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Note: Sample cells to investigate solid/liquid interfaces with neutrons

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The design of sample cells to study solid/liquid interfaces by neutron reflection is presented. Use of standardized components and a modular design has allowed a wide range of experiments that include grazing incidence scattering and conventional small-angle scattering. Features that reduce background scattering are emphasized. Various flow arrangements to fill and replenish the liquid in the cell as well as continuous stirring are described. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4906518>]

In the past 25 years, the measurement of specular reflection of neutrons at glancing angles has become a widely used technique to investigate the structure and composition of solid/liquid interfaces.^{1–3} Experiments have investigated adsorbed surfactants, polymers, proteins, and model membranes. It is usual to allow the incident beam to pass through the solid substrate and, entering by the edge almost perpendicular to the beam, the reflection occurs from a large, smooth face. The design of sample holders for these measurements has evolved and a number of improvements have facilitated a range of different experiments that study *in-situ* reactions, the influence of temperature change, and other effects. Principles for design of optimized measurement cells are presented below in the context of a specific modular design that can be adapted flexibly to a range of experiments. Some older designs of cells have been illustrated in the literature¹ and photographs⁴ shown but there is little explicit discussion about the principles or even the choice of materials. An interesting design for specific experiments to give very low background uses specially machined silicon crystals with a very thin recess for liquids and filling ports.⁵

Sample holders are designed to hold a thick, smooth, and flat substrate that is sealed against a container for liquids that has ports for fluid flow. Some important criteria are that the solutions can be exchanged readily, either for measurements with different contrasts such as H₂O and D₂O, to change the concentration of adsorbate, or to modify conditions with different chemicals or changes of pH. Exchange is usually achieved by pumping appropriate solutions to displace the contents of the cell. For some studies, it is desirable that the surface should always remain in contact with liquid as it could change if dried or even simply exposed to air.

In order to measure conveniently at different angles, the reflecting interface must be at the centre of rotations of the circles of the reflection instrument. The space available for the necessary translations is often limited and so a compact design is required. Some instruments work with a horizontal reflecting surface while for others a vertical geometry is used. The cells described below and shown in Figure 1 can be used readily in either geometry as indicated in Figure 2.⁶ The

modular concept with various supports and liquid flow arrangements enables a very broad range of experiments.

The design includes several features to improve the performance as regards reflection measurements. The surfaces of the metal frames are cut away to allow a wide range of angles for the incident beam and to measure grazing incidence scattering. Reflecting substrates with areas of 50 × 50 mm² can be mounted. Large areas are desirable to maximize the signal but limits are imposed by transmission of the neutron beam through the length of the crystal. Avoiding as far as possible that there are flat surfaces in the beam parallel with the reflecting interface diminishes the chance of stray reflections. Addition of an extra absorbing mask to shield scattering from the bulk liquid and the support can significantly reduce the background. A simple design with an absorber on a micrometer translation was used initially but an improved, compact design with an absorber made by 3D printing⁷ that can be used in both horizontal and vertical mounting arrangements has been tested. Normally the cell and mounts are assembled with stainless steel screws. For experiments with polarized neutron beams, they can be replaced with brass screws. In general, these are less desirable as they are more prone to be activated by scattered neutrons or when translated into the beam if multiple cells are mounted on a sample changer. The aluminum frames can also be mounted directly, or with plastic spacers for temperature isolation, on optical table kinematic mounts (Thor Labs, KB75) that are used on some instruments.

The design of inlets and outlets for the liquid is not entirely trivial: they need to optimize the fluid flow for various different experiments. It is frequent that solutions can have significantly different densities and/or viscosities. Flow and displacement of possible air bubbles can also depend strongly as to whether the reflecting surface is mounted vertically or close to horizontal. The cell components can be used in a variety of combinations to provide appropriate flow. A small magnetic stirrer “flea” in a recess in the polycarbonate back is driven by an external motor with an attached magnet and creates a flow pattern that provides efficient mixing. It is convenient to adjust the stirring speed and, for other applications,⁸ we have found a unipolar stepper motor to provide reliable performance at low cost. An identical motor (16HS, McLaren Servo Supplies Ltd., www.mclennan.co.uk) and electronic driver⁹ were used for the reflection cell.

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FIG. 1. Diagram of cell with cutaway view of holder for a substrate, liquids, and gasket. A magnetic stirrer is shown in this assembly.

Options to use different filling arrangements with two, three, or four ports to optimize flow for different experiments are shown in Figure 3. For a simple experiment, one inlet, at the bottom when the cell is mounted vertically, with an outlet on the opposite corner on the top works well with slow displacement of the liquid. Two inlet ports are used for mixing two reagents *in-situ*. If it is desired, for reasons of density, to fill some solutions from the top and others from the bottom, four ports can be chosen. A dense fluid filled from the bottom will displace a lighter fluid through an outlet at the top and vice-versa. If the inlet and outlet ports are all connected to controlled valves, this can be automated in a sequence of measurements. Use of specific back pieces or gaskets for the different inlet/outlet arrangements minimizes dead volume that is not exchanged by flow and eases cleaning. Inlet and outlet ports have been prepared with $\frac{1}{4}$ in. 28 UNF screw threads and flat bottoms to take Omnifit connectors (see www.omnifit.com) for tubing and valves. This allows easy filling with either liquid chromatography pumps or syringes. Typical filling speeds are 2 ml min^{-1} .

The choice of materials for construction is important. PTFE (polytetrafluoroethylene) or other fluorinated polymers are convenient to contain solutions and for connectors as they

FIG. 2. Possible orientations with cell mounted for (a) reflection and grazing incidence scattering, (b) transmission SANS, (c) horizontal surface for reflection, (d) shows the assembly with two neutron transparent windows and a PTFE gasket with integral filling ports as used in (b).

FIG. 3. Schematic diagram showing different flow arrangements for (a) simple fluid displacement, (b) mixing of reagents with one outflow, and (c) opposite inlet and outlets if required for fluids of different densities. A slot in the polycarbonate back piece provides for distribution of the fluid across the cell.

can withstand vigorous cleaning, and after soaking in appropriate solvents, do not leach surface active materials. Unfortunately, there is a tendency to creep but retaining a machined gasket in a polycarbonate frame diminishes this problem and avoids the reduction in usable life of alternative designs. For work with aqueous solutions, polycarbonate has good resistance to acids and a variety of cleaning agents such as alcohols and alkanes. An advantage is that it is transparent and visual inspection of the filling of the cell is possible. It can be machined readily and a smooth finish that retains the transparency is straightforward to achieve. While other material such as PEEK (polyetheretherketone) offers better resistance to alkali, it is less compatible with acids and is not transparent.

The flexibility of the design includes the possibility to assemble the cell with two neutron-transparent crystals, which could be the same or different materials, rather than a polycarbonate back. This allows measurement of reflection from two different surfaces or, if the sample holder is rotated by 90° , measurement of scattering in transmission geometry to understand the structure of the material in the bulk of the liquid that is in contact with the surfaces. This arrangement with a PTFE gasket machined with in-built filling ports is shown in Figure 2(d). For reflection studies, the substrates can vary in thickness between 8 and 12.5 mm. The support is symmetric and the cell, when vertical, can be mounted for measurements either to the left or the right of the incident beam.

The temperature of the interface is maintained by circulating water from a bath through the channels in the mounting plates. Small nylon spacers can be inserted to reduce heat transfer to the support. A four-wire, M5 threaded, platinum resistance temperature sensor (Pt100) is screwed directly in the metal frame adjacent to the crystals. A robust sensor that is reliably fixed to the cell allows direct control of the sample temperature. Measurements between 15 and 60°C are possible without any additional temperature insulation. Details of the various components are described in supplementary material.⁹

Typical neutron reflectivity data for a cationic surfactant solution (hexadecyltrimethylammonium bromide at three

FIG. 4. Reflectivity curve for a sapphire/D₂O surfactant solution interface. The inset shows the comparison of total counts for similar measurements with an absorbing mask to reduce background (blue diamond) and without mask (open red squares).

times the critical micelle concentration) in D₂O against a sapphire substrate are shown in Figure 4. The benefit of an adjustable mask to screen the background scattering is evident with measurements of reflectivity below 10^{-6} . The significant reduction in background measured on a position sensitive detector is shown in the insert. As most of the background scattering is observed at large $Q = (4\pi/\lambda) \sin \theta$, where λ is the wavelength and θ is the angle of incidence, this enables substantial improvement in the minimum reflectivity that is measurable.

The cells described have been used for a variety of experiments with surfactants, polymers, proteins, and particles. They have also been adapted for *in-situ* reactions triggered either by addition of chemicals or illumination with UV light. Ergonomic features such as small recesses to locate components and rubber supports to avoid too much stress on crystals have made the cells particularly easy to assemble. In conclusion, the modular design, with standardization of many components that are easily fabricated or purchased, allows many different experiments and easy upgrades of the design to be incorporated as new instruments are commissioned or ideas for experiments develop.

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- ⁹See supplementary material at <http://dx.doi.org/10.1063/1.4906518> that describes details of component parts (motors, electronics, fluid connections, etc.).