Using molecular dynamic simulations to describe the solid-liquid phase transition of lead nanoparticles with different nano-geometries

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Abstract

In this study, three lead (Pb) nanoparticles, including cone, sphere and cylinder, are modeled and melted using molecular dynamic (MD) simulations. The choice of initial geometries mainly affects the initial and middle stages of phase transition. Initially, the melting point of the cone model is much lower than other two models. This is because the transition of the cone model is induced by its sharp edge, which is prone to be melted. Then, the transition of all models keeps toward the centre of mass. Meanwhile, cone and cylinder models are deformed into spheres. The deforming rate is higher than transition. Finally, all three models were fully melted into the shape of the spheres. Therefore, initial Pb nano-geometries do not affect the final stage of the phase transition.

1. Introduction

As a critical non-ferrous metal material, lead (Pb) is broadly applied in medical, mechanical and energy storage products [1]. For example, the Pb battery has been applied as a utility energy source for the automotive industry [2]. However, many pieces of research pointed out that Pb is also a potential threat to human health, such as urinary, cardiovascular and neurologic diseases [3].

In decades, the nano-sized Pb particle also has attracted researchers’ concern. D L Zhang et al reported that the Pb nanoparticles were precipitated from Pb/Al solid solution at 325 °C–380 °C [4]. Xiao Ming Chen et al found that the melting of the Pb nanoparticles surface brought the peak of internal particle friction [5]. Sunil K. Karna et al measured that the magnetic moment of icosahedral Pb particles with 7 nm was about 140 times larger than that of Face Centered Cubic (FCC) Pb particles with 6 nm [6]. Anna Moros et al analyzed the melting point and enthalpy of Pb nanoparticles, which were embedded with aluminum polycrystalline [7]. Seyed Hossein Hosseinia prepared the nanocomposite with Pb nanoparticles [8]. Sadhasivam Thangarasu et al developed the Pb-carbon hybrid battery using Pb nanoparticles [9].

In terms of the melting behaviours of Pb nanoparticles, molecular dynamic (MD) simulations could be a credible researching approach. Previously, MD simulations were applied to describe phase transitions of various metals, such as Ir/Rh nanoalloys [10], Al nanoparticles [11–13], bulk Al [14], Ag57Cu13 nanoalloy [15], Fe [16, 17], W [18], Ta [19], Li [20], Au-Pd nanoalloys [21], Pd34Pt14 nanoalloy [22], Zr68Pd32 nanowires [23], Ag nanoparticles [24], Nb (1 1 0) nanofilm [25], Fe-Ni-Cr nanoparticles [26] and so on. In this study, we are mainly focused on the melting process of Pb nanoparticles. The initial aim of this investigation was not only about the phase transition of Pb nanoparticle itself, but also the difference caused by various nano-geometries.
2. Method: MD simulations

As figure 1 shows, three initial models, including sphere, cylinder and cone, were built for the present study. In which, their lattice constant was 4.95 Å, and the type of crystal was FCC. Totally, there were 17265, 26256, and 9060 Pb atoms in those models respectively. Then, all three models were placed at the centre of a 40×40×40 nm³ simulation box with periodical boundaries respectively. After a 1 ns release process at 300 K, all models were linearly heated until 800 K in 1 ns, which means that the set heating rate was about 500 K ns⁻¹. With Nose [27]/Hoover [28] thermostat theory, the entire heating process was linearly controlled by the canonical

Table 1. Summary of all programs applied in this study.

| Software | Version | Usage | Citation |
|----------|---------|-------|----------|
| LAMMPS | 64bit-15Apr2020 | MD simulations platform | [30] |
| VMD     | 1.9.3   | Atomic structural analysis | [31] |
| OVITO   | 3.0.1   | Rendering the configuration | [32] |

Figure 1. The configuration of three initial models.

Figure 2. The system potential energy of three models.
Figure 3. The MSD plot of three models.

Figure 4. Evaluation of atomic displacements during phase transitions.
ensemble (NVT). The timestep of all above simulations was 1 fs, and the temperature damping parameter was 100 fs.

In this MD simulation study, an Embedded-Atom Method (EAM) force field was utilized to describe the atomic interactions. This EAM force field was developed and trained by Kun Wang et al [29]. Additionally, all programs used in this investigation and article are listed in table 1 below.

3. Results and discussion

3.1. Energy and displacement

Above all, the solid-liquid phase transition is evaluated by the plots of system potential energy. As shown in figure 2, the entire heating simulations bring up the potential energy of the three models. Along with the appearance of phase transition, all three plots show the jump of potential energy in various degrees. It seems that the vertical deviation of the potential energy jump represents the extent of transition, and the horizontal position of jump represents the melting point of the nanoparticle. Therefore, the cone-like Pb model has the lowest melting point and extent of transition. Despite the absolute value of energy, sphere and cylinder models show a similar transition process. In order to further confirm the transition temperatures, Mean Square Displacement (MSD) of three models are plotted as figure 3. In which, the extent of atomic movement could be represented by the slope of plots. The displacement of Pb atoms is accelerated with the happening of phase transition. It is obtained that the melting point of the cone model is about 560 K, while both cylinder and sphere models are melted at about 640 K. This result is in good agreement with figure 2. Comparing with the melting point of tabulated bulk Pb [7], the value for the cone-like model is obviously declined.
Furthermore, the distribution of atomic displacement during transition is analyzed as well. Figures 4(a)–(c) are plotted for cone, sphere and cylinder models respectively. While scanning vertically, a peak of displacement appeared at the top, bottom and middle of the cone. This is because the deformation started from both edges to the center. Similarly, cylinder model shows two peaks toward the centre. As an isotropy geometry, the distribution for the sphere model is almost equal. Additionally, figure 4(d) shows that the value distribution of the sphere model is more narrow than the anisotropy cylinder model.

3.2. Morphology and microstructure
In this section, the phase transition process of each model is discussed according to the particle configuration and crystal style identifications. Figures 5–7 illustrate the melting process of cone, sphere and cylinder models, respectively. In those figures, the left column is the overall morphology, and the right column is the cross-section of nanoparticle with 1 nm thick. The transition is demonstrated by the decline of Pb atoms in FCC style lattice. Whatever the initial nano-geometry was, the melted Pb nanoparticles are finally formed as irregular spheres with high kinetics.

Generally, all three models have shown an inward transition process. Due to the vertically asymmetric microstructure, the melting of the cone model was prone to start at the sharp edge. So the melting point of which was lower than other models. Then, the liquid phase spread to the core of the nanoparticle. Although the upper edge melted earlier than the bottom, it doesn’t mean that the upper half of nanoparticle melted earlier as well. The observed final region with solid phase is still on the mass centre of the melted cone model. Next, the sphere model shows the lowest change in nano-geometry during the transition. Different from the cone model, there is no clear starting site of sphere melting. The liquid phase spreads to the core of the sphere from all 360 degrees.
Finally, the transition of the cylinder model is similar to the sphere model. According to the cross-section of the cylinder, the spread rate of the liquid phase in each direction is equal as well. Additionally, the deformation of the cylinder and cone models make them deform into the spheres, so the final stage of all models are accurately the same. Therefore, the deformation rates are higher than the spread of the liquid phase. They have different beginnings, but the same ending.

4. Conclusion

MD simulations have been performed to investigate the critical effect of initial geometry on Pb nanoparticle transitions. The rank order of their melting points is cone < sphere = cylinder. The decline of cone melting temperature is induced by its sharp edge. On contrast, sphere and cylinder models are melted simultaneously from their surface. All models experience an inward transition process. Associated with the enlarging of the liquid phase, cone and cylinder models are deformed into spheres. Before fully melted, those models have been the same on shapes. To some extent, the final stage of the cone and cylinder could also be considered as the melting of the sphere. As an isotropy nano-geometry, the change of sphere model during transition is too little to be directly observed. Despite the sharp edge of the cone, the spread rates of the liquid phase from all directions are almost equal. At last, the phase transition of all models ended at the mass centre of the final spheres.

Figure 7. The phase transition process of the cylinder model.
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Data availability statement
The data that support the findings of this study are available upon reasonable request from the authors.

ORCID iDs

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