Dynamics and unsteady morphologies at ice interfaces driven by D$_2$O–H$_2$O exchange

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The growth dynamics of D$_2$O ice in liquid H$_2$O in a microfluidic device were investigated between the melting points of D$_2$O ice (3.8 °C) and H$_2$O ice (0 °C). As the temperature was decreased at rates between 0.002 °C/s and 0.1 °C/s, the ice front advanced but retreated immediately upon cessation of cooling, regardless of the temperature. This is a consequence of the competition between diffusion of H$_2$O into the D$_2$O ice, which favors melting of the interface, and the driving force for growth supplied by cooling. Raman microscopy tracked H/D exchange across the solid H$_2$O–solid D$_2$O interface, with diffusion coefficients consistent with transport of intact H$_2$O molecules at the D$_2$O ice interface. At fixed temperatures below 3 °C, the D$_2$O ice front melted continuously, but at temperatures near 0 °C a scalloped interface morphology appeared with convex and concave sections that cycled between growth and retreat. This behavior, not observed for D$_2$O ice in contact with D$_2$O liquid or H$_2$O ice in contact with H$_2$O liquid, reflects a complex set of cooperative phenomena, including H/D exchange across the solid–liquid interface, latent heat exchange, local thermal gradients, and the Gibbs–Thomson effect on the melting points of the convex and concave features.

Ice formation is arguably the most common crystallization process on Earth, ranging from the formation of atmospheric snow and ice to annual cycles of freezing and thawing of ground water. Ice has more solid phases than any other substance, with 17 polymorphs reported (1) and another predicted (2). The growth dynamics of common, hexagonal (Ih) ice are essential in climate modeling, mitigating structural damage due to freeze–thaw cycles (3, 4), glacier dynamics (5), cryobiology and cryopreservation (6), and the design of new materials through ice templating (7). Heavy water (D$_2$O) also adopts the same Ih structure and crystal habit as light water (H$_2$O) (8), but melts at higher temperatures $T_m$ = 3.8 °C vs. $T_m$ = 0 °C, respectively. D$_2$O has been used as a solvent in the cold preservation of organs (9). The higher melting temperature and lower vapor pressure of D$_2$O are essential for estimating millennial global temperatures through analysis of deuterium composition in ice cores (10). The fractionation of water isotopomers is a manifestation of preferential freezing of D$_2$O with respect to H$_2$O, which affects the distribution of environmental deuterium (11, 12). Isotopic fractionation also can occur through H/D exchange, a process that has been investigated at temperatures ranging from −178 °C to −2 °C (13–20). H/D exchange at lower temperatures (up to −103 °C), has been investigated by measurement of changes in isotopic composition in thin stratified films of D$_2$O–H$_2$O–HDO (1–100 nm in thickness) (13, 14, 17, 19). The diffusion of tritium into bulk H$_2$O ice has been measured over the range −35 °C to −2 °C (18, 20), with diffusion coefficients spanning seven orders of magnitude. Comparison of diffusion coefficients for ice films and bulk crystals from measurements performed over such a large range of temperatures may be problematic because (i) extrapolation of Arrhenius behavior may not be reliable over the temperature range; (ii) different diffusion mechanisms may be operative at lower temperatures compared with those at higher temperatures (interstitial ion migration vs. vacancy migration); (iii) thin ice films may be polycrystalline or even amorphous, compared with the single crystallinity of bulk ice; and (iv) thin ice films tend to have more defects than single crystals, affording larger-than-actual diffusion rates in films (17). Herein, we describe ice crystallization on the surface of a D$_2$O crystal in liquid water within a microfluidic device for which temperature can be controlled with a precision of 0.001 °C and a stability of ±0.002 °C. At a constant temperature below the melting point of D$_2$O, 3.8 °C, the crystal interface melted slowly. As the system was cooled continuously at a sufficiently high rate, the ice front advanced, but retreated immediately after cooling ceased, signaling exchange of H for D in the solid D$_2$O that reduced the ice melting temperature. At a constant system temperature (the temperature that was measured by the thermistor), the liquid–solid interface exhibited oscillatory and unsteady morphologies owing to the combined effects of H/D exchange, latent heat dissipation, local thermal gradients, and the Gibbs–Thomson effect.

D$_2$O–H$_2$O Phase Diagram

Several investigations of ice-containing mixtures of H$_2$O and D$_2$O (21–23), and implicitly HOD, have been reported, relying on vibrational spectroscopic assays of HOD through the appearance of separate O-H and O-D vibrational bands. These reports, however, have not addressed the melting (or freezing) habits of H$_2$O:D$_2$O mixtures. Measurement of the melting points across a range of H$_2$O:D$_2$O compositions can permit construction

Significance

Freezing and melting of ice are one of the most common events on Earth. The dynamics of ice crystallization are relevant to climate research, mitigating frost damage in agriculture and construction, glacier dynamics, tissue and food preservation, and transportation. We describe the use of microfluidic devices, accompanied by precise temperature control, to examine the effect of H/D isotope exchange between liquid light water and solid heavy water on ice growth dynamics. These studies revealed unusual morphologies at the ice surface in contact with the liquid, including curious unsteady morphological features that give the appearance of oscillation due to complex interplay of H/D exchange, thermal gradients, and local surface curvature.

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of a phase diagram, which in turn can be used to deduce the equilibrium composition of a H$_2$O–D$_2$O liquid–solid interface during growth or melting. This was achieved by insertion of a small amount of premixed solutions (0.5 μL total volume) with various H$_2$O:D$_2$O compositions into an oil droplet resting on a sapphire disc placed on a custom-built cold stage (Fig. S1). The oil droplet was then topped with a glass coverslip, extruding the oil and leaving water trapped between the coverslip and the sapphire disc (24). The assembly was cooled to −20 °C and then heated slowly to melt the ice partially, affording a disk-shaped single crystal of ice. Optical microscopy was used to determine the melting temperature of the single crystal, enabling construction of a simple binary phase diagram, which displayed a linear relationship between the melting temperature and isotopic composition (Fig. 1).

**H$_2$O Crystal Growth on D$_2$O Ice**

Crystal growth resulting from ice deposition on a D$_2$O crystal in liquid H$_2$O was examined in a microfluidic device that initially contained neat D$_2$O. The temperature of the cold stage was controlled to within ±0.001 °C. After lowering the temperature to −20 °C to freeze the liquid in the microfluidic channel, the resulting D$_2$O ice was melted partially at 3.6 °C until a well-formed single crystal remained in the channel. The length of these crystals ranged from 80 μm to 800 μm. The channel dimensions of the primary compartment prescribed their width and height (150 μm and 20 μm, respectively). The liquid D$_2$O surrounding the crystal was then replaced with H$_2$O, and the temperature was lowered immediately to a value below 3 °C to limit melting of the crystal. The reliability of this protocol was assessed using an indicator dye that enabled visualization of the displacement of D$_2$O by H$_2$O. Injection of an H$_2$O solution containing sunset yellow dye FCF (for coloring food; 1% wt/wt; CAS no. 2783-94-0) into the microfluidic channel confirmed plug flow displacement of the liquid D$_2$O. All subsequent experiments were performed without sunset yellow, however. At constant system temperature below the D$_2$O melting point, the D$_2$O crystal interface melted, as observed by the retreat of the interface, signaling a continuous reduction in the melting point due to H/D exchange across the interface. For example, at 1 °C the solid–liquid interface retreated at a rate of ca. 0.5 μm/s. This exchange, which melts the interface, adds H to the D$_2$O ice while enriching the solution near the solid interface with D.

When the temperature was decreased at a rate of 0.002–0.1 °C/s from an initial temperature between 2 °C and 0.2 °C, the growth front of a D$_2$O crystal in contact with the added liquid H$_2$O advanced, which can be attributed to freezing of liquid near the interface that contained D$_2$O from prior melting of the interface. This new layer must have a composition governed by the phase diagram in Fig. 1. If the temperature was held constant after continuous cooling, this newly crystallized region melted over a few seconds. For example, lowering the temperature from 0.786 °C to 0.682 °C at 0.02 °C/s resulted in rapid growth of ice on the D$_2$O crystal, accompanied by the formation of a distinct interface between the new H$_2$O-rich ice and the D$_2$O ice (Fig. 2 A and B). After the cooling was stopped and the cold stage stabilized at 0.699 °C, the H$_2$O-rich ice melted rapidly at 2.2 μm/s to the original D$_2$O crystal boundary, after which the remaining D$_2$O crystal melted more slowly at 0.25 μm/s, limited by H/D exchange across the interface (Fig. 2 C and D). Above 0.002 °C/s, the growth rate of the ice front increased linearly with increasing cooling rate (Fig. S2). Raman microscopy of the newly formed H$_2$O-rich ice performed on an area ~10 μm from the D$_2$O ice front revealed compositions near those expected from the phase diagram in Fig. 1 (Fig. S3).

In another experiment in which the temperature was lowered from 0.745 °C at 0.01 °C/s, the D$_2$O ice interface exhibited an unsteady scalloped morphology (Fig. 3 A–E and Movie S1). The cellular features of this interface merged to form a flat ice front upon further cooling (Fig. 3 F and G). Like the crystal in Fig. 2, the solid–solid interface between the D$_2$O crystal and the added H$_2$O ice was readily apparent (Fig. 3 G, dashed box). Upon cessation of cooling the ice growth stopped, and the ice

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**Fig. 1.** Binary phase diagram for H$_2$O:D$_2$O mixtures determined from visual observation of freezing/melting (red circles) and the predicted melting points (black line). The phase diagram follows a simple linear dependence between melting temperature and isotopic composition. Inset shows an ice crystal formed in a 75%-H$_2$O–25%-D$_2$O mixture at 0.996 °C. The disc-shaped morphology is typical of crystals grown across the isotopic range. The upper face of the disc corresponds to the ⟨0001⟩ plane. (Scale bar, 10 μm.)

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**Fig. 2.** (A) A D$_2$O crystal in H$_2$O liquid. (B) The crystal grew after lowering the temperature, revealing a distinct interface between the oval D$_2$O crystal in the center and the surrounding H$_2$O crystal. The dashed oval is a visual aid. (C) After raising the temperature, the newly formed ice retreated. (D) Raising the temperature melted the entire H$_2$O crystal, leaving the D$_2$O crystal with the original shape intact. (Scale bar, 20 μm.)
front retreated again to the position of the former D$_2$O crystal interface (Fig. 3H). The unsteady cellular features were not observed at cooling rates exceeding 0.02 °C/s (Fig. S4). Collectively, the cellular features in Fig. 3 suggest nonlinear behavior that results from a competition between the timescales for cooling and H/D exchange, the former promoting growth and the latter promoting melting of the ice interface. Both processes require exchange of latent heat. When the driving force (supercooling) is large (Fig. 3 D–G), growth becomes more competitive than H/D exchange, and the advancing growth front is flat, absent of cellular features. Notably, these features were not observed for D$_2$O ice in contact with D$_2$O liquid or H$_2$O ice in contact with H$_2$O liquid; thus any explanation must involve H/D exchange and diffusion as well as thermal effects.

The interface between D$_2$O and H$_2$O crystals was examined during rapid lowering of the temperature of a D$_2$O crystal in contact with liquid H$_2$O from 0.998 °C to −0.211 °C. The liquid in the channel froze, creating a noticeable discontinuity between the D$_2$O crystal and the new H$_2$O ice (Fig. S5). The interface between the D$_2$O and H$_2$O crystals gradually blurred, becoming imperceptible after ∼20 min (Fig. S5 C–E). The discontinuity suggests a grain boundary between the old (D$_2$O-rich) and the new (H$_2$O-rich) ice, which may reflect a disordered liquid layer that persisted during freezing, possibly akin to quasi-liquid layers invoked for grain boundary melting (25). It is reasonable to suggest that the optical contrast across the width of the discontinuity stems from a different refractive index ($\eta = 1.24$ if amorphous) compared with hexagonal ice ($\eta = 1.3$) (26). The disappearance of this region likely reflects restructuring of the disordered region to match the lattice of the solid ice on either side. This process would require molecular motion, and it is reasonable to expect that the timescale would be comparable to that for diffusion. The blurring of the H$_2$O–D$_2$O discontinuity at the solid–solid interface formed as described above suggests a change in structure or composition due to H/D exchange, widening a mixed interface accompanied by the formation of HOD.

The changes in the composition of the D$_2$O single ice crystal were measured by Raman microscopy at subfreezing temperatures in the range −0.2 °C to −0.5 °C, which were performed with a precision of ±0.001 °C and spatial resolution of ±0.5 μm. The Raman microscope was focused on the D$_2$O side of the conjoined H$_2$O–D$_2$O ice crystal, 10 μm from the original D$_2$O–H$_2$O interface. The reduction in D$_2$O content and the increase in H/D exchange were evident from changes in the intensity and the position of the $\nu_{OD}$ bands between 2200 cm$^{-1}$ and 2600 cm$^{-1}$ (Fig. S6). Initially, the spectrum revealed $\nu_{OD}$ stretching modes typical for pure D$_2$O at 2337 cm$^{-1}$ and 2483 cm$^{-1}$ (23, 27). Over time, the intensity of the D$_2$O peaks decreased concomitant with a shift of the 2337 cm$^{-1}$ peak toward 2440 cm$^{-1}$ (Fig. 4). The amount of H/D was determined by measuring the reduction in the integrated intensity in the region of interest and by using a calibration curve of predetermined H$_2$O:D$_2$O compositions (Materials and Methods and Figs. S6 and S7). The diffusion coefficient of H$^+$ (or H$_2$O) into the D$_2$O ice was determined using a standard seminfinite slab model (Eq. 1), where $C_O$ is the H$_2$O fraction at the D$_2$O–H$_2$O interface (determined from the phase diagram), $C_C$ is the H$_2$O fraction at a distance $x$ from the D$_2$–H$_2$O interface, $x$ is the distance from the D$_2$–H$_2$O interface where the Raman measurement is positioned ($x = 10 \pm 0.5$ μm), $D$ is the diffusion coefficient, and $t$ is time. A reasonable fit of Eq. 1 to the data afforded $D = 0.59 \pm 0.1 \times 10^{-10}$ cm$^2$·s$^{-1}$ (Fig. 4). Notably, the timescale for diffusion of H$_2$O through a typical 3-μm-thick layer using this value of $D$ is ∼25 min, comparable to the time for near disappearance of the interface region in Fig. S5E.

$$C = C_o \left[1 - \text{erf} \left(\frac{x}{2\sqrt{Dt}}\right)\right]$$  

The aforementioned diffusion coefficient compares favorably to the values of $D = 1.0 \pm 0.2 \times 10^{-10}$ cm$^2$·s$^{-1}$ reported for D$_2$O diffusion in polycrystalline ice at −1.8 °C and $D = 0.1 \pm 0.1 \times 10^{-10}$ cm$^2$·s$^{-1}$ for T$_2$O diffusion in single-crystal ice at −10 °C (18, 29). Using the reported value of $D_{\text{D$_2$O}} = 10.63$ cm$^2$·s$^{-1}$ measured for T$_2$O diffusion in a single crystal of H$_2$O ice (18), the data in Fig. 4 were consistent with an activation energy $E_a = 58.7 \pm 0.2$ kJ/mol. This value is comparable to that reported for T$_2$O in ice, $E_a = 59.8 \pm 6.7$ kJ/mol (18); diffusion of T$_2$O into natural single ice crystals, $E_a = 65.7 \pm 8.3$ kJ/mol (22); and the activation energy for desorption of H$_2$O from 6-μm-thick ice films (58.1 ± 0.8 kJ/mol) (30). In contrast, the diffusion coefficient for HF, which may diffuse as an intact molecule or as ions, in single ice crystals at −10 °C was reported as $D = 0.8 \pm 0.5 \times 10^{-6}$ cm$^2$·s$^{-1}$, substantially larger than the values above (31). Collectively, these data implicate diffusion of intact water molecules through a vacancy mechanism for H/D exchange in the D$_2$O crystal (8, 18, 32).
Unsteady Interface Morphologies

As described above, when the temperature of the microfluidic channel containing a D$_2$O crystal in contact with liquid H$_2$O was lowered quickly from ca. 2.6 °C to a constant temperature in the range 2.6–0.6 °C, the flat ice front grew, but then retreated, with lower rates of retreat at lower temperatures. Cooling the device from 2.6 °C to below 0.6 °C also resulted in an initial period of growth followed by retreat of the H$_2$O-rich ice front. Once the ice front retreated to the original D$_2$O crystal interface, unsteady morphologies like those in Fig. 3 were observed, growing and melting in an unsteady, almost oscillatory, manner across the interface (Fig. 5 and Movie S2). These unsteady morphologies were not observed for D$_2$O ice in contact with D$_2$O liquid or H$_2$O ice in contact with H$_2$O liquid, arguing against impurities as a major factor in their formation. The interface was decorated with convex features having radii of curvature ranging from 5 μm to 15 μm, alternating with deep concave features having large negative curvature. Under constant system temperature, the convex and concave features cycled every 20–120 s, persisting during a slow retreat of the average position of the D$_2$O crystal interface, which typically required 8 h to traverse the length of the microfluidic chamber (3.6 mm, Movie S3). These unsteady morphologies vanished if the temperature was raised by >0.025 °C (Movie S2). In a few trials, the convex and concave features of the interface coalesce in successive cycles to give the appearance of wavelike patterns, denoted by the vertical dashed lines in Fig. 5. Most experiments, however, reveal an unsteady cycling of the interface morphology, usually with new convex features emerging out of regions of sharp negative curvature where shrinking convex features intersect the interface. The evolution of the curved features was not a consequence of crystal anisotropy (Fig. S8).

These observations suggest that the growth and dynamics of the unsteady morphologies depend on a complex set of cooperative phenomena as described below, including H/D exchange from the H$_2$O-rich liquid into the D$_2$O-rich ice crystal, latent heat exchange, local thermal gradients, and the Gibbs–Thomson effect on the melting points of the convex and concave features. The Gibbs–Thomson effect (33) predicts that the melting temperature of a curved interface, $T_m$, can be calculated using Eq. 2, where $T_m$ is the melting temperature of the bulk ice (which is nearly equal to the temperature measured by the thermistor mounted in a copper plate beneath the microfluidic device; Fig. S1), $\gamma$ is the energy of the solid–liquid interface, $\kappa$ is the curvature or reciprocal radius of the curved feature, and $L$ is the latent heat of ice. The $\kappa$ term is positive when the feature is convex (34). Convex features (positive curvature) are susceptible to melting because $T_i > T_m$, whereas concave features (negative curvature) can promote ice growth because $T_i < T_m$. Using the range of curvature radii observed here, a surface tension $\gamma = 0.033$ J·m$^{-2}$ and $L = 3.34 \times 10^{-3}$ J·m$^{-3}$, the magnitude of the $T_i$ values for the convex and concave features is anticipated to be in the range 0.001 $\leq |T_i| \leq 0.005$ °C. This small difference is within the precision of temperature control and measurement in the microfluidic device (as measured at the thermistor), which is viewed as essential for the observation of the unsteady morphologies that otherwise would go unnoticed.

$$\frac{T_m}{T_i} = 1 - \left( \frac{\kappa}{L} \right)$$

Considering the above factors, a preliminary framework for understanding the growth and dynamics of the unsteady interface morphology was constructed. Ice grows initially upon cooling because of the presence of D$_2$O near the interface, which diffuses into the liquid phase, creating a supercooled condition. The ice then retreats when H$_2$O diffuses into the solid phase, inducing melting as $T_m$ decreases. During this growth and retreat, the cellular features form on the interface, possibly because of the nonequilibrium conditions created by the requirement for effective exchange of latent heat during freezing and melting following the temperature step. Once the unsteady morphologies appear, melting of the convex features, aided by the Gibbs–Thomson effect, enriches the concentration of D$_2$O molecules in the liquid above it due to preferential freezing of D$_2$O at the lower temperature. Heat transfer between the convex and concave regions may then occur, aided by the difference in thermal diffusivities. The thermal diffusivity of ice (1.50 × 10$^{-2}$ cm$^2$·s$^{-1}$) is 10 times greater than that of liquid water or poly(dimethylsiloxane) (PDMS) (1.50 × 10$^{-3}$ cm$^2$·s$^{-1}$ and 1.00 × 10$^{-3}$ cm$^2$·s$^{-1}$, respectively) and 3 times greater than the glass bottom of the microfluidic chamber (5.50 × 10$^{-3}$ cm$^2$·s$^{-1}$).

Latent heat absorbed by melting of the convex features could therefore lower the temperature and hence supercool the concave interface. Considering the latent heat of fusion and the heat capacity of solid ice, and assuming an idealized adiabatic condition, a convex feature modeled as a hemicylinder with a 5-μm radius and a 20-μm height absorbs latent heat that would lower the temperature of an adjacent hemicylinder of equal volume in the adjacent solid region by 0.16 °C. Notably, local irradiation of a region of the unsteady ice interface at a constant system temperature with a 980-nm IR laser resulted in ice growth at neighboring (not irradiated) regions (Movie S4), which is consistent with the release of D$_2$O into the liquid near the ice interface upon melting and the supercooling effect. Moreover, the expected content of D$_2$O at x = 5 μm and t = 20 s, based on the diffusivity in the liquid (D = 10$^{-5}$ cm$^2$·s$^{-1}$), is consistent with the composition ofmixed ice expected at the constant system temperature (Fig. 1).

This heuristic framework demands a more quantitative understanding of the growth and dynamics of the unsteady morphologies. A typical starting point is a linear stability analysis of the ice front. It is well known that a flat interface may be linearly unstable under certain conditions, notably when subject to undercooling in the liquid, which gives rise to the well-known...
Mullins–Sekerka instability (34, 35). The observations here cannot be explained by a Mullins–Sekerka instability, which would predict a melting front to be stable. Moreover, nonplanar morphologies for H₂O ice contacting H₂O liquid or D₂O ice contacting D₂O liquid were never observed. Therefore, both temperature and concentration diffusion must be included in a linear stability analysis, but such an analysis appears to be analytically intractable here.

Consequently, numerical simulations were attempted to validate pieces of the heuristic framework and to explore the values of parameters that might give rise to unsteady morphologies. Phase-field simulations (36) that included thermal diffusion, concentration diffusion, and surface energy effects (Supporting Information) were performed, allowing for different diffusion constants in the solid and liquid phases and a concentration-dependent melting temperature (with respect to the amount of H in D₂O ice). Numerical limitations prevented simulations using the measured diffusivities or melting temperatures; therefore, simulations were aimed toward capturing the dynamics qualitatively. The initial configuration for the simulations included pure D₂O solid at one end of the domain separated by a sharp, possibly curved interface from a domain of pure liquid H₂O. The temperature at both ends of the domain was fixed at the same constant value (see Table S1 for the parameter values used in the phasefield simulations).

Simulations of a flat interface upon imposing a constant temperature between the Tₘ values for D₂O and H₂O usually exhibited either melting or freezing, but with a transition region at intermediate temperatures where the interface froze initially and then melted (Fig. S9). This change in direction was due to a high initial flux of D₂O into the liquid phase, creating a supercooled condition that causes the interface to freeze, followed by a slower flux of H₂O into the solid phase, lowering the melting temperature and causing melting. The timescales and temperature profile in the simulations differed from those in the experiment, which also exhibited freezing followed by melting. Nevertheless, the simulations support the premise that the direction of interface motion reflects the difference in the timescales of the fluxes of D₂O and H₂O between liquid and solid and the subsequent coupling to the melting temperature.

The evolution of an interface that began with a nonflat (sinusoidal) shape also was explored. Simulations clearly reveal that the temperature of a convex feature is higher than the temperature of the surroundings (i.e., the constant system temperature), which provokes its disappearance through melting. Conversely, the adjacent concave feature is cooler, which will provoke freezing in this region and a lower D₂O concentration above it due to preferential freezing of D₂O at the lower temperature (Fig. S10B). This preliminary modeling did not find evidence of a linear instability, however, and it could not replicate the proposed feedback between the convex and concave features. Instead, all interfaces eventually decayed to a flat morphology, and the locations of the convex and concave features never moved (Figs. S10C and S11B, for example.)

These preliminary numerical investigations are limited by numerous factors—most notably grid resolution, numerical stiffness that makes use of the experimental parameter values impractical, and a 10-dimensional parameter space that has not yet been examined exhaustively. The discrepancy between the numerical results and experimental observations also may reflect other, as yet unidentified physics. Perhaps defects that form during the continuous oscillatory-like cycling of melting and freezing at the interface play a role; or perhaps the morphologies are oscillating between nonplanar, quasi-steady ice fronts, which are known to exist in simpler systems (34). Although the modeling reported here was numerical, it would be useful to explore whether there is a parameter regime in which the planar interface is linearly unstable, and it still seems possible that improved theory could predict unsteady dynamics like those seen in the experiments (37).

Collectively, the observations described herein reveal that ice crystallization can still surprise, generating behavior that cannot be explained readily by nonlinear models. Liquid exchange around a single crystal of ice in a microfluidic device, combined with highly precise temperature control, created conditions in which the competing influences of heat transfer, surface curvature, and H/D exchange afforded unusual and persistent features
that melted and froze cyclically on the ice interface as it retreated due to melting. Preliminary numerical simulations captured the freezing and melting of a flat interface and the relationship between thermal and concentration fluxes at the interface, as well as a dependence of the fluxes on surface curvature. Further modeling is required, however, to capture the sensitive coupling and feedback between temperature and concentration fluxes, as well as other physical factors, which produce the oscillatory behavior. Although oscillating growth fronts have been reported during condensation of water on thin metal films that imposed a temperature gradient (38), to our knowledge, the unsteady morphologies observed here have not been observed previously on ice interfaces, and they appear to be unique to D2O solid–H2O liquid interfaces. The behavior is somewhat reminiscent of oscillations observed during vapor–liquid–solid growth of sapphire nanowires, however (39). Moreover, the microfluidic device configuration enabled measurement of self-diffusion of water in single crystals of ice, using Raman microscopy. The methodology described here promises utility for investigations of other crystalline materials, and we anticipate it can lead to further discoveries in ice crystallization, including the effects of ice crystallization inhibitors.

Materials and Methods

Microfluidic Solution Exchange Experiments. A temperature-controlled cold stage that was previously described in ref. 24 was placed on an inverted microscope (DMIRE2; Leica Microsystems Inc.). The temperature of the cold stage could be adjusted with a precision of ±0.001 °C and stability of ±0.002 °C (Fig. 51). A SCMOS (2yla 5.5; Andor) camera was used to acquire images. A sapphire disc (2.5 cm diameter) was placed between the cold stage and the microfluidic device to minimize temperature gradients. Immersion oil was introduced to the surface of the sapphire disc, and the microfluidic chip was then placed on top of the sapphire disc. The microfluidic channels were filled with 99.96% D2O (Cambridge Isotopic Laboratories) and the temperature decreased to ca. −20 °C to freeze the D2O in the channel. The temperature was then increased to melt the ice blocking the inlet and outlet and to form a D2O single ice crystal, with a distinct boundary. The D2O channels were then heated with doubly distilled H2O to crystallize a D2O–H2O–HDO solid–liquid interface. A 980-nm IR laser (Wuhan Laserlands Laser Equipment Co.) was used for local ice melting.

Raman Shift Measurements. The H/D composition of ice crystals and H2O/HDO diffusion into D2O ice were measured with a Raman microscope (DXR Raman microscope; Thermo Fisher Scientific), using a 532-nm excitation laser operating at 10 mW, with a 40× objective and slit width of 50 μm. Due to the upright configuration of the microscope, the cold stage was mounted upside down so that the channel was accessible to the Raman excitation beam. The exchange of D2O with H2O was performed in a manner similar to that described above. After the D2O–H2O solid–liquid interface was created, the temperature was decreased to −0.2 °C to −0.5 °C to freeze the liquid H2O in the channel. Raman measurements were collected on a region of the D2O ice crystal located 0.5 μm from the original D2O–H2O solid–liquid interface. Data were collected at regular intervals using an exposure time of 15 s, and the final intensity for each interval was calculated from the sum of 15 measurements. The Raman spectra of the time-lapse measurements were background subtracted and baseline corrected before determination of the total intensity. The intensities used to evaluate the diffusion coefficient were calculated from the integral of the intensity between 2200 cm\(^{-1}\) and 2500 cm\(^{-1}\), the range that captures the bands attributable to \(\nu_2\) and \(\nu_3\) for both D2O and HDO (Fig. S6). The intensity data were corrected using a calibration curve for various compositions of D2O–H2O mixtures (Fig. S7), although this did not substantially affect the fit of the data or the calculated diffusion constant (Eq. 1).

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