Full details – ISIS(STFC-RAL) / OU Co-funded Facility Development and Utilisation PhD Studentship

“Exploiting Neutrons to Unveil Star-Formation: Exploring Dynamical Amorphous Ice Systems”

Lead Supervisor (OU) Dr Helen Fraser (helen.fraser@open.ac.uk)
Lead Supervisor (ISIS (STFC-RAL)) Dr Tom Headen (tom.headen@stfc.ac.uk)

PhD: This studentship will combine condensed matter experimental techniques in neutron scattering, with molecular dynamics simulations, asking:

“How is the structure and porosity of Amorphous Solid Water (ASW) impacted by the presence of adsorbates?
What impact will this behaviour have on the physics and chemistry of icy materials in star- and planet-forming environments?”.

The student programme is focused around three specific objectives:
(a) to study ASW ice-adsorbate systems with ISIS using NIMROD and SAN2D to test how adsorbates effect the ice structure and porosity, focusing on CH$_3$OH and CO$_2$.
(b) to design and develop a dedicated low-pressure / low-temperature experimental system for forming, manipulating and destroying multi-component condensed molecular systems, for studying astrophysical ice analogues + adsorbates with NIMROD and SANS2D and
(c) to couple large-scale molecular dynamics simulations of multi-component ice formation / evolution with measurable properties from neutron scattering studies, including material density, porosity, structure, clathrate formation and H-bonding.

Essential Requirements for PhD Candidates

1. Able to study full time for 3.5 years from 1st Oct 2020
2. Minimum 2:1 (or equivalent) MPhys / MChem / MSci
3. Willingness to study across 2 centres, Open University (1st, 3rd & 4th Years) and ISIS (2nd Year)
4. EU or UK citizen (for fee purposes)
5. Previous experimental research project experience in physics or chemistry
6. IELTS pass at > 7.5 (if English is not your native language and your final Masters exams were not taught and examined in English)

Desirable (not obligatory) Requirements for PhD Candidate

1. Able to demonstrate how they work well as part of a diverse team, particularly during periods of intensive work under pressure
2. Previous experience of large-scale facilities experiments
3. Strong written and oral communicator (in English)
4. Some experience of experiment design and development, particularly if this involved cryogenics, gas handling or vacuum systems
5. Previous evidence of experience with molecular dynamics simulations

The student will receive a maintenance grant of ~ £15,009 per year (2019-2020 rate), with all academic fees covered.
Research Environment and Training

As with all co-funded ISIS facility development studentships, this studentship is based on a strong partnership between the host university (Open University) and ISIS Neutron Source Facility at RAL, Harwell. The PhD is therefore co-supervised by two lead supervisors, one at the OU (Dr Helen Fraser) and one at ISIS (Dr Tom Headen). Both supervisors have experience with experimental design and development and neutron scattering – Dr Headen also brings expertise in theoretical modelling and neutron studies of disordered materials and Dr Fraser astrochemical knowledge. In addition, the student will have a 2nd supervisor at the OU (Dr Jimena Gorfinkel with expertise in theoretical chemistry) and a pastoral tutor, independent of the academic supervisory team. The student will be registered at the Open University throughout their PhD studies and graduate from the OU. Whilst the 1st, 3rd and 4th years will be spent at the OU’s Milton Keynes campus in the School of Physical Sciences, the student will be located at the ISIS Neutron Facility near Harwell, Oxfordshire for the entire 2nd year of study. This arrangement will lead to the student gaining greatest benefit from the research environments at both institutions, achieving the scientific and facilities development aims of the studentship, and enable the student to undertake all the usual PhD training, particularly during their 1st year of studies, and the 3rd/4th year “writing up” period. We will encourage the student to publish their scientific findings and present their work at national and international Meetings. The student will be encouraged to attend the renowned ISIS and Oxford Neutron Training schools, and have access to a varied of training and employability opportunities through STFC the OU and SEPNET.

You can follow these links to find further details about the School of Physical Sciences at the OU, the OU School of Physical Sciences PhD Programme as well as the ISIS Neutron and Muon Source and ISIS Disordered Materials Group.
**Background Motivation:** Interstellar ice, dominated by Amorphous Solid Water (ASW) is the largest molecular reservoir (after H₂) in the universe. In the laboratory, as in space, the porosity of ASW is strongly influenced by prevailing formation parameters such as the deposition temperature and the angle of incidence and ASW has huge capacity to adsorb gases. It is assumed the meta-stable interstellar ASW loses porosity as a function of time or temperature as star-formation progresses. This porosity change is astrochemically vital as it alters the total ASW surface area from ~ 2000 m²/g to ~ 0.1 m²/g, changing the surface available for chemical catalysis, accounts for discrepancies between (observed) gas-phase and solid-state abundances of volatile interstellar molecules due to gas-trapping in the pores (most importantly of H₂ and CO – the primary coolant gases in the star-formation cycle) and affects how icy grains might “stick” to form the early seeds of planets and cometary nuclei. Such changes are attributed to loss of ice porosity, so to consolidate astrochemical models with observations, astrochemists need to quantify pore growth, in terms of size, shape and spacing in the ice structure as it grows, and how these properties change as the ice is thermally processed. This information can be uniquely obtained from neutron scattering studies.

A plethora of laboratory experiments and molecular dynamics simulations have converged to conclude that structures of ASW ice grown above 77 K (compact ASW or c-ASW) differ in porosity from those formed below 77 K (porous or p-ASW) and both differ from cubic crystalline ice, I_h, formed on heating ASW to beyond 150 K; the exact I_h structure may even exhibit ice “memory”, being reliant on both the ASW it forms from, and even never be found in a “pure” form – rather as a disordered ice “mixed” with the hexagonal form (h). However, whilst conclusive experimental evidence exists that nanopores disappear as ASW is heated, micro-porosity persists; the debate rages as to whether pores “cluster” and grow before collapsing or not. How this pore-collapse process happens remains a mystery, and furthermore, except in neutron scattering studies, porosity can only be probed indirectly – using adsorbate gases – and no-one has a clue of the extent to which adsorbate molecules impact ASW pore-structure or evolution during (a) its growth and (b) its thermal / temporal evolution. These scenarios affect all the physical and chemical attributes of ASW that are so vital in modelling interstellar astrochemistry. Furthermore, despite strong evidence to the contrary from condensed matter physics, suggesting clathrate-hydrates can only be formed via pressurisation of water ices, the astronomy ice literature implies clathrate hydrates can form in interstellar and cometary ices as “polluted” ASW is warmed, based on observational and laboratory spectroscopic assignments to adsorbate-H₂O (ice) features.

All these processes will be investigated experimentally during this PhD, and the first data on this project will actually be obtained prior to the student’s start date – so that data for analysis will be available from day 1 of the PhD studies.

**Facility Development:** Over the past 5 years, our experiments on NIMROD and SANS2D have exploited the development of instrumental techniques that have pushed the boundaries of both instruments. Our development of a proof of concept in situ sample-environment has proven we can study ASW growth and thermal evolution with neutrons showing our vapour-deposited ASW exhibits both granularity and porosity, both of which evolve as a function of deposition time, deposition temperature and thermal heating - five independent analyses of the SANS region converged to form the same picture of the nano-porosity. From these models we have evolved methods to describe the size and shape of our ASW nano-pores, test how these parameters vary as a function of the surface temperature during ice deposition, evolve as the ice is heated, hold a “memory” of the growth conditions, and disappear between 100 and 120 K. When compared to earlier studies of pre-prepared (D₂O) ASW samples, held under liquid N₂ conditions, it is clear that the evolution of the pores exposed to L.N₂ is different beyond 100 K to those of ASW ices grown in situ – suggesting adsorbates do play a role in changing ASW pore structure and evolution.
However, ASW formation is pressure-temperature sensitive. Our existing experimental set-up is limited to 20 K base temperature, and bin pressures $> 1 \times 10^{-4}$ Torr. The latter is “right at the edge” of the pressure regime where amorphous ices can be expected to be formed on a cold-plate by vapour deposition without some degree of crystallisation occurring. N$_2$, CH$_4$ and CO, the “best” (and most well-documented) adsorbate probes of ASW, readily desorb at these temperatures. So a new sample environment is required, capable of reaching pressure below $1 \times 10^{-8}$ Torr and temperatures of 10 K or less, suited to in situ sample growth, heating and destruction. A major part of this PhD is to design and construct a new experimental bin suited to these requirements, fully UHV compatible and with a 10 K cryostat, exploiting the mechanical design and existing experimental facilities at the OU, coupled with the expertise of RAL Space (Prof Brian Ellison) and ISIS. The system will be tested and integrated during Y2 of the PhD and the student’s residence at ISIS.

**Combining Theory and Experiment:** Our group have also developed molecular dynamics code (first with DL POLY but, as parallelisation was required, using GROMACS) constrained by TIPPP4P-ice, to simulate vapour-deposited water-ice growth (of 500 H$_2$O molecules in a $35 \times 35 \, \text{Å}^2$ x-y-periodic box) as a function of substrate temperature, and now have over 900 ASW structures from which properties such as porosity, H-bonding and a visual structural image can be extracted. Whilst these structures act as useful benchmark and starting point, we now need to “warm them up” and “make them bigger” to truly be able to simulate effects we can observe in neutron scattering studies. GROMACS has a number of neutron simulation packages associated with it as a basis to start modelling neutron outcomes from our icy metastable materials. The final challenge of this studentship is to work on this coupling of theory and experiment, building links in Y2 to the Scientific Computing Department of STFC (Dr Tom Griffin)- work anticipated to progress into Year 3 of the student’s study.