Degeneracy

• Ideally: frustration induces ground state degeneracy, and spins fluctuate amongst those ground states down to low temperature

• e.g. triangular lattice Ising antiferromagnet

Wannier (1950):

\[ \Omega = e^{S/k_B} \quad S \approx 0.34Nk_B \]
Estimate degeneracy?

- Dual representation
- honeycomb lattice
Estimate degeneracy?

- Dual representation
- Focus on the frustrated bonds
Estimate degeneracy?

- Dual representation
  - color “dimers” corresponding to frustrated bonds
  - “hard core” dimer covering
Estimate degeneracy?

- Dual representation
  - A 2:1 mapping from Ising ground states to dimer coverings
Dimer states

- First exercise: can we understand Wannier’s result?
- Count the dimer coverings
Dimer states

- Consider the “Y” dual sites
  - each has 3 configurations
  - this choice fully determines the dimer covering
- But we have to make sure the Y$^{-1}$ sites are singly covered. Make a crude approximation:
  - Prob(dimer) = 1 - Prob(no dimer) = 1/3
  - Prob(good Y$^{-1}$) = 2/3 * 2/3 * 1/3 * 3 = 4/9
- Hence

\[
\Omega \approx 3^N \left( \frac{4}{9} \right)^N = e^{N \ln(4/3)}
\]

\[
S \approx 0.29 \, N \, k_B \quad \text{Wannier} \quad S \approx 0.34 \, N \, k_B
\]
Spin (and water) Ice

- This simple NN AF Ising model is rather idealized
- You may expect that there are always perturbations that split this degeneracy and change the physics
- BUT...turns out that something similar happens in spin ice, which really seems to be an almost ideally simple material - by accident!
Water ice

• Common “hexagonal” ice: tetrahedrally coordinated network of O atoms - a wurtzite lattice

• Must be two protons in each H$_2$O molecule - but they are not ordered
Ice entropy

- Giauque 1930's measured the "entropy deficit" by integrating C/T from low T and comparing to high T spectroscopic measurements

![Calorimeter diagram]

**Fig. 1.**—Calorimeter.

**Fig. 2.**—Heat capacity in calories per degree per mole of ice.

<table>
<thead>
<tr>
<th>Temperature, °K.</th>
<th>Entropy, cal./deg./mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.022</td>
</tr>
<tr>
<td>10-273.10°K., graphical</td>
<td>9.081</td>
</tr>
<tr>
<td>Fusion 1435.7/273.10</td>
<td>5.257</td>
</tr>
<tr>
<td>273.10-298.10°K., graphical</td>
<td>1.580</td>
</tr>
<tr>
<td>Vaporization 10490/298.10</td>
<td>35.220</td>
</tr>
<tr>
<td>Correction for gas imperfection</td>
<td>0.002</td>
</tr>
<tr>
<td>Compression R ln 2.3756/760</td>
<td>-6.886</td>
</tr>
</tbody>
</table>

Cal./deg./mole = 44.28 ± 0.05

The difference between the spectroscopic and calorimetric values is 0.82 cal./deg./mole.
Pauling argument

- Pauling made a simple “mean field” estimate of the entropy due to randomness of the protons, which turns out to be quite accurate

\[ \Omega = e^{S/k_B} = \]

\[ 2^{2N} \times \left( \frac{6}{16} \right)^N = \left( \frac{3}{2} \right)^N \]

each bond \( \bigcirc \) constraints

\[ \binom{4}{2} = 6 \]

allowed configurations each \( \bigcirc \)

\[ S = k_B \ln(3/2) = 0.81 \text{Cal/deg} \cdot \text{mole} \]

c.f. \( S_{\exp} = 0.82 \pm 0.05 \text{Cal/deg} \cdot \text{mole} \]
Classical realization: spin ice

• Rare earth pyrochlores Ho$_2$Ti$_2$O$_7$, Dy$_2$Ti$_2$O$_7$: spins form *Ising doublets*, behaving like classical vectors of fixed length, oriented along *local* easy axes

\[ \vec{S}_i = \hat{e}_i \sigma_i \]