The ice surface in premelting and freezing: transition dynamics and metastable states

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The premelting of ice is well known, but not about how the premelted and solid surfaces convert into each other. In this work, the transition dynamics between two phases are revealed with large-scale molecular dynamics simulations. Supercooling and superheating states exist in the transition, and are overcome by nucleation-like processes. The natural inhomogeneity of ice surface enhances nuclei formation, while it only accelerates premelting but not freezing. Furthermore, the complete freezing of ice surfaces may be hindered by the stacking order mismatch between nuclei. This work points out the importance of metastable states in premelting studies, and calls attention to their potential effects on related physics.
The premelting of ice, known as the existence of a quasi-liquid layer (QLL) on the ice surface below melting point, has been recognized for more than 170 years since Faraday's experiment in 1850[1]. Due to its important role in various environmental processes[2-5] and the rich physics inside[6-8], premelting has been of research interest for decades[8]. There're considerable researches about the onset of premelting[9-15], the thickness[16-21] and structure[21-27] of QLL, how it behaves during growth or evaporation[28-32], and its interaction with external solvents[33-38] or confinements[39-43].

Despite the progress, there're still several questions about premelting that remain unsolved. There're large discrepancies within the premelting onsets and QLL thicknesses reported in the literature[8, 44], and it's doubted if a particular “transition temperature” exists[45]. Droplets are found on QLL at certain ranges of temperature and vapor pressure[30], but the microscopic mechanism of how they emerge and disappear is still unclear. Besides, the premelting is suggested to explain the well-known slippy of ice[46-49], but the scope and validity of such explanations are under challenge[50-52].

Notably, these issues are somewhat related to a less-emphasized topic: how do the QLL and unpremelted “solid” surface transit into each other. Indeed, the transition kinetics could be important for interpreting results of various studies about premelting, since metastable phases may play a role in them (just like the bulk solid-liquid transition[53]). Besides, it may also be relevant to more specific phenomena: the appearance of droplets is related to the ice surface converting between multiple structures[30], and the tribology of ice may be affected by the additional melting induced by sliding and pressures[49, 54-55]. Therefore, understanding how QLL appears and freezes would be helpful for both studying premelting and understanding physics related to premelting. However, few researches had focused on the transition dynamics between QLL and solid surfaces, and none have provided a microscopic description as far as we know.

Molecular dynamics (MD) simulations are widely adapted in premelting research[8], because of their molecule-level resolution and ability to fine-control external conditions. In this paper, we present a picture of the transition dynamics between QLL and solid surfaces by MD simulation. In particular, we observed the supercooling and superheating states during the transition, as an analog to their bulk version. Both directions of transition roughly follow the nucleation picture, but also shows qualitatively different behavior from common scenarios. Notably, the surface inhomogeneity of ice induces the formation of certain nuclei, but they only promote the transition from solid surfaces to QLL and not inversely. Furthermore, the mismatch of stacking orders between nuclei can hinder the complete freezing of QLL. In this work we adopted the ML-mW water model[56], a reparameterization of the coarse-grained mW model[57] with improved performance on multiple properties. The ML-mW model exhibits a complete premelted first bilayer near the melting point, agreeing with SFG experiments[11] and the full atomic TIP4P/Ice model (supporting information / SI, Sec. 1). It’s also significantly more efficient than full atomic models[58] thus allowing large-scale simulations. Its melting point is found to be 295.83±0.5K by the direct coexistence technique[58-59] (SI Sec. 2). To identify the extent of premelting, we use the proportion of solid molecules[60] in each bilayer as an order parameter. An order parameter of 1.0 indicates a solid ice crystal and 0.0 means the complete loss of order. MD simulations are performed with LAMMPS[61] and accelerated
by INTEL package, with structural visualizations carried out by OVITO (see SI, Methods section for the detailed setup).

![Image of Figure 1](image)

**Figure 1. Overview of the static premelting behavior.** (a) the order parameter (proportion of solid molecules) as functions of temperature, for first 3 bilayers on the surface. Gray shadow: estimated melting point of ice. Green shadow: estimated onset of premelting ($T_p$, see SI Sec. 3). (b) the structure of QLL at 294.5K, sliced for first 3 bilayers, in a 20*20 nm lattice. Colors represent the structural type of each water molecule (see legends). (c) the structure of solid surface at 293.1K.

The static profile of premelting for the ML-mW model is summarized in Fig. 1. There’s a single specific onset of premelting temperature for this model, where the first 2 bilayers of surface lose their order simultaneously (Fig. 1(a)). This onset is further determined as $T_p$=293.85±0.15K (green shadow in Fig. 1(a); see SI Sec. 3). The premelting behaves like a 1st-order phase transition, where the order parameters change abruptly at $T_p$. In the premelted surface with $T>T_p$, the 1st bilayer is mostly melted and the 2nd bilayer is mixed with solid and liquid (Fig. 1(b)). In the solid surface with $T<T_p$, only a small fraction of liquid exists in the 1st bilayer and barely any exist in the 2nd bilayer (Fig. 1(c)). The proportion of liquid molecules in the 1st bilayer grows slowly with temperature, but the solid part always dominates when $T<T_p$ (Fig. 1(a)). The premelting mainly involves first 2 bilayers and the 3rd bilayer is mostly intact in both scenarios.

To study the transition between QLL and solid surface, a series of simulations are performed starting from either solid or premelted surface, in a range of temperatures near $T_p$ (293.1~294.5K). Thermodynamically, the melting of solid surfaces should occur under temperatures higher than $T_p$, and similar in the opposite direction. Transitions between two phases are indicated by the change of order parameter in first 2 bilayers. The results of all such trials are summarized in Fig. 2(a). Notably, the transition between two phases doesn’t occur immediately when it’s thermodynamically favored. Indeed, the solid surface is stable in a 100 ns simulation up to 294.3K, ~0.5K higher than $T_p$; while the melted surface is stable in 100 ns down to 293.3K, ~0.5K lower than $T_p$ (Fig. 2(a)). These results indicate the existence of supercooling and superheating for the premelting transition, at least in a short time. These metastable phases bring in total uncertainty of ~1K on the premelting onset, which may be relevant to observations about different measurements of QLL during heating and cooling. This uncertainty is smaller than the discrepancy between the $T_p$ reported by various experiments, though. However, we speculate that the metastable states may be relevant in larger temperature ranges if premelting occurs at lower temperatures, as suggested in another water model (SI Sec. 4).
Figure 2. Supercooling and superheating of the ice surface. (a) the order parameters of first 2 bilayers, at the end of simulations in 20*20 nm lattices lasting 100 ns each. QLL start = simulations started from QLL (premelted surface); SS = solid surface. Green shadow: estimated onset of premelting. (b) the order parameters of first 2 bilayers during a QLL -> SS transition at 293.1 K. (c) an SS -> QLL transition at 294.5 K.

Fig. 2(b) and (c) demonstrate two instances of transition processes between two phases. Both of them go through some time before an abrupt change of order parameters, confirming the existence of metastable phases. But the premelting and freezing transition also show different features: the 1st bilayer of the supercooled phase has a stable order parameter before transition (Fig. 2(b)), but that of the superheated phase fluctuates rather heavily (Fig. 3(c)). This is similar to the impression of its bulk counterpart, where supercooling is considered much more stable than superheating\[^{65}\]. Such contrast also implies a difference in the transition mechanism between two directions, as we will discuss soon.

To investigate the transition between two phases in more detail, we performed large-scale (70*70 nm) MD simulations and visualized the structural change of ice surfaces. The conditions are selected so that (1) the metastable phases can exist for a reasonably long time; (2) transitions are still observable in the timescale of an MD simulation.

Figure 3. The structure of ice surface during a solid -> premelted transition. Colors represent different structural types (see legends in Fig. 1). Pure white means no molecules in that region of the bilayer, i.e. holes. The lattice size is ~70*70 nm. The simulation is performed at 294.2 K, starting from a perfect ice surface. (a1~a4) the 1st bilayer, at 10/100/150/187 ns of the simulation. (b1~b4) the 2nd bilayer. Some holes and liquid nuclei are circled (see main text).
Fig. 3 shows a typical process of premelting, from solid surface to QLL. In the beginning, the 1st bilayer is a regular mixture of solid and liquid (a1), similar to the equilibrium state at lower temperatures (Fig. 1(c)). After some time, however, holes start to appear in the 1st bilayer (a2, circled); meanwhile, some liquid regions in the 2nd bilayer become larger (b2, circled). One liquid region in the 2nd bilayer grows further later (b3, circled), with larger holes and liquid region in the corresponding 1st bilayer (a3, circled). The liquid region continues to grow (a4, b4) until occupying the whole surface, completing the phase transition.

It’s interesting to compare this process with the more familiar counterpart, the bulk liquid-solid transition. In the latter scenario, the supercooling/superheating phases turn into stable phases by a nucleation process: nuclei (i.e. small clusters) of the stable phase are randomly generated by thermal fluctuations, and nuclei large enough can grow continuously into bulk\cite{66}. Indeed, if we only look at the 2nd bilayer, the premelting transition looks similar to the classical nucleation: the liquid nuclei appear in the solid background (b1~b2), and one of them grows continuously into the whole surface (b3~b4). However, considering 2 bilayers together reveals a unique feature of premelting: liquid nuclei on the ice surface are not randomly generated. Namely, the growing liquid nuclei in Fig. 3(b) is located close to a large hole in Fig. 3(a), and it is not a coincidence: generally, liquid molecules in the 2nd bilayer are more likely to appear around holes in the 1st bilayer (SI Sec. 5). In other words, holes in the 1st bilayer lead to a surface inhomogeneity promoting the premelting transition. This effect arguably comes from two aspects: (1) holes in the 1st bilayer directly expose those regions of the 2nd bilayer to the air, making them more vulnerable to thermal perturbations; (2) large liquid regions are sometimes found near holes in the 1st bilayer (see Fig. 3(a2), for example), so the region beneath them more likely consists of liquid too.

The freezing direction, where QLL turns into the solid surface, is illustrated in Fig. 4. Notably, large holes are found in the 1st bilayer of QLL (Fig. 4(a); circled in a1-a2). In the beginning, the 2nd bilayer is mainly composed of liquid, with solid islands of varied sizes straggling in it (b1). After some time, large solid islands appear in the 2nd bilayer where holes in the 1st bilayer locate (b2, a2, circled). At the first glance, this seems to be an analog to the premelting direction discussed earlier (Fig. 3): holes in the 1st bilayer promote the phase transition. However, the large nuclei under holes don’t grow further in this case. Indeed, it’s another nucleus away from holes that finally grows larger (a3, b3, circled), and spread into the whole surface (a4, b4). And it doesn’t look like a coincidence either: though more studies may be required for a conclusion, it seems that solid nuclei under holes are unlikely to grow or induce freezing (SI Sec. 6).

Such observation reveals the different roles of holes during surface melting and freezing: though holes exist in both scenarios, they seem to only promote the transition to premelted phases, but not reversely. This contrast probably traces back to the origin of holes on ice surfaces: the molecule redistribution between bilayers. Namely, molecules in the 1st bilayer move into lower and upper layers during premelting (SI Sec. 7), resulting in lower molecule density thus growing holes (SI Sec. 8). Growing holes allow the nuclei under holes to grow, which may further trigger the phase transition. In the freezing direction however, the holes tend to shrink instead (SI Sec. 8), confining the nuclei under them and preventing them from spreading into the whole surface. Therefore, holes don’t help the transition to the freezing phase.
Figure 4. The structure of ice surface during a premelted -> solid transition. Colors represent different structural types (see legends in Fig. 1). The lattice size is ~70*70 nm. The simulation is performed at 293.3 K, starting from a premelted surface. (a1~a4) the 1st bilayer, at 10/140/280/350 ns of the simulation. (b1~b4) the 2nd bilayer. Some holes and solid nuclei are circled (see main text).

Another notable thing is that the solid grown from the supercooled QLL is partially stacking disordered ice (b3, b4, cubic molecules shown as blue). It only represents a single observation though and we don’t consider that a general rule. However, such stacking disorders might also exist in real ice surfaces frozen from QLL, considering the belief that stacking disordered ice is kinetically favored during crystallization[67]. Furthermore, molecules from different nuclei (e.g. under holes) may have different stacking orders within the 2nd bilayer (b3), because of their different origin. As a result, the boundary region between stacking orders remains liquid to the end of simulation (b4) due to lattice mismatch. The lifetime of such boundaries is unknown yet, but they might survive longer if the holes in the 1st bilayer are large, which could result from holes merging to reduce their “edge” energy in a longer timescale.

So far, we have discussed the surface inhomogeneity of QLL and its implication for the transition dynamics. In real scenarios, the ice surface may undergo growth or evaporation. Such processes can lead to an ice surface not being terminated with one full bilayer, altering the surface structure including the inhomogeneity. Specifically, excess molecules beyond one bilayer can “fill” the holes and ultimately lead to clusters on the surface (SI Sec. 9). However, it’s yet unsure if the filling of holes can make the unpremelted phase more stable.

In this study we used the ML-mW water model, which shows a 1st-order premelting transition at several Kelvins below the melting point (Fig. 1). However, this is not an established conclusion and other water models may behave very differently. Models like the original mW show a completely continuous premelting transition[21, 45], and the premelting onset reported by different simulations can differ by dozens of Kelvins[11, 15, 21, 25-26, 45]. So it’s not surprising if other water models have different premelting dynamics, not to mention experiments with highly variable conditions. However, currently it’s difficult to remove this ambiguity, as
we have to rely on empirical classical force fields for computational efficiency. These force fields are usually built with the main focus on bulk properties, making them less reliable for premelting studies. To move towards a more definitive conclusion, an efficient force field of water focusing on the ice surface is desired. Nevertheless, we still feel it helpful to provide a potential picture of the transition dynamics here in prior, indicating the importance of metastable phases, and showing how QLL may behave under a scaling not frequently touched.

To sum up, we have provided a molecular-level picture of the transition dynamics between the premelted and solid ice surfaces. Supercooling and superheating phases exist in the premelting transition, and generally the supercooled phase has smaller fluctuation. The transition between phases roughly follows the nucleation picture, and holes in ice surfaces promote nuclei generation. Nuclei induced by holes can grow and lead to a full transition to the premelting phase, but not to the inverse direction. Sometimes the freezing process leads to the coexistence of different stacking orders in the same bilayer, due to having multiple nuclei concurrently. Further studies may focus on developing water models specifically target ice surfaces, and re-evaluating the premelting behavior of ice including transition dynamics.

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Supporting Information

For the article: The ice surface in premelting and freezing: transition dynamics and metastable states

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Methods

Some of the simulation setup has been mentioned in the main text; this section will describe them in more detail.

ML-mW

The ML-mW model is used in most simulations in this work. The lattice parameter is determined by an NPT simulation at 294 K, resulting in \(a=b=0.45015 \text{ nm}, c=0.73487 \text{ nm}\). The variation of lattice parameter due to temperature change is \(< 0.0001 \text{ nm}\) in the temperature range studied in this paper and is neglected. All simulations are performed in the NVT ensemble unless otherwise noted, using the Nose-Hoover thermostat\(^{[1-2]}\) with a relaxation time of 1.25 ps. The timestep for MD is 5 fs. A slab with 10 bilayers is used for simulating the ice surface. The bottom 2 bilayers are fixed during the simulation (by excluding them from time integration and thermostating), and the top 8 bilayers are movable. A reflective layer is placed above the ice surface to avoid losing molecules. A vacuum layer exists between the ice surface and reflective layer, with thickness \(>> 0.4 \text{ nm}\) (\(\approx\) the cutoff of ML-mW model). Periodic boundary conditions are imposed in two other directions.

The original mW

The original mW model is used in several places of SI. Most of the simulation setup is same as ML-mW except for the force field parameters. The lattice parameter used for mW model is \(a=b=0.4427 \text{ nm}, c=0.72028 \text{ nm}\).\(^{[3]}\)

TIP4P/Ice

The TIP4P/Ice model\(^{[4]}\) is used in several places of SI. These simulations are performed with GROMACS\(^{[5-6]}\) for better performance. The ice structures are generated by the GenIce2 software\(^{[7-8]}\) with a density of 0.90634 \text{ g/cm}^3. GenIce2 generates ice structures with stochastic arrangements of hydrogen atoms and zero net dipole moment. A slab with 10 bilayers is used for simulating the ice surface. No molecules are fixed in the simulation (i.e. it is a double-sided slab). All reported statistics about the ice surface are averaged for both sides. Periodic boundary conditions are imposed in all directions. A large vacuum layer (~3x thickness of the slab) is placed “between” two sides to reduce interactions between periodic images. Note that whole molecules should not be split apart when adding the vacuum layer. The velocity-Verlet integrator and Nose-Hoover thermostat are used for better comparability with LAMMPS. All simulations are performed in the NVT ensemble with a thermostat relaxation time of 1.25 ps. The timestep for MD is 2 fs. The coulomb part of interaction is calculated by the fast smooth particle-mesh Ewald method, with the short-range part cut at 0.9 nm. The van der Waals part is calculated with a plain cut-off of 0.9 nm, with long-range corrections for energy and pressure. The linear center-of-mass velocity is removed every 100 steps to mitigate the drifting of slab.

Getting the stable phase

In the main text, we showed the existence of supercooling/superheating in premelting. They introduce some difficulty in finding the (thermodynamic) stable phase, since these metastable phases may persist in a finite-time simulation. To find the stable phase in such scenarios, we used a scheme similar to the direct-
coexistence technique for finding bulk melting points. First, the premelted and solid ice are prepared independently in advance, by NVT simulations in corresponding temperature ranges (e.g. 295 and 293 K). After that they're concatenated together (Fig. S1):

The obtained structure is slightly relaxed to avoid molecule overlap, then the regular NVT simulation is performed. Note that the simulations at performed at constant volume (instead of constant pressure in its bulk version), since the surface doesn't affect lattice parameters of bulk ice (because it only takes up an infinitesimal portion of molecules in the real world, where the “slab” contains many bilayers). At the thermodynamic limit, a certain phase will dominate the surface after sufficient time, telling us the stable phase at this temperature. In finite-size simulations, the dominating phase may vary in a narrow temperature range and an estimate of the premelting onset is derived. This scheme is used in Fig. 1(a) (with a total lattice size of 20*10 nm) and SI Sec. 3 (total lattice size of 40*20 nm).

Splitting bilayers
In this work, we split the ice surface into multiple bilayers to analyze its order and structure. For the mW and ML-mW models, this can be done by counting from the fixed layers at bottom. Namely, the bisector of two bottom layers is found first, and other bisectors are derived by successively adding the height of one bilayer. For the TIP4P/Ice model, the bisector of two middle layers is found first instead, by averaging the z coordinate of all oxygen atoms. In this approach, all bilayers except the top two have almost same number of molecules, and the bisector of top two bilayers is very close to the local minimum of molecule distribution histogram in z direction. The change of molecule numbers in top two layers is induced by premelting (SI Sec. 7).

Structure identification
The molecules in ice surfaces are categorized by their local structures through this work. This is done by the method described in Appendix A of ref. 9 (i.e. the “identify diamond structure” modifier in OVITO). For our purpose, the 1st and 2nd neighbors of hexogen/cubic molecules are also counted into the corresponding structures (the molecules themselves are on site but their neighbors are probably not). For the three-atom TIP4P/Ice model, only oxygen atoms are considered during the identification.
Existence of complete premelting in several water models

The ML-mW model claims an improvement over the original mW on several properties, and a general accuracy comparable to higher-level water models\cite{10}. However, its premelting properties have not been touched before this work, and it would be desired to compare its premelting behavior with other popular water models. In this section, we will discuss the stable surface structures of three water models (mW, ML-mW, TIP4P/Ice) near the melting point. To this end, a 10*10 nm perfect ice surface is built for each of these three models, and they’re simulated near the melting point of each model for 10 ns. The results are shown in Fig S2.

![Figure S2](image)

**Figure S2.** Ice surface near melting point in three water models, sliced for the 1st and 2nd bilayer. Colors represent structural types (see Fig. 1, main text). Only oxygen atoms are shown for the TIP4P/Ice model. (a) ice surfaces after 10 ns of simulation each. Temperature: ML-mW -> 295.7K (T_m-0.13K), mW -> 275.7K (T_m+1K\cite{11}), TIP4P/Ice -> 270K (T_m+0.2K\cite{12}). (b) the ice surface of mW model after rapidly throwing molecules and 25 ns of simulation (throw at the rate of 0.2 molecules/fs, with initial velocities of 0.2~0.3 nm/ps towards surface. 1 bilayer is thrown in total). The ice surfaces keep a similar structure in the 25 ns simulation, i.e. it’s at least a metastable phase.

The ML-mW and TIP4P/Ice models share similar features near the melting point: the 1st bilayer is almost completely melted, while the 2nd bilayer is mainly liquid with some solid islands in them (Fig. S2(a)). But the original mW model is very different: the 1st bilayer is only partially melted at a temperature higher than the melting point, and the 2nd bilayer is still mostly solid (Fig. S2(a)). In other words, the mW ice never completely premelts. To eliminate the effect of potential metastable phases, we tried to artificially make a completely premelted surface for the mW model by rapidly throwing molecules to the surface. It turns out that the mW model does have a completely premelted phase (Fig. S2(b), and see captions), but coexistence tests reveal that it’s still only metastable even above the melting point (not shown here). Therefore, the mW model doesn’t seem to have a thermodynamically stable complete premelting, while two other models have.

Such difference points out the importance of force field choice in premelting studies. However, at this moment, we don’t think it necessarily means “ML-mW and TIP4P/Ice behaves similarly in premelting” or
“ML-mW is better than mW”. Indeed, the TIP4P/Ice model is reported to show premelting down to 200K\cite{13} (see SI Sec. 4), while the ML-mW shows that only at several Kelvins below the melting point. For our purpose, the ML-mW model is adopted because it’s the only water model (as far as we know) that has complete premelting and allows large-scale (e.g. 70*70 nm) simulations performance-wise. The more basic problem is that most empirical force fields are designed for bulk properties, so ice surface properties like premelting are somewhat hit-or-miss (see main text).

Comparison between water models also points out another topic, namely the premelting behavior of different materials may vary drastically (as they already did in different water models). It’ll be interesting to study the premelting behavior in more types of materials, and potentially figure out internal factors affecting them. For example, it had been suggested that the continuous premelting of the mW model is caused by a negative solid-liquid-vapor line tension\cite{14}, though the latter property may be difficult to touch since liquid in QLL is different from the bulk.
2 The melting point of ML-mW model

In the original paper of ML-mW model, the melting point is reported as 289K. To study its premelting behavior, we re-determined the melting point with higher accuracy using the direct-coexistence technique. The model used in direct-coexistence simulations is ~7.2*5.5*13.2 nm in size and has ~16000 molecules in total, half filled by water and half filled by ice. A large model reduces stochastic error and systematic error caused by the difference between NPT and the exact NP,T ensemble[15-16]. 5 independent runs (with different random seeds for initial velocities) are performed for each temperature under the NPT ensemble. Each run lasts for 200 ns, or until a certain phase dominates the system. The results are summarized in Tabl. S1. The estimated melting point is 295.83±0.5K.

| Temperature/K | 295  | 295.33 | 295.67 | 296  | 296.33 |
|---------------|------|--------|--------|------|--------|
| Solid         | 5    | 5      | 1      | 0    | 0      |
| Liquid        | 0    | 0      | 0      | 0    | 5      |
| Undetermined  | 0    | 0      | 4      | 5    | 0      |

Table S1. The result of direct-coexistence tests for the ML-mW model. "Undetermined" means neither phase dominated the system after 200 ns of simulation.
3 The premelting onset of ML-mW model

The premelting onset of ML-mW model is determined by the coexistence technique demonstrated in the Methods section (Fig. S1), with total system sizes of 40*20 nm. 4 independent runs with different random seeds for initial velocities are performed for each temperature. Each run lasts for 75~235 ns. The results are summarized in Tabl. S2; the estimated transition temperature is 293.85±0.15K. This is shown as the green shadow in Fig. 1(a) and 2(a) of main text.

| Temperature / K | 293.7 | 293.8 | 293.9 | 294.0 |
|-----------------|-------|-------|-------|-------|
| Solid           | 4     | 1     | 1     | 0     |
| Premelted       | 0     | 1     | 2     | 4     |
| Undetermined    | 0     | 2     | 1     | 0     |

*Table S2. The results of premelting coexistence tests. "Undetermined" means neither phase dominates the system at the end of simulations.*
4 Stability of metastable phases under lower transition temperatures

In the ML-mW model, supercooling and superheating can be observed but only in a small temperature range (~1K). This is partly because the premelting temperature is high (near the melting point), so molecules on the surface diffuse quickly. To demonstrate this, here we consider the metastable phases in the TIP4P/Ice model with a much lower premelting onset. For this purpose, simulations are performed starting from either perfect or premelted surface at three temperatures: 180, 200, and 220 K. Each simulation is performed in a 10*10 nm lattice and lasts for 100 ns.

![Figure S3](image1)

Figure S3. The order parameters of first 2 bilayers, during 100 ns simulations at (a) 180 K (b) 200 K (c) 220 K. SS=solid surface. Vertical lines on the right indicate the difference in order parameters between supercooled and superheated phases at the end of simulations.

Fig. S3 shows the evolution of surface order during the simulations. Notably, the liquid and solid phases don’t reach the same state during the simulation: there’s a non-zero difference between order parameters of the same bilayer at the end (vertical lines on the right). The difference is larger when the temperature is lower, indicating that the transition is kinetically limited. As a result, metastable phases can survive in a wider range of temperatures (e.g. 180~220 K in Fig. S3), especially on the colder side. Indeed, we found that the coexistence technique for premelting (Methods section) doesn’t work well at such temperatures because the kinetics are so forbidding that a boundary doesn’t help much.

![Figure S4](image2)

Figure S4. Surface diffusion in the 1st bilayer. Only horizontal displacement is considered, and the overall drift of bulk is removed beforehand. (a) the distribution of molecule displacement during the 100 ns simulations. The frequency is normalized so that the total area under each curve is same. Curves are slightly smoothed for better appearance. (b) the mean squared displacement (MSD) as functions of time. The framed region at the bottom-right corner is magnified on the right. The diffusion coefficients are proportional to the slopes at equilibrium (not really achievable here, but can be approximated by the ending part of simulations).
The effect of low temperatures can be better understood by checking the surface diffusion. Fig. S4(a) shows the total horizontal displacement of molecules in the 1st bilayer in simulations. The QLL and solid phases have similar profiles for molecule displacements, and the QLL phase diffuses only slightly faster. Indeed, the diffusion of both phases is quite slow, especially at low temperatures (180 and 200 K) where the molecule displacement is comparable to the lattice parameters. In other words, the “QLL” behaves like a solid glass for diffusion at these temperatures (where two phases don't merge yet). The mean square displacement (MSD) of molecules demonstrates this further (Fig. S4(b)): the difference in diffusion coefficient between two phases is minor and much less than that caused by temperature change. The slow diffusion means neither of the two phases is kinetically eager to convert into the other, leading to metastable phases existing in a wide range of temperatures. It also implies that the surface structure is not everything for premelting: certain physical properties, like the diffusion coefficient, may have no direct relation to the structure. In other words, multiple premelting “onset” may exist even for the same force field, depending on the physical properties of interest.
Distribution of liquid nuclei during the premelting transition

In the main text, we discussed the surface structure of ice during the premelting transition, and noted the forming of liquid nuclei near holes (Fig. 3, main text). To demonstrate this as a general tendency, we plot out the frequency of liquid molecules appearing in the 2nd bilayer during the “quasi-equilibrium period” (i.e. after holes have formed and before the phase transition actually happens). This is shown in Fig. S5(a). Except for the nuclei finally triggering transition (the solid white circle), several other nuclei are also found (dashed white circles). Fig. S5(b)~(f) show the structure of 1st bilayer at several typical time, with significant holes circled out. Notably, most of the holes (solid circles) are found near the location of nuclei. Furthermore, high liquid frequency (in Fig. S5(a)) generally corresponds to large and long-life holes: for example, holes around two regions with highest frequencies in (a) are found in all of the five timepoints, and these holes consistently grow in the simulation. Such correspondence indicates the relation between holes and liquid nuclei during the premelting transition.

Figure S5. Relation between holes and liquid nuclei. (a) the frequency distribution of liquid molecules appearing in bilayer 2, during 25~125 ns of the simulation. Some nuclei (regions with high frequencies) are circled out (see text). (b~f) the 1st bilayer at five points during the simulation. Some holes are circled out (see text). Colors represent structural types (see Fig. 1, main text).

It should be pointed out however, this relation is not deterministic due to intrinsic randomness in nuclei formation. For example, some holes (dashed circles in (b)~(f)) don’t seem to have corresponding nuclei. In other words, holes increase the chance of finding nuclei, but they don’t guarantee that nuclei exist. Besides, the liquid regions in bilayer 1 may also help the formation of liquid nuclei in bilayer 2, though likely to a weaker extent.
6 Solid nuclei under holes are unlikely to grow

In the main text (Fig. 4), we demonstrated an instance where nuclei under holes are large but didn’t trigger the freeze of QLL. To see if this is a general tendency, we summarized all appearances of nuclei during the simulation before the phase transition is triggered (Fig. S6(a)). Notably, most of the nuclei are small (~100 molecules; also see Fig. 4(b) in main text), and most small nuclei are not located under holes (blue circles, Fig. S6(a)). However, when it comes to larger nuclei (> 1000 molecules), the proportion of nuclei under holes increases significantly and indeed reached near 100% (orange line in right panel). In other words, large nuclei are much more likely to appear under holes. Nevertheless, it’s finally a nucleus not under holes induced the transition (blue arrow). Though probably come from pure luck, it still seems to indicate that nuclei under holes are unlikely to trigger the transition.

It’ll be instructive to check out the behavior under other temperatures. Fig. S6(b) shows the distribution of nuclei during a simulation under 293.5 K. Small nuclei still take the majority, but there is an increasing number of large nuclei, especially for those > 2000 molecules. Meanwhile, almost all these large nuclei are found under holes (orange circles). However, no phase transition is observed during this 400 ns simulation. Of course, it may be simply because the critical nucleus size (if it’s a thing at all) is larger; but combining the increase of large nuclei and nuclei under holes, it may also be related to the nature that nuclei under holes don’t trigger transitions, even if they’re large.

At lower temperatures things go different. At 293.1 K (Fig. S6(c)) the nuclei under holes become much fewer; the general sizes of nuclei also become smaller and the transition occurs in a short time (blue arrow). It is probably because of the higher “nucleation rate” at lower temperatures, so the nuclei under holes don’t have a significant advantage anymore; also more nuclei generated means single nuclei are smaller.

Figure S6. Statistics of nuclei in supercooled QLL, at (a) 293.3 (b) 293.5 (c) 293.1 K. Left panel: nuclei appeared in the simulations. Each circle represents one solid nucleus (> 100 molecules) in one frame. Nuclei are identified by cluster analyses within solid molecules in the 2nd bilayer: solid molecules with distance < 0.35 nm belong to the same nuclei. Orange color means the nucleus is under a hole, and blue means not. "If a nucleus is under a hole" is determined by whether molecules in bilayer 1 are found within 1 nm (horizontal distance) around the center of mass of the nuclei. For this purpose, only molecules belonging to the largest cluster in bilayer 1 are considered, to avoid interference from scattered molecules in holes. This crude approach does make some misjudges (e.g. from concave nuclei or occasional small holes on large nuclei) but the accuracy is enough for discussion here. Blue arrows in (a) and (c) represent the nuclei triggering the phase transition. Right panel: blue: histogram of nuclei size distribution. The X-axis represents the average number of nuclei in one frame in the corresponding size interval (the system size is ~70*70 nm). Note that bar lengths are in log scale. Orange: the percentage of nuclei under holes in each size interval, in linear scale from 0% to 100%. Very large nuclei (beyond the topmost bars) are not included in the right panel because of lacking sufficient samples.
 Redistribution of molecules between bilayers in premelting

In the main text, we have shown the appearance of holes in QLL. Indeed, it can be related to the redistribution of molecules between bilayers on the surface. To demonstrate this, first we define “layer concentration” (LC) to describe how “dense” a bilayer is (ref. [3] but in a more general way):

\[ LC_X = \frac{N_X}{A\sigma_{\text{perfect}}} \]

Where \( LC_X \) is the LC of bilayer X, \( N_X \) is the number of molecules in this bilayer, \( A \) is the area of this bilayer (in a given lattice), and \( \sigma_{\text{perfect}} \) is the number of molecules per area in perfect ice. By this definition, perfect ice has \( LC=1.0 \) for all bilayers, and real systems are scaled accordingly by their density in each bilayer. An increase of LC for a certain bilayer indicates molecules flowing into that bilayer, and vice versa.

To study the vertical exchange of molecules during premelting, an MD run is performed at four temperatures (250/293.5/295/290 K) successively, with each temperature lasting for 20 ns. The LC of bilayer 0~3 are shown in Fig. S7 (“bilayer 0” means the region above bilayer 1, assuming the bilayer 1 is of one bilayer, i.e. 0.73487 nm thick). At low temperatures (250 K), each bilayer keeps its density (0~20 ns, Fig. S7). The story begins at 293.5 K, where the transition point is not reached yet but the surface already become somewhat disordered (similar to Fig. 1(c)). At this temperature, some molecules start to leave the 1st bilayer (20~40 ns), giving a slight decrease (<5%) of density in bilayer 1. After the premelting transition occurs (45~60 ns), the LC of bilayer 1 drops further (15~20%), and that of bilayer 0 and 2 increase. In other words, the molecules in bilayer 1 move to upper and lower layers in the premelting transition, and bilayer 1 becomes less dense so holes grow. On the other hand, the molecules in bilayer 0 and 2 go back to bilayer 1 after the surface refreeze (60~80 ns), leading to a denser bilayer 1 and shrinking holes.

Figure S7. Layer concentration of bilayer 0, 1, 2, and 3 (see text for definition), during an MD simulation at 250, 293.5, 295, and 290 K, successively. The y-axis is broken in the middle. Each temperature lasts for 20 ns (time boundaries are shown as dashed vertical lines). The system size is ~20*20 nm.
The tendency of hole sizes during premelting and freezing

As stated in the main text, premelting leads to growing holes on the surface while freezing leads to shrinking holes. Such tendency can be illustrated by the evolution of hole sizes during transitions, as shown in Fig. S8. Notably, holes in the premelted surface tend to grow slightly ((a), before (1)), probably reflecting a (slow) equilibration process in the surface. However, the hole sizes drop significantly after the surface freezing has reached the holes ((a), after (2)). In other words, surface freezing triggers the shrinking of holes. For the premelting side (S8(b)), the holes are growing for the most time, just like that shown in Fig. 3. Moreover, the size of the largest hole increase sharply after the phase transition actually starts ((b), after (3)). Generally speaking, the holes tend to grow in the premelting direction.

Figure S8. Sizes of 1st and 2nd largest holes in the system, during (a) freezing at 293.3 K (Fig. 4), and (b) premelting at 294.2 K (Fig. 3). Vertical lines: the approximate time of (1) the freezing transition has started, (2) the solid phase has reached the edge of the largest hole, and (3) the premelting transition has started. To measure the size of holes, molecules belong to the largest cluster in bilayer 1 are extracted (see captions of Fig. S6). Holes are identified as connected regions (considering periodic images) not covered by any molecule in the XY-plane, assuming each molecule has a radius of 0.35 nm. Large fluctuations in a short time (almost “vertical” in the curves) are caused by adjacent holes merging and detaching, which are irrelevant to our discussion here.
9 QLL with excess molecules on the surface

Until now all of our simulations begin from full-bilayer terminated ice surfaces, or systems with same number of molecules as that. In real systems the ice may undergo growth or evaporation, leading to excess molecules beyond one full bilayer on the surface. To study those scenarios, we may introduce excess molecules by throwing molecules toward a full-bilayer terminated surface (see captions of Fig. S9). These excess molecules may fill the holes and lead to clusters on surface, as shown in Fig. S9 (colored in red). Notably, most of clusters sit on the liquid region of bilayer 1 when the temperature nears the premelting onset (293.5/294 K). This is quite different from clusters observed in the original mW model, where most clusters sat on the solid region$^{39}$. At lower temperatures (293 K), more clusters are found above solid regions. It’s yet unclear if such contrast implies a crossover in relative stability of clusters’ locations, or it’s merely because more solid exists in bilayer 1 at low temperatures.

Figure S9. Ice surfaces with 20% extra molecules (20% means “20% of a full bilayer”; e.g. if a regular system has 10 bilayers and each bilayer has 10,000 molecules, then the current system has 102,000 molecules, with extra 2,000 molecules added on the surface). Upper panels: both bilayer o and 1 are shown. Molecules in bilayer 0 (see SI Sec. 7) are colored in red; see legend in Fig. 1 for other molecules. Lower panels: only bilayer 1 is shown. Temperatures are shown at the top. The system size is ~70*70 nm. Each simulation starts from a perfect ice surface and lasts for 125 ns. Extra molecules are added at the beginning of simulations, by smashing one molecule to the surface every 0.5 ps, with initial velocities of 0.2~0.3 nm/ps towards the surface. The high molecule addition rate is selected in hope of taking the system away from the initial structure, so it’s more likely to reach the thermodynamic stable state later (though it’s not guaranteed).

When more extra molecules exist on the surface, clusters grow further along with the liquid region beneath them (Fig. S10(a1-a2)), and may connect together and isolate the solid regions in bilayer 1 (a1-b2). Following this trend, the clusters will finally occupy the whole bilayer 0 (c1-d2); at this moment it may form either a premelted or solid surface ((d) shows a premelted surface), depend on temperature and kinetics details.
In the main text, we have seen that the premelting transition is primarily driven by holes. Since excess molecules on the surface fill the holes, we may expect the unpremelted phase becomes more stable. However, detailed studies on this could be difficult, as the coexistence technique becomes unreliable (the “cluster on liquid” phase is inhomogeneous on such a large scale that cannot be neglected at general MD simulation sizes).
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