

Characterizing Ice Crystal Growth Behavior Under Electric Field Using Phase Field Method

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In this article, the microscale ice crystal growth behavior under electrostatic field is investigated via a phase field method, which also incorporates the effects of anisotropy and thermal noise. The multiple ice nuclei's competitive growth as disclosed in existing experiments is thus successfully predicted. The present approach suggests a highly efficient theoretical tool for probing into the freeze injury mechanisms of biological material due to ice formation during cryosurgery or cryopreservation process when external electric field was involved. [DOI: 10.1115/1.3142978]

Keywords: microscale ice crystal, phase field method, electric field, cryobiology

1 Introduction

Freeze injury induced by ice formation is usually considered as the main killer of cells during cryosurgery or cryopreservation [1]. A two-factor hypothesis proposed by Mazur et al. [2], the intracellular ice formation (IIF) at rapid cooling rates and solution effects at slow cooling rates, has served well to explain the mechanism of freeze injury. The biological materials would be subjected to damage due to extracellular and intracellular ice formations during freezing. For the cryopreservation at supercooling temperature, the occurrence of IIF is the single most important factor determining whether or not cells will survive freezing [3]. So far, many cryopreservation methods have been successfully developed. Among the many efforts ever made, the electrostatic field was recently proposed to improve the output of the cryopreservation process [4–6]. To better understand the detailed events occurring in such practice, it is rather important to model and predict the microscale ice crystal formation and growth behavior, and thus characterize the effects of several core factors, such as undercooling, anisotropy, thermal noise, external electric field, etc. In fact, the interaction between the cell and ice during freezing is becoming a hot topic and has attracted much attention in the cryobiology area [7,8]. However, it is still a rather difficult task to track the

evolution of the solidification front and quantify the interaction between the cell membrane and ice in detail. Among various theoretical approaches ever developed, the phase field method is rather flexible in characterizing the crystal formation and has been extensively adopted to model solidification process in materials science [9]. This method can effectively simulate the interaction between the solidification front and foreign particles [10]. Recently, some authors [11,12] begun to pay attention to possible application of this method in cryopreservation. In the present work, this theoretical strategy was extended to characterize the ice crystal formation under electrostatic field and describe multiple ice nuclei's competitive growth behavior.

2 Theoretical Model

It has been well known that phase transition from water to ice begins with a nucleation process, which means re-arrangement of water atoms to form ice crystal. When the radius of ice seed satisfies $r \geq r_c = \sigma T_M / L \Delta T$, it will continue to grow. The growth rate depends on the dynamical state of the ice-water interface, such as the surface tension and the temperature at interface. In addition, the effects of the external electric field on the ice formation have been demonstrated in both theoretical and experimental researches. As the molecular dynamics simulated [13], a dc field with a magnitude of $E = 5.0 \times 10^9$ V/m could induce crystallization of supercooled water. Recently, experiments [4–6,14] have demonstrated that the external electric field can effectively affect water nucleation and ice growth. A lower electrostatic field strength in the range of $E = 10^3 - 10^5$ V/m, which is easily obtained in experiments, can induce increase in the nucleation temperature of water [6] and the asymmetric growth of ice [4].

The influence of low electrostatic field strength on water nucleation and ice growth may be attributed to the dipole polarization of water molecules by the electrostatic field. Under the electrostatic field, the phase transition must overcome excess energy $\Delta G^E = E \Delta \mu$, where $\Delta \mu = \mu_w - \mu_i$ is the difference of electrical dipole moments between water and ice. However, for the low electrostatic field strength ($E < 10^5$ V/m), ΔG^E is much smaller than L and can be negligible. In other words, the water molecules with dipole moments may follow the Boltzmann distribution function $p = A \exp(\mu_w E \cos \varphi / kT)$ [6], and get in the most stable state with the maximum energy along the direction of the electrostatic field ($\varphi = 0$). Although for the low electrostatic field magnitude, the value variation of p with respect to φ is rather small in bulk phase, the effects of electrostatic field may become largely strong at the interface and affect the dynamical state of the interface [4]. The polar water molecules (or clusters) may be torqued, re-arranged, and forced to join the ice lattice via a special orientation and position under action of the electrostatic field. Thus the rate of attachment (or detachment) of water molecules on the ice interface is affected by external electrostatic field. In order to characterize such influence of the electrostatic field, the surface tension should be modified as $\exp(\lambda \cos(\theta - \varphi))\sigma$ during the ice growth, where λ is proportional to $\mu_w E / kT$.

It is noteworthy that a major part of the biological media is a saline solution, which generally includes various ions, such as Na^+ and Cl^- . Under the electrostatic field, these positive and negative ions take completely different movement and gather near the corresponding electrodes, which in turn induces nonuniform distribution of ions. In addition, the heterogeneous structure of ions, such as their different sizes, also leads to different ion behaviors. These behaviors induced by the electrostatic field will affect the dynamical process of the ice interface and further strengthen the asymmetric growth of ice [4]. Thus, the effects of the ions under the electrostatic field should also be reflected by modifying the surface tension. That means a model with generalized purpose should incorporate such effects of ions coupling with the electrostatic field on the dynamical behavior of the ice interface. The present note is dedicated to investigate the effects of the electrostatic field

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on the ice interface but is not to completely characterize the effects of ions, which will be addressed in further work.

In this note, a dimensionless phase field model [15] is adopted to characterize the ice growth. A nonconserved phase field ϕ ($\phi = 0$ is corresponding to ice and $\phi = 1$ to water) describes the transition from water to ice, which is driven by undercooling. A conserved dimensionless temperature field u is used to characterize the energy variation due to temperature diffusion and phase transition. It reads as

$$\phi_t = m \nabla \cdot (B(\theta) \nabla \phi) + m \varepsilon^{-2} \phi(1 - \phi)[\phi - 0.5 + 30 \varepsilon a S u \phi(1 - \phi)] \quad (1)$$

$$u_t = \nabla^2 u - S^{-1} 30 \phi^2 (1 - \phi)^2 \phi_t + \psi(x, y, t) \quad (2)$$

where

$$B(\theta) = \begin{pmatrix} \gamma^2(\theta) & -\gamma'(\theta)\gamma(\theta) \\ \gamma'(\theta)\gamma(\theta) & \gamma^2(\theta) \end{pmatrix} \quad (3)$$

In the above equations, the term ψ represents the thermal noise, which indicates the fluctuation of temperature, and $u = (T - T_M) / \Delta T$. $\gamma(\theta) = 1 + \varsigma \cos n(\theta - \theta_0)$ denotes the dimensionless anisotropic surface tension and $\theta = \arctan(\phi_y / \phi_x)$, where θ_0 is the angle between the reference direction and the x -axis. Four dimensionless parameters are defined as follows:

$$m = \frac{\nu \sigma T_m}{\kappa L}, \quad \varepsilon = \frac{\delta}{w}, \quad a = \frac{\sqrt{2} w}{12 d}, \quad S = \frac{c_p \Delta T}{L} \quad (4)$$

where $d = c_p \sigma T_m / \rho L^2$ [15].

From the above dissection, the effects of electrostatic field with low magnitude can induce change of the surface tension with the form $\sigma_E = \exp(\lambda \cos(\theta - \varphi)) \sigma$. Thus in the phase field model, the dimensionless anisotropic surface tension should be modified as $\gamma_E(\theta) = \exp(\lambda \cos(\theta - \varphi)) \gamma(\theta)$. The value of λ is proportional to $\mu_w E / kT$, which characterizes the strength of electric field. In our simulations, the value of λ is chosen in the range 0.02–0.2 and $\varphi = 0$, which indicates that the orientation of electric field is along the positive x -axis.

3 Results

The physical properties of water [11] used in the simulation are listed below: $\kappa = 1.31 \times 10^{-3} \text{ cm}^2/\text{s}$, $L = 333.5 \text{ J}/\text{cm}^3$, $T_M = 273.15 \text{ K}$, $c_p = 4.212 \text{ J}/\text{cm}^3 \text{ K}$, and $\sigma = 7.654 \times 10^{-6} \text{ J}/\text{cm}^2$. The length scale w is considered as $2.7 \times 10^{-4} \text{ cm}$. Thus the phase field model parameters for all the simulations, according to Wang et al. [15], can be fixed with $\varepsilon = 0.005$, $m = 0.035$, $a = 400$, and $S = 0.5$, respectively, which corresponds to the cooling temperature of 233.56 K.

An explicit time-differencing scheme is adopted to solve ϕ -equation, and an implicit Crank–Nicolson algorithm is chosen for solving the u equation. All the simulations are performed in a two-dimensional domain with 1500×1500 grid points ($\Delta x = 10^{-2}$ and $\Delta t = 10^{-4}$) under the Neumann boundary conditions. The initial condition of the phase field for single ice nucleus is set for $\phi = \frac{1}{2} [\tanh((r - r_c) / 2\sqrt{2}\varepsilon) + 1]$. The initialization of the dimensionless temperature is $u = -\phi$ for all the simulations, which corresponds to the initial temperature T_M in solid and $T_M - \Delta T$ in liquid.

Simulations indicate that the influence of surface tension anisotropy on the shape of ice is more evident compared with that on the growth rate. The variation of the anisotropy strength does not significantly change the velocity at the dendritic tip, which is strongly affected by the local cooling strength. Fourfold and sixfold dendritic ice crystals are often observed in experiments. Figure 1(a) shows a fourfold dendritic ice crystal evolving from an initial circle shaped seed. The thermal noise, which often induces the temperature fluctuation at the interface, is considered as the main reason of sidebranching growth [16]. A sixfold dendritic ice with sidebranching is shown in Fig. 1(b). It is necessary to con-

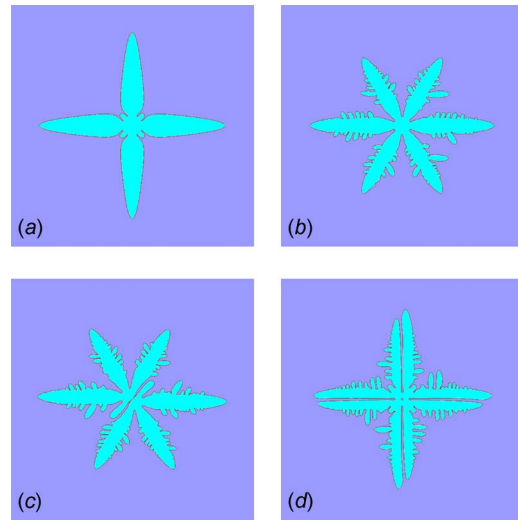


Fig. 1 Microscale dendritic ice crystal patterns with (a) fourfold structures without thermal noise, (b) sixfold structures with thermal noise, and (c) two seed and (d) four seed competitive growth. The parameters $\gamma = 0.04$ and $n = 4$ in (a) and (d), and $\gamma = 0.02$ and $n = 6$ in (b) and (c). The angle $\theta_0 = 0$ for (a)–(d).

sider the influence of the other crystal seeds on the ice growth. Figures 1(c) and 1(d) represent two seed and four seed competitive growths, which results in the crease of growth for both collided dendrites and preferred growth in directions of unhindered grains.

Under the electrostatic field, the growth of dendritic ice crystals would display asymmetry behavior. As indicated in Fig. 2, the main branches parallel to the electrostatic field grow faster than the other branches. One can also observe that the growth of the sidebranching is strengthened along the direction of the electric field and weakened along the inverse direction. The above influence could further become clearer by increasing the value of λ (comparing Fig. 2(b) with Fig. 2(c)), which indicates that a stronger magnitude of electrostatic field would strengthen the asymmetric growth of ice. Figure 2(d) shows how the reference direction affects the ice growth under electric field. The above results

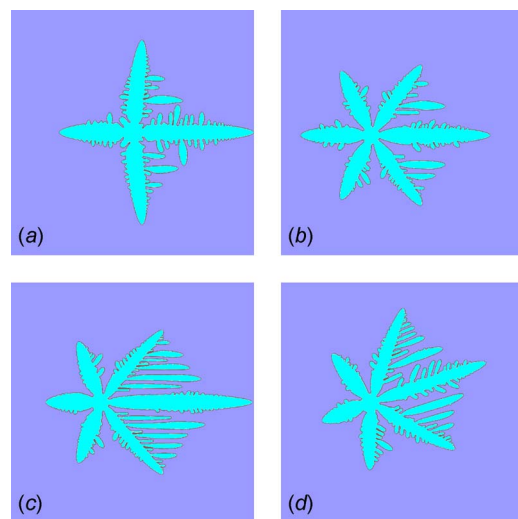


Fig. 2 The influence of electric field on ice crystal growth at (a) $\gamma = 0.04$, $n = 4$, and $\lambda = 0.1$; at (b) $\gamma = 0.02$, $n = 6$, and $\lambda = 0.1$; and at (c) and (d) $\gamma = 0.02$, $n = 6$, and $\lambda = 0.2$. The angle $\theta_0 = 0$ for (a)–(c) and $\theta_0 = \pi/9$ for (d).

concerning the effects of electric field are in good accordance with the qualitative analysis in Ref. [6] and the experimental observation in Ref. [4].

In summary, in the present work, we have successfully demonstrated that the phase field method can effectively reproduce microscale ice crystal growth, and characterize the effects of external electric field. We also presented the influence of thermal noise on ice growth and multiple ice nuclei's competitive growth. Although the results as presented in this note are very consistent to experimental observation, the influence of electrostatic field on ice crystal growth, in fact, is rather complex, and cannot be completely figured out by only modifying the surface tension. In addition, our discussion is mainly limited to pure water, and the aqueous solution in biological materials often have many ions such as Na^+ and Cl^- , which can affect the ice growth more strongly under the electric field. Therefore, it is urgently needed to make further efforts along this direction. The present modified phase field method offers a useful start tool to tackle such tough theoretical issue.

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Nomenclature

a	= dimensionless parameter
A	= proportional constant
c_p	= specific heat ($\text{J}/\text{cm}^3 \text{K}$)
d	= capillary length
E	= strength of electrostatic field (V/m)
ΔG^E	= excess energy
k	= Boltzmann's constant
L	= heat of fusion (J/cm^3)
m	= dimensionless parameter
n	= n -fold dendritic ice crystals
p	= Boltzmann distribution
r	= radius of ice seed
r_c	= critical radius
S	= Stefan number
T_M	= melting temperature (K)
ΔT	= degree of supercooling (K)
u	= dimensionless temperature
w	= length scale (cm)
γ	= dimensionless surface tension
δ	= length scale for the interface
ε	= dimensionless interface thickness
s	= strength of the anisotropy
θ	= normal direction of interface

θ_0	= reference direction
κ	= thermal diffusivity (cm^2/s)
λ	= dimensionless parameter
μ_w	= electrical dipole moments of water
μ_i	= electrical dipole moments of ice
ν	= dimensionless interface kinetic coefficient
σ	= surface tension (J/cm^2)
ϕ	= parameter for phase field
φ	= direction of electrostatic field
ψ	= thermal noise

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