THE JOURNAL OF CHEMICAL PHYSICS **147**, 174502 (2017)

The accretion of the new ice layer on the surface of hexagonal ice crystal and the influence of the local electric field on this process

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(Received 6 July 2017; accepted 18 October 2017; published online 7 November 2017)

The process of creation of a new layer of ice on the *basal* plane and on the *prism* plane of a hexagonal ice crystal is analyzed. It is demonstrated that the ordering of water molecules in the already existing crystal affects the freezing. On the basal plane, when the orientations of water molecules in the ice block are random, the arrangement of the new layer in a cubic manner is observed more frequently—approximately 1.7 times more often than in a hexagonal manner. When the water molecules in the ice block are more ordered, it results in the predominance of the oxygen atoms or the hydrogen atoms on the most outer part of the surface of the ice block. In this case, the hexagonal structure is formed more frequently when the supercooling of water exceeds 10 K. This phenomenon is explained by the influence of the oriented electric field, present as a consequence of the ordering of the dipoles of water molecules in the ice block. This field modifies the structure of solvation water (i.e., the layer of water in the immediate vicinity of the ice surface). We showed that the structure of solvation water predetermines the kind of the newly created layer of ice. This effect is temperature-dependent: when the temperature draws nearer to the melting point, the cubic structure becomes the prevailing form. The temperature at which the cubic and the hexagonal structures are formed with the same probabilities is equal to about 260 K. In the case of the *prism* plane, the new layer that is formed is always the hexagonal one, which is independent of the arrangement of water molecules in the ice block and is in agreement with previous literature data. For the *basal* plane, as well as for the *prism* plane, no evident dependence on the ordering of water molecules that constitute the ice block on the rate of crystallization can be observed. *Published by AIP Publishing.* https://doi.org/10.1063/1.4994612

I. INTRODUCTION

A crystal of hexagonal ice, even if its crystallographic structure is nearly perfect, can still show a significant degree of disorder. This is due to the possibility of different spatial orientations of water molecules that are built in the crystal lattice of ice. In fact, it is said that water molecules in hexagonal ice crystals are usually randomly oriented, which results in a zero dipole moment of the whole structure. However, the same may not always be true for the surface of ice. It can be heterogeneous since the number of dangling O–H bonds and their relative positions on the surface can change. It is possible that a particular pattern of dangling O–H bonds on the ice surface might be preferred (the one that provides a minimum value of the ice surface free energy). Because of that it is reasonable to ask if the state of the ice surface in contact with liquid water has an influence on the kinetics of the freezing of water or on the structure of the newly accumulated layer of ice. In the case of freezing of pure water, it seems that the original order pattern should fade quickly.[1] However, the state of the surface of ice may be of importance to the action of antifreeze proteins (AFPs). These proteins are able to prevent the growth of an ice crystal, thanks to their ability to irreversibly bind to the ice surface (to various crystallographic planes, depending on the protein type[2]). The mechanism responsible for the adsorption is still debated.[3]

The available data concerning the arrangement of the O–H bonds at the surface (and its possible implications for freezing and melting) usually concern the "bare" ice surface (the ice-vacuum interface). Fletcher[4] was the first one who pointed out that there is a preferred pattern—estimated temperature, in which this structure should be stable, was very low (about 30 K for the *basal* and 70 K for the *prism* plane). Results reported for higher temperatures, below 200 K, are inconclusive. Buch *et al.*[5] suggested that in these temperatures, the *basal* plane of ice may be, at least partially, ordered and this order corresponds to the structures proposed by Fletcher. On the other hand, recently published work of Avidor and Allison[6] undermines that conclusion, claiming that Fletcher's structures cannot be the predominant ones (if they exist at all). Moreover, the energy of stabilization of the ordered structures is relatively small,[4] so at temperatures close to the melting point of ice, the ordering disappears completely due to the thermal motions. However, even if there is no specific or preferred pattern, the relative positions of dangling O–H bonds on the ice surface may still have an influence on the water freezing process, as other authors pointed out.

Batista and Jónsson[7] asked what was the influence of dangling O–H bonds on the adsorption energy of a single

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water molecule on the ice surface. Studies were conducted at 140 K, the adsorption occurred at the ice-vacuum interface, and TIP4P water model was used. The authors noted that there are three molecules in the surface that are close to the adsorbing molecule. Therefore, adsorption sites on the ice surface are different due to different orientations of water molecules in their surroundings. The authors proposed to divide the sites into groups, taking into account the number of dangling O–H bonds in theirs immediate vicinity. Type A sites, with one dangling O–H bond next to them, had the highest adsorption energy—these were the sites that were occupied by the adsorbing molecules first. A little less favorable were B sites, surrounded by two dangling O–H bonds. When there were no dangling O–H bonds in the vicinity of an adsorption site, the adsorption energy was much lower than for A and B sites. When there were three dangling O–H bonds close to the site, the adsorption did not occur. Quantum-mechanical calculations performed by others[8] confirmed that A and B sites have the highest adsorption energy. Conclusions drawn by Batista and Jónsson[7] can be summarized as follows: the adsorption of a single water molecule on the *basal* plane of ice takes place in the corner or in the middle of a six-membered ring created by the water molecules belonging to the ice surface. The condition for the adsorption to occur is the presence of one or two dangling O–H bonds in the immediate vicinity of the adsorption site. The adsorption energy depends, according to the authors, on the strength of the local, effective electric field generated by the dangling O–H bonds close to the adsorption site—the biggest contribution comes from the dangling O–H bonds in the immediate vicinity of this site. However, some authors pointed out that when considering the influence of the electric field on the adsorption energy, contributions originating from dangling O–H bonds located up to 10 Å from the adsorption site should be taken into account.[9]

The role of the dangling O–H bonds was also acknowledged during the analysis of ice pre-melting. Namely, Bishop *et al.*[10] studied the mechanism of pre-melting of the *basal* plane of ice. The authors analyzed the behavior of two ice surfaces, differing in the number of dangling O–H bonds. They noticed that the temperatures, in which the melting begins, are different for both surfaces. In an attempt to pinpoint the origin of this behavior, the authors introduced a global order parameter, which was the measure of heterogeneity of dangling O–H bonds distribution. It turned out, however, that the global order of dangling O–H bonds could not really explain the observed differences in the melting temperatures. Further and more careful analysis led to the conclusion that the local order of dangling O–H bonds is more important. Sites on the surface of ice with higher "density" of dangling O–H bonds ("hot spots") had lower melting temperature.

In conclusion, we can say that the state of the ice surface has a great importance when it comes to the ice melting process or growth of new layers of ice on the crystal surface. However, it should be noted that the results discussed above refer to a "bare" ice surface (the ice-vacuum interface). In this case, the adsorption of a single water molecule is influenced only by its interaction with the ice surface. For this reason, an attempt to extend these conclusions to the solid-liquid interface may be problematic. Moreover, as Buch *et al.*[5] pointed out, adsorption of molecules on the surface may strengthen, modify, but also disturb original order patterns which can play an important role in the formation of new ice layers, especially in the case of the solid-liquid interface. To the best of our knowledge, there are no reports concerning the influence of the number or the order of dangling O–H bonds for the melting/freezing of ice at the solid-liquid interface. For this reason, but also bearing in mind the role, that dangling O–H bonds may hypothetically play in the action of antifreeze proteins, we decided to undertake this study.

II. METHODS

A. Simulation procedure

The results were obtained using computer simulations. They were carried out with the molecular dynamics package Amber12.[11] The temperature was kept constant by the weak coupling to an external bath (τ_T = 1.0 ps) using the Berendsen thermostat.[12] The pressure (1 bar) was kept constant by the weak coupling method (τ_p = 1.0 ps). The particle-mesh Ewald method was used for electrostatic interactions. A cutoff of 1.2 nm for nonbonding interactions was used. Equations of motion were integrated with a relatively small (in relation to the simulation temperatures) time step, 2 fs. As Rozmanov and Kusalik[13] showed, too high value of the time step significantly affects the observed water freezing rate.

B. Selection of water model

The chosen water model was TIP4P/Ice.[14] Its freezing temperature, 272 K, is very close to the experimental value. The creators of the TIP4P/Ice water model convincingly argue that their model "greatly improves the melting properties of previous potentials. But, contrary to the case of TIP5P, the improvement in the melting properties is done without deteriorating the other computed quantities."[14]

C. System setup

Simulated systems consisted of an ice block, built from 1330 TIP4P/Ice water molecules (7 layers of hexagonal ice, 190 water molecules in each layer), surrounded by another 15 858 water molecules (liquid water). Two planes of the block were *basal* planes of hexagonal ice (approximately 3.8 × 3.8 nm) and two planes were *prism* planes (approximately 3.8 × 2.5 nm). Distances between the surfaces of ice and the simulation box walls were equal to 3.0 nm for the *basal* planes and 1.5 for the rest of the surfaces. Therefore, the ice block was surrounded by liquid water from all sides. The purpose of that was to eliminate the influence of periodic boundary conditions on the water freezing process, which was pronounced especially in the case of the *basal* plane.[15] To avoid melting of ice on the edges of the block, the coordinates of oxygen atoms in the block were constrained (the harmonic force constant was 2 kcal $Å^{-2}$ mol^{-1}).

Two types of systems were analyzed: the ones with the ice block with a nonzero overall dipole moment and the ones with the ice block with a close to zero overall dipole moment. 120 independent copies of the first and the second type of

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the system were analyzed. They differed with (liquid) water molecules coordinates and specific order of dangling O–H bonds on the ice surfaces.

Results are presented as averages, obtained from the analysis of these 120 copies, for temperatures from the range 250 K–270 K. Detailed description of the procedure of the preparation of the systems was included in the supplementary material to the present publication. The time of the simulation was equal to 60 ns for every system.

III. RESULTS AND DISCUSSION

A. General characteristic of the systems

Simulations of the studied systems were carried at temperatures 250 K, 257.5 K, 261 K, 265 K, and 270 K. The progress of the freezing of solvation water on the *basal* and *prism* planes of the ice block was analyzed. To follow it, a CHILL+ algorithm[16] was used. This recently developed algorithm can distinguish different forms of ice (hexagonal and cubic) and detect the so-called interfacial ice—a structure that appears on the ice-water interface; its ordering is intermediate between that of ice and tetrahedrally coordinated liquid.[17]

For our research, we chose a system that consists of an ice block surrounded on all sides by liquid water. This choice was made to avoid the influence of periodic boundary conditions on the freezing process.[15]

There is also another advantage of this choice. The formation of a new ice layer starts by the formation of a nucleus that needs to reach a temperature-dependent critical size.[18] Our system is relatively small which hampers the growth of the nucleus. At higher temperatures, closer to the ice melting point, our system reaches a steady state, when the ice nuclei continuously form and dissolve. Thus, assuming that this steady state is equivalent to an equilibrium state, investigation of this dynamic equilibrium offers an opportunity to evaluate the role of the state of the ice surface.

However, in this case, the effects resulting from the existence of sharp edges of the ice block may occur. To lessen their influence on the results, we analyzed the properties of solvation water covering up only the middle area of every surface of the ice block: this area consisted of water molecules that were located at a distance of at least 0.5 nm from the edges of the block (Fig. S1 in the supplementary material).

In our work, we analyzed two types of systems, which we called ASYM and RAND. Both of them consisted of 120 independent copies prepared as described in detail in the supplementary material. We adopted the following definition of the dangling O–H bonds: if an axis of an O–H bond of some water molecule located at a selected plane of the ice block forms with this plane an angle greater than 45°, then we recognize this hydrogen atom as dangling. ASYM and RAND systems differed by the number of dangling O–H bonds in the middle parts of the ice block surfaces—the parts that were next to the analyzed solvation water (Fig. S1 in the supplementary material). For the ASYM systems, the average number of dangling O–H bonds at the *basal* planes was (78 ± 8)% on one side and (22 ± 4)% on the other side, while at the *prism* planes, it was (65 ± 5)% on one side and (32 ± 4)% on the other side. The number after ± sign is the standard deviation from the average calculated over the 120 copies mentioned above. Therefore, the overall number of dangling O–H bonds was very similar in each copy, but the specific arrangement of these dangling O–H bonds on the planes was different in each copy. The initial number and arrangement of dangling O–H bonds remained almost unchanged during the whole simulation (60 ns). In the case of the RAND systems, the average number of dangling O–H bonds was (48 ± 5)% and (49 ± 4)% for two *basal* planes. For the prism planes, the values were similar, also equal to about 50%.

B. Density distribution functions and the scope of the solvation layer

In the first step, we determined the distribution of solvation water density in the vicinity of the ice surface (see the supplementary material). The course of the density distribution function (Fig. S2 in the supplementary material) allowed us to choose the scope of the analyzed solvation layers, which was 0.35 nm and 0.58 nm.

C. Dynamics of ice layer formation

Formation of a new ice layer on the already existing ice surface is a complex process, which is initiated by a formation of an ice nucleus, followed by its growth and association of the neighboring nuclei into a larger structure.[15] The lower the temperature, the easier the process of nucleation takes place—at temperatures close to the freezing temperature, critical ice nucleus size, that allows for subsequent stable growth, becomes greater and thus the probability of forming it rapidly decreases. For example, Hudait *et al.*[18] reported that for a monoatomic water model mW, at temperature 270 K, the critical size of the ice nucleus is about 180–280 water molecules. The melting temperature of this model, determined by the authors, is equal to (273 ± 0.5) K. The systems examined by us were relatively small (the bilayer of ice at the *basal* plane consisted of only 190 water molecules). It means that at temperatures close to the ice melting point (272 K for TIP4P/Ice water model), the formation of a sufficiently large ice nucleus may be hindered. This is the reason why the freezing is complete only in systems with high degree of supercooling (250 K), while at the higher temperatures (257.5 K, 261 K, 265 K, and 270 K), the systems apparently reached a steady state, in which ice nuclei of both forms of ice are formed and dissolved, staying in equilibrium with surrounding liquid water. Two examples of this process, for ASYM system, can be found in Fig. S3 in the supplementary material. This dynamic equilibrium offers an opportunity to evaluate the role of the state of the ice surface—a number and/or the arrangement of the dangling O–H bonds—on the tendency to form a new (hexagonal or cubic) layer. In the available literature, there is no reference to this problem. Even though cubic ice is less thermodynamically stable than hexagonal ice, the difference between their free energies is relatively small (the value obtained by computer simulations with a mW water model was on the order of about 0.1 kJ/mol,[19] while the experimental value was estimated to be equal to about 0.05 kJ/mol[20]). This means that in temperatures close to the freezing temperature of water, both forms should occur with almost the same probability. However, the situation is different: both experiment[21] and simulations[18]

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show that the content of the cubic structure in the freezing water is different than the content of the hexagonal structure, and it depends on the temperature (the amount of the cubic structure decreases when the temperature increases).

Process of ice freezing proceeds differently for the *basal* and *prism* plane of ice; therefore, the results obtained for those planes will be presented separately.

1. Basal plane

CHILL+ algorithm,[16] which we used as a tool for the analysis of the state of the systems, is able to detect hexagonal and cubic structures, and—at the same time—allows to evaluate the content of liquid (or more disordered) water in the freezing mixture. When we follow the process of the freezing of water at 250 K, in the first solvation shell (up to 0.35 nm), it can be seen that the systems have a tendency to evolve in two main directions: the formation of a hexagonal or cubic structure (Fig. 1). We noticed that the system in which the crystallization process started with the cubic (or hexagonal) form of ice, afterwards, in most cases, ended up with the solvation water frozen entirely as cubic (or hexagonal) ice. At this temperature and after 60 ns, only a small number (no more than 2%–3%) of the systems were in a state, in which the content of cubic and hexagonal structures in the freezing layer was comparable. Usually, the final (that is after 60 ns of simulation) content of one of the forms of ice was much higher than the other, exceeding 95%. However, at higher temperatures: 257.5 K, 261 K, 265 K, and 270 K, the behavior of the systems was different. Liquid water does not freeze entirely—for example, at 265 K the amount of water molecules that can be classified as liquid water (from the structural point of view) was equal to about 40% ÷ 50%. The emerging ice nuclei could have a hexagonal or cubic structure—during the simulation, we observed constant processes of formation, dissolution, and reformation of the same or different crystallographic structure of ice (Fig. S3 of the supplementary material). As it was mentioned before, these fluctuations were the result of the small size of the block. It was impossible to create simultaneously many neighboring ice nuclei on the surface of ice and to combine them into one greater and stable ice nucleus.

The fact that we observed the growth of hexagonal and cubic structures on the *basal* plane is in agreement with the results described by other authors. Carignano *et al.*[22] showed that there are hexagonal and cubic layers growing on the *basal*

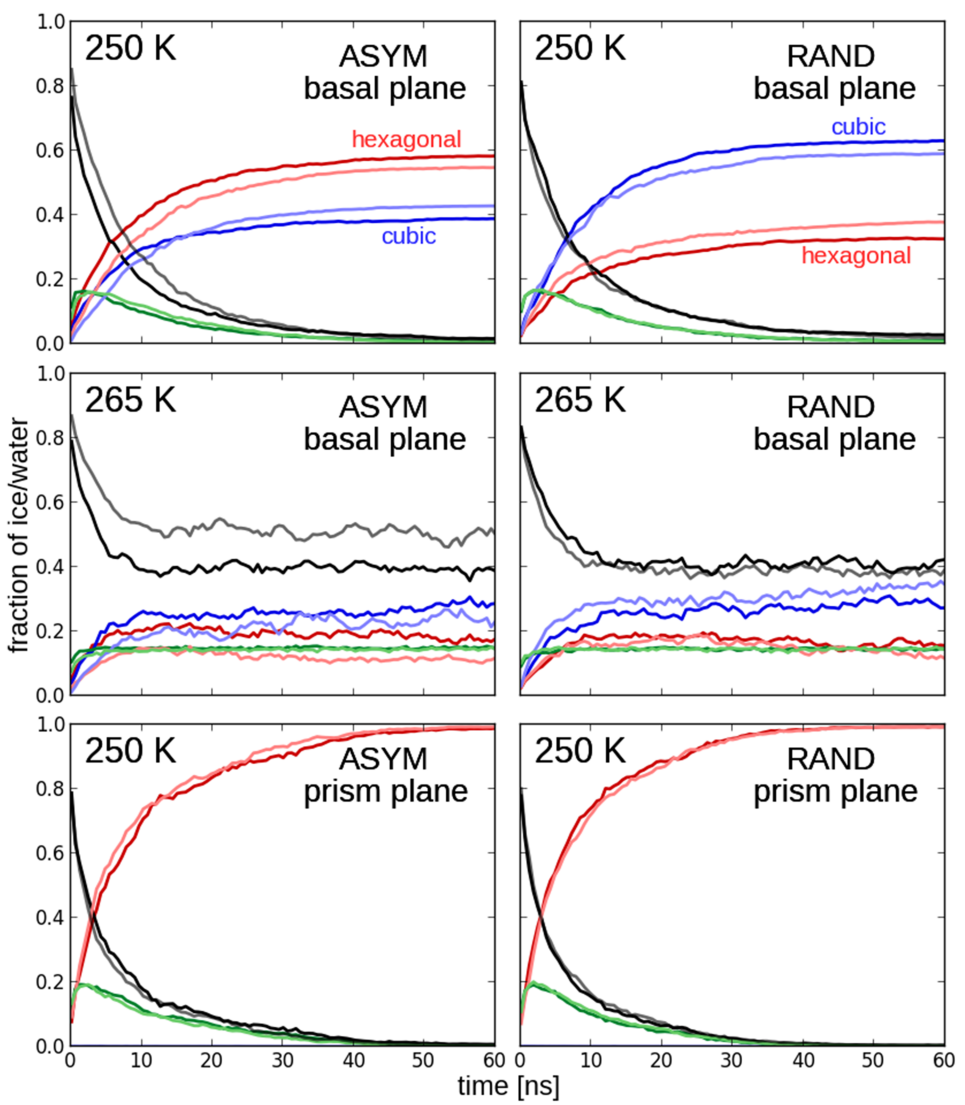

FIG. 1. The fraction of solvation water molecules (from the first solvation shell, up to 0.35 nm from the ice surface) that can be classified as a hexagonal structure (red) and cubic structure (blue). The interfacial ice is in green and the structure classified as a liquid is in black. Two shades correspond to two investigated planes (two *basal* and two *prism*). In the case of the ASYM systems, the lines in darker color correspond to planes with the higher content of the dangling O–H bonds. These are the averages for 120 ASYM systems and 120 RAND systems. The time changes during 60-ps-long simulation are presented. Note the reverse order of the amount of hexagonal and cubic structures for ASYM and RAND systems at 250 K.

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plane. Carignano[23] compared ice growth on hexagonal and cubic surfaces (on *basal* and (111) planes, respectively). The research demonstrated that new ice layers growing on the ice surface can have both hexagonal and cubic structures, regardless of the initial structure of the ice, but layers of the cubic structure occur more often. Similar conclusions were drawn by Seo *et al.*[15] and Choi *et al.*,[24] who estimated the average ratio of cubic to hexagonal ice as 2.4:1 and 2.5:1. Recently, Hudait *et al.*[18] conducted research, in which they observed ice growth on the *basal* plane of hexagonal ice. The results showed that in each of the studied temperatures, the new ice that emerged was a mixture of hexagonal and cubic structures. In temperatures close to the melting point, new ice layers were either cubic or hexagonal. When the degree of supercooling became higher, cubic and hexagonal structures could coexist within one layer (separated by the line of crystal lattice defects). This effect is easy to understand, when bearing in mind the strong temperature dependence of the size of the critical ice nucleus. When it comes to the homogeneous ice nucleation, it appears that, strictly speaking, neither a hexagonal nor cubic structure is formed, but a stacking-disordered material with cubic and hexagonal sequences.[25]

Figure 1 illustrates the time dependence of a fraction of hexagonal and cubic structures in the solvation layer, averaged over all 120 studied systems. Two conclusions arise immediately from this figure. First, at 250 K, systems ASYM and RAND behave differently: in ASYM systems, the hexagonal structure is preferred (CUB/HEX ratio, cubic to hexagonal structure content, is equal to about 0.7), while in RAND systems, the cubic form of ice is preferred (CUB/HEX ratio is equal to about 1.7). Second, in ASYM systems, the preference of one ice form over another generally does not depend on the number of dangling O–H bonds. After raising the temperature to 265 K, the situation is different: in RAND and ASYM systems, the cubic structure is more favored and the CUB/HEX ratio is more or less the same for both, equal to about 1.7. This is roughly the same value that we observed in the case of the RAND systems at 250 K.

As we already mentioned, at 250 K the form of ice that emerged first usually continued to grow and expand until the whole solvation shell was frozen. It indicates that it is decided very early which form of ice is going to be finally formed on the *basal* plane. We investigated the structure of solvation water (up to 0.58 nm from the surface of ice) in these early moments—during the first 0.06 ns of the simulation. In this short time, the crystallization is not yet advanced, but the structure of solvation water has already changed to enable it to turn into ice later on. The choice of low temperature, 250 K, offers also another advantage, which is small thermal motions. Thanks to that, the structural effects are enhanced and can be observed more easily. We examined whether the early changes in the structure of solvation water can be connected with the structure of the new layer of ice that is finally formed. We analyzed the positions of water molecules (relatively to the underlying surface of ice) and their orientations (as described by the vector of the dipole moment). To this aim, we calculated the average number of molecules occupying consecutive points in space (with a step equal to 0.01 nm), taking into account these first 0.06 ns of the simulation. Moreover, we also calculated the energies of the dipoles of water molecules in the local electric field generated by the ice block.

We clearly observed some well-defined points in space which are occupied significantly more often than other. This can be seen in Fig. 2. A similar feature was described by Seo *et al.*,[15] who investigated the growth on the *basal* plane of hexagonal ice. We divided the frequently occupied spots into three groups. The first group (called P1, represented by red spots in Fig. 2) is the spots located next to the most outer water molecules at the surface of the ice block. Water molecules from the solvation layer that occupy these spots create hydrogen bonds with the surface of the ice block. The energy of dipoles of these water molecules in the electric field is relatively low, its mean value ranges from about −31 kJ/mol for the ASYM systems and the plane with 78% of dangling O–H bonds to about −22 kJ/mol ÷ −26 kJ/mol for the rest cases.

The second group (P2, cyan spots in Fig. 2) is the spots above these water molecules in the ice block that constitute the inner sublayer of the most outer part of the ice block. The molecules in spots P2 occupy the rest of the nodes of the hexagonal net. These spots are a little farther from the surface of the ice block than the P1 spots (by about 0.08 nm). The positions of the P1 and P2 spots can be observed in Fig. 2. The P2 spots are also about ten times less frequently occupied than P1 spots. The energy of dipoles of water molecules in P2 spots is higher than in P1 spots and equal to about −3.8 kJ/mol and −5.7 kJ/mol in RAND and ASYM systems, respectively. If these spots become occupied and hydrogen bonds are created with molecules from the P1 spots, it can lead to the formation of a new ice layer that will have a hexagonal structure.

The third group (P3, orange spots in Fig. 2) is the spots above the middle of the six-membered rings of the hexagonal ice. Similar to the P2 spots, they are also a little farther from the surface of the block than the P1 spots and less frequently occupied than the P1 spots. The energy of dipoles of water molecules in P3 spots is higher as well, equal to about −3.7 kJ/mol and −5.4 kJ/mol in RAND and ASYM systems, respectively. If these spots become occupied and hydrogen bonds are created with molecules from the P1 spots, it can lead to the formation of a new ice layer that will have a cubic structure.

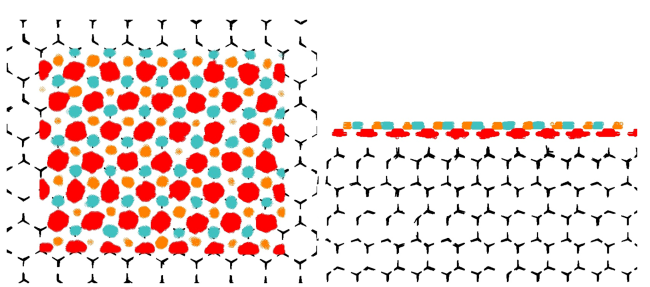

FIG. 2. The spots where water molecules from the first and second solvation shells of the *basal* plane of hexagonal ice place themselves most frequently. The ice block is in black lines. The spots P1 are in red, the spots P2 and P3 are in cyan and orange (see text). Left: The view perpendicular to the *basal* plane. Right: Side view, parallel to the *basal* plane, which highlights the difference of the distance of the spots P1, P2, and P3 to the surface of the ice block. This picture was made for the ASYM systems and the basal plane with 22% of the dangling O–H bonds (for the first 0.06 ns of the simulation at 250 K). The picture was generated in VMD.[38]

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The spots P3 are more frequently occupied than P2 in RAND systems (the ratio P3/P2 is equal to 1.96) but significantly less frequently occupied than P2 in ASYM systems (the ratio P3/P2 is equal to 0.40). Since in RAND systems the cubic structure is the prevailing form and in ASYM systems the hexagonal structure is the prevailing form (Fig. 1), these results demonstrate the connection between the early structure of the solvation water and the final structure of the new layer of ice. It was also found that the increase in the temperature leads to the increase of the ratio P3/P2, which correlates with the increase of the amount of the cubic structure in the system.

In ASYM systems, the ratio P3/P2 is almost the same for both *basal* planes—the one with 22% of the dangling O–H bonds (0.42) and the one with 78% of the dangling O–H bonds (0.39). Therefore, the sheer state of the surface of ice, characterized by the lack or presence of dangling O–H bonds, does not determine the kind of ice that crystallizes on the surface. Rather, the determining factor is the ordering of the dipoles of water molecules in the ice block that gives rise to a distinctly oriented electric field. Two features of this field matter when the new ice is formed—its intensity and the direction of its vector. The electric field is present in RAND and ASYM systems. Its mean intensity in both systems is roughly comparable for short distances from the surface of ice (from 0.17 nm to 0.35 nm, see Table S1 in the supplementary material). Farther away, it becomes about two times stronger for ASYM systems. More importantly, the mean (i.e., calculated over the whole investigated surface area of ice and the distances from 0.17 nm to 0.35 nm) direction of the vector of the electric field is very different for RAND and ASYM systems. In RAND systems, it is perpendicular to the surface of ice and in ASYM systems, it is askew. It is also about ten times shorter in the case of the RAND systems than in the case of the ASYM systems. The shortness of the mean vector is a result of the fact that the directions of the vector of the electric field intensity can change abruptly from place to place in the case of the RAND systems. The dipoles of water molecules tend to arrange themselves, on average, in the general direction of the vector of the local electric field generated by the ice block, especially in the first solvation shell (as indicated by the low energy of the dipoles in P1 spots).

Water molecules from the second solvation shell also arrange themselves more or less parallel to the vector of the electric field (although the energy of the dipoles in P2 and P3 spots is higher than for P1 spots), but they are also constrained by the necessity to create hydrogen bonds with the molecules from the first solvation layer (P1 spots) in order to form a new layer of ice. In new layers of hexagonal ice, the interaction with the directed electric field promotes the orientation of water molecules that echoes the underlying pattern of the hexagonal ice block, with the bonds between oxygen and hydrogen atoms aligned along the edges of the six-membered rings. Actually, knowing the structure of the surface of ice (the orientations of the water molecules at the surface) and the direction of the electric field, we are able to predict the most preferred conformations of water molecules occupying spots P1. After that, we can check whether this configuration would favor adsorption in P2 (hexagonal structure) or P3 (cubic structure) spots. According to this estimate, in the ASYM systems, the spots P2 would be favoured over P3 (Fig. S4 in the supplementary material). This estimate of ratio of the molecules occupying spots P3 and P2 is equal to about 0.8 and is comparable to the observed ratio of the molecules visiting spots P3 and P2 in ASYM systems, which is equal to about 0.4. It also is comparable to the observed ratio of the amount of cubic to hexagonal structure (CUB/HEX = 0.7 for ASYM system at 250 K).

The increase of the temperature reduces the influence of the electric field on the orientation of the molecules and results in a more frequent occurrence of the cubic structure also in the ASYM systems. This is illustrated in Fig. 1. The temperature dependence of the ratio of the amount of cubic to hexagonal structure, CUB/HEX, can be approximated by the Arrhenius equation (see Fig. 3). The activation energy can be estimated as about 28 kJ/mol, which is comparable to the energy of reorientation of the dipole of water molecule in the electric field, experienced by the water molecules in the solvation shell (the dipole moment of the TIP4PIce water molecule is 2.426 D[14]). As we can see, the equal probability of formation of both forms of ice in ASYM systems occurs at about 260 K. This temperature should depend on the strength of the electric field.

In RAND systems, the direction of the mean vector of the field in the first solvation shell is perpendicular to the surface of the block of ice (this is because the molecules of solvation water are closer to the surface hydrogen atoms than to the surface oxygen atoms). In these systems, the frequency of formation of the cubic structure is constantly greater than that of the hexagonal structure. The CUB/HEX ratio is equal to about 1.7, irrespectively of temperature. Therefore, in this case, the electric field is, apparently, not responsible for the prevalence of the cubic structure. It could be possible that the deciding factor may be the interaction of the newly created ice layer with the surrounding water, not with the surface of ice, as suggested by Takahashi.[26,27]

The influence of the external electric field on the crystallization of water was studied by experiment[28–30] and molecular dynamics.[31–34] It is believed that the electric field exceeding 10^9 V/m facilitates the nucleation and significantly raises the melting temperature of ice.[34] Some results reported in the above mentioned references (Yan *et al.*[31–34]) at first glance may seem to contradict with ours. These authors observed that the presence of the electric field equal to about 5×10^9 V/m

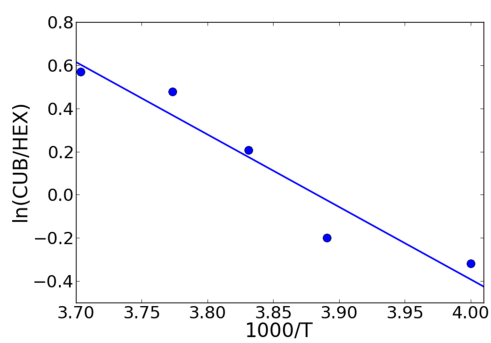

FIG. 3. The Arrhenius plot of the CUB/HEX ratio for ASYM systems. The estimated activation energy is 28 kJ/mol.

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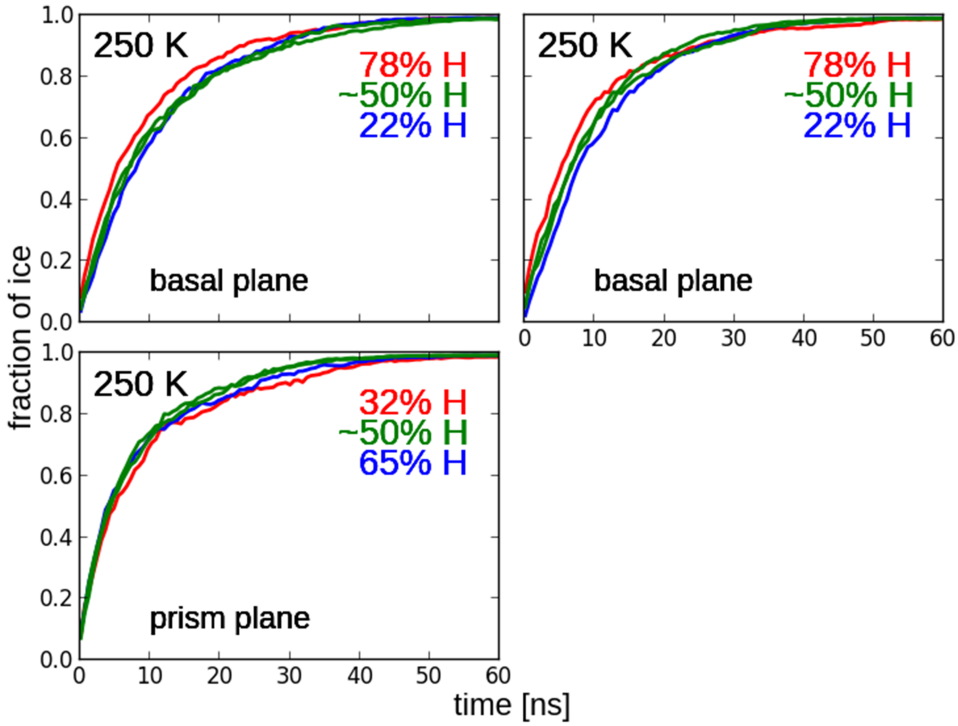

FIG. 4. The growth rate of hexagonal structure (left) and cubic structure (right) in solvation water (up to 0.35 nm from the ice surface) at *basal* planes (top) and *prism* planes (bottom). All data are for simulations at 250 K. Next to the *prism* plane, we do not observe any cubic structure. The amounts of the dangling O–H bonds at the surfaces of the ice block are given.

easily promoted the formation of layers of cubic ice on a flat wall. In these parts of the simulated systems where the field was not present, both cubic and hexagonal structures could be found. However, our results do not describe nucleation in the presence of an external electric field but the accumulation of new layers of ice on the already existing matrix—the *basal* plane of hexagonal ice. In the cited papers, the ice that was formed under the influence of the electric field did not expand by growing on the *basal* surface. This is why we do not believe that our observations contradict with these results.

Existing literature data do not allow us to infer if (and how) the electric field may affect the growth rate of new ice layers on the surface of the ice block. To answer this question, we analyzed (at 250 K) the rate of freezing for cubic and hexagonal structures, in the vicinity of the *basal* plane, for ASYM and RAND systems. Results of this analysis are presented in Fig. 4. As it can be seen, freezing rates for both forms of ice in the case of the *basal* plane are very similar and they seem to be independent of the state of the ice surface (number of dangling O–H bonds), as well as of the presence of the electrical field.

This fragment of our work can be summarized as follows. The oriented electric field, present as a result of ordering of water molecules in the ice block, can modify the structure of solvation water (i.e., water in the immediate vicinity of the ice surface). This modification of the structure of water predetermines the kind of a newly created layer of ice. Thus, the oriented electric field, present as a result of ordering of the water molecules in the ice block, promotes the formation of the hexagonal form of ice over the cubic form. This is clearly observed for high supercooling, exceeding 10 K, but not in higher temperatures, when the supercooling drops to 5 K or less. Simultaneously, we do not observe an influence of the state of the *basal* surface on the freezing rate. The growth rates of hexagonal and cubic structures on the *basal* planes are very similar and do not seem to depend on the number of dangling O–H bonds and the electric field generated by the ice block.

2. Prism plane

On the *prism* plane, water freezing process leads to hexagonal structure only. It agrees with observations of other authors.[22] In Fig. 4, we presented results depicting the ice freezing rate. It can be clearly seen that—compared to the *basal* plane—the ice growth is noticeably faster.

Pronounced difference between the ice growth rates in the case of the *basal* and *prism* planes is known and was described and explained before.[35,36]

IV. CONCLUSIONS

As mentioned in the Introduction, the state of the surface of ice (number and arrangement of dangling O–H bonds) might play a role in the freezing and melting processes. However, factors that determine whether the newly formed ice layer on the *basal* plane is hexagonal or cubic are not known. Understanding the role of the state of the surface of ice may be important from the point of view of understanding the mechanism of action of AFPs. According to one of the concepts, when the protein molecule approaches the surface of ice, a "solidification" of water between both surfaces occurs.[37] If this concept is close to the truth, then the role of the state of the surface may be very important.

As we present, the state of the existing ice, on which the freezing occurs, can influence this process. We investigated ice blocks with more ordered and disordered water molecules. Although we suspect that in nature a long-range ordering of water molecules may be rather exceptional, it is possible

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that it may occur locally. The orientational ordering of water molecules in the ice block leads to the presence of a directed electric field in the vicinity of the ice block. This field modifies the structure of solvation water (i.e., the layer of water in the immediate vicinity of the ice surface). We showed that the structure of solvation water predetermines the structure of a newly created layer of ice (hexagonal or cubic). This effect is temperature-dependent. The field is responsible for the greater preference to form a hexagonal structure than to form a cubic structure on the basal plane in high supercooling, exceeding 10 K. Since a protein molecule can also generate an electric field, it cannot be ruled out that this phenomenon may have implications for the action of AFPs.

In the case of the *prism* plane, we do not observe the influence of the ordering of water molecules in ice on the structure of the new layer, which is always hexagonal. We observe that the freezing proceeds faster on the *prism* plane than on the *basal* plane, but we do not see any clear influence of the state of the surface (dangling O–H bonds) or the electric field on the freezing rate. Also, two forms of ice, cubic and hexagonal, seem to grow with the same rate on the *basal* plane.

SUPPLEMENTARY MATERIAL

See supplementary material for detailed description of the simulation procedure, description of density distribution functions, picture of solvation layers, diagrams depicting formation and dissolution of ice at 265 K, and mean electric field intensities.

ACKNOWLEDGMENTS

The calculations were carried out at the Academic Computer Center (TASK) in Gdańsk. This research was supported in part by PL-Grid Infrastructure.

[1] S. Nie, N. C. Bartelt, and K. Thürmer, Phys. Rev. B **84**, 035420 (2011).
[2] J. D. Madura, K. Baran, and A. Wierzbicki, J. Mol. Recognit. **13**, 101 (2000).
[3] J. Grabowska, A. Kuffel, and J. Zielkiewicz, J. Chem. Phys. **145**, 075101 (2016).
[4] N. H. Fletcher, Philos. Mag. B **66**, 109 (1992).
[5] V. Buch, H. Groenzin, I. Li, M. J. Shultz, and E. Tosatti, Proc. Natl. Acad. Sci. U. S. A. **105**, 5969 (2008).
[6] N. Avidor and W. Allison, J. Phys. Chem. Lett. **7**, 4520 (2016).
[7] E. R. Batista and H. Jónsson, Comput. Mater. Sci. **20**, 325 (2001).
[8] C. Thierfelder, A. Hermann, P. Schwerdtfeger, and W. G. Schmidt, Phys. Rev. B **74**, 045422 (2006).
[9] Z. Sun, D. Pan, L. Xu, and E. Wang, Proc. Natl. Acad. Sci. U. S. A. **109**, 13177 (2012).
[10] C. L. Bishop, D. Pan, L. M. Liu, G. A. Tribello, A. Michaelides, E. G. Wang, and B. Slater, Faraday Discuss. **141**, 277 (2009).
[11] D. A. Case, T. A. Darden, T. E. Cheatham III, C. L. Simmerling, J. Wang, R. E. Duke, R. Luo, R. C. Walker, W. Zhang, K. M. Merz, B. Roberts, S. Hayik, A. Roitberg, G. Seabra, J. Swails, A. W. Götz, I. Kolossváry, K. F. Wong, F. Paesani, J. Vanicek, R. M. Wolf, J. Liu, X. Wu, S. R. Brozell, T. Steinbrecher, H. Gohlke, Q. Cai, X. Ye, J. Wang, M.-J. Hsieh, G. Cui, D. R. Roe, D. H. Mathews, M. G. Seetin, R. Salomon-Ferrer, C. Sagui, V. Babin, T. Luchko, S. Gusarov, A. Kovalenko, and P. A. Kollman, *AMBER 12 Reference Manual* (University of California, San Francisco, 2012).
[12] H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola, and J. R. Haak, J. Chem. Phys. **81**, 3684 (1984).
[13] D. Rozmanov and P. G. Kusalik, J. Chem. Phys. **136**, 44507 (2012).
[14] J. L. F. Abascal, E. Sanz, R. García Fernández, and C. Vega, J. Chem. Phys. **122**, 234511 (2005).
[15] M. Seo, E. Jang, K. Kim, S. Choi, and J. S. Kim, J. Chem. Phys. **137**, 154503 (2012).
[16] A. H. Nguyen and V. Molinero, J. Phys. Chem. B **119**, 9369 (2015).
[17] E. B. Moore and V. Molinero, J. Chem. Phys. **132**, 244504 (2010).
[18] A. Hudait, S. Qiu, L. Lupi, and V. Molinero, Phys. Chem. Chem. Phys. **18**, 9544 (2016).
[19] E. Małolepsza and T. Keyes, J. Chem. Theory Comput. **11**, 5613 (2015).
[20] Y. P. Handa, D. D. Klug, and E. Whalley, J. Chem. Phys. **84**, 7009 (1986).
[21] T. L. Malkin, B. J. Murray, C. G. Salzmann, V. Molinero, S. J. Pickering, and T. F. Whale, Phys. Chem. Chem. Phys. **17**, 60 (2015).
[22] M. A. Carignano, E. Baskaran, P. B. Shepson, and I. Szleifer, Ann. Glaciol. **44**, 113 (2006).
[23] M. A. Carignano, J. Phys. Chem. C **111**, 501 (2007).
[24] S. Choi, E. Jang, and J. S. Kim, J. Chem. Phys. **140**, 014701 (2014).
[25] A. Zaragoza, M. M. Conde, J. R. Espinosa, C. Valeriani, C. Vega, and E. Sanz, J. Chem. Phys. **143**, 134504 (2015).
[26] T. Takahashi, J. Cryst. Growth **59**, 441 (1982).
[27] T. Takahashi and T. Kobayashi, J. Cryst. Growth **64**, 593 (1983).
[28] D. Ehre, E. Lavert, M. Lahav, and I. Lubomirsky, Science **327**, 672 (2010).
[29] A. Belitzky, E. Mishuk, D. Ehre, M. Lahav, and I. Lubomirsky, J. Phys. Chem. Lett. **7**, 43 (2016).
[30] K. Carpenter and V. Bahadur, Langmuir **31**, 2243 (2015).
[31] J. Y. Yan and G. N. Patey, J. Phys. Chem. Lett. **2**, 2555 (2011).
[32] J. Y. Yan and G. N. Patey, J. Phys. Chem. A **116**, 7057 (2012).
[33] J. Y. Yan and G. N. Patey, J. Chem. Phys. **139**, 144501 (2013).
[34] J. Y. Yan, S. D. Overduin, and G. N. Patey, J. Chem. Phys. **141**, 074501 (2014).
[35] H. Nada and Y. Furukawa, J. Cryst. Growth **283**, 242 (2005).
[36] M. A. Carignano, P. B. Shepson, and I. Szleifer, Mol. Phys. **103**, 2957 (2005).
[37] E. Kristiansen and K. E. Zachariassen, Cryobiology **51**, 262 (2005).
[38] W. Humphrey, A. Dalke, and K. Schulten, J. Mol. Graphics **14**, 33 (1996).

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