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Improved analytical formulas for x-ray and neutron reflection from surface films

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A general and exact expression for x-ray and neutron reflectance and transmittance is given in terms of an integral of the real-space scattering-length-density profile fluctuation of the film, with respect to an arbitrary constant reference density level, over the wave function inside the film. Various special cases and approximations are then derived from this exact form by suitable approximations of the wave function. In particular, two practical approximate formulas are derived which are improvement over the corresponding distorted-wave Born approximations. One is for an arbitrary film deposited on a known substrate and the other for a free liquid surface. Numerical results are used to illustrate the accuracy of these formulas.

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I. INTRODUCTION

The reflectance and transmittance of specular reflection of plane waves of x ray and neutrons from one-dimensional surface films have been given recently in [1] in the so-called small curvature approximation (SCA). This approximation was proven to reduce to and is more accurate than the standard Born approximation, the distorted-wave Born approximation (DWBA), and the WKB approximation. It was also shown that it is accurate from high-Q region down to the region very close to the critical edge. However, around the critical edge, it produces some oscillatory deviations from the exact result. These deviations are thought to be due to the existence of a bare-substrate Fresnel reflection term in the Green's function employed in the SCA. Around the critical edge, this term remains as a propagating mode when it should have become evanescent, thus causing an artificial interference effect. To correct for this effect, a more general and better Green's-function formulation of the reflection is developed in this paper.

The reflection and transmission of a plane wave e^{ik_0z} by a surface film on top of a semi-infinite substrate are illustrated in Fig. 1. The free liquid surface is just a special case of Fig. 1 when the substrate scattering length density is made identical to that of the bulk liquid. The scattering length densities are 0, $\rho(z)$, and ρ_s in the air, the film, and the substrate, respectively. The corresponding one-dimensional wave numbers are k_0, $k(z)$, and k_s defined by $k_0=2\pi\sin\theta/\lambda$, $k(z)=[k_0^2-4\pi\rho(z)]^{1/2}$, and $k_s=(k_0^2-4\pi\rho_s)^{1/2}$ with θ denoting the grazing angle of incidence and λ the free-space wavelength of the incident wave. The reflected wave is re^{-ik_0z} and the transmitted wave te^{ik_sz} with r and t being the reflectance and transmittance to be found. The one-dimensional wave function $U(z)$ satisfies the following Helmholtz equations in the three regions shown in Fig. 1:

$$U''(z)+k_0^2U(z)=0,\quad z\le -d \tag{1.1a}$$

$$U''(z)+\bar{k}^2U(z)=-(k^2-\bar{k}^2)U(z),\quad -d\le z\le 0 \tag{1.1b}$$

$$U''(z)+k_s^2U(z)=0,\quad z\ge 0 \tag{1.1c}$$

where $\bar{k}$ is an arbitrary reference wave number to be chosen properly so that the above-mentioned artificial interference effect can be eliminated. It should be pointed out that, for the neutron, $U(z)$ is the z dependence of the corresponding three-dimensional wave function ϕ defined as $\phi(x,y,z)=\varphi(x,y)U(z)$, while for s-wave x rays, i.e., with polarization vector perpendicular to the plane of incidence, $U(z)$ represents the z dependence of the electric-field intensity $E(x,y,z)=F(x,y)U(z)$. For p-wave x rays, i.e., with polarization within the plane of incidence, it is not possible to cast $U(z)$ in the above form, and the theory presented in this paper does not apply.

To solve Eqs. (1.1a)–(1.1c), the general Green's-function approach is followed [2,3]. Using the geometry

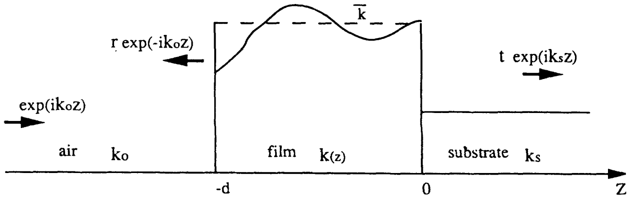

FIG. 1. Illustration of the reflection and transmission of a plane wave by a surface film on top of a substrate.

in Fig. 1, it is straightforward to derive the Green's function as

$$g(z,z')=C_r e^{-ik_0 z}[e^{i\bar{k}z'}+R_r e^{-i\bar{k}z'}], \quad z\le -d \tag{1.2a}$$

$$g(z,z')=C_t e^{ik_s z}[e^{-i\bar{k}z'}+R_1 e^{i\bar{k}(2d+z')}], \quad z\ge 0 \; . \tag{1.2b}$$

Using the Green's functions, one easily obtains the exact general expressions for the reflectance r and transmittance t as

$$r=\bar{R}+C_r\int_{-d}^{0}dz'(k^2-\bar{k}^2)U(z')[e^{i\bar{k}z'}+R_r e^{-i\bar{k}z'}] \; , \tag{1.3a}$$

$$t=\bar{T}+C_t\int_{-d}^{0}dz'(k^2-\bar{k}^2)U(z')[e^{-i\bar{k}z'}+R_1 e^{i\bar{k}(2d+z')}] \; , \tag{1.3b}$$

with

$$C_r=\frac{iC}{2\bar{k}}T_1 e^{i(\bar{k}-k_0)d}, \quad C_t=\frac{iC}{2\bar{k}}T_r, \quad C=\frac{1}{1-R_1R_r e^{2i\bar{k}d}} \tag{1.3c}$$

and

$$\bar{R}=C(-R_1+R_r e^{2i\bar{k}d})e^{-2ik_0 d}, \quad \bar{T}=CT_fT_r e^{i(\bar{k}-k_0)d} \; , \tag{1.3d}$$

where $R_1=(\bar{k}-k_0)/(\bar{k}+k_0)$, $R_r=(\bar{k}-k_s)/(\bar{k}+k_s)$, $T_1=2\bar{k}/(\bar{k}+k_0)$, $T_r=2\bar{k}/(\bar{k}+k_s)$, and $T_f=2k_0/(k_0+\bar{k})$. Compared to [1], the unique element introduced here is the reference $\bar{k}$, which can be chosen in various ways without changing the validity of the solution Eqs. (1.3a) and (1.3b). In Sec. II, various choices of $\bar{k}$ will be discussed and the resultant reflectances compared with the known results. For a free liquid surface and a film deposited on a known substrate, two very accurate formulas will be presented in Sec. II and numerical comparisons with the exact results will be used to demonstrate their accuracies in Sec. III.

II. SPECIAL CASES AND PRACTICAL APPROXIMATE FORMULAS

Since $\bar{k}$ is an arbitrary constant, one can choose different values for it to obtain different forms of exact expressions for r and t.

(a) If $\bar{k}$ is chosen to be $\bar{k}=k_0$, corresponding to choosing the reference level to be the air, then r and t reduce to

$$r=R+\frac{i}{2k_0}\int_{-d}^{0}dz'(k^2-k_0^2)U(z')[e^{ik_0z'}+Re^{-ik_0z'}] \; , \tag{2.1a}$$

$$t=T+\frac{i}{2k_0}T\int_{-d}^{0}dz'(k^2-k_0^2)U(z')e^{-ik_0z'} \; , \tag{2.1b}$$

with $R=(k_0-k_s)/(k_0+k_s)$ and $T=2k_0/(k_0+k_s)$. Equations (2.1a) and (2.1b) are then identical to the exact results given in [1]. In order to obtain a close-form expression for r and t, approximation of the wave function $U(z)$ in the film has to be made. It turns out that for this choice of $\bar{k}$, it is difficult to obtain a good approximate $U(z)$ which reproduces the correct reflectivity near the total reflection edge (see Ref. [1]).

(b) However, if $\bar{k}$ is chosen to be $\bar{k}=k_s$, then Eq. (2.1a) becomes

$$r=Re^{-2ik_0d}+A\int_{-d}^{0}dz'(k^2-k_s^2)U(z')e^{ik_sz'} \; , \tag{2.2a}$$

$$A=\frac{i}{k_0+k_s}e^{i(k_s-k_0)d} \; , \tag{2.2b}$$

which is again exact but simpler. The choice of $U(z)$ then becomes easier.

(i) Now, the wave function $U(z)$ in Eq. (2.2a) can be approximated very accurately by the following choice (see [1]):

$$U(z)=B\left[\exp\left[\int_0^z ik\,dz\right]+r_b\exp\left[-\int_0^z ik\,dz\right]\right] \; , \tag{2.3a}$$

$$B=\frac{t_fe^{-ik_0d}\exp\left[\int_{-d}^{0}ik\,dz\right]}{1+r_br_f\exp\left[\int_{-d}^{0}2ik\,dz\right]} \; . \tag{2.3b}$$

Here $r_f=(k_0-k_f)/(k_0+k_f)$, $r_b=(k_b-k_s)/(k_b+k_s)$, $t_f=2k_0/(k_0+k_f)$, and $k_f=(k_0^2-4\pi\rho_f)^{1/2}$ and $k_b=(k_0^2-4\pi\rho_b)^{1/2}$. Note that ρ_f is calculated by taking the average of the density profile $\rho(z)$ at the front end of the film ($z=-d$) over a region of thickness $\Delta=2\pi/Q_c$, Q_c being the value of $Q=2k_0$ at the critical edge. The quantity ρ_b is similarly calculated at the rear end of the film ($z=0$). This approximation of $U(z)$ is obtained from the SCA result Eqs. (2.14a) and (2.14b) in [1] by neglecting the derivative $k'(z)$ for simplicity. Equation (2.3a) will be accurate for most practical purposes because the phase relation and the multiple reflections between the front and the back interfaces are both correctly accounted for. Substitution of (2.3a) into Eq. (2.2a) gives

$$r=Re^{-2ik_0d}+AB\int_{-d}^{0}dz'(k^2-k_s^2)e^{ik_sz'}\left[\exp\left[\int_0^{z'}ik\,dz\right]+r_b\exp\left[-\int_0^{z'}ik\,dz\right]\right] \; . \tag{2.4}$$

This is a good approximate formula for a film deposited on a known substrate and will be shown in Sec. III to be an improvement over the DWBA Eq. (2.6c) and the result in [1, Eq. (2.15a)].

(ii) For a free liquid surface, the surface structure gradually merges into the bulk. In this case $r_b=0$ for sufficiently large d such that all the surface structure is included. Then, k_s is equal to the bulk value of the liquid. If the bulk wave number is denoted by $\bar{k}$, we have

$$r=Re^{-2ik_0d}+D\int_{-d}^{0}dz'(k^2-\bar{k}^2)e^{i\bar{k}z'}\exp\left[\int_0^{z'}ik\,dz\right] \; , \tag{2.5a}$$

where

$$D=\frac{it_f e^{-2ik_0 d}\exp\left[\int_{-d}^{0}(\bar{k}+k)dz\right]}{(k_0+\bar{k})}\ . \tag{2.5b}$$

This is an excellent approximate formula for free liquid surfaces.

(c) If the choice for $\bar{k}$ is such that

$$\bar{k}^2=\frac{1}{d}\int_{-d}^{0}k^2(z)dz\ , \tag{2.6a}$$

and we use the exact wave function inside a film having a constant scattering-length density $\bar{\rho}$, which is

$$U(z)=CT_f e^{-ik_0 d}e^{i\bar{k}d}[e^{i\bar{k}z}+R_r e^{-i\bar{k}z}]\ , \tag{2.6b}$$

then Eq. (1.3a) reduces to a simple expression

$$r=\bar{R}+C_0[\Delta\tilde{\rho}(2\bar{k})+R_r^2 e^{4i\bar{k}d}\Delta\tilde{\rho}(-2\bar{k})]\ , \tag{2.6c}$$

with $C_0=iC^2T_1T_f e^{-2ik_0 d}/(2\bar{k})$ and $\bar{R}$ already defined in Eq. (1.3d). Note that $k^2-\bar{k}^2=-4\pi(\rho-\bar{\rho})=-4\pi\Delta\rho(z)$ and $\Delta\tilde{\rho}$ denotes the half-space Fourier transform of $\Delta\rho(z)$. Equation (2.6c) is the DWBA approximation currently proposed to be used to treat very thin surface films ($d<400$ Å) deposited on a highly reflecting substrate [4,5]. This approximation is not accurate for the case of thicker films and weakly reflecting substrates as will be seen in Sec. III.

(d) Finally, in order to obtain the well-known Born approximation [6], the film and the substrate as a whole are regarded as a finite material region localized within

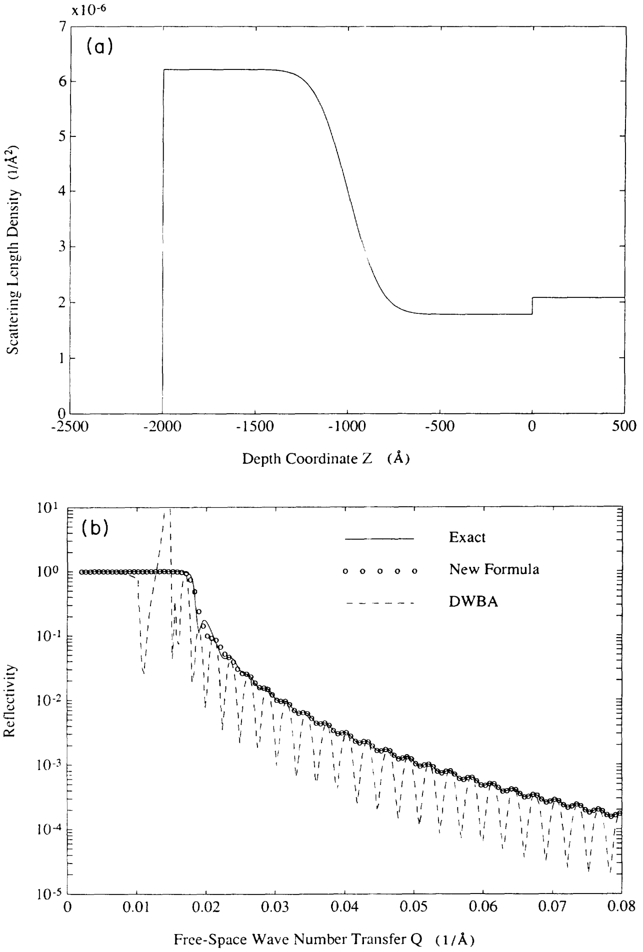

FIG. 2. Comparison of Eq. (2.4) with the exact result and the distorted-wave Born approximation Eq. (2.6c). (a) The scattering-length-density profile used for comparison is an error function profile between two polymer layers on top of a silicon substrate as commonly used in neutron reflection study of polymer-polymer interdiffusion [8]. (b) The calculated reflectivity using Eq. (2.4) is plotted in circles together with the exact result (solid line) and the DWBA approximation (dashed line). Q is the free-space wave-number transfer defined by $Q=2k_0$.

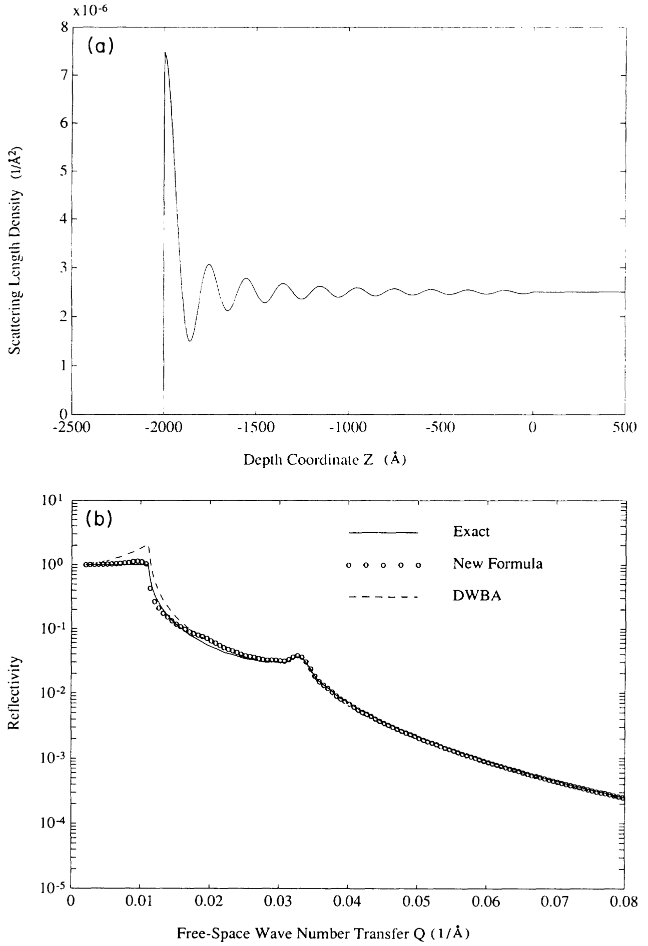

FIG. 3. Comparison of Eq. (2.5a) with the exact result and the distorted-wave Born approximation Eq. (2.6c). (a) The scattering-length-density profile used for comparison is superposition of an oscillating component on a bulk liquid as given by $\rho(z)=\rho_b+\rho_1[\sin k(z+z_0)/k(z+z_0)]\cdot e^{-(z+z_0)/\xi}$, where $\rho_b=2.5\times10^{-6}$ Å^{-2}, $\rho_1=5.0\times10^{-6}$ Å^{-2}, $k=\pi/100$ Å^{-1}, $z_0=2000$ Å, and $\xi=2000$ Å. This oscillatory profile simulates our recent finding on free microemulsion surfaces [9]. (b) The calculated reflectivity using Eq. (2.5a) is plotted in circles together with the exact result (solid line) and the DWBA approximation (dashed line). Q is the free-space wave-number transfer defined by $Q=2k_0$.

$(-\infty,+\infty)$ and $\bar{k}$ in Eq. (1.3a) is chosen to be k_0. Then the integration limits in Eq. (1.3a) become $(-\infty,+\infty)$. Since the region to the right of the film-substrate combination consists of air, we can put, in Eq. (1.3a), $R_1=R_r=0$, $T_1=1$, $\bar{R}=0$, and $C_r=1/2k_0$. If we further approximate the wave function inside the film-substrate combination by the incident wave e^{ik_0z}, we obtain, noting that $k^2-k_0^2=-4\pi\rho(z)$,

$$r=\frac{i}{2k_0}\int_{-\infty}^{+\infty}dz'(k^2-k_0^2)\cdot e^{2ik_0z'}$$

$$=\frac{-4\pi i}{Q}\int_{-\infty}^{+\infty}dz'\rho(z')\cdot e^{iQz'}\;, \tag{2.7a}$$

where $Q=2k_0$. A partial integration further reduces the expression to the well-known form

$$r=\frac{4\pi}{Q^2}\int_{-\infty}^{+\infty}dz'\frac{d\rho(z')}{dz'}\cdot e^{iQz'}\;. \tag{2.7b}$$

This approximation is only accurate for values of Q larger than about five times the critical edge [1],

III. NUMERICAL COMPARISONS AND CONCLUSIONS

In this section, the accuracy of the formulas Eqs. (2.4) and (2.5a) are tested by comparisons with the exact results calculated through Parrat's recursion relation [7]. The DWBA approximation Eq. (2.6c) is also calculated and compared with Eqs. (2.4) and (2.5a).

For Eq. (2.4), an error function scattering length density profile illustrated in Fig. 2(a) is used. The profile is typical of the DPS-HPS (deuterated-protonated polystyrenes) polymer-polymer interdiffusion profile on top of a silicon substrate [8]. The calculated reflectivity from Eq. (2.4) (the squared modulus of r) is plotted in circles in Fig. 2(b) together with the exact result in solid line. The DWBA result from Eq. (2.6c) is in dashed line. Equation (2.4) agrees very well with the exact result. The DWBA approximation suffers from the artificial interference effect due to the large step at the rear interface when the average profile is taken as shown by Eq. (2.6a). Equation (2.4) is without doubt superior to DWBA. It is also better than the result in [1] since the fluctuations around the critical edge is suppressed in Eq. (2.4). We found through numerical analysis that the condition of validity for the DWBA approximation is that the substrate has a very high scattering length density, i.e., is highly reflecting, and that the film structure can be approximated closely by a small perturbation superimposed on a constant scattering-length-density background. Consequently, it is more likely to be accurate for x-ray reflection than for neutron reflection because the highest available substrate scattering length densities are about one order of magnitude greater for the former than for the latter. The strong oscillations of the DWBA result in Fig. 2(b) are just due to the low neutron scattering length density of silicon and the large difference of the error function profile from a constant layer.

For Eq. (2.5a), a free surface scattering-length-density profile as given in Fig. 3(a) is used. The profile is representative of those found in microemulsion [9]. The calculated reflectivity using Eq. (2.5a) is plotted in circles in Fig. 3(b) together with the exact result in solid line. The DWBA result is in dashed line. Again it is found that Eq. (2.5a) is fairly accurate over the entire Q range and it is an improvement over the DWBA.

In summary, we found two formulas Eqs. (2.4) and (2.5a) which are fairly simple and very accurate. They are reducible to and more accurate than the DWBA approximation as well as the Born approximation [1]. Numerical calculations using the above two profiles for various choices of $\bar{k}$ have shown that $\bar{k}=k_s$ is the best choice for the approximate wave function $U(z)$ given by Eq. (2.3a). The reason for this is that $\bar{k}=k_s$ eliminates the artificial interface at $z=0$ in the Green's function so that around the critical edge there is no propagating wave to disturb the correct evanescent wave in the film.

Finally, it is also important to point out the utility of the theory developed in this paper as compared to the well-known Parrat numerical recursion relation. First, the integral-equation formulation can be used as the reference reflection to derive the expression for the diffuse nonspecular scattering due to surface roughness as well as volumetric inhomogeneities [10] by the perturbation method while it is impossible to achieve this using the recursion relation. Second, the formulas derived in this paper may be used to do mathematical inversion of the reflectance data by a matrix inversion method to reconstruct the real-space scattering-length-density profiles [11] while the recursion relation cannot be used in this way. Third, the development in this paper constitutes a coherent formation of the reflection theory which yields in a natural way the well-known Born, distorted-wave Born, and WKB approximations, which are used in practice by many authors [4–6,12].

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[1] Xiao-Lin Zhou, Sow-Hsin Chen, and Gian P. Felcher, J. Phys. Chem. **95**, 9025 (1991).

[2] Xiao-Lin Zhou, Gian P. Felcher, and Sow-Hsin Chen, Physica B **173**, 167 (1991).

[3] C.-T. Tai, *Dyadic Green's Functions in Electromagnetic Theory* (Intext Educational Publishers, Scranton, 1971), pp. 35 and 36.

[4] M. K. Sanyal *et al.* (unpublished).

[5] B. L. Carvalho *et al.* (unpublished).

[6] J. Als-Nielsen, Z. Phys. B **61**, 411 (1985).

[7] G. Parrat, Phys. Rev. **95**, 359 (1954).

[8] G. P. Felcher, A. Karim, and T. P. Russell, J. Non-Cryst.

Solid **131-133**, 703 (1991).

[9] Lay-Theng Lee *et al.* (unpublished results).

[10] S. K. Sinha, E. B. Sirota, S. Garoff, and H. B. Stanley, Phys. Rev. B **38**, 2297 (1988).

[11] Xiao-Lin Zhou, Sow-Hsin Chen, and G. P. Felcher, in *Inverse Problems in Scattering and Imaging,* edited by M. Bertero and E. R. Pike, Malvern Physics Series (Hilger, Bristol, 1992), p. 109.

[12] K. Kjer and J. Als-Nielsen, Thin Solid Films **157**, 17 (1982).