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Rapid growth of ice crystal dendrite tips in dilute solution of trehalose

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ABSTRACT

We use Mach-Zehnder interferometry to measure ice-crystal tip radii and growth rates in dilute aqueous solutions of trehalose over a range of concentrations. Although trehalose at high concentrations is a well-known inhibitor of ice crystal growth in aqueous solution, we find that the ice instead grows faster with the trehalose concentrations below about 8 wt%, with a peak tip velocity near 2 wt%. By directly measuring the 3D morphology of the growing ice crystals with the interferometer, we find that the dendrite tip in solution becomes thinner and sharper than that in pure water, causing the more rapid growth of ice.

1. Introduction

Trehalose is well known as an inhibitor of ice crystal growth in aqueous solution. For example, Sei et al. [1] reported a suppression of the growth rate of growing ice crystals with increasing trehalose concentration of 20.8 to 52.1 wt%. To help understand the phenomenon, Uchida et al. [2] measured the viscosity of aqueous solution at various trehalose concentrations, finding that the viscosity in solutions of less than 10 wt% are same as that of pure water, and the values increase with increasing concentration over than 10 wt%. They concluded that the decreasing amount of free water in the solution increases the viscosity and reduces the growth rate of ice.

Other materials inhibit ice growth, including antifreeze proteins (AFP) [3,4], carboxylated ε-poly-L-lysine [5], antifreeze glycoproteins [6], and ice-nucleation-active (INA) bacteria [7,8]. The inhibition can be selective to crystal orientation. For example, the face of adhesion to the ice surface depends on the molecular structure of the AFP [3,4]. On the other hand, Nada et al. [8] measured the growth rates of ice crystals in aqueous solutions with INA bacteria and found that the growth rate in the *c*-axis direction decreases with increasing concentration, but increases in the *a*-axis direction. After observing growing steps on the basal plane, they concluded that selective binding of bacterial ice-nucleating proteins along the {0 0 0 1} plane was causing a decrease in growth rate in the *c*-axis direction, allowing an increase in growth rate in the *a*-axis direction.

Unlike isotropic dendrite crystals (e.g., succinonitrile) that have a relatively simple tip shape characterized by a single tip radius, an ice dendrite crystal has an asymmetrical tip characterized by two tip radii. As shown in Fig. 1a, we designate the tip radius on the basal plane as R_1 (projected to the {0 0 0 1} plane), and that on the plane perpendicular to the basal plane as R_2 (projected to the $\{0\,\bar{1}\,1\,0\}$ plane) [9,10]. But despite this asymmetry, the growth velocity V of an ice dendrite tip (direction to *a*-axis) is consistent with the universal theory [10] that assumes the marginal stability of a symmetrical tip shape [11–13].

Recently, we discovered a concentration-dependent maximum growth rate of ice dendrite crystal in dilute aqueous solutions with trehalose. In this study, we use Mach-Zehnder interferometry to examine the growth rate and the 3D morphology of growing ice dendrites at various concentrations and various supercoolings. Using the resulting measurements, we discuss the growth mechanism of a rapidly growing ice dendrite.

2. Experimental

Our experimental apparatus was designed and built to study free-growth and 3D observations of growing ice crystals. As it is nearly the same as that described previously [9], we give just a brief description here.

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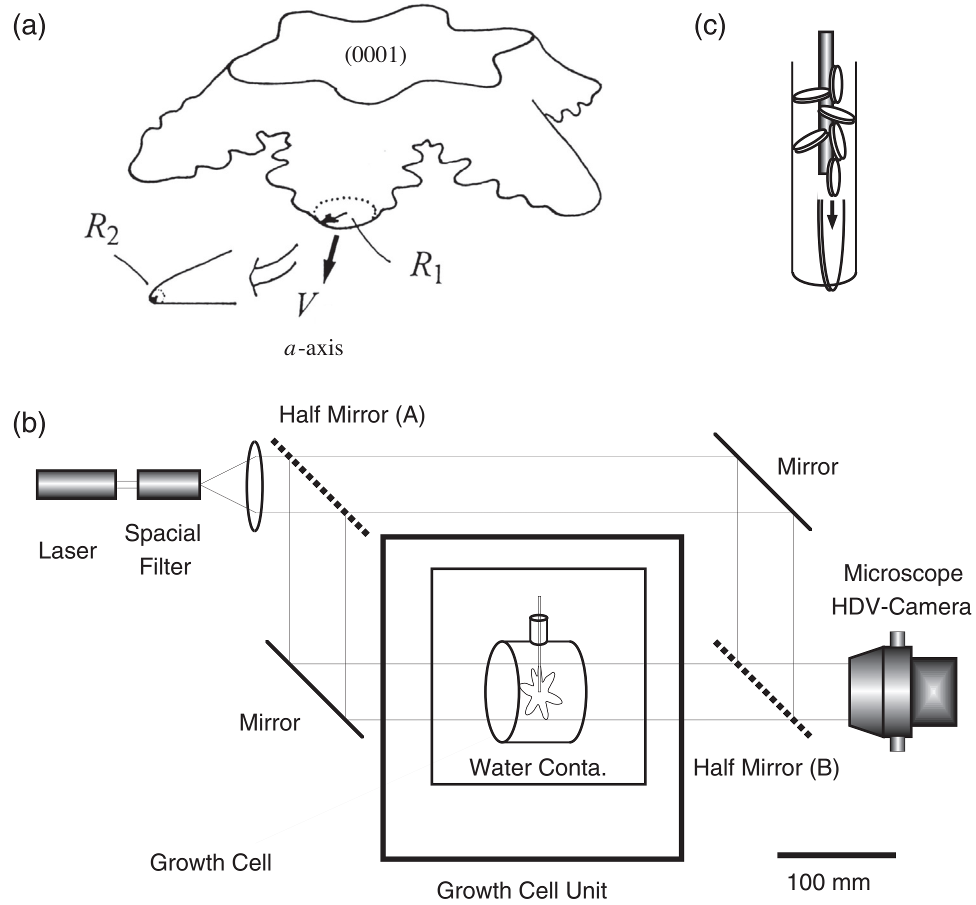

Fig. 1. Experimental system and apparatus. (a) Relevant parameters of the ice-crystal dendrite: the tip growth velocity V (direction to a-axis), the tip radius on the basal plane R_1 (projected to the $\{0\,0\,0\,1\}$ plane), and that on the plane perpendicular to basal plane R_2 (projected to the $\{0\,\bar{1}\,1\,0\}$ plane). (b) Mach-Zehnder interferometer. (c) Nucleation of ice crystals in a glass capillary.

An optical cell (ϕ50 mm × 50 mm) is used for the growth cell and filled with distilled and filtrated pure water with electrical conductivity 18.2 MΩ with or without trehalose (Fig. 1b). The temperature of this growth solution is kept constant within 0.01 K by stirring a transparent non-freezing ethylene-glycol aqueous solution in water container around the growth cell. The degree of supercooling refers to the specific freezing-point depression in solution of the trehalose by determining the specific equilibrium of that solution by observing the ice-crystal response.

A glass capillary is used to support the growing crystal. To nucleate the crystal, we insert a chilled wire inside the capillary as shown in Fig. 1c. Many ice crystals nucleate on the surface of chilled wire, but ice crystal grown in water has anisotropic growth direction: grow as disk-like shape. After the ice grows down the inside of the capillary, one single ice crystal exits the tip and starts growing freely, we turn the capillary parallel to the image plane. Fig. 2 shows two examples. The growth velocity of the tip does not depend on the crystal size except in the initial stage (not part of our measurements). The two tip radii (R_1 and R_2) are also constant values, except during tip splitting at low supercooling.

For the 3D observations, we use a Mach-Zehnder interferometer. In this system, by adjusting the mirror while observing the interference fringes, we can obtain the setting in which the fringes on the crystal track equi-thickness regions of the ice crystal (similar to contours in a topographic map). Fig. 3a′ and b′ are two examples. The thickness interval of each interference fringe is given as $d(m+1) - d(m) = l/|n_{\mathrm{ice}} - n_{\mathrm{water}}| = 24.4\ \mu\mathrm{m}$, where the fringe order m = integer, the wavelength $l = 635$ nm, the refractive index of ice $n_{\mathrm{ice}} = 1.30756$, and the refractive index of water $n_{\mathrm{water}} = 1.33361$. Here, we assume the dilute trehalose solution has the same value of the refractive index as pure water. By cutting the reference path (upper path in Fig. 1b), this system changes to a schlieren system as shown in Fig. 3a and b.

The tip radius on the basal plane R_1 is measured by comparison of the perimeter to a parabola tip on the basal plane. The tip radius on the plane perpendicular to the basal plane R_2 is measured in the same image plane by determining the analogous parabola, but instead based on the crystal thickness and distances from the tip of dendrite to the first two fringes on the line to the center of crystal (Fig. 1a). In trehalose solution, it was difficult to determine the position of fringe because of the roughness of surface. Then we determined the position of fringe by average fringe curve on the picture as shown thin lines in Fig. 3b'.

3. Results and discussion

Morphologies of growing ice crystals in both pure water and dilute trehalose solution are shown in Fig. 2. As the ice structure is hexagonal, one may expect the growing crystals to have six main branches of similar length. But the images in Fig. 2 show less growth downward. The growth of the downward branch is inhibited by an effect of thermal convection. In particular, latent heat warms the solution adjacent to the crystal, increasing this solu-