Dynamic REIXS Liquid Cell

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NSERC CRSNG

Canadian Light Source Inc.

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Introduction

The vast majority of | biological chemical interfacial ecological colloidal medical | processes occur in wet environments

These applications motivate the study of electronic structure of liquid solutions using soft x-ray emission

Most liquids have high vapour pressure:
- incompatible with required vacuum conditions

Approaches

Free Liquid MicroJet
Injected directly into the vacuum
Turbulent
Far from thermodynamic equilibrium
Vapour sheath

Static Cell
Biological radiation damage
Film Development
Local heating
- Bubble formation
- Temperature control

Flow-Through Cell
Refreshed by a pressure gradient,
Responds to stress

REIXS Beamline

The Resonant Elastic and Inelastic X-ray Scattering (**REIXS** shown above) beamline currently under construction at the Canadian Light Source (**CLS**) will be outfitted with the flow cell apparatus capable of spectroscopy of liquids under ultrahigh vacuum conditions.

The REIXS beamline will have an energy range of 80-2000 eV with a tens of microns scale spot size from an elliptically polarizing undulator source.

It is expected that from time to time the 100 nm membrane separating the liquid sample from the ultrahigh vacuum environment will rupture during operation due to the pressure drop across it. Such an event may be potentially harmful to the optical detector housed in the vacuum chamber. We assess these risks.

Abstract

Compared to studies of solids or gases, research into the electronic structure of liquid solutions is a relatively recent field. Although vacuum-incompatible and technically challenging, spectroscopy of liquid phase materials is desirable for the many biological, chemical and medical processes which occur in wet solutions. The Resonant Elastic and Inelastic X-ray Scattering (REIXS) beamline currently under construction at the Canadian Light Source (CLS) will be outfitted with an apparatus capable of spectroscopy of liquids under ultrahigh vacuum conditions. A flow-through cell, in which the sample is steadily refreshed by a pressure gradient, removes many of the problems associated with conventional static cells, in which radiation exposure may easily damage and locally heat the sample causing bubble formation and disallowing temperature control. We present our flow cell setup for spectroscopy on liquids and liquid-solid interfaces.

The REIXS beamline will have an energy range of 80-2000eV with a tens of microns scale spot size from an elliptically polarizing undulator source. Photons enter the flow cell through a 100nm silicone nitride membrane. Emitted X-rays proceed through this same window and are collected in the spectrometer.

The difference in pressure between the outlet and the inlet reservoirs moves material through the circuit. Previous apparati operated at atmospheric pressures resulting in a large pressure gradient across the thin membrane. With this design, the inlet reservoir sets the pressure within the line. Standard operating procedure will be to maintain the pressure in the line just above the material's vapourization pressure, although users will have the ability to vary this condition. The force on the window can thus be minimized while maintaining a liquid phase sample.

In case of a membrane rupture the circuit volume has been reduced wherever possible. The channels are fitted with fast closing isolation valves both upstream and downstream of the copper sample cell. The valves are triggered by a pressure sensor and have a closing time of 5 ms. Our free jet formation calculations predict that a negligible amount of sample is contributed within this time.

We have preformed pressure predictions indicating a manageable rise in pressure in the case of a rupture. Upon membrane failure, a pressure wave passes through the liquid reducing its pressure and causing a loss of thermodynamic equilibrium. As a result the liquid begins to boil. Boiling is initiated at nucleation sites (typically solid/liquid or liquid/gas interfaces). The heat required for evaporation and cavitation is obtained from the liquid itself. Bubbles grow with expansion and eventually disperse the cooled liquid. There is no environmental temperature to keep them in the liquid state and the liquid freezes. It has been previously observed that a large fraction of the liquid freezes upon vacuum exposure. Ice blocks the orifice and sample escapes slowly after initial exposure. To protect optical instrumentation from what material is emitted a fast shutter valve (10ms) is inserted to partition the vacuum chamber until UHV is reestablished. The windows can be quickly replaced by retracting the flow cell manifold into a separately venting chamber.

Liquid Circuit Design

For **photon-in/photon-out** experiments
Retractable arm for easy replacement of windows without venting the measurement
Pressure difference betweeen inlet and outlet reservoirs controls flow rate

Designed around the **100 nm** thick silicon nitride **window**
Clamped by the cell block

Separates liquid from ultrahigh vacuum of REIXS spectrometer and beamline

Pressure in the line set as high as atmospheric
or as low as just above the vaporization pressure

Force on membrane can be minimized while maintaining liquid state

Large pressure gradients and prolonged irradiation cause **ruptures**

Fast Shutting Valves

Vacuum-side Valves
cut of the source of fluid
close at a speed of 10 ms
Upstream and Downstream Valves
defending vacuum chamber equipment
isolation valves close in 5 ms
ensure free jet cut off

Free Jet Stage

Until the downstream valves close the rupture will act like the orifice of a free jet.

Isentropic Compressible Jet

$$G = \frac{\dot{m}}{A} = \rho v$$
$$= p\left(\frac{V}{c}\right)\sqrt{\frac{\gamma}{RT}}$$
$$= \frac{p_o}{\sqrt{T_o}}\sqrt{\frac{\gamma}{R}}\frac{M}{\left(1 + \frac{\gamma-1}{2}M^2\right)^{(\gamma+1)/[2(\gamma-1)]}}$$
$$= C\frac{p_o}{\sqrt{T_o}}$$

Choked Jet Flow

$$G^* = \left(\frac{\dot{m}}{A}\right)_{max}$$
$$= \frac{p_o}{\sqrt{T_o}}\sqrt{\frac{\gamma}{R}}\sqrt{\left(\frac{2}{\gamma+1}\right)^{(\gamma+1)/(\gamma-1)}}$$
$$= 0.04042\frac{p_o}{\sqrt{T_o}}$$

Assuming the entire window blows out, in the time it takes for the vacuum-side valve to close only 0.22% molecules originally upstream of the valves can

Catastrophic Rupture Dynamics

Immediate vaporization of liquids is considered in the context of containment failure of highly pressurized liquids. Vessel rupture may result in total and instantaneous loss of liquid inventories in the form of a rapidly expanding cloud. A catastrophic event is said to occur when a significant portion of the vessel contents is lost in an infinitesimally short time. Notice that this is conceptually cler to our situation than a compressible jet.

The liquid depressurizes
A fraction of the liquid flashes to form a vapor
The previous step brings the remaining liquid to its boiling point
The expanding vapor entrains part of the liquid as solid droplets

Upon failure, a pressure wave passes through the liquid reducing its pressure and causing a loss of thermodynamic equilibrium. As a result the liquid starts to boil. Boiling is initiated at nucleation sites (usually interfaces). The boiling causes gaseous bubbles to form in liquid. This is called cavitation. The heat required for evaporation and cavitation is obtained from the liquid itself. The bubbles grow as expansion flashes and eventually break the liquid into cooled chunks which have contributed all of their internal energy to the expansion. In our case, there is no environmental temperature to keep them in the liquid state and they freeze.

$$x_H = \frac{h_{f1} - h_{f2}}{h_{g2} - h_{f2}}$$

Using standard temperature-pressure tables the flashed vapour fraction is estimated as 0.0419.
96% is instantly frozen upon the event of a catastrophic rupture.

Ice Obstruction

This compares well with previous findings. It has been observed in previous apparatii that only 0.94% of the liquid in the lines is ejected into the vacuum chamber. This is because immediately upon vacuum exposure the liquid freezes effectively blocking the orifice. This obstruction and the effects of cell geometry have not been included in our estimates.

Pressure Rise

Before the window fails the measurement chamber (internal volume = 0.0641m³) is at equalibrium with a pressure on the order of 10^{-11} mbar at room temperature.

Upon a rupture, free jet flow during valve closure supplements the entire contents of the line below the isolation point. Only 4.2% of this matter is vaporized and free to raise the chamber pressure.

After sample exposure the measurement chamber is estimated to be at 10^{-5} mbar.