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Size and temperature consideration in the liquid layer growth from nanovoids and the melting model construction

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HIGHLIGHTS

- A united model for the crystal melting point from nanovoids is established.
- Melting point increases with decreased void size.
- The result is expected from the negatively curved surface of the void.
- The prediction is agreed well with the MD simulation results.

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ABSTRACT

A new model for the solid melting point $T_m(D)$ from nanovoids is proposed through considering the liquid layer growth behavior. This model, which does not have any adjustable parameter, introduces the classical thermodynamic treatment, i.e., the liquid nucleation and growth theory, for nanoparticle melting. With increased void diameter D, $T_m(D)$ approaches to T_{m0}. Moreover, $T_m(D) > T_{m0}$ for a small void (T_{m0} is the bulk melting point). In other words, the solid can be significantly superheated especially when D decreases, even if the difference of interface energy is larger than zero. This finding can be expected from the negatively curved surface of the void. The model predictions are consistent with the molecular dynamic (MD) simulation results for argon solids. Moreover, the growth of liquid layer from void surface relies on both size and temperature, which directly determine liquid layer thickness, and only when liquid layer thickness reaches to a critical value, can void become instable.

1. Introduction

Numerous melting-related phenomena are unsolved fundamental material problems, and are thus the subject of continuous experimental and theoretical studies [1,2]. Such phenomena include surface premelting, melting below bulk thermodynamic melting point T_{m0}, and superheating above T_{m0} during very fast heating [3,4]. Usually, heterogeneous nucleation on free surfaces occurs as a result of reduction in surface energy [5,6], i.e., $\Delta\gamma$ ($=\gamma_{sv} - \gamma_{sl} - \gamma_{lv}) > 0$ (γ is the interface energy; s, l, and v denote solid, liquid, and vapor phase, respectively; and Δ means the difference), which inevitably leads to the appearance of a molten nanometer-thick layer [7,8], The decrease in melting point with the reduction in particle diameter D down to nanoscale is widely accepted [9,10] because of the increase in the surface-to-volume ratio, and it has also been found for nanostructured materials as the grain size decreases [11]. A significant amount of superheating can be achieved if surface melting is suppressed, for example, in nanoparticles embedded in a matrix [12,13] or in computer simulations using periodic boundary conditions [5,14,15]. Several attempts to clarify the mechanisms of melting induced by defects such as vacancies [16,17], interstitials [18] and lattice dislocations [19–21] have also been made. The results of these studies show that defect-induced melting requires localized disorder as a solid is heated toward its T_{m0}.

Nanovoids, which can be defined as clusters consisting of many vacancies in a given matrix, exist in many real materials. As is known, vacancy concentration plays an important role and the melting point will decrease with vacancy concentration enhanced, which can be found in some studies [22–27] where the models by considering vacancy concentration in melting point for nanoparticles are constructed. The corresponding melting point of nanoparticles is always lower than T_{m0}. However, this phenomenon does not occur for nanovoids. The key difference between them is

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surface curvature. Although $\Delta\gamma > 0$, solid superheating exists, and the melting point higher than T_{m0} increases with void size D dropping [28–31]. Moreover, some other thermodynamic properties from nanovoid surfaces have a similar size effect, and the widely accepted reason is the negatively curved surfaces [28]. Thus far, the simplest treatment is to adjust the curvature value. However, the mechanism of melting from voids is still unknown and requires further research [32,33].

For melting, surfaces have the potential to become liquid nuclei to melt solids, except for surfaces with $\Delta\gamma < 0$, because of the higher stability of the surface even above T_{m0} [34]. As long as $\Delta\gamma > 0$ is satisfied, surface melting generally occurs and leads to the formation of a liquid layer, and then complete melting occurs under melting point. This process can also be found in MD simulation for a void. As presented by Bai and Li [35], there are four stages for the argon solid melting from a void surface: (I) the solid is stable and characterized by a stable solid–vapor interface; (II) the surface melts and the solid coexists with a stable, thin layer of liquid nucleating around the void surface; (III) the partially melted solid fills the void, the liquid and solid coexist, and the solid host is stable; and (IV) compete melting. It is clear nanovoids have a similar melting process to that of nanoparticles [36–38], despite the distinct difference, i.e., curvature: a liquid layer nucleates and grows on the void surface with T enhanced. Thus, the derivatives and conclusions for flat or positively curved surfaces can be applied to negatively curved ones to some extent. Based on this consideration, the thermodynamic theory of liquid nucleation and growth for nanoparticles melting is introduced and extended into nanovoids in this work to clarify the melting process from nanovoids and explain the inherent mechanism. The effects of both void size D and temperature T on the liquid layer thickness and the corresponding melting point are modeled. With liquid layer growing, the critical condition for melting is also predicted. The established theoretical model shows a good agreement with MD simulation results.

2. Model

According to the thermodynamic treatment for nanoparticles [39–41], a similar melting process from a void surface is considered. As the temperature is gradually increased, a liquid layer first forms on the void surface, and continuously increases until solid completely becomes liquid. Fig. 1 shows the schematic of this melting behavior. The bulk solid is infinite with a nanovoid, and any other defect or surface is neglected as shown in Fig. 1a. In the melting process, a liquid layer nucleates and grows around the void surface in Fig. 1b. To resolve the liquid layer thickness with temperature enhanced, the change in Helmholtz free energy between the system of the complete solid (Fig. 1a) and that of the non-melted solid with a liquid layer around void (Fig. 1b) should be calculated. Firstly, from a thermodynamic perspective, the Helmholtz free energy of a system with a completely solid (Fig. 1a) can be read:

$$F_s = \mu(T,P)N_s - P_sV_s + \gamma_{sv}A_{sv} \tag{1}$$

where $\mu(T, P)$, a function of the local temperature T and pressure P, is the chemical potential per atom; the surface area (A_{sv}) is related to the void size D; and the volume (V_s) is determined by the total number of atoms in a system (N_s). In Eq. (1), $\mu(T, P)$ can be obtained in reference to the bulk melting point T_{m0} and the externally applied pressure P_0 [41]:

$$\mu(T,P) = \mu(T_{m0},P_0) - s_s(T - T_{m0}) + v_s(P - P_0) \tag{2}$$

where s_s and v_s are the entropy and volume per atom of solid, respectively. In Eq. (2), for any non-plane surface, the pressure on surface P is no longer P_0, and an additional pressure arising from the curvature effect is created. For a nanovoid with diameter D, the difference of pressure can be denoted as $P - P_0 = 4f/D$ according to the Laplace–Young equation, where f is the surface stress of a solid–vapor interface. This additional pressure P in Eq. (2) induced by surface curvature is the primary difference, which leads to different change in melting point for nanoparticles and nanovoids when compared with bulk. Then, by combining this P with Eq. (2) and substituting them into Eq. (1), the final Helmholtz free energy of this fully solid system is rewritten:

$$F_s = \mu(T_{m0},P_0)N_s - s_s(T - T_{m0})N_s - v_s\left(\frac{4f}{D}\right)N_s - \left(P_0 - \frac{4f}{D}\right)V_s + \gamma_{sv}A_{sv} \tag{3}$$

The term involved in Eq. (3) (the surface stress f) can be deleted and Eq. (3) can be simplified as the following expression:

$$F_s = \mu(T_{m0},P_0)N_s - s_s(T - T_{m0})N_s - P_0V_s + \gamma_{sv}A_{sv} \tag{4}$$

Then the Helmholtz free energy for the system of the unmelted solid with a liquid layer could be established in a similar way with

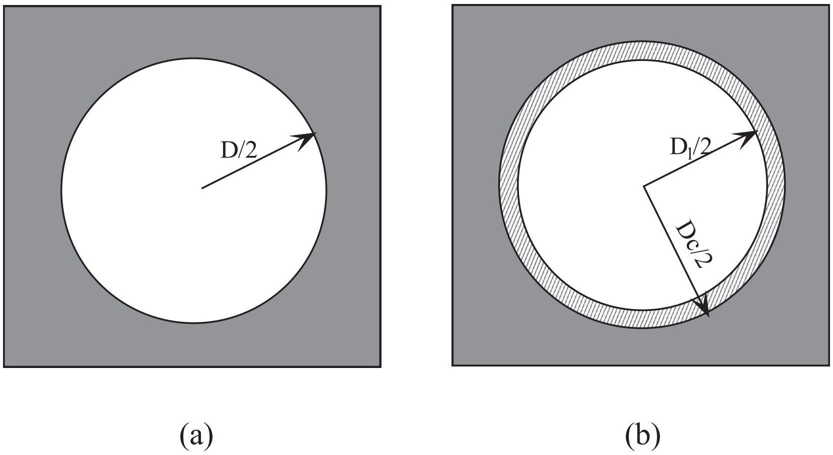

Fig. 1. The two configurations demonstrating the melting process from a void: (a) fully solid phase with a void of diameter D, (b) solid crystal with a liquid layer around the void, forming a solid–liquid interface (of diameter D_c) and liquid–vapor interface (of diameter D_l).