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ABSTRACT

A disordered quasi-liquid layer of water is thought to cover the ice surface, but many issues, such as its onset temperature, its thickness, or its actual relation to bulk liquid water, have been a matter of unsettled controversy for more than a century. In this perspective article, current computer simulations and experimental results are discussed under the light of a suitable theoretical framework. It is found that using a combination of wetting physics, the theory of intermolecular forces, statistical mechanics, and out-of-equilibrium physics, a large number of conflicting results can be reconciled and collected into a consistent description of the ice surface. This helps understand the crucial role of surface properties in a range of important applications, from the enigmatic structure of snow crystals to the slipperiness of ice.

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I. INTRODUCTION

On March 12, 1936, a team of Japanese researchers led by Nakaya succeeded in creating the first ever artificial snow crystal in a snow chamber under controlled conditions.¹ After several years of further research, the results were summarized and collected in the diagram that now bears his name.^{1–5} The Nakaya diagram maps crystal habits as a function of temperature and humidity of the surrounding atmosphere (Fig. 1). The complex structures that form as supersaturation is increased can be relatively well understood under the framework of crystal growth science.^{3,5,6} However, the surprising transformation of solid hexagonal prisms from plate-like to columnar-like and back to plate-like as temperature decreases has remained a mystery ever since.^{3–5}

Nakaya understood that the only way to interpret the experimental observations was to assume that the surface structure of ice must be highly complex. For this reason, he revisited an old hypothesis by Faraday, who first conjectured that ice below its melting point bares a microscopically thin liquid layer on its surface.⁷ Based on this idea, he performed experiments, later improved by Hosler and Goldshlak, to measure the adhesion of ice beads.^{8,9} The teams concluded that the adhesion and its dependence on humidity was likely to result from the premelting layer conjectured by Faraday. However, due to the lack of adequate experimental tools, the hypothesis remained unconfirmed. Delightful reports on the ingenuity and perspicacity of early researchers to probe the ice surface for a premelting film using rudimentary experimental apparatus may be found in Refs. 10–12.

Two decades later, Kuroda and Lacmann borrowed an original idea from Stransky on premelting mediated crystal growth¹³ and formulated a consistent theory of ice growth from the vapor. Their working hypothesis was that the basal and prism faces of ice undergo a sequence of surface phase transitions. Switching from one surface phase to another would cause abrupt shifts in the relative growth rates of the basal and prism faces, thereby accounting for the puzzling plate-to-column transformations depicted in the Nakaya diagram.^{14,15}

Kuroda went on to conduct ellipsometry and x-ray diffraction studies that were among the first few direct evidences for the presence of a quasi-liquid layer of melt water on the ice surface.^{16,17} Following these studies, the field experienced a surge of renewed activity, with numerous measurements and estimates of the quasi-liquid layer thickness carried out using a variety of modern spectroscopic and mechanical techniques.^{17–27}

Within a decade, these experimental measurements confirmed what had remained a plausible hypothesis for more than a hundred years.

Paradoxically, the experimental confirmation of the premelting phenomenon in ice did not settle the issue altogether. Estimates of the precise thickness of the quasi-liquid layer varied by orders of magnitude, according to most reviews.^{28–31} In this context, the discussion shifted to whether the quasi-liquid layer maintains a finite thickness up to the triple point or whether it diverges and becomes infinitely thick. In the language of adsorption science, this corresponds to asking whether a complete surface melting transition

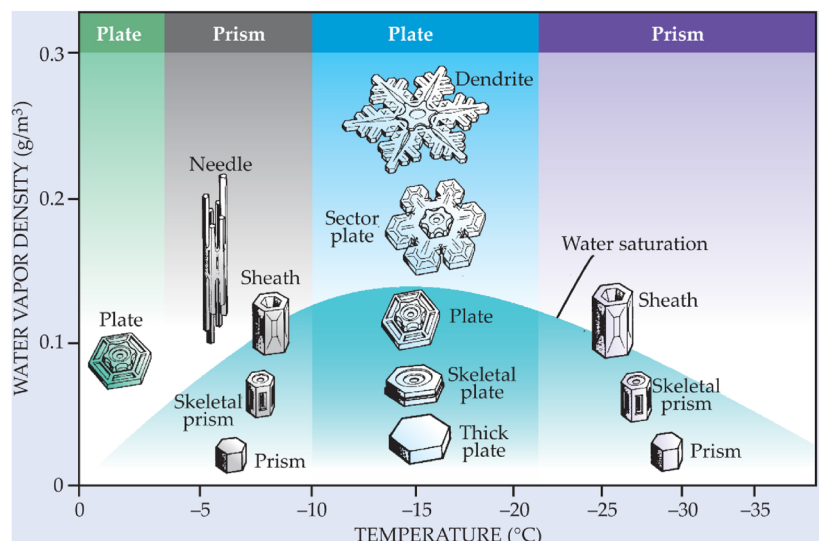


FIG. 1. Diagram of snow crystal morphology, a descendant of the early Nakaya diagram due to Kobayashi.² The figure displays the habit of ice crystals grown in the atmosphere as a function of temperature and excess water vapor density over ice saturation. The origin of the complex shapes that appear as saturation increases is relatively well understood. The reason why simple hexagonal prisms grown at low vapor saturation change from plates, to columns, and back again to plates as temperature decreases has remained a mystery ever since Nakaya first published his results. Reproduced with permission from Y. Furukawa and J. S. Wettlaufer, *Phys. Today* **60**(12), 70–71 (2007). Copyright 2007 AIP Publishing LLC.

exists (the complete wetting of water on ice) or whether surface melting remains incomplete at three phase coexistence (the partial wetting of water on ice).³²

Regardless of actual measurements of the quasi-liquid layer thickness as a function of temperature, experimental observations dating back to the late 1960s showed that water does not completely wet the ice surface. Early observations of water droplets formed on ice^{33–35} were confirmed several years later^{18,36,37} and have been reported during the past decade with high-quality imaging.^{38–44} Surprisingly, this implies that the surface of ice is mildly hydrophobic, or at least not completely hydrophilic.

Interestingly, once the presence of liquid water droplets on the ice surface was confirmed by direct optical microscopy imaging, Faraday's original hypothesis came under renewed scrutiny.⁴⁵ More recently, Sazaki and collaborators—at the Institute for Low Temperature Science, founded by Nakaya and later home to Kuroda—have raised serious concerns about this hypothesis,^{38,41,42,46} while studies on the ice surface using macroscopic probes have lead Bonn *et al.* to question the significance of ice premelting altogether.^{43,47,48}

Of course, ice premelting is thought to have important implications in many fields other than crystal growth. This includes atmospheric physics,³⁰ glaciology, soil science,²⁹ and tribology.⁴⁹ However, disputes and controversies on the role of premelting films extend into nearly all these topics.^{10–12,29–31,50,51} In this introduction, I have highlighted its relevance to crystal growth science, as seeking for an explanation of the Nakaya diagram has proved to be an exceptional motivation to delve into a variety of important topics in chemical physics, including wetting physics, capillary wave and crystal growth theory, renormalization theory, intermolecular forces, liquid-state theory, and out-of-equilibrium physics.

In this perspective article, I discuss how a selected blend of concepts from these wide range of fields, together with the help of computer simulations,^{52–64} allows interpreting and reconciling a large body of apparently conflicting empirical evidence into a unified and consistent picture of the structure and dynamics of premelting films. This includes some of the most relevant puzzles reported in recent reviews:^{31,46,65} How can the observation of elementary

steps be reconciled with the presence of significant premelting? Why do liquid droplets appear well above water-vapor saturation? Most notably, what is the reason for the alternation of crystal habits in the Nakaya diagram?

Often, this requires delving into rather intricate and subtle discussions. The readers less interested in the finer details of wetting physics and crystal growth can get an overall impression of the field by going through Secs. II, VI, IX, XI, and XII only, while a read through Sec. XII may be sufficient to get a broad picture of the current understanding and future challenges.

II. MODERN EMPIRICAL EVIDENCE OF ICE PREMELTING

The experimental measurement of ice premelting thickness has been reviewed in a large number of papers.^{18,25,26,28,30,31,41} All of them agree that the data exhibit enormous dispersion, with discrepancies spanning several orders of magnitude. However, the large extent of scatter can be reduced significantly by a judicious selection of experimental results. As noted in Ref. 29, there is no reason to expect that the premelting film thickness should be equal for surface and interfacial premelting. Indeed, computer simulations show that interfacial premelting structure is similar to that of surface premelting only for very hydrophobic substrates.⁶⁴ Considering the case of surface premelting alone significantly reduces the number of available measurements.^{16,18,20,23,25–27,66,67} However, out of all these studies, the early results by Golecki and Jaccard using proton backscattering are clearly outliers⁶⁶ and can be ruled out. Furthermore, studies using atomic force microscopy are necessarily invasive and are prone to capillary condensation in between the tip and the surface,⁶⁸ so they are left out too. A final selection accounting for all the remaining measurements since 1990, using widely different non-invasive techniques, such as ellipsometry, x-ray scattering, and infra-red, sum frequency, or fluctuation spectroscopy lead to a rather different picture, with results differing by at most one order of magnitude for temperatures below about -1°C (Fig. 2). The scatter remains bracketed within one order of magnitude even up to

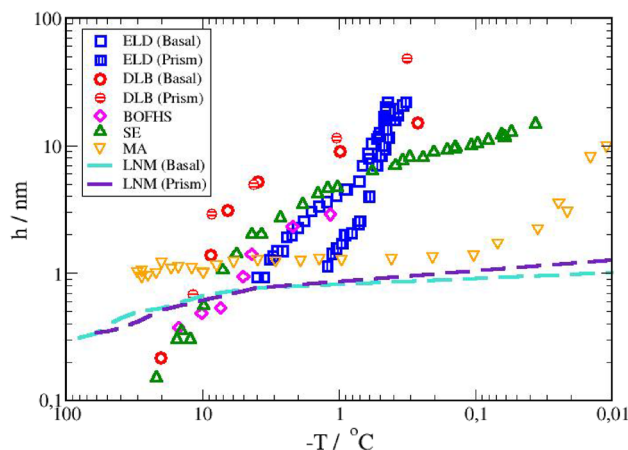


FIG. 2. Extent of ice premelting. A selection of all non-invasive experimental results since 1990 for temperatures up to -1°C lead to premelting film thicknesses that agree within an order of magnitude. Experimental results are from Elbaum *et al.*¹⁸ (ELD), Dosch *et al.*²⁰ (DLB), Blum *et al.*²⁴ (BOFHS), Sadchenko and Ewing (SE),²⁵ and Mitsui and Aoki²⁷ (MA). Representative results from computer simulations are provided for the TIP4P/Ice model from Llombart *et al.*⁵⁷ (LNM).

temperatures of -0.1°C if the results of Ref. 21 are discarded. All of these experimental measurements confirm that a premelting layer appears on the ice surface, with thicknesses that increase from the sub-nanometer scale to at most 10 nm in the temperature interval between -20 and -1°C . This appears somewhat higher but within reasonable agreement with computer simulation results for different water models, which consistently show the formation of a disordered liquid layer on the ice surface.^{52,53,55–57,68–75} Indeed, the extent of ice premelting can be quantified in computer simulations using suitable order parameters that allow distinguishing whether a water molecule is found in a liquid-like or solid-like environment (Fig. 3).^{76,77} Using such parameters, simulation studies report film thicknesses that lie in the sub-nanometer range up to about -1°C below the model's

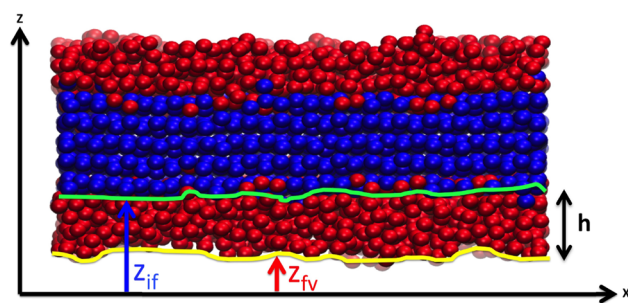


FIG. 3. Snapshot of an ice–vapor interface as obtained in computer simulations for the TIP4P/Ice model. The red particles correspond to water molecules in a liquid-like state. The blue molecules are in a solid-like state as determined using a suitable order parameter. The interfacial structure may be characterized by two fluctuating surfaces, which bound the premelting film from the ice and vapor bulk phases. Reproduced with permission from Llombart *et al.*, *Sci. Adv.* 6, eaay9322 (2020). Copyright 2020 Author(s), licensed under a Creative Commons Attribution 4.0 License.

triple point and then grow somewhat above the nanometer thickness at higher temperatures.^{55–57,68,69,71,74,78}

However, notice that in strict sense, the direct comparison between computer simulations and experiments can only be done for studies probing uncontaminated and atomically smooth ice surfaces with well-defined orientation. This requires dedicated preparation of single mono-crystals grown by layer by layer deposition from the vapor.^{5,16,18,38,40,42} In most laboratories, measurements have been performed from rapid vapor deposition^{24,26} or water freezing,^{25,27,67} which produces polycrystalline samples with uncontrolled smoothness unless extra care is exercised.²⁰ In practice, it seems from Fig. 2 that the premelting film thickness remains constrained within one order of magnitude irrespective of the smoothness or surface orientation. Particularly, the current uncertainties in experiments do not seem to settle whether the film thickness is significantly different in basal or prism surfaces, but results from computer simulations suggest this difference is constrained within tenths of a nanometer.^{56,57,63,69}

III. A TOY MODEL OF (COMPLETE) SURFACE MELTING

Despite the empirical evidence discussed in Sec. II, the significance of equilibrium ice premelting has been contested occasionally,^{41,43,45} so it is now instructive to consider a minimal model of the ice/vapor interface approaching three phase coexistence.

To set the scene, let us consider a low temperature bulk solid in equilibrium with bulk vapor at two phase coexistence. Increasing the temperature while remaining at solid–vapor coexistence, the system moves along the *sublimation line*, and approaches the *triple point*, where solid, liquid, and vapor phases become equally stable and can coexist simultaneously under the same thermodynamic conditions (Fig. 4).

Premelting, viewed as an equilibrium phenomenon, is the study of how the metastable liquid phase (*l*) intrudes at the interface between the coexisting bulk solid (*s*) and vapor phases (*v*) in the vicinity of a metastable liquid–vapor coexistence line (Fig. 3). For many substances, this can only occur as the system approaches the triple point. For the special case of ice, however, notice that the metastable prolongation of the liquid–vapor coexistence line runs very close to the sublimation line all the way from the triple point down to very low temperatures.

In order to gain a microscopic understanding of this problem, let us borrow tools from statistical field theory and assume that there is a suitable *order parameter*, ϕ , which adopts widely different values for the bulk solid and vapor phases.

An order parameter can be simply the system's density. However, in order to characterize the high symmetry of a solid, a more sophisticated order parameter may prove convenient.^{79,80} For the special case of ice premelting, for example, one can choose some suitable measure of the tetrahedral order, which allows distinguishing different ice polymorphs from the liquid or vapor phases.^{71,76,77,81}

A microscopic characterization of the interfacial properties can now be afforded by introducing an order parameter field, $\phi(z)$, which describes how the order parameter changes continuously from its value in the bulk solid to its value in the bulk vapor along the perpendicular direction to the solid–vapor interface, z .

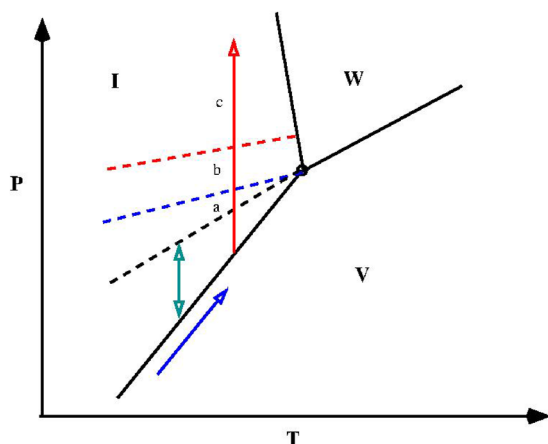


FIG. 4. Phase diagram of water in the neighborhood of the triple point. The full black lines illustrate the equilibrium phase boundaries, including the *sublimation line* separating ice from vapor and the *condensation line*, separating liquid water from vapor. The black dashed line is the metastable prolongation of the condensation line. Equilibrium premelting occurs for a path along the sublimation line, as indicated by the blue arrow. The equilibrium thickness of the premelting film is dictated by the distance of the sublimation line to the metastable prolongation of the condensation line, as indicated by the green segment. The red line indicates a non-equilibrium path, with three different regimes as described in Sec. IX. In region a, below the kinetic condensation line, indicated by the blue dashed line, ice grows but the premelting film remains in a steady state of constant thickness. In region b, above the kinetic condensation line, the premelting film remains in steady state but vapor can condense and form droplets atop. In region c, above the kinetic spinodal line, condensation occurs faster than freezing, the premelting film diverges and ice freezes in a wet mode.

Within the square gradient approximation, the excess surface free energy of the interface, $\Delta\omega$, may be obtained in terms of $\phi(z)$, as a sum of bulk free energies adopted by the system along the interface. An additional square gradient term accounts for the cost of creating the inhomogeneity,

$$\Delta\omega = \int dz \left\{ f(\phi) + \frac{1}{2} C \left(\frac{d\phi}{dz} \right)^2 \right\}. \quad (1)$$

Here, $f(\phi)$ is the bulk free energy of the system as measured in excess to the value of the bulk coexisting phases, while C is a system's parameter which sets the scale of the surface tension.

This free energy model, already employed by van der Waals, is also known under the name of Cahn–Hilliard theory or Landau–Ginzburg–Wilson Hamiltonian. In that context, it has proven instrumental in understanding the structure of interfaces,⁸² nucleation,^{83,84} and critical phenomena at two phase coexistence.^{85,86} Here, one usually introduces a dimensionless order parameter and assumes the bulk free energy is a simple bi-quadratic potential, $f(\phi) = (1 - \phi^2)^2$, with minima $\phi = \pm 1$ corresponding to the bulk phases at coexistence. Since Eq. (1) is analogous to a classical Lagrangian, the optimal order parameter field, which minimizes the surface free energy, satisfies the analog of an energy conservation principle and can be expressed as

$$f(\phi) = \frac{1}{2} C \left(\frac{d\phi}{dz} \right)^2. \quad (2)$$

The solution of this equation for the bi-quadratic potential provides the well-known result for the structure of an interface at two phase coexistence,^{82,87}

$$\phi(z) = \tanh(\kappa z), \quad (3)$$

where κ is an inverse correlation length in the scale of the molecular diameter.

Related models have also been applied previously to the study of premelting, under the assumption that the bulk solid and liquid phases behaves as an inert substrate.^{71,88,89} This maps premelting behavior to a problem that is known in the literature as short-range wetting.^{32,90} However, this obviates altogether the essence of premelting, which corresponds to the approach of two coexisting phases to a triple point.

A simple way to remedy this deficiency is to modify the bi-quadratic potential to account for the intrusion of a third phase with an order parameter in between those of the bulk solid and liquid phases, i.e., $f(\phi) = (1 - \phi^2)^2(t + \phi^2)$, where $t \propto 1 - T/T_t$ is a measure of the under-cooling [Fig. 5(a)]. The Euler–Lagrange equation, Eq. (2), can be solved exactly for this potential, yielding⁸⁹

$$\phi(z) = \frac{\sqrt{t} \tanh(\kappa z)}{\sqrt{t + 1 - \tanh^2(\kappa z)}}. \quad (4)$$

This result nicely describes the essence of premelting. For deep under-cooling, t is much larger than $1 - \tanh^2(\kappa z)$ for all z , and Eq. (4) becomes virtually equal to the sharp $\tanh(\kappa z)$ interfacial profile that is typical for two phases at coexistence. When the system approaches the triple point, however, $t \rightarrow 0$, the order parameter profile adopts a value $\phi(z) \approx \sqrt{t}$ close to zero as long as $1 - \tanh^2(\kappa z)$ in the denominator remains larger than t . This occurs in an increasingly larger range of z values as t vanishes. Accordingly, the model predicts a gradual increase of the liquid phase in between the solid and the vapor phases on approaching the triple point [see Fig. 5(b)].

In order to understand how this premelting film thickens, we define a film thickness as the distance between the two points where $\phi(z) = \pm 1/2$. Plugging this condition into the profile Eq. (4) shows that the film thickness presents a logarithmic divergence,

$$h = -\kappa^{-1} \ln t. \quad (5)$$

Whence, it is predicted that a bulk liquid phase will intrude between the solid and vapor phases at the triple point. This is a case of a *complete surface melting* transition, which is akin to the complete wetting transition of a liquid at the solid–vapor interface. The name serves here to emphasize that the premelting film diverges at the triple point and distinguishes the alternative outcome of *incomplete* surface melting, which corresponds to the situation where the premelting film remains finite at the triple point. A key concept is to recognize that the complete surface melting of the solid, viewed as an *equilibrium* phenomenon, can only occur *exactly at the triple point*. Indeed, this is the only thermodynamic state where three equilibrium macroscopic bulk phases can coexist simultaneously.

To gain further insight into the problem, it is convenient to express the excess surface free energy of Eq. (1) implied by the profile $\phi(z)$ of Eq. (4) in terms of the film thickness. Using Eq. (2) together with Eq. (5), this gives exactly to leading order,

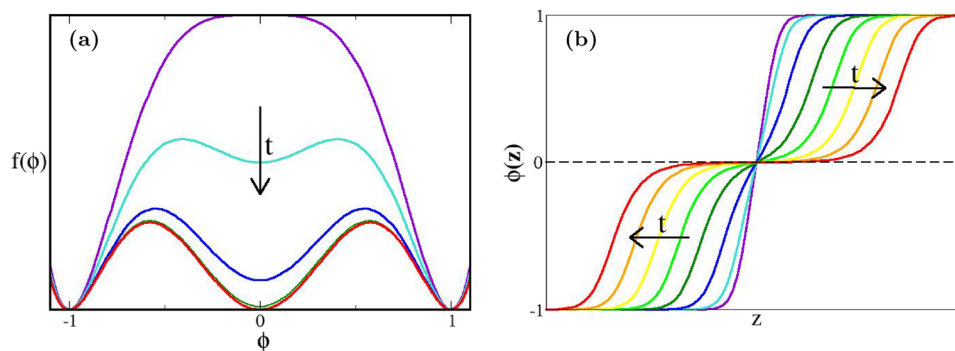


FIG. 5. Toy model of surface premelting. (a) Free energy of a two-phase system approaching the triple point. At high under-cooling, the free energy exhibits two minima of equal height, corresponding to coexistence of the two phases. Along the sublimation line, a metastable minimum gradually emerges as under-cooling decreases. At the triple point, all three minima reach the same free energy. (b) Corresponding order parameter profiles, showing the gradual enrichment of the metastable phase as under-cooling decreases. Lines from violet to red indicate system behavior in order of decreasing under-cooling, as highlighted by the black arrows.

$$\Delta\omega(h) = \gamma_{sl} + \gamma_{lv} + Be^{-\kappa_t h} - \Delta p h, \quad (6)$$

where γ_{sl} and γ_{lv} are the solid–liquid and liquid–vapor surface tensions, B is a positive constant in the scale of the surface tension, κ_t is the correlation length at the triple point, and $\Delta p \propto t$ is the pressure difference between the metastable liquid phase and the coexisting bulk solid or vapor phases.

Another key concept is to acknowledge that $\Delta\omega$ is actually the surface tension of the solid–vapor interface, γ_{sv} , expressed explicitly as a function of its equilibrium film thickness, $h(t)$. By virtue of Eq. (5), it follows that the Young condition for complete wetting is met exactly at the triple point. This serves to emphasize the relation of complete surface melting with the wetting transition. However, importantly, it shows explicitly that at temperatures below the triple point, a solid–vapor interface can exhibit a significant amount of interfacial premelting without it meeting exactly the wetting condition. This result is often not well-appreciated.

Using the above-mentioned results, it is also possible to discuss what precisely can be understood as the onset of premelting.^{31,65,74} The model shows that premelting appears in a *continuous* fashion, as a gradual flattening of the interfacial profile at the interface position $z = 0$, i.e., there is no particular thermodynamic signature in the density profile of the solid–vapor interface signaling a premelting threshold. The best that can be done is to notice that the flattening of the interfacial density is the result of the stabilization of the liquid phase at a metastable minimum of the free energy surface. This is the only feature that can be identified as the theoretical onset of surface premelting. However, the signature of the metastable minimum is hardly detectable in the order parameter profile until the minima of $f(\phi)$ become sufficiently close in energy, i.e., $t \approx 0$. Therefore, for practical matters, the onset cannot be identified until the change in slope and the emerging liquid film at $z = 0$ is above the chosen experimental probe's detection threshold.

IV. WETTING PHYSICS

From this exactly solvable model, the continuous buildup of a liquid film between the solid and vapor phases, and its divergence at the triple point appear as a very general feature of systems

approaching three phase coexistence. It is, therefore, tempting to consider complete surface melting as a universal feature of solid–vapor interfaces.⁷¹ However, the model free energy of Eq. (1) has important limitations.

First, it is based on a small-gradient, long wave-length approximation to the free energy. This misses fine molecular details, such as packing correlations between the repulsive core of the molecules,⁹¹ which can only be accounted with a multicomponent order parameter.^{80,92} Second, it assumes implicitly that the molecular interactions are short ranged in nature. The model is, therefore, not able to account for the role of long-range interactions with algebraic decay such as van der Waals forces.³²

In order to afford a more general description of interfacial premelting, it is convenient to borrow tools of wetting physics.^{32,93} Here, one is concerned with the behavior of an equilibrium solid–vapor interface as the vapor phase approaches liquid–vapor coexistence. For the premelting of a single component system, the condition of solid–vapor coexistence may be achieved by moving along the sublimation line, while the approach to liquid–vapor coexistence may be achieved by heating toward the triple point along this line. Therefore, the framework of equilibrium wetting physics can be fully mapped to the premelting problem *as long* as one moves along the sublimation line (Fig. 4).

Let us then assume a large parcel of ice is in phase equilibrium with an infinite amount of water vapor at temperature T and vapor pressure $p_{sv}(T)$. This implies that, in a fixed sub-volume enclosing the ice–vapor interface, the system is in a grand canonical ensemble, with a chemical potential that is set by the pressure of the water vapor. This observation is convenient because the chemical potential is a scalar that remains constant throughout the system and allows completely characterizing the thermodynamic state.^{94,95} As a bonus, the grand canonical free energy of a bulk system is merely given by $\Omega = -pV$ and is, therefore, the only free energy that can be assessed from knowledge of mechanical properties solely. This allows us to estimate the free energy cost of replacing the bulk vapor with a liquid layer off coexistence as $-\Delta p A h$, where $\Delta p(T, \mu) = p_l(T, \mu) - p_v(T, \mu)$ is the pressure difference between bulk liquid and vapor pressures at the temperature and chemical potential imposed by the water vapor reservoir, and A is the area of the interface.

The surface free energy of the solid–vapor interface per unit surface as a function of the film thickness can then be written as^{56,58,63}

$$\Delta\omega(h) = \gamma_{sl} + \gamma_{lv} + g(h) - \Delta p h, \quad (7)$$

where $g(h)$ is the *interface potential*, which measures the excess surface free energy of the liquid film with respect to its bulk value; while $-\Delta p h$ accounts for the free energy cost of replacing a vapor layer of thickness h by equal amounts of metastable bulk liquid.

The fact that the surface free energy of the premelting film is measured with respect to that of a bulk liquid does not imply that the premelting film is assumed to behave exactly as a liquid. Instead, by definition, $g(h)$ is introduced here as a free energy excess with respect to the bulk liquid so as to account for such differences. In practice, it is found that $g(h)$ becomes extremely small for films of barely one nanometer thickness.⁶⁰ This shows that the bulk free energy of the liquid phase is indeed a good reference state for measuring the free energy of the film and justifies the name of “*quasi-liquid layer*” that is often employed in place of “premelting.”

In addition to the quantitative measure of free energies, the role of $g(h)$ is to describe the propensity of the premelting film to grow as three phase coexistence is approached. By definition, $g(h) \rightarrow 0$ as $h \rightarrow \infty$. Therefore, a monotonously decaying trend of $g(h)$ implies that the state of minimal surface free energy corresponds to a bulk liquid film formed on the ice surface, such that the minimum $h \rightarrow \infty$. On the other hand, when $g(h)$ exhibits an absolute minimum at finite thickness, it corresponds to a case where the surface free energy is smaller for h finite than $h \rightarrow \infty$, i.e., such that the extent of premelting remains limited and there is, therefore, the absence of complete surface melting.

By comparing Eq. (7) with Eq. (6), we see that for the exactly solvable model of Sec. III, $g(h) = Be^{-\kappa_l h}$ is a monotonously decaying function corresponding to a case of complete surface melting.

Away from the triple point, with $\Delta p h$ finite, the interface potential determines the equilibrium film thickness via the minimization of Eq. (7) with respect to h . This leads right away to

$$\Pi(h_e) = -\Delta p, \quad (8)$$

where $\Pi = -dg(h)/dh$ is the *disjoining pressure* as introduced by the Russian school of colloidal science.^{96–98} In the geophysics community, $\Pi(h)$ is often known as the thermo-molecular force.^{29,99}

This result shows that the film thickness may be considered as depending on the single variable Δp , which characterizes the approach of the vapor to liquid–vapor coexistence. Since the vapor at pressures close to the sublimation line behaves virtually as an ideal gas, $\Delta p(T)$ can be accurately approximated to $\Delta p(T) = \rho_l k_B T \ln p_{sv}(T)/p_{lv}(T)$, where ρ_l is the density of the bulk liquid, k_B is Boltzmann’s constant, and p_{sv} is the coexistence vapor pressure over $\alpha = s, l$.^{56,58} This shows explicitly that the equilibrium premelting thickness need not be measured strictly in terms of a distance away from the triple point. Rather, it is dictated by the distance of the sublimation line to the metastable prolongation of the condensation line. In water, these two lines run very close together all the way down to 0 K, an observation that could explain the unexpected report of ice premelting at very low temperature.¹⁰⁰ Assuming Clausius–Clapeyron behavior for the vapor

pressures, this equation simplifies to $\Delta p = \rho_l \Delta h_{sl} (T - T_t)/T_t$, where Δh_{sl} is the enthalpy of melting. The result is quantitatively correct down to 10 °C but remains qualitatively correct for at least –50 °C.⁶³

Unfortunately, the interface potential is usually not known exactly. Under these circumstances, Eq. (8) is not a predictive tool, but rather, a practical means for obtaining information of the related disjoining pressure from knowledge of the equilibrium film thickness.^{56,58,63,64} Thus, if one has reliable measurements of h_e as a function of temperature, together with computations of Δp from bulk thermodynamics, Eq. (8) provides the disjoining pressure right away.^{56,58,63}

The reader might wonder what is the point of mapping h_e to $\Pi(h)$ via Δp , if the experimental measurements right away provide h_e as a function of temperature, which is a simpler variable. The answer is that once $\Pi(h)$ is known, Eq. (8) shows that h_e is a natural function of the single variable $\Delta p(T, p)$. This allows predicting equilibrium thickness for arbitrary thermodynamic states from knowledge of a set of measured states. For the case of surface premelting, knowledge of $\Pi(h)$ obtained for equilibrium states along the sublimation line, allows predicting the properties of premelting films in moderately out-of-equilibrium conditions of arbitrary temperature and pressure, as we shall discuss later in Sec. IX.⁵⁸

This concept may be easily tested without invoking out-of-equilibrium conditions for the closely related case of interfacial premelting, where premelted equilibrium states can now occur for

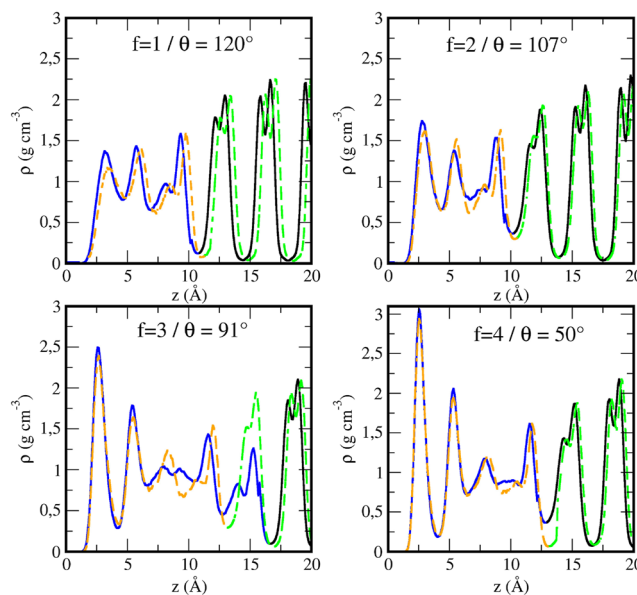


FIG. 6. Characterization of film structure on substrates of different wettability as indicated by the contact angle, θ . Interfacially premelted films in widely different conditions but equal disjoining pressure are very similar. The density profiles indicated by the dashed lines were obtained at $T = 266$ K and $p = 1$ bar; the ones in a continuum line are obtained at $T = 262$ K and $p = 400$ bars. The region of density profiles with a majority of liquid-like molecules is depicted in either orange or blue; that where the majority is formed by solid-like molecules is indicated by green and black. Reproduced with permission from Baran *et al.*, J. Phys. Chem. C **129**, 4614–4631 (2025). Copyright 2025 American Chemical Society.

arbitrary values of temperature and pressure.⁶⁴ In this context, Eq. (8) allows predicting equilibrium film thicknesses at arbitrary thermodynamics states from measurements of film thickness along a single isobar. This shows that the natural measure of distance away from a point in the melting line (T_m, p_m) is neither $T - T_m$, nor $p - p_m$, but the pressure difference $\Delta p(T, p)$. In a recent study, it was shown that this mapping also holds for the prediction of the interfacial structure of the premelting film, as illustrated in Fig. 6.⁶⁴

V. SURFACE INTERMOLECULAR FORCES

The other important reason why wetting physics formalism can be proof as a formidable benchmark for understanding ice premelting is that the interface potential $g(h)$ has its origin in molecular interactions. Therefore, one can use a large body of well-understood results on the theory of intermolecular forces^{101,102} to constrain $g(h)$ and make important qualitative statements about its behavior.⁶⁰

The first simple insight one can make is that the interface potential of a premelting film may be divided into short and long range contributions additively as

$$g(h) = g_{sr}(h) + g_{vdw}(h). \quad (9)$$

Here, $g_{sr}(h)$ is a short-range contribution with exponentially fast decay, which results from packing correlations,^{98,103–105} short range attractive interactions,^{96,101} and finer effects such as renormalizable surface fluctuations.^{98,103} In addition, $g_{vdw}(h)$ is a long-range contribution that stems from the van der Waals interactions and decays in algebraic fashion.^{101,106–108}

A. Packing and layering effects

Borrowing tools from liquid state theory, the short-range contribution is expected to obey the following equation:^{98,103–105}

$$g_{sr}(h) = B_2 e^{-\kappa_2 h} - B_1 e^{\kappa_1 h} \cos(q_o h - \alpha), \quad (10)$$

where B_i are positive coefficients, κ_i are inverse decay lengths in the scale of the molecular diameter, q_o is a wave-vector which sets the pitch of the packing correlations, and α is an unknown phase.

In this expression, the first term is a monotonous decaying function which reduces the film's free energy as h increases. Accordingly, this term promotes surface melting, as predicted by the toy model of Sec. III and previous studies.^{71,103} To a higher order of approximation, however, it is required to account for the packing correlations of the water molecules, which produce next to leading order contributions of damped oscillatory form.⁹¹ At the mean field level, the presence of this term suggests that the interface potential could exhibit local minima and generate a sequence of layering transitions.¹⁰³ At a higher level of approximation, surface capillary waves can renormalize the mean field expectation and suppress the predicted layering transitions.^{98,103}

Figure 7 shows an example for the disjoining pressure curve $\Pi = dg/dh$ of the prism face as obtained from computer simulations using the TIP4P/Ice model of water.¹⁰⁹ The curve is computed by first measuring the equilibrium premelting thickness as a function of temperature [Fig. 7(a)], mapping this to the corresponding value of $\Delta p(T)$, as obtained accurately from thermodynamic integration, and plotting $\Delta p(T)$ as a function of $h_e(T)$ [Fig. 7(b)].⁵⁶

The results show a monotonous decrease in the disjoining pressure. Therefore, the amplitude of the oscillations predicted in Eq. (10) is too small to allow for the appearance of minima of the interface potential for films of less than several nanometers. In this fluctuation dominated regime, the oscillations predicted in the mean field approximation are washed away, and there is no longer a “layering transition” in the thermodynamic sense.^{98,103} However, the signature of underlying mean field transitions can survive as a flattening of the interface potential within given ranges of film thickness. In the computer simulations of Ref. 56, these rounded transitions could be observed as a marked oscillatory behavior of the inverse interfacial susceptibility [inset of Fig. 7(b)], which can be measured as the second derivative of the interface potential.

Interestingly, experimental studies using sum frequency generation (SFG) spectroscopy observed a stepwise blue shift in the OH stretch signal, which was interpreted as a hint of layer by layer growth at the basal surface of ice at about 257 K.^{72,110} According to the computer simulations, this signal could correspond to enhanced surface fluctuations at a rounded layering transition, but the current

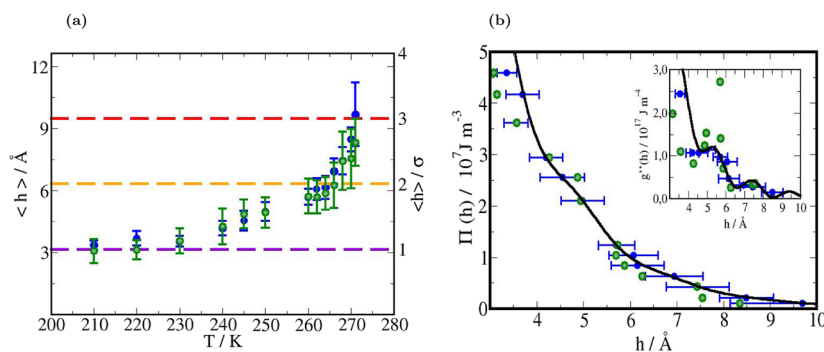


FIG. 7. Calculation of disjoining pressures. (a) Film thickness measured at solid–vapor equilibrium for the primary prism face as a function of temperature. (b) The results are mapped to the corresponding Laplace pressure difference, Δp , between bulk water and vapor at the same chemical potential to produce a disjoining pressure isotherm. The symbols are results from computer simulations for the TIP4P/Ice model. The lines are a fit to the asymptotic result of Eq. (10). The inset shows inverse susceptibilities as calculated from the simulations (symbols) and predicted from the second derivative of the interface potential (lines), displaying regions of enhanced surface fluctuations. Reproduced with permission from Llombart *et al.*, Phys. Rev. Lett. **124**, 065702 (2020). Copyright 2020 American Physical Society.

simulation results suggest that this is not a strict thermodynamic transition. Unfortunately, surface phase transitions in the fluctuation dominated regime exhibit strong system size effects, and further simulations with larger systems might be necessary to settle the issue.

To summarize, all computer simulation studies support the emergence and gradual growth of premelting films, with a film thickness of about 1–2 nm 1 K away from the triple point.^{55–58,63,69,71} A detailed analysis suggests that in this range, there are enhanced surface fluctuations on growing from one bilayer to the next, but not a thermodynamic layering transition of the premelting film in the thermodynamic sense. Extrapolation of the fits beyond the range of film thicknesses achieved in simulation suggest that the oscillatory term of Eq. (10) could in principle lead to very shallow minima of the interface potential for the basal face,^{56,63} but not for the prism face. However, the resulting minima are so shallow that they are very likely to vanish due to surface capillary waves. Under this assumption, the short-range contribution of the interface potential is a monotonously decreasing function, which effectively promotes a situation of complete surface melting for both the basal and prism faces, in a way similar to the prediction of the toy model of Eq. (6).

B. van der Waals forces and the absence of complete melting

The above-mentioned discussion suggests that, as long as short-range forces are concerned, ice should exhibit complete surface melting. However, as shown in Eq. (9), the interface potential also contains contributions that result from the van der Waals interactions between molecules. These forces have an algebraic decay, so that, for sufficiently thick premelting films they will dominate over the short range forces, which decay exponentially fast. Therefore, the ultimate fate of the interface potential for thick wetting films will be dictated, not by the short range forces, but by the weak van der Waals forces.

Unfortunately, it is not possible to directly assess the role of van der Waals forces by means of computer simulations for two reasons. The first and most important is that the van der Waals forces in computer simulations are cutoff beyond a truncation radius of about one nanometer, and this has been no exception in the study of ice premelting. The second is that, even if the interactions were calculated effectively, say, as in a lattice sum,¹¹¹ the accuracy required to measure the effect of such forces would be likely prohibitive. Among other things, reaching a thick film beyond the nanometer requires approaching the triple point in the sub-Kelvin scale very carefully, but in practice, the uncertainty in the triple point of usual force fields is on the scale of 1–2 K.

Fortunately, the nature of surface van der Waals forces is rather well understood and allows constraining the interface potential without the need of involved computer simulations. Indeed, borrowing the tools of surface physics, we can describe the role of van der Waals forces on a wetting film by means of the following equation:^{106,107,112}

$$g_{vdw}(h) = -\frac{A(h)}{12\pi h^2}, \quad (11)$$

where $A(h)$ is the so called Hamaker constant. The full account of the h -dependent Hamaker constant requires very involved quantum-electrodynamic considerations,¹⁰⁷ but to the accuracy that can be achieved in current experiments, we can simplify the problem

to the range of h less than 100 nm, where $A(h)$ depends only weakly on the film thickness.⁶⁰

In this situation, corresponding to $A(h \rightarrow 0) = A$, the van der Waals forces are fully dominated by high-frequency dipole fluctuations of the electronic degrees of freedom. These, in practice, are modeled in computer simulations and most theoretical approaches by a dispersive London term between water molecules at the pair level, which decays as $-C_{vdw}/r^6$. Such contributions can be summed up in the pair additive approximation of Hamaker,¹¹³ which has been revisited more recently under the framework of (thermodynamic) density functional theory of wetting films.^{32,108,114} For the special case of surface premelting, the result reduces to^{53,60,63}

$$A = \pi^2 C_{vdw} (\rho_v - \rho_l)(\rho_s - \rho_l). \quad (12)$$

For most substances, the density of the solid phase is larger than that of the liquid phase and the Hamaker constant is negative. In such case, the van der Waals contribution to the interface potential becomes positive and favors complete surface melting. However, a well-known anomaly of water is that the density of ice is smaller than that of liquid water. This means that the Hamaker constant ruling ice premelting is positive, a fine detail that was already noticed by Nozières.¹¹⁵ The implication is that the van der Waals forces take a negative value and inhibit the formation of a thick wetting film. So, whatever is the behavior of the short-range contribution, and whether it adopts minima due to the oscillations of the packing term or not, the contribution of the van der Waals forces is to inhibit the growth of the premelting film. As a result of this balance, the interface potential must have a minimum at intermediate distances, leading to a case of incomplete surface melting. Furthermore, notice that this behavior is generic and arises from the nature of the bulk ice and water phases, so that, to leading order, it does not depend on the nature of the exposed surface plane.

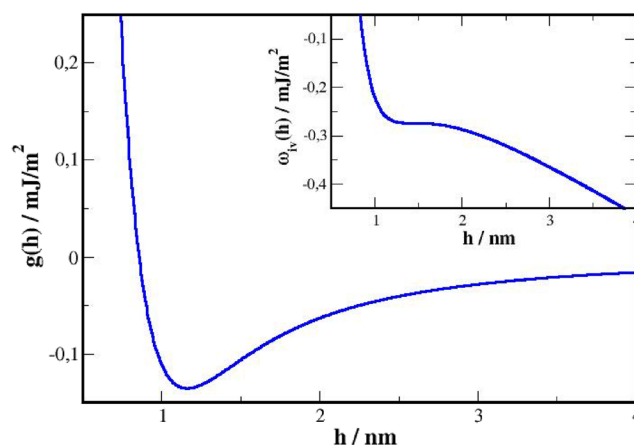


FIG. 8. Minimal model of the interface potential of ice premelting as obtained from a single decaying exponential function and a constant positive Hamaker constant. The minimum of the interface potential leads to an equilibrium premelting film thickness at the triple point of about 1 nm. Inset: Away from the triple point, the surface free energy of Eq. (7) picks up the $-\Delta\phi h$ term, until the minimum vanishes at a wetting spinodal point. Reproduced with permission from Luengo-Márquez *et al.*, *J. Chem. Phys.* **157**, 044704 (2022). Copyright 2022 AIP Publishing LLC.

C. A minimal model of ice premelting

Based on the discussion in Secs. V B and V C, a minimal model of ice premelting needs to account for the growth of the premelting film due to short-range structural forces and the inhibition of further growth by long-range van der Waals forces. Ignoring the small oscillatory term, such behavior can be described with the following interface potential:

$$g(h) = Be^{-\kappa h} - \frac{A}{12\pi h^2}. \quad (13)$$

The result obtained by parameterization to data for the primary prism face (Fig. 8) shows a shallow minimum at a thickness of barely one nanometer, which inhibits complete surface melting under conditions of solid–vapor coexistence.⁶⁰ However, as soon as the system is moved away from the sublimation line, Δp in Eq. (9) can increase sufficiently that the overall free energy minimum vanishes completely at a *wetting spinodal point* (Fig. 8, inset). Eventually, this can lead to the complete wetting of the system, as discussed in Sec. IX.

D. Digression: Into the realm of quantum electrodynamics

The minimal model discussed above describes the qualitative behavior of ice premelting for film thicknesses less than hundreds of nanometers. Beyond this range, intermolecular forces become dominated by very subtle quantum electrodynamic effects that are usually ignored altogether.¹⁰¹ Indeed, as emphasized in Eq. (11), the Hamaker “constant” is actually not a constant, but displays a very rich and complex behavior as the thickness of the premelting film becomes large. The full quantitative behavior of $A(h)$ can only be determined within the framework of Dzyaloshinskii–Lifshitz–Pitaevskii (DLP) theory,¹¹² which has been used extensively by Boström and collaborators to address a number of related problems in ice premelting.^{59,117–121} Unfortunately, DLP theory is not amenable to an easy qualitative interpretation and requires involved numerical calculations.¹⁰⁷ For this reason, a simple analytical approximation was worked out recently solely for this purpose.⁵⁴

The rationale here is that van der Waals forces emerge from dipole fluctuations at all frequencies of the spectral range. The Hamaker function $A(h)$ is, therefore, a sum of contributions of all frequencies. In practice, for films smaller than a hundred nanometers or so, the Hamaker function is fully dominated by high-frequency dipole fluctuations and is approximately given as⁵⁴

$$A_{\omega>0}(h) = \frac{3\hbar c v_\infty}{32\sqrt{2}} \frac{n_l}{n_s^2 + n_l^2} \frac{n_v^2 - n_l^2}{n_s^2 + n_l^2} f(h), \quad (14)$$

where $\hbar$ is Planck’s constant, c is the speed of light, $v_\infty \approx 0.01 \text{ nm}^{-1}$ is a wave-number corresponding to the principal electronic transition of water, n_i are refractive indices in the visible, and finally, $f(h)$ is a crossover function, which remains close to unity for all $h v_\infty \ll 1$. In this regime of small h , the above-mentioned equation accounts for correlated electronic dipole fluctuations as dictated by the material’s refractive indices. As an anomaly of water, the refractive index of the solid phase is smaller than that of the liquid phase, $n_s < n_l$, which results in a positive Hamaker constant, exactly as predicted by Eq. (12).

However, as the film thickness gradually increases, quantum-electrodynamic effects gradually suppress the contributions from high-frequency dipole fluctuations, leading to the vanishing of the crossover function approximately as⁵⁴

$$f(h) = \frac{1}{v_\infty h} \left[\left(2 + \frac{3}{2} v_T h \right) e^{-v_T h} - (2 + v_\infty h) e^{-v_\infty h} \right], \quad (15)$$

where v_T is a thermal wave-number in the micrometer scale. From this equation, it is possible to assess easily that for $h v_\infty \ll 1$, $f(h) \approx 1$, which justifies the Hamaker approximation for sufficiently thin films. When the film thickness increases such that $h v_T < 1 < h v_\infty$, $f(h)$ gradually decreases as $1/h$, leading to the regime of retarded Casimir interactions. Finally, when $h v_T > 1$, the crossover function vanishes exponentially fast, leading to complete suppression of high-frequency contributions to the intermolecular forces. In this little appreciated regime, the Hamaker function now becomes dictated by static contributions alone and is given by

$$A_{\omega=0} = \frac{3}{4} \frac{(\epsilon_s - \epsilon_l)(\epsilon_v - \epsilon_l)}{(\epsilon_s + \epsilon_l)(\epsilon_v + \epsilon_l)} k_B T, \quad (16)$$

where, relative to Eq. (14), the dipole fluctuations are now described in terms of the static dielectric constants, ϵ_i . Since in this case $(\epsilon_l - \epsilon_s) < 0$, the change from high-frequency dominated to low-frequency dominated behavior leads to a sign reversal of the Hamaker function, which changes from being positive for h small, as anticipated by Eq. (12), to being negative for h larger than the micrometer scale. This means that $A(h)$ shifts from inhibiting surface melting at $h < \mu\text{m}$, to promoting surface melting at large $h > \mu\text{m}$.^{60,122}

In practice, whether one considers the simple description of Eq. (12) or the complex $A(h)$ function from DLP theory, the interface potential exhibits an absolute free energy minimum at intermediate film thicknesses, so that the equilibrium state of the ice surface at the triple point corresponds to a case of incomplete surface melting. If, however, for whatever reason, a large fluctuation moves the film thickness into the range where $A(h)$ has become negative, the surface intermolecular forces could lead the system to surface melt spontaneously.

Elbaum and Schick pioneered the use of DLP theory as a tool for the study of ice premelting.¹¹⁶ Their results anticipated that van der Waals forces inhibit ice premelting for films in the nanometer scale. Unfortunately, they used a poor parameterization of the dielectric functions of water and ice and predicted erroneously a negative Hamaker constant promoting surface premelting as $h \rightarrow 0$. To add to this confusion, Limmer and Chandler approximated the Hamaker constant at small h using the static contribution that is relevant only at large h , but predicted the correct behavior due to an error in the sign convention in Eq. (11).⁷¹

The problem has since then been revisited, and new, more reliable parameterizations of the dielectric response confirm that the Hamaker function is positive in all the range from $h = 0$ to the micrometer scale as described above.^{60,122} Unfortunately, most of the work on DLP performed before 2020, including also work by myself,¹¹⁹ has relied on the parameterization of Elbaum and Schick and could be unreliable for premelting films smaller than the nanometer.

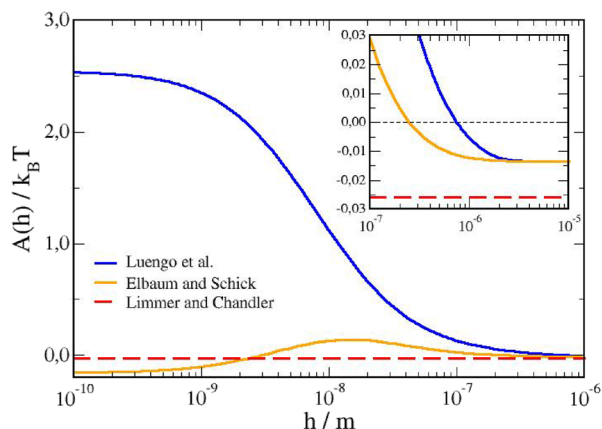


FIG. 9. Hamaker functions as predicted by DLP theory. The blue lines represent results for $A(h)$ as calculated from an accurate parameterization of the dielectric response of water and ice by Luengo-Márquez *et al.*⁶⁰ For small h , $A(h)$ is positive, as predicted by Eq. (12), and inhibits surface melting. For large h , $A(h)$ changes sign, becomes negative, and favors surface melting. The inset shows the sign reversal occurs at about 760 nm. The orange lines represent results from Elbaum and Schick, which suffer from a poor parameterization of the dielectric response.¹¹⁶ The sign of $A(h)$ is correct for films of thickness larger than 3 nm. The red dashed lines represent results from Limmer and Chandler.⁷¹ Adapted from Luengo-Márquez *et al.*, J. Chem. Phys. **157**, 044704 (2022). Copyright 2022 AIP Publishing LLC.

Figure 9 shows the full h dependence of the Hamaker function with a recent reliable parameterization of the dielectric properties⁶⁰ and compares it to previous calculations.^{71,116} The results of Luengo-Márquez *et al.* are in qualitative agreement with Fiedler *et al.*¹²² (not shown), but Boström *et al.* have ever since opted for the parameterization of dielectric properties presented in Ref. 60.

VI. WATER DROPLETS ON ICE

As discussed above, the theoretical considerations show that pure ice does not exhibit complete surface melting. However, the experimental measurements of premelting thickness are far less clear and often appear to favor the opposite conclusion, as evidenced from the positive slopes of $h(T)$ in a log-log plot (Fig. 2). Yet, for a long time, there has been compelling experimental evidence that water does not completely wet the ice surface. This evidence comes from the recurrent observation of water droplets formed on its surface, first reported by Knight.^{33,35}

The presence of water droplets has ever since been confirmed by a number of studies through the years,^{18,34,36} including photographs of water droplets on the basal surface of hexagonal ice micro-crystals³⁷ and large millimeter drops on polycrystalline ice.^{43,44,123,124} However, it was not until the past ten years that the quality of the reported pictures has allowed us to appreciate this finding widely.^{38,41,42,46}

According to Young's equation, the surface tension of a solid-vapor interface is related to the equilibrium contact angle as $\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta_e$. This means that droplets with a finite contact angle, $\theta_e > 0$, have a surface tension less than $\gamma_{sl} + \gamma_{lv}$ and do not meet Young's condition of complete wetting. Therefore, the observation of water droplets implies necessarily a case of incomplete surface melting.

How can we then reconcile the experimental observations of incomplete wetting with the reported divergence of premelting film thickness as temperature approaches the triple point?

The key point, as suggested by Sazaki and collaborators,^{38,41} is that conventional techniques such as x-ray dispersion,²⁰ spectroscopy,^{24,25} or ellipsometry,¹⁶ do not allow telling whether the water-like signal of the experimental probe is due to the continuous growth of a uniform liquid layer or due to the spatially heterogeneous spreading of liquid droplets. In fact, studies by Elbaum *et al.*¹⁸ are likely the only ones to have combined simultaneously a reflectometer to measure film thickness and an interference microscope to visualize the ice surface. In their experiments, they could confirm that close to the triple point, the gradual growth of the premelting film thickness was eventually followed by the formation of condensed water droplets, which produced an apparent diverging film thickness.¹⁸ This shows that the use of conventional techniques becomes unreliable in the close neighborhood of the triple point. The reason is that the condensation and sublimation lines are very close to each other and eventually meet exactly (Fig. 4). Therefore, it suffices a minimal local fluctuation for the vapor to become supersaturated over water and move the solid-vapor interface away from equilibrium conditions. This results in vapor condensation and the appearance of inhomogeneities and instabilities. Under such conditions, the ice-vapor interface no longer corresponds to an equilibrium uniform state and the measured water-like signal can no longer be trusted as a measure of the equilibrium film thickness.

The take away message from the experimental side is that (1) experimental probes of film thickness confirm the formation of liquid-like layers on the ice surface and (2) contact angle measurements confirm that ice exhibits only incomplete surface melting. This scenario is consistent with observations from computer simulations and agrees with the picture that emerges from the physics of intermolecular forces,^{53,58,60,115,116,122} although a full understanding of the origin of the incomplete surface melting has emerged only recently.^{56,60}

Paradoxically, the experimental observation of liquid droplets on the ice surface has often been interpreted as illustrating the complete lack of equilibrium ice premelting,^{38,41–43,45,46,123} which is obviously at odds with experimental measurements of film thickness.^{18,20,25,27} This conflict emerges from a misunderstanding of Young's equation, where it is often assumed that γ_{sv} accounts for the surface tension of a *bare* interface between the unrelaxed ice surface and its vapor. At high temperature, the *equilibrium* solid-vapor interface can exhibit a significant amount of surface disorder consistent with the existence of a premelting film and γ_{sv} may become significantly different from the expected value for a perfect unrelaxed interface obtained by cleavage of the solid phase.

The key issue here is to realize that the surface free energy of Eq. (7) becomes the exact solid-vapor surface tension when evaluated for the equilibrium film thickness, h_e , as dictated by Eq. (8). Indeed, replacing the equilibrium condition into Eq. (7) must provide the ice-vapor surface tension by definition, whence

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} + g(h_e) + \Pi(h_e)h_e. \quad (17)$$

Akin to the result of the exactly solvable model, Eq. (6), this equation shows explicitly that the ice-vapor interface in thermodynamic equilibrium can exhibit an adsorbed liquid film of finite thickness

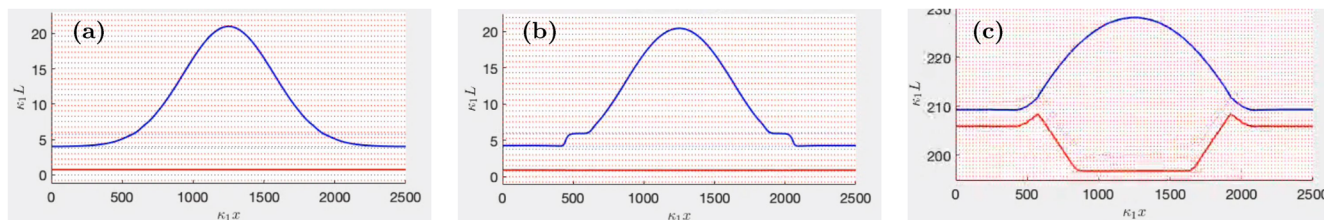


FIG. 10. Mesoscopic modeling of water droplets on ice. The figure shows the time evolution of a liquid droplet deposited under conditions of supersaturation over water (kinetic condensation line). The blue line depicts the liquid/vapor surface, while the red line describes the position of the ice/water surface. (a) Notice that the drop sits on top of a premelting film. (b) Transiently, droplets governed by an interface potential with two minima can exhibit a second film thickness next to the rim of the drop. (c) For sufficiently long times, as water vapor condenses, the surfaces elevate by condensation and ice gradually freezes within the drop. Reproduced with permission from Sibley *et al.*, Nat. Commun. **12**, 239 (2021). Copyright 2021 Author(s), licensed under a Creative Commons Attribution 4.0 License.

without necessarily meeting the Young condition for wetting. Particularly, equating Eq. (17) to Young's condition for a droplet of liquid on a solid substrate, one gets an equation for the contact angle at the triple point,

$$\cos(\theta_e) = 1 + \frac{g(h_e)}{\gamma_{lv}}. \quad (18)$$

This explicitly provides the contact angle of a droplet formed atop a premelting film of equilibrium thickness h_e [cf. Fig. 10 for the numerical calculation of a water droplet profile consistent with Eq. (18)].

This now shows again that observation of water droplets on the ice surface found in many different experiments over the years^{18,33–37,39,42–44} need not rule out the presence of an equilibrium wetting film of finite thickness below the liquid droplet, as occasionally assumed.^{38,41–43,45,46,123}

The confusion is likely to result from an alternative convention for the surface free energy which is often found in the literature,^{29,65}

$$\Delta\omega(h) = (\gamma_{sl} + \gamma_{lv} - \gamma_{sv})I(h) + \gamma_{sv} - \Delta\phi h. \quad (19)$$

Comparing this result with Eq. (7), one can easily relate $I(h)$ with the interface potential, $g(h)$, whereupon, both results are fully equivalent. However, assuming that $I(h) = 0$ for $h = 0$ from the outset^{29,65} leads to the misleading interpretation that the solid–vapor interface need be understood as a bare ice–vapor interface with no premelting whatsoever. Actually, the above-mentioned equation is completely equivalent to Eq. (7), with the understanding that $I(h) = 0$ holds not for $h = 0$, but for $h = h_e$.

It is noteworthy that the calculations of interface potentials as described above predict a shallow minimum at an equilibrium film thickness slightly above $h_e \approx 1$ nm, with $g(h_e)$ in the scale of -10^{-1} mJ/m².^{60,63} Using Eq. (18), this shows that atop the premelting film of nanometer thickness, a water droplet with contact angles ranging from 2.5° to 3.5° can form. This appears to be in rather fair agreement with observation of water droplets formed spontaneously by condensation or melting on pristine ice facets under very nearly equilibrium conditions, which are reported to fall in the range of 0.6°–2.3°.^{18,34,42,46,65}

Intiguously, experiments performed with macroscopic droplets on the order of a 1 mm radius provide significantly larger contact angles.^{33,43,44,123} In two recent experiments,^{43,44} liquid water droplets above the melting point were gently deposited on ice and the relaxation process was followed carefully until full arrest

of the contact line. For ice at a temperature close to its melting point, these experiments consistently reported contact angles of 12°, in agreement with the early observation of Knight.³³ However, the deposition process here is an extremely complex problem in fluid mechanics, as the droplets are formed under conditions of significant temperature and chemical potential gradients between the outer atmosphere, the water droplet, and the underlying ice. Therefore, despite that the relaxation process was carefully followed and checked for the attainment of *mechanical equilibrium*, it is unlikely that this corresponds to the conditions of experiments where spontaneous droplet formation was observed by gentle condensation of the vapor at nearly *thermodynamic equilibrium*.^{18,34,46}

A possible hypothesis is that the arrest of the contact line in the macroscopic experiments is the result of some yet not fully understood non-equilibrium process related to the pinning of the contact line due to freezing.¹²⁴ Be as it may, a striking observation of these experiments is the increase in contact angle as the temperature of the ice surface decreases,^{43,44} reaching an amazing value of 150° at 180 K.⁴³ Further work on wetting dynamics and capillarity is needed to understand this behavior and its relation to the low temperature ice surface.¹²⁵

VII. IS THE OBSERVATION OF SURFACE STEPS CONSISTENT WITH ICE PREMELTING?

From the above-mentioned discussions, there appears to emerge a consistent picture indicating that ice does not completely surface melt, but it does build up a significant premelting film attaining the scale of the nanometers at the triple point.

This view arises from the critical analysis of experimental measurements of premelting film thickness,^{18,20,24,25,27} experimental observation of water droplets,^{18,34,37,39} computer simulations,^{55–57,68,69,71,74,78} and theoretical considerations.^{53,56,60,63}

However, this interpretation is yet to meet an important challenge.

In experiments performed by the Hokaido team, atomically smooth ice surfaces were prepared by epitaxial deposition from pure water vapor. This careful sample preparation, together with advanced optical microscopy, have allowed in the past decade to observe (and report) the ice surface with unprecedented detail.^{39,42,46} Particularly, it was shown that the basal ice surface at exceedingly small supersaturation exhibits elementary steps in perfect agreement with the expected lattice structure and results in crystal growth by

terrace spreading or spiral growth.^{39,42,46} However, the general wisdom in crystal growth theory is that this kind of *smooth* surfaces are in a highly ordered, low temperature state.^{126–129} The question then arises that how can one reconcile the step formation expected for a highly ordered surface, with the highly disordered state expected for a premelted surface? Sazaki and collaborators interpreted their own observation as evidence for the lack of premelting layers on the ice surface, most noticeably, in Ref. 41, but have thereafter sometimes stand by,⁴⁶ sometimes moderated this claim.^{65,130}

However, a recent combination of simple models, borrowed from crystal growth theory and capillary wave theory, shows that the observation of significant premelting and step formation are both mutually acceptable and reconcilable.^{52,53,58}

A. Healing distance of a surface

Before embarking into the details, however, it is worth digressing on the healing distance, a concept that is important in the theory of wetting on patterned substrates.¹³¹ The question here is whether a thin film deposited on a patterned substrate will “heal” the holes left by the pattern and lead to a fully flat liquid–vapor surface or, alternatively, whether it will adapt to the substrate and lead to a liquid–vapor surface that reveals the shape of the pattern. The decision depends on a balance between the free energy cost of increasing the surface area by following the pattern and the free energy cost of healing the surface by changing the preferred equilibrium film thickness. The former cost is governed by the liquid–vapor surface tension, γ_{lv} , while the latter is controlled by the interface potential, $g(h_e)$. The result emerging from the theory of wetting is that there is a relevant healing distance, or correlation length, $\xi = \sqrt{\gamma_{lv}/g''(h_e)}$ [with g'' the second derivative of $g(h)$ with respect to h], which dictates the film’s decision. If the surface tension is very large, ξ is large, and the film fills all holes with lateral dimension smaller than the healing distance to save the cost of creating extra surface area (as the film’s height remains correlated over length scales larger than the pattern relief); however, if the interface potential is strong, ξ is small, and the liquid film will follow the shape of the pattern to save the free energy cost of perturbing the film thickness away from its equilibrium value (as the pattern relief is now of a greater scale than the film height correlation length).

It perspires that, for liquid films with a healing distance smaller than the typical distance between neighboring steps, one could envisage a premelting liquid film that would adapt to the steps. Optical observation of the ice surface would then exhibit traces of the steps created on the buried solid surface despite the presence of a highly disordered premelting film atop.

Using our data for g'' shown in Fig. 7, together with the surface tension of liquid water, we find that $\xi \approx 1$ nm for the basal face approaching T_t . This is somewhat larger than the scale of a step, ca. one molecular diameter, but much smaller than the typical distance between steps observed in experiment. This suggests that a premelting film could indeed faithfully mimic the shape of the solid ice underneath, so that the apparent conflicting observations of ice premelting and surface steps can be reconciled.

B. Smooth and rough interfaces

The discussion above is appealing, but it does not explain why and when does a crystal plane show steps and terraces as does the

basal plane of ice crystals or whether such surface steps can be observed in a premelted interface.

To understand this, it is required to make the important distinction between smooth and rough crystal interfaces.^{127,129,132,133} Smooth interfaces are those that are bound to the underlying crystal lattice. They exhibit perfectly terminated crystal planes and show limited surface height fluctuations of the order of one or a few lattice spacings. On the other hand, rough interfaces unbind from the underlying crystal lattice and exhibit very large surface fluctuations, very much as in fluid interfaces. This apparently sophisticated distinction is crucial for the behavior of a crystal. In the absence of surface defects, smooth surfaces can only grow by a slow activated process of two dimensional nucleation, where a small critical terrace is formed and then spreads horizontally along the surface. On the other hand, rough surfaces can grow without an activation barrier in a continuous fashion and exhibit growth rates that are linear in the saturation. As temperature increases, smooth surfaces gradually become disordered and can become rough across a so called, roughening transition. This transition was first conjectured in a famous paper by Burton, Cabrera, and Frank in the late 1950s.¹³⁴ However, the fine details were not understood until the late 1970s,^{135–137} where it was fully characterized and shown to be a fluctuation dominated phase transition of the Kosterlitz–Thoules type.^{127,129,133}

Since both roughening and premelting are surface disorder phenomena, the question then is, whether the roughening transition must necessarily occur before the appearance of significant surface premelting or not. If this were the case, the observation of steps on the basal plane would imply that there can be no premelting indeed, as suggested by Sazaki *et al.*^{40–42} However, simple considerations suggest that this need not be the case. Indeed, at the ice–water interface, the basal plane is thought to remain smooth up to the triple point. This expectation is supported by evidences of two dimensional nucleation of ice from its melt,¹³⁸ the visual observation of elementary steps in vicinal planes,¹³⁹ and the indication of layer-wise growth in molecular dynamics simulations.^{140–142} Since the ice–water interface can be considered as a limiting case of a premelted surface with a film of infinite thickness, one can then expect intuitively that a buried basal surface under a thin premelting film should also be able to remain smooth up to the triple point.

In order to substantiate this claim, it is required to take explicitly in consideration the complex structure of the premelted interface. This can be achieved by describing the premelted layer in terms of an ice/water surface, $z_{sl}(\mathbf{x})$, and a water/vapor surface, $z_{lv}(\mathbf{x})$, which bound the layer in between the bulk ice and vapor phases at arbitrary points $\mathbf{x}$ in a flat horizontal reference plane parallel to the interface (Fig. 3).^{52,53,57}

The free energy cost of a given realization of the ice/water surface profile may be assessed by means of the sine–Gordon Hamiltonian as¹²⁷

$$\Delta\Omega_{\text{SG}} = \int d\mathbf{x} \left(\frac{1}{2} \tilde{\gamma}_{sl} (\nabla z_{sl})^2 - u \cos \left(\frac{2\pi}{b} z_{sl} \right) \right), \quad (20)$$

where the first term accounts for the free energy cost of increasing the surface area, as dictated by the solid–liquid surface stiffness (for practical matters, the difference between a stiffness coefficient $\tilde{\gamma}$ and the corresponding surface tension γ can be ignored here), while the second term penalizes the deviations of the ice/water surface away

from the underlying lattice spacing, b , with u being a lattice strength parameter.

For a simple solid–liquid interface, the distinction between rough and smooth interfaces can be made quantitatively by the calculation of the surface height fluctuations. However, for practical matters, it proves convenient to better consider the problem by transforming the surface profile, $z(\mathbf{x})$, into Fourier space, as $z(\mathbf{q})$, with $\mathbf{q}$ being a wave-vector along the plane of the interface. This is convenient because it allows obtaining simple analytical results for the sine–Gordon Hamiltonian. Particularly, the mean squared surface fluctuations are given in Fourier space as^{127,143}

$$\langle \delta z_{sl}^2(q) \rangle = \frac{k_B T}{A} \frac{1}{w + \gamma_{sl} q^2}, \quad (21)$$

where $w \propto u$ is a renormalized lattice strength parameter, which sets how strongly is the solid surface tied to the underlying lattice. At low temperature, w is finite, and the surface fluctuations $\langle z^2(q) \rangle$ remain finite at all wave-vectors. However, as the temperature increases, w is renormalized by thermal fluctuations and eventually vanishes at the roughening temperature, $T_R \propto \gamma_{sl} b^2$, irrespective of the cohesive energy of the lattice. Above this temperature, there is no longer a cutoff in the denominator of Eq. (21) and the surface height fluctuations diverge in the limit of small wave-vectors. Thus, the distinction between finite or diverging height fluctuations allows identifying whether a simple interface is rough or smooth.

For the more complex problem of a premelted interface, one needs to further account for the surface fluctuations of the water/vapor surface, bounding the premelting film from the vapor phase. This can be achieved by using the so-called capillary-wave Hamiltonian,^{82,144}

$$\Delta \Omega_{CW} = \int d\mathbf{x} \left(\frac{1}{2} \gamma_{lv} (\nabla z_{sl})^2 + g(h) \right), \quad (22)$$

where, again, the first term accounts for the free energy cost of increasing the water/vapor surface area, while the second term, with $g(h)$ being the interface potential, penalizes excursions of the premelting film thickness away from the preferred equilibrium value [as dictated by Eq. (8)].

The total surface free energy of the premelted interface is obtained as a sum of the sine–Gordon and capillary-wave Hamiltonians, Eqs. (20) and (22), which are coupled via the premelting film thickness, $h(\mathbf{x}) = z_{lv}(\mathbf{x}) - z_{sl}(\mathbf{x})$.

This coupled SG + CW model of surface fluctuations can be solved approximately,^{52,53,57} using an elegant renormalization method due to Saito (notice that this approach was erroneously attributed to Safran in the original Ref. 52).¹³⁷ In this case, the outcome is an expression for the surface height fluctuations of the ice/water and water/vapor surfaces, as well as the corresponding cross correlations,

$$\begin{aligned} \langle |z_{sl}^2(\mathbf{q})| \rangle &= \frac{k_B T}{A} \frac{g'' + \gamma_{lv} q^2}{w g'' + (g'' \Sigma + w \gamma_{lv}) q^2 + \gamma^2 q^4}, \\ \langle |z_{lv}^2(\mathbf{q})| \rangle &= \frac{k_B T}{A} \frac{w + g'' + \gamma_{sl} q^2}{w g'' + (g'' \Sigma + w \gamma_{lv}) q^2 + \gamma^2 q^4}, \\ \langle z_{sl}(\mathbf{q}) z_{lv}^*(\mathbf{q}) \rangle &= \frac{k_B T}{A} \frac{g''}{w g'' + (g'' \Sigma + w \gamma_{lv}) q^2 + \gamma^2 q^4}, \end{aligned} \quad (23)$$

where $\Sigma = \gamma_{sl} + \gamma_{lv}$, $\gamma^2 = \gamma_{sl} \gamma_{lv}$, and $g'' = d^2 g / dh^2$.

Despite the increased algebraic complexity, the overall behavior of these compound interfaces is very similar to that of the isolated ice–water interface described in Eq. (21). Indeed, for finite w , it is seen that all surface fluctuations remain finite in the limit of $q \rightarrow 0$. However, when w vanishes, all three surface fluctuations diverge in the limit of small wavelengths. The difference is that, now, the roughening transition occurs for $T_R \propto \Sigma b^2$,⁵² which is significantly higher than the roughening transition at the ice–water interface (as anticipated in Ref. 145 from purely qualitative arguments). This confirms that (1) the premelted basal interface can remain smooth all the way up to the triple point and (2) there is no conflict between the observation of surface steps on the basal face and the existence of substantial ice premelting.

C. Digression: Can ice crystals be overheated?

Most crystalline solids are difficult to overheat because they start melting instantaneously at their surface.^{115,146} However, it has been suggested that the observation of water droplets on the ice surface could imply the possibility to overheat ice.³⁵ The rationale is that melting at the surface can only proceed by increasing the equilibrium premelting film thickness, which, in the absence of complete surface melting lies in a free energy minimum (cf. Fig. 8) and is thus reluctant to move away from the minimum.⁶³ In practice, however, the free energy minimum is very shallow, as discussed before. However, smooth interfaces are known to grow epitaxially by activated nucleation, and whence, are also expected to have an activation barrier for the epitaxial layers to melt.¹⁴⁷ This provides an additional reason for overheating. Indeed, Elbaum *et al.* reported that the basal ice surface could survive overheating of up to 0.2–0.3 °C,¹⁸ while droplets on the basal ice surface at very nearly the melting point have been reported in work by Gonda and Sei.³⁷ In computer simulations, perfect ice mono-crystals exposed only at the basal surface could be superheated up to 2 °C, but similar behavior for the prism face was not found.⁶³

VIII. THE EQUILIBRIUM STRUCTURE OF PREMELTING FILMS

From the previous sections, it becomes clear that the ice–vapor interface has a complex three-dimensional structure featuring a significant layer of disordered water on top of bulk ice. Therefore, reducing the problem to the characterization of a single dividing surface, as is usual in surface thermodynamics, misses out plenty of interesting details.

A more detailed and insightful characterization may be achieved by using the ice/water and water/vapor surface profiles, $z_{sl}(\mathbf{x})$ and $z_{lv}(\mathbf{x})$, discussed above. Using these definitions, it is possible to monitor the deviations of the local surface height, $\delta z(\mathbf{x})$, from the instantaneous average position, $\bar{z}$, for either the ice/water, $\delta z_{sl}(\mathbf{x}) = z_{sl}(\mathbf{x}) - \bar{z}_{sl}$, or water/vapor surfaces, $\delta z_{lv}(\mathbf{x}) = z_{lv}(\mathbf{x}) - \bar{z}_{lv}$. The identification of these rather sophisticated order parameters turns out to be extremely useful and allows identifying a number of structural transformations on the ice surface.

As an example, Fig. 12(a) shows the probability distribution of $\delta z_{sl}(\mathbf{x})$ and $\delta z_{lv}(\mathbf{x})$ as temperature increases from $\Delta T = T - T_t = -82$ K to $\Delta T = -2$ K on the equilibrium basal surface of ice as described by the TIP4P/Ice model. At the lowest temperature, the distribution of surface heights is a narrow Gaussian, as expected

for a sharp low temperature interface. In the language of the statistical thermodynamics of soft solid interfaces,^{148–152} this state is designed as an ordered flat (OF) phase. As temperature increases, steps and terraces start to proliferate on the ice surface, as revealed by the multi-modal character of the probability distribution. A surface structure with proliferation of terraces but limited surface height fluctuations is known as a disordered flat phase (DOF), as first identified by Rommelse and den Nijs in simple column models of the solid interface.¹⁴⁸ Finally, at yet higher temperature, the multi-modal probability distribution vanishes and now becomes a broad Gaussian distribution. This transformation occurs concurrently with a significant increase in the premelting thickness, so it appears that the interface trades the entropy of step proliferation in the DOF phase, for the translational entropy of the liquid-like water molecules. This last surface phase was named as a high-temperature reconstructed (HT-RF) phase in Ref. 57, although the name of flat premelted (FP) phase would have been more appropriate.

The distinction between OF and HT-RF phases, with unimodal distributions, and the DOF phase, with a multi-modal distribution of surface heights, can be seen in Fig. 12(c), which displays a heatmap of the instantaneous surface height fluctuations. Corresponding to the DOF phase, the basal surface becomes heterogeneous and correlated up and down domains of the surface height are clearly visible. A similar heterogeneous distribution of surface heights was also observed in studies of the mW model for the basal face at low temperatures.^{68,74}

The study of the prism facet also reveals the existence of three different surface phases, albeit with the phase transitions occurring at significantly different temperatures from those observed for the basal face.⁵⁷ A related study for the TIP4P/2005 water model studied the height–height surface correlations in real space and also found evidence of the existence of three different phases on basal and prism faces of ice.⁷⁸

The characterization of different surface phases at the ice–vapor interface is extremely appealing, as it could provide for the explanation of the Nakaya diagram. Indeed, one expects that the crystal growth rates could change significantly across the surface phase transitions, resulting in non-monotonous behavior. Without any other factual evidence, Kuroda and Lacmann made the bold hypothesis in 1982 that the ice surface should exhibit three different surface phases. They conjectured that a mismatch in the transition temperatures in prism and basal facets could lead to the alternating growth rates that are required to explain the Nakaya diagram.¹⁴ Four decades after the formulation of the Kuroda–Lacmann theory, computer simulations appear to support that hypothesis.⁵⁷

This conjecture seems reasonable and appealing, but it remains to be substantiated with actual predictions of the crystal growth rates. This begs the following questions: (1) How representative is the equilibrium surface structure during the out-of-equilibrium growth process of ice in the atmosphere? (2) How could the crystal growth rates be calculated from the equilibrium surface properties?

IX. PREMELTING FILMS AWAY FROM THE SUBLIMATION LINE

In practice, the ice–vapor interface can only be realized under equilibrium conditions for state points along the sublimation line, a situation which is actually more the exception than the rule.

Indeed, ice samples in the atmosphere will be most often found under conditions away from equilibrium.⁵ In this situation, the interface does no longer remain uniform, but will display pattern formation, inhomogeneities, and instabilities.¹⁵³ However, contrary to some simple situations, the departure from equilibrium cannot be fully interpreted just as a measure of the distance of the vapor away from the sublimation line. The vicinity of the (metastable) liquid–vapor coexistence line means that, together with the sublimation/desublimation processes, it is necessary to account for the competing evaporation/condensation process of the marginally metastable liquid phase (cf. Fig. 4).

A simple manifestation of departure from equilibrium that was already mentioned is the spontaneous formation of water droplets by vapor deposition on the ice surface.^{18,34,37,38} According to the Laplace equation, this phenomenon can only occur when the pressure inside the liquid phase is larger than that in the surrounding vapor phase.⁸² In material equilibrium, with both phases at equal chemical potential, this occurs as soon as the vapor is saturated over water.

However, the experiments performed by the Hokaido team show that water droplets on the ice surface form only under conditions of significant supersaturation over water vapor, when the pressure is increased beyond a temperature-dependent threshold that lies well above the condensation line (cf. Fig. 11).^{41,42}

In order to understand this behavior, it is convenient to extend the free energy model of premelting films, Eq. (7), which is only valid along the coexistence line, to the general case of arbitrary pressure of the vapor phase, p_v , i.e.,⁵⁹

$$\Delta\omega(h) = \gamma_{sl} + \gamma_{lv} + g(h) - (p_s - p_v)z_{sl} - (p_l - p_v)z_{lv}, \quad (24)$$

where p_s and p_l are the pressures of the corresponding bulk phases at equal temperature and chemical potential as the mother vapor phase, while z_{sl} and z_{lv} are the heights of the ice/water and water/vapor surfaces bounding the premelting liquid film from below and above, respectively, with the premelting film thickness now given as $h = z_{lv} - z_{sl}$.

This is a simplified free energy model that accounts for a uniform out-of-equilibrium solid/vapor interface. Borrowing tools from fluctuation theory and near equilibrium physics, this free energy may be used to describe the dissipative dynamics of the interface.⁸⁶ The key issue here is that the dynamics of a system close to equilibrium is dictated by deviations of the free energy from its equilibrium value. Particularly, it is expected that the time derivative of the relevant variables is linear in the free energy gradients. Therefore, the growth rate at the ice/water surface bounding the premelting film from below, which results from freezing/melting events, may be qualitatively described as $r_{sl} \propto -k_{sl}\partial\Delta\omega/\partial z_{sl}$, with k_{sl} being the kinetic growth coefficient. In analogy, the growth rate at the water/vapor surface bounding the film from above, which results from condensation/evaporation events, may be described as $r_{lv} \propto -k_{lv}\partial\Delta\omega/\partial z_{lv}$, with k_{lv} being the corresponding rate coefficient.⁵⁸ The evolution of the solid/liquid bounding surface will be dictated by the occurrence of freezing/melting events, and so $dz_{sl}/dt \propto r_{sl}$. On the other hand, the evolution of the liquid/vapor surface is mainly given as a result of condensation/evaporation events, but also depends on the freezing/melting events of the lower surface due to the difference in density of ice and water, whence $dz_{lv}/dt \propto r_{lv} - r_{sl}$.

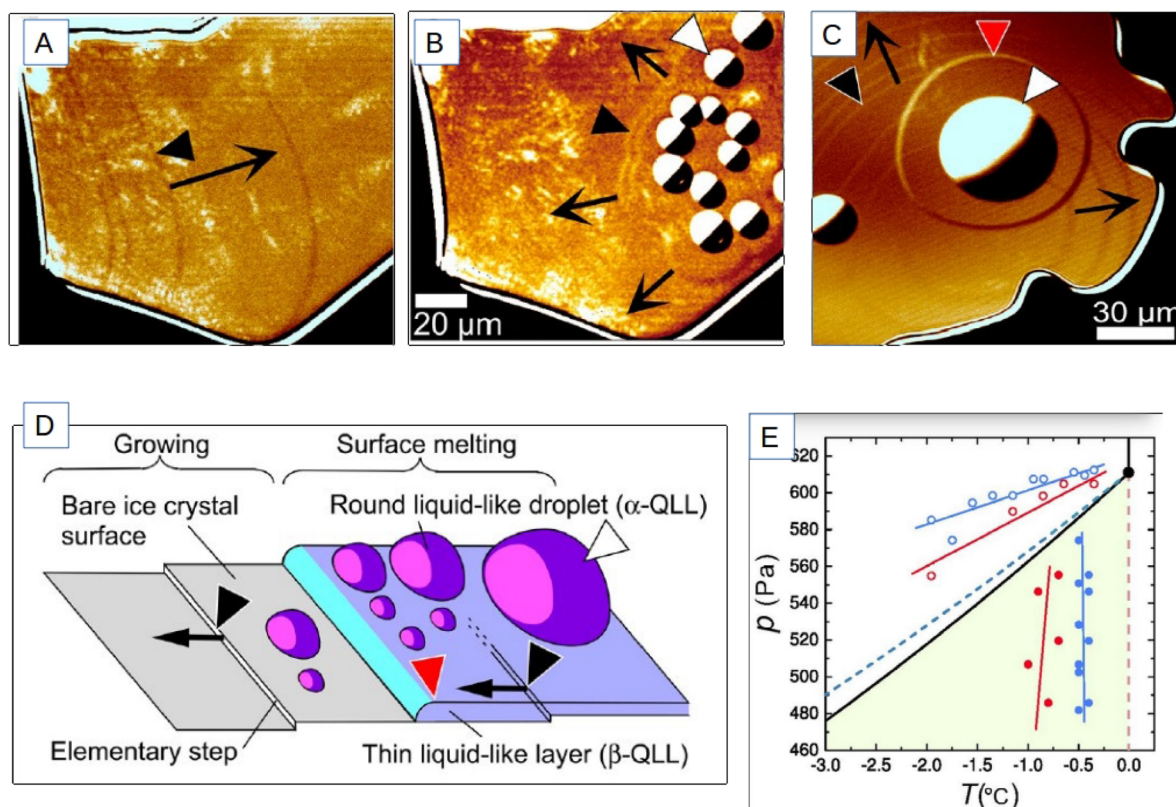


FIG. 11. Experimental observation of the ice basal face in the neighborhood of the triple point. (a) At slight supersaturation, elementary steps appear and spread horizontally. (b) At higher saturation, droplets condense on the surface. (c) At yet higher saturation, thick premelting films can appear below the droplets. (d) Sketch showing, from left to right, the sequence of events observed in panels (a)–(c), as interpreted in Ref. 38. (e) The ice phase diagram, illustrating the phase boundary lines indicated by the black line, and the metastable prolongation of the condensation line represented by the blue dashed line. The red line shows the region where condensation of water droplets first appears. The blue line shows the region where a second wetting film below the liquid droplets first appears. Notice the similarity with the sketch of Fig. 4 predicted from the theory described in Sec. IX. Panels (a)–(d) reproduced with permission from Sazaki et al., Proc. Natl. Acad. Sci. U. S. A. 109, 1052–1055 (2012). Copyright 2012 Authors. Panel (e) reproduced with permission from Murata et al., Proc. Natl. Acad. Sci. U. S. A. 113, E6741–E6748 (2016). Copyright 2016 Authors, licensed under a Creative Commons license.

Using this set of phenomenological equations, it is possible to show that there exists a *quasi-stationary* regime where ice can gently grow ($dz_{sl}/dt > 0$) or melt ($dz_{sl}/dt < 0$) while the premelting film remains in a steady state of constant film thickness ($dh/dt = 0$). It corresponds to a physical situation where the lower surface of the premelting film freezes at the same rate as water vapor condenses on the upper surface. This is an extremely relevant observation that was already recognized by Kuroda and Lacmann^{14,15,154} and discussed qualitatively in computer simulation studies.^{68,70,155–157} A modern rewrite in the language of wetting physics provides the condition for the quasi-stationary regime in striking resemblance with the equilibrium condition of premelting films, Eq. (8),⁵⁸

$$\Pi(h_{qs}) = -\Delta p_k, \quad (25)$$

where h_{qs} stands here for the steady state film thickness in the quasi-stationary regime, while the kinetic Laplace pressure, Δp_k , is the out-of-equilibrium analog of Δp in Eq. (8),

$$\Delta p_k = \frac{\rho_l k_{lv}}{\rho_s k_{sl} + \rho_l k_{lv}} [p_l - p_v] - \frac{\rho_s k_{sl}}{\rho_s k_{sl} + \rho_l k_{lv}} [p_s - p_l]. \quad (26)$$

The simple model described above provides a valuable framework for the understanding of growth morphology of premelting films. First of all, it shows that the notion of a well-defined premelting film remains meaningful under out-of-equilibrium conditions,^{154,158} second, it shows that the corresponding steady state premelting film thickness can be measured from knowledge of the equilibrium disjoining pressure and the kinetic coefficients of the growth process; and third, it shows that the expected wetting behavior of the quasi-stationary regime can be described in analogy to that expected for a wetting film on an inert substrate.¹⁵⁸

Particularly, it is known that the condition for mechanical equilibrium of a liquid droplet on an inert substrate is a positive Laplace pressure, $\Delta p > 0$. So, similarly, in the quasi-stationary regime, with a living substrate feeding from the premelting film, the condition of mechanical equilibrium of the droplet now becomes $\Delta p_k > 0$.⁵⁸ Solving for the marginal condition $\Delta p_k(p_v, T) = 0$ provides a *kinetic condensation line*, which dictates the pressure at which a droplet can first start growing atop the liquid/vapor surface (cf. the blue dashed line of Fig. 4). This can be worked out easily from the above-mentioned equation and leads to a kinetic phase boundary line of Clausius–Clapeyron type,

$$\ln p_{kc}/p_t = \frac{\Delta H_{kc}}{R} \left(\frac{1}{T_t} - \frac{1}{T} \right), \quad (27)$$

where p_{kc} stand for the *kinetic condensation pressure* and $\Delta H_{kc} > \Delta H_{lv}$ is an effective enthalpy of vaporization. This is always larger than the equilibrium vaporization enthalpy, ΔH_{lv} , so that the condition for a droplet condensing on top of the growing premelted ice surface lies always above the equilibrium condensation line, in full agreement with the observations of the Hokaido team [cf. red line of Fig. 11(e)].^{41,42}

Another relevant phase line corresponds to the solution of Eq. (25) in the special case that the steady state thickness h_{qs} attains the value corresponding to the wetting spinodal, i.e., where the second derivative of the interface potential $g(h)$ first vanishes. The kinetic spinodal line lies above the kinetic coexistence line and describes the phase points where a quasi-stationary regime can no longer hold (cf. the red dashed line of Fig. 4). In this situation, the freezing rate at the ice/water surface can no longer match the condensation rate at the water/vapor surface, so that the premelting film thickness starts growing without bounds. This corresponds to a situation of *kinetic* complete surface melting, where the ice sample is freezing underneath the liquid film, but the liquid film thickness is diverging due to vapor condensation at a faster pace.⁵⁸

The kinetic phase boundaries can be extended to a temperature higher than T_t , where they then describe the evaporative regime of the ice crystal. In this case, the kinetic spinodal line dictates the conditions where the evaporation at the water/vapor surface can no longer match the rate of melting at the ice/water surface. The crystal here will exhibit wet evaporation and actually disappear from a puddle of water. In between this line and the liquid–vapor coexistence line, there lies a prolongation of the kinetic condensation line, which bounds the regions of thermodynamic variables where water droplets can form as a result of ice melting. This rather unexpected behavior was reported by Asakawa and collaborators, as a set of boundary lines running almost parallel to the melting line. Intriguingly, the lines measured in Ref. 42 were slightly below T_t , rather than above T_t , as predicted in the kinetic model described here. A shift of the triple point due to the presence of impurities could help explain the discrepancy with respect to the theoretical expectation.

The different growth regimes discussed in this section are sketched in a qualitative manner shown in Fig. 4, to be compared with the experimental results of Fig. 11(e). However, an important thing to notice is that the quasi-stationary growth regime described here and the corresponding kinetic boundary lines are not a universal feature of the substance. As recognized by Kuroda and Gonda a long time ago,¹⁵⁴ they crucially depend on the growth mechanism followed by the crystal. Depending on the crystal plane, initial conditions, and sample history, this can be nucleated, spiral, or linear growth. The linear growth discussed above, however, is the one leading to the simplest algebraic results and is used here for the sake of illustration.

In practice, under out-of-equilibrium conditions, there occur film instabilities, and the mean field free energy model of Eq. (24), corresponding to films of uniform thickness, is not sufficient to describe the complex out-of-equilibrium dynamic that actually takes place. However, accounting for inhomogeneities using the SG-CW free energy model of Sec. VII B allows describing

complex non-equilibrium phenomena in remarkable agreement with experimental findings (cf. Fig. 10).⁵⁸

Be as it may, the kinetic phase diagram that emerges from this theoretical treatment appears to be extremely relevant for the understanding of crystal growth in the atmosphere. Particularly, the formation of complex crystal habits displayed in the Nakaya diagram occurs somewhat above the equilibrium condensation line.¹⁵⁹ It is very tempting to speculate that this threshold of complex habit behavior is related to the first emergence of water vapor condensation effects on the crystal surface as described by the Kinetic condensation line.⁵⁸ Confirmation of this hypothesis would have a significant impact in the understanding of crystal growth from the vapor.

X. STEP FREE ENERGIES AND THE NAKAYA DIAGRAM

From the above-mentioned discussion, it follows that in a narrow region of supersaturation in between the sublimation line and the kinetic condensation line, which is relevant for snowflake growth in the atmosphere,⁵ ice grows gently under a steady state regime of constant premelting thickness.¹⁴ This corresponds to the linear response regime, where the growth rates are dictated by the equilibrium surface structure, as discussed in Fig. 12. Indeed, in linear response theory, the out-of-equilibrium dynamics of a system is fully dictated by the correlated dynamics of the system in equilibrium.^{86,160}

The fluctuation formula of Eq. (23) then becomes very valuable. Fitting these equations to the spectrum of surface fluctuations as obtained from computer simulations [Fig. 12(d)] allows assessing the value of the lattice strength parameter, w . Not surprisingly, this, together with the surface stiffness coefficients, sets the free energy cost of creating an elementary step of height b on the crystals' surface.

Using results from the sine–Gordon model of crystalline interfaces,^{127,161} the free energy cost to create a step on the ice/water surface amounts to $\beta_{sl} = \frac{2b^2}{\pi^2} \sqrt{\gamma_{sl} w}$.¹⁶² In the presence of premelting it is also required to account for the cost of rising the water/vapor surface above the step so formed. By analogy with the previous result, it is expected that this free energy cost will be given by $\beta_{lv} = \frac{2b^2}{\pi^2} \sqrt{\gamma_{lv} g''}$.⁵⁷ The total free energy cost of creating a step on the premelted surface must then be given as $\beta = \beta_{sl} + \beta_{lv}$.⁵⁷

The rationale of these two equations may be understood as follows: the deviation of a surface from planarity bears a free energy cost related to the increase of surface area, which can be measured as $\propto \gamma (dz/dx)^2 dx$, with the squared derivative of $z(x)$ used as a measure of the surface area increment.^{127,162} On average, the surface height increases by an amount equal to the full step height $dz = b$ over a horizontal distance on the scale of the surface correlation length, $dx = \xi$. This is $\xi_{sl} = \sqrt{\gamma_{sl}/w}$ or $\xi_{lv} = \sqrt{\gamma/g''}$ for either the ice/water and water/vapor surfaces, respectively. Then, the calculation of $\gamma(b/\xi)^2 \xi$ leads to the previous results up to numerical factors.

Figure 13 compares the step free energies of prism and basal facets of ice crystals obtained from computer simulations for the TIP4P/Ice model.⁵⁷ The results are in order of magnitude agreement with measurements obtained directly from the growth of snow crystals^{5,163} and show a non-monotonous behavior, as required to explain the Nakaya diagram. Indeed, the step free energies appear

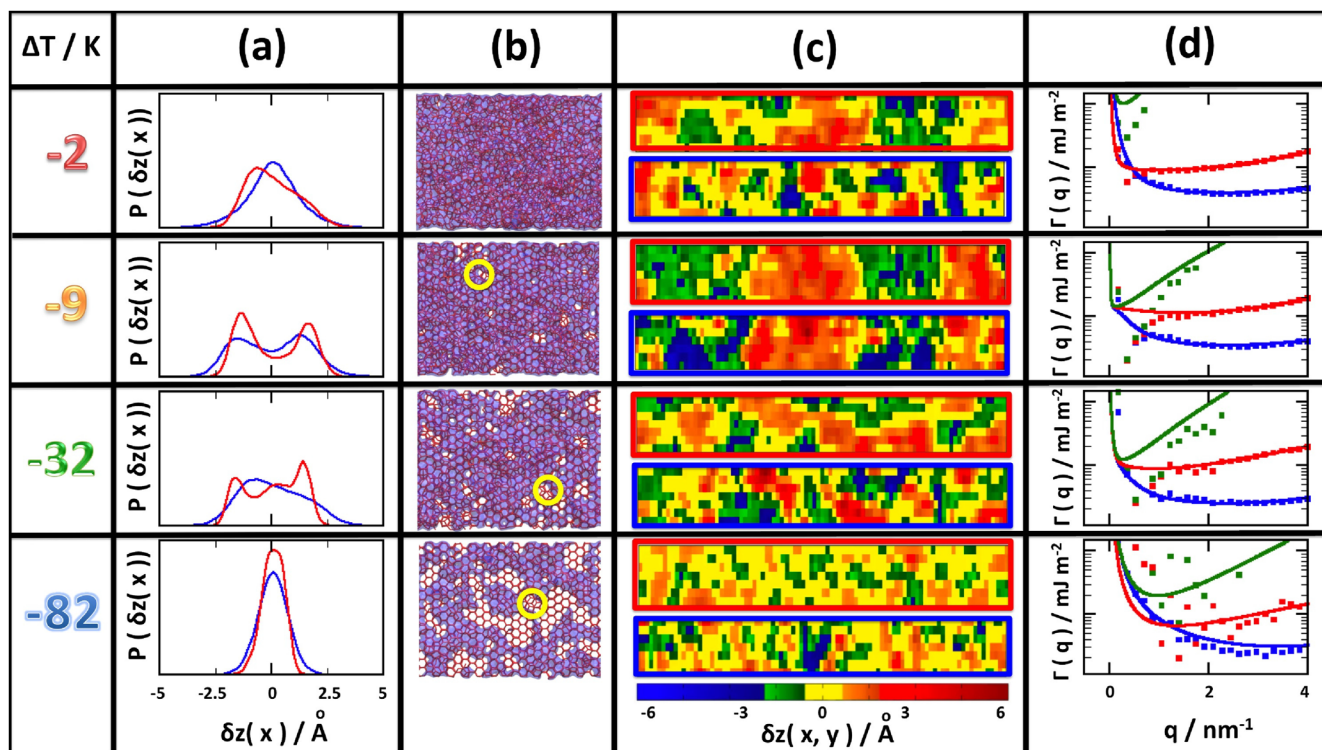


FIG. 12. Equilibrium structure of the ice basal face as described by the TIP4P/Ice model. (a) The probability density of film heights reveals two surface phase transitions as shown by the transformation from unimodal to bimodal and back to unimodal distributions as temperature increases. (b) Snapshots of surface coverage of liquid-like molecules on top of the bulk ice. (c) Heat map of height distributions shows the emergence of thick correlated up and down domains at intermediate temperatures. (d) The spectrum of surface height fluctuations can be fitted to an analytical model of Eq. (23) in order to estimate step free energies (cf. Fig. 13). Reproduced with permission from Llombart *et al.*, *Sci. Adv.* **6**, eaay9322 (2020). Copyright 2020 Author(s), licensed under a Creative Commons Attribution 4.0 License.

higher or lower for either the basal or prism facets in alternating order.

Crystal growth in the atmosphere is thought to occur by 2d nucleation,^{3,5,164,165} but possibly also as a result of dislocations at

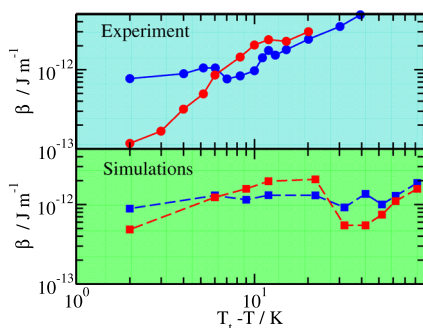


FIG. 13. Step free energies of basal (blue) and primary prism (red) faces. The top panel shows experimental results, as reported in Ref. 163. The bottom panel shows simulation results for the TIP4P/Ice. In both cases, the step free energies alternate sequentially between the basal and prism faces as expected for the plate–column–plate transitions observed in the Nakaya diagram. Reproduced with permission from Llombart *et al.*, *Sci. Adv.* **6**, eaay9322 (2020). Copyright 2020 Author(s), licensed under a Creative Commons Attribution 4.0 License.

the edge of the crystals.^{40,41,159,166} In either case, the growth rates are inversely related to the step free energies. According to the results of Fig. 13, in the close neighborhood of the triple point, the prism face has lower step free energies and grows faster than the basal face, leading to formation of plate-like crystal habits. As temperature decreases, the step free energy of the prism face becomes larger than that of the basal face, the growth rate of the basal face takes over, and crystals adopt a columnar habit. Eventually, a new crossover between step free energies takes place and crystals adopt again a plate-like habit. This scenario as explained from the measurement of step free energies under equilibrium conditions has been confirmed for the same water model by measurement of the relaxation dynamics of thick liquid films adsorbed on ice.¹⁵⁷

The alternating behavior of crystal growth rates of ice from the vapor has been reported in a number of experiments over the years^{165–168} but a molecular explanation of this unusual behavior has remained elusive. However, thanks to the atomic scale resolution of computer simulations, the development of reliable force fields for water,^{109,169} and the formulation of a suitable theoretical framework for the analysis of computer simulations,^{52,53,57} a consistent explanation appears to emerge. The ice surface structure is extremely complex and cannot be explained in terms of the traditional crystal surface models based on the surface diffusion of isolated adatoms that is adequate for the description of high energy solids very far

away from their triple point. Contrary to this venerable picture, the ice surface exhibits all the way from 200 K to its melting point a significant amount of self-adsorption which increases with temperature and reaches the nanometer thickness in the neighborhood of the triple point. In this process, the basal and prism surfaces undergo a number of structural rearrangements,^{56,78} with profound impact on the crystal growth dynamics. The result of these transformations is that the growth rates become higher or lower for either the basal or prism facets in alternating order. While the detailed structure of the surface phases is different, the underlying reason for the alternating growth rates is very much as anticipated by Kuroda and Lacmann many years ago.¹⁴

XI. HOW LIQUID IS QUASI-LIQUID?

In wetting physics, emphasis is made on the condensation of liquid films on a substrate. Of course, it is understood that as long as the thickness of the film remains finite, the film is not strictly a bulk liquid, but there never is a need to emphasize this in the theoretical framework, whether condensation occurs in the form of a liquid film or a liquid droplet.

In the study of ice premelting, one assumes that the premelting film has its origin in the melting of ice-like molecules. However, as far as a thermodynamic description of the equilibrium ice–vapor interface is required, there is no need what so ever to consider whether the film is formed by ice melting or vapor deposition. In fact, from a dynamical point of view, the rates of adsorption/desorption and freezing/melting need to be exactly equal at equilibrium.

However, it has been traditional in the study of the ice–vapor interface to refer to the surface disordered layer as the *quasi-liquid* layer. This is fine, but it puts the emphasis of the problem on how different this could be from the expected bulk liquid, suggesting enigmatic properties and an aura of mystery.

Yet, if human kind had to give up computer simulations and be left with one single qualitative take away message from now more

than 50 years of practice, it would be that macroscopic constitutive laws can be qualitatively trusted down to the nanometer scale. Within my experience, this statement holds for all molecular liquids and the quasi-liquid layer is found not to be an exception.

Within a few Kelvin of the triple point, most computer simulations^{55–57,68,69,71,74,78} and experimental probes^{18,24,25,27} indicate that the thickness of the premelting film has reached that scale. Based on this thumb rule, the quasi-liquid layer at the triple point is indeed very much like liquid water despite its limited thickness.

The first evidence comes from the study of droplets. At the triple point, the ice–vapor surface tension differs from the sum of ice–water (~ 30 mN/m, from Ref. 170) and water–vapor surface tensions (~ 75.7 mN/m, from Ref. 171) by $g(h_e)$, the minimum of the interface potential. From Eq. (18), this can be equated to $g(h_e) \approx -\frac{1}{2}\gamma_{lv}\theta^2$. Using the upper bound of contact angles observed in experiment, the correction cannot possibly exceed ~ -2 mN/m, which is actually less than the uncertainty in current estimates of the ice–water surface tension and no more than 2 % of the result expected in the case of complete wetting, $\sim 75 + 30 = 105$ mN/J. So, whatever the quasi-liquid layer is, it is sufficient to exhibit surface tensions that do not differ by more than 2% from the value expected for bulk liquid water at the interface of either ice or water vapor.

Another evidence comes from the study of surface fluctuations of the premelting film as studied from computer simulations.⁵² Using an adequate order parameter,^{76,77} it is possible to resolve the surface fluctuations of the ice/film and film/vapor surfaces that bound the premelting film from the bulk phases and measure their corresponding wave-vector-dependent surface tensions. These can then be compared to the wave-vector-dependent surface tensions of independent simulations for the ice–water and water–vapor interfaces. The results of this comparison (Fig. 14) show that the ice/water and water/vapor surfaces of the premelting film fluctuate independently and match exactly those corresponding to interfaces of the bulk phases up to wave-vectors of $q \approx 1.5$ nm⁻¹. This means that, for undulations of less than ~ 3 nm, these surfaces respond to perturbations exactly as the interfaces between bulk ice–water and

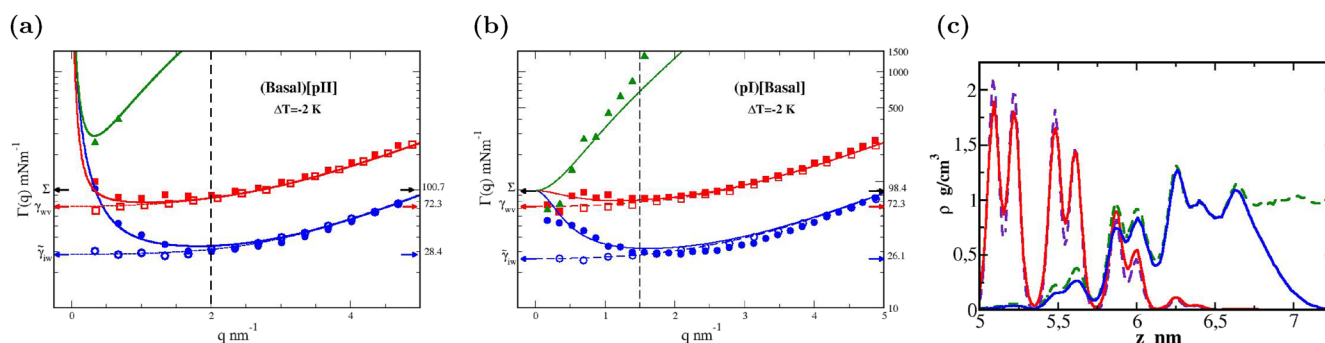


FIG. 14. Interfacial structure and surface fluctuations of ice close to the triple point. Panels (a) and (b) show the spectrum of surface fluctuations for the basal and prism faces in the near vicinity of the triple point, as described by the TIP4P/2005 model of water. The results are displayed as wave-vector-dependent surface tensions of the ice/water (blue) and water/vapor (red) surfaces, together with the coupled correlations (green). The symbols represent results from computer simulations, while the lines represent fits to the model of Eq. (23). The corresponding surface tensions for interfaces of bulk water with either bulk ice or bulk vapor are indicated by the empty symbols and look equal to those of the premelting film up to $q = 2$ nm⁻¹, as indicated by the black dashed line. Panel (c) compares density profiles of the premelting film (continuous lines) with those of the ice/water and water/vapor interfaces (dashed lines). The red and blue full lines are density profiles of solid-like and liquid-like molecules of the premelting film, respectively. The violet and green dashed lines are densities of solid-like and liquid-like molecules from the ice/water and water/vapor interfaces, respectively. Reproduced with permission from Benet *et al.*, Phys. Rev. Lett. **117**, 096101 (2016). Copyright 2016 American Physical Society.

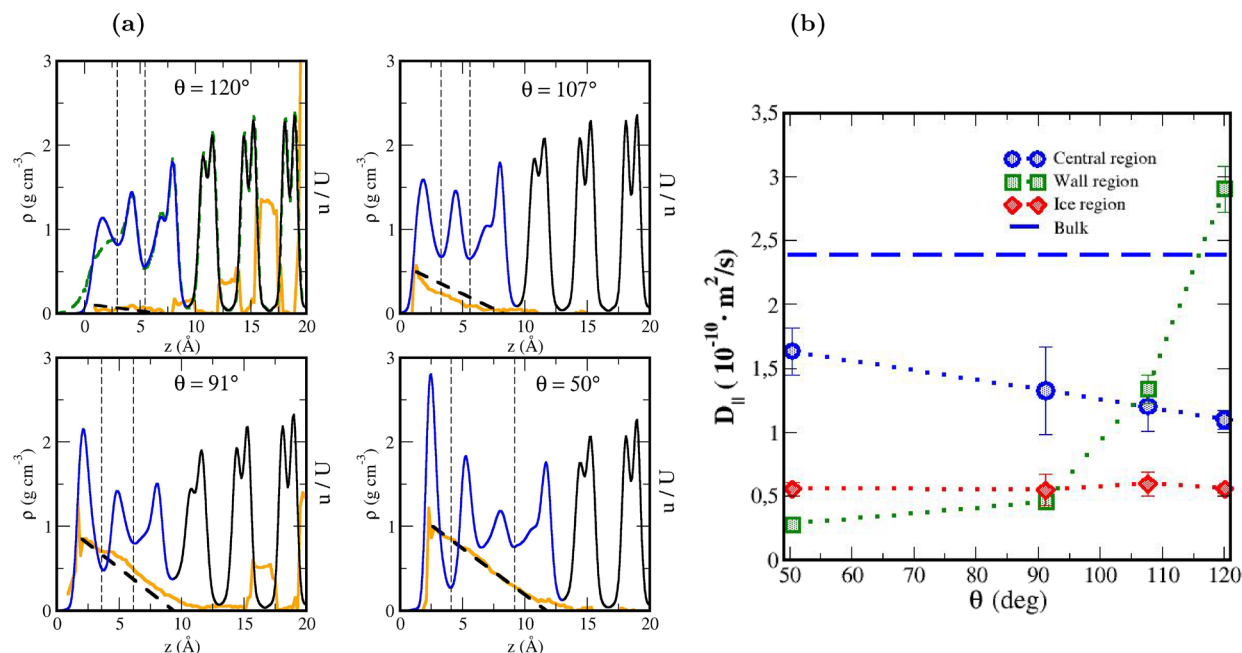


FIG. 15. Rheology of premelting films at $T = -8^\circ\text{C}$ as described by the TIP4P/Ice model. The results are shown for ice at the interface with four substrates with differing water contact angles. (a) Density profiles are indicated by either blue (for regions with liquid-like molecules as the majority phase) or black (for regions with solid-like molecules as the majority phase) continuous lines. The orange line represents the corresponding flow profiles resulting when the substrate slides at a speed of 5 m/s on the ice surface. The dashed black lines represent predictions for Couette flow, with slopes as given by the corresponding bulk water viscosity. (b) Diffusion coefficients calculated for the parallel motion of liquid-like molecules. The blue dashed line represents the result corresponding to bulk undercooled water. This is compared to parallel diffusion coefficients of water-like molecules in three different regions of the premelted layer, as indicated by the dashed black lines of panel (a). The blue circles correspond to liquid-like molecules within the central region of the premelting film. The green squares correspond to molecules within the wall adsorption layer. The red diamonds correspond to the molecules in the ice adsorbed layer. Reproduced with permission from Baran *et al.*, *Proc. Natl. Acad. Sci. U. S. A.* **119**, e2209545119 (2022). Copyright 2022 Authors, licensed under a Creative Commons Attribution-NonCommercial-NoDerivs 4.0 International (CC BY-NC-ND) license.

water–vapor. The resemblance between surface fluctuations of premelting films and bulk water may be understood by comparison of the corresponding density profiles, which are almost the same at the interfacial regions [Fig. 14(c)].

For fluctuations of a larger scale, the bounding surfaces eventually start noticing the finite thickness of the premelting film and become highly correlated. Eventually, they must behave as one single fluctuating surface.¹⁰³ The distinction can then become dramatic depending on the surface anisotropy. The basal face is smooth, so that it effectively has an infinite stiffness to surface fluctuations. However, all other faces of ice are rough at the triple point⁶³ and will exhibit a compound surface tension very close to the sum of $\gamma_{sl} + \gamma_{lv}$, as discussed above.

The question then remains as to whether the small extent of liquid in between the surfaces is sufficient to exhibit a dynamic response similar to bulk water. Computer simulations are particularly insightful as they allow monitoring single molecule motion without perturbing the system. Unfortunately, measurements of self-diffusion coefficients are difficult to interpret, as they strongly depend on the location of molecules within the premelting film.^{73,75,172} The results typically show that molecules close to the ice/water surface have a low diffusivity, while those at the water/vapor surface exhibit enhanced diffusion.⁷³ However, bulk properties cannot be expected for the three dimensional motion of

the molecules because of the strong confinement in the direction perpendicular to the film. Indeed, the motion in this direction can even become sub-diffusive or glassy-like because of the locking and freezing of the molecules at the ice/water surface.¹⁷² On the other hand, measuring the diffusion parallel to the interface for liquid-like molecules within the film yields a rather different picture. In this case, the water molecules exhibit self-diffusion coefficients that are very close to those obtained for bulk undercooled water at the same temperature (Fig. 15). This is sufficient for the film to display an almost bulk-like rheological response when sheared. Indeed, simulations of the TIP4P/Ice model displayed a velocity pattern consistent with Couette flow and a shear stress similar to that expected for bulk water, albeit with slip lengths in the scale of several nanometers (Fig. 15).⁶¹ These results appear strongly in conflict with experimental measurements of viscosity coefficients estimated from the spreading of a liquid droplet sitting on ice, which were found to be 20–200 times larger than for bulk water.^{46,65,173} However, based on the description of wetting dynamics of premelting films, the motion of the contact line in a liquid drop is often dictated, not by the spontaneous flow of the liquid film, but by the growth rate of the ice surface underneath.⁵⁸ Therefore, the flow of a liquid film next to a droplet need not be a faithful proxy of the fluid properties. Indeed, the current understanding of nanofluidics is that there is no reason to expect such large viscosities in films of nanometer thickness.¹⁷⁴

XII. FUTURE CHALLENGES

The topic of ice premelting has been a puzzling problem of chemical physics, with long standing debates over its mere existence, the order of magnitude of the film thickness, its resemblance with the liquid phase, and its significance in important atmospheric processes such as snow flake growth. Unfortunately, some of the conflicts result from interpretations that concentrate on one single laboratory's piece of evidence and disregard other sources and experimental methodologies. Using a wider perspective and a suitable theoretical framework, many of the apparently conflicting observations are actually found to be mutually consistent and complementary.

In this perspective, I have shown that blending a number of theoretical tools, including wetting physics,^{56,58,60} intermolecular forces,⁶⁰ statistical mechanics of crystal growth,^{52,53} out-of-equilibrium physics,⁵⁸ and computer simulations,^{52,53,55–57,61,63,64} a consistent picture is gradually emerging, which allows reconciling a large body of apparently conflicting experimental results.

In this view, it appears that an equilibrium premelting film of sub-nanometer thickness gradually builds up atop pristine ice surfaces along the sublimation line^{31,65} and reaches a thickness of the order of one nanometer in the neighborhood of the triple point, whereupon, attractive van der Waals forces inhibit further growth in a case of incomplete surface melting.⁶⁰ The nanometer thickness is sufficient for the premelting liquid film to exhibit properties that are very similar to those expected for bulk liquid water.^{52,61,174}

While the equilibrium film thickness is bound by van der Waals intermolecular forces,⁶⁰ diverging liquid films can emerge readily for small deviations away from equilibrium, when supersaturation is above a stability limit, as dictated by the crystal growth mechanism and the underlying intermolecular forces. In this situation, the vapor condensation occurs at a faster pace than the freezing of the water film in contact with the solid surface so that the liquid film gradually diverges in thickness. In this peculiar scenario, ice growth from the vapor proceeds in a wet mode, by freezing from the liquid film formed atop.⁵⁸ This is a case of *kinetic* surface melting, which could easily be mistaken with *equilibrium* surface melting but is, in fact, an out-of-equilibrium phenomenon.

Below the liquid film's stability limit, but above a kinetic condensation line, liquid droplets can condense from the vapor atop a marginally stable premelting film, leading to the appearance of inhomogeneities on the ice surface. The condensation of a droplet at water supersaturation or above is actually the expected behavior and such droplets should not be confused with uniform equilibrium layers expected in equilibrium.

In between the sublimation line and the kinetic condensation line, growth proceeds in a quasi-stationary mode, whereby accretion of ice occurs while a stable premelting film remains in a steady state regime of constant thickness.^{14,15,154} This premelting film, even at sub-nanometer length-scales that occur at strong under-cooling, has a profound impact on the crystal surface structure and promotes a sequence of structural surface phase transitions,⁵⁷ similar to those conjectured by Kuroda and Lacmann many years ago.¹⁴ As a result, growth rates of the basal and prism faces crossover twice and lead to the alternation of columnar and plate-like hexagonal prisms described in the celebrated Nakaya diagram.^{1,4,5}

In this account, a significant progress in the qualitative understanding of equilibrium and out-of-equilibrium premelting films appears to emerge. However, there still remain important problems to be understood and a large number of properties to constrain within reasonable accuracy.

Indeed, the conclusions drawn in this perspective rely to a great extent on computer simulations, which have been used both as a standalone characterization technique and as an essential tool for the interpretation of experiments.^{72,175,176} However, simulations have some limitations. The most apparent for the study of ice premelting close to the triple point is the uncertainty in the determination of melting temperatures, which due to system size effects and unavoidable simulation artifacts (finite time step, truncation of interactions) is of the order of 1 K.⁶³ On the other hand, at lower temperatures that are relevant for the study of incipient surface disorder, classical molecular dynamics could be unreliable at least in quantitative terms, as the strong libration frequencies of water molecules result in significant nuclear quantum effects.¹⁷⁷ Be as it may, most of the studies of ice premelting by computer simulations have been performed with fixed point charge models,^{109,169} which do not deal with environment-dependent polarizability effects that could become very important at an interface. Another problem is that most fixed charged models predict a very small vapor pressure,¹⁷⁸ which could be a matter of concern. Current advances in force field modeling are promising¹⁷⁹ and preliminary assessments of the extent of ice premelting by means of accurate first-principle models, such as MDPol, seem to confirm the most significant features observed with classical force fields.¹⁷⁵ Qualitative agreement from machine learned density functional potentials would be also welcome, and some work in this direction has been published recently.^{176,180} Another important issue in the study of ice premelting with computer simulations is the initial preparation of ice surfaces. Both basal and primary prism faces have a bilayer structure, and initial configurations can be prepared with a fully terminated or a half terminated bilayer. Some of the work reported in this study for the basal face was prepared with a half terminated bilayer,^{55–57} while that of the prism face was prepared with a fully terminated bilayer. Exactly what surface preparation is more relevant to the experimental situation is unclear, and further work in this direction is required to understand the actual self-adsorption state of equilibrium premelting.

Most of this perspective article has been concerned with ice premelting above 200 K. However, the ice surface at lower temperatures is also of relevance for the understanding of atmospheric and extraterrestrial physics and poses interesting fundamental problems concerning the organization of dangling hydrogen bonds,¹⁸¹ the competition between cubic and hexagonal ice,¹⁸² and surface reconstruction.^{183,184} Some time ago, Fletcher suggested that the ice surface at low temperature could be stabilized by adapting ordered hydrogen bond arrangements, in a so called Fletcher stripe phase.¹⁸³ This hypothesis has been explored in some studies for frozen realizations of bulk ice,^{185,186} but some work remains to understand how thermal agitation could change the picture and what is the role of the conjectured order/disorder transition in the emergence of translational surface disorder.¹⁸⁷ A particularly interesting question is how the disordering of the Fletcher surface phase could be coupled to the underlying bulk hydrogen bond network and whether the Fletcher phase is consistent with the hydrogen bond disordered network of

ice Ih.^{176,187} Recent experimental work shows that the low temperature surface reconstruction of epitaxially grown patches could be actually far more complicated than previously envisaged.¹⁸⁴

To great extent, of course, the progress that has been achieved rests on a large body of experimental evidence gathered from a number of different techniques over the past few decades. In recent times, scrutiny of the interfacial structure using sum frequency generation (SFG) spectroscopy has received a great deal of attention, as it promises to disentangle bulk from surface properties better than other probes.^{22,24,72,181,188} Unfortunately, the interpretation of the non-linear electronic polarizability, the difficulties of band assignment, and the actual depth of the surface probe are highly controversial topics among expert practitioners, which considerably limit the significance of the surface spectra so retrieved.^{189,190} In this regard, current interpretation of the results relies to a great extent on the comparison of synthetic spectra obtained from computer simulations and some promising advances in this direction have been reported very recently.^{175,176}

However, the most insightful and clear experiments appear to be those which combine in one or another way advanced microscopy techniques, together with an exquisite control of the vapor pressure.^{18,38} Without this, the entanglement between freezing and condensation, which is prone to occur inevitably as the triple point is approached, leads to very difficult interpretation. Great progress could be achieved if somehow the Brewster reflectometry used by Elbaum and collaborators to measure film thickness¹⁸ could be combined with the advanced optical microscopy and vapor pressure control achieved by Sazaki and collaborators.^{38,42} This would allow characterizing film thicknesses of the pristine ice faces in equilibrium, as well as the condensation effects that take place out of equilibrium. In this regard, it is important to notice that most of the work of the Hokaido team reports results close to crystal edges, which are expected to be indeed the most dynamically active.^{3,5} Yet, it is required to fully understand to what extent the complex phenomenology they observe is related to general features of the smooth mono-crystal surface or to the proliferation of dislocations and other defects caused from strain that often occur at the crystal edges. The ice crystallites that are studied in that work are obtained from vapor deposition on silver iodide, which has a small but significant lattice mismatch. As far as understanding atmospheric crystal growth, this could pose problems because the thickness of the resulting crystal is often not known and the role of the underlying silver iodide mold in creating crystal defects is not fully understood. Ideally, the studies should be performed on perfect single monocrystals.^{5,191} A dream experiment would be the scanning of pristine hexagonal ice prisms grown from the vapor (diamond dust),⁵ with a combination of Brewster angle reflectometry,¹⁸ and advanced optical microscopy,³⁸ in exquisite vapor pressure control.⁴²

Be as it may, the current equipment available in Hokaido appears to be in a situation to confirm salient features of the kinetic phase diagram that emerges from the theoretical approach. Particularly, the formation of complex crystal habits displayed in the Nakaya diagram occurs somewhat above the equilibrium condensation line.¹⁵⁹ It is very tempting to speculate that this threshold of complex habit behavior is related to the first emergence of water vapor condensation effects on the crystal surface as described by the kinetic condensation line. However, the theoretical model shows

that the steady state regime of crystal growth depends on the growth mechanism. Experiments have shown that, under favorable circumstances, either nucleated or spiral growth can be observed. Is it possible to detect the dependence of the kinetic condensation line on the prevailing growth mechanisms?

A significantly simpler experimental challenge would be to test the theoretical prediction of kinetic surface melting beyond the kinetic spinodal line. In experiments, this would be detected as a temperature-dependent threshold supersaturation where the ice surface becomes unstable and a strong condensation effect is observed throughout the whole crystal surface. It is tempting to hypothesize that this regime could be related to hail formation. One way or the other, the confirmation of the most salient features of the kinetic phase diagram would be a major experimental achievement.

On the theoretical side, the best estimates of interface potentials clearly support a situation of incomplete wetting, with a shallow minimum of the interface potential at thickness of about one nanometer that is consistent with the droplet contact angles obtained for vapor condensation.^{18,42} However, there are a number of important problems that are still difficult to explain from the model of surface intermolecular forces suggested here.

First, on qualitative grounds, it is not clear how to interpret the observation of a thick liquid film that appears to emerge below condensed liquid droplets at supersaturation.^{38,42} This phenomenology corresponds to the stabilization of a second minimum of the interface potential at intermediate film thickness.⁴² On theoretical grounds, this could result from either (1) oscillatory behavior of the short range contribution of the interface potential⁵⁶ or (2) the stabilization of a secondary minimum due to van der Waals forces,⁶⁰ both of these situations are possible in principle. However, the film observed in experiments is about 9 nm thick. This is too large to be the result of oscillations and too small to be the result of the sign reversal of the Hamaker constant. Therefore, the problem rests to be solved. An important question here then is whether the formation of these thick films is actually an equilibrium or a non-equilibrium phenomena. Indeed, both kinetic and thermodynamic interpretations of this observation may be found in the literature^{41,42} and a full discussion on why should one or the other be favored is still lacking. If the thermodynamic interpretation were to be confirmed, then the only theoretical explanation that could be given within the current understanding of wetting and intermolecular forces is as follows: there is no secondary wetting state that could become an absolute minimum of the surface free energy. However, if a droplet is formed at supersaturation and then local saturation at the contact line decreased transiently below the kinetic condensation line, a metastable minimum of the free energy would appear that could drive the formation of the observed film. Confirmation of this scenario would require rather involved theoretical calculations of the diffusion limited evaporation/condensation dynamics in the neighborhood of the drop.

Second, on quantitative grounds, the separation between the kinetic phase lines of the kinetic phase diagram is given mainly by the depth of the interface potential.⁵⁸ However, the current estimate of this minimum is less than one mJ/m², which is extremely small.^{60,63} Based on this calculation, the kinetic phase lines displayed in Fig. 11 should lie very close to each other and differ by less than a Pascal.^{58,60} The current experimental observations, however, show

lines that are separated by several Pascals.⁴² The reason for this discrepancy is not understood but could perhaps be related to diffusion limited growth of the droplets, a feature not accounted for in the theoretical calculations.⁵⁸

Another relevant conceptual problem refers to the role of electrostatic effects. In the study of aqueous interfaces, the interface potential always features an important contribution from electrostatic interactions. These have been discarded altogether in the current survey, under the assumption that water is neutral. However, in view of the shallow minimum of the interface potential, weak electrostatic effects could become significant at long range; e.g., is there a role of electrical effects in creating a second minimum of the interface potential? Currently, both experimental^{21,28} and theoretical reports^{31,192} suggest that the first few ice layers below the premelting film could exhibit significant Bjerrum defects, leading to an effective surface charge at the ice/water surface. This, together with charge accumulation from water's self-dissociation, might play a role in the properties of premelting films,²⁸ but an assessment with simple force fields is simply beyond reach. The formulation of a simple Poisson–Boltzmann theory is possible. However, unfortunately, this requires imposing boundary conditions at the ice/water and water/vapor interfaces that currently appear not well understood. Indeed, the electrical nature of the water/vapor interface is a highly controversial issue and even the definition and sign of the electric potential difference between the bulk phases appears to be unsettled.¹⁹³ Yet, a far less discussed topic that is needed to interpret the role of electrostatics is the boundary condition for the ionic force at the solid phase, i.e., what is the pH of bulk ice? This was a problem that attracted the attention of Eigen¹⁹⁴ but does not seem to have been a matter of inquiry in the literature ever since. Understanding both of these fundamental problems of chemical physics is interesting *per se* and is absolutely necessary in order to assess whether electrostatic interactions promote or inhibit surface melting, and to what extent.

Regarding the shallowness of the interface potential, it is interesting to recall the discrepancy of contact angle measurements of macroscopic and microscopic droplets.¹²⁵ If the contact angle of 12° measured for large droplets was to be confirmed as the correct macroscopic equilibrium contact angle, the depth of the free energy minimum of the interface potential would increase significantly and some of the problems mentioned above could be remedied. This begs the following question: Could the discrepancy be related to line tension effects? Unfortunately, assessing line tensions close to a wetting transition is challenging, and even the sign of the line tension remains a controversial issue.¹⁹⁵ However, notice that assuming a negative line tension would imply that the contact angle decreases as the droplets become smaller,^{196,197} bringing into agreement the discrepancies between microscopic and macroscopic realizations of water droplets on ice. Yet, it is clear that the early stages of droplet deposition on the ice surface do not correspond to full thermodynamic equilibrium, so one cannot rule out that the discrepancy is related to pinning of the contact line by frozen water in some extremely complex out-of-equilibrium process.

This perspective has focused essentially on the study of pure ice samples. Yet, one of the most important motivations in the study of ice premelting is its role in the scavenging of atmospheric gases.¹⁹⁸ Our current understanding on the way trace gases and other impurities are adsorbed in the premelting layer and partitioned between

the bulk and interface remains rather limited.¹⁹⁹ Experiments and computer simulations have been carried out recently on selected adsorbents^{27,30,55,78,200–203} but a general understanding on this topic is still missing and requires further study.

Beyond surface ice premelting, it has been amply verified that liquid-like layers can also be significant at interfaces^{204–206} and some recent computer simulations confirm this for a wide range of substrates.^{61,207–209} However, there is still a large room for understanding the role of a substrate on ice premelting and what interfacial characteristics enhance or inhibit growth of quasi-liquid layers.⁶⁴ These interfacially premelted layers apparently exhibit close to bulk like properties⁶¹ and can provide for a lubrication effect in ice sliding.^{61,62}

In summary, significant progress in the understanding of ice premelting has been gathered in the past decade, but there remains a great room for further research. A promising but formidable challenge could be to combine microscopic insight toward the formulation of a crystal growth law (Fig. 13) with advances in the mesoscopic modeling of crystal habits.^{5,210–212} This could address a major task pending since first tackled by Kepler in 1611.²¹³ Can we possibly predict *ab initio* the shape of snow crystals in the atmosphere from the underlying principles of physics?

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AUTHOR DECLARATIONS

Conflict of Interest

The author has no conflicts to disclose.

Author Contributions

Luis G. MacDowell: Conceptualization (equal); Data curation (equal); Funding acquisition (equal); Methodology (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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