

SANS from Adsorbed Polymer Layers

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SUMMARY: One of the areas in which small-angle neutron scattering (SANS) has had a profound impact over the last twenty years is the investigation of polymers and surfactants adsorbed at the solid/liquid and liquid/liquid interfaces. This is of course also an area of considerable commercial importance. Control of the structure of an adsorbed layer is thus a key priority of the colloid scientist. Equally important, however, is the ability to probe the arrangement of the adsorbed polymer molecules and to extract quantitative information from what might well be a complex, multicomponent system. SANS in combination with the principle of deuterium contrast variation is uniquely placed to provide this information.

Introduction

The first objective of any SANS experiment is to determine the differential scattering cross-section as a function of the scattering vector, $(d\Sigma/d\Omega)(Q)$, for a sample, since it is this quantity which contains all the information about the shape, size, and interactions between the scattering centres (here given the subscript “p” for particles)^[1,2]. It may be expressed thus

$$\frac{\partial \Sigma}{\partial \Omega}(Q) = N_p V_p^2 (\Delta\rho)^2 P(Q) S(Q) + B \quad (1)$$

where N_p is the number concentration of particles, V_p is the volume of one particle, $(\Delta\rho)^2$ is the contrast $(= (\rho_p - \rho_m)^2)$ where ρ_p is the neutron scattering length density of the particles and ρ_m that of the dispersion medium), $P(Q)$ is the form (or shape) factor, $S(Q)$ is the structure factor (normally engineered to have a minimal contribution to the scattering in the experiments under discussion in this paper), and B is the background signal.

From a properly designed and executed SANS experiment, it may be possible to obtain values for the surface area per unit volume of the substrate, estimates of the thickness of the adsorbed layer, a measure of how much polymer or surfactant is present within the layer, and a description of how it is arranged - the *volume fraction profile*, $\Phi(z)$ ^[3]. It is $\Phi(z)$ which will be the focus of this paper^[4-6].

SANS From Adsorbed Polymer Layers

Before considering methods of analysis involving $\Phi(z)$, it is worth remembering that, just as in any conventional light scattering experiment, SANS can be used to elucidate the shape of the particles in a dispersion. If that shape is not too complex - and emulsion droplets, polymer latices and pigment particles can usually be well approximated as spheres, for example - then a measure of the size of those particles can be deduced by the application of, say, the Guinier approximation ^[7]. If the measurement is repeated in the presence of a layer of adsorbed polymer or surfactant, then the difference between the two sizes may be used to estimate the thickness of the layer. The drawback with this approach is that SANS is relatively insensitive to the few, well-solvated, but highly-extended, polymer “tails” at the periphery of the adsorbed layer.

The “Core-Shell” Model

This approach assumes that a particle and its adsorbed layer (given the subscript “l”) can be modelled as two homogeneous, concentric spheres; see Fig. 1a.

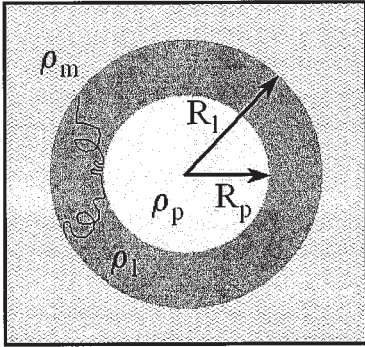


Figure 1a. A schematic representation of the “core-shell” model of a particle with an adsorbed layer. Notice how the model under-describes the actual structure in the layer. See the main text for an explanation of the symbols.

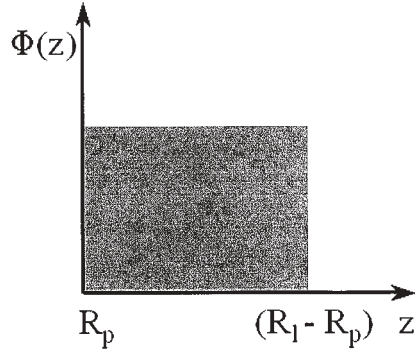


Figure 1b. The volume fraction profile corresponding to the “core-shell” model depicted in Fig. 1a.

If $P(Q, R_l)$ and $P(Q, R_p)$ are the form factors for spheres of radii R_l and R_p , respectively, then the overall scattering from such a composite particle is

$$\frac{\partial \Sigma}{\partial \Omega}(Q) = \frac{16\pi^2}{9} N_p P(Q) S(Q) + B \quad (2)$$

where

$$P(Q) = \left[(\rho_1 - \rho_m)^2 F(Q, R_1)^2 \right] + \left[2(\rho_1 - \rho_m)(\rho_p - \rho_1) F(Q, R_p) F(Q, R_1) \right] + \left[(\rho_p - \rho_1)^2 F(Q, R_p)^2 \right] \quad (3)$$

and

$$F(Q, R_1)^2 = R_1^6 P(Q, R_1)$$

$$F(Q, R_p)^2 = R_p^6 P(Q, R_p)$$

Clearly, when $\rho_1 = \rho_m$, that is, when the adsorbed layer is contrast-matched to the dispersion medium, only the scattering from the core of the composite particle is observed. A more useful scenario, though, occurs when $\rho_p = \rho_m$, i.e., when the core is contrast-matched to the dispersion medium. Then, the form factor describes the scattering from a spherical shell of thickness $(R_1 - R_p)$ and scattering length density ρ_1 :

$$\begin{aligned} P(Q) &= \left[(\rho_1 - \rho_m) F(Q, R_1) - (\rho_1 - \rho_m) F(Q, R_p) \right]^2 \\ &= \left[(\rho_1 - \rho_m) F(Q, R_1) + (\rho_p - \rho_1) F(Q, R_p) \right]^2 \end{aligned} \quad (4)$$

The drawback with this approach is that it assumes the scattering length density within the adsorbed layer is uniform (i.e., that $\Phi(z)$ is a step function; more commonly referred to as a “block” profile); see Fig. 1b.

As will become apparent, this assumption is not very satisfactory in the case of polymers, although the “core-shell” model does work reasonably well for adsorbed layers of short-chain surfactants. Two excellent examples of the application of this approach to such systems are the work of Ottewill and co-workers^[8-12] and Cummins *et al.*^[13].

The “Inversion” Technique

The great advantage of this approach is that it does not presuppose a form for $\Phi(z)$. In fact, this technique is actually capable of determining it. In addition to showing how the average density of polymer segments varies with distance, z , in the direction perpendicular to the interface, $\Phi(z)$ also provides several measures of the layer thickness, the adsorbed amount (from the integral under the curve) and the average fraction of bound segments (from the proportion of segment density within a finite distance of $z = 0$).

The inversion technique has essentially evolved in two forms; one due to Crowley^[14] and co-workers from studies of both grafted^[15,16] and, in particular, physically adsorbed polymers^[3-5,17-19], and the other due to Auvray^[20] and co-workers, principally from studies of grafted polymer layers^[21-29]. The principle difference between the two forms is that Auvray and

co-workers specifically consider the contribution to the scattering that arises from segment density fluctuations in the adsorbed layer, whereas Crowley and coworkers generally ignore this contribution. The latter argue that such fluctuations are generally unimportant except in a few special cases, such as in systems with dense grafted layers ^[21,30,31] and indeed the scattering from the fluctuation term is very weak for polymer layers that are neither very dense nor comprise high-molecular-weight polymers.

The starting point for both derivations is a variation of Eq. 1, viz.

$$\frac{\partial \Sigma}{\partial \Omega}(Q) = N_p P(Q) S(Q) + B \quad (5)$$

where (cf. Eqs 2-4)

$$P(Q) = [(\rho_p - \rho_m) F_p(Q) + (\rho_l - \rho_m) F_l(Q)]^2 \quad (6)$$

$F_p(Q)$ represents the *intraparticle* form factor for the core particle and $F_l(Q)$ the *intralayer* form factor for the adsorbed polymer. The inversion technique therefore properly considers the separate contributions to the scattering from both the particle and the adsorbed layer.

If the curvature of the surface is small compared to Q , that is, if $QR_p \gg 1$, then Eq. 6 may be expanded to give

$$P(Q) = [(\rho_p - \rho_m)^2 F_p(Q)^2] + [2(\rho_p - \rho_m)(\rho_l - \rho_m) F_p(Q) F_l(Q)] + [(\rho_l - \rho_m)^2 F_l(Q)^2] \quad (7)$$

from which it can be seen that the first term (called $I_2(Q)$ by Crowley *et al.* or $I_{gg}(Q)$ by Auvray *et al.*; the subscript “g” is for grain, i.e. particle) describes the contribution to $P(Q)$ arising from the core particle, the third term (called $I_0(Q)$ by Crowley *et al.* or $I_{pp}(Q)$ by Auvray *et al.*; the subscript “p” in their case is for polymer) describes the contribution from the adsorbed layer, and the second term (called $I_1(Q)$ by Crowley *et al.* or $I_{pg}(Q)$ by Auvray *et al.*) is a particle-surface interference term.

Using an independent notation, where the subscript “p” signifies the particle and the subscript “l” signifies the (adsorbed) layer, these three terms may be written explicitly thus:

$$I_{pp}(Q) = (\delta_p - \delta_m)^2 \frac{2\pi A_p}{Q^4} \left[1 + \frac{1}{Q^2 R_p^2} \right] \quad (8)$$

$$I_{pl}(Q) = (\delta_p - \delta_m)(\delta_l - \delta_m) \frac{4\pi A_p}{Q^4} \left[\int_0^t \Phi(z) \cos(Qz) dz - QR_p \int_0^t \Phi(z) \sin(Qz) dz \right] \quad (9)$$

$$I_{ll}(Q) = (\delta_l - \delta_m)^2 2\pi A_p \left[\frac{1}{Q^2} \left| \int_0^t \Phi(z) \exp(iQz) dz \right|^2 + \tilde{I}_{ll} \right] \quad (10)$$

where A_p is the surface area per unit volume of a particle (usually expressed as S_p/V_p in the Auvray derivation, where $S_p = 4\pi R_p^2$ for spherical particles), t is the maximum extent of the

adsorbed layer and $\tilde{I}_{||}$ is related to the density-density correlation function that describes fluctuations in the adsorbed layer. It is the $\tilde{I}_{||}$ term in Eq. 10 that the Crowley derivation does not treat implicitly.

The $I_{pp}(Q)$ term

Equation 8 is simply a statement of the well-known Porod law^[32], the Q^{-4} dependence of the particle scattering being general result for a surface fractal.

The $I_{pl}(Q)$ term

If $QR_p \gg 1$, Eq. 9 reduces to the sine Fourier transform of $\Phi(z)$, that is

$$I_{pl}(Q) \approx -(\rho_p - \rho_m)(\rho_l - \rho_m) \frac{4\pi A_p}{Q^3} \int_0^\infty \Phi(z) \sin(Qz) dz \quad (11)$$

Thus, by subtracting the scattering obtained at contrast match for the particles ($\rho_p = \rho_m$) from the scattering obtained “off-contrast” ($\rho_l \neq \rho_p \neq \rho_m$), multiplying the result by Q^3 and taking the Fourier transform, it is possible to obtain $\Phi(z)$. In fact, this was the method used to derive the very first volume fraction profile from SANS data^[15,16]. This route to $\Phi(z)$ has both advantages and disadvantages. In its favour are that inversion only requires a Fourier transform, the procedure is not affected by the form of $\Phi(z)$, and (importantly) it is independent of the fluctuation term $\tilde{I}_{||}$. The downside, however, is that when the particles are not at contrast match, the $I_{pp}(Q)$ term is the dominant contribution to the observed scattering. This much stronger signal can be subtracted (either by using the scattering obtained when the adsorbed layer is at contrast match or by using Porod’s law), but the resulting $I_{pl}(Q)$ scattering can then suffer from a poor signal-to-noise ratio. One way to overcome this drawback is to maximize A_p and Auvray and co-workers have demonstrated that $I_{pl}(Q)$ can be obtained with good statistics when the polymers are adsorbed in dispersions of macroporous particles^[25,26].

The $I_{||}(Q)$ term

The more direct route for obtaining $\Phi(z)$ is from the scattering when the particles are at contrast match ($\rho_p = \rho_m$). Under this condition, $P(Q)$ in Eq. 7 reduces to Eq. 10. Unfortunately, because it is the *modulus* of the integral that is measured experimentally, the transformation of the first term in the brackets is complicated by the need to introduce a phase factor, $\exp(i\phi Q)$, where ϕ is unknown. Fortunately the particle surface can be used as a phase

reference point (since $\Phi(z) = 0$ for $z < 0$) and this allows φ to be determined using a dispersion integral relationship^[14,16]. $\Phi(z)$ can then be obtained by Hilbert transformation of the $I_{||}(Q)$ scattering data. This procedure always generates a possible $\Phi(z)$ though some rapidly decaying functional forms for $\Phi(z)$ can be problematical. In practice, very few functions are limited by this constraint. A physically realistic $\Phi(z)$ can also be back-transformed into reciprocal space and compared with the actual experimental scattering data, for example using a maximum entropy minimization^[33].

Figure 2a shows the volume fraction profile for a block copolymer adsorbed at the liquid-liquid interface in an emulsion^[34] and was obtained by inversion of the $I_{||}(Q)$ scattering. The shape of this profile, whilst typical of a physically adsorbing block copolymer, is clearly very different to the block profile assumed by the “core-shell” model. When the polymer chains in the adsorbed layer are “grafted” (terminally-attached) to the interface, the volume fraction profile often displays a maximum, see Fig. 2b.

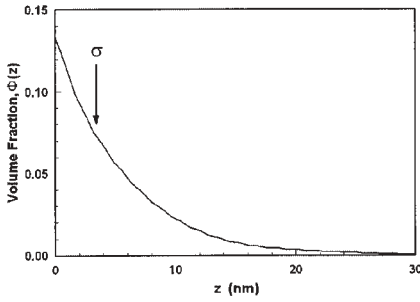


Figure 2a. The volume fraction profile for the PEO-PPO-PEO block copolymer Pluronic F127 (Poloxamer 407) adsorbed at the interface in a perfluorodecalin-in-water mesoscopic emulsion system (from Ref. 34). Also shown is the position of the second moment of the profile.

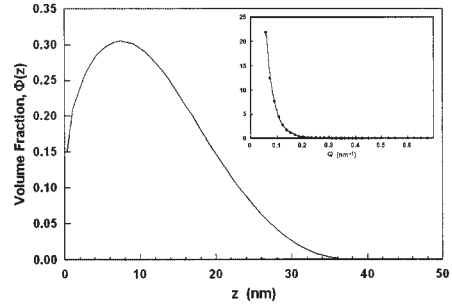


Figure 2b. The volume fraction profile that best describes the structure of the adsorbed layer formed by perdeuterated PS ($M_w \sim 24000$) grafted to colloidal silica particles dispersed in DMF (from Ref. 31). $\Gamma \sim 6.5 \text{ mg m}^{-2}$. The inset shows the corresponding experimental (•) and calculated (—) scattering data.

Neglecting fluctuations, and provided $R_p \gg t$ and $Q\sigma < 1$, the exponential term in Eq. 10 can be expanded to yield

$$I_{||}(Q) \approx (\rho_l - \rho_m)^2 \frac{2\pi A_p M^2}{Q^2} \exp(-Q^2 \sigma^2) \quad (12)$$

where the normalisation constant, M (Auvray *et al.* use the symbol γ), is given by

$$M = \int_0^l \Phi(z) dz = \frac{\Gamma}{\delta} \quad (13)$$

Γ is the mass of polymer adsorbed per unit area and δ is the bulk density. σ , the *second moment about the mean*, of $\Phi(z)$ is defined as

$$\sigma^2 = \langle z^2 \rangle - \langle z \rangle^2 \quad \text{where } \langle z^n \rangle = M^{-1} \int_0^l \Phi(z) z^n dz \quad (14)$$

and the *root-mean-square thickness*, t_{rms} , as

$$t_{\text{rms}} = \langle z^2 \rangle^{1/2} \quad (15)$$

Physically, σ provides an estimate of the average distance of the centre-of-mass of an adsorbed layer from the interface. For a “block” profile of thickness l , $\sigma^2 = l^2/12$.

Substituting expressions for A_p and M (Eq. 13) into Eq. 12, and noting that the latter expression is per unit volume, then leads to the very useful result

$$\frac{\partial \Sigma}{\partial \Omega}(Q) \approx (\rho_i - \rho_m)^2 \left[\frac{6\pi\phi_p}{Q^2} \frac{\Gamma^2}{\delta^2 R_p} \exp(-Q^2 \sigma^2) \right] + B \quad (16)$$

Equation 16 describes the scattering from the adsorbed polymer layer in a dilute, non-interacting system where the substrate is at contrast match. This expression can be model-fitted to the observed scattering to obtain values for Γ and σ , and in the case of the data responsible for Fig. 2a yielded values of $\Gamma = 1.9 \text{ mg m}^{-2}$ and $\sigma = 2.3 \text{ nm}$.

An additional parameter that can be determined with a knowledge of the volume fraction profile is the average bound fraction, $\langle p \rangle$, given by the expression

$$\langle p \rangle = M^{-1} \int_0^l \Phi(z) dz \quad \text{where } l \approx 1 \text{ nm}^{[4]} \quad (17)$$

This is the average fraction of segments in adsorbed polymer molecules that are bound to the interface or, in other words, the fraction of segments in “trains”. As an example, for the $\Phi(z)$ depicted in Fig. 2a, it is found that $\langle p \rangle \approx 14 \%$.

Equations 12 and 16 work well if the adsorbed layer has a reasonable extent but the limiting behaviour of Eq. 10 causes problems if the adsorbed layer is relatively thin, as is often the case with short-chain surfactants. Acknowledging this, Crowley has recently formulated an extension to the method outlined above^[35]. It relies on the fact that there is a narrow range of Q over which the “sheet-like” scattering from the adsorbed layer dominates other contributions (specifically, the particle and particle-layer interference scattering when $Q \leq \sigma^{-1}$, and the specular Porod’s law scattering when $Q \geq \pi/R_p$). However, this new formalism cannot provide the volume fraction profile for the adsorbed layer.

The $\tilde{I}_{||}$ term

Auvray *et al.* have shown that it is possible to draw analogies between de Gennes scaling description of semidilute polymer solutions ^[36] and the structure of adsorbed layers ^[25,26]. They show that any concentration fluctuations in the adsorbed layer manifest themselves as a contribution to the scattering (cf. Eqs 10 and 12) of the form

$$\tilde{I}_{||} \propto \frac{1}{(aQ)^n} \quad (18)$$

where a is the size of a polymer segment. A slightly modified functional form is necessary with dense adsorbed layers, as is discussed below. Three different categories of fluctuation contribution have been identified, each characterized by its own scaling exponent n . Only two have been verified experimentally. In all cases, n is positive, and so $\tilde{I}_{||}$ decays as Q increases.

(a) Physically adsorbed layers where $R_p \gg t$

When the thickness of the adsorbed layer is relatively small compared to the radius of the substrate particle, $\Phi(z)$ is predicted to decay as $z^{-4/3}$ over the range $a < z < Q^{-1}$. Under such conditions, $n = 4/3$. However, experimental evidence suggests that this behaviour is not universal ^[3].

(b) Physically adsorbed layers where $R_p \leq t$

When the thickness of the adsorbed layer is of the same order as the radius of the substrate particle, $n = 5/3$. However, the scaling of $\Phi(z)$ has not yet been established.

(c) Grafted layers

When the polymer is grafted (terminally-attached) to the surface of the substrate, or possibly where a block copolymer is adsorbed at high coverage, a “brush-like” adsorbed layer develops. This type of adsorbed layer structure can be characterized by parabolic or Gaussian volume fraction profiles (i.e., $\Phi(z) \propto z^{-2}$) and a length scale, ξ , related to the distance between anchor points. In this category of adsorbed layer the fluctuation contribution varies as

$$\tilde{I}_{||} \propto \frac{1}{1+(\xi Q)^2} \quad (19)$$

The “Scaling” Methodologies

By combining Eqs 10 and 18, a very generic description of the scattering from an adsorbed layer can be formulated, viz.

$$\frac{\partial \Sigma}{\partial \Omega}(Q) = \frac{U}{Q^2} + \frac{V}{Q^n} + B \quad (20)$$

where U and V are constants and $4/3 \leq n \leq 2$. Multiplying Eq. 20 through by Q^n , and neglecting the term in Q^{n-2} (except when $n = 2$), then gives

$$Q^n \frac{\partial \Sigma}{\partial \Omega}(Q) \approx W + B Q^n \quad (21)$$

A graph of $Q^n (d\Sigma/d\Omega)(Q)$ versus Q^n can thus be used to estimate the magnitude of the fluctuation contribution.

SANS from Adsorbed Layers in Ultra-Concentrated Dispersions

Crowley and co-workers have also developed a description of the scattering from film-forming polymer latex dispersions^[37]. As the dispersion medium evaporates, capillary forces drive the polymer latex particles together. Locally-flat bilayers (Plateau borders^[38]) develop where the particle surfaces meet and, in some instances, the initially spherical particles may deform into rounded polyhedra. This obviously has implications for any adsorbed layer.

This treatment relies on the fact that when $QR_p > \pi$, only specular scattering from the bilayer region is observed. This scattering is the sum of two contributions. The first of these is simply the self-scattering from the individual particle surfaces forming the bilayer (i.e., $I_{pp}(Q)$, Eq. 8). The second contribution, $\Delta I_{pp}(Q)$, which is the important one when $\phi_p > 0.74$ is due to interference effects between adjacent particle surfaces in the bilayer and is given by

$$\Delta I_{pp}(Q) = -(\rho_p - \rho_m)^2 \frac{4\pi A_B}{Q^4} \cos(Q\Delta_0) \quad (22)$$

where A_B is the surface area of a bilayer of thickness Δ_0 .

Review

Small-angle neutron scattering (SANS) is one of the most successful experimental techniques for probing the number and arrangement of polymer or surfactant molecules in an adsorbed layer and can yield quantitative information that can be directly compared with other measurements.

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