In this work, the solidification of liquid iron with or without external magnetic field was investigated by using two molecular dynamics methods, namely direct cooling and two-phase simulation. The influence of external magnetic field on the solidification is characterized by the critical temperature and radial distribution functions. Our computational results show that under external magnetic field, the solidification point tends to decrease significantly. By further analyzing the diffusion coefficients and viscosity, we attribute the effect to the stronger fluctuation of liquid iron atoms driven by the external magnetic field.

Key words: Nucleation, Iron, Magnetic field, Molecular dynamics

I. INTRODUCTION

The parameters of solidification process, such as nucleation rate and growth rate, determine the characteristics of solidification structure. It is of great value in industrial application to study the mechanism and controlling of solidification nucleation in electromagnetic metallurgy. The research of solidification process and the progress of solidification technology promote the birth and development of many kinds of new materials and their forming technology.

In recent years, there have been several pioneer studies of investigating liquid-solid phase transition mechanism using molecular dynamics (MD) simulations, such as the homogeneous nucleation of supercooled hot metal by Shibuta et al. [1], the continuous process of homogeneous nucleation and grain growth of a supercooled iron solution by Okita et al. [2], and the grain formation mechanism of Cu-at.19.9Al shape-memory alloy by Ozgen et al. [3]. However, all these previous works have not considered the effects of external magnetic field.

The experiments related to application of external magnetic fields in the solidification of metals date back to the early 20th century. The initial research was to use magnetic field to stir the liquid metal to improve the metallurgical structure, e.g. applying alternating magnetic field to the ingot during solidification by Langenberg et al. [4] and the investigation of rotating magnetic field effect on Si content and eutectic fraction in aluminum alloy by Roplekar et al. [5]. Vives et al. invented the method of electromagnetic oscillation in the solidification process of metal, with the application of a static magnetic field and alternating magnetic field, which produced an alternating electromagnetic force in
the melt and melt vibration, for realizing the grain refinement, gas removal and improvement of the filling capacity [6, 7].

The MD simulations of iron-related materials have significant industrial value, such as the enhanced photocatalytic performance of ordered mesoporous Fe-doped CeO$_2$ catalysts for the reduction of CO$_2$ with H$_2$O, and the joint modification of g-C$_3$N$_4$ coupling and Fe doping to improve the visible-light-driven activity of TiO$_2$ reported by Li et al. [8–10]. Besides, the iron has relatively well-defined force field parameters, allowing us to test the effects from external magnetic field. The structure of iron is simple and easy to simulate, so it is an ideal choice for this work.

II. METHODS

The solidification process of liquid iron has been simulated here by molecular dynamics, using the program of large scale atomic molecular massively parallel simulator (LAMMPS) [11]. The initial simulation cell is prepared from bcc crystal structure of iron with periodic boundary conditions, containing 16000 atoms and with the shape of cubic box as 57.33 Å×57.33 Å×57.33 Å. Then the system is melted by heating to 3000 K, for a 0.05 ns equilibration as shown FIG. S1 in Supplementary materials. The MD simulations are carried out in an isothermal-isobaric (NPT) ensemble. The temperature is lowered from 3000 K by cooling down to 1000 K with the Nosé-Hoover chain thermostat [12, 13] under chosen cooling speed. In this work, four different cooling speeds have been tested. The Andersen method [14] barostat is used for controlling pressure (at 1 atm). The velocity-Verlet algorithm is used to propagate the classical motion equation with a time step of 1 fs. The Visual Molecular Dynamics (VMD) [15] package is used for structure monitoring and trajectory analysis, and the visualization and analysis software Ovito [16] is used for output data generated in our molecular dynamics simulations.

Embedded atom method (EAM) potential fitted by Chamati et al. [17] is employed as the interatomic potential for the Fe–Fe interaction. In EAM potential, the total energy of a monoatomic system has the form

$$E_{tot} = \frac{1}{2} \sum_{ij} V(r_{ij}) + \sum_i F(\hat{\rho}_i)$$  

where $V(r_{ij})$ is the pair interaction energy between atoms $i$ and $j$ separated by a distance $r_{ij}$ and $F$ is the embedding energy of an atom $i$ as a function of the host electron density $\hat{\rho}_i$.

The effective Hamiltonian is used to simulate the magnetic effect. In brief, an additional force field parameter, spin, is assigned to each iron atom. A Zeeman effect model term is added into the original Hamiltonian for simulating the interaction between the spins and the external magnetic field [18]:

$$H_{\text{Zeeman}} = -g \sum_{i=0}^{N} \mu_i \vec{s}_i \cdot \vec{B}_{\text{ext}}$$  

where $\vec{B}_{\text{ext}}$ is the external magnetic field, $g$ is the Lande $g$-factor (specified as $g=2.0$), $\vec{s}_i$ is the unitary vector describing the orientation of spin $i$, and $\mu_i$ is the atomic moment of spin $i$ given as a multiple of the Bohr magneton $\mu_B$ ($\mu_i \approx 2.2$ in bulk iron). One should also keep in mind that the spins also interact with each other. This effect is described by another term of the effective Hamiltonian, as [19]:

$$H = \sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j$$  

The temperature effects are accounted for by connecting the spin to a thermal bath using a Langevin thermostat [20]. A random torque and a transverse dissipation are applied to each spin $i$ according to the following stochastic Landau-Lifshitz-Gilbert (sLLG) equation:

$$\frac{d\vec{s}_i}{dt} = \frac{1}{(1 + \lambda^2)} [(\vec{\omega}_i + \vec{\eta}) \times \vec{s}_i + \lambda \vec{s}_i \times (\vec{\omega}_i \times \vec{s}_i)]$$  

with $\lambda$ being the transverse damping and $\vec{\eta}$ being a random vector. The components of the random vector are drawn from a Gaussian probability distribution. Their amplitude is defined as a proportion of the target temperature $T$ of the thermostat [21]. And in the practical implementation, a symplectic propagator is used on the spin system [22]. In this work, we calculate the solidification point, 1D/2D radial distribution function (RDF) of liquid iron melted from bcc crystal lattice, with and without external magnetic field of 10 T. We use four different cooling rates including 1.0 K/ps, 0.67 K/ps, 0.05 K/ps and 0.04 K/ps, for the above calculations. We also employ the two-phase method to observe the hysteresis phenomenon of solid-liquid phase transition in the processes of heating and cooling.
III. RESULTS AND DISCUSSION

From a characteristic trajectory, the structures of the system before, during and after the phase transition without external magnetic field are shown in FIG. 1(a, b, c). It can be seen in FIG. 1(b) that the phase transition of the system begins at the upper right corner, since atoms in that area appear in bcc structure as visualized by Ovito. The nucleation would appear randomly during the cooling process, as seen in FIG. S2 in Supplementary materials. The ordered phase grows gradually and eventually dominates the simulated system, as shown in FIG. 1(c). The corresponding radial distribution functions of these structures (shown in FIG. 1(g, h, i)) reveal that the second peak of the RDF is split into two peaks, which proves that the system has undergone a phase transition. Meanwhile the third and fourth peaks in liquid state are split into two pairs of peaks, and become sharper as the temperature goes down.

The two-phase method can avoid the hysteresis phenomenon of solid-liquid phase transition during the heating and cooling. In this work, we also apply a two-phase method to validate our simulated results. The initial structure is prepared from liquid state prepared at 3000 K as one half, and the solid state structure prepared at 1000 K as the other half (shown in FIG. 1(d)). We can see again that the phase transition begins with the formation of small nuclei at random locations in the system (FIG. 1(e)) and eventually spreads to the whole system (FIG. 1(f)).

The recorded phase transition temperatures are listed in Table I. From the table, one can see clearly the difference of solidification temperature for iron when external magnetic field is applied, although the non-equilibrium feature of the MD protocol used in this work causes inevitable deviation. Apart from that, we also collect the solidification curves (in FIG. 2(a–d)) from monitoring the volume as an order parameter varying with temper-
FIG. 2 (a) The solidification curve without external magnetic field, and (b) zoom-in of (a) near the abrupt change in volume. (c) The solidification curve with 10 T magnetic field, and (d) zoom-in of (c) near the abrupt change in volume. The hysteresis loops formed by the solidification curve and the melting curve (e) without magnetic field and (f) with a 10 T magnetic field.

TABLE I Solidification temperatures in the MD calculations.

<table>
<thead>
<tr>
<th>Cooling rate (K/ps)</th>
<th>T /K</th>
<th>Fluctuation /K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 T</td>
<td>10 T</td>
</tr>
<tr>
<td>1.0</td>
<td>1550.87</td>
<td>1523.60</td>
</tr>
<tr>
<td>0.67</td>
<td>1521.13</td>
<td>1557.61</td>
</tr>
<tr>
<td>0.4</td>
<td>1556.43</td>
<td>1542.35</td>
</tr>
<tr>
<td>0.4(two-phase)</td>
<td>1564.33</td>
<td>1590.40</td>
</tr>
<tr>
<td>0.4(heating)</td>
<td>2488.07</td>
<td>2487.96</td>
</tr>
<tr>
<td>0.04</td>
<td>1600.21</td>
<td>1587.46</td>
</tr>
<tr>
<td>0.04(two-phase)</td>
<td>1614.31</td>
<td>1578.36</td>
</tr>
</tbody>
</table>

nature. When the system is cooling, there is an abrupt change of volume for phase transition in the range of 1500–1600 K with or without external magnetic field. As can be seen from FIG. 2(e, f), the midpoint of the hysteresis loop is about 2022 K without an applied magnetic field and it is about 2015 K with a 10 T magnetic field. The external magnetic field thus causes a slight decrease of the phase transition point.

To obtain insights of the functionality of the magnetic field, we analyzed radial distribution function of the system without or with external magnetic field (shown in FIG. 3). The RDF in a system of particles reflects the atomic distributions in one-dimension statistical average and describes how density varies as a function of distance from a reference particle. In detail, it is a variable as the number or probability of atoms appearing at different distances. The first peak means the average number of atoms as the nearest neighbor of an atom, and the second peak means the average number of the next nearest neighbor of an atom. Because liquid phase has only short-ranged order, the RDF of liquids is parallel to the x-axis after several (two to three in general) peaks of nearest neighbors, and the peaks are fat and smooth. The higher the temperature is, the more drastically the thermal motion of the atom does, so that the lower heights and wider width of peaks are. In the bcc iron, the nearest neighbor atom of the body-centered atom is located at the eight vertices of the cell, and the next-nearest neighbor atoms are centered in the neighboring cells. Therefore, under cooling, the first peak is increasing and the valley is decreasing, which shows that the short-ranged order of the system is increasing. And the second peak is split at lower temperature, which means that the system has undergone a phase transition. The number of the third nearest neighbor is larger than that of the second nearest neighbor in the bcc iron system, so the third peak is higher than the second one.
The changes of energies and structures without or with 10 T magnetic field during the cooling processes are given in FIG. 4. The potential energy and total energy of the system have drastic changes, while the magnetic energy changes very slightly when the simulation time extends to more than 3900 ps, no matter whether there is an external magnetic field or not. The structure of a large number of particles in the system changes from liquid to bcc at the same time point. The process of energy and particle structure changes can be seen more clearly in the inset images in the middle of each image. These changes are relatively continuous, rather than jumps. Therefore, the solidification phase transition of bcc iron can be considered as a second-order phase transition. The two-dimensional RDFs before and after phase transition are also analyzed to show more clearly the distribution of atoms in the system.

FIG. 5 reveals tendency of solidification points without and with applied magnetic field. The critical temperature $T_c$ decreases under magnetic field with a cooling rate of 1.0 K/ps, but seems to increase with the cooling rate 0.67 K/ps. It is anticipated that a faster rate for cooling should cause the more non-equilibrium effect. Besides, we utilized two different protocols, direct cooling and two-phase simulation, to mutually validate the convergence of the results. When the cooling rate is reduced to 0.4 K/ps and 0.04 K/ps, the tendency becomes clearer. With only one exception of two-phase method with 0.4 K/ps cooling rate, all other three simulations, 0.4 K/ps direct cooling, 0.04 K/ps direct cooling and 0.04 K/ps two-phase cooling, $T_c$ decreases with the magnetic field. The exception suggests in two-phase method, the numerical results are more sensitive to the cooling rate. From the results, it can also be seen the two-phase method with cooling rate of 0.4 K/ps has larger fluctuation, making further evidence of sensitivity with cooling rate for the two-phase method.

The change of diffusion coefficient of iron atoms in liquid phase at 3000 K under magnetic field can be justified readily using the Einstein relation as follows [23]:

$$D = \int_0^\infty d\tau \langle v_x(\tau) v_x(0) \rangle$$

(5)
FIG. 4 The changes of energies and structures ratio (a, c) without magnetic field or (b, d) with 10 T during the cooling processes. $E_k$ is the kinetic energy, $E_p$ is the potential energy, $E_m$ is the magnetic energy, and $E_{tot}$ is the total energy.

FIG. 5 Relationship of solidification point without (left) or with (right) external magnetic field under four chosen cooling speeds (1.0 K/ps, 0.67 K/ps, 0.4 K/ps and 0.04 K/ps). The heights of the rectangles represent the phase transition temperature range. The short horizontal lines in the middle of these rectangle refer as their midpoints.

According to Eq.(5), the diffusion coefficients of the systems without and with magnetic field could be obtained as $1.53 \times 10^{-5}$ cm$^2$·s$^{-1}$ and $1.81 \times 10^{-5}$ cm$^2$·s$^{-1}$, respectively. With diffusion coefficients, one can also obtain the viscosity from Stokes-Einstein equation [24]:

$$D = \frac{k_BT}{6\pi\eta r}$$

where $k_B$ is the Boltzmann constant, $T$ is the temperature, $\eta$ is the viscosity, and $r$ is the hydrodynamic radius, usually replaced by the atoms covalent radius (126 pm here), as described in Ref.[17]. According to Eq.(6), the viscosities are calculated to be $1.14 \times 10^{-2}$ Pa·s and $0.96 \times 10^{-2}$ Pa·s without and with external magnetic field, respectively. When the temperature is reduced from 3000 K to 1823 K, the viscosity without magnetic field is extrapolated to be $6.93 \times 10^{-3}$ Pa·s, in excellent agreement with the literature value $6.44 \times 10^{-3}$ Pa·s [25]. It is thus determined that the diffusion coefficient of liquid iron increases with the applied magnetic field whereas the viscosity is suppressed. These results suggest that iron atoms fluctuate more actively in an external magnetic field. Therefore, under the effect of magnetic field, atoms are harder to nucleate upon cooling and the solidification point of liquid iron will be lower. From here we can understand the effect on nucleation dynamics in the presence of an external magnetic field. On the other hand, from other experiments on the solidification of liquid aluminum, Li et al. found that the diffusion of the atoms decreases and the viscosity increases under external magnetic field [26]. So there seems to be no general rule for the effect of external magnetic field on the nucleation processes for liquid iron.
**IV. CONCLUSION**

In summary, we have applied two MD simulation methods, namely direct cooling and two-phase simulation, to investigate the dynamics of solidification of iron without and with external magnetic field. Our results show that the iron undergoes solidification at the temperature range of 1500–1600 K. During the solidification, we have observed the process of nucleation in the simulated system, and the position of nucleation is stochastic. By analyzing heating-cooling hysteresis loops, 1D and 2D radial distribution functions with or without magnetic field, we have found the magnetic field to effectively decrease the solidification temperature. From our results of diffusion coefficient and viscosity, we attribute this effect to the increasing fluctuations of atoms in the liquid iron.

**Supplementary materials:** The simulation box of liquid iron from bcc crystal structure with periodic boundary conditions, containing 16000 atoms which was melted by heating to 3000 K. Multiple repetitive molecular dynamics simulations of solidification show the random nucleation.

**V. ACKNOWLEDGMENTS**

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