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Molecular dynamics simulations of the melting process of Pb nanofilms

Botao Liu

School of Materials Science and Engineering, Central South University, Changsha, China

8204190118@csu.edu.cn

Abstract. Metallic nanofilms have attracted plenty of research interests because of their important applications in integrated circuits and thermoelectric conversion technology. However, there has not been much research discussing the thermodynamic properties of nanometal films with thickness less than 5 nanometers. To fill this research gap, this article investigates the melting behavior of Pb nanofilms through molecular dynamic simulations. The results show that most nanofilms experience a turning point in their potential energy during melting, followed by a sharp decrease due to the collapse of their previous two-dimensional structure. The melting temperature of nanofilms is found to decrease with decreasing thickness, following the trend predicted by the Safaei model, except for nanofilms with 1-3 atomic layers, which exhibit an abnormally high melting point. It is suggested that this anomaly is due to the reconstruction of nanofilms into a more stable structure, possibly the {111} plane. This study can inspire research on the thermal stability and structural evolution of nanometal films and aid in their future design and preparation.

Keywords: molecular dynamics, melting process, Pb nanofilms.

1. Introduction

Metallic nanofilms, as a type of nanomaterials, are of great significance in modern industries like integrated circuits and thermoelectric conversion technology because of their unique electrical and thermal performances [1]. To ensure the reliability and capability of nanofilms, it is very important to understand their thermal stability, and as a fundamental parameter of materials, melting point can help better study their thermodynamic properties.

Nowadays, plenty of experiments and theories have already suggested that the melting point of nanomaterials is highly depending on their sizes [2-5]. As the sizes of nanoparticles decrease, the surface-to-volume ratios of particles will soar substantially, and the atoms distributed on the surface have totally different cohesive condition with the atoms distributed in the bulk, which will significantly change their thermodynamic properties. A specific result of this reason is that the melting point of nanoparticles decreases as their size reduces. As for the exact numerical relationship between these two parameters, Safaei et al. proposed a reasonably mathematical model by utilizing the proportional relationship between the cohesive energy of surface atoms and internal atoms, which is also applicable for calculating the melting point of nanofilms [6]. The equation can be written as

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$$\frac{T_{mn}}{T_{mb}} = 1 - (1 - q)\frac{n_s}{n_t} \quad (1)$$

where T_{mn} and T_{mb} are respectively the melting temperature of nanoparticle and bulk, q is a parameter representing the coordination number ratio of surface to volume, n_s and n_t are respectively the numbers of surface atoms and total atoms. Their work also suggests that the calculated theoretical values are in best agreement with experimental value when q = 1/8 or 1/4. However, for nanofilms with thickness less than 5 nm, there has not been much research discussing them. Therefore, it is of great interest to carry out a further study to better understand the melting behavior of nanofilms with thickness less than 5 nanometers.

For ultrathin films, the limited experimental conditions make it hard to directly measure their melting processes [7]. Fortunately, the availability of computational simulations has provided a promising avenue for addressing this challenge. Molecular dynamic (MD) simulation is an essential simulation technique studying the movements and interactions of molecules based on the classical mechanics models and potential functions to predict the materials behaviors [8]. This approach enables the numerical exploration of underlying mechanisms and regulations governing material properties, thereby circumventing the limitations of conventional empirical and intuitive research. In this paper, MD simulation is utilized to study the melting processes of the Pb nanofilms with thickness under 10 nm.

2. Computational methodologies

2.1. Potential function

The embedded-atom method (EAM) is a commonly used atomic-scale computational method for simulating the structure and properties of metallic materials [9]. It is based on the interatomic interactions, represented as the embedded energy of an atom's charge in the surrounding electron density of other atoms. This method can account for the electron structure of metal atoms and their interactions, providing relatively accurate computational results. The EAM method has been successfully applied in simulating the mechanical properties, thermodynamic properties, point defect behaviors, and phase transitions of metals [10]. In this paper, EAM function from Hoyt et al. is used to characterize the interatomic interactions of Pb [11].

2.2. MD simulation

The basic parameter of the physical properties of Pb are listed in Table 1. The initial size of simulation box is set as $20a_0 \times 20a_0 \times 20a_0$ in this work. The supercells are initialized with a (001) plane size of $20a_0 \times 20a_0$ in the x-direction [100] and y-direction [010], and nine different thicknesses are calculated for the z-direction [001] (L_n, n = 1, 2, 3, 4, 5, 6, 7, 8, 9, representing the number of atom layers). The periodic boundary conditions are used in three directions. All atoms are arranged in an FCC crystal lattice within the supercell. Then, each Pb nanofilm is heated from 20 K to 1000 K within 1×10^6 time steps in NPT Ensemble (P = 0 atm).

Table 1. The basic parameter of the physical properties of Pb.

Lattice Structure	Lattice Parameter a_0(nm)	Relative Atomic Mass m	$T_{mb}(K)$
fcc [12]	4.95 [12]	207.2 [13]	600.6 [14]

The length of every time step is 1 fs. The Nose-Hoover thermostat is used for the temperature control of the system [15].

3. Results and discussion

To investigate the changes of the system state with the increase of temperature, the potential energy of per Pb atom is recorded every 10000 steps. As shown in Figure 1, it can be seen that the potential energy of nine nanofilms all increases linearly with the temperature before and after the melting point.

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When the temperature reaches the melting points, for L1 to L3 and L6 to L9 nanofilms, their potential energy will experience a turning point and undergo a period of accelerated increase, followed by another turning point and a sharp decrease. However, for L4 and L5 nanofilms, their potential energy will not experience the first turning point (which is regarded as the melting point) but will decrease directly. The unique drop of potential energy is because during the melting process, the previous two-dimensional structure of nanofilms will collapse, which will make the entire system transform into the bulk structure. Therefore, the surface energy of the system reduces, leading to the drop of the potential energy. Such phenomenon is also observed in the study from Zhou et al. and Wen et al. [16,17]. the reason is assumed that the energy barrier for structure collapse in L4 and L5 nanofilms is so low that their potential energy does not need to undergo the period of rapid heating stage before the sharp drop. It is also notable that the caloric curve of L1 nanofilm and L2 nanofilm will overlap for a period before melting. It is because the single atomic layer of Pb [001] cannot exist stably and will rapidly collapse into a two-atomic layer structure.

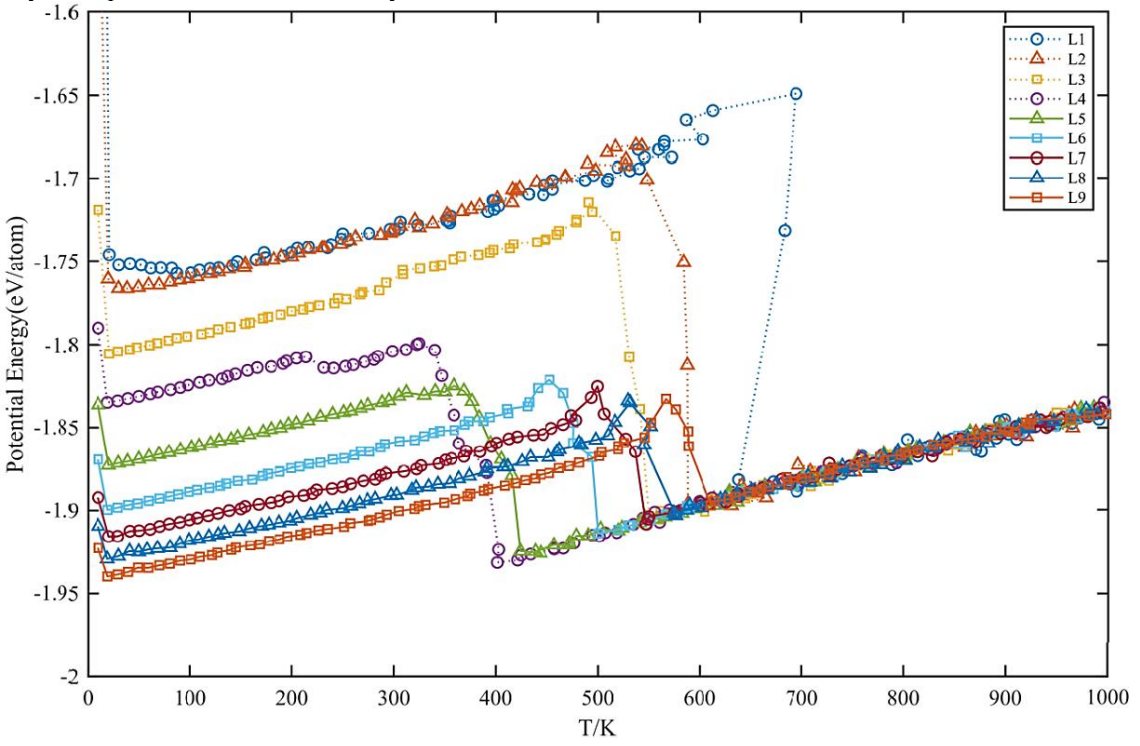

Figure 1. The potential energy as a function of temperature for Pb nanofilms.

Then, to investigate the relationship between Pb nanofilms melting temperature and its thickness, L1 to L9 nanofilms' melting points are plotted in Figure 2 and compared to the Safaei's model, formula (1). As for the term n_s/n_t in formula (1), in nanofilm system, it can be approximated as the number of surface atomic layers divided by the total number of atomic layers, which is $2/n$. For parameter q, two curves of Safaei's model are respectively plotted with $q = \frac{1}{4}$ and $q = \frac{1}{8}$. In Figure 2, it can be clearly seen that the melting point of nanofilms L4 to L9 decreases with decreasing thickness, following the trend predicted by the Safaei model. However, for nanofilms L1, L2, and L3, their melting points anomalously increase with decreasing thickness. From the observation of the structure change of the L2 nanofilm during simulation (Figure 3), it is speculated that this anomalous increase is because Nanofilms with fewer atomic layers are more likely to exhibit wave-like deformations, which can lead to the formation of more thermally stable structures. Referring to the work of Zhou et al. [16], it is speculated that the more stable structure should be the Pb {111} plane, which has a denser stacking and thus lower surface energy. Apart from L2 nanofilm, such deformation can also be observed in L1 and L3 nanofilms.

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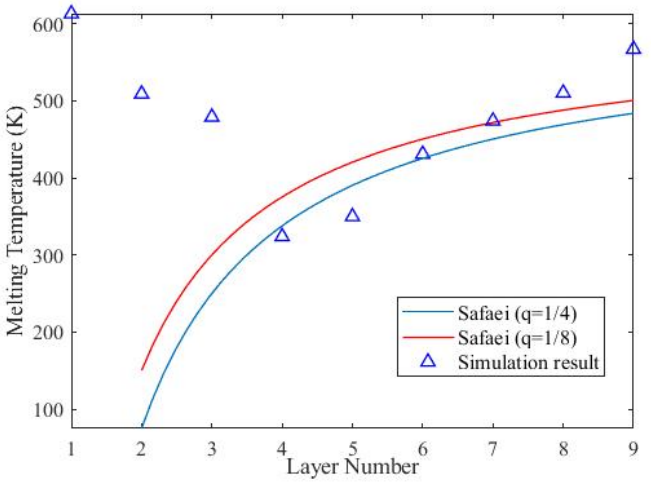

Figure 2. The melting point of nanofilms with different layer numbers (compared with Safaei model [6]).

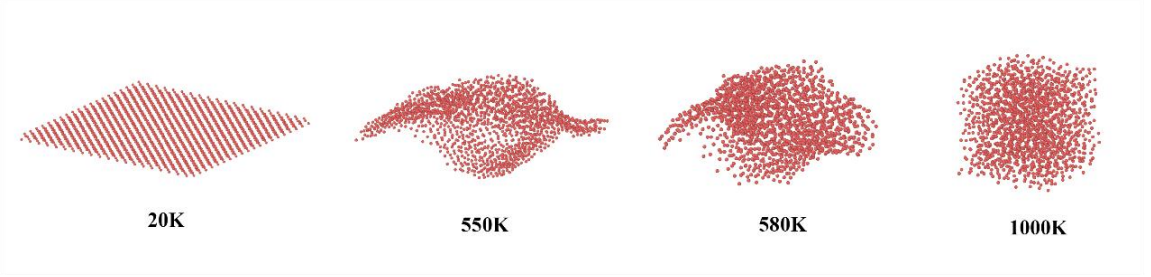

Figure 3. The 3D structure of L2 nanofilm at 4 typical temperatures.

4. Conclusion

In this work, the melting process of Pb nanofilms was investigated with difference thickness via MD simulation. The result shows that when the temperature reaches the melting points, the potential energy of most nanofilms undergoes a turning point, experiencing a period of accelerated increase, followed by another turning point and a sharp decrease. It is suggested that the unique drop in potential energy is due to the collapse of the previous two-dimensional structure of nanofilms during the melting process, transforming the entire system into a bulk structure. Meanwhile, the result of the melting temperature of Pb nanofilms as a function of thickness illustrates the nanofilm with 1 to 3 atomic layers have abnormally high melting points, it is speculated that this phenomenon is because of the reconstruction of nanofilms into more stable structure and one possible structure is {111} plane. Overall, this is the first study to discover the unusual high melting point of nanofilms at the scale of several-atom layers (1-3 layers). This work can provide inspiration for the research on the thermal stability and structural evolution of nanometal films and help in the future design and preparation of nanometal films. Future research could more deeply explore the mechanisms underlying this unusual high melting point of nanofilms.

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