

## Why is the cubic structure preferred in the newly formed ice?

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Molecular dynamics was employed to explain the preference for the cubic structure in newly formed crystals of ice. The results showed that in supercooled liquid water the molecules connected by hydrogen bonds are more likely to adopt relative orientations similar to the ones characteristic for cubic ice. The observed preference for certain relative orientations of molecules in the hydrogen-bonded pairs results in the higher probability of the formation of ice with the cubic structure. On that basis it was concluded that the main reason for the increased probability of the formation of cubic ice in solidifying water is the distinctive structure of liquid water.

Under ambient pressure, water solidifies into ice which is a mixture of two forms of ice - hexagonal and cubic - despite the fact that the hexagonal form is thermodynamically more stable.<sup>1</sup> This observation has been confirmed for a wide range of temperatures, both by experiment<sup>2-5</sup> and computer simulations<sup>6-11</sup>. Moreover, it was shown that in many cases the content of cubic ice in the newly formed crystals is greater than the amount of hexagonal form<sup>7,8,10-15</sup> (Fig. 1) and that the ratio of cubic to hexagonal ice content increases as the temperature decreases.<sup>11</sup>

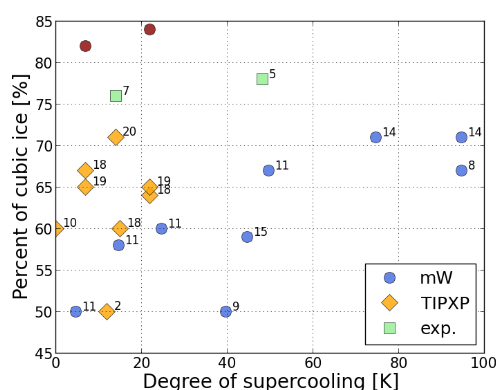


Fig. 1 Dependence of cubic ice content in the crystals of ice on the degree of water supercooling (blue points – mW water model<sup>8,9,11,14,15</sup>, green points – experiment<sup>5,7</sup>, orange points – TIPXP family of water models<sup>2,10,18,19,20</sup>, dark red points – values predicted by the model, see text)

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As can be seen in Fig. 1, the results obtained both by experiment and computer simulations are similar. There might be several reasons for the observed discrepancies, one of which is the research methodology. For example, in the case of computer simulations, the employment of the periodic boundary conditions or the size of the simulation system may have a significant influence on the results. Interestingly, in the case of the results obtained by the computer simulations conducted using the monoatomic water model mW, the content of cubic ice was generally lower compared to the results obtained with the use of different water models or by experimental methods. It seems that the type of model of water used in the simulations is another factor that may affect the results.

Over the years, a number of attempts have been made to find the causes of this phenomenon. Carignano<sup>7</sup> suggested that the process of freezing of water progresses according to the so-called Ostwald rule. The rule states that during the solidification of a liquid phase the crystal structure of the lowest stability crystallises first. Other authors<sup>8,16</sup> showed that in terms of stability, the cubic and hexagonal forms of ice differ only to a small extent, which cannot explain the difference in the content of both structures in the newly formed ice. Based on that information, it was concluded that the preference for cubic ice may have a kinetic basis, not a thermodynamic one<sup>8</sup>. If that is the case, cubic ice might be preferred as a result of a greater number of ways in which a new water molecule can be added to an existing crystal of ice or due to a lower activation energy of an addition of a new water molecule to a crystal of ice. On the other hand, it was argued<sup>15</sup> that the entropy might be an important factor to consider - the number of planes on which ice can be stacked is greater for the cubic form of ice. Another possible explanation for the observed preference is connected with the shape of ice nuclei<sup>17</sup>. Crystals with a high content of hexagonal ice are asymmetric which makes them less stable compared to the crystals of cubic ice. Despite the growing amount of data, the reason for the preference for the cubic structure in the newly formed crystals of ice is still unclear.

Previous research concentrated on this topic was focused mainly on the analysis of the energy and entropy changes during the process of freezing of water<sup>8,11,16,17</sup>. In this work a different approach was adopted in which the focus was on the structure of the hydrogen bond network in the supercooled liquid water. The main concept of the work can be presented as follows.

Pairs of water molecules connected by hydrogen bonds that can be found in the hexagonal and cubic ice are arranged in a different manner. The difference lies in the relative spatial orientation of the molecules that form these pairs. Pairs of water molecules connected by hydrogen bonds can also be found in the liquid water and sometimes the relative orientation of molecules in those pairs is similar to the one observed for the hexagonal or cubic structure of ice. The probabilities of finding a pair of water molecules with the relative orientation characteristic for the hexagonal ( $p_{hex}$ ) and cubic ( $p_{cub}$ ) structure of ice in liquid water were characterized in this study and were shown to be different. This difference could be responsible for the fact that cubic ice is created more often than the hexagonal one.

In order to put this idea to the test, computer simulations (with the use of Amber12<sup>21</sup> molecular dynamics package) were carried out. The TIP4P-Ice water model was used, which – as it was shown before<sup>22</sup> – correctly reproduces the phase diagram of water at temperatures close to the water melting point under moderate pressures. Firstly, a simulation system consisting of 12 665 molecules of liquid water located in a rectangular simulation box was simulated at several temperatures in the range of 250 – 300 K (a detailed description of the simulation procedure was included in the ESI). Secondly, a series of computer simulations was conducted for the systems composed of a crystal of hexagonal ice (located in the centre of the simulation box) submerged in liquid water, at two temperatures: 250 K and 265 K. A detailed description of the preparation and simulation procedure of those systems can be found in the previous work<sup>18</sup>. In both cases, as a measure of the relative orientation of water molecules connected by hydrogen bonds the dihedral angle  $\phi$  was used. The  $\phi$  angle (Fig. 2) is defined as an angle between two intersecting planes, where each plane contains two vectors:  $\overline{OO}$  (vector that connects oxygen atoms of two neighbouring molecules) and  $\overline{OD}$  (which lies on the bisector of the H-O-H angle of the water molecule; see also Fig. S1 in ESI).

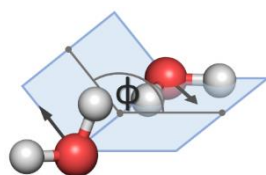


Fig. 2 Definition of a  $\phi$  angle between two water molecules connected by a hydrogen bond (the bisectors of the H-O-H angles for both water molecules are indicated by arrows)

In Fig. 3, the distributions of the  $\phi$  angles in two types of systems: consisting of only liquid water (at different temperatures) and consisting of crystals of ice submerged in liquid water were presented. In the case of the latter, the systems in which a new layer of hexagonal or cubic ice was present at the end of the simulation (after 18 ns; the presence of newly formed ice was detected with the use of CHILL+ algorithm<sup>23</sup>) were selected for the analysis. In those systems, the values of the  $\phi$  angles were determined for pairs of molecules consisting of water molecules which form the surface of the basal plane of the ice crystal and water molecules of the (solidified) solvation layer of ice (green lines in Fig. 3).

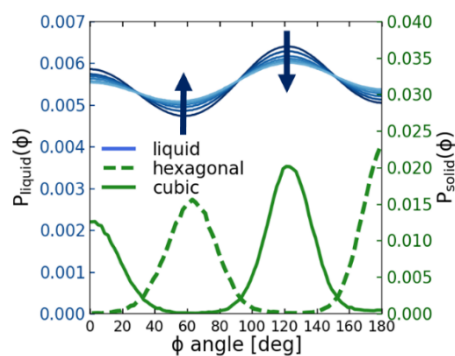


Fig. 3 Distributions of the  $\phi$  angles for the pairs of water molecules connected by the hydrogen bonds in liquid water (blue lines) at temperatures in the range of 250-300 K (the darkest line corresponds to the temperature of 250 K, the brightest one – 300 K; arrows shows the direction of temperature increase) and for pairs of molecules located in the adjacent layers of the newly formed hexagonal (green dashed line) and cubic ice (green solid line)

The results obtained for supercooled liquid water are presented in Fig. 3 with the blue lines. As can be seen, there is a clear preference for the angles close to  $0^\circ$  and  $120^\circ$ . The preference for those angles occurs at all studied temperatures (in the range of 250 – 300 K); it is also clear from Fig. 3 that the preference is strengthened as the temperature decreases.

In order to relate the structure of water and the content of cubic and hexagonal structures in ice, the relative orientations of pairs of water molecules in ice should be analysed. In the ideal crystal of ice, each molecule of water is connected by hydrogen bonds with four neighbouring molecules. Three of those molecules are located within the same layer of ice as the central molecule (when layers perpendicular to the stacking direction are considered) and the relative orientations of the molecules that create those pairs are the same for the cubic and hexagonal structure of ice. The last bond connects the water molecules that are located in the adjacent layers of ice. In the case of hexagonal structure of ice,  $\phi$  values for these pairs of water molecules are equal to about  $60^\circ$  or  $180^\circ$ , while for the cubic ice the  $\phi$  values are close to  $0^\circ$  or  $120^\circ$ . In the newly formed ice, where the water molecules are not perfectly ordered, the distributions of the  $\phi$  angles are quite broad (Fig. 3 – green lines). Nevertheless, even at this stage of the process of freezing, the characteristic features of both forms of ice are clearly visible.

When the distributions of the  $\phi$  angles in liquid water are compared with the distributions obtained for newly formed ice it can be seen that there is a preference for the pairs of water molecules in liquid water to adopt the relative orientations similar to the ones characteristic of cubic ice. This preference may be the reason for the higher probability of the formation of cubic ice in the solidifying water when compared to the hexagonal structure. In that case, also the ratio of the content of both forms of ice in the newly formed ice should depend on the temperature: as the temperature decreases, the content of cubic ice increases. This conclusion is consistent with the literature data concerning the content of hexagonal and cubic ice (see Fig. 1).

With the histograms presented in Fig. 3, it is possible to estimate the probability that a given pair of water molecules (connected by the hydrogen bond) in liquid water will have a relative orientation similar to the one observed for the hexagonal (“hex”) or cubic (“cub”) form of ice. In order to estimate that probability, the integration of the distribution of the  $\phi$  angles (in liquid

water) around the values characteristic for both structures has been performed. The adopted width of the integration interval was equal to  $20^\circ$  ( $\pm 10^\circ$  around the values of the  $\phi$  angles characteristic for cubic and hexagonal ice). For example, the probabilities calculated for the temperature of 250 K were equal to:  $p_{hex} = 0.1440$  and  $p_{cub} = 0.1856$ ; the values obtained for other temperatures are included in Table S1 in the ESI.

If each of the pairs of water molecules with a given configuration (“hex” or “cub”) were the nucleus of the crystallization, then the  $p_{cub}$  to  $p_{hex}$  ratio should reflect the ratio of the content of cubic and hexagonal ice formed in the solidifying liquid. However, the situation is different: as Choi et al.<sup>20</sup> showed, during the formation of a new layer of solid on the basal plane of ice there is a competition between larger clusters of water molecules with a hexagonal and cubic structure. Only clusters that are large enough have a chance for further growth and transformation into a full layer of ice. In other words, the structure of the new layer of ice is determined by the orientation of not one, but many neighbouring water molecules, which belong to the liquid phase, but at the same time are located close to the surface of the ice crystal (basal plane of hexagonal ice or (111) plane of cubic ice) and form pairs with the surface water molecules of the crystal. If the orientations of the molecules in the solvation layer (relative to the surface water molecules of the ice) correspond to “hex” or “cub” configurations and if the size of the formed cluster exceeds a certain minimum value, then the ice layer with the corresponding structure will be formed.

Let's assume that the minimum (critical) size of the cluster is equal to  $N$ . In that case, the final content of both forms of ice will be determined by the probability of the formation of the clusters consisting of  $N$  water molecules (denoted as  $p^{(N)}_{hex}$  for the hexagonal ice or  $p^{(N)}_{cub}$  for the cubic ice). The ratio of the probabilities  $p^{(N)}_{hex}$  and  $p^{(N)}_{cub}$  should reflect the ratio of the content of the cubic and hexagonal structures in the newly formed ice. For that reason, the key questions that should be addressed are about the minimum size of the cluster ( $N$ ), the probability of its occurrence and the temperature dependence of both these quantities.

In order to estimate the minimum size of the cluster ( $N$ ), the process of freezing of water on the basal plane of the ice crystal (which has the same structure as (111) plane of cubic ice) was analysed. When the process of freezing begins, molecules of liquid water that are located close to the surface of an ice crystal start to change their orientations to match the crystal lattice of the ice. The progress of this process can be followed with the use of the  $\phi$  angles formed between the water molecules that build the surface of the ice and the neighbouring molecules of liquid water. Therefore, for all of the simulated systems, all molecules of liquid water that were connected by the hydrogen bonds with the basal plane of ice were found. In the next step, the values of the  $\phi$  angles were determined for the selected pairs of molecules. Depending on those values, each molecule of solvation water was then assigned to one of the three groups: “cub”, “hex” or “other”. It was assumed that the selected molecule belonged to the “cub” group when the corresponding value of the  $\phi$  angle was within the range of  $\pm 10^\circ$  around the values of  $0^\circ$  or  $120^\circ$  and to the “hex” group for angles within the range of  $\pm 10^\circ$  around the values of  $60^\circ$  or  $180^\circ$ . Water molecules that did not meet any of the above conditions were assigned to the “other”

group. Thanks to this procedure, from all water molecules in the solvation shell of the basal plane of ice, only the ones that adopted the optimal orientation to become a part of the solid phase of a given structure were selected. The next step of the analysis was to find the size of the clusters which consisted of water molecules belonging to the same groups. The changes in the size of the clusters for the “cub” and “hex” groups in time were analysed, for all simulated systems.

Based on the data obtained, an attempt was made to estimate how large the cluster of water molecules assigned to the “cub” or “hex” group should be to determine the direction of the process of freezing. For different values of  $N$ , in each simulation system, the moment when the cluster of a given size appeared for the first time was determined. In the next step, the structure of this cluster was compared to the structure of ice at the end of the simulation (in most of the cases at this moment the solvation layer of ice was fully solidified). The percentage of systems in which the structure of the starting cluster (of a given size) has been preserved until the end of the simulation is presented in Fig. 4.

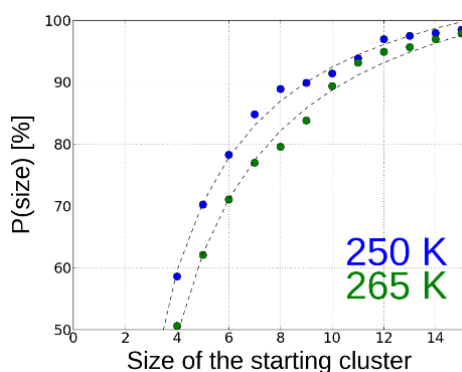


Fig. 4 The probability of the formation of a full layer of ice of the same structure as a starting cluster of a certain size as the function of the size of the starting cluster

The probability of the formation of a full layer of ice of the same structure as a starting cluster was higher for larger clusters. As it can be expected, the obtained results vary depending on the temperature (and thus on the degree of supercooling) and show that the probability of the formation of a full layer of ice of the same structure as the starting cluster of a given size decreases with increasing temperature. Based on the data obtained, the size of a minimum (critical) cluster can be estimated as 9 and 10 molecules at 250 K and 265 K, respectively, which corresponds to the sizes of the cluster for which the obtained probability was close to 90% or higher.

Knowing the probabilities of  $p_{cub}$  and  $p_{hex}$  in liquid water and the size of a minimum cluster ( $N$ ), an attempt can be made to estimate the probabilities of a formation of such clusters ( $p^{(N)}_{hex}$  and  $p^{(N)}_{cub}$ ) at the pre-existing ice lattice. For this purpose, the following model system has been constructed.

The matrix corresponding to the crystal lattice of the surface of the basal plane of hexagonal ice (which is the same as the surface of (111) plane of cubic ice) was generated. It was assumed that every outer molecule in the ice crystal (every node of the matrix) creates one new hydrogen bond outside from the pre-existing ice. The relative orientations of the molecules



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of liquid water participating in these hydrogen-bonded pairs were assigned to be as in cubic ice, as in hexagonal ice or other, with the probabilities equal to  $p_{hex}$ ,  $p_{cub}$  and  $p_{other} = 1 - (p_{hex} + p_{cub})$ . Then the probabilities of all the pairs, which are next to each other, having the same (“cub” or “hex”) structure and creating one cluster of a given size  $N$  (or larger) were calculated. As it was argued before, the probability of the formation of a cluster of a minimum (critical) size and “cub” or “hex” structure should reflect the probability of the formation of a new ice layer of the same structure. With  $N$  equal to 9 at 250 K and 10 at 265 K, the final content of the cubic form of ice was estimated as equal to 84% and 82%, respectively (for comparison with the experimental data see Fig. 1).

As can be expected, the probability of the formation of a cubic structure was higher for a higher degree of supercooling. Moreover, at both temperatures, the model predicts a preference for the cubic structure of ice. However, the values obtained are higher than the experimental ones. This should not be surprising considering the fact that the model is very simple and randomly assigns orientations to every molecule of water present in the solvation layer of the ice crystal, neglecting the influence of other factors. On the other hand, this method confirms that the preference for the cubic structure of ice is directly related to the structure of the liquid water or – more precisely – to the preference for certain relative orientations of water molecules connected by hydrogen bonds. In light of this limitation, the predicted content of hexagonal and cubic ice in the newly formed ice can be considered as close to the experimental values and the values obtained by the computer simulations.

### Conclusions

The conducted research clearly shows that the reason for the preference for the cubic structure of newly formed ice can be associated with the structure of liquid water (simulated with the TIP4P-Ice water model). The increased probability for the pairs of water molecules in liquid water, connected by hydrogen bonds, to adopt mutual orientations similar to the ones characteristic for cubic ice translates into the increased probability of the formation of ice with that structure. The most important factor here seems to be the probability of the formation of a cluster consisting of water molecules with a similar orientation relative to the water molecules in the ice crystal (“hex” or “cub”) of a certain minimum size. The formation of such a cluster determines the process of freezing of liquid water, leading to the creation of a new layer of ice with the same structure. The model presented in this work also allows us to understand why the content of cubic ice in the freezing water increases with the increase of the water supercooling.

### Conflicts of interest

There are no conflicts to declare

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