

# A Primer on Ice

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# Chapter 1

## Introduction to ice

Water forms many different crystal structures in its solid form. These provide insight into the potential structures of ice even in its liquid phase, and they can be used to calibrate pair potentials used for simulation of water [9, 14, 15]. In crowded biological environments, water may behave more like ice than bulk water. The different ice structures have different dielectric properties [16].

There are many crystal structures of ice that are topologically tetrahedral [1], that is, each water molecule makes four hydrogen bonds with other water molecules, even though the basic structure of water is trigonal [3]. Two of these crystal structures (Ih and Ic) are based on the same exact local tetrahedral structure, as shown in Figure 1.1. Thus a subtle understanding of structure is required to differentiate them.

We refer to the tetrahedral structure depicted in Figure 1.1 as an exact tetrahedral structure. In this case, one water molecule is in the center of a square cube (of side length two), and it is hydrogen bonded to four water molecules at four corners of the cube. The triples of numbers represent the Cartesian coordinates of the various water locations. The distance between oxygen centers in these coordinates is  $\sqrt{3}$  for the waters that are directly hydrogen bonded, as indicated by the dotted lines in Figure 1.1, and the distance between the next-nearest neighbors is  $2\sqrt{2}$ . The actual distance for ice Ih or Ic is believed to be 2.76 Ångstroms, so to convert our coordinates to Ångstroms we must multiply by 1.5935. We will see that the density of ice Ih and Ic in our units is one water per eight cubic units, which corresponds to about one water per 32.37 cubic Ångstroms.

The ice structures are not simple repeats of this basic cube. Instead, this unit is utilized in different ways to form different forms of ice I. In other forms of ice, this tetrahedral structure is distorted, but the four hydrogen bonds remain.

Notice that we have not specified the location of the hydrogen (donors) for the hydrogen bonds in Figure 1.1. We use dotted lines to indicate the hydrogen bonds inside the cube, independent of where the hydrogens are located. In general, there are six different specifications for the hydrogens for the central water molecule located at the center of the box, since there are four possible locations for each pair of hydrogens:

$$6 = \binom{4}{2}.$$

For each of these six pairings, it is easy to see that there is a compatible assignment of hydrogens

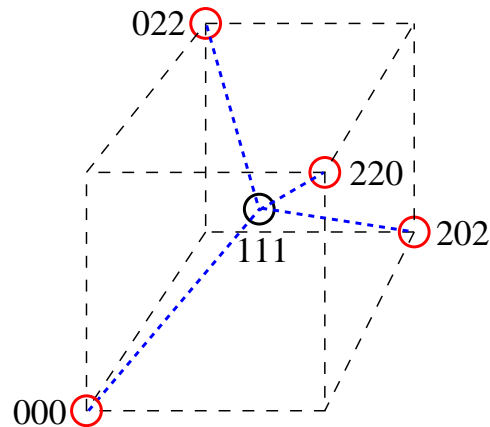


Figure 1.1: The tetrahedral basis for the crystal structures of both forms of ice I. The triples of numbers are the Cartesian coordinates of the water positions in a cube of side two units. Forms the basis for both the cubic structure of the diamond lattice for ice Ic and the hexagonal structure of ice Ih.

for the four corner water molecules (each edge must contain precisely one hydrogen). However, when one continues this process to their neighbors, constraints on the hydrogen positions become significant. In some forms of ice, the positions of the hydrogens are fixed, and we can indicate the directions of the hydrogen bonds by arrows (cf. Figure 3.1).

One way to think of the structure of ice is as a graph with a type of periodic structure. In this way, there is a natural finite graph that generates this periodic structure [12]. These graphs differentiate the different forms of ice, and they help to visualize the structure. Let us introduce these notions more precisely.

## 1.1 Lattices in $\mathbb{R}^3$

A lattice is a very simple notion, a set of points generated by shifting the origin in three directions repeatedly. They are specified by three vectors as in (2.9) or (2.18).

**Definition 1.1** *Suppose that  $g^1, g^2, g^3 \in \mathbb{R}^3$  are not co-planar. A lattice  $\mathcal{L}(g^1, g^2, g^3)$  in  $\mathbb{R}^3$  is the set of points*

$$\mathcal{L}(g^1, g^2, g^3) = \left\{ x_\alpha = \sum_{i=1}^3 \alpha_i g^i \mid \alpha \in \mathbb{Z}^3 \right\},$$

where  $g^1, g^2, g^3 \in \mathbb{R}^3$  are called the generators of the lattice.

Thus a lattice just consists of the vertices of a tiling of  $\mathbb{R}^3$  obtained with simple boxes with possibly slanted sides. Lattices make sense in any number of dimensions, with the number of generators being the dimension. The vertices of the parallelograms in Figure 2.2 provide an example

of a lattice in two dimensions. Since we are primarily interested in three-dimensional lattices, we have simplified to this case.

A lattice forms a group under the addition

$$x_\alpha + x_\beta = \sum_{i=1}^3 (\alpha_i + \beta_i) g^i \quad \forall \alpha, \beta \in \mathbb{Z}^3, \quad (1.1)$$

and this group is isomorphic to  $\mathbb{Z}^3$ . We can denote this isomorphism by  $\phi$ , where

$$\phi(\beta) = x_\beta \quad \forall \beta \in \mathbb{Z}^3. \quad (1.2)$$

The **fundamental domain** of a lattice  $\mathcal{L}(g^1, g^2, g^3)$  is the set

$$\Omega_{\mathcal{L}} = \{y = x_1 g^1 + x_2 g^2 + x_3 g^3 \mid x \in \mathbb{R}^3, 0 \leq x_i \leq 1, i = 1, 2, 3\}. \quad (1.3)$$

The shapes of the fundamental domain of a lattice are crucial in determining certain symmetries of crystals, and they are useful in visualizing the repeating pattern of crystals. However, these symmetries are primarily of interest when determining the vertex positions based on X-ray data.

## 1.2 Crystals in $\mathbb{R}^3$

A crystal is more complex than a lattice. It has a set of points  $\mathcal{P} \subset \mathbb{R}^3$  that form the basis for the crystal unit, and these are shifted throughout space using a lattice. Typically,  $\mathcal{P} \subset \mathbb{R}^3$  is a finite set.

**Definition 1.2** *We say that a set  $\mathcal{P} \subset \mathbb{R}^3$  is non-degenerate with respect to a lattice  $\mathcal{L}(g^1, g^2, g^3)$  if for any  $p, q \in \mathcal{P}$  and  $x_\alpha \in \mathcal{L}(g^1, g^2, g^3)$ ,  $p = q + x_\alpha$  implies  $x_\alpha = 0$ .*

**Definition 1.3** *Suppose  $g^1, g^2, g^3 \in \mathbb{R}^3$  are the generators of a lattice  $\mathcal{L}(g^1, g^2, g^3)$ , and  $\mathcal{P} \subset \mathbb{R}^3$  is non-degenerate with respect to  $\mathcal{L}(g^1, g^2, g^3)$ . A **crystal**  $\mathcal{C}$  in  $\mathbb{R}^3$  is a graph  $\mathcal{C} = (\mathcal{V}, \mathcal{E})$  whose vertices  $\mathcal{V}$  comprise a set of points*

$$\mathcal{V} = \{x_\alpha + p \mid p \in \mathcal{P}, x_\alpha \in \mathcal{L}(g^1, g^2, g^3)\}, \quad (1.4)$$

and whose edges  $\mathcal{E}$  are also generated by a finite set  $\mathcal{S} \subset \mathcal{V} \times \mathcal{V}$  of edges:

$$\mathcal{E} = \{(x_\alpha + v^1, x_\alpha + v^2) \mid (v^1, v^2) \in \mathcal{S}, x_\alpha \in \mathcal{L}(g^1, g^2, g^3)\}. \quad (1.5)$$

One simple crystal  $\mathcal{C}(g^1, g^2, g^3)$  is based on a lattice  $\mathcal{L}(g^1, g^2, g^3)$ , with  $\mathcal{P} = \{(0, 0, 0) \in \mathbb{R}^3\}$  and  $\mathcal{S} = \{(0, g^i) \mid i = 1, 2, 3\}$ . Notice that the set  $\mathcal{S}$  is not a set of edges based on points in  $\mathcal{P}$ . That is, the pair  $(\mathcal{P}, \mathcal{S})$  does not form a graph itself.

## 1.3 Comparing crystals

Ice forms many different crystal forms under different temperature and pressure conditions. We would like to have ways to compare them that compare, contrast and differentiate them. We will see that some of the commonly used concepts do not distinguish between common ice forms.

### 1.3.1 Quotient graph

For any crystal  $\mathcal{C} = (\mathcal{V}, \mathcal{E})$  generated from a lattice  $\mathcal{L}(g^1, g^2, g^3)$ , the natural lattice group defined via (1.1) acts on  $\mathcal{C}$  in a natural way, and it leaves the crystal invariant:

$$\begin{aligned} x_\beta(x_\alpha + p) &= x_\alpha + x_\beta + p = x_{\alpha+\beta} + p, \\ x_\beta(v^1, v^2) &= (x_\beta + v^1, x_\beta + v^2), \end{aligned} \tag{1.6}$$

for all  $\beta \in \mathbb{Z}^3$ . Note that we can think equivalently of (1.6) defining the action of  $\mathcal{L}(g^1, g^2, g^3)$  on  $\mathcal{C}$ , or the action of  $\mathbb{Z}^3$  on  $\mathcal{C}$ , where we make the obvious identification. Thus it is natural to consider the quotient graph  $\mathcal{C}/\mathcal{L}(g^1, g^2, g^3)$  with respect to this group action. Let us define this quotient graph.

The vertices of this quotient graph are equivalence classes of vertices in  $\mathcal{V}$ . We say two points  $v^1, v^2 \in \mathcal{V}$  are equivalent with respect to the group  $\mathcal{L}(g^1, g^2, g^3)$  if, for some  $\beta \in \mathbb{Z}^3$ ,

$$v^1 = v^2 + x_\beta. \tag{1.7}$$

We define  $\mathcal{V}/\mathcal{L}(g^1, g^2, g^3)$  to be the set of equivalence classes with respect to the equivalence relation (1.7). Each  $v^i = p^i + x_{\alpha_i}$ , so (1.7) means that

$$p^1 = p^2 + x_\gamma \tag{1.8}$$

for some  $\gamma \in \mathbb{Z}^3$ . Since we assume that  $\mathcal{P}$  is non-degenerate with respect to  $\mathcal{L}(g^1, g^2, g^3)$ , (1.8) implies that

$$p^1 = p^2. \tag{1.9}$$

Thus any  $[v] \in \mathcal{V}/\mathcal{L}(g^1, g^2, g^3)$  can be written as  $p + x_\alpha$  for a unique  $p \in \mathcal{P}$ :  $[v] = [p]$ . Thus there is a natural injection  $\mathcal{V}/\mathcal{L}(g^1, g^2, g^3) \subset \mathcal{P}$ . Since  $[p] \in \mathcal{V}$  for all  $p \in \mathcal{P}$ , this is an isomorphism.

For edges  $e \in \mathcal{E}$ , let us use the notation  $e_i$  for the vertices of the edge:  $e = (e_1, e_2)$ . We say that  $e$  and  $\hat{e}$  are equivalent with respect to the group  $\mathcal{L}(g^1, g^2, g^3)$  if, for some  $\beta \in \mathbb{Z}^3$ ,

$$e_i = \hat{e}_i + x_\beta \quad \forall i = 1, 2. \tag{1.10}$$

We define  $\mathcal{E}/\mathcal{L}(g^1, g^2, g^3)$  to be the set of equivalence classes with respect to the equivalence relation (1.10). Note that  $[e] = [\hat{e}]$  implies that  $[e_i] = [\hat{e}_i]$  for  $i = 1, 2$ . Therefore, for each ‘‘edge’’  $[e] \in \mathcal{E}/\mathcal{L}(g^1, g^2, g^3)$ , we can identify two vertices  $[e_i]$  for  $i = 1, 2$ . Thus there is a natural injection

$$\mathcal{E}/\mathcal{L}(g^1, g^2, g^3) \subset \mathcal{V}/\mathcal{L}(g^1, g^2, g^3) \times \mathcal{V}/\mathcal{L}(g^1, g^2, g^3) \subset \mathcal{P} \times \mathcal{P}. \tag{1.11}$$

Thus we can think of  $\mathcal{E}/\mathcal{L}(g^1, g^2, g^3)$  as providing edges between vertices  $\mathcal{V}/\mathcal{L}(g^1, g^2, g^3)$ , and this defines the graph  $\mathcal{C}/\mathcal{L}(g^1, g^2, g^3)$ , called the **fundamental finite graph** of the crystal [12]. We will see that this graph can distinguish between different crystal structures of ice.

distance	$N_h$	$N_c$
1.7321	4	4
2.8284	12	12
2.8868	1	
3.3166	9	12
4.0000	6	6
4.0415	6	
4.3589	9	12
4.6188	2	
4.8990	18	24
5.1962	9	16
5.4160	12	
5.4467	3	
5.6569	6	12
5.6862	6	
5.9161	18	24
total	121	122

Table 1.1: Radial distances between oxygen centers in two different forms of ice one: ice Ih and ice Ic. The left column is the radial distance and the second and third columns are the numbers of water molecules at that distance:  $N_h$  for ice Ih and  $N_c$  for ice Ic.

### 1.3.2 Radial distribution function

The **radial distribution function** is one measure often used. The primary one in the context of ice is the oxygen-oxygen radial distribution function. This is a type of probability distribution function related to the likelihood of finding a neighboring oxygen at a given distance  $r$ .

For true crystals, such a distribution is discrete, that is, a sum of delta functions at distinct distances, due to the fact that the positions of the atoms in (1.4) has a periodic structure. Moreover, all crystals based on the local tetrahedral structure in Figure 1.1 have the property that the first (smallest  $r$ ) nonzero part of the radial distribution is the same, corresponding to the fact that each oxygen has four neighbors at a distance of  $\sqrt{3}$  in the coordinates of Figure 1.1. The second nonzero part of the radial distribution is also the same, corresponding to the fact that the (twelve) next nearest neighbors are at the opposite corners of a cube of side two, and thus are all at a distance of  $2\sqrt{2}$  in the coordinates of Figure 1.1.

There is a significant difference between the radial distribution function and the radial density function. The latter is the former divided by  $4\pi r^2$ . Thus the first peak for tetrahedral water would have a height of  $1/3\pi$  and the second peak would have a height of  $3/8\pi$ .

Although the first two points of the radial functions for ice Ih and Ic are the same (see Table 1.1), their overall distributions are quite different. Ice Ic has a sparser set of distribution points than Ih as illustrated in Table 1.1. This pattern continues for larger distances; there are 96 distances in Ic less than twenty, but 239 distances in Ih less than twenty. (Both crystals have thirty molecules at



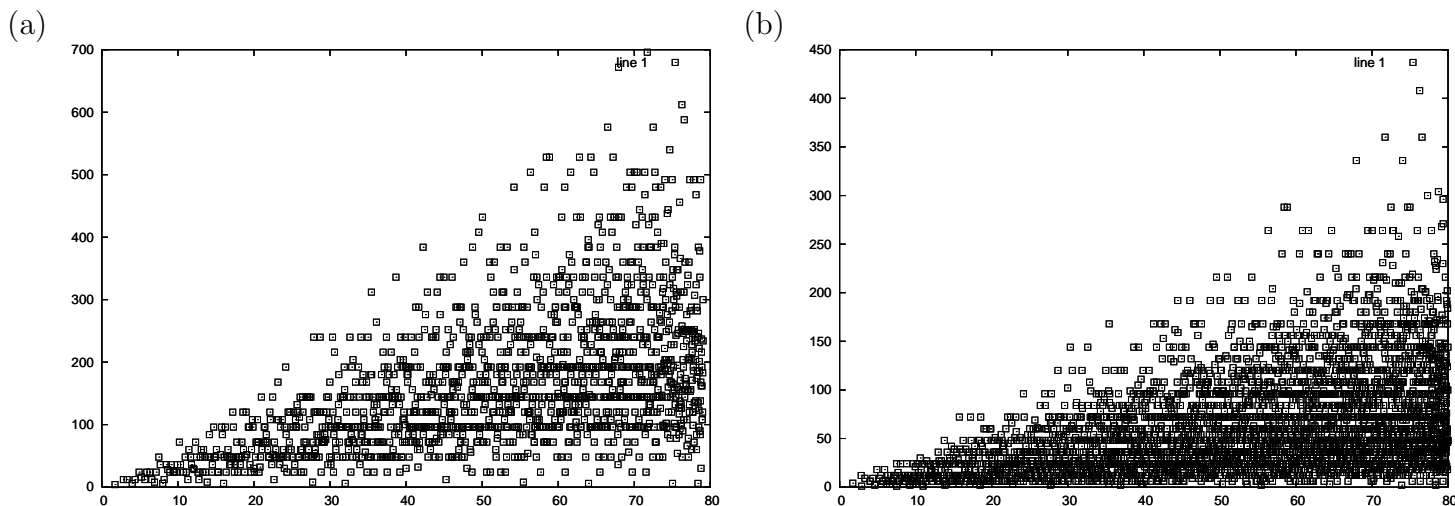


Figure 1.2: The radial distribution of ice Ic (a) and ice Ih (b).

a distance of twenty.)

### 1.3.3 Local graph structure

In some cases, the local graph of hydrogen bonds can be instructive. For crystals, this structure is repeated, so we can look at a single instance. In Figure 1.3, we show the water molecules (vertices indicated by circles) surrounding the central green water, together with the hydrogen bonds (edges). The blue waters are the nearest neighbors, magenta waters are next-nearest neighbors, and the black circles indicate next-next-nearest neighbors. Notice that four of them are marked in red because they are involved in a cycle.

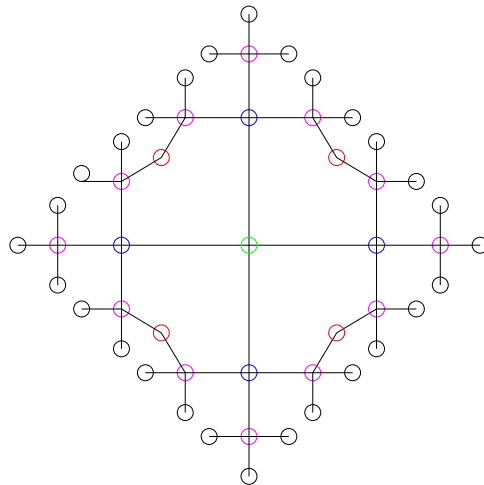


Figure 1.3: The local graph of hydrogen bonds in both forms of ice I.



# Chapter 2

## Ice I structures

The most common phase of ice on earth is Ih, the hexagonal form of ice [6, 11]. However, another form (Ic) also occurs in the atmosphere [10]. Both of these have what we call exact tetrahedral structure, as depicted in Figure 1.1. In this structure, one water molecule is in the center of a square cube, and it is hydrogen bonded to four water molecules at four corners of the cube, as depicted in Figure 1.1.

It is surprising that two different crystalline structures can be formed from this basic unit. One objective here is to examine mathematical tools that can describe how they differ. In addition, other forms of ice form nearly tetrahedral structures that have four bonds, although not with the same lengths and angles as depicted in Figure 1.1.

### 2.1 Ice Ih

The crystal structure of ice Ih is identical to the hexagonal diamond structure of carbon, known as Lonsdaleite [8]. This structure is also known as wurtzite [5]. The structure can be visualized in several ways. It can be viewed as parallel sheets made of a hexagonal network of hydrogen bonds, as shown in Figure 2.1. This figure provides the top view of a single sheet in the crystal and depicts three of the hydrogen bonds formed by each water molecule, each of which is represented by a vertex in Figure 2.1(a). There are alternating colors because the water molecules make alternating hydrogen bonds with either the sheet above or the sheet below. In our rendering, the red waters make bonds with waters directly above them, and the magenta waters make bonds with waters directly below them. Obscured in Figure 2.1(a) are the vertical undulations in the sheets. This is made clear when we realize that the hydrogen bonds around each vertex must form exact tetrahedral bonds with their neighbors, as depicted in Figure 1.1. Thus the red waters, which make bonds with waters directly above them, have all of the hydrogen bonds in Figure 2.1(a) projecting down. Thus the red waters are at the top of the undulations in the sheets. The reverse is true for the magenta waters.

We can complete the picture by considering neighboring sheets and their interconnecting hydrogen bonds, as shown in Figure 2.1(b). We have drawn the neighboring sheets with blue and green waters to make them distinct from the red and magenta ones. We have depicted in Figure 2.1(b)

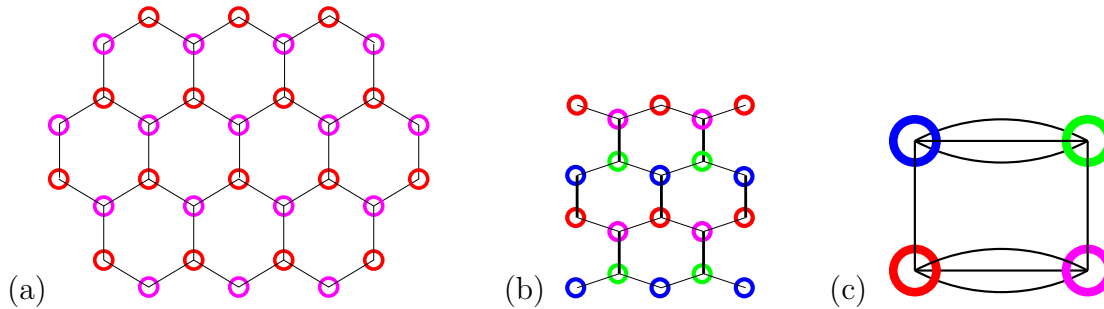


Figure 2.1: The hexagonal structure of ice Ih. (a) Top view of a single layer. The red water oxygens are located above the plane of the figure. In addition to the three hydrogen bonds depicted by lines, they are also hydrogen bonded to waters in another layer above the plane. The magenta water oxygens are located below the plane of the figure and are hydrogen bonded to waters in a layer below the plane. (b) Side view of the hexagonal structure of ice Ih. Hydrogen bond linkages between the red-magenta and the blue-green layers are shown using a thicker line. (c) Fundamental finite graph [12, 13] of the hydrogen bond linkages.

the edge view of a vertical slice through the crystal sheets. Now we see the undulations of the sheets that were obscured in Figure 2.1(a). We can also see that we can view the blue-green sheets as a reflection of the red-magenta sheets. The newly revealed hydrogen bonds are depicted in Figure 2.1(b) via darker lines; the lighter lines indicate hydrogen bonds already seen in Figure 2.1(a).

In Figure 2.1(c), the fundamental finite graph (Section 1.3.1) of the connections [13] is depicted. This reflects the fact that each water is connected to three waters within its horizontal sheet and one water in a neighboring sheet. For example, there are three different ways for a magenta water to be hydrogen bonded to a red water, and one way for it to be bonded to a green water.

The amplitude of the wiggles in Figure 2.1(b) can be obtained by reference to Figure 1.1. The plane of the green points passes through the points  $(0, 2, 2)$ ,  $(2, 0, 2)$ ,  $(2, 2, 0)$ , and the center of the triangle generated by these points is  $(4/3)(1, 1, 1)$ . Thus the distance from the blue water and the green plane is  $\sqrt{3}/3 = 1/\sqrt{3}$ . Thus the wiggles above and below a mean plane are  $\pm c$  where  $c = 1/2\sqrt{3} = (1/6)\sqrt{3}$ .

The basic symmetry of Ih ice is known as monoclinic. The top view of the crystal unit domain is a simple parallelogram, as shown in Figure 2.2(a). In Figure 2.2(b), data is provided to determine the dimensions of the crystal unit. The parameter  $a = \sqrt{2}$ , since the distance between two next-nearest neighboring water oxygens, e.g., two blues in Figure 2.2(b), is  $2\sqrt{2}$ . The blue waters fall in a plane parallel to the plane of Figure 2.2, so the three dimensional distance is the same as the two dimensional distance. The parameter  $b$  is the side length of a 60 degree right triangle, where the other side length is  $a = \sqrt{2}$ . Thus  $b = \sqrt{6}$ .

We recall the parameter  $c = (1/6)\sqrt{3}$  for the amplitude of the ‘wiggle’ below and above the plane of the figure in Figure 2.2. Thus the points in the unit cell in the plane of the figure in

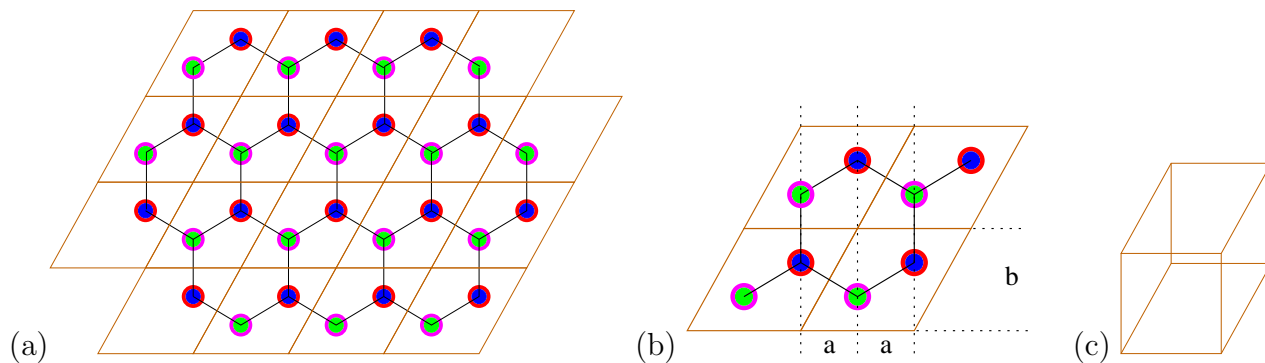


Figure 2.2: The monoclinic symmetry of ice Ih. (a) The repeating crystal unit in the  $(x, y)$ -plane, generated by  $g_1$  and  $g_2$ . (b) Notation to determine the distance  $a$ ; note that  $b = \sqrt{3}a$ . (c) Three-dimensional unit cell.

Figure 2.2 are ( $p_0$  is green,  $p_1$  is blue)

$$\begin{aligned} p_0 &= (a, b/3, c) = (\sqrt{2}, \sqrt{2}/\sqrt{3}, (1/6)\sqrt{3}), \\ p_1 &= (2a, 2b/3, -c) = (2\sqrt{2}, 2\sqrt{2}/\sqrt{3}, -(1/6)\sqrt{3}). \end{aligned} \quad (2.1)$$

We can check the values of  $a, b, c$  by using the fact that the distance between oxygen centers is  $\sqrt{3}$ , that is,  $\|p_1 - p_0\| = \sqrt{3}$ . Thus

$$\|p_1 - p_0\|^2 = 2 + \frac{2}{3} + \frac{1}{3} = 3.$$

The remaining points in the unit cell ( $p_2$  is magenta,  $p_3$  is red) are

$$\begin{aligned} p_2 &= (\sqrt{2}, \sqrt{2}/\sqrt{3}, (7/6)\sqrt{3}), \\ p_3 &= (2\sqrt{2}, 2\sqrt{2}/\sqrt{3}, (3/2)\sqrt{3}), \end{aligned} \quad (2.2)$$

which can be determined as follows. Green and magenta waters ( $p_0$  and  $p_2$ ) are hydrogen bonded, and thus they are at a distance  $\sqrt{3}$ , and moreover their  $x$  and  $y$  coordinates are the same. Thus  $p_2 - p_0 = (0, 0, \sqrt{3})$ . The red waters are above the magenta waters by an amount  $2c = 1/\sqrt{3} = \sqrt{3}/3$ .

Note that

$$\|p_3 - p_1\|^2 = 3 \left( \frac{3}{2} + \frac{1}{6} \right)^2 = 3 \left( \frac{5}{3} \right)^2 = \frac{25}{3}, \quad (2.3)$$

so that  $\|p_3 - p_1\| = 5/\sqrt{3} \approx 2.89$ , slightly larger than the next-nearest neighbor distance of  $2\sqrt{2}$ .

The generators of the lattice for the infinite crystal as in Definition 1.3 for the ice Ih crystal are therefore

$$g^1 = (2a, 0, 0) = (2\sqrt{2}, 0, 0), \quad g^2 = (a, b, 0) = (\sqrt{2}, \sqrt{6}, 0), \quad g^3 = (0, 0, (8/3)\sqrt{3}), \quad (2.4)$$

where the  $z$ -axis translation is easily determined from Figure 2.1(b), as follows. The crystal unit repeat distance in the  $z$ -direction consists of two components: one is the distance between oxygen

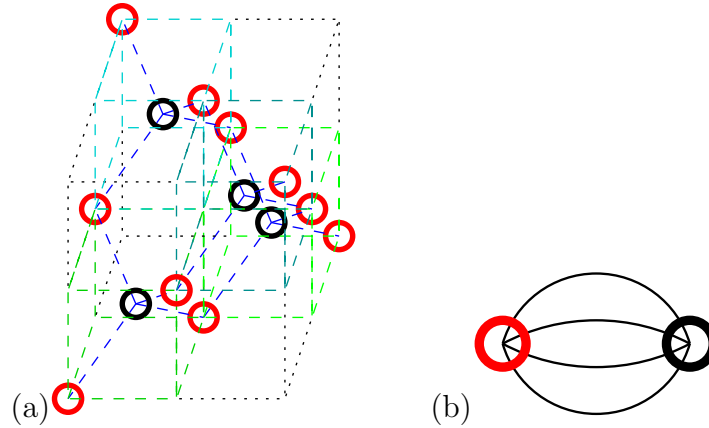


Figure 2.3: Crystal structure of ice Ic. (a) Cubic lattice unit of ice Ic. (b) Fundamental finite graph [12] of the hydrogen bond linkages.

centers  $\sqrt{3}$  and the other is the oscillation in the layer, which has magnitude  $c = 1/2\sqrt{3}$ . Both of these elements get repeated twice in the crystal unit. Thus  $g_3^3 = 2\sqrt{3} + 2/\sqrt{3} = 8/\sqrt{3}$ . An internal check is available regarding the volume of the unit cell,

$$2a \cdot b \cdot g_3^3 = (2\sqrt{2})(\sqrt{6})(8/\sqrt{3}) = 32. \quad (2.5)$$

This means that the water density is one water per 8 cubic units. We will see that this matches exactly the density of ice Ic.

Generators for the edges for the infinite crystal as in Definition 1.3 for the ice Ih crystal are

$$(p_0, p_1), \quad (p_0, p_2), \quad (p_0, p_1 - g^1), \quad (p_0 + g^2, p_1), \quad (p_1 - g^3, p_1). \quad (2.6)$$

## 2.2 Ice Ic

The location of water molecules in the ice Ic lattice is the same as the diamond (carbon) lattice. The placement of waters in a cube is indicated in Figure 1.1. In Figure 2.3, we depict water molecules in a cube of side four. This has four sub-cubes of size two each, each containing a molecule at its center, as well as four void cubes. The symmetry of the diamond (ice Ic) crystal is often called face-centered cubic, since there are atoms at each corner of the cube of side four at and at the center of each face.

The location of the waters  $\mathcal{P}$  in the unit cube that can be used to generate the infinite crystal as in Definition 1.3 are

$$\begin{aligned} p_0 = 000, \quad p_1 = 111, \quad p_2 = 220, \quad p_3 = 022, \quad p_4 = 202, \\ p_5 = 331, \quad p_6 = 133, \quad p_7 = 313, \end{aligned} \quad (2.7)$$

where we use the abbreviation  $xyz$  to stand for  $(x, y, z)$  for vectors in  $\mathbb{R}^3$ , in keeping with the notation in Figure 1.1. Notice that the last three vectors, which correspond to the subcube centers

in Figure 2.3 other than 111, can be written as the vector sum of 111 and the third, fourth and fifth vectors, the positions of the waters at the corners of the subcube in Figure 1.1. That is,

$$p_i = p_{i-3} + p_1, \quad i = 5, 6, 7. \quad (2.8)$$

The generators of the lattice for the infinite crystal as in Definition 1.3 for the ice Ic crystal are

$$g^1 = 400, \quad g^2 = 040, \quad g^3 = 004. \quad (2.9)$$

The density of ice Ic is eight molecules in 64 units cubed, or one molecule per 8 cubic units.

The relation (2.8) suggests that the diamond (ice Ic) crystal can be generated by a smaller number of generators [12, 13]. So we consider crystal generators

$$P_0 = 000, \quad P_1 = 111, \quad (2.10)$$

together with lattice generators

$$G^1 = 220, \quad G^2 = 022, \quad G^3 = 202. \quad (2.11)$$

Then (2.8) implies that

$$p_{i+3} = G^i + p_1, \quad i = 2, 3, 4. \quad (2.12)$$

Of course we also have

$$p_{i+1} = G^i + p_0, \quad i = 1, 2, 3. \quad (2.13)$$

Similarly, we have

$$g^1 = G^1 - G^2 + G^3, \quad g^2 = G^1 + G^2 - G^3, \quad g^3 = -G^1 + G^2 + G^3, \quad (2.14)$$

Thus we have shown that the set of crystal vertices generated from (2.11) and (2.10) contain all of the crystal vertices generated from (2.9) and (2.7).

The fact that the crystal with a smaller number of generators does not generate more points can be proved by a density argument. The volume of the fundamental domain of the diamond crystal can be computed as follows. We use the change of variables (2.14), which we can write as

$$\begin{pmatrix} g^1 \\ g^2 \\ g^3 \end{pmatrix} = \begin{pmatrix} 1 & -1 & 1 \\ 1 & 1 & -1 \\ -1 & 1 & 1 \end{pmatrix} \begin{pmatrix} G^1 \\ G^2 \\ G^3 \end{pmatrix}. \quad (2.15)$$

Thus the fundamental domain for the lattice  $\mathcal{L}(G^1, G^2, G^3)$  has volume  $16 = 64/4$ , since

$$\det \begin{pmatrix} 1 & -1 & 1 \\ 1 & 1 & -1 \\ -1 & 1 & 1 \end{pmatrix} = 4. \quad (2.16)$$

Thus the density of molecules in the crystal generated from (2.11) and (2.10) is again one molecule per eight cubic units. Therefore the two crystals are the same.

This confirms that the fundamental finite graph of the diamond (ice Ic) crystal is as shown in Figure 2.3(b) [12, 13].



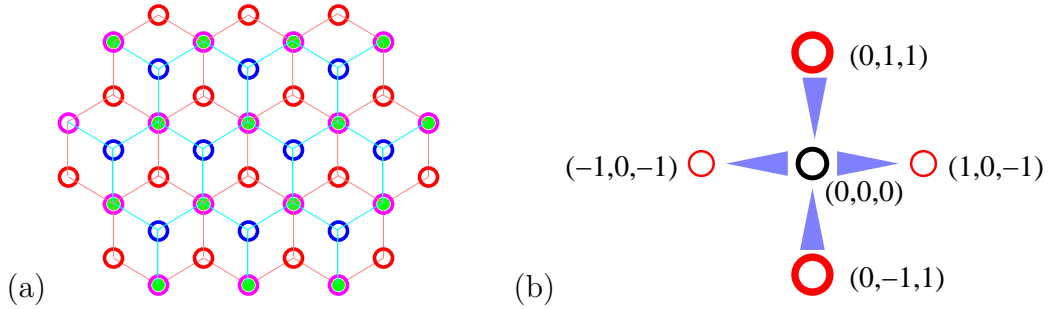


Figure 2.4: The hexagonal view of the ice Ic crystal structure. (a) Overlay of two layers. The bottom blue-green layer is shifted so that only the green waters lie directly below (and are hydrogen bonded to) the magenta waters. The blue waters are not hydrogen bonded to any of the waters in the red-magenta layer shown, but rather are hydrogen bonded to waters in a layer (not shown) below the blue-green layer. (b) The basic tetrahedral unit. The blue triangles indicate hydrogen bonds, and the direction of the triangle indicates the direction in or out of the plane.

## 2.3 Second view of the Ic crystal structure

The ice Ic (diamond) crystal structure is closely related to the Ih structure of ice. It involves the same hexagonal sheets as indicated in Figure 2.1. In this case, there are three such sets of parallel layers, running in transverse directions. So to be precise, we must pick one normal direction for definiteness, which we will call the  $z$  axis. In the case of ice Ih, there is only one normal direction to the parallel sheets determined by the direction of the regular hexagonal holes.

For ice Ic, instead of hydrogen bonding to reflected layers above and below, they are hydrogen bonded to layers above and below that are shifted, as is shown in Figure 2.4(a) for two layers. We imagine that the blue-green layer is below the red-magenta layer. Thus we see the green waters below the magenta waters. The red waters in the red-magenta layer are also hydrogen bonded to blue waters in an unseen blue-green layer above. Thus the two blue-green layers are shifted as well and do not lie on top of each other from this perspective.

There is also another description of the ice Ic (diamond) crystal, involving a smaller set of generators and lattice unit domain. We pick a set of coordinates  $(\hat{x}, \hat{y}, z)$  rotated by 45 degrees in the plane perpendicular to the  $z$ -axis. In these coordinates, the location of the waters  $\mathcal{P}$  in the unit cube that can be used to generate the infinite crystal as in Definition 1.3 are

$$\hat{p}_0 = (0, 0, 0), \quad \hat{p}_1 = (\sqrt{2}, 0, 1), \quad \hat{p}_2 = (\sqrt{2}, \sqrt{2}, 2), \quad \hat{p}_3 = (0, \sqrt{2}, 3). \quad (2.17)$$

The generators of the lattice for the infinite crystal as in Definition 1.3 for the Ic crystal in these coordinates are

$$\hat{g}^1 = (2\sqrt{2}, 0, 0), \quad \hat{g}^2 = (0, 2\sqrt{2}, 0), \quad \hat{g}^3 = (0, 0, 4). \quad (2.18)$$

The relation between the coordinates in Figure 1.1 and the points in (2.18) and (2.17) is given by

$$x = \frac{\hat{x} - \hat{y}}{\sqrt{2}}, \quad y = \frac{\hat{x} + \hat{y}}{\sqrt{2}}. \quad (2.19)$$

Thus the  $(x, y, z)$  coordinates  $q_i$  of  $\hat{p}_i$  compare with the points  $p_i$  of (2.7) as follows:

$$\begin{aligned} q_0 &= (0, 0, 0) = p_0, & q_1 &= (1, 1, 1) = p_1, & q_2 &= (0, 2, 2) = p_3, \\ q_3 &= (-1, 1, 3) = (3, 1, 3) - (4, 0, 0) = p_7 - g^1. \end{aligned} \quad (2.20)$$

Similarly, the  $(x, y, z)$  coordinates  $h^i$  of the lattice vecotrs  $\hat{g}^i$  are

$$h^1 = (2, 2, 0) = \frac{1}{2}(g^1 + g^2), \quad h^2 = (-2, 2, 0) = \frac{1}{2}(-g^1 + g^2), \quad h^3 = g^3. \quad (2.21)$$

Inverting these relations, we find

$$g^1 = h^1 - h^2, \quad g^2 = h^1 + h^2, \quad g^3 = h^3. \quad (2.22)$$

Thus any point of the form in the ice Ic crystal can be written as

$$p_j + \sum_{i=1}^3 m_i g^i = p_j + (m_1 + m_2)h^1 + (m_2 - m_1)h^1 + m_3 h^3. \quad (2.23)$$

To see that this is in the crystal described by (2.17) and (2.18), we have to relate the rest of the  $p_i$ 's to the  $q_i$ 's. Thus we collect all of the relationships here, some of which have previously been derived:

$$\begin{aligned} p_0 &= q_0 \\ p_1 &= q_1 \\ p_2 &= (2, 2, 0) = h^1 = q_0 + h^1 \\ p_3 &= q_2 \\ p_4 &= (2, 0, 2) = q_2 - h^2 \\ p_5 &= (3, 3, 1) = q_1 + h^1 \\ p_6 &= (1, 3, 3) = q_3 + h_1 \\ p_7 &= q_3 + g^1 = q_3 + h^1 - h^2. \end{aligned} \quad (2.24)$$

This proves that

$$\mathcal{V}(p_0, \dots, p_7; g^1, g^2, g^3) \subset \mathcal{V}(q_0, \dots, q_3; h^1, h^2, h^3) = \widehat{\mathcal{V}}(\hat{p}_0, \dots, \hat{p}_3; \hat{g}^1, \hat{g}^2, \hat{g}^3). \quad (2.25)$$

The fact that

$$\mathcal{V}(p_0, \dots, p_7; g^1, g^2, g^3) = \mathcal{V}(q_0, \dots, q_3; h^1, h^2, h^3) = \widehat{\mathcal{V}}(\hat{p}_0, \dots, \hat{p}_3; \hat{g}^1, \hat{g}^2, \hat{g}^3) \quad (2.26)$$

is a simple consequence of a density argument. The former crystal has eight points per cube of size  $4^3 = 64$  units-cubed, whereas the latter has four points per box of volume  $2\sqrt{2} \times 2\sqrt{2} \times 4 = 32$  units-cubed. Thus they both have the same density of one point per eight units-cubed, and hence they must be equal. If some point were in the latter and not in the former, this would happen consistently (periodically) and this would violate the equality of densities.

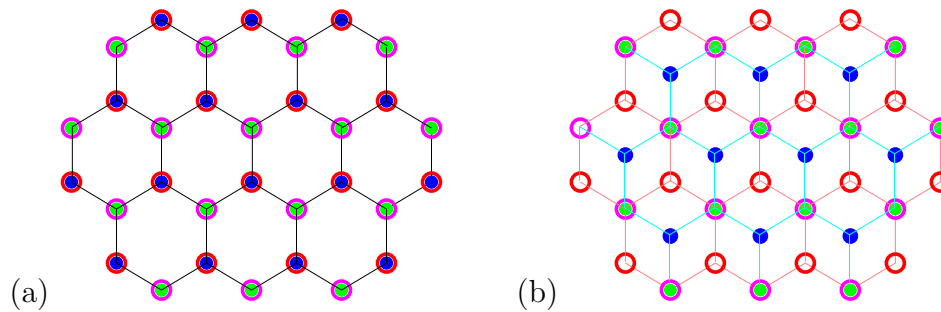


Figure 2.5: Comparison of the hexagonal views of the ice Ih (a) and Ic (b) crystal structures. In both structures, the blue waters are not hydrogen bonded to any of the waters in the red-magenta layer shown, but rather are hydrogen bonded to waters in a layer (not shown) below the blue-green layer. The magenta and green waters are hydrogen bonded.

## 2.4 Alternating Ih/Ic layered structures

The two ice I structures are compared and contrasted in Figure 2.5. Since both the Ih and Ic crystals can be constructed one layer at a time, it is clear that layered structures can be built with arbitrary alternations between Ih and Ic layers. More precisely, when adding an additional layer, a choice can be made to add a reflection (Ih) or shift (Ic) of the previous layer. This construction preserves the exact local tetrahedral structure depicted in Figure 1.1 or Figure 2.4(b).

# Chapter 3

## Ice II structure

The structure of ice II [7] is different from the ice I structures in several ways, but it can also be compared with ice Ih in useful ways. It is useful to think of ice II as being derived from ice Ih in terms of hexagonal columns, each of which is formed of an alternating structure of hexagonal rings as depicted in Figure 3.1. The columns themselves no longer form simple hexagonal attachments, however. Note that the alternating hexagons are not perfectly aligned in ice II, cf. Figure 1 in [2] or Figure 2a in [4].

Thus there are two types of rings: the blue-green rings form hydrogen bonds to the red-magenta rings above and below, much like the connections formed between layers in ice Ih. However, the layers in this case are quite different, as the red-magenta rings do not make hydrogen bonds with the blue-green rings directly above or below them. Instead, the red-magenta rings form hydrogen bonds with neighboring hexagonal columns, as depicted in Figure 3.2.

Unlike ice Ih and Ic, ice II is hydrogen-ordered (or proton-ordered). This means there is exactly one prescribed direction for each of the hydrogen bonds formed at each oxygen center. Thus we can depict the hydrogen bonds via an oriented graph, as indicated in Figure 3.2. Also, the local structure of ice II is significantly altered from the perfect tetrahedral structure of ice Ih and Ic. This is consistent with the fact that water is itself not tetrahedral in structure [3]; it is trigonal, but the flexibility of hydrogen bonds allows the formation of both perfect and approximate tetrahedral structures.

For ice II, the hexagonal columns are somewhat free-standing, connected by hydrogen bonds to other hexagons, but the connections themselves do not form a hexagonal structure as in ice Ih. Each of the hexagonal columns is constructed using alternating layers of hexagons as depicted in Figure 3.1. Thus there are green-blue hexagons and red-magenta hexagons which stack on top of each other. Oscillations in the water heights around the mean are indicated for the blue-green hexagon; the solid line hexagon depicts the mean height. The units used in [7] are based on the unit of repeat in the direction orthogonal to the plane of Figure 3.2, which is the same as the direction parallel to the center of the hexagonal columns in Figure 3.1 (i.e., the horizontal axis); one of these units is approximately 6.25 Å. The length of the hydrogen bonds shown in Figure 3.1 corresponds to about 0.57 units in the direction parallel to the center of the hexagonal columns, whereas the distances between nonbonded oxygens is only 0.43 units. In Figure 3.2, which is a caricature of

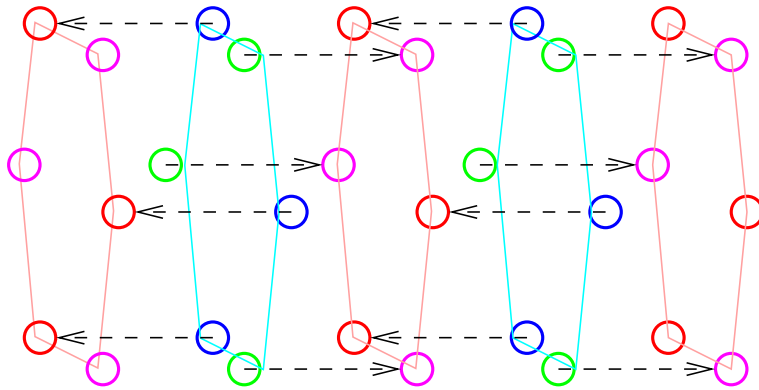


Figure 3.1: The structure of the hexagonal columns in ice II. Side view of hydrogen bond structure between the two types of rings in ice II. Oscillations in the oxygen displacements from the mean are indicated for the blue-green hexagon; the solid line hexagon depicts the mean position along the axis of the hexagonal column.

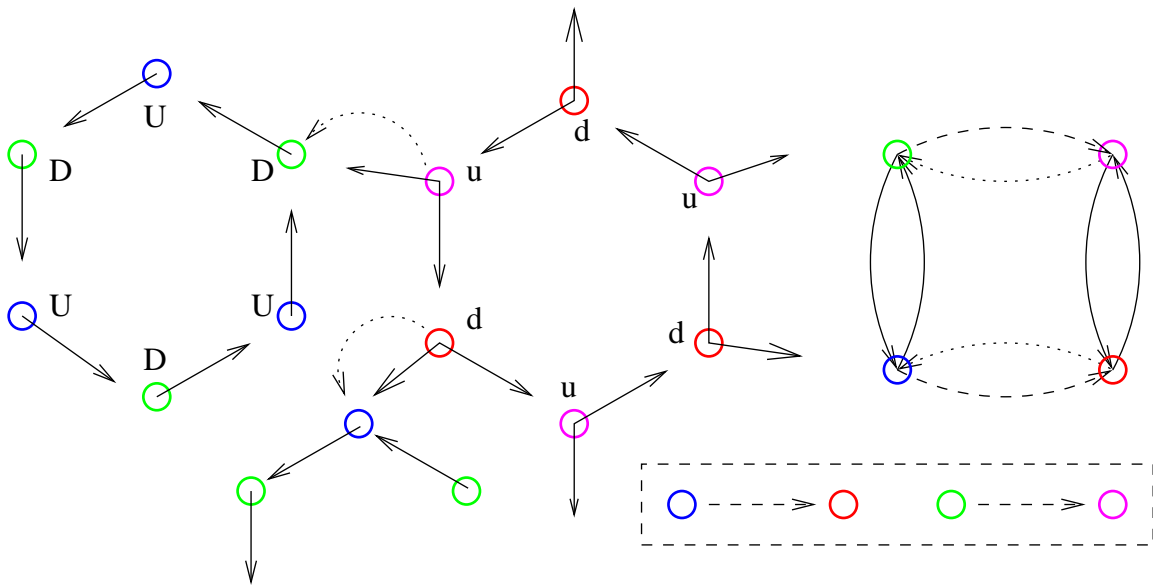


Figure 3.2: Hydrogen bond structure in the two types of rings in ice II. The dashed lines in the dashed box indicate the hydrogen bonds made perpendicular to the plane of the figure, whose directions are indicated by U and D (up and down). The lower case letters ‘u’ and ‘d’ (up and down) indicate the orientation of the hydrogen bond acceptor regions on the oxygens. The dotted lines indicate hydrogen bonds made between two different hexagonal columns. The graph to the right depicts the topology of the hydrogen bond connections [12].

Figure 2 in [7], the top view of each of these hexagons is shown, together with the hydrogen bonds made between two different hexagonal columns, indicated by a dotted line.

The alternating colors mark the alternating directions of the hydrogen bonds (from the oxygen center towards the two hydrogens in each water molecule). In the left hexagon, only one of the hydrogen bonds is seen as the other is (alternately) going out of the page or into the page; the directions for these hydrogen bonds are indicated by capital letters for Up and Down. The pattern of these hydrogen bonds is indicated by the dashed lines in the dashed box: e.g., green waters have hydrogens below the plane of the page making a hydrogen bond with magenta oxygens. The small letters indicating ‘u’ and ‘d’ in the red-magenta hexagons also indicate the directions of the hydrogen bonds, but in this case in reverse. These hydrogen bonds are depicted by arrows that are visible in the plane of the page; the larger arrows indicate ones coming up out of the page, and the smaller arrows indicate ones going down. Thus the letter ‘u’ does not indicate the direction of this hydrogen bond, but rather the direction of the donor pair for the hydrogen bond connecting to it. Thus the magenta water oxygen is the acceptor for the hydrogen bond to the green water above it. Note that the ‘u’ does indicate the position of the acceptor, which is up since the hydrogen bond emanating from the magenta water is down. So the capital letters U and D indicate directions of the hydrogen bond donor pairs, whereas the lower case letters indicate the orientation of the oxygen acceptor region.

The red-magenta hexagons are very nearly planar, but the green-blue hexagons are less so. This allows the out-of-plane hydrogen bonds to be more nearly orthogonal to the plane of Figure 3.2. The units used in [7] are based on the unit of repeat in the direction orthogonal to the plane of Figure 3.2. In these units, the oscillation of the red and magenta oxygen centers is about  $\pm 0.02$  around the mean plane, whereas the green and blue oxygen centers are about  $\pm 0.05$  from the mean plane. The greens and reds are below their means, and the magentas and blues are above their means.

The dotted lines in Figure 3.2 indicate the sideways connections between hexagonal tubes. To clarify the picture, we indicate all the sideways hydrogen bonds emanating from one hexagon on the left in Figure 3.3. To complete the picture, we have indicated all of the acceptors of hydrogen bonds for the green-blue waters. These cannot be easily combined in a planar plot, one key feature of ice II. It is worth noting that Figure 2b in [4] indicates only one direction for the linkages between hexagonal columns, whereas Figure 3.3 shows that they go both up and down (if they did not go both ways, there would be significant compressibility of the ice II hexagonal columns).

In Figure 3.3, we have indicated the mean height of the various hexagons in the units just introduced. We see that there is an oscillation in mean heights of the connected hexagons. The alternation in elevation between hexagonal columns is depicted in Figure 3.4, which shows the elevations of nearby blue-green hexagons. For every hexagon at elevation  $2/3$ , there is one below it at elevation  $-1/3$ . Thus we can view the variation as an oscillation of size  $\pm 1/3$ .

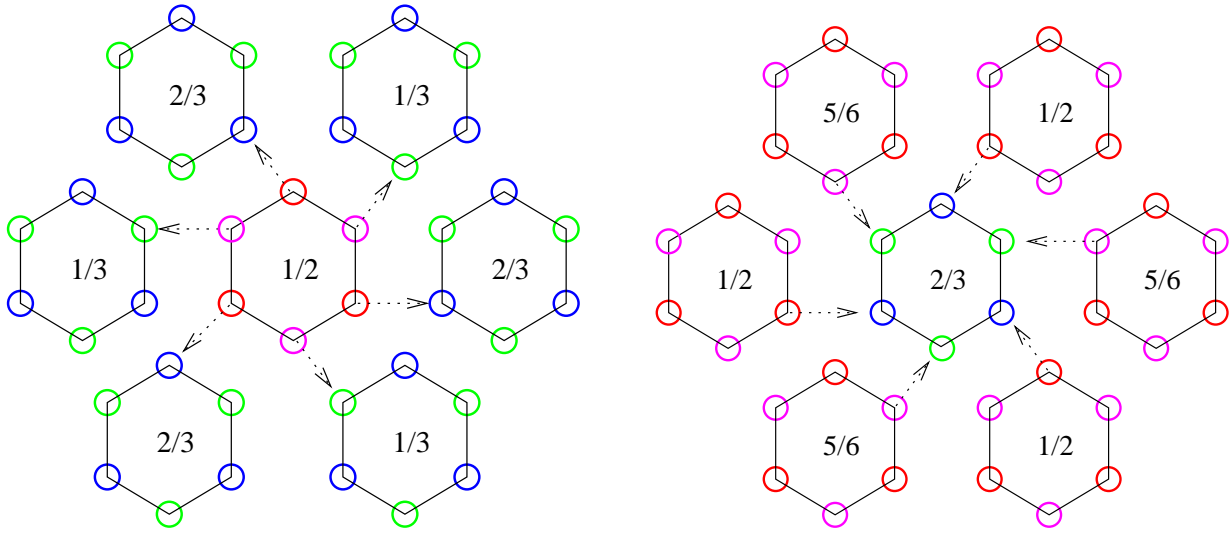


Figure 3.3: Schematic of one class of hydrogen bonds that link different hexagonal columns. The fractions in each hexagon indicate the mean elevation of the hexagon.

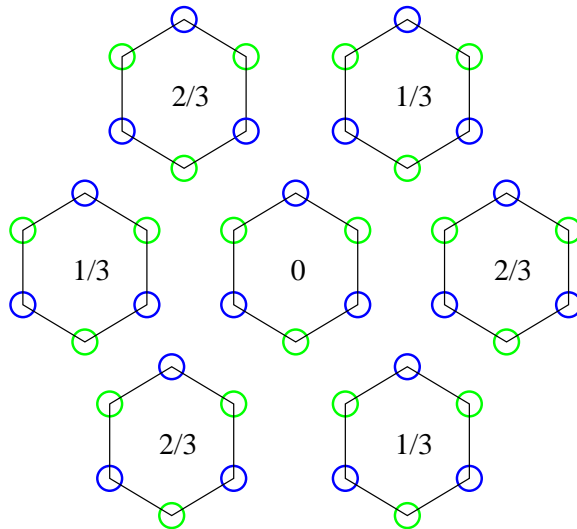


Figure 3.4: Top view of alternating elevations of nearby blue-green hexagons. For every hexagon at elevation  $2/3$ , there is one below it at elevation  $-1/3$ .

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