HOMOGENEOUS NUCLEATION AND INNER STRUCTURE EVOLUTION IN NUCLEUS Fe FROM CLASSIC MOLECULAR DYNAMICS SIMULATION

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Abstract

Molecular dynamic simulation was used to study the solidification process of liquid Fe with Sutton-Chen potential. Bond orientational order (BOO) parameters and Voronoi polyhedron index (VPI) method, named BOO+VPI method, were applied to identify atomic local structure and local volume precisely. During the solidification process, two large clusters were detected, one is an imperfect five-fold twinning structure, and the other is a lamellar structure. In addition, the density and order of the two clusters were analyzed along with their growth. All analyses suggest that the density and the order of the crystal nucleus increase gradually with the increase of the size, and the order of the crystal nucleus with the five-fold twinning structure is higher. Meanwhile, the embryos are always found in high structure-ordered region instead of high density region.

Introduction

Crystallization[1, 2] plays a prominent role in physical, chemical and material science. Meanwhile, crystal nucleation from an undercooled melt is one of the fundamental process during solidification. Despite this, even for simple metals such as Fe[3] or model system such as hard spheres[4-6], nucleation is far from being well understood at a microscope level.

In addition, although crystal nucleation has been the subject of extensive experiment and theoretical study[7]. Our understanding of crystal nucleation and growth regime at the microscope level is still limited. Due to lack a reliable quantitative understanding of crystallization at present, it deserves more studies on this topic, especially for the phase transition, so the application of molecular dynamic (MD) simulation becomes more and more important.

A large number of experiments[8] and simulations[9, 10] show that the formation of stable solid from super-cooled melt is an extremely complicated process. The most popular view is that the pre-critical nuclei exists in high bond orientational order regions, with the collective effect of density fluctuation[11-13] and bond-order fluctuation, when a crystallite reaches the critical size for which the energy gain for volume growth overcomes the free energy penalty for surface formation. After that, the critical nuclei undergo upon a rapid growth process until the complete solidification.

There are two basic theories about solidification, one is the classical nucleation theory[14, 15], the other one is two-step nucleation theory[15]. The classical nucleation theory holds that the formation of the critical crystal nucleus is the collective action of the density fluctuation and the structure fluctuation[16, 17], moreover, the two order parameters proceed simultaneously. However, two-step nucleation theory, formulated by Ostwald, states that the density and

structure fluctuation that result in a crystalline nucleus occurring not simultaneously, but in sequence. The structure fluctuation follows or superimposed on the density fluctuation, which promotes the formation of the critical crystal nucleus. Moreover, Ostwald's step rule emphasizes that the nucleus formed from the melt is in the phase closest in free energy to the liquid phase.

All the time, most studies were concentrated on model system, such as hard sphere model and Lennard-Jones fluid model[18, 19]. With regard to the Lennard-Jones fluid model, a large number of simulation shows that its pre-critical nuclei has a body-centered cubic (BCC) structure rather than stable face-centered cubic (FCC) structure, then, as the crystalline reaches critical size, the core position is filled with FCC structure, while in the surface, a high degree of BCC ordering is attained.

In this letter, we present a molecular dynamics study of the solidification of liquid Fe. The main purpose of this research is to study the morphological and structural changes of the clusters in the process of solidification of Fe and the variation of the density and order of the clusters with different shapes and sizes. Specific comparative analysis is presented in the conclusion part.

Computational experiment procedure

The MD simulations were performed on iron with 1024000 Fe atoms by a Sutton-Chen potential[20]. The potential energy U is written as the sum of a contribution arising from pairwise interactions and a contribution of a many-body term

$$U = \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} \varepsilon \left(\frac{a}{r_{ij}}\right)^{n} - \varepsilon C \sum_{i=1}^{N} \sqrt{\rho_i}$$

(1)

in which r_{ij} is the distance between atom i and atom j, N is the number of atoms in the system, ε is a parameter with dimensions of energy, and besides, the density term ρ_i is given by

$$\rho_i = \sum_{j \neq i} \left(\frac{a}{r_{ij}}\right)^{m}$$

(2)

a is a parameter with dimensions of length. n and m are positive integer.

We use the set of parameters as follows: $\varepsilon=0.0006eV$ $a=0.36467nm$ $n=15$ $m=4$ and $C=1104.7351$

First of all, we built a supercell, which is composed of 12800 perfect BCC atoms, then heat it up to 3000K to make it melt completely. The system was then cooled to 1833K and to achieve the state of equilibrium completely we made the system undergo upon a relaxation process at this temperature with 10^6 steps.

In the second step, we made a combination among 8 copies of this system, thus, a new system consisting of 1024000 Fe atoms was established.

Finally, in order to observe the nucleation and growth process, the system was cooled from 1833K to 1710K, we equilibrated the system for 5.5×10^5 steps and other 5×10^4 steps for the sake of statistics.

The Berendsen thermostat was applied to control the temperature for every step and the Andersen method was applied for controlling pressure. Besides, the equations of atomic motion were integrated by the Verlet-Velocity algorithm with a time step of 2fs. The periodic boundary conditions were applied for the whole system.

Results and Discussion

We tracked the whole solidification to observe the evolution of cluster structure. During this process, the continuous attachment and disattachment between clusters led to the formation of two big clusters. One is a lamellar structure, named cluster_1 and the other is an imperfect five-fold twinning structure, named cluster_2. The large clusters defined here are those whose size exceed 1000 at a certain time and its final size divide the initial size must more than 100, in other words, during the whole solidification the size of cluster expanded one hundred times. Then, cluster_1 and cluster_2 merged into a larger cluster at 100.2ps, named cluster_1_2, owing to the collision. After that, system realized complete solidification.

To identify crystalline particles and atomic local volume, we make full use of the local orientational order parameter[21] and Voronoi polyhedron index (VPI) method. It is useful to characterize local packing symmetries with local orientational order parameter. At the same time, it is convenient to follow the formation of solid clusters and to distinguish between different polymorphs. As defined in Eq.(3)

$$\overline{q_{lm}}(i) \equiv \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(\hat{r}_{ij}) \tag{3}$$

From the $\overline{q_{lm}}(i)$ we can construct local invariants,

$$q_l(i) \equiv [\frac{4\pi}{2l+1} \sum_{m=-l}^{l} |\overline{q_{lm}}(i)|^2]^{\frac{1}{2}} \tag{4}$$

and

$$\hat{\omega}_l(i) \equiv \frac{\sum_{\substack{m1,m2,m3 \\ m1+m2+m3=0}} \begin{pmatrix} l & l & l \\ m_1 & m_2 & m_3 \end{pmatrix} \overline{q_{lm_1}}(i)\overline{q_{lm_2}}(i)\overline{q_{lm_3}}(i)}{[\sum_{m=-l}^{l} |\overline{q_{lm}}(i)|^2]^{\frac{3}{2}}} \tag{5}$$

Two particles i and j are defined as neighbors if the distance between them is less than 3.45Å (corresponding to first minimum in pair-correlation function of liquid Fe) A pair of neighboring particles is connected if dot-product $q_6(i)\cdot q_6(j)$ is larger 0.5. At the same time, if the number of connections with its neighboring particles exceeds 7, therefore we identify it as solid-like particle[21].

What's more, to identify the crystal polymorphs, we take advantage of the diverse symmetries that the crystal have on the W_6 and W_4 axis. The BCC structure can be distinguished from closed-packed crystals such as hexagonal close-packed (HCP) and FCC, since W_6 is positive in the former whereas negative for the latter. At the same time, the FCC structure and HCP structure can be characterized by the distribution of W_4, thus, W_4 is good to distinguish between FCC crystals (for which it has negative value) and HCP crystals (for which it has positive value).

Figure 1a and 1b present the change of the fraction of different crystal structure in the whole solidification process of the two clusters. Figure 1a shows that the fraction of BCC structures steadily decreases at the expenses of both FCC and HCP structures. Moreover, the fraction of HCP is higher than that of FCC before aggregation. Figure 1b shows that the percentage of HCP is floating in 40%~50%, the fraction of FCC increases as cluster get bigger (In general, the HCP atoms are concentrated in the position of the five-fold axis, meanwhile, the majority of FCC atoms are gathered in the intermediate zone between two axis, both the FCC and HCP atoms directly contribute to the formation of imperfect five-fold twinning structure) and the fraction of BCC atoms decreases gradually. At the moment of aggregation, the fraction of different crystal

polymorphs exhibit a mutation. The fraction of HCP atoms presents a dump and the fraction of FCC atoms displays a sharply increases. The reason for this phenomenon is that in terms of cluster_1, $f_{FCC} \approx 23\%$, $f_{HCP} \approx 54\%$, while with respect to cluster_2, $f_{FCC} \approx 33\%$, $f_{HCP} \approx 42\%$, so the phenomenon of the mutation is inevitable. The final steady state of the whole solidification process is as follows: $f_{HCP} > f_{FCC} > f_{BCC}$.

The most serious discrepancy between Figure 1a and 1b is the change tendency of the fraction of FCC atoms in the two clusters. It is evident that the fraction of FCC atoms not increases monotonously but with the tendency of increasing gradiently in cluster_2.
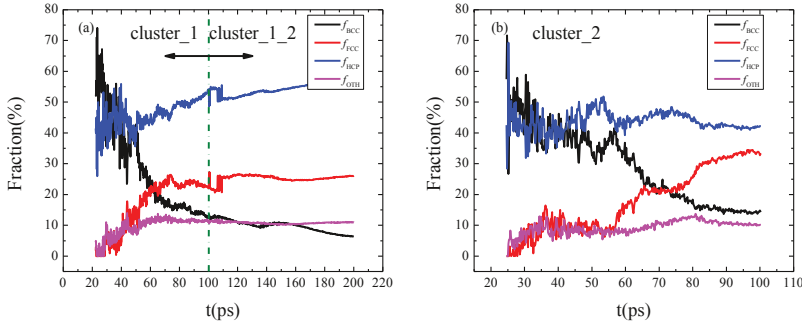

Figure 1. The fraction of different structure components, such as BCC (black line) FCC (red line) HCP (blue line) and OTH (pink line), in the nucleated cluster as a function of simulation time. The vertical dashed line indicates aggregation between two clusters. If solid-like atoms do not belong to BCC-like structure or closed-packed structure, then, it is considered as OTH atoms.

We make a detailed analysis about the internal composition of the two clusters in the last part. Next, we also make a comparison between density and the value of the order parameters, belonging to the two clusters. Figure 2 shows that the density of cluster_1 is the same as that of cluster_2 to a large extent, no matter it is in the surface or in the core. In contrast, the value of structure order parameter in the core of cluster_2 is somewhat higher than the value of the order parameter in the core of cluster_1. In terms of the order parameter in the surface, it reaches the same value almost. As a consequence, the value of the order parameter in cluster_2 is higher than that of cluster_1. In addition, the density of cluster_1 and cluster_2 are increasing with time in terms of the whole cluster. The important point to note is that the value of order parameter in cluster_2 increases gradiently. We suspect that the appearance of this phenomenon may be related to its internal structure. In particular, it is most easily seen that the amplitude of fluctuation of two parameters is larger in surface than in core, which contributes to the diffusion properties of the interface between clusters and super-cooled melt.
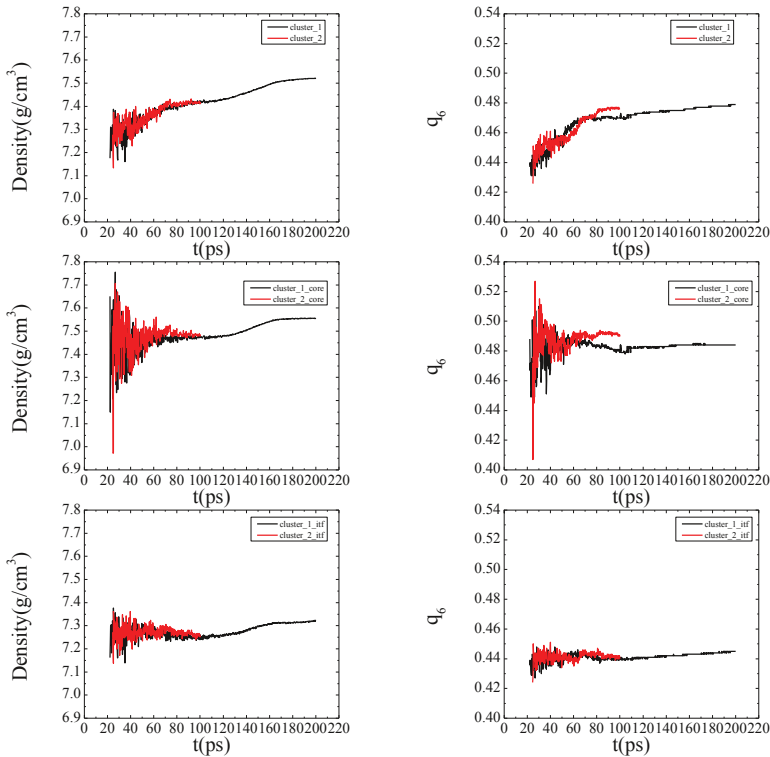
Figure 2. The comparison of density and order parameters in the whole cluster, core and interface of cluster_1 (black line) and cluster_2 (red line). The curve reflects the relationship of the density and the structure order parameters with simulation time.

As discussed in the above, the density and order change with the time during the solidification process. In the following part, we will show the distribution of density and the order in different regions of the two clusters. As we can seen from Figure 3(a) and Figure 3(b) that the density and the order decrease both from core to interface and from interface to liquid no matter in the lamellar structure or in the imperfect five-fold twinning structure. Besides, we make a detailed analysis about the distribution of density and the order in the different partition, including core and interface, which belong to cluster itself, in addition to cloud1, cloud2, cloud3 and cloud, which respond to the local liquid environment around clusters. It is not surprised to see that the density and the order increase in an extremely small extent, which attributes to the existence of some small solid cluster in the local liquid environment. In addition, there are some important points where density distribution is broadly in agreement with that in the lamellar structure, whereas the distribution of the order presents different characteristics, which the value of the local order parameter, corresponding to core, in cluster_2 is higher than that in cluster_1, leading to the order of the imperfect five-fold twinning structure is higher than the lamellar structure. It

is evident from the curve presented in Figure 3(c) and 3(d), with respect to the phenomenon mentioned above.
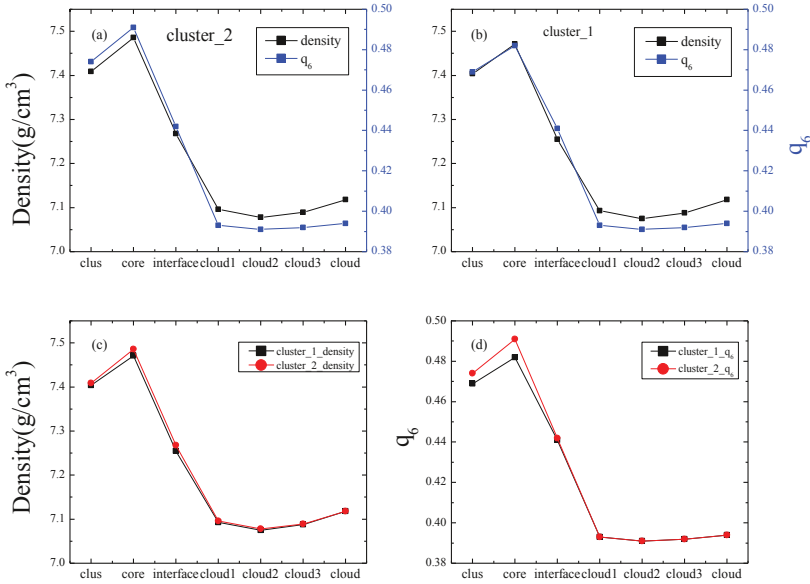

Figure 3. The distribution of the density and the order in different partition, including clus (clus represents cluster itself), core, interface, cloud1, cloud2, cloud3 and cloud. Data are averaged over simulation time.

In the following, we will discuss the relationship among density, the degree of order and size of the two large clusters. As can be seen from Figure 4, it increases with the time for density, the order and size. Moreover, the change tendency of density is similar with that of the order, its slope of curve reduce gradually. When it comes to size, it is apparent that cluster size is increases with time gradually and the slope is progressively increasing. Compared to cluster_1, the trend of cluster_2 is the same as cluster_1 to a large extent. On one hand, we cannot ignore the common features of the two clusters, but, on the other hand, we must contemplate the difference between the two clusters. In terms of cluster_2, the value of order parameters is higher than that of cluster_1 ultimately, but its size is smaller that of cluster_1. What's more, the trend of order in cluster_2 is gradient growth. In the following, we will present results of the two clusters that its density and order are increasing with size. In other words, the greater of the size, the larger of the corresponding density and the order of the two clusters.
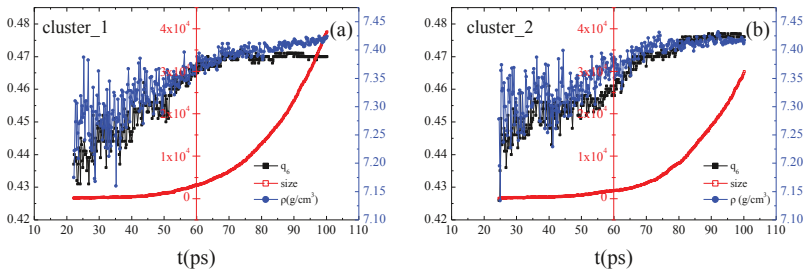
Figure 4. The density (blue), size (red) and the order (black) as a function of time in cluster_1 and cluster_2.

Finally, we also observe that the embryos are always found in high structure-ordered region instead of high density region, which is agreement with the results from the gaussian core model[22] and it has been presented in other paper.

Conclusions

In this paper, we illustrate the solidification process of liquid Fe and make a detailed analysis on the growth process. By tracing the whole solidification process of super-cooled liquid Fe, we have found two large clusters, one is a lamellar structure and the other is an imperfect five-fold twinning structure. Then, we make a brief illustration about the relationship among the density, order, and size of the two clusters. All analyses suggest that the density and the order of the crystal nucleus are gradually increasing with the increase of the size, which is similar with hard sphere model and the order of the crystal nucleus with the five-fold twinning structure is higher. Besides, we also find that the embryos are always found in high structure-ordered region instead of high density region.

Acknowledgment

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