Using supercomputers to answer simple questions: how does salt dissolve, why is ice slippery, and more…

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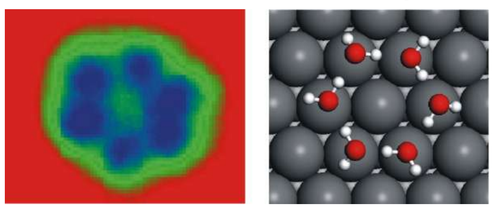
The **ICE** group - www.chem.ucl.ac.uk/ice - aims at understanding important phenomena in surface-, materials-, and nano-science. Using concepts from quantum mechanics to statistical mechanics, we apply and develop methods and computer simulations to study, for instance, chemical reactions at surfaces and processes of environmental relevance. Water is a major focus of our work. Some examples of our recent research are given below. Ultimately much of our work comes down to answering simple, even childish, questions such as how salt dissolves, why ice is slippery, how ice nucleates, melts, and so on. These questions might seem simple but to provide reliable answers which stand up to the test of experiment or bring fundamental insight they must be tackled with sophisticated ab initio approaches which require some of the world's most powerful supercomputers – such as Legion – to be solved.

Nano-scale Ice nucleation and the initial stages of cloud formation

• Heterogeneous ice nucleation plays a key role in fields as diverse as atmospheric chemistry and biology. Over the last few years we have been working closely with experimentalists to understand precisely how solid surfaces encourage water molecules to aggregate into ice. Our first principles simulations have revealed, for example, the structure of the "smallest piece of ice" – a six molecule water hexamer -, the first ever supported ice structure built from pentagons, and they have shed light on how the natural ice nucleating agent kaolinite makes ice in the troposphere.

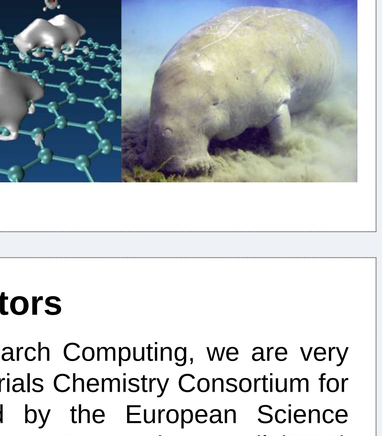
Experiment **Theory**



• Talented experimentalists with expensive microscopes such as a Scanning Tunnelling Microscope (STM) can measure very small things. The colourful image on the far left is a single water hexamer sitting on a Cu(111) surface. The radius of this ice particle is about 0.0000000005 metres. That's only half a nanometre.

• With theory, lots of cpu time, and some patience, we determined the precise atomic structure of the ice hexamer [1,2]. We also learned about the nature of hydrogen bonds at metal interfaces. (Hydrogen bonds are some of the weakest but most important bonds in nature. In addition to holding ice together they hold, for example, DNA and many proteins in shape.) We found that water molecules at noble metal surfaces don't like to bond to the surface and *accept* H bonds at the same time.

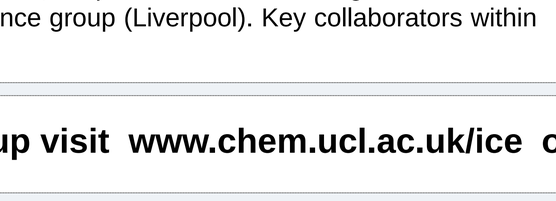
• Having identified and characterised the smallest piece of ice as a single water hexagon it came as great surprise to discover that when ice nucleates on a different Cu surface it forms long perfectly straight ice chains and that these ice chains were built out of *water pentagons* [3].
• The image on the right shows the structure we determined for the pentagon chains on the bottom with an STM image of the ice "rods" on the top.
• This is the first characterisation of an extended ice structure built from pentagons. It reveals an unanticipated structural adaptability of water-ice films, demonstrating that the presence of the substrate can be sufficient to favor non-hexagonal structural units. This realization may be an important step towards the identification of new anthropogenic ice nucleating agents for seeding clouds and making rain.



• An important natural ice nucleating agent is the clay mineral, kaolinite ($Al_2Si_2O_5(OH)_4$), which plays a prominent role in ice nucleation and cloud formation in the upper atmosphere. We are working on trying to understand the basic atomic level processes involved in such catalytic ice nucleation processes on kaolinite. Recently our simulations have shown that kaolinite readily produces a single layer of hexagonal ice, which is just as stable as bulk ice [4].

Dugongs grazing on Graphene!

• Serious number crunching simulations are also fun. Whilst using first principles to understand the wetting of graphene – a single sheet of graphene and the first true 2D crystal - our simulations on Legion predicted that water molecules "ride grazing dugongs across the surface!"
• The computer generated image on the right shows how the electron density rearranges when water adsorbs on graphene.



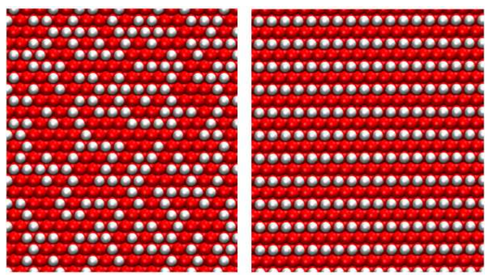
Support, Sponsors & Collaborators

• As well as generous allocations of computer time from UCL Research Computing, we are very grateful to the London Centre for Nanotechnology and the UK's Materials Chemistry Consortium for additional computational resources. Our work is also supported by the European Science Foundation through a European Young Investigator Award, the European Research Council (ERC) through an "ERC Staring Grant", the EPRSC, and the Royal Society.

• Equally important are our strong collaborations with other international theory groups such as those headed by Matthias Scheffler (Berlin), Enge Wang (Beijing), and Alessandro Laio (Trieste), as well as our many excellent experimental collaborators, in particular Karina Morgenstern's STM group (Hannover) and Andrew Hodgson's surfce science group (Liverpool). Key collaborators within UCL include Dario Alfe, Mike Gillan, and Ben Slater.

The Ice Surface is Superchilled

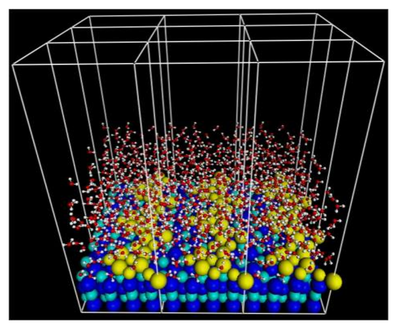
• We all know that ice becomes slippery some 20-40 K below its bulk melting point. Less is known, however, about the surface of ice at lower temperatures such as those experienced by ice crystals in the upper atmosphere.

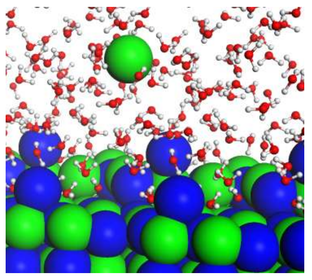


• Our first principles simulations show that although bulk ice is a proton disordered solid, at the surface, protons order [5]. Electrostatic repulsion between protons at the surface causes them to order, effectively making the surface "superchilled". This insight into the ice surface is likely to have implications for the equilibrium crystal shape of ice crystals or catalytic reactions which take place on their surfaces.

Density Oscillations in a Nanoscale Water Film on Salt: Insight from Ab Initio Molecular Dynamics

• The salt-water interface is one of the most important and common on earth, playing a prominent role in disciplines such as atmospheric science and biology. Despite the apparent simplicity of such interfaces, arguably the most fundamental question of what the nature and structure of the liquid water/salt interface is under ambient conditions remains unclear.
• We have addressed this issue with an ab initio molecular dynamics simulation of a nanoscale liquid water film on NaCl [6]. A pronounced layering is observed in the film, with the density exhibiting a damped oscillatory behaviour in the direction of the surface normal.

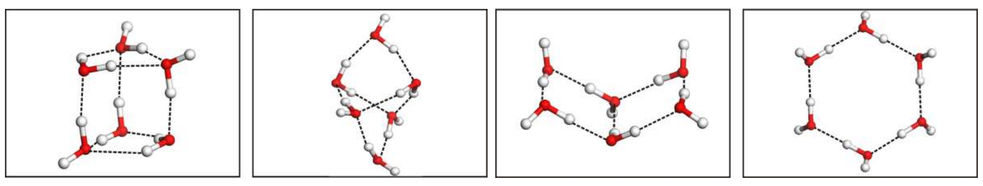




• Currently we are using accelerated molecular dynamics techniques on Legion to answer the question of how a salt crystal dissolves.
• The image on the left shows a snapshot of a simulation capturing in intimate detail the precise moment a chlorine ion (green) breaks away from a sodium chloride crystal into the water above.
• We're all familiar with salt dissolving in water, but this is the first time the molecular-level process has been modeled entirely with quantum mechanics.

Testing quantum mechanics for verrrrry small energies

• Most of the "first principles" simulations we do are with a theory known as density-functional theory (DFT). This is a very powerful theory. In principle it is exact but in practice it relies on an approximation for how electrons interact with each other. We are tackling the issue of the accuracy of DFT through extensive series of studies of small gas phase water clusters [7], water-molecule complexes [8], and water-solid interactions [9].
• These benchmark studies with techniques such as Møller-Plesset perturbation theory, coupled cluster, or quantum Monte Carlo often come with extreme computational burdens. The science they produce tends to be mostly boring numbers. However, these benchmarks are essential to establish the accuracy of more traditional methods such as DFT, and help to ensure that the numbers we produce stand the test of time and experiment.



• The four structures above are some of the low energy arrangements of a gas phase water hexamer. Which one has the lowest energy has been hotly debated for decades. Our simulations have helped to resolve this debate [7].

Publications

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[9] B. Li, A. Michaelides, and M. Scheffler, Surf. Sci. 602, L135 (2008).

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