Neutron and X-ray scattering methods developed by this research group are used to study the structure and dynamics on the nanometre and picosecond space/time scales. Adsorption, self-assembly at interfaces, polymers, the imitation of biomineralisation phenomena using "template" molecules and, most recently, the structure and denaturation of proteins at interfaces are current areas of interest. The insights gained are used to guide chemical synthesis in making new materials with interesting physicochemical properties. One recent highlight has been the first determination of the thermodynamic parameters for protein denaturation in the 50 Angstroms surface layer of a protein solution. By comparison with denaturation in the bulk, the contribution of the surface forces can be measured quantitatively. Another is the first measurement of the interfacial structure of an emulsion surface by neutron reflectivity. "Micro breaking" of the emulsion at the interface with a solid surface has been detected.

Our collaboration with Orica Ltd on the structure and stability of high internal phase oil/water emulsions has produced scientifically interesting and practically useful information. We continue to show that structural relationships at the nanoscale have importance for rheological and other properties. Scattering methods continue to give new quantitative information about how the surfactant stabilises these systems. Studies by the same methods on milk fat membrane in collaboration with the Dairy Research Corporation and Food Science Australia have continued using selective deuteration of membrane components.

Surface Structure of Protein Solutions

We have made the first studies of thermal denaturation at the air-water interface of protein solutions. Measurements up to 70°C were possible using the energy dispersive reflectometer at the ISIS pulsed neutron source. The energy dispersive nature of this instrument has provided the unique advantage for these measurements to overcome the effects of evaporation and condensation. Denaturation of both lysozyme and b-lactoglobulin in the 50 Angstroms surface layer occurs at temperatures up to 20°C lower than in the bulk solution. Furthermore by using the thickness of the denaturing layer as an ordered parameter we have been able to calculate the surface contribution to the enthalpy of denaturation of these proteins. The work has important consequences for protein as templates in biology and in connection with protein fouling of surfaces. Work has begun on the chemical denaturation of interfacial layers. This looks promising. *(with M.J. Henderson, A. Perriman, and S.A. Holt [ISIS, Rutherford Appleton Lab., UK])*

Synthesis and Characterisation of Emulsions using Pure and Mixed Surfactants

Our previous work has shown that mixtures of surfactants may be important for controlling both the rheology and the stability of high internal phase emulsions. Work this year on several series of polyisobutylene surfactant and SMO surfactant mixtures have shown that such mixtures can produce properties unobtainable with pure surfactants. Our methods of neutron contrast variation have been used to

identify the interfacial structures from many of these mixtures. Correlation of these nanostructure measurements with rheological, surface tension and other measurements is revealing interesting phenomena. In related work the properties of these surfactants at the air-water interface has been studied by classical methods and reflectometry. This has shown that for insoluble surfactants in general, it is necessary to invoke imperfections in the spread monolayers such as aggregation, lateral segregation and polynya formation. *(with M.J. Henderson, P.A. Reynolds, and E.P. Gilbert [ANSTO, Lucas Heights])*

Growth of Highly Ordered Mesoporous Films

Our studies on the growth of highly ordered silicate films have now disentangled two mechanisms leading to film growth under different physical conditions. The millisecond refelctometer in our lab (see below) has greatly aided the study of the mechanism. We are now able to record data on the time scale of a few minutes (for the whole reflectivity pattern) and different phases in the growth process for hermetically sealed air-water interfaces have been recorded. Currently the mechanism of the "switch" for the surfactant sphere to rod transition is under study since short induction times are now accessible with our instruments. An exciting recent development is the growth of titanium dioxide films *at the air-water interface* using new chemistry. *(with M.J. Henderson, D. King)*

Millisecond Reflectometer Development

The tests on the "Bragg rotor" version of the millisecond reflectometer have now been successfully concluded and a major report written. At the same time the instrument has been moved to the GX-13 rotating anode source to obtain the highest possible laboratory X-ray intensities. At that source we have also tested dispersive energy diode detectors as an alternative to the Bragg rotor system for "low count rate" si*tuations*. By working away from the critical edge, counting with either the "Iglet" detector or the avalanche photo-diode system (developed for the Bragg rotor) is *now* possible. We have found that for the avalanche photo-diode system count rates up to 0.5 MHz are acceptable without serious double quantum counting and with the Iglet count rates (at 2% energy resolution) up to 50 kHz are acceptable. With these systems we have been able to record X-ray reflectivity data, with correct scale factor, *and able to be processed* by our suite of programs. *(with T.L. Dowling, M.J. Henderson, D.J. King)*

Ion and Solvent Transfers at Nickel Hydroxide Films Exposed to LiOH

The intercalaction/deintercalation of ion and solvent within the $Ni(OH)_2$ film matrix during oxidation and reduction is crucial to the response time of any device based on this material, e.g. the alkaline battery. Our previous study of this solid/liquid interface enabled a unique solution to the ion and solvent transfers during the charge/discharge cycle -under potentiodynamic control- using the combined electrochemical quartz crystal microbalance and probe beam deflection instrument (constructed at the University of Leicester). In order to reveal potential *vs.* time-dependent processes, we have now applied a potentiostatic control function and extracted the time dependencies of ion and solvent fluxes in a chronoamperometric experiment. Combining the EQCM/PBD-derived fluxes of individual mobile species with their molar volumes, the implied changes in film volume, driven by redox switching can be estimated. *(with M.J. Henderson, and A.R. Hillman, H. French [U. Leicester, UK])*

X-ray Reflectivity Study of Milk Proteins (dominated by □-casein) at the Air-milk Serum Interface and their Response to Fat Content and Temperature

The surface structure of dispersed emulsions play a key role in stability of the system. Proteins being one of the most important surface active components in foods stabilise interfaces by self-interaction, resulting in a stiff visco-elastic adsorbed layer. These interactions are sensitive to disruptive effects of lipids. Previous kinetics studies by the group (Holt, S.A. and White, J.W., 1999. *Phys. Chem. Chem. Phys.*, 1, 5139-5145) using the X-ray reflectivity method to investigate the surface adsorption of milk proteins indicate that □-casein had a stronger affinity for the air-liquid interface compared to whey proteins. It has been shown that initially a dense protein layer, with the thickness of 20Å is formed, then a second more diffuse layer with lower volume density of protein follows. Here we report the conformational changes occurred at the air-milk serum interface due to the effects of milk fat content, temperature and the milk preparation technique (*i.e.* homogenisation *vs* microfluidisation).

In the effect of fat content on the adsorption of protein into the interface the key conclusion is that at lower temperatures the surface composition remains unchanged. The compositional changes, however, become significant at room temperature indicating adsorption of less reflective-water-soluble components into the surface layer. Repulsive interactions between casein aggregates are also involved. Microfluidised samples, having the advantage of smaller particle size, prove to be more stable to fat or temperature effects compared to the corresponding homogenised milks. *(with R. Heidari)*

Small Angle X-ray Scattering Studies on the Milk Fat Globule Membrane (MFGM)

The functional properties of fats are very important in many food systems. The type of dispersion, the solid-liquid fat ratio and the occurring crystal form have a strong influence on the behaviour of the entire edible fat system. The milk fat globule membrane (about 10nm in cross-section) consists of a complex mixture of proteins, glycoprotein, enzymes, phospholipids, triglycerides, cholestrol and other minor lipids. It is generally presumed that saturated fats and triglycerides contract when they solidify or transform from an unstable to a more stable crystalline form. However, considerable expansion (up to 20%) in many saturated triglycerides and hydrogenated fats have also been reported (Hvolby 1974).

Present study on MFGM using small angle scattering method has consistently indicated the presence of a crystal with a Bragg spacing of 41Å and a melting point of 37°C corresponding to a minor triglyceride in milk. The small angle scattering from this crystal, revealed in all milk samples tested here (*i.e.* both homogenized and microfluidised milks), has not yet been reported in the literature. More detailed SAXS experiments with simulated MFGM will provide quantitative information on possible involvement of other MFGM components in the formation of the observed crystal and its biochemical significance. *(with R. Heidari, T.L. Dowling)*

http://rsc.anu.edu.au/white.html