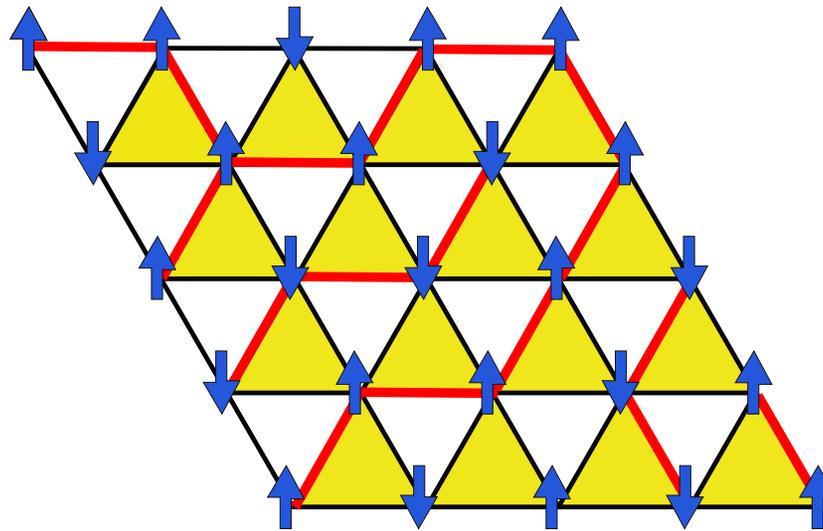


# Degeneracy

- Ideally: frustration induces ground state degeneracy, and spins fluctuate amongst those ground states down to low temperature
- e.g. triangular lattice Ising antiferromagnet



1 frustrated  
bond per  
triangle

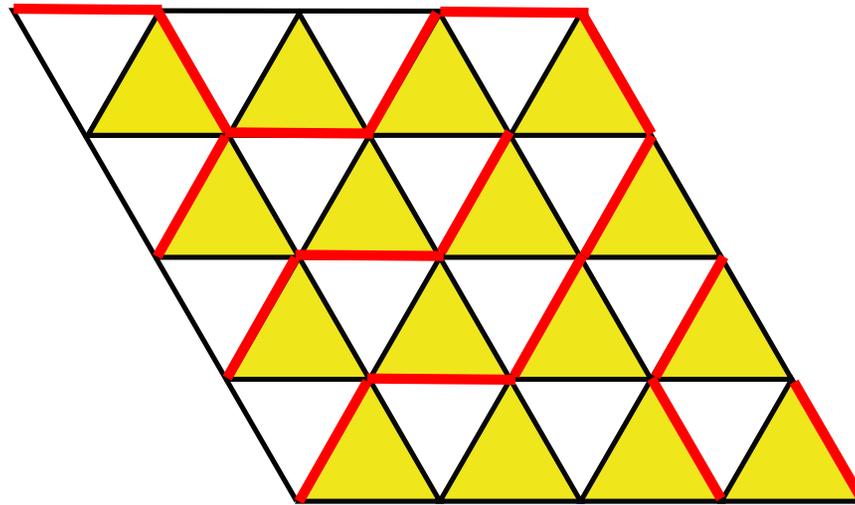
Wannier (1950):

$$\Omega = e^{S/k_B}$$

$$S \approx 0.34Nk_B$$

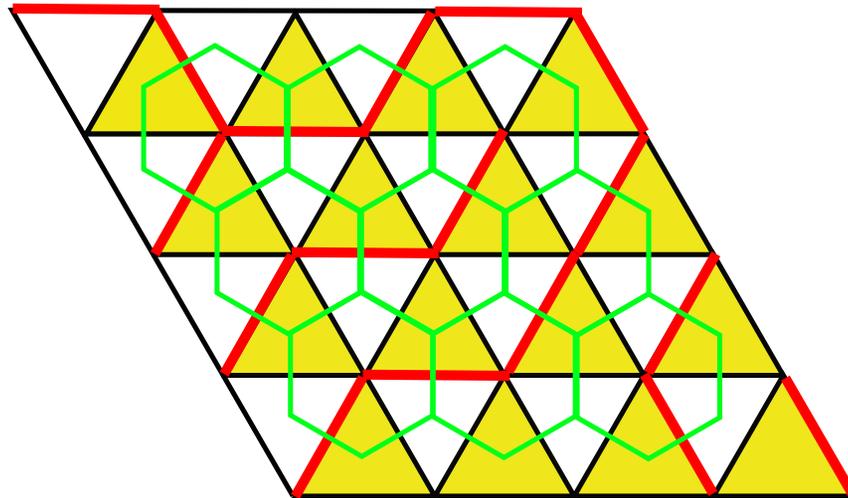
# Estimate degeneracy?

- Dual representation
  - honeycomb lattice



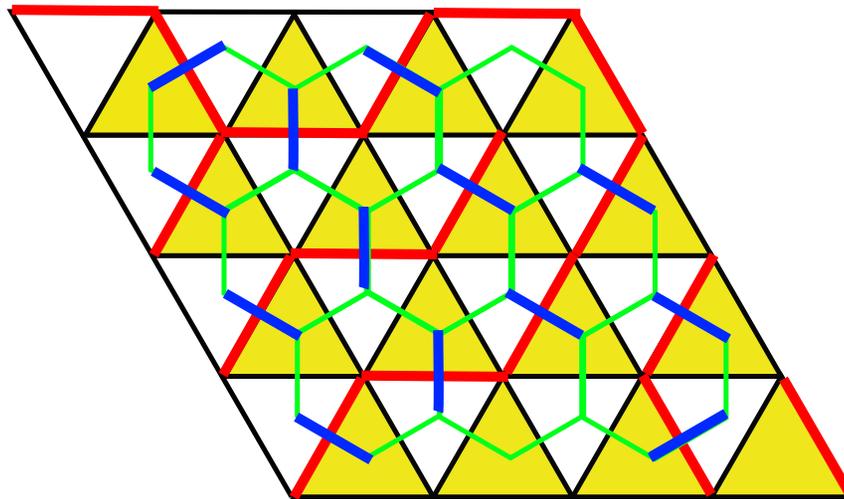
# Estimate degeneracy?

- Dual representation
  - focus on the frustrated bonds



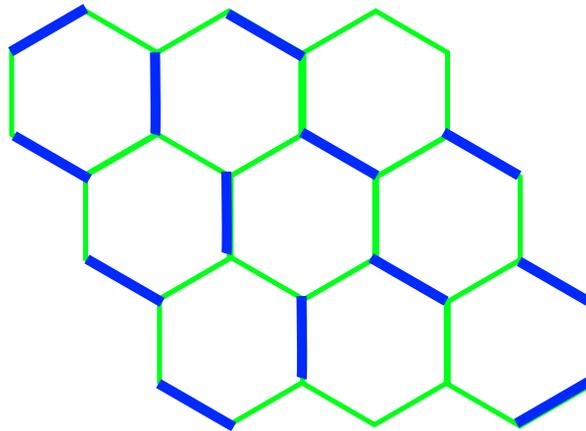
# Estimate degeneracy?

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



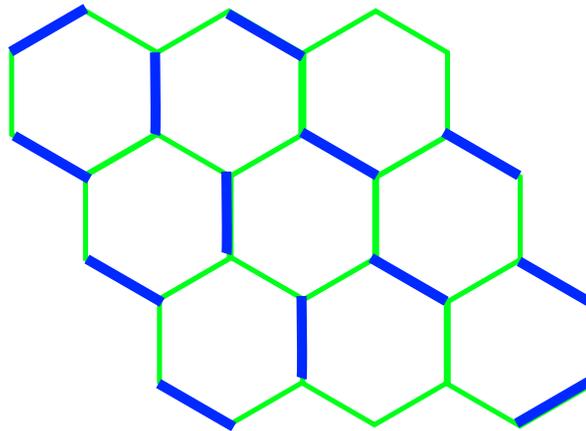
# Estimate degeneracy?

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

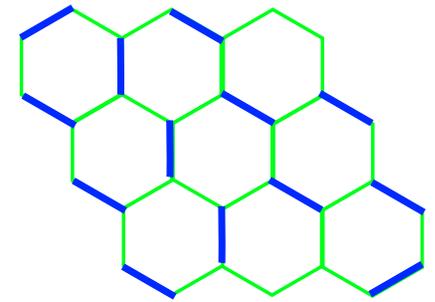


# Dimer states

- 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



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

$$S \approx 0.29 N k_B$$

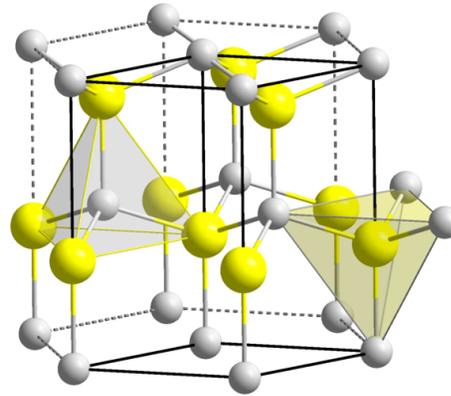
Wannier  $S \approx 0.34 N k_B$

# Spin (and water) Ice

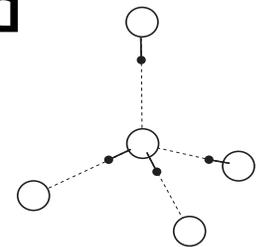
- This simple NN AF Ising model is rather idealized
- You may expect that there are always perturbations that split this degeneracy and change the physics
- BUT...turns out that something similar happens in spin ice, which really seems to be an almost ideally simple material - by accident!

# Water ice

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



- Must be two protons in each H<sub>2</sub>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

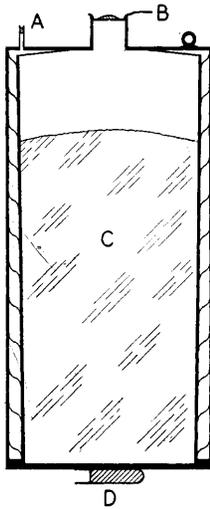


Fig. 1.—Calorimeter.

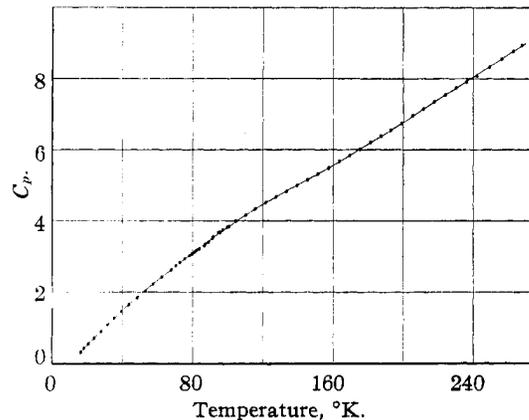


Fig. 2.—Heat capacity in calories per degree per mole of ice.

TABLE III

CALCULATION OF ENTROPY OF WATER

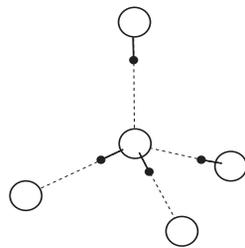
0-10°K., Debye function $h\nu/k = 192$	0.022
10-273.10°K., graphical	9.081
Fusion 1435.7/273.10	5.257
273.10-298.10°K., graphical	1.580
Vaporization 10499/298.10	35.220
Correction for gas imperfection	0.002
Compression $R \ln 2.3756/760$	-6.886

Cal./deg./mole  $44.28 \pm 0.05$

cal./deg./mole. 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



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

allowed configurations each O

$$\Omega = e^{S/k_B} =$$

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

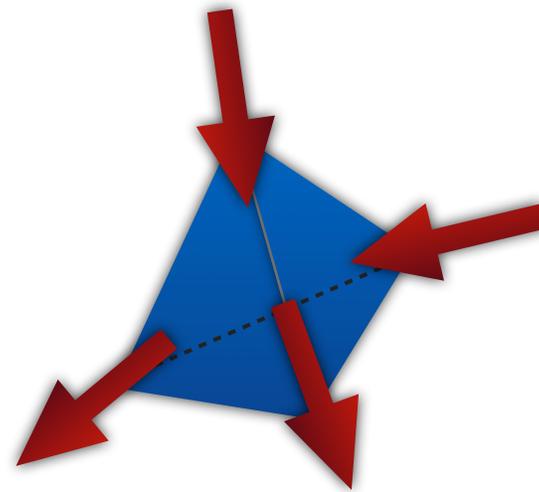
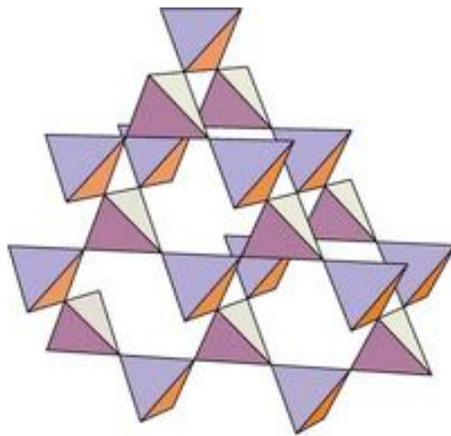
each bond O constraints

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

$$\text{c.f. } S_{\text{exp}} = 0.82 \pm 0.05 \text{ Cal/deg} \cdot \text{mole}$$

# Classical realization: spin ice

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



$$\vec{S}_i = \hat{e}_i \sigma_i$$