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# Submicrometer-scale molecular dynamics simulation of nucleation and solidification from undercooled melt: Linkage between empirical interpretation and atomistic nature

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ABSTRACT

Nucleation and solidification from the undercooled iron melt are investigated from the atomistic point of view by large-scale molecular dynamics (MD) simulations up to 12 million atoms in systems of the submicrometer-scale. There exist some amount of atoms with icosahedral configuration in the undercooled iron melt and these atoms increase with decreasing temperature. It is expected that accumulation of atoms with icosahedral configuration in the initial $\beta$-relaxation regime of nucleation is the key to initiate the formation of bcc phase. On the other hand, mobility of atoms in the undercooled melt decreases drastically with decreasing temperature. These two competing factors in the atomistic scale are considered to derive a critical temperature at which nucleation rate becomes maximum, which agrees with a classical theory for homogeneous nucleation. Moreover, the Avrami exponents during solidification are approximately estimated to be close to 3 and 4 in two- and three-dimensional grain growths, respectively, which also agrees with empirical interpretation. Our novel approach utilizing the high parallel efficiency of the GPU supercomputer successfully links the empirical interpretation in metallurgy with the atomistic behavior of nucleation and solidification, which enlarges the application range of MD simulations for the study of structural materials.



## 1. Introduction

Solidification microstructures have been widely studied since they directly affect properties of products of metals and alloys. Therefore, many efforts have been made over many years [1,2] to control the solidification microstructures as planned as well as to understand fundamental natures of solidification. However, it is still challenging to control solidification microstructures with a high degree of accuracy since the solidification process is affected by many aspects of physics over wide spatiotemporal scales. Moreover, it is generally difficult to observe these processes directly by experimental approaches, although several pioneering works have achieved in situ observations of the solidification process [3–8]. Therefore, computational studies have contributed to shedding light on the nature of the solidification and subsequent grain growth processes. For example, Monte-Carlo (MC) simulations have been widely employed to investigate grain growth [9–11], recrystallization [12], weld solidification [13] and so on. The front tracking method [14,15] and cellular automata [16–19] are also employed to examine grain growth [15,16,18] and dendritic growth [14,17,19]. In addition, phase-field simulations [20–23] have become a major tool to investigate solidification microstructures [24–27] since it is not necessary to explicitly track the position of a sharp interface in complex microstructural patterns in the phase-field model. Combined with the recent rapid progress in high-performance computational environments [27], phase-field simulations now cover some aspects of multiple physics during solidification such as the competitive growth of dendrites [28–30] and the effect of convection [31–33]. The lattice Boltzmann method [34,35] is also useful for a large-scale fluid computation in solidification problem. Moreover, a dendritic needle network (DNN) model [7,36] is recently proposed for the multiscale modeling of

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dendritic spacing selection during solidification. Most of above-introduced computational studies are based on continuum or lattice-based models.

On the other hand, molecular dynamics (MD) simulations have contributed the understanding of the nature of solidification microstructures from the atomistic point of view [27,37,38]. As major examples, MD simulations have been widely employed to estimate interfacial properties at high temperature since it is not straightforward to measure them directly in the production process. For example, the solid–liquid interfacial energy of metals has been widely investigated using various techniques such as the cleaving technique [39–41] applying an external cleaving potential to estimate the anisotropic solid–liquid interfacial energy, the capillary fluctuation method [42–45] in which the interfacial stiffness is extracted from the fluctuation of the solid–liquid interface profile, the small particle method [46–49] based on the Gibbs–Thomson effect in small nanoparticles in an undercooled melt. In addition, the kinetic coefficient of a solid–liquid interface and its anisotropy have been investigated [44,48]. The representative values of interfacial parameters estimated from MD simulations are well summarized in Ref. [27]. In parallel with the estimation of interfacial properties, MD simulations are also utilized to discuss the atomic dynamic behaviors in undercooled melts. It has been confirmed from various MD studies [50–53] that individual atoms in undercooled melts are trapped in transient cage structures in a short relaxation time (called $\beta$–relaxation regime) and those atoms need sufficiently long relaxation time (called $\alpha$–relaxation regime) to escape from the cages. Nucleation from such undercooled melts are also investigated by MD simulations [53–56], which have showed that the formation of nucleus is related to the dynamical heterogeneity in the $\alpha$–relaxation regime. In particular, Hou et al. [53] revealed that there exist many icosahedral clusters in the undercooled melt of sodium in the initial $\beta$–relaxation regime, and subsequently icosahedral clusters disaggregate followed by the formation of many bcc clusters at the $\alpha$-relaxation regime. Moreover, there are many computational studies focusing on the fundamental aspect of nucleation from the atomistic viewpoint. For example, Auer and Frenk [57] discussed the discrepancy in the nucleation rate from those obtained using classical nucleation theory and the hard-sphere model. Bokeloh et al. [58] investigated nucleation in undercooled nickel by a combination of differential scanning calorimetry (DSC) experiments and MC simulation and found a nonspherical geometry of crystalline clusters, fluctuating between prolate and oblate shape at a given size. Non-classical nucleation behavior from supercooled nickel during rapid quenching is also investigated by the MD simulation [59], which concluded that the saddle point droplet consists of randomly stacked planar structures with an in-plane triangular order at nucleation. Although these studies have shed light on the nature of nucleation from the atomistic point of view, these studies are limited to the formation of one nucleus (or a few nuclei) using the systems consisting of 10–100 thousand atoms. Several pioneering works have achieved nucleation in large systems with more than million atoms in the early stages [60,61]. However, it is not straightforward in general to achieve nucleation naturally in the large system with more than million atoms due to the computational limitation, whereas it is essential to investigate the multiple-nucleation in the large system in order to discuss solidification microstructures precisely.

Under such circumstances, we have developed our own code for carrying out MD simulations on a graphics processing unit (GPU), which enables the handling of one million atoms in MD simulations over a period of nanoseconds and has a computation time of several days [62–64]. Using this code on a GPU supercomputer, we successfully achieved the statistical sampling of multiple-nucleation and subsequent microstructure formation processes in the quasi-two dimensional cell with one million atoms [65], which revealed that the nucleation rate and the incubation time of nucleation as functions of temperature have characteristic shapes with a nose at the critical temperature. That is, the knowledge obtained only from the trajectory of atoms agrees well with a classical theory from the macroscopic point of view. This new insight shows us new possibility to link empirical interpretation in metallurgy with the atomistic behavior of nucleation and solidification assisted by large-scale MD simulations. One of important attempts in this direction is to shed light on dominant atomistic processes hardly uncovered within a classical nucleation theory by elucidating statistical behavior of $\beta$– and $\alpha$–relaxation processes and also by identifying a dominant factor(s) competing with such relaxation processes. Furthermore, it is an important and challenging issue to evaluate a central quantity in a continuum theory for growth process by means of the atomistic simulations. To this end, homogeneous nucleation and solidification are closely investigated by large-scale MD simulations up to 12 million atoms in systems of submicrometer–scale, which are performed on the GPU supercomputer, TSUBAME2.5. In particular, the two competing factors dominating homogenous nucleation [2,65] and the Avrami exponent showing the growth mode during phase transformation [66,67], which are typical empirical indices regarding solidification microstructures, are closely discussed from the atomistic point of view.

## 2. Simulation methodology

The simulation methodology basically follows previous studies [63–65]. The Finnis–Sinclair (FS) potential [68] is employed for the interatomic potential between iron atoms, which is one of the most established potentials for body-centered-cubic (bcc) metals. It has been confirmed in previous studies that the FS potential can reproduce the solidification from the undercooled iron melt both in cluster [69–71] and bulk [63–65] systems accurately. The total energy of the FS potential, $E$, is expressed as follows:

$$E = \frac{1}{2}\sum_i \sum_j V_{ij}(r_{ij}) - A\sum_i \sqrt{\rho_i} \tag{1}$$

$$V_{ij}(r_{ij}) = \begin{cases} (r_{ij}-c)^2\left(c_0 + c_1 r_{ij} + c_2 r_{ij}^2\right) & (r_{ij} \le c) \\ 0 & (r_{ij} > c) \end{cases} \tag{2}$$

$$\rho_i = \sum_{j \ne i} \phi(r_{ij}) \tag{3}$$

$$\phi(r_{ij}) = \begin{cases} (r_{ij}-d)^2 + \beta\dfrac{(r_{ij}-d)^3}{d} & (r_{ij} \le d) \\ 0 & (r_{ij} > d) \end{cases}, \tag{4}$$

where $V$ is the repulsive term, $r_{ij}$ is the bond length between atoms $i$ and $j$, $\rho$ is the total electronic charge density at the site of atom $i$, which is constructed by the rigid superposition of atomic charge densities $\phi$, $A$ is the binding energy, $c_0$, $c_1$, and $c_2$ are the free parameters used for fitting experimental data, $c$ and $d$ are cutoff parameters assumed to lie between the second-nearest- and third-nearest-neighbor atoms, $\beta$ is a parameter used to introduce a maximum value of $\phi$ within the first-nearest-neighbor distance. The parameters for bcc iron from the original FS paper are employed [68] (Table 1). A leapfrog method is used to integrate the classical equation of motion with a time step of 5.0 fs. A Berendsen