Allowance for microscopic effects in the electrodynamics of metal surfaces

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A calculation method is developed that makes it possible to take into account the influence of the spatial dispersion and of the microscopic properties of a surface on the optical characteristics of the interface between a metal and vacuum. The method is based on the use of the Riemann boundary-value problem scheme. The equations are rearranged in such a way that they contain only electromagnetic-field components that vary slowly near the surface. The problem of the additional boundary conditions, which is being discussed in the literature, does not arise in this case. It becomes possible to express the observable quantities in terms of the spectral characteristics of the unbounded metal and of the integral characteristics of the surface. The method developed is applicable to the solution of the following concrete problem: 1) the calculation of the optical characteristics in the hydrodynamic model of the metal, and 2) the elucidation of the influence of the surface structure on the dispersion law of the surface plasmons. The results are compared with the experimentally measured dependences of the frequencies of the surface plasmons on the potential discontinuity in electrochemical systems.

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1. INTRODUCTION

The advances in the experimental technique, and particularly modulation spectroscopy[1] and the spectroscopy of attenuated total internal reflection,[2] have made it possible to obtain for the light-reflection coefficients and surface-wave characteristics quantitative data that are much more accurate than the earlier ones. In the visible range and in the near ultraviolet, the observed relative effects of the influence of the electronic structure of the surface of the metals turned out to be much larger in a number of cases than the natural parameter $a\omega/c$, where a is a quantity of the order of the atom size, ω is the frequency, and c is the speed of light. To this day, there is no satisfactory theory of these effects. Such a theory should take into account in suitable fashion both the dispersion of the dielectric constant in the metal and the microscopic effects on its surface. The problems encountered in this case are described in Refs. 3 and 4.

One of these problems is the insufficient number of ordinary conditions for the field discontinuities on the metal boundary in the case of a macroscopic description, when more than two volume modes appear. Many variants of the additional boundary conditions (ABC) are contained in the literature and are critically reviewed in Ref. 4, where it is emphasized that the total microscopic problem of the reflection of light does not require, in principle, any additional boundary conditions. It is proposed in Ref. 4 to carry out the calculations using microscopic models. It is clear, however, that the microscopic characteristics should enter at $a\omega/c \ll 1$ only in the form of some averaged parameters that depend little on the details of surface models which are usually remote from reality. The elucidation of the form of these parameters and the derivation of microscopic equations for the electromagnetic field, accurate to first nonvanishing order in $a\omega/c$, was one of the principal tasks of the present paper. To this end, we have reduced our problem to the Riemann boundary-value problem[5] previously used in a number of physical problems,[6] and have shown that it has a unique solution for any number of volume modes. The gist of the method consists of using the consequences of the analytic properties of the Fourier components of the fields and of the response functions, which automatically account for all the conditions on the surface of the metal. This approach is an extension of Ref. 7, where light reflection was described by using the Wiener–Hopf mathematical formalism. In contrast to Ref. 7 and to papers of like character,[8,9] in which it was possible to consider only the case of an abrupt boundary of a homogeneous metal, the method used here makes it possible to take into account simultaneously both the influence of the spatial dispersion and the influence of the surface structure. Another question that arises in the problems under consideration and is being discussed to this day in the literature[10] concerns the uncertainties that arise in the analysis of the microscopic equation for field components that vary rapidly at the surface. The ensuing difficulties are eliminated in the present paper by restructuring the equations in such a way that only field components that are slowly varying on the surface (and are continuous in the macroscopic theory) are left. This procedure was proposed and used earlier in Refs. 11 and 12.

The developed general scheme is used in this paper to solve two problems of practical interest. First, in Sec. 4 we consider the influence of the properties of the surface on the reflection coefficients and on the dispersion law of surface excitations in the hydrodynamic model of a metal. Second, in Sec. 5 we consider the influence of the potential discontinuity applied to a metal surface on the dispersion law of surface plasmons; this influence was investigated experimentally in Refs. 13.

2. INITIAL EQUATIONS

We consider a metal that occupies the left-hand half-space $x_1 < 0$, where the plane $x_1 = 0$ lies near the macroscopically smooth boundary of a lattice of positive ions.

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A monochromatic electromagnetic wave $\mathbf{E}(\omega, \mathbf{x})$ is incident on the metal and has an amplitude $\mathbf{E}^0$, a frequency ω, and a wave vector $\mathbf{k}^0$ that lies in the (x_1, x_2) plane. We start from electromagnetic-field equations of the form

$$\left(\delta_{ij}\nabla^2 - \frac{\partial^2}{\partial x_i \partial x_j}\right) E_j(\omega, \mathbf{x}) + \frac{\omega^2}{c^2}\int \varepsilon_{ij}(\omega, \mathbf{x}, \mathbf{x}') E_j(\omega, \mathbf{x}')\, d^3\mathbf{x}' = 0, \tag{1}$$

where summation over like indices is implied. We have introduced in (1), in the linear-response approximation, a term with nonlocal dielectric constant $\varepsilon_{ij}(\omega, \mathbf{x}, \mathbf{x}')$. We put

$$\varepsilon_{ij}(\omega, \mathbf{x}, \mathbf{x}') = \varepsilon_{ij}(\mathbf{x}, \mathbf{x}') = \varepsilon_{ij}^0(\mathbf{x}-\mathbf{x}')\theta(-x_1') + \delta\varepsilon_{ij}(\mathbf{x}_\parallel - \mathbf{x}_\parallel', x_1, x_1') + \delta_{ij}\delta(\mathbf{x}-\mathbf{x}')\theta(x_1), \tag{2}$$

where $\varepsilon_{ij}^0(\mathbf{x}-\mathbf{x}')$ is the dielectric constant of the homogeneous metal[1)] and $\mathbf{x}_\parallel = (0, x_2, x_3)$. The term $\delta\varepsilon_{ij}(\mathbf{x}_\parallel - \mathbf{x}_\parallel', x_1, x_1')$, which takes into account the influence of the surface, decreases rapidly over microscopic distances at $|x_1|, |x_1'| \to \infty$, and we assume that

$$\left|\int \delta\varepsilon_{ij}(\mathbf{x}_\parallel, x_1, x_1')\, dx_1 dx_1' d^2\mathbf{x}_\parallel\right| \ll \frac{c}{\omega}\left|\int \varepsilon_{ij}^0(\mathbf{x})\, d^3\mathbf{x}\right|. \tag{3}$$

The inequality (3) is equivalent to the condition that the distances over which the influence of the boundary on the electronic properties of the homogeneous attenuates is small compared with the wavelength of the light. According to contemporary notions, this distance is of the order of $\hbar p_f^{-1}$, where p_f is the momentum on the Fermi surface.[14] We emphasize that even if (3) is satisfied the term with $\delta\varepsilon_{ij}$ in (2) is decisive when it comes to describing experiments similar to those considered in Sec. 5, in which one measures the influence of the modulation of the properties of metal surfaces on the optical characteristics.

To abbreviate the notation, we assume in (2) that averaging is carried out at $|x_1| \gg a$ over the three-dimensional crystal cell; this assumption is justified when long-wave components of the fields are considered and there are no short-wave longitudinal modes.[15] Averaging over the two-dimensional cell in the direction along the metal surface is carried out at all x_1. We change over hereafter from functions of the coordinates $x_\parallel$ to their Fourier components. The conserved value of the projection of the wave vector on the plane of the surface $\mathbf{k}_\parallel = \mathbf{k}_\parallel^0$ in the arguments of the functions will as a rule be omitted. In place of Eqs. (1) and of the diverging-wave boundary condition we can write down the integral equation

$$E_i(\omega, \mathbf{k}_\parallel, x_1) = E_i(x_1) = E_i^0 \exp(-ik_1^0 x_1) + \frac{i}{2k_1^0}\frac{\omega^2}{c^2}\int dx_1 dx_1' \times\left\{\exp(ik_1^0|x_1 - x_1'|)\left(\delta_{ij} - \frac{c^2 k_i k_j}{\omega^2}\right)[\varepsilon_{jl}(x_1', x_1'') - \delta(x_1' - x_1'')\delta_{jl}]E_l(x_1'')\right\}; \quad \varepsilon_{jl}(x_1, x_1') \equiv \varepsilon_{jl}(\mathbf{k}_\parallel, x_1, x_1'), \tag{4}$$

where $\mathbf{k}_\parallel = (0, k_2, k_3)$ and k_1 is the operator $-i\partial/\partial x_1$. On changing to the Fourier component with respect to the coordinate x_1, the operation k_1 turns into ordinary multiplication.

Following the Ewald scheme[16,17] we represent the one-dimensional Green's functions that enters in (4)

$$\exp[ik_1^0|x_1 - x_1'|] = 2i\theta(x_1 - x_1')\sin[k_1^0(x_1 - x_1')] + \exp[-ik_1^0(x_1 - x_1')]. \tag{5}$$

Substituting (5) in (4) we obtain two equations:

$$E_i^0 = -\frac{i}{2k_1^0}\frac{\omega^2}{c^2}\int dx_1' dx_1'' \left\{\exp(ik_1^0 x_1')\left(\delta_{ij} - \frac{c^2 k_i k_j}{\omega^2}\right) \times[\varepsilon_{jl}(x_1', x_1'') - \delta(x_1' - x_1'')\delta_{jl}]E_l(x_1'')\right\};$$

$$E_i(x_1) = -\frac{1}{k_1^0}\frac{\omega^2}{c^2}\int_{-\infty}^{x_1} dx_1' \int_{-\infty}^{\infty} dx_1'' \left\{\sin k_1^0(x_1 - x_1') \times\left(\delta_{ij} - \frac{c^2 k_i k_j}{\omega^2}\right)[\varepsilon_{jl}(x_1', x_1'') - \delta(x_1' - x_1'')\delta_{jl}]E_l(x_1'')\right\}. \tag{6}$$

The first equation in (6) is obtained from the condition that the terms proportional to $\exp(-ik_1^0 x_1)$, cancel out as $x_1 \to -\infty$. It determines the normalization of $E_i(x_1)$ and, since we seek hereafter only the ratios of the field amplitudes, it is of no importance to us. We introduce the notation

$$D_i(x_1) = \int \varepsilon_{ij}(x_1, x_1')E_j(x_1')\, dx_1'. \tag{7}$$

It follows[16] from (6) that the relative increment of the functions $E_2(x_1)$, $E_3(x_1)$ and $D_1(x_1)$ is of the order $a\omega/c$ when x_1 changes near $x_1 = 0$ by amounts equal to atomic distances. We recall that in the macroscopic theory it is precisely these field components which have no discontinuities on the surface. With the aid of the tensor $\varepsilon_{(1)}^{-1}(x_1, x_1') \equiv \varepsilon_{(1)}^{-1}(\mathbf{k}_\parallel, x_1, x_1')$, defined by the condition[2)]

$$\int \varepsilon_{11}(x_1, x_1'')\varepsilon_{(1)}^{-1}(x_1'', x_1')\, dx_1'' = \delta(x_1 - x_1'), \tag{8}$$

we can express the field components that vary rapidly near the surface, particularly $E_1(x_1)$, in terms of $E_2(x_1)$, $E_3(x)$, and $D_1(x_1)$. Taking into account the already mentioned properties of $\delta\varepsilon_{ij}(x_1, x_1')$, we can furthermore put in (6), at the accuracy employed,

$$\int \delta\varepsilon_{ij}(x_1, x_1')E_j(x_1')\, dx_1' = \Gamma_{ij}(x_1)E_j^s, \tag{9}$$

where the quantities E_j^s are the values of the slowly varying functions of x_1 at $x_1 = 0$:

$$E_1^s = D_1(0), \quad E_2^s = E_2(0), \quad E_3^s = E_3(0). \tag{10}$$

The coefficients $\Gamma_{ij}(x_1)$ introduced in (9) are equal to

$$\Gamma_{11}(x_1) = \int dx_1' dx_1'' \delta\varepsilon_{11}(x_1, x_1')\varepsilon_{(1)}^{-1}(x_1', x_1''),$$

$$\Gamma_{ij}(x_1) = \int dx_1' \delta\varepsilon_{ij}(x_1, x_1') - \int dx_1' dx_1'' dx_1''' \delta\varepsilon_{i1}(x_1, x_1')\varepsilon_{(1)}^{-1}(x_1', x_1'')\varepsilon_{1j}(x_1'', x_1'''), \quad j = 2, 3. \tag{11}$$

3. GENERAL SOLUTIONS OF THE FIELD EQUATIONS

After substituting (2) in the second equation of (6) and using (9), Eq. (6) is transformed at $x_1 > 0$ into a relation that expresses the field in the right-hand half-space $E_i^+(x_1) = E_i(x_1)\theta(x_1)$ in terms of the field $E_i^-(x_1) = E_i(x_1)\theta(-x_1)$ in the left-hand half-space and of the values of E_j^s. The natural method of solving such equations is to use the mathematical formalism of the Riemann boundary problem.[5] To this end, we change over to Fourier transforms. From the second equation of (6), taking (2) and (9) into account, we then obtain

$$E_i^-(k_1)+E_i^+(k_1)=\frac{\omega^2}{c^2}\left(\delta_{ij}-\frac{c^2k_ik_j}{\omega^2}\right)\frac{1}{k^2-\omega^2/c^2+ik_1\delta}$$
$$\times[(\varepsilon_{jl}^0(k_1)-\delta_{jl})E_l^{-1}(k_1)+\Gamma_{jl}(k_1)E_l^+]. \quad \delta\to+0. \tag{12}$$

The term $ik_1\delta$ in the denominator of the Green's function in (12) will not be explicitly written out hereafter. To solve the Riemann problem it is necessary to consider the analytic properties of the functions $\varepsilon_{ij}^0(k_1)$ and $\Gamma_{ij}(k_1)$ that enter in (12).

Confining ourselves for simplicity to the case of metals with nearly spherical Fermi surface, we put at $\mathbf{k}_\parallel=\mathbf{k}_\parallel^0$

$$\varepsilon_{ij}^0(\mathbf{k})=\varepsilon_T(|\mathbf{k}|)\delta_{ij}+[\varepsilon_L(|\mathbf{k}|)-\varepsilon_T(|\mathbf{k}|)]k_ik_j/k^2. \tag{13}$$

The form of the dependence of $\varepsilon_{T,L}(|\mathbf{k}|)$ on k_1 is connected with the form of the spectrum of the excitations in the unbounded metal, which includes in the general case N transverse and M longitudinal modes. These modes correspond to k_1 values $\pm v_T^{(n)}(\mathbf{k}_\parallel^0)$ and $\pm v_L^{(m)}(\mathbf{k}_\parallel^0)$ ($n=1,\ldots,N$; $m=1,\ldots,M$), which are at fixed $\mathbf{k}_\parallel=\mathbf{k}_\parallel^0$ the respective roots of the equations

$$k_1^2+(\mathbf{k}_\parallel^0)^2-\frac{\omega^2}{c^2}\varepsilon_T(|\mathbf{k}|)=0, \quad \varepsilon_L(|\mathbf{k}|)=0. \tag{14}$$

The quantities $v_T^{(n)}, v_L^{(m)}$ have positive imaginary components corresponding to damping. Without loss of generality, we can assume that $\varepsilon_{T,L}(|\mathbf{k}|)$ are analytic functions of k_1 in the band $|\mathrm{Im}k_1|<1/a$. This assumption is equivalent to the natural condition that $\varepsilon_{T,L}(\mathbf{x})$ decrease exponentially with increasing $|x_1|$. The behavior of $\varepsilon_{ij}^0(k_1)$ as $k_1\to\infty$ in the analyticity band is characterized by the condition

$$\varepsilon_{ij}^0(k_1)\to\delta_{ij}\varepsilon_i^0 \quad \text{as} \quad |k_1|\to\infty, \tag{15}$$

where ε_i^0 is the local component of the dielectric constant. The quantities $\Gamma_{ij}(k_1)$, in view of the connection between $\Gamma_{ij}(x_1)$ and $\delta\varepsilon_{ij}(x_1,x_1')$ in accordance with formulas (11), are also analytic functions of k_1 in the band $|\mathrm{Im}k_1|<1/a$ and satisfy, being Fourier transforms of quadratically integrable functions, the condition

$$\Gamma_{ij}(k_1)=o(1), \quad |k_1|\to\infty. \tag{16}$$

We resolve the Fourier components of the quantities $E_i^\pm(x_1)$ into longitudinal and transverse components with the aid of the following definitions:

$$\begin{aligned}E_L^\pm(k_1)&=k_iE_i^\pm(k_1)=k_1E_1^\pm(k_1)+k_2E_2^\pm(k_1),\\ E_{TE}^\pm(k_1)&=e_{ijl}k_jE_i^\pm(k_1)=k_2E_3^\pm(k_1),\\ E_{TM}^\pm(k_1)&=(\delta_{ij}\delta_{il}-\delta_{il}\delta_{jl})k_jk_lE_i^\pm(k_1)=k_1k_2E_2^\pm(k_1)-k_2^2E_1^\pm(k_1),\end{aligned} \tag{17}$$

where e_{ijl} is a completely antisymmetrical tensor, and the second equalities are the consequence of the particular choice of the coordinate frame. The quantities $E_{TE}+(k_1)$ and $E_{TM}+(k_1)$ coincide, apart from the coefficients, with the amplitudes of the electric-field intensities respectively in the s- and p-polarized waves. From (17) we get the relation

$$E_{TM}^\pm(k_1)-k_1E_L^\pm(k_1)=k^2E_1^\pm(k_1), \tag{17'}$$

which determines the connection between E_{TM} and E_L at $k^2=0$. From (12), (13), and (17) we get the equations

$$\begin{aligned}E_L^+(k_1)&=-\varepsilon_L(k_1)E_L^-(k_1)-k_i\Gamma_{ij}(k_1)E_j^s,\\ \left(k^2-\frac{\omega^2}{c^2}\right)E_{TE}^+(k_1)&=-\left(k^2-\frac{\omega^2}{c^2}\varepsilon_T(k_1)\right)E_{TE}^-(k_1)\\ &+\frac{\omega^2}{c^2}e_{ijl}k_j\Gamma_{il}(k_1)E_l^s,\\ \left(k^2-\frac{\omega^2}{c^2}\right)E_{TM}^+(k_1)&=-\left(k^2-\frac{\omega^2}{c^2}\varepsilon_T(k_1)\right)E_{TM}^-(k_1)\\ &+\frac{\omega^2}{c^2}(\delta_{ij}\delta_{il}-\delta_{il}\delta_{jl})k_ik_j\Gamma_{ik}(k_1)E_k^s.\end{aligned} \tag{18}$$

The quantities $E_{L,TE,TM}^+(k_1)(E_{L,TE,TM}^-(k_1))$, by virtue of the definition $E_i^\pm(x_1)$, are analytic functions of k_1 at $\mathrm{Im}k_1>0$ ($\mathrm{Im}k_1<0$). To solve Eqs. (18) we need additional conditions on the behavior of $E_{L,TE,TM}^-(k_1)$ as $|k_1|\to\infty$ in the half-plane $\mathrm{Im}k_1<0$. As shown in the Appendix,

$$\begin{aligned}E_{TE}^-(k_1)|_{|k_1|\to\infty}&=-i(k_2/k_1)E_3^s, \quad E_{TM}^-(k_1)|_{|k_1|\to\infty}=-ik_2E_2^s,\\ E_L^-(k_1)|_{|k_1|\to\infty}&=-i(E_1^s+\tilde\gamma_{ij}E_j^s),\end{aligned} \tag{19}$$

where the constant $\tilde\gamma_{ij}$ is expressed in terms of ε_{ij}^0 and Γ_{ij} in accordance with formula (A.2).

The solution of Eqs. (18) in accordance with the general scheme of Ref. 5, based on the use of the already mentioned analytic properties of $\varepsilon_{ij}^0(k_1)$ and $\Gamma_{ij}(k_1)$ and on Eq. (17'), is given in the Appendix. As a result, the quantities $E_{TE}^+(k_1)$ and $E_{TM}^+(k_1)$, which determine the fields outside the metal, are given by

$$\begin{aligned}E_{TE}^+(k_1)&=\frac{1}{(k_1+i\delta)^2+(k_\parallel^0)^2-\omega^2/c^2}f_{TE}(k_1),\\ E_{TM}^+(k_1)&=\frac{1}{(k_1+i\delta)^2+(k_\parallel^0)^2-\omega^2/c^2}f_{TM}(k_1),\end{aligned} \tag{20}$$

where the functions $f_{TE}(k_1)$ and $f_{TM}(k_1)$, which have only pole singularities at $\mathrm{Im}k_1\geq -1/a$, are equal to

$$\begin{aligned}f_{TE}(k_1)&=\left[R_{TE}(k_1)+\frac{\omega^2}{c^2}\left(k_1+\frac{i}{a}\right)^{N-1}k_2\varkappa_{3i}^+(T,k_1)E_i^s\right]\\ &\times\left[\Omega_T^+(k_1)\left(k_1+\frac{i}{a}\right)^{N-1}\right]^{-1},\\ f_{TM}(k_1)&=\left\{R_{TM}(k_1)+\frac{\omega^2}{c^2}\left(k_1+\frac{i}{a}\right)^{N-1}k_2[k_1\varkappa_{2i}^+(T,k_1)\right.\\ &\left.-k_2\varkappa_{1i}^+(T,k_1)]E_i^s\right\}\left[\Omega_T^+(k_1)\left(k_1+\frac{i}{a}\right)^{N-1}\right]^{-1}.\end{aligned} \tag{21}$$

The polynomials $R_{TE}(k_1)$ and $R_{TM}(k_1)$ and the function $\Omega_T^+(k_1)$ and $\varkappa_{ij}^+(T,k_1)$, which enter in (21) and are defined in the Appendix, are expressed in terms of the quantities ε_{ij}^0, $\varepsilon_{(1)}^{-1}$ and Γ_{ij} for any number of natural volume modes of the metal. In Eqs. (20) and (21) are left exactly two undetermined constants, E_2^s and E_3^s, in accord with the number of independent amplitudes in the incident wave.

To obtain the observed quantities, we turn to the coordinate representation and consider the asymptotic forms as $x_1\to\infty$. Using the analytic properties of the functions in (20), we have

$$\begin{aligned}E_p^+(x_1)&=\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp(-ik_1x_1)E_p^+(k_1)\,dk_1|_{x_1\to\infty}\\ &=-\frac{i}{2k^0}\{f_p(k_1^0)\exp(-ik_1^0x_1)-f_p(-k_1^0)\exp(ik_1^0x_1)\},\end{aligned}$$
$$p=TE, TM, \quad (k_1^0)^2=\omega^2/c^2-(k_\parallel^0)^2. \tag{22}$$

In the expressions for $E_{TM}^+(x_1)$ and $E_{TE}^+(x_1)$, only two waves remain as $x_1\to\infty$, corresponding to the poles in

(20) closest to the real axis k_1 and proportional respectively to $\exp(\pm ik_1^0 x_1)$. The coefficient of $\exp(-ik_1^0 x_1)$ can be set equal to the amplitude of the field in the wave incident on the metal, so that we can eliminate the two remaining constants E_2^s, E_3^s. The coefficient of $\exp(ik_1^0 x_1)$ specifies the sought amplitudes of the reflection coefficients $r_{TE}(k_1^0)$ and $r_{TM}(k_1^0)$, which take the form

$$r_{TE}(k_1^0)=\frac{f_{TE}(-k_1^0)}{f_{TE}(k_1^0)}, \quad r_{TM}(k_1^0)=\frac{f_{TM}(-k_1^0)}{f_{TM}(k_1^0)}. \tag{23}$$

The values of $\omega_s \equiv \omega_s(k_\parallel)$, which are the roots of the equation

$$f_{TM}(k_1^0)=0, \tag{24}$$

correspond to the possibility of existence of solutions with one wave at $x_1>0$, which attenuates as $x_1 \to \infty$. For real ω_s, such solutions correspond to surface modes that attenuate in both directions as $|x_1| \to \infty$. Complex ω_s with small imaginary components correspond to surface resonances that attenuate either because of the decay of the wave that goes into the interior of the metal, or because of the absorption over the characteristic time $(2|\mathrm{Im}\omega_s|)^{-1}$.

4. OPTICAL CHARACTERISTICS IN THE HYDRODYNAMIC MODEL OF A METAL

We consider a problem in which the traditional[18] expression

$$\varepsilon_L(\omega,\mathbf{k})=\varepsilon_T(\omega,\mathbf{k})=\varepsilon(\omega,\mathbf{k})=\varepsilon_0(\omega)-\frac{\omega_p^2}{\omega^2-\beta^2k^2+i\omega/\tau} \tag{25}$$

is used for the bulk dielectric constant of a metal. The transition from the dielectric properties of the metal to the properties of a vacuum, however, will not be assumed here, as is customary, to be jumplike. We assume only for the sake of brevity that the surface has axial symmetry, i.e., $\Gamma_{ij}(x_1)=\delta_{ij}\Gamma_i(x_1)$, $\Gamma_2(x_1)=\Gamma_3(x_1)$, and that $\Gamma_i(x_1)=0$ at $x_1<0$. The last condition can be satisfied if the quantities $\Gamma_i(x_1)$, which characterize the deviations from the volume properties, decrease over atomic distances from the surface, and there is a definite leeway in the choice of the position of the surface. In this case there can propagate in the volume of the metal two transverse volume modes with $k_1=\pm v_T^{(1)}$, $\pm v_T^{(2)}$ and one longitudinal mode with $k_1=\pm v_L$, where

$$\begin{aligned}
&\varepsilon_L(\omega,k)=\varepsilon_0(\omega)\frac{k_1^2-v_L^2}{k_1^2-v_\mu^2},\\
&k^2-\frac{\omega^2}{c^2}\varepsilon_T(\omega,k)=\frac{(k_1^2-v_T^{(1)2})(k_1^2-v_T^{(2)2})}{k_1^2-v_\mu^2},\\
&(v_T^{(1,2)})^2=\frac{1}{2}\left[\varepsilon_0(\omega)\frac{\omega^2}{c^2}+\mu^2\right]\\
&\pm\left\{\frac{\omega_p^2}{\beta^2}\frac{\omega^2}{c^2}+\frac{1}{4}\left[\varepsilon_0(\omega)\frac{\omega^2}{c^2}-\mu^2\right]^2\right\}^{1/2}-k_\parallel^2,\\
&(v_L)^2=(v_\mu)^2-\frac{\omega_p^2}{\beta^2\varepsilon_0(\omega)}, \quad (v_\mu)^2=\mu^2-k_\parallel^2, \quad \mu^2=\frac{\omega^2}{\beta^2}+\frac{i\omega}{\beta^2\tau}.
\end{aligned} \tag{26}$$

The functions $\Omega_T^{\pm}(k_1)$ and $\Omega_L^{\pm}(k_1)$ are equal to unity under the case under consideration.

Using Eqs. (A.7) and (A.8), we find that the Fourier transforms of the fields inside the metal take at $\mathrm{Im}k_1<0$ the form

$$\begin{aligned}
&E_{TE}^-(k_1)=-ik_2E_3^s\frac{k_1-v_\mu}{(k_1-v_T^{(1)})(k_1-v_T^{(2)})},\\
&E_{TM}^-(k_1)=-ik_2E_2^s\frac{(k_1+A)(k_1-v_\mu)}{(k_1-v_T^{(1)})(k_1-v_T^{(2)})},\\
&E_L^-(k_1)=-i(1+\bar\gamma_{11})E_1^s\frac{k_1-v_\mu}{\varepsilon_0(\omega)(k_1-v_L)}.
\end{aligned} \tag{27}$$

Substituting (27) in (A.9) we get

$$\begin{aligned}
&A=\frac{k_2^4-k_2^2[v_T^{(1)}v_T^{(2)}-v_L(v_T^{(1)}+v_T^{(2)})]}{k_2^2(v_T^{(1)}+v_T^{(2)}-v_L)+v_T^{(1)}v_T^{(2)}v_L},\\
&(1+\bar\gamma_{11})E_1^s=-k_2\varepsilon_0(\omega)E_2^s\frac{v_L^2+k_2^2}{k_2^2(v_T^{(1)}+v_T^{(2)}-v_L)+v_T^{(1)}v_T^{(2)}v_L}
\end{aligned} \tag{28}$$

Using next (21)–(23) and (A.7), we obtain expressions for the amplitudes of the reflection coefficients $r_{TE}(k_1^0)$ and $r_{TM}(k_1^0)$ of s- and p-polarized light, respectively, in the form

$$\begin{aligned}
&r_{TE}(k_1^0)=\left[(k_1^0-v_T^{(1)})(k_1^0-v_T^{(2)})+i\frac{\omega^2}{c^2}(k_1^0-v_\mu)\Gamma_\parallel\right]\\
&\times\left[(k_1^0+v_T^{(1)})(k_1^0+v_T^{(2)})-i\frac{\omega^2}{c^2}(k_1^0+v_\mu)\Gamma_\parallel\right]^{-1}\frac{k_1^0+v_\mu}{v_\mu-k_1^0},\\
&r_{TM}(k_1^0)=\left\{(k_1^0-v_T^{(1)})(k_1^0-v_T^{(2)})(k_1^0-A)+i\frac{\omega^2}{c^2}(k_1^0-v_\mu)\right.\\
&\times\left.\left[k_1^0\Gamma_\parallel+k_2\Gamma_\perp\frac{E_1^s}{E_2^s}\right]\right\}\left\{(k_1^0+v_T^{(1)})(k_1^0+v_T^{(2)})(k_1^0+A)\right.\\
&\left.-i\frac{\omega^2}{c^2}(k_1^0+v_\mu)\left[k_1^0\Gamma_\parallel-k_2\Gamma_\perp\frac{E_1^s}{E_2^s}\right]\right\}^{-1}\frac{v_\mu+k_1^0}{v_\mu-k_1^0},
\end{aligned} \tag{29}$$

where

$$\Gamma_\perp=\int_0^\infty\Gamma_1(x_1)dx_1, \quad \Gamma_\parallel=\int_0^\infty\Gamma_2(x_1)dx_1=\int_0^\infty\Gamma_3(x_1)dx_1 \tag{30}$$

and the coefficients A and E_1^s/E_2^s are determined from (28). The parameters β and τ in the expression (25) for the bulk dielectric constant usually satisfy the inequalities

$$\beta \ll c, \quad \beta \ll \omega_p/k_\parallel, \quad \omega\tau \gg 1,$$

so that

$$\begin{aligned}
&(v_T^{(1)})^2=\frac{\omega^2}{c^2}\left[\varepsilon_0(\omega)-\frac{\omega_p^2}{\omega(\omega+i/\tau)}+O\left(\varepsilon_0(\omega)\frac{\beta^2}{c^2}\right)\right]-k_\parallel^2,\\
&(v_T^{(2)})^2=v_\mu^2[1+O(\varepsilon_0(\omega)\beta^2/c^2)].
\end{aligned} \tag{31}$$

Far from the volume-plasmon frequencies, i.e., at $|\omega^2-\omega_p^2/\varepsilon_0(\omega)| \gg \beta^2k_\parallel^2$, we obtain from (28) with the aid of (31)

$$\begin{aligned}
&A=\frac{k_\parallel^2}{v_T^{(1)}}\left[1+O\left((|\varepsilon_0(\omega)|)^{1/2}\frac{\beta}{c}\right)\right],\\
&(1+\bar\gamma_{11})E_1^s=-k_2E_2^s\frac{\varepsilon_0(\omega)v_L}{v_T^{(1)}v_T^{(2)}}\left[1+O\left((|\varepsilon_0(\omega)|)^{1/2}\frac{\beta}{c}\right)\right].
\end{aligned} \tag{32}$$

In this case the expressions for the light-reflection coefficients agree in the zeroth order in $|\varepsilon_0|^{1/2}\beta/c$ and $\omega\Gamma_i/c$ with the known Fresnel formulas.[16] It should be noted that in expression (25) foe the dielectric constant, and accordingly (27) for $E_L^-(k_1)$, when dispersion is excluded, acquire an incorrect behavior as $k_1 \to \infty$ if we simply set the parameter β equal to zero, and this behavior affects substantially the results of the calculations. The reason is that $\varepsilon(\omega,\mathbf{k})$ and $E_L^-(k_1)$ tend as $k_1 \to \infty$ in a nonuniform fashion to their limiting values in β. If we assume $\beta=0$ from the very outset, then formu-

las (28) and (32) take the modified form

$$E_1^s/E_2^s = -k_2\varepsilon(\omega,0)/v_T^{(1)}. \quad (33)$$

Expression (29) for $r_{TM}(k_1^0)$ agrees in first order in $\omega\Gamma_i/c$, when (33) is taken into account, with the formulas previously obtained without allowance for spatial dispersion,[11,12] and differs from the result obtained when the limit $\beta \to 0$ is taken in the final expression. An analysis of formulas (29) shows that at $\Gamma_i(k_1) = 0$ the influence of the spatial dispersion on the reflection coefficient of s-polarized light is particularly substantial at $|\varepsilon_0(\omega)| \gg 1$, i.e., at frequencies corresponding to interband transitions in the metal. In the case of p-polarized light the influence of the spatial dispersion is significant, in addition, at frequencies close to those of the volume plasmons.

The reflection coefficient (29) of p-polarized light has a pole corresponding to the existence of a surface plasmon. In the simplest case $\Gamma_i(k_1) = 0$, but when spatial dispersion is taken into account we obtain for the dispersion law of the surface plasmon, in the nonrelativistic limit at $\varepsilon_0(\omega) = 1$, the relation

$$\omega_s = \frac{\omega_p}{\sqrt{2}}\left[1 + \frac{1}{2\sqrt{2}}\frac{\beta|\mathbf{k}_\parallel|}{\omega_p} - \frac{i}{\sqrt{2}}\left(\frac{1}{\omega_p\tau} + \frac{1}{2}\frac{\beta|\mathbf{k}_\parallel|}{\omega_p}\right) + O\left(\left(\frac{\beta k_\parallel}{\omega_p}\right)^2\right)\right] \quad (34)$$

Relation (34) is similar to that obtained in Ref. 18 in the so-called dielectric model,[3)] and differs from the latter only in the coefficient in front of the term that depends linearly on $|\mathbf{k}_\parallel|$ in the imaginary part of ω_s. In the case of the dielectric model, the quantities $\Gamma_\perp$ and $\Gamma_\parallel$ do not vanish but are equal to $\Gamma_\perp = 0$, $\Gamma_\parallel = i\beta\omega_p^2/2\omega^3$, and this leads to the usual result. As seen from (34), the presence of spatial dispersion leads to an additional surface-plasmon level width that depends on $|\mathbf{k}_\parallel|$. The position of the level of the surface plasmon also depends on $|\mathbf{k}_\parallel|$, and the coefficient of the term linear in $|\mathbf{k}_\parallel|$ is positive.[4)] This conclusion agrees with the results of measurements of the dispersion law of surface plasmons propagating along an aluminum-vacuum boundary.[19]

5. INFLUENCE OF THE SURFACE STRUCTURE ON THE DISPERSION OF SURFACE PLASMONS

In this section we confine ourselves to media that can be described by a local dielectric constant $\varepsilon(\omega) = \varepsilon(\omega, k)|_{k=0}$, i.e., we assume that $\beta = 0$. In contrast to Sec. 4, however, we do not assume here that $\Gamma_i(x_1) = 0$ at $x_1 < 0$. In this case Eq. (24) for the dispersion of the surface plasmons takes the form

$$\left\{\frac{1}{\varepsilon_1}\left(\varepsilon_1\frac{\omega^2}{c^2} - k_\parallel^2\right)^{1/2} + \frac{1}{\varepsilon(\omega)}\left(\varepsilon(\omega)\frac{\omega^2}{c^2} - k_\parallel^2\right)^{1/2}\right\}$$
$$-i\left\{\frac{1}{\varepsilon_1\varepsilon(\omega)}\left(\varepsilon_1\frac{\omega^2}{c^2} - k_\parallel^2\right)^{1/2}\left(\varepsilon(\omega)\frac{\omega^2}{c^2} - k_\parallel^2\right)^{1/2}\Gamma_\parallel + k_\parallel^2\Gamma_\perp\right\} = 0, \quad (35)$$

where ε_1 is the dielectric constant of the external medium, which is no longer assumed to be vacuum, and

$$\Gamma_\perp = \frac{1}{\varepsilon(\omega)}\int_{-\infty}^{0}\Gamma_1(x_1)\,dx_1 + \frac{1}{\varepsilon_1}\int_0^{\infty}\Gamma_1(x_1)\,dx_1,$$
$$\Gamma_\parallel = \int_{-\infty}^{\infty}\Gamma_2(x_1)\,dx_1. \quad (36)$$

In a three-layer model, which is characterized by introduction of a dielectric constant ε_2 which does not depend on the coordinates x_1 and x_1', of an intermediate layer with a finite transverse dimension d, Eq. (35) goes over into the equations obtained in Refs. 3 and 21. The second term in the left-hand side of (35) takes into account the influence of the surface layer. This term turns out to be relatively small in the parameter $a\omega/c$ in the case considered below. Using this circumstance, we can write down the following dispersion law for the frequency of the surface plasmons:

$$\omega_s(k_\parallel) = \omega_s^0(k_\parallel) - B(\omega_s^0)\,|\mathbf{k}_\parallel|\,[\Gamma_\parallel - \varepsilon_1\varepsilon(\omega)\Gamma_\perp]; \quad (37)$$
$$B(\omega) = \frac{2(\varepsilon_1)^{1/2}[-\varepsilon(\omega)]^{1/2}}{[\varepsilon(\omega)-\varepsilon_1][\varepsilon_1 d\ln\varepsilon(\omega)/d\omega + 2(\varepsilon_1+\varepsilon(\omega))/\omega]}.$$

Here $\omega_s^0(k_\parallel)$ is the frequency of the surface plasmon that propagates along the boundary of a two-phase system $\varepsilon(\omega)/\varepsilon_1$, which is the solution of the equation

$$k_\parallel^2 = \frac{\omega^2}{c^2}\frac{\varepsilon_1\varepsilon(\omega)}{\varepsilon_1+\varepsilon(\omega)}. \quad (38)$$

From (35)–(37) we see that the influence of the structure of the surface layer on the dispersion law should be particularly substantial at large $|\mathbf{k}_\parallel|$, at which the quantity $\varepsilon(\omega)$ approaches $-\varepsilon_1$. This conclusion agrees with experimental results.[13]

Equation (37) can be used to describe the dependence of the experimentally obtained[13] dependence of the frequency of the surface plasmons on the potential discontinuity on a metal-electrolyte boundary. In the calculation of the dielectric constant we shall take into account the influence of the potential drop φ on the distribution of the electron density near the surface. To describe this effect, we retain in the dielectric constant only the plasmon component. By the same token we disregard the effects of the influence of the potential drop on the electronic transitions. Noticable effects of similar type can be expected only in the parameter interval corresponding to proximity of the threshold of external photoemission or to resonant frequencies of transitions in a double layer.

In the considered very simple model we have

$$\varepsilon_{ij}(x_1, x_1') = \delta_{ij}\varepsilon(x_1)\delta(x_1 - x_1') = \left[\varepsilon_1 + (\varepsilon(\omega)-\varepsilon_1)\frac{\rho(x_1)}{N_e}\right]\delta(x_1 - x_1')\delta_{ij}, \quad (39)$$

where N_e is the concentration of the electrons in the volume of the metal and $\rho(x_1)$ is the electron density, which depends on the distance to the surface. Near the zero-charge point[22] the function $\rho(x_1)$ can be represented in the form

$$\rho(x_1) = \rho_0(x_1) - \frac{Q}{e}f(x_1), \qquad \int_{-\infty}^{\infty} f(x_1)\,dx_1 = 1. \quad (40)$$

Here Q is the metal-surface charge and depends on the potential drop, while $\rho_0(x_1)$ is the distribution of the electron density at the zero-charge point at $Q = 0$, and $f(x_1)$ does not depend on Q. The explicit form of the functions $\rho_0(x_1)$ and $f(x_1)$ for a number of metals were obtained in Refs. 23. Under the foregoing assumptions, we obtain from (36), (39), and (40) the following expressions for the quantities $d\Gamma_\parallel/d\varphi$ and $d\Gamma_\perp/d\varphi$, which

enter in (37) and specify the dependences of the surface-plasmon frequency on the potential drop

$$\frac{d\Gamma_{\parallel}}{d\varphi}=\frac{d}{d\varphi}\int_{-\infty}^{\infty}\{\varepsilon(x_1)-[\varepsilon(\omega)\theta(-x_1)+\varepsilon_1\theta(x_1)]\}\,dx_1=\frac{\varepsilon_1-\varepsilon(\omega)}{eN_e}C(\varphi),$$

$$\frac{d\Gamma_{\perp}}{d\varphi}=\frac{d}{d\varphi}\int_{-\infty}^{\infty}\{[\varepsilon(\omega)\theta(-x_1)+\varepsilon_1\theta(x_1)]^{-1}-[\varepsilon(x_1)]^{-1}\}\,dx_1 \tag{41}$$

$$=\frac{\varepsilon_1-\varepsilon(\omega)}{eN_e}C(\varphi)\int_{-\infty}^{\infty}f(x_1)\left[(\varepsilon(\omega)-\varepsilon_1)\frac{\rho_0(x_1)}{N_e}+\varepsilon_1\right]^{-2}dx_1,$$

where $C(\varphi)=dQ/d\varphi$ is the differential capacitance of the double layer.[22] We note that in the case $\mathrm{Re}\,\varepsilon(\omega)<0$ and small damping in the volume of the metal ($\mathrm{Im}\,\varepsilon(\omega)\ll 1$) we have

$$|\mathrm{Im}\,d\Gamma_{\parallel}/d\varphi|\ll|\mathrm{Re}\,d\Gamma_{\parallel}/d\varphi|,$$

and the value of $\mathrm{Im}\,d\Gamma_{\perp}/d\varphi$ remains of the same order as $\mathrm{Re}\,d\Gamma_{\perp}/d\varphi$, and can be expressed in the form

$$\mathrm{Im}\frac{d\Gamma_{\perp}}{d\varphi}=\frac{\pi N_e}{\varepsilon(\omega)-\varepsilon_1}\frac{C(\varphi)}{e}\left\{\frac{df(x_1)}{dx_1}\left(\frac{d\rho_0(x_1)}{dx_1}\right)^{-2}\right\}_{x_1=x_1^0}. \tag{42}$$

To determine (42) we used the already noted[11,24] circumstance that the main contribution to $\mathrm{Im}\,\Gamma_{\perp}$ in the case of small volume damping is made by the region near the point $x_1=x_1^0$, where $\mathrm{Re}\,\varepsilon(x_1^0)=0$. In the case of metals, $x_1^0=1$–2 Å and $(df(x_1)/dx_1)_{x_1^0}<0$.

Measurements[13] of the spectra of attenuated total internal reflection from the (111) face of Ag in a 0.5 M solution of $NaClO_2$ have shown that at $\hbar\omega_s^0=3$ eV, at potentials more positive than the zero-charge point, $d\hbar\omega_s/d\varphi\approx-2\times10^{-2}$ eV/V and $|d\hbar\omega_s/d\varphi|$ is much less than this value for potentials more negative than the zero charge. At the same time, according to (37) and (41) the natural frequency of the plasmon surface satisfies the relation

$$\frac{1}{C(\varphi)}\frac{d\hbar\omega_s}{d\varphi}=\zeta, \tag{43}$$

where the constant ζ is expressed in terms of the bulk dielectric constants and the distribution function of the charge in the surface layer. As seen from the figure, the experimental-data reduction in Ref. 13 confirms Eq. (43). It is important here that the differential capacitance of the considered system changes strongly (by an approximate factor of five) in the vicinity of the zero-charge potential,[25] which lies in the measurement interval. The results of the experiments of Ref. 13 confirm also the conclusion that follows from (37) and (42) that the width of the surface-plasmon level should increase with increasing potential drop.

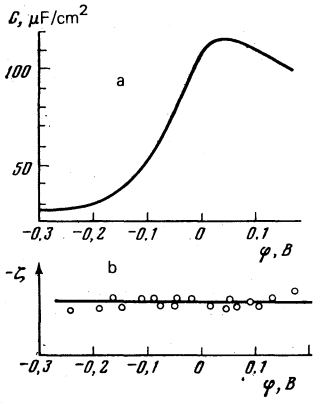

FIG. 1. Experimental check on Eq. (43). Top—dependence of the capacitance C on φ in accordance with the data of Ref. 25; the potential is reckoned from the zero-charge point $Q=0$. Bottom: straight line—calculation by formula (43), circles—experimentally measured values of $d\hbar\omega_s/d\varphi$,[13] divided by the values of $C(\varphi)$ shown in the upper figure. The quantity ζ [Eq. (43)] is plotted in arbitrary units.

6. CONCLUSION

The calculation method developed in Secs. 2 and 3, based on a solution of Riemann boundary-value problem, makes it possible to express the light-reflection coefficients and the dispersion of surface excitations in terms of the spectral characteristics of the volume of the crystal and the properties of its surface. In the considered method, a condition on the behavior of the Fourier components of the fields as $k_1\to\infty$ is used in place of the ordinary boundary conditions on the surface, which entails certain difficulties, as stated in the Introduction. Using the information that follows from the field equations (6) on the analytic properties of these Fourier components, as well as the connection given by relations of the type (17′) between the longitudinal and transverse components, it becomes possible to obtain an unambiguous solution of the problem of light reflection in the first nonvanishing order in the parameter $a\omega/c$, without resorting to concrete microscopic models. The surface properties enter in the observed quantities via a finite number of parameters Γ_{ij}, which are expressed in terms of averaged microscopic characteristics. Such a description makes it possible to dispense with the so-called three-layer model customarily used to take into account the influence of the surface, wherein the microscopic effects are described with the aid of the macroscopic Drude formula and which contradicts qualitatively, for example, the results of experiments on electroreflection.[26] It is important that in contrast to the three-layer model, in the considered approach it becomes possible to describe satisfactorily effects connected with the strong enhancement of the p-polarized field in the surface layer, which occurs whenever $\mathrm{Re}\,\varepsilon(\omega,x_1)$ approaches zero. These effects include, in particular, the appearance of a specific absorption.

An essential feature of the present paper is the study of the coefficients of the asymptotic forms of the waves at large distances from the surface. This yields, for example, the dispersion laws of the surface excitations in the form of conditions that these coefficients become infinite (the appearance of poles). Such an approach yields in general form, by starting from the spectral properties, important characteristics of the dispersion laws, in analogy with the procedure used in the investigation of the properties of the S matrix in the quantum-mechanical scattering theory.

The application, in Sec. 4, of the developed theory, to the so-called hydrodynamic model of a metal has made it possible to determine the frequency intervals in

which, for example, in modulation measurements, it is necessary to take simultaneously into account the spatial dispersion and the influence of the microscopic structure of the surface. The derived formulas show a nonuniform dependence of the observed quantities on the microscopic parameters that enter both in the spatial dispersion and in the characteristics of the surface. The use of the theory has made it possible to obtain in Sec. 5, for the first time ever, a description, consistent with experiment, of the influence of the surface potential drop on the dispersion law of the surface plasmons. The obtained formulas make it possible to use the experimental data on the dispersion law to draw conclusions concerning the electronic structure of the surfaces.

APPENDIX

To solve Eqs. (18) by the Riemann boundary-value-problem method it is necessary to supplement them with conditions on the behavior of $E^-_{L,TE,TM}(k_1)$ as $|k_1|\to\infty$ in the half-plane $\mathrm{Im}k_1<0$. According to (15) and (17) we have

$$E_{TE}^-(k_1)=k_2\int_{-\infty}^{0}e^{ik_1x_1}E_3(x_1)\,dx_1=k_2\int_{-\infty(1-i\delta)}^{0}e^{iy}E_3\left(\frac{y}{k_1}\right)\frac{dy}{k_1}\underset{k_1\to\infty}{=}-\frac{ik_2}{k_1}E_3^s,$$

$$E_{TM}^-(k_1)=\int_{-\infty}^{0}e^{ik_1x_1}[k_1k_2E_2(x_1)-k_2^2E_1(x_1)]\,dx_1\underset{k_1\to\infty}{=}-ik_2E_2^s,$$

$$E_L^-(k_1)=k_1\frac{1}{\varepsilon_{11}^0(k_1)}[D_1^-(k_1)-\varepsilon_{12}^0(k_1)E_2^-(k_1)-\varepsilon_{13}^0(k_1)E_3^-(k_1)$$

$$-\gamma_{1j}(k_1)E_j^s]+k_2E_2(k_1)\underset{k_1\to\infty}{=}\frac{1}{\varepsilon_1^0}k_1(D_1^-(k_1)-\gamma_{1j}(k_1)E_j^s)\underset{k_1\to\infty}{=}-i\frac{1}{\varepsilon_1^0}(E_1^s+\tilde\gamma_{1j}E_j^s). \tag{A.1}$$

Estimates of the integrals in (A.1) are obtained by introducing a new integration variable $y=k_1x_1$ and deforming the integration contour with allowance for the fact that $\mathrm{Im}k_1<0$. The constant $\tilde\gamma_{ij}$ in (A.1) is the discontinuity, at $x_1=0$, of the function $\gamma_{ij}(x_1)$, the value of which is obtained from the equality obtained with the aid of (2), (7), and (9),

$$D_1^-(x_1)-\int_{-\infty}^{\infty}\varepsilon_{1j}^0(x_1-x_1')E_j^-(x_1')\,dx_1'=\theta(-x_1)\Gamma_{1j}(x_1)E_j^s$$

$$-\int\theta(x_1)\varepsilon_{1j}^0(x_1-x_1')\theta(-x_1')E_j(x_1')\,dx_1'=\gamma_{1j}(x_1)E_j^s\left[1+O\left(\frac{a\omega}{c}\right)\right], \tag{A.2}$$

$$\tilde\gamma_{1j}=-i\lim k_1\int_{-\infty}^{\infty}e^{ik_1x_1}\gamma_{1j}(x_1)\,dx_1\quad\text{as}\quad k_1\to\infty.$$

We now represent the factors $k^2-\omega^2c^{-2}\varepsilon_T(k_1)$ and $\varepsilon_L(k_1)$, which enter in (18), in the band $|\mathrm{Im}k_1|<1/a$ in the form

$$k^2-\frac{\omega^2}{c^2}\varepsilon_T(k_1)=\frac{\Omega_T^-(k_1)}{\Omega_T^+(k_1)(k_1^2+1/a^2)^{N-1}}\prod_n(k_1^2-v_T^{(n)2}),$$

$$\varepsilon_L(k_1)=\frac{\varepsilon_1^0\Omega_L^-(k_1)}{\Omega_L^+(k_1)(k_1^2+1/a^2)^{M}}\prod_m(k_1^2-v_L^{(m)2}), \tag{A.3}$$

where $\Omega^+_{L;T}(k_1)$ ($\Omega^-_{L,T}(k_1)$) are analytic functions at $\mathrm{Im}k_1>-1/a$ ($\mathrm{Im}k_1<1/a$). From the aforementioned properties of $\varepsilon_T(k_1)$ and $\varepsilon_L(k_1)$ it follows that $\Omega^\pm_{L,T}$ can be expressed with the aid of the Cauchy formula in the form

$$\Omega_{L,T}^{\pm}(k_1)=\exp\left\{\mp\frac{1}{2\pi i}\int_{-\infty\mp i/a}^{\infty\mp i/a}\ln\Omega_{L,T}(\xi)\frac{d\xi}{\xi-k_1}\right\},$$

$$\Omega_T(k_1)=\left[k^2-\frac{\omega^2}{c^2}\varepsilon_T(k_1)\right]\left(k_1^2+\frac{1}{a^2}\right)^{N-1}\Big/\prod_n(k_1^2-(v_T^{(n)})^2);$$

$$\Omega_L(k_1)=\varepsilon_L(k_1)\left(k_1^2+\frac{1}{a^2}\right)^{M}\Big/\varepsilon_1^0\prod_m(k_1^2-(v_L^{(m)})^2). \tag{A.4}$$

The functions $\Omega^\pm_{T,L}$ in (A.3) were chosen such that $\Omega^\pm_{T,L}(k_1)\to1$ as $k_1\to\infty$ in their analyticity region. We expand next the product $\Omega^\pm_{T,L}(k_1)\Gamma_{ij}(k_1)$ in the band $|\mathrm{Im}k_1|<1/a$ into a sum of functions $\varkappa^\pm_{ij}(k_1)$ that are analytic, respectively, at $\mathrm{Im}k_1>-1/a$, $\mathrm{Im}k_1<1/a$:

$$\Omega_p^+(k_1)\Gamma_{ij}(k_1)=\varkappa_{ij}^+(p,k_1)+\varkappa_{ij}^-(p,k_1),\quad p=T,L, \tag{A.5}$$

where, taking into account the properties of $\Omega^\pm_{T,L}(k_1)$ and $\Gamma_{ij}(k_1)$, we can equate

$$\varkappa_{ij}^{\pm}(p,k_1)=\mp\frac{1}{2\pi i}\int_{-\infty\mp i/a}^{\infty\mp i/a}\Omega_p^+(\xi)\Gamma_{ij}(\xi)\frac{d\xi}{\xi-k_1}. \tag{A.6}$$

With the aid of (A.3) and (A.5) we can rewrite Eqs. (18) in the form of three equations whose right- and left-hand sides contain functions that are analytic at $\mathrm{Im}k_1<0$ and $\mathrm{Im}k_1>0$, respectively. Correspondingly, the two parts of these equations are analytic continuations of each other and constitute throughtout an analytic function of k_1, they are equal (when the behavior of $E^-(k_1)$ as $k_1\to\infty$), which follows from (A.1), is taken into account) to certain polynomials, which we shall designate by $R_L(k_1)$, $R_{TE}(k_1)$ and $R_{TM}(k_1)$. This solves the Riemann boundary-value problem,[5] with

$$E_{TE}^-(k_1)=\left[-R_{TE}(k_1)+\frac{\omega^2}{c^2}\left(k_1+\frac{i}{a}\right)^{N-1}k_2\varkappa_{3i}^-(T,k_1)E_i^s\right]$$

$$\times\left[\prod_n(k_1^2-(v_T^{(n)})^2)\Omega_T^-(k_1)\right]^{-1}\left(k_1-\frac{i}{a}\right)^{N-1},$$

$$E_{TM}^-(k_1)=\left\{-R_{TM}(k_1)+\frac{\omega^2}{c^2}\left(k_1+\frac{i}{a}\right)^{N-1}k_2[k_1\varkappa_{2j}^-(T,k_1)\right.$$

$$\left.-k_2\varkappa_{ij}^-(T,k_1)]E_j^s\right\}\left[\prod_n(k_1^2-(v_T^{(n)})^2)\Omega_T^-(k_1)\right]^{-1}\left(k_1-\frac{i}{a}\right)^{N-1},$$

$$E_L^-(k_1)=\left[-R_L(k_1)-\left(k_1+\frac{i}{a}\right)^{M}k_i\varkappa_{ij}^-(L,k_1)E_j^s\right]$$

$$\times\left[\varepsilon_1^0\prod_m(k_1^2-(v_L^{(m)})^2)\Omega_L^-(k_1)\right]^{-1}\left(k_1-\frac{i}{a}\right)^{M}. \tag{A.7}$$

Comparing the functions on the right- and left-hand sides in (A.7) as $k_1\to\infty$, we find that $R_{TE}(k_1)$, $R_{TM}(k_1)$, and $R_L(k_1)$ are polynomials of degree N, $N+1$, and M, respectively, i.e., the degree of the polynomials depends on the number of natural modes of the metal. The next task is to determine the coefficients in the polynomials $R(k_1)$. We use first the condition that $E^-(k_1)$ should have no poles in the lower half-plane and consequently the numerators in (A.7) should vanish at k_1 corresponding to zeros of the denominators that lie in the lower half-plane at $k_1=-v_T^{(n)}$ and $k_1=-v_L^{(m)}$, respectively. Taking into account Eqs. (A.1), we get

$$R_{TE}(k_1)=ik_2E_3^s\prod_{n=1}^{N}\left\{k_1+v_T^{(n)}-\frac{\omega^2}{c^2}i\left(\frac{i}{a}-v_T^{(n)}\right)^{N-1}\right.$$
$$\left.\times\varkappa_{3i}^-(T,-v_T^{(n)})E_i^s\left[E_3^s\prod_{n'\neq n}(v_T^{(n')}-v_T^{(n)})\right]^{-1}\right\},$$

$$R_{TM}(k_1)=ik_2E_2^s(k_1+A)\prod_{n=1}^{N}\left\{k_1+v_T^{(n)}+i\frac{\omega^2}{c^2}\left(\frac{i}{a}-v_T^{(n)}\right)^{N-1}\right.$$
$$\left.\times\left[E_2^s\prod_{n'\neq n}(v_T^{(n')}-v_T^{(n)})\right]^{-1}\frac{1}{A-v_T^{(n)}}[v_T^{(n)}\varkappa_{2j}^-(T,-v_T^{(n)})+k_2\varkappa_{ij}^-(T,-v_T^{(n)})]E_j^s\right\},$$

$$R_L(k_1)=i[E_i^s+(\bar{\varkappa}_{ij}+\tilde{\varkappa}_{ij})E_j^s]\prod_{m=1}^{M}\left\{k_1+v_L^{(m)}\right.$$
$$-i\left(\frac{i}{a}-v_L^{(m)}\right)^{M}\left[\prod_{m'\neq m}(v_L^{(m')}-v_L^{(m)})\right]^{-1}$$
$$\left.\times\frac{[v_L^{(m)}\varkappa_{ij}^-(L,-v_L^{(m)})-k_2\varkappa_{2j}^-(L,-v_L^{(m)})]E_j^s}{E_i^s+(\bar{\varkappa}_{ij}+\tilde{\varkappa}_{ij})E_j^s}\right\},\qquad(A.8)$$

where

$$\tilde{\varkappa}_{ij}=i\lim\varkappa_{ij}^-(L,k_1)k_1\quad\text{as}\quad k_1\to\infty.$$

Equations (A.7) and (A.8) contain four not yet determined constants, $E_i^s(i=1,2,3)$ and A. Their number can be reduced with the aid of (17′), from which we get at $k^2=0$ the two conditions

$$[E_{TM}^-(k_1)-k_1E_L^-(k_1)]=0\quad\text{for}\quad k_1=\pm ik_\parallel^0.\qquad(A.9)$$

At $k_1=ik_\parallel^0$ it is necessary to substitute in (A.9) the analytic continuation $E_{TM}^-(k_1)$ and $E_L^-(k_1)$, from the region $\mathrm{Im}\,k_1<0$ into the region $0<\mathrm{Im}\,k_1=k_\parallel^0\ll 1/a$ specified by formulas (A.7), which are valid also at $\mathrm{Im}\,k_1<1/a$. It is convenient to use Eqs. (A.9) to eliminate the constants A and E_1^s, which are not connected directly with the asymptotic form of $E(x)$ as $x_1\to-\infty$. In terms of these constants, (A.9) is a system of two equations whose solutions are too unwiedly to write out here explicitly.

Solving Eqs. (18) with the aid of (A.7), we obtain Eqs. (20) and (21).

[1)]It is convenient, for the subsequent analysis, to eliminate from the first term of the right-hand side of (2) the seemingly natural factor $\theta(-x_1)$; this can always be done by including in the second term of (2) the expression $-\varepsilon_{ij}^0(x_1-x_1')\,\theta(x_1)\,\theta(-x_1')$ which is localized near the surface (at $x_1=x_1'=0$). In the dielectric model considered in Sec. 4, $\delta\varepsilon_{ij}$ in (2) is simply equal to this expression.

[2)]We note that the quantity $\varepsilon_{(1)}^{-1}(x_1,x_1')$ does not coincide in the general case with the component, defined in standard fashion, of the inverse tensor $(\varepsilon^{-1}(x_1,x_1'))_{11}$.

[3)]This model corresponding to a choice of the dielectric constant in the form

$$\varepsilon_{ij}(x_1,x_1')=\delta_{ij}[\varepsilon^0(x_1-x_1')\theta(-x_1)\theta(-x_1')+\delta(x_1-x_1')\theta(x_1)].$$

[4)]We note that the question of the choice of the sign of $|\mathbf{k}_\parallel|$ in the dispersion law was the cause of a controversy both in the analysis of the experimental data of Ref. 19 and in the theory of this phenomenon.[20]

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