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Neutron reflectivity and small angle neutron scattering: An introduction and perspective on recent progress

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ABSTRACT

In recent years both neutron reflectivity, NR, and small angle neutron scattering, SANS, have been applied to the study of increasingly complex surface and interfacial properties. The methodology and advantages of using these neutron scattering techniques to probe surfaces and interfaces will be briefly outlined. Some recent examples of surfactant, polymer and polymer–surfactant adsorption at the air–water, liquid–solid, and liquid–liquid planar interfaces are highlighted. These are contrasted by some examples of the nature of adsorption on colloidal sol particles and emulsion droplets.

1. Introduction

The nature of surfaces and interfaces and the adsorption of species such as surfactants, polymers, polyelectrolytes and proteins to surfaces and interfaces are central to a vast range of domestic, industrial, technological, biological and medical processes and applications. There are a wide range of surface sensitive techniques available, which include atomic force microscopy, AFM, ellipsometry and optical reflectometry, fluorescence spectroscopy and other surface spectroscopic probes such as sum frequency spectroscopy, SFS, second harmonic generation, SHG, surface plasmon resonance, SPR, and surface sensitive FTIR, and x-ray reflectivity and scattering. Each of these techniques offers a particular perspective on surface and interfacial properties. However the neutron scattering techniques of NR and SANS offer unique and particular properties that make them powerful techniques for the study of surface and interfaces.

Apart from known strongly absorbing elements (such as Cd, Gd, and Sm) the absorption cross-section of cold/thermal neutrons is small, making them a penetrating probe that does relatively little radiation induced damage. Hence they can be used non-invasively to probe buried interfaces. However, the major advantage of neutron scattering arises from the different scattering power (characterised by the neutron scattering length, b) associated with different isotopes. This is especially valuable in organic molecules as the scattering lengths of H and D have different magnitudes and sign (b for H is -0.374×10^{-12} cm and for D is 0.6674×10^{-12} cm). The scattering length density, ρ, and refractive index, n, are defined in terms of b as,

$$\rho = \sum_i b_i N_i \tag{1}$$

where b_i and N_i are the neutron scattering length and number density of species i, and

$$n^2 = 1 - \frac{\lambda^2}{\pi}\rho \tag{2}$$

where λ is the neutron wavelength.

Hence by D/H isotopic substitution (labelling) the refractive index distribution can be manipulated. In particular, as will be demonstrated later, judicious choice of labelling makes SANS and NR surface specific.

2. Neutron scattering

Apart from the non-invasive nature of neutron scattering, the accessibility of buried interfaces, and the ability to manipulate the refractive index distribution in the system, the length scales accessible, ~10 to 5000 Å, are well matched to the length scales of a majority of the surface and interfacial phenomena of interest. The length scale probed is determined by the scattering vector Q, given by $Q = 4\pi\sin\theta/\lambda$, where θ is the scattering angle or grazing angle of incidence. The recent treatise by Sivia [1••] is an excellent introduction to many aspects of neutron and x-ray scattering, and in particular to SANS and NR.

The specular reflectivity of neutrons, R(Q), from a planar surface or interface is related to the refractive index or scattering length density distribution in a direction perpendicular to the surface. In the kinematic approximation [2] this is expressed as,

$$R(Q) = \frac{16\pi^2}{Q^2}\left|\int \rho(z)e^{-iQz}dz\right|^2. \tag{3}$$

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The reflectivity can be expressed in terms of the kinematic approximation above or using the exact approach more familiar in thin film optics [2–5]. For a thin film at the interface between two bulk phases the reflectivity is,

$$R = \frac{r_{01}^2 + r_{12}^2 + 2r_{01}r_{12}\cos(2\beta_1)}{1 + r_{01}^2 r_{12}^2 + 2r_{01}r_{12}\cos(2\beta_1)} \tag{4}$$

where the subscripts 0, 1, and 2 refer to the upper phase, the thin film, and the sub-phase respectively, $\beta = k_1 n_1 d_1$ is the optical path length, n_1 is the refractive index of the thin film, d_1 is the film thickness, and k_0 and k_1 are the neutron wave vectors in the upper phase and in the monolayer normal to the interface. The Fresnel coefficients are given by $r_{ij} = (p_i - p_j)/(p_i + p_j)$ where $p_i = n_i \sin\theta_i$.

Eq. (4) can be simplified to

$$R(Q) = \frac{16\pi^2}{Q^4}\left[(\rho_1 - \rho_0)^2 + (\rho_2 - \rho_1)^2 + 2(\rho_1 - \rho_0)(\rho_2 - \rho_1)\cos Qd\right]. \tag{5}$$

For a thin film at the interface between air ($n = 1$) and a subphase with $n = 1$, Eq. (5) further simplifies to,

$$R(Q) = \frac{16\pi^2}{Q^4}(2\rho)^2 \sin\left(\frac{Qd}{2}\right)^2. \tag{6}$$

For more complex surface structures the optical matrix method [5], which describes the interface as a series of thin layers with a characteristic matrix per layer describing its optical properties, is readily adapted. Alternatively, within the kinematic approximation as defined in Eq. (3), the interfacial region can be divided into distributions that represent the different components at the interface [6•], and then the reflectivity can be written as,

$$R(Q) = \frac{16\pi^2}{Q^2}\left[\sum_i b_i^2 h_{ii} + \sum_i \sum_{j<i} 2b_i b_j h_{ij}\right]. \tag{7}$$

The self partial structure factors, h_{ii}, in Eq. (7) are one dimensional Fourier transforms of $n_i(z)$, and the cross-partial structure factors, h_{ij}, relate to the relative positions of the distributions defined by h_{ii}.

The fundamentals of SANS are described in a number of articles, see for example Refs. [7,8]. Small angle scattering is the scattering in the forward direction [8], arises from the coherent superposition of the scattered waves and is expressed as a differential scattering cross-section, σ, per solid angle, Ω. It can be expressed as a summation of the amplitude weighted phase shifts or an integral of the scattering length density distribution ρ(r), such that,

$$\frac{d\sigma}{d\Omega} = \left\langle \left| \sum_j b_j \exp\left(i\underline{Q}.\underline{R}_j\right) \right|^2 \right\rangle = N\left\langle \left| \int_V \rho(r)\exp\left(i\underline{Q}.\underline{r}\right)dr \right|^2 \right\rangle_Q \tag{8}$$

where N is the number of scattering objects and V the sample volume. For a dilute solution of monodisperse scattering objects (in solid or liquid solution) then,

$$\frac{d\sigma}{d\Omega} = N\left\langle F^2(Q) \right\rangle_Q \tag{9}$$

where the form factor F(Q) contains information about the particle or scattering object size and shape,

$$F(Q) = \int_V [\rho(r) - \rho_s]\exp(iQ.r)dr. \tag{10}$$

For more concentrated solutions the higher particle concentrations result in inter-particle interactions and correlations becoming important, and these are characterised by a structure factor, S(Q). Hence dσ/dΩ is then expressed in its simplest form as [9•],

$$\frac{d\sigma}{d\Omega} \approx NS(Q)P(Q) \tag{11}$$

where P(Q) is $\langle F^2(Q) \rangle_Q$, and a range of different expressions for the form factor for different particle geometries, spheres, concentric shells, ellipses, and rods, exist. To make the scattering surface specific, the factor $(\rho(r) - \rho_s)$ is crucial. For example, for a core-shell form factor, adjusting the scattering length density ρ(r) (through D/H isotopic substitution) such that the core and solvent are identical renders the scattering sensitive only to the interfacial layer.

3. Adsorption onto colloidal particles and emulsion droplets: the contribution from SANS

Scattering techniques, and especially SANS, have been extensively used to study the adsorption of polymers and surfactants onto colloidal particles and emulsion droplets. Oberdisse [10] recently reviewed the adsorption and grafting onto colloidal interfaces using scattering techniques. Understanding adsorption onto colloidal particles and droplets is important in the context of colloidal stabilisation and involves both charge and steric stabilisation and the generation of functionalised surfaces.

3.1. Colloidal particles

The pioneering work in the area of polymer adsorption is encapsulated in some key papers by Cosgrove et al. [11,12]. The scattering from a colloidal system with adsorption can be written as,

$$I(Q) = I_0(Q) + \Delta\rho I_1(Q) + \Delta\rho^2 I_2(Q) \tag{11}$$

where $I_o(Q)$ arises from the adsorbed polymer layer, and $I_2(Q)$ and $I_1(Q)$ are from the particle and particle-surface interference. At zero contrast, $\Delta\rho_p = 0$ (particle index matched to the solvent),

$$I(Q) = I_0(Q) = \frac{8\pi^2 r_o^2 \Delta\rho_s^2}{Q^2}\left|\int_0^t \phi(z)e^{iQz}dz\right|^2 \tag{12}$$

which reduces to a simple sine transform of the polymer volume fraction distribution, φ(z), at $Qr_o \gg 1$. Using inversion techniques [11] they were able to show that the PEO volume fraction distribution on the surface of a polystyrene latex particle did not follow the expected scaling laws. This same approach showed how changing the solvency of the PEO layer by temperature and added electrolyte resulted in a collapse of the adsorbed PEO layer, which could be interpreted in terms of the dispersion stability. The same approach can be applied to other colloidal particles with different geometries. Nelson et al. [13] explored the adsorption of a Pluronic tri-block copolymer onto Laponite clay particles and determined both the adsorbed amounts and the structure of the adsorbed layer, as the Pluronic structure was altered.

In more concentrated colloidal dispersions Qiu et al. [14] extracted the volume fraction distribution of PEO adsorbed onto colloidal silica particles from the average scattering term. A collapse of the adsorbed layer due to repulsion arising from neighbouring particles was observed.

The scattering from the adsorbed layer can be expressed as an average term and a fluctuation term,

$$I(Q) = \overline{I_0(Q)} + I_F(Q) \tag{13}$$

where $\overline{I_0(Q)}$ is the scattering from the average of the adsorbed layer, and $I_F(Q)$ is the scattering from concentration fluctuations within the layer. Inclusion of the fluctuation term showed that the polymer layer became