specification of the simulation models.

<table>
<thead>
<tr>
<th>Simulation No</th>
<th>(d_1)</th>
<th>(d_2)</th>
<th>Morphology</th>
<th>Atoms contained</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10a</td>
<td>10a</td>
<td>Solid sphere</td>
<td>4246</td>
</tr>
<tr>
<td>2</td>
<td>10a</td>
<td>16a</td>
<td>Solid sphere</td>
<td>10712</td>
</tr>
<tr>
<td>3</td>
<td>10a</td>
<td>24a</td>
<td>Solid sphere</td>
<td>31020</td>
</tr>
<tr>
<td>4</td>
<td>16a</td>
<td>16a</td>
<td>Solid sphere</td>
<td>17178</td>
</tr>
<tr>
<td>5</td>
<td>16a</td>
<td>24a</td>
<td>Solid sphere</td>
<td>37486</td>
</tr>
<tr>
<td>6</td>
<td>24a</td>
<td>24a</td>
<td>Solid sphere</td>
<td>57794</td>
</tr>
<tr>
<td>7</td>
<td>10a</td>
<td>10a</td>
<td>Hollow sphere</td>
<td>3964</td>
</tr>
<tr>
<td>8</td>
<td>10a</td>
<td>16a</td>
<td>Hollow sphere</td>
<td>8448</td>
</tr>
<tr>
<td>9</td>
<td>10a</td>
<td>24a</td>
<td>Hollow sphere</td>
<td>18664</td>
</tr>
<tr>
<td>10</td>
<td>16a</td>
<td>16a</td>
<td>Hollow sphere</td>
<td>12932</td>
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<td>12</td>
<td>24a</td>
<td>24a</td>
<td>Hollow sphere</td>
<td>33364</td>
</tr>
</tbody>
</table>

To establish the initial MD system for sintering simulation, as shown with the configurations in figures 1(a) and (b), respectively. In addition, a set of simulations for equilibrium are also conducted at different temperatures (e.g. 10, 98, 198 and 298 K) which is much lower than the melting point. To avoid the deviation from the equilibrium and extra driving force induced by the deformation of particle, the potential energy curves and configurations of the particles are examined to ensure that the equilibrium durations are long enough and the entire systems can approach the minimum energy state. All configurations in these simulations show that the hollow spheres are able to remain the initial morphology with a cavity interior after the equilibrium, and thus are ready for the sequent sintering simulation. In this study, we focus on the models prepared at the room temperature of 298 K.

2.2. MD simulations

In the MD simulations of sintering, non-periodical boundary conditions are used along all the three dimensions. The interatomic interactions are modelled on embedded-atom method (EAM) force field [32]. The total energy \(U\) for a system of \(N\) atoms is described as

\[
U = \sum_{i=1}^{N} F_i(\rho_i) + \frac{1}{2} \sum_{j \neq i} \Phi_{ij}(r_{ij}),
\]

where \(F_i\) is the embedding function, \(\rho_i\) is the electron density at atom \(i\), \(\Phi_{ij}\) is a pair interaction function, and \(r_{ij}\) is the distance between atom \(i\) and \(j\). The detailed parameters of the EAM for Ag atoms, which are specified in the study of Foiles et al [33], are utilized in this study to describe between Ag atoms.

After the initial MD model is established, the simulation is carried out at room temperature (298 K) with isochoric-isothermal (NVT) ensemble using the Nosé–Hoover thermostat [34, 35] and velocity-Verlet integrator [36]. This equilibration lasts for 1 ns to mimic the solid state sintering at 298 K. Subsequently, the system temperature is linearly increased to model the laser sintering. It is shown that the temperature of the metal nanoparticles due to laser heating is approximately linear [37]. For simplification, the laser heating of metal nanoparticles is simulated by linearly increasing the nanoparticle temperature. Three heating rates of 0.04, 0.2 and 1 K ps\(^{-1}\) are considered for each simulation case as listed in Table 1. The system temperature is computed and monitored every 10 steps during the simulations of the heating process. If the difference between the computed and desired temperatures is greater than 1 K, the atomic velocities are rescaled in order to make sure that the system temperature is reset to the desired value. For all simulations, a time step of 2 fs is used. No heat loss to the environment is considered.
that an atom travels in the sintering process:

$$\text{MSD} = \frac{1}{N} \sum_{i=1}^{N} \left[ r_i(t) - r_i(0) \right]^2,$$

where \( N \) is the total number of atoms, \( t \) is time, and \( r \) is the position of each atom. The MSD is computed based on the initial coordinates of atoms at the beginning of the subsequent laser sintering.

### 3. Solid state sintering at room temperature

From the simulation results, it is found that the solid state sintering of two bare nanoparticles can occur at room temperature without any laser irradiation, due to their ultrafine sizes and relatively large atomic potential gradients. The evolution of the particle deformation during solid state sintering at room temperature is illustrated in figure 2, with the snapshots of the atomic configurations obtained at different time steps corresponding to the points A, B, C and D on the neck width curves. The two nanoparticles are initially separated without laser heating applied yet (points A in figure 2), and the system temperature is maintained at 298 K. At points B, it can be clearly seen that the two nanoparticles move towards each other and become connected with a rapid neck formation. A relatively stable dumbbell-shaped particle is then formed in the later stage (see points C and D). This phenomenon of solid state sintering at room temperature can be observed in all the cases for both solid and hollow nanoparticles with different sizes.

The time histories of neck width and number density of classified disordered and surface atoms for both solid (simulation 2) and hollow (simulation 8) nanoparticles are also shown in figure 2. At the early stage of the solid sintering from points A to B, a rapid neck growth occurs with the emergence of grain boundary consisting of non-crystalline atoms, and thus results in a sudden increase of the disordered-atom fraction (corresponding to the first peak on the number density curve). Then, during the thermal equilibration, particularly in the fast neck growth stage (e.g., from point B to C in figure 2(a), and point B to D in figure 2(b)), partial dislocation cores are nucleated from the neck region, and quickly lead to a slippage along the \( \{1\ 1\ 1\} \) close-packed plane, forming the intrinsic stacking faults. Since partial dislocation cores also consist of non-crystalline atoms which are determined by CNA, their nucleation results in another increase of the disordered-atom fraction (corresponding to the second peak on the number density curve). After the first peak (temporary grain boundary) and second peak (partial dislocation cores) of the number density curve, it can also be found that the surface-atom fraction finally decreases to a lower value than that in the initial status. This reflects the reduction of total free surface area and implies that the decrease of free energy due to this reduced surface area is the main driving force [25] for the solid state sintering at room temperature.

As shown in the configuration on points C and D in figure 2(a), a partial dislocation core is initially nucleated from the neck region, then passes through the whole section of the smaller nanoparticle, leaving a stacking fault behind, and finally ends on the other side of the free surface, forming stable stacking faults in the lattice during the later solid sintering process. This process indicates that the lattice structure deformation is mainly mediated by the partial dislocation activity. Another different scenario is that spontaneous generation of dislocations near the neck still occurs, but forms transient stack faults that later can disappear, as shown in configurations on points C and D in figure 2(b). In all the cases modelled in this paper, stable stacking faults were formed in simulations 1, 2 and 7, in which relatively small particles were included. Transient stacking faults were found in most simulations (simulations 3–6, 8, 9 and 11) with the increase of the particle size. These results confirm that the plastic deformation via dislocation generation is an important mechanism [21, 42], which contributes in a major way to the sintering of both solid and hollow nanoparticles. However, both stable and transient slippages of the lattice can be observed during the solid state sintering at the room temperature, which is not obviously shown in the previous work [19, 23].

Furthermore, either stable or transient stacking faults were observed to occur in the smaller one for each pair if the two sphere sizes are not identical (see the configurations in figure 2), indicating that the partial dislocations and lattice slips are more prone to form in smaller particles. This finding could be explained by the mechanical rotation that occurs to some degree in virtually all the simulations reported in this study, which is similar to the phenomenon in the previous work [42]. Additional simulation of different initial orientations including \( \langle 1\ 1\ 0\ \rangle \) and \( \langle 1\ 1\ 1\ \rangle \) combined with \( \langle 1\ 0\ 0\ \rangle \) were also performed, and it was found that the dislocations can be easily formed and slide on \( \langle 1\ 1\ 1\ \rangle \) planes in the \( \langle 1\ 1\ 0\ \rangle \) directions during

![Figure 2. Time histories of neck width and number density of surface and disordered atoms for (a) solid and (b) hollow nanoparticle pair of 10a versus 16a. The insets are the atomic configurations at various time steps.](image-url)
the solid sintering with an obvious mechanical rotation due to the initial misorientation [21]. Similarly, for the particle pairs focused on in the current study, the mechanical rotation is found to be especially obvious in smaller nanoparticles, and the dislocations thus are easily found in the smaller ones because of the relative crystalline misorientation. As illustrated in both figures 2(a) and (b) at the point B, the smaller spheres rotate to a certain angle at the onset of neck formation. After the disordered atoms in the neck region recrystallize to fcc structure, it can be found that the ‘upper’ smaller nanoparticles start to rotate back and forth around a ‘balance position’, which is much more obvious for the hollow cases. That is why there are more ‘small oscillations’ on the neck width curve during the stable stage for the hollow particles after the neck is formed.

4. Laser sintering

The resulting dumbbell shape nanoparticles at 298 K are then subjected to laser irradiation. Each particle pair is heated linearly from 298 K to 1098 K (or 1298 K for some larger size particle cases to obtain the melting points) and the laser heating lasts for 20 ns, 4 ns and 0.8 ns, corresponding to the heating rates of 0.04, 0.2 and 1 K ps$^{-1}$, respectively. A typical configuration evolution for the laser sintering of a hollow nanoparticle pair, as well as the corresponding gyration radius changing, is illustrated in figure 3. The neck width and MSD evolutions for the solid and hollow particle pairs are plotted against temperature in figures 4–6.

4.1. Deformation evolution of the particle pair

Generally, for each nanoparticle pair with different sizes, no matter whether it is hollow or solid, there are two turning points on the axis of temperature (as indicated by the two vertical dash lines in figure 3 or the two arrows in the following figures 4 and 5), marking the rapid drops of the gyration radii but the fast growths of the neck widths. Thus, the deformation evolution of the nanoparticle pair during the laser sintering process could be divided into three stages: relatively stable stage, transition stage, and melting stage.

In the relatively stable stage, which is referred to as the quasi-equilibrium state, the neck growth rate of the two nanoparticles is lower and relatively stable, in comparison with that in the later transition stage (see figures 4 and 5). The gyration radius curve also exhibits a relatively smooth feature, which also indicates that the shape change and deformation of the particles are not very severe in this early stage of laser sintering.

The end of the low neck growth rate stage is followed by the transition stage. As the temperature increases, the nanoparticles experience a transition from solid state to premelting state and quasi-liquid state. The neck growth rate becomes faster than that in the previous stage and the gyration radius starts to decreases to a lower value. The structure deformation is much more severe, along with both plastic deformation and surface melting. As a result, the number density of the disordered atoms is continuously increasing and becomes dominant over the fcc atoms ($>0.5$) in the entire system. Specifically for the hollow spheres, atoms on the two inner free surfaces as well as the outer free surface begin to move very fast, and the inner hollow space becomes smaller and smaller during this stage (see the configurations at points C and D in figure 3). Driven by curvature induced surface diffusion, the so-called ‘spherication’ process [19] begins and the two particles keep moving towards each other to form into one sphere. This transition stage is also accompanied by a small portion of lattice structure changing from fcc to hcp (visually found in the configuration at point D), which is similar to the phenomenon reported for metallic nanorods by Wang and Dellago [43] but has not been observed clearly in the previous study [19] on the laser sintering of nanoparticles. This lattice structural transition can be a very important mechanism related to the heating rate effect on the hollow nanoparticle sintering, as will be discussed later in this paper.

Lastly, as the temperature increases to the second turning point, the most rapid reduction of the gyration radius occurs, with the simultaneous ascending of the neck growth rate and MSD in figures 4–6. These sudden changes with steep slopes shown on the curves indicate the onset of the melting stage with the coalescence of the two particles. For the hollow nanoparticles, the shell structures finally collapse in this stage and the inner vacant spaces disappear, filled with a large number of amorphous atoms. As illustrated by the configurations at points E and F in figure 3, the melting tends to occur and drive all the atoms from the two particles together to form one sphere. At point F around 1098 K, the fraction of the disordered and surface atoms finally reaches 100%, denoting that the entire transition from fcc crystal structure to amorphous is fully accomplished.

4.2. Size and heating rate effects

Figure 4 demonstrates the laser heating rate effect on the neck width growth of different-sized solid sphere pairs. By
Figure 4. Comparison of the neck width in the simulations 1–6 for the solid nanoparticle pairs at three different laser heating rates.

comparing the curves in figures 4(a)–(f), it is found that at each specific heating rate, melting or coalescence would start at a higher temperature when the particle diameter becomes larger. This size effect at a constant heating rate also holds for the hollow nanoparticle case, as compared by each panels in figure 5. In figure 6, the temperature at which the MSD increases significantly indicates the occurrence of melting. From all the simulations for both hollow and solid pairs with different sizes, the results of MSD again confirm the arguments of the size effect discussed above. To determine the melting temperature more accurately, the dependence of the potential energy on temperature during different heating processes for each individual solid and hollow particle is evaluated (partially shown in figure 7). Similar to previous work [44, 45], the melting transition for the nanoparticles can be clearly identifiable by the sharp rise in energy over a relative small range of temperature change. Thus the melting temperatures are collected from these energy curves and plotted in figure 8. The error bars indicate the amplitudes of the melting ranges, taken from the starting points and end points of the large upward jumps in the energy curves, and the symbols their centres. It can be found that the size-dependent melting temperature is valid for both solid and hollow particles at the same heating rate. These results confirm the theoretical demonstration from Buffat and Borel [10] that the melt point increases with the increase of size, and are also in good agreement with previous work [19, 23, 45].

Another finding for each solid nanoparticle case is that the neck width during the transition stage (the region between the two arrows in figure 4) is larger when the heating rate becomes lower, in spite of the neck width showing almost independently on the heating rate during the relatively stable stage (the region before the first arrow). The corresponding MSD curves can also show the same trend, that is, at the same temperature for each solid particle pair (e.g. figure 6(a)), the MSD increases with the decrease of heating rates. This phenomenon can be explained by the duration of the laser heating. At a lower heating rate, it needs more time to raise the temperature from 298 K to a certain value. Thus, the whole sintering process lasts longer and the atoms in the particles have longer time to interact with each other. As a result, the sintering becomes more thorough and the atoms would be much farther from their initial positions, leading to a larger neck width and MSD value.

A very interesting phenomenon is observed when the hollow nanoparticles are considered in the sintering process. Compared to those in figure 4, the results in figure 5 for all the hollow particle cases show an inverse trend of the temperature for fast neck growth at the end of the transition stage, as the heating rate is increased from 0.2 K ps$^{-1}$ to 1.0 K ps$^{-1}$. This indicates that melting stage happens beforehand on the temperature axis for the hollow spheres at an ultrahigh heating rate, which is quite different from that in the solid particle cases. In figures 5 and 6(b), the second arrow in each panel suggests the steep increases of the neck growth rate and MSD.
Figure 5. Comparison of the neck width in the simulations 7–12 for the hollow nanoparticle pairs at three different laser heating rates. Which occur at a lower temperature for the heating rate of 1.0 K ps\(^{-1}\). This implies that besides the size and heating rate, the geometrical structure of the nanoparticle could also play an important role in the sintering process.

This inverse trend can be found much more clearly in figure 9, which plots the melting temperature versus heating rate for both solid and hollow particle pairs with different sizes. Similarly, as shown in figure 10, the temperature for the fast neck growth to start and end are also collected from the curves at different heating rates in figures 4 and 5, and defined as the coalescence temperature for the particle pairs in this study. As can be seen, the hollow particles show a very different tendency from the solid ones. For each hollow particle pair, the melting point and coalescence temperatures show an obvious inverse trend with the increase of heating rate at a high level, as plotted in figures 9(b) and 10(b).

4.3. Comparison of hollow and solid particles

To gain insight into the effect of hollow structure on the inverse trend of fast neck growth temperature with the increase of heating rate to an ultrahigh level, a comparative study between the deformation evolutions of the solid and hollow spheres is conducted in detail, as shown in figure 11. To better understand the evolution of the inner free surface in hollow spheres, the variation of the cavity at different heating rates is also calculated and plotted in figure 12.

In figures 11(a) and (b), the crystalline structure of atoms is identified to understand the lattice transition during the sintering at various heating rates. The statistic distributions of the surface and disordered atoms with respect to temperature at three different heating rates actually reveal quite different patterns between the solid and hollow spheres. For the solid particles in figure 12(a), the three number density curves of the surface and disordered atoms almost coincide with each other as the temperature increases, until the first melting temperature of the lowest heating rate case is reached (see the curves from the initial point at 298 K to point C). In contrast, the number density curves of hollow particles in figure 11(b) start to show much divergence right after point A at a lower temperature, until the entire crystal structure in all three cases transits to amorphous after point D with the fraction of disordered atoms equaling 100%. Specifically, at the same high heating rate of 1.0 K ps\(^{-1}\), by comparing the configurations in figures 11(a) and (b), it can be found that introducing the inner free surfaces in hollow nanoparticles actually facilitates the surface diffusion and melting from both outside and inside, which makes the entire structure more unstable and easier to collapse. The initial larger surface-atom fraction in the hollow spheres also implies the increased number of active atoms and the increased free surface-area-to-volume ratio, so that the surface tension-driven-atomic migration becomes more dominant than that in the solid spheres during the sintering. Hence, the hollow nanoparticles tend to coalesce into one sphere more thoroughly.
than the solid ones at the same temperature level, as comparing the configurations at points C and D in figures 11(a) and (b).

Furthermore, for each specific hollow particle pair, the inverse trend of fast neck growth temperature at an ultrahigh heating rate could be explained by the different lattice structure transition from that at a low heating rate. The different way of structure transition under different heating rates can be inferred by the curves in figure 11(b), in which the fraction of disordered
atoms for the 1.0 K ps\(^{-1}\) case is larger than those for the other two lower heating rate cases (see points B, C and D). It also can be demonstrated by the gyration radius versus temperature curves at different heating rates plotted in figure 11(c). For the two lower rates of 0.04 K ps\(^{-1}\) and 0.2 K ps\(^{-1}\), the drops of gyration radius curves are step-like. In contrast, the rapid reduction of the gyration radius for the 1.0 K ps\(^{-1}\) happens at a lower temperature and appears much smoother, which is consistent with the inverse trend of the neck-growth/MSD versus temperature curves in figures 5 and 6. The step-like feature of the gyration radius evolution at lower heating rates is mainly due to the structure reconfiguration as well as the lattice transformation, which can be explained by the sliding of the lattice structure [19] in the early neck growth stage, and the transformation from fcc to hcp structure later during the premelting stage.

From the atomic configurations of the hollow particles at the lower heating rate of 0.04 K ps\(^{-1}\), as discussed above in section 4.1, in the transition stage with the plastic deformation (see point B in figure 3), a lot of intrinsic stacking faults (hcp atoms) are formed in the particles. These defects can disappear with the recrystallization of the lattice structure as the temperature rises (see point C in figure 3). Later in the end of the transition stage when premelting occurs, the re-formation of the hcp atoms are observed at points D and E. However, the same hollow particle pair shows a different scenario of structure deformation at the highest heating rate of 1.0 K ps\(^{-1}\), as illustrated by the atomic configurations in figure 11(b). As discussed earlier, the higher heating rate means that there is a shorter duration to heat the system from 298 K to a desired value, thus the duration for the interactions among the atoms is limited, which makes it harder to form regular planer defects. Instead of lattice sliding, the surface diffusion and melting from both inside and outside dominate the entire process of the laser sintering.

These arguments stated above can be further confirmed by a quantitative comparison of the hcp atoms density in figure 11(d) for the three different heating rates. For the 0.04 K ps\(^{-1}\) and 0.2 K ps\(^{-1}\) cases, the number density of hcp atoms becomes much higher than that in the 1.0 K ps\(^{-1}\) case after \(\sim 698\) K. That is the reason why the corresponding fraction of disordered atoms in figure 11(b) becomes smaller, which postpones the thorough transition from crystal to amorphous state. On the other hand, the curves of normalized cavity volume (the ratio of current cavity volume to initial cavity volume) versus temperature in figure 12 for the hollow spheres are also consistent with the tendency predicted by figures 11(c) and (d). Similar to the decrease of gyration radius curves, the reduction of the cavity volume is more stepwise and starts to occur at a much lower temperature below the melting point, at the lowest heating rate of 0.04 K ps\(^{-1}\). This result confirms that structural reconfiguration induced by the lattice sliding in the hollow shells, is an important mechanism during the low heating rate process. In contrast, at the highest heating rate of 1.0 K ps\(^{-1}\), the lattice structure transformation from fcc to hcp becomes much less dominant, and only a very small portion of hcp atoms is found in figure 11(d). Meanwhile, the sudden drop on the smoother cavity volume curve around the melting stage in figure 12 implies the direct collapse of the hollow interior instead of the thorough structural adjustment and reconfiguration. The transition from the fcc structure directly to disordered state is more likely to happen at this ultrahigh heating rate, which makes hollow spheres prone to coalescence and melt earlier at a lower temperature.

5. Conclusions

Based on MD simulations, a comparative study of both solid and hollow spherical silver nanoparticles with different sizes under laser sintering is conducted systematically in this paper. Three heating rates of 0.04 K ps\(^{-1}\), 0.2 K ps\(^{-1}\) and 1 K ps\(^{-1}\) are considered. Major findings from the study are summarized as follows:

- The solid state sintering of both solid and hollow nanoparticles can occur spontaneously at room temperature, and plastic deformation via partial dislocation activities and lattice slips are important mechanisms which contribute in a major way to the sintering of both solid and hollow nanoparticles. Either stable or transient stacking faults have been observed to occur in the smaller one in a pair if the two sphere sizes are not identical, indicating that the partial dislocations and lattice slips are more prone to form in smaller particles. Mechanical rotation can also be found during the neck growth, which is more obvious in the hollow nanoparticles.
The deformation evolution of the nanoparticle pair during laser sintering process can be mainly divided into three stages: relatively stable stage, transition stage, and melting stage. At each specific heating rate, it is found that melting starts at a higher temperature when the particle diameter becomes larger for both solid and hollow nanoparticles. An interesting inverse trend of the temperature for fast neck growth has been observed at the end of the transition stage for all the hollow particle cases, as the heating rate rises from 0.2 K ps$^{-1}$ to ultrahigh 1.0 K ps$^{-1}$, which is quite different from the solid nanoparticle cases. This phenomenon implies that in addition to the size and heating rate, the geometrical structure of the nanoparticle could also play an important role in the sintering process.

In hollow nanoparticles, more active atoms and larger free surface-area-to-volume ratio make the surface-tension-driven atomic migration more dominant than that in the solid spheres during the laser sintering. At a low heating rate, the plastic deformation combined with structural reconstructions induced by the lattice sliding in the hollow shells is found to be an important mechanism during the heating process. At an ultrahigh heating rate, though there is still a small portion of hcp atoms formed, transition from fcc crystal directly to disordered structure from both outside and inside becomes more dominant, facilitated by the introduction of the inner free surfaces in hollow shells. The entire hollow particle pairs thus show an obvious tendency to coalesce and melt at a lower temperature level than with a low heating rate.

The findings reported in this paper might be useful for the future investigation of different kinds of nanoparticle sintering in which both solid and hollow structures are involved. In a real laser sintering process, controlling heat flux is more common and easier than controlling temperature. Further investigations can be focused on the sintering process of particles heated by means of constant heat flux. Meanwhile, different metallic particles besides the silver ones studied currently, should be considered in the future study to better understand the effect of interior structures during the sintering process.

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Figure 12. Normalized cavity volume as a function of temperature for the hollow particle pairs of (a) $10a$ versus $10a$ and (b) $16a$ versus $16a$ at different heating rates.

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