



Phase field simulations of ice crystal growth in sugar solutions



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ABSTRACT

We present the first model ever, that describes explicitly ice crystal growth in a sugar solution during freezing. This 2-D model uses the phase field method, supplemented with realistic, and predictive theories on the thermodynamics and (diffusion) kinetics of this food system. We have to make use of a novel type of phase field to obtain realistic, micron-sized ice crystals, and exclusion of sugar from the crystalline phase. Via simulation of a single ice crystal, we identify important time scales governing the growth. These time scales are also important for the coarsening of the ice morphology in freezing systems with multiple ice crystals. These simulations show that the average ice crystal size is governed by the freezing rate via a power law, similar to an empirical relation from literatures, which is deduced from experiment. The presented model is viewed as a good basis for even more realistic simulations of crystal growth in food.

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1. Introduction

The size and shape of ice crystals are important measures for the quality of frozen foods, like ice cream or frozen soft fruits [1]. Small rounded ice crystals are desired for ice cream with a soft and creamy texture. Other foods are frozen as a means of preservation. For frozen foods having a cellular tissue, it is important that the ice crystals remain smaller than the cell size, otherwise they will puncture them – rendering an unappetizing, mushy food after thawing. Freezing is also used for texturing foods like the traditional Japanese food, kori-tofu [2]. Here, often larger crystals are desired to render a fibrous structure to the soy gel. This freeze texturing is nowadays also used for non-food applications like scaffolds of biomaterials and other advanced materials [3,4].

In our previous research we have used freeze-drying to structure vegetables for enhanced hydration [5]. In that research we have derived an empirical relation for the mean ice crystal size as a function of freezing rate [6]. Our literature review has shown that there are several (semi-) empirical relations, which quite differ from each other. We expect that also the composition of the food is of importance, but none of the empirical relations takes that into account. Hence, there is a need for more theoretical understanding how the ice crystal size can be controlled via freezing rate and food formulation. Such understanding is also advantageous for frozen foods like ice cream, which are reformulated to contain less sugars to improve the health effects of this indulgent food.

The theoretical understanding of ice crystal growth at the microscale we like to obtain from phase field simulations [7]. Currently, this numerical method is mainly used to describe the evolution of the microstructure of alloys during solidification. The so-called phase field indicates whether the material is either solid or liquid. In the interfacial region, the phase field is a smooth function that varies in between its extremal values, which are used to indicate the bulk solid and liquid phases. The interfacial region has a finite width, which is several times larger than the grid spacing. Therefore, this numerical method is also called the diffuse interface method.

The evolution of the phase field and the solute concentration field are governed by a free energy functional. Often, the evolution of the concentration field is driven by diffusion only, with the chemical potential as the driving force. However, in the liquid phase both fields can be subject to flow, driven by gradients in hydrostatic and osmotic pressures. The driving forces for diffusion and flow, the chemical potential and osmotic pressure are derived from the above mentioned free energy functional. In this aspect the phase field method is very related to the Cahn–Hilliard method of spinodal decomposition of alloys and polymer blends [8,9]. We have used similar models earlier to describe (surfactant-stabilized) emulsions [10–13].

Via its coupling to the free energy functional, it is relatively straightforward to link the phase field method to realistic, thermodynamic descriptions of complex food materials [14]. Often, foods are structured via phase transitions [15], which are handled relatively straightforwardly in the phase field method. Not only solidification, but also boiling phenomena can be treated [16].

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Having developed realistic descriptions of the thermodynamics of complex foods including sugars [17,18], and a realistic description of diffusion in these materials [19], we are in the position to apply the phase field method to realistic simulations of microstructural developments of sugar solutions during freezing. Only recently, the phase field method has been applied to freezing of mixtures of water and a solute, namely salt [20,21]. However, for these mixtures simplified approximations are used for the thermodynamics and the diffusion. Here, we intend to use realistic, and predictive theories, which do not require any approximations.

In this paper we will report our first results of the application of the phase field method to freezing of sucrose solutions, which is taken as a model system for ice cream. The only non-realistic restrictions of the model we will impose are: (1) the simulations will be performed in 2-D, and (2) we do not assume anisotropy in the interfacial tension, which is normally assumed in the phase field method to model dendritic growth. However, as said above, dendritic growth is not stimulated in ice-creams, and microstructures of frozen foods indicate that cellular crystal growth dominates in normal food freezing operations [1,6]. Furthermore, we envision that the 2-D representation of the crystals are cross sections of the cellular crystals. Cellular ice crystals grow in the direction of the temperature gradient, and their cross section is about circular. In the 2-D plane the temperature gradient will be assumed zero. The cross sectional size of the cellular ice crystals is often the length scale of interest for the morphology of frozen foods [5]. Hence, we do expect the simulated ice morphology to be comparable to that of slowly frozen sugar solutions.

Below, we will investigate the growth of single seed crystals, and multiple seed crystals. Crystallization takes place in 4 steps: (1) nucleation, (2) recalescence, (3) growth and (4) coarsening. However, there is a large difference in time and length scales governing each step. Hence, we will focus on the last 2 steps only. Seed crystals are placed in the computational domain at the start of the simulation. We will particularly focus on the interaction between growth, coarsening and freezing rate. For single seed crystals we first focus on the numerical aspects of the developed model, and investigate the important time scales of the crystallization process. In the latter case, we examine the impingement of crystals, and the interaction of coarsening and freezing rate.

2. Phase field model

2.1. Governing equations

To describe non-isothermal solidification of aqueous solutions, we need to describe in principle three fields: the energy density e , the solute volume fraction ψ , and the phase field ϕ – which is equivalent to the volume fraction of ice. In the phase field method, the total energy density e is decomposed in sensible energy density q and a contribution due to latent heat:

$$e = q - L_{ice}\phi \quad (1)$$

with L_{ice} the specific enthalpy of fusion for ice, measured in J/m^3 . The sensible energy density is linear with temperature:

$$q = [\phi C_{p,ice} + (1 - \phi)C_{p,w}](T - T_m) \quad (2)$$

$C_{p,i}$ is the specific heat of the material i , in units of $(\text{J/m}^3/\text{K})$. To simplify the initial presentation of the model, we have assumed implicitly that specific heat of the liquid phase is dependent of the solute concentration. T_m is the melting temperature of ice – which is taken as the reference temperature for the energy.

The energy balance is written with the change in latent heat in the right-hand-side of the equation:

$$\partial_t q = \nabla k(\phi, \psi) \cdot \nabla T + L_{ice} \partial_t \phi \quad (3)$$

The equation will be solved for q , and $\partial_t \phi$ will follow from the evolution of the phase field, as described below. The thermal conductivity of ice and sugar solution is different, and it is thus a function of ϕ and ψ .

The ice volume fraction evolves according to Allen–Cahn [7]:

$$\frac{1}{\tau_\phi} \partial_t \phi = - \frac{\delta f}{\delta \phi} \quad (4)$$

$\delta f / \delta \phi$ is the variational derivative of the free energy functional against the phase field order parameter. The free energy functional f will be given below.

The solute volume fraction evolves as:

$$\partial_t \psi = \nabla M_\psi \cdot \nabla \frac{\delta f}{\delta \psi} \quad (5)$$

The mobility M_ψ is related to the moisture diffusivity, D_m , via $M_\psi = D_m \psi(1 - \psi)$. $\delta f / \delta \psi$ is the chemical potential difference, $\tilde{\mu}_\psi$, the driving force for diffusion. It is also derived from the free energy functional, via the derivative of the free energy against the solute volume fraction ψ .

The total free energy density is decomposed into two parts: $f = f_\psi + f_\phi$, which are a function of ψ and ϕ respectively. f_ψ is the free energy density of the sugar solution, which is described by the Flory–Huggins (FH) theory [17,18]. In case of $\phi = 0$, it reads:

$$\frac{f_\psi}{RT} = \frac{1}{N} \psi \ln(\psi) + (1 - \psi) \ln(1 - \psi) + \chi \psi(1 - \psi) \quad (6)$$

χ is the Flory–Huggins interaction parameter, and N is the ratio of molar volume between solute and water. Below, we will adjust this contribution to the free energy to account for exclusion of sugar from the crystalline phase.

The other contribution to the free energy, f_ϕ , enables the coexistence of two phases: the ice crystal phase, and the unfrozen sugar solution. To this end, we use the Cahn–Hilliard formulation with a double well potential – where the energy barrier is temperature dependent [7]:

$$\frac{f_\phi}{RT} = 2H\phi^2(1 - \phi)^2 + \frac{\kappa}{2}(\nabla\phi)^2 + X(T - T^{eq})g(\phi) \quad (7)$$

with $g'(\phi) \approx \delta(x) = h(\phi)^N$ with $h(\phi) = 4\phi(1 - \phi)$ and N an integer number. $g'(\phi)$ approximates the Dirac-delta function, and thus $g(\phi)$ approximates the Heaviside function. T^{eq} is the (local) freezing temperature of the aqueous solution, which depends on the local sugar concentration ψ , as determined by the FH theory [17]. The last term is inspired by the snow model of Plapp and coworkers [22]. The form of the free energy functional f_ϕ is explained in more detail below.

The supercooling $\Delta T = T - T^{eq}$ will tilt the double well potential, as shown in Fig. 1. Between the two wells there is an energy barrier of height, which equals, $\Delta h = H/8$ at $T = T^{eq}$. If the solution is supercooled, the potential well of the solid phase ($\phi = 1$) lowers, as well as the energy barrier Δh . If the potential well of the solid phase is lower than that of the liquid phase, this phase is thermodynamically favoured. Only the solid phase is stable, and the liquid phase will be metastable or supercooled.

The squared gradient term in the free energy functional represents the surface free energy of the solid–liquid interface. The order parameter ϕ will develop into a tanh profile, for which the squared gradient term is an approximation of the delta-function [11]. The thickness of the diffuse interface thickness ζ is related to the height of the energy barrier H , and the interfacial free energy κ . Via the properties of $g(\phi)$ the wells of the potential remain at $\phi = 0$ and $\phi = 1$ [23]. The free energy difference between the two wells equals the free energy difference between solid and liquid phase and must remain smaller than the height of the energy

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