Current Opinion in Colloid & Interface Science 9 (2005) 390–395

Current Opinion in
COLLOID and
INTERFACE SCIENCE

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Conformation, directed self-assembly and engineered modification: some recent near surface structure determinations by grazing incidence small angle X-ray and neutron scattering

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Available online 18 December 2004

Abstract

Some recent developments in grazing incidence small angle scattering (GISAS) technique are reviewed. The emphasis is on the application of GISAS to elucidating the effects of geometrical surface constraint on self-assembled systems and the effect of modification of interfaces or molecular subassemblies to direct the formation of more complex structures.

Keywords: Off-specular; X-ray; Neutron; Surface; Interface; Thin-film; GISAS; GISANS; GISAXS

1. Introduction

Emerging and maturing over the last 20 years, specular reflectivity of X-ray and neutron beams (SR, SXR and SNR) is now widely used to study layered microstructure—as the laterally averaged scattering power, electron density or isotopic neutron scattering length density, respectively, perpendicular to an interface [1,2]. Since the translational invariance of the interface that these techniques assume can never be perfectly achieved, some fraction of the incident radiation will unavoidably be scattered off-specularly. Grazing incidence small angle scattering (GISAS) by X-rays (GISAXS) or neutrons (GISANS) is simply the small angle scattering that arises from inhomogeneities at or near an interface on the same "large scales" ~1–100 nm of macromolecular structure probed by their bulk counterparts SAXS and SANS. For strictly interfacial inhomogeneities, the length scale sampled along the direction of the incident beam is actually rather greater, magnified from this range by a factor of about the cosecant of the grazing angle—an effect familiar from the operation of optical diffraction gratings at grazing incidence [3].

In the early days of specular reflection studies, GISAS was an inconvenient background underlying the specular signal and often subtracted from that signal incorrectly due to a misunderstanding of its behavior and limited offset sampling carried out with single element detectors. In the last decade, broader sampling in scattering vector made possible as an ever increasing number of reflection geometry instruments are equipped with one- and two-dimensional position sensitive detectors (PSDs), and improved theoretical understanding has allowed this scattering to emerge in its own right as a probe of layered structure morphologies.

GISAS techniques share to a great extent the advantages and disadvantages of their bulk counterparts: as Fourier techniques with high penetration, they provide global statistical information on subsurface structures as opposed to the narrow field surface sampling of direct imaging methods, but as indirect methods they suffer from the inversion problem. In the case of neutrons magnetic sensitivity and the use of isotopic scattering contrast overcome the relative weaknesses of currently available sources in special cases.

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doi:10.1016/j.cocis.2004.10.005

2. GISAS technique and analysis

Fig. 1 shows a schematic of the scattering geometry for specular reflectivity and GISAS for an interfacial sample in the xy plane of incident beam with wavevector $\mathbf{k}_i$ in the xz plane, showing the incident and exit grazing angles α_i and α_f and the deviation angle ϕ of the scattered wavevector $\mathbf{k}_f$ projected onto the sample plane. For specular reflection $\alpha_f=\alpha_i$ and $\phi=0$ so the scattering vector $\mathbf{Q}\equiv\mathbf{k}_f-\mathbf{k}_i$ is normal to the surface and has magnitude $Q_R=2k\ \sin\alpha_i$.

For off-specular scattering, the components of the scattering vector are:

$$Q_z = k(\sin\alpha_f + \sin\alpha_i)$$

$$Q_y = k\cos\alpha_f\sin\phi$$

$$\begin{aligned} Q_x &= k(\cos\alpha_f\cos\phi - \cos\alpha_i) \\ &\cong -\left(Q_z(\sin\alpha_f - \sin\alpha_i) + Q_y\sin\phi\right)/2 \\ &\approx -\left(Q_z(Q_z - Q_R) + Q_y^2\right)/2k \end{aligned}$$

We consider the simple case in which most GISAS intensity occurs due to inhomogeneities, which are uniformly distributed below the interface—for instance voids or embedded nanoparticles within a solid matrix, or a colloidal solution. For α_i above the critical value for total reflection α_C, some fraction of the beam $R[Q_R]$ will be specularly reflected and a fraction $T[\alpha_i]=T[Q_R]=1-R[Q_R]$ will be transmitted into the interface and refracted by it making a smaller angle α'_i to the interface as it enters the solution (denoting in-substrate quantities with primes). If this transmitted beam is scattered within the substrate with a wave vector transfer such that it travels back toward the interface at a grazing angle $\alpha'_f<\alpha_f$ before being transmitted and refracted upon exit to α_f. Since wavevector components parallel to an interface are unchanged upon refraction, the parallel components of the in-substrate scattering vector and that observed at a downstream detector will be equal, so $Q'_y=Q_y$ and $Q'_x=Q_x$. Applying the laws of refraction at the interface, we can show that the perpendicular components are related as:

$$Q'_z = \left(\sqrt{(2Q_z - Q_R)^2 - Q_C^2} + \sqrt{Q_R^2 - Q_C^2}\right)\Big/2$$

Where $Q_C=2k\ \sin\alpha_C$ is the critical scattering vector for total external reflection [4].

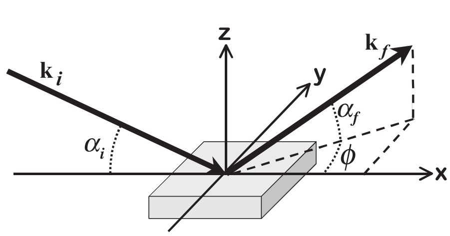

Fig. 1. Scattering geometry for specular reflection and GISAS measurements.

In this simple case, the in-substrate differential macroscopic scattering cross-section (Σ_s) will be related to the differential cross-section (σ) measured at the detector:

$$\frac{d\Sigma_s}{d\Omega'}[Q'] \approx \frac{d\sigma}{d\Omega}[Q]/Ad'_{\text{eff}}\ \frac{\sin\alpha_f}{\sin\alpha_f'}\,T[\alpha_i]T[\alpha_f]$$

This corrects the solid angle for refraction (the sin ratio) and interfacial transmissions [5], and as in conventional bulk SAS we correct for the effective sample volume—in this case, accounting for refraction as well as absorption. The volume term here, Ad'_{eff}, is the irradiated interfacial area multiplied by refractive probe depth $d'_{\text{eff}}\sim\alpha'_i\alpha'_f/\mu(\alpha'_i+\alpha'_f)$, where μ is the absorption coefficient of the sample.

Fig. 2 illustrates two typical recent GISAS scans. Fig. 2(a) shows 2D PSD GISAXS (Q_y,Q_z) scattering at a single incident angle from a coexisting hexagonal and worm-like self-assembled silica mesostructures on a silicon substrate. (See also Doshi et al. [6•], discussed below.) Fig. 2(b) shows a multi-angle SNR/GISANS scan series of a surfactant membrane solution at a quartz interface taken with a z directed 1D PSD converted to (Q_x,Q'_z) coordinates. A distinct difference in periodicity between structures at and the quartz surface and in the near surface bulk is indicated by the offset between the peaks in the specular (Q_x=0) and off-specular GISANS peaks. (See also Hamilton et al. [7•], discussed below.) Similar data sets are obtained in time-of-flight (TOF) neutron SNR/off-specular measurements over a range of incident wavelengths at constant angle.

In cases in which there is a limited coherence with depth in the substrate (for instance most solution studies), the transport theory corrections outlined above treating refractive distortion and reflection of the incident and scattered waves as separable processes are easy to apply and hold fairly well [7•,8]. In general, however, there is a coherent relationship between inhomogeneities and interfaces. Roughness is the canonical example and off-specular Yoneda scattering exiting an interface by selective reflection at the critical angle the observed consequence [9]. There may be a degree of correlation of roughness between multilayer interfaces or of scattering aggregates within extended lateral structures (for example: the preferential embedding of coated nanoparticles in self-assembled polymeric multilayers investigated by Lauter-Pasyuk et al. [10••]). A full Distorted Wave Born Approximation (DWBA) approach is then necessary to deal with dynamical effects: significant coherent multiple reflection and interference of both the incident and scattered waves. A DWBA approach was first introduced to reflectivity studies by Vineyard's analysis of grazing incidence surface diffraction [11] and an extensive formalism for off-specular scattering studies of rough interfaces and roughness correlations in multilayers has been developed by Sinha et al. [12], Sanyal et al. [13], Pynn [14], Holy and Baumbach [15] and Schlomka et al. [16] among others. Many of the articles cited