Chapter 2

Ground state degeneracy of Ising and related models

In this chapter, we will discuss the ground state degeneracy of discrete models. We will start with an exact calculation of the residual entropy of the antiferromagnetic Ising model on the triangular lattice using a pfaffian technique. We will then turn to models where there is no exact result, and we will show that surprisingly accurate estimates can be obtained by an approach invented by Pauling in the context of water ice, with direct consequences for spin ice, the magnetic analog of water ice.

2.1 Ising model on the triangular lattice

Quite amazingly, it is possible to calculate exactly the residual entropy of the Ising antiferromagnet on the triangular lattice. This remarkable result has first been derived by Wannier directly in the Ising language. Here we will take a slightly different path. We will first map the ground state manifold of the Ising model onto dimer coverings of its dual lattice, the honeycomb lattice. Then we will formulate the counting of these dimer coverings in terms of a pfaffian. This formulation is very useful because it allows one to discuss qualitatively the nature of the correlations in the ground state manifold of Ising models very simply in terms of Grassman variables, and also because it leads to deep insight into the properties of quantum dimer models which have been introduced to describe a class of quantum spin liquids.

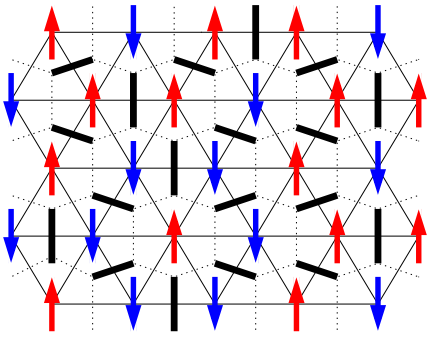

Figure 2.1: Mapping of a ground state of the Ising antiferromagnet onto a dimer covering of the honeycomb lattice.

2.1.1 Mapping onto dimer coverings of the honeycomb lattice

Consider a ground state of the Ising antiferromagnet. In each triangle, there are two bonds with antiparallel spins and minimal energy, and one with parallel spins and maximal energy. This bond is said to be frustrated. If we draw a line across the frustrated bonds joining the centers of the triangles adjacent to this bond, we define a dimer covering of the honeycomb lattice. Since there is only one frustrated bond per triangle, dimers never share a site.

Conversely, given a dimer covering of the honeycomb lattice, one can reconstruct a ground state of the Ising model by choosing the orientation of one spin, and by following the rule that two spins on a bond crossed by a dimer are parallel. Since the first spin can be up or down, one can actually associate two ground states of the Ising model to a dimer covering. They are related by a global reversal of the spins.

2.1.2 Pfaffian technique to count dimers

The number of dimer coverings corresponds to the number of ways of grouping pairs of adjacent (nearest-neighbor) sites. This can be expressed as a sum of permutations between sites with the help on an adjacency matrix:

$$Z = \frac{1}{\left(\frac{N}{2}\right)!2^{N/2}} \sum_p b(p_1,p_2)b(p_3,p_4)\dots b(p_{N-1},p_N) \tag{2.1}$$

where the sum over $P = \{p_1, \ldots, p_N\}$ runs over the permutations of $1, \ldots, N$, and where the adjacency matrix is defined by

$$b(i,j) = \begin{cases} 1 \text{ if } i,j \text{ adjacent} \\ 0 \text{ otherwise.} \end{cases} \tag{2.2}$$

The sum has to be divided by $(N/2)!$ to correct fot multiple couting because of permutations between pairs, and by $2^{N/2}$ to correct for multiple counting because of permutations within pairs.

This sum is not a standard object, but under certain circumstances it can be expressed as the pfaffian of a matrix, which is itself related to its determinant and can thus be evaluated using standard linear algebra techniques.

Definition: If one superimposes two dimer coverings, the result is a *transition graph* that consists of loops containing an even number of sites.

Theorem: Assume that it is possible to attach to each adjacent pair an arrow such that, around each loop that belongs to a possible transition graph between dimer coverings, the number of arrows in each direction is odd. Let us further define the Kasteleyn matrix:

$$a(i,j) = \begin{cases} 1 \text{ if } i,j \text{ ajdacent and } i \to j \\ -1 \text{ if } i,j \text{ ajdacent and } i \leftarrow j \\ 0 \text{ otherwise.} \end{cases} \tag{2.3}$$

Then,

$$Z = \left| \frac{1}{\left(\frac{N}{2}\right)! 2^{N/2}} \sum_p \varepsilon(p) a(p_1, p_2) \ldots a(p_{N-1}, p_N) \right| \tag{2.4}$$

where $\varepsilon(p)$ is the sign of the permutation.

Proof: This will be clearly true is, for all permutations, i.e. for all dimer coverings, the sign of $\varepsilon(p)a(p_1,p_2)\ldots a(p_{N-1},p_N)$ is the same. Now, let us consider two dimer coverings C and C' corresponding to two permutations p and p' and calculate the product $\varepsilon(p)a(p_1,p_2)\cdots \times \varepsilon(p')a(p'_1,p'_2)\ldots$. To go from one to the other, one just has to shift sites around loops of the transition graph. This implies that

$$\varepsilon(p') = \varepsilon(p) \prod_l \varepsilon(l) \Rightarrow \varepsilon(p)\varepsilon(p') = \prod_l \varepsilon(l)$$

where the product over l runs over the loops of the transition graph, and $\varepsilon(l)$ is the signature of the cyclic permutation around the loop. Now, for the sites belonging to a given loop, the product of the matrix elements of

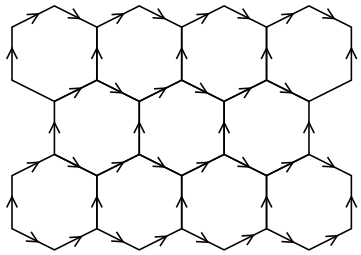

Figure 2.2: Arrow configuration of the Kasteleyn matrix for the honeycomb lattice. With this choice, the number of arrows that go anticlockwise is odd for all loops belonging to a transition graph. These loops are of even length and must encompass an even number of sites.

the matrix a of C and C' will be negative because the number of arrows in each directions is odd, and the sign of the cyclic permutation around this loop is negative because the number of sites is even[1]. So, for each loop, the final sign entering the product is positive, implying that the overall sign of the product is positive, hence that the terms in the sum have the same sign for all configurations.

Now,

$$\text{Pf } a = \frac{1}{\left(\frac{N}{2}\right)!2^{N/2}} \sum_p \varepsilon(p) a(p_1,p_2)\dots a(p_{N-1},p_N) \tag{2.5}$$

is an object known as the *pfaffian* of the skew-symmetric matrix $a(i,j)$, and its square is equal to the determinant of a. So finally,

$$\boxed{Z = \sqrt{\det a}} \tag{2.6}$$

On a periodic lattice, the matrix a can be interpreted as a (non-hermitian) tight-binding problem, and the determinant is the product of the eigenvalues of a, which can readily be calculated using Bloch theorem.

2.1.3 Entropy of dimer coverings on the honeycomb lattice

For the honeycomb lattice, it is indeed possible to find an arrow configuration that satisfies the condition of the lemma. An example can be found in Fig.2.2.

[1] The cyclic permutation of n objects can be decomposed into the product of $n-1$ transpositions, implying that its sign is $(-1)^{n-1}$.

To find the eigenvalues of $a(i,j)$, let us formulate the problem as a tight-binding problem. To each site i we associate a ket $|i\rangle$. The objective is to diagonalize the operator

$$\hat{O} = \sum_{i,j} a(i,j)|i\rangle\langle j|$$

On the honeycomb lattice, there are two sites per unit cell, defining two sublattices A and B. Let's define the Fourier transforms on the two sublattices:

$$|\vec{k}\rangle_A = \frac{1}{\sqrt{N_u}} \sum_{i\in A} e^{i\vec{k}.\vec{R}_i}|i\rangle \Rightarrow |i\rangle = \frac{1}{\sqrt{N_u}} \sum_{\vec{k}} e^{-i\vec{k}.\vec{R}_i}|\vec{k}\rangle_A \text{ for } i \in A$$

and

$$|\vec{k}\rangle_B = \frac{1}{\sqrt{N_u}} \sum_{i\in B} e^{i\vec{k}.\vec{R}_i}|i\rangle \Rightarrow |i\rangle = \frac{1}{\sqrt{N_u}} \sum_{\vec{k}} e^{-i\vec{k}.\vec{R}_i}|\vec{k}\rangle_B \text{ for } i \in B$$

where N_u is the number of unit cells. The operator $\hat{O}$ can be written

$$\begin{aligned}\hat{O} &= \sum_{i\in A}\sum_{\vec{\tau}} (a(i,i+\vec{\tau})|i\rangle\langle i+\vec{\tau}| + a(i+\vec{\tau},i)|i+\vec{\tau}\rangle\langle i|) \\ &= \sum_{i\in A}\sum_{\vec{\tau}} \frac{1}{N_u} \sum_{\vec{k}_1,\vec{k}_2} (e^{-i(\vec{k}_1-\vec{k}_2).\vec{R}_i} e^{i\vec{k}_2.\vec{\tau}} a(i,i+\vec{\tau})|\vec{k}_1\rangle_A\langle\vec{k}_2|_B \\ &\quad + e^{i(\vec{k}_1-\vec{k}_2).\vec{R}_i} e^{-i\vec{k}_2.\vec{\tau}} a(i+\vec{\tau},i)|\vec{k}_2\rangle_B\langle\vec{k}_1|_A)\end{aligned}$$

where $\vec{\tau}$ are the vectors going from one site to its nearest neighbors. Since

$$\frac{1}{N_u} \sum_{i\in A} e^{-i(\vec{k}_1-\vec{k}_2).\vec{R}_i} = \delta_{\vec{k}_1\vec{k}_2}$$

the operator $\hat{O}$ can be rewritten

$$\hat{O} = \sum_{\vec{k}} \hat{O}(\vec{k})$$

with

$$\hat{O}(\vec{k}) = \sum_{\vec{\tau}} e^{i\vec{k}.\vec{\tau}} a(i,i+\vec{\tau})|\vec{k}\rangle_A\langle\vec{k}|_B + \sum_{\vec{\tau}} e^{-i\vec{k}.\vec{\tau}} a(i+\vec{\tau},i)|\vec{k}\rangle_B\langle\vec{k}|_A$$

Since the set of kets $|\vec{k}\rangle_A$ and $|\vec{k}\rangle_B$ form and orthonormal basis of the full Hilbert space, the eigenvalues of the operators $\hat{O}(\vec{k})$ obtained by diagonalizing each of them in the subspace spanned by $|\vec{k}\rangle_A, |\vec{k}\rangle_B$ will be eigenvalues of $\hat{O}$.

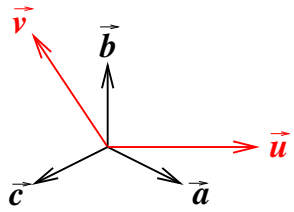

Figure 2.3: Definition of the basis vectors of the honeycomb lattice $\vec{u}$ and $\vec{v}$, and of the vectors $\vec{a}$, $\vec{b}$ and $\vec{c}$ going from one site to its nearest neighbours.

For the honeycomb lattice, there are three vectors $\vec{\tau}$, say $\vec{a}$, $\vec{b}$ and $\vec{c}$. If we choose the basis vectors $\vec{u},\vec{v}$ according to Fig. 2.3, they satisfy $\vec{a}+\vec{b}+\vec{c}=\vec{0}$, $\vec{a}-\vec{c}=\vec{u}$ and $\vec{b}-\vec{a}=\vec{v}$, leading to $\vec{a}=(\vec{u}-\vec{v})/3$, $\vec{b}=(\vec{u}+2\vec{v})/3$, $\vec{c}=(-2\vec{u}-\vec{v})/3$. If we write the vector as $\vec{k}=x\vec{u}^*+y\vec{v}^*$, then, from the definition of the reciprocal lattice, one gets: $\vec{k}.\vec{a}=(2\pi x-2\pi y)/3$, $\vec{k}.\vec{b}=(2\pi x+4\pi y)/3$ and $\vec{k}.\vec{c}=(-4\pi x-2\pi y)/3$. Besides, with the arrow convention of Fig. 2.2, the matrix elements are given by $a(i,i+\vec{a})=+1$, $a(i,i+\vec{b})=+1$ and $a(i,i+\vec{c})=-1$, leading to

$$f(\vec{k})\equiv\sum_{\vec{\tau}}e^{i\vec{k}.\vec{\tau}}a(i,i+\vec{\tau})=e^{i(2\pi x-2\pi y)/3}(1+e^{2\pi iy}-e^{2\pi ix})$$

With this definition, we need to diagonalize the operator

$$\hat{O}(\vec{k})=f(\vec{k})|\vec{k}\rangle_A\langle\vec{k}|_B-f(\vec{k})^*|\vec{k}\rangle_B\langle\vec{k}|_A$$

in the subspace spanned by $|\vec{k}\rangle_A,|\vec{k}\rangle_B$, i.e. we look for α, β and λ such that

$$\hat{O}(\vec{k})(\alpha|\vec{k}\rangle_A+\beta\langle\vec{k}|_B)=\lambda(\alpha|\vec{k}\rangle_A+\beta\langle\vec{k}|_B).$$

This leads to $\lambda\beta=-\alpha f(\vec{k})^*$ and $\lambda\alpha=\beta f(\vec{k})$. We deduce from these equations that the eigenvalues satisfy

$$\lambda^2=-|f(\vec{k})|^2\Rightarrow\lambda_\pm(\vec{k})=\pm i|f(\vec{k})|$$

They are complex conjugate, and their product is given by

$$\lambda_+(\vec{k})\lambda_-(\vec{k})=|f(\vec{k})|^2=3+2\cos(2\pi y)-2\cos(2\pi x)-2\cos(2\pi(x+y)).$$

The determinant of the matrix $a(i,j)$, which is the equal to the product of its eigenvalues, is thus given by

$$\det a=\prod_{\vec{k}}|f(\vec{k})|^2$$

Coming back to the counting of dimers, the number of coverings is given by $Z = \sqrt{\det a}$, and the entropy per site by

$$s = \frac{1}{N} \ln Z = \frac{1}{N} \frac{1}{2} \sum_{\vec{k}} \ln |f(\vec{k})|^2,$$

where N is the number of sites. In the thermodynamic limit, one can replace the sum by an integral, according to

$$\frac{1}{N_u} \sum_{\vec{k}} \to \int d\vec{k}$$

Since there are two sites per unit cell, $N = 2N_u$, and the entropy per site of dimer coverings on the honeycomb lattice is given by

$$\begin{aligned} s_{\rm hc}^{\rm dimer} &= \frac{1}{4} \int_0^1 dx \int_0^1 dy \ln[3 + 2\cos(2\pi y) - 2\cos(2\pi x) 2\cos(2\pi(x+y))] \\ &= 0.161532... \end{aligned}$$

2.1.4 Residual entropy of the Ising antiferromagnet on the triangular lattice

Since each dimer configuration on the honeycomb lattice gives rise to two ground states of the Ising model, the number of ground states of the Ising antiferromagnet on the triangular is given by $\Omega = 2Z$. The residual entropy per site is thus given by

$$s_{\rm tri}^{\rm Ising} = \frac{1}{N_t} \ln Z + \frac{\ln 2}{N_t}$$

In the thermodynamic limit, the second term is negligible, and, since the number of sites of the triangular lattice is half that of its dual honeycomb lattice, the residual entropy is twice that of dimer coverings on the honeycomb lattice:

$$\begin{aligned} s_{\rm tri}^{\rm Ising} &= \frac{1}{4} \int_0^1 dx \int_0^1 dy \ln[3 + 2\cos(2\pi y) - 2\cos(2\pi x) 2\cos(2\pi(x+y))] \\ &= 0.323065... \end{aligned}$$

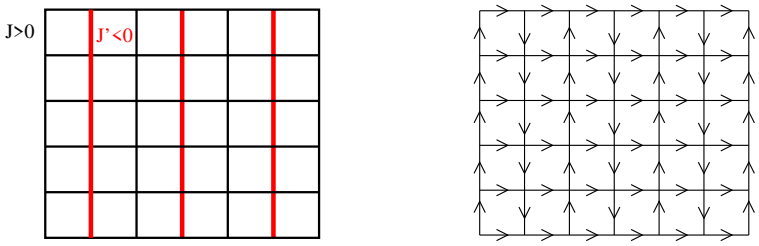

Figure 2.4: Left: Villain fully frustrated model on the square lattice. Right: Arrow configuration of the Kasteleyn matrix on the square lattice.

2.2 Other Ising models

2.2.1 Fully frustrated Ising model on the square lattice

The square lattice is a bipartite lattice, but if the number of antiferromagnetic bonds around each square plaquette is odd, then it is impossible to satisfy all bonds. This can be easily implemented by imposing that the bonds on every other vertical line are ferromagnetic while all other bonds are antiferromagnetic (Villain model). Then on each plaquette one can satisfy at most 3 bonds. This can be achieved in an infinite number of ways. To see this, one can again map the problem onto a dimer covering problem on the dual lattice, which is also a square lattice, by drawing a dimer across the unsatisfied bond of every plaquette.

This dimer covering has again a pfaffian solution. An arrow configuration that fulfills the condition of the theorem is given by horizontal arrows going right on each bond, and vertical arrows alternating between up and down on every other line. This defines a periodic problem with a two-site unit cell. However sites of a given sublattice are not only coupled to sites of the other sublattice, so it is better to write the operator $\hat{O}$ as:

$$\hat{O} = \sum_{i\epsilon A}\sum_{\vec{\tau}} a(i,i+\vec{\tau})|i\rangle\langle i+\vec{\tau}| + \sum_{i\epsilon B}\sum_{\vec{\tau}} a(i,i+\vec{\tau})|i\rangle\langle i+\vec{\tau}|$$

After Fourier transform, $\hat{O} = \sum_{\vec{k}} \hat{O}(\vec{k})$, where $\hat{O}(\vec{k})$ is of the form

$$\hat{O}(\vec{k}) = g_A(\vec{k})|\vec{k}\rangle_A\langle\vec{k}|_A + f(\vec{k})|\vec{k}\rangle_A\langle\vec{k}|_B - f(\vec{k})^*|\vec{k}\rangle_B\langle\vec{k}|_A + g_B(\vec{k})|\vec{k}\rangle_B\langle\vec{k}|_B$$

For the square lattice, $f(\vec{k}) = 2i\sin(\pi x)$, $g_A(\vec{k}) = 2i\sin(2\pi y)$ and $g_B(\vec{k}) = -2i\sin(2\pi y)$. The product of the eigenvalues is the determinant of the ma-

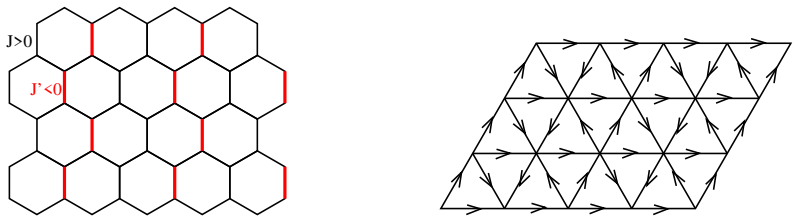

Figure 2.5: Left: Fully frustrated model on the honeycomb lattice. Right: Arrow configuration of the Kasteleyn matrix on the triangular lattice.

trix

$$\begin{pmatrix} g_A(\vec{k}) & f(\vec{k}) \\ -f(\vec{k})^* & g_B(\vec{k}) \end{pmatrix}$$

and is given by $4\sin^2(2\pi y) + 4\sin^2(\pi x)$, leading to a residual entropy per site

$$s_{\rm sq}^{\rm dimer} = s_{\rm FFsq}^{\rm Ising} = \frac{1}{4}\int_0^1 dx \int_0^1 dy \ln[4\sin^2(2\pi y)) + 4\sin^2(\pi x))] = 0.291561...$$

This is both the residual entropy of dimer coverings on the square lattice and of the fully frustrated Ising model on the square since the dual lattice is the same as the original lattice with the same number of sites.

2.2.2 Fully frustrated Ising model on the honeycomb lattice

Similarly, one can define the fully frustrated Ising model on the honeycomb lattice by imposing an odd number of antiferromagnetic bonds around the hexagons. This can be achieved by imposing that half the vertical bonds are ferromagnetic (see Fig). This problem can be mapped onto the problem of dimer coverings on the triangular lattice, the dual lattice of the honeycomb lattice. The arrow configuration that satisfies the condition for the pfaffian calculation again defines a periodic problem with a two site unit cell (see Fig), and the matrix to be diagonalized for each $\vec{k}$ has the same form as for the square lattice with $g_A(\vec{k}) = 2i\sin(2\pi y)$, $g_B(\vec{k}) = -2i\sin(2\pi y)$, and $f(\vec{k}) = 2i\sin(\pi x) - 2\cos(\pi x + 2\pi y)$. Its determinant is given by $4\sin^2(2\pi y) + 4\sin^2(\pi x) + 4\cos^2(\pi x + 2\pi y)$, leading to an entropy per site for the dimer

covering problem

$$s_{\rm tri}^{\rm dimer} = \frac{1}{4}\int_0^1 dx \int_0^1 dy \ln[4\sin^2(2\pi y) + 4\sin^2(\pi x) + 4\cos^2(\pi x + 2\pi y)]$$

$$= 0.428595...$$

Since the number of sites of the honeycomb lattice is twice that of the dual triangular lattice, the residual entropy per site of the fully frustrated Ising model on the honeycomb lattice is given by

$$s_{\rm FFhc}^{\rm Ising} = \frac{1}{8}\int_0^1 dx \int_0^1 dy \ln[4\sin^2(2\pi y) + 4\sin^2(\pi x) + 4\cos^2(\pi x + 2\pi y)]$$

$$= 0.214297...$$

2.2.3 Ising model on kagome lattice

It is not always possible to map the ground state manifold of a frustrated Ising model onto a dimer covering problem that one can solve exactly. Then counting the number of ground states exactly is not possible, and reliable estimates can only be obtained with some kind of numerical approach (e.g. graph expansions, finite-size scaling of exact counting on small clusters, or tensor networks). However, there is a simple approach due to Pauling that often gives excellent results. Let's illustrate it on the Ising kagome antiferromagnet. The kagome lattice can be seen as a lattice of corner-sharing triangles. On each triangle, the energy is minimized by configurations with two spins up and one spin down, or two spins down and one spin up. There are 6 such configurations out of a total of $2^3 = 8$ configurations. Pauling's idea is to use this constraint to reduce the total number of Ising configurations on the kagome lattice. If we denote by N the number of sites, the number of configurations is 2^N. Now, including up and down triangles, the number of triangles is equal to $2N/3$. So Pauling's approach consists in correcting the number of configurations by a factor $(6/8)^{2N/3}$, leading to the following estimates for the number of ground states on N sites:

$$\Omega = 2^N \times \left(\frac{6}{8}\right)^{2N/3},$$

and for the residual entropy

$$s = \frac{1}{N}\ln\Omega = \ln 2 + \frac{2}{3}\ln(3/4) \simeq 0.501359...$$

This should be compared to the numerical estimate $s \simeq 0.5018...$ (Nagle). The agreement is remarkably good.

Note that this entropy is much larger than on the triangular lattice: the number of ground states grows as $\Omega \simeq (1.6517)^N$. As we shall see when discussing correlations, this is reflected into very different behaviours for the two lattices (algebraic correlations for the triangular lattice, exponential correlations for the kagome lattice).

Pauling's approach would be exact on a Bethe lattice, and it works well for the kagome because the triangles are only connected by loops of length 6. For the triangular lattice, which is very different from a Bethe lattice, it leads to the estimate $s = \ln(3/2) = 0.4054...$, significantly larger than the exact result $s = 0.3230...$ derived in the previous section.

2.3 Spin ice

The ground state degeneracy of a classical system has been measured in two pyrochlore compounds that realize what is known as spin ice: $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$. In these compounds, the total momentz $J = L + S$ of Dy and Ho is very large (15/2 and 8, respectively), and they sit at the vertices of a pyrochlore lattice. The crystal field forces each moment to lie along the direction that joins the centers of the two tetrahedra to which it belongs. In addition, the exchange interaction is ferromagnetic, and on each tetrahedon the energy is minimized when two spins point toward the center and two spins away from the center, or 2 spins in and 2 spins out. This problem can be mapped to that of ice water. Indeed, at low temperature water crystallizes into a structure where the oxygen atoms sit on the dual lattice of the pyrochlore lattice (i.e. there is one oxygen at the center of each tetrahedron), and the hydrogen atoms sit on the bonds connecting nearest-neighbor oxygens, but on each tetrahedron two of them are closer to the central oxygen to build a water molecule (spin in), and the two others are further apart from it (spin out), closer to neighboring oxygen atoms.

With 2 in, 2 out, the number of allowed configurations per tetraheron is equal to 6 while the total number of states is equal $2^4 = 16$. This led Pauling (1943) to estimate the number of configurations as

$$\Omega \simeq 2^N \left(\frac{6}{16}\right)^{N_{\rm tetra}} = \left(\frac{3}{2}\right)^{N/2}$$

since the number of tetrahedra $N_{\rm tetra} = 2N/4 = N/2$ is half the number of

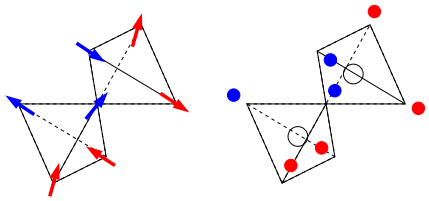

Figure 2.6: 2 spins: one in, one out. → best situation: 2 in, 2 out. Similar to water: 0 at the center of tetrahedra, H make water molecules → 2 in, 2 out.

sites, and the residual entropy per site as

$$s = \frac{1}{2}\ln(3/2) = 0.2027...,$$

very close to the numerical estimate $s \simeq 0.2050....$ This entropy has been measured in water by Giauque (1943), and much more recently in spin ice by Ramirez et al (1999). The measurement is indirect. It relies on measuring the specific heat, and on extracting the entropy from it according to:

$$S(T) - S(T_0) = \int_{T_0}^{T} \frac{C\mathrm{d}T}{T} \tag{2.7}$$

When $T \to +\infty$, the entropy per site must go to $\ln 2$. So if there is a residual entropy per site s at $T = 0$, the difference $[S(T) - S(T_0)]/N$ must tend to $\ln 2 - s$ when $T_0 \to 0+$ and $T \to +\infty$. The residual entropy s appears as a missing entropy as compared to high temperature expectation $\ln 2$. This is quite accurately what has been measured by Ramirez et al in zero field.

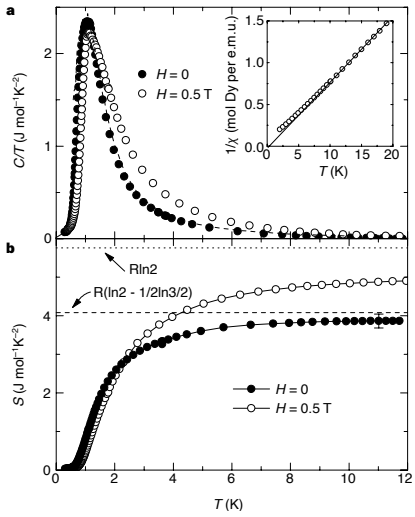

Figure 2.7: a) Specific heat of $Dy_2Ti_2O_7$; b) Entropy obtained by integrating C/T from very low temperature. In zero field, the missing entropy is very close to Pauling's estimate of the residual entropy. (After Ramirez et al, Nature 1999.)