Scattering from liquid-Liquid interfaces

The liquid/liquid interface remains an important area of chemistry due to its widespread application in practical systems in which the formation, stability and breakdown of liquid/liquid dispersions (emulsions) are involved. Liquid/liquid interfaces are essential constituents of biological systems as well as being involved in many chemical separation processes. Understanding how the organisation of molecules at liquid/liquid interfaces influences the system performance is of utmost importance in these applications. Due to the continued development of neutron reflectometry over the past decade, major advances have been made into the investigation of the structure of surfaces and interfaces. Although the technique has advanced greatly, the area of interfacial science concerning the liquid/liquid interface has received relatively little attention by this method.

The lack of progress in the development of neutron reflectometry at liquid/liquid interfaces is attributable neither to a lack of effort or to the suitability of the technique. Overcoming the drastic attenuation of a neutron beam upon transmission through a liquid medium remains the major obstacle. The advances made so far have revolved around the ability to form and maintain a thin oil film, from a volatile oil vapour phase, through which the neutron beam is transmitted. Although by this approach the condensation method has proved successful, it possesses two limitations. First, it is restricted to the study of volatile oils and therefore to the adsorption of oil-insoluble molecules. Second, the maintenance of a uniform condensed oil layer is a difficult and time-consuming task. In order to address these shortcomings we recently developed a new, versatile approach for the investigation of the structure of adsorbed polymers and surfactants at oil/water interfaces which complements the condensation method. This approach is suitable for the study of oil-soluble, water-soluble and insoluble amphiphiles as well as being amenable to the use of non-volatile oils. Neutron reflectometery is used to resolve these buried interfaces.

Neutron reflectometery

Neutrons show many optical properties analogous to those of electromagnetic *s*-wave radiation and the normal laws of optics such as Snell’s law and Fresnel’s equations are applicable. Analogously to optical reflectometry, specular neutron reflectometry is used to determine the (neutron) refractive index profile $n(z)$ normal to an interface (z is the coordinate normal to the interface). Thermal neutrons have wavelength comparable with interatomic spacing and can be used to resolve structural features with sub-molecular resolution. Neutron reflectivity is a technique sensitive to the average neutron refractive index, n, profile normal to an interface. The dispersive refractive index can be written as

$$n(\lambda) \approx 1 - \frac{\lambda^2}{2\pi} Nb + i \frac{\lambda}{4\pi} N\sigma \qquad (1)$$

where λ is the neutron wavelength, $Nb = \sum_i N_i b_i$ and $N\sigma = \sum_i N_i \sigma_i$, with N_i the number density, b_i the coherent scattering length, and σ_i the absorption and incoherent cross-section of nucleus i. The multiple Nb is known as the scattering length density of a medium with refractive index n. According to eq. (1), the large difference in the scattering lengths of ^{1}H (b = –3.7406 fm) and ^{2}H (b = 6.671 fm) can be exploited in hydrogenous systems. For our present purpose it is convenient to replace σ with the linear absorption coefficient $\chi = \chi(\lambda)$ which embraces all loss processes and is determined from transmission measurements.

Since Nb is approximately linearly related to the volume fraction composition. The reflectivity can be calculated using, among other methods, the standard optical-matrix method and the parameters of the proposed layer model can be optimised using nonlinear least-squares fitting. The Gaussian interfacial roughness used in the modelling is the r.m.s. roughness of the interface. For a relatively thin (typically < 10 μm) oil film, the reflections from both the Si–oil and oil–water interfaces contribute to the measured reflectivity. If the incidence angle and the Si–oil and oil–water scattering contrasts are appropriate, total reflection from both these interfaces occurs and two critical edges are observed; the locations of these edges correspond to total reflection from the Si–oil (high-λ edge) and Si–water (low-λ edge interfaces. The intensity of the low-λ edge is reduced in magnitude due to the attenuation by the oil film. The decrease in intensity between the two critical edges is used to calculate the oil-film thickness using the Beer-Lambert law – the transmission, $T = T(\lambda)$, at a given wavelength is $T = \exp(-\chi l)$, where l is the pathlength – and this is incorporated in the reflectivity calculations. The analysis of the reflectivity data for these fluid-fluid systems is based on the thick film approximation for the calculation of the overall reflectivity, R_{tot}, from the Si–oil–water composite interface. A comprehensive description of the experimental procedure and the data analysis from these buried interfaces will be given.

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