Application of CP2K to ice problems
Ice phase diagram

15 known crystalline ice phases

Several amorphous forms (e.g. see Martonak et al. JCP 2005)

Many phases are order/disorder pairs e.g. Ih/XI, V/XIII, VII/VIII

XII found in 1998, 3 further phases reported 2006-2009
Why ice is like an old mattress

Vacancies in ice

Bulk vacancy energy constant $0.74\text{eV} \pm 0.025\text{eV}$

Surface vacancy energy varies by $\sim 0.8\text{eV}$ and $\sim 0.5\text{eV}$ in outermost layer
Dipoles in perfect ice

Dipole variance is an intrinsic property of crystalline ice proton disordered phases
Dipole moment correlated with vacancy energy
Why does this variance arise?

- Each molecular dipole sits in a frustrated lattice exhibiting orientational disorder.
- In the bulk, due to proton disorder and the symmetry of oxygen network, the molecule feels an average field.
- At the surface, the symmetry is lowered and local environment has a strong influence on the local ESP.
- Generic property - e.g. spin ice, hydrates.

As part of this study, ADMM was used to compute PBE0 dipole moments on 288 molecule cells with an overhead 100% w.r.t PBE.
Consequences

- Around 10% of surface sites are comparatively very weakly bound
- At low temperature admolecules formed (proto-QLL)
- All vacancy energies lowered upon vacancy-admolecule formation
- Influence on pre-melting and reaction chemistry
The ice XV problem

see The polymorphism of ice: five unresolved questions, Salzmann et al., PCCP, 2011

What Governs the Proton Ordering in Ice XV?
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ABSTRACT: Powder neutron diffraction and Raman spectroscopy experiments for ice XV, the recently discovered proton-ordered polymorph of ice VI, suggest that the protons arrange in an antiferroelectric structure with $P\overline{1}$ symmetry, contrary to several density functional theory predictions of a ferroelectric $Cc$ structure. Here, we find that higher-level fragment-based second-order perturbation theory (MP2) and coupled cluster theory (CCSD(T)) electronic structure calculations predict that the experimentally proposed proton ordering is indeed slightly more stable than the other possible structures. These calculations reveal a close competition between the structure with the strongest local hydrogen bonding ($Cc$) and the one with the most favorable “delocalized” hydrogen bond cooperativity effects ($P\overline{1}$), with the latter being preferred by $\sim$0.4 kJ/mol per molecule. The results reiterate the importance of viewing ice networks as a whole instead of focusing on pairwise hydrogen-bonding interactions.

SECTION: Molecular Structure, Quantum Chemistry, and General Theory

Ice XV/VI have the largest variation in hydrogen bond angle of any phase.

Problem solved?
Key ice XV structures

2Cl

9A2
Accuracy of CP2K

Largest discrepancy 0.06 kJ/mol

GPW approach very comparable with full PW
Varying HF and vdW does not change the order of stability.
RI-MP2

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&END XC_FUNCTIONAL
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  &INTERACTION_POTENTIAL
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&KIND O
  BASIS_SET cc-TZ
  RI_AUX_BASIS_SET RI_TZ
  POTENTIAL GTH-HF-q6
&END KIND
&END SUBSYS


96 molecules
1078s on 3840 processors (Archer)
RI-MP2 results

2048 hybrid nodes: NVIDIA-Tesla-K20X graphical processing unit and 8 Intel-Xeon-E5 processors. 2048 GPUs, 16384 CPUs (organized as 4096x4 MPIxOMP). On average the full cell optimization is converged in 20 steps. Average Timing per step: 390 s, Average Timing per step, RI-MP2 part: 320 s

$9A2 = Cc$ most stable

Theory still predicts exptl (2Cl) structure to be metastable
dRPA results

$O(N^4)$

<table>
<thead>
<tr>
<th>Basis Functions</th>
<th>Machine</th>
<th>Timing (s)</th>
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A possible new ice I phase?

• Work esp. by Ben J. Murray et al. (Leeds) (e.g. *Nature*, 2005) has highlighted the potential importance of cubic ice.

• How trustworthy are potential models for modelling cubic ice and nucleation? (cubic ice typically formed in brute force crystallisation studies despite being metastable w.r.t hexgonal ice)

• Assess proton ordering to establish any intrinsic bias (using DFT as a benchmark)
Comparing Ih and Ic

2 clear favoured configurations

Xlh

Xlc
A possible new ice phase?

XIh

XIc

Structures are isoenergetic

XIc a possible competing phase?

Table 3  Comparison of ice XIh and ice XIc energies and structures obtained with VASP using hard PAW potentials and DMC

<table>
<thead>
<tr>
<th>Density functional</th>
<th>Cohesive energy/kJ mol(^{-1})</th>
<th>Volume/H(_2)O/Å(^3)</th>
<th>O-HO bond angle (°)</th>
<th>(\Delta H_{c-&gt;l}/J) mol(^{-1})</th>
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<td>Ice XIc</td>
<td>Ice XIh</td>
<td>Ice XIc</td>
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<td>DMC</td>
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<td>-57.84 ± 0.22</td>
<td>31.18 ± 0.22</td>
<td>31.28 ± 0.31</td>
</tr>
</tbody>
</table>

Z Raza et al., PCCP, 2011
Ice $\text{XIIa/XIIc}$ revisited

**PBE**

-1655.6800

**MP2**

\(~60\text{J/mol}\)

-1650.8400

**RPA**

\(~40\text{J/mol}\)

-1663.760

$\text{XIIh}$ has an extra molecule in the second coordination shell - vdW stabilised

*Mauro del Ben, Joost VandeVondele, BS, Christoph Salzmann unpublished results*
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