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Interpretation of differential reflectance studies of metal surfaces

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Formulas are derived which relate differential surface power absorption spectra for s- and p-polarized light to differential reflectance data, frequency by frequency. The formulas, which are exact for jellium, do not involve the use of Fresnel equations or any theoretically calculated parameters.

Because they contain information on the excitation spectra of surfaces, differential optical reflectance measurements are potentially a powerful means for understanding the structure of surfaces in general, and constitute one of the main hopes for characterizing solid–liquid and solid–high-density-gas interfaces.[1] It is clear, and this point has of course been made before,[2] that the quantity of interest for surface characterization is the surface power absorption spectrum and not simply the reflectance, since the latter represents a complicated mixture of absorptive and reactive effects, from both bulk and surface. However, until now it has not been shown how to derive surface absorption spectra from reflectance measurements, without the use of a classical three-phase model.[3] For s-polarized light impinging on a flat surface, the classical picture does give an essentially correct description of surface optical properties because $E^{\perp}$, the electric field normal to the surface, vanishes identically while the tangential field $\vec{E}^{\parallel}$ is almost constant.[4] However, when $E^{\perp} \neq 0$ the classical picture gives an unphysical description of the electromagnetic field in the immediate vicinity of a surface, and thus should not be used to analyze absorption spectra with the hope of characterizing the atomic layers that comprise it.[3] There are several reasons why the classical picture breaks down when $E^{\perp} \neq 0$:

(1) It is discontinuous—typically in a classical calculation the dielectric function ϵ is taken to jump discontinuously at each interface. The continuity of the normal displacement $D^{\perp}$ then implies that $E^{\perp}$ jumps discontinuously in inverse proportion to ϵ. One is then faced with two difficulties in interpreting surface optical data. First, where is the discontinuity surface relative to the atoms? And second, why should a calculation of electron excitation by a discontinuous field give a meaningful description of the actual physics?

(2) It is local—microscopically the relation between total electric field and induced current is given by a nonlocal conductivity tensor, $\overleftrightarrow{\sigma}(\vec{r},\vec{r}\,';\omega)$, ω being the frequency. The conductivity is only effectively local when the field varies slowly on an atomic scale. This is not true of $E^{\perp}$ near a surface.[4] $D^{\perp}$ varies slowly, not $E^{\perp}$.[5,6]

(3) It is incomplete—above the plasma frequency the matching conditions derived from Maxwell's equations do not suffice to determine the fields. An "additional boundary condition" (ABC) is required before the theory is well defined.[7]

These problems have been addressed in several papers over the last five years. It has been shown, for jellium at least, how to calculate electromagnetic fields both below and above the plasma frequency using a nonlocal description of surface dielectric response.[8] (Sample results are shown in Fig. 1.) The microscopic response theory has been shown to explain both the great enhancement of photoemission seen from Al below the plasma frequency and its frequency dependence, while the classical theory fails to account for either.[9] Exact microscopic formulas for surface reflectance have been derived for both s- and p-polarized light incident on flat jellium.[4] These formulas show that for p-polarized light the surface response function is essentially an inverse dielectric function[5,6] while for s polarization it is directly the surface contribution to ϵ that matters.

Despite these advances in the microscopic theory of surface dielectric response, an answer to one fundamental question has not been given: How shall one *use* p-polarization surface reflectance data to characterize surfaces?[10] More specifically, for example, what good does it do to know that the surface response function for p-polarized light is related to an inverse dielectric function? The present paper is an attempt to answer this question by showing *for metals* how the desired quantity,[2] the surface power absorption spectrum, can be derived from surface reflectance data without the introduction of a classical three-phase model. The results are stated in terms of simple formulas relating power absorption to exact surface response functions. The latter can be derived from angle-of-incidence-dependent differential reflectance measurements, as has been discussed before.[5] An interesting

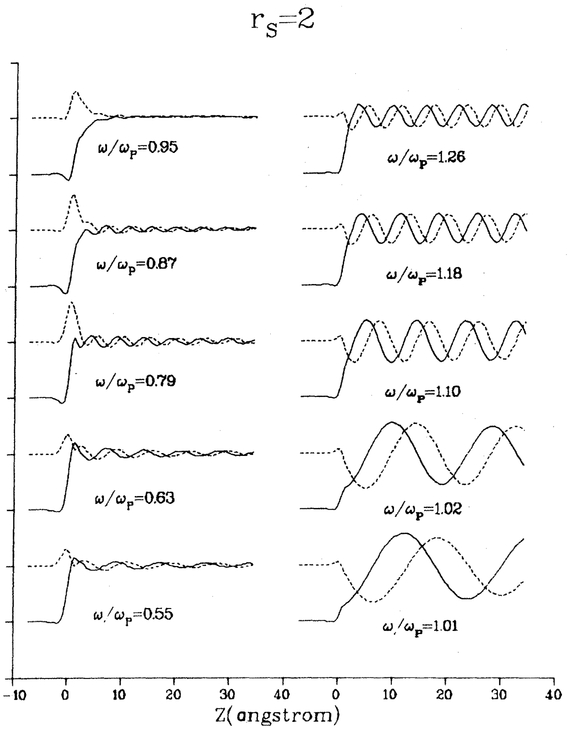

FIG. 1. Real (solid lines) and imaginary (dashed lines) parts of $[E^{\perp}(z)/E^{\perp,\mathrm{cl}}(\mathrm{ins})-1]/[1-\epsilon(\omega)]$ for a jellium surface of electron gas radius $r_s=2$, for various frequencies. Notice the peak in the imaginary part of the fields for $\omega<\omega_p$, the plasma frequency. As explained in the text, the area under this peak is directly related to the total surface photoelectric excitation cross section. Above ω_p, the corresponding statement is more complicated because the photoexcited plasmons obscure the surface photoemission peak. The method used to obtain these results is discussed at length in Ref. 8.

"spin-off" of the discussion is an interpretation of the peak in $\mathrm{Im}[E^{\perp}(z)/E^{\perp}(\mathrm{inside})]$ found (see Fig. 1) in the neighborhood of the jellium surface when $\omega<\omega_p$.[8] The area under this peak is directly proportional to total surface photoexcitation cross section. A theory which does not produce this peak does not include surface photoexcitation. A theory which attributes such a peak to small "surface dielectric constant" represents the surface photoeffect wrongly, in that the effect is the result of a sharp gradient in the dielectric function,[9] *not* its near vanishing.[11]

In what follows, I show qualitatively, then more precisely, how the microscopic theory yields formulas for surface power absorption for *s*- and *p*-polarized light. The important result of earlier, detailed investigations[4-6] is that the microscopic theory simply generalizes the classical conditions that $\vec{E}^{\parallel}$ and $D^{\perp}$ are constant across a surface. Thus for long wavelength (or small wave vectors, $q\equiv\omega/c$), one finds

$$\vec{E}^{\parallel}(z;\vec{q}_{\parallel},\omega)\approx\text{const} \tag{1}$$

and

$$D^{\perp}(z;\vec{q}_{\parallel},\omega)=\int dz'\,\epsilon^{zz}(z,z';\vec{q}_{\parallel},\omega)E^{\perp}(z';\vec{q}_{\parallel},\omega)$$
$$=\epsilon(\omega)E^{\perp}(in;\vec{q}_{\parallel},\omega). \tag{2}$$

Here $\vec{q}_{\parallel}$ is the tangential conponent of the incident beam wave vector $\vec{q}$, $\epsilon(\omega)$ is the bulk $q\rightarrow 0$ dielectric function, and $E^{\perp}(in;\vec{q}_{\parallel},\omega)$ is the classical $E^{\perp}$ just inside the surface. The dielectric tensor $\epsilon^{zz}(z,z';\vec{q}_{\parallel},\omega)$ is nonlocal, i.e., is not proportional to $\delta(z-z')$, and is related to the conductivity by

$$\epsilon^{zz}(z,z';\vec{q}_{\parallel},\omega)=\delta(z-z')+\frac{4\pi i}{\omega}\sigma^{zz}(z,z';\vec{q}_{\parallel},\omega). \tag{3}$$

Off-diagonal components of ϵ or σ can be ignored for $\vec{q}_{\parallel}\rightarrow 0$.[4]

Equation (2) immediately shows that $E^{\perp}(z;\vec{q}_{\parallel}\rightarrow 0,\omega)$ is related to $\int\epsilon^{zz}(z,z')^{-1}dz'$, where $\epsilon^{zz}(z,z')$ is thought of as a matrix. Thus as a number of authors have noted,[5,6] the z component of the field in the surface region is governed by a response function which is related to "an inverse dielectric function." The significance of this result for the surface power absorption can be seen readily.

The power absorption of a solid per unit area is given by[12]

$$P=\tfrac{1}{2}\int dz\,\mathrm{Re}[\vec{E}^{*}(z;\vec{q}_{\parallel},\omega)\cdot\vec{j}(z;\vec{q}_{\parallel},\omega)]$$
$$=\tfrac{1}{2}\int dz\,dz'\,\mathrm{Re}[\vec{E}^{*}(z;\vec{q}_{\parallel},\omega)\cdot\overleftrightarrow{\sigma}(z,z';\vec{q}_{\parallel},\omega)$$
$$\cdot\vec{E}(z';\vec{q}_{\parallel},\omega)]. \tag{4}$$

The parallel component of $\vec{E}$ is constant across the surface. Thus its contribution to P is directly proportional to the real part of the (z-integrated) conductivity or the imaginary part of the dielectric function. In contrast, $E^{\perp}$ is related to the inverse dielectric function, $\epsilon^{-1}(z,z')$. Thus the contribution of $E^{\perp}$ to the power absorption is roughly proportional to $|\epsilon^{-1}|^2\mathrm{Im}\epsilon$ or $\mathrm{Im}\epsilon^{-1}$. This result bodes ill for the objective of characterizing surface structure by correlating an absorption spectrum with an optical joint density of states (OJDOS) since the peaks of such an OJDOS, which correspond to peaks in $\mathrm{Im}\epsilon$, may well give rise to minima of $\mathrm{Im}\epsilon^{-1}$.[13] On the other hand, we are not at liberty to alter the physics of the surface dielectric response to suit our convenience.

The relevance of a quantity of the nature of $\mathrm{Im}\,\epsilon^{-1}$ to the power absorption associated with $E^{\perp}$ means nothing other than that when ϵ is resonant, the normal surface field is correspondingly diminished, and thus the power absorption which is proportional to the field square times the OJDOS is *anti*resonant.

I now make this argument precise, obtaining exact results for surface power absorption by a (jelliumlike) metal. In a differential reflectance measurement, one wishes to determine the surface contribution to dP/du, the derivative of the power absorption with respect to an experimentally accessible parameter u which affects surface properties, such as the electric field in metallic electroreflectance,[1] or the coverage of some adsorbate. In general, there will also be a "bulk" contribution to dP/du equal to the u derivative of the transmitted electric field intensity times the unmodulated bulk power absorption. The bulk component of dP/du is of little intrinsic interest and one wishes to eliminate it specifically from consideration. This can be accomplished by breaking the z integral of Eq. (4) into integrals over $z \leqslant Z$ and $z \geqslant Z$, where Z is an arbitrary "cutoff" value of z, well inside the surface but much less so than a light wavelength. (The solid is assumed to occupy the right half-space.) In the region $z \geqslant Z$, $E^{\perp}(z)$ is of the form

$$E^{\perp}(z) = \vec{\mathrm{T}}\, e^{i q_{\perp}' z} + \hat{u} T^{z} p_{\omega} e^{i(k^{L} + i0^{+})z}, \tag{5}$$

where $q_{\perp}'$ is the normal component of the classical "inside" wave vector, $\vec{\mathrm{T}}$ differs from the classical transmission amplitude by terms of $O(q)$, and p_{ω} and k^{L} are the amplitude and wave vector of the bulk plasmon which is photoexcited if $\omega > \omega_{p}$ (see Fig. 1). $E^{\perp}$ and $\vec{\mathrm{T}}$ depend on $\vec{\mathrm{q}}_{\parallel}$ and ω of course. This dependence has been suppressed for clarity.

The bulk contribution to dP/du is the term which is proportional to $d|\vec{\mathrm{T}}|^{2}/du$. This latter quantity is of $O(q)$ in the long-wavelength limit, but the bulk contribution to dP/du is of $O(1)$ because

$$\int_{Z}^{\infty} dz \exp(-2z\, \mathrm{Im} q_{\perp}') \approx \frac{1}{2\, \mathrm{Im} q_{\perp}'}, \tag{6}$$

which is manifestly of $O(q^{-1})$.

The remaining contributions to dP/du from $z \geqslant Z$ together with all the contributions from $z \leqslant Z$ constitute the interesting surface power absorption spectrum. For long-wavelength light, making use of the rotational invariance of $\overleftrightarrow{\sigma}(z, z'; 0, \omega)$, Eq. (4) implies that

$$\frac{dP}{du} = \tfrac{1}{2}\,\mathrm{Re}\left(|\vec{\mathrm{E}}^{\parallel,\mathrm{cl}}|^{2} \int dz\, dz' \,\frac{d}{du}\, \sigma^{xx}(z, z'; 0, \omega) + |E^{\perp,\mathrm{cl}}(\mathrm{out})|^{2} \int dz\, dz' \,\frac{d}{du}\, [\mathcal{E}^{*}(z) \sigma^{zz}(z, z'; 0, \omega) \mathcal{E}(z')] \right), \tag{7}$$

where here and henceforth dP/du is defined as the *surface component only* of the differential power absorption. In Eq. (7), $\vec{\mathrm{E}}^{\parallel,\mathrm{cl}}$ is the classical value of the tangential electric field and $E^{\perp,\mathrm{cl}}(\mathrm{out})$ is the classical outside value of the normal component. $\mathcal{E}(z)$ is defined by

$$\mathcal{E}(z) \equiv E^{\perp}(z) / E^{\perp,\mathrm{cl}}(\mathrm{out}). \tag{8}$$

It is the z component of $\vec{\mathrm{E}}(z)$ normalized to its classical value just outside the surface. Note that the integrals of Eq. (7) converge because the u derivatives localize the integrands near the surface.

It is immediately apparent that the contribution of $\vec{\mathrm{E}}^{\parallel}$ to dP/du is simpler than that of $E^{\perp}$. The latter can, however, be made tractable by proving an "optical theorem," i.e., a theorem relating a "total cross section" to a "forward scattering amplitude." According to Eqs. (2) and (3), $\mathcal{E}(z)$ satisfies[14]

$$\mathcal{E}(z) = 1 - \frac{4\pi i}{\omega} \int dz' \sigma^{zz}(z, z') \mathcal{E}(z'). \tag{9}$$

[This equation thus says nothing other than $D^{\perp}(z) \approx \mathrm{const.}$] Equation (9) immediately yields

$$\mathrm{Re}\,\mathcal{E}^{*}(z) \int dz' \sigma^{zz}(z, z') \mathcal{E}(z') = \frac{\omega}{4\pi}\, \mathrm{Im}[\mathcal{E}^{*}(z)], \tag{10}$$

which when substituted into Eq. (7) gives

$$\frac{dP}{du} = \tfrac{1}{2}\left(|\vec{\mathrm{E}}^{\parallel,\mathrm{cl}}|^{2} \int dz\, dz' \,\frac{d}{du}\, \mathrm{Re}\, \sigma^{xx}(z, z') + |E^{\perp,\mathrm{cl}}(\mathrm{out})|^{2} \,\frac{\omega}{4\pi} \int dz \,\frac{d}{du}\, \mathrm{Im}\,\mathcal{E}^{*}(z) \right). \tag{11}$$

The relation between the surface power absorption and the reflectance for p-polarized light follows from this result.

Before proceeding, however, it is worth considering the meaning of the numerical results for $\mathcal{E}(z)$, shown in Fig. 1, in the light of Eq. (11). Notice that for $\omega < \omega_{p}$, $\mathcal{E}(z)$ has a real part that looks roughly like a smoothed version of the step-function behavior that $\mathcal{E}(z)$ would show classically, and an imaginary part peaked at the surface. Equation (11) tells us what this imaginary part means. The area under it corresponds to the surface power absorption associated with $E^{\perp}$. In the jellium model underlying the calculation, the *only* loss mechanism is surface photoelectric excitation, and that is therefore what $\mathrm{Im}\mathcal{E}(z)$ represents. Any "model $\mathcal{E}(z)$" that does not manifest such a peak does not take proper account of the surface photoelectric effect. Note that there is here a question of self-consistency. $\mathrm{Im}\mathcal{E}(z)$ both *causes* and is the result of surface photoemission.

I turn now to the question of determining dP/ds by reflectance measurements. It is convenient to define two surface response functions, $d_{\parallel}(\omega)$ and $d_{\perp}(\omega)$, for electric vectors parallel and perpendicular to the surface. These response functions have the dimensions of length and accordingly may be thought of as "optical surface positions." They are given by

$$d_{\parallel}(\omega) \equiv Z - \frac{4\pi i}{\omega}\,\frac{1}{\epsilon(\omega)-1}\int_{-\infty}^{Z} dz \int_{-\infty}^{\infty} dz'\sigma^{xx}(z,z') \quad (12)$$

and

$$d_{\perp}(\omega) \equiv Z - \frac{\epsilon(\omega)}{\epsilon(\omega)-1}\left[\int_{-\infty}^{Z} dz\,[1-\mathcal{E}(z)] + \int_{Z}^{\infty} dz\left(\frac{1}{\epsilon(\omega)} - \mathcal{E}(z)\right)\right]. \quad (13)$$

The cutoff Z is defined as above. $d_{\perp}(\omega)$ is well defined because $\mathcal{E}(z) \to 1$ as $z \to -\infty$ [cf. Eqs. (8) and (9)], and

$$\mathcal{E} \to [1/\epsilon(\omega)][1 + p(\omega)\exp(ik^{L} - 0^{+})z\,]$$

as $z \to +\infty$ [cf. Eq. (5)]. $d_{\parallel}(\omega)$ is Z independent because

$$\frac{4\pi i}{\omega}\int dz'\sigma^{xx}(z \to \infty, z') = \epsilon(\omega) - 1\,. \quad (14)$$

These definitions of surface response functions are equivalent to those which have been used in Refs. 5 and 6, as is shown in the Appendix below, as long as one remains below the plasma frequency. For $\omega \geq \omega_{p}$, Eq. (13) remains perfectly adequate while a surface response function based on an "$\epsilon^{-1}(z,z')$" is not obviously so.(15)

It is straightforward to express dP/du in terms of $d(d_{\parallel})/du$ and $d(d_{\perp})/du$. Equation (12) yields

$$\int dz\,dz'\,\frac{d}{du}\,\sigma^{xx}(z,z') = \frac{i\omega}{4\pi}\,[\epsilon(\omega)-1]\,\frac{d}{du}\,[d_{\parallel}(\omega)], \quad (15)$$

while Eq. (13) implies that

$$\int dz\,\frac{d}{du}\,\mathcal{E}(z) = \frac{\epsilon(\omega)-1}{\epsilon(\omega)}\,\frac{d}{du}\,[d_{\perp}(\omega)]. \quad (16)$$

Thus

$$\frac{dP}{du} = \frac{\omega}{8\pi}\left[\,|\vec{\mathrm{E}}^{\parallel,\mathrm{cl}}|^{2}\,\mathrm{Im}\left([1-\epsilon(\omega)]\,\frac{d}{du}\,[d_{\parallel}(\omega)]\right) + |E^{\perp,\mathrm{cl}}(\mathrm{out})|^{2}\,\mathrm{Im}\left(\frac{1-\epsilon(\omega)}{\epsilon(\omega)}\,\frac{d}{du}\,[d_{\perp}(\omega)]\right)\right]. \quad (17)$$

This expression may be written in terms of the incident flux $F \equiv c|\vec{\mathrm{E}}^{0}|^{2}/8\pi$ for s- and p-polarized light. For s polarization one has

$$\frac{dP^{(s)}}{du} = qF\,|1 + r^{(s),\mathrm{cl}}|^{2}\,|\epsilon(\omega) - \sin^{2}\theta\,|\gamma_{\parallel}(\omega)\,, \quad (18)$$

where

$$\gamma_{\parallel}(\omega) \equiv \mathrm{Im}\left([1-\epsilon(\omega)]\,\frac{d}{du}\,d_{\parallel}(\omega)\right). \quad (19)$$

θ is the angle of incidence, and $r^{(s),\mathrm{cl}}$ is the classical, s-polarization reflection amplitude. For p polarization one has

$$\frac{dP^{(p)}}{du} = qF\left|\frac{1 + r^{(p),\mathrm{cl}}}{\epsilon(\omega)}\right|^{2} \times \{\,[\epsilon(\omega) - \sin^{2}\theta\,]\gamma_{\parallel}(\omega) + \sin^{2}\theta\,\gamma_{\perp}(\omega)\}\,, \quad (20)$$

where

$$\gamma_{\perp}(\omega) \equiv \mathrm{Im}\left([1-\epsilon(\omega)]\epsilon^{*}(\omega)\,\frac{d}{du}\,[d_{\perp}(\omega)]\right) \quad (21)$$

and $r^{(p),\mathrm{cl}}$ is the classical amplitude for p-polarized light.

Equations (18)–(21) are the main results of this paper. They give dP/du for s- and p-polarized incident light in terms of $\epsilon(\omega)$, $d(d_{\parallel})/du$, and $d(d_{\perp})/du$. These quantities can be obtained directly from reflectance measurements, as I now review.

An exact (for jellium) theory of the surface contributions to reflectance[4] gives the following results for the complex reflection amplitudes for s- and p-polarized light

$$r^{(s)} = r^{(s),\mathrm{cl}}[1 + 2iq_{\perp}d_{\parallel}(\omega)], \quad (22)$$

$$r^{(p)} = r^{(p),\mathrm{cl}}(\,1 + 2iq_{\perp}\{d_{\parallel}(\omega) + [d_{\perp}(\omega) - d_{\parallel}(\omega)] \times [\epsilon(\omega)^{-1} - q_{\perp}^{2}/q_{\parallel}^{2}]^{-1}\}\,)\,. \quad (23)$$

Here $q_{\perp} \equiv q\cos\theta$. Thus the differential reflection coefficients for s and p polarization are given by[16]

$$\frac{1}{R^{(s),\mathrm{cl}}}\,\frac{dR^{(s)}}{du} = -4q_{\perp}\,\frac{d}{du}\,[\mathrm{Im}\,d_{\parallel}(\omega)] \quad (24)$$

and

$$\frac{1}{R^{(p),\mathrm{cl}}}\,\frac{dR^{(p)}}{du}=-4q_{\perp}\,\frac{d}{du}\,\mathrm{Im}\left(d_{\parallel}(\omega)+\frac{d_{\perp}(\omega)-d_{\parallel}(\omega)}{\epsilon^{-1}(\omega)-\cot^{2}\theta}\right). \tag{25}$$

The differential reflectance for s polarization directly determines $\mathrm{Im}d[d_{\parallel}(\omega)]/du$. The θ dependence of $dR^{(p)}/du$ can then be used to determine the real and imaginary parts of $d[d_{\perp}(\omega)-d_{\parallel}(\omega)]/du$.[5] One still needs the real part of $d(d_{\parallel})/du$ to compute the power absorption, however. This is a familiar problem in the classical analysis of reflectance data. It can be solved entirely within the context of s-polarization measurements. That is, $\mathrm{Re}[d(d_{\parallel})/du]$ can be obtained by measuring a differential phase change on reflection, via Eq. (22), or by carrying out a Kramers-Kronig analysis using the measured $\mathrm{Im}[d(d_{\parallel})/du]$.[17]

Once one has performed the analysis just described, substitution of the measured values of $d(d_{\perp})/du$ and $d(d_{\parallel})/du$ into Eqs. (19) and (21) yields $dP^{(s)}/du$ and $dP^{(p)}/du$. Thus the differential power spectrum is obtained from reflectance data without the use of Fresnel formulas or any theoretically calculated parameter.

In view of the success of the jellium picture in describing surface photoemission from Al,[9] this metal would be an excellent choice for a test of the formulas derived here. Such a test might involve the measurement of the change in loss spectrum with adsorption under UHV conditions, using electrons and by monitoring reflectance changes. It is not obvious how successful the application of the jellium-surface results will be in the case of non-free-electron metals, such as Ag and Au for which many electroreflectance measurements have been reported.[1] Certainly, the azimuthal anisotropy reported for Ag(110) (Ref. 18) is beyond the ability of the jellium model to describe. In the results of Kötz and Kolb (KK),[19] it is seen that the electroreflectance of Ag is very different for s and p polarization, for θ sufficiently far from 0°. This is in accord with Eqs. (24) and (25). At the plasma frequency [where $\epsilon^{-1}(\omega)=0$], KK observe a dramatic dip in the p-polarization electroreflectance. That an anomaly should be observed at this frequency is in agreement with Eq. (25), because $\epsilon^{-1}(\omega)$, in the denominator of the second term of this equation, becomes quite large at the plasma frequency [for Ag, $\epsilon^{(2)}(\omega_p)\sim 0.2$ (Ref. 20)]. However, according to Eqs. (24) and (25), if $\epsilon(\omega)\approx 0$, the electroreflectance for s and p polarization should be nearly equal. KK's results do not obey this behavior. One wonders whether this is because $(d/du)\{\mathrm{Im}[d_{\perp}(\omega_p)-d_{\parallel}(\omega_p)]\}$ is particularly large, or whether a failure of the jellium model to describe Ag is at fault. Experimental tests of the jellium theory and extension of the theory to include non-free-electron behavior would obviously be desirable in answering this question.

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APPENDIX

The purpose of this appendix is to show the relation between $d_{\parallel}(\omega)$ and $d_{\perp}(\omega)$ and the corresponding surface response functions Λ_x and Λ_z defined in Refs. 5 and 6. Λ_x is defined by

$$\Lambda_x\equiv\int dz\left(\int dz'\epsilon^{xx}(z,z')-\epsilon^{\mathrm{cl}}(z)\right), \tag{A1}$$

where for a vacuum-metal interface in the neighborhood of $z=0$

$$\epsilon^{\mathrm{cl}}(z)\equiv\Theta(-z)+\epsilon(\omega)\Theta(z). \tag{A2}$$

Substitution of Eqs. (A2) and (3) into Eq. (A1) and introduction of the cutoff Z on the z integral then yields

$$\Lambda_x=\frac{4\pi i}{\omega}\int_{-\infty}^{Z}dz\int_{-\infty}^{\infty}dz'\sigma^{xx}(z,z')-[\epsilon(\omega)-1]Z. \tag{A3}$$

Comparing Eqs. (A3) and (12), we see that

$$d_{\parallel}(\omega)\equiv[1-\epsilon(\omega)]\Lambda_x. \tag{A4}$$

For Λ_z, one has the definition

$$\Lambda_z\equiv\int dz\left(\int dz'\epsilon^{-1}(z,z')-\frac{1}{\epsilon^{\mathrm{cl}}(z)}\right), \tag{A5}$$

which has meaning for $\omega<\omega_p$.[15] We proceed via Eqs. (3) and (9) which imply that

$$\mathcal{E}(z)\equiv\int dz'\epsilon^{-1}(z,z'). \tag{A6}$$

Thus

$$\Lambda_z=\int dz\left(\mathcal{E}(z)-\frac{1}{\epsilon^{\mathrm{cl}}(z)}\right) \tag{A7}$$

or, using Eq. (A2),

$$\Lambda_z=\int_{-\infty}^{0}dz[\mathcal{E}(z)-1]+\int_{0}^{\infty}dz\left(\mathcal{E}(z)-\frac{1}{\epsilon(\omega)}\right). \tag{A8}$$

To show the relation of this expression to that for $d_{\perp}(\omega)$, Eq. (13), we first check that $d_{\perp}(\omega)$ is Z independent. Thus

$$\frac{d}{dZ}\, d_\perp(\omega) = 1 - \frac{\epsilon(\omega)}{\epsilon(\omega)-1}\left(1 - \frac{1}{\epsilon(\omega)}\right) = 0\,, \tag{A9}$$

which is the desired result. Since Z is arbitrary, we set it equal to zero in Eq. (13), and thus find that

$$\Lambda_z = \frac{\epsilon(\omega)-1}{\epsilon(\omega)}\, d_\perp(\omega)\,. \tag{A10}$$

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[14] The "$q_\parallel \to 0$" and "ω" have been suppressed in writing $\sigma^{zz}(z,z')$.

[15] Specifically, a plasmon represents a zero of the bulk dielectric function which makes a very careful definition of $\epsilon^{-1}(z,z')$ essential.

[16] These formulas have the usual classical limits, as has been shown in detail in Ref. 3. For example, for a three-phase model with a local conductivity $\sigma(z) = \sigma^a\Theta(z)\Theta(d-z)+\sigma^b\Theta(z-d)$, Eq. (12) implies that $d_\parallel = d(1-\sigma^a/\sigma^b)$. Therefore, Eq. (24) yields $(R^{(s),\mathrm{cl}})^{-1} \times (dR^{(s),\mathrm{cl}}/ds) = 4qd\cos\theta\,\mathrm{Im}(\sigma^a/\sigma^b)$, which is the McIntyre-Aspnes result (Ref. 3).

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