The Structure and Entropy of Ice and of Other Crystals with Some Randomness of Atomic Arrangement

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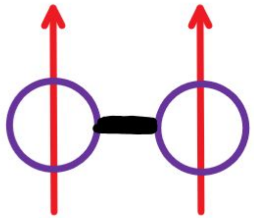
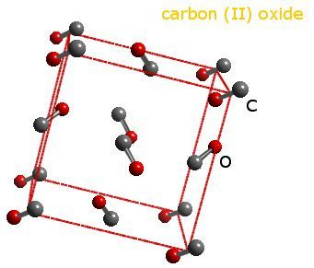
Pauling, L. (1935). The structure and entropy of ice and of other crystals with some randomness of atomic arrangement. Journal of the American Chemical Society, 57(12), 2680-2684. doi:10.1021/ja01315a102

Prior Work on Entropy and Crystal Structures

- At low T, orthohydrogen molecules rotate as freely as in the gas [1-2].
- Molecules in crystal structures of carbon monoxide and nitrous oxide must choose between two specific orientations [3-5].



Orthohydrogen



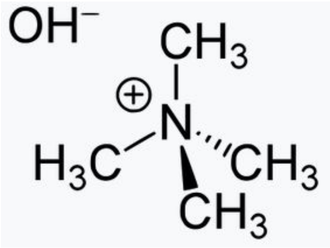
Structure of CO (WebElements)

- Each oxygen atom in ice is tetrahedrally surrounded by four other oxygen atoms and bonded to these atoms by hydrogen bonds [6-8].

A Short History of the Hydrogen Bond

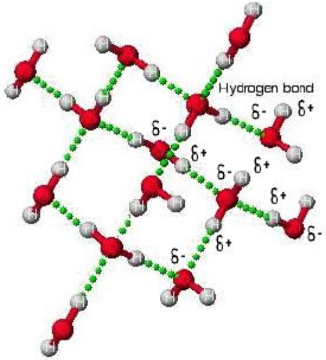
1912

Hydrogen bonds account for some bases being weaker than others



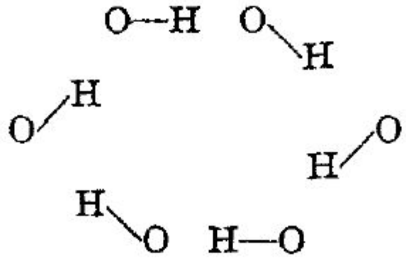
1920

Hydrogen bonding within water is described



1935

Linus Pauling questions the precise positioning of hydrogen atoms within ice crystals

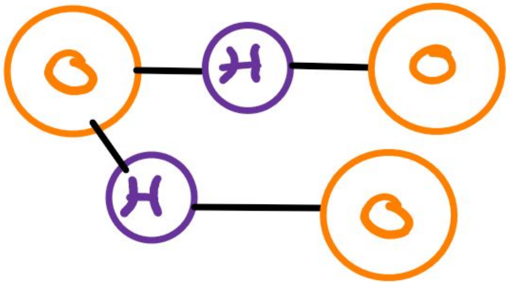


With several years of research in crystal structures, Pauling gets to work on theorizing the structure of ice!

The Questions at Hand

1. How far apart are oxygen and hydrogen atoms within ice?

2. Does each hydrogen atom lean closer to one oxygen than the other? Or, are they always halfway between?



3. Is the hydrogen atom free to choose where it lies between two O atoms regardless of other H atoms?

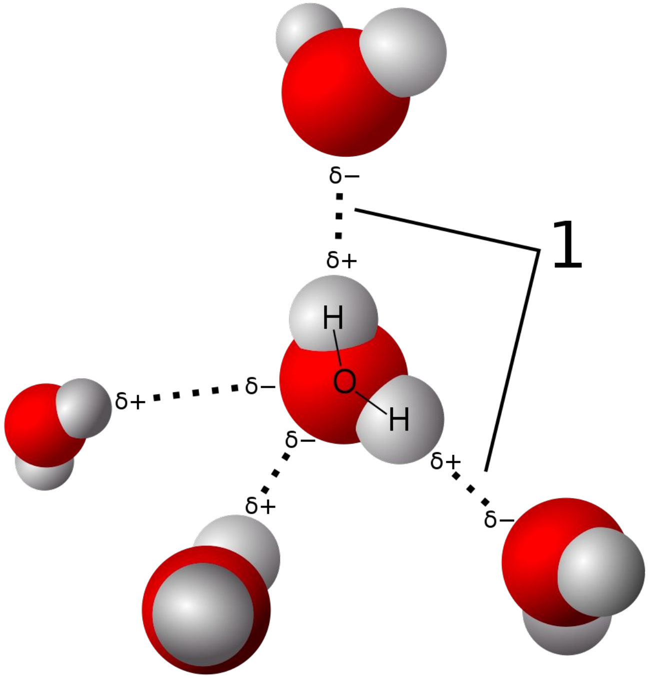
4. What does this tell us about the residual entropy of molecules in ice, and does it agree with previous experiments?

$$S = k\ln(W)$$

Pauling's Four Postulates

- O-H distance and H-O-H angle
- Orientation of each water molecule
- Orientation of the four adjacent molecules
- Ignore non-adjacent molecules

A large number of possible configurations in an ice crystal!



Hydrogen bonds between water molecules

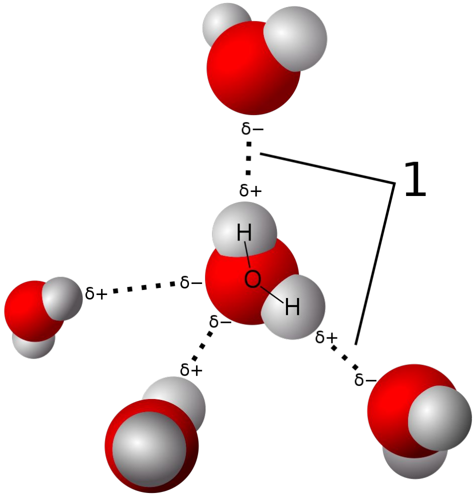
Pauling's calculation of the entropy of ice

For *N* water molecules, the number of possible configurations is

$$W = ({}^6/_4)^N = ({}^3/_2)^N$$

Another argument:

$$W = 2^{2N}({}^3/_8)^N = ({}^3/_2)^N$$



The entropy of an ice crystal with *N* moles of water is thus

$$R \ln {}^3/_2 = 0.805 \text{ E. U.}$$

How does this calculation hold up?

Residual entropy obtained from data:

- Heat capacity of ice:
  - 44.23 E.U. (Giauque & Ashley 1933)
  - **44.28 E.U.** (Giauque & Stout 1936)
- Spectroscopy of water vapor:
  - **45.101 E.U.** (Gordon 1934)

Difference = 0.82 E.U.

Ortho-para explanation: $^{3}/_{4} R \ln 2 = 1.03$

Pauling's theory: $R \ln {}^{3}/_{2} = 0.805$ E. U.

A sort of meta-analysis

This paper does an extraordinary job at

- Setting up the problem
  - The very first thing Pauling writes is of exposition of previous works

> Investigations of the entropy of substances at low temperatures have produced very important information regarding the structure of crystals, the work of Giauque and his collaborators being particularly noteworthy. For example, the observed entropy of crystalline hydrogen shows that even at very low temperatures the molecules of orthohydrogen in the crystal are rotating about as freely as in the gas;[1] subsequent to this dis-

- Making explicit all assumptions used throughout the entire paper

(about as explicit as one can be)

> (1) In ice each oxygen atom has two hydrogen atoms attached to it at distances of about 0.95 Å., forming a water molecule, the HOH angle being about 105° as in the gas molecule.
>
> (2) Each water molecule is oriented so that its two hydrogen atoms are directed approximately toward two of the four oxygen atoms which surround it tetrahedrally, forming hydrogen bonds.
>
> (3) The orientations of adjacent water molecules are such that only one hydrogen atom lies approximately along each oxygen–oxygen axis.
>
> (4) Under ordinary conditions the interaction of non-adjacent molecules is not such as to appreciably stabilize any one of the many configurations satisfying the preceding conditions with reference to the others.

- Being clear and explicit when certain assumptions are being used
  - Refers to them as condition/assumption 1-4

Further Observations

The cogs of the research enterprise are in full force here:

- Pauling is able to create such an influential work while staying completely on the theory side

- Pauling can be incredibly terse at times, but that is to (somewhat) be expected

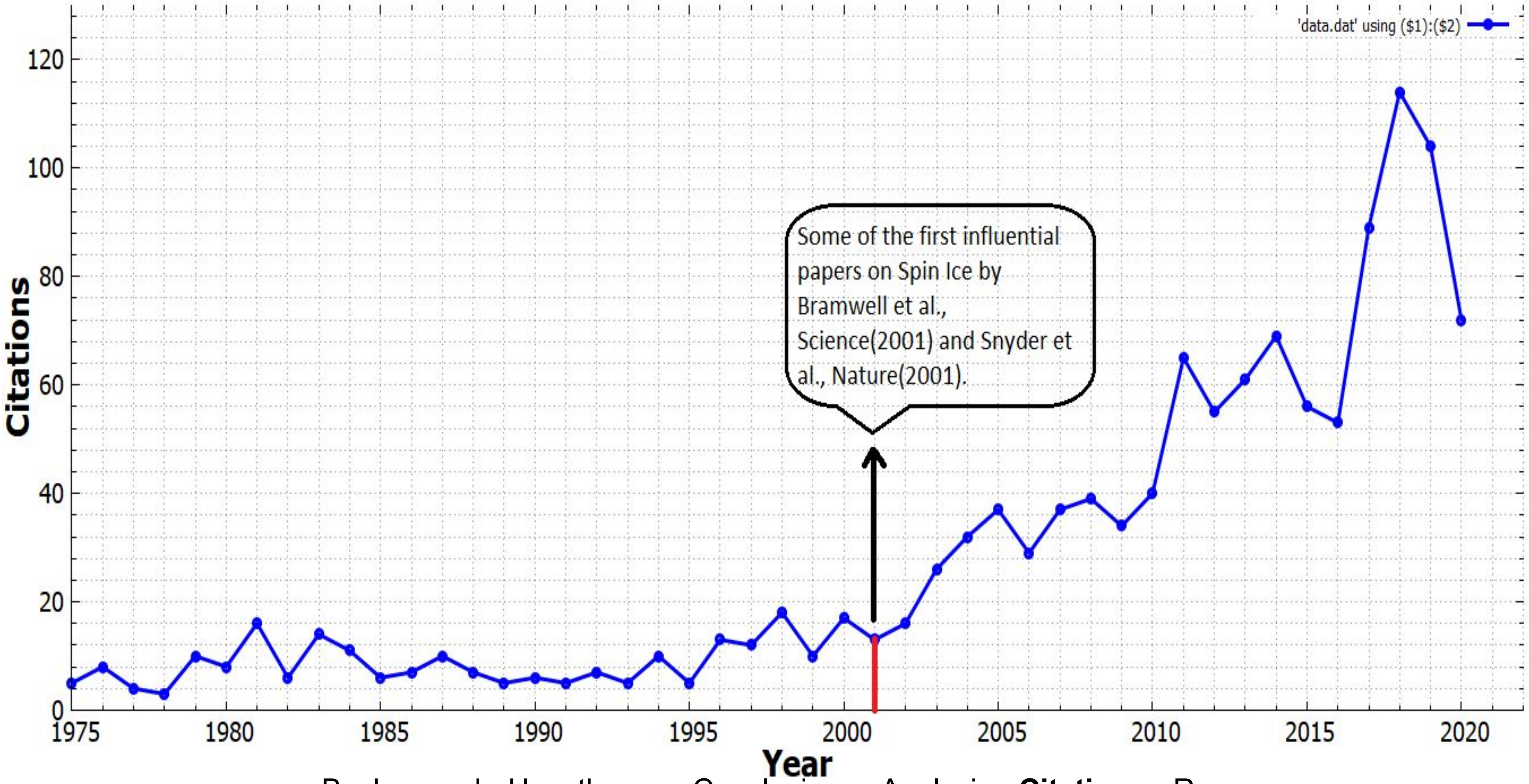
Proposition 1. This is a proposition.

Proof. The proof is left as an exercise for the reader.

Proposition 2. This is another proposition.

Proof. The proof is left as an exercise for the reader and it's closer to the relevant proposition.

Citation data



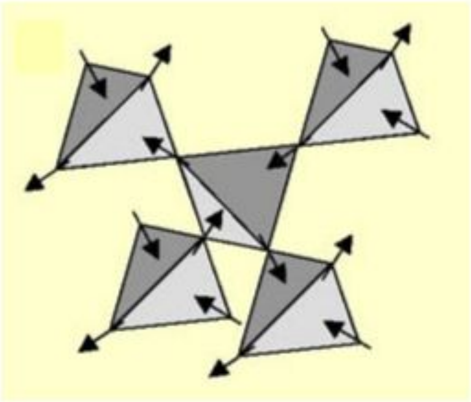
Citation evaluation

- Total number of citations: 1185
- What are the general trends in the citation data? Does the work have any significance in modern day physics?
- Is the model proposed generalizable to study problems in other areas of condensed matter physics? Spin Ice, Vertex models.

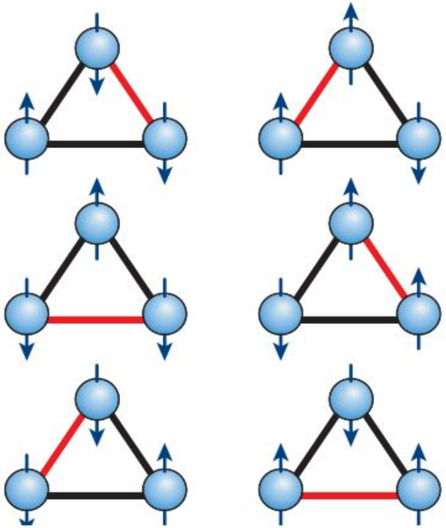
Spin Ice

- Replace binary configuration of each Hydrogen atom by a spin. Similar to the water Ice, this has a extensive ground state entropy due to the multiple spin configuration satisfying the Ice rules. Eg. $Di_2Ti_2O_7$, $Ho_2Ti_2O_7$.

- Such extensive ground state entropy is more generally achieved using frustrated systems, like for example Mott insulators interacting through competing interactions(mostly achieved through some triangular geometry). Ex. Antiferromagnetic triangular lattice(S_o=0.323kBN[Wannier, 1950])

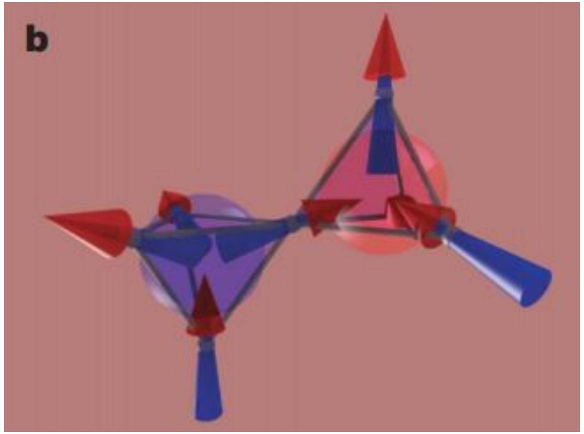


Snyder et al., Nature (2001)

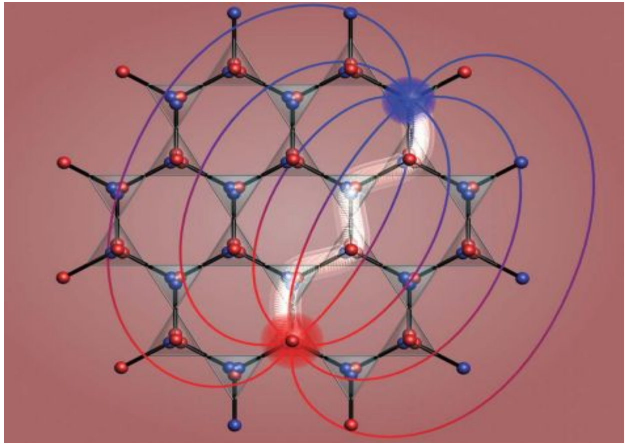


Balents, Nature(2010)

Spin Ice cont.



C. Castelnovo et al., Nature(2006)



C. Castelnovo et al., Nature(2006)

- Ideas which further enhance the potential of the model, hinting towards exciting physics: fractionalized excitations, possibilities of realizing phases of matter which go beyond the Landau-Ginzburg paradigm.

Quantum spin liquids

Instead of the classical spin ice, which can be viewed as a finite temperature thermal phase, described by statistical mechanics, we now consider QSLs which are zero-temperature quantum many-body ground states described using coherent states (superposition of all configurations in the low energy sector).

Properties:

- Extensive ground state entropy.
- No ‘ordered’ state even at T=0K. Ground state manifolds; fluctuation induced order. Explaining QSL GSs, RVB theory and high-Tc SC.
- Phase transitions cannot be described using an order parameter.
- Give rise to fractionalized excitations coupled to emergent gauge fields. Emergence more fundamental than reductionism?(Xiao-Gang Wen in Quantum Field Theory of Many-Body Systems(2007))

What You Should Know

- Pauling established a formula to calculate residual entropy (RE) at very low temperatures
    - Proven through establishment of assumptions and checked via calculation
- Using this, we learn that the calculated RE from experiments reveals the structure of the ice crystal
- Leading the way for spin ice and QSLs ---->
    - See further readings

References and Reading Suggestions

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