

## A low-wave-vector expansion for reflectivity

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We expand an accurate, closed-form equation for the reflectivity in a power series around  $q_2=0$ , where  $q_2$  is the  $z$  component of the wave-vector transfer in a film of constant composition. We examine, in particular, the case where  $q_2=0$  at the critical edge. Such an example might be realized through a neutron-reflectivity experiment on a microemulsion that exhibits surface layering. We find the coefficients of this low-wave-vector expansion to be the moments of the scattering-length density profile. We demonstrate how the first moment of the profile can be obtained from an accurate reflectivity measurement.

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Specular reflectivity has enjoyed a recent popularity because it is a sensitive probe of the scattering-length density profile normal to the reflection surface. And because the scattering-length density can be explicitly linked to molecular composition, the reflectivity technique is seen as an important surface-science tool. Neutron reflectivity, for example, has been used to quantify the surface segregation of deuterated polymer, in an otherwise miscible blend of deuterated and protonated polymer [1]. X-ray reflectivity has been used to observe and quantify the structure of self-assembled surfactant films on silicon [2] and the surface-induced structure of liquid-crystal films on their approach to the smectic- $A$  transition [3]. A recent review article describes these and other systems [4].

What is common to all reflectivity experiments is the need to fit the data with a model of the scattering-length density profile. And whenever a model is used, there are the concomitant questions concerning the uniqueness of the fitted model. Some have reduced the ambiguity of their model through the use of contrast variation [5], while others have supported their model with reasonable physical arguments. Still others have complemented their reflectivity studies with direct surface probes [6]. Of the studies that have relied solely on reflectivity, most have used only data far from  $q_c$ , the critical wave vector for total reflection, where multiple-scattering effects are not important and the Born approximation holds. In this Brief Report, we show how model-independent information on the profile can be extracted from accurate measurements close to the critical edge. Our message here is not that contrast variation, reasonable physical arguments, or secondary probes are without merit. We merely seek to counter the conventional wisdom that views low-wave-vector data as not interpretable and, therefore, useless.

The utility of reflectivity data near  $q_c$  has been largely hampered by the lack of accurate, closed-form expressions for the reflectivity. In an exact calculation, the profile is divided into many slabs, each of constant

scattering-length density; the reflectivity from this composite medium is then calculated using a recursion relation developed from standard optics [7]. This relation, however, becomes unwieldy for more than three layers, and so does not lend itself to a low-wave-vector expansion. In the Born approximation, refraction is ignored and the reflectivity can be related to the modulus of the Fourier transform of the  $z$ -dependent derivative of the scattering-length density [8,9]. This closed-form expression, however, is inaccurate near the critical edge, where refractive effects are important.

The starting point of our approach is a closed-form equation that accurately approximates the reflectivity from thin films ( $\delta < 600$  Å), even near  $q_c$ . This equation has been recently developed within the distorted-wave Born approximation (DWBA) [10]. In the DWBA, one accounts for refraction by envisioning the actual film, with its depth-dependent variations in scattering-length density  $\rho(z)$ , to be comprised of a homogeneous slab of average scattering-length density  $\rho_0$ , and thickness  $\delta$ , and a difference film, which records  $\Delta\rho(z)=\rho(z)-\rho_0$  between the air-film ( $z=0$ ) and film-substrate ( $z=\delta$ ) interfaces. The net wave vector within the film is stripped of any depth dependence and assigned a value corresponding to this average film,  $q_2=(q^2-16\pi\rho_0)^{1/2}$ . In fact, such an approximation has been previously combined with the Born approximation equation to produce a kind of modified Born expression [11]: here  $q_2$  is substituted for  $q$ , the vacuum wave vector, in the Fourier transform. This modification, however, also produces inaccurate reflectivities at low wave vectors.

The success of the DWBA stems from the explicit separation of the average and difference films. Consider, for example, the case where the substrate and the average film have the same scattering-length density. The average film is then no longer a slab, but a step, and  $\delta$  is the distance from the air-step interface over which the deviations from  $\rho_0$  disappear. Such a profile might be realized for a microemulsion that exhibits surface layering, where the layers are regions of  $D_2O$  and protonated oil, separat-

ed by surfactant. In this case, we expect  $\rho(z)$  to oscillate about, and finally decay to, a bulk scattering-length density  $\rho_0$ . The neutron reflectivity from this layered film can be expressed as a perturbation on the reflectivity [ $R_0(q)=|r_0(q)|^2$ ] from the uniform, bulk microemulsion with no surface layering:

$$R(q) = \left| ir_0(q) + \frac{4\pi}{q} [1 + r_0(q)]^2 \int_0^\delta \Delta\rho(z) e^{iq_2 z} dz \right|^2. \quad (1)$$

Figure 1, where the exact, DWBA, and modified Born reflectivities are calculated from the neutron scattering-length density profile of a hypothetical surface-layered microemulsion, bears witness to the accuracy of the DWBA and the inaccuracy of the modified Born approximation, near the critical edge. The Born result, which is not shown here, is inaccurate up to  $q = 3q_c$ .

If  $\rho(z)$  oscillates equally about  $\rho_0$ , then  $\int_0^\delta \Delta\rho(z) dz$  will vanish, and so, at  $q_2 = 0$ ,  $R(q) = R_0(q)$ . It therefore makes sense to expand  $R(q) - R_0(q)$  around  $q_2 = 0$ . Even if  $\rho(z)$  oscillates only approximately equally about  $\rho_0$ , which might be the case for an actual microemulsion,

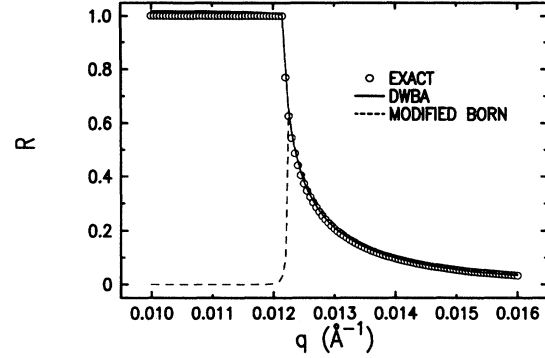


FIG. 1. Exact, DWBA, and modified Born reflectivities, calculated from the profile of Fig. 2(a). Note that the ordinate scale is linear.

$\int_0^\delta \Delta\rho(z) dz$  will be negligible, and the expansion still holds. This expansion yields  $R(q) - R_0(q)$  in terms of the moments [ $M_j = \int_0^\delta z^j \Delta\rho(z) dz$ ] of the difference profile  $\Delta\rho(z)$ .

$$R(q) = R_0(q) + \left[ \frac{8\sqrt{\pi}}{\sqrt{\rho_0}} M_1 \right] q_2 + \left[ \frac{16\pi}{\rho_0} M_1^2 - \frac{8}{\rho_0} M_1 \right] q_2^2 + \left[ -\frac{16\sqrt{\pi}}{\rho_0^{3/2}} M_1^2 + \frac{17}{4\sqrt{\pi}\rho_0^{3/2}} M_1 - \frac{4\sqrt{\pi}}{3\sqrt{\rho_0}} M_3 \right] q_2^3 + \left[ \frac{9}{\rho_0^2} M_1^2 - \frac{3}{2\pi\rho_0^2} M_1 + \frac{4}{3\rho_0} M_3 - \frac{16\pi}{3\rho_0} M_1 M_3 + \frac{4\pi}{\rho_0} M_2^2 \right] q_2^4 + O(q_2^5). \quad (2)$$

By fitting  $R(q) - R_0(q)$  to a polynomial and matching the coefficients of this polynomial to those of Eq. (2), the lower moments of  $\Delta\rho(z)$  can be obtained. For a fit,  $R_0(q)$  need not be measured separately:  $R_0(q)$  is the Fresnel reflectivity of a step with height  $\rho_0$ —a value that can be found through an accurate measurement of  $q_c = \sqrt{16\pi\rho_0}$  of the layered film. In the DWBA, after all,  $\delta$  and  $\Delta\rho(z)$  are both small enough to not affect  $q_c$ ;  $q_c$  is, instead, just a measure of the bulk film upon which the layering resides.

Some examples of how this moment analysis might be applied with neutron-reflectivity data are shown in Figs. 2 and 3. In Fig. 2(a), we plot a hypothetical scattering-length density profile of a surface-ordered microemulsion composed of  $D_2O$ , protonated oil, and protonated surfactant;  $\rho(z)$  oscillates about, and then decays to,  $\rho_0$ , the bulk value, which is approximately midway between  $\rho_{D_2O} = 6.38 \times 10^{-6} \text{ \AA}^{-2}$  and  $\rho_{oil} = -4.8 \times 10^{-7} \text{ \AA}^{-2}$ . This profile was generated using an exponentially damped cosine function:  $\rho(z) = \rho_{D_2O}\phi + \rho_{oil}(1 - \phi)$ , where  $\phi$  is given by  $\phi = \frac{1}{2} + \frac{1}{2} e^{-(z/\xi)} \cos(2\pi z/D)$ . Here we have chosen  $D = 200 \text{ \AA}$  and  $\xi = 100 \text{ \AA}$ . This set of parameters is consistent with a recent observation of layering at the air-film interface of a bicontinuous microemulsion [12]. Figure 2(b) shows a plot of  $R(q) - R_0(q)$  and its corresponding fourth-order-polynomial fit;  $R(q)$  and  $R_0(q)$  were generated from the profile of Fig. 2(a);  $R(q)$  was cal-

culated using the exact recursion relation. From a fit of  $R(q) - R_0(q)$ , we obtain the first moment of the difference profile to be  $-0.00274$  when the actual first (difference) moment is  $-0.00260$ . It is not practical to accurately obtain the second or third moments, which are buried in the coefficients of the third- and fourth-order terms. In Fig. 3(a), we also show the scattering-length density of a surface-ordered microemulsion, but here we use  $H_2O$  and deuterated oil ( $\rho_{H_2O} = -5.6 \times 10^{-7} \text{ \AA}^{-2}$  and  $\rho_{oil} = 6.5 \times 10^{-6} \text{ \AA}^{-2}$ ); we have again used the exponentially damped cosine function with  $D = 200 \text{ \AA}$  and  $\xi = 100 \text{ \AA}$ . Figure 3(b) shows a plot of  $R(q) - R_0(q)$ , generated from the profile in Fig. 3(a), and its corresponding fourth-order-polynomial fit. We obtain the first moment of the difference profile to be  $0.00250$  when the actual first (difference) moment is  $0.0268$ . These two examples show that both surface excess and depletion can be measured in a model-independent fashion: in Fig. 2, where  $\rho(z) > \rho_0$  near the air-microemulsion interface, we determine  $M_1 < 0$ ; in Fig. 3, we cause a surface depletion in scattering-length density and we, accordingly, measure  $M_1 > 0$ .

As might be expected, Eq. (2) is only accurate for  $q_2\delta < 1$ , and since  $\delta$  is typically  $600 \text{ \AA}$ , any moment analysis usually applies only for  $q_c < q < 1.03q_c$ . In Fig. 1, this corresponds to  $q < 0.0126$ . It should also be noted that Eq. (2) ignores resolution ( $\Delta q$ ). Our calculations

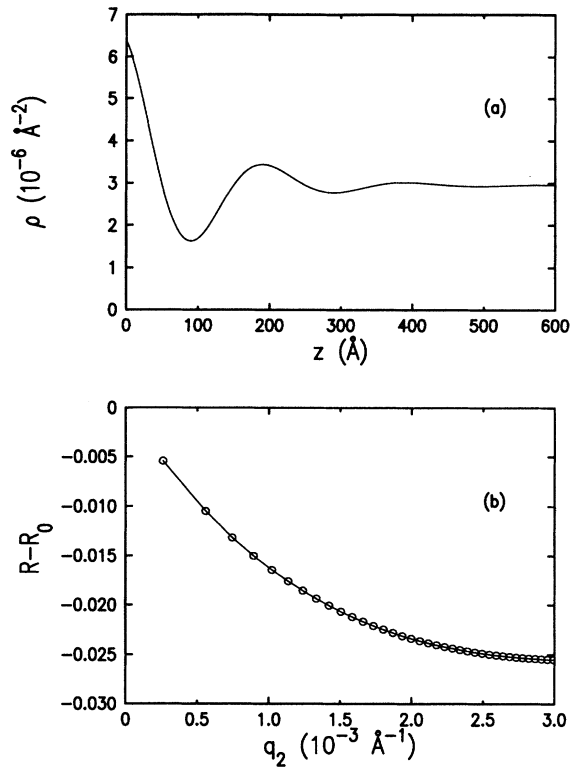


FIG. 2. (a) Scattering-length density profile of a hypothetical surface-layered microemulsion composed of  $D_2O$ , protonated oil, and surfactant; (b) the difference curve  $R(q) - R_0(q)$  is fit to a fourth-order polynomial:  $R(q) - R_0(q) = 7.56 \times 10^7 q_2^4 - 1.128 \times 10^6 q_2^3 + 7.38 \times 10^3 q_2^2 - 22.51 q_2 - 3.79 \times 10^{-5}$ .

show that, for  $\Delta q < 10^{-5} \text{ \AA}^{-1}$ , Eq. (2) can be applied, as is; for larger  $\Delta q$ , the expression should be convolved with the resolution function before fitting the difference curve. Also, in any actual experiment,  $R(q)$  would have to be measured to within 0.3% [ $\Delta R(q) < 0.3\%$ ]; presumably, this type of accuracy can be achieved near the critical edge, where the number of incident and reflected particles are approximately equal. This moment analysis could also be used with x-ray reflectivity data, where the large number of incident, monochromatic photons allows for both a low  $\Delta q$  and a low  $\Delta R(q)$ . In a typical x-ray experiment, however,  $\Delta \rho(z)$  rarely changes by more than 30%, and so  $R(q)$  would have to be measured even more accurately. Here we have chosen examples from neutron

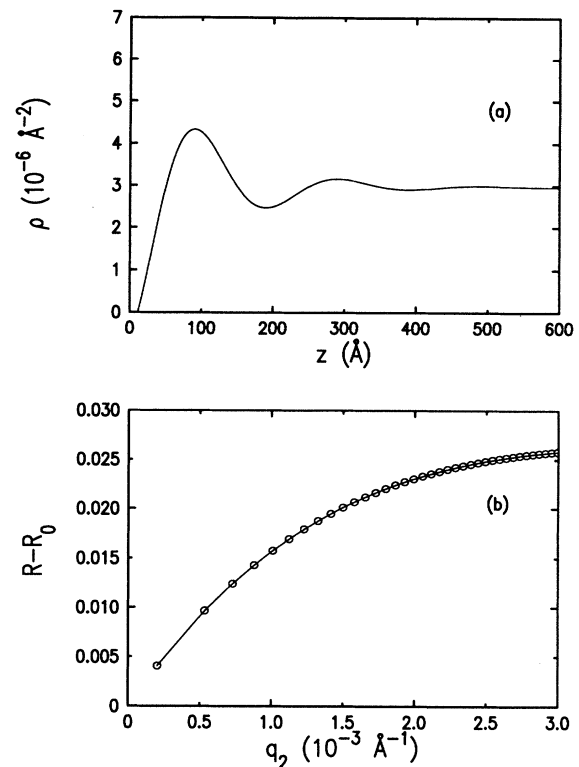


FIG. 3. (a) Scattering-length density profile of a hypothetical surface-layered microemulsion composed of  $H_2O$ , deuterated oil, and surfactant; (b) the difference curve  $R(q) - R_0(q)$  is fit to a fourth-order polynomial:  $R(q) - R_0(q) = -6.46 \times 10^7 q_2^4 + 9.72 \times 10^5 q_2^3 - 6.56 \times 10^3 q_2^2 + 21.28 q_2 + 1.78 \times 10^{-5}$ .

reflectivity because this technique, through isotopic labeling, allows for the possibility of larger changes in  $\rho(z)$  and, therefore, a larger difference between  $R(q)$  and  $R_0(q)$ . In summary, we note that, while the requirements for this analysis are demanding, accurate measurements of  $R(q)$  near  $q_c$  could serve the useful purpose of revealing the first moment of the difference profile. And this model-independent information could be used to complement information obtained from other means.

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