

The Double-Pyramid Structure of Dendritic Ice Growing From Supercooled Water

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Abstract.

It is known that ice growing freely from supercooled water has a morphological transition at $T = -2.7^\circ\text{C}$, from a flat dendritic structure at higher temperatures to a twelve-sided double-pyramid structure at lower temperatures. The double-pyramid structure, which can be described as two hollow six-sided pyramids joined at their apices, is built from dendrites growing in well defined growth directions which are non-crystallographic in the planes normal to the basal plane while their projections on the basal plane retain the hexagonal symmetry. Similar structures have been reported in other hexagonal materials. In order to understand better the growth mechanism, we measured the temperature field in the water around the growing crystals by using the temperature dependence of its refractive index. Since this dependence happens to be zero at the freezing point for *regular water* (H_2O), we use *heavy water* (D_2O), and achieve considerably greater sensitivity. The free growth experiments performed with heavy ice reveal that their morphological behavior is similar to regular ice, as well as their velocities and the angle between the pyramids as a function of supercooling. The temperature measurements showed that the interaction between the two sides of the pyramid via the temperature field is weak.

This leads to the conclusion that the solution for the growth mode of the dendrites should be found in the single dendrite level. Explanations of this phenomenon are discussed in the light of recent advances in dendritic growth theory - in particular the concept of microscopic solvability - combined with the behavior of the surface tension and the kinetic effect as a function of crystallographic orientation. It can be shown that growth in a low symmetry direction leads to an asymmetrically growing crystal and to asymmetry in the observed temperature field.

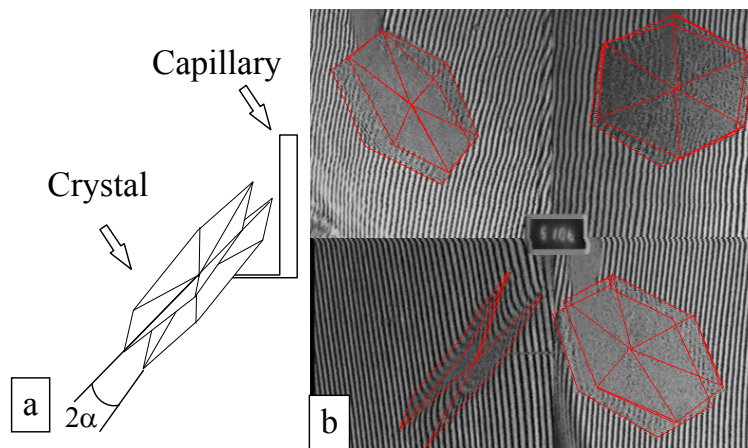


Figure 1

(a) Drawing of a double pyramid crystal growing from a bent capillary. (b) A crystal growing from heavy water at 3.85°C supercooling is observed simultaneously from four directions. The crystal edges have been emphasized and the interference fringes can be seen in the background.

1. Introduction

Ice crystals growing from the melt have been investigated in the past by many researchers[1,2,3,4,5]. It was found that the shape of an ice crystal at small supercooling (less than 2.7°C below the freezing point) is quasi-two-dimensional i.e., a flat crystal, with a rich in-plane structure having hexagonal symmetry. The envelope of the crystals is shape preserving. At higher supercooling (>2.7°C) the ice grows in a different morphology. Instead of six $\langle 11\bar{2}0 \rangle$ growth directions in the plane normal to the hexagonal axis, a twelve-sided double pyramid (dodecaconal) is observed (Fig. 1). This structure is built from dendrites which grows in defined directions $\langle 11\bar{2}z \rangle$, where z represent the component of the direction perpendicular to the basal plan. While the projection of the growth direction on the basal plane is not changed and the hexagonal symmetry is retained, the angle of the pyramid changes continuously as a function of the initial supercooling. That means that z is not discrete and the growth is along non-rational directions. The z -component increases with the supercooling and has typical value 0.2 at >5°C supercooling (Fig. 2). At supercooling of more then 5.5°C more complex structure including secondary splitting is observed [2].

There are other materials with double pyramid structure, such as liquid crystals[6], smoke particles[7], and ^3He - ^4He crystals[8]. The hexagonal symmetry is common to all. In these crystals there is a two fold symmetry in one direction and a six fold symmetry in the perpendicular plane which suggest that the low symmetry is needed in order to get a non crystallographic growth direction.

Theoretical research on dendritic growth has concentrated on the morphology of the single dendrite, whereas the growth of an array of dendrites has received relatively little attention[9,10]. However it is reasonable to suppose that the properties of a single dendrite dictate the behavior of the array. Since the experimental evidence is that an array of dendrites grows in a non crystallographic direction it follows that we might look for circumstances under which a single dendrite does likewise. In the case of liquid crystals where the pyramidal structures are also observed, individual dendrites grow with asymmetrical tips [11] which have been explained in terms of anisotropic thermal conductivity of the fluid [12], but this explanation can not apply in the case of water.

Brener and Levine [13] have suggested on theoretical grounds that anisotropic crystals could select low symmetry growth directions if the orientations of minimum surface tension (capillary length) and minimum kinetic growth coefficient were not related by reflection symmetry. They demonstrate in a two dimensional example that the selected growth orientation then depends continuously on the degree of supercooling. In this paper we hypothesize that ice crystals are an example of this behavior.

2. Methods

We grow (heavy) ice from supercooled (heavy) water. The experimental set-up includes a chamber filled with water whose temperature is controlled to 0.01°C. The chamber is viewed by four interferometers from different directions. More details can be found in references [14,15]. The nucleation is initiated by an electric pulse, a method called electrofreezing [16]. The crystal is nucleated by this method in a water-filled capillary with a narrow tip from which it emerges into the supercooled water where it grows freely. The capillary can be bent to give preference to certain orientations (Fig. 1). The growth process is monitored by an interferometer along each of the four directions. From each interferogram a projection of the temperature field in the water in the vicinity of the crystal is deduced [14]. The 10mm field of view gives reasonable time to observe fast growing crystals with a resolution of 50µm. However, this resolution is not enough to observe individual dendrites in the high velocity regime (supercooling greater than 3°C). The interferometric method uses the temperature dependence of refractive index. Since this dependence happens to be zero at the freezing point for *regular water* (H_2O), we use *heavy water* (D_2O), and achieve an order of magnitude greater sensitivity.

3. Results

Heavy ice crystals were grown in the range of 0.5°C to 8.5°C supercooling. At temperatures above 1.1°C (i. e. 2.7°C supercooling) the crystals grow as flat plates. Below this temperature the crystals grow in the double pyramid manner as described in the Introduction. Figure 1 shows a crystal growing from heavy water supercooled by 3.85°C . We studied the development and growth of the pyramidal structure in heavy ice (Figure 2) and found similar velocities and angles to those measured by Ryan[17] in regular water. Our experimental set-up [14] also enables us to measure some important aspects of the temperature field of the water in the vicinity of the crystal by optical means. In figure 3 the projection of the field in the vicinity of the pyramidal structure is shown. From a slice of the projection parallel to the hexagonal axis one can see that the decay length of the field is considerably less than the separation of the growing tips. From this it is possible to deduce that the interaction between the two sides of the pyramid via the temperature field is negligible. This lead to the conclusion that the non-crystallographic growth direction is independent of the overall structure, and suggests that the single dendrite growth theory is suitable to deal with this problem.

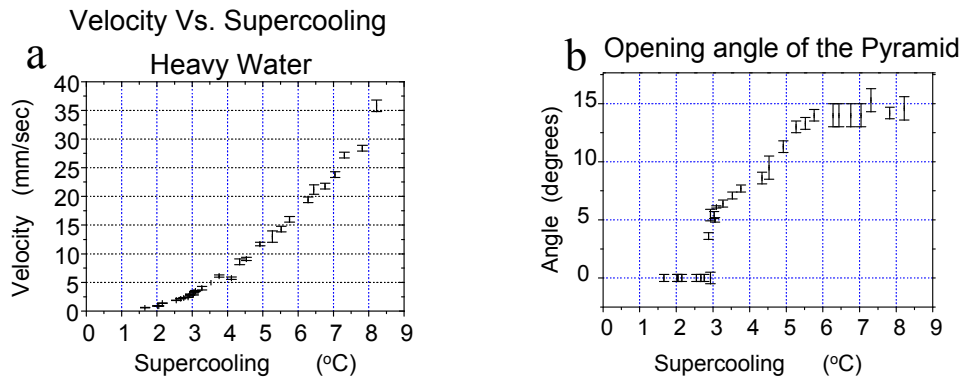


Figure 2
(a) The velocity of heavy water dendrite as a function of supercooling; (b) The angle between the pyramid faces and the basal plane (half of the opening angle), as a function of supercooling

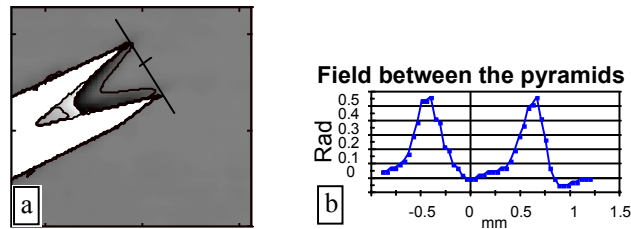


Figure 3.
(a) Projection of the temperature field measured in the vicinity of the double pyramid structure.
(b) Cross section of the field along the line shown in (a).

4. Theoretical background on dendritic growth

In order to discuss possible explanations of the non-crystallographic dendritic growth we describe briefly the basic tenets of the micro-solvability theory [18]. Diffusion-limited growth is based on the following assumptions:

a) The temperature field obeys the heat diffusion equation:

$$(1) \quad \partial T / \partial t = D \nabla^2 T$$

where D is the thermal diffusion coefficient.

b) There exists a crystal shape which is preserved in time. This implies that the temperature of the interface also does not change. To achieve this, conservation of energy at the interface is required:

$$(2) \quad L V_n = \mathbf{n} \cdot (D C_p \nabla T)_{\text{solid}} - (D C_p \nabla T)_{\text{liquid}}$$

where L is the latent heat. It is emitted by the phase transformation at a rate proportional to the normal velocity V_n , and is conducted away from the interface in order to maintain constant temperature.

c) Boundary conditions: the temperature at infinity is constant, $T(\infty) = T_\infty$ and lower than the melting temperature T_m . The interface temperature is:

$$(3) \quad T_i = T_m (1 - d_1(\theta, \varphi) \kappa_1 - d_2(\theta, \varphi) \kappa_2) - \beta(\theta, \varphi, V_n)$$

where T_i is the temperature at the interface and T_m is the melting temperature of a flat crystal. The angles θ and φ indicate the orientation of the interface with respect to two orthogonal axes. The anisotropic capillary length is (d_1, d_2) and the curvature is (κ_1, κ_2) , with respect to the same axes. The kinetic supercooling is $\beta(\theta, \varphi, V_n)$ which indicates the deviation from equilibrium on the interface for a given orientation and normal velocity. It might be more convenient to discuss the normal velocity as a function of the kinetic supercooling $V_n = V_n(\theta, \varphi, \beta)$, which is the inverse function of $\beta(\theta, \varphi, V_n)$. The micro-solvability theory relates the selection of growth direction to the anisotropy of β and d and it is now considered that the anisotropy is crucial to the existence of stable growth morphologies. In the light of the above remarks, we now suggest a few scenarios which can explain the morphological transition from the flat structure to the double pyramid structure.

First, let us neglect the surface tension and consider only the anisotropic behavior of the velocity as a function of the interface supercooling. In order to explain a morphological transition in this case the dependence of velocity V_n must be inseparable from its dependence on orientation, i.e.:

$$(4) \quad V_n \neq f(\theta, \varphi) \cdot g(\beta).$$

This is a generalization of Ryan's proposal[2], in which he treated the growth velocity as a vectorial sum of the velocity in the basal plan and the growth perpendicular to it. The crystal grows in the direction which has minimum β for the given V_n . In this approach the morphological transition is seen as the result of a change in the growth manner in the basal direction (c direction) from layer-by-layer growth [19] to continuous growth, or in another words kinetic roughening[20]. One should remark that, while growth in non-crystallographic direction is influenced by the velocities in the different crystallographic direction it is not a simple vector summation, as explained by Wettlaufer et al. [21] In the present case, the anisotropy in the kinetic effect of ice can be explained by different entropy barriers due to different configuration needed to add a molecule to the a surface and the c surface (Jackson et al. [22]). It is quite conceivable that β has maxima along all high symmetry directions, and therefore has its minima in low symmetry directions. The fact that the hexagonal symmetry is retained, indicates the independence of the two orthogonal direction φ, θ .

On the other hand, one can assume that the important parameter governing the growth direction is the anisotropy of the surface stiffness $\gamma + \gamma''$, which is proportional to d . Growth then occurs in the direction of minimum d . This approach has been implemented by Gonzalez-Cinca et al.[23] who have compared two dimensional phase field simulation of diffusion limited growth with the morphologies of liquid crystals. An important feature of this simulation is the inclusion of the cusp in the surface tension which introduce a delta

function into the stiffness. Since this is a numerical simulation it does not bring out the reason for the change in orientation as a function of supercooling.

If both kinetic and surface tension effects play comparable parts, Brener and Levine [13] have suggested that the transition could result from competition between them; this does not require dependence of these parameters on temperature. In particular, they showed that a continuous change in the growth direction results if the symmetry is low.

5. Discussion

One aspect of this problem is that the shape of a crystal growing in a non-crystallographic orientation should not be symmetrical with respect to the growth direction[11,17]. While the kinetic and capillary effects are themselves symmetrical with respect to the crystallographic orientation, if the growth axis is tilted, it follows that the temperature is not uniform on the interface. The inner surface of the pyramid will be warmer than the outside since the two have the same orientation but are growing at different velocities [17]. The temperature map Fig. 3 appears to confirm this result, but one must take into account the partial obscuration of the field by the concavity of the pyramid on its outside. However, asymmetry of the crystal shape is also noticeable in flat crystals growing in the symmetry plane[5], and the temperature map [24] also confirms this. It is not clear yet what symmetry-breaking mechanism is responsible for this phenomenon; it is possible that convection in the water may be involved, but it may be connected with the anisotropy of β and d .

6. Conclusions

These experiments represent the first direct observation of temperature fields around growing crystals. The experiments on heavy ice (which crystallizes similarly to regular ice) have demonstrated that the two branches of the double pyramidal structure grow independently. This suggests that the origin of this structure is at the single dendrite level, but the experiments have not yet led to a distinction between the different theories leading to asymmetry.

We think that further investigation of the interface parameter as well as theoretical work on this problem is important in order to understand the growth of nonisotropic materials

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