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Liquid phase sintering of two roughened ice crystals in sucrose solution: A comparison to theory and simulation

R.S. Farr [a,*], A. Luque [b], M.J. Izzard [c], M. van Ginkel [c]

[a] Unilever R&D Vlaardingen, Olivier van Noortlaan 120, AT 3133, The Netherlands
[b] CEIT and Tecnun, University of Navarra, Paseo Manuel Lardizabal 15, 20018 San Sebastian, Spain
[c] Unilever R&D Colworth, Sharnbrook, Bedford MK44 1LQ, UK

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ABSTRACT

We construct an approximate analytic expression for the growth of the neck between two sintering roughened crystals in contact with a melt. The result combines recent work on early phase sintering [R.S. Farr, M.J. Izzard, Phys. Rev. E 77 (2008) 041608], and a numerical method presented here, based on Legendre polynomials. The expression gives an estimate which covers all times from very early to near equilibrium, and includes the effect of a grain boundary between the two crystals. The predictions are then compared to experiments on sintering of ice crystals in a sucrose solution.

1. Introduction and the equations of surface evolution

When a crystal is allowed to come into equilibrium against a melt, then it will eventually reach the Wulff shape, which can be obtained by the following construction [1]: let the free energy per unit area of a plane surface of the crystal (in contact with the melt) be given by $\gamma(\mathbf{n})$, where $\mathbf{n}$ is a unit vector normal to the surface, then we define a set of points $\mathbf{p}(\mathbf{n}) \propto \mathbf{n}\gamma(\mathbf{n})$, where the constant of proportionality sets the size of the crystal. We define the set of planes through the set of points $\mathbf{p}(\mathbf{n})$, each perpendicular to $\mathbf{n}$, and then the Wulff shape is the inner envelope of all these planes.

As seen most clearly in the terrace-ledge-kink model [2,3], one expects the surface free energy $\gamma(\mathbf{n})$ to have a cusp for planes oriented close to a crystallographic direction (so called vicinal planes). From the Wulff construction, this leads to the equilibrium crystal shape having facets, which are molecularly flat, save for isolated surface vacancies and molecular islands [4]. However, at a particular temperature, the free energy cost for the formation of molecular islands vanishes, as does the cusp in the surface free energy. The crystal surface becomes rough on a molecular scale, but smooth and curved on a macroscopic scale. This 'roughening transition' is different for different crystallographic symmetry directions: for example, in ice, the basal direction remains faceted up until melting, while the prism planes roughen at a temperature around 257–260 K, when against water under pressure [5] or fructose solutions [6].

When roughened portions of two crystals (each in contact with a melt) are brought into gentle contact at constant temperature, they will begin to sinter, forming a neck. If there is an orientational misalignment between the two crystal lattices (which is the case in general), then the neck will also include a grain boundary. Where this grain boundary meets the crystal/melt interface, there will locally be a notch [7] with a dihedral angle θ_0 given from simple force balance by

$$2\gamma\cos(\theta_0/2) = \gamma_{gb} \tag{1}$$

where γ is the (approximately isotropic) surface free energy per unit area of the crystals against the melt, and γ_{gb} that of the grain boundary (which will be a function of the orientational mismatch).

During this process, and subsequently, the evolution of the shapes of the crystals is driven by the fact that a molecule at a curved surface has a chemical potential μ which depends on the mean curvature κ. In linearized form, the well-known Gibbs-Thomson relation between the two quantities is

$$\mu = \mu_0 + \Omega_v\gamma\kappa, \tag{2}$$

where μ_0 is the chemical potential for a molecule at a flat surface, Ω_v is the molecular volume, and κ is positive for a convex crystal surface.

* Corresponding author. Tel.: +31104605360; fax: +31104606747.
E-mail address: robert.farr@unilever.com (R.S. Farr).

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Molecules therefore have a tendency to leave regions of high positive mean curvature, where their chemical potential is relatively high, and to attach to regions of lower or negative (i.e., concave) mean curvature. To do so, they may diffuse through either the melt, the crystal lattice (by movement of vacancies), or along the crystal surface [7]. In vapor-phase sintering, diffusion along the crystal surface is often the dominant path, because the concentration of molecules in the vapor is low, as is the concentration and mobility of vacancies in the crystal [8,7].

For liquid phase sintering, the concentration of the relevant molecules in the bulk of the melt may be comparable to that at the crystal surface, and therefore the much larger cross sectional area available for diffusion in the bulk will tend to make this the dominant channel for diffusive transport.

Assuming that bulk diffusion limited re-crystallization is the dominant mode of neck growth, then the concentration of diffusing species in the melt will be governed by a (usually non-linear) diffusion equation. To proceed, we make three important assumptions:

First, that thermal diffusion is much faster than mass diffusion (so that the temperature remains approximately constant and uniform). This is the usual case for liquids, where the ratio of diffusivities is typically around 10^3 [9].

Second, that the concentration difference induced by the surface curvature is small enough that the non-linearity in the diffusion equation is negligible. We see from the diffusivity data in Fig. 1 of Ref. [10] that for cold sucrose solutions (which is the focus of the present paper), a 1% change in sucrose concentration can lead to a change in sucrose self diffusivity of 5–10%. However, using Eq. (5) and the calculations from Section 4 below, we see that moving from a flat ice crystal surface to one with a radius of curvature of 0.1 μm corresponds (at a temperature of 262 K) to a change in sucrose concentration of around 0.1%. This second approximation is therefore seen to be reasonably accurate for cold sucrose/ice systems studied with a light microscope.

Third, we assume that the transients of the diffusion equation have died out, which can be justified once the relevant equations have been constructed, and is discussed below in more detail in the argument leading up to Eq. (21).

Under these circumstances, the volume fraction $\phi(\mathbf{r})$ at position $\mathbf{r}$ in the melt of the type of molecules which can form the crystal is governed by Laplace's equation

$$\nabla^2\phi = 0. \tag{3}$$

Furthermore, the growth rate of the crystal in a direction normal to its surface is given by

$$v_n = D\frac{\partial\phi}{\partial\mathbf{n}}\bigg|_{\text{surface}}, \tag{4}$$

where D is the relevant (material) diffusivity. Using the linearized form of the Gibbs–Thomson relation (Eq. (2)), the boundary condition on $\phi(\mathbf{r})$ becomes

$$\phi(\mathbf{r})|_{\text{surface}} = \phi_0 + \frac{\Omega_v T\gamma\kappa}{L}\frac{d\phi_0}{dT}, \tag{5}$$

where $\phi_0(T)$ is the equilibrium value of ϕ against a flat crystal surface at (absolute) temperature T and L is the latent heat of fusion per molecule.

Eqs. (3)–(5) then determine the evolution of the system in exactly the same manner as the LSW theory of Ostwald ripening [11–13].

Suppose the co-ordinates of a point in space are denoted by $(x_{\text{true}},y_{\text{true}},z_{\text{true}})$ and the time by t_{true}, then we can introduce a capillary length for bulk diffusion limited evolution, given by $l_C = \gamma\Omega_v/L$ and dimensionless space, time and concentration variables $x = x_{\text{true}}/l_C$, $t = t_{\text{true}}D(Td\phi_0/dT)/l_C^2$ and $\psi = (\phi-\phi_0)/(Td\phi_0/dT)$. Eqs. (3)–(5) then assume the simple form

$$\nabla^2\psi = 0, \quad v_{\text{norm}} = \frac{\partial\psi}{\partial\mathbf{n}}\bigg|_{\text{surface}}, \quad \psi|_{\text{surface}} = \kappa. \tag{6a, b, c}$$

where v_{norm} is now the dimensionless normal velocity and κ the surface mean curvature in the re-scaled (dimensionless) co-ordinates.

2. Theoretical results

Recent theoretical work [14] has shown that the very early stages of the growth of necks is governed by the behaviour of a travelling- or solitary-wave solution to Eqs. (6). The picture is that the cross section of the neck resembles that shown in Fig. 1, where a teardrop-shaped end forms at the outer edge of the neck.

Analysing this behaviour in Ref. [14] leads to a power-law dependence of r_n (the neck radius scaled by l_C) on the scaled time t. Specifically,

$$\frac{dr_n}{dt} \approx \frac{4}{r_n^3}I(\theta_0)R, \tag{7}$$

where R is the harmonic mean of the radii of the two spherical crystals (non-dimensionalized using the capillary length l_C), and $I(\theta_0)$ is a number which describes the effect of the dihedral angle at the grain boundary on the neck growth rate.

To simplify further, we introduce a new variable u (related to the size of the neck r_n), and a re-scaled time t' through

$$u = r_n/R \text{ and } t' = t/R^3. \tag{8a, b}$$

Eq. (7) then tells us that for small t',

$$u(t') \approx 2(I(\theta_0)t')^{1/4}. \tag{9}$$

From the calculations in Ref. [14], it is possible to obtain a numerical approximation to the function $I(\theta_0)$ (where θ_0 is measured in radians), namely

$$I(\theta_0) \approx 0.200\theta_0^2 - 0.0161\theta_0^3. \tag{10}$$

3. Numerical results

Section 2 discussed a recent theoretical model for sintering at very early times. In order to study bulk diffusion limited evolution at late times, we adopt a numerical approach, using spherical polars (r,θ), by expanding the concentration field ψ and the boundary of the crystals $r_0(\theta)$ as a series in Legendre polynomials $P_n(\cos\theta)$ in the following manner:

$$\psi(r,\theta,t) = \Psi_0 + \sum_{n=1}^{n_{\max}}\Psi_{2n}\frac{P_{2n}(\cos\theta)}{r^{2n+1}}, \tag{11}$$

$$r_0(\theta,t) = \rho Z(\theta) + \sum_{n=0}^{n_{\max}}R_{2n}P_{2n}(\cos\theta), \tag{12a}$$

where

$$Z(\theta) \equiv \cot(\theta_0/2)|\cos\theta| + \sqrt{\cot^2(\theta_0/2)\cos^2\theta + 1}. \tag{12b}$$

The R's, Ψ's and ρ are all functions of the non-dimensionalized time t. The series is truncated to a fixed order, which sets the resolution of the simulation, in contrast to voxel-based simulation approaches (for example Ref. [15]), where the resolution is determined by an explicit voxel size.

The functional form of Eq. (12a) consists of two terms: an initial angle-dependent function $Z(\theta)$, multiplied by the coefficient ρ, and a series of Legendre polynomials in $\cos(\theta)$, with the R's as coefficients. The function $r = \rho Z(\theta)$ describes a surface composed of two equal spheres with centres at equal distances from the origin along