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Investigating the quasi-liquid layer on ice surfaces: a comparison of order parameters†

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Ice surfaces are characterized by pre-melted quasi-liquid layers (QLLs), which mediate both crystal growth processes and interactions with external agents. Understanding QLLs at the molecular level is necessary to unravel the mechanisms of ice crystal formation. Computational studies of the QLLs heavily rely on the accuracy of the methods employed for identifying the local molecular environment and arrangements, discriminating between solid-like and liquid-like water molecules. Here we compare the results obtained using different order parameters to characterize the QLLs on hexagonal ice (Ih) and cubic ice (Ic) model surfaces investigated with molecular dynamics (MD) simulations in a range of temperatures. For the classification task, in addition to the traditional Steinhardt order parameters in different flavours, we select an entropy fingerprint and a deep learning neural network approach (DeepIce), which are conceptually different methodologies. We find that all the analysis methods give qualitatively similar trends for the behaviours of the QLLs on ice surfaces with temperature, with some subtle differences in the classification sensitivity limited to the solid–liquid interface. The thickness of QLLs on the ice surface increases gradually as the temperature increases. The trends of the QLL size and of the values of the order parameters as a function of temperature for the different facets may be linked to surface growth rates which, in turn, affect crystal morphologies at lower vapour pressure. The choice of the order parameter can be therefore informed by computational convenience except in cases where a very accurate determination of the liquid–solid interface is important.

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1 Introduction

Quasi-liquid layers develop on ice surfaces at temperatures below the bulk melting point.^{1–4} This interesting pre-melting phenomenon is related to the structure of the ice surfaces,^{5–7} influences the growth and morphology of ice crystals,^{8–10} and mediates chemical reactions at the vapour–ice interface.^{11,12} Since their prediction about 160 years ago by Michael Faraday,¹³ the existence of such QLLs has been confirmed by a variety of experimental techniques, including photoelectron spectroscopy,¹⁴ glancing angle X-ray,^{15,16} ellipsometry,¹⁷ atomic

force microscopy,^{18,19} etc.^{20–24} These methods, however, did not reach a consensus on the QLL thickness and the temperature associated with the onset of pre-melting, which depend on the probes used.^{25–28} Meanwhile, extensive efforts contributed by computer simulations support that the thickness of the QLLs is directly correlated with temperature.^{29–33}

Hexagonal ice (Ih) is the most common among the many phases of ice, as it is found at ambient conditions.^{34,35} The Ih structure determines the sophisticated hexagonally-symmetric shape of snowflakes. It is usually obtained by freezing water at ordinary temperature. Vapour deposition at a lower temperature can produce cubic ice (Ic), which is a metastable structure with the oxygens arranged in a diamond lattice.^{36,37} The structures of Ih and Ic are distinct, but the differences are subtle: the local arrangement of the four first neighbours is similarly tetrahedral,³⁸ with differences emerging in the second coordination shell. In fact, the Ih second hydration shell contains 12(+1) molecules, whereas that of Ic contains 12 with a different arrangement. The extra water molecule in the Ih second shell,³⁹ anharmonic nuclear vibrations⁴⁰ and nuclear-quantum effects^{41,42} can be linked to the greater stability of Ih over Ic.

Ih has three main crystal surfaces: the basal (0001), the primary prism (10 $\bar{1}$ 0) (prism1) and the secondary prism ($\bar{1}$ 2 $\bar{1}$ 0)

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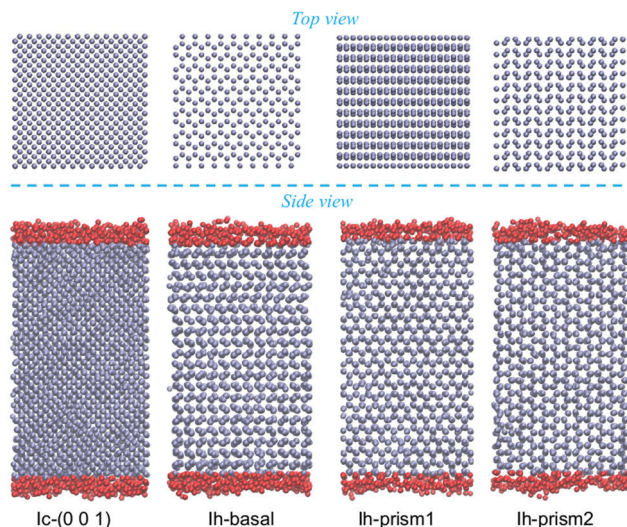


Fig. 1 The slab models used to study the (001) surface of Ic and the basal, primary and secondary prism surfaces of Ih. Top panels: cross sections of the ice phase parallel to the surface; bottom panels: view perpendicular to the surface for exemplary MD snapshots at 260 K showing the two quasi-liquid layers with liquid-like molecules identified by the local Steinhardt parameter lq_3 coloured in red. Only oxygen atoms are shown.

in pairs with intra-bilayer spacing of 0.929 Å and inter-bilayer spacing at 3.738 Å; the primary prism slab consists of 48 layers of 120 atoms each, also arranged in pairs, with intra-bilayer spacing of 1.296 Å and inter-bilayer spacing of 2.766 Å; the secondary prism slab consists of 40 equally spaced layers at a distance of 2.275 Å, each composed of 144 molecules. The cubic slab consists of 56 equally spaced layers at a distance of 1.561 Å, each composed of 98 molecules.

The reference MD simulations for bulk Ih and bulk Ic are performed at the temperature of 250 K and 260 K. Bulk water is studied at 300 K and 280 K, and supercooled at 260 K and 250 K. The MD simulations for Ih slabs are conducted at temperatures between 240 K and 270 K, in 5 K intervals. The MD simulations for the Ic slab are conducted at temperatures between 200 K and 270 K, in 10 K intervals. The simulations are carried out using the LAMMPS (Dec 9, 2014 version) package.⁶⁸ The cutoffs for the long-range Coulomb and van der Waals interactions are set to 12 Å. A time step of 1 fs is used. Temperature and pressure are controlled with Nosé–Hoover thermostat and barostat with relaxation times of 100 fs and 1000 fs, respectively.

To equilibrate the reference bulk ice, 10 ns of *NPT* simulation are performed at zero pressure at the temperature of 250 K and 260 K. Once the *NPT* simulations are complete the final *NPT* configuration (atomic positions and supercell) are used to run *NVT* simulations for 20 ns. For the bulk supercooled water, the final *NPT* configuration is subjected to a fast-melting process at 400 K for 10 ns in the *NVT* ensemble. Then, a 10 ns cooling process is performed to the target temperature progressively (300 K, 280 K, 260 K and 250 K), followed by 10 ns *NVT* simulations. The trajectories selected to analyze are the last 9 ns of the *NVT* simulations; the diffusivity of the

supercooled water was checked by analysing the mean square displacements. Only the oxygen atoms are considered for structure classification. The protocol and parameters of the MD simulations for the Ih and Ic slabs are similar to the reference bulk ice, but longer simulations are run. 10 ns of *NPT* simulations are run to equilibrate the system followed by 100 ns of *NVT* simulations; in the last 90 ns statistics are collected for analysed with datasets containing MD snapshots at 10 ps intervals. The simulations at 270 K are run for 400 ns to improve the sampling due to large fluctuations close to the melting point.

2.2 Analysis details

Analyzing the QLLs relies on the method used to discriminate liquid-like molecules from ice-like molecules. In this work, we analyze atomistic trajectories sampling ice surfaces to characterize the QLLs by using Steinhardt order parameters, entropy fingerprints and the DeepIce method.⁶⁴ The analysis details are introduced below. The analyses with Steinhardt parameters and entropy fingerprints are done using PLUMED 2.5.1,^{52,69} while the DeepIce analysis uses an in-house code.⁶⁴

2.2.1 Steinhardt parameters. Steinhardt order parameters distinguish between crystal and liquid-like molecular configurations on the basis of the coherence of their orientational order with that of their neighbours.⁶⁸ We adopt this method because it is more general than other local order parameter choices (such as common neighbor analysis (CNA)^{48,70}), it does not depend on specific crystal structures, and does not require the definition of a reference frame. SOPs are in fact based on spherical harmonics, which introduce the inherent rotational invariance necessary to classify environments, irrespectively of their orientation.⁵⁰ In SOPs the choice of the most suitable angular component l depends on the structures to classify. The global Steinhardt order parameter q_l for particle i is defined as:

$$q_l(i) = \sqrt{\frac{4\pi}{(2l+1)} \sum_{m=-l}^l |q_{lm}(i)|^2} \quad (1)$$

where the $(2l+1)$ components are computed as:

$$q_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b} Y_{lm}(\mathbf{r}_{ij}). \quad (2)$$

l is an integer parameter (in this work we test $l = 3, 4, 6$), $Y_{lm}(\mathbf{r}_{ij})$ are the spherical harmonics calculated for the vector \mathbf{r}_{ij} connecting particle i to the neighbouring particle j , and $N_b(i)$ is the number of nearest neighbours of particle i within a chosen cutoff distance.

The local average- q_l (laq_l) introduces averages over the first neighbour shell of a given particle and the particle itself.⁵⁰ This improves the classification accuracy compared to the global parameter q_l , as longer-range information is accounted for.^{41,50} laq_l is defined as:

$$laq_l(i) = \sqrt{\frac{4\pi}{(2l+1)} \sum_{m=-l}^l |\bar{q}_{lm}(i)|^2} \quad (3)$$



entropy fingerprint e and le approaches. In the classification process, the use of just one order parameter to distinguish water molecules from ice is named “single classification”, while “double classification” denotes when two order parameters are simultaneously used.

The probability distribution of SOPs and entropy fingerprints of ice and supercooled water provide an intuitive reference to determine the threshold values to distinguish different structures of ice and water and is shown in Fig. 2 for representative cases, with all the investigated cases available in the ESI,† Fig. S1. The probability distributions are normalized to one and are calculated at both 250 K and 260 K to evaluate temperature effects. The q_l parameters do not have the potential to classify different ice structures and water because their distributions for ice and water overlap for large intervals of values. Moreover, I_h and I_c are degenerate with respect to q_l , i.e. their respective q_l distributions overlap completely, making q_l unable to distinguish between ice polymorphs. Locally averaged parameters such as lq_3 , laq_3 , lq_4 and laq_4 are able to distinguish water and different ice structures with similarly good results. When compared to the corresponding q_l parameters, the overlap area between ice and water is significantly reduced, and the overlap area between different I_h and I_c is also reduced. Among these parameters, lq_3 and laq_3 can distinguish water from ice clearly. Instead, it is more difficult to distinguish water and I_h using the lq_4 and laq_4 parameters. The lq_3 parameter is also the best for discriminating I_h from I_c . Finally, lq_6 and laq_6 are good choices to distinguish water and ice structures, but they cannot distinguish different ice structures as I_h and I_c ; lq_6 and laq_6 distributions overlap significantly.

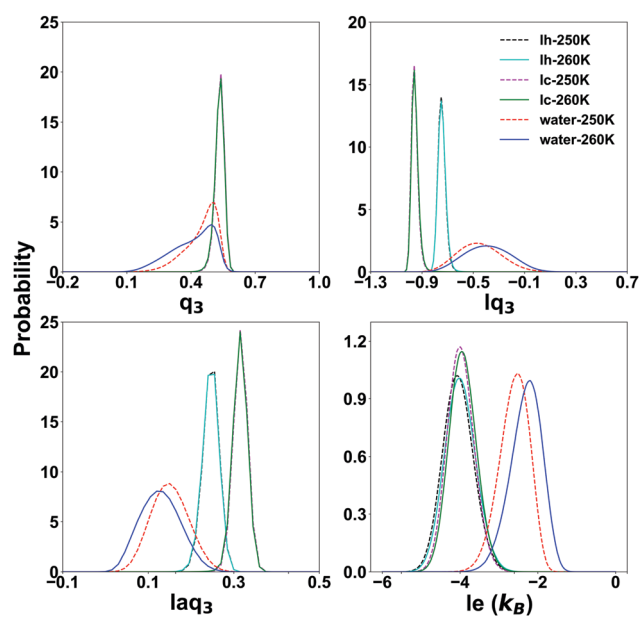


Fig. 2 The probability distribution of the Steinhardt parameters lq_3 and laq_3 and the local entropy fingerprint le for bulk water and ice at 250 K and 260 K.

The entropy fingerprint e and its local average le are very effective in distinguishing water from ice, with le providing a better separation, similarly to the effect of local averaging in the Steinhardt parameters and basically the same threshold for I_h and I_c . However, these parameters cannot separate I_c and I_h .

Focusing on the local parameters that can clearly distinguish water from ice, we determine the discriminating threshold by taking the point of intersection between the curves of water and ice as the threshold, testing the effect of temperature at 250 K and 260 K. The thresholds and the overlap integrals between the corresponding probability distribution are shown in Table 1.

The effect of the temperature is overall small, with the overlap integral being slightly smaller at 260 K. Hence it is justifiable to use the threshold determined at 260 K for all the investigated temperatures. Choosing a sharp threshold is an approximation which will inevitably result in failure to detect some water molecules, although the smaller is the overlap integral the smaller is the probability to miss them. We will compare the different methods to identify these hard-to-identify molecules in a subsequent section, and select for the comparison lq_3 , laq_3 and le . They can be used individually or in combination ($le + lq_3$ or $le + laq_3$) to exploit the features of both entropy and Steinhardt parameters. Examples of joint $le + lq_3$ and $le + laq_3$ distributions are shown in Fig. 3.

3.2 Characterizing QLLs on Ice slabs

After determining the relevant thresholds for local SOPs and entropy fingerprint in the bulk, we can use such cutoffs to locate the molecules in the quasi-liquid layers on the different ice slabs. Using single and double classification to identify the QLLs, we can visualize the MD trajectories to observe the QLLs on the ice surfaces. No molecule in the QLLs of the different surfaces of I_h and I_c is found to evaporate from the surface. This result allows us to conclude that under all the tested temperature conditions and for the sampled times, the ice surfaces are stable. Even at 270 K, surfaces do not melt and

Table 1 Top: the thresholds for bulk water and ice (I_h or I_c) discrimination using the local Steinhardt parameters (lq_l and laq_l with $l = 3, 4, 6$) and entropy fingerprint (le) at 250 K and 260 K; bottom: the overlap of the probability distribution for water and ice (I_h and I_c) of the local Steinhardt parameters (lq_l and laq_l with $l = 3, 4, 6$) and entropy fingerprint (le) in the bulk systems at 250 K and 260 K

Threshold	$le(k_B)$	lq_3	laq_3	lq_4	laq_4	lq_6	laq_6
250 K-water- I_h	-3.33	-0.68	0.21	0.42	0.26	0.49	0.38
260 K-water- I_h	-3.17	-0.67	0.20	0.41	0.25	0.48	0.37
250 K-water- I_c	-3.33	-0.84	0.26	0.60	0.34	0.53	0.40
260 K-water- I_c	-3.18	-0.82	0.26	0.58	0.34	0.52	0.39
Overlap	$le(k_B)$	lq_3	laq_3	lq_4	laq_4	lq_6	laq_6
250 K-water- I_h	0.076	0.192	0.134	0.216	0.325	0.056	0.032
260 K-water- I_h	0.047	0.076	0.087	0.192	0.264	0.054	0.032
250 K-water- I_c	0.072	0.009	0.012	0.025	0.020	0.028	0.014
260 K-water- I_c	0.044	0.008	0.007	0.023	0.018	0.029	0.025
250 K- I_h - I_c	0.813	0.021	0.066	0.068	0.043	0.522	0.520
260 K- I_h - I_c	0.894	0.007	0.073	0.078	0.047	0.512	0.543



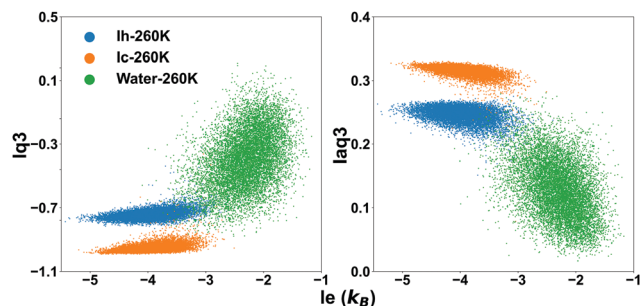


Fig. 3 The distribution of the values of the local entropy fingerprint le and either or laq_3 for bulk water (green dots), Ih (blue dots) and Ic (orange dots) at 260 K.

yield a QLL with stationary thickness. The techniques used did not identify spurious liquid-like molecules at the surfaces of the perfect ice slabs.

The time-evolution of the number of liquid-like molecules on the two surfaces of the ice slabs in the MD trajectories are shown in Fig. 4 as calculated using the local entropy fingerprint

as order parameter, as an example, and in Fig. S2–S5 of the ESI† for the lq_3 , laq_3 , le and their combinations. While the numbers vary depending on the classification methods, the trends are consistent. In particular, when using double classification, the number of molecules classified as liquid-like on all ice surfaces (Ih and Ic) is lower than that when using the corresponding single classification, due to the more stringent requirement to satisfy simultaneously two criteria. From the graphs in Fig. 4, we can observe that, as the temperature gradually rises, the QLLs on the different ice surfaces grow in thickness. In particular, in the temperature range between 260 and 270 K, the number of liquid-like molecules on Ic surface increases substantially. This behaviour is also shown by both Ih-prism1 and Ih-prism2 surfaces when the temperature changes from 265–270 K, while the number of liquid-like molecules on the Ih basal surface fluctuates more strongly than those on the prismatic surfaces in the temperature range 255–260 K.

The time-evolution of the number of molecules in QLLs on different ice surfaces is also investigated using DeepIce with 10 and 16 nearest neighbours. The time evolution on all

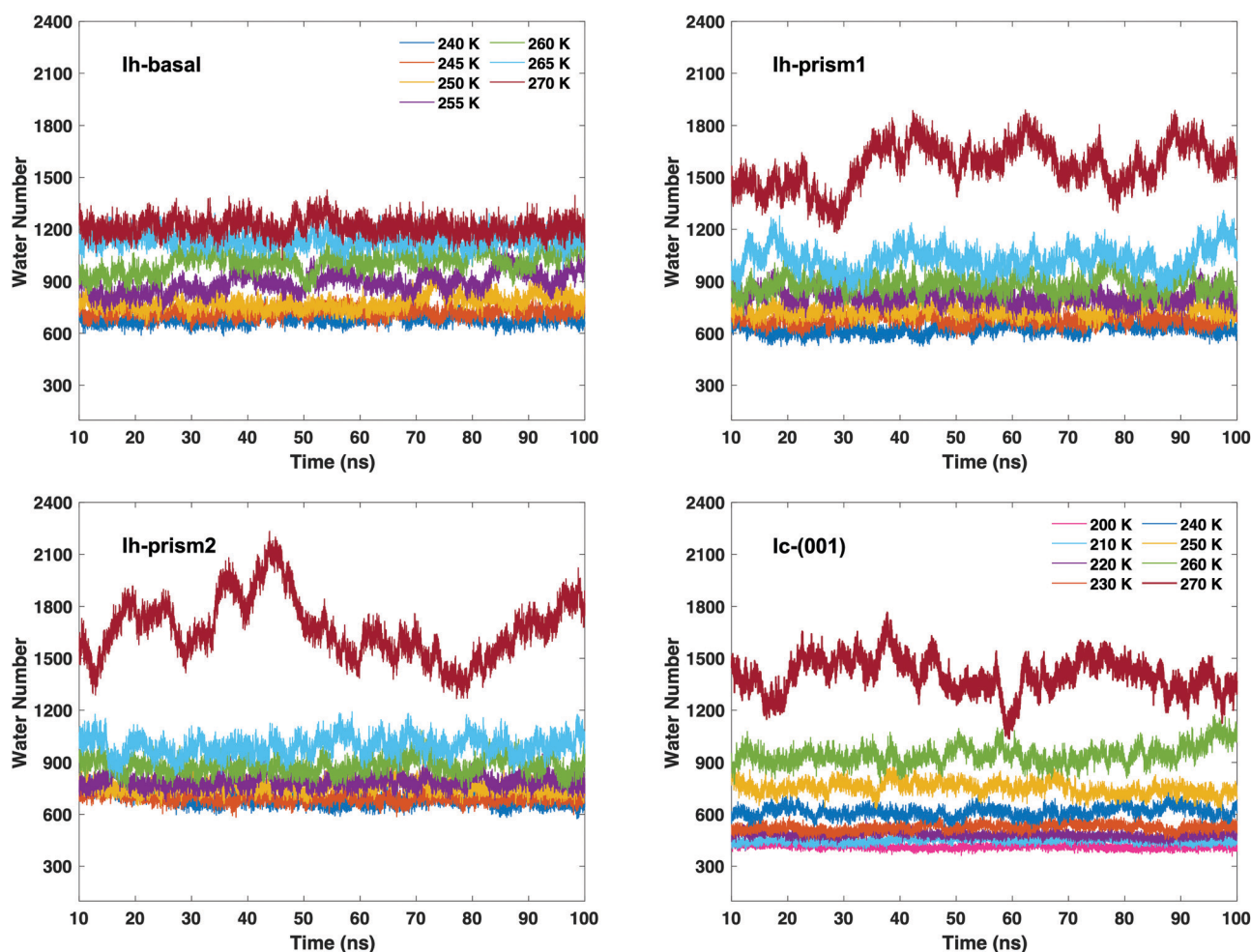


Fig. 4 Time-evolution of the number of liquid-like molecules in QLLs on the basal (top-left panel, with temperature legend for Ih), prism1 (top-right panel), and prism2 (bottom-left panel) surfaces of Ih in the 240–270 K range of temperature and on the (001) surface of Ic (bottom-right panel, with temperature legend for Ic) in the 200–270 K range of temperature, using the local entropy fingerprint le as order parameter.

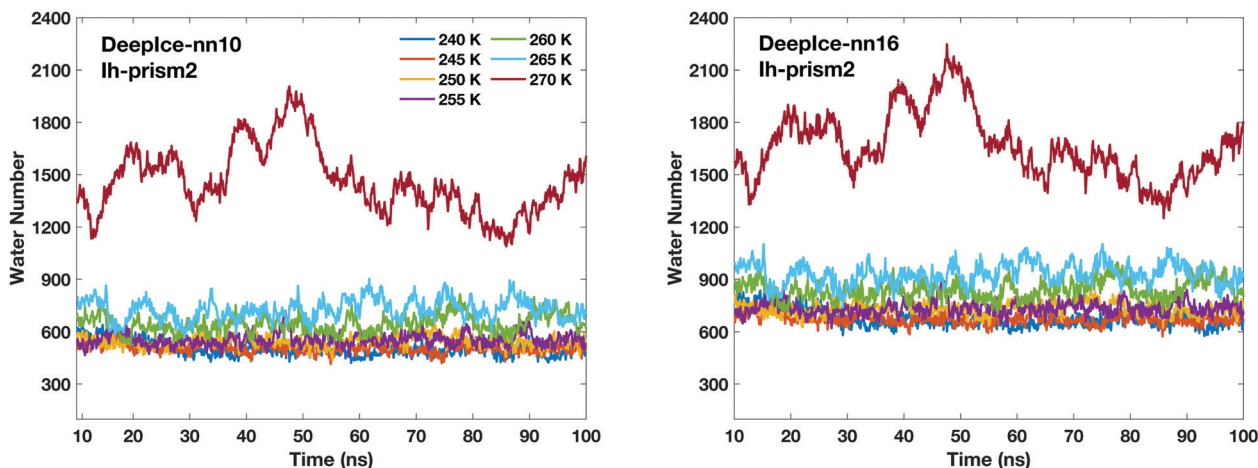


Fig. 5 Time-evolution of the number of liquid-like molecules in QLLs on the Ih prism2 surface using Deeplce with 10 nearest neighbours (left panel) and 16 nearest neighbours (right panel).

surfaces is consistent with the trend generated by using the local SOPs and entropy fingerprint in Fig. 4. Hence we only show the comparison on the Ih prism2 surface here in Fig. 5 when different numbers of neighbours are used for Deeplce. The graphs for the other ice surfaces are included in the ESI† in Fig. S6. The average number of liquid-like molecules obtained using 16 nearest neighbours are larger than the results obtained with 10 nearest neighbours. Hence, using 16 nearest neighbours tend to identify more liquid-like disordered molecules on the three different Ih surfaces than when 10 is used. This reason may be due to the second shell that can improve the ability to distinguish water and ice structures. The comparison between the nearest neighbours 10 and 16 is further discussed later on.

The average number of liquid-like molecules in the QLLs as a function of the system's temperature defined by local SOPs and entropy fingerprint, single, double classification and Deeplce is shown in Fig. 6 for a selection of cases. Error bars represent the standard deviation in the trajectories and capture the amplitude of fluctuations observed in Fig. 4 and 5. The Ic data in the top-left panel is shown for different methods, while the Ih data is shown for the different surfaces with the same classification method. The number of liquid-like molecules in QLLs on all ice surfaces increases as the temperature increases as expected. The results obtained by using different order parameters and Deeplce show large standard deviations close to the melting point 270 K, which corresponds to the dramatic fluctuation of the number of liquid-like molecules on the prismatic planes and Ic in Fig. 4 and 5; for the Ih basal surface the fluctuations and corresponding standard deviations are larger at 255–260 K. For the Ic surface, the curve shows a gentle upward trend against the temperature rise; overall le detects more liquid-like molecules than lq_3 and there is a subset of molecules detected either by le or lq_3 which therefore are counted in the double classification scheme. In general, the number of liquid-like molecules in QLLs on different ice surfaces fluctuates around a particular averaged value, with

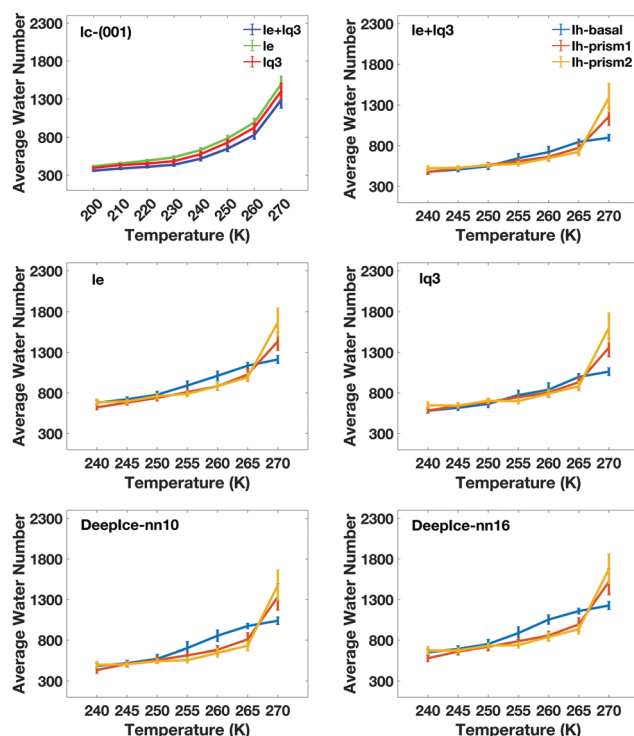


Fig. 6 The average number of liquid-like molecules in QLLs on Ic and Ih surfaces as a function of temperature defined by the local Steinhart parameter lq_3 , the local entropy fingerprint le in single and double classification, and Deeplce (nn10 and nn16) for the Ih surfaces.

fluctuations which increase as the temperature increase, as expected and previously observed in MD simulations when using TIP4P/Ice and other water models.⁶ Below 270 K, the number of liquid-like molecules on different ice surfaces is similar for Ih; when the temperature is close to 270 K, the order of the number of liquid-like molecules on Ih surfaces is basal plane > primary prismatic plane > second prismatic plane, but an inversion, although small is observed around 260 K,

more noticeable when the local entropy order parameter is used. In the range of 250 K to 265 K, the curves of basal and prismatic planes using le are better separated than those using lq_3 ; this separation is even more clear for the results obtained with DeepIce and interestingly is approximately in the range of temperature where there is an change of morphology in ice crystals with hexagonal prism shape, from platelets to needles to platelets again.⁹

Previous simulations with TIP4P/Ice⁶ predicted a different order of thickness close to the melting point, with the basal surface characterized by a thicker QLL, followed by the primary prism and then by the secondary prism surfaces. Besides differences due to the use of a tetrahedral order parameter, the trends are similar except at high temperature. The discrepancies are likely to be due to a difference in sampling, which is substantially longer in our work at 270 K; our slabs are also larger. Size and sampling effects are more significant close to divergence and the melting point, which have still not been investigated in detail. Simulations with different water models (mW and TIP5P-Ew) also predicted a thinner QLL for the basal with respect to the primary prism surface close to the melting point.^{33,77}

To obtain a result independent from the size of the supercell, we can evaluate the thickness of the QLLs (in Å) as follows:¹⁹

$$d \text{ (Å)} = \frac{\bar{n}_l M}{2\rho N_{AV} S 10^{-24}} \quad (10)$$

where \bar{n}_l is the average number of liquid-like molecules during the simulation time, $M = 18.01574 \text{ g mol}^{-1}$ is the molecular weight of water, N_{AV} is the Avogadro number, ρ is the density of water in units of g cm^{-3} , S is the size of the ice surface exposed to vacuum. The 2 in the denominator take into account that the ice slab models have two independent QLLs at both ends. The calculations here use the vacuum-facing surface area of the supercell at the end of the *NPT* simulations at the relevant temperature, as used in the *NVT* simulations. However, the variation with temperature of the cell cross-sections calculations are fairly small. Specifically these cross sections are within $1984.76\text{--}1998.97 \text{ Å}^2$ for the Ic (001) surface, $2120.09\text{--}2126.26 \text{ Å}^2$ for the Ih basal surface, $1999.12\text{--}2003.67 \text{ Å}^2$ for the Ih prism1 surface, and $2068.07\text{--}2082.14 \text{ Å}^2$ for the Ih prism2 surface. In principle, there are also slight differences in the density of water at different temperatures. The density of the TIP4P/Ice water model at the melting point is close to 0.99 g cm^{-3} ,⁶⁶ and this value is adopted here for the evaluation of the thickness.

The calculated thickness in Å of the QLLs on Ic and Ih surfaces using the various recipes are summarized in Tables S1 and S2 in the ESI,[†] respectively. Here, the thickness of QLLs on Ic (001) surface calculated by lq_3 , le in single and double classification and on Ih surfaces defined by le are shown in Fig. 7 as an example. The Ic data in the bottom-left panel are shown for different recipes, while the Ih data in the top-left are shown for the different surfaces with the same classification method le . Even at temperature as low as 200 K, the liquid layer

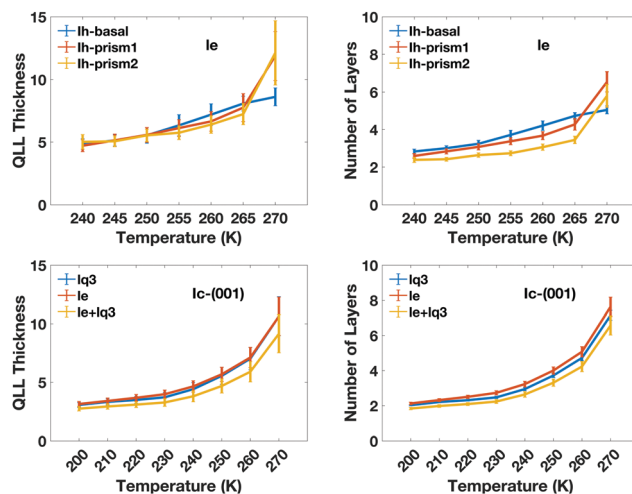


Fig. 7 Left panel: The thickness of QLLs (in Å) on Ih surfaces defined by the local entropy fingerprint le (top) and on the Ic surface defined by the local Steinhardt parameter lq_3 , the local entropy fingerprint le in single and double classification (bottom) as a function of temperature. Right panel: The number of ice-equivalent layers in the QLLs on the different ice surfaces as a function of temperature.

still appears on the ice surface with some thickness. Single and double classification methods both confirmed that the thickness of QLLs gradually increased with the increase of temperature. When the temperature is below 270 K, the thicknesses of QLLs at different ice surfaces at a specific temperature are close to each other.

We can also interpret the results in term of the number of ice-equivalent layers in the QLL, which is independent on the supercell, and reflects the arrangement in bilayers of the basal and prism1 Ih surfaces and in single layers of the Ih prism2 and the (001) Ic surfaces. The number of water molecules in each layer is 98 on the Ic (001) plane, 120 on the basal and primary prismatic planes, and 144 on the secondary prismatic plane. Hence, the number of layers can be calculated by dividing the average number of water molecules in QLLs by the water number in each layer. The results of the ice-equivalent number of layers for a single surface per slab are plotted in Fig. 7, to provide an idea of how many ice-equivalent layers are involved in the surface pre-melting. At 270 K the number of ice-equivalent layers on prismatic planes fluctuates by 2 to 3 as the error bar shows. This illustrates that additional layers start to melt and this transition causes the thickness of the melted layer to fluctuate more. The interface between the quasi-liquid layer and the ice is where the relevant crystallization and melting process occur, which causes the increase or decrease of the QLLs. The number of ice-equivalent layers on the basal plane is more stable with a fluctuation range from 1 to 2 ice-equivalent layers. This is linked to the rate of premelting and surface energy for different planes.⁴³

In the direction orthogonal to the surface, the QLL shows a “layered” structure, not necessarily corresponding to the number of ice-equivalent layers in Fig. 7, which can be monitored through the oxygen density in the direction orthogonal to the



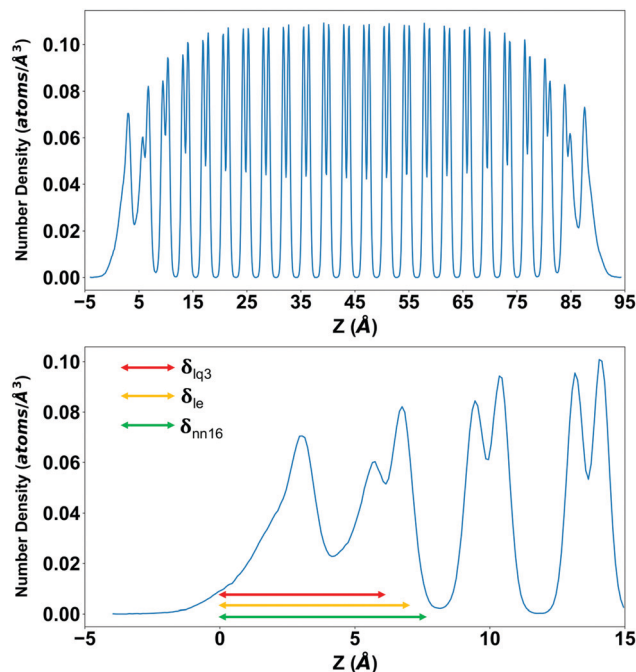


Fig. 8 Top: the oxygen density profile in the direction orthogonal to the basal surface for the Ih slab at 260 K. Bottom: the oxygen density profile close the Ih basal surface at 260 K with a comparison of the average QLL thicknesses obtained with lq_3 (red arrow), le (yellow arrow) and DeepIce-nn16 (green arrow).

surface. As an example, the oxygen density for the Ih basal slab at 260 K is shown in Fig. 8, compared with the thickness estimated with a selection of methods: 7.50 ± 0.42 Å when calculated with DeepIce-nn16, 7.20 ± 0.43 Å with le , and 6.13 ± 0.39 Å with lq_3 . The QLL extends approximately to the first minimum with zero density of the density profile, and has a three-peak structure showing a degree of layering.

We also characterize the “character” of the liquid-like molecules in the QLLs by calculating, as a function of temperature, the average values of the order parameters for the water-like molecules, which are shown in Fig. 9. The le values of different ice Ih surfaces reflect the degree of disorder captured through entropy, which increases with temperature. It is interesting to note that the value of le for the basal plane between 250 K and 265 K is higher than that of the primary prism plane, which again may be correlated with the rate of growth and crystal morphology. This is consistent with experiments, where the interfacial water organization of the basal surface was found to undergo a transition from one to two molten bilayers at 257 K.⁴³ However, the prism planes proceed in a continuous pattern with progressive melting, resulting in the cross-over. laq_3 on all Ih surfaces shows a downward trend, but again with cross-overs for the basal and prism faces, while lq_3 does not show this behaviour. The DeepIce results do not provide information on the character of the liquid-like molecules as they do not have a associated order parameter of variable value.

To complement the information of the average order parameters, an exemplary snapshot of one of the Ih prism2 surfaces

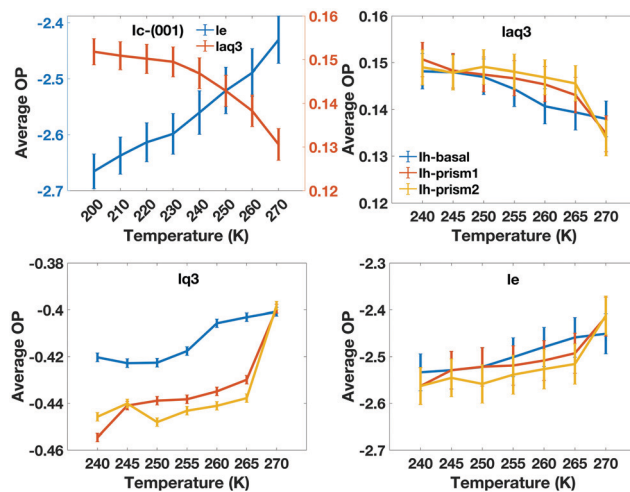


Fig. 9 The average value of laq_3 , lq_3 , and le for the liquid-like molecules on the Ih surfaces and the average value of laq_3 and le for the liquid-like molecules on the Ic-(001) surface as a function of temperature.

at 270 K, hence at conditions characterized by large fluctuations, is shown in Fig. 10, where the oxygen atoms are coloured according to the values of either le (top) or lq_3 (bottom). The two order parameters have different characteristic distributions for crystal and liquid-like molecules, as shown in Fig. 2 and evident in Fig. 10, with the occasional misclassified molecule. Instantaneous inhomogeneities are observable on the surfaces which may show in-plane patterns, as investigated for ice^{26,33} and other liquid surfaces.⁷⁸

3.3 Comparison of recipes for characterizing the QLLs

The single classification (lq_3 , laq_3 , and le), the double classification (lq_3 – le , laq_3 – le), and DeepIce (nn10 and nn16) recipes have all proved to be overall good at distinguishing between liquid-like and ice molecules and thus at defining the quasi-liquid

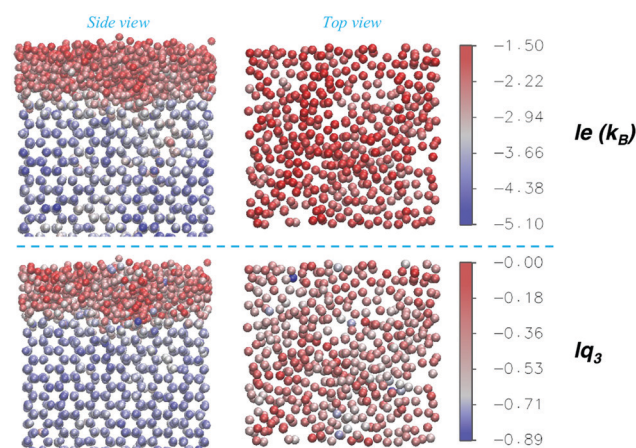


Fig. 10 The spatial distribution of the order parameters le (top panels) and lq_3 (bottom panels) in exemplary MD snapshot of a Ih prism2 surface at 270 K, viewed from the side (left) and top (right) with respect to the surface. Only oxygen atoms are shown, coloured according to the value of the order parameters. The thresholds of for the crystal/liquid classification are $-3.17 k_B$ for le and -0.67 for lq_3 .

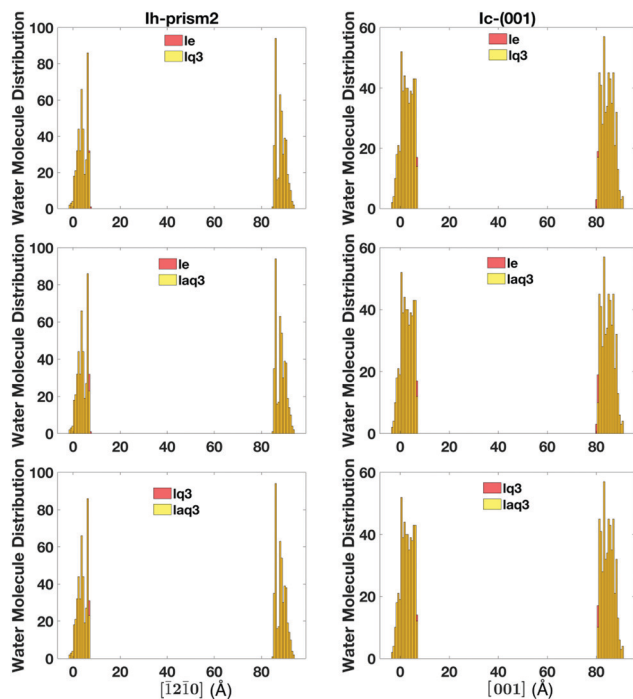


Fig. 11 The histogram of the liquid-like molecules in QLLs detected by lq_3 , laq_3 , and le on Ic and Ih prism2 surfaces at 260 K.

layers, giving qualitatively similar results. However, there are still some discrepancies in the definition of liquid-like molecules using the different recipes, which lead to errors in the accuracy of the final quantitative definition of the QLLs. Hence, we need to perform a comparative study of these recipes.

The number of liquid-like molecules defined by lq_3 and laq_3 is always slightly smaller than the number of liquid-like molecules defined by le . By comparing the results obtained with lq_3 and le we observe that the difference mainly occurs at the ice-QLL interface, as shown in an example in Fig. 11 for the Ic and Ih prism2 slabs at 260 K, where the histograms show the location of the liquid-like molecules in the direction perpendicular to the surfaces. Here the number of liquid-like molecules identified by le but not by lq_3 or laq_3 is rather small, with laq_3

detecting slightly less liquid-like molecules than lq_3 . le tends to identify more complete layers at the liquid-ice interface. Other surfaces show similar results with again some differences at the solid-liquid interfaces.

A comparison of DeepIce with 10 and 16 nearest neighbours is illustrated in Fig. 12 with an example of an MD snapshot for the Ih prism2 surface at 270 K. From this graph, compared to nn16, nn10 misses a certain amount of liquid-like molecules, which suggests that when the two nearest complete shells are taken into account, more information is provided for the classification of the molecule phase. By comparing DeepIce-nn16 with le we find that the results are very similar as illustrated in Fig. 12, with a few liquid-like molecule difference in this particular example.

From these results DeepIce-nn16 and le have similar identification capacity, followed by lq_3 and laq_3 . From the computational point of view, DeepIce-nn16 is time-consuming in the datasets preparation stage, and calculations using le as implemented in PLUMED are more expensive because of the calculation of the $g(r)$ than those using laq_3 and lq_3 .

4 Conclusions

In this work, the QLLs on ice Ih and Ic have been systematically studied as a function of temperature by using different classification recipes. Molecular dynamics simulations showed that the size of QLLs increases as the temperature increases as expected. Among these recipes, the 3rd order local and local average Steinhardt parameters (lq_3 and laq_3) and the local entropy fingerprint (le) are all good at distinguishing ice and water molecules, with le identifying extra liquid molecules at the ice-liquid interface. The neural network DeepIce with 16 nearest neighbours in the datasets provides similar results to le , while using only 10 nearest neighbours tend to miss in Ih the identification of some liquid-like molecules at the QLL-ice interface compared with nn16 and le . The Steinhardt and entropy order parameters further provide some measure of the character of the molecules in the QLLs, which DeepIce cannot do. This can shed some light into the different temperature behaviour of the Ih basal and prism surfaces and its relation to the temperature-dependent morphology of hexagonal prism shaped crystals at low vapour pressure.^{9,79} The cross-overs of le and laq_3 and of the QLL size as function of temperature for the Ih surfaces nicely correlates with the variation in crystal morphology.

There are some differences in computational costs for the various methods, in the implementation we use, with DeepIce needing time in the datasets preparation and le some extra expenses with respect to the local Steinhardt parameters. As the order parameters were developed for bulk systems and used without modifications, it is interesting to observe that they do not seem to have problems at the surface level, but show some differences at the ice-QLL interface, which is a bulk-like environment. DeepIce is trained to recognize undercoordinated atoms at surfaces.

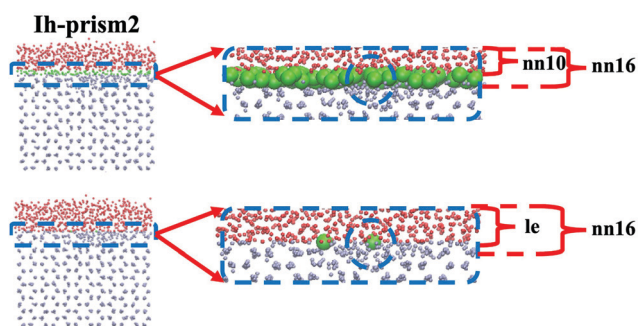


Fig. 12 Comparison of the liquid-like molecules at Ih prism2 surfaces detected by DeepIce-nn10, nn16, and le for an exemplary snapshot at 270 K. Highlighted in green are the liquid-like molecules which cannot be identified by DeepIce-nn10 compared to nn16 in the top panel, and by le compared to nn16 in the bottom panel.



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