

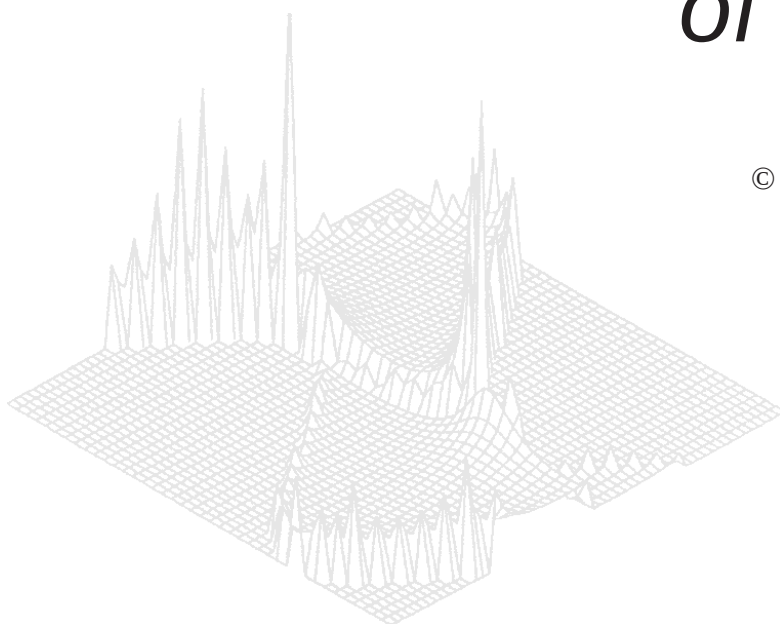
---

CSIRO PUBLISHING

---

# *Australian Journal of Physics*

Volume 50, 1997  
© CSIRO Australia 1997



A journal for the publication of  
original research in all branches of physics

**[www.publish.csiro.au/journals/ajp](http://www.publish.csiro.au/journals/ajp)**

All enquiries and manuscripts should be directed to

*Australian Journal of Physics*

**CSIRO PUBLISHING**

PO Box 1139 (150 Oxford St)

Collingwood

Vic. 3066

Australia

Telephone: 61 3 9662 7626

Facsimile: 61 3 9662 7611

Email: [peter.robertson@publish.csiro.au](mailto:peter.robertson@publish.csiro.au)



Published by **CSIRO PUBLISHING**  
for CSIRO Australia and  
the Australian Academy of Science



## Neutron and X-ray Reflectometry: Solid Multilayers and Crumpling Films\*

*Anthony S. Brown,<sup>A</sup> Stephen A. Holt,<sup>B</sup> Paul M. Saville<sup>C</sup> and John W. White<sup>A</sup>*

<sup>A</sup> Research School of Chemistry, Australian National University,  
GPO Box 414, Canberra, ACT 2601, Australia.

<sup>B</sup> School of Physics, Australian Defence Force Academy, University College,  
University of New South Wales, Canberra, ACT 2600, Australia.

<sup>C</sup> Department of Chemistry, University of Leicester, University Road,  
Leicester, LE1 7RH, United Kingdom.

### *Abstract*

The structures of films and interfaces at the molecular level can be determined from specular reflectivity measurements using neutrons and X-rays. A general introduction to the principles of neutron and X-ray reflectometry is given. Illustrative examples of the application of neutron and X-ray reflectometry to problems of chemical and physical interest are presented.

### 1. Introduction

Neutron and X-ray reflectometry have emerged in recent years as the premier techniques for investigating the structures of surfaces, interfaces and thin films at the molecular level. Reflectometry is being applied to problems in very diverse fields of research, and with Australia's increasing capability in this area and greater access to instruments it seems timely to raise general awareness of reflectometry within the Australian scientific community. The aim of this paper is to provide a very general introduction to the principles of reflectometry and the sort of information it can provide, together with a series of illustrative examples drawn from our recent work at the Research School of Chemistry. The focus will be on specular reflectivity, a technique which can provide details of film and interface structures normal to the plane. Related techniques, such as diffuse and off-specular reflectivity and grazing incidence diffraction, can yield information about in-plane structure and crystallinity, but are beyond the scope of the present article: recent reviews of these rapidly advancing areas of research are available in the literature (e.g. Dietrich and Haase 1995, and references therein; Als-Nielsen *et al.* 1994; Foster 1993).

Australia has a significant stake in the newly commissioned neutron reflectometer known as SURF at the Rutherford Appleton Laboratory in the UK, as well as easy access to the older and higher-resolution instrument known as CRISP. At the Research School of Chemistry, in collaboration with the Australian Defence Force Academy, we are currently commissioning Australia's first X-ray reflectometer, designed as a prototype for possible implementation at the Australian National

\* Refereed paper based on a contribution to the ANZIP 20th Condensed Matter Physics Meeting held at Charles Sturt University, Wagga Wagga, NSW, in February 1996.

Beamline at the Photon Factory in Japan. Australia is also currently involved in the design process for instruments to be built at the Advanced Photon Source in Chicago, including planning for the construction of an X-ray reflectometer.

## 2. Basic Concepts

Neutrons and X-rays undergo reflection and refraction at the interface between two media having different refractive indices. Reflectivity measurements provide a sensitive probe of the variation of refractive index (and hence chemical composition) through interfaces. The refractive index  $n$  of a material can be written as:

$$n = 1 - (\delta - i\beta). \quad (1)$$

The imaginary component arises when the material is absorbing. The real part of  $1 - n$  is usually of the order of  $10^{-5}$ – $10^{-6}$ , and because  $\text{Re } n < 1.0$  there is a critical angle of incidence below which total reflection of X-rays and neutrons occurs.

Different sign conventions for the X-ray and neutron cases have led to some confusion in the literature. Hayter and Mook (1989) have introduced a convention applicable to both neutron and X-ray refractive indices which we will follow here. Accordingly, the real and imaginary components of the refractive index for a material are given for neutrons as:

$$\delta = \frac{\lambda^2}{2\pi} N b = \frac{\lambda^2}{2\pi} N_A \sum_i \frac{\rho_i}{A_i} (b_{0,i} + b'_i), \quad (2)$$

$$\beta = \frac{\lambda \mu_N}{4\pi} = \frac{\lambda^2}{2\pi} N_A \sum_i \frac{\rho_i}{A_i} |b''_i|, \quad (3)$$

and for X-rays as:

$$\delta = \frac{\lambda^2}{2\pi} r_0 \rho_e = \frac{\lambda^2}{2\pi} r_0 N_A \sum_i \frac{\rho_i}{A_i} (f_{0,i} + f'_i), \quad (4)$$

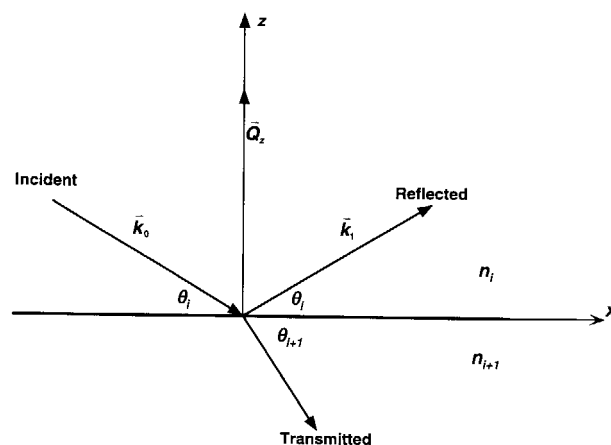
$$\beta = \frac{\lambda \mu_X}{4\pi} = \frac{\lambda^2}{2\pi} r_0 N_A \sum_i \frac{\rho_i}{A_i} |f''_i|, \quad (5)$$

where  $N_A$  is Avogadro's number,  $r_0$  the classical electron radius ( $2.82 \times 10^{-13}$  cm),  $\lambda$  the wavelength of the incident radiation,  $\rho_i$  the physical density in the sample of element  $i$  with atomic weight  $A_i$ , and  $\mu_N$  and  $\mu_X$  the neutron and X-ray linear attenuation coefficients, respectively.

The neutron refractive index depends upon the bound coherent scattering length  $b_0$ , and the real and imaginary dispersion terms  $b'$  and  $b''$ , where the imaginary component is related to the absorption and incoherent scattering cross sections (Penfold 1991a). The dispersion corrections are usually negligible and  $\beta$  can often be ignored. The X-ray refractive index depends (analogously) upon the atomic scattering factor  $f_0$  and the dispersion terms  $f'$  and  $f''$ . In the reflectivity experiment only forward scattering is of interest and  $f_0$  is then equal to the atomic number. Absorption is more problematic for X-rays than neutrons:  $f'$  and

$f''$  are usually not negligible and  $\beta$  can consequently be significant, particularly for heavier elements. It is convenient to use the quantities  $Nb$  and  $r_0\rho_e$ , where  $N$  is the number density of scattering centres and  $\rho_e$  is the apparent electron density (including the effects of the real dispersion correction). Because of the close analogies between the neutron and X-ray expressions, we will use the term 'scattering length density' to refer to both  $Nb$  and  $r_0\rho_e$  though it strictly applies only to the former. The modulus signs in equations (3) and (5) allow tabulated values of  $b''$  and  $f''$  to be taken from any source as described by Hayter and Mook (1989).

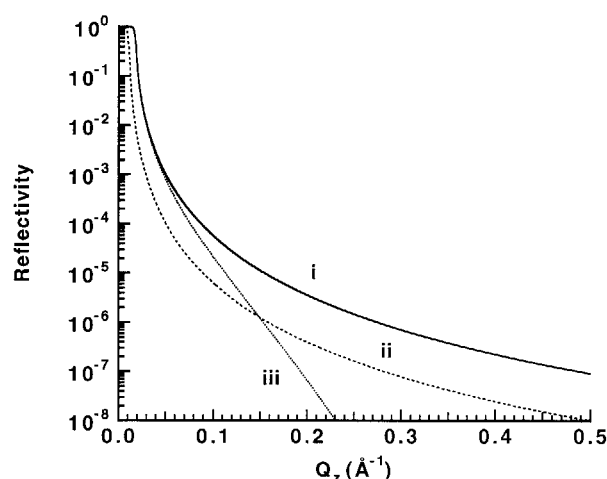
The variation of atomic number through the periodic table is obviously smooth and orderly, while the variation of neutron scattering length is apparently random even between isotopes of the same element. Neutron and X-ray reflectivity therefore display a very different sensitivity to sample composition and may provide complementary information which can be used to great effect.



**Fig. 1.** Geometry of the specular reflection experiment.

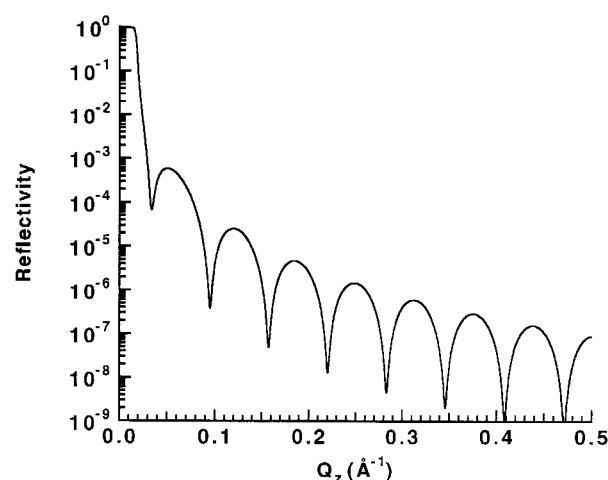
The geometry for a reflectivity experiment is illustrated schematically in Fig. 1. Radiation with wavevector  $\vec{k}_0$  is incident on the interface between two media with refractive indices  $n_i$  and  $n_{i+1}$  at an angle  $\theta_i$ . In general, some of the radiation will be reflected with wavevector  $\vec{k}_1$ , and some transmitted. The calculation of the intensities of reflected and transmitted radiation is formally equivalent to the solution of the Schrödinger equation for the interaction of a particle with a potential barrier (Schiff 1955). The transmission and reflection coefficients depend upon the height and thickness (scattering length density and thickness) of the barrier and the momentum of the incident radiation (photons or neutrons). In the case of specular reflection the angle of incidence is equal to the angle of reflection, the wavevectors  $\vec{k}_0$  and  $\vec{k}_1$  are confined to the  $xz$  plane and are equal in magnitude, and the magnitude of the scattering vector is  $Q_z = |\vec{Q}_z| = |\vec{k}_0 - \vec{k}_1| = (4\pi/\lambda)\sin\theta$ . Because of these constraints, specular reflection yields information on the variation of composition through the interface and normal to it.

The essence of a specular reflectivity experiment is to measure the reflectivity  $R$  of the sample as a function of scattering vector magnitude  $Q_z$ , where the reflectivity is defined as the ratio of intensities of reflected and incident beams. Fig. 2 shows simulated reflectivity profiles for two air/liquid interfaces illustrating several pertinent features. The reflectivity of an ideally smooth, sharp interface (known as the Fresnel reflectivity) is proportional to  $Q_z^{-4}$ , and this behaviour imposes several constraints on the measurement and analysis of reflectivity profiles. One consequence of the Fresnel reflectivity is the large dynamic range which must be accommodated by the detection and counting system: reflectivities can vary by 6–8 orders of magnitude depending upon the sample. A second consequence is that the range of useful scattering vectors accessible in the experiment (and hence the ability to resolve features in the composition profile) is limited by how quickly the reflectivity falls to background. Backgrounds become significant for neutrons at  $Q_z$  about  $0.25\text{--}0.35\text{ \AA}^{-1}$ , while for X-rays the range is extended by a factor of about three (Lu *et al.* 1996). The other feature to note in Fig. 2 is the presence of a critical angle  $Q_{z,c}$ , below which the incident radiation is completely reflected by the interface, i.e. the reflectivity is unity. The critical angle is larger for materials having higher scattering length density. When an interface is rough or diffuse the reflectivity falls off even more rapidly than the  $Q_z^{-4}$  dependence of the Fresnel reflectivity [see Fig. 2(iii)].



**Fig. 2.** Simulated reflectivity profiles for air/liquid interfaces. Fresnel reflectivities (i.e. interface roughness is  $0.0\text{ \AA}$ ) are shown for air/liquid interfaces where the scattering length densities are (i)  $6.0 \times 10^{-6}\text{ \AA}^{-2}$  and (ii)  $2.0 \times 10^{-6}\text{ \AA}^{-2}$ . The effect of interface roughness is shown in (iii), where the interface in (i) has been modified by a roughness of  $10\text{ \AA}$ . Note that a background has not been included in the simulation.

The effect of adding a thin film of another material to the interface is shown in Fig. 3. Interference between beams reflected from the two interfaces now present gives rise to modulations in the reflectivity known as ‘Kiessig fringes’. The fringe spacing is related to the film thickness, while the depth of the oscillations is dependent on the magnitude of the differences in scattering length densities of the air and film and between the film and substrate (Foster 1993).



**Fig. 3.** Simulated reflectivity profile for a monolayer film at the air/liquid interface. The film is 100 Å thick with a scattering length density of  $3.0 \times 10^{-2} \text{ Å}^{-2}$  while that of the subphase is  $6.0 \times 10^{-6} \text{ Å}^{-2}$ . Both interfaces are sharp (i.e. roughnesses are 0.0 Å) and no background has been included.

### 3. Instrumentation

Reflectometer designs fall into two broad categories: energy-dispersive or angle-dispersive. The CRISP and SURF neutron reflectometers (Penfold 1991*b*) at the Rutherford Appleton Laboratory are typical of energy-dispersive instruments, in which  $Q_z$  is varied by having an incident beam composed of a range of different wavelengths impinge on the sample at a fixed angle of incidence. This has a number of advantages, including short data collection times (since the reflectivities at each  $Q_z$  are recorded simultaneously) and constant beam footprint on the sample. It is a geometry which is, perhaps, less well-suited to X-ray reflectometers because of the difficulties associated with generating sufficient intensity of white radiation, although several energy-dispersive X-ray instruments have been described in the literature (Metzger *et al.* 1994; Roser *et al.* 1994) and appear to yield excellent results.

Angle-dispersive instruments achieve variation of  $Q_z$  with a fixed wavelength source by varying the angle of incidence. Our X-ray reflectometer is an angle-dispersive design, shown schematically in Fig. 4 and described by Jamie *et al.* (1995). It has a horizontal sample stage which allows measurements to be made on liquid surfaces and liquid-supported films as well as solid samples. Measurements can be made at angles of incidence in the range 0.0–3.4 degrees (0.00–0.48 Å<sup>−1</sup> for CuK<sub>α</sub> radiation) in steps of 0.0007 degrees (0.0001 Å<sup>−1</sup>).

### 4. Data Analysis

The observation of Kiessig fringes in a reflectivity profile can allow direct determination of the film thickness,  $d$  (Foster 1993):

$$d = \frac{2\pi}{\Delta Q}, \quad (6)$$

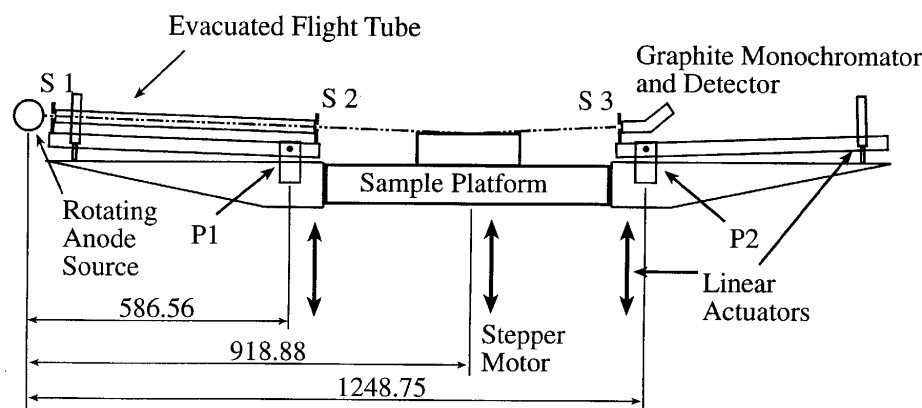


Fig. 4. Schematic view of the X-ray reflectometer recently commissioned at the Research School of Chemistry, showing the features of an angle-dispersive design. The dimensions are in millimetres. P1 and P2 refer to the points about which the flight tube and detector arms pivot.

where  $\Delta Q$  is the spacing between two successive minima in the profile. The example in Fig. 3 has  $\Delta Q = 0.0628 \text{ \AA}^{-1}$ , corresponding to a film thickness of  $100 \text{ \AA}$  (as used in the simulation).

If the sample contains regularly repeated layers, such as a Langmuir–Blodgett film or a multiple quantum well device, constructive interference results and Bragg peaks become evident in the reflectivity profile. The characteristic spacing of the repeat unit  $d$ , can be calculated from the peak positions thus (Foster 1993):

$$d = \frac{2\pi}{Q_{\text{corr}}}, \quad (7)$$

where  $Q_{\text{corr}} = (Q_{\text{ex}}^2 - Q_c^2)^{1/2}$  is the peak position  $Q_{\text{ex}}$  corrected for the shift caused by the presence of the total reflection region defined by the critical angle  $Q_c$ .

Further information can be obtained by more complex data analysis methods. A number of methods based on modelling the reflectivity profile have been developed, but a comprehensive survey of these is beyond the scope of this article. Descriptions of several alternative methods can be found in the literature (e.g. Foster 1993; Russell 1990; Penfold and Thomas 1990; Als-Nielsen *et al.* 1994; Lee and Milnes 1995; Pederson and Hamley 1994; Lu and Thomas 1995).

The approach used in our laboratory is that described by Penfold (1991*c*), based on methods developed in classical optics. The system of interest is modelled as discrete layers of uniform scattering material with three adjustable parameters per layer: the scattering length density, the layer thickness and the roughness or diffuseness of the interface with the adjoining layer. The reflectivity is then calculated using an optical transfer matrix method due to Abeles (1948). The parameters of the model are then adjusted iteratively to achieve the best least-squares fit to the data.

A major difficulty which arises in the analysis of reflectivity data is the loss of phase information in the experiment: the ‘phase problem’ common to all scattering experiments. Unfortunately it is not generally possible to find a

unique model to fit the data, and indeed it is often possible to find physically or chemically unreasonable models which fit the data well. Sivia *et al.* (1991) have listed a number of other consequences of the loss of phase information which can limit the chances of success in the modelling process.

## 5. Experimental Design

Careful experimental design can greatly enhance the likelihood of obtaining an unambiguous model. In the experimentalist's favour is the fact that a significant amount of prior knowledge about the sample is usually available. For example, in the preparation of a multiple quantum well device or Langmuir–Blodgett film the approximate composition and thickness of each layer may be known as well as the order in which various layers are deposited. Under such circumstances many completely inappropriate models can be immediately discarded and the modelling proceeds from a position of partial knowledge.

Suitable isotopic substitution of substrate and film material can help resolve model ambiguities in neutron reflectometry. The most common substitution for systems of chemical interest is deuteration of hydrogenous materials, though the possibilities are somewhat more restricted for non-hydrogenous systems. Varying the isotopic compositions of the various components of an interface in this way (and without otherwise disturbing the chemistry) leads to a number of different reflectivity profiles for the system which reduces model ambiguities by placing further constraints on the model. With the advent of synchrotron X-ray sources it is possible, in principle, to do the analogous experiment by measuring reflectivity profiles using incident radiation with wavelengths close to, and far from, the absorption edge for an element in the sample. By changing the apparent electron density in this way (i.e. varying  $f'$  in equation 4) a number of profiles may be obtained which will again impose constraints on the model.

## 6. Illustrative Examples

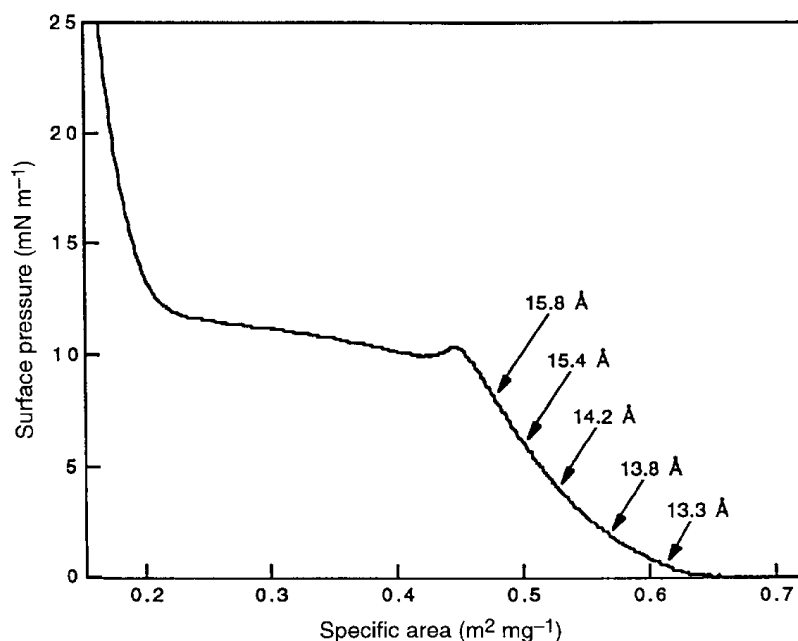
Our work with Langmuir films (thin films at the air/liquid interface) has been conducted using neutrons, while the commissioning of our new laboratory X-ray reflectometer has seen new interests developed in thin solid films of various sorts. Our applications of neutron reflectometry to the study of polymer surfactants are described in more detail in Saville *et al.* (1993, 1994, 1995), White *et al.* (1994) and Gentle *et al.* (1993). The X-ray results presented here are of a preliminary nature, since our modelling and simulation software is currently undergoing significant development to handle our X-ray data appropriately.

### *(6a) Surface Chemistry of Polymeric Surfactants at the Air/Water Interface*

The vast majority of our current knowledge of Langmuir films is based on the interpretation of surface pressure–area ( $\Pi$ -A) isotherm data, which can be thought of as the two-dimensional analogue of the more familiar pressure–volume (P-V) isotherm for three-dimensional systems. The area displayed in a  $\Pi$ -A isotherm can be the film area (the physical dimension of the film), the specific area (area per mass of surfactant in the film), or the molecular area (area occupied by a single molecule in the film).  $\Pi$ -A isotherms for simple short-chain surfactants generally show features characteristic of two-dimensional gaseous, liquid and solid phases with smooth transitions between them. At sufficiently high surface pressures,

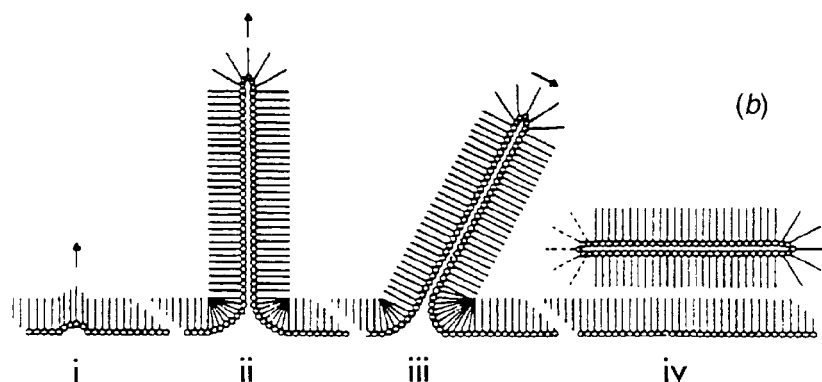
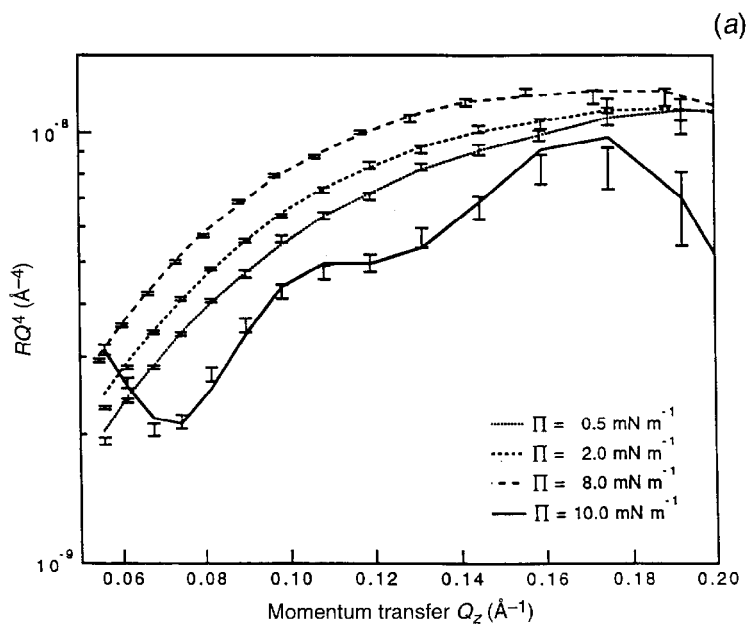
monolayer films of such materials will buckle and collapse to form multilayer structures.

In contrast to simple surfactants, polymeric materials are always composed of molecules having a range of molecular weights, and their molecular weights are typically much larger than those of simple surfactants. As a consequence, polymeric surfactants display a range of more complex temperature- and molecular weight-dependent  $\Pi$ - $A$  isotherm behaviours, which we wish to understand at the molecular level. Features of particular interest are: the transition from surfactant to non-surfactant behaviour as a function of molecular weight exhibited by some polymeric surfactants, the effect of polymer conformation (shape) on their properties, and their response to externally applied stresses such as pressure and temperature.



**Fig. 5.**  $\Pi$ - $A$  isotherm for a polystyrene surfactant, PS-OH, with average molecular weight  $973 \text{ g mol}^{-1}$ , showing the monolayer thicknesses determined by neutron reflectivity for the low-pressure fluid region. [Reproduced from Saville (1995).]

A typical isotherm for a polystyrene surfactant (PS-OH) with an average molecular weight of  $973 \text{ g mol}^{-1}$  is shown in Fig. 5. Neutron reflectivity profiles were measured at a number of surface pressures for fully deuterated PS-OH spread on two different subphases:  $\text{D}_2\text{O}$  and air contrast matched water (ACMW, a mixture of  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$  with scattering length density the same as for air). Modelling of the data indicated that the film is initially composed of a monolayer of surfactant with a thickness of  $13.3 \text{ \AA}$  at a surface pressure of  $0.5 \text{ mN m}^{-1}$ . As the film is compressed to higher surface pressures it becomes thicker as the polymer chains are forced to become closer packed and more linear in conformation. At a surface pressure of  $10 \text{ mN m}^{-1}$  the film ruptures and undergoes a structural transition to a monolayer overlaid by islands of trilayer.



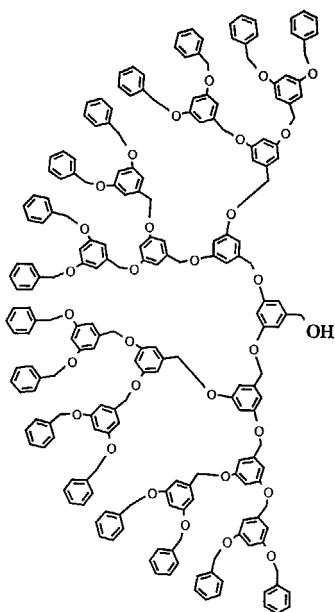
**Fig. 6.** (a)  $RQ_z^4$  plots for a film of deuterated PS-OH on ACMW in the fluid region at increasing surface pressures. The appearance of fringes at  $\Pi = 10 \text{ mN m}^{-1}$  indicates the collapse of the monolayer to form a trilayer structure. The figure is reproduced from Saville (1995). (b) Schematic representation of the mechanism proposed for the collapse of the monolayer film to a trilayer structure. As the surface pressure increases the film weakens (i), begins to fold (ii), bends over towards the surface (iii), before finally collapsing to form a trilayer (iv). The diagram has been adapted from Ries and Swift (1987).

The reflectivities of the film on an ACMW subphase are shown in Fig. 6a, where the contribution of the Fresnel reflectivity is removed by plotting  $RQ_z^4$  rather than  $R$ . The change from monolayer to multilayer is clearly indicated in the sudden appearance of fringes in the reflectivity profile between  $\Pi = 8.0 \text{ mN m}^{-1}$

and  $\Pi = 10.0 \text{ mN m}^{-1}$ . The likely structural changes of the film are shown schematically in Fig. 6b.

*(6b) Surface Chemistry and Conformation of Dendrimers*

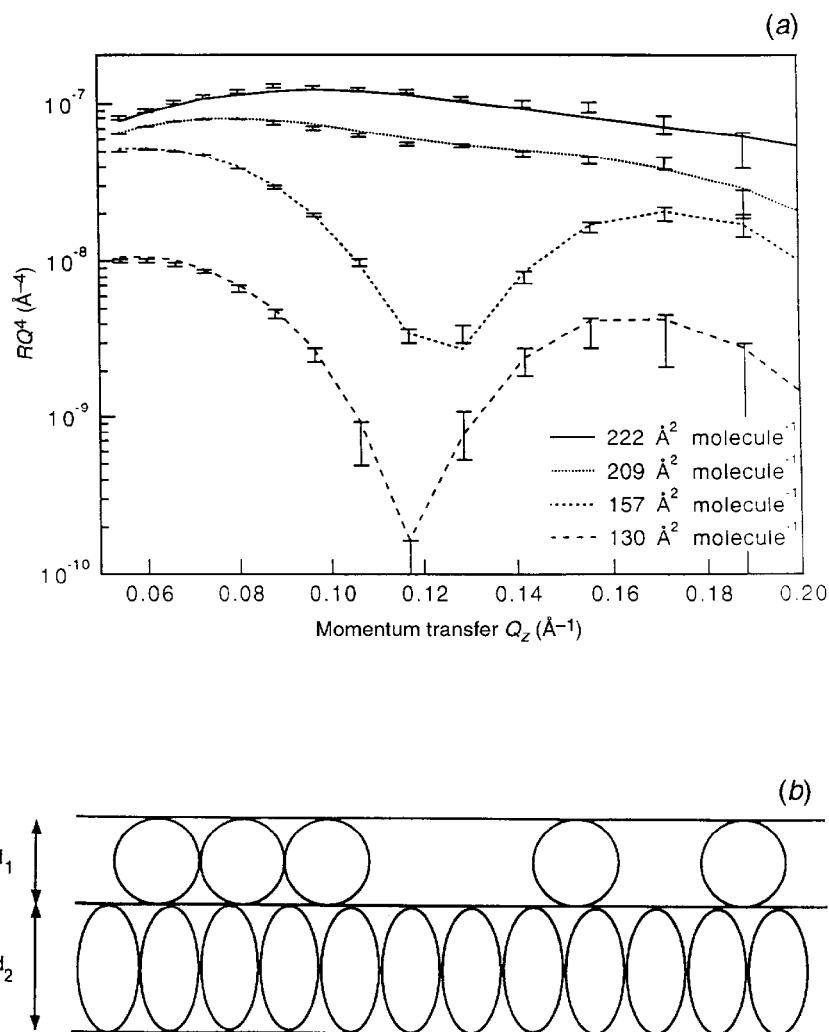
We have undertaken similar studies of the surface chemistry of a family of novel and relatively new polymers known as dendrimers. An example, designated as [G-4]-OH (fourth generation, -OH terminated), is illustrated in Fig. 7. These molecules may act as two-dimensional surfactants spread out on the surface, or pack in two dimensions at the interface, or adopt a variety of different shapes depending on the balance of externally applied stress and internal (including solution) forces.



**Fig. 7.** Molecular structure of a dendrimer, [G-4]-OH. [Reproduced from Saville (1995).]

The  $\Pi$ -A isotherms of these materials show pronounced maxima and minima. Surface reflectivity can give the structural correlates of this thermodynamic behaviour. The isotherm data for [G-4]-OH suggest that a monolayer film collapses to a multilayer structure at higher surface pressures, though in contrast to the PS-OH example, the final structure has a non-integral number of layers. This seemingly irrational result is explicable when the neutron reflectivity results are analysed. Reflectivity data were collected for Langmuir films spread on  $\text{D}_2\text{O}$  and ACMW subphases. The onset of multilayer formation is again easily seen in the  $RQ^4$  plots (see Fig. 8a) where fringe development occurs at surface pressures corresponding to molecular areas of between  $157$  and  $209 \text{ \AA}^2 \text{ molecule}^{-1}$ .

Modelling of the reflectivity data indicates that the molecules adopt a roughly spherical conformation at low surface pressures and become increasingly elongated as the surface pressure is increased. Further compression causes the film to rupture and undergo a transition to a bilayer structure in which the layer nearest the subphase is composed of close packed prolate spheroids and the overlayer



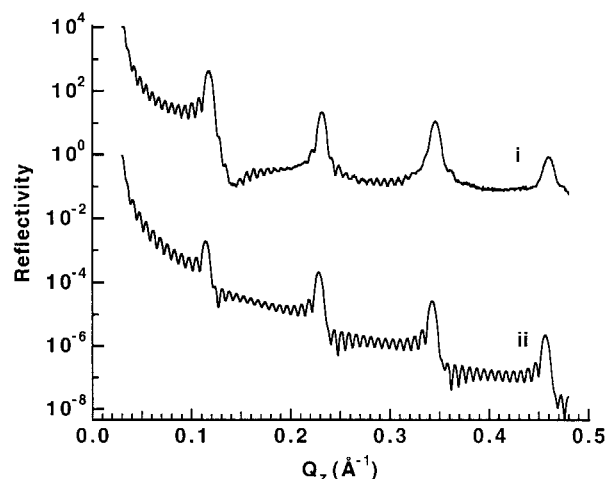
**Fig. 8.** (a)  $RQ_z^4$  plots for a film of partially deuterated [G-4]-OH on ACMW. The appearance of fringes at molecular areas less than  $209 \text{ \AA}^2 \text{ molecule}^{-1}$  indicates the collapse to a bilayer structure. (b) The bilayer structure proposed for [G-4]-OH on the basis of the neutron reflectivity modelling. The circles and ellipses represent a molecular envelope enclosing the individual molecules. [Reproduced from Saville (1995).]

is composed of sparsely packed near-spherical molecules. This model is shown schematically in Fig. 8b.

#### (6c) Solid Multilayer Films

Monolayer films at the air/liquid interface can be deposited onto solid substrates in a controlled manner to produce solid multilayer films (Langmuir-Blodgett (LB) films) with potentially useful chemical and physical properties. The X-ray reflectivity profile for an LB film composed of 31 layers of barium arachidate

deposited head-to-head and tail-to-tail onto a silicon substrate is shown in Fig. 9(i). The profile shows Kiessig fringes corresponding to a total film thickness of 853 Å, and Bragg peaks corresponding to a layer repeat distance of 55 Å, calculated according to equations (6) and (7). These figures accord well with what is known about the film from its preparation and the molecular dimensions of barium arachidate. A simulated profile calculated using estimated values of the relevant physical densities, compositions and interface roughnesses is also shown in Fig. 9(ii) for comparison. Further software developments already under way will allow us to model such multilayer materials directly.

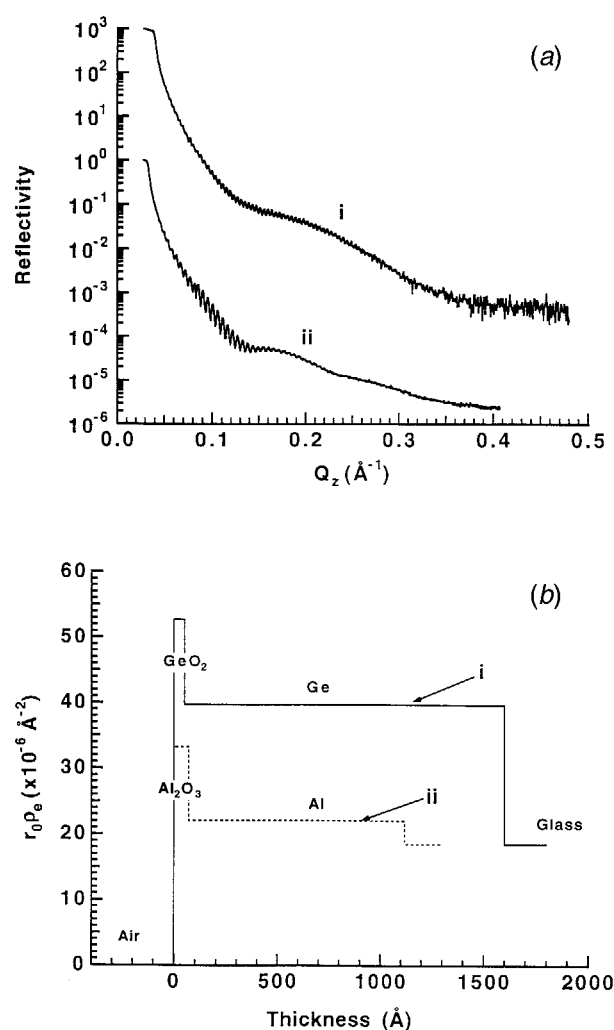


**Fig. 9.** (i) Experimental and (ii) simulated X-ray reflectivity profiles for an LB film composed of 31 layers of barium arachidate on a silicon substrate. Note that the experimental profile has been offset upwards arbitrarily for clarity.

#### (6d) Thin Metal and Semiconductor Films on Solid Substrates

Fig. 10a shows the X-ray reflectivity profiles for a germanium film and an aluminium film deposited onto glass substrates by a sputtering technique. The profile for the germanium film shows high-frequency modulations in the reflectivity corresponding to a total film thickness of 1600 Å, and a lower-frequency modulation indicating the presence of a second layer of material with a thickness of 50 Å, probably an oxide coating. The aluminium film shows similar features, with a total thickness of 1120 Å including a layer of 70 Å. Our preliminary modelling of these profiles indicates that they are extremely sensitive to the details of interfacial roughness. Proposed scattering length density profiles for these samples are shown in Fig. 10b.

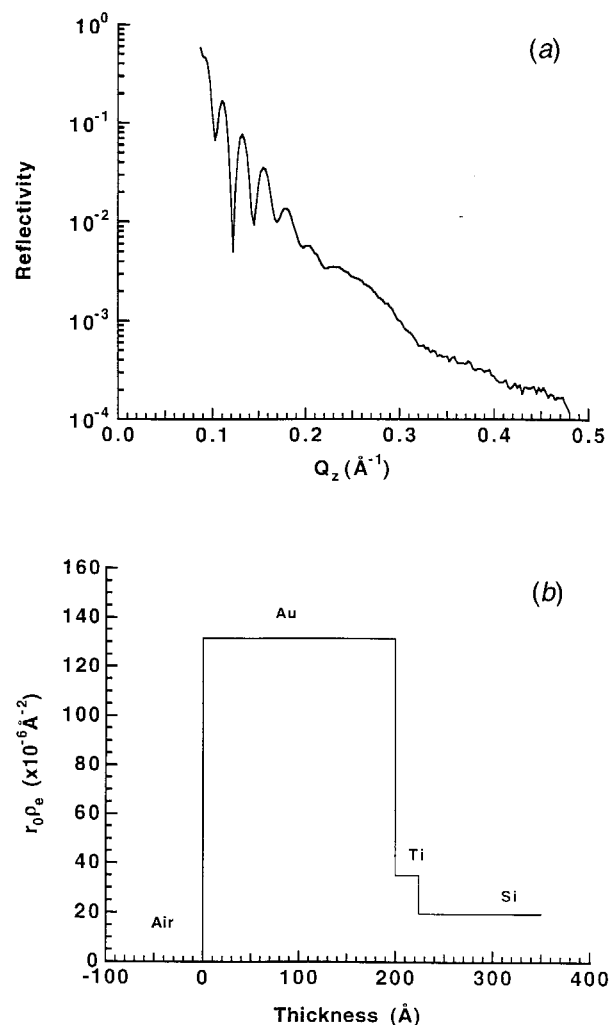
The final example illustrates a two layer film in which the thicknesses are somewhat smaller than the germanium and aluminium films. The reflectivity of a film composed of 200 Å gold overlaid on 24 Å of titanium and deposited on a silicon substrate is shown in Fig. 11. The large difference in scattering length density between gold and air is reflected in the deep valleys in the profile, and the length scale of 200 Å is easily seen in the fringe spacing. The proposed scattering length density profile for this sample is shown in Fig. 11b.



**Fig. 10.** (a) X-ray reflectivity profiles for thin solid films on glass substrates: (i) 1600  $\text{\AA}$  film of germanium and (ii) 1120  $\text{\AA}$  film of aluminium. Both films consist of two layers, the top layer probably an oxide. Note that (i) has been offset upwards arbitrarily for clarity. (b) The proposed scattering length density profiles corresponding to the reflectivities shown in (a). No interface roughnesses have been applied.

## 7. Concluding Remarks

Neutron and X-ray reflectometry provide a means of characterising surfaces, thin films and interfaces on a length scale of 10–2000  $\text{\AA}$  in a straightforward and non-destructive manner. In particular, specular reflectivity measurements are sensitive to the composition variation normal to the surface, film thickness and interfacial roughness.



**Fig. 11.** (a) X-ray reflectivity profile for a thin metal film consisting of 200  $\text{\AA}$  gold and 24  $\text{\AA}$  titanium deposited on a silicon substrate. (b) The proposed scattering length density profile corresponding to the reflectivity shown in (a). No interface roughnesses have been applied.

## References

- Abelès, F. (1948). *Ann. Phys. (Paris)* **3**, 33.  
 Als-Nielsen, J., Jacquemain, D., Kjaer, K., Leveiller, F., Lahav, M., and Leiserowitz, L. (1994). *Phys. Rep.* **246**, 251.  
 Dietrich, S., and Haase, A. (1995). *Phys. Rep.* **260**, 1.  
 Foster, M. (1993). *Crit. Rev. Anal. Chem.* **24**, 179.  
 Gentle, I. R., Saville, P. M., White, J. W., and Penfold, J. (1993). *Langmuir* **9**, 646.  
 Hayter, J. B., and Mook, H. A. (1989). *J. Appl. Cryst.* **22**, 35.  
 Jamie, I. M., Dowling, T. L., Holt, S. A., and Creagh, D. C. (1995). Proc. Third Congress of the Vacuum Society of Australia, pp. 25–7 (Vacuum Society of Australia).  
 Lee, E. M., and Milnes, J. E. (1995). *J. Appl. Cryst.* **28**, 518.  
 Lu, J. R., and Thomas, R. K. (1995). *Nucl. Instrum. Methods A* **354**, 149.

- Lu, J. R., Lee, E. M., and Thomas, R. K. (1996). *Acta Cryst. A* **52**, 11.
- Metzger, T. H., Luidl, C., Pietsch, U., and Vierl, U. (1994). *Nucl. Instrum. Methods A* **350**, 398.
- Pedersen, J. S., and Hamley, I. W. (1994). *Physica B* **198**, 16.
- Penfold, J. (1991*a*). Rutherford Appleton Laboratory Report RAL-91-023.
- Penfold, J. (1991*b*). *Physica B* **173**, 1.
- Penfold, J. (1991*c*). In 'Neutron, X-ray and Light Scattering' (Eds P. Lindner and Th. Zemb), p. 223 (Elsevier: Amsterdam).
- Penfold, J., and Thomas, R. K. (1990). *J. Phys.: Condens. Matter* **2**, 1369.
- Ries, H. E., and Swift, H. (1987). *Langmuir* **3**, 853.
- Roser, S. J., Felici, R., and Eaglesham, A. (1994). *Langmuir* **10**, 3853.
- Russell, T. P. (1990). *Mater. Sci. Rep.* **5**, 171.
- Saville, P. M. (1995). PhD thesis, Australian National University, Canberra.
- Saville, P. M., Gentle, I. R., White, J. W., Penfold, J., and Webster, J. R. P. (1994). *J. Phys. Chem.* **98**, 5935.
- Saville, P. M., Reynolds, P. A., White, J. W., Hawker, C. J., Fréchet, J. M. J., Wooley, K. L., Penfold, J., and Webster, J. R. P. (1995). *J. Phys. Chem.* **99**, 8283.
- Saville, P. M., White, J. W., Hawker, C. J., Wooley, K. L., Penfold, J., and Fréchet, J. M. J. (1993). *J. Phys. Chem.* **97**, 293.
- Schiff, L. I. (1955). 'Quantum Mechanics', p. 92 (McGraw-Hill: New York).
- Sivia, D. S., Hamilton, W. A., and Smith, G. S. (1991). *Physica B* **173**, 121.
- White, J. W., Kerr, J. C. H., Penfold, J., Saville, P. M., and Thomas, R. K. (1994). In 'Progress in Pacific Polymer Science 3' (Ed. K. P. Ghiggino), p. 99 (Springer: Berlin-Heidelberg).