Experiments on the dynamic wetting of growing icicles

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Abstract. The distinctive shape of an icicle is the outcome of a highly non-equilibrium process involving heat and mass transport in the presence of fluid flowing over an evolving topography. It has previously been shown that the ripple patterns with a near universal wavelength that are observed on many icicles are correlated with small levels of impurities in the feed water. Models of icicle shape evolution, and of the origin of the ripple pattern, require a detailed understanding of how liquid water flows over a growing icicle. The impurity effect is not accounted for by any existing model of ripple formation. Here, we explore this flow dynamics using laboratory-grown icicles with a fluorescent dye as an impurity. Contrary to previous models, we find that the ice is incompletely wetted by the liquid phase, and that the whole process is much more stochastic than has been previously assumed. In addition, the presence of impurities modifies the wetting properties of the ice surface, while the emerging topography interacts with the liquid distribution. There is evidence for mixed-phase ice. These observations must inform any successful model of an impurity-driven rippling instability. Our results have general implications for the morphological evolution of many natural, gravity-driven, wet ice growth processes.

1. Introduction

The morphology of ice formed from liquid water flowing over a growing surface presents a challenging free-boundary problem. Such "wet ice growth" [1] is found during atmospheric ice build-up on aircraft [2] and power lines [3], on growing hailstones [4, 5], and on growing icicles [6–10]. A common factor to all of these scenarios is a thin deposit of water on the ice surface, which gradually freezes to add to the ice. For icicles and other structural ice, this water flows due to gravity and is held on the surface by capillary forces, but the details of this flow *in situ* are not well understood.

Icicles form in a sub-freezing atmosphere from water dripping off an overhang. This water freezes, releasing its latent heat to the air or the supporting structure. An icicle grows as more water flows down the ice surface, freezing on the icicle wall (increasing diameter), or at the tip (increasing length). More heat can be removed at the tip, so the icicle's length grows faster than its diameter [7], leading to its familiar elongated shape. Icicles grown from impure water exhibit ripples about their circumference [10]. These

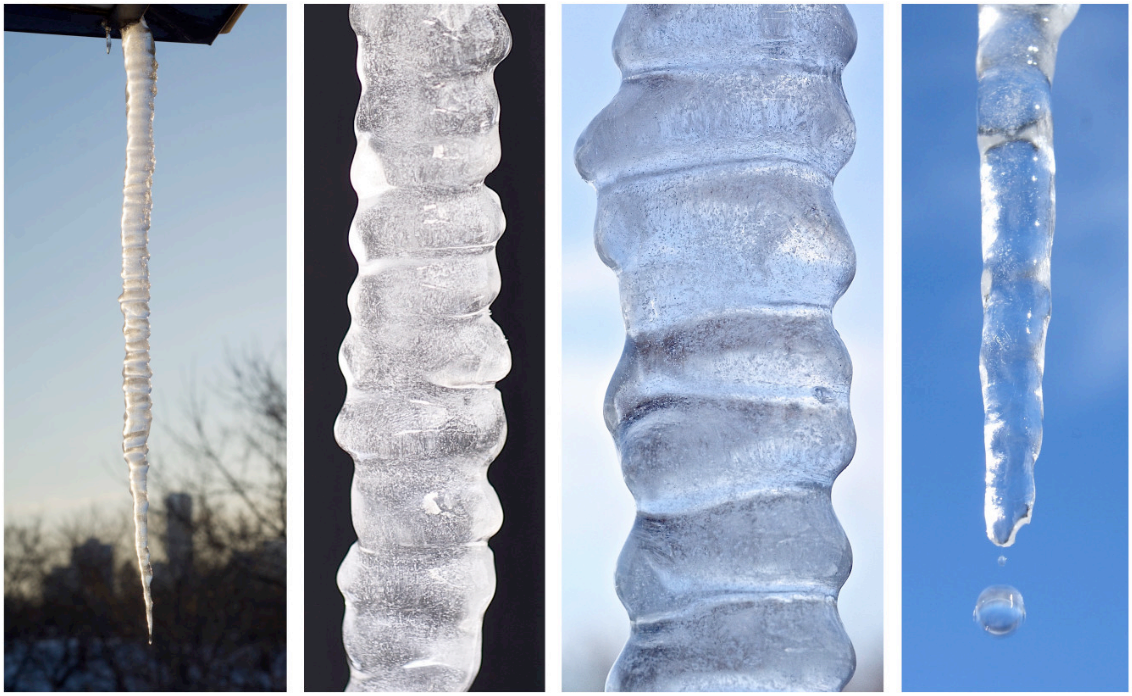

Figure 1. Various images of natural icicles. The first image shows a complete icicle from root to tip. The next two images show detailed views of typical ripple patterns. The final image shows a tip shedding a mm-scale droplet.

ripples, which are common on natural icicles (see figure 1), have been attributed to a pattern-forming morphological instability [8, 11–17], but their dependence on impurities has not been explained through theory. Ripples are observed to have a near-universal wavelength of ∼1 cm. The motivation of the present work is to explore the long time dynamics of the liquid water on the surface of growing icicles, with an eye to better understanding the mechanisms that lead to ripple formation.

We experimentally probed the dynamics of liquid water on the surface of icicles with the use of a strongly fluorescent dye added to the feed water. The dye acts as the impurity which triggers the ripple pattern, and an indicator for the liquid water. The apparatus and the composition of the feed water are described in section 2 and section 2.1 below.

In section 3, we observe that the liquid does not cover the entire ice surface, but rather descends in rivulets, leaving behind patches of liquid. What's more, in section 3.1, we show that the amount of liquid retained on the surface is strongly correlated with the amount of impurities. In section 3.2, we show that the distribution of liquid is also correlated with the upper surfaces of the ripples and matches their observed upward migration.

Our results shed important light on the unresolved question of why impurities are required for ripple formation. We show that icicles grown with impurities retain surface water quite differently than those without. To investigate processes that may affect the liquid distribution, we use cylinders of ice as a substrate and modify the surfaces to isolate single properties. Those results are presented in section 4. In section 5, we discuss the implications of these observations for theories of ripple formation, while section 6 presents a brief conclusion.

2. The experiment

We grew icicles by dripping near-freezing water onto a slowly rotating support in a temperature-controlled, purpose-built laboratory machine. The machine is an improved version of the one used in previous studies [9, 10]. To cool the air, refrigerated antifreeze solution was pumped through the interior aluminum walls of the chamber, while circulating fans blew the interior air through heatsinks on the walls to maintain an even temperature. Having turbulent air inside the chamber suppresses the tendency for icicles to grow multiple tips [9]. The chamber temperature was measured with thermocouples at three heights, and was held constant to ±0.1°C within a range of 0.5°C, top to bottom. We grew icicles at air temperatures in the range of -13.5°C to -18°C.

Humidity within the chamber was continuously monitored by a probe (Dracal USB-TRH300). Measurements of humidity are difficult below the frost point [18]; we pumped desiccated air into the chamber during initial cool-down, but the relative humidity rose quickly to 85% once the water drip started to form an icicle. A small amount of evaporative cooling contributes to the heat transfer away from the growing ice [19].

Water was introduced at the top of the chamber at a steady drip rate from a temperature controlled nozzle, which maintained a feed water temperature just above freezing. The feed water fell a short distance onto a pointed wooden support, which was rotated slowly. The 8 minute support rotation period was fast compared to the time it takes to form an icicle (at least 4 hours), but slow compared to the fluid mechanical time scale of the water flow. The centrifugal acceleration produced by rotation was negligible compared to the acceleration due to gravity. The main purpose of rotation was to allow all sides of the icicle to be imaged. Rotating the support with the nozzle slightly off axis helped distribute the water evenly over the wooden support and also helps average out thermal asymmetries in the chamber, encouraging the axisymmetry of the icicle. Previous studies [9, 10, 20] have examined both rotated and non-rotated icicles and found no significant differences in shape or ripples away from the support region. Unfrozen water that fell from the icicle tip was drained out the chamber via a gently heated funnel.

From the side of the chamber, a 36 MP SLR camera (Nikon D810) captured images at 16 evenly spaced, indexed, angular support positions. Using edge detection and the rotational position, it was possible to reconstruct the full three dimensional shape of the growing icicle as a function of time. Images were taken under white LED illumination, allowing frontal views of the water distribution to be measured. In addition to monitoring the growing icicle with the SLR, we also recorded 30 fps HD video during some runs, which allowed the fastest fluid mechanical time scales to be qualitatively observed.

2.1. source water

Many different dissolved impurities can trigger the rippling instability. In this work, *sodium fluorescein* ($Na_2C_{20}H_{12}O_5$) was used as both a dye and the instability-triggering impurity. When icicles are grown with fluorescein dye and illuminated with white light, they fluoresce green in patches where liquid water is present while the ice appears orange. The effects can be seen in figure 2. This fluorescent quenching is due to a saturation of fluorescein; as the liquid water freezes, the concentration of sodium fluorescein increases, and the fraction of fully dissociated fluorescein molecules decreases, quenching fluorescence and turning the dye orange.

The emissivity of fluorescein is dependent on its charge: the dianion emits strongly in the green band near 520 nm, while the cation and neutral forms do not [21]. The fluorescein dye used in the source water is at low enough concentration that it near-fully dissociates into two sodium cations, and a fluorescein dianion. This behaviour of flourescein has also been used to visualize the freezing of capillary flows [22, 23].

We grew icicles in a series of decreasing concentrations. Each series started with a relatively high concentration of feed water impurities added to distilled water, which was then diluted by half for each subsequent icicle. We maintained the same flow rate and air temperature within each series, but varied it between series. Five of these series are presented here, as summarized in Table 1. The source water for Series 2 through 5 was degassed under vacuum for 10 minutes using an aspirator before each icicle was grown.

The flow rates we used were near the upper end of the flow rate ranges used in previous icicle growth experiments. Meano *et al.* [8] used flow rates between 0.2 g/min and 2.1 g/min, while Chen *et al.* [9, 10, 20] used between 0.5 g/min and 3.2 g/min. Higher flow rates can result in no icicle growth at all, depending on air temperature and the temperature of the feed water [20]. Our flow rates were consistent with robust icicle growth at the air temperatures shown in Table 1.

1035 ppm of sodium fluorescein matches the ionic molal concentration of a 240 ppm NaCl solution, so these results can be compared to previous work [10] that used *sodium chloride* (NaCl) as the impurity. The ionic concentration stated in mMol/kg counts the number of dissociated ions per kg of water. Our highest value of 8.46 mMol/kg is equivalent to 247 ppm NaCl, which is roughly equal to the highest concentration for icicles previously observed to have consistently upward moving ripples [10]. Even this maximum impurity concentration is rather low in absolute terms; it is only four times the impurity concentration of Toronto tap water [10], and less than 1% of 35 ppt standard sea water. Ripples are observed at concentrations as low as 16 ppm sodium fluorescein.

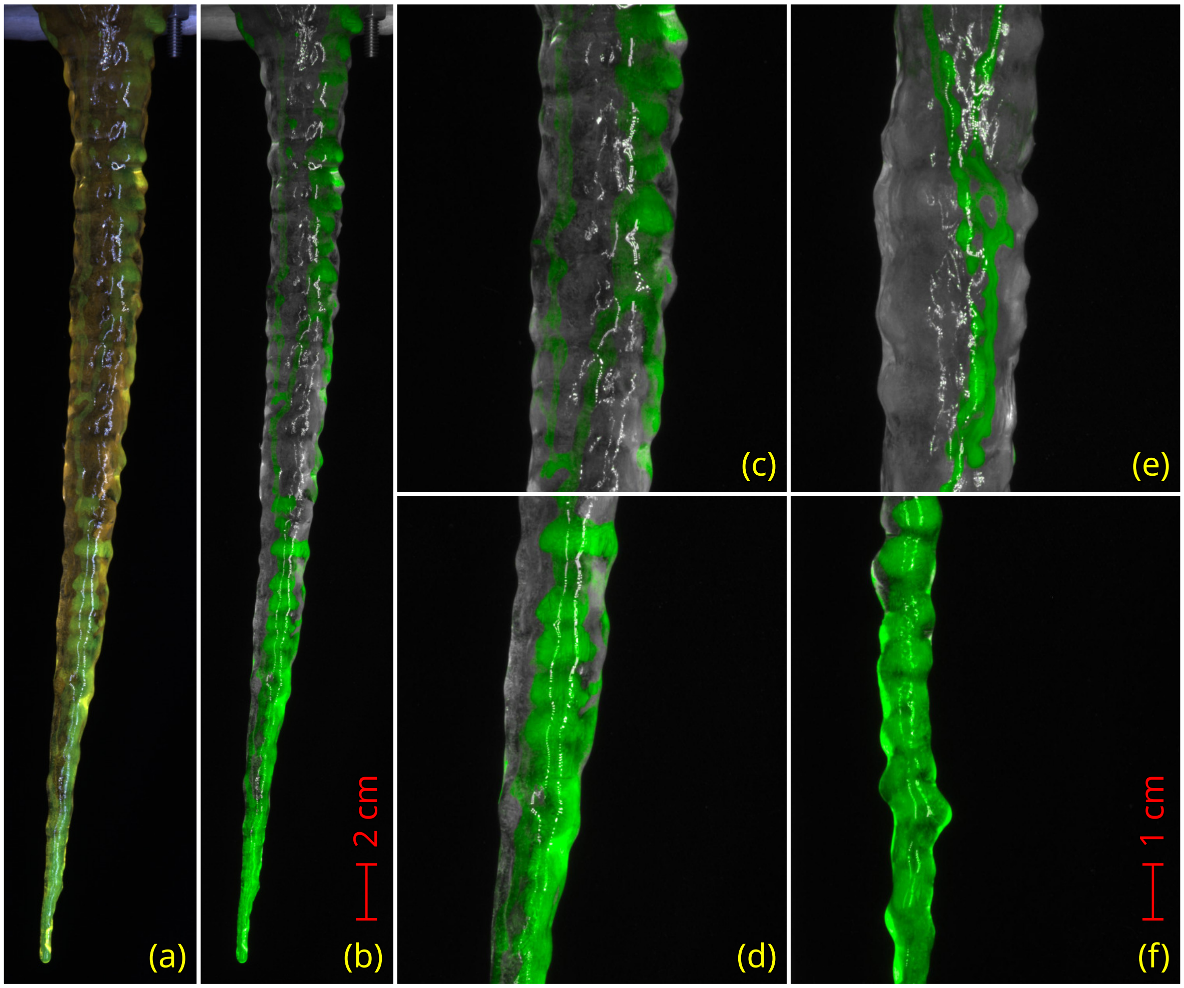

Figure 2. An example of an icicle dyed with 129 ppm sodium fluorescein. The quenched orange colour can be seen in the unaltered image (a), and the fluorescent green can be isolated (b) to locate liquid on the surface. Close-ups show patches of liquid on the upper side of ripples (c), (d). At a later time, thinner rivulets with complex branching are present (e), while the tip remains covered (f). **A movie version of this figure is included in the supplementary information.**

Table 1. Experimental parameters for the five series of icicles studied, comprising a total of 39 icicles. *The 32 ppm icicle for Series 1 had incomplete data due to a camera malfunction and has been omitted. †The NaCl solution in Series 5 was dyed with 8 ppm Sodium Fluorescein.

Series Number	Impurity	Initial Concentration (mMol/kg)	Number of icicles	flow rate (g/min)	air temperature (°C)
1	Sodium Fluorescein	4.13	6*	3.0	-14
2	Sodium Fluorescein	2.06	7	3.0	-17
3	Sodium Fluorescein	8.26	8	3.0	-14
4	Sodium Fluorescein	8.46	10	2.0	-14
5	Sodium Chloride†	31.1	7	3.0	-14

The fifth series of icicles uses sodium chloride (NaCl) as the primary impurity and 8 ppm sodium fluorescein dye. This amount of dye can be seen clearly by the camera, but has little effect on the actual freezing dynamics. We observed that when fluorescein comprises a smaller fraction of the impurities, the fluorescence does not quench as quickly. This series of icicles are more transparent, emit green light for longer times, and appear less orange after fully freezing. While the same behaviour of the liquid is observed, the fluorescence measurements had to analyzed separately from the other four series.

3. Water distribution

The water which freezes to form the icicle generally does not completely cover the ice surface except in a short region near the tip. Over most of the icicle, the water flows down in a number of thin rivulets, leaving trails of water, but on icicles grown with higher concentrations of dye in the source water, there are also patches of fluorescent liquid adhering to the surface. These patches are wider and last longer than the trails. The rivulets may branch or reconnect with trails left by past rivulets, or feed into patches of liquid, and usually have a complex morphology as seen in figure 2.

One can feel a rough texture on the surface at fluorescent patches by scraping it with a fingernail, indicative of dendritic growth or spongy ice. We are unable to image the microstructure directly in the current experiments. The clearer, uncovered portions of the icicle are quite smooth. The surface coverage tends to increase with dye concentration, a trend that is visualized in figure 3, and quantified in section 3.1 below.

The surface liquid is transient, but evolves slowly enough to be identified over several rotations of the icicle (*i.e.* over $\sim$15 minutes). The lifetime of rivulets and patches is short compared to the full growth time, so that the icicle above the tip area is built up stochastically from the contribution of many rivulets and patches.

3.1. Surface coverage

The relationship between the source water dye concentration and the amount of surface covered by liquid is our first evidence of a connection between the configuration of surface liquid deposits and the formation mechanism of icicle ripples. It is apparent to the eye in figure 3 that higher concentration icicles retain more fluorescent liquid on their surfaces. We can quantify this observation using image processing.

The green colour of fluorescence matches the negative a channel in the CIE-LAB colourspace. We used a Canny edge detector [24] to find the icicle shape, and isolated the a channel as the fluorescent *intensity* of each pixel. The CIE-LAB colourspace is a reference standard, in which the a and b channels are colour axes with 0 as colourless and values further from zero having more saturated colour. Our images typically ranged from 0 (grey) to -60 (green) in the a channel. For some measurements, the image was

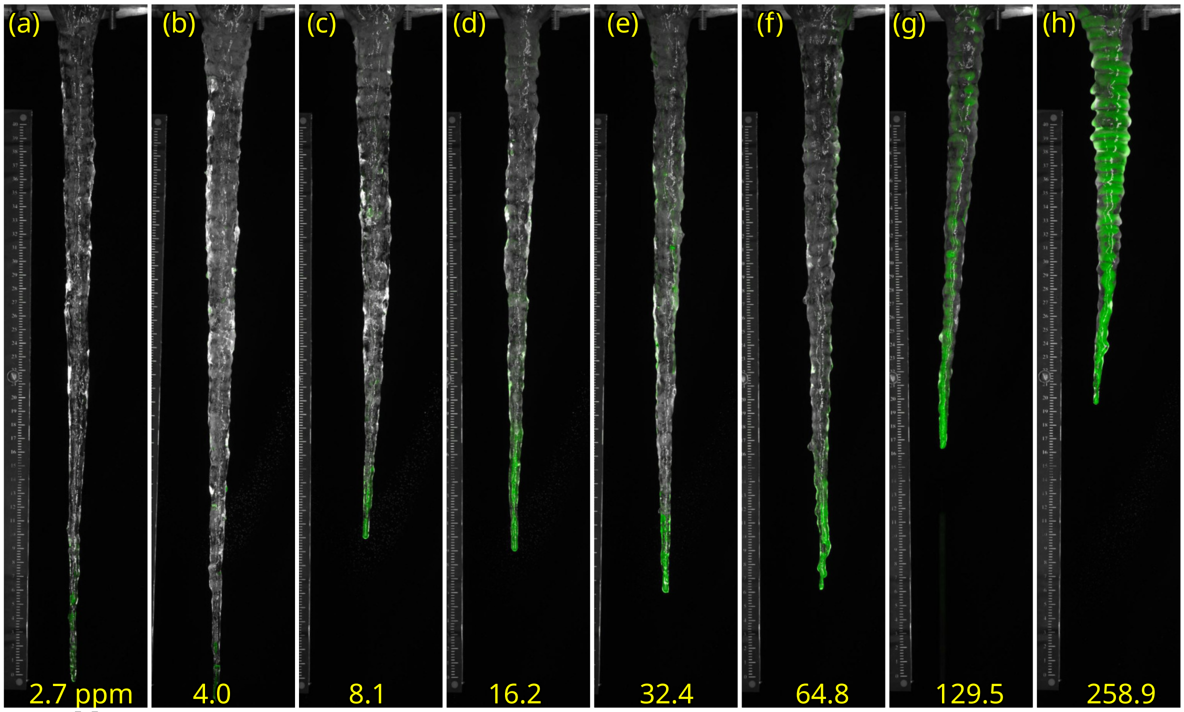

Figure 3. Each icicle of Series 2 pictured 2.5 hours into its growth. There is a clear correlation between the concentration and the amount of surface covered by liquid. In this series, the icicles grown with higher concentration are also shorter, thicker and exhibit more prominent ripples.

segmented by thresholding the intensity so that anything below a = -6 was counted as liquid. Choosing a threshold of -6 included all pixels with fluorescence, while reducing background noise.

Assuming a circular cross section, we "unrolled" each image and mapped each pixel to an area on the icicle surface. The intensity and liquid area measurements were summed around the circumference, and recorded as a function of the distance from the root. A rolling time average was then applied over one full rotation (16 frames). This image processing pipeline is illustrated in figure 4.

Figure 5 shows the surface area, covered area, and liquid fraction, plotted against time for a sample icicle. The trends shown are typical for all icicles with a constant water feed rate. At first, liquid covers the whole icicle while the area grows nearly linearly and the covered area matches the surface area. This continues up to a certain time, after which the covered area plateaus and remains roughly constant for the rest of the growth time. The liquid fraction, conversely, stays close to 100% in the early stages, then falls off as $1/t$.

In order to compare icicles across different concentrations, the median covered area between 2 hours and 4 hours was selected to characterize the maximum supported liquid area. This statistical quantity varies significantly with concentration, as seen in figure 6, with higher concentrations consistently supporting more liquid. This quantifies

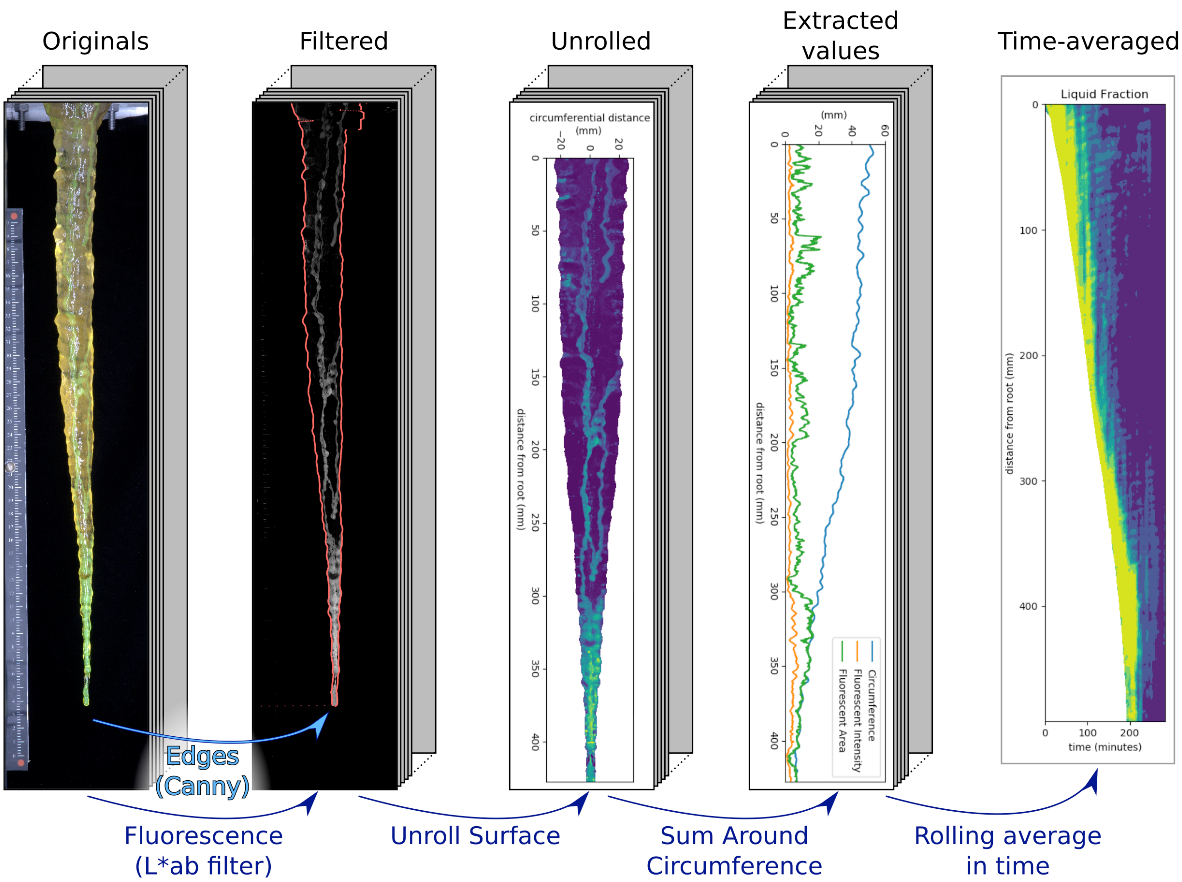

Figure 4. The image processing pipeline. The original image is filtered to extract edges and fluorescence. The icicle is "unrolled" and the fluorescence signal is summed around the circumference. All quantities are then time-averaged over a full rotation.

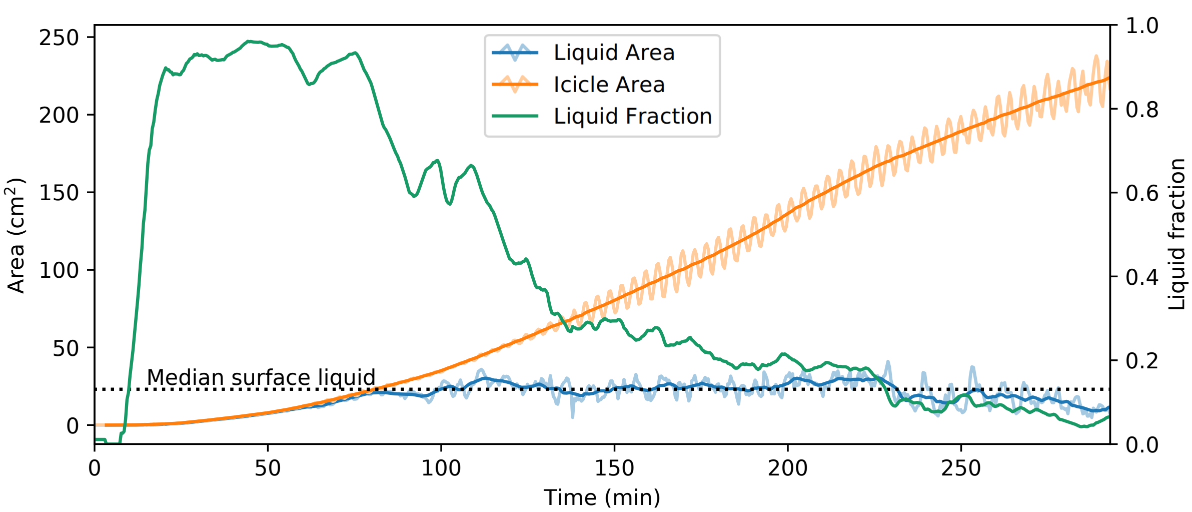

Figure 5. Total surface areas on an icicle ($Q = 3.0$ g/min, $T = -14.0°$C, $c = 1027$ μmol/kg) during its growth. All icicles show a common pattern; liquid covers the entire surface until a certain size is reached, after which the liquid area remains constant through the rest of the icicle growth.

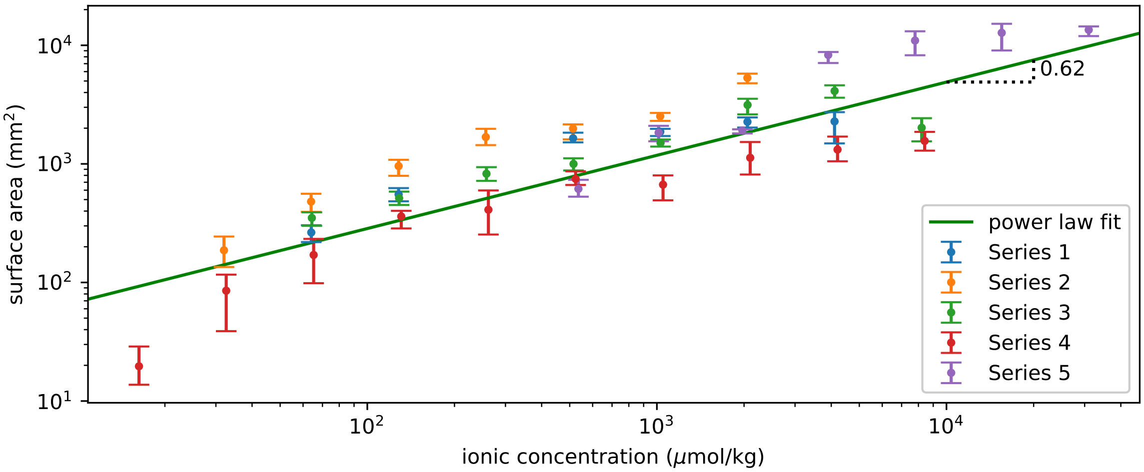

Figure 6. The median liquid covered area for icicles grown with varying feed water concentrations. Flow rates and temperatures for each series are outlined in Table 1. Higher concentrations support more liquid at the surface, following a power-law trend for most of the range of concentrations, with an exponent of 0.62 ± 0.04. Series 4, which had a lower flow rate, shows the same trend but has a consistently lower covered area than the others.

the trend observable by eye in figure 3. A phenomenological fit of this trend to a simple power-law gives $L \propto c^{0.62}$, where L is the liquid-covered area and c is the concentration. This important and somewhat counterintuitive result has strong implications for any theory of the rippling instability, as discussed in section 5 below.

Previous experimental work has established that the presence of ripples depends only on the concentration of impurities [10]; we also observe this in our dyed icicles. Clear ripples are present for concentrations above 64 ppm sodium fluorescein, while there are brief hints of ripples at some lower concentrations. The icicles with lower concentration that exhibited ripples were all part of Series 2, which had colder ambient air. Series 2 also consistently had higher surface coverage. The significant dependence of liquid coverage on concentration strongly suggests that the arrangement of surface liquid is directly linked to the mechanism of ripple formation. This inference is strengthened by the fact that in Series 2, we find ripples at lower concentrations than under other conditions, and also more liquid retained on the icicle surface. Furthermore, in all cases, the additional retained liquid appears to be contained in wider patches, rather than thin rivulets. To further establish the relationship between ripples and surface coverage, in the next section we compare the spatial distribution of liquid surface water, measured by fluorescence, to the topography of the icicle, measured by edge detection.

3.2. Liquid on ripples

In this section, we employ correlation techniques to reveal connections between ripples and surface liquid coverage. Visual inspection of rippled icicles shows that the liquid water often sits on the upper surface of a ripple. An example of this is highlighted in figure 2. This distribution makes intuitive sense, because low Reynolds number gravity-driven flow might be expected to cause liquid to accumulate of the upper surface, while draining it from the underside. Accumulation on the upper surface, leading to additional ice growth there, would also intuitively explain the observed upward migration of ripples [8, 10].

We quantitatively compared the liquid distribution to the topography using cross-correlation. The topography on the sides of the icicle can be measured directly using edge detection on the images. The liquid, however, is identified with fluorescence on the front surface, facing the camera. Because the icicle was rotated right-to-left in the view of the camera, we cross-correlated the right edge to the fluorescence one quarter rotation later. The fluorescent intensity for the middle 3/8 of the "unrolled" icicle surface (as described in section 3.1) was used to estimate the liquid distribution. In order to focus only on the ripple pattern, we de-trended both the topography and the fluorescence using a discrete cosine transform, and identified the cross-correlation peak closest to zero.

Figure 7 shows results for the cross-correlation between the right edge and the fluorescent intensity for a particular icicle. For that icicle, between 90 minutes and 210 minutes of growth, the median offset distance between the fluorescence signal and the topography was 3.41 mm, or about 1/3 the ripple wavelength, with the liquid preferentially located on the upper side of the ripple.

These measurements were repeated for all icicles that exhibited ripples. The liquid areas were consistently above the ripples, with a median displacement of 1.88 mm and mode of 3.1 mm over all rippled icicles. Icicles without ripples cannot be analyzed the same way, because both the amount of liquid and variation in topography were too small to reliably measure.

The results of this section show that higher dye concentration in the source water is correlated with much higher surface liquid coverage, with the additional liquid preferentially located on the upper surface of the emergent ripples. This coverage increase is more than a geometric flow effect, however, as the coverage pattern becomes dominated by patches rather than rivulets, with the patches associated with increased surface roughness.

The important effect of of impurity concentration on surface wettability is most obvious on icicles grown at the highest concentrations, where nearly the whole surface above and below the ripples is covered. These icicles have a distinct surface roughness that can be readily observed by scratching. This rough surface probably retains more liquid water because of its increased wettability *via* the Wenzel effect [25]. Similar surface roughness can be detected on the upper side of ripples at medium concentrations, while non-rippled icicles have very smooth surfaces. It is likely that the presence of impurities also directly modifies the surface energy of the ice; ionic impurities trapped at surfaces are known to effect contact angles and other equilibrium wetting properties [26].

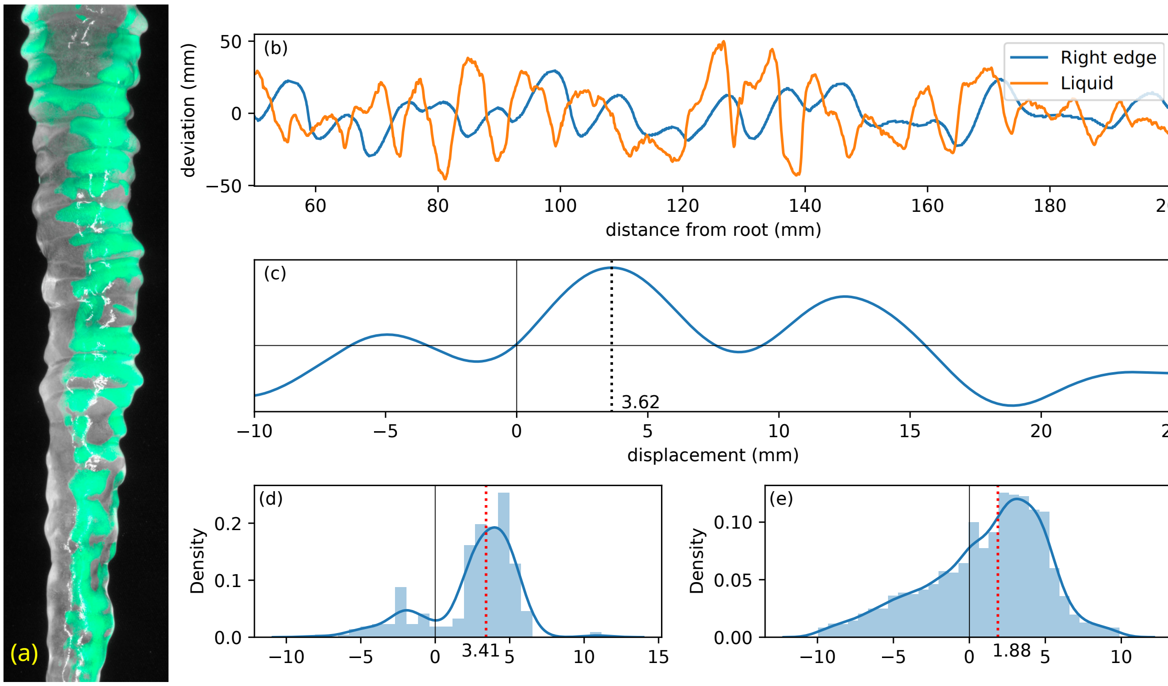

Figure 7. A rippled icicle with dye concentration of 259 ppm (2053 μmol/kg), grown at flow rate 3.00 g/min and air temperature -16°C. (a) It is clear by eye in a saturated false-colour image that patches of liquid tend to be located above the ripples. (b) A plot of the topography (blue) and fluorescent intensity (orange) for this frame shows that fluorescence peaks several mm in advance of the topography. (c) A cross-correlation of these two measurements gives a offset-distance of 3.62 mm at that time. (d) The distribution the peak closest to zero in the cross-correlation for each frame has a clear bias for liquid sitting above ripples, with a median offset (red dotted line) of 3.41 mm. (e) This offset in the cross-correlation is still evident when the cross-correlation peaks are averaged over of all rippled icicles.

In the following section, we investigate the influence of these effects by growing ice on preformed cylindrical substrates designed to separately test the effect of various properties of the ice surface.

4. Cylindrical substrates

In previous sections, we saw that the amount and location of liquid on the surface of an icicle is affected by the concentration and topography. The surface of ice is an area of active research, with many unanswered questions about contact angle, surface energy, and the nature of the quasi-liquid surface layer [27–29]. While quite interesting, these theories and experiments concern pure ice under very controlled conditions near equilibrium. Because icicles grow far from equilibrium and from a complex flow involving moving contact lines, we focus here only on the macroscopic phenomena that may affect the wetting dynamics underlying icicle growth. The concentration may play a role through its modification of the surface energy, or by creating a rough surface and

cylinder	concentration (ppm)	flow rate (g/min)	temperature (°C)	treatment
control	184	3.0	-13.7	No surface treatment.
dye bands	184	3.0	-13.7	Saturated sodium fluorescein solution painted in bands to create regions of high surface concentration of dye.
roughened	184	3.0	-13.7	Sanded with 120 grit emery cloth to create a rough surface.
grooved	184	3.0	-13.7	grooves of various widths sawn into the cylinder to approximate ripples.
truncated	440	3.0	-11.5	no surface treatment, short cylinder.

Table 2. The characteristics of a series of runs in which dyed water was dripped onto rotating preformed cylinders of ice with various surface treatments and lengths. All cylinders were initially formed in a mold using distilled water.

reservoirs (*e.g. via* dendritic growth). Larger scale topography can trap water in small depressions, or slow the gravity-driven flow.

To isolate these effects, we replaced the wood support with various long pre-formed cylinders of ice which acted as substrates for subsequent ice formation. The cylinders were frozen in a copper pipe mold, from distilled water which had been degassed under vacuum for 30 minutes. A cotton string core reinforced the otherwise fragile cylinders. Table 4 lists the properties of each cylinder. For each cylinder, dyed water was delivered to the top of the rotating cylinder in the same way as before.

Strikingly, no ripples form at any time during the growth of the *control* cylinder, seen in figure 8. From start to finish, very little liquid water is retained on the surface. All of the water descends quickly in thin rivulets, between 2 mm and 5 mm in width, and only a few patches dwell on the surface. This flow leads to a slow radial growth rate of 2.4 mm/h, with the impure ice eventually reaching a diameter several times that of the original pure ice substrate. It was apparent that the ice that formed on the *control* cylinder is quite different from that of normal impure icicles grown under otherwise identical conditions. The additional ice is still impure, as is evident from its orange color, but is more transparent than the other icicles and cylinders, which suggests fewer impurities were trapped.

The three long surface-modified cylinders from table 4 are shown in figure 9. We modified the surface concentration by painting dye on some regions (*dye bands*), surface roughness by sanding (*roughened*), and the surface topography by sawing grooves (*grooved*). Placing these features in the middle of a long cylinder also isolates the effects from the start and end of a finite domain. In each case, the resulting ice accretion pattern differed from the control, each exhibiting some ripples, but in no case did they sustain a large amplitude ripple pattern resembling that of an icicle grown under the

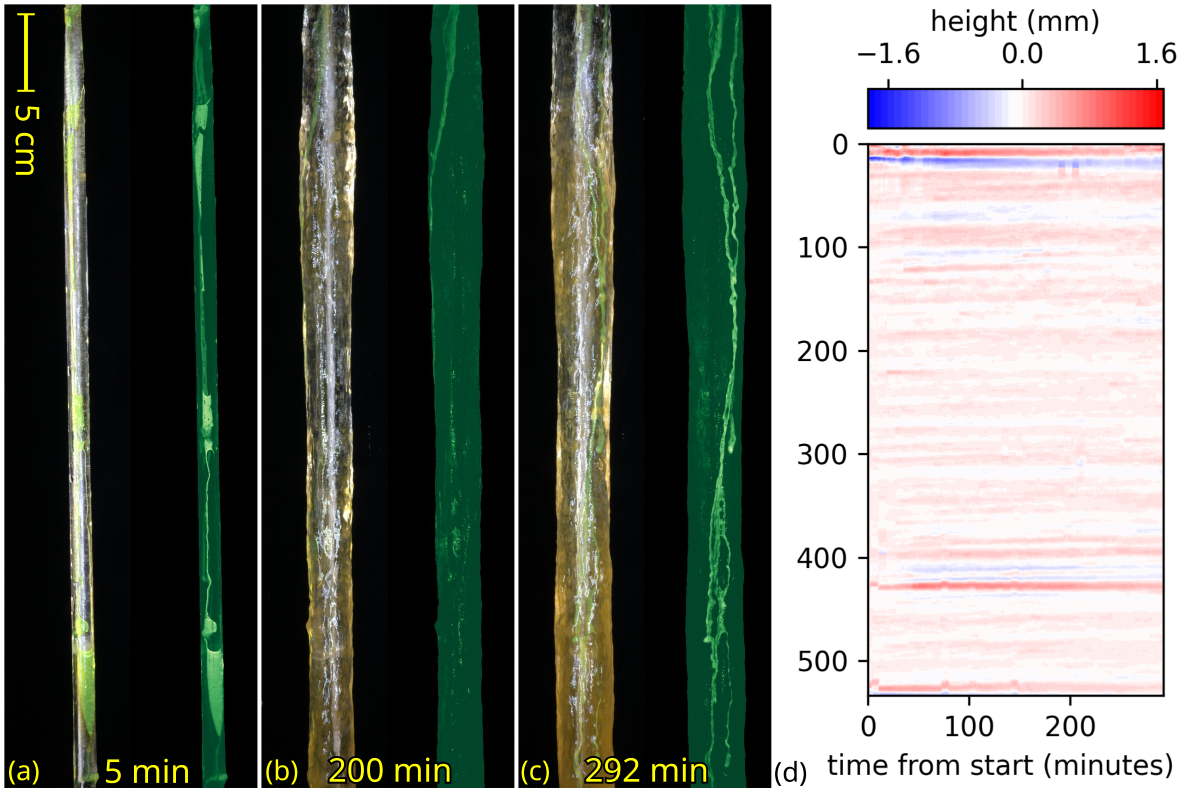

Figure 8. The control cylinder, imaged at various times during growth, shown next to a false colour image to highlight the liquid regions. Branching and merging of rivulets is clearly visible in panel (c). Panel (d) shows the deviation of right edge from its mean throughout growth. No clear ripple pattern forms.

same conditions.

Some small ripples briefly formed below the largest band of fluorescein on the *dye bands* cylinder, as indicated in figure 9. However, the ripples never spanned the circumference of the cylinder, and their growth was not sustained. The initial ripples remained small, then slowly smoothed out over the remaining hours of growth. In early times, the liquid spread out over more of the surface below that large band, so that more liquid was retained in the region where ripples began to form. At 18 minutes, we measured the liquid width as 6.3-10.4 mm (25^{th} to 75^{th} percentile) above the wide band, and 13.5-18.1 mm below the wide band. The increased width compared to the *control*, even above the wide band, may be caused by the less concentrated bands near the top of the cylinder. At late times, the liquid distribution on the *dye bands* cylinder resembled the thin rivulets of the *control* cylinder, but the ice itself was much more opaque and bumpy at the $\sim$1 cm scale. This liquid coverage was also reflected in the radial growth rate: for early growth, the rate was 3.5 mm/h, while at later times it matched the *control*'s gowth of 2.4 mm/h. In the first few minutes, the band appears to have released dye into the water, changing the concentration in the downstream region where small ripples formed.

The topographic features on the *grooved* cylinder, indicated on figure 9(b), had some significant effect on ripple formation. The thinnest grooves had a very minor effect that would be easy to miss, but a 5 mm wide groove caused a large rib that spanned the circumference of the cylinder, followed by a small train of ripples that formed upstream. These ripples began immediately because the wide groove held more water at its top, leading to more liquid covering the entire surface above the wide groove. But again, at later times, less water was retained on the surface, and ripple growth was not sustained. The first ripples that formed above the wide groove lasted the longest, and remained as the highest diameter after all the ripples smoothed out. The appearance of the ice in well-coated areas was very similar to the ice of the *dye bands* cylinder.

Ripples quickly formed on the *roughened* cylinder and became disordered at later times. These ripples nevertheless remained considerably smaller in amplitude than those that would be formed on an icicle grown with the same flow rate and concentration. However, of the three long cylinders, the *roughened* cylinder showed the greatest initial difference in liquid distribution as compared to the *control*. Liquid water clearly spread more widely than in the previous cases, covering half the circumference over most of the length. The spread was widest at the onset, and narrower lower down the icicle, because most of the water had been used up by then. For the first hour, larger patches remained on the surface, preferentially on the upper surface of ripples. After another 30 minutes, the water began to descend in small rivulets as seen on the *control*. We believe this is because the ice began to freeze over completely before more liquid replenished the reservoirs. When the ice is frozen completely, the surface becomes smooth and impurities are isolated from the surface, so it behaves like the pure ice of the *control* cylinder. The radial growth rates were nearly identical to the *dye bands* cylinder: 3.6 mm/h at the start, and 2.4 mm/h later in growth.

The *truncated* cylinder, which was simply a shorter version of the *control*, strikingly illustrates the difference between ice growth on cylindrical substrates and in icicles. It is analyzed in detail in figure 10. The first ripple formed around the bottom edge of the *truncated* cylinder, and more were robustly generated along the length of the pendant icicle. Eventually, additional ripples started to form on the *truncated* cylinder above the first one, and became visible at 100 minutes and 160 minutes into icicle growth. This upward propagation is consistent with the tendency of icicle ripples to travel upward during growth for low impurity concentrations [10]. The source water flowed uninterrupted down the surface of the cylinder in rivulets as in the *control* cylinder, then fed a conventional icicle at its base. As growth progressed, the icicle forming below the base became thicker than the section on the preformed cylinder.

The stark contrast in water adhesion and diameter growth between the *truncated* cylinder and its pendant icicle shows that there is a fundamental difference in the surface characteristics between the impure ice in an icicle and impure ice formed on a pure substrate, as in the *control*. It seems likely that the internal structure of the ice in each case differs as well.

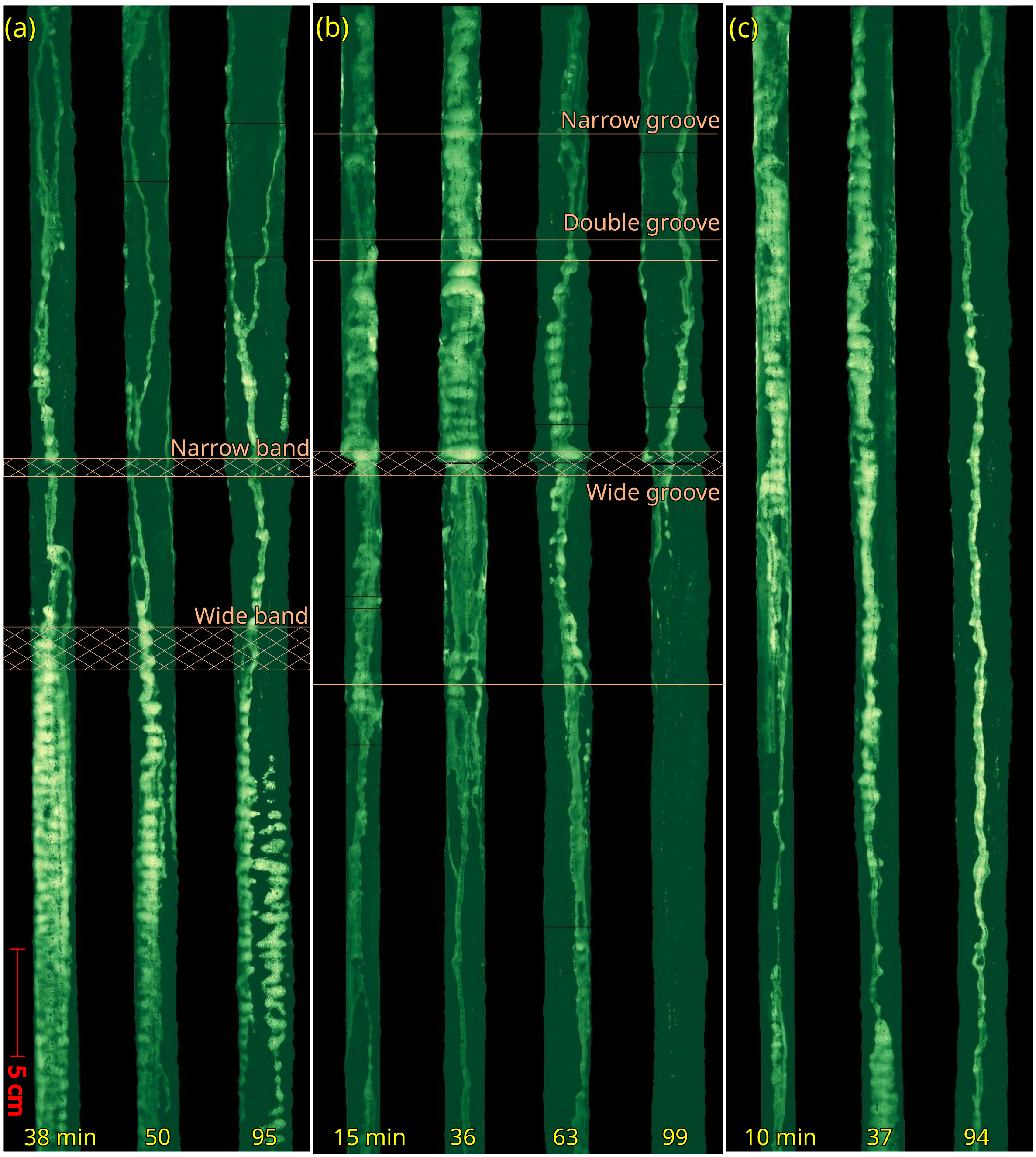

Figure 9. Three long cylinders with surface modifications and how they affect liquid distribution and ripple formation. The areas with more liquid coverage exhibit ripples. (a) The *dye bands* cylinder exhibits transient ripples directly below the wide band with the highest concentration, but below not the narrower bands. (b) The *grooved* cylinder developed a train of transient ripples above the largest groove (indicated by the arrow). Narrow grooves had almost no effect. (c) The *roughened* cylinder exhibits the most consistent spreading of liquid along its length and the formation of small disordered ripples.

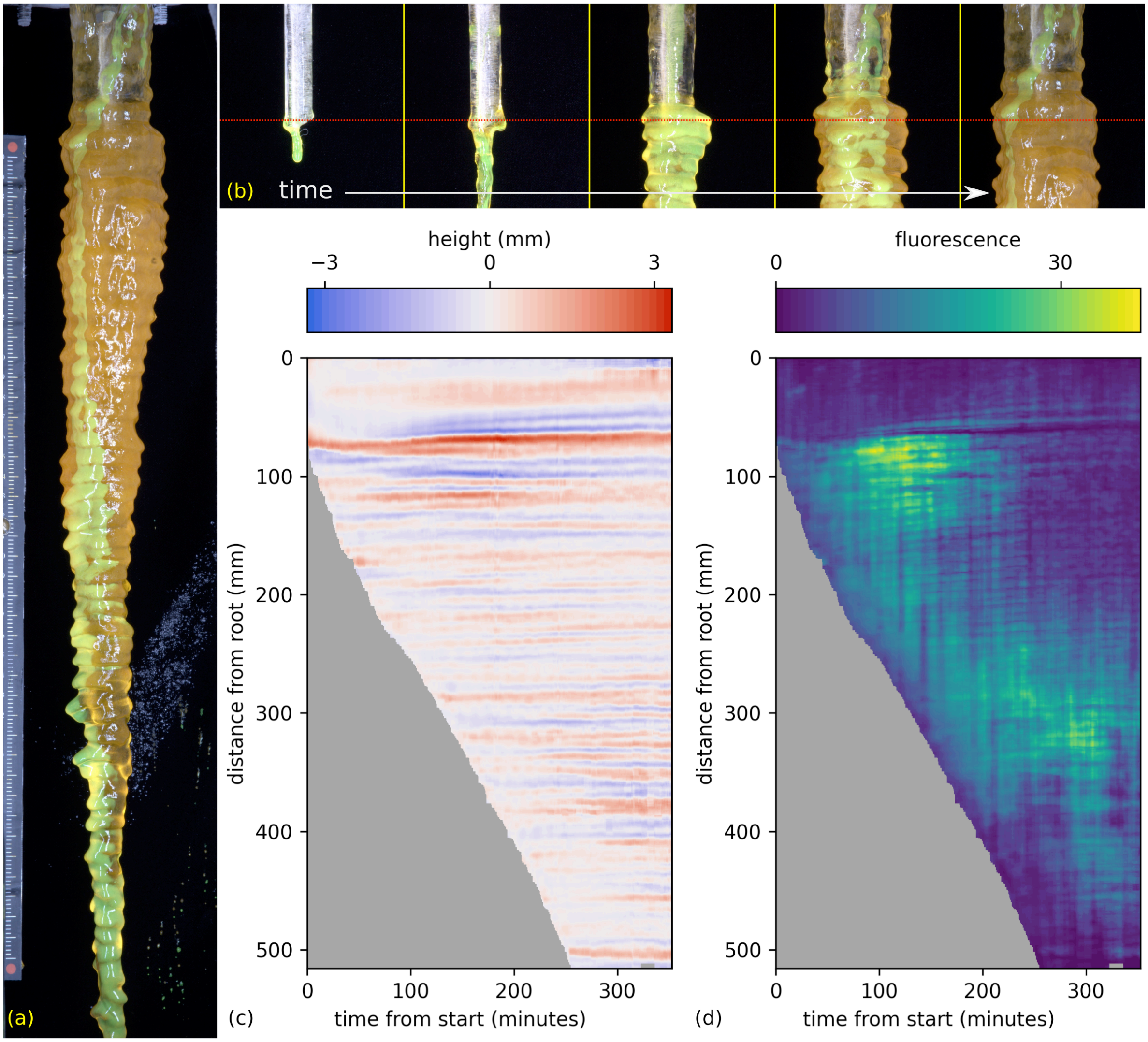

Figure 10. The *truncated* cylinder: (a) forms a typical icicle from its base, which grows thicker than the ice grown over the cylinder. (b) The first ripple starts just below the end of the cylinder, then migrates upward. New ripples form above the first, as shown in (b), and in (c), a space-time image of the topography. (d) A space-time image of the fluorescence shows that almost all the liquid is retained on the new ice, and correlates well to the ripples. The vertical bands in (d) are a result of only half the icicle being visible in any one image.

The ripples that formed on the pendant icicle, as well as the few just above the end of the *truncated* cylinder, were more persistent, and grew more robustly to a much larger amplitude than any ripples in the other cylinder experiments. These observations have important implications for any theory of ripple formation, as discussed in section 5 below.

5. Discussion

A common assumption to all existing models of icicle growth is that the icicle is fully ensheathed by a thin flowing water film [30]. A uniform thin film flow is the basis of several theories to explain the ripple instability [8, 11–17], and the overall shape of icicles [31]. Within the thin film, a typical Reynold's number of 0.1 - 4.0 can be estimated for ordinary conditions [8], provided there is a laminar Poiseuille flow. However, the actual situation is that the flow is spatially and temporally intermittent, preferring to flow down the surface in rivulets, except for a short region near the tip.

The assumption of a completely wetted surface might seem to be justified in equilibrium because solid ice is known to support a quasi-liquid layer of water on its surface which would appear to favour complete wetting [32], and a hence a zero contact angle. However, it is well established that the existence of a quasi-liquid layer does not imply a zero contact angle [28], and that, in fact, the surface tension balance at the contact line provides for a positive contact angle. At warmer temperatures, complete wetting is observed because there is a liquid layer for another reason [29]. This liquid layer disappears at about -13°C, near the temperature where our experiments were done. Other experiments [27] on the structure of the ice surface find that there is a disordered surface as low as -90°C with additional layers melting above -16°C, and quasi-liquid drops and film above -2°C. Previous icicle experiments [9, 10, 20] have shown that the ambient temperature does not strongly effect the emergence of ripples, other than to vary their overall speed of growth; there is no obvious change in the phenomena near -13°C.

The relevance of purely thermodynamic considerations is suspect, however, because the surface of a growing icicle is an open system driven far from equilibrium by latent heat release and flow, giving rise to large temperature and concentration gradients. Our observations indicate that the icicle surface is in a highly dynamic state with only partial liquid coverage of the surface. We now turn our our attention to the existing continuum theories of icicle ripples, since our observations speak mainly to macroscopic phenomena.

The first continuum theory of icicle ripples is due to Ogawa *et al.* [11]. Subsequently, in a series of papers, Ueno *et al.* [12–17] elaborated upon a physically similar model using different approximations and different assumptions about certain boundary conditions. Ueno *et al.* also explored several different heat transfer mechanisms in the surrounding air, going beyond simple diffusion. First, and most fundamentally, both the Ogawa and Ueno models treat the emergence of the ripples as the outworking of a linear instability away from a simplified basic flow state. The problem is treated as axisymmetric, so that the icicle is assumed to be covered by a uniform sheath of flowing liquid water in the basic flow state. The overall shape of the icicle is ignored and it is treated as planar. The basic flow state is assumed to be a simple, steady parabolic shear flow with surface tension and its internal fluid-mechanical instabilities are ignored. Furthermore, the water is assumed to be pure. Under certain assumptions about temperature boundary conditions on each side of the water film ‡, these models both produce a linear instability whose most unstable mode is a traveling ripple with about the observed universal wavelength. The Ogawa model predicts that the ripples should travel downward, while the Ueno model predicts upward motion. Experimentally, ripples are observed to travel upward at lower impurity concentrations, and downward for higher concentrations [10]. An analogous, but chemically more complex model has been proposed to explain ripples on stalactites [33].

Previous work [10] has shown that impurities are essential for the emergence of ripples, falsifying both the Ogawa and Ueno models which take no account of impurities. Both models, furthermore, predict ripples on pure water icicles which are not observed. We have attempted to generalize the Ueno model [34,35] to include impurities by adding the physics of impurity transport; the advection and diffusion of concentration and its associated boundary conditions. Our generalized Ueno model contains the coupling of temperature and concentration at the growing ice water interface to include the effect of freezing point depression. The generalized Ueno model consequently has different temperature boundary conditions than the original Ueno model, which leaves the temperature of the ice water interface unconstrained [15]. It thus does not reduce to the original model when the concentration of impurities is set to zero. The generalized Ueno model produces an instability, but fails to predict a wavelength because the growth rate of the fastest growing linear mode diverges at short wavelengths [34]. At present, we have no convergent, axisymmetric continuum linear stability theory based on a simplified basic flow state which also accounts for impurities §.

The surface of an icicle is not fully ensheathed in a liquid film, except for a short region near the tip. Instead, the flow state consists of transient rivulets and longer lasting patches of liquid. The amount of liquid retained on the surface is tied to both concentration, and the size of ripples. With higher concentrations, more liquid is retained, and larger, more robust ripples form. This trend is consistent among different temperatures and flow rates. While an Ogawa- or Ueno-like linear instability might be relevant near the tip, it is evident that the ripples grow from a much more stochastic flow pattern than is assumed by an axisymmetric model. The actual unsteady flow state does not reduce to a simple parabolic shear profile, even in time average. Thus it is more plausible that the concentration-dependent flow patterns couple positively with the topography evolution to cause ripples.

‡ The Ogawa model constrains the temperature of the ice-water interface to be equal to the melting temperature of ice. This boundary condition, if generalized to include freezing point depression, would the same as the one used in our generalized Ueno model. The Ogawa and Ueno models also differ in the way they treat the surface tension at the free water surface, and in the details of the long wavelength approximation.

§ We have not attempted to generalize the Ogawa model to include impurities. It is presently unclear if such a generalized Ogawa model would suffer the same divergence at large wavenumber as the generalized Ueno model.

Furthermore, if the icicle is ensheathed in liquid water, as in axisymmetric models, it follows that the water must be supercooled, in order that the latent heat released at the ice water interface be transported radially outward. This is not the case for the observed flow state, in which it is possible for the liquid in the rivulets to remain above freezing, while surrounding areas of bare ice may be colder. Significant azimuthal temperature gradients will certainly exist. Thus the temperature distribution, as well as the concentration distribution which is transported by the same flow, will be very different than allowed by any axisymmetric model. Further studies of the temperature distribution on growing icicles would help illuminate these points.

The liquid also preferentially dwells on the upper surface of ripples/topography, which would help explain the upward migration of ripples that has been previously observed [8–10, 20], reinforcing the hypothesis that the flow patterns provide positive feedback to the topography evolution. Topography would be expected to modulate the downslope effect of gravity, but there may also be other causes of this localization. Notably, the ice on the upper surfaces of the ripples has a rough texture, which may enhance the wetting there.

Our investigations using cylindrical substrates demonstrate that the flow of water over the surface of actively growing ice depends on surface texture, presence of impurities at the surface, gravity, and topography (both slopes, and cylinder terminations). On conventional icicles at high concentration, liquid is increasingly drawn onto rough areas of the surface and interacts with the topography differently than at low concentration. The failure of the control cylinder to produce ripples despite sufficient feedwater concentration suggests a further potential positive feedback between topography, concentration, and the exposed (internal) structure of impure ice.

The *banded* and *roughened* cylinders show some spreading of liquid due to roughness and trapped impurities, leading to small-amplitude ripples. However, a stop in the flow as caused by a wide groove (*grooved* cylinder) or the end of the substrate (*truncated* cylinder) has a more significant effect. A notable difference between the surface effects (*banded* and *roughened* cylinders) and the topographic effects (*grooved* and *truncated* cylinders) is that ripples do not always wrap around the circumference to form ribs. For the ripples to wrap around the icicle, it appears that the liquid must first wrap around the whole icicle. This can be seen most clearly at the end of a surface (e.g. at the tip or above a groove). Most rippled icicles have ripples that wrap completely around the circumference, which suggests that the ripple is initiated at the tip, consistent with the ripples seen propagating up from the end of the *truncated* cylinder.

The very different shape evolution of the *truncated* cylinder and its pendant icicle points to a significant difference between the actively growing ice, and the "inactive" preformed ice. The ice actively growing from impure water may have a higher concentration of impurities trapped near the surface, and also the rough texture that was emulated in the *banded* and *roughened* cylinders. The liquid is also wider in those areas, suggesting that it spreads out around the surface more easily. Once some ice has completely frozen over, fully encapsulating the impurities, it behaves differently: the surface does not retain as much liquid, but instead allows it to freely flow in rivulets to the bottom of the ice. This suggests a further potential positive feedback between topography, concentration and the internal structure of the impure ice may be present. More experiments will be required to uncover the distribution of impurities trapped in the ice.

Freezing point depression due to the presence of impurities may still play a minor role in the actual rivulet-dominated flow. The rough surface texture observed on ripples can trap the impurities inside a spongy ice matrix. According to mushy layer theory [36], as the solid fraction increases without adequate transport of impurities, the local concentration increases, further depressing the freezing point. These mechanisms can cause additional changes to the local temperature and freezing rate that are not captured in a solid ice model. One such effect could be a slower freezing rate relative to the flow and spreading rates, enhancing the interaction between the incoming feed water and the "wet" areas on the surface. It is not possible to observe these dynamic effects directly with the current experiment due to its limited time resolution and the difficulty of isolating transient rivulets on growing icicles. Experiments focussing on an individual, controlled rivulet may shed light on these small-scale processes. For example, one could measure the advancing contact angle and velocity of the front of a rivulet on an inclined plane of ice. Monier *et al.* have recently performed a similar experiment [23], but on aluminum with different temperature conditions.

Finally, our observations challenge the assumption that the ripples are the result of a linear instability. Rather, they suggest that small but finite perturbations might be required to trigger the appearance of ripples. A linear instability would have been expected to produce ripples on the *control* cylinder, but no ripples were observed. Ripples only appeared on the *grooved* cylinder when a sufficiently large topographic perturbation was encountered. On the other hand, rippling was also observed on the *roughened* cylinder without finite topography, as long as a sufficient amount of liquid was retained by the rough surface.

6. Conclusion

Any theoretical model of wet ice growth must account for the flow and redistribution of liquid water over the evolving topography of the ice surface. The liquid flow and distribution, in turn, determines the pattern of latent heat released as the ice grows, and thus the advection and diffusion dynamics of the local temperature. When impurities are present, their partial exclusion by the growing ice gives rise to a flux of concentration, which is also advected and diffused in the flowing liquid. Finally, the gravity driven flow of liquid water over the topography must also account for surface tension forces, and in the case of partial liquid coverage, mobile contact lines and wetting effects. Solving for the emerging shape of the ice requires closing the complex feedback loop between shape and the transport of heat and impurities. On an icicle, this shape evolution exhibits pattern formation: the appearance of slowly translating ripples with a near-universal wavelength. How can these ripples be explained? Our observations put strong constraints on any model of ripple formation.

We have shown through experiment that the flow of liquid over icicles is a much more complicated and stochastic process than was previously thought. In particular, we have uncovered the effect that small levels of impurities, previously shown to be crucial to the appearance of ripples, has on the wetting properties of the ice surface. In general, impurities cause the ice surface to retain more water, and to change the overall pattern of flow toward wider rivulets and more discrete patches of liquid.

Linear stability-based theories of ripples, which assume a simple thin-film flow, cannot account for the impurity effect and do not explain how ripples grow even as the bulk of the water flows down the surface in discrete rivulets. An explanation of the ripples must be sought in the way in which the highly stochastic water flow couples both to the topography and to the strongly impurity-enhanced local dynamic wetting properties of the ice. Any complete theory of icicle morphology must account for these surface properties in addition to the interplay between the evolving shape and the transport of heat and impurities.

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