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Exact microscopic theory of surface contributions to the reflectivity of a jellium solid*

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Exact microscopic formulas are derived for the surface optical properties of a jellium solid. The comparison of these formulas to those derived classically by McIntyre and Aspnes shows that for *s*-polarized light, the parametrization of surface-reflectance data using the classical theory is a valid procedure, but that for *p*-polarized light, because short-wavelength fields are induced in the surface region, the classical assumption of local dielectric response is invalid, and thus the classical prescription for parametrizing surface reflectance data is unphysical.

I. INTRODUCTION

Until the present, little theoretical attention has been given to the optical experiments that can be used as probes of surface electronic structure, namely, surface reflection spectroscopy[1] and ellipsometry.[2] Consequently, the data from these experiments (changes in reflectivities for *s*- and *p*-polarized light as a function of frequency and impurity adsorption) are generally analyzed in terms of a simple classical model, as propounded, e.g., by McIntyre and Aspnes[3] (MA). The MA model, which is a natural generalization of the picture ordinarily used in the analysis of bulk optical data, assumes that a sample may be represented as a semi-infinite bulk dielectric, having a sharp surface and a local dielectric constant $\epsilon^b(\omega)$, covered by a thin selvedge layer of uniform thickness d and of local dielectric constant $\epsilon^a(\omega)$ (see Fig. 1). The purpose of the present paper is to analyze the validity of this model from a microscopic point of view, and thus to decide how physical a parametrization of surface optical data it provides. The conclusions reached are that in the case of *s*-polarized light, for which the electromagnetic field varies slowly in the surface region, the MA model yields quite a reasonable approximation to the microscopic theory. However in the *p*-polarized case, because the field varies sharply across the surface, the use of a *local* surface dielectric function is invalid, and the MA model is therefore generally in poor correspondence with the microscopic results.

In calculating *bulk* optical properties, the description of a sample as a dielectric medium with a sharp surface and having a local dielectric constant is mainly an approximation insofar as the typically rather small effects of atomic discreteness (or "local-field effects"[4]) are neglected. That is, by virtue of the fact that light wavelengths are very long compared to microscopic distances, the details of surface structure as well as the nonlocality of the sample's dielectric function can generally be ignored.[5] Thus apart from local-field effects, the classical model for *bulk* optical properties is in fact microscopically correct.[5]

The question addressed in the present paper is the extent to which the same is true for the MA model's description of the *surface* contributions to optical reflectivity. That is, ignoring local-field effects, the correspondence is explored between the predictions of the MA model and those of the most-general nonlocal microscopic jellium model, for surface optical properties. The main results obtained are the following:

(i) As noted above, for *s*-polarized light, the MA model provides a quite reasonable parametrization of surface-reflectance data. The reason for the good correspondence between the MA model and the microscopic jellium picture is that for *s*-polarized light, the electric field is purely tangential to the surface, and therefore is slowly varying everywhere in space, even across the surface region. This slow variation can be understood most simply as a consequence of the classical matching condition for the tangential electric field $\vec{E}_{\parallel}$ at a dielectric interface, namely,

$$\vec{E}_{\parallel}(\text{outside}) = \vec{E}_{\parallel}(\text{inside}), \tag{1.1}$$

which in the microscopic case translates into the statement that $\vec{E}_{\parallel}$ is essentially constant in the surface region.[6] Because $\vec{E}(\vec{r})$ is slowly varying, for *s*-polarized light, the nonlocal relation

$$\vec{J}(\vec{r}) = \int \overleftrightarrow{\sigma}(\vec{r},\vec{r}\,')\cdot\vec{E}(\vec{r}\,')\,d^3r' \tag{1.2}$$

between the current $\vec{J}(r)$ and the electric field $\vec{E}(r')$ [via the nonlocal conductivity tensor, $\overleftrightarrow{\sigma}(\vec{r},\vec{r}\,')$] reduces, to a very good approximation,[7] to the local relation

$$\vec{J}(\vec{r}) \approx \left(\int \overleftrightarrow{\sigma}(\vec{r},\vec{r}\,')\,d^3r'\right)\cdot\vec{E}(\vec{r}). \tag{1.3}$$

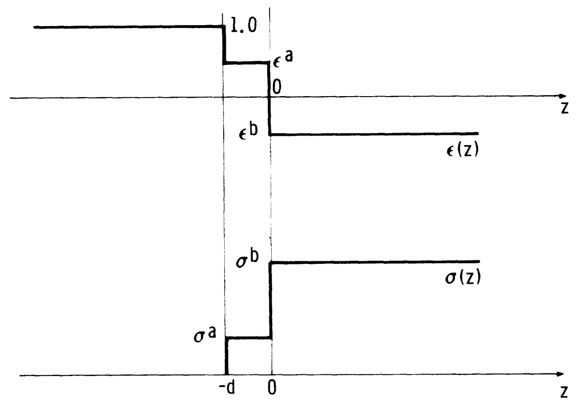

FIG. 1. Schematic illustration of MA model (Ref. 3) for surface contributions to optical reflectivity. The conductivity and the dielectric constant jump to their "selvedge" values at $z=-d$ and to their bulk values at $z=0$.

Thus, identifying the quantity

$$\overleftrightarrow{\sigma}_{\rm loc}(\vec{r}) \equiv \int \overleftrightarrow{\sigma}(\vec{r},\vec{r}')\, d^3r' \tag{1.4}$$

as the local conductivity tensor, one sees that the only serious approximation in the MA model, for s-polarized light, is the replacement of smoothly varying $\overleftrightarrow{\sigma}_{\rm loc}(\vec{r})$ by the piecewise constant model conductivity (cf. Fig. 1)

$$\overleftrightarrow{\sigma}_{\rm MA}(\vec{r}) = 1 \begin{cases} 0, & z<-d, \\ \sigma^a, & -d<z<0, \\ \sigma^b, & 0<z \end{cases} \tag{1.5}$$

(where z is the coordinate normal to the surface). As a consequence, while the MA model formula for the surface correction to $\mathcal{R}^{(s)}_{\rm cl}$, the classical reflectivity for s-polarized light, is[3]

$$\Delta\mathcal{R}^{(s)}/\mathcal{R}^{(s)}_{\rm cl} = 4q_\perp d\, {\rm Im}(\sigma_a/\sigma_b), \tag{1.6}$$

with

$$q_\perp = 2\pi \cos\theta_i/\lambda \tag{1.7}$$

(where λ and θ_i are, respectively, the wavelength and the angle of incidence of the light), the microscopic theory yields the very similar *exact* formula

$$\frac{\Delta\mathcal{R}^{(s)}}{\mathcal{R}^{(s)}_{\rm cl}} = 4q_\perp \int dz\, {\rm Im}\left(\frac{\overline{\sigma}^x(z)}{\overline{\sigma}^x(\infty)}\right), \tag{1.8}$$

where

$$\overline{\sigma}^x(z) \equiv \int d^3r'\, \sigma^{xx}(\vec{r},\vec{r}'). \tag{1.9}$$

[$\sigma^{xx}(\vec{r},\vec{r}')$ means the x-x component of $\overleftrightarrow{\sigma}(\vec{r},\vec{r}')$. $\overline{\sigma}^x(z)$ is independent of x and y by virtue of the assumption of two-dimensional translational invariance, i.e., of a jelluim solid.]

(ii) For p-polarized light matters are quite different. In this case the electric field has a component normal to the surface, which, as one would expect from the classical matching conditions, undergoes rapid spatial variation in the surface region, even for a long-wavelength incident beam.

Because E^z varies as rapidly as $\overleftrightarrow{\sigma}(\vec{r},\vec{r}')$ does in the surface region, one may not approximate the nonlocal relation between $\vec{J}(\vec{r})$ and $\vec{E}(\vec{r}')$, Eq. (1.2), by the local relation, Eq. (1.3). Thus it is hard to

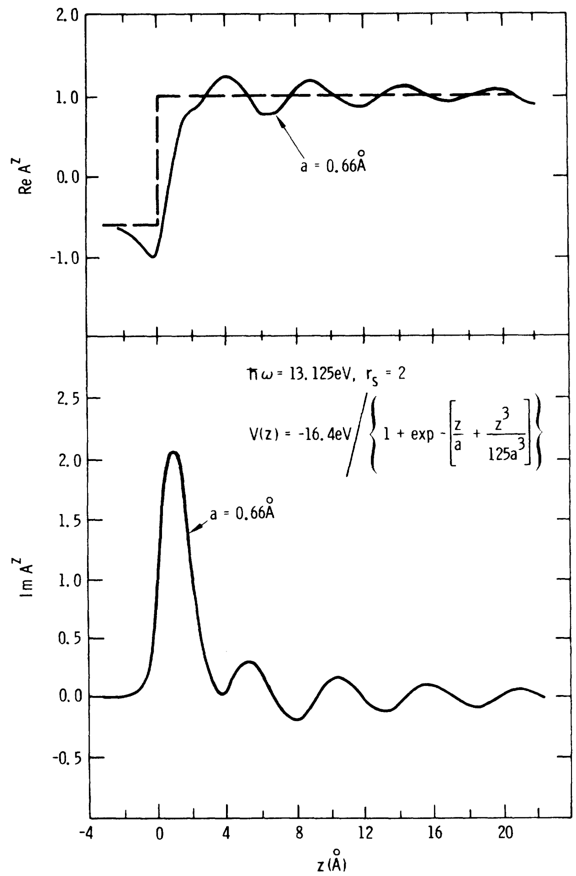

FIG. 2. Spatial behavior of the normal component of the vector potential $A^z(z)$ [note: $E^z(z) \equiv (i\omega/c)A^z(z)$] in the neighborhood of a jellium-vacuum interface (taken from Ref. 6, Fig. 4). The curves shown were calculated using the random phase approximation for electron gas radius $r_s=2$ and for $\hbar\omega = 13.125$. The jellium surface here corresponds to the single-electron potential barrier $V(z) = -V_0/\{1+\exp-[z/a+(z/5a)^3]\}$, with $V_0 = 16.4$ eV and $a = 0.66$ Å. $A^z(z\to\infty)$ has been normalized to 1. Note that $A^z(z)$ undergoes rapid phase as well as magnitude oscillations in the surface region. It is not clear how best to choose an MA model dielectric function to calculate a classical $A^z(z)$ for comparison. In the upper panel I show the classical form of ${\rm Re}A^z(z)$ assuming no selvedge layer ($d=0$) and $\epsilon^b(\omega)$ equal to the bulk jellium value for $r_s=2$ and $\hbar\omega=13.125$ eV (dashed curve). For the same classical model ${\rm Im}A^z(z)$ is identically zero.

see why a model based on a local dielectric constant such as $\epsilon^a(\omega)$ should give a useful description of the surface response to p-polarized light.

In addition, as is illustrated in Fig. 2, the microscopic calculation of E^z leads to a spatial dependence which is very different from the classically predicted step-function behavior. It is therefore doubly difficult to see why values of $\epsilon^a(\omega)$ and d, chosen to give agreement between the MA model and reflectivity data for p-polarized light, should have any physical content.

In the microscopic theory, the formula for the surface correction to $\mathcal{R}_{cl}^{(p)}$, the classical reflectivity for p-polarized light, is found to be

$$\frac{\Delta\mathcal{R}^{(p)}}{\mathcal{R}_{cl}^{(p)}}=4q_\perp \operatorname{Im}\left\{\int dz\, z\,\frac{d}{dz}\left[q_\parallel^2\frac{\epsilon^T(0,\omega)}{\epsilon^T(0,\omega)-1}\frac{E^z(z)}{E^z(\infty)}+[q_\parallel^2-q^2\epsilon^T(0,\omega)]\left(\frac{\bar{\sigma}^x(z)}{\bar{\sigma}^x(\infty)}-\theta(z)\right)\right]\Big/[q_\parallel^2-q_\perp^2\epsilon^T(0,\omega)]\right\}. \quad (1.10)$$

In Eq. (1.10), $\epsilon^T(0,\omega)$ is the bulk transverse dielectric constant at wave-vector zero and frequency ω,[8] $\vec{q}_\parallel$ and $q_\perp$ are, respectively, the wave vectors along and normal to the surface for the incident beam, and $q_\perp'$ is the normal component of the wave vector of the refracted beam inside the sample. Finally, "∞" means a value of z deep inside the solid.[9] [$\bar{\sigma}^x(z)$ is defined in Eq. (1.9).]

Equation (1.10) does reduce to the MA formula

$$\frac{\Delta\mathcal{R}^{(p)}}{\mathcal{R}_{cl}^{(p)}}=4q_\perp d\operatorname{Im}\left(\frac{\epsilon^a-\epsilon^b}{1-\epsilon^b}\,\frac{q^2\epsilon^b-q_\parallel^2(1+\epsilon^b/\epsilon^a)}{q_\parallel^2-q_\perp^2\epsilon^b}\right), \quad (1.11)$$

where

$$\epsilon^{a,b}\equiv 1+(4\pi i/w)\sigma^{a,b} \quad (1.12)$$

when one assumes a conductivity tensor of the form of Eq. (1.5) (see Appendix); and for normal incidence ($q_\parallel=0$, $q_\perp=q$), where s and p polarization are indistinguishable, Eqs. (1.10) and (1.11) do reduce respectively to Eqs. (1.8) and (1.6). However, in general there is no obvious relation between the formulas of Eqs. (1.10) and (1.11), analogous to that between Eqs. (1.6) and (1.8) for the s-polarized case.

In order to interpret Eq. (1.10) it should be noted that by Poisson's equation, the quantity dE^z/dz is essentially[10] proportional to the surface charge induced as the p-polarized light is refracted. Thus Eq. (1.10) shows that $\Delta\mathcal{R}^{(p)}/\mathcal{R}_{cl}^{(p)}$ is a measure of the dipole moment of the induced surface charge.

The remainder of this article is organized as follows: In Sec. II, the results discussed above are derived from first principles, i.e., the microscopic formulas for $\Delta\mathcal{R}^{(p)}/\mathcal{R}_{cl}^{(p)}$ and $\Delta\mathcal{R}^{(s)}/\mathcal{R}_{cl}^{(s)}$ are obtained starting from Maxwell's wave equation, using the most general, nonlocal jellium conductivity tensor. In Sec. III these formulas are tabulated together with their MA model counterparts. Finally, in an Appendix it is shown how Eq. (1.10) reduces to the MA result for p-polarized light, assuming a conductivity tensor of the form of Eq. (1.5).

II. OPTICAL PROPERTIES OF JELLIUM SURFACE

In this section, I derive exact formulas for the surface contributions to the reflectivity of a flat-surfaced jellium solid for both s- and p-polarized incident light. The formulas reveal that for p-polarized light, the surface contribution to the reflectivity is a measure of the dipole moment of the surface charge induced by the incident beam, as the solid tries to screen out the light. For s-polarized light the surface contribution to the reflectivity measures the distance over which the conductivity tensor of the solid heals to its bulk form.

The restriction to a flat "jellium" solid, of course, amounts to the assumption that the solid's conductivity tensor $\bar{\sigma}(\vec{r},\vec{r}\,';\omega)$ is of the two-dimensionally translation-invariant form $\bar{\sigma}(\vec{\rho}-\vec{\rho}\,';z,z';\omega)$, where $\vec{\rho}\equiv(x,y)$, and the surface normal points in the z direction. With this assumption, the wave vector of the electromagnetic field along the surface, $\vec{q}_\parallel$, is a good quantum number, and the Maxwell wave equation for the vector potential $\vec{A}_{\vec{q}_\parallel,\omega}(z)$ assumes the form[6]

$$\left[\frac{d^2}{dz^2}-q_\parallel^2+\left(\frac{\omega}{c}\right)^2\right]\vec{A}_{\vec{q}_\parallel,\omega}(z)-\left(\hat{u}_z\frac{d}{dz}+i\vec{q}_\parallel\right)\left(\hat{u}_z\frac{d}{dz}+i\vec{q}_\parallel\right)\cdot\vec{A}_{\vec{q}_\parallel,\omega}(z)=-\frac{4\pi i\omega}{c^2}\int dz'\,\bar{\sigma}_{\vec{q}_\parallel,\omega}(z,z')\cdot\vec{A}_{\vec{q}_\parallel,\omega}(z'), \quad (2.1)$$

or equivalently,

$$\vec{A}_{\vec{q}_\parallel,\omega}(z)=\int_z^\infty dz'\frac{\sin q_\perp(z-z')}{q_\perp}\left[\frac{4\pi i\omega}{c^2}\int dz''\,\bar{\sigma}_{\vec{q}_\parallel,\omega}(z',z'')\cdot\vec{A}_{\vec{q}_\parallel,\omega}(z'')-\left(\hat{u}_z\frac{d}{dz'}+i\vec{q}_\parallel\right)\left(\hat{u}_z\frac{d}{dz'}+i\vec{q}_\parallel\right)\cdot\vec{A}_{\vec{q}_\parallel,\omega}(z')\right]. \quad (2.2)$$

In writing Eqs. (2.1) and (2.2), the gauge has been chosen in which the scalar potential is identically zero. The unit vector $\hat{u}_z$ points in the plus-z direction. The quantity $q_\perp$ is defined by

$$q_\perp \equiv [(\omega/c)^2 - |\vec{q}_\parallel|^2]^{1/2}. \tag{2.3}$$

And finally, $\overleftrightarrow{\sigma}_{\vec{q}_\parallel,\omega}(z,z')$ is the two-dimensional Fourier transform of $\overleftrightarrow{\sigma}(\vec{\rho}-\vec{\rho}\,';z,z';\omega)$.

In the derivation which follows, the jellium surface is assumed to lie in the neighborhood of the plane $z=0$, with the bulk of the solid occupying the half-space $z>0$. Thus for z or z' smaller than minus a few Å, $\overleftrightarrow{\sigma}_{\vec{q}_\parallel,\omega}(z,z')$ is essentially zero. (Since $\overleftrightarrow{\sigma}_{\vec{q}_\parallel,\omega}$ is a short-ranged function of $|z-z'|$ one need only specify where z or z' lies.) On the other hand, for z or z' greater than a few Å, $\overleftrightarrow{\sigma}_{\vec{q}_\parallel,\omega}(z,z')$ has healed to its bulk jellium form, i.e.,

$$\overleftrightarrow{\sigma}_{\vec{q}_\parallel,\omega}(z,z') \xrightarrow[z,z'>\text{ a few Å}]{} \overleftrightarrow{\sigma}^{\infty}_{\vec{q}_\parallel,\omega}(z-z') = \int \frac{dk_\perp}{2\pi}\, e^{ik_\perp(z-z')}\left(\sigma^{(1)}[(q_\parallel^2+k_\perp^2)^{1/2};\omega]\,\overleftrightarrow{1} + \frac{(\vec{q}_\parallel,k_\perp)(\vec{q}_\parallel,k_\perp)}{|\vec{q}_\parallel|^2+k_\perp^2}\,\sigma^{(2)}[(q_\parallel^2+k_\perp^2)^{1/2};\omega]\right). \tag{2.4}$$

(This form is fixed by rotational invariance.[11])

The reason one can derive exact formulas for the surface contributions to the reflectivity of a jellium solid is that a long-wavelength expansion for $\vec{A}_{\vec{q}_\parallel,\omega}(z)$ can be extracted from Eq. (2.2) *without one's actually having to solve the equation.* As they must, the zeroth-order terms in the expansion yield the classical formulas for the reflectivity of a flat, semi-infinite solid. The first-order terms, however, are more interesting; they describe the surface contributions to the reflectivity, and they do so exactly.

The method used to construct the long-wavelength expansion of Eq. (2.2) is as follows. The z' integral in the equation is divided into two integrals, over the domains $(-\infty, Z)$ and (Z,∞), where Z is chosen to lie sufficiently far into the bulk (~ a few Å) that for z or $z' \gtrsim Z$, $\overleftrightarrow{\sigma}_{\vec{q}_\parallel,\omega}(z,z')$ has healed to its bulk form [cf. Eq. (2.4)]. The integral over (Z,∞) can then be carried out trivially, because $\vec{A}_{\vec{q}_\parallel,\omega}(z)$ must behave as a plane wave in the isotropic medium which occupies the region $z \gtrsim Z$, and the result has a straightforward long-wavelength expansion. At the same time, the integral over $(-\infty, Z)$ can be directly expanded in powers of $q_\perp$ and $q\equiv\omega/c$, because (for light such that $\hbar\omega \lesssim 200$ eV) these quantities are much smaller than the inverse surface thickness.

Thus one begins by defining the quantities $\vec{A}^{\rm I}_{\vec{q}_\parallel,\omega}(z;Z)$ and $\vec{A}^{\rm II}_{\vec{q}_\parallel,\omega}(z;Z)$ by

$$\vec{A}^{\rm I}_{\vec{q}_\parallel,\omega}(z;Z) \equiv \int_Z^\infty dz'\,\frac{\sin q_\perp(z-z')}{q_\perp}\left[\frac{4\pi i\omega}{c^2}\int dz''\,\overleftrightarrow{\sigma}_{\vec{q}_\parallel,\omega}(z',z'')\cdot\vec{A}_{\vec{q}_\parallel,\omega}(z'') - \left(\hat{u}_z\frac{d}{dz'}+i\vec{q}_\parallel\right)\left(\hat{u}_z\frac{d}{dz'}+i\vec{q}_\parallel\right)\cdot\vec{A}_{\vec{q}_\parallel,\omega}(z')\right] \tag{2.5}$$

and

$$\vec{A}^{\rm II}_{\vec{q}_\parallel,\omega}(z;Z) = \vec{A}_{\vec{q}_\parallel,\omega}(z) - \vec{A}^{\rm I}_{\vec{q}_\parallel,\omega}(z;Z). \tag{2.6}$$

The expression for $\vec{A}^{\rm I}_{\vec{q}_\parallel,\omega}(z;Z)$ may be immediately simplified by using the trigonometric identity

$$\sin q_\perp(z-z') \equiv \sin q_\perp(z-Z)\cos q_\perp(Z-z') + \cos q_\perp(z-Z)\sin q_\perp(Z-z'). \tag{2.7}$$

Combining Eqs. (2.2), (2.5), and (2.7), one finds that

$$\vec{A}^{\rm I}_{\vec{q}_\parallel,\omega}(z;Z) = \left(\cos q_\perp(z-Z) + \frac{\sin q_\perp(z-Z)}{q_\perp}\frac{d}{dZ}\right)\vec{A}_{\vec{q}_\parallel,\omega}(Z), \tag{2.8}$$

an expression which only involves $\vec{A}_{\vec{q}_\parallel,\omega}(z)$ evaluated in the bulk region of the solid.

To complete the evaluation of $\vec{A}_{\vec{q}_\parallel,\omega}(z;Z)$, one determines the behavior of $\vec{A}_{\vec{q}_\parallel,\omega}(z)$ with $z\sim Z$ by substituting into Eq. (2.2) the ansatz[12,13]

$$\vec{A}_{\vec{q}_\parallel,\omega}(z) \xrightarrow[z\gtrsim Z]{} \vec{T}_{\vec{q}_\parallel,\omega}e^{iq'_\perp z}. \tag{2.9}$$

One easily finds,[6,13] using Eq. (2.4), that Eq. (2.9) does indeed solve Eq. (2.2) provided that $\vec{T}_{\vec{q}_\parallel,\omega}$ and $q'_\perp$ satisfy the secular equation

$$(q_\perp'^2 - q_\perp^2)\vec{T}_{\vec{q}_\parallel,\omega} = q^2(4\pi i/\omega)\sigma^{(1)}(q';\omega)\,\vec{T}_{\vec{q}_\parallel,\omega} + [(q^2/q'^2)(4\pi i/\omega)\sigma^{(2)}(q';\omega)+1] \times \vec{q}\,'(\vec{q}\,'\cdot\vec{T}_{\vec{q}_\parallel,\omega}), \tag{2.10}$$

wherein

$$\vec{q}\,' \equiv (\vec{q}_\parallel, q'_\perp) \tag{2.11}$$

and

$$q\equiv\omega/c. \tag{2.12}$$

Equation (2.10) is solved by taking the dot product of both sides with $\vec{q}'$, yielding the equation

$$(\vec{q}'\cdot\vec{T}_{\vec{q}_\parallel,\omega})\epsilon^{(L)}(q';\omega)=0, \tag{2.13}$$

where $\epsilon^{(L)}(q';\omega)$, defined by

$$\epsilon^{(L)}(q';\omega)\equiv 1+(4\pi i/\omega)[\sigma^{(1)}(q';\omega)+\sigma^{(2)}(q';\omega)], \tag{2.14}$$

is the longitudinal bulk dielectric constant. Assuming that

$$\epsilon^{(L)}(q';\omega)=0 \tag{2.15}$$

has no solution at the frequency ω,[12] Eq. (2.13) simply requires that

$$\vec{q}'\cdot\vec{T}_{\vec{q}_\parallel,\omega}=0 \tag{2.16}$$

or that $\vec{A}_{\vec{q}_\parallel,\omega}(z)$ be transverse for $z\gtrsim Z$. Substituting Eq. (2.16) back into Eq. (2.10) one finds an additional condition, namely,

$$q_\perp'^2=q_\perp^2+q^2[\epsilon^T(q';\omega)-1], \tag{2.17}$$

where $\epsilon^T(q';\omega)$, the transverse bulk dielectric constant, is defined by

$$\epsilon^T(q';\omega)\equiv 1+(4\pi i/\omega)\sigma^{(1)}(q';\omega). \tag{2.18}$$

Adding $q_\parallel^2$ to both sides of Eq. (2.17) one sees that this equation is equivalent to the familiar formula

$$q'^2/\epsilon^T(q';\omega)=q^2. \tag{2.19}$$

One may now complete the calculation of $\vec{A}^{\rm I}_{\vec{q}_\parallel,\omega}(z;Z)$. According to Eq. (2.17), $q_\perp'$ will be a small quantity if $q_\perp$ and q are. Therefore, since $Z\approx$ a few Å, one has from Eq. (2.9) that

$$\vec{A}_{\vec{q}_\parallel,\omega}(z\approx Z)=\vec{T}_{\vec{q}_\parallel,\omega}(1+iq_\perp'z-\tfrac{1}{2}q_\perp'^2z^2+\cdots). \tag{2.20}$$

Thus for z within a few Å of the surface, expanding the trigonometric functions in Eq. (2.8) and substituting from Eq. (2.20), one finds the formula

$$\vec{A}^{\rm I}_{\vec{q}_\parallel,\omega}(z;Z)\approx\{1+\tfrac{1}{2}(q_\perp'^2-q_\perp^2)Z^2+[iq_\perp'-Z(q_\perp'^2-q_\perp^2)]z-\tfrac{1}{2}q_\perp^2z^2+O(q^3)\}\vec{T}_{\vec{q}_\parallel,\omega}. \tag{2.21}$$

It remains to find a similar formula for $\vec{A}^{\rm II}_{\vec{q}_\parallel,\omega}(z;Z)$. Using the identity (charge conservation)

$$\left(\hat{u}_z\frac{d}{dz}+i\vec{q}_\parallel\right)\cdot\left(\vec{A}_{\vec{q}_\parallel,\omega}(z)+\frac{4\pi i}{\omega}\int dz'\,\vec{\sigma}_{\vec{q}_\parallel,\omega}(z,z')\cdot\vec{A}_{\vec{q}_\parallel,\omega}(z')\right)\equiv 0, \tag{2.22}$$

which follows directly from Eq. (2.1), $\vec{A}^{\rm II}_{\vec{q}_\parallel,\omega}(z;Z)$ may be written in the form

$$\vec{A}^{\rm II}_{\vec{q}_\parallel,\omega}(z;Z)\equiv\int_z^Z dz'\,\frac{\sin q_\perp(z-z')}{q_\perp}\times\left[q^2\vec{1}+\left(\hat{u}_z\frac{d}{dz'}+i\vec{q}_\parallel\right)\left(\hat{u}_z\frac{d}{dz'}+i\vec{q}_\parallel\right)\right]\cdot\frac{4\pi i}{\omega}\int dz''\,\vec{\sigma}_{\vec{q}_\parallel,\omega}(z',z'')\cdot\vec{A}_{\vec{q}_\parallel,\omega}(z''). \tag{2.23}$$

In order to proceed, it is convenient to specify at this point whether one is looking at the case of s- or p-polarized light. Let us consider the case of s-polarized light first, and to be specific, let us assume the incident beam to have its electric vector in the x direction. Then $\vec{q}_\parallel$ will necessarily point in the y direction, and from Eq. (2.23) one obtains the expansion through second order

$$A^{{\rm II}\,x}_{\vec{q}_\parallel,\omega}(z;Z)=q^2\int_z^Z dz'\,(z-z')\times\frac{4\pi i}{\omega}\int dz''\,\sigma^{xx}_{\vec{q}_\parallel,\omega}(z',z'')A^x_{\vec{q}_\parallel,\omega}(z''). \tag{2.24}$$

Note that terms involving $\sigma^{xy}_{\vec{q}_\parallel,\omega}$ and $\sigma^{xz}_{\vec{q}_\parallel,\omega}$ do not appear in Eq. (2.24); this fact is a consequence of rotational invariance in the x-y plane, which implies that these off-diagonal components of the conductivity tensor are of $O(q_xq_y)$ and $O(q_x)$, respectively.

In the case of p-polarized light, it turns out that one only needs to know the value of $\vec{A}^{\rm II}_{\vec{q}_\parallel,\omega}(z;Z)$ through first order in the small wave vectors. Thus for p-polarized light one writes

$$A^{{\rm II}\,z}_{\vec{q}_\parallel,\omega}(z;Z)=\int_z^Z dz'\,(z-z')\frac{d}{dz'}\left(\hat{u}_z\frac{d}{dz'}+i\vec{q}_\parallel\right)\cdot\frac{4\pi i}{\omega}\int dz''\,\vec{\sigma}_{\vec{q}_\parallel\omega}(z',z'')\vec{A}_{\vec{q}_\parallel,\omega}(z'')+\cdots \tag{2.25}$$

and

$$\vec{A}^{\rm II\,\parallel}_{\vec{q}_\parallel,\omega}(z;Z)=i\vec{q}_\parallel\int_z^Z dz'\,(z-z')\frac{d}{dz'}\times\frac{4\pi i}{\omega}\int dz''\,\sigma^{zz}_{\vec{q}_\parallel,\omega}(z',z'')A^z_{\vec{q}_\parallel,\omega}(z'')+\cdots. \tag{2.26}$$

[In writing Eq. (2.26), rotation invariance in the x-y plane has again been used.)

Both of these equations may be written in simpler forms. Specifically, using Eq. (2.22), Eq. (2.26) may be rewritten

$$\vec{A}^{\rm II\,\parallel}_{\vec{q}_\parallel,\omega}(z;Z)=i\vec{q}_\parallel\int_z^Z dz'\,(z-z')\frac{d}{dz}A^z_{\vec{q}_\parallel,\omega}(z'), \tag{2.27}$$

while integrating by parts, Eq. (2.25) assumes the form

$$A^{IIz}_{\vec{q}_\parallel,\omega}(z;Z)=\frac{4\pi i}{\omega}\int dz''\left[\sigma^{z\gamma}_{\vec{q}_\parallel,\omega}(Z,z'')-\sigma^{z\gamma}_{\vec{q}_\parallel,\omega}(z,z'')\right]A^{\gamma}_{\vec{q}_\parallel,\omega}(z'')+i\vec{q}_\parallel\int_z^Z dz'\int dz''\,\frac{4\pi i}{\omega}\,\vec{\sigma}_{\vec{q}_\parallel,\omega}(z',z'')\cdot\vec{A}_{\vec{q}_\parallel,\omega}(z''). \tag{2.28}$$

(Summation on the repeated index $\gamma=x,y,z$, is implied.)

At this point one collects results. Combining Eqs. (2.21), (2.24), (2.27), and (2.28), via Eq. (2.26), one has for s-polarized light with the electric vector in the x direction, the equation

$$A^{x}_{\vec{q}_\parallel,\omega}(z)=T^{x}_{\vec{q}_\parallel,\omega}\left(1+iq'_\perp z+(q'^2_\perp-q^2_\perp)(\tfrac{1}{2}Z^2-Zz)-\tfrac{1}{2}q^2_\perp z^2+q^2\int_z^Z dz'(z-z')\,\frac{4\pi i}{\omega}\,\bar{\sigma}^{x}_{0,\omega}(z')+O(q^3)\right), \tag{2.29}$$

where $\bar{\sigma}^x(z')$ is defined by

$$\bar{\sigma}^{x}_{\vec{q}_\parallel,\omega}(z')\equiv\int dz''\,\sigma^{xx}_{\vec{q}_\parallel,\omega}(z',z''). \tag{2.30}$$

For p-polarized light, one has the pair of equations

$$A^{z}_{\vec{q}_\parallel,\omega}(z)=(1+iq'_\perp z)T^{z}_{\vec{q}_\parallel,\omega}+\frac{4\pi i}{\omega}\int dz''\left[\sigma^{z\gamma}_{\vec{q}_\parallel,\omega}(Z,z'')-\sigma^{z\gamma}_{\vec{q}_\parallel,\omega}(z,z'')\right]A^{\gamma}_{\vec{q}_\parallel,\omega}(z'')$$
$$+i\vec{q}_\parallel\int_z^Z dz'\int dz''\,\frac{4\pi i}{\omega}\,\vec{\sigma}_{\vec{q}_\parallel,\omega}(z',z'')\cdot\vec{A}_{\vec{q}_\parallel,\omega}(z'') \tag{2.31}$$

and

$$\vec{A}^{\parallel}_{\vec{q}_\parallel,\omega}(z)=(1+iq'_\perp z)\vec{T}^{\parallel}_{\vec{q}_\parallel,\omega}+i\vec{q}_\parallel\int_z^Z dz'\,(z-z')\,\frac{d}{dz'}\,A^{z}_{\vec{q}_\parallel,\omega}(z'). \tag{2.32}$$

It is by studying the asymptotic properties of these equations as z is taken out into the vacuum, that one derives expressions for the reflectivity of the jellium solid.

Consider first the case of s-polarized light. For z sufficiently far into the vacuum that $\vec{\sigma}_{\vec{q}_\parallel,\omega}(z,z')\approx 0$, $\vec{A}_{\vec{q}_\parallel,\omega}(z)$ must [see, e.g., Eq. (2.17)] be a linear combination of plane waves traveling toward and away from the surface. That is, $\vec{A}_{\vec{q}_\parallel,\omega}(z)$ is of the form

$$\vec{A}_{\vec{q}_\parallel,\omega}(z\to\infty)=\vec{A}^{0}_{\vec{q}_\parallel,\omega}e^{iq_\perp z}+\vec{R}_{\vec{q}_\parallel,\omega}e^{-iq_\perp z}, \tag{2.33}$$

where, of course, $\vec{A}^0_{\vec{q}_\parallel,\omega}$ and $\vec{R}_{\vec{q}_\parallel,\omega}$ can be identified as the vector magnitudes of the incident and reflected waves, respectively. In the long-wavelength limit, for z in the vacuum but small in magnitude compared to $q_\perp^{-1}$, Eq. (2.33) has the series expansion

$$\vec{A}_{\vec{q}_\parallel,\omega}(z)\approx(\vec{A}^{0}_{\vec{q}_\parallel,\omega}+\vec{R}_{\vec{q}_\parallel,\omega})[1-\tfrac{1}{2}q^2_\perp z^2+O(q^4_\perp)]$$
$$+(\vec{A}^{0}_{\vec{q}_\parallel,\omega}-\vec{R}_{\vec{q}_\parallel,\omega})[iq_\perp z+O(q^3_\perp)]. \tag{2.34}$$

The expression for the reflectivity, for s-polarized light is obtained by comparing the x component of Eq. (2.34) with Eq. (2.29) term by term, according to powers of z.[14] Thus one obtains the microscopically accurate matching conditions

$$A^{0x}_{\vec{q}_\parallel,\omega}+R^{x}_{\vec{q}_\parallel,\omega}=T^{x}_{\vec{q}_\parallel,\omega}[1-\tfrac{1}{2}(q'^2_\perp-q^2_\perp)\alpha^2+\cdots] \tag{2.35}$$

and

$$A^{0x}_{\vec{q}_\parallel,\omega}-R^{x}_{\vec{q}_\parallel,\omega}=T^{x}_{\vec{q}_\parallel,\omega}[q'_\perp/q_\perp+(1/iq_\perp)(q'^2_\perp-q^2_\perp)\beta], \tag{2.36}$$

where α and β are defined by the formulas

$$\alpha^2\equiv\int_{-\infty}^{Z}dz'\,z'\left(\frac{\bar{\sigma}^{x}_{0,\omega}(z')}{\bar{\sigma}^{x}_{0,\omega}(\infty)}-\theta(z')\right) \tag{2.37}$$

and

$$\beta\equiv\int_{-\infty}^{Z}dz'\left(\frac{\bar{\sigma}^{x}_{0,\omega}(z')}{\bar{\sigma}^{x}_{0,\omega}(\infty)}-\theta(z')\right). \tag{2.38}$$

[$\theta(z)$ is the ordinary step function.] In deriving Eqs. (2.35)–(2.38), one makes use of Eq. (2.17) and of the fact[15] that

$$\bar{\sigma}^{x}_{0,\omega}(z\to\infty)\equiv\bar{\sigma}^{x}_{0,\omega}(\infty)=(\omega/4\pi i)[\epsilon^{T}(0,\omega)-1]. \tag{2.39}$$

From Eqs. (2.35) and (2.36) one can immediately solve for the reflectivity, $\mathcal{R}^{(s)}_{\vec{q}_\parallel,\omega}$ for s-polarized light. One obtains the result, to first order in $q_\perp$ and $q'_\perp$,

$$\mathcal{R}^{(s)}\equiv|\mathcal{R}^{x}_{\vec{q}_\parallel,\omega}/A^{0x}_{\vec{q}_\parallel,\omega}|^2=\mathcal{R}^{(s)}_{\rm cl}[1+4q_\perp\,{\rm Im}\beta+O(q^2)], \tag{2.40}$$

in which the classical reflectivity $\mathcal{R}^{(s)}_{\rm cl}$ is given by

$$\mathcal{R}^{(s)}_{\rm cl}\equiv(1-q'_\perp/q_\perp)/(1+q'_\perp/q_\perp). \tag{2.41}$$

Substituting Eq. (2.38) into Eq. (2.40), and noting that the value of Z in Eq. (2.38) can be set equal to ∞ without affecting the result, one obtains the final formula for $\mathcal{R}^{(s)}$

$$\mathcal{R}^s = \mathcal{R}_{cl}^{(s)}\left[1 + 4q_\perp \int_{-\infty}^{\infty} dz' \,\mathrm{Im}\left(\frac{\bar{\sigma}^x_{0,\omega}(z')}{\bar{\sigma}^x_{0,\omega}(\infty)}\right)\right]. \qquad (2.42)$$

Notice that the $O(q_\perp)$ correction in Eq. (2.42) measures the width of the region over which $\bar{\sigma}^x_{0,\omega}(z)$ rises from zero to its bulk value. Thus this correction is a surface property. Also notice that in limit of the MA model,[3] commonly used in the interpretation of surface reflectance measurements, Eq. (2.42) yields the expected result. The MA model assumes a semi-infinite solid occupying the half-space $z \geq 0$ and having a local dielectric constant ϵ^b (b for "bulk"), covered by a selvedge layer of thickness d, having local dielectric constant ϵ^a [cf., Eq. (1.5)]. In this case, then, Eq. (2.42) yields the formula

$$\mathcal{R}^{\mathrm{MA}} = \mathcal{R}_{cl}^{(s)}\{1 + 4q_\perp d\,\mathrm{Im}[(\epsilon_a - 1)/(\epsilon_b - 1]\}, \qquad (2.43)$$

which is the MA result.[3]

Let us now turn to the case of p-polarized light. It is again true, for z in the vacuum but small in magnitude compared to $q_\perp$, that $\vec{A}_{\vec{q}_\parallel,\omega}(z)$ is of the form given in Eq. (2.34). In order to obtain an expression for the reflectivity in this case, however, it is convenient to match Eq. (2.34) to Eqs. (2.31) and (2.32).[13] Thus one must learn how to extract the $z \to -\infty$ behavior of $\vec{A}_{\vec{q}_\parallel,\omega}(z)$ from these latter equations.

To begin, note that according to Eq. (2.32), $\vec{A}_{\vec{q}_\parallel,\omega}(z)$ is constant to zeroth order in $\vec{q}_\parallel$ and $q'_\perp$. Thus, since by rotational invariance in x-y planes, $\sigma^{zx}_{\vec{q}_\parallel,\omega}(z,z')$, $\sigma^{zy}_{\vec{q}_\parallel,\omega}(z,z')$, and $\sigma^{xy}_{\vec{q}_\parallel,\omega}(z,z')$ are, respectively, of $O(q^x_\parallel)$, $O(q^y_\parallel)$, and $O(q^x_\parallel q^y_\parallel)$, and since by two-dimensional translation invariance

$$\int dz'\,\sigma^{zx}_{\vec{q}_\parallel,\omega}(z,z') = \int dz'\,\sigma^{zy}_{\vec{q}_\parallel,\omega}(z,z') \leq O(q^2_\parallel), \qquad (2.44)$$

all the terms in Eq. (2.31) involving off-diagonal components of $\bar{\sigma}_{\vec{q}_\parallel,\omega}(z,z')$ are negligible, and Eq. (2.31) may be rewritten

$$A^z_{\vec{q}_\parallel,\omega}(z) = (1 + iq'_\perp z)T^z_{\vec{q}_\parallel,\omega} + \frac{4\pi i}{\omega}\int dz''\,[\sigma^{zz}_{\vec{q}_\parallel,\omega}(Z,z'') - \sigma^{zz}_{\vec{q}_\parallel,\omega}(z,z'')]A^z_{\vec{q}_\parallel,\omega}(z'') + i\vec{q}_\parallel\cdot\vec{T}^\parallel_{\vec{q}_\parallel,\omega}\int_z^Z dz'\,\frac{4\pi i}{\omega}\,\bar{\sigma}^x(z'). \qquad (2.45)$$

This equation may be reduced further by taking advantage of Eqs. (2.9) and (2.4) for the behavior of $A^z_{\vec{q}_\parallel,\omega}(z'')$ and $\sigma^{zz}_{\vec{q}_\parallel,\omega}(z\approx Z,z'')$. Using these equations the term involving $\sigma^{zz}_{\vec{q}_\parallel,\omega}(Z,z'')$ in Eq. (2.45) can be evaluated, leading to the result

$$A^z_{\vec{q}_\parallel,\omega}(z) = [\epsilon^T(0,\omega) + iq'_\perp z]T^z_{\vec{q}_\parallel,\omega} - \frac{4\pi i}{\omega}\int dz''\,\sigma^{zz}_{\vec{q}_\parallel,\omega}(z,z'')A^z_{\vec{q}_\parallel,\omega}(z'')$$
$$+ [\epsilon^T(0,\omega) - 1]iq'_\perp Z T^z_{\vec{q}_\parallel,\omega} + i\vec{q}_\parallel\cdot\vec{T}^\parallel_{\vec{q}_\parallel,\omega}\int_z^Z dz'\,\frac{4\pi i}{\omega}\,\bar{\sigma}^x(z'). \qquad (2.46)$$

Finally, using Eqs. (2.16) and (2.39), the last two terms of Eq. (2.46) can be combined, to equal

$$[\epsilon^T(0,\omega) - 1]\,iq'_\perp T^z_{\vec{q}_\parallel,\omega}\int_z^Z dz'\left(\theta(z') - \frac{\bar{\sigma}^x(z')}{\bar{\sigma}^x(\infty)}\right). \qquad (2.47)$$

Thus as $z \to -\infty$, Eq. (2.46) yields the expression for $A^z_{\vec{q}_\parallel,\omega}(z)$,

$$A^z_{\vec{q}_\parallel,\omega}(z \to -\text{“}\infty\text{”})$$
$$\to T^z_{\vec{q}_\parallel,\omega}(\epsilon^T(0,\omega) - iq'_\perp\{z + [\epsilon^T(0,\omega) - 1]\beta\} + O(q^2_\perp)), \qquad (2.48)$$

where β is defined in Eq. (2.38).

Equation (2.48) may be compared with Eq. (2.34) to yield the matching equations

$$A^{0z}_{\vec{q}_\parallel,\omega} + R^z_{\vec{q}_\parallel,\omega}$$
$$= T^z_{\vec{q}_\parallel,\omega}\{\epsilon^T(0,\omega) - iq'_\perp\beta\,[\epsilon^T(0,\omega) - 1]\} + O(q^2_\perp) \qquad (2.49)$$

and

$$A^{0z}_{\vec{q}_\parallel,\omega} - R^z_{\vec{q}_\parallel,\omega} = (1/iq_\perp)T^z_{\vec{q}_\parallel,\omega}[iq'_\perp + O(q^2)]. \qquad (2.50)$$

Of these equations, Eq. (2.49) will be useful in determining the surface contribution to the reflectivity for p-polarized light, but Eq. (2.50) will not, because it does not reveal what are the first-order corrections to the classical matching condition for $A^{0z}_{\vec{q}_\parallel,\omega} - R^z_{\vec{q}_\parallel,\omega}$. In order to obtain a second useful matching condition, then, one returns to Eq. (2.32), which implies that, as $z \to -\text{“}\infty\text{”}$,

$$\vec{A}^\parallel_{\vec{q}_\parallel,\omega}(z \to -\text{“}\infty\text{”}) \to (1 + iq'_\perp z)\vec{T}^\parallel_{\vec{q}_\parallel,\omega}$$
$$+ i\vec{q}_\parallel\left(zT^z_{\vec{q}_\parallel,\omega}[1 - \epsilon^T(0,\omega)] + \int_\infty^{-\infty} dz'\,z'\,\frac{d}{dz'}A^z_{\vec{q}_\parallel,\omega}(z')\right), \qquad (2.51)$$

the derivation of this equation depending on the fact that to zeroth order in the small wave vectors, according to Eq. (2.40),

$$A^{z}_{\vec{q}_{\parallel},\omega}(z) \to \begin{cases} T^{z}_{\vec{q}_{\parallel},\omega}, & z \to \text{“}\infty,\text{”} \\ \epsilon^{T}(0,\omega) T^{z}_{\vec{q}_{\parallel},\omega}, & z \to -\text{“}\infty.\text{”} \end{cases} \quad (2.52)$$

To obtain a useful matching condition from Eq. (2.51) one makes use of the transverseness conditions necessarily satisfied by $\vec{A}^{0}_{\vec{q}_{\parallel},\omega}$ and $\vec{R}_{\vec{q}_{\parallel},\omega}$, viz.,

$$\begin{aligned} &\vec{q}_{\parallel}\cdot \vec{A}^{0\parallel}_{\vec{q}_{\parallel},\omega} + q_{\perp} A^{0z}_{\vec{q}_{\parallel},\omega} = 0, \\ &\vec{q}_{\parallel}\cdot \vec{R}^{\parallel}_{\vec{q}_{\parallel},\omega} - q_{\perp} R^{0z}_{\vec{q}_{\parallel},\omega} = 0, \end{aligned} \quad (2.53)$$

and that satisfied by $\vec{T}_{\vec{q}_{\parallel},\omega}$, Eq. (2.9). Using these equations, the comparison of Eqs. (2.34) and (2.51) yields the matching condition

$$A^{0z}_{\vec{q}_{\parallel},\omega} - R^{0z}_{\vec{q}_{\parallel},\omega} = T^{z}_{\vec{q}_{\parallel},\omega}\left(\frac{q'_{\perp}}{q_{\perp}} - \frac{i|\vec{q}_{\parallel}|^{2}}{q_{\perp}}\int_{-\infty}^{\infty} dz' z' \frac{d}{dz'}\mathfrak{A}_{\omega}(z') + O(q_{\perp}^{2})\right), \quad (2.54)$$

in which $\mathfrak{A}_{\omega}(z)$ is the zeroth-order solution to Eq. (2.46), normalized to 1 at $z\to\infty$. That is, $\mathfrak{A}_{\omega}(z)$ satisfies the equation[16]

$$\mathfrak{A}_{\omega}(z) = \epsilon^{T}(0,\omega) - \frac{4\pi i}{\omega}\int \sigma^{zz}_{0\omega}(z,z')\mathfrak{A}_{\omega}(z'). \quad (2.55)$$

Equations (2.54) and (2.49) may now be combined to give an expression for the reflectivity of a jellium solid for p-polarized light $\mathfrak{R}^{(p)}$ to first order in the small wave vectors. One finds that[17]

$$\mathfrak{R}^{(p)} = \mathfrak{R}^{(p)}_{\text{cl}}\left\{1 + 4q_{\perp}\,\text{Im}\left[\frac{\epsilon^{T}(0,\omega)}{q'^{2}_{\perp} - q_{\perp}^{2}\epsilon^{T2}(0,\omega)}\left(|\vec{q}_{\parallel}|^{2}\int dz\; z\frac{d\mathfrak{A}_{\omega}}{dz} - \frac{q'^{2}_{\perp}\beta[\epsilon^{T}(0,\omega)-1]}{\epsilon^{T}(0,\omega)}\right)\right]\right\}, \quad (2.56)$$

where $\mathfrak{R}^{(p)}_{\text{cl}}$ is the classical reflectivity for p-polarized light, given by

$$\mathfrak{R}^{(p)}_{\text{cl}} = \frac{1 - q'_{\perp}/q_{\perp}\epsilon^{T}(0,\omega)}{1 + q'_{\perp}/q_{\perp}\epsilon^{T}(0,\omega)}. \quad (2.57)$$

[Equation (2.56) is identical to Eq. (1.10), since $E^{z}(z) \equiv (i\omega/c)A^{z}(z)$ in the gauge for which the scalar potential is identically zero.]

Two straightforward checks of Eq. (2.56) can be carried out: (i) One can show that the result is independent of the choice of origin of z, and (ii) one can verify that Eq. (2.56) agrees with the classical solution of the MA model. This second check is sketched in the Appendix; the first is accomplished in what follows.

Suppose that the origin of z is shifted so that $z \to z+d$. Then, using Eq. (2.52), one finds that

$$\int_{-\infty}^{\infty} z\frac{d}{dz}\mathfrak{A}_{\omega}(z) \to \int_{-\infty}^{\infty} z\frac{d}{dz}\mathfrak{A}_{\omega}(z+d) = \int_{-\infty}^{\infty} z\frac{d}{dz}\mathfrak{A}_{\omega}(z) - d[1-\epsilon^{T}(0,\omega)]. \quad (2.58)$$

At the same time, using Eq. (2.38) (with Z taken to ∞), one has that

$$\beta \to \int_{-\infty}^{\infty} dz\left(\frac{\bar{\sigma}^{x}(z+d)}{\bar{\sigma}^{x}(\infty)} - \theta(z)\right) = \int_{-\infty}^{\infty} dz\left(\frac{\bar{\sigma}^{x}(z)}{\sigma^{x}(\infty)} - \theta(z)\right) + d. \quad (2.59)$$

Thus the shift in origin causes a change of the surface term in Eq. (2.56) proportional to

$$d\,\text{Im}\left[\frac{\epsilon^{T}(0,\omega)}{q'^{2}_{\perp} - q_{\perp}^{2}\epsilon^{T2}(0,\omega)} \times\left(q_{\parallel}^{2}[\epsilon^{T}(0,\omega)-1] - \frac{q'^{2}_{\perp}[\epsilon^{T}(0,\omega)-1]}{\epsilon^{T}(0,\omega)}\right)\right]. \quad (2.60)$$

However, according to Eq. (2.17),

$$q'^{2}_{\perp} - q_{\perp}^{2}\epsilon^{T2}(0,\omega) = [\epsilon^{T}(0,\omega)-1]\{q^{2} - [\epsilon^{T}(0,\omega)-1]q_{\perp}^{2}\}, \quad (2.61)$$

while

$$q_{\parallel}^{2} - q'^{2}_{\perp}/\epsilon^{T}(0,\omega) = \{q^{2} - [\epsilon^{T}(0,\omega)+1]q_{\perp}^{2}\}/\epsilon^{T}(0,\omega). \quad (2.62)$$

Substituting these equations into Eq. (2.60) shows that the latter expression equals

$$d\,\text{Im}(1) = 0, \quad (2.63)$$

or in other words that Eq. (2.56) for $\mathfrak{R}^{(p)}$ is independent of the choice of origin, as it should be.

In conclusion, it is worth remarking on the physical significance of Eq. (2.56). According to Poisson's equation, the induced charge excited when a p-polarized light beam strikes a surface $\delta n_{\omega}(z)$ is given by

$$\delta n_{\omega}(z) = -\frac{i\omega}{4\pi c}\left(i\vec{q}_{\parallel} + \hat{u}_{z}\frac{d}{dz}\right)\cdot \vec{A}_{\vec{q}_{\parallel},\omega}(z), \quad (2.64)$$

or in the limit $q_{\parallel}\to 0$,

$$\delta n_{\omega}(z) = -\frac{i\omega}{4\pi c}T^{z}_{\vec{q}_{\parallel},\omega}\frac{d}{dz}\mathfrak{A}_{\omega}(z). \quad (2.65)$$

Thus, according to Eq. (2.56) the surface contribution to $\mathcal{R}^{(p)}$ measures the quantity

$$\int dz\, z\, \frac{\delta n_{\omega}(z)}{T^{z}_{\vec{q}_{\parallel},\omega}} \tag{2.66}$$

about an origin fixed by the value of β. That is, the surface correction to $\mathcal{R}^{(p)}$ measures the dipole moment of the induced charge-density fluctuation.

III. RECAPITULATION AND DISCUSSION OF RESULTS

For convenience I tabulate here (in Table I) the microscopic and classical results for the surface contributions to the reflectivity of a jellium solid, for s- and p-polarized light.

For s-polarized light one sees in Table I that the microscopic and classical formulas for $\Delta\mathcal{R}/\mathcal{R}_{cl}$ are closely similar. However, the microscopic formula for p-polarized light explicitly depends on the spatial behavior of $A^{z}_{\vec{q}_{\parallel},\omega}(z)$ in the surface region and only reduces to the classical formula if $A^{z}_{\vec{q}_{\parallel},\omega}(z)$ is of the classical step function form of Eq. (A5) (see Appendix). Thus the parametrization of data using the classical formula for p-polarized light appears at the very best to be a procedure requiring considerable caution, one for which an independent experimental test would be highly desirable. Such a test might involve, for example, a separate determination of the classical surface optical constants of an optically isotropic adlayer (such as an adlayer of inert gas atoms), using first s- and then p-polarized light.[18] According to the microscopic formulas developed here, one would expect that the value determined for $\epsilon^{a}(\omega)$ will depend on which polarization was used, a result which would clearly contradict the idea underlying the classical picture.

Regarding prospects for further theoretical work, it should be noted that the jellium model is itself, of course, not an exact model of a real solid. Thus it seems reasonable to ask, for example, whether the existence of local-field effects in a real crystal might not invalidate the classical picture even for s-polarized light. A complete answer to this question awaits the extension of surface reflectance theory to the crystalline case. However, it does seem reasonable to expect that surface local-field effects will not be significantly stronger in determining surface optical properties than bulk local-field effects are[4] in the determination of bulk optical properties.

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APPENDIX

In this appendix I sketch the derivation of the statement that if the conductivity tensor is taken to be of the form assumed by McIntyre and Aspnes[3] (MA), namely,

$$\overline{\sigma}(\vec{r},\vec{r}\,';\omega)=\overline{1}\delta(\vec{r}-\vec{r}\,')\begin{cases}0, & z<-d,\\ \sigma^{a}, & -d<z<0,\\ \sigma^{b}, & z>0,\end{cases} \tag{A1}$$

then Eq. (2.56) reduces to MA's formula for the surface contribution to the reflectivity for p-polarized light,[3]

$$\frac{\Delta\mathcal{R}^{(p)}}{\mathcal{R}^{(p)}_{cl}}=-4q_{\perp}d \times \mathrm{Im}\left[\left(\frac{\epsilon^{a}-\epsilon^{b}}{1-\epsilon^{b}}\right)\frac{q^{2}-|\vec{q}_{\parallel}|^{2}(\epsilon^{a}+\epsilon^{b})/\epsilon^{a}\epsilon^{b}}{q^{2}-|\vec{q}_{\parallel}|^{2}(1+\epsilon^{b})/\epsilon^{b}}\right], \tag{A2}$$

where

$$\epsilon^{a,b}\equiv 1+(4\pi i/\omega)\sigma^{a,b}. \tag{A3}$$

The derivation is straightforward. Substituting Eq. (A1) into Eq. (2.38) immediately yields the expression for β,

TABLE I. Formulas for $\Delta\mathcal{R}^{(s,p)}/\mathcal{R}^{(s,p)}_{cl}$ from the microscopic theory and from the MA model (Ref. 3).

Polarization	s	p
Microscopic $\dfrac{\Delta\mathcal{R}}{\mathcal{R}_{cl}}$	$4q_{\perp}\int dz\,\mathrm{Im}\dfrac{\overline{\sigma}^{x}(z)}{\overline{\sigma}^{x}(\infty)}$ $\overline{\sigma}^{x}(z)\equiv\int d^{3}r'\,\sigma^{xx}(\vec{r},\vec{r}\,';\omega)$	$4q_{\perp}\,\mathrm{Im}\left\{\int dz\,z\dfrac{d}{dz}\left[q_{\parallel}^{2}\dfrac{\epsilon^{T}(0,\omega)}{\epsilon^{T}(0,\omega)-1}\dfrac{A^{z}(z)}{A^{z}(\infty)} + [q_{\parallel}^{2}-q^{2}\epsilon^{T}(0,\omega)]\left(\dfrac{\overline{\sigma}^{x}(z)}{\overline{\sigma}^{x}(\infty)}-\theta(z)\right)\right]\Big/[q_{\parallel}^{2}-q_{\perp}^{2}\epsilon^{T}(0,\omega)]\right\}$
MA model $\dfrac{\Delta\mathcal{R}}{\mathcal{R}_{cl}}$	$4q_{\perp}d\,\mathrm{Im}\left(\dfrac{\sigma^{a}(\omega)}{\sigma^{b}(\omega)}\right)$ $\epsilon^{a,b}(\omega)\equiv 1+\dfrac{4\pi i}{\omega}\sigma^{a,b}(\omega)$	$4q_{\perp}d\,\mathrm{Im}\left[\dfrac{\epsilon^{a}(\omega)-\epsilon^{b}(\omega)}{1-\epsilon^{b}(\omega)} \times\left(\dfrac{q^{2}\epsilon^{b}(\omega)-\{1+\epsilon^{b}(\omega)/\epsilon^{a}(\omega)\}q_{\parallel}^{2}}{q_{\parallel}^{2}-q_{\perp}^{2}\epsilon^{b}(\omega)}\right)\right]$

$$\beta = \frac{\sigma^a}{\sigma^b} d \equiv \frac{\epsilon^a - 1}{\epsilon^b - 1} d . \tag{A4}$$

Substituting Eq. (A1) into Eq. (2.55), yields the behavior of $\mathcal{A}_\omega(z)$,[8]

$$\mathcal{A}_\omega(z) = \begin{cases} \epsilon^b, & z < -d, \\ \epsilon^b/\epsilon^a, & -d < z < 0, \\ 1, & z > 0 \end{cases} \tag{A5}$$

(which one could have guessed immediately from the classical matching condition which states that ϵA^z is continuous across a dielectric interface). From Eq. (A5) one finds that

$$\int dz\, z d \frac{\mathcal{A}_\omega(z)}{dz} = -d\epsilon^b \left(\frac{1}{\epsilon^a} - 1\right) . \tag{A6}$$

Equations (A4) and (A6) may now be substituted into Eq. (2.56), leading, after some algebraic manipulation, precisely to the MA result, Eq. (A2).

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[1]J. Anderson, G. W. Rubloff, M. A. Passler, and P. J. Stiles, Phys. Rev. B 10, 2401 (1974); J. B. Restorff and H. D. Drew, Proceedings of the 35th Annual Conference on Physical Electronics, University Park, Pennsylvania, 1975 (unpublished); a recent theoretical paper by A. J. Bennett and D. Penn [Phys. Rev. B 11, 3644 (1975)] treats the shapes of surface reflectance resonance shapes within an Anderson model—it does not address the question of the nonlocality of surface dielectric response which is treated here.

[2]G. A. Bootsma and F. Meyer, Surf. Sci. 14, 52 (1969); the most elaborate theory of ellipsometry in print, by P. W. Atkins and A. D. Wilson, ibid. 22, 433 (1970), treats absorbate atoms rather completely but the substrate quite classically. In any case this paper has not yet been applied in any data analysis.

[3]J. D. E. McIntyre and D. E. Aspnes, Surf. Sci. 24, 417 (1971). Note that in this paper an unusual sign convention is adopted for wave vectors and frequencies (i.e., plane waves traveling in the plus-z direction are taken to be of the form $\exp(-iq_\perp z + i\omega t)$). As a consequence the reflectivity formulas derived there appear to differ by a sign from those derived here. In fact there is no discrepancy; because of MA's sign convention, their dielectric constants are the complex conjugates of those used here.

[4]The most complete calculation of such effects, to date, is that of W. Hanke and L. J. Sham, Phys. Rev. Lett. 33, 582 (1974). See also J. A. Van Vechten and R. M. Martin, *ibid.* 28, 446 (1972); S. L. Adler, Phys. Rev. 126, 413 (1962); and N. Wiser, *ibid.* 129, 62 (1963).

[5]Apart from, e.g., the anomalous skin effect, and photogeneration of plasmons.

[6]P. J. Feibelman, Phys. Rev. B 12, 1319 (1975).

[7]Expanding $\vec{E}(\vec{r}\,')$ in a Taylor series about the point $\vec{r}$, one sees that the quality of the approximation is governed by the smallness of the ratio of the range of $\vec{\sigma}(r, r')$ as a function of $|\vec{r} - \vec{r}\,'|$ to the distance over which $\vec{E}(\vec{r})$ varies appreciably.

[8]$\epsilon^T(0, \omega)$ becomes $\epsilon^b(\omega)$ in the MA model.

[9]Deep on a microscopic scale but at a depth small compared to $|q'_\perp|^{-1}$.

[10]This proportionality would be exact if $|\vec{q}_\parallel|$ were zero.

[11]P. M. Platzman and P. A. Wolff in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1973), Suppl. 13.

[12]Bulk plasmon photoexcitation is here being ignored. At frequencies such that plasmons can be excited Eq. (2.9) should also contain a longitudinal term of the form $\vec{L}_{q\parallel\omega} \exp(iq_\perp^L z)$, where $q_\perp^L$ is determined by the equation, $\epsilon^L(q_\perp^L, \omega) = 0$, where ϵ^L is the bulk longitudinal dielectric function.

[13]See P. J. Feibelman, Phys. Rev. B 12, 4282 (1975).

[14]It is verified below that the results obtained are independent of the choice of origin of z, as they ought to be.

[15]Reference 6, Appendix A.

[16]Note in passing that this equation expresses precisely two pieces of physical information, the classical matching condition

$$\mathcal{A}_\omega(z \to -\infty) = \epsilon^T(0, \omega) \mathcal{A}_\omega(z \to \infty)$$

and current conservation, which, as $|\vec{q}_\parallel| \to 0$, is expressed [cf. Eq. (2.22)] by the equation

$$\frac{d}{dz}\left(\mathcal{A}_\omega(z) + \frac{4\pi i}{\omega} \int dz' \sigma_{0\omega}^{zz}(z, z') \mathcal{A}_\omega(z')\right) = 0 .$$

[17]Note that

$$\mathcal{R}^{(p)} \equiv |\vec{R}_{\vec{q}_\parallel,\omega}|^2 / |\vec{A}^0_{\vec{q}_\parallel,\omega}|^2 = |R^z_{\vec{q}_\parallel,\omega}|^2 / |A^{0z}_{\vec{q}_\parallel,\omega}|^2$$

because [cf. Eq. (2.53)] for p-polarized light

$$|\vec{R}^\parallel_{\vec{q}_\parallel,\omega}|^2 / |\vec{A}^{0\parallel}_{\vec{q}_\parallel,\omega}|^2 = |R^z_{\vec{q}_\parallel,\omega}|^2 / |A^{0z}_{\vec{q}_\parallel,\omega}|^2 .$$

[18]This suggestion is due to G. W. Rubloff (private communication).