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Hydrodynamic Theory of Surface-Plasmon Dispersion

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The dispersion of surface-plasma oscillations is calculated analytically, using the Bloch hydrodynamic model for an electron gas and solving Maxwell's equations in the absence of retardation effects. This study is based on an approximation for a constitutive relation which provides a useful alternative to previous model descriptions of the surface. It is found that at long wavelengths the surface-plasmon dispersion relation includes a term which is linear in the momentum parallel to the surface and which is half as large as in the case of a study for specular reflection. In contrast to hydrodynamic treatments for specular reflection, the present one leads to an appreciable Landau damping of the surface-plasma oscillations. The magnitude of this Landau damping is roughly consistent with the results of a recent numerical study of plasmons for a more realistic model of the surface. Also discussed in some detail are the charge-density fluctuations associated with the surface plasmon, and a useful relation is established between the amplitudes of bulk- and surface-charge oscillations. In an appendix it is shown that when the imaginary part of the hydrodynamic dielectric function is neglected, one is led to surface modes which are quite different from the usual surface plasmon. Finally the results for surface plasmons are compared with those which are obtained for surface phonons in a metal film and the relationship between two different recent analyses of the surface-phonon problem is discussed in some detail.

I. INTRODUCTION

The dependence of the surface-plasmon frequency on the momentum parallel to the surface of a semi-infinite electron gas is potentially interesting, because of its sensitivity to the details of the electronic properties of the surface. Although experimental data on the dispersion of surface plasmons are scarce, many theoretical studies of this effect have appeared in recent years.[1–12]

The models which have been used in detailed analyses do not differ significantly as far as the description of the surface is concerned. Both in classical or semiclassical and in fully quantum-mechanical treatments, the surface is usually idealized as a perfectly reflecting well-defined boundary, from which the electrons are scattered specularly. In the classical and quasiclassical theories, the unperturbed electron density is assumed to be constant in the occupied space right up to the surface, at which it falls off abruptly to zero. The additional assumption—namely, that in the presence of an induced density fluctuation, all the particles which strike the surface are reflected specularly—then enters as a boundary condition for the perturbed electron distribution function. In first-principle quantum-mechanical treatments, the condition of specular reflection is automatically incorporated by describing the surface by means of an infinite potential step which terminates the unperturbed potential of the bulk. In this model the equilibrium electron density may vary because of quantum-mechanical interference between incoming and reflected particle waves. Both the quasiclassical and quantum-mechanical treatments may be referred to as "sharp-surface models" in the sense that, in both cases, the perturbed electron density is forced to vanish outside a suitably placed effective surface.

Recently, however, Bennett[13] and Beck and Celli[14] have presented two different numerical calculations of the surface-plasmon dispersion relation which go beyond the simple sharp-surface model. Bennett[13] treats a surface where the electron density falls off to zero from its bulk value over a finite width in the surface region, using the hydrodynamic model for the electron gas. The quantum-mechanical calculation of Beck and Celli[14] starts out from an appropriate finite-step surface potential, to which the electrons are allowed to adjust self-consistently in an approximate way. The results of these recent studies differ strongly from those of the earlier calculations[2–4,9–11] and are in much closer agreement with the available data, as

obtained from fast electron transmission experiments[15,16] and from an analysis of inelastic-low-energy-electron-diffraction (ILEED) measurements.[17]

It is well-known that, like bulk plasmons, the surface plasmon is not a true eigenmode oscillation of an electron gas, even in the absence of any dissipative effects (e.g., collision damping). A bulk plasmon of appropriate wavelength may decay by exciting electron-hole pairs in the single-particle continuum. This leads to an imaginary part in the frequency of the plasmon, which is known as Landau damping. Unlike for bulk plasmons, the Landau damping of surface plasmons is not severely restricted by momentum conservation, because the density fluctuation associated with such a mode incorporates all Fourier components in the direction perpendicular to the surface. Therefore Landau damping of a surface plasmon is usually expected to exist for all wavelengths. The various theories of surface plasmons do not agree concerning the magnitude of the Landau damping, but we note that the self-consistent calculation of Beck and Celli[14] leads to a much larger damping than is found in most of the previous sharp-surface treatments.

In this paper surface plasmons are studied, using the Bloch hydrodynamic model for the electron gas[18] and assuming a sharp surface in the sense discussed above. This model was first applied to surface plasmons by Ritchie[2] and has subsequently been used and discussed by several authors.[3,9,19,20] We recall that these studies assume a uniform equilibrium electron density in the metal and specular reflection (or equivalent boundary conditions) on an infinite potential barrier at the surface. These assumptions are rather unrealistic, since the actual equilibrium density does not have the form of an abrupt step, and the potential barrier at the surface is not infinite (being of the order of the Fermi energy plus the work function). Our starting point is a simple approximation for the constitutive relation which enters in the study of Maxwell's equations. This constitutive relation is formally similar to one derived in a treatment of the anomalous skin effect[21] for diffuse reflection at the surface. However, from the evidence given in Sec. II, it is unlikely to describe diffuse reflection in the present case, although no detailed proof for this does exist. Our approximation consists in replacing the dielectric kernel in the general constitutive relation by its asymptotic expression in the bulk region, in a similar spirit as the equilibrium density profile is replaced by the bulk electron density in previous hydrodynamic studies.[3,9,19,20] An approximation on the equilibrium density profile is avoided in the present case. The results of the present and of the earlier hydrodynamic studies will complement each other in the sense that they are typical for models where an inhomogeneous quantity of interest is replaced by its analog in a bulk system. In the following I shall refer to the previous hydrodynamic treatment as the case of specular reflection (as is customary) and to the new treatment as a dielectric approximation (DA).

Although in some respects the results based on the sharp-surface hydrodynamic model are superseded by self-consistent calculations using finite-step surface potentials, I feel that it is appropriate to give a complete discussion for the case of the DA before passing on to finite barrier models. Indeed, this study leads to much more insight than the calculation for specular reflection,[2] into the basic qualitative features that can be expected of surface plasmons in metals. This is particularly evident from the fact that in the hydrodynamic treatment for the DA, unlike for specular reflection, one finds a Landau damping as is generally expected for surface plasmons. In the hydrodynamic model the Landau damping corresponds to the decay of a surface plasmon into excitations which are transverse soundlike modes, rather than electron-hole pairs. Note that in the work of Bennett[13] the possibility of Landau damping has not been considered, although it may be small in this case. Finally, we expect the analytical results to be useful for the comparison with numerical studies of the surface-plasmon dispersion relation of the type mentioned above.

The paper is divided up as follows: In Sec. II, I discuss the hydrodynamic model and use Maxwell's equations to formulate the dielectric response problem for the determination of the surface-plasmon dispersion relation. For clarity's sake and in order to illustrate the striking differences between the results for the DA and for specular reflection, I shall discuss both cases in parallel. In Sec. III, I present the detailed calculation of the surface-plasmon frequency and of the Landau damping, and also discuss the charge-density fluctuations associated with the surface-plasmon mode. These results are strongly dependent not only on the real part, but also on the imaginary part of the hydrodynamic dielectric function. In Appendix A the rather different surface-plasmon modes which are obtained when the dielectric function is approximated by its real part are studied, whereby, in particular, the possibility of Landau damping is neglected. In Sec. IV, I compare my results with earlier calculations and with experiment, as well as with the results for surface phonons in a metal film. A more detailed analysis of the similarities and differences between the results for surface plasmons and surface phonons and between two different recent studies of the surface-phonon problem is given in Appendix B.

II. MODEL AND DIELECTRIC RESPONSE FORMULATION

As discussed in Sec. I, I use the hydrodynamic model for the dielectric response of a homogeneous electron gas (i.e., with no surface effects present), which is moving in a uniform background of positive ionic charge. The bulk dielectric function at frequency ω and wave vector k is then given by[18]

$$\epsilon(k,\omega)=1-\frac{\omega_p^2}{\omega^2-\beta^2k^2+i\omega/\tau}\ , \tag{1}$$

where ω_p is the free-electron plasma frequency and the constant β^2 is defined by

$$\beta^2=\tfrac{3}{5}v_F^2 \quad (v_F=\text{Fermi velocity})\ ; \tag{2}$$

a value which is obtained by requiring the bulk plasmon dispersion relation, $\epsilon(k,\omega)=0$, to agree with the random-phase-approximation (RPA) result for an infinite electron gas. The imaginary term in the denominator of Eq. (1) represents an effective collision damping. In the framework of a sharp-surface model, the response of a bounded system to an external perturbation is specified completely by a constitutive relation, which is eventually expressed in terms of the bulk dielectric function.

In the present analysis of surface plasmons I consider a metal half-space confined to the region $z>0$ and bounded by vacuum for $z<0$. The use of a half-space rather than a film geometry is sufficient as long as one is not interested in the coupling between plasmons localized at different surfaces in space, which is important for very thin films. The study of surface plasmons then proceeds in two steps. One first solves Maxwell's equations to determine the induced fields inside and outside the metal surface. Next, one matches the appropriate field components on the surface at $z=0$, which leads to an implicit dispersion relation for surface-plasmon modes. I shall use the electrostatic approximation and put $c=\infty$, which restricts the validity of my results, typically, to wave vectors $k>\omega_p/c\simeq 0.005k_F$. In the absence of any external charge distribution, Maxwell's equations then reduce to $\vec{\nabla}\times\vec{E}(\vec{r},t)=0$ and $\vec{\nabla}\cdot\vec{D}(\vec{r},t)=0$ (Poisson's equation), where $\vec{E}(\vec{r},t)$ and $\vec{D}(\vec{r},t)$ denote the electric and displacement fields at $\vec{r}$, t, respectively. Because of translational invariance parallel to the surface, it is convenient to Fourier analyze the various fields $\vec{F}(\vec{r},t)$ with respect to $\vec{\nu}=(x,y)$ and t. Two-dimensional wave vectors parallel to the surface are denoted by $\vec{k}_\parallel$ and we use the notation $\vec{F}(z,\vec{k}_\parallel,\omega)\equiv[\vec{F}_\parallel(z), F_z(z)]$ for the Fourier components parallel and perpendicular to the surfaces as well as $F_\parallel(z)=\vec{F}_\parallel(z)\cdot\vec{k}_\parallel/k_\parallel$. The real components of the fields at wave vector $k_\parallel$ and frequency ω are defined by

$$\vec{F}(\vec{r},t;\vec{k}_\parallel,\omega)=\vec{F}(z,\vec{k}_\parallel,\omega)e^{i(\vec{k}_\parallel\cdot\vec{\nu}-\omega t)}+\text{c.c.} \tag{3}$$

The constitutive relation is of the general form

$$\vec{D}(z,\vec{k}_\parallel,\omega)=\int_0^\infty dz'\,\epsilon(z,z',\vec{k}_\parallel,\omega)\vec{E}(z',\vec{k}_\parallel,\omega)\ , \quad z>0\ . \tag{4}$$

The more familiar expression which relates the current density $\vec{j}(z,\vec{k}_\parallel,\omega)$ at the point z to the electric field at points z'[21] is obtained from Eq. (4) by using the well-known definition of $\vec{D}(z,\vec{k}_\parallel,\omega)$. In the case of a homogeneous infinite system, the integration in Eq. (4) would extend from $-\infty$ to ∞ and the kernel $\epsilon(z,z',\vec{k}_\parallel,\omega)$ would be just the Fourier transform in z space of the bulk dielectric constant, which is only a function of $z-z'$. When surfaces are present, this kernel is inhomogeneous and its precise form as a function of both z and z' is not known. However, it reduces asymptotically to the bulk dielectric constant for z and z' far away from the surface.

The constitutive relation (4) takes a simple form if the true equilibrium density profile is replaced by the bulk electron density up to a sharp surface and if electrons are assumed to be reflected specularly at the surface. By means of a simple phenomenological argument,[3] one finds in this case

$$D_\parallel(z)=\int_0^\infty dz'\,[\epsilon(z-z',k_\parallel,\omega)+\epsilon(z+z',k_\parallel,\omega)]\,E_\parallel(z')\ , \tag{5a}$$

$$D_z(z)=\int_0^\infty dz'\,[\epsilon(z-z',k_\parallel,\omega)-\epsilon(z+z',k_\parallel,\omega)]\,E_z(z')\ , \quad z>0 \tag{5b}$$

where $\epsilon(z,k_\parallel,\omega)\equiv\epsilon(|z|,k_\parallel,\omega)$ is the Fourier transform with respect to k_z of the bulk dielectric function. It is seen that the kernels in Eqs. (5) do not reduce to the correct form, $\epsilon(z-z',k_\parallel,\omega)$ for z and z' far away from the surface.

This difficulty is avoided in the new DA introduced in Sec. I, where one replaces $\epsilon(z,z',\vec{k}_\parallel,\omega)$ everywhere by its asymptotic expression in the bulk region:

$$\vec{D}(z,\vec{k}_\parallel,\omega)=\int_0^\infty dz'\,\epsilon(z-z',k_\parallel,\omega)\vec{E}(z',\vec{k}_\parallel,\omega), \quad z>0\ . \tag{6}$$

Note, incidentally, that the effective surfaces in Eqs. (5a), (5b), and (6) lie generally at different positions than the true surface in Eq. (4), which divides the vacuum region from the region where the electron density in the nonuniform system is different from zero.

Although it has been stated that Eq. (6) is associated with diffuse reflection of electrons at the surface,[22] it appears that this assertion is largely unfounded. The existence of such a connection was inferred from the formal analogy between Eq. (6) and a constitutive relation for diffuse reflec-

tion[23] derived in a treatment of the anomalous skin effect.[21] However, note that in the anomalous skin effect[21] one is dealing with noninteracting electrons and a kernel which does not depend on $k_{\parallel}$, whereas in the present problem bot the electron interactions and the dependence of $\epsilon(z, k_{\parallel}, \omega)$ on $k_{\parallel}$ play a central role. Furthermore, while in the discussion of the anomalous skin effect, the equilibrium electron density is assumed to be constant everywhere, this assumption is not implicit in the use of approximation (6). For these reasons, the existence of any precise connection between Eq. (6) and the assumption of diffuse surface scattering is rather improbable. Incidentally, note that the mentioned constitutive relation of Ref. 21 cannot describe diffuse reflection exactly, since, as is well known, it is based on a formulation of a diffuse condition which does not conserve particles.[21]

As discussed in Sec. I, the constitutive relations (5a), (5b), and (6) should be regarded as belonging to a class of approximations where an inhomogeneous quantity [of which the equilibrium electron density $n_0(z, k_{\parallel})$ and the dielectric kernel $\epsilon(z, z', \vec{k}_{\parallel}, \omega)$ are typical examples] is replaced by its analog in the bulk region. The assumption of specular reflection which leads to Eqs. (5) corresponds then to the additional approximation of placing an infinite potential barrier at the surface. This is a general characterization of the difference between the two methods, whereas, for example, a distinction in terms of surface-scattering mechanisms would hinge on the uniform static density approximation.[21] As seen from Eqs. (5) and (6) the two methods are equivalent in the case where the dielectric constant is local, $\epsilon(k, \omega) \equiv \epsilon(\omega)$. In such a case, one is therefore describing a system where both the equilibrium electron density and the dielectric kernel are replaced by bulk values.

Due to the phenomenological nature of the present treatment, the density fluctuation associated with the surface plasmon is expected to include both surface- and bulk-charge contributions. In addition to being well-known in elementary electrostatics,[24] surface charges are quite familiar in the context of surface collective modes. The surface plasmon which is found when the electron gas is described by a local dielectric constant[20,25] and the phonons in metal films discussed in Appendix B are two kinds of elementary excitations where surface charge is involved in the induced density fluctuation. On the other hand, the surface plasmon obtained in a nonlocal treatment for specular reflection does not involve any surface-charge fluctuation, which indicates that this case is an exception in the framework of phenomenological treatments. Indeed, the condition of specular reflection prevents any accumulation of charge on the surface.

We now proceed to write the electrodynamic wave equation for the component $E_{\parallel}(z)$ of the electric field in the region occupied by the system. For the case $\omega^2 > \beta^2 k_{\parallel}^2$, the Fourier transform of Eq. (1) is given by

$$\epsilon(|z|, k_{\parallel}, \omega) = \delta(z) + i(\omega_p^2/2\beta\Omega')\,\mathrm{sgn}\omega\, e^{i(\Omega'/\beta)\,\mathrm{sgn}\omega|z|}, \tag{7}$$

where, to linear order in τ^{-1},

$$\Omega' = \Omega(1 + i\omega/2\tau\Omega^2), \quad \Omega = (\omega^2 - \beta^2 k_{\parallel}^2)^{1/2}. \tag{8}$$

For real ω, Eq. (7) has the property

$$\epsilon(|z|, k_{\parallel}, -\omega) = \epsilon^*(|z|, k_{\parallel}, \omega), \tag{9}$$

which guarantees that the displacement field which corresponds to the real electric field components of the form (3) is real. Also note that Eq. (7) is rather sensitive to the analytic structure of Eq. (1) at large k, where, of course, hydrodynamics ceases to be a good approximation. Therefore the calculations using this form for $\epsilon(|z|, k_{\parallel}, \omega)$ should, in principle, be regarded as model calculations based on a long-wavelength approximation for the dielectric function. The same general remark also applies, of course, to the use of Eq. (1) in the Ritchie–Marusak expression for the surface-plasmon dispersion relation for specular reflection.[3,9] Nevertheless, it is known that in this case the use of Eq. (1) leads to results which are identical to the earlier results of Ritchie, based on purely hydrodynamic arguments.[2] In addition, these results are surprisingly close, for small $k_{\parallel}$, to those which are obtained with much more rigorous dielectric functions.[3,4,9] Thus for our purpose the approximation involved in using Eq. (1) does not seem to be too restrictive.

In order to display in detail the differences between the results for the DA and for specular reflection, I shall discuss both cases, using the same general method. Recall that the specular case is usually discussed by a different procedure, based on Fourier transformation with respect to all spatial coordinates. By combining Maxwell's equations, using Eqs. (5a), (5b), (6), and (7), one is led to the following coupled equations for $E_{\parallel}(z)$ and $E_z(z)$ in the occupied half-space ($\omega > 0$):

$$\frac{d^2E_{\parallel}(z)}{dz^2} - k_{\parallel}^2 E_{\parallel}(z) = i\frac{\omega_p^2 k_{\parallel}}{2\beta\Omega'}\left\{k_{\parallel}\int_0^{\infty} dz'\,[G(z, z') + G(z, -z')]\,E_{\parallel}(z') + (\Omega'/\beta)\int_0^{\infty} dz'\,[G(z, z')\,\mathrm{sgn}(z - z') - G(z, -z')]\,E_z(z')\right\} \quad \text{(specular case)} \tag{10}$$

$$= i\frac{\omega_p^2 k_\parallel}{2\beta\Omega'}\left\{k_\parallel\int_0^\infty dz'\, G(z,z')E_\parallel(z') + (\Omega'/\beta)\int_0^\infty dz'\, G(z,z')\,\mathrm{sgn}(z-z')E_z(z')\right\} \quad \text{(DA case)}, \tag{11}$$

$$E_z(z) = \frac{1}{ik_\parallel}\frac{dE_\parallel(z)}{dz}, \tag{12}$$

where

$$G(z,z') = e^{i(\Omega'/\beta)|z-z'|}.$$

These equations, which look rather complicated, may be readily converted into a much simpler differential equation. Indeed, by differentiating Eqs. (10) and (11) twice and eliminating the integral terms, we obtain for both cases

$$\frac{d^4E_\parallel(z)}{dz^4} - (k_\parallel^2+\gamma^2)\frac{d^2E_\parallel(z)}{dz^2} + k_\parallel^2\gamma^2E_\parallel(z) = 0, \tag{13}$$

where

$$\gamma = (1/\beta)(\omega_p^2 - \Omega'^2)^{1/2}. \tag{14}$$

The solution of Eq. (13), which is bounded for $z\to\infty$, is

$$E_\parallel(z) = a'e^{-k_\parallel z} + b'e^{-\gamma z}, \tag{15}$$

where a' and b' are integration constants whose values are fixed by the external charge distribution by which the system is perturbed. Since $E_\parallel(z)$ includes only exponentially decaying terms, one may simplify Eqs. (10) and (11) by means of partial integrations, using Eq. (12). This yields the electrodynamic wave equations

$$\frac{d^2E_\parallel(z)}{dz^2} - \left(k_\parallel^2+\frac{\omega_p^2}{\beta^2}\right)E_\parallel(z) = \frac{i\omega_p^2}{2\beta\Omega'}\left(k_\parallel^2+\frac{\Omega'^2}{\beta^2}\right)\times\int_0^\infty dz'\,[G(z,z')+G(z,-z')]\,E_\parallel(z') \quad \text{(specular case)} \tag{16}$$

$$= -\frac{\omega_p^2}{2\beta^2}e^{i(\Omega'/\beta)z}E_\parallel(0^+) + \frac{i\omega_p^2}{2\beta\Omega'}\left(k_\parallel^2+\frac{\Omega'^2}{\beta^2}\right)\times\int_0^\infty dz'\, G(z,z')E_\parallel(z'), \quad z>0 \quad \text{(DA case)}, \tag{17}$$

from which Eq. (13) may also be obtained. Here $E_\parallel(0^+)$ denotes the value of $E_\parallel(z)$ just inside the occupied region. Note that because the fields vanish exponentially at large distances, all integrals in Eqs. (10) and (11) are well-defined at the finite $k_\parallel$ of interest, even for $\tau\to\infty$. Therefore the derivation of Eqs. (16) and (17) from Eqs. (10) and (11) does not depend significantly on the presence of a nonvanishing effective collision damping.

Since the linear integrodifferential equations for $E_\parallel(z)$ are of second order, the complete solutions of the form (15) must only depend on one arbitrary constant. A relation between a' and b' is obtained by substituting Eq. (15) into Eqs. (16) and (17), respectively. This leads, in each case, to the condition that a certain expression which depends on z only through a proportionality factor $e^{i(\Omega'/\beta)z}$ must be zero for all z, which requires the coefficient of this factor to vanish. In this way one obtains

$$\frac{a'}{b'} = -\frac{\gamma}{k_\parallel}\frac{\Omega'^2+\beta^2k_\parallel^2}{\omega_p^2} \quad \text{(specular case)}, \tag{18}$$

$$\frac{a'}{b'} = -\frac{k_\parallel}{\gamma+i(\Omega'/\beta)}\left(1+i\frac{\gamma\Omega'}{\beta k_\parallel^2}\right) \quad \text{(DA case)}. \tag{19}$$

III. SURFACE-PLASMON DISPERSION RELATION AND DENSITY FLUCTUATION

The boundary conditions from which the dispersion relation for surface modes is obtained are that $E_\parallel(z, k_\parallel, \omega)$ and $D_z(z, k_\parallel, \omega)$ must be continuous across the surface $z=0$. These conditions are a direct consequence of Maxwell's equations as written in the form of $dD_z(z)/dz + ik_\parallel D_\parallel(z) = 0$ (Poisson's equation) and of Eq. (12). The explicit expressions of $D_z(z)$ are obtained from Eqs. (5b), (6), (7), (12), and (15). The results are

$$D_z(z) = i\frac{k_\parallel^2-\gamma^2}{k_\parallel^2+\Omega'^2/\beta^2}a'e^{-k_\parallel z} \quad \text{(specular case)} \tag{20}$$

and

$$D_z(z) = i\frac{k_\parallel^2-\gamma^2}{k_\parallel^2+\Omega'^2/\beta^2}a'e^{-k_\parallel z} - \frac{\omega_p^2}{2\beta k_\parallel\Omega'}\left(\frac{k_\parallel a'}{k_\parallel+i(\Omega'/\beta)}+\frac{\gamma b'}{\gamma+i(\Omega'/\beta)}\right)\times e^{i(\Omega'/\beta)z}, \quad z>0 \quad \text{(DA case)}. \tag{21}$$

The exponentially decreasing fields in the vacuum region $z<0$ are given by

$$E_\parallel(z) = a''e^{k_\parallel z}, \tag{22a}$$

$$D_z(z) = -ia''e^{k_\parallel z}, \tag{22b}$$

and are proportional to the arbitrary constant a''.

First, consider the specular case. The matching of Eqs. (15) and (20) to Eqs. (22) at $z=0$ yields a pair of linear homogeneous equations between a', b', and a'', which must be solved together with (18). Thus the determinant Δ of the coefficients in these equations must vanish. This is, of

course, the condition for the existence of self-induced oscillations in the system, which determines the surface-plasmon dispersion relation. From $\Delta = 0$ one obtains the equation

$$2(\omega^2/\omega_p^2)\eta - 1 - k_\parallel/\gamma = 0 \ , \tag{23}$$

where

$$\eta = 1 + i/\omega\tau$$

in the linear approximation for the collision damping effect. Combining the above relation for $\gamma/k_\parallel$ with definitions (8) and (14) leads to the explicit result

$$\gamma = \frac{1}{2}\left[\left(\frac{2\omega_p^2}{\beta^2 k_\parallel^2} + 1\right)^{1/2} - 1\right] k_\parallel$$

$$= \frac{\omega_p}{(\sqrt{2})\beta}\left(1 - \frac{\beta k_\parallel}{(\sqrt{2})\omega_p} + \cdots\right) , \tag{24}$$

and to the exact expression for the surface-plasmon frequency:

$$\omega^2 = (1/2\eta)[\omega_p^2 + \beta k_\parallel (2\omega_p^2 + \beta^2 k_\parallel^2)^{1/2} + \beta^2 k_\parallel^2] \ . \tag{25}$$

This yields the well-known hydrodynamic dispersion relation,[2,19,20] including collision damping[9]:

$$\omega = \frac{\omega_p}{\sqrt{2}}\left[1 - \frac{i}{(\sqrt{2})\omega_p\tau} + \left(\frac{3}{10}\right)^{1/2}\left(\frac{v_F k_\parallel}{\omega_p}\right)\right.$$

$$\left. + \frac{3}{20}\left(\frac{v_F^2 k_\parallel^2}{\omega_p^2}\right) + O\left(\frac{v_F^3 k_\parallel^3}{\omega_p^3}\right)\right] \quad \text{(specular case)} \ , \tag{26}$$

in which the dispersion correction is linear at long wavelengths. In Eq. (26), I have neglected the linear effect of the collision damping on the dispersion terms.

In the DA case the calculation is somewhat more complicated. The condition $\Delta = 0$ which determines the solution of Eq. (19) and of the equations obtained by matching the fields in Eqs. (15) and (21) to Eqs. (22) at $z = 0$ yields the implicit dispersion relation

$$\frac{1}{k_\parallel}\left(\gamma + i\,\frac{\Omega'}{\beta}\right) + i\,\frac{\omega_p^2\gamma}{2\beta k_\parallel^2\Omega'} - \left(2 - \frac{\omega_p^2}{2\Omega'(\Omega' + i\beta k_\parallel)}\right)$$

$$\times\left(1 + \frac{i\gamma\Omega'}{\beta k_\parallel^2}\right) = 0 \ . \tag{27}$$

After some rearrangement of terms, using Eq. (8), this equation may be rewritten in the more useful general form

$$2\,\frac{\omega^2}{\omega_p^2}\,\eta - 1 - \frac{k_\parallel}{\gamma}\,\frac{\omega^2}{\omega_p^2}\,\eta - \frac{\beta^2 k_\parallel^2}{\omega_p^2}\left[2 - \frac{\omega_p^2}{2\omega^2\eta} - \frac{k_\parallel}{\gamma}\left(1 + \frac{\omega_p^2}{2\omega^2\eta}\right)\right]$$

$$+ i\,\frac{\beta k_\parallel}{\omega_p^2}\,(\omega^2\eta - \beta^2 k_\parallel^2)^{1/2}\left[1 + \frac{\omega_p^2}{2\omega^2\eta} - \frac{k_\parallel}{\gamma}\left(2 - \frac{\omega_p^2}{2\omega^2\eta}\right)\right] = 0 \ . \tag{28}$$

We first observe that in the limit $\beta \to 0$, Eq. (28) has the solution $\omega = \omega_p/\sqrt{2}$, which corresponds to the usual surface-plasmon mode. The real part of Eq. (28) for $\tau \to \infty$ may be readily compared with the corresponding Eq. (23) for specular reflection. In particular, it follows from a trivial iteration of Eq. (28) that the linear term in the dispersion of the surface-plasmon frequency is just half as large in the DA case as in the specular case. Because of the presence of the imaginary part, Eq. (28) has only solutions for complex frequencies at finite $k_\parallel$. The imaginary part of the surface plasmon frequency for $\tau \to \infty$ corresponds to Landau damping. In the present case the Landau damping results from the decay of surface-plasmon excitations into transverse soundlike waves, which occur as poles in the dielectric function (1). Of course, in a more realistic treatment, based on the Lindhard dielectric function, the Landau damping would be due to the decay of the plasmons into electron-hole pair excitations created in the single-particle spectrum.

In order to find the explicit solution of Eq. (28), we first make the approximation of neglecting the effect of the collision damping on the dispersion terms in the surface-plasmon frequency, in addition of treating it only to lowest order. This allows us to replace η everywhere by the result of the lowest-order iteration, namely $\eta_0 = 1 + i(\sqrt{2})/\omega_p\tau$. Next we write the solution in the form $\omega = \omega_1 - i\omega_2$ and introduce the quantities $u = \omega_1/\omega_p$ and $v = \omega_2/\omega_p$. For the purpose of iterating Eq. (28) with respect to the terms in $k_\parallel$ and determining the solution through quadratic order in $\beta k_\parallel/\omega_p$, we write $u = 1/\sqrt{2} + u_1 + u_2$ and $v = v_1 + v_2$, where u_1 and u_2, v_2 are of first and second order in $\beta k_\parallel/\omega_p$, respectively, whereas v_1 is of first order in τ^{-1} and in $\beta k_\parallel/\omega_p$. Finally we expand all quantities in Eq. (28), including γ and Ω', through order $\beta^2 k_\parallel^2/\omega_p^2$ and equate to zero the real and imaginary parts of Eq. (28) at each order. After somewhat lengthy but straightforward calculations, we arrive at the following expression for the surface-plasmon frequency:

$$\omega = \frac{\omega_p}{\sqrt{2}}\left\{1 + \frac{1}{2}\left(\frac{3}{10}\right)^{1/2}\left(\frac{v_F k_\parallel}{\omega_p}\right) + \frac{51}{80}\,\frac{v_F^2 k_\parallel^2}{\omega_p^2} - i\left[\frac{1}{(\sqrt{2})\omega_p\tau} + \left(\frac{3}{10}\right)^{1/2}\left(\frac{v_F k_\parallel}{\omega_p}\right)\right] + O\left(\frac{v_F^3 k_\parallel^3}{\omega_p^3}\right)\right\} \quad \text{(DA case)} \ , \tag{29}$$

where definition (2) has been used. Note that the quadratic term in the Landau damping is identically zero in this case. The most striking differences between Eqs. (26) and (29) lie in the magnitude of

the linear term in the surface-plasmon dispersion and in the occurrence of an appreciable Landau damping in the DA case, which is completely absent in the specular case. Detailed comparison with other calculations and with experiment is given in Sec. IV.

From the details of the above calculation it follows that our results depend as much on the presence of the imaginary part as on that of the real part of the function $\epsilon(|z|, k_\parallel, \omega)$. The reason for this is simply that the imaginary part of Eq. (1), which is nonzero only at the transverse sound-wave poles $\omega = \beta k$ $(\tau \to \infty)$, leads to nonvanishing contributions at all frequencies in z space. One may, however, inquire about the nature of the results in the case where only the real part of Eq. (1) for $\tau \to \infty$ (Cauchy principal part) is used in the calculation. *A priori*, this cannot be ruled out as a possible limiting case, from the point of view of the hydrodynamic equation from which Eq. (1) is derived. However, such a calculation leads to very different results from those obtained above, which further illustrates the role of the imaginary part of Eq. (1) for the derivation of a surface-plasmon mode of the usual type. These results, whose study follows rather closely the one presented above, are discussed in Appendix A.

The remaining part of this section is devoted to the analysis of the nature of the charge-density fluctuations which are associated with the surface-plasmon modes discussed above. The comparison of the results for the DA and for specular reflection from this point of view leads to additional information regarding the physical differences between these two cases. In the framework of a sharp-surface model the total density fluctuation may include, in general, not only a bulk-charge fluctuation $\delta\rho_B(z, k_\parallel, \omega)$, but also a surface-charge fluctuation $\delta\rho_S(z, k_\parallel, \omega)$, which is located on the surface of the bounded system. One has by definition

$$\delta\rho_B(z, k_\parallel, \omega) = -\left(\frac{dP_z(z)}{dz} + ik_\parallel P_\parallel(z)\right)\theta(z) ,$$

where $4\pi\vec{P}(z) = \vec{D}(z) - \vec{E}(z)$ is the induced polarization and $\theta(z)$ is the unit step function [$\theta(z) = 1$ for $z > 0$ and $\theta(z) = 0$ for $z < 0$]. In the electrostatic approximation, Maxwell's equations then lead to

$$4\pi\delta\rho_B(z, k_\parallel, \omega) = -\frac{i}{k_\parallel}\left(\frac{d^2E_\parallel(z)}{dz^2} - k_\parallel^2 E_\parallel(z)\right)\theta(z) . \tag{30}$$

On the other hand, the induced surface-charge density on the plane surface at $z = 0$ is given by the discontinuity of $E_z(z)$ at $z = 0$ (Ref. 24):

$$4\pi\delta\rho_S(z, k_\parallel, \omega) = [E_z(0^+) - E_z(0^-)]\,\delta(z) , \tag{31}$$

where $E_z(0^+)$ and $E_z(0^-)$ are the fields evaluated just inside and just outside the system, respectively. This expression for the surface-charge density is a direct consequence of Poisson's equation.

In the specular case we obtain, by inserting Eq. (15) in Eq. (30),

$$4\pi\delta\rho_B(z, k_\parallel, \omega_s) = ik_\parallel(1 - \gamma^2/k_\parallel^2)b' e^{-\gamma z}\theta(z) , \tag{32}$$

where γ is given by Eq. (24) and ω_s denotes the surface-plasmon frequency [Eq. (25)]. Because of the large magnitude of the wave vector $\omega_p/(\sqrt{2})\beta$, it follows that the bulk density fluctuation is strongly peaked near the surface and that its amplitude is proportional to $\omega_p^2/\beta^2 k_\parallel^2$ at long wavelengths. On the other hand, the matching of $E_\parallel(z)$ leads to the relation

$$a'' = a' + b' , \tag{33}$$

so that from Eq. (31), using Eqs. (12), (15), (18), and (22a), we find

$$\delta\rho_S = 0 . \tag{34}$$

The absence of a surface charge in the density fluctuation is, of course, expected from the assumption of specular reflection. Since in this case all the particles striking the surface are scattered back into the metal in specular directions, there is no net accumulation of charge on the surface.

In the DA case $\delta\rho_B(z, k_\parallel, \omega_s)$ is also of the general form of Eq. (32), but the parameter γ is now obtained by substituting Eq. (29) in the definition (14). In the considered approximation, γ turns out to be independent of the collision damping and is given explicitly by

$$\gamma = \frac{\omega_p}{(\sqrt{2})\beta}\left[1 - \frac{1}{\sqrt{2}}\left(\tfrac{1}{2} - i\right)\frac{\beta k_\parallel}{\omega_p} + \cdots\right] . \tag{35}$$

By comparing Eqs. (35) and (24) we see that in the present case the real part of the linear term in the square bracket is half as large as in Eq. (24) and, in addition, an imaginary part appears as a result of the Landau damping. Thus we find that for the DA, the bulk density fluctuation, which decays rapidly as one moves away from the surface, is modulated by an additional oscillatory contribution of wavelength $4\pi/k_\parallel$. By inserting Eq. (35) into Eq. (32) we obtain the explicit expression

$$4\pi\delta\rho_B(z, k_\parallel, \omega_s) = -ik_\parallel\frac{\omega_p^2}{2\beta^2 k_\parallel^2} \times\left[1 - \sqrt{2}\left(\tfrac{1}{2} - i\right)\frac{\beta k_\parallel}{\omega_p} + \cdots\right]b' e^{-\gamma z}\theta(z) . \tag{36}$$

Incidentally, note that the bulk density fluctuation [Eq. (32)] satisfies the relation

$$\left(\frac{d^2}{dz^2} - \gamma^2\right)\delta\rho_B(z, k_\parallel, \omega) = 0 , \quad z > 0 \tag{37}$$

which is the basic equation of the hydrodynamic model.[2] On the other hand, the amplitude of the

surface-charge fluctuation at the surface $z=0$ may be written in the form

$$4\pi\delta\rho_S(z,k_\parallel,\omega) = i\left[1+\frac{\gamma}{k_\parallel}\left(1-2\frac{\omega^2}{\omega_p^2}\eta\right)+2i\frac{\Omega'\beta k_\parallel}{\omega_p^2}\left(1-\frac{\gamma^2}{k_\parallel^2}\right)\right]b'\delta(z)\,, \tag{38}$$

where we have used Eqs. (31), (12), (15), and (22a) and eliminated a' and a'' by means of Eqs. (19) and (33), which remains, of course, valid in the DA case. Finally, by substituting Eq. (35) and the expression[26]

$$\Omega' = \frac{\omega_p}{\sqrt{2}}\left[1+\frac{1}{\sqrt{2}}\left(\tfrac{1}{2}-i\right)\frac{\beta k_\parallel}{\omega_p}+O\left(\frac{\beta^2k_\parallel^2}{\omega_p^2}\right)\right]\,, \tag{39}$$

obtained from Eqs. (29) and (8), into Eq. (38), the surface-charge density associated with the surface plasmon of frequency ω_s is found to be

$$4\pi\delta\rho_S(z,k_\parallel,\omega_s) = -i\left[i\frac{\omega_p}{(\sqrt{2})\beta k_\parallel}-\left(1+\frac{5i}{4}\right)+O\left(\frac{\beta k_\parallel}{\omega_p}\right)\right]b'\delta(z)\,. \tag{40}$$

Note that, by analogy with Eq. (3), the true charge-density fluctuation associated with a plasmon of frequency $\omega_s(k_\parallel)$ is given by

$$\delta\rho\ (\vec{\mathbf{r}},t) = [\delta\rho_B(z,k_\parallel,\omega_s)+\delta\rho_S(z,k_\parallel,\omega_s)] \times e^{i(\vec{\mathbf{k}}_\parallel\vec{\rho}-\omega_s t)}+\text{c.c.}$$

As anticipated, we thus find that in the DA case, the charge-density fluctuation associated with the surface plasmon includes a surface-charge contribution which does not appear in the specular case. The expression for the bulk density fluctuation Eq. (36) evaluated at a point 0^+ just inside the occupied half-space, may be combined with Eq. (40) to give

$$-i\frac{\omega_p}{(\sqrt{2})\beta}\delta\rho_S(z,k_\parallel,\omega_s) = \left[1-\frac{3\sqrt{2}}{4}\left(\frac{\beta k_\parallel}{\omega_p}\right)+\cdots\right]\delta\rho_B(0^+,k_\parallel,\omega_s)\delta(z)\,, \tag{41}$$

which shows that the ratio of the bulk- and surface-charge-density fluctuations at $z=0$ scales as the characteristic wave vector $\omega_p/(\sqrt{2})\beta$ for $k_\parallel=0$. Because of the largeness of $\omega_p/(\sqrt{2})\beta$, one thus expects $(1/e)\delta\rho_S$ to be small compared to $[(1/e)\delta\rho_B(0^+,k_\parallel,\omega_s)]^{2/3}$ (e = electron charge).

I believe that in the framework of the sharp-surface models, the present treatment in the DA is more generally valid than the treatment for specular reflection, because it allows the density fluctuation associated with the surface plasmon to have both bulk- and surface-charge contributions. This conclusion is further substantiated by the fact that for the DA (unlike for specular reflection), one gets a Landau damping, a feature which is generally expected of surface plasmons for all values of the momentum. In a certain sense one may consider the DA model to be intermediate between the specular model, in which the density fluctuation consists entirely of bulk charge, and the local dielectric function model[25] in which, on the contrary, the fluctuation involves only surface charge. Of course the local model is not accessible, in general, as a special limit of the present treatment because Eq. (7) is the Fourier transform of Eq. (1) only for $\beta\neq 0$.

IV. DISCUSSION AND CONCLUDING REMARKS

For the purpose of comparing the dispersion relation (29) with other calculations and with available experimental results, the surface-plasmon frequency $\omega_s(k_\parallel)$ is written as a function of momentum parallel to the surface in the general form

$$\omega_s(k_\parallel) = \frac{\omega_p}{\sqrt{2}}\times\left(1-i\gamma_0+(a_1-ia_2)\frac{v_Fk_\parallel}{\omega_p}+(b_1-ib_2)\frac{v_F^2k_\parallel^2}{\omega_p^2}+\cdots\right)\,. \tag{42}$$

The numerical values of a_1, a_2, b_1, and b_2, which are obtained in the various theories, are compared in Table I for free-electron densities corresponding to Al and Mg, for which experimental results are available. For brevity I have excluded from the comparison the results obtained by using the full RPA dielectric constant of the free-electron gas (Lindhard function) in a numerical solution of the general dispersion relation of Ritchie and Marusak for specular reflection.[3,9] These results have been determined for particular values of free-electron gas densities and the values of a_1 and a_2 are rather similar to Wagner's results based on the Boltzmann equation.[9]

The only results in Table I which relate to experiment are those of Bagchi *et al.*,[17] which have been extracted from an analysis of the ILEED data for Al. The numerical values for the quantum-mechanical RPA theory of Heger and Wagner are obtained from Ref. 10 using the relations

$$(0.166r_s)^{1/2} = \frac{k_{FT}}{2k_F} = \frac{\sqrt{3}}{4}\frac{\hbar\omega_p}{\epsilon_F}$$

(ϵ_F is the Fermi energy and k_{FT} is the Thomas–Fermi wave vector) and the values for $\hbar\omega_p$ and ϵ_F quoted in Ref. 14. The remaining values, which are presented for the cases of Al and Mg (except the last values for a_2), are obtained from those listed by Beck and Celli[14] by making the change of variable

$$\frac{k_\parallel}{k_F} = \frac{\hbar\omega_p}{2\epsilon_F}\frac{v_Fk_\parallel}{\omega_p}$$

in their form for the dispersion relation and using their values for $\hbar\omega_p$ and ϵ_F. The last values of a_2 listed for Al and Mg are based on the formula

$$a_2 = \frac{\pi}{16}\left(\frac{2}{3}\right)^{1/4}\left(\frac{k_{FT}}{2k_F}\right)^{1/2}, \tag{43}$$

which follows from an expression for the Landau damping derived by Feibelman,[6] using the RPA along with a surface model with a step in the density profile.

It follows from Table I that the present value of the linear coefficient a_1 in the dispersion is appreciably smaller (and the Landau-damping coefficient a_2 much larger) than the corresponding values obtained in previous quasiclassical calculations[2-4,9] for specular reflection. In fact our value for a_1 is similar to the values obtained in infinite-barrier quantum-mechanical calculations,[10,11] but the result for a_2 is an order of magnitude larger than those given in these latter calculations. For the reasons given before, I believe that the results for the DA case are more realistic than those for specular reflection, at least for the simple model which has been analyzed.

Compared to the quasiclassical results for specular reflection,[2-4,9] the present value for a_1, like those obtained in infinite barrier quantum-mechanical calculations, appears to be in closer agreement with the small negative value obtained from experiment by Bagchi *et al.*[17] (in the range $10^{-2} \leq k_{\parallel} \leq 1$ Å^{-1}), as well as with the result of Beck and Celli's finite-barrier treatment. Furthermore, we recall that Kunz's experimental data[15] on fast-electron energy loss in thin Mg films show that $\mathrm{Re}\omega_s(k_{\parallel})$ first decreases and then increases for increasing values of $k_{\parallel}$, lying in the range $0.02 \leq k_{\parallel} \leq 0.4$ Å^{-1}. Similar data obtained by Kloos[16] for the case of Al show, however, no evidence for any variation of $\mathrm{Re}\omega_s(k_{\parallel})$ with $k_{\parallel}$ at short wavelengths. On the other hand, the present value for the coefficient a_2 in the Landau damping is larger than all previous theoretical values, but note that it is much more consistent with the results of Beck and Celli and of Feibelman than the earlier quasiclassical results. It is also appreciably larger than the value obtained by Bagchi *et al.* for Al, although the method which they use to fit the experimental results does not give a precise estimate of a_2. Finally, note that an analysis of semiconductor tunneling data by Ngai *et al.*[27] leads to values of a_2 which agree with the relatively large values predicted by Eq. (43). The same analysis seems to indicate that the tunneling data can be described using the value $a_1 = 0$ while being inconsistent with the large values obtained in the qusiclassical calculations for specular reflection.

In this paper I have ignored retardation effects. These effects are important at long wavelengths

TABLE I. Numerical values of the coefficients of the linear and quadratic terms in the dispersion of the surface-plasmon frequency and of the Landau damping at long wavelengths. Here $\alpha = k_{FT}/2k_F$, where k_{FT} and k_F are the Thomas–Fermi and Fermi wave vector, respectively.

	Source	a_1	b_1	γ_0	a_2	b_2
This work		0.2738	0.6375	$[(\sqrt{2})\omega_p\tau]^{-1}$	0.5477	0
Ritchie[a]		0.5477	0.15	$[(\sqrt{2})\omega_p\tau]^{-1}$	0	0
Wagner[b]		0.5578	•••	•••	0.0307	•••
Kanazawa[c]		0	1.2	•••	0	0
Al $\alpha = 0.528$	Bagchi *et al.*[d]					
	Preferred	−0.073	1.116	0.15	0.079	•••
	Acceptable	0.055	0.67	0.16	0.079	•••
	Beck and Celli[e] (Finite barrier)	−0.074	0.94	0	0.218	0.405
	Infinite barrier RPA calculations					
	Heger and Wagner[f]	0.191	•••	0	0.0297	•••
	Beck[g]	0.367	0.369	0	0.0079	0.016
	Feibelman[h]	•••	•••	0	0.129	•••
Mg $\alpha = 0.644$	Beck and Celli[e] (Finite barrier)	−0.174	1.116	0	0.181	0.525
	Infinite barrier RPA calculations					
	Heger and Wagner[f]	0.111	•••	0	0.0297	•••
	Beck[g]	0.338	0.428	0	0.0067	0.0149
	Feibelman[h]	•••	•••	0	0.142	•••

[a]Reference 2. [b]Reference 4. [c]Reference 1. [d]Reference 17. [e]Reference 14. [f]Reference 10. [g]Reference 11. [h]Reference 6.

where the free radiation field is strongly coupled to the surface-plasmon oscillations in the crossing region of the photon dispersion line with the unperturbed surface-plasmon dispersion curve. The effect of retardation on the surface-plasmon frequency has been extensively studied using a local approximation for the dielectric function.[28] The modification of these effects when dispersion is included in the dielectric function has also been analyzed in various approximations for the case of specular reflection.[9] In this case the implicit equation which determines the eigenmodes of the coupled photon-plasmon system must be solved numerically. The study of retardation effects in the case of the DA would be much more complicated than for specular reflection.

To conclude this section, I briefly compare the above results for surface plasmons with those which are obtained for surface phonons in metals, from the point of view of the density fluctuations associated with these modes. The interested reader is referred to Appendix B for the explicit calculation of the density fluctuation in the phonon case and for a detailed comparison and discussion of two recent studies of the phonon problem[29,30] in different contexts. The surface phonons in a metal film may be studied by starting from the dielectric function

$$\epsilon(k,\omega)=\epsilon(\omega)+k_{\mathrm{FT}}^2/k^2\ ,\quad \epsilon(\omega)=1-\omega_M^2/\omega^2\ , \tag{44}$$

whose zero's describe the bulk phonon modes in a model,[31] where the ions are treated as a high-frequency plasma and the free electrons are assumed to screen out instantaneously any charge fluctuation associated with the slowly moving ions. Here ω_M denotes the ion plasma frequency and $1+k_{\mathrm{FT}}^2/k^2$ is the static Thomas–Fermi dielectric constant of the free-electron gas. The use of the Fourier transform of Eq. (44) in the approximate constitutive relations (5a), (5b), and (6) enables one, in principle, to study surface phonons by following a method similar to the one applied in Secs. I and II. However, because of the nature of the phonon model, (5a) and (5b) cannot be traced back to assumptions about the surface scattering in the present case, in contrast to the situation for surface plasmons. This is discussed in Appendix B, where it is shown furthermore that the surface phonons have quite different properties, depending on whether Eqs. (5) or Eq. (6) is used. These differences manifest themselves in ways other than in the plasmon case. In particular, we find that for both constitutive relations the induced density fluctuation includes surface-charge contributions and that, unlike in the plasmon case, the surface charge plays an essential role for the existence of surface-phonon modes. Also, the bulk density fluctuation for a surface phonon may extend much further into the bulk than for surface plasmons, where it remains essentially localized within the distance $(\sqrt{2})\beta/\omega_p$ from the surface. By means of a detailed argument it is shown that the use of the constitutive relations (5a) and (5b) is unjustified for a realistic description of surface phonons in a metal, but that, nevertheless, the results obtained with this expression correspond to an interesting limiting case.

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APPENDIX A: SURFACE-PLASMON MODES BASED ON REAL DIELECTRIC FUNCTION

Here, I shall briefly study the dispersion relation for surface plasmons in the case where collision damping is neglected and where one approximates the dielectric function (1) by its real part for $\tau\to\infty$. This latter function is nothing but the Cauchy principal part of Eq. (1), whose Fourier transform for $\omega^2>\beta^2k_\parallel^2$ is the real expression

$$\epsilon(|z|,\ k_\parallel,\omega)=\delta(z)-\frac{\omega_p^2}{2\beta\Omega}\sin\frac{\Omega}{\beta}|z|\ . \tag{A1}$$

As will become clear later on, Maxwell's equations can be solved in this case only for a film geometry. Thus, consider a film of thickness $2a$ which is confined between $z=-a$ and $z=a$ and which extends to infinity in the xy plane. For the DA the constitutive relation is of the same form as Eq. (6), except that the integration is now from $-a$ to a. I shall not discuss the case of specular reflection, because the form of the constitutive relation for a film in the specular case[22] renders the use of the method of Secs. II and III somewhat complicated. However, note that this case could be readily discussed by using the results of Wagner,[4] who derived a general dispersion relation of the same type as the Ritchie–Marusak expression[3] for a film geometry. The use of Eq. (6) and (A1) in Maxwell's equations leads to the following integrodifferential equation for the fields inside the film:

$$\frac{d^2E_\parallel(z)}{dz^2}-\left(k_\parallel^2+\frac{\omega_p^2}{\beta^2}\right)E_\parallel(z)=-\frac{\omega_p^2}{2\beta^2}$$

$$\times\left(E_\parallel(-a^+)\cos\frac{\Omega}{\beta}(z+a)+E_\parallel(-a^-)\cos\frac{\Omega}{\beta}(z-a)\right)$$

$$-\frac{\omega_p^2}{2\beta\Omega}\left(k_\parallel^2+\frac{\Omega^2}{\beta^2}\right)\int_{-a}^{a}dz'\sin\frac{\Omega}{\beta}|z-z'|E_\parallel(z')\ . \tag{A2}$$

This equation may be converted into a differential equation which is identical to Eq. (13). Since we are considering the case of a film, we must use the general solution of this equation, which reads

$$E_{\parallel}(z) = a' e^{-k_{\parallel} z} + b' e^{-\gamma z} + c' e^{k_{\parallel} z} + d' e^{\gamma z} \ . \tag{A3}$$

The substitution of (A3) in (A2) reduces this equation to a linear combination of $\sin(\Omega/\beta)z$ and $\cos(\Omega/\beta)z$, which must vanish for all ω and $k_{\parallel}$. This condition can be satisfied only if the coefficients of both functions are identically zero, which leads to

$$b' = d' = 0 \ , \tag{A4}$$

in the limit $k_{\parallel} a \gg 1$, $\gamma a \gg 1$, which corresponds to the neglect of coupling effects between two plasmons localized near $z = -a$ and $z = a$, respectively. Note that because of the fact that the integral in (A2) includes terms proportional to $\sin(\Omega/\beta)z$ as well as to $\cos(\Omega/\beta)z$, one is always led to two conditions to be verified by the arbitrary constants in the solution of Eq. (13). This solution must therefore include both the exponentially decreasing and increasing terms as displayed in (A3). As a result the calculation using the kernel (A1) leads to a solution only for the case of a film geometry, since, in particular, the remaining two constants cannot be determined by the two matching conditions at one surface alone. The expression of $D_z(z)$ given by Eq. (6) reduces to

$$D_z(z) = -i\left(1 - \frac{\omega_p^2}{\omega^2}\right)(c' e^{k_{\parallel} z} - a' e^{-k_{\parallel} z})$$

$$- i \frac{\omega_p^2}{2\omega^2} \frac{\beta}{\Omega} e^{k_{\parallel} a}\left[\left(k_{\parallel} \sin\frac{\Omega}{\beta}(z-a) + \frac{\Omega}{\beta}\cos\frac{\Omega}{\beta}(z-a)\right)c'\right.$$

$$\left. + \left(k_{\parallel}\sin\frac{\Omega}{\beta}(z+a) - \frac{\Omega}{\beta}\cos\frac{\Omega}{\beta}(z+a)\right)a'\right], \tag{A5}$$

again for $k_{\parallel} a \gg 1$ and $\gamma a \gg 1$. The matching of $D_z(z)$ and $E_{\parallel}(z)$ inside the film to exponentially decreasing fields outside [of the form (22) for $z < -a$] yields a system of four linear homogeneous equations between the four integration constants in the fields inside and outside the film. After some algebra the solutions of the corresponding secular determinant may be written as a pair of transcendental equations for the surface-plasmon frequencies as a function of the momentum parallel to the surface:

$$\omega^2 = \frac{\omega_p^2}{2}\cos^2\frac{\Omega a}{\beta}\left(1 - \frac{\beta k_{\parallel}}{\Omega}\tan\frac{\Omega a}{\beta}\right) \tag{A6}$$

and

$$\omega^2 = \frac{\omega_p^2}{2}\sin^2\frac{\Omega a}{\beta}\left(1 + \frac{\beta k_{\parallel}}{\Omega}\cot\frac{\Omega a}{\beta}\right) \ . \tag{A7}$$

These equations could be easily solved graphically for special values of the parameters. It follows that, although in the present "thick-film" limit there is no overlap between the electric fields associated with surface plasmons localized at different surfaces, their frequencies do actually depend on thickness. This rather peculiar feature is a consequence of the use of the dielectric function (A1). The above equations lead to a linear dispersion to lowest order in $k_{\parallel}$. Furthermore for $k_{\parallel} = 0$, instead of a single surface plasmon of frequency $= \omega_p/\sqrt{2}$, one finds a family of modes, whose frequencies given by

$$2x^2 = \cos^2\alpha x \tag{A8}$$

and

$$2x^2 = \sin^2\alpha x \ , \quad x = \omega/\omega_p \ , \quad \alpha = \omega_p a/\beta \tag{A9}$$

are distributed between $\omega = 0$ and $\omega = \omega_p/\sqrt{2}$. Since α is rather large for realistic values of the parameters, the number of solutions of (A8) and (A9) will generally be large.

To conclude, recall that Landau damping of surface plasmons can only occur when the imaginary part of the dielectric function (1) is included. The present results show, however, that the neglect of this imaginary part has a much more drastic effect in that it profoundly modifies the nature of the surface-plasmon modes which are obtained in this case. Note that the results of this appendix may be more useful as an illustration of this point than from the point of view of practical applications. This is because they depend, in an essential way, on the neglect of the imaginary part of $\epsilon(k, \omega)$, an approximation which, from a general physical point of view, would seem to be reasonable only if it would not have any major consequences for the surface-plasmon dispersion relation. However, we observe that for appropriate parameter values, Bennett's model[13] also predicts the existence of several surface-plasmon modes at long wavelengths, whose frequencies lie, however, in the high-frequency range $\omega_p/\sqrt{2} \leq \omega \leq \omega_p$. In common with the calculation of this appendix, Bennett's theory does not allow for an imaginary part (which for $\tau \to \infty$ describes the excitation of soundlike bulk modes) in the hydrodynamic electron gas equation, from which Eq. (1) is derived.

APPENDIX B: SURFACE PHONONS IN A METAL FILM

The purpose of this appendix is twofold. First I want to establish a parallelism between the present work on surface plasmons and the recent dielectric studies of surface phonons in metal films.[29,30] My analysis is centered on the comparison of the charge-density fluctuations associated with both kinds of modes; which is, of course, of some intrinsic interest. On the other hand, the approaches used by Griffin and Harris (GH) and by Heinrichs (H) in the phonon case are quite different and lead to very different results, so that a detailed analysis of the origin of these differences is needed. Such a study can be developed very conveniently in the framework of the dielectric method used in Secs. II and III, and constitutes our second

objective here.

In the work of GH the surface phonons are studied by means of the collisionless Boltzmann equation, using a sharp-surface model. The dispersion relation for phonons in a half-space obtained by GH is formally identical to the well-known result of Ritchie and Marusak[3] and is expressed in terms of a bulk response function. On the other hand, the theory described by H is based on the solution of Maxwell's equations (for $c \to \infty$) for a film geometry, using the approximation (6) for the constitutive relation and the model bulk dielectric function (44). For simplicity the following discussion is specialized to the case of a semi-infinite system occupying the region $z > 0$ and bounded by vacuum. In the theory of H, such a half-space system is appropriate only for the discussion of true surface modes[30] for which the quantity α^2 defined by

$$\alpha^2 = k_\parallel^2 + k_{FT}^2/\epsilon(\omega) \tag{B1}$$

is positive. In this paper I have changed the notation in an obvious way from that of Ref. 30.

We find that the results of GH may be derived in the present dielectric formulation by using a constitutive relation of the form of Eqs. (5). This is not surprising in view of their formal equivalence to the Ritchie–Marusak formula.[29] In order to show this we substitutue Eqs. (5) in Maxwell's equations, using the Fourier transform[30] of Eq. (44), which leads to the simple differential equation [compare to Eq. (15) of Ref. 30]

$$\frac{d^2 E_\parallel(z)}{dz^2} - \alpha^2 E_\parallel(z) = 0 , \tag{B2}$$

in the absence of any external charge distribution. By matching the bounded solution

$$E_\parallel(z) = b e^{-\alpha z} , \quad z > 0 \tag{B3}$$

and the corresponding expression for $D_z(z)$, given by (5a), (5b), (12), and (B3), to fields in the vacuum of the form (22), we obtain the following dispersion relation for surface phonons in the metal half-space:

$$(\alpha/k_\parallel)\epsilon(\omega) + 1 = 0 . \tag{B4}$$

This equation is identical to Eq. (3.20a) of Ref. 29 and gives rise to a surface-mode branch which extends in the whole frequency range between $\omega = 0$ and $\omega = \omega_M$.[29] The arbitrary constant which is present in (B3) is fixed by the external probe by which the collective oscillations in the system are excited. Finally, by using Eqs. (30), (31), (12), (22), and the result $a'' = b$ [matching of $E_\parallel(z)$] the bulk- and surface-charge-density fluctuations associated with the surface phonons are found to be

$$4\pi\delta\rho_B(z, k_\parallel, \omega) = -i[k_{FT}^2/\epsilon(\omega)k_\parallel]\, b e^{-\alpha z}\theta(z) , \tag{B5}$$

$$4\pi\delta\rho_S(z, k_\parallel, \omega) = i(1 + \alpha/k_\parallel) b\delta(z) , \tag{B6}$$

where α is determined by the explicit solution of (B4). By introducing the Fourier components of the potential $V(z) = (i/k_\parallel)E_\parallel(z)$, we then obtain

$$4\pi\delta\rho_B(z, k_\parallel, \omega) = k_{FT}^2[V(z)/-\epsilon(\omega)]\theta(z) . \tag{B7}$$

On the other hand, for $\alpha^2 > 0$, the theory of H leads to an implicit dispersion relation for surface phonons (for the discussion of the solution, see Ref. 30) which is given by

$$\left(3 + \frac{\alpha}{k_\parallel}\right)\epsilon(\omega) + \frac{3}{2}\,\frac{k_{FT}^2}{k_\parallel^2} + 4 = 0 . \tag{B8}$$

Furthermore, one finds

$$E_\parallel(z) = b'(e^{-\alpha z} + e^{-k_\parallel z}) , \quad z > 0 \tag{B9}$$

$$a'' = 2b' \quad \text{[matching of (22a) and (B9)]} , \tag{B10}$$

$$4\pi\delta\rho_B(z, k_\parallel, \omega) = -i[k_{FT}^2/\epsilon(\omega)k_\parallel]\, b' e^{-\alpha z}\theta(z) , \tag{B11}$$

$$4\pi\delta\rho_S(z, k_\parallel, \omega) = i(3 + \alpha/k_\parallel) b'\delta(z) , \tag{B12}$$

of which Eqs. (B11) and (B12) are obtained from Eqs. (30) and (31), using Eqs. (12), (22), (B9), and (B10). Although $\delta\rho_B$ given by Eq. (B11) is of the same form as Eq. (B5) its relation to the potential differs from Eq. (B7) since by using Eq. (B9) we obtain

$$4\pi\delta\rho_B(z, k_\parallel, \omega) = \frac{k_{FT}^2}{-\epsilon(\omega)}\left(V(z) - \frac{i}{k_\parallel}\, b' e^{-k_\parallel z}\right)\theta(z) . \tag{B13}$$

The parameter α in these expressions is given by the solutions of (B8) that satisfy (B1), from which it follows that, in this case, the surface modes only exist at high frequencies.[30] At lower frequencies one finds a different kind of modes, which can no longer be identified as true surface modes.[30]

In both treatments the parameter α, which determines the range of the bulk density fluctuations (B5) and (B11), takes all real values between 0 and ∞ when the frequency and wave vector vary along the surface-phonon dispersion curve. It follows, therefore, that the bulk density fluctuation associated with a surface phonon may extend quite far into the bulk of the system. This shows a difference with the results for surface plasmons where the bulk charge fluctuation is found to be localized within a distance of the order of $(\sqrt{2})\beta/\omega_p$ from the surface.

Turning to the surface charges, note that Eqs. (B6) and (B12) include contributions due to both the electrons and the ions. The fact that the ions lead to a surface-charge fluctuation is, of course, expected, since they are treated in a local approximation. From this it follows that the surface charge plays an essential role for the existence of surface phonons, since if the ions were present

alone, the density fluctuation would, in fact, only consist of surface charge.[25] As a result, the surface phonons would not exist if one would require surface charges to be absent, by demanding continuity of $E_z(z)$ instead of $D_z(z)$ on the surface. On the other hand, recall that surface plasmons exist even when surface charges are absent, as in the specular case.

Another point which is worth emphasizing is that in the static approximation, where the electrons adjust instantaneously to any charge imbalance caused by the ions, the surface-scattering mechanism does not enter in the description of surface-phonon modes. Indeed, in the static case one has no control on the actual motion of the electrons as a function of time. This is nothing but a consequence of the fact that in the Thomas–Fermi approximation there is no equation of motion for the electron density fluctuation in the usual sense. It is thus clear that surface-scattering boundary conditions do not arise in the discussion of the problem, at least within the Thomas–Fermi approximation. It follows that, in particular, the constitutive relations (5a) and (5b) are not related to specular reflection in the case where $\epsilon(z, k_{\parallel}, \omega)$ is given by the Fourier transform of Eq. (44). This becomes even more obvious after recalling that the condition of specular reflection, unlike the DA discussed in Sec. II, would be incompatible with the existence of a surface-charge fluctuation of the type found above [Eq. (B6)].

Without detailed calculations it is, of course, impossible to make any statements as to whether the electronic surface charge might be removed by using a dynamic dielectric function for the electrons, instead of the Thomas–Fermi expression. If this would be the case for an appropriate dielectric function, the calculation based on Eqs. (5) would correspond to specular reflection. Judging from the results obtained in Sec. III for the case of surface plasmons, we expect that such calculations would yield more realistic results in the case of the DA than in the case of specular reflection. At present, however, we are primarily concerned with situations where the Thomas–Fermi approximation is nearly exact and where considerations about the reflection of the electrons at the surface are largely irrelevant, as discussed above. It follows that since in the present case one cannot associate Eqs. (5) with specular reflection, one is forced to look for other possible justifications for using this expression. The situation is different in the case of Eq. (6) which, unlike Eqs. (5), appears as a natural first approximation of the true constitutive relation, since it corresponds to replacing the kernel $\epsilon(z, z', \vec{k}_{\parallel}, \omega)$ by its bulk expression.

Going back to the above expressions, we observe that (B7) is identical to the linearized Thomas–Fermi equation for a homogeneous system where the potential is screened by the dielectric function of the ions, whereas (B13) includes an additional term. This shows a basic difference between the constitutive relations (5a) and (5b) and (6) as applied to the present problem. Note, however, that since (B9) differs from (B3) only by a solution of Poisson's equation in the vacuum region, the bulk density fluctuation given by Eqs. (30) and (B9) satisfies the following differential form of the Thomas–Fermi equation in $\vec{r}$ space:

$$\nabla^2\left(4\pi\delta\rho_B(\vec{r}, \omega) + k_{\mathrm{FT}}^2 \frac{V(\vec{r}, \omega)}{\epsilon(\omega)}\right) = 0\,, \quad z > 0 \qquad \text{(B14)}$$

which is the analog of Eq. (37) in the plasmon case. It follows from Eq. (B7) that in the GH theory, the inhomogeneity which is caused by the introduction of the surface does not spread into the bulk, since this equation describes a system where the static electron density profile is replaced by the bulk density. However, such an inhomogeneity appears in this case in the form of the surface charge (B6), which clearly corresponds to a modification of the Thomas–Fermi model through the introduction of an effective sharp surface.[32] Whereas (B7) corresponds to a well-defined approximation (see Sec. II), the introduction of the surface charge [Eq. (B6)] is somewhat arbitrary, since the meaning of Eqs. (5) is unclear in the present case. On the contrary, Eqs. (B13) and (B12) show that in the theory of H the inhomogeneity (or "diffuseness") which is introduced by the surface spreads into the bulk as well as on the surface, since the right-hand side of Eq. (B13) includes a term which would not appear in the Thomas–Fermi equation for a homogeneous system. This is not unreasonable, since, *a priori*, it seems quite unlikely that within a sharp-surface model, one can adequately simulate the electronic properties of a true perturbed surface in terms of a surface inhomogeneity alone. Therefore the results based on the constitutive relation (6) are expected to be much more general than those based on Eqs. (5) since they correspond to less restrictive assumptions about the modifications which are required in the Thomas–Fermi model in order to simulate electronic inhomogeneities in the framework of a sharp-surface model. It should be emphasized that these modifications are not introduced arbitrarily, but that in the case of Eq. (6) they follow from the approximation of replacing the true kernel in the constitutive relation for the bounded system by its bulk expression. This is indeed the most natural first approximation if one believes that the inhomogeneity near the surface is of secondary importance in the final results compared to the presence of the surface itself.

In conclusion, I feel that there is no true justification for using the constitutive relations (5a) and (5b) in connection with the phonon model [Eq. (44)]. The main objection against it is that it corresponds to oversimplified and somewhat arbitrary assumptions about the way the introduction of a sharp surface affects the relationship between the induced density fluctuation and the induced potential. In light of the above considerations, the calculation based on Eqs. (5) has, nevertheless, the virtue of indicating under what limiting conditions one may expect a surface-mode branch to exist down to $\omega = 0$. We believe that in the absence of any more detailed microscopic derivation of the true inhomogeneous kernel $\epsilon(z, z', k_{\parallel}, \omega)$ for the phonon case, the most reasonable approximation is to replace it by its bulk expression, as done in Ref. 30. Also, recall that this approximation becomes exact for positions z and z' sufficiently far away from the surface, whereas the kernels in Eqs. (5) do not have this important property.

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[26]In connection with Eq.(39) we remark that the Fourier transform (7) of $\epsilon(k,\omega)$ is based on the assumption $\mathrm{Im}\Omega' > 0$ for $\omega > 0$, which is indeed verified for the definition (8) of Ω' when ω is real. On the other hand, when w is equal to the surface-plasmon frequency $\omega_s(k_{\parallel})$, which includes collision and Landau damping, we find that Ω' has a small negative imaginary part (for $k_{\parallel} \neq 0$) in the DA case and a vanishing imaginary part in the specular case. One is thus faced with an inconsistency with respect to the assumption on which (7) is based, at least to the considered order of approximation. In view of this difficulty and because the starting point of the present theory is the response function $\epsilon(z, k_{\parallel}, \omega)$ rather than $\epsilon(k,\omega)$, we are led to *define* $\epsilon(z, k_{\parallel}, \omega)$ by Eq.(7) for all frequencies, recalling that, in general, it corresponds to the Fourier transform of (1) for real frequencies only. The usefulness of this definition lies in the fact that for specular reflection it leads to the well-known result for the surface-plasmon dispersion relation, whereas in the DA case it yields the known value for the collision damping effect and a Landau-damping of the sign appropriate to Fourier components which oscillate as $e^{-i\omega t}$, as is, in fact, assumed in Eq. (1). One may hope that for more accurate dielectric functions the above type of difficulty does not arise, although this would have to be checked explicitly in each particular case.
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