Proposed Sample Environments for FREIA

1 Outline

The range of possible samples that will be used on FREIA are quite varied to cover the wide-ranging science case.

Therefore, we should firstly look towards the most generic sample environments that will definitely be required at FREIA (and ESTIA). Our second consideration should be how best to exploit the high performance of the instrument. FREIA is optimised for studying dynamic systems with changing structure over short periods of time. Such changes may be induced by internal and external influences, such as temperature, chemical reactions or adsorption processes, humidity, etc. The third consideration is the ever-growing demand and interest in performing in situ and/or simultaneous characterisation of the system under investigation with NR (and XRR). The fourth, and final, consideration is the automation of sample changes. This concept probably needs the most thought/creativity as it is currently the least considered sample environment aspect at neutron facilities.

1.1 Sample types

Sample sizes will vary from approximately 1 cm^2 to potentially 20 x 40 cm in the case of a large liquid trough. Some typical samples are listed below, but these are by no means comprehensive.

i. Free liquid interfaces

- A free water (H2O or D2O or a mix) or buffer solution "sub-phase" onto which is spread an insoluble monolayer such as a phospholipid. The spreading of this monolayer is usually achieved by depositing onto the surface small quantities of a chloroform or methanol solution containing the required molecule.
- The same as above but the sub-phase will contain a compound of interest that is expected to interact with the surface monolayer. These compounds may be expensive or difficult to produce (e.g. proteins) so the volume of the sub-phase may be important (low volume means less material to achieve the same concentration).
- A free liquid (not necessarily water) which contains some surface-active species that will adsorb to the interface forming a layer that can be resolved using reflectometry.
- A Liquid-liquid interface (e.g. oil and water). One of the liquids would contain some surface-active species that will adsorb to the interface forming a layer that can be resolved using reflectometry.

ii. Solid interfaces

- A solid sample onto which a thin film has been deposited (e.g. polymer). Typically, the roughness of the solid has a big impact on the success of a reflectometry experiment so the solids typically used are those that can be polished to be close to atomically flat (roughness of the order 10Å), such as silicon or sapphire.
- A solid-liquid sample. The solid is usually chosen to be transparent to neutrons so that the incident beam does not need to be transmitted through the liquid phase (which could contain large amounts of hydrogen and therefore contribute significantly to the incoherent background scattering). The sample is oriented with the solid on the top. The surface of the solid will have on it a layer of some that can be resolved using reflectometry. This layer may have been formed in-situ via the adsorption of some surface-active species from solution, or made offline by means of a technique such as Langmuir-Schaffer dipping. In

order to obtain multiple neutron scattering length density contrasts for the same monolayer, the liquid can be exchanged with another.

iii. Samples with in-situ techniques

- A range of other samples are also possible, including samples that require the in-situ integration of parallel techniques such as rheometry. These techniques will have varying requirements on space and geometry.

2 Sample Environment Equipment Summary

The importance of appropriate sample environment provision for the success of FREIA cannot be over emphasised. The sample environment for soft matter reflectometry experiments is much more specialised than for other neutron instruments at ESS.

The proposed sample environments for FREIA which are given below, fall into three categories depending on their urgency, scientific impact and frequency of use: *essential*, *highly desirable*, *desirable* or *potentially interesting*. Below this list is a general assessment of all the considered sample environments, ranked from 1-5 depending on their perceived priority (1 = low; 3 = essential for day two; 5 = essential for day one). For each case we have justified their need by their *scientific case*, what each needs to be able to do (*required specification*), what it needs in terms of sample environment supplies (*required services*) and integration (*required integration*).

Essential:

i. Thermostated and atmospherically controlled sample changer for liquid troughs
ii. Multiple Langmuir Troughs (traditional and including small volumes)
iii. Thermostated and atmospherically controlled sample changer for solid-gas samples
iv. Thermostated sample changer for solid-liquid samples with associated cells, syringe & HPLC pumps

Highly desirable:

v. Sample changer with appropriately adapted Langmuir Trough system
vi. Liquid-liquid sample environment with associated syringe & HPLC pumps
vii. Monolayer changer system for liquid surfaces

Desirable:

viii. Electrochemistry cell & associated potentiostat
ix. Chemical Reaction Cells & (reactive) gas handling
x. In-situ Brewster Angle Microscope / Ellipsometer
xi. In-situ FTIR
xii. Rheometer

Potentially interesting:

xiii. Pool equipment (cryostat, magnets etc)
xiv. High pressure cell
xv. Over-flowing cylinder
xvi. In-situ Spin Coater??

Ancillary equipment & facilities

(some specific equipment that will support the user programme in addition to the general chemistry & biology facilities for sample preparation)

- Appropriate storage capacity for activated samples (depends on the design of cells)

- Facilities for cleaning solid samples using Piranha solution
- Langmuir-Blodgett and Langmuir-Schäfer systems
- Brewster Angle Microscope / Ellipsometer
- Tensiometers
- Quartz Crystal Microbalance
- Tip sonicator
- UV / Ozone Cleaner

3 Sample Stack

The instrument should have the following items effectively permanently installed:

- Passive vibration isolation
- A sample stack that conforms to ESS standards and which allows sufficient sample motion and space for all SEE listed below
- Active vibration isolation
- Alignment laser & interferometer for auto alignment (of liquid surfaces in particular)

These items are completely essential for day 1. As such they will be considered during the instrument detailed design and fully specified then.

4 SEE Scientific case and specification

There is a significant difference between the solid and free-liquid samples to be used on FREIA in that the solid samples will be rotated to allow higher incident and reflected angles, while the liquids samples necessarily remain horizontal. In order to fully exploit the maximum sample-detector angle on FREIA the solid sample environments should allow incident and reflected angles of up to **25°**. Liquid samples should cover up to **4°** for the entry window and **6°** for the exit window. Sample environments should be fitted to ensure that the sample centre is a constant distance to the detector every time they are installed. It is assumed almost all the environments below will need access to power and the network and so has not been stated explicitly. The lengths of sample environments given below refer to their length in the neutron beam and width is the horizontal distance perpendicular to the beam direction.

Low backgrounds will be crucial in achieving optimal performance, particularly for liquid samples. The SEE should therefore be designed to at least not contribute to the background scattering and ideally reduce it. This is true for all environments and is therefore assumed.

Given the very high neutron flux incident on samples, their activation is potentially significant. All SEE therefore needs to be designed with this in mind, using materials that do not activate where possible, and with appropriate shielding where it is not. The possibility that active samples cannot be quickly removed by a user also needs to be considered, both in terms of the number of cells available and in allowing for appropriate storage capacity.

In all cases flexibility is important and SEE should be adaptable to user supplied samples or equipment.

In certain cases (indicated below), significant development work will be required to realise the full potential of the instrument. This is likely to take several years and significant man-power and will need to occur significantly before the equipment is actually needed on the instrument.

i. Thermostated and atmospherically controlled sample changer for liquid troughs (priority = 5)

Scientific case	Many experiments do not require active control of surface pressure (although the capacity to measure the surface pressure will remain useful). Samples in these experiments will therefore consist of a small PTFE (or similar material) trough into which the sample liquid is poured. Many such samples may require small volumes (for example, because the price of the required deuteration is otherwise prohibitive). Such small volumes are generally achieved by making the troughs very shallow, while maintaining the overall surface area to ensure a flat surface. A range of different possibilities will be required to suit the range of different samples possible. For example, many typical surfactant studies in water will benefit from larger troughs since they are not limited by volume, whereas a study of ionic liquids may require very small volumes in troughs that are made from materials other than PTFE. With measurement times of the order of minutes, the ability to change samples remotely to avoid frequent user access to the cave is essential. Equally the ability to change the liquid sub-phase without removing the monolayer would be very helpful.
Sharing Possibilities	None
Required specification	o Minimum of 10-20 PTFE troughs mounted and another 20-40 offline (for simultaneous preparation) o Integrated surface pressure sensors for each position o Ability to mount user supplied troughs o Low volume troughs and alternative material options, e.g. Delrin, Macor, PEEK (min. another 30 troughs) o Independent heating/cooling & temperature control o Individually controlled atmosphere enclosure(s) with heated windows to prevent condensation o Humidity control up to 95% rel. humidity o Easy access and integration with sample stack **REQUIRES DEVELOPMENT WORK** o Troughs that allow exchangeable sub-phase o HPLC pumps with capacity for 4 inlet channels & enough outlets for mounted cells o Alternative syringe pumps for small volumes
Service requirements	o Water and/or oil bath for heating o Temperature control capacity for up to 20 independent control loops o Humidity control system o Independent thermometers o Inert (e.g. N_2) or humidified gas supply
Integration requirements	o Auto alignment with feedback from interferometer during measurement to compensate for evaporation o Time-stamping of readings from surface pressure

ii. Multiple Langmuir Troughs (traditional and including small volumes) (priority = 5)

Scientific case	A Langmuir Trough is a (usually PTFE) container with barriers that can move over the surface to control the surface area available to a monolayer of insoluble amphiphilic molecules. Measurement of the surface pressure (related to the surface tension) vs area per molecule can give information about the packing and thermodynamics of the monolayer in question. Existing commercial Langmuir troughs are available but these do not necessarily meet all the requirements for use on FREIA.
Sharing Possibilities	None
Required specification	o At least 3 standard commercial Langmuir Troughs with varying liquid volumes (large, medium & small) o Associated control system o An atmosphere and temperature-controlled enclosure (including heated windows to avoid condensation and heated lid to avoid drips from above) o Easy access to sample surface o Repeatable mounting system within enclosure o Aspirator pumps with chemical waste disposal
Service requirements	o Water and/or oil bath for heating o Independent thermometer o Inert (e.g. N_2) or humidified gas supply o Aspirator pump (vacuum pump with trap for liquids)
Integration requirements	o Integrated with commercial software (e.g. LabView) or controllable through instrument software o Auto alignment with feedback from interferometer during measurement to compensate for evaporation o Time-stamping of readings from trough system

iii. Thermostated and atmospherically controlled sample changer for solid-gas samples (priority = 5)

Scientific case	Almost all of the sample environments will require temperature control. The temperature range and precision required of this control will vary substantially with the specific samples. For example, a typical experiment looking at biomolecules (lipids & proteins) will operate in the range 0 to 80°C with precision of the order ±1°C. Meanwhile an organic photovoltaic (polymer) study could require much higher temperatures of up to 500°C and precision of the order ±0.1°C. Solid samples are relatively easy to combine with a simple sample changer stage. However, on FREIA the number of samples will be high and therefore the arrangement of the samples needs to be appropriate to facilitate this. Not all experiments will require a sample changer but the individual requirements are similar.
Sharing Possibilities	There is some overlap with the requirements for similar equipment on ESTIA
Required specification	o Positions for 10-20 solid samples with independent temperature control o A range of heater options (cartridge heaters, peltier etc) o Heating rates up to 100°C per minute o Steady state control precision of ±0.1°C o Sample changes using kinematic mounts with appropriate integration for samples & heaters o Individually or shared controlled atmosphere enclosure(s) with heated windows to prevent condensation o Humidity control up to 95% rel. humidity o Easy access and integration with sample stack to allow sample alignment & tilting
Service requirements	o Temperature control capacity for up to 20 independent control loops o Humidity control system o Inert (e.g. N_2) or humidified gas supply
Integration requirements	

iv. Thermostated sample changer for solid-liquid samples with associated cells, syringe & HPLC pumps (priority = 5)

Scientific case	Over may years there have been as many iterations of designs of solid-liquid cells. These vary in detail depending on the specific requirements of the sample. However, the general principles are the same. A solid sample (silicon, quartz sapphire etc.) is clamped onto a trough (typically PEEK or similarly inert plastic) and sealed by an o-ring on the sample surface. The plastic trough has inlets and outlets through which it is possible to flow liquid. In the more advanced cells this flow is kept laminar to avoid turbulence that can disrupt the adsorbed monolayer. Water can then be flowed through the cell using an HPLC pump, and in this way, it is possible to exchange the contrast of the water by flowing mixtures of H2O and D2O in the appropriate proportions. It is also expected that experienced users will provide their own cells and it is likely that these will have been optimised for use at existing facilities. It is therefore essential the mounting for solid liquid cells on FREIA is adaptable to these existing designs.
Sharing Possibilities	There is some overlap with the requirements for similar equipment on ESTIA but these cells will not necessarily be easily transferred to FREIA. The sample size difference means that a solid-liquid cell optimised for ESTIA will be too small for FREIA.
Required specification	o Minimum of 10 solid-liquid cells mounted and another 20 offline (for simultaneous preparation) o Ability to mount user supplied cells (appropriate sizes for other facilities) o Low volume and small cell alternative options (another 30 cells) o HPLC pumps with capacity for 4 inlet channels & enough outlets for mounted cells o Alternative syringe pumps for small volumes o Independent heating/cooling & temperature control
Service requirements	o Water and/or oil bath for heating o Temperature control capacity for up to 20 independent control loops o Independent thermometers
Integration requirements	o Auto-alignment system

v. Sample changer with appropriately adapted Langmuir Trough system for high through-put (priority = 4)

Scientific case	The high performance of FREIA may mean that measurements are completed within a few minutes. For a Langmuir trough system the ability to change surface pressure will some additional measurements and increase time between sample changes. Similarly changes of temperature may also be of interest and could increase the time between sample changes. However, these are not necessarily required nor can they be considered efficient use of beam time. It is also important to enhance the user experience by allowing reasonable times between sample changes where possible.
Sharing Possibilities	None
Required specification	**REQUIRES DEVELOPMENT WORK** o Medium sized Langmuir troughs (10 x 20cm?) adapted to allow exchange of the sub-phase o Adaptable to smaller troughs o HPLC pump with at least 2 channels and switch for at least 3 samples o A system that can mount and swap between 3 (or more) Langmuir troughs without spillages or disturbance of the surface o Associated control system o An atmosphere and temperature-controlled enclosure (including heated windows to avoid condensation and heated lid to avoid drips from above) o Easy access to sample surface o Repeatable mounting system within enclosure o Aspirator pumps with chemical waste disposal
Service requirements	o At least 3 independent water and/or oil baths for heating/cooling o Independent thermometers o Inert (e.g. N_2) or humidified gas supply o Integrated HPLC tubing with appropriate inlets/outlets o Aspirator pump (vacuum pump with trap for liquids)
Integration requirements	o Controllable through instrument software o Auto alignment with feedback from interferometer during measurement to compensate for evaporation o Time-stamping of readings from trough system

vi. Liquid-liquid sample environment with associated syringe & HPLC pumps (priority = 4)

Scientific case	The current state-of-the-art liquid-liquid cells used for neutron reflectometry are not as well developed as the solid-liquid cells. However, the fundamental principles are quite similar. There are two strategies for looking at the liquid-liquid interface. The first basically uses a solid-liquid cell. A frozen macroscopic oil layer is deposited onto a solid (silicon) sample prior to assembly of the cell. (For example, this may be done by spin coating.) This is then filled with water in the measurement orientation (with the solid and oil layer at the top). The second approach is to have a free liquid trough in an enclosure with inert windows. The second liquid can be injected from above once the interface has been provisionally aligned. It is likely that these designs will develop in the coming years, so FREIA will provide one or two generic liquid-liquid sample environments that can be used by as many users as possible. Temperature control, HPLC pumps and sample changing possibilities are all possible for these environments
Sharing Possibilities	None
Required specification	**REQUIRES DEVELOPMENT WORK** o HPLC pump with at least 2 channels and switch for at least 3 samples o A system that can mount and swap between 3 (or more) liquid-liquid troughs without disturbance of the surface o Associated control system o Easy access o Repeatable mounting system o Temperature control
Service requirements	o Water and/or oil bath for heating o Independent thermometers o Inert (e.g. N_2) or humidified gas supply o Integrated HPLC tubing with appropriate inlets/outlets o Independent thermometers
Integration requirements	

vii. Monolayer changer system for liquid surfaces (priority = 3)

Scientific case	Another approach to enabling automatic sample changes is to use a robot to spread and remove monolayers from a surface. This is possible in principle and could allow for additional flexibility in sample changing. The cleanliness of liquid troughs is crucial to the success of experiments so automation of such a process is challenging and will require significant development effort.
Sharing Possibilities	None
Required specification	**REQUIRES DEVELOPMENT WORK** o Robot with micro-syringe and aspirator capabilities o Integration with Langmuir troughs and/or standard trough sample environments described above o Some method of feedback to confirm sample cleanliness o Ability to refill sub-phase from below o Temperature control
Service requirements	o Water and/or oil bath for heating o Independent thermometers o Inert (e.g. N_2) or humidified gas supply o Integrated HPLC tubing with appropriate inlets/outlets o Aspirator pump (vacuum pump with trap for liquids)
Integration requirements	o Cleanliness feedback system to be defined? o Controllable through instrument software o Auto alignment with feedback from interferometer during measurement to compensate for evaporation o Time-stamping of readings from trough system

viii. Electrochemistry cell & associated potentiostat (priority = 3)

REQUIRES DEVELOPMENT WORK

The cells for electrochemistry will be instrument or even experiment specific. A standardised cell that resembles solid-liquid cells and can be mounted in the same sample changers should be provided. Similarly, the liquid-liquid cells may be adaptable to allow for the inclusion of the required electrodes.

There is some overlap with the requirements for similar equipment elsewhere since a potentiostat does not care about the sample geometry. Integration of a potentiostat with the control system and appropriate time-stamping will be required.

An example cell is described in the following reference:

Lauw et al. Review of Scientific Instruments 81, 074101 (2010); DOI: 10.1063/1.3455178

ix. Chemical Reaction Cells & (reactive) gas handling (priority = 3)

One of the key drivers in the science case is to look at the kinetic of changes in samples. A good fraction of such experiments will look at chemical changes that result from reactions at the interfaces. The details will be quite varied but the sample environment should be similar to those already described, but with additional requirements for chemical inertness. This can be problematic for things like Ozone or other reactive gasses. Gas handling and ozone generation (UV lamps) are likely to be of use to other instruments so FREIA would probably use a pool gas handling system where appropriate. COSHH extraction systems within the instrument cave will also be required

x. In-situ Brewster Angle Microscope / Ellipsometer (priority = 3/2)

REQUIRES DEVELOPMENT WORK

In general an additional technique perpendicular to the neutron beam adds information about the sample that can be beneficial in terms of the interpretation of neutron data. A BAM or Ellipsometer (or both) can be used and this has been done on existing instruments. However, the complexity of setting up and aligning these systems is difficult which means that they are not well suited to being put on and taken off an instrument. In principle the system could be compatible with both air-liquid and solid-liquid samples. But these do have different constraints and this will make set-up more difficult. Significant development work would be required to ensure that mounting and dismounting can be done in a routine manner.

The choice of BAM or ellipsometry is also not trivial since commercial equipment that is suited for BAM does not necessarily make a good ellipsometer & vice versa.

xi. In-situ FTIR (priority = 3/2)

REQUIRES DEVELOPMENT WORK

Recent developments have shown the possibility of performing in-situ IR measurements in combination with neutron reflectometry. There are several potential techniques that could be incorporated and as such a range of possible developments exist.

An example reference:

Skoda et al. RSC Adv., (2017), 7, 34208 DOI: 10.1039/c7ra04900e

xii. Shear Cell / Rheometer (priority = 3/2)

This equipment would be shared with SANS instruments with adaptations to look at surfaces. See LoKi SEE document.

xiii. Pool equipment (cryostat, magnets etc) (priority = 2)

Scientific case	Occasional experiments may require SEE from the ESS pool. These items could include an electromagnet (<1T), a vacuum chamber & cryostats etc.
Sharing Possibilities	This equipment is not core to the FRIEA Science case therefore would only be accessed through the pool and rarely used.
Required specification	o Relevant adaptations for mounting samples with a horizontal surface

Service requirements	o Liquid Helium o CCR compressors o Helium gas o Vacuum pumps
Integration requirements	o Standardised mounting for rapid change-over of pool equipment o the Cave design will try to incorporate a Sample Environment Labyrinth if possible. o Helium recovery system?

xiv. High pressure cells (priority = 2)

REQUIRES DEVELOPMENT WORK

High pressure gas cells are potentially required. FREIA would be able to use a pool gas handling system.

xv. In Over-flowing cylinder (priority = 1)

REQUIRES DEVELOPMENT WORK

This is currently a specialist technique that is not routine and only used by 1-2 research groups. However, the technique has the potential to be able to take advantage of FREIA and could be more generally useful for a wider user base.

xvi. In-situ Spin Coater or other processing techniques (priority = 1)

REQUIRES DEVELOPMENT WORK

The potential for high speed measurements on FREIA mean that it may be possible to investigate thin films during processing. For example, spin coating of polymer films. The techniques are likely to be quite challenging and would require significant development, with specifications that are defined by the experiment.