Direct Fitting of Grazing-Incidence Neutron and X-ray Reflectivity Profiles using the Kinematic Approximation

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(Received 21 September 1994; accepted 13 January 1995)

Abstract

At present, neutron and X-ray reflection data have been analysed either by modelling, using the optimal-matrix method, or by the fitting of partial structure factors arising from application of the kinematic approximation. Here the direct and simultaneous fitting of neutron and X-ray reflection profiles measured for a series of isotopic variations of the same interface is described. The interface is described as consisting of several components, which are either groups of atoms in a molecule or a whole molecule itself. In this work, the density distributions of the components perpendicular to the interface are described as Gaussian or tanh functions. These forms are chosen because they have analytical Fourier transforms. Fitting reflectivity profiles rather than partial structure factors reduces the sensitivity of the analysis to imperfections in one or more data sets. With existing kinematic methods, it is difficult to combine X-ray and neutron measurements. The new method readily allows such a combination, which is of importance if the capacity for isotopic substitution is limited or information about the counter-ion distribution is desired. It is also demonstrated that constraints posed by the stoichiometry of the interfacial species, by volume filling and molecular geometry, or from the results of the application of other experimental techniques, may readily be incorporated into the new fitting procedure.

Current methods of analysis – the optical-matrix method

The optical-matrix method allows the exact reflectivity to be calculated of any interface that may be described by a series of uniform-composition blocks. There are two formulations, one due to Born & Wolf (1975), and one due to Abeles, see for example Heavens (1955). The latter has been found to be more convenient because it may be modified to allow a roughness to be applied to the boundary between the blocks, as described by Penfold (1988).

When data are fitted, a chemical model of the interface is proposed. Provided the number of blocks is not too large, it is a relatively simple matter to restrict the models tested to those that are physically realistic, for example by applying the constraint that the volume fraction at the interface should never exceed unity, or that the model should be consistent with charge neutrality or the known stoichiometry of the system. The scattering-length density and thickness of each uniform-density block are evaluated and these are used to calculate the reflectivity profile. A comparison is made between the theoretical and experimental profiles. Poor agreement indicates that the proposed model is incorrect; however, good agreement does not necessarily imply that the structure of the interface has been found, because a unique scattering-length density profile does not give rise to a unique reflection profile. This difficulty is reduced by the use of isotopic variation, most commonly H/D substitution.

At interfaces involving the liquid phase, it is unrealistic to treat the density distribution normal to the interface in terms of a few uniform-composition regions or blocks. The distribution of matter at an interface will have some smooth variation from one bulk phase to the other. In particular, the existence of sharp boundaries between the blocks has the effect of enhancing the amplitude of interference phenomena, which are rarely strongly observed in reflection profiles of liquid interfaces. In principle, it is possible to break the interface up into a greater number of blocks but this often renders the problem impossible to solve whilst maintaining the various constraints posed by the system.

Current methods of analysis – the kinematic approximation method

A review of the theory

The application of the kinematic or weak scattering approximation to the analysis of grazing-incidence reflectivity data from layers adsorbed at interfaces is
described in detail by Crowley, Lee, Simister & Thomas (1991). The specular component of the reflectivity of a macroscopically flat interface is given by

$$ R(q) = \frac{(16\pi^2/q^4)}{q^2} \hat{\rho}(q)^2. \tag{1} $$

where $\hat{\rho}(q)$ is the one-dimensional Fourier transform of $\rho(z)$, the scattering-length density variation normal to the interface:

$$ \hat{\rho}(q) = \int_{-\infty}^{\infty} \exp(-iqz)\rho(z) \, dz. \tag{2} $$

or, alternatively,

$$ R(q) = \frac{(16\pi^2/q^4)}{q^2} \hat{\rho}^{(1)}(q)^2, \tag{3} $$

where $\rho^{(1)}(z)$ is the differential of $\rho(z)$, $d\rho(z)/dz$, and $\hat{\rho}^{(1)}(z)$ is its one-dimensional Fourier transform.

The scattering-length density profile normal to an interface may be expressed in terms of the distribution of the species present, for example, surfactant, solvent and air. In some instances, it is relevant and useful to break down molecules at the interface further, for example a surfactant molecule may be treated as a head group and a hydrocarbon chain.

If the scattering-length density profile normal to the interface is considered in terms of its constituent species, then

$$ \rho(z) = \sum_i b_i n_i(z). \tag{4} $$

where $n_i(z)$ is the number density of the species $i$ at a depth $z$ and $b_i$ is its scattering length. Thus, if the interface consists of three components (for example surfactant head group, chain group and water) denoted 1, 2 and 3, then the above equation may be rewritten as

$$ \rho(z) = b_1 n_1(z) + b_2 n_2(z) + b_3 n_3(z). \tag{5} $$

The partial structure factor between species $i$ and $j$ may be defined as follows:

$$ h_{ij}(q) = \text{Re} \left[ \hat{n}_i(q)\hat{n}_j^*(q) \right]; \tag{6} $$

when $i$ and $j$ are the same, this simplifies to

$$ h_{ii}(q) = |\hat{n}_i(q)|^2. \tag{7} $$

$\hat{n}_i(q)$ is the one-dimensional Fourier transform of $n_i(z)$, the average number-density profile of a group, $i$, in the direction normal to the interface. These relationships can also be written in terms of the differential of $n_i(z)$, denoted $n_i^{(1)}(z)$, and its Fourier transform, $\hat{n}_i^{(1)}(q)$.

The resulting partial structure factor in this case is $h^{(1)}(q)$.

$$ \hat{n}_i(q) = \int_{-\infty}^{\infty} \exp(-iqz)n_i(z) \, dz. \tag{8} $$

Because the Fourier transforms are one-dimensional, the two sets of equations are equivalent; hence, the following direct relationship between $h(q)$ and $h^{(1)}(q)$ results:

$$ q^2 h(q) = h^{(1)}(q). \tag{9} $$

The partial structure factors are related to the number-density distributions of the groups, or species, $i$ and $j$ via (6) and (7).

Substitution of (5), (6) and (7) into (3) for a three-component system gives

$$ R(q) = (16\pi^2/q^4)[b_1^2 h_{11}(q) + b_2^2 h_{22}(q) + b_3^2 h_{33}(q) + 2b_1 b_2 h_{12}(q) + 2b_1 b_3 h_{13}(q) + 2b_2 b_3 h_{23}(q)]. \tag{10} $$

These partial structure factors, $h_{ij}$, may be obtained by solution of the appropriate simultaneous equations of the form of (10). For a three-component system, six reflection profiles are required in order to obtain all the partial structure factors. In general, for a system of $n$ components, a minimum of $\frac{1}{2}n(n + 1)$ reflectivity measurements are required. Because (10) is valid for both neutrons and X-rays, an X-ray reflection measurement may be used as one of the $\frac{1}{2}n(n + 1)$ contrasts.

Because the weak scattering approximation has been invoked, expressions of the form of (10) are only valid over the momentum transfer range where multiple scattering is uncommon, that is, where the reflectivity is less than $10^{-2}$. The expression derived by Crowley (1993) may be used to correct experimental data to give the kinematic reflectivity, $R(q)$ in (10):

$$ R(q) = R_f(q) + \left[ \frac{1}{2} + \left(1 - \frac{q^2}{q_c^2}\right)^{1/2}\right]^2 \times \frac{R_{\text{obs}}(q) - R_f(q)}{[1 - R_f(q)]}, \tag{11} $$

where $R_f$ is the Fresnel reflectivity of a smooth interface between the two bulk phases of interest and $q_c$ is the critical momentum transfer. $R_k$ is the kinematic reflectivity of a smooth flat interface between the bulk phases. $R_f$ and $R_k$ are given by the expressions

$$ R_f = \frac{[1 - (1 - q_z^2/q^2)^{1/2}]^2}{[1 + (1 - q_z^2/q^2)^{1/2}]} \tag{12} $$

and

$$ R_k = (16\pi^2/q^4)(\rho_1 - \rho_2)^2. \tag{13} $$

where $\rho_1$ and $\rho_2$ are the scattering-length densities of the two bulk phases.

Therefore, experimental data over the whole range of momentum transfer, not just those significantly above the critical angle, may be used for the purposes of determination of interfacial structure using the kinematic approximation.

**Analysis of partial structure factors**

Because reflectivity is measured over a limited range of momentum transfer, it is impossible to invert the
Partial structure factors in order to obtain the number-density profiles directly. Previously, it has been common practice to fit self partial structure factors assuming a functional form for the relevant number-density distribution, using (7). It is usual to assume that the solvent number-density distribution is described by a tanh function.

\[ n_s(z) = \left( n_{\text{bulk}} / 2 \right) \left[ 1 + \tanh \left( z / \zeta \right) \right] \]  

(14)

where \( n_{\text{bulk}} \) is the number density of the bulk solution, \( n_s(z) \) the number density of the solvent at a depth \( z \) and \( \zeta \) a width parameter. The resulting self partial structure factor is

\[ h_{ii}(q) = \left( n_{\text{bulk}}^2 / q^2 \right) \left( \pi q / 2 \right)^2 \cosh \left( \pi q / 2 \right) \]  

(15)

Species adsorbed at the interface are assumed to have a number-density profile described by a Gaussian function.

\[ n_i(z) = n_i^0 \exp \left( -4z^2 / \sigma_i^2 \right) \]  

(16)

where \( n_i^0 \) is the number density at the peak of the Gaussian distribution and \( \sigma_i \) is the full width of the distribution at 1/e of its maximum height. The surface excess of \( i \) is given by

\[ \Gamma_i = 1 / A_i = \sigma_i n_i^0 \pi^{1/2} / 2 \]  

(17)

where \( \Gamma_i \) is the coverage in molecules \( \text{Å}^{-2} \) and \( A_i \) is the area per molecule in \( \text{Å}^2 \). The resulting self partial structure factor is

\[ h_{ii}(q) = (1 / A_i^2) \exp \left( q^2 \sigma_i^2 / 8 \right) \]  

(18)

Application of the shift theorem of Fourier transforms (see, for example, Bracewell, 1978), results in the following expression for the cross partial structure factor \( h_{ij} \):

\[ h_{ij}(q) = \text{Re} \left[ h_i(q) h_j(q) \exp (iq\delta) \right] \]  

(19)

where \( \delta \) is the distance between the centres of the two distributions. If the two distributions in question, \( n_i(z) \) and \( n_j(z) \), are positive, even and symmetrical about their centre, e.g. Gaussian, then

\[ h_{ij}(q) = \left| h_i(q) h_j(q) \right|^{1/2} \cos (q\delta) \]  

(20)

If, however, one of the distributions is odd, e.g. tanh, and one even, then

\[ h_{ij}(q) = \pm \left| h_i(q) h_j(q) \right|^{1/2} \sin (q\delta) \]  

(21)

where the sign is chosen to ensure a positive \( h_{ij} \).

Hence, provided that the distributions of \( i \) and \( j \) are either both even or one even and one odd, application of (20) or (21) allows \( \delta \) to be evaluated.

The methods outlined above have been used to analyse neutron reflection data on a variety of systems, mostly at the liquid–vapour interface; see, for example, Lu, Hromadova, Simister, Thomas & Penfold (1994), Lu, Simister, Thomas & Penfold (1993), Lu, Marrocco, Su & Thomas (1993) and Lu, Lee, Thomas, Penfold & Flitch (1993). However, some features of the method limit is usefulness.

If the components present at the interface can be exactly contrast-matched to air, then reflection profiles from systems in which all but one component is null scattering give the self partial structure factor for the nonmatched component directly. In this case, the errors in that partial structure factor may be quantified by reference to the errors in the original reflection measurement. Cross partial structure factors are obtained by taking differences of two or more data sets and thus their errors are harder to assess. If such contrast-matching is impossible, the partial structure factors may be obtained by solution of the simultaneous equations of the form of (10). Because the data sets contribute to the determination of a particular partial structure factor to varying degrees, errors in the reflection measurements cannot be readily translated into errors in the partial structure factors.

The problem of errors in the reflection profiles has been discussed by Lu, Simister, Thomas & Penfold (1993). These authors were concerned primarily with investigating the effects of errors caused by poor background subtraction and systematic errors in the scaling of the reflection data. They showed that such errors could have a profound influence on the shape and magnitude of the extracted partial structure factors and the resulting fitted number-density profiles.

In order to obtain a complete set of partial structure factors for an interface consisting of \( n \) components, it is necessary to obtain \( \frac{1}{2} n(n+1) \) sets of reflection data. Often, this is not possible. The types of systems where this method fails are those in which H/D substitution is not possible in all the components, for example one component is a fluorocarbon-based material, or one or more components may be complex, a protein or a polymer. For these systems, at worst, it is impossible to extract any partial structures at all; at best, only those factors associated with components that can be matched can be extracted. For these systems, at present there is no alternative but to model the reflectivity using the optical-matrix method.

In many instances, it is important to be able to analyse X-ray and neutron reflection data together. X-ray reflection data may provide a vital additional contrast in systems where H/D substitution is impossible to achieve. In addition, X-rays are generally more sensitive to counter-ions and a combination of the two techniques may be the only way of studying counter-ion structure. In order to extract partial structure factors from a combination of neutron and X-ray data, the X-ray data must be binned identically to the neutron data and all X-ray data outside the momentum-transfer range of the neutron measurement discarded. Thus, the great advantage of X-ray reflection, namely its large momentum-transfer range, is lost.

Often, some information concerning the interfacial structure may already be known. For example, stoichiometry or charge neutrality may dictate the relative
numbers of components. Volume filling may constrain the number of components present, molecular geometry may constrain the possible separation of components, and information about the coverage of a species may be known from other experimental techniques, for example surface tension. Ideally, such information should be incorporated in the data analysis. However, to date, some such information has been included in an ad hoc manner through scaling of certain selected data sets using model calculations, see for example Lu, Simister, Thomas & Penfold (1993).

Fitting reflectivity profiles directly

Introduction

From the above discussion, it is clear that the optical-matrix method is cumbersome to apply, describes the interface in an unrealistic fashion and may not treat surface roughness in a satisfactory manner. However, with this method it is possible, although tedious, to apply physical constraints to the interfaces used in the calculations and there is no problem with a parallel treatment of X-ray and neutron data.

Existing methods based on the kinematic approximation have the advantage that they model the interface in a realistic way and are less cumbersome to apply. However, in many systems of interest a full set of partial structure factors or partial structure factors involving components of interest cannot be extracted owing to a lack of suitable contrasts. In many cases, the existing contrasts, when combined with physical constraints and/or information from other experiments, should still prove sufficient to give reliable information about the interfacial structure. However, with the existing method this is not possible.

Even when they can be reliably extracted, fitting of the partial structure factors is not ideal. They are strongly sensitive to imperfections in the data, the combination of X-ray and neutron reflection data fails to make use of the greatly enhanced momentum-transfer range of the X-ray data, and physical constraints are difficult to apply.

We now describe a new method of data analysis that is based on the kinematic approximation but, because it fits the reflectivity profiles directly, overcomes the principal disadvantages of the partial-structure-factor method.

Theory

Provided the number-density distributions of the various components can be described by functions whose Fourier transforms are also analytical functions, equations of the form of (10) give an analytical expression for the reflectivity in terms of the momentum transfer, the scattering lengths of the components and the parameters describing their distributions. The best-fit parameters may be obtained by a non-linear least-squares procedure in which the quantity to be minimized is $F(i, q)^2$, where

$$F(i, q) = \sum_i \sum_q [\log R_{\text{obs}}(i, q) - \log R_{\text{calc}}(i, q)].$$  \hfill (22)

where the summation is performed over all values of momentum transfer, $q$, and over all data sets from different isotopic combinations, $i$. The minimization therefore yields the best combined fit to all sets of data that are assumed to have equal weighting. Each $R_{\text{calc}}(i, q)$ is given by all equation of the form of (10) with the scattering lengths appropriate to the contrast $i$. The logarithm of the reflectivity is used in (22) because this optimizes the scaling of the problem to ensure an efficient solution by the chosen algorithm. It also gives an even weighting to all the data points, even though the reflected signal changes by several orders of magnitude over the momentum-transfer range of the experiment.

For a system comprising two absorbed species at the air–water interface, (10) may be written explicitly:

$$R_{\text{calc}}(q) = (16\pi^2/q^2)((b_1^2/A_1^2) \exp (-q^2\sigma_1^2/8) + (b_2^2/A_2^2) \exp (-q^2\sigma_2^2/8))$$

$$+ (b_1^2b_2^2/(q^4)(\zeta\pi q/2)^2 \coth^2 (\zeta\pi q/2))$$

$$\pm 2b_1b_2[(1/A_1A_2) \exp [-q^2((\sigma_1^2 + \sigma_2^2)/8)]^{1/2} \times \cos \theta_{12} \pm 2b_1b_{so}}$$

$$\times [(n_{so}/q A_1) \exp (-q^2\sigma_1^2/8)(\zeta\pi q/2)^2]$$

$$\times \coth^2 (\zeta\pi q/2))^{1/2} \sin q\delta_{12}$$

$$\pm 2b_2b_{so}[(n_{so}/q^2 A_2) \exp (-q^2\sigma_2^2/8)(\zeta\pi q/2)^2]$$

$$\times \coth^2 (\zeta\pi q/2))^{1/2} \sin q\delta_{23}).$$ \hfill (23)

The parameters describing the number-density distributions of the two adsorbed species are $A_1$ and $A_2$, the areas per molecule of species 1 and 2, $\sigma_1$ and $\sigma_2$ the full width at 1/e of the maximum height of the two Gaussian number-density distributions, and $\delta_{12}$ the centre-to-centre separation of the two distributions. The water number-density distribution is described as a tanh function and its only adjustable parameter is $\zeta$, a width parameter defined in (14). The offsets of the centres of the two Gaussian distributions from the centre of the solvent distribution are given by $\delta_{1s}$ and $\delta_{2s}$.

Because (23) is valid for both neutrons and X-rays, both types of data may be combined. No truncation of the X-ray data is required, so full use may be made of their extended range in momentum transfer.

It can be seen by reference to (23) that only the magnitudes and not the signs of the distribution offsets, $\delta_{ij}$, can be determined without recourse to independent information. The magnitudes of the $\delta_{ij}$'s are not all independent. Even if no assumptions are made concerning the relative positions of the components in the interface, only certain sets are physically consistent. Often, the relative positions of components within the interface are known or inferred. For example, in the case
of a charged surfactant, common sense dictates that the
distribution of hydrocarbon chain is further from the bulk
solution phase than the charged headgroup. Application
of this assumption allows the general statement of the
relation between the $\delta_i$'s of (23) $|\delta_{12}| = |\delta_{11} \pm \delta_{22}|$, to be
written as:

$$\delta_{12} = \delta_{11} - \delta_{22}, \quad (24)$$

where the positive direction is defined as away from
the bulk solution in the direction of the vapour. Thus,
$\delta_{12}$ may be eliminated from the fitting procedure.
Similar arguments apply in more complex systems,
but the ability to infer the sign of the offsets may be
limited because there are more possible offset sign
combinations. In addition, in cases where the magnitude
of offsets is similar to the accuracy of their determina-
tion, it may also not be possible to determine the sign.
Whatever the system, no solution can be regarded as
physically valid unless the magnitudes of the offsets are
consistent.

Stoichiometry or the requirement for charge neutrality
may provide relationships between the coverages of the
adsorbed species that may lead to the removal of one or
more area terms from the fitting procedure. In some
instances, the coverage of a component may already be
known from some independent measurement, for exam-
ple surface tension or pressure/area isotherm measure-
ments. In this case, the relevant quantity may be
constrained to the known value and not varied in the
fitting procedure. Such constraints vary from system to
system but are easily and simply dealt with in this
method.

Other constraints, which are equally important and
difficult to incorporate in existing methods based on the
kinematic theory, are space filling and geometry. It is
important that the volume-fraction profile resulting from
the number-density-distribution parameters is physically
sensible. There appear to be two ways of dealing with this
is the present method.

(i) The solvent number-density distribution could be
calculated numerically to ensure a complete filling of
space based on the known volumes of the components.
Because this number-density profile would not have a
functional form it would have to be Fourier transformed
numerically to obtain the self solvent partial structure
factor for incorporation in (10). This procedure is not
only cumbersome, it is also only valid for adsorption at
the solid–liquid or liquid–liquid interfaces. At the air–
water interface, the surface is rough and complete space
filling up to the vapour phase does not occur.

(ii) A second possibility, which we have chosen to
adopt, is to assume that the water distribution is described
by a tanh function and to use the total volume-fraction
profile of the interface calculated from the adjustable
parameters and the known volumes of the components to
generate a weighting factor, $W$. The quantity to be
minimized then becomes $[WF(i, q)]^2$, where $F(i, q)$ is
still given by (22). A convenient form for $W$ is:

$$W = \exp[10.0(V_{\text{max}} - 1.1)] \quad \text{for } V_{\text{max}} > 1.1;$$

$$W = 1.0 \quad \text{for } V_{\text{max}} < 1.1. \quad (25)$$

$V_{\text{max}}$ is the maximum value of the volume-fraction
profile. This weighting factor effectively constrains the
volume-fraction to be physically reasonable, restricting
the maximum by which it can exceed the bulk density to
10%. In principle, geometric constraints, for example
those that place an upper limit on the separation of two
components in the same molecule, may be dealt with in a
similar manner.

It is also possible to include weighting factors to
account for statistical errors. However, in the results
shown below, we have chosen not to do this. Care must
be taken in using statistical errors as weighting factors in
reflectivity experiments because systematic errors, intro-
duced especially by instrumental resolution, occur at low
values of momentum transfer where statistical errors are
smallest.

From the above discussion, it can be seen that the
incorporation of constraints has the effect of reducing the
number of independent variables in equations of the form
of (23). Thus it is possible that fewer than the $3n(n + 1)$
contrasts may be required in order to evaluate the
independent parameters.

**Example of the direct-fitting method**

We choose to illustrate the use of this new method of
data analysis by examining the soluble surfactant
C$_{16}$H$_{33}$N(CH$_3$)$_3$Br, C$_{16}$TAB, adsorbed at the air–solution
interface. The data were obtained using the CRISP
reflectometer located on the ISIS neutron spallation
source at the Rutherford-Appleton Laboratory, England
(Penfold, Ward & Williams, 1987) by Lu, Hromadova,
Simister, Thomas & Penfold (1994). The bulk solution
concentration was $9.1 \times 10^{-4} \, \text{M}$, just below the critical
micelle concentration, or CMC, $9.2 \times 10^{-4} \, \text{M}$ (Mukerjee
& Mysels, 1971). The area per adsorbed molecule at this
concentration was determined by surface-tension mea-
surements to be 44.5 Å$^2$. Isotopes were synthesized in
which the chain-bound H atoms (dC$_{16}$TAB), the head-
group H atoms (hC$_{16}$TAB), and all H atoms
d(C$_{16}$dTAB) were replaced by D atoms. In addition, an
isotope was produced by mixing hC$_{16}$TAB and
0C$_{16}$dTAB such that the hydrocarbon chains were exactly
contrast-matched to air. This isotope is referred to as
0C$_{16}$hTAB. Solutions were prepared both in D$_2$O and in
null scattering water, CM0. In addition, X-ray reflection
data measured by Styrkas (1994) on a home-built
instrument at the Physical Chemistry Laboratory, Oxford,
were also available. The reflection measurements used in
this study are summarized in Table 1.

The raw neutron reflectivity data were scaled to give
absolute values by reference to the reflection from the
clean D$_2$O–air interface. The scaling was checked by the

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**Table 1**

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Description</th>
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<tbody>
<tr>
<td>D$_2$O-air</td>
<td>Clean D$_2$O–air interface</td>
</tr>
<tr>
<td>D$_2$O-D$_2$O</td>
<td>D$_2$O-D$_2$O interface</td>
</tr>
<tr>
<td>D$_2$O-CM0</td>
<td>D$_2$O-null scattering water</td>
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</tbody>
</table>

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**Note:** The table is not fully transcribed here, but the text provides a summary and includes details about the neutron and X-ray reflectivity experiments performed on a surfactant solution.
plotting of reflection data measured on D$_2$O solutions as $q^2R(q)$ versus $q$ and a check that the plot extrapolated to a value at $q = 0.0$ of $16\pi^2n_{so}^2b_{so}$, where $n_{so}$ and $b_{so}$ are the solvent bulk number density and scattering length, respectively. The X-ray reflectivity was measured in absolute units by a direct comparison to the incident beam intensity. For each data set, a flat background was determined by inspection and was subtracted from the raw signal. All data, X-ray and neutron, measured using a nonmatched solvent were corrected to give the kinematic reflectivity using (11). This correction was negligible at all but the lowest $q$ values.

The interface was treated as consisting of three components, hydrocarbon chains, tetramethylammonium bromide head groups and water. The concentration of surfactant in the bulk solution was such that treating the bulk solution as pure water did not introduce any appreciable error. In the least-squares fitting procedure, the areas per molecule of the head and chain, $A_1$ and $A_2$ in (23), were constrained to have the same adsorbed concentration of C$_{n}$TAB $9.1 \times 10^{-4}$ M CMC $9.2 \times 10^{-4}$ M

<table>
<thead>
<tr>
<th>Component volumes</th>
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<tbody>
<tr>
<td>Group or molecule</td>
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<tr>
<td>C$<em>{16}$H$</em>{35}$-</td>
</tr>
<tr>
<td>-N(CH$_3$)$_4$</td>
</tr>
<tr>
<td>Br$^-$</td>
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<td>H$_2$O</td>
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The best-fit parameters obtained by direct fitting are similar to those reported from an analysis of the partial structure factors. The main advantage of the direct method is that with it it is straightforward to ensure that the parameters are consistent. In the partial-structure-factor method, consistency is harder to achieve, especially when the number of components becomes large. This is illustrated in the present example by a slight inconsistency in the three offsets, $\delta_{ch}$, $\delta_{cs}$, and $\delta_{ks}$. The main disagreement between the two methods comes in the thickness of the head group. In the PSF analysis, the figure of $14 \AA$ comes from fitting the head-group self PSF. This in turn comes from a single reflection measurement, (c) in Table 1. In the direct method, the head self PSF is determined by all reflection measurements in which the head-group is not null-scattering rather than a single data set. Because scattering from the head group is relatively weak, its parameters are very sensitive to the amount and nature of the data used to evaluate them and this accounts for the discrepancy between the $\sigma_h$ values of Table 3. This can also be seen by reference to the results of Table 4.

It is also interesting to investigate to what extent the same information may be obtained with fewer than the six contrasts required for the partial structure factor analysis, and which, if any, of the contrasts are vital to the analysis. In Table 4, we show the results of performance of the minimization with only five of the six neutron contrasts, and one example of the use of four neutron measurements and one X-ray measurement. In order to compare the quality of the fits, the value of $F(i, q)$, defined in (22), normalized by the number of data points in the multiple data sets, is given.

As can be seen from Table 4, in most cases reducing the number of data sets used in the analysis does not change the structural parameters significantly. However, it is clear from the table that in order to obtain a realistic and accurate thickness for the head-group region it is important to include a set of data in which only that region is deuterated. This requirement may be relaxed if X-ray data are available, because that measurement is sensitive to Br$^-$ counter-ions present in the head-group region. In general, the extent to which a meaningful determination of the structure of an $n$-component interface when fewer than $\frac{1}{2}n(n + 1)$ contrasts are available will depend on:

(a) which contrasts are available;
(b) the desired spatial resolution compared with the momentum-transfer range of the experimental data;

<table>
<thead>
<tr>
<th>Table 1. Summary of data for C$_{16}$TAB</th>
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<tbody>
<tr>
<td>CMC</td>
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<td>Concentration of C$_n$TAB</td>
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<td>X-ray data</td>
</tr>
</tbody>
</table>
| Neutron data (contrasts used)           | (a) $dC_{16}hTAB$ in cm0  
(b) $dC_{16}dTAB$ in cm0  
(c) $0C_{16}hTAB$ in cm0  
(d) $dC_{16}hTAB$ in D$_2$O  
(e) $dC_{16}dTAB$ in D$_2$O  
(f) $hC_{16}dTAB$ in D$_2$O |
Fig. 1. Best fit to the combined set of six neutron reflection profiles of Table 1 (a)-(f). The parameters of the fit are given in Table 3.

Fig. 2. (a) The total volume fraction profile and (b) the individual component volume fraction profiles for (i) water, (ii) the trimethylammonium bromide head group and (iii) the hydrocarbon chain corresponding to the fit to the six sets of neutron reflection data (a)-(f) in Table 1. The parameters of the fit are given in Table 3.
Table 3. Best-fit parameters for 9.1 \times 10^{-4} M C_{16}TAB solution

<table>
<thead>
<tr>
<th>C_{16}TAB parameter</th>
<th>Area (Å²)</th>
<th>δ_{σh} (Å)</th>
<th>δ_{σx} (Å)</th>
<th>σ_{c} (Å)</th>
<th>σ_{s} (Å)</th>
<th>ζ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSF analysis</td>
<td>43.0</td>
<td>8.0</td>
<td>9.0</td>
<td>2.0</td>
<td>16.5</td>
<td>14.0</td>
</tr>
<tr>
<td>Direct analysis</td>
<td>44.5</td>
<td>8.7</td>
<td>9.3</td>
<td>0.6</td>
<td>16.6</td>
<td>17.8</td>
</tr>
</tbody>
</table>

Table 4. Fitted parameters obtained by the use of various combinations of data

<table>
<thead>
<tr>
<th>Data sets used (see Table 1)</th>
<th>\langle f(i, q) \rangle</th>
<th>σ_{c} (Å)</th>
<th>σ_{s} (Å)</th>
<th>δ_{σh} (Å)</th>
<th>δ_{σx} (Å)</th>
<th>ζ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a), (b), (c), (d), (e), (f)</td>
<td>5.7 × 10^{-3}</td>
<td>16.6</td>
<td>17.8</td>
<td>9.3</td>
<td>0.6</td>
<td>7.6</td>
</tr>
<tr>
<td>(b), (c), (d), (e), (f)</td>
<td>6.3 × 10^{-3}</td>
<td>16.6</td>
<td>17.8</td>
<td>9.3</td>
<td>0.6</td>
<td>7.6</td>
</tr>
<tr>
<td>(a), (c), (d), (e), (f)</td>
<td>6.3 × 10^{-3}</td>
<td>16.3</td>
<td>16.1</td>
<td>9.5</td>
<td>0.0</td>
<td>7.4</td>
</tr>
<tr>
<td>(a), (b), (d), (e), (f)</td>
<td>4.2 × 10^{-3}</td>
<td>16.2</td>
<td>26.4</td>
<td>9.3</td>
<td>1.4</td>
<td>7.4</td>
</tr>
<tr>
<td>(a), (b), (c), (e), (f)</td>
<td>5.2 × 10^{-3}</td>
<td>16.7</td>
<td>17.5</td>
<td>10.2</td>
<td>1.6</td>
<td>7.5</td>
</tr>
<tr>
<td>(a), (b), (c), (d), (f)</td>
<td>3.7 × 10^{-3}</td>
<td>16.5</td>
<td>17.5</td>
<td>8.6</td>
<td>1.8</td>
<td>7.7</td>
</tr>
<tr>
<td>(a), (b), (c), (d), (e)</td>
<td>5.2 × 10^{-3}</td>
<td>15.9</td>
<td>17.8</td>
<td>9.4</td>
<td>0.6</td>
<td>6.7</td>
</tr>
<tr>
<td>(a), (b), (c), (d), and X-ray</td>
<td>3.7 × 10^{-2}</td>
<td>18.0</td>
<td>14.0</td>
<td>9.4</td>
<td>1.4</td>
<td>8.0</td>
</tr>
</tbody>
</table>

(c) the availability of independent information on the system.

However, of all data-analysis methods, the direct-fitting method is the only one in which external information can be used to aid in the determination of the structure; it is thus likely to be of great use in systems where the scattering length of one or more components may not be varied, for example with fluorocarbon species and many proteins.

Discussion

We have described a new method of neutron and X-ray reflection data analysis. The number-density distributions of the components present in the interface are described by smooth functions, for example Gaussian or tanh functions, which have analytical forms for the Fourier transforms. The method has the advantage compared with modelling by means of the optical-matrix method that it is not only less cumbersome to apply but describes the interface in a more realistic way. Unlike previous methods based on the kinematic approximation, the reflectivity profiles themselves are fitted, rather than the partial structure factors extracted from the data. The new method is more realistic because the partial structure factors, especially the cross terms, are extremely sensitive to imperfections in the data, and the propagation of errors from reflection profile to partial structure factor may not always be followed. The present method can also be readily adapted to incorporate physical constraints provided by volume-filling arguments, stoichiometry, geometry and other experimental measurements in order to aid the determination of the structure.

We have chosen to illustrate the use of the new method by analysing neutron reflection data of C_{16}TAB adsorbed at the solution–air interface. Lu, Hromadova, Simister, Thomas & Penfold (1993) had analysed the data by a combination of optical-matrix modelling and analysis of partial structure factors. The conclusions arrived at are qualitatively similar to those previously obtained. We also demonstrate that it is possible to come to broadly similar conclusions using fewer than the six contrasts required in the partial-structure-factor method, and that the number of sets of neutron data required may be further reduced if X-ray reflection data is available. This reduction in the number of data necessary is a consequence both of not requiring the partial structure factors explicitly and the incorporation of physical constraints in the fitting procedure. This method is likely to prove of great importance, especially in systems where contrast variation is limited or it is not possible to exactly contrast-match all the components.

References
