

Article

Substrate Orientation Dependence of Local Ordering and Crystal Nucleation in Al Melts

Qi Zhang ^{1,*} , Yamei Jin ², Sai Tang ³ and Jiankai Ma ⁴¹ College of Electronic and Information Engineering, Anshun University, Anshun 561000, China² College of Chemistry and Chemical Engineering, Anshun University, Anshun 561000, China; 15739333181@163.com³ Powder Metallurgy Research Institute, Central South University, Changsha 410083, China; s.tang@csu.edu.cn⁴ Xi'an Rare Metal Materials Institute Co., Ltd., Xi'an 710016, China; jkma@mail.nwpu.edu.cn

* Correspondence: qzhang@mail.nwpu.edu.cn

Abstract

Heterogeneous nucleation is almost invariably responsible for the solidification of metals in practice, and this process governs the fabrication techniques for numerous advanced materials. Hence, a profound understanding of the physical essence of heterogeneous nucleation at the atomic scale is urgently required. In this study, we systematically investigate the substrate orientation dependence of liquid ordering and crystal nucleation in Al melts using molecular dynamics simulations (MD). Results show that the ability of nanoparticles to promote crystal nucleation originates from their capacity to facilitate the formation of crystal-like structures at the melt–substrate interface. Regarding the influence of substrate orientations on the ordered layers at the Al liquid–solid interface, the following trends are observed: the (111) plane has the strongest induction ability, followed by the (110) and then the (100) planes. For in-plane ordering, the (100) plane exhibits the highest order, followed by the (111) plane, with the (110) plane being the weakest. Notably, despite its highest atomic density in the first-ordered layer, the (111) substrate suffers from lower atomic mobility than the (100) and (110) substrates, hindering rapid rearrangement into the FCC structure. The synergy of the layer-by-layer growth mode, strong templating efficiency, and high atomic mobility leads to the fastest crystal growth for the (100) orientation.

Keywords: crystal nucleation; molecular dynamics simulation; atomic structure ordering; substrate–liquid interface

1. Introduction

Heterogeneous nucleation is a key step in the solidification process of metals, playing a critical role in controlling grain structure, eliminating shrinkage porosity and voids, and optimizing mechanical properties [1–9]. Under actual production conditions, various nanoscale heterogeneous particles are inevitably present in aluminum and its alloy melts, including native oxides (e.g., Al_2O_3) [10–15], externally added nucleating agents (e.g., TiB_2 , Al_3Ti) [6,7,16], and in situ formed intermetallic compounds [17,18]. To date, several high-melting-point compounds have been identified as effective nucleation substrates for α -Al. Specifically, Al_3Ti (tetragonal D_{022} , $a = 4.62 \text{ \AA}$, $c = 8.594 \text{ \AA}$) and TiB_2 (hexagonal, $a = 3.038 \text{ \AA}$, $c = 3.239 \text{ \AA}$) are the key nucleant particles in Al–Ti–B refiners [7]. TiC (face-centered cubic, $a = 4.328\text{--}4.60 \text{ \AA}$) serves as the primary nucleant phase in Al–Ti–C master alloys, while AlB_2 (hexagonal) has been identified as a metastable phase that can form during grain refiner synthesis [19]. Experimental studies indicate that the crystallographic matching



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between the substrate and α -Al is a key factor governing nucleation efficiency [20–22]. For Al_3Ti , the interatomic spacing misfit (f_r) between the close-packed rows of Al and Al_3Ti can be as low as 0.73% ($\langle 110 \rangle \text{Al} // \langle 021 \rangle \text{Al}_3\text{Ti}$, $f_r = 0.73\%$), with an interplanar spacing mismatch of only 1.65% ($\{111\} \text{Al} // \{112\} \text{Al}_3\text{Ti}$, $f_d = 1.65\%$) [7]. TiB_2 has a lattice misfit of approximately 4.2% with α -Al, though its nucleation potency is enhanced by the formation of an Al_3Ti layer on its surface. TiC exhibits strong (111) orientation, which can be tailored by B doping to improve its nucleation efficiency [23,24]. Furthermore, Yang et al. [21] identified an Al/TiC_x nucleation interface featuring an Al-interfacial transition layer with a sandwich-like structure composed of Al and Ti elements, exhibiting the orientation relationship of $[011]\text{Al} // [011]\text{TiC}_x$ and a (111) $[011]\text{Al}$ plane inclined at 21° to the (111) $[011]\text{TiC}_x$ plane. This interfacial transition layer reduces the atomic mismatch between Al and TiC_x and thereby promotes Al nucleation. More generally, it is suggested that the substrate is considered an efficient inoculant when the planar disregistry is less than about 10% [20].

Given the above, the heterogeneous interfaces formed between these nanoparticles and metallic melts profoundly influence the nucleation energy barrier, nucleation kinetics, and the resulting solidification microstructure. Therefore, a thorough atomic-scale understanding of how the substrate influences the atomic structures of the metallic melts and subsequent nucleation is essential for controlling solidification microstructures and properties. Owing to the rapid advancement of experimental technologies and simulation methods, numerous studies [10,13,25–32] have revealed that a heterogeneous interface induces the formation of an ordered interfacial layer in the region between metallic melts and a substrate, which in turn plays a decisive role in the heterogeneous nucleation process [33–35]. As early as 1981, Bonissent et al. [25] demonstrated, via molecular dynamics (MD) simulations, that liquid atoms in contact with the (111) and (100) surfaces of a face-centered cubic (FCC) crystal adopt a layer-like distribution parallel to the solid surface. Since then, numerous researchers have observed analogous layered ordered structures at liquid–substrate interfaces using both simulations and experimental techniques. Oh et al. [13] conducted in situ observations using high-resolution electron microscopy and revealed the formation of a layered ordered structure of finite thickness at the interface between Al melt and the (0006) surface of single-crystal Al_2O_3 at 1023 K, providing the first experimental evidence for the existence of such an ordered interfacial layer at the liquid–substrate interface. Gandman et al. [26] found that Al melt can form ordered structures on different crystal planes of a single-crystal Al_2O_3 substrate, and that the degree of ordering shows a strong orientational dependence on the sapphire facet planes, with the interfacial layer on the (0006) plane exhibiting the highest degree of order. Using an embedded atom model (EAM) combined with MD, Palafox et al. [27] observed that a pre-freezing layer of crystalline Pb with a thickness of two to three atomic planes was formed at the Pb/Cu interface; however, the structure of the Pb melts at Cu (111) and Cu (100) substrates was significantly different, and the nucleation of FCC Pb was considerably more difficult on the Cu (100) substrate.

These studies confirm that liquids exhibit enhanced ordering in contact with various substrates, manifesting as out-of-plane ordering (where liquid atoms form layers parallel to the interface) and in-plane ordering within each layer. The degree of ordering is highly dependent on the nature of the substrates, particularly their crystalline orientation. To further elucidate the influence of substrate orientation, Men et al. [28,29] examined the liquid ordering and growth kinetics at Al interfaces with (100), (110), and (111) orientations. Their results demonstrated that in-plane ordering persists across five, five, and three atomic layers, respectively. Subsequently, they proposed that the (100) and (110) interfaces may undergo reconstruction during solidification, rendering them rougher than their (111)

counterpart—a phenomenon that could serve as the physical origin of growth anisotropy in FCC metals. Employing MD simulations in conjunction with a newly developed COMB3 potential, Yan et al. [30,31] systematically investigated the homogeneous (100), (110), and (111) interfaces between solid and liquid Al, revealing that in-plane ordering exhibits a strong dependence on substrate orientation, extending to six, ten, and three out-of-plane layers for the (100), (110), and (111) interfaces, respectively.

Despite many studies devoted to understanding liquid–solid interfacial properties and liquid ordering in Al, the vast majority of existing molecular dynamics studies on heterogeneous nucleation have adopted sandwich-type configurations, in which a liquid film is confined between two parallel substrate surfaces. In such geometries, the number of liquid atoms is typically limited to only a few thousand, with liquid layer thicknesses often less than 20 Å. However, finite-size effects in nucleation simulations have been systematically documented in the literature. Mahata et al. [36] demonstrated that for homogeneous nucleation of Al, Fe, and Mg liquids, systems containing fewer than 1 million atoms exhibit significant size dependence in diffusion properties and nucleation rates, and only when the system size exceeds approximately 2 million atoms do the properties of interest become fully converged. For heterogeneous nucleation, Hussain et al. [37] identified three distinct regimes—spanning, proximal, and converged—depending on the relationship between the critical nucleus size and the simulation box dimensions, and showed that finite-size artifacts arise when nuclei span across or approach their periodic images. In the commonly used sandwich-type geometries, the combination of thin liquid films and small in-plane dimensions can lead to spurious interactions between the two confining surfaces and between nuclei and their periodic images, potentially compromising the reliability of the observed interfacial ordering and nucleation behavior. Furthermore, extensive research on homogeneous nucleation has demonstrated that short-range and medium-range ordered structures within the melts are crucial for crystal nucleation and phase selection during solidification [34,38–42]. Nevertheless, current investigations have largely focused on in-plane and out-of-plane ordering of the melt in the vicinity of the substrate, while the influence of substrate on melt local structures, particularly a systematic investigation on the atomic structural evolution from short-to-medium range as well as the crystal nucleation process, remains largely unexplored. In light of the above, this work takes liquid Al as the research object and systematically investigates the influence and underlying mechanisms of differently oriented substrates on the liquid structures and the subsequent nucleation. The goal is to establish the intrinsic relationships among substrate orientation, interfacial structure and nucleation behavior, thereby providing theoretical support for optimizing grain refinement technologies for aluminum alloys.

2. Computational Methods

2.1. Molecular Dynamics Simulation

All MD simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS, version 03 Mar 2020, Sandia National Laboratories, Livermore, CA, USA) [43]. The embedded atom method (EAM) potential for Al, developed by Mendeleev et al. [44], was employed to investigate the liquid–solid phase transition. This potential has been extensively used in previous studies on Al crystallization [41]. Furthermore, we have calculated the melting temperature of Al using the solid–liquid coexistence method and obtained a value of 926 K [41], which is in excellent agreement with the experimental value of 933 K. This confirms that the potential correctly describes the thermodynamic balance between solid and liquid phases, which is critical for simulations of heterogeneous nucleation near the melting point. Additionally, we have compared the radial distribution functions (RDFs) of liquid Al calculated using this potential with

experimental data at the temperatures of 1000 K and 1300 K [41]. The results show excellent agreement in both peak positions and peak heights, confirming that the potential accurately captures the short-range and medium-range ordering characteristics of liquid Al that are central to our analysis of substrate-induced ordering. These validations lend strong support to the investigations presented in this work. Nevertheless, we acknowledge the inherent limitations of the EAM formalism, including the neglect of electronic degrees of freedom and potential deviations under extremely high undercooling conditions. However, since our simulations are conducted in the near-melting regime where the potential is well validated, we believe these limitations do not compromise the main conclusions of this work.

Temperature control was achieved using Nosé–Hoover thermostats. We calculated the density, stress, and potential energy profiles of the solid–liquid coexistence systems in NVT runs at expected temperatures. This thermostat was selected because it properly generates the canonical ensemble and allows for physically correct temperature fluctuations, which is essential for studying nucleation phenomena. The velocity–Verlet algorithm was used to integrate the Newton’s motion equations with a time step of 2 fs in all simulations. It should be noted that the 2 fs time step is a standard and well-validated choice in the MD simulation community for aluminum and other metallic systems. Especially, we note that previous MD studies specifically investigating substrate-induced ordering and heterogeneous nucleation in aluminum–substrate and other substrate–liquid systems have consistently used time steps of 2 fs [45,46]. Equilibration was confirmed by monitoring the instantaneous temperature at 2 ps intervals throughout the simulations. As a representative case, the 800 ps production runs—which were used to calculate the structural and dynamical properties—were performed with a target temperature of 1000 K. The measured average temperature was 1000.012 K, deviating from the target by a mere 0.012 K, with a standard deviation of ± 1.17 K. Notably, this observed fluctuation is nearly identical to the theoretical canonical fluctuation of ± 1.155 K expected for a 500,000-atom system at 1000 K, providing strong evidence that the thermostat faithfully samples the canonical ensemble. These findings collectively confirm that our 800 ps production runs achieved exceptional temperature stability.

The initial model for the heterogeneous nucleation process mediated by nanoparticles was established as follows: (1) An FCC crystalline Al system containing 500,000 atoms was relaxed at 2500 K for 100 ps to obtain a liquid structure in equilibrium state, and then cooled to $0.8T_m$ and relaxed for another 100 ps. (2) A cubic region of a certain size was selected at the center of the liquid Al, and all atoms within this region were removed. (3) Cubic nanoparticles of FCC Al were constructed with crystallographic orientations perpendicular to the *z*-direction being (100), (110), and (111) planes, respectively, matching the size of the cubic region in step (2). A gap of approximately 2 Å was maintained between the nanoparticle and the surrounding liquid to ensure no atomic overlap. This value was selected based on the following: (i) it is approximately half of the Al nearest-neighbor distance, placing liquid atoms within the attractive range of the substrate potential without core overlap; (ii) it is consistent with the equilibrium solid–liquid interfacial layer spacing reported in previous MD studies of Al systems [47]; and (iii) it matches the interfacial spacing measured in experimental studies of metal–solid interfaces using in situ X-ray scattering and HRTEM (FEI Titan 80–300 S/TEM, Thermo Fisher Scientific, Hillsboro, OR, USA) [26,48]. The lattice constant was taken as the equilibrium lattice constant of Al at its melting point, i.e., $a_{\text{Al}} = 4.12$ Å. (4) The constructed nanoparticle was then embedded into the liquid Al. The initial configurations of the nanoparticle-undercooled liquid systems established following the above procedure are shown in Figure 1. The dimensions of the liquid Al and the nanoparticles are listed in Table 1, from which it can be seen that the total number of atoms in each system is comparable.

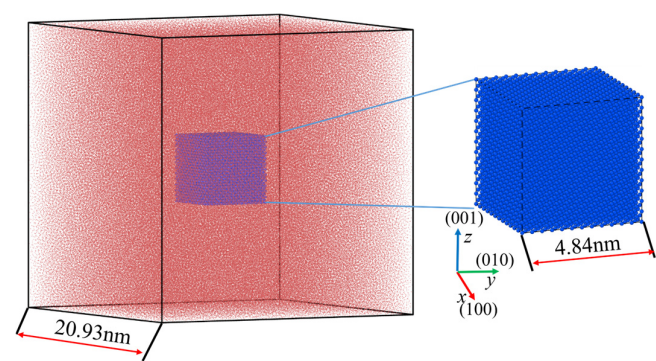


Figure 1. Initial configuration of the calculation system: blue and red balls represent solid nanoparticles and Al melt, respectively.

Table 1. System size of initial liquid-nanoparticle configurations.

Surface Orientation	Nanoparticle Size (Å ³)	Number of Nanoparticle Atoms	Number of Liquid Atoms
(100)	48.64 × 48.64 × 48.64	7813	491,901
(110)	57.2 × 48.54 × 57.2	9600	489,254
(111)	57.2 × 48.54 × 56.05	10,240	488,382

Regarding the establishment of the initial liquid–substrate configurations with different crystalline orientations, as shown in Figure 2, to eliminate non-physical interactions between the lower surface of the substrate and the upper surface of the liquid, a vacuum region was introduced above the liquid phase. The length in the z-direction of the vacuum region is approximately four times the total height of the substrate and the liquid (about 100 nm in this work). The blue regions in Figure 2 represent the substrates with upper surfaces oriented along the (100), (110), and (111) crystallographic planes, respectively, with a lattice constant of 4.12 Å. These substrates were kept fixed during the simulations. This pinned-substrate approach offers two main advantages [35]: (1) it enables simulations at high temperatures without melting or deforming the substrate, allowing it to be treated as a high-melting-point substrate; (2) it eliminates interference from chemical interactions between the liquid and the substrate, making it suitable for studying the effects of substrate properties (such as crystallographic orientation, lattice mismatch, and surface roughness) on the liquid microstructure and heterogeneous nucleation. Based on this model, the following analysis focuses on characterizing the structural features and interfacial ordering of the Al melts at the solid–liquid interface.

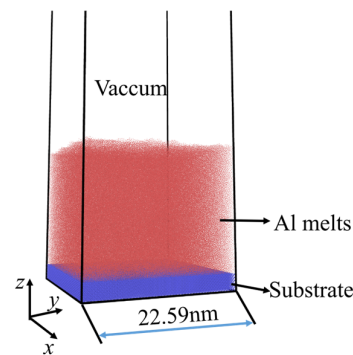


Figure 2. Initial configuration of liquid–solid phase simulations. Blue and red atoms represent Al substrate and melts, respectively.

2.2. Methodology of Structural Analysis

2.2.1. Radial Distribution Function

The radial distribution function (RDF), $g(r)$, describes the probability density of finding an atom at a distance r from a given central atom. As one of the most effective and commonly used tools for characterizing the structure of liquids, amorphous solids, and crystalline phases, it can be expressed for a monatomic system as follows [49]:

$$g(r) = \frac{V}{N^2} \left\langle \sum_{i=1}^N \frac{n(r)}{4\pi r^2 \Delta r} \right\rangle \quad (1)$$

where V denotes the volume of the simulated system, N is the total atom count, and $n(r)$ represents the number of atoms surrounding a central atom within the spherical shell from r to $r + dr$; the bin size dr used for the RDF calculation was $0.05 \text{ \AA}$. Note that the RDFs of liquid Al obtained from each of the substrate–liquid systems were averaged over the last 2×10^5 steps, following an initial 1×10^5 equilibration steps.

2.2.2. Bond Order Orientational Parameter

To discriminate between crystal-like and liquid-like atoms, the local bond-orientational order parameter was computed during simulations. The complex vector $Q_{lm}(i)$ for atom i is defined as follows [50]:

$$Q_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(\mathbf{r}_{ij}) \quad (2)$$

where $N_b(i)$ is the number of atoms neighboring atom i , Y_{lm} is the set of spherical harmonics of degree l with order $m \in [-l, l]$, and $\mathbf{r}_{ij}$ is the vector between atoms i and j . The orientation of each bond $\mathbf{r}_{ij}$ connecting particles i and j can be described by two angles: the azimuthal angle $\phi(\mathbf{r}_{ij})$ and polar angle $\theta(\mathbf{r}_{ij})$, denoted as $\phi_{i,j}$ and $\theta_{i,j}$ respectively. Therefore, Equation (2) takes the form:

$$Q_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(\theta_{i,j}, \phi_{i,j}) \quad (3)$$

Then, a bond between atoms i and j was established when $S_{ij} = \sum_{m=-6}^6 Q_{6m}(i) Q_{6m}^*(j) > 0.7$, with Q_{6m}^* being the conjugate of Q_{6m} . Based on the number of bonded neighbors (N_b), atoms were categorized as follows: those with more than 10 neighbors were crystalline (long-range order, LRO), those with fewer than 5 were liquid-like, and those with 5 to 10 were solid-like precursors. The thresholds of 10 and 5 neighbors were selected based on the ideal coordination number of the FCC crystal structure, which is 12. In an ideal FCC lattice, each atom has 12 nearest neighbors. However, at finite temperatures near the melting point, thermal vibrations and the presence of defects cause deviations from this ideal value. Therefore, atoms with more than 10 bonded neighbors are classified as crystalline (maintaining long-range order), those with fewer than 5 as liquid-like (lacking local orientational order), and those with 5 to 10 as solid-like precursors (exhibiting medium-range order). These thresholds are consistent with those used in previous computational studies of crystallization and melt ordering in metallic systems [42,43]. Furthermore, the averaged bond order parameter (a-BOP) [50] was adopted to probe the structural ordering in undercooled melts and to identify crystal symmetries, i.e., FCC, BCC, and HCP phases. The a-BOP is given by [50]

$$\bar{q}_l(i) = \left(\frac{4\pi}{2l+1} \sum_{m=-l}^l |\bar{q}_{lm}(i)|^2 \right)^{1/2} \quad (4)$$

where $\bar{q}_{lm}(i) = \frac{1}{\tilde{N}_b(i)} \sum_{j=0}^{\tilde{N}_b(i)} Q_{lm}(j)$, and the sum from $j = 0$ to $\tilde{N}_b(i)$ runs over all neighbors of particle i plus particle i itself.

The criteria employed to distinguish the various crystalline phases (namely, BCC, FCC, and HCP) have been well established and are described in detail in our previous study [40]. Specifically, atoms with an a-BOP value of $\bar{q}_6 \geq 0.4$ are defined as long-range ordered structures. Subsequently, atoms are identified as BCC phase when $0.016 < \bar{q}_4(i) < 0.056$, as the HCP structure when $0.056 \leq \bar{q}_4(i) \leq 0.115$, and as the FCC structure when $\bar{q}_4(i) > 0.115$. In what follows, the averaged bond-orientational order parameter is used to discriminate the crystal order, and the parameter N_b is used to differentiate solid-like precursor atoms from liquid-like atoms. All simulated atomic configurations were visualized with OVITO (Open Visualization Tool, version 3.15.1) [51].

3. Simulation Results and Discussion

3.1. Effects of Nanoparticles on Crystallization

Figure 3 illustrates the solidification process of undercooled liquid Al at $0.8T_m$ (740 K) in the presence of FCC nanoparticles with different orientations. In the figure, purple, green, red, and pink atoms represent crystal-like, FCC, HCP structures and solid nanoparticles, respectively. Liquid atoms are omitted to clearly highlight the nucleation process. For all three nanoparticle orientations, the nucleation process is essentially consistent: liquid atoms first attach to the nanoparticle surface to form crystal-like structures, as shown in Figure 3a,d,g. Over time, the number of crystal-like atoms increases, and they gradually transform into an FCC structure, leading to continuous crystal growth. During crystal growth, a substantial number of crystal-like atoms remain attached to the surface of the formed FCC structure to reduce the liquid–solid interfacial energy, thus facilitating the subsequent crystal growth. Furthermore, clear growth anisotropy is observed, indicating that the growth rates of different crystallographic planes vary significantly. Specifically, the growth rates of the crystallographic planes, from fastest to slowest, follow the order (100), (110), and (111).

This phenomenon is consistent with the previous MD findings of Hoyt et al. [52] concerning the kinetic coefficients of various crystallographic planes in face-centered cubic Ag and Au, i.e., $\mu_{100} > \mu_{110} > \mu_{111}$, in which the calculated growth rates for the (100) and (110) planes are in agreement with the predictions of the BGJ model [53]. Furthermore, Hoyt et al. found that $\mu_{100}/\mu_{110} = \sqrt{2}$, which matches the ratio of their respective interplanar spacings. However, according to the BGJ mode, the crystallization rate is proportional to the interplanar spacing d . Accordingly, the (111) plane, having the largest interplanar spacing, should exhibit the fastest growth rate—a prediction that clearly contradicts the MD results. The underlying reason for this discrepancy remains highly debated. Hoyt et al. [54] proposed that at the solid–liquid interface of the (111) plane, liquid atoms tend to form numerous island-like stacking faults, which subsequently transform into the FCC structure. In contrast, near the (100) and (110) planes, liquid atoms directly form the FCC structure, thereby slowing the growth kinetics of the (111) plane. Huitema et al. [55], on the other hand, suggested that the kinetic coefficients of crystal growth are governed by two factors: the in-layer ordering process of liquid atoms and the densification process involving interlayer hopping. The growth of the (100) and (110) planes is primarily controlled by the former, whereas the growth of the (111) plane is mainly determined by the latter. Based on the existing research outlined above, it is evident that an in-depth analysis of the microstructure on the liquid side of the solid–liquid interface is essential for elucidating the anisotropy of crystal growth kinetics.

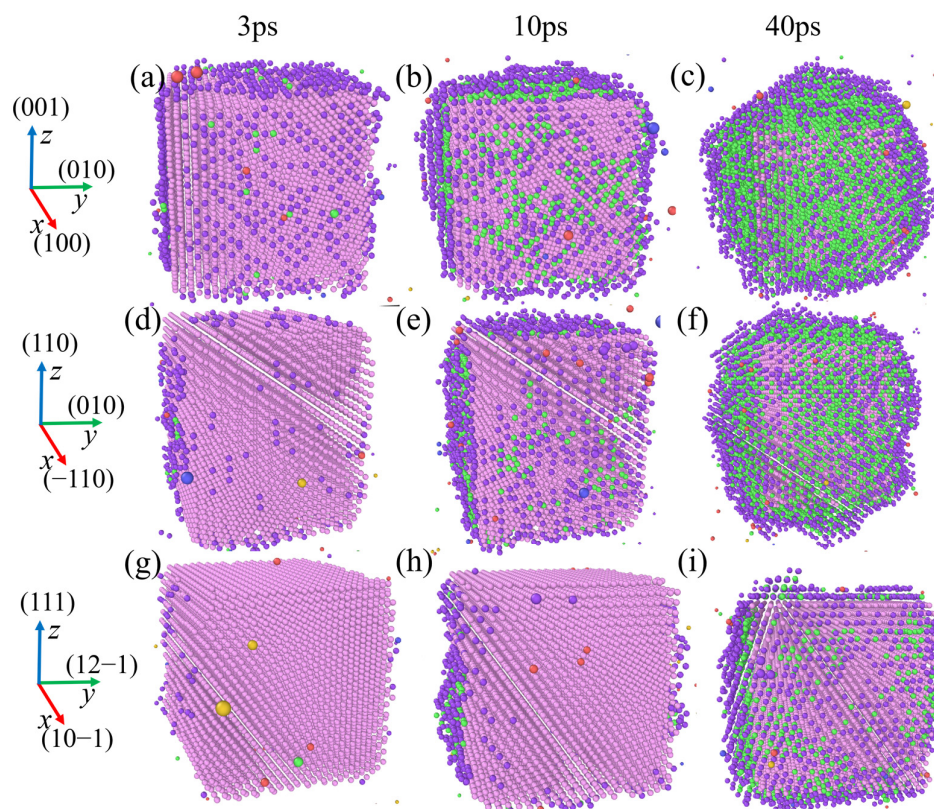


Figure 3. Snapshots of structural evolution of systems with different Al nanoparticles during isothermal annealing at $0.8T_m$: (a–c) (100); (d–f) (110); (g–i) (111). Purple, green, red, pink, and yellow atoms represent crystal-like, FCC, HCP structures, solid nanoparticles and icosahedral atoms, respectively.

According to our previous findings on the correlation between local atomic structure in undercooled melts and crystal nucleation, the formation of medium-range ordered (MRO) crystal-like structures within the undercooled melts is the prerequisite for crystal nucleation [40,56]. Therefore, here we further analyze the influence of nanoparticles on the evolution of crystalline (FCC, HCP and BCC phases) and crystal-like structures in the liquid phase. Figure 4a,b illustrate the evolution of these structures during the isothermal relaxation of liquid Al at $0.8T_m$ in the presence of nanoparticles with different orientations. For comparison, the structural evolution curves for homogeneous nucleation of liquid Al at $0.8T_m$ are also presented.

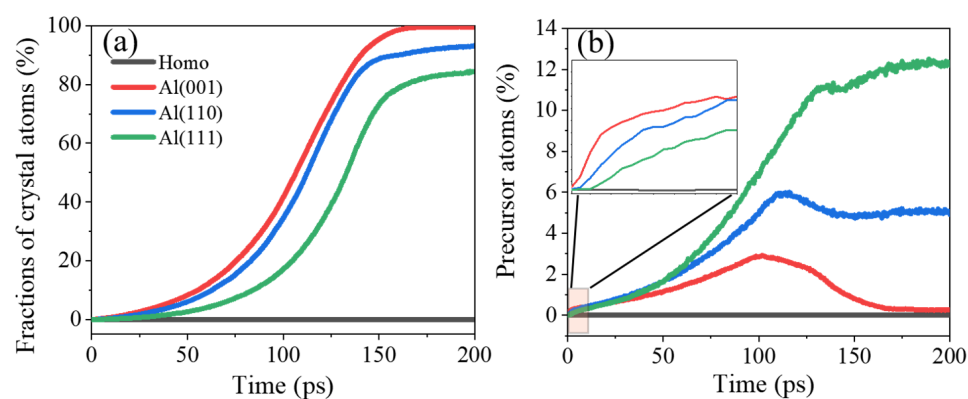


Figure 4. Evolution of atomic structures in melts during solidification: (a) Fractions of crystalline atoms; (b) Fractions of precursor atoms; inset represents the enlarge image of square area in (b).

Figure 4a directly demonstrates the crystallization-promoting effect of nanoparticles. Notably, nanoparticles with the (100) orientation exhibit a more pronounced promoting effect than those with the (110) or (111) orientations. To elucidate the underlying mechanism associated with the forming ability of precursor (solid-like) atoms, Figure 4b presents the orientational dependence of nanoparticle effects on the evolution of solid-like structures. Overall, as the crystallization proceeds, the number of solid-like atoms in the melt continuously increases. Among the three orientations, the (111) nanoparticle system exhibits the largest number of such clusters, followed by the (110) system, while the (100) orientation shows the fewest. This behavior is primarily attributed to the faster crystallization rate of the (100)-oriented heterogeneous system, leading to a rapid transformation of solid-like structures into the FCC structure, whereas the opposite is true for the (111) heterogeneous core. Furthermore, it can be observed that nearly 12% of the total atoms remain as solid-like atoms after crystallization is complete, ultimately existing as defects within the crystal in the (111) system. The evolution rule for solid-like structures seems unable to explain the crystal growth anisotropy shown in Figure 4a; therefore, particular attention should be focused on the efficiency of nanoparticles in inducing the formation of solid-like precursors during the early stage of nucleation. As shown in the inset of Figure 4b, the number of crystal-like structures evolves during the first 10 ps. It is evident that (100) nanoparticles have the strongest ability to induce the formation of crystal-like structures, followed by (110) nanoparticles, with (111) nanoparticles being the weakest, which is consistent with the crystallization rates illustrated in Figure 4a.

Based on the above analysis, it can be reasonably inferred that the ability of nanoparticles to promote the formation of crystal-like structures is the primary reason for the differences in crystallization rates among the three orientations. In other words, the ability of a crystallographic plane to facilitate the formation of crystal-like structures may determine its growth kinetics. Therefore, it is necessary to further analyze and characterize the structural features of the liquid phase at the interface between different oriented crystallographic planes and the liquid.

3.2. Effects of Substrate on the Liquid Structure

3.2.1. Averaged Structural Information of Melts

To thoroughly analyze the influence of various oriented substrates on the melt structure, the RDF was employed to obtain the averaged structural information of melts, as shown in Figure 5. Figure 5a presents the RDF curves of the steady-state melt at 1000 K. It can be easily observed that RDF curves of melts are significantly affected by the presence of substrates. Specifically, the peak intensities of the RDF curves for the melt under the influence of each substrate are notably higher than those of the substrate-free homogeneous melt, indicating that the degree of structural ordering from short range to long range in the melt is markedly enhanced. Furthermore, the RDF curves for the melt under the (100) and (110) substrates are nearly identical, and their intensities are significantly higher than those of the Al melt under the influence of the (111) substrate. Similar results are also obtained in the RDF curves of the melts at 930 K (Figure 5b), confirming the reliability of these findings. This observation strongly suggests that the (100) and (110) substrates possess comparable abilities to induce melt ordering, both of which are significantly greater than that of the (111) substrate, aligning with the crystallization rate differences presented in Figure 4.

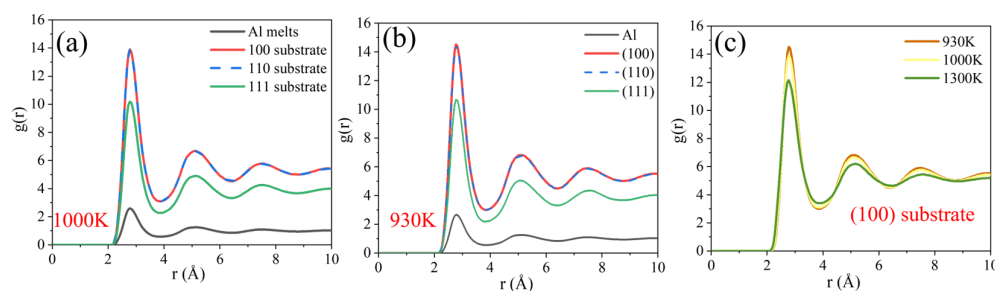


Figure 5. RDF curves of the Al melts under the effect of different oriented substrate: (a) 1000 K; (b) 930 K; (c) RDF of Al melts in the presence of (100) substrate at different temperatures.

3.2.2. In-Plane and Out-of-Plane Ordering Adjacent to Interface

To establish a connection between the structural characteristics of the liquid phase above the melting point and the solidification behavior at undercooled temperatures, this section analyzes the influence of substrate orientation on the structural ordering of the liquid phase above the melting point. Figure 6 shows the visualized atomic structure of liquid Al in the substrate–liquid system at 1000 K. It can be clearly observed that for substrate–liquid systems with different crystallographic orientations, the liquid atoms exhibit pronounced layering characteristics along the z -direction near the interface—a behavior that can be referred to as the “preordering” of the liquid phase. Kauffmann et al. [17,26] categorized the preordering of liquids into two types: in-plane ordering and out-of-plane ordering. From the magnified views, all three systems exhibit two to three relatively distinct ordered liquid layers. Therefore, to gain a deeper understanding of the influence of crystallographic orientation on liquid ordering, a quantitative analysis of both out-of-plane and in-plane ordering of the liquid phase is necessary.

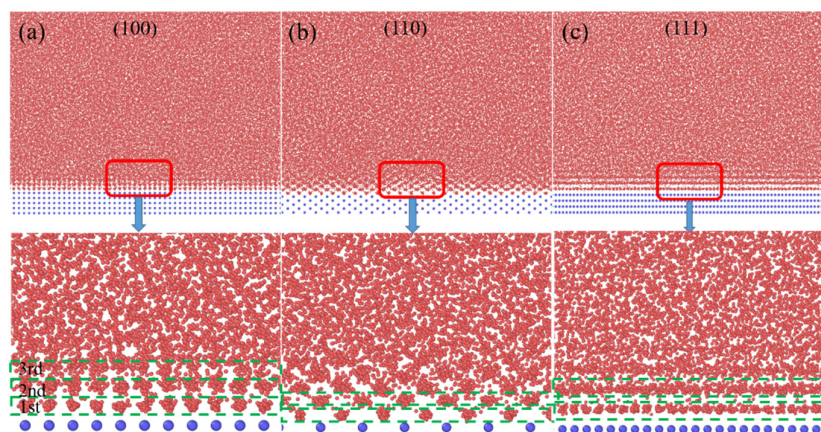


Figure 6. Snapshots of atomic structures of substrate–liquid system at 1000 K: (a) (100); (b) (110); (c) (111). Dash lines denote ordering layer, blue and red balls represent solid substrate and Al melt, respectively.

(a) Analysis of out-of-plane ordering

For out-of-plane ordering, the atomic number density distribution function ρ along the direction normal to the solid–liquid interface is generally used as a characterization method. ρ is a continuous function that can simultaneously reflect both the solid-like and liquid-like characteristics of the liquid phase at the solid–liquid interface. It can be defined as [47]

$$\rho(z) = \frac{\langle N_z \rangle}{L_x L_y \Delta z} \quad (5)$$

where N_z is the number of atoms within the range from $z - \Delta z/2$ to $z + \Delta z/2$ at time t , the angle brackets denote time-averaging, Δz is the bin size (one-tenth of the interplanar spacing), and L_x and L_y represent the dimensions of the simulation box in the x and y directions, respectively. To improve the statistics, for each substrate orientation, we performed three independent simulation trajectories under identical thermodynamic conditions ($T = 1000$ K, NVT ensemble). Each trajectory was initialized from a different set of initial velocities drawn from a Maxwell–Boltzmann distribution at 1000 K, using different random seeds for the velocity assignment. All reported density profiles represent averages over these independent runs. In addition, the diffusion coefficients were calculated using the Einstein relation, which relates the mean square displacement (MSD) to the diffusion coefficient within each layer to characterize the diffusion behavior of the ordered layers: $D = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |r_i(t) - r_i(0)|^2 \rangle$, where $r_i(t)$ is the position of atom i at time t , and the angle brackets denote an ensemble average over all atoms and time origins. The MSD was computed for each atomic layer parallel to the substrate surface, and the diffusion coefficient was extracted from the linear regime of the MSD versus time curve. Relevant data were statistically analyzed over the final 20 ps of the isothermal relaxation simulations, which lasted up to 800 ps. The final reported diffusion coefficient is the mean across the three independent trajectories, with error bars representing the standard deviation across the three independent runs. This approach provides robust statistics while remaining computationally feasible for our 500,000-atom system.

Figure 7 presents the distribution curves of atomic number density and diffusion properties for the (100), (110) and (111) oriented substrate–liquid systems. In the figure, regular density peaks exceeding $0.45 \text{ atom}/\text{\AA}^3$ diverge with the substrate orientation. Starting from the substrate–liquid interface, the atomic density profiles exhibit an oscillatory decreasing trend along the z -direction, indicating the presence of layering phenomena in the liquid phase at the interface. At distances far from the interface, the atomic density remains nearly constant ($\sim 0.053 \text{ atom}/\text{\AA}^3$), corresponding to the interior region of the liquid, which suggests that the degree of ordering gradually decreases from the interface to the bulk liquid. For substrate–liquid systems with (100), (110), and (111) orientations, five to seven ordered atomic layers can be observed, as illustrated in Figure 7. Specifically, the atomic densities of the first ordered layers are $0.174 \text{ atom}/\text{\AA}^3$, $0.124 \text{ atom}/\text{\AA}^3$, and $0.251 \text{ atom}/\text{\AA}^3$, respectively. This suggests not only the strongest interfacial interaction between the (111) substrate and the liquid but also a high degree of spatial confinement. In comparison, the (110) and (100) substrates exhibit both weaker substrate–liquid interactions and a lower degree of out-of-plane ordering.

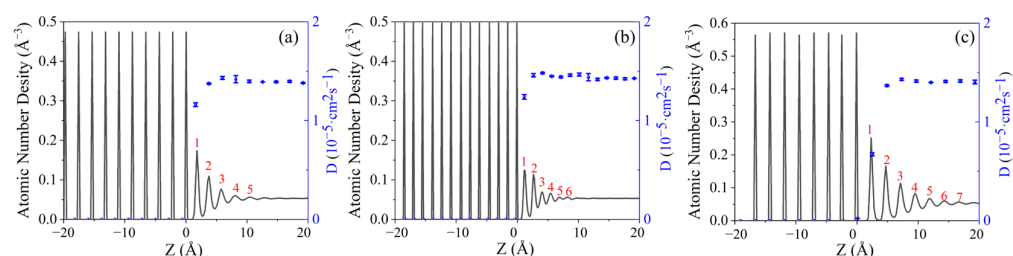


Figure 7. The density profile $\rho(z)$ (black curves) of the substrate and Al melts as a function of z , in which the diffusive properties (blue dots with error bars) were also involved: (a) (100); (b) (110); (c) (111), red numbers 1–7 denote the sequential numbers of the ordered layers.

Furthermore, it can be observed that the distribution of diffusion coefficients exhibits certain general characteristics: from the solid–liquid interface toward the bulk liquid, the atomic diffusion ability gradually increases for each ordered layer, and the mobility of atoms in the liquid is significantly stronger than that of atoms located at the inter-

face. More importantly, the atomic mobility of the first ordered layer on the (111) plane ($0.69 \times 10^5 \text{ cm}^2 \cdot \text{s}^{-1}$) is noticeably lower than that on the (100) ($1.17 \times 10^5 \text{ cm}^2 \cdot \text{s}^{-1}$) and (110) planes ($1.25 \times 10^5 \text{ cm}^2 \cdot \text{s}^{-1}$), which likely arises from the strongest interaction between atoms of substrate and liquid, as well as the highest atomic density of the first ordered layer on the (111) surface compared to (100) and (110) surfaces.

The density distribution can generally be considered a direct consequence of Boltzmann's law, which states that atomic density is proportional to $\exp(-U/k_b T)$, where U and T are the potential energy and temperature at a given position within the system, respectively, and k_b is the Boltzmann constant. The periodically arranged substrate atoms create local low-energy potential wells, which trap liquid atoms and cause them to vibrate around these wells, thereby leading to the formation of the first ordered layer. Similarly, once the first ordered layer is formed, it generates analogous local potential wells that promote the formation of the second ordered layer, and so on. Based on ab initio molecular dynamics simulations (AIMD), Ma et al. [57] found that since the vibrational amplitude of liquid atoms at the interface is much larger than that of substrate atoms, the potential wells generated by atoms in each ordered layer are not stable at fixed positions but vary over time. Furthermore, as the number of ordered layers increases, the vibrational characteristics of atoms within the layers gradually become stronger, reflected by the diffusion property distribution of each ordered layer in Figure 7. This intrinsically makes it increasingly difficult for subsequent ordered layers to form stable potential wells. Consequently, as the distance from the substrate increases, the depth of the potential wells gradually decreases, leading to a successive attenuation in the degree of order of each layer, until eventually the formation of further ordered layers can no longer be induced.

Based on the above analysis, it can be understood that interlayer ordering at the solid–liquid interface is not the key, nor the sole, factor leading to the anisotropy of crystal growth. Furthermore, the in-plane diffusion properties of atoms within each ordered layer are likely related to in-plane ordering and the arrangement of atoms within the layer. Therefore, this study further characterizes and analyzes the in-plane ordering in detail.

(b) In-plane-ordering of Al melts

The two-dimensional density distribution $\rho_{xy}(\vec{r})$ was used to further characterize the in-plane ordering and in-plane structure of each ordered layer. A square grid was defined in the $x - y$ plane for each ordered layer, with spatial steps of $\Delta x = \Delta y = 0.5 \text{ \AA}$. In addition, to better visualize the periodic structure within the ordered layers, the two-dimensional structure factor $S_{xy}(\vec{k})$ was also calculated, which is expressed as [35]

$$S_{xy}(\vec{k}) = \langle |\rho_{xy}(\vec{k})|^2 \rangle \quad (6)$$

In the equation, $\rho_{xy}(\vec{k})$ is the Fourier transform of the two-dimensional density $\rho_{xy}(\vec{r})$. To calculate the two-dimensional structure factor $S_{xy}(\vec{k})$, the structure factor of atomic configurations per 1 ps was computed, and a statistical average was taken over the transient values for a simulation duration of 100 ps.

Figure 8 presents the in-plane two-dimensional density of the first to fifth ordered layers in the substrate–liquid system, along with the corresponding two-dimensional structure factors (shown in the upper-right insets). For each oriented substrate–liquid system, the two-dimensional in-plane density of the first ordered layer exhibits a regular periodic arrangement, indicating that the atomic arrangement within this layer is well-ordered and possesses a strong crystalline symmetry consistent with the orientation of the substrate. For the (100) substrate, the induced in-plane ordering extends to the fourth layer, whereas for the (110) and (111) substrates, it persists only up to the third layer. By

the fourth layer, the two-dimensional density distribution becomes disordered, and the two-dimensional structure factor begins to show a halo-ring, indicating that the in-plane structure exhibits liquid-like characteristics. Moreover, as the distance from the interface further increases, the halo-ring becomes brighter, and the structure becomes increasingly disordered. This means that moving from the interface toward the liquid interior, the structure gradually approaches that of a disordered melt, reflecting the strong regulatory effect of the substrate surface on the liquid structure. The simulation results are in good agreement with experimental observations [17].

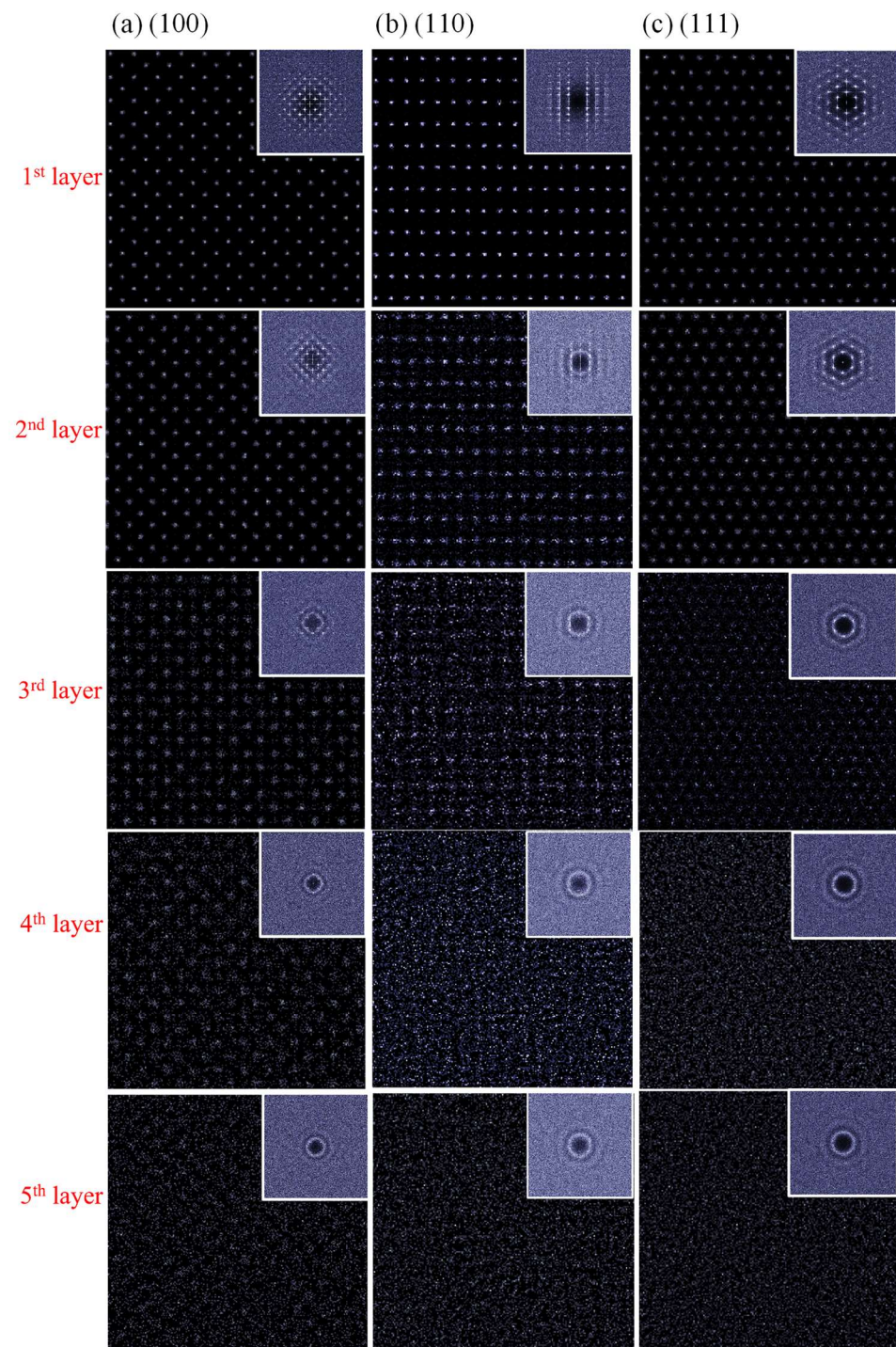


Figure 8. Two-dimensional density and Fourier structure factor (insets) plots for different systems under the temperature of 1000 K: (a) (100) substrate–melt system; (b) (110) substrate–melt system; (c) (111) substrate–melt system.

The average number of bonded neighbors (N_b), presented in Figure 9, further quantifies the degree of atomic arrangement ordering per layer. N_b decreases gradually with increasing layer number. Notably, N_b for the first layer of the (100) system approaches 10, reflecting an ordered structure near crystallinity, whereas the (110) and (111) systems yield N_b values of 6 and 8, respectively, indicating less-ordered structures. Additionally, the second layer of the (100) system retains a solid-like arrangement, unlike the other systems which become liquid-like. These results demonstrate that while the (111) substrate induces relatively strong out-of-plane ordering, the (100) orientation possesses a superior capacity for in-plane ordering, with the (110) orientation being the weakest in this regard.

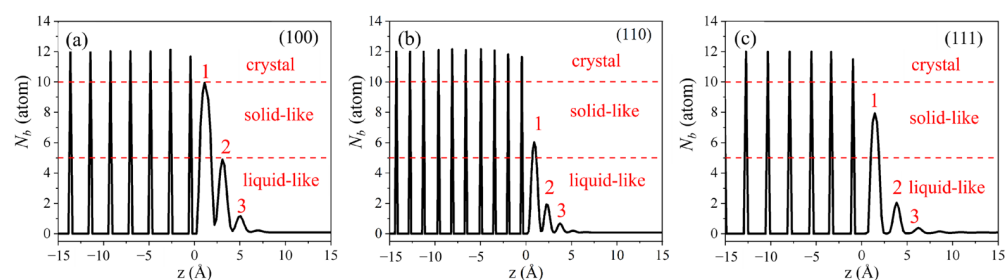


Figure 9. Number of bonded neighbors N_b of the substrate and Al melts as a function of distance z at 1000 K: (a) (100); (b) (110); (c) (111), the red numbers 1–3 denote the sequential numbers of the ordered layers.

3.3. Mechanism of Nucleation and Growth on Substrates

Figure 10 shows snapshots of simulation cells during the crystal nucleation and growth from undercooled Al melt ($0.8T_m$) on (001), (110) and (111) orientation substrate. The results indicate that, regardless of the substrate orientation, Al melt rapidly forms an out-of-plane ordering parallel to the interface upon the initiation of the solidification simulations. Once the out-of-plane ordering forms, those atoms in the first ordering layer tend to transform into FCC structures through slight position adjustment. However, we can observe that the first layer atoms in (100) and (110) systems succeed in forming FCC structures much more easily than in the (111) substrate, as illustrated in Figure 10(a1,b1,c1). This deviation can be ascribed to the differences in atomic number density as well as the atom mobility adjacent to substrates. As revealed above, the first ordering layer with the (111) substrate shows higher atomic density yet lower atomic mobility relative to that of the (100) and (110) substrates, making it difficult for atoms to quickly rearrange into the FCC structure. In contrast, the (100) and (110) ordered layers allow such transformation more readily. Subsequently, after crystallization of the first ordered layer, atoms in the second layer undergo local adjustment to become crystalline, facilitated by the highly ordered atoms of the first layer. Concurrently, the first two crystallized layers promote in-plane and out-of-plane ordering in the adjacent melts, leading to further crystallization. Notably, during crystal growth, liquid atoms ahead of the (110) interface exhibit a considerably lower degree of ordering than those ahead of the (100) and (111) interfaces, as reflected by the fewer purple solid-like atoms attached to the crystal surface, consistent with results illustrated in Figures 8 and 9. This process repeats successively, achieving layer-by-layer crystallization and eventual growth of the entire crystal until the melt is fully solidified. As a result, (111)-oriented crystals grow much more slowly than their (100) and (110) counterparts, as shown in Figure 10. This study reveals the microscopic mechanism by which heterogeneous interfaces regulate the atomic structures and nucleation behavior of liquid metals, providing a theoretical basis for optimizing the grain refinement process of aluminum alloys and designing efficient nucleating agents.

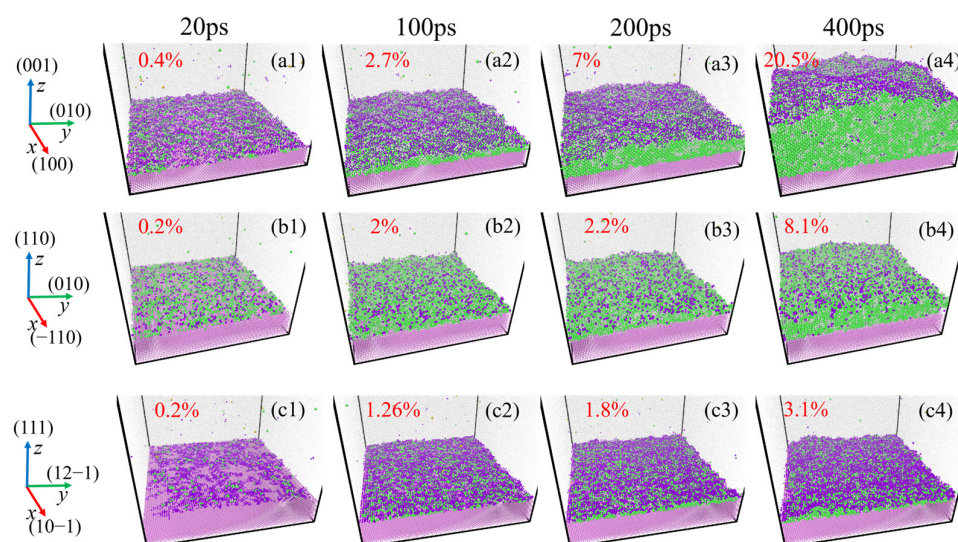


Figure 10. Snapshots of simulation cells during nucleation and crystal growth from undercooled Al melt on (a1–a4) (100) plane, (b1–b4) (110) plane and (c1–c4) (111) plane. Green, purple and pink atoms represent Al atoms with FCC structure, solid-like structure and atoms belonging to substrates, respectively. FCC and solid-like atoms are defined by a-BOP and Nb. The value shown in the upper left corner of the figure represents the crystallinity of the melt at the corresponding moment.

4. Conclusions

In this study, we systematically investigated the effects of substrate orientation on the structural ordering of Al melts and the subsequent heterogeneous nucleation behavior. The main conclusions are as follows:

- (1) The results show that the promoting effect of nanoparticles on crystal nucleation originates from their ability to facilitate the formation of crystal-like structures in metallic melts.
- (2) The influence of substrates with different crystallographic orientations on the ordering of the Al melts adjacent to the interface can be summarized as follows: the (111) surface exhibits the strongest ability to induce out-of-plane ordering, followed by the (110) and (100) surfaces. With respect to in-plane ordering, the layer adjacent to (100) substrate shows the highest degree of order, followed by the (111) orientation, while the (110) plane exhibits the lowest. The first ordering layer with the (111) substrate shows higher atomic density yet lower atomic mobility compared with that of the (100) and (110) substrates, making it difficult to quickly rearrange into the FCC structure. Layer-by-layer crystallization realizes successive crystal growth.
- (3) The synergistic effect of the layer-by-layer growth mode, the strong induction of liquid ordering, and the favorable atomic mobility enable the (100)-oriented crystal to grow the fastest. In contrast, the relatively weaker in-plane ordering and lower atomic mobility result in the slowest growth for the (111) orientation.

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Conflicts of Interest: Author Jiankai Ma was employed by the company Xi'an Rare Metal Materials Institute Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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