Atomic investigation of steady-state dendrite tips by using phase-field crystal method

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Abstract. Steady-state dendrite growth is controlled by the states of dendrite tips, thus the morphology and growth kinetics of dendrite tip have always been a highly-studied issue in the field of dendrite growth. A crucial problem is to find out the factors influencing the morphology of dendrite tip, and to clarify their working mechanism. Since dendrite tip is at micrometer or even atomic scale, interface energy may probably plays an important role during the formation and stabilization of dendrite tips. Investigations of this issue at atomic scale is of significant because it can help us to clearly observe the morphology evolution of dendrite tip fundamentally, and specifically reveal the relationship between interface energy anisotropy and dendrite tip morphology. We investigate growth kinetics and morphology of dendrite tips at atomic scale by using phase-field crystal simulation. Atomic scale steady-state dendrite tips are obtained at different interface energy anisotropy and growth driving force. It is shown that the morphology of the forefront of dendrite tip varies periodically with time, which is related to the behavior of atom attachment during the steady-state growth of dendrite tip. Moreover, we demonstrate that growth driving force determines the overall shape of dendrite tip, but exerts little influence on the morphology of the forefront of dendrite tip which actually is determined by interface energy anisotropy. The dendrite tip of high interface energy anisotropy often presents sharp shape which is in favour of the formation of dendrite tip. Nevertheless, the shape of dendrite tip approaches to circle with decreasing magnitude of interface energy anisotropy, indicating that it is more difficult for the formation of dendrite tip under the circumstance of lower interface energy anisotropy.

1. Introduction

Steady-state dendrite growth is controlled by the states of dendrite tips, thus the morphology and growth kinetics of dendrite tip have always been a highly-studied issue in the field of dendrite growth. For the study of dendritic growth, a crucial problem is to find out the factors influencing the morphology of dendrite tip, and to clarify their working mechanism. Macroscopically, Ivantsov solution, experimental results, and phase field simulation illustrate that the product between dendrite tip radius R and growth velocity V or V^2 is a constant. Therefore, R is decreasing nonlinearly with undercooling or supersaturation if assuming V increases linearly with undercooling or supersaturation. That is to say that the overall shape of dendrite tip is affected by macroscopic driving force such as undercooling or supersaturation [1,2].

Moreover, since dendrite tip is at micrometer or even atomic scale, interface energy may probably plays an important role during the formation and stabilization of dendrite tips. As we know, the Wulff theory elucidates the close relationship between interface energy anisotropy and equilibrium crystal
shape. The round or sharp corners of equilibrium crystal shape are attributed to the magnitude of interface energy anisotropy. So it is interesting to explore that whether the dendrite tip morphology is also closely related to interface energy anisotropy or not. Microscopic solvability theory suggests that interface energy anisotropy is indispensable during the formation of dendrite tip, and illustrates that the stability criterion constant being related to the steady-state of dendrite tip is a function of interface energy anisotropy. Moreover, phase field simulations have obtained similar results. Phase field simulations have not only reproduced the steady-state growth of dendrite tips at micrometer or larger scale, but also verified the dependence of stability criterion constant on interface energy anisotropy as indicated by the microscopic solvability theory. Nevertheless, these works only have explained the importance of interface energy anisotropy on dendrite tip, failing to tell us clearly how interface energy anisotropy affects dendrite tip.

Solving this problem requires us to conduct research at atomic scale which can help us to clearly observe the morphology evolution of dendrite tip fundamentally, and specifically reveal the relationship between interface energy anisotropy and dendrite tip morphology. A more microscopic research can contribute a better understanding about dendrite tip formation, and atomic scale investigations may provide us with the most direct picture for structure and shape of dendrite tip. However, to observe dendrite growth at atomic scale still faces formidable difficulties and challenges in experimental and numerical studies at present.

To present atomistic resolution analysis of morphology of the dendritic growth front for different strength of anisotropy of the interfacial energy, in this study, we employ a new methodology—phase-field crystal (PFC) model, which has the unique advantage of simulating crystal growth at atomic length scale and at diffusive time scale. For the purpose of acquiring a better understanding about dendrite tip growth kinetics and morphology microscopically, we firstly study growth kinetics of steady-state dendrite tip, and then investigate the dependence of dendrite tip morphology on growth driving force and interface energy anisotropy. It is found that interface energy anisotropy determines the morphology of the forefront of dendrite tip, while growth driving force tends to exert its effects on the overall morphology of dendrite tip.

2. Method and simulation details
Based on the classical density functional theory (CDFT) of freezing, Elder et al. invented the phase-field crystal (PFC) model. Like CDFT, the PFC model is formulated as the free-energy function with respect to scaled density related to atom number density,

\[ F(\psi) = \int d^3 \{ \frac{\psi}{\bar{\rho}_0} [ -\varepsilon + (1 + \nabla^2)^2 \psi + \psi^4] \} \],

where \( \psi \) is the scaled coarse-grained (ensemble- or time- averaged) atomic number density field, \( \varepsilon \) is related to the crystalline anisotropy. \( \psi \) is periodic in crystal phases, while uniform in liquid phase. Compared with conventional phase-field simulation in which the crystallographic information of solid phase is smeared, the PFC model is capable of visualizing the atom configuration of solid phases with various crystal structures.

The simulation parameter \((\varepsilon, \bar{\rho}_0)\) is chosen based on 2D PFC phase diagram. The crystalline anisotropy increases with increasing \( \varepsilon \). The initial density of liquid phase is \( \bar{\rho}_0 \) which determines the growth driving force. The crystal growth begins with a circular nucleus with radius's length about five times of the lattice constant. The circular nucleus locates at the center of the simulation box and is surrounded by homogenous liquid. The initial density of the nucleus is given by one-mode approximation which reads,

\[ \psi = A[\cos(qx)\cos(qy/\sqrt{3}) - \cos(2qy/\sqrt{3})/2] + \bar{\rho}_0, \]

where \( A \) is the amplitude of the density waves, and \( q \) is the magnitude of the principal reciprocal lattice vectors with the value of \( \sqrt{3}/2 \). Thus, the lattice constant of hexagonal structure is given by \( a = 2\pi/q \). The dimensionless grid size is \( dx = \pi/4 \), and the time step is \( dt = 0.75 \).
3. Results and discussion

Fig. 1 describes the growth kinetic and morphology of steady state dendrite growth when \((\varepsilon, \bar{\nu}_0) = (0.3, -0.34)\). As shown in Fig. 1(a) the shape of smoothed density profiles on the front of solid-liquid interface remains unchanged after dendrite growth reaches steady-state, and the length of the diffusion field in liquid phase converges with time as shown in the inset figure in Fig. 1(a). These aspects suggest that the density diffusion field around dendrite tip can reach a steady-state, allowing the growth velocity and the minimum density on the front of solid-liquid interface to converge after a transient stage, i.e., the dendrite tips grow in a constant velocity after a short transient stage.

Fig. 1(c) describes the change of density minimum in the liquid phase on the front of dendrite tip. The periodic characteristics reflect the growth mechanism. As shown in Fig. 1(d), the peak corresponds to the generation of a new layer in the vicinity of the forefront of dendrite tip, and the valley indicates that the new layer has already been fully occupied by atoms. Our simulation shows

Figure 1. The growth kinetics and morphology of steady-state dendrite growth. (a) The shape of smoothed density profiles along the direction of dendrite arm at various times, where \(L\) is the length of the diffusion field, and \(\bar{\nu}_{\text{min}}\) the minimum density of liquid phase on front of solid-liquid interface. The inset figure in (a) show that \(L\) will converge when dendrite growth reaches to steady-state. (b) The change of growth velocity \(V\) and \(\bar{\nu}_{\text{min}}\) with time. (c) The variation of
during a very short time. (d) the morphology of the forefront of dendrite tip corresponding to time A-F in (c).

**Figure 2.** The dendrite morphology of dendrite tip at different growth driving force ($\bar{\psi}_0$) under the same interface energy anisotropy with $\varepsilon=0.3$. (a) $\bar{\psi}_0=-0.3575$, (b) $\bar{\psi}_0=-0.345$, (c) $\bar{\psi}_0=-0.3425$, and (d) $\bar{\psi}_0=-0.34$. The left figure in (a)-(d) is the overall shape of dendrite, while the right one corresponds to the forefront part of dendrite tip.

**Figure 3.** The comparison between the morphology of equilibrium crystal and dendrite tip at different interface energy anisotropy ($\varepsilon$): (a) and (b) $\varepsilon=0.4$; (c) and (d) $\varepsilon=0.3$; and (e) and (f) $\varepsilon=0.25$.

that the morphology of dendrite tips at atomic scale varies between the two circumstances periodically. Experimental study at microscopic scale also find that the morphology of dendrite tip present similar
oscillation. For the convenience, we regard the morphology corresponding to valleys as the dendrite tip morphology in this study.

As shown in Fig. 2, the morphology of the forefront of dendrite tip doesn’t change with growth driving force under the same interface energy anisotropy when $\varepsilon = 0.3$, though overall shape of dendrite tip varies substantially with growth driving force. The part of contour lines corresponding to the forefront of dendrite tip overlap, but they begin to separate at the position away from the forefront of dendrite tip. Therefore, though overall radius of dendrite tips shows obvious dependence on growth driving force, the morphology of the dendrite tip is independent of growth driving force. Thus, it is interesting to explore the factors determining dendrite tip morphology at atomic scale.

As shown in Fig. 3, we compare the morphology of the corner of equilibrium crystal with the forefront of dendrite tip. For the case of high interface energy anisotropy, both the equilibrium crystal and dendrite tip present sharp shape. For the case of intermediate interface energy anisotropy, the dendrite tip and equilibrium crystal tip present a small round shape limited by two small facets; For the case of weaker interface energy anisotropy, the round shape at dendrite tip becomes wider compared with Fig. 3(c) and (d). However, no dendrite can be obtained if decreasing interface energy anisotropy further, because the interface energy is too weak to sustain dendrite tip. Though the overall morphology of dendrite tip shows great differences, the local atom configuration at the corners of equilibrium crystal and dendrite tips is almost the same. As we know, the local part of the corner is greatly determined by interface energy anisotropy. Therefore, it is inferred that the morphology of the forefront of dendrite tip is determined by interface energy anisotropy.

4. Conclusion

In this work, through phase-field crystal simulation, we study the steady-state dendrite tip growth kinetics and morphology at atomic scale. It is shown that atomic scale morphology of the forefront of dendrite tip varies periodically with time, which is resulted from the behaviours of atom attachment at dendrite tip. Moreover, being consistent with previous studies, the radius of the overall dendrite tip decreases with increasing driving force, but the radius of the forefront of dendrite tip generally shows little dependence on driving force. We find that the morphology of the forefront of dendrite tip is mainly determined by interface energy anisotropy. Dendrite tip obtained under high interface energy anisotropy often has sharp dendrite with high curvature, which is in favour of dendrite tip formation. For the case of low interface energy anisotropy, the radius of the forefront part of dendrite tip increases steeply with decreasing anisotropy, which is disadvantage for the formation of dendrite.

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