How ice grows: role of surface liquid films and water droplets

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Close to the triple point, the surface of ice is covered by a thin liquid layer which crucially impacts growth and melting rates. Experimental probes cannot observe the growth processes below this layer, and classical models of growth by vapor deposition do not account for the formation of these wetting films. Here, we develop a mesoscopic model of liquid-film mediated ice growth, and identify the various resulting growth regimes. At low saturation, freezing proceeds by terrace spreading, but the motion of the buried solid is conveyed through the liquid to the outer liquid-vapor interface. At higher saturations water droplets condense, a large crater forms below, and freezing proceeds undetectable beneath the droplet. Our approach is a generalized framework that naturally models freezing close to three phase coexistence and provides a first principle theory of ice growth and melting that is much need in the geosciences.

Keywords: Ice, Surface melting, Crystal growth, Thin-film dynamics, Computer simulations.

I. INTRODUCTION

The growth and melting of ice plays a crucial role in numerous processes, from the precipitation of snowflakes [1], to glacier dynamics [2], scavenging of atmospheric gases [3] or climate change [4]. Yet, despite ice ubiquity both in large masses on the poles and as tiny crystals in the atmosphere, we still do not fully understand how ice actually grows (or melts) [5-8].

Conflicting experimental measurements of ice growth rates [9-13] have been analyzed under a framework of classical crystal growth based on direct deposition from the vapor phase, followed by the subsequent two dimensional migration of adatoms onto surface kinks [14]. However, the last two decades have witnessed great progress in the experimental characterization of the ice/vapor interface at equilibrium [7]. Results from different experimental techniques [15-19], as well as computer simulations confirm that the surface disorder of ice grows steadily as the triple point is approached, and what is sometimes referred to as a ‘quasi-liquid layer’ of premelted ice is formed on its surface [20-24]. Unfortunately, classical growth models based on the terrace-ledge scenario do not account for the impact of premelting films at all and attempts to incorporate this effect have met only limited success [25-27].

The difficulty to incorporate the role of premelting films on crystal growth theories is also encountered in many systems of interest in materials science. Whether in the growth of proteins from solution, or the deposition of calcium carbonate on tissues, there is a growing body of evidence reflecting the need to account for alternative growth pathways not addressed in classical crystal growth theories [28-30]. Quite generally, when growth occurs close to a triple point, the role of a third intervening phase can become very significant, as it will absorb between both bulk phases forming a liquid film, and even condense into liquid droplets on the growing substrate [31-34]. In this situation, the role of the precursor phase is difficult to assess. On the one hand, it can accelerate crystal growth by lowering step free energies, but also, simultaneously, it competes with the crystal for the scarcely saturated mother vapor phase. Accordingly, the understanding of the crystal growth mechanism requires to characterize the adsorbed film, the film thickness and the likelihood of droplet formation.

The problem is akin to one encountered in the theory of wetting, where one studies how a metastable liquid phase (say, water), adsorbs at the interface between a solid substrate (ice) in contact with a vapor (water vapor) as the liquid/vapor coexistence line is traversed [35]. For an inserted substrate, wetting is very well understood in terms of the underlying interface potential $g(h)$ that measures the free energy of the adsorbed film as a function of film thickness $h$ [36]. But what is the significance of $g(h)$, and how can one define a film thickness in systems out of equilibrium, where the substrate is feeding from the adsorbed film at the expense of the mother phase? Here, we combine state of the art computer simulations, equilibrium wetting theory and thin-film modeling to describe the kinetics of the ice surface in the vicinity of the triple point within a general framework for wetting on reactive substrates. Our results show that as the vapor saturation increases, ice first grows by terrace spreading below a premelting film with a well defined stationary thickness. At higher saturations, however, the premelting layer thickness diverges, and growth actually proceeds from below a bulk water phase. In between these two regimes, at intermediate saturations, droplets condense on the ice surface and growth proceeds mainly under the droplets. The different regimes are separated by well defined kinetic phase lines, whose location can be mapped to an underlying equilibrium interface potential.
familiar quantity in the study of wetting \cite{35,36}.

Here we show that a batch of simulations performed along the sublimation line can be exploited to calculate an approximate interface potential for the premelting film. To see this, we write the effective surface free energy per unit surface area at solid/vapor coexistence as \( \omega(h) = g(h) - \Delta p_{lv}(T)h \), where \( \Delta p_{lv}(T) \) is the pressure difference between the liquid and vapor bulk phases at the solid/vapor coexistence chemical potential. This can be readily calculated by thermodynamic integration from available data (see Methods and \cite{38}), while the surface free energy may be obtained from the probability \( P(h) \) to observe a given global film thickness during the course of the simulation with lateral area \( A \), as \( A\omega(h) = -k_B T \ln P(h) \) \cite{39,41}. Using histogram reweighting techniques, the piecewise functions \( \omega(h) \) at different temperatures can be combined to build the interface potential over the whole range of film thicknesses \( h \) that are observed (Fig. 2). To obtain the potential for even larger values of \( h \), additional theory needs to be invoked.

Close to the triple point, the short range (mean-field) form of the interface potential exhibits oscillations due to molecular packing effects, taking the form \cite{12,13}:

\[
g_{sr}(h) = C_2 \exp(-\kappa_2 h) - C_1 \exp(-\kappa_1 h) \cos(q_0 h^2 + \alpha),
\]

where \( C_i \) are positive constants, \( \kappa_1 \) and \( \kappa_2 \) are inverse decay lengths (whichever is shorter is the inverse bulk correlation length), and \( q_0 \approx 2\pi/d \), where \( d \) is the molecular diameter. Additionally, there are algebraically decaying contributions to the interface potential which stem from the long range van der Waals interactions, originating from fluctuations of the electromagnetic field. Elbaum and Schick \cite{40} parametrized the dielectric response of ice and water to numerically calculate these contributions with Dzyaloshinskii-Lifshitz-Pitaevsky theory. Following Ref. \cite{47}, we show that the resulting crossover of retarded to non-retarded interactions is given accurately as

\[
g_{caw}(h) = -B h^{-3} \left[ 1 - f \exp(-ah) - (1 - f) \exp(-bh) \right],
\]

where \( f \) is a parameter that accounts for the relative weight of infrared and ultraviolet contributions to the van der Waals forces, \( a \) is a wavenumber in the ultraviolet region, while \( b \) falls in the extreme-ultraviolet and accounts for the suppression of high frequency contributions (see the Supplementary Information (SI) for further details).

Combining these, we obtain \( g(h) = g_{sr}(h) + g_{caw}(h) \) and fit our computer simulation results to this form, with \( C_i, \kappa_i, q_0 \) and \( \alpha \) as fit parameters. In fact, the simulation results can be fitted very accurately to \( g_{sr}(h) \) alone \cite{38}, but extrapolation of the simulation results to larger \( h \) is required to describe the behavior at saturation. Therefore, in the parameter search we impose that \( g(h) \) exhibits minima at energies \( \sim 10^{-5} \text{J/m}^2 \), as observed in experiment \cite{35}. The constrained fit yields an interface

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Predicted wetting phase diagram for the ice/vapor surface with linear growth. On the left is the equilibrium phase diagram of water in the neighborhood of the triple point. The solid lines are the melting (black), vaporization (blue) and sublimation (red) lines. The dashed lines are metastable prolongations of the melting and vaporization lines. Dotted red and blue lines are kinetic transition lines which describe the transitions observed in experiments between the states illustrated on the right, namely (a) a homogeneous surface, (b) a droplet on top of a homogeneous surface and (c) a spreading film below a droplet \cite{33}. The green dotted line is the kinetic spinodal line where quasi-stationary states are no longer stable. The kinetic transition lines shown here have been calculated using the model in Eqs. (3) \cite{34}, assuming linear growth \((w = 0)\) and an interface potential 30 times larger than that obtained in this work, in order to spread the lines for ease of viewing.}
\end{figure}
FIG. 2. Interface potential for a water film adsorbed on ice as calculated from computer simulations. The small red circles are simulation results obtained from piecewise histogram reweighting. The larger black circles are results obtained by integration of the related disjoining pressure as determined recently [23]. The dark solid blue line is a fit to the simulation results, constrained to exhibit two minima. The inset shows details of the primary $\alpha$ and secondary $\beta$ minima, which are not visible on the scale of the main figure. For ordinary wetting, a transition from $\alpha$ to $\beta$ occurs at a pressure of $\Delta p = 46000$ Pa above liquid-vapor saturation (light blue).

potential in good agreement with the available simulation data — see Fig. 2. Consistent with expectations from renormalization theory, the shallow minima in the interface potential are more widely spaced than one would expect from mean field theory, located at $h_\alpha = 16.0$ Å and $h_\beta = 24.5$ Å. We refer to these two as the $\alpha$- and $\beta$-minima, respectively, and this interface potential provides a transition between a thin $\alpha$ and a thick $\beta$ film at sufficiently large supersaturation.

B. Kinetics of crystal growth and droplet condensation

1. Interface Hamiltonian

The interface potential is adequate for describing equilibrium properties of homogeneous films. However, in order to account for droplets like that depicted in Fig. 3 and other such inhomogeneities, we must extend our description. Building on previous work [21, 48–50], we begin by constructing a coarse-grained free energy (effective Hamiltonian) with all the required physics, consisting of a coupled sine-Gordon plus Capillary Wave (SG+CW) Hamiltonian with bulk fields,

$$\Omega = \int \left[ \frac{\gamma_{sl}}{2} \left( \nabla L_{sl} \right)^2 + \frac{\gamma_{lv}}{2} \left( \nabla L_{lv} \right)^2 - u \cos(q_z L_{sl}) \right. $$
$$ \left. + g(L_{lv} - L_{sl}) - \Delta p_{sl} L_{sl} - \Delta p_{lv} L_{lv} \right] dx. \tag{3}$$

The first two terms account for the free energy cost to increase the surface area of the solid/liquid and liquid/vapor surfaces in a longwave approximation, where $\gamma_{sl}$ and $\gamma_{lv}$ are the solid/liquid interfacial stiffness coefficient and the surface tension, respectively. The cosine term accounts for the energy cost $u$ to move the solid/liquid surface $L_{sl}$ away from the equilibrium lattice spacing, as dictated by the wave-vector $q_z = 2\pi/d_B$, where $d_B$ is the lattice spacing between ice bilayers at the basal face. This simple model is known to describe adequately nucleated, spiral and linear growth [21, 51]. The interface potential coupling the two surfaces seeks to enforce the equilibrium thickness of the premelting film $h = L_{sl} - L_{lv}$. The last two terms account for the bulk energy of the system as measured relative to the (reservoir) vapor phase with fixed chemical potential $\mu$, where $\Delta p_{sl} = p_s(\mu) - p_l(\mu)$ is the pressure difference between the bulk solid and liquid phases, where $\Delta p_{lv} = p_l(\mu) - p_v(\mu)$ is the pressure difference between the bulk liquid and vapor phases. These two terms account for the free energy change due to growth/melting of the solid phase at the expense of the premelting film, and exchange of matter between the latter and the vapor via condensation/evaporation.

FIG. 3. Illustration of a possible surface feature with annotations for our two-dimensional gradient dynamics model setup. Two evolving interfaces are shown: the solid-liquid surface (in red) at reference height $z = L_{sl}(x, t)$ and above the liquid-vapor interface at reference height $z = L_{lv}(x, t)$. The solid and vapour phases are modelled as extending infinitely below and above, respectively.

2. Gradient driven dynamics

The motion of the solid/vapor interface in the presence of a premelting film necessitates us to account explicitly for the different dynamical processes occurring at both the solid/liquid and liquid/vapor surfaces [25, 27]. On the one hand, $L_{sl}$ evolves as a result of freezing/melting at the solid/liquid surface and on the other hand, $L_{lv}$ evolves as a result of both the condensation/evaporation at the liquid/vapor surface and freezing/evaporation at the solid/liquid surface. Finally, we must also account for advective fluxes of the premelting film over the surface. In practice, since we are concerned only with small deviations away from equilibrium, we can assume the dynamics is mainly driven by free energy gradients with respect to the relevant order parameters [55]. Accordingly, we treat the freezing/melting and condensation/evaporation in terms of non-conserved gradient dynamics, and the advective fluid dynamics of the premelting film using a
thin-film (lubrication) approximation, whence
\[
\begin{align*}
\frac{\partial L_{sl}}{\partial t} &= -k_{sl} \frac{\delta \Omega}{\delta L_{sl}} \\
\frac{\partial L_{lv}}{\partial t} &= \nabla \left[ \frac{h^3}{2\eta} \nabla \frac{\delta \Omega}{\delta L_{lv}} \right] - k_{lv} \frac{\delta \Omega}{\delta L_{lv}} + k_{sl} \frac{\Delta \rho}{\rho_l} \frac{\delta \Omega}{\delta L_{sl}}
\end{align*}
\]  
(4)

where \(k_{sl}\) and \(k_{lv}\) are kinetic growth coefficients that determine the rate of crystallization and condensation at the solid/liquid and liquid/vapor surfaces, respectively, \(\eta\) is the viscosity in the liquid film and \(\Delta \rho = \rho_s - \rho_l\), where \(\rho_s\) and \(\rho_l\) are the densities of the solid and liquid, respectively. Models with some similar features were developed in [30] [51].

C. Kinetic phase diagram

The time evolution predicted by Eqs. 3–4 is extremely rich and varied and the full range can only be obtained numerically. However, if we assume that the surface is on average flat, then we obtain equations that enable us to predict the outcome of the numerical simulations and determine an accurate kinetic phase diagram. Coarse-graining the evolution over the time period required to form a single new plane of the crystal, we replace the time derivatives of \(L_{sl}\) and \(L_{lv}\) by their average values (denoted as \(\langle . \rangle\)), yielding
\[
\begin{align*}
\langle \partial_t L_{sl} \rangle &= \pm k_{sl} \sqrt{\phi_{sl}^2 - w^2} \\
\langle \partial_t L_{lv} \rangle &= k_{lv} \phi_{lv} - (\Delta \rho/\rho_l) \langle \partial_t L_{sl} \rangle
\end{align*}
\]  
(5)

where \(w = q_{l,lv}, \phi_{sl} = \Delta p_{sl} - \Pi, \phi_{lv} = \Delta p_{lv} + \Pi\) and \(\Pi(h) = -\partial_h g(h)\) is the disjoining pressure. The \(\pm\) sign corresponds to either freezing (\(\phi_{sl} > 0\)) or sublimation (\(\phi_{sl} < 0\)).

Despite the simplifications made, the dynamics predicted by Eq. 5 is still fairly complex. Firstly, it shows that deterministic growth cannot occur for \(\phi_{sl}^2 < w^2\). The locus \(\phi_{sl}^2 = w^2\) encloses a region where the crystal front only advances via nucleation and growth of new terraces. The initial stages of this occur against the free energy gradient, and can only be described by adding additional appropriate random noise contributions to Eq. 4 [52] [53]. For \(\phi_{sl}^2 > w^2\), corresponding to the onset of kinetic roughening, growth proceeds deterministically and there is no free energy barrier to surmount for the liquid to freeze onto the ice surface. For these thermodynamic conditions, it is possible to find a regime of quasi-stationarity where the solid and liquid phases grow at the same rate, i.e. where \(\langle \partial_t L_{lv} \rangle - \langle \partial_t L_{sl} \rangle = 0\), and so the average film thickness is constant. Significantly, this condition also yields
\[
\Pi(h) = -\Delta p_k(p_v, T),
\]  
(6)

where the kinetic overpressure \(\Delta p_k\) is a function of the thermodynamic conditions and depends parametrically on the kinetic coefficients and growth mechanism (see SI for further details). In the limit where the substrate is inert and fixed, i.e. with \(k_{sl} = 0\), then \(\Delta p_k = p_l - p_v\), and the above result is precisely the Derjaguin equation for the equilibrium thickness of an adsorbed liquid film on an inert substrate [33] [36]. This is very convenient, because we can then predict the outcome of the nonequilibrium dynamics by analogy with what we would expect for an equilibrium film with an effective Derjaguin overpressure \(\Delta p_k\). Likewise, one sees that an effective interface potential \(\omega_k(h) = g(h) - \Delta p_k h\) determines the dynamics of the system in the quasi-stationary regime, showing that the growth behavior in this regime is exactly as one would expect for an inert substrate with overpressure \(\Delta p_k\).

This observation allows us to determine the kinetic phase diagram, identifying the regions in \((p, T)\) space where the different outcomes of the interfacial wetting dynamics is to be expected. From the shape of the equilibrium interface potential, we find the kinetic phase diagram features a line of kinetic coexistence, where \(\Delta p_k = 0\), a line of transitions between the states at the \(\alpha\) and \(\beta\) minima of \(g(h)\), and a kinetic spinodal line. The details of the phase diagram depend on the precise form of \(g(h)\) and on the assumed growth mechanism, but for the simplest case of purely linear growth, with \(w = 0\), the lines are qualitatively arranged as in Fig. 4.
D. Results for the interface dynamics

Using gas kinetic theory, crystal growth theory, and literature data for water and ice\[59,61\], we estimate the model parameters $k_{sd}, k_{lv}, \nu, \gamma_{sd}, \gamma_{lv}, \Delta p_{sd}$ and $\Delta p_{lv}$. These data, combined with the interface potential $g(h)$ from computer simulations, allows us to draw the kinetic phase diagram in Fig. 4. The shaded area surrounding the sublimation line is the region where crystal growth is a slow activated process, only proceeding via step nucleation and growth, and is seldom observed in experiments. In the absence of any impurities to speed up the nucleation, in this regime the substrate is effectively unreactive for time scales smaller than the inverse nucleation rate, and behaves according to the equilibrium interface potential, Fig.5-a. Over the small range of temperatures where the liquid-vapor coexistence line lies inside this region, the substrate is effectively inert. In practice, the experimental systems reported in\[33\] contain dislocations, so the crystal freezes by spiral growth and the region of unreactive wetting shown in Fig. 4 for the SG+CW model is not observed.

In our simulations (Fig. 5(b-e) and Movie S1), an initial terrace mimicking a local defect on the solid/liquid surface $L_{sl}$, not observable by optical means, triggers the formation of a corresponding terrace on the liquid/vapor surface $L_{lv}$, with a step height equal to the solid lattice spacing. Crystal growth then proceeds by the spreading of the terrace, and the motion of this terrace on the solid phase is conveyed to the external liquid/vapor surface and can be observed directly by confocal microscopy (c.f. Fig S1 in Ref.\[33\]). Once the new full crystal lattice plane is formed, growth becomes stuck until a new critical nucleus is formed stochastically.

Crossing the line of nucleated growth towards higher saturation, such that $\phi_{sl} > w$, the thermodynamic driving force for crystal growth is large enough to beat the bulk crystal field, and growth then occurs without activation, as in a kinetically rough surface\[51,53\]. However, if $\phi_{sl}$ is only marginally larger than $w$, the process occurs in a stepwise fashion, occurring with large time intervals of no growth, followed by height increments equal to the lattice spacing $d_{l}$ in a short time. On further increasing $\phi_{sl}$, crystal growth then proceeds in a truly quasi-stationary manner while the premelting film thickness remains constant, consistent with Eq. (9).

Interestingly, traversing the metastable prolongation of the liquid-vapor coexistence line does not change the growth behavior in any way. Although $\Delta p_{lv}$ is now positive, $\Delta p_{k}$ is still negative, so the thickening of $h$ is still uphill in the effective free energy $\omega_{k}(h)$: i.e. the system behaves as if it is effectively undersaturated with respect to liquid-vapor coexistence and the vapor/liquid interface cannot advance faster than the crystal/liquid interface (c.f. Fig. 5-f). A liquid droplet quenched to this region of the kinetic phase diagram is never stable – see Fig. 5(g-j) and Movie S2. Instead, at the contact line of the droplet, terrace formation on the ice is triggered by the action of the disjoining pressure. The crystal then grows and the droplet flattens out, in order to reach a quasi-equilibrium film thickness consistent with Eq. (9).

As a transient during the process, the premelting film thickness $h$ can be stable in the $\beta$ film state, reminiscent of the ‘sunny side up’ states observed in experiment\[33\]. Subsequently, the droplet disappears, leaving an Aztec pyramid shaped solid surface feature that is covered by a premelting film with thickness of the $\alpha$ state. Finally, the inhomogeneity completely disappears, and growth proceeds in a strictly quasi-stationary manner with a flat surface.

The situation changes significantly when saturation is raised above the kinetic liquid-vapor coexistence line, where $\Delta p_{k} > 0$. For thick enough films, $h$ can now move downhill in the effective surface free energy (Fig. 5-k). In this regime, small fluctuations or crystal defects that locally increase the film thickness beyond the spinodal thickness of $g(h)$ trigger the formation of large liquid droplets on top of the premelting film, as observed in experiments—see Fig. 5(l-o) and Movie S3; c.f. Fig. 1-D from\[33\]. Essentially, when $\Delta p_{k} > 0$ the liquid pressure is large enough to sustain the tension of the droplet surface. However, the droplet cannot be fully stable here, since the system is open. The fastest way to decrease the overall free energy while the solid phase grows is to form a large crater below the droplet and then for the two interfaces to separate. Likewise, a droplet quenched to this region behaves initially as described above for droplets below the kinetic liquid-vapor coexistence. The difference is that once a few terraces have been formed at the rim, the crystal grows thereon inside the droplet towards its center by creating a premelting film of $\alpha$ thickness, without the droplet curvature flattening out (Fig. S3 and Movie S5). As growth proceeds, the interface profiles take a transient shape like that of droplets on soft substrates\[52\] with the solid surface growing higher in the contact line region. A crater develops, but is then filled by the growing solid, before the droplet disappears.

Increasing further the pressure above the kinetic $\alpha \rightarrow \beta$ transition line, the free energy of the $\beta$ film becomes less than that of the $\alpha$ film (Fig. 5-p). Thus, it is favorable for the droplet rim to grow a $\beta$ film at the cost of the $\alpha$ film, leading to the ‘sunny side up’ state found experimentally at sufficiently high saturation—see Fig. 5(q-t) and Movie S4; c.f. Fig 1-A from\[33\]. However, eventually the saturation is large enough that the $\beta$ film metastable minimum is washed away by the linear term $\Delta p_{k} h$ in $\omega_{k}(h)$. In this case, the system becomes highly unstable (i.e. linearly unstable to perturbations), and small satellite droplets can form, either in the neighborhood of a larger droplet, or directly from a single local perturbation on the solid surface (Fig. S4 and Movie S6), a situation that very much resembles experimental observations—see Movies S1 and S2 from Ref.\[33\]. Eventually, in the long time limit the inhomogeneities disappear completely, and the premelting film thickness diverges. Crystal growth then proceeds below a macroscopically thick...
FIG. 5. Surface dynamics at different state points in the kinetic phase diagram, with various initial conditions. Each row corresponds to the points marked in Fig. 4. In the first column (f,k,p) show the corresponding effective free energies $\omega_k(h)$ that determine quasi-stationary growth, while (a) instead shows the binding and sine-Gordon potentials, since no quasi-stationary growth occurs at this state point. The remaining columns show the solid/liquid and liquid/vapor surfaces at significant milestones in the time evolution (solid red and blue lines, respectively). The dashed red lines indicate the surface location for fully formed ice bilayers, and dashed blue lines show the corresponding heights of a premelting film at the $\alpha$ or $\beta$ minima, as a guide to the eye. (a-e) Typical evolution in the the nucleated regime at $(p,T) = (455, 269.5)$ (° in Fig. 4). A small terrace nucleated on the solid/liquid surface triggers the formation of a similar terrace on the liquid/vapor surface and then spreads horizontally (Movie S1). (f-j) A droplet quenched to a pressure just below the kinetic liquid-vapor coexistence line at $(p,T) = (514, 269.5)$ (× in Fig. 4). Small terraces are formed at the rim of the droplet and then spread (Movie S2). (k-o) A surface defect for $(p,T) = (517.5, 269.5)$ (× in Fig. 4) above kinetic liquid-vapor coexistence, triggers the formation of a liquid droplet, which evolves to form a crater, then ice grows into the droplet, before vanishing (Movie S3). (p-t) A droplet at $(p,T) = (518.5, 269.5)$ (+ in Fig. 4) above the kinetic $\alpha \rightarrow \beta$ transition, develops a $\beta$ film at the edges and an expanding crater below (Movie S4).

wetting film that feeds on the surrounding bulk vapor.

III. DISCUSSION

We have formulated a theory that rationalizes the behavior of out-of-equilibrium premelting films and wetting on reactive substrates. For quasi-stationary states with net crystal growth but constant premelting film thickness, there exists an effective free energy that allows us to predict the nonequilibrium dynamics in complete analogy with equilibrium wetting theory of inert substrates. Using computer simulations and theory, we estimate the interface potential of premelting water films on ice. Inputting this into our model, we are able to explain and calculate the experimental observation of two kinetic transition lines, at which water droplets and then a thick wetting film emerge. Our results demonstrate that the complex dynamics of a buried solid surface can be conveyed to the experimentally accessible outer surface of the quasi-liquid film. Accordingly, the motion of the experimentally accessible outer surface may be used to interpret the hidden dynamics of the inner surface. Furthermore, our model uncovers additional behaviors that could in future be explored experimentally with different techniques. For instance, the transition between the two potential minima controls the long-time behaviour of the solid under a droplet: either ice grows into the droplet, or forms an expanding crater below. We also confirm that observation of terrace translation, spiral growth and nucleation observed in experiment is fully consistent with the existence of large surface disorder consisting of a nanometer thick premelting film observed in simulations [20, 21, 23, 24].
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Appendix A: Methods

1. Computer simulations

Simulations of an equilibrated ice slab in the NVT ensemble are performed in the temperature range 210–270 K for the TIP4P/Ice model using GROMACS. For each temperature, an independent histogram of the laterally averaged film thickness h is obtained and used to calculate g(h) as described in the text and SI. The form for g(h) in Eqs. (1)–(2) is then fitted to these results. Parameter values and further details are given in the SI.

2. Gradient Dynamics

Numerical computations of the dynamics of the thin-film equations are performed using the method of lines, similar to that used in Ref. [53], but with a periodic pseudospectral method for the spatial derivatives. Further details are given in the SI.

3. Model Parameters

Phase coexistence data required to compute ∆pvl, ∆pvc, structural properties of ice, and surface tension coefficients are obtained from the literature as described in the SI. The kinetic growth coefficients kvl and kvc are estimated from Frenkel and gas kinetic theory, and the sine Gordon parameter is chosen to match step free energies from the literature as described in the SI.
AUTHOR INFORMATION

Contributions

D.N.S. performed gradient dynamics simulations. P.L. E.G.N. and L.G.M calculated interface potential. D.N.S., A.J.A. and L.G.M constructed the continuum model. L.G.M. designed research. D.N.S., A.J.A. and L.G.M wrote paper.

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II. CALCULATION OF THE INTERFACE POTENTIAL

A. Definition of the interface potential

The excess grand potential $\Omega$ (Landau free energy) per unit area for a liquid film of thickness $h$ on a planar solid surface in equilibrium with a bulk vapor phase with chemical potential $\mu$ and temperature $T$ is

$$\frac{\Omega + p_v V}{A} = \gamma_{sl} + \gamma_{lv} + g(h; T) - \Delta p_{lv}(T, \mu)h$$

$$= \gamma_{sl} + \gamma_{lv} + \omega(h; T, \mu),$$

where $V$ is the volume of the system, $A$ is the area of the surface, $\gamma_{sl}$ is the solid/liquid interfacial tension, $\gamma_{lv}$ is the liquid/vapor interfacial tension, $g(h)$ is the interface potential for the film at liquid-vapor coexistence, often referred to as the binding potential, and $\Delta p_{lv}(T, \mu) = p_l(T, \mu) - p_v(T, \mu)$ is the pressure difference of the bulk liquid and vapor phases at the chemical potential of the bulk vapor. The potential $\omega(h; T, \mu)$ is the effective interface potential that determines the interfacial phase behavior.

In relevant previous work, the interface potential of liquid films adsorbed on an inert substrate was calculated by performing grand-canonical simulations at liquid-vapor coexistence \[62 \square 66\]. In that case, $\omega(h; T, \mu) = g(h; T)$, and the free energy may be evaluated from

$$A \omega(h; T, \mu) = -k_B T \ln P(h),$$

where $P(h)$ is the probability distribution of $h$, collected during the grand canonical simulation with enhanced sampling techniques and $k_B$ is Boltzmann’s constant. Effectively, the procedure is equivalent to performing a series of canonical simulations at different film thicknesses \[67\].

For the case of a one component system with liquid adsorbed at the solid/vapor interface, the above method cannot be applied, because the three phase system at fixed temperature only exists at equilibrium at the solid/vapor coexistence chemical potential. Instead, we perform a set of fixed-$NVT$ simulations at different temperatures ($N$ is the number of molecules), similar to previous calculations in studies of the interface potential for grain boundary premelting \[30 \square 68\].

For a liquid film adsorbed at the solid/vapor interface along the sublimation line $(T, \mu_{sv}(T))$, Eq. \[1\] gives

$$\omega(h; T, \mu_{sv}) = g(h; T) - \Delta p_{lv}(T)_{|sv}h,$$

where $g(h; T)$ is the interface free energy for the film along the liquid-vapor coexistence line, and $\Delta p_{lv}(T)_{|sv} = p_l(T, \mu_{sv}) - p_v(T, \mu_{sv})$ is the pressure difference between liquid and vapor bulk phases at the solid-vapor coexistence chemical potential.

Performing simulations of the solid phase at constant temperature, initiated in a vacuum, the system equilibrates into a state of solid/vapor coexistence, with a premelting liquid film at the interface with thickness dictated by imposed thermodynamic conditions. At this temperature, the film thickness fluctuates according to a probability distribution $P(h; T, \mu_{sv})$, which can easily be collected during the course of the simulation, as shown in Fig. \[5\].

The interface potential in the range of observed film thicknesses may be calculated as

$$g(h; T) = -\frac{k_B T}{A} \ln P(h; T, \mu_{sv}) + \Delta p_{lv}(T)_{|sv}h + C_T,$$

where $C_T$ is an arbitrary constant. By performing a sequence of simulations at different temperatures, one obtains a set of piecewise potentials $g(h; T_i)$, which overlap for small ranges of $h$, provided the simulations are performed at sufficiently close temperature intervals. The right hand panel of Fig. \[5\] shows the set of piecewise functions obtained at a series of different temperatures, with values as indicated in the key. Since the temperature dependence of $g(h; T)$ is small, the piecewise function can be combined into a single continuous interface potential by choosing suitable constants $C_T$. The resulting function is continuous and shows no apparent singularities, consistent with the assumption of weak temperature dependence of the various piecewise terms $g(h; T_i)$.
B. Calculation of the pressure difference $\Delta p_{lv}(T)|_{sv}$

In order to evaluate the interface potential, we must first determine $\Delta p_{lv}(T)|_{sv}$. We start from the Gibbs-Duhem thermodynamic relation

$$Nd\mu = -SdT + Vdp,$$

(5)

where $S$ is the entropy. From this we obtain the following equivalent pair of relations

$$d\mu = -sdT + \frac{1}{\rho}dp,$$

$$dp = \rho sdT + pd\mu,$$

where $s = S/N$ is the entropy per particle and $\rho = N/V$ is the number density. At phase coexistence, $\mu$, $p$ and $T$ are equal in the two coexisting phases. Hence, along the the solid (subscript $s$) and vapor (v) coexistence line we have $d\mu_s = d\mu_v$, $dp_s = dp_v$, and $dT_s =dT_v$. Therefore, from the first of these together with Eq. (6) we obtain the familiar Clausius-Clapeyron equation for the variation of the vapor pressure along the sublimation line

$$\frac{dp}{dT}|_{sv} = \frac{\rho_v s_v - s_s}{\rho_s - \rho_v}.$$  

(8)

Similarly, from Eq. (7) we obtain

$$\frac{d\mu}{dT}|_{sv} = \frac{\rho_v s_v - \rho_s s_s}{\rho_s - \rho_v}.$$  

(9)

Thus, from Eq. (8) the variation of vapor pressure along the sublimation line is

$$dp_{v}|_{sv} = \rho_s \rho_v \frac{s_s - s_v}{\rho_v - \rho_s}dT,$$

(10)

whereas the pressure variations of the liquid phase is given more generally by Eq. (7) as

$$dp_{l} = \rho_l s_l dT + \rho_l d\mu.$$  

(11)

However, we must evaluate the liquid pressure along the sublimation line, so $\mu$ is not an independent variable. Rather, it is given by the Clausius-Clapeyron type Eq. (9), and thus

$$dp_{l}|_{sv} = \rho_l s_l dT + \rho_l \frac{\rho_v s_v - \rho_s s_s}{\rho_s - \rho_v}dT.$$  

(12)
Therefore, the variation of \( d(p_l - p_v)\)|\(_{sv}\) along the sublimation line is obtained from Eqs. (10) and (12) after some rearrangements, as

\[
d(p_l - p_v)|_{sv} = \left. \frac{\rho_s \rho_l \partial s_l - \rho_v \partial s_l + \rho_l \partial s_v - \rho_v \partial s_l s_s + \rho_s \rho_v s_s - \rho_s \rho_v s_v}{\rho_s - \rho_v} \right|_{sv} dT. \tag{13}
\]

In principle, this equation could be integrated starting from the triple point, where \( p_l - p_v = 0 \), down to lower temperatures, by using experimental or simulation data for entropies and densities along the sublimation line. To achieve this, we first notice that the zeroth order integrated form of this equation may be found in Elbaum and Schick [46].

Here, we take a different more convenient approach by expressing this equation in terms of liquid-vapor and solid-vapor coexistence pressures, which are known from experiments with great accuracy. To achieve this, we first notice \( \rho_v \ll \rho_l \) and \( \rho_v \ll \rho_s \). Therefore, the exact result in Eq. (13) can be greatly simplified with only a very small loss in accuracy, to

\[
d(p_l - p_v)|_{sv} = -\rho_l (s_s - s_l) dT|_{sv}. \tag{14}
\]

Now, we write

\[
(s_s - s_l)|_{sv} = [(s_s - s_v) - (s_l - s_v)]|_{sv}. \tag{15}
\]

Furthermore, assuming the vapor behaves as an ideal gas so that (i) \( s = -k_B (\ln(\Lambda^3 \rho) - 1) \), where \( \Lambda \) is the thermal de Broglie wavelength, and (ii) \( \rho = p/k_B T \), we can write the vapor entropy at the sublimation line in terms of the entropy of the incompressible liquid phase at the condensation line as

\[
s_v|_{sv} = s_v|_{lv} + k_B \ln \frac{p_{lv}}{p_{sv}}. \tag{16}
\]

Substituting this into Eq. (15) and noting that the entropy of the incompressible liquid phase hardly changes at all, which means that we may approximate \( s|_{sv} = s|_{lv} \), so that from Eq. (15) and Eq. (16) we can write

\[
(s_s - s_l)|_{sv} = (s_s - s_v)|_{sv} - (s_l - s_v)|_{lv} + k_B \ln \frac{p_{lv}}{p_{sv}}. \tag{17}
\]

Substituting this into Eq. (14) then yields:

\[
d(p_l - p_v)|_{sv} = -\rho_l \left[ (s_s - s_v)|_{sv} - (s_l - s_v)|_{lv} + k_B \ln \frac{p_{lv}}{p_{sv}} \right] dT, \tag{18}
\]

where now both \( (s_s - s_v)|_{sv} \) and \( (s_l - s_v)|_{lv} \) are actual entropies of phase change. Invoking the Clausius-Clapeyron Eq. (8) for these two quantities, assuming \( \rho_v \ll \rho_s \), \( \rho_v \ll \rho_l \) and making the ideal gas approximation \( \rho = k_B T \rho \), we obtain

\[
-(s_s - s_v)|_{sv} = \frac{k_B T}{p_{sv}} \left. \frac{dp}{dT} \right|_{sv}, \tag{19}
\]

and a similar expression for \( (s_l - s_v)|_{lv} \). Substituting these into Eq. (18), we obtain the sought expression for \( d(p_l - p_v)|_{sv} \) explicitly in terms of vapor pressures along sublimation and condensation lines as

\[
d(p_l - p_v)|_{sv} = \rho_l d \left( k_B T \ln \frac{p_{sv}}{p_{lv}} \right). \tag{20}
\]

Integrating this equation from the triple point to a desired arbitrary temperature, we obtain

\[
\Delta p_{lv}(T)|_{sv} = \rho_l k_B T \ln \frac{p_{sv}}{p_{lv}}. \tag{21}
\]

This is the same result obtained in [38] by alternative means. We use explicit expressions obtained for the vapor pressures of the TIP4P/Ice model to calculate the required pressure difference for use in Eq. (4).
C. Surface van der Waals forces

Elbaum and Schick calculated the van der Waals force contributions to the interface potential using Lifshitz theory \[46\]. The results are obtained only in numerical form from quadrature, which is not convenient for numerical purposes. Here we derive an accurate analytical approximation, along the lines of Ref. \[47\]. The results are obtained only in numerical form from quadrature, which is not convenient for numerical purposes.

Quite generally, the van der Waals forces between two media, 1 and 2, across a media \(m\) enclosed between infinite slabs of media 1 and 2, give rise to an interface potential of the form

\[
g_{vdw}(h) = -\frac{A(h)}{12\pi h^2},
\]

(22)

where \(A(h)\) is the Hamaker function. In a well known approximation to Lifshitz theory, this is given as

\[
A(h) = \frac{3}{2} k_B T \sum_{n=0}^{\infty} R(\omega_n)[1 + r_n]e^{-r_n},
\]

(23)

where the prime indicates that the first term is weighted by a factor of \(1/2\), \(r_n = 2\epsilon_m^{1/2} \omega_n h/c, \omega_n = \omega_T n, \omega_T = 2\pi k_B T/h\), and \(\epsilon_m\) is the dielectric constant of the layer of thickness \(h\). The function \(R(\omega_n)\) is a complicated expression that depends on the frequency dependent dielectric constants of the material and the film thickness \(h\) \[47\]. For practical purposes, it can be approximated via the simpler expression

\[
R(\omega_n) = \left( \frac{\epsilon_1 - \epsilon_m}{\epsilon_1 + \epsilon_m} \right) \left( \frac{\epsilon_2 - \epsilon_m}{\epsilon_2 + \epsilon_m} \right),
\]

(24)

where \(\epsilon_1\) and \(\epsilon_2\) are the frequency dependent dielectric constants of the media enclosing the layer of thickness \(h\). At this stage it is convenient to single out the \(n = 0\) term in Eq. (23), and to further approximate the remaining sum into an integral. Then

\[
g_{vdw}(h) = -\frac{A_{\omega=0}}{12\pi h^2} - \frac{A_{\omega>0}(h)}{12\pi h^2},
\]

(25)

where

\[
A_{\omega=0} = \frac{3}{4} \left( \frac{\epsilon_1 - \epsilon_m}{\epsilon_1 + \epsilon_m} \right) \left( \frac{\epsilon_2 - \epsilon_m}{\epsilon_2 + \epsilon_m} \right) k_B T,
\]

(26)

and

\[
A_{\omega>0}(h) = \frac{3\hbar c}{8\pi \epsilon_m^{1/2}} \int_{\nu_T}^{\infty} R(\nu)[1 + \nu h]e^{-\nu h} d\nu,
\]

(27)

where the sum over angular frequencies has been transformed into an integral over wavenumbers \(\nu = 2\epsilon_m^{1/2} \omega/c\) and \(\nu_T = 2\epsilon_m^{1/2} \omega_T/c\).

Elbaum and Schick parametrized the dielectric properties of water and ice, and argued that the term \((\epsilon_i - \epsilon_m)\) of the function \(R(\nu)\) changes sign at ultra-violet frequencies, such that \(R(\nu) < 0\) in the infra-red, but \(R > 0\) at the extreme ultra-violet and beyond. In view of this, we split the integral of Eq. (27) and write:

\[
A_{\omega>0}(h) = \frac{3\hbar c}{8\pi \epsilon_m^{1/2}} \int_{\nu_T}^{\nu_{UV}} R(\nu)[1 + \nu h]e^{-\nu h} d\nu + \frac{3\hbar c}{8\pi \epsilon_m^{1/2}} \int_{\nu_{UV}}^{\nu_{\infty}} R(\nu)[1 + \nu h]e^{-\nu h} d\nu,
\]

(28)

where \(\nu_{UV}\) is the frequency at which \(R(\nu)\) is maximum. The first integral can now be evaluated using the first mean value theorem, and the second using the second mean value theorem, yielding

\[
A_{\omega>0}(h) = \frac{3\hbar c}{8\pi \epsilon_m^{1/2}} R(\nu_{IR})[(2 + \nu_T h)e^{-\nu_T h} - (2 + \nu_{UV} h)e^{-\nu_{UV} h}] + \frac{3\hbar c}{8\pi \epsilon_m^{1/2}} R(\nu_{UV})[(2 + \nu_{UV} h)e^{-\nu_{UV} h} - (2 + \nu_{\infty} h)e^{-\nu_{\infty} h}].
\]

(29)

This is an exact quadrature for suitably chosen frequencies \(\nu_{IR}\) and \(\nu_{\infty}\), satisfying \(\nu_T < \nu_{IR} < \nu_{UV}\), and \(\nu_{UV} < \nu_{\infty} < \infty\). Collecting terms, the above expression simplifies to

\[
A_{\omega>0}(h) = \frac{3\hbar c}{8\pi \epsilon_m^{1/2}} R(\nu_{IR})[\nu_T h - f(2 + \nu_{UV} h)e^{-\nu_{UV} h} - f(2 + \nu_{\infty} h)e^{-\nu_{\infty} h}],
\]

(30)
where $f = R(\nu_{UV}) / R(\nu_{IR})$. Eq. (30) provides a simple analytic expression which properly captures the crossover from retarded to non-retarded interactions, as well as the suppression of retarded interactions at large distances and the temperature dependence of the van der Waals forces.

Assuming that the relevant wave-numbers are well separated, such that $\nu_T \ll \nu_{UV} \ll \nu_\infty$, we find the following four distinct regimes as $h$ increases:

- The subnanometer range, $\nu_\infty h \ll 1$, describes either the $h \to 0$ or $T \to 0$ behavior of $A_{\nu>0}$. Expanding all the exponentials in Eq. (30), one finds that the terms of order $h^0$ inside the square brackets cancel exactly. Retaining then the leading order terms in $h$, one finds

$$A_{\nu>0}(h) = \frac{3\hbar \nu_\infty}{4\pi} R(\nu_{UV}).$$  \hspace{1cm} (31)

In this regime $A_{\nu>0}$ recovers the standard low temperature asymptotic limit that is well known in the literature. In particularly, $A_{\nu>0}$ is independent of $h$ and one can talk appropriately of a Hamaker constant.

- For $\nu_{UV} h \ll 1 \ll \nu_\infty h$, the last term in Eq. (30) is exponentially suppressed, and $A_{\nu>0}$ develops an explicit $h$ dependence

$$A_{\nu>0}(h) = \frac{3hc}{4\pi \epsilon_m^{1/2}} R(\nu_{UV}).$$ \hspace{1cm} (32)

Using this expression in Eq. (22), we recover the standard result for retarded van der Waals interactions. In this range, the free energy has naturally shifted from an $h^{-2}$ to an $h^{-3}$ dependence, while the sign of the interactions remains dominated by the UV dielectric response.

- For $\nu_T h \ll 1 \ll \nu_{UV} h$, the last two terms of Eq. (30) are suppressed, and the retarded interactions cross over from an ultraviolet dominated regime, to an infrared dominated regime

$$A_{\nu>0}(h) = \frac{3hc}{4\pi \epsilon_m^{1/2}} R(\nu_{IR}),$$ \hspace{1cm} (33)

since $R(\nu_{IR})$ and $R(\nu_{UV})$ have opposite signs, the Hamaker function changes sign from positive to negative as the film thickness becomes larger than the cross-over wave-length $\nu_{UV}$ lying in the nanometer length scale.

- Finally, for $\nu_T h \gg 1$, only the first term of Eq. (30) remains. This results in an exponentially decaying retarded interaction corresponding to the expected suppression of $A_{\nu>0}$ at microwave distances [69, 70], with

$$A_{\nu>0}(h) = 3k_B T R(\nu_{IR}) e^{-\nu_T h}.$$ \hspace{1cm} (34)

For practical purposes, we are only interested in modeling van der Waals forces out to distances of the order of decades of nanometers from the surface, so we assume $\nu_T h \ll 1$, and simplify Eq. (30) to

$$g_{vdw}(h) = \frac{B}{h^3} \left[ 1 - f \exp(-\nu_{UV} h) - (1 - f) \exp(-\nu_\infty h) \right],$$ \hspace{1cm} (35)

where now $B$, $f$, $\nu_{UV}$ and $\nu_\infty$ are parameters chosen to best model the results of Elbaum and Schick in the range of 1 to 10 nm. For sufficiently large $f > 1$, this equation gives the expected crossover in the decay form of $g(h)$ from $\sim h^{-2}$ to $\sim h^{-3}$ dominated regimes found for the ice/water/air interface.

Figure 7 shows a comparison of the exact results from Lifshitz theory together with the fit to Eq. (2), showing excellent agreement for the set of parameters displayed in Table 1. Since we find that $g_{vdw}(h)$ is a factor of 1/100 smaller than $g_{sr}(h)$ in the range $h < 10 \text{ Å}$, the van der Waals forces therefore only become relevant at large distances, where $g_{sr}(h)$ becomes negligible due to the exponential decay form that it has.

D. Fit to the interface potential

The computer simulation results for the interface potential are fitted to the expression $g(h) = g_{sr}(h) + g_{vdw}(h)$, with $g_{sr}(h)$, the structural short range contribution:

$$g_{sr}(h) = C_2 \exp(-\kappa_2 h) - C_1 \exp(-\kappa_1 h) \cos(q_0 h + \alpha)$$ \hspace{1cm} (36)
We use the coefficients $C_1$, $\kappa_2$, $\kappa_1$, $q_0$ and $\alpha$ as fitting parameters, setting $\kappa_2 = 2\kappa_1$, for simplicity. Since the interface potential obtained from simulation is exact up to an additive constant, we seek parameters by minimizing the least square deviations from the corresponding disjoining pressure $\Pi(h) = -\partial_h g(h)$. We include also a constraint in the minimization to force the minimum of the interface potential to be at $g_{\text{min}} = -5.9 \times 10^{-5}$ J/m$^2$, consistent with the observed contact angle of a droplet on an $\alpha$ film. The parameter values obtained from this fitting are to be found in Table I.

The value found for $q_0$ is consistent with a strong renormalization away from the value one would expect from mean field theory \cite{42,44}.

| Property        | Value                  |
|-----------------|------------------------|
| $C_1$           | $3.143 \times 10^{-5}$ J/m$^2$ |
| $C_2$           | $4.116 \times 10^{-2}$ J/m$^2$ |
| $\kappa_1$      | $2.043 \times 10^8$ m$^{-1}$ |
| $q_0$           | $7.148 \times 10^9$ m$^{-1}$ |
| $\alpha$        | $5.144^\circ$         |
| $B$             | $7.875 \times 10^{-31}$ Jm |
| $f$             | 1.106 (unitless)       |
| $a$             | $3.03 \times 10^7$ m$^{-1}$ |
| $b$             | $5.0 \times 10^8$ m$^{-1}$ |
| $\alpha$-minimum| 1.6 nm                |
| $\beta$-minimum | 2.4 nm                |
| $\Pi^*, \alpha - \beta$ transition | $-4.60 \times 10^4$ Pa |
| $\Pi^*, \beta$ spinodal          | $-1.02 \times 10^5$ Pa  |

E. Computer Simulations

We use the GROMACS package to perform Molecular Dynamics simulations of the TIP4P/Ice model \cite{37}. The equations of motion are integrated using the Leap-Frog algorithm, with a time step of 3 fs. Bond and angle constraints are applied using the LINCS algorithm. The canonical ensemble is sampled using thermostated dynamics with the velocity rescale algorithm \cite{71}. The Lennard-Jones interactions are truncated at a distance of 9 \AA. Electrostatic interactions are evaluated using the Particle Mesh Ewald algorithm with the same real space cutoff. We calculate the reciprocal space term using a total of $80 \times 64 \times 160$ vectors in the $x, y, z$ reciprocal directions, respectively. We use a 0.1 nm grid spacing and fourth order interpolation scheme for the charge structure factor. For the initial configuration, we perform an $NpT$ simulation at 1 bar to obtain the equilibrium lattice parameters, and use the equilibrium values to create the initial $NVT$ configuration. Simulations are carried out in systems consisting of of $8 \times 8 \times 5$ unit cells of...
III. INTERFACE DYNAMICS: THE SINE GORDON + CAPILLARY WAVE MODEL

The dynamics of the premelting film, i.e. of the solid/liquid and liquid/vapor interfaces \( L_{sl} \) and \( L_{lv} \), respectively, is governed by the free energy in Eq. (3) of the main text, together with the gradient dynamics equations in Eq. (4) of the main text. This dynamics incorporates the influence of freezing/melting at the solid/liquid surface, condensation/evaporation at the liquid/vapor surface, as well as terrace and droplet spreading.

Obviously, this model does not incorporate any effects related to thermal gradients. However, it is believed that for films less than approximately 100 nm, disjoining pressure effects largely dominate over thermo-capillary effects [49]. Also, the experiments we describe are performed over fairly long time scales, so that local thermal equilibrium is reached, since growth and evaporation events appear to be reversible and reproducible [33]. The model assumes the lubrication approximation for the advective dynamics of the thin liquid film, which is accurate provided the characteristic wavelength of the lateral height variations is larger than the thickness of the liquid layer. Note also that the evolution of \( L_{sl} \) with added random noise is known to show an activated dynamics when the driving force \( \Delta p \) is smaller than \( w = q_z u \), so if noise were included, our model would incorporate the expected crossover from nucleated growth at small \( \Delta p \) to linear growth at large \( \Delta p \) [52, 58]. As it is, our model does not describe the formation of critical nuclei, but it does describe well the subsequent growth. The nucleated dynamics of the stochastic model is described at length in Ref. [74] while the crossover to linear growth is discussed in [53, 75].

Using the free energy functional and gradient dynamics, Eqs. (3) and (4) in the main text, we obtain the following time evolution equations for \( L_{sl} \) and \( L_{lv} \):

\[
\begin{align*}
\frac{\partial L_{sl}}{\partial t} &= -k_{sl}[\gamma_{sl} \nabla^2 L_{sl} + w \sin(q_z L_{sl}) - \phi_{sl}], \\
\frac{\partial L_{lv}}{\partial t} &= (\nabla \cdot \frac{k_{lv}^2}{\rho} \nabla + k_{lv})[\gamma_{lv} \nabla^2 L_{lv} + \phi_{lv}] - \frac{\Delta \rho}{\rho_l} \frac{\partial L_{sl}}{\partial t},
\end{align*}
\]

where \( w = q_z u \), \( \phi_{sl} = \Delta p_{sl} - \Pi \) and \( \phi_{lv} = \Delta p_{lv} + \Pi \), while \( \Delta p_{sl} = p_s - p_l \) and \( \Delta p_{lv} = p_l - p_v \). The dynamics exhibited by this pair of coupled partial differential equations is very rich, and the full gamut can only be found by solving numerically. However, analytic results can be obtained for the long-time average behavior, i.e. for the growth speeds. For \( \phi_{sl}^2 < w^2 \), ice growth (corresponding to \( L_{lv} \) increasing) cannot occur, because the thermodynamic force \( \phi_{sl} \) is not sufficient to overcome the sinusoidal pinning potential. Therefore, growth proceeds by the horizontal spread of terraces with velocity \( \frac{\pi}{4} k_{sl}(\frac{2\pi}{\gamma_{sl}})^{1/2} \phi_{sl} \) [53, 76]. For \( \phi_{sl}^2 > w^2 \), the driving potential \( \phi_{sl} \) overcoming the sinusoidal potential, and uniform growth can occur. However, if \( \phi_{sl} \) is only marginally larger than \( w \), the process occurs in a stepwise fashion, with a long interval in which there is almost no growth, followed by fast growth over a short time period, leading to a height increment of \( \approx 2\pi/q_z \), i.e. of one ice lattice spacing. This process repeats recursively with a period \( \tau = 2\pi/q_z \sqrt{\phi_{sl}^2 - w^2} \), so that the average growth rate is \( k_{sl} \sqrt{\phi_{sl}^2 - w^2} \). For large \( \phi_{sl} \), this provides the usual ‘linear growth’ mode of rough interfaces, but in the limit \( \phi_{sl} \approx w \), the linear growth mode can be much slower than the horizontal translation of terraces.

pseudo-orthorhombic geometry, each containing 16 molecules. More details of how we perform our simulations may be found in Refs. [21, 38, 50, 72].

During the course of each of our simulations, we identify structurally liquid-like molecules using the \( q_0 \) order parameter [73]. Once these molecules are identified, we determine the locations of the liquid-vapor and solid-liquid surfaces as explained in Ref. [72]. From these two surfaces, we calculate the local film thickness as the difference between these, \( h(x) = L_{lv}(x) - L_{sl}(x) \). For the calculation of the interface potential, the local film thickness for a given configuration is laterally averaged, in order to obtain the average liquid film thickness. The set of global film thicknesses obtained during the course of the simulation are used to compute the probability histograms \( P(h) \), from which \( g(h) \) can be calculated as indicated in Eq. (4). The resulting interface potential is therefore renormalized, on the scale of the simulation box. Results for \( P(h) \) are collected by performing simulations over a series of different temperatures in the range 210 to 271 K; the particular values used are given in the key of Fig. 6.
A. Mean field dynamics and kinetic phase diagram

For flat films, the average growth rate over time scales much larger than $\tau$ is then given by

$$
\begin{align*}
\langle \frac{\partial L_{sl}}{\partial t} \rangle &= \pm k_{sl} \sqrt{\phi_{sl}^2 - w^2} \\
\langle \frac{\partial L_{sv}}{\partial t} \rangle &= k_{lv} \phi_{lv} - \frac{\Delta p}{\rho_l} \langle \frac{\partial L_{sl}}{\partial t} \rangle
\end{align*}
$$

(2)

where the plus sign stands for freezing, and the minus sign for sublimation. Subtracting one from the other, we obtain the average speed of the liquid film thickness growth

$$
\langle \frac{\partial h}{\partial t} \rangle = k_{lv} \phi_{lv} \pm \frac{\rho_s}{\rho_l} k_{sl} \sqrt{\phi_{sl}^2 - w^2}.
$$

(3)

This result becomes particularly simple for the case when $w = 0$, where surface roughening occurs. In the case that we are interested in, where $w \neq 0$ and $p > p_{sv}$ so that the height of the ice grows, the condition that the liquid thickness is stationary $\langle \partial_h h \rangle = 0$ is achieved for $\phi_{lv} \geq 0$, $\phi_{sl} \geq 0$, and $\phi_{sl} - w^2 \geq 0$. In the marginal case where $\phi_{sl} = w$, then we need $\phi_{lv} = 0$. Solving these two conditions simultaneously corresponds to $\Delta p_{sl} + \Delta p_{lv} = \pm w$. Using the approximate but nonetheless accurate thermodynamic relations for the pressure differences given below in Eqs. (14) and (15), these condition may be solved as a function of $T$, yielding the following equation for the boundary

$$
p_{ns}(T) = p_{sv}(T)e^{\pm \frac{w}{k_B T}}.
$$

(4)

States between the sublimation line $p_{sv}(T)$ and the boundary line $p_{ns}(T)$ neither grow nor sublimate because the surface $L_{sl}$ can not grow in the absence of thermal activation.

For the more general case when $\phi_{sl}^2 - w^2 \geq 0$, the stationarity condition is achieved as a solution of the equation

$$
k_{lv} \phi_{lv} \pm \frac{\rho_s}{\rho_l} k_{sl} \sqrt{\phi_{sl}^2 - w^2} = 0.
$$

(5)

It corresponds to the condition that the liquid/vapor and solid/liquid surfaces grow at the same rate. Only one solution exists, given that the surface growth rates are monotonic. However, in order to solve explicitly we need to square each term. The resulting equation then has two solutions, each of the same magnitude but with opposite sign. Of course, one is unphysical. Therefore, squaring in Eq. (5) we obtain

$$
p_{sl}^2 k_{sl}^2 \phi_{sl}^2 - p_{lv}^2 k_{lv}^2 \phi_{lv}^2 = p_{sl}^2 k_{sl}^2 w^2,
$$

(6)

under the condition that $p_{lv} > p_{sv}(T)$. This provides a quadratic equation for $\Pi$ as a function of $p_{lv}$ and $T$, so one obtains

$$
\Pi = -\Delta p_k,
$$

(7)

with

$$
\Delta p_k = -\frac{f_s^2 \Delta p_{sl} + f_l^2 \Delta p_{lv} \pm f_s [f_l^2 (\Delta p_{sl} + \Delta p_{lv})^2 + (f_s^2 - f_l^2) w^2]^{1/2}}{(f_s^2 - f_l^2)},
$$

(8)

where $f_s = \rho_s k_{sl}$ and $f_l = \rho_l k_{lv}$. Thus, the solution may formally be written in exactly the same form as the equilibrium condition for the adsorption on an inert substrate, with the Laplace pressure difference $\Delta p = p_t - p_v$ replaced by a kinetic pressure difference $\Delta p_k$ which depends on the growth mechanism and rate constants. Likewise, an effective potential exists whose extrema are stationary states of the underlying dynamics.

Alternatively, Eq. (6) may be solved for $p_{lv}$ as a function of $\Pi$ and $T$, with the result:

$$
\rho_l k_B T \ln \frac{p}{p_{lv}} + \Pi = -\frac{\Delta p C \pm \left[\kappa^2 \rho_l^2 C^2 + \rho_l^2 w^2 (\Delta p^2 - \kappa^2 \rho_l^2)\right]^{1/2}}{\Delta p^2 - \kappa^2 \rho_l^2},
$$

(9)

where $\kappa = \rho_l k_{lv}/\rho_s k_{sl}$ and $C = \rho_s \rho_l k_B T \ln \frac{p_{sv}}{p_{lv}} - \rho_s \Pi$. In this case, the result corresponding to $w = 0$ and $\Pi = 0$ (for a rough ice surface) is obtained for the ‘+’ root. Three kinetic transition lines in the phase diagram can be identified from these equations and are worth noting:
• The line of kinetic coexistence occurs when $\Delta p_k = 0$. This is a line in the phase diagram $p_v(T)$ that can be obtained from Eq. (6), for the choice $\Pi = 0$. States with pressure above this line have film thicknesses corresponding to the portion of $\Pi < 0$.

• The kinetic spinodal line, which occurs when $\Delta p_k = \Pi_{\text{spin}}$, with $\Pi_{\text{spin}}$ the value at which the interface potential $g(h)$ predicts that the liquid/vapor interface $L_v$ becomes linearly unstable, i.e. has a spinodal. This condition leads to a line $p_{\text{spin}}(T)$ that can be obtained from Eq. (6), for the choice $\Pi = \Pi_{\text{spin}}$. In our work we are principally interested in when the state at the $\beta$ minimum in the potential becomes linearly unstable (spinodal).

• The line of $\alpha \to \beta$ kinetic transition. A particularly interesting situation is that where a thin and a thick film coexist as marginally stable extrema in the regime where $\omega_k(h)$ has a double well form. The condition of ‘kinetic coexistence’ is obtained by solving for the two film thickness $h_1$ and $h_2$ satisfying

$$\begin{cases}
\omega_k(h_1) = \omega_k(h_2) \\
\Pi(h_1) = -\Delta p_k \\
\Pi(h_2) = -\Delta p_k
\end{cases} \tag{10}$$

The first condition imposes equal effective free energy for both films, and the other two impose that both states obey the quasi-stationary condition at equal kinetic overpressure $-\Delta p_k$. As an alternative, these equations may be written more concisely as:

$$\begin{cases}
g(h_1) + \Pi(h_1)h_1 = g(h_2) + \Pi(h_2)h_2 \\
\Pi(h_1) = \Pi(h_2)
\end{cases} \tag{11}$$

Once the value of $\Pi$ that satisfies the condition is known, the pressure $p_v$ at which the condition is met can be obtained by solving Eq. (6) for $p_v(T)$ using the appropriate value of $\Pi$ in Eq. (9).

From these observations we are able to construct the highly detailed kinetic phase-diagram shown in Fig. 4 of the main text, which is an essential tool for understanding at different state points the numerical results obtained from the coupled gradient dynamics partial differential equations in Eq. (4) of the main text.

B. Thermodynamic functions and the equilibrium phase diagram

The pressure differences between solid/liquid and liquid/vapor phases are the thermodynamic driving forces that lead to the growth of the ice and the liquid from the vapor. To determine these differences requires knowledge of the equilibrium phase diagram, i.e. to know the pressure as a function of temperature along the condensation and sublimation lines, $p_{sl}(T)$ and $p_{sv}(T)$, respectively. We obtain these by assuming they follow from the Clausius-Clapeyron equation. This approximation is excellent for the sublimation line [77], and remains good for the vaporization line down to 260 K [61]. They are given by

$$\ln \frac{p_{sv}}{p_t} = \frac{\Delta H_{sv}}{R} \left( \frac{1}{T_t} - \frac{1}{T} \right), \tag{12}$$

$$\ln \frac{p_{lv}}{p_t} = \frac{\Delta H_{lv}}{R} \left( \frac{1}{T_t} - \frac{1}{T} \right), \tag{13}$$

where $T_t$ and $p_t$ are the temperature and pressure at the triple point, $R$ is the gas constant, $\Delta H_{sv}$ is the molar enthalpy change for sublimation and $\Delta H_{lv}$ is the molar enthalpy change for condensation.

Since ice and water can both be treated as effectively being incompressible, the pressure changes which are relevant to this study are very small. Therefore, the pressure differences can accurately be approximated by

$$p_l - p_v = \rho_l RT \ln \frac{p_v}{p_{lv}(T)}, \tag{14}$$
\[ p_s - p_v = \rho_s RT \ln \frac{p_v}{p_{sv}(T)}. \]  

Using Eqs. (12)–(15), we obtain explicit expressions for the liquid-vapor and ice-liquid overpressures as

\[ p_l - p_v = \rho_l RT \ln \frac{p_v}{p_t} - \frac{\rho_l \Delta H_{lv}(T - T_t)}{T_t}, \]

\[ p_s - p_l = (\rho_s - \rho_l) RT \ln \frac{p_v}{p_t} + \left( \frac{\rho_l \Delta H_{lv} - \rho_s \Delta H_{sv}}{T_t} \right)(T - T_t). \]

Notice that the pressure difference between the solid and liquid phases decreases as the ambient vapor pressure increases. The triple point data required for the implementation of Eqs. (12)–(17) may be found in Table II.

**TABLE II. Triple point data of water. Conversion from mass to molar units performed assuming \( M_w = 18.015 \) g/mol.**

| Property | Value | Reference |
|----------|-------|-----------|
| \( T_t \) | 273.16 K | [59] |
| \( T_t \) | 0.1 C | [59] |
| \( p_t \) | 611.65 Pa | [59] |
| \( \rho_l \) | 55 498 mol/m\(^3\) | [59] |
| \( \rho_s \) | 50 888 mol/m\(^3\) | [60] |
| \( \rho_v \) | 0.2694 mol/m\(^3\) | [59] |
| \( \Delta H_{sv} \) | 51 059 J/mol | [61] |
| \( \Delta H_{lv} \) | 45 051 J/mol | [61] |
| \( \Delta H_{sl} \) | 6 008 J/mol | [61] |

**C. Numerical solution of the model**

Numerical computations of the dynamics of the interfaces predicted by our coupled partial differential equation model in Eqs. (1) (i.e. Eqs. (3) and (4) of the main text) are performed using a method of lines technique similar to that used in Ref. [64]. The method is extended to evolve the two interfaces (solid-liquid, and liquid-vapor), with coupling terms involving mass transfer and the two interface potentials naturally included. However, we evaluate the spatial derivatives in a different manner, which significantly increases the rate of numerical convergence. This was done because for the evolution of the solid-liquid interface, a pinning effect in the horizontal direction can occur if too few mesh points are used. Consequently, rather than using an extremely large number of points in the finite difference scheme used in [64], here we implement a periodic pseudospectral method.

The numerical method uses results from Ref. [78], discretising on a regular (periodic) grid and uses a band-limited interpolant derived using the discrete Fourier transform and its inverse to form the differentiation matrices which act in real space (see chapter 3 of [78] for details). The periodicity enabled by the premelting film avoids the need to evolve actual contact lines, in comparison to some of our previous work using pseudospectral discretisation [79, 80]. For the time stepping, the ode15s Matlab variable-step, variable-order solver is used [81]. Our numerical calculations are performed on the nondimensionalised version of the model equations. We find that choosing \( \kappa_1^{-1} \approx 0.49 \) nm and \( 3\eta/(\kappa_1 \gamma_{lv}) \approx 0.11 \) ns as our units of length and time in the nondimensionalisation works well.

To explore the effectiveness of our model to at least qualitatively reproduce the phenomena observed in the experiments and to confirm the validity of the analytical predictions for the different behaviors in the different \((p_v, T)\) regions of the phase diagram, we perform an extensive set of full numerical simulations, for a range of state points covering all the different growth regimes. Of course, the observed behavior also depends on the effective surface free energy \( \omega_k(h) \), which includes ice surface effects on the evolution of the interfaces, and on the initial conditions. A comprehensively large variety of initial conditions (i.e. the \( t = 0 \) profiles of the two interfaces) have also been trialled, especially for planar interfaces (at different separations, usually based on the heights corresponding to the \( \alpha \) or \( \beta \) minima) with either small imperfections in the solid, or an initial perturbation of the liquid surface, or both. The results presented in the paper are drawn from the following three different initial condition types: Firstly, a planar solid-liquid surface with a Gaussian droplet shaped perturbation in the liquid-vapor interface, given by

\[ L_{lv} = d_B + h_0 + A_f \exp[-((x - x_L/2)/x_{wf})^2], \]

\[ L_{sl} = d_B, \]

\[ \Delta H_{sv} = \text{51,059 J/mol}, \]

\[ \Delta H_{lv} = \text{45,051 J/mol}, \]

\[ \Delta H_{sl} = \text{6,008 J/mol}, \]

\[ \kappa_1^{-1} \approx \text{0.49 nm}, \]

\[ 3\eta/(\kappa_1 \gamma_{lv}) \approx \text{0.11 ns}, \]

\[ \omega_k(h) \]
where \( h_0 \) is an initial separation (such as the height of the \( \alpha \) minimum), \( x_L \) is the size of the periodic domain (taken as \( x_L = 2500 \kappa_1^{-1} \)) in all simulations presented here, \( A_f = 17 \kappa_1^{-1} \) is the height of the Gaussian perturbation and \( x_w \) is a measure of its width. We typically set \( x_w = 450 \kappa_1^{-1} \) for the results presented here.

The other two forms for the initial conditions are

\[
L_{sl} = d_B + \frac{A_i}{2} d_B \left[ \tanh \left( \frac{x - (x_L - x_{wi})/2}{10 \kappa_1^{-1}} \right) - \tanh \left( \frac{x - (x_L + x_{wi})/2}{10 \kappa_1^{-1}} \right) \right],
\]

\[
L_{lv} = d_B + h_0,
\]

which corresponds to a planar liquid-vapor surface, together with an ice-liquid interface that has on it a small imperfection of height \( A_i \) that is an integer multiple of the height of a single ice terrace, that protrudes either into or away from the liquid, and has width \( x_{wi} \). Values used in the work presented here are \( \{A_i, x_{wi}\} = \{1, x_{wi} = x_L/16\} \) and \( \{A_i, x_{wi}\} = \{10, x_{wi} = 9x_L/16\} \).

Fig. 5 of the main text displays snapshots from four typical simulations, and here we show snapshots from two additional simulations in Figs. 8–9. The full time evolutions of all six simulations can be seen in the movies included as supplementary material, named Movies S1–S6.

FIG. 8. Snapshots as described in the caption of Fig. 5, but here corresponding to droplet above the kinetic liquid-vapor coexistence at \( (p,T) = (517.5, 269.5) \), which is the point indicated with a “\( \bullet \)” symbol in Fig. 4.

D. Kinetic coefficients for the growth rate laws

1. Growth of the liquid/vapor surface

For an infinitely thick premelting film with a flat liquid-vapor surface, Eq. (1) for the growth rate of the surface becomes

\[
\frac{\partial L_{lv}}{\partial t} = k_{lv} \Delta p_{lv}.
\]

Replacing \( p_l - p_v \approx \rho k_B T (p - p_{lv})/p_{lv} \) in the term for condensation/evaporation rate, we find

\[
\frac{\partial L_{lv}}{\partial t} \approx k_{lv} \rho k_B T (p - p_{lv})/p_{lv}.
\]

This result can be compared to the Knudsen-Hertz law, which reads

\[
\frac{\partial L_{lv}}{\partial t} = k_{KH} (p - p_{lv}),
\]


TABLE III. Temperature dependent coefficients. \( T \) refers to absolute temperature in K. \( T_c \) refers to temperature in the Celsius scale.

| Property | Value | Source |
|----------|-------|--------|
| \( d_B \) | \( 0.37 \times 10^{-9} \) m | 1 |
| \( \rho_{lv} \) | \( \rho_{lv}/(R_c T) \) | ideal gas law |
| \( T_c \) | \( T - 273.15 \degree C \) | Celsius scale |
| \( \rho_l \) | \( 55502 + 3.4549T_c - 0.4464T_c^2 \ldots \) | S2 S3 |
| \( \rho_s \) | \( 50885 - 9.71T_c - 0.03T_c^2 \) mol m\(^{-3} \) | 1 |
| \( \gamma_{sl} \) | \( (28 + 0.25T_c) \times 10^{-3} \) J/m\(^2 \) | 1 |
| \( \gamma_{lv} \) | \( (75.7 - 0.1775T_c) \times 10^{-3} \) J/m\(^2 \) | 84 |
| \( \eta \) | \( 1.39 \times 10^{-4}(T/225 - 1)^{-1.64} \) kg m\(^{-3} \) s\(^{-1} \) | 85 |
| \( u \) | \( 1.3 \times 10^{-4} \) J/m\(^2 \) | This work |
| \( k_{lv} \) | \( 3.4 \times 10^{-10} \rho_{lv}T^{-1/2} \times 10^{-3} \) m/s Pa | Knudsen-Hertz law |
| \( k_{sl} \) | \( 6.4k_{lv} \) | |

where \( k_{KH} = \alpha_{lv}/\rho_l(2\pi m_w k_B T)^{1/2} \), and where \( \alpha \) is the sticking coefficient, or fraction of vapor molecules that stick to the interface upon collision and \( m_w \) is the mass of a water molecule. Therefore, we find

\[
k_{lv} = \frac{\rho_{lv}}{\rho_l k_B T} k_{KH}.
\]

We calculate \( k_{lv} \) using the thermodynamic data reported in Table III. We also assume \( \alpha_{lv} = 1 \) for the attachment of pure water vapor onto the ice surface, consistent with all current molecular simulation studies [72, 86-88].

2. Growth of the solid/liquid surface

For an infinitely thick premelting film with flat solid-liquid interface, Eq. (1) for the growth rate of the surface becomes

\[
\frac{\partial L_{sl}}{\partial t} = k_{sl} \Delta p_{sl}.
\]

Replacing \( p_s - p_v \approx \rho_s \Delta H_{sl} \frac{T - T_i}{T_i} \) in the term for the freezing/melting rate we find

\[
\frac{dL_{sl}}{dt} \approx k_{sl} \rho_s \Delta H_{sl} \frac{T_i - T}{T_i}.
\]

This result can be compared to the law of linear growth for a crystal from the melt which holds at large undercooling [1],

\[
\frac{dL_{sl}}{dt} = k_{LG}(T_i - T).
\]

The result for the rate constant suggested by Librecht [89], \( k_{LG} = 0.07 \) cm/s K, leads to \( k_{sl} = 6 \times 10^{-10} \) m/s Pa. However, the slope of the kinetic coexistence line is determined by the ratio \( k_{sl}/k_{lv} \), and we find that the slopes observed in experiments can only be reproduced for \( k_{sl}/k_{lv} \approx 6.4 \), which is about a factor of 10 smaller. It seems likely that the kinetic coefficient for growth from the premelting film could be significantly smaller than that from the melt, since the interface is considerably smoother [21]. Therefore, in our calculations we set \( k_{sl} = 6.4k_{lv} \).

E. Size of the region where nucleated dynamics occurs

For \( h \to \infty \), our model gives an equation for the dynamics of \( L_{sl} \) that corresponds to the growth of ice within supercooled water. This is

\[
\frac{\partial L_{sl}}{\partial t} = k_{sl} (\gamma_{sl} \nabla^2 L_{sl} - u q_z \sin(q_z L_{sl}) + \Delta p_{sl}),
\]

(27)
which is a forced overdamped sine-Gordon equation. The growth is nucleated for $u q_z > \Delta \rho_{sl}$, and otherwise linear
in time [58, 74]. Therefore, we can obtain an order of magnitude estimate for the parameter $u$ from the value of the
temperature where there is a crossover from nucleated to linear growth of ice in supercooled water. According to
Pruppacher [1], this occurs at about $T - T_t \approx 2K$. Using $p_s - p_l = \rho_s \Delta H_{sl} \Delta T / T_t$, we find

$$u = \frac{b}{2\pi} \rho_s \Delta H_{sl} \frac{\Delta T^*}{T_t}.$$  

(28)

Using $\Delta T^* = 2K$ as suggested from results in Ref. [90], and $d_B = 0.37$ nm, we find $u = 1.3 \times 10^{-4}$ J/m$^2$. This
is about five times larger than the results obtained from computer simulations, which yield $u = 2.8 \times 10^{-5}$ J/m$^2$
[21] [24] [52]. The value we use is given in Table III.

F. Viscosity

In principle, the lubrication approximation on which our thin film dynamics model is based on uses as input the
bulk liquid viscosity. Some studies suggest there is a large enhancement of the viscosity of premelting films (c.f. [91])
over the bulk value. However, this appears to remain as an unsolved issue, with very recent high-profile studies being
published [92]. Thus, here we use here the viscosity of supercooled bulk water as reported in Table III. Changing the
value of the viscosity in our model will not qualitatively change our results.

IV. MOVIES

• Movie S1: Movie corresponding to Fig. 5 (a-e).
• Movie S2: Movie corresponding to Fig. 5 (f-j).
• Movie S3: Movie corresponding to Fig. 5 (k-o).
• Movie S4: Movie corresponding to Fig. 5 (p-t).
• Movie S5: Movie corresponding to Fig. 8.
• Movie S6: Movie corresponding to Fig. 9.