

Why are snowflakes hexagonal?

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Overview

- 1 Ice Ih and Ic and proton disorder.
 - Introduction.
- 2 Results.
 - Results for protonated ice.
- 3 Sanity checks.
 - Vibrational pressure.
 - Beyond principal axes approximation effects.
- 4 Origin of differences in anharmonicity.
 - Dominant contributions to anharmonicity.
- 5 Conclusions and next steps.

Differences in stacking of hexagonal layers.

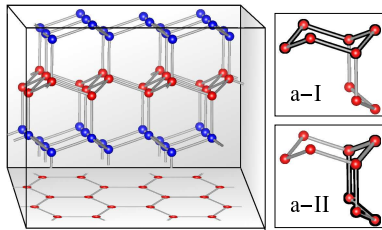


Figure : Hexagonal ice, Ih (blue).
 ABAB stacking of bilayers.
 a-I and a-II show chair and boat
 form hexamers, respectively, the two
 basic building blocks of Ih.

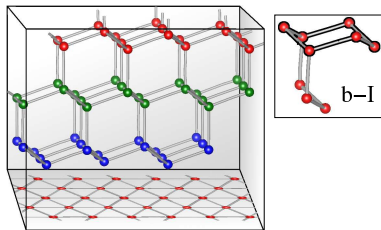


Figure : Cubic ice, Ic (red).
 ABC stacking of bilayers.
 b-I shows a chair form hexamer.
 Cubic ice does not contain boat
 form hexamers.

Proton disorder in a nutshell.

- Bernal-Fowler ice rules.
 - 1 Each oxygen is covalently bonded to two hydrogen atoms.
 - 2 Each oxygen accepts and donates two hydrogen bonds from/two other oxygens.

Defect-free ice consists of tetrahedrally coordinated water molecules bound in a hydrogen bond network.

Proton disorder in a nutshell.

- Bernal-Fowler ice rules.
- Pauling's residual configurational entropy.
Pauling's residual configurational entropy [1] has been confirmed experimentally by measuring the entropy differences between pure and KOH-doped ice [2, 3]. The configurational free energies of bulk Ih and Ic are almost identical, since they are effectively determined by the tetrahedral coordination of the molecules [4].

Proton disorder in a nutshell.

- Bernal-Fowler ice rules.
- Pauling's residual configurational entropy.
- Choice of polytypes for this study.
 - 16 symmetry-unique eight-molecule Ih configurations [5] and
 - 11 symmetry-unique proton-ordered Ic configurations [6].

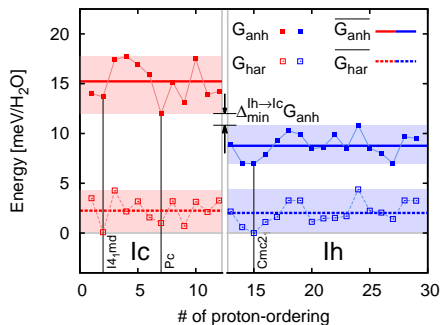


Figure : Harmonic free energies, G_{har} , (empty squares) and total free energies, G_{anh} , (filled squares), measured with respect to $G_{\text{har}}^{\text{XIh}}(\text{Cmc}2_1)$.

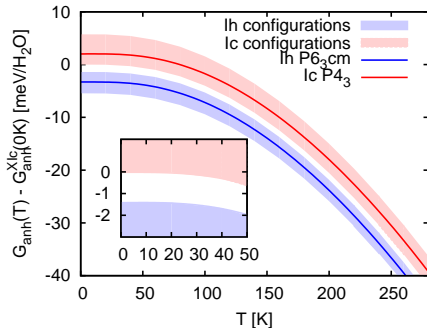


Figure : Anharmonic vibrations stabilise Ih with respect to Ic across a wide temperature range.

Vibrational pressure - Results.

- Vibrational pressure of $\sim 0.45 \pm 0.05$ GPa.
- Zero temperature expansion of $\sim 4\%$ which agrees well with other *ab initio* DFT and path-integral MD studies [7].
- Expanded volumes including vibrations agree with experiment to within $\sim 1\%$.
- Vibrational frequencies and anharmonicity do not change significantly upon evaluation at the expanded volume.

Coupling of vibrational modes.

- Next level of approximation: coupling of vibrational modes.
- Pairwise coupling of vibrational modes already requires mapping of 2D Born-Oppenheimer surfaces and scales as N^5 .
- Calculations for the primitive unit cells of ice Ih and Ic indicate that including pairwise coupling of vibrational modes leads to a small increase in the differences in anharmonicity between ice Ih and Ic.

Origin of differences in anharmonicity - I.

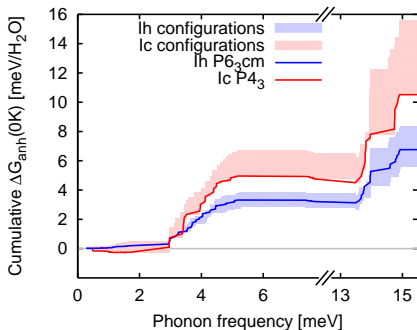


Figure : Cumulative anharmonic energies as a function of frequency.

Results averaged over proton-orderings.

Phase	u_{anh} [Å]	u_{har} [Å]	Δu [Å]
Ih	0.225	0.227	-0.002
Ic	0.220	0.225	-0.005

Table : RMS displacements of the protons at the harmonic, u_{har} , and anharmonic level, u_{anh} , and the difference due to anharmonicity, Δu .

Origin of differences in anharmonicity - II.

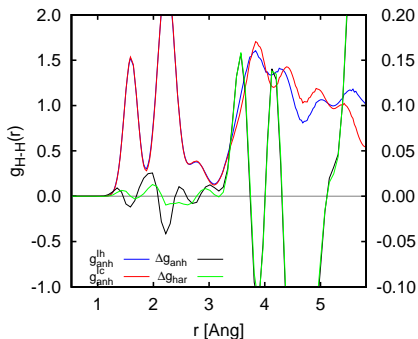


Figure : H-H RDFs for Ih (blue) and Ic (red).

For $r < 3 \text{ \AA}$

At the harmonic level (green), the difference between Ih and Ic, $\Delta g_{har} \equiv g_{har}^{Ih} - g_{har}^{Ic}$, is minimal. At the anharmonic level (black), the difference between Ih and Ic, $\Delta g_{anh} \equiv g_{anh}^{Ih} - g_{anh}^{Ic}$, is non-negligible.

For $r > 3 \text{ \AA}$:

The differences in the static structures of Ih and Ic become dominant.

Structural origin of differences in anharmonicity.

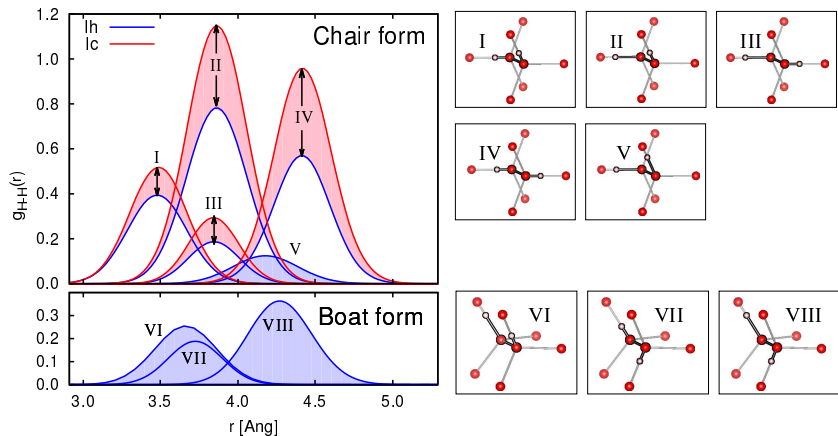


Figure : Anharmonic H-H RDF decomposed into contributions from different bonding configurations of fourth-nearest neighbour pairs of protons.

Conclusions and next steps.

Relevance of Ih and Ic:

- climate modelling and the simulation of ice nucleation and formation.
- potential relevance in biological sciences in the context of cryopreservation.

Importance of anharmonic vibrations:

- in hydrogen bonded molecular crystals: likely to be crucial in correctly describing the energy differences between very similar such polymorphs, e.g., in pharmaceutical science.
- in various other examples as in B. Monserrat's talk.
- at ice surfaces (basal and prism surfaces in Ih and basal in Ic).
- around impurities or other defects.

Ice Ih and Ic and proton disorder.
Results.
Sanity checks.
Origin of differences in anharmonicity.
Conclusions and next steps.

Acknowledgements.

The logo for EPSRC (Engineering and Physical Sciences Research Council) features the letters 'EPSRC' in a bold, maroon serif font. The text is centered between two horizontal teal lines.

HECToR



Bibliography I

- [1] L. Pauling.
The structure and entropy of ice and of other crystals with some randomness of atomic arrangement.
Journal of the American Chemical Society, 57:2680–2684, 1935.
- [2] Y. Tajima, T. Matsuo, and H. Suga.
Phase transition in KOH-doped hexagonal ice.
Nature, 299:810–812, 1982.
- [3] S. M. Jackson and R. W. Whitworth.
Thermally-stimulated depolarization studies of the Ice XI-Ice Ih phase transition.
Journal of Physical Chemistry B, 101:6177–6179, 1997.
- [4] J. F. Nagle.
Lattice Statistics of Hydrogen Bonded Crystals. The Residual Entropy of Ice.
Journal of Mathematical Physics, 7:1484–1491, 1966.

Bibliography II

- [5] K. Hirsch and L. Ojamäe.
Quantum-chemical and force-field investigations of ice Ih: computation of proton-ordered structures and prediction of their lattice energies.
Journal of Physical Chemistry B, 108:15856–15864, 2004.
- [6] Z. Raza, D. Alfè, C. G. Salzmann, J. Klimeš, A. Michaelides, and B. Slater.
Proton ordering in cubic ice and hexagonal ice; a potential new ice phase – XIc.
Physical Chemistry Chemical Physics, 13:19788–19795, 2011.
- [7] R. Ramírez, N. Neuerburg, M.-V. Fernández-Serra, and C. P. Herrero.
Quasi-harmonic approximation of thermodynamic properties of ice Ih, II, and III.
Journal of Chemical Physics, 137:044502, 2012.

Convergence behaviour.

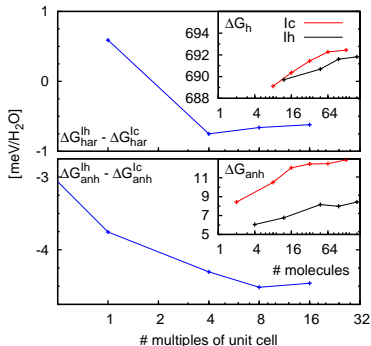


Figure : Convergence of the harmonic (top) and anharmonic contributions (bottom) to the vibrational energy with supercell size.

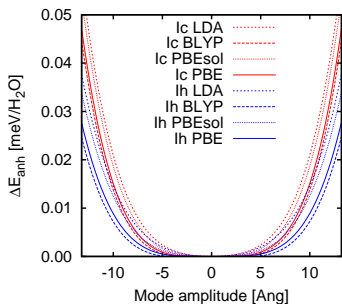


Figure : Anharmonic components of the BO energies,
 $\Delta E_{\text{anh}} \equiv E_{\text{anh}} - E_{\text{har}}$, for the

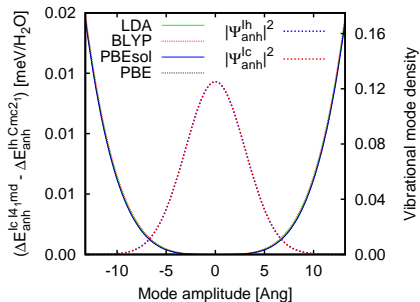


Figure : The differences in ΔE_{anh} between the highest energy vibrational modes in Ih and Ic for different density functionals are

Energetics.

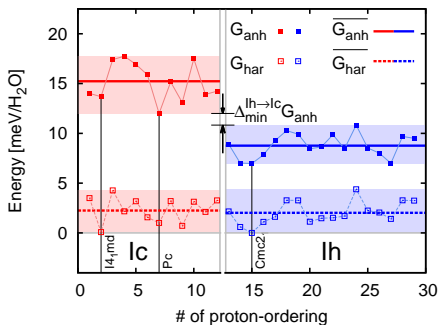


Figure : Protonated ice.

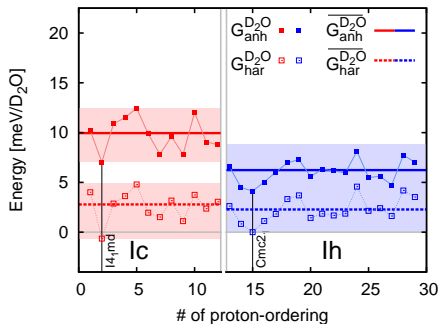


Figure : Deuterated/heavy ice.

G_{har} (empty squares) and G_{anh} (filled squares) measured with

Vibrational pressure - Self-consistency problem.

Initial static equilibrium structure.

Structure relaxed at ambient pressure.

Harmonic approximation to the BO surface.

Evaluate phonon modes and frequencies.

Anharmonic calculation.

Evaluate anharmonicity and resultant phonon pressure.

Equilibrium structure at expanded volume due to lattice vibrations.

Rerelax equilibrium structure taking into account phonon pressure.

Check for self-consistency.

If phonon pressure matches ambient pressure, then exit self-consistency loop.

Final structure at expanded volume due to lattice vibrations.

The phonon pressure matches the external ambient pressure.