Hydrodynamic model for surface plasmons in metals and degenerate semiconductors*

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A hydrodynamic model is used to study the effect of the electron-density profile at the surface on surface-plasmon modes. The model consists of an extension of Bloch's original hydrodynamic model to study an inhomogeneous electron gas capable of self-oscillations about a ground state given by the Hohenberg-Kohn-Sham theory of the inhomogeneous electron system. We write down an expression for the conductivity tensor which formally contains all relevant information within the context of our hydrodynamic formulation. The qualitative features of the model are illustrated by detailed numerical calculations for smooth electron-density profiles. The dispersion relation of both regular surface-plasmon and higher-multipole excitations (which occur for sufficiently diffuse profiles) are studied for a wide range of wave vectors from the optical ($\omega \sim cq$) to the nonretarded or electrostatic limit.

I. INTRODUCTION

In recent years there has been considerable interest in the subject of collective modes of excitation at the surface of metals and highly doped semiconductors. Despite the substantial amount of work done on the subject there has been as yet no satisfactory treatment of the nature of these modes in the optical region ($q \sim \omega/c$). Surface oscillations in this, the "retarded" limit, have been studied almost exclusively using a local approximation for the bulk dielectric function.[1] Although the effects of dispersion (i.e., q dependence) in this bulk dielectric function have been studied in the case of specular reflection,[2] the issue still remains that these formulations have "prejudiced" the problem from the start by the introduction of a *bulk* response function. Furthermore, the surface has almost always been idealized as a sharp, mathematical boundary.

This paper is a generalization of a previous one[3] (hereafter referred to as I) in which the surface plasma oscillations in metals were studied in the longitudinal ($c = \infty$) approximation, using a generalized hydrodynamic formulation. We now allow for the effect of retardation, i.e., the fact that the electromagnetic fields due to the fluctuation of the sources in the system travel with a finite velocity c. Our formulation is devised in such a way that a realistic, i.e., smoothly varying, electronic density at the surface is allowed for. We also treat surface and bulk excitations on an equal footing. In this sense our procedure is in the same spirit as that of Harris and Griffin,[4] who used the random-phase approximation (RPA). Although these authors cast their theory in a fairly general way, they obtained explicit results only after expanding the conductivity tensor in powers of ω^{-1} and keeping only the leading term (nonlocal effects being thus lost) and only for a sharp metal-vacuum interface. One of the aims of this paper is to investigate how useful information about the electron surface structure can be obtained from the study of the surface collective behavior, and as such, it belongs in the line of work initiated by Feibelman[5] in the electrostatic limit.

In I, special emphasis was placed on how the generality of our approach allowed quite naturally for the presence of additional branches in the dispersion relation[6] and a physically appealing condition for their existence was provided for a simple dynamical model. We now reinvestigate the same question in the retarded limit. We believe this is the first time that this has been done.

Surface plasmons in metals and semiconductors have been detected by electron-energy-loss measurements,[7] by low-energy-electron diffraction[8] (LEED), and by optical means.[9] (For a recent review on surface plasmons in solids see Ref. 10, where further references can be found.) However, the additional branches or "higher multipoles" have not been detected to date. In I we suggested a way of measuring these modes, namely, by performing LEED experiments on layers of alkalis chemisorbed on the surface of a high free-electron density metal. We believe that our present investigation provides the qualitative picture for proposing that those modes could be observed by attenuated-total-reflection (ATR) measurements[9] done on the same systems or on appropriate semiconductor surfaces.

This paper is divided up as follows: in Sec. II we present the general formalism, with emphasis on the physics behind it. We write down an expression for the conductivity tensor which in principle contains all relevant static (i.e., self-consistent electron contour in the ground state) and dynamic information within the context of a hydro-

dynamic formulation. Given the difficulty of applying conventional many-body techniques to the highly inhomogeneous systems under consideration, the hydrodynamic approach offers a workable, albeit approximate alternative. This is the main motivation for the several recent papers using a hydrodynamic formulation of the inhomogeneous electron gas.[6,11-16] Some important points are examined in a general context (that is, without having to specify a particular form for the density functional $G[n]$ which appears in Euler's equation), like the *approximate* nature of some conclusions reached previously in the electrostatic ($c=\infty$) limit, this being defined here as the region in $q-\omega$ space such that $\omega c^{-1} \ll q$. We point out that in general, hydrodynamic effects do enter into the equation for the transverse part of the field associated with the charge fluctuation, a qualitative feature which does not appear to be recognized in the literature. Thus, another objective pursued in this paper is to point out the need for further theoretical study of the problem of the dynamic response of the surface to electromagnetic fields. Section II can be considered then as a first step in that direction.

In Sec. III we apply the formalism of Sec. II to find the surface electronic collective spectrum for surfaces with smoothly varying density profiles. A simple ansatz for the pressure term in Euler's equation is made. In this section we speculate on the experimental possibilities opened by our qualitative results. For the benefit of those interested mainly in this aspect of the problem we have written Sec. III in such a way that it can be read almost independently of Sec. II.

In Sec. IV we present a critical discussion of the theory we developed in the previous sections. We indicate the desirability to improve our approximations and the physico-mathematical reasons why we cannot, at the present time, go beyond the simplifying assumptions of Sec. III. On the other hand, we emphasize that our theory is formulated in such a way that it leaves room for improvement and provides a general framework for studying the response of diffuse surfaces to electromagnetic fields. We also express the need for experimental evidence to guide us in a program of achieving results of quantitative significance, and to ultimately justify or disqualify the model we present in this paper.

II. FORMULATION OF THE SURFACE-COLLECTIVE-MODE PROBLEM

A. Generalized hydrodynamics

We begin by recalling that Bloch introduced the hydrodynamic theory of the electron gas in order to study the normal modes of oscillation about the ground state of a system as defined in the Thomas-Fermi model.[17] The basic idea of what follows (and this was first discussed by Ying[11] in the electrostatic approximation, $c=\infty$) is to extend Bloch's approach and consider an inhomogeneous electron system capable of self-oscillations about a ground state given by the Hohenberg-Kohn-Sham theory of the inhomogeneous electron gas.[18] We thus express the total energy of the system as[11]

$$H = G[n(\vec{r},t)] + \tfrac{1}{2}\int d^3r\, n(\vec{r},t)\left|\vec{\nabla}\psi - \frac{1}{c}\vec{A}\right|^2 + \tfrac{1}{2}\int d^3r\, d^3r' \frac{n(\vec{r},t)\,n(\vec{r}',t)}{|\vec{r}-\vec{r}|} - \int d^3r\, V_{\text{back}}(\vec{r})\,n(\vec{r},t). \tag{2.1}$$

Here $\psi(\vec{r},t)$, the velocity potential, is defined by

$$-\vec{\nabla}\psi(\vec{r},t) = \vec{v}(\vec{r},t) - 1/c\,\vec{A}(\vec{r},t), \tag{2.2}$$

and $\vec{v}(\vec{r},t)$ is the particle velocity, $n(\vec{r},t)$ is the particle density ($n\vec{v}=\vec{J}$ being the particle current density), and $\vec{A}(\vec{r},t)$ is the vector potential of the electromagnetic field produced by the charge fluctuations. The functional $G[n(\vec{r},t)]$ (Refs. 3, 11, 18) represents the exchange, correlation, and internal kinetic energies of the electron system. $V_{\text{back}}(\vec{r})$ is the electrostatic potential due to the neutralizing positive background. We assume the jellium model for this background. Unless otherwise specified, atomic units ($m=|e|=\hbar=1$) are used in this paper. Since we are interested in self-oscillations of the electron system, we have not included any external electromagnetic fields in Eq. (2.1). (Their introduction is straightforward.) In Eq. (2.1) we have assumed the Coulomb gauge, but this places no restriction on the theory once the basic equations [Eqs. (2.7) and (2.8)] are obtained.

We now assume that the field $n(\vec{r},t)$ is canonically conjugate to the field $\psi(\vec{r},t)$ and, hence, Hamilton's equations follow[19]:

$$\frac{\delta H}{\delta\psi(\vec{r},t)} = -\frac{\partial}{\partial t}n(\vec{r},t), \tag{2.3}$$

$$\frac{\delta H}{\delta n(\vec{r},t)} = \frac{\partial\psi(\vec{r},t)}{\partial t}. \tag{2.4}$$

We note that the derivatives on the left-hand side of Eqs. (2.3) and (2.4) are functional derivatives. Then, with H given by Eq. (2.1), Eqs. (2.3) and (2.4) give, respectively:

$$\frac{\partial}{\partial t}n = \vec{\nabla}\cdot\left[n\left(\vec{\nabla}\psi - \frac{\vec{A}}{c}\right)\right], \tag{2.5}$$

and

$$\frac{\partial \psi}{\partial t} = \frac{1}{2}\left|\vec{\nabla}\psi - \frac{1}{c}\vec{A}\right|^2 + \frac{\delta G}{\delta n} - V_{\text{back}} + \int d^3r' \frac{n(\vec{r}', t)}{|\vec{r} - \vec{r}'|}. \tag{2.6}$$

We can rewrite Eqs. (2.5) and (2.6) in a more familiar looking form by eliminating ψ in favor of $\vec{v}$ and $\vec{A}$. Thus, Eqs. (2.5) and (2.6) can be rewritten

$$\frac{\partial}{\partial t} n + \vec{\nabla} \cdot \vec{J} = 0, \tag{2.7}$$

and

$$n \frac{d}{dt} \vec{v} = -n(\vec{E} - \vec{\nabla} V_{\text{back}}) - \frac{1}{c} \vec{J} \times \vec{B} - n\vec{\nabla} \frac{\delta G[n]}{\delta n}, \tag{2.8}$$

where use was made of the identity

$$(\vec{v} \cdot \vec{\nabla})\vec{v} + (1/c)[\vec{v} \times (\vec{\nabla} \times \vec{A})] = \tfrac{1}{2}\vec{\nabla}[(\vec{\nabla}\psi - \vec{A}/c)^2]$$

and, as usual,

$$\vec{E} = -\frac{1}{c}\frac{\partial}{\partial t}\vec{A} - \vec{\nabla}\phi,$$

with

$$\phi = -\int d^3r' \frac{n(\vec{r}', t)}{|\vec{r} - \vec{r}'|} \quad \text{and} \quad \vec{B} = \vec{\nabla} \times \vec{A}.$$

We emphasize that, as in I, the term $n\nabla(\delta G/\delta n)$ enters Euler's equation as a generalization of the gradient of the conventional density-dependent pressure. In order to describe small amplitude self-sustaining oscillations we assume that the dynamical variables n, $\vec{J}$, and $\vec{E}$ depart slightly from their equilibrium values, that is, we write down:

$$n(\vec{r}, t) = n_0(\vec{r}) + n_1(\vec{r}, t); \quad \vec{J}(\vec{r}, t) = \vec{J}_1(\vec{r}, t);$$

$$\vec{E}(\vec{r}, t) = \vec{E}_0(\vec{r}) + \vec{E}_1(\vec{r}, t); \quad \frac{\delta G}{\delta n} = \left(\frac{\delta G}{\delta n}\right)_0 + \left(\frac{\delta G}{\delta n}\right)_1,$$

and obtain

$$\vec{E}_0 - \vec{\nabla} V_{\text{back}} + \vec{\nabla}\left(\frac{\delta G}{\delta n}\right)_0 = 0, \tag{2.9}$$

$$\frac{\partial n_1}{\partial t} + \vec{\nabla} \cdot \vec{J}_1 = 0, \tag{2.10}$$

and

$$\frac{\partial}{\partial t}\vec{J}_1 = -n_0(\vec{r})\vec{E}_1 - n_0(\vec{r})\vec{\nabla}\left(\frac{\delta G}{\delta n}\right)_1. \tag{2.11}$$

A few points are worth noting here. Firstly, writing $\vec{E}_0 = -\vec{\nabla}\phi_0$, Eq. (2.9) gives $-(\phi_0 + V_{\text{back}}) + (\delta G/\delta n)_0 = \mu$ (μ is a constant which one identifies as the chemical potential). This equation, as proved by Hohenberg and Kohn[18] is exact (of course the exact form of the functional $G[n_0]$ is not known) for the ground state of the inhomogeneous system and was used (in a different, but equivalent, version) by Lang and Kohn[20] to compute the self-consistent density contours in the ground state of the metal-vacuum system. Secondly, the magnetic field does not enter Eq. (2.11) because $\vec{B}_0 = 0$, i.e., because of the absence of an external static magnetic field. Thirdly, although $\phi_0(\vec{r})$ does not appear explicitly in Eq. (2.11), it is effectively taken into account via the self-consistent density $n_0(\vec{r})$, the solution to the unperturbed problem, Eq. (2.9). Equations (2.10) and (2.11) are the basic equations in our description of the small amplitude self-oscillations of the electron system. We supplement them with the full set of Maxwell's equations. As usual, upon elimination of the magnetic field $\vec{H}$, one obtains (for the fluctuating variables):

$$\vec{\nabla} \times (\nabla \times \vec{E}_1) = -\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\vec{E}_1 + \frac{4\pi}{c^2}\frac{\partial}{\partial t}\vec{J}_1 \tag{2.12}$$

and

$$\vec{\nabla} \cdot \vec{E}_1 = -4\pi n_1. \tag{2.13}$$

One convenient way to proceed is to Fourier transform all the space-time functions into $\vec{k} - \omega$ space. We assume all variables to be continuous, differentiable functions of $\vec{r}$. Note that we can make this assumption because, for instance, in the metal surface problem, we allow the density n_0 to be a smooth function of z, the coordinate normal to the surface. In fact, in principle, it should be the solution to Eq. (2.9).[20] It is then straightforward to show that

$$E_i(\vec{k}, \omega) = \frac{4\pi i}{\omega(\omega^2 - c^2k^2)}(\omega^2\delta_{ij} - c^2k_ik_j)J_j(\vec{k}, \omega) \tag{2.14}$$

(where the summation convention is used and, as in the rest of the paper, the subindices denoting first-order quantities are dropped). We remark that for the inhomogeneous medium the variables with physical meaning are the wave packets constructed from the corresponding Fourier amplitudes.

B. Conductivity tensor

Following Harris and Griffin[4] we now introduce the constitutive relation

$$J_i(\vec{k}, \omega) = \int \frac{d^3k'}{(2\pi)^3} \sigma_{ij}(\vec{k}, -\vec{k}', \omega) E_j(\vec{k}', \omega). \tag{2.15}$$

If there were an external electromagnetic field, then σ_{ij} would represent the response to the total, local, electric field. Note that σ_{ij}, the "conductivity tensor," is not a true "response function" as defined in the general theory of linear response[21]

to external perturbations.

Then, one way to cast the equation that determines the dispersion relation of both bulk and surface collective modes is obtained by combining Eqs. (2.14) and (2.15):

$$E_i(\vec{k},\omega)=\frac{(4\pi i)}{\omega(\omega^2-c^2k^2)}(\omega^2\delta_{ij}-c^2k_ik_j)\times\int\frac{d^3k'}{(2\pi)^3}\sigma_{jl}(\vec{k},-\vec{k}',\omega)E_l(\vec{k}',\omega). \tag{2.16}$$

The problem thus posed reduces, in principle, to finding the conductivity tensor $\sigma_{ij}(\vec{k},-\vec{k}'\omega)$ and then solving the integral equation (2.16). As in I we write down, in general:

$$\left(\frac{\delta G}{\delta n}\right)_1=\hat{L}(n_0)n_1. \tag{2.17}$$

A remark on the operator $\hat{L}(n_0)$ may be in order here. The expressions for it are borrowed from the theory in its static limit, whether the system is isolated, Eq. (2.9),[22] or in the presence of a static perturbation.[23] We shall have more to say on this in Sec. IV, but for future reference we state here that if we ignore the gradient terms[22] in G, then $\hat{L}$ is just a function of position [through its dependence on $n_0(\vec{r})$] which we shall denote by $p(\vec{r})$. For brevity we shall refer to this as the Thomas-Fermi approximation for $\hat{L}$, although the exchange and correlation contribution of the homogeneous system would be included.

Then, using Eqs. (2.17) and (2.10) in Eq. (2.11) we obtain

$$i\omega J_i(\vec{r},\omega)+(i/\omega)n_0(\vec{r})\partial_i[\hat{L}\partial_jJ_j(\vec{r},\omega)]=n_0(\vec{r})E_i(\vec{r},\omega). \tag{2.18}$$

We now take the $\vec{k}$-Fourier transform of Eq. (2.18). It is straightforward to show that

$$\int d^3r\,e^{-i\vec{k}\cdot\vec{r}}n_0(\vec{r})\partial_i[\hat{L}(\vec{r})\partial_jJ_j(\vec{r},\omega)]=-\int\frac{d^3k'}{(2\pi)^3}\hat{A}_i(\vec{k},\vec{k}')k_j'J_j(\vec{k}',\omega),$$

where

$$\hat{A}_i(\vec{k},\vec{k}')\equiv\int\frac{d^3k''}{(2\pi)^3}k_i''n_0(\vec{k}-\vec{k}'')\hat{L}(\vec{k}'',\vec{k}'), \tag{2.19}$$

with

$$\hat{L}(\vec{k}'',\vec{k}')\equiv\int d^3r\,e^{-i\vec{k}''\cdot\vec{r}}\hat{L}(\vec{r})e^{i\vec{k}'\cdot\vec{r}}.$$

Note that in the Thomas-Fermi approximation, $\hat{L}(\vec{r})\to p(\vec{r})$ and $\hat{L}(\vec{k}'',\vec{k}')\to p(\vec{k}''-\vec{k}')$. In addition,

$$\int d^3r\,e^{-i\vec{k}\cdot\vec{r}}n_0(\vec{r})E_i(\vec{r},\omega)=\int\frac{d^3k'}{(2\pi)^3}n_0(\vec{k}-\vec{k}')E_i(\vec{k}',\omega),$$

so that the Fourier transform of Eq. (2.18) can be written

$$i\omega J_i(\vec{k},\omega)=\frac{i}{\omega}\int\frac{d^3k'}{(2\pi)^3}\hat{A}_i(\vec{k},\vec{k}')k_j'J_j(\vec{k}',\omega)+\int\frac{d^3k'}{(2\pi)^3}n_0(\vec{k}-\vec{k}')E_i(\vec{k}',\omega). \tag{2.20}$$

Making use of Eq. (2.15) into Eq. (2.20) we can write down an integral equation for $\sigma_{ij}(\vec{k},-\vec{k}',\omega)$. Rather than doing that we just note that

$$k_j'J_j(\vec{k}',\omega)=(\omega/4\pi i)k_j'E_j(\vec{k}',\omega).$$

Then writing $E_i(\vec{k}',\omega)=E_l(\vec{k}',\omega)\delta_{il}$, utilizing Eq. (2.15) on the left-hand side of Eq. (2.20), and imposing that the resulting equation holds for all $E_l(\vec{k}',\omega)$, we obtain at once,

$$\sigma_{il}(\vec{k},-\vec{k}',\omega)=(-i/\omega)n_0(\vec{k}-\vec{k}')\delta_{il}+(-i/4\pi\omega)\hat{A}_i(\vec{k},\vec{k}')k_l'. \tag{2.21}$$

This tensor (once an expression for $\hat{L}$ is chosen) should be useful in the study of optical properties of diffuse surfaces. Unlike any other conductivity tensor one finds in the literature, it could provide a starting point for studying, for instance, changes in reflectance due to the excitation of higher-multiple surface plasmons, whose existence depends on our keeping the second term on the right-hand side of Eq. (2.21). This is, in effect, what is implicitly done in Sec. III, where the simple ansatz (see I)

$$n_0\vec{\nabla}\left(\frac{\delta G}{\delta n}\right)_1=\beta^2\vec{\nabla}n_1 \tag{2.22}$$

(β^2 being a constant) is made. In fact, it is straightforward to show that in this case,

$$\sigma_{il}(\vec{k},-\vec{k}',\omega)=\left(-\frac{i}{\omega}\right)n_0(\vec{k}-\vec{k}')\delta_{il}+\left(\frac{-i\beta^2}{\omega}\right)\frac{n_0(\vec{k}-\vec{k}')k_ik_l}{\omega^2-\beta^2k^2}. \tag{2.23}$$

Despite the crudeness of this approximation, we shall see in Sec. III that it contains a lot of interesting physics when used in conjunction with a "realistic" electron contour at the surface. We remark that even the simple expression [Eq. (2.23)] is more general than the one used by Harris and Griffin[4] in their high-frequency expansion of the RPA, which corresponds to setting $\beta^2=0$, i.e., dropping all hydrodynamic dispersive effects. This local approximation is also implicit in the

more conventional treatments of the surface-plasmon problem in the retarded region.[1,24] In Sec. IV we comment on the reasons which inhibit us at the present moment from using a (presumably) more accurate expression for $\hat{A}$ [that is, for $\hat{L}(n_0)$].

Substituting Eq. (2.21) into Eq. (2.16), we obtain:

$$E_i(\vec{k},\omega) = \frac{4\pi}{\omega^2 - c^2k^2}\int \frac{d^3k'}{(2\pi)^3} n_0(\vec{k}-\vec{k}')E_i(\vec{k}',\omega) + \frac{(4\pi)(-c^2)k_i}{\omega^2(\omega^2-c^2k^2)}\int \frac{d^3k'}{(2\pi)^3} n_0(\vec{k}-\vec{k}')k_l E_l(\vec{k}',\omega) + \frac{4\pi i}{\omega^2-c^2k^2}\int \frac{d^3k'}{(2\pi)^3}\hat{A}_i(\vec{k},\vec{k}')n(\vec{k}',\omega) + \frac{(4\pi i)(-c^2)k_i}{\omega^2(\omega^2-c^2k^2)}\int \frac{d^3k'}{(2\pi)^3}k_j\hat{A}_j(\vec{k},\vec{k}')n(\vec{k}',\omega). \tag{2.24}$$

We find it convenient to take the scalar and vector products of $\vec{k}$ and Eq. (2.24). We obtain, respectively:

$$\omega^2\vec{k}\cdot\vec{E}(\vec{k},\omega) = 4\pi\int\frac{d^3k'}{(2\pi)^3}n_0(\vec{k}-\vec{k}')\vec{k}\cdot\vec{E}(\vec{k}',\omega) + 4\pi i\int\frac{d^3k'}{(2\pi)^3}\vec{k}\cdot\hat{A}(\vec{k},\vec{k}')n(\vec{k}',\omega), \tag{2.25}$$

and

$$(\omega^2-c^2k^2)\vec{k}\times\vec{E}(\vec{k},\omega) = 4\pi\int\frac{d^3k'}{(2\pi)^3}n_0(\vec{k}-\vec{k}')\vec{k}\times\vec{E}(\vec{k}',\omega) + 4\pi i\int\frac{d^3k'}{(2\pi)^3}\vec{k}\times\hat{A}(\vec{k},\vec{k}')n(\vec{k}',\omega). \tag{2.26}$$

We emphasize that the second term on the right-hand side of Eq. (2.26) introduces hydrodynamic effects into the equation for the "transverse" part of the field. [If we were to quantize the theory, what this is saying is that hydrodynamic effects will, in general, affect the "photon component" of the coupled photon-plasmon (polariton) mode.] This effect vanishes if the simple ansatz Eq. (2.22) is made (because of $\hat{A}$ being then proportional to $\vec{k}$) and, of course, it is absent in all local (i.e., $\beta^2=0$) theories.

C. Example: homogeneous system

Here:

$$n_0(\vec{k}-\vec{k}') = (2\pi)^3\bar{n}_0\delta(\vec{k}-\vec{k}'),$$

where $\bar{n}_0$ is a constant (equal to the background density). Assume, for simplicity, a Thomas-Fermi approximation to $\hat{L}$. Then

$$\hat{L}(\vec{k}'',\vec{k}') - p(\vec{k}''-\vec{k}') = (2\pi)^3\bar{p}\delta(\vec{k}''-\vec{k}')$$

[with $\bar{p}=p(\bar{n}_0)$]. Eq. (2.19) gives

$$\hat{A}_i(\vec{k},\vec{k}') = (2\pi)^3\beta^2_{\text{Th-F}}\,k_i\delta(\vec{k}-\vec{k}'), \tag{2.27}$$

where we have called $\beta^2_{\text{Th-F}}\equiv\bar{n}_0\bar{p}_0$. Then, using $\vec{k}\cdot\vec{E}(\vec{k},\omega)=4\pi i\,n(\vec{k},\omega)$, Eq. (2.25) reduces to

$$\omega^2 n(\vec{k},\omega) = \omega_p^2 n(\vec{k},\omega) + \beta^2_{\text{Th-F}}k^2 n(\vec{k},\omega)$$

($\omega_p^2\equiv 4\pi\bar{n}_0$) and hence there can exist a nonvanishing $n(\vec{k},\omega)$ (in the absence of external changes) if and only if

$$\omega^2 = \omega_p^2 + \beta^2_{\text{Th-F}}\,k^2.$$

This is the bulk plasmon dispersion relation (note, however, that $\beta^2_{\text{Th-F}}\neq\frac{3}{5}v_F^2$). Also, with $\hat{A}$ given in Eq. (2.27), Eq. (2.26) simplifies to

$$(\omega^2-c^2k^2)\vec{k}\times\vec{E}(\vec{k},\omega) = \omega_p^2\vec{k}\times\vec{E}(\vec{k},\omega),$$

thus, there exists a nonzero transverse electromagnetic field if and only if

$$\omega^2 = \omega_p^2 + c^2k^2,$$

which is the photon dispersion relation, modified by the coupling of the photon field with the electron system. Finally, note that the reason why Eqs. (2.25) and (2.26) are decoupled in the homogeneous system is that $\hat{A}$ as given by Eq. (2.27) is proportional to $\vec{k}$ [that this holds true for a more general choice of $\hat{L}$ can be seen in Eq. (2.19), with $n_0(\vec{k}-\vec{k}'') = (2\pi)^3\bar{n}_0\delta(\vec{k}-\vec{k}'')$].

D. Surface-problem geometry

We assume z to be the coordinate normal to a planar jellium surface and assume translation invariance in the plane $(x-y)$. We thus consider $\vec{k}$ as having a well-defined component $\vec{q}$ parallel to the jellium surface. Without loss of generality we take $\vec{q}$ to be along the x axis: $\vec{k}\equiv(q,0,k_z)$.

Rather than working with Eqs. (2.25) and (2.26) we prefer to use the differential equations which are their equivalents. They are obtained by transforming Eqs. (2.25) and (2.26) back into r space. For the geometry just defined we obtain:

$$\frac{\partial}{\partial z}\left(n_0(z)\frac{\partial}{\partial z}[\hat{L}(n_0)\,n(qz\omega)]\right) + [\omega^2-\omega_p^2(z)-q^2n_0(z)\,\hat{L}(n_0)]n(qz\omega) + E_z(q,z,\omega)\frac{\partial}{\partial z}n_0(z) = 0 \tag{2.28}$$

and

$$i\omega\frac{\partial}{\partial z}J_x(qz\omega)+\omega q\,J_z(qz\omega)=\frac{\partial}{\partial z}[n_0(z)E_x(qz\omega)]-iqn_0(z)E_z(qz\omega)+iq\frac{\partial}{\partial z}[n_0(z)\hat{L}(n_0)n(qz\omega)]$$
$$-iqn_0(z)\frac{\partial}{\partial z}[\hat{L}(n_0)n(qz\omega)]. \tag{2.29}$$

In order to write down Eq. (2.29) use was made of the equation

$$4\pi i\,\omega(\vec{\nabla}\times\vec{J})=(\omega^2+c^2\nabla^2)(\vec{\nabla}\times\vec{E}),$$

which follows from Eq. (2.12). We have assumed the so-called p polarization, $\vec{E}=(E_x,0,E_z)$. Note that Eq. (2.29) is just the curl of Euler's equation for the present geometry. In fact, we wrote it down for the sake of completeness, since in the remainder of this paper we shall use Eq. (2.29) together with Euler's equation.

We now express the field $\vec{E}$ in terms of the sources. Equation (2.14) can be rewritten

$$E_i(\vec{k},\omega)=-ik_i\phi(\vec{k},\omega)+(i\omega/c)A_i(\vec{k},\omega), \tag{2.30}$$

where

$$\phi(\vec{k},\omega)\equiv\frac{4\pi c^2}{\omega^2-c^2k^2}n(\vec{k},\omega),$$

$$A_i(\vec{k},\omega)\equiv\frac{4\pi c}{\omega^2-c^2k^2}J_i(\vec{k},\omega). \tag{2.31}$$

Note that

$$\vec{k}\cdot\vec{A}(\vec{k},\omega)-\frac{\omega}{c}\phi(\vec{k},\omega)=\frac{4\pi c}{\omega^2-c^2k^2}[\vec{k}\cdot\vec{J}(\vec{k},\omega)-\omega n(\vec{k},\omega)]=0,$$

i.e., ϕ and $\vec{A}$ as defined by Eq. (2.31) satisfy the Lorentz condition. Then, performing simple contour integrations we obtain:

$$\phi(q,z,\omega)=\frac{(-2\pi)}{(q^2-\omega^2/c^2)^{1/2}}\int dz'e^{-(q^2-\omega^2/c^2)^{1/2}|z-z'|}\times n(q,z',\omega) \tag{2.32}$$

and

$$A_i(q,z,\omega)=\frac{(-2\pi)}{c(q^2-\omega^2/c^2)^{1/2}}\int dz'e^{-(q^2-\omega^2/c^2)^{1/2}|z-z'|}\times J_i(q,z',\omega).$$

In deriving Eq. (2.32) from Eq. (2.31) we have required $q\gtrsim\omega/c$, which in any case is the region of the $(q-\omega)$ plane which is of interest in the surface-plasmon problem. Using Eqs. (2.31) and (2.32) we can write down the expressions for $E_x(qz\omega)$ and $E_z(qz\omega)$ which are needed in Eqs. (2.28) and (2.29), the two coupled integrodifferential equations for the surface collective problem. [From now on we shall omit the labels (q,ω) in the argument of the fluctuating variables.]

E. Electrostatic limit

Mathematically, it can be defined by setting $c=\infty$. Then, the theory developed in I follows.[5] However, we want to analyze what was done in I within the context of the retarded problem. Recalling Eq. (2.32) we see that a necessary condition to do that is $q\gg\omega/c$. Then,

$$\phi\to\frac{-2\pi}{q}\int dz'\,e^{-q|z-z'|}n(z') \quad\text{and}\quad E_z\to-\frac{\partial\varphi}{\partial z}.$$

We then replace this expression for E_z into Eq. (2.28) and, for the sake of simplicity in the argument, assume a Thomas-Fermi approximation to $\hat{L}$. If $q\ll\omega/\beta_{\text{Th-F}}$, and if we assume that $n(z)\to0$ as $z\to-\infty$ (deep inside the solid), then q can be treated as a small number in Eq. (2.28) and we recover what was done in I. Our procedure is consistent since, under the conditions just stated, the solution to Eq. (2.28) in the limit $q\to0$ (but $\omega/c\ll q$ first) is $n(z)\sim e^{-(\omega/\beta_{\text{Th-F}})|z|}$, $(\omega\sim\omega_p)$. However, note that the conclusions of I now have to be considered as approximate, in other words, to hold only to zeroth order in the small quantity ω_p/qc. In particular, the frequency of the regular plasmon is expected to deviate from its "canonical" value of $\omega_p(z=-\infty)/\sqrt{2}$. (See Sec. III.)

In order to further emphasize this point, let us consider the equation of continuity

$$iqJ_x+\frac{\partial}{\partial z}J_z-i\omega n=0. \tag{2.33}$$

Now, the existence of the higher multipoles could be explained by noting (see I) that if charge is to be conserved, $(J_z)_{z=0}=0$, [$z=0$ being the point on the z axis where $n_0(z)$ is assumed to vanish]. Thus *when* $q\to0$ Eq. (2.33) requires that

$$\int dz\,n_{q=0}=0,$$

and this condition was shown to allow for the existence of more than one surface-plasmon branch. It is then of physical importance to ensure that there exists a typical length, λ, in the dynamic

surface problem, such that $\lambda^{-1} \gg q \gg \omega/c$. Now, since $n(z) \sim e^{-(\omega_p/\beta_{\text{Th-F}})|z|}$, then $\lambda \equiv (\omega_p/\beta_{\text{Th-F}})^{-1}$. Writing down Eq. (2.33) in dimensionless units, the first term on the left-hand side will be proportional to (λq) and can then be neglected. We can then expect to find the higher-multipole branches in the retarded region (for appropriate surface diffusenesses) and their frequencies in the $q > \omega/c$ region will be given to zeroth order in ω/qc by the values obtained in the $c = \infty$ approximation.[3] We remark that, however, the clear-cut classification of these modes as multipoles holds only in the aforementioned limit $c = \infty$, $q = 0$. Nonetheless, we shall retain the language, i.e., we shall refer to multipole fluctuations in the identification of the various plasmon branches in the retarded region.

III. APPLICATION TO SIMPLE MODELS

As an application of the formulation and physical picture developed in Sec. II, we now present the solution to idealized models for the electron density at a free metal-vacuum interface (Fig. 1.) As mentioned in Sec. II, this "static" model is here accompanied by the simple dynamical ansatz [Eq. (2.22)], which corresponds to the "usual" type of hydrodynamics. Thus, the dynamics of the system we consider in this section is implicitly contained in the conductivity tensor given by Eq. (2.23). We remark that, however, our ansatz is not exactly equivalent to Bennett's pressure term[6] since, having lost self-consistency by the introduction of an arbitrary $n_0(z)$, the static potential $\phi_0(z)$ should enter Euler's equation. However, Bennett's numerical results do not show a marked qualitative dependence on the value of this term (compare Figs. 3 and 4 in Ref. 6).

The two basic equations in this section are

$$\beta^2 \frac{\partial^2 n(z)}{\partial z^2} + [\omega^2 - \omega_p^2(z) - \beta^2 q^2] n(z) + E_z(z) \frac{\partial}{\partial z} n_0(z) = 0 \quad (3.1)$$

[where $\omega_p^2(z) = 4\pi n_0(z)$] and

$$i\omega J_i(z) = n_0(z) E_i(z) + \beta^2 \partial_i n(z). \quad (3.2)$$

Equations (3.1) and (3.2) are, respectively, Eq. (2.28) and Euler's equation [Eq. (2.11)] after Eq. (2.22) is used. Note that the form of Eq. (3.1) is the same in both the retarded and the nonretarded ($c = \infty$) limits. However, in the former case there are two contributions to $E_z(z)$:

$$E_z(z) = 4\pi h'(z) + 4\pi(\omega/c^2) g(z). \quad (3.3)$$

Here $\alpha \equiv (q^2 - \omega^2/c^2)^{1/2}$ and we have defined, for all z:

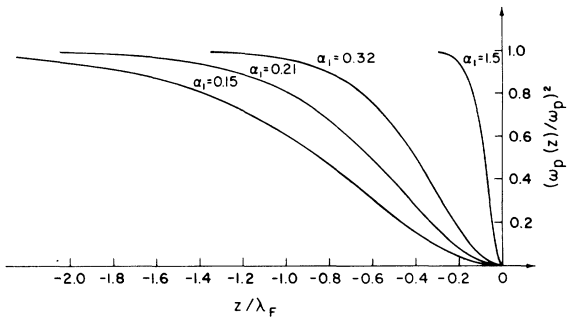

FIG. 1. Electron-density profiles $n_0(z)/n_0(-\infty) = 1.01 \times (1 - \cosh^{-2} \alpha_1 z)$ for four different values of α_1 (Å^{-1}). Abscissa is measured in Fermi wavelengths ($\lambda_F = 2\pi/k_F$) appropriate to sodium (one Fermi wavelength equals 6.82 Å). Points z_0 such that $n_0(z) = n_0(-\infty)$ [and beyond which the corresponding profile was replaced by the value $n_0(-\infty)$] are: $\alpha_1 = 1.5 \rightarrow z_0 = -0.29$; $\alpha_1 = 0.32 \rightarrow z_0 = -1.36$; $\alpha_1 = 0.21 \rightarrow z_0 = -2.07$; $\alpha_1 = 0.15 \rightarrow z_0 = -2.90$.

$$h(z) = -\frac{1}{2\alpha} \int_{-\infty}^{0} dz'\, e^{-\alpha|z-z'|} n(z') \quad (3.4)$$

and

$$g(z) = -\frac{i}{2\alpha} \int_{-\infty}^{0} dz' e^{-\alpha|z-z'|} J_z(z'). \quad (3.5)$$

From Eqs. (3.4) and (3.5) it follows that:

$$n(z) = h''(z) - \alpha^2 h(z) \quad (3.6)$$

and

$$J_z(z) = (-i)[g''(z) - \alpha^2 g(z)], \quad (3.7)$$

where, as in the rest of this section, we denote differentiation with respect to z by a prime. We remark that $n_0(z)$ has been taken to vanish for $z > 0$ (being otherwise arbitrary for $z < 0$, that is, inside the metal). Making use of Eqs. (3.3) and (3.6) we transform Eq. (3.1) into the following differential equation:

$$\beta^2 h''''(z) - \beta^2[\alpha^2 + \gamma^2(z)] h''(z) - [\omega_p^2(z)]' h'(z) + \beta^2 \alpha^2 \gamma^2(z) h(z) + (\omega/c^2)[\omega_p^2(z)]' g(z) = 0, \quad (3.8)$$

where

$$\beta^2 \gamma^2(z) \equiv \omega_p^2(z) + \beta^2 q^2 - \omega^2. \quad (3.9)$$

Similarly, substituting Eq. (3.7) into the z component of Eq. (3.2) and utilizing Eqs. (3.3) and (3.6) we obtain

$$g''(z) - \kappa^2(z) g(z) - (\beta^2/\omega) h'''(z) + (1/\omega)[\omega_p^2(z) + \beta^2 \alpha^2] h'(z) = 0. \quad (3.10)$$

Here we have defined

$$c^2 \kappa^2(z) = \omega_p^2(z) + c^2 q^2 - \omega^2. \quad (3.11)$$

Note that the term that introduces $g(z)$ in Eq. (3.8)

vanishes in the case of the homogeneous medium (as well as in the electrostatic limit). Hence the explicit coupling between Eqs. (3.8) and (3.10) is due to our allowing for a smooth density profile at the surface.

We now cast the above system of differential equations in a form appropriate for numerical integration. We define the 6×1 column function vector $u(z)$ by

$$u^t(z)=[h(z);h'(z);h''(z);h'''(z);g(z);g'(z)] \tag{3.12}$$

(where the superscript "t" denotes transpose), and 6×6 function matrix $\mathfrak{M}(z)$ by

$$\mathfrak{M}(z)=\begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ -\alpha^2\gamma^2(z) & [\omega_p^2(z)]'/\beta^2 & \alpha^2+\gamma^2(z) & 0 & -\omega[\omega_p^2(z)]'/\beta^2c^2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & -[\omega_p^2(z)+\beta^2\alpha^2]/\omega & 0 & \beta^2/\omega & \kappa^2(z) & 0 \end{bmatrix} . \tag{3.13}$$

Then the following matrix equation is equivalent to the system of equations (3.8) and (3.10):

$$u'(z)=\mathfrak{M}(z)u(z). \tag{3.14}$$

At this point we have to consider a specific model for the function $\omega_p^2(z)$ [that is, for $n_0(z)$]. A choice for $\omega_p^2(z)$ which, as shown in I, yields analytical solutions in the nonretarded limit, is the smooth function

$$\omega_p^2(z)=\omega_p^2(1-\cosh^{-2}\alpha_1 z), \tag{3.15}$$

where ω_p is the plasma frequency deep inside the solid ($z\to-\infty$). This function is shown in Fig. 1 for various values of α_1. We find this choice quite useful to study the sensitivity of the surface collective behavior to the shape and diffuseness of the electron profile at the surface. Actually, for numerical convenience we modified this definition of $\omega_p^2(z)$ slightly by multiplying the function $(1-\cosh^{-2}\alpha_1 z)$ by a numerical factor very close to unity and approximating the resulting function by unity for $z<z_0$, where z_0 is the value of z at which this function reaches the value of one. (It is these "modified" profiles which are shown in Fig. 1.) We checked that this "perturbation" of Eq. (3.15) did not have any significant effect in our results. For instance, the critical values of α_1 for which the successive multipoles first appear are known analytically for $\omega_p^2(z)$ as given by Eq. (3.15), and it was verified numerically that the modified profiles gave essentially the same critical values.

Now the system (3.14) has six linearly independent solutions. For z less than z_0 we can write down the solutions with no difficulty. The three well-behaved ones are

$$y_1(z)=\begin{bmatrix} 1 \\ \gamma \\ \gamma^2 \\ \gamma^3 \\ -\dfrac{\beta^2\omega\gamma}{\omega_p^2-\omega^2} \\ -\dfrac{\beta^2\omega\gamma^2}{\omega_p^2-\omega^2} \end{bmatrix}\times e^{\gamma z};\quad y_2(z)=\begin{bmatrix} 1 \\ \alpha \\ \alpha^2 \\ \alpha^3 \\ -\dfrac{\omega_p^2\,\alpha}{\omega(\alpha^2-\kappa^2)} \\ -\dfrac{\omega_p^2\,\alpha^2}{\omega(\alpha^2-\kappa^2)} \end{bmatrix}\times e^{\alpha z};\quad y_3(z)=\begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ \kappa \end{bmatrix}\times e^{\kappa z}, \tag{3.16}$$

where γ and κ refer to the values of $\gamma(z)$ and $\kappa(z)$ at $z=-\infty$. Then the general solution to Eq. (3.14) for $-\infty<z<0$ is

$$u(z)=Ay_1(z)+By_2(z)+Dy_3(z). \tag{3.17}$$

The analytic continuation of the three solutions (3.16) into the diffuse region $z_0<z<0$ was obtained numerically, using a Runge-Kutta method.

Outside the solid ($z>0$) $g(z)$ is given by

$$g(z)=Fe^{-\alpha z},\quad z>0. \tag{3.18}$$

We note that knowing $g(z)$ for all z and $n(z)$ for

$z<0$ [$n(z)$ vanished identically for $z>0$], we can calculate all the other variables for all z, as can be seen from Eqs. (3.3), (3.4), and (3.7) and the following two expressions for E_x and H_y:

$$iqE_x(z) = -2\pi\alpha \int_{-\infty}^{0} dz'\, e^{-\alpha|z-z'|}\, n(z') + \left(-4\pi\frac{\omega}{c^2}\right) g'(z), \tag{3.19}$$

and

$$\frac{cq}{4\pi} H_y(z) = \frac{\omega}{2} \int_{-\infty}^{0} dz'\, e^{-\alpha|z-z'|}\, \mathrm{sgn}(z-z')\, n(z') + i J_x(z) - (\omega^2/c^2)\, g(z). \tag{3.20}$$

Now, at $z=0$ we have three boundary conditions: $(J_x)_{z=0^-} = 0$ [note that from Eq. (3.18) we infer that $J_x = 0$ outside the solid], and the continuity of $g(z)$ and $g'(z)$. Since the integrals on the right-hand side of Eqs. (3.19) and (3.20) are continuous, the continuity of E_x and H_y at $z=0$ is thus ensured. We can find a further relation between A, B, and D by the following argument. For $z<z_0$, Eqs. (3.6), (3.16), and (3.17) give

$$n(z) = (\gamma^2 - \alpha^2) A e^{\gamma z}. \tag{3.21}$$

Hence, for $z<z_0$

$$\int_{-\infty}^{0} dz'\, e^{-\alpha|z-z'|}\, \mathrm{sgn}(z-z')\, n(z') = 2\gamma A e^{\gamma z} - e^{\alpha z}\left((\gamma+\alpha) e^{(\gamma-\alpha)z_0} A + \int_{z_0}^{0} dz'\, e^{-\alpha z'} n(z')\right). \tag{3.22}$$

At this point it is convenient to recast Eq. (3.10) as an integrodifferential equation as follows:

$$g''(z) - \kappa^2(z)\, g(z) = -\frac{\omega_p^2(z)}{2\omega} \int_{-\infty}^{0} dz'\, e^{-\alpha|z-z'|}\, \mathrm{sgn}(z-z')\, n(z') + \frac{\beta^2}{\omega} n'(z). \tag{3.23}$$

Then, substituting Eqs. (3.21) and (3.22) in Eq. (3.23) we obtain, for $z<z_0$, the equation

$$g''(z) - \kappa^2 g(z) = -\gamma\omega\left(1 - \frac{\beta^2}{c^2}\right) A e^{\gamma z} + \frac{\omega_p^2}{2\omega} e^{\alpha z}\left((\gamma+\alpha) e^{(\gamma-\alpha)z_0} A + \int_{z_0}^{0} dz'\, e^{-\alpha z'} n(z')\right),$$

whose general solution is

$$g(z) = D e^{\kappa z} - \frac{\beta^2\gamma\omega}{\omega_p^2 - \omega^2} A e^{\gamma z} - \frac{c^2}{2\omega} e^{\alpha z}\left((\gamma+\alpha) e^{(\gamma-\alpha)z_0} A + \int_{z_0}^{0} dz'\, e^{-\alpha z'} n(z')\right). \tag{3.24}$$

Now, according to Eqs. (3.12) and (3.17):

$$g(z) = A y_1^{(5)}(z) + B y_2^{(5)}(z) + D y_3^{(5)}(z) \tag{3.25}$$

(where the superscripts label the row in the column vectors y_i, $i=1,2,3$). Then taking Eq. (3.25) for $z<z_0$, utilizing Eq. (3.16) and comparing with Eq. (3.24) we obtain,

$$(-2\alpha) B = (\alpha+\gamma) e^{(\gamma-\alpha)z_0} A + \int_{z_0}^{0} dz'\, e^{-\alpha z'} n(z'). \tag{3.26}$$

Finally, noting that

$$\int_{z_0}^{0} dz'\, e^{-\alpha z'}\left[h''(z') - \alpha^2 h(z')\right] = \left[h'(0) + \alpha h(0)\right] - e^{-\alpha z_0}\left[h'(z_0) + \alpha h(z_0)\right],$$

and recalling Eq. (3.6) then Eq. (3.26) simplifies to give

$$h'(0) + \alpha h(0) = 0. \tag{3.27}$$

This condition can be rewritten

$$A\left[y_1^{(2)}(0) + \alpha y_1^{(1)}(0)\right] + B\left[y_2^{(2)}(0) + \alpha y_2^{(1)}(0)\right] + D\left[y_3^{(2)}(0) + \alpha y_3^{(1)}(0)\right] = 0. \tag{3.28}$$

Thus, the dispersion relation of the surface collective modes reduces to finding the zeros of the following 4×4 determinantal equation:

$$\Delta = \begin{vmatrix} [y_1^{(2)}(0) + \alpha y_1^{(1)}(0)] & [y_2^{(2)}(0) + \alpha y_2^{(1)}(0)] & [y_3^{(2)}(0) + \alpha y_3^{(1)}(0)] & 0 \\ [y_1^{(4)}(0) - \alpha^2 y_1^{(2)}(0)] & [y_2^{(4)}(0) - \alpha^2 y_2^{(2)}(0)] & [y_3^{(4)}(0) - \alpha^2 y_3^{(2)}(0)] & 0 \\ y_1^{(5)}(0) & y_2^{(5)}(0) & y_3^{(5)}(0) & -1 \\ y_1^{(6)}(0) & y_2^{(6)}(0) & y_3^{(6)}(0) & \alpha \end{vmatrix} = 0. \tag{3.29}$$

Here Δ is the determinant of the coefficients of the 4×4 homogeneous system of equations for the unknowns A, B, D, and F.

In Figs. 2 and 3 we exhibit the dispersion relations obtained by numerically solving Eq. (3.29) for several values of α_1. In order to show the dependence of the dispersion relations on the shape of the electron-density profile we shall also make reference to the dispersion curves given in Ref. 25 for a simpler two-step density model. It was found convenient to measure z in units of λ_F, the Fermi wavelength and to express Eq. (3.14) in dimensionless form. In this theory the only parameter characterizing the dynamics of the electron system is its bulk density, so that upon making Eq. (3.14) dimensionless[26] all the elements of the matrix $\mathfrak{M}(z)$ can be expressed in terms of r_s, the (bulk) Wigner-Seitz radius. For definiteness we took $r_s=3.99$, which corresponds to the bulk density of sodium. This value of r_s, lying in the middle of the metallic range, can be considered to be a representative one. (Figure 1 in Ref. 25 applies to this same value of r_s.) The values of α_1 for which the dispersion curves are presented here can be given physical significance by recalling the critical values of α_1 for which successive multipole excitations first appear (I). Now, the dipole model first shows up (at $\omega=\omega_p$) for $\alpha_1\equiv\alpha_1^{(\mathrm{dip})}=\omega_p/\beta\sqrt{2}$. Then, with $\beta^2=\frac{3}{5}v_F^2$ and $r_s=3.99$, $\alpha_1^{(\mathrm{dip})}=0.73$ Å^{-1}. (We remark that $\alpha_1^{(\mathrm{dip})}\sim r_s^{-1/2}$ Å^{-1}.) The quadrupole mode first appears (at $\omega=\omega_p$) when $\alpha_1\equiv\alpha_1^{(\mathrm{quad})}=\alpha_1^{(\mathrm{dip})}/\sqrt{6}\simeq0.29$ Å^{-1}. The octopole mode is first "bound" for $\alpha_1\equiv\alpha_1^{(\mathrm{oct})}=\alpha_1^{(\mathrm{dip})}/\sqrt{15}=0.18$ Å^{-1}. The profiles corresponding to these limiting values of α_1 can be found in I. The most abrupt profile shown in Fig. 1 corresponds to $\alpha_1=1.5$ Å^{-1} and the associated dispersion relation (as shown in Fig. 2) has the expected "regular plasmon" behavior. We remark that the slope for $q>\omega/c$ is less than for the abrupt model, $\alpha_1\to\infty$, which is the $a=0$ dispersion curve in Fig. 1 of Ref. 25. The next contour shown in Fig. 1 corresponds to $\alpha_1=0.32$ Å^{-1}. In Fig. 2 we present the ensuing dispersion curves. The dipole mode is already well bound and the regular plasmon branch never reaches the value $\omega_{sp}=\omega_p/\sqrt{2}$. The next dispersion relation given in Fig. 2 corresponds to the contour drawn for $\alpha_1=0.21$ in Fig. 1. The

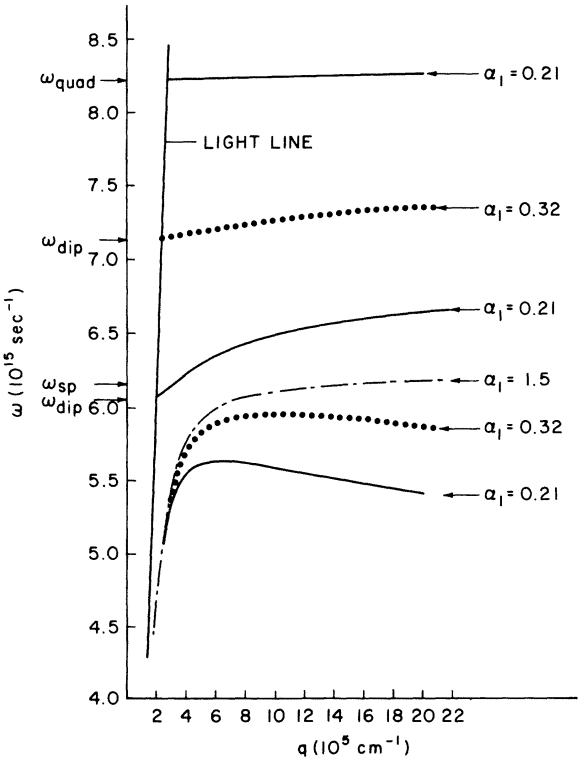

FIG. 2. Dispersion relation for three values of α_1(Å^{-1}). Corresponding electron contours are shown in Fig. 1. $q=0$ values of the frequencies of the dipole and quadrupole modes (for the corresponding values of α_1) obtained in the $c=\infty$ limit are given on the ordinate axis.

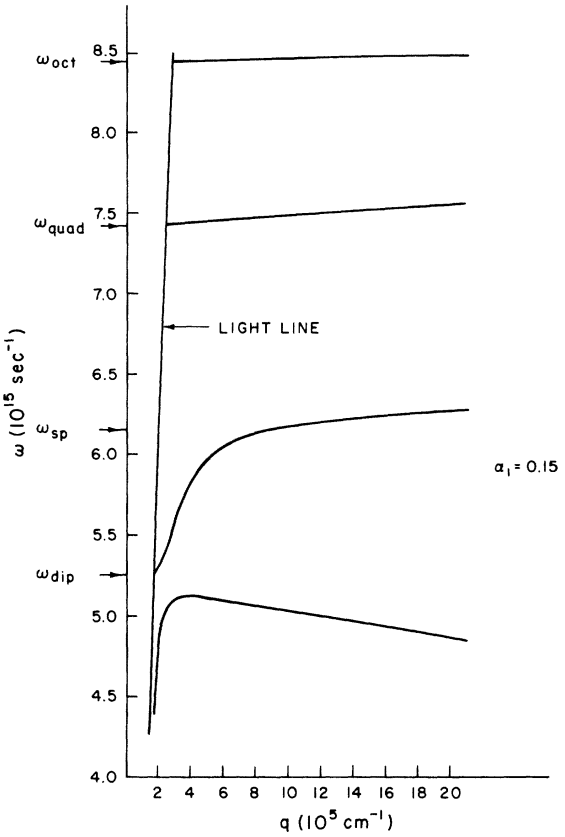

FIG. 3. Dispersion relation for the profile shown in Fig. 1 for $\alpha_1=0.15$ Å^{-1}. $q=0$ values of the dipole, quadrupole, and octopole modes obtained in the $c=\infty$ limit are shown on the ordinate axis.

quadrupole mode has already appeared, showing little dispersion; the dipole branch intersects the light line slightly below ω_{sp} and the regular plasmon branch is pushed further below ω_{sp}.[27] Figure 2 makes evident that the lower two modes appear to interact in the optical region and this prevents the crossing of their dispersion curves. We note that this effect creates a gap in the surface collective spectrum at a frequency slightly below ω_{sp}. One qualitative difference between the results of Fig. 2 and those of Fig. 1 of Ref. 25, is that there is a range of values of α_1 ($0.22 < \alpha_1 < 0.29$) such that both the dipole and quadrupole modes lie above ω_{sp}, whereas for the two-step model (for the parameters chosen in Ref. 25) the dipole was already below ω_{sp} before the quadrupole was bound. That is, the two-step model binds the higher multipoles "more strongly" once they are well bound. The last contour shown in Fig. 1 corresponds to $\alpha_1 = 0.15$ Å^{-1} and the associated dispersion curves are presented in Fig. 3. The octopole mode is already bound and is practically flat throughout the optical region. The quadrupole branch shows little dispersion also. The dipole mode, being well below ω_{sp} appears to interact with the regular plasmon branch in the optical region. We remark that the two lower branches in Fig. 3 look very much like the corresponding branches (not shown in Fig. 1, Ref. 25) for $a = 4$ Å in the two-step model. However, in the latter case for that value of a those are the only two branches, whereas in Fig. 3 the quadrupole and the octopole modes are present.

We believe this discussion shows quite vividly the strong dependence of the surface collective dispersion relation in the optical region on both the shape of the electron contour at the surface and its diffuseness. If the qualitative effects our theory predicts are indeed observable (and we emphasize that the multipole branches are a reality in the case of classical plasmas), then two points of prime interest to the experimentalist would be the location of the intersection of the higher-multipole branches and the light line, and the "gap" in the dispersion curves below ω_{sp}. We feel that the new qualitative phenomena described here should stimulate experimental search for the higher multipoles with the attenuated-total-reflection (ATR) method[9] at surfaces of high free-electron-density metals with layers of chemisorbed alkalis. The theoretical model of chemisorption due to Lang[28] is most helpful in visualizing the experiment we are proposing, since chemisorbing one or more layers corresponds in this model to varying the diffuseness of the electron contour at the surface. The qualitative results reported here for the optical region, together with the relative simplicity of the ATR method (as compared with the extremely complicated reduction analysis[8] to obtain the plasmon-dispersion relation in the electrostatic region from the LEED data), seem to render preference to the optical method in the search for the existence of the higher-multipole modes. We note that since in this paper we have not included any damping effects, the ATR experiment we are suggesting should be performed keeping the incident angle fixed and scanning the photon energy, so as to avoid the backbending of the dispersion curve.[29]

IV. DISCUSSION

We have illustrated with simple models the importance of taking into account hydrodynamic effects in the problem of electron collective motion in diffuse surfaces in the retarded region. Previous work in the subject has generally assumed otherwise[30]; namely, that for $q \sim \omega/c$ hydrodynamic dispersion was not important. In the light of our results this simplifying assumption seems warranted only for very abrupt surfaces. On the other hand, we show in the Appendix that hydrodynamic effects play no role in the problem of "guided"[24] s-polarized electromagnetic waves in inhomogeneous media.

The main qualitative feature of the theory of Sec. II lost by the ansatz Eq. (2.22), stems from the disappearance of hydrodynamic effects from Eq. (2.26), which gives the "photon component" of the coupled plasmon-photon mode. How important an effect that would be is only a matter of conjecture at the present moment.

In order to obtain results of quantitative significance we probably should use the theory of Sec. II with a more elaborate choice for the operator $\hat{L}(n_0)$ (that is, for the density functional $G[n]$), and retain self-consistency by using the self-consistent solutions $n_0(z)$(Ref. 20) to Eq. (2.9). We note, however, that the smooth profiles used in Sec. III are not so different from the self-consistent ones[20] to expect our arbitrary choice [Eq. (3.15)] to be a serious shortcoming. We rather think that if future experimental evidence indicates significant departures from the results of Sec. III, they would have to be accounted for by an appropriate choice of $\hat{L}$. We remark that a change in $\hat{L}$ has a more significant effect in the theory, since that change will, in general, alter the order of the differential equations of the problem. As mentioned in Sec. II, the expressions for $\hat{L}$ we have available are the ones proposed for the ground state of the system.[22,23] In our theory, however, we need to apply them over a wide range of frequencies up to frequencies of the order of the plasma frequency. Perhaps a simple remark will illustrate the diffi-

culty we face here. It is well known[31] that in the homogeneous system, assuming the ideal-gas adiabatic law to hold, the pressure-density relation at low frequencies (acoustic region) is that appropriate for the three kinetic degrees of freedom of the particles, whereas at high frequencies (plasmon region) it is that appropriate for a system with only one translational degree of freedom. This means that even in this simple case we should really interpolate β^2 from its high-frequency value of $\frac{3}{5}v_F^2$ to $\frac{5}{9}$ of that value, which is the correct number for low frequencies. Hence, in the much more complicated case of the strongly inhomogeneous electron system we are concerned with, one would expect that the low-frequency functionals will have to be modified at high frequencies. This physical argument has a mathematical counterpart which we now present very succinctly. If we assume, in an asymptotic sense, the validity of the expansion of the functional $G[n]$ in powers of the gradient of the density,[18] and utilize the expression for G used by Smith[22] in his static studies of metal surfaces, we obtain the following expression for $\hat{L}[n_0]$:

$$\hat{L}(n_0) = p(n_0) + \frac{1}{36}\frac{1}{n_0}\left(q^2 - \frac{\partial^2}{\partial z^2} + \frac{\partial}{\partial z}\frac{n_0'}{n_0}\right), \tag{4.1}$$

where

$$p(n_0) = \tfrac{1}{3}(3\pi^2)^{2/3} n_0^{-1/3} - \tfrac{1}{3}(3\pi^{-1})^{1/3} n_0^{-2/3} - (0.1 n_0^{-1/3} - 1.55\times 10^{-4} n_0^{-2/3})/(0.079 + n^{1/3})^3. \tag{4.2}$$

The three terms that add up to give $p(n_0)$ are due, respectively, to the contributions of the local kinetic, exchange, and correlation energies (i.e., the kinetic, exchange, and correlation energies of a homogeneous electron system with the local value of the density) to the functional G. The second term on the right-hand side of Eq. (4.1) is due to the first gradient correction to the kinetic energy.

Now, using Eq. (4.1) in Eqs. (2.28) and (2.11) in conjunction with the self-consistent profiles of Lang and Kohn[20] [we remark that the self-consistent density $n_0(z)$ falls off to zero *exponentially* outside the metal; this is really the only feature of $n_0(z)$ that is relevant to the present argument] we find that the ensuing differential equations have regular singular points at $z = \pm\infty$. Hence, they can be solved by the method of indices utilized, for example, in Ref. 23. Now, unfortunately, the roots of the indicial equation are such that[32] in the high-frequency region there is one more well-behaved solution in the tail region ($z \to +\infty$) of the electron distribution than in the bulk region ($z \to -\infty$), and thus we cannot match the solutions obtained on both sides of $z = 0$ (which is some convenient point on the z axis) to obtain the surface-plasmon dispersion relation. This problem subsists if we include the next term in the gradient expansion for the kinetic-energy functional. There are, in fact, three such terms.[33] On the other hand, no such problems arises in the $\omega \to 0$ limit. Now, owing to the lack of first-principle density functionals for frequencies other than zero, we must try phenomenological frequency-dependent modifications of the static functionals. But here, of course, the problem is the lack of experimental data to fit to. Since the higher multipoles have not been detected to date, and the regular plasmon branch measured on clean surfaces is relatively well fitted in the optical region by local theories, i.e., dropping $\hat{L}$ altogether, our being able to improve on the theory of Sec. III appears to be dependent on further progress on the experimental side. Despite the present "truncated" stage our theory is in, we emphasize that the theory of Sec. II offers a program of work which we think can be brought to a more sophisticated level than the approximations of Sec. III, should the experimental evidence so require. We hope that the results of this paper and this discussion will stimulate experimental work along the lines proposed in Sec. III.

Finally, let us make two further remarks. Firstly, there could be an objection that using a hydrodynamic model is not justified in the surface problem because of the low-electron density that exists in the tail region. Actually, this same objection could be posed to the use of RPA theories,[4,5] since the local $r_s \to \infty$ in the tail region. The answer to this objection is, as usual, that the model will find its ultimate justification if it is able to account for the experimental evidence, and again, this remains an open question. We can also offer the following argument. It is argued[34] that the reason the density-functional theory works so well in the evaluation of (static) quantities like work functions is that those quantities depend on integrals over the entire surface region, rather than just the tail. Now, as proved in I, this same property holds true in the surface-plasmon problem. More precisely, at least in the electrostatic $q > \omega/c$ region, the dispersion relation of both regular plasmon and higher multipoles is given in terms of integrals over all space of the density fluctuations.

Secondly, in this paper we have implicitly assumed that the surface collective excitations we dealt with are sufficiently long-lived that meaningful results can be obtained from a theory like ours, which ignores damping effects. Experimental evidence[35] seems to indicate that damping effects are not too serious in the optical region (at least for

the surface-plasmon branch). Of course, we could always introduce an effective collision time and associated viscous force in Euler's equation, but the very use of a hydrodynamic formulation means that the electron-hole pairs are left out and hence we cannot introduce a genuine Landau (collisionless) damping in our theory. Now, for the low temperatures we are concerned with in this paper, it is not obvious that the complications which would follow from the introduction of collisional damping would mean an improvement of the theory. We rather feel that estimates of the damping of surface plasmons, which (unlike the case of bulk plasmons) will occur at all wavelengths, should be done via microscopic theories. To close this comment we note that we think that the conclusions drawn by Heinrichs[12] in the $c=\infty$ limit do not apply to our theory. Heinrichs, who took a different hydrodynamic approach, based on the use of the hydrodynamic *bulk* dielectric constant, claims that when the possibility of Landau damping is neglected the spectrum of surface-plasmon modes changes radically. However, we find little, if any, overlapping between his theory and ours. In his paper the differential equations for charge fluctuations and electrostatic fields have constant coefficients. Nowhere does the density $n_0(z)$ enter the theory, and in fact he finds his theory (Appendix A in Ref. 12) to have no solution in the metal-vacuum interface case. In brief, the modes Heinrichs found for the slab geometry appear to have nothing to do with the higher multipoles discussed in I and in this paper.

APPENDIX

In this Appendix we first show that hydrodynamic effects play no role in the case of the s-polarized mode, $\vec{E}=(0,E_y,0)$. In inhomogeneous media, the possibility of existence of electromagnetic waves with this polarization and with a spatial behavior such that the wave oscillates near the surface and decays exponentially in the bulk region, has recently been investigated by Conwell,[24] using a local theory. In order to make a comparison with her paper let us write down the following two differential equations, which are obtained transforming Eqs. (2.25) and (2.26), respectively, into $\vec{r}$ space:

$$\vec{\nabla}\cdot[n_0(\vec{r})\vec{\nabla}\hat{L}(n_0)n(\vec{r})]+[\omega^2-\omega_p^2(\vec{r})]n(\vec{r},\omega)+\vec{\nabla}n_0(\vec{r})\cdot\vec{E}(\vec{r},\omega)=0, \quad \text{(A1)}$$

and

$$c^2\vec{\nabla}^2[\vec{\nabla}\times\vec{E}(\vec{r},\omega)]+[\omega^2-\omega_p^2(\vec{r})]\vec{\nabla}\times\vec{E}(\vec{r},\omega)-\vec{\nabla}\omega_p^2(\vec{r})\times\vec{E}(\vec{r},\omega)=\vec{\nabla}\times[\omega_p^2(\vec{r})\vec{\nabla}\hat{L}\,n(\vec{r},\omega)]. \quad \text{(A2)}$$

Now, for the surface geometry considered in this paper and for the s polarization, $\vec{\nabla}n_0(z)\cdot\vec{E}(\vec{r},\omega)=0$, so that one possible solution to Eq. (A1) is,

$$n(\vec{r},\omega)\equiv 0. \quad \text{(A3)}$$

With this choice, then, the eventual solutions to Eq. (A2) will not correspond to plasmon modes. Also, Eq. (A2) adopts the simpler (homogeneous in $\vec{E}$) form:

$$c^2\nabla^2(\nabla\times\vec{E})+[\omega^2-\omega_p^2(\vec{r})]\nabla\times\vec{E}(\vec{r},\omega)-\vec{\nabla}\omega_p^2(z)\times\vec{E}(\vec{r},\omega)=0. \quad \text{(A4)}$$

We emphasize that, having disappeared from Eq. (A4), hydrodynamic effects have no bearing on the present problem, in contrast to the plasmon case analyzed in this paper. For the sake of completeness we now show how Eq. (A4) reduces to Conwell's[24] starting equation. We first note that

$$\vec{\nabla}\omega_p^2(z)\times\vec{E}(\vec{r},\omega)=-E_y(z)\frac{\partial}{\partial z}\omega_p^2(z)\hat{e}_x,$$

where $\hat{e}_x$ is the unit vector on the x direction. Thus, taking the x component of Eq. (A4) we obtain, after little rearrangement

$$c^2\left(-q^2+\frac{\partial^2}{\partial z^2}\right)\frac{\partial}{\partial z}E_y(z)+\omega^2\frac{\partial}{\partial z}E_y(z)-\frac{\partial}{\partial z}[\omega_p^2(z)E_y(z)]=0, \quad \text{(A5)}$$

where, as in the text, q is directed along the x axis. We integrate Eq. (A5) once and impose the boundary condition that $E_y(z)\to 0$ as $z\to\infty$. Then,

$$\frac{\partial^2E_y(z)}{\partial z^2}+\left(\frac{\omega^2-\omega_p^2(z)}{c^2}-q^2\right)E_y(z)=0, \quad \text{(A6)}$$

and defining $\epsilon(z,\omega)=1-\omega_p^2(z)/\omega^2$, we obtain

$$\frac{\partial^2E_y(z)}{\partial z^2}+\left(\epsilon(z,\omega)\frac{\omega^2}{c^2}-q^2\right)E_y(z)=0. \quad \text{(A7)}$$

which is the differential equation studied by Conwell to investigate the possibility of obtaining "guided" solutions, or more specifically, solutions which oscillate near $z=0$ and then decay exponentially as $z\to\infty$. We emphasize that here Eq. (A7) does not depend upon the assumption of a local theory. It is simply that nonlocal (hydrodynamic) effects do not enter. Finally, we note that if $c\to\infty$ then Eq. (A7) reduces to Laplace's equation and hence Conwell's modes do not have an electrostatic limit, which is a reflection of the fact that these modes are not polaritons. We thus think that the name Conwell gave these modes — namely, guided plasmons — is a misnomer.

We close this appendix by showing how Eqs. (A1) and (A2) reduce to the differential equation studied

by Guidotti *et al.*[24] in their local theory of plasmons in inhomogeneous media. The local limit corresponds to neglecting all hydrodynamic effects and thus we set $\hat{L}=0$. Then Eqs. (A1) and (A2) give, respectively,

$$[\omega^2-\omega_p^2(z)]n(\vec{r},\omega)+\vec{\nabla}n_0(z)\cdot\vec{E}(r,\omega)=0 \tag{A8}$$

and

$$c^2\nabla^2(\vec{\nabla}\times\vec{E})+[\omega^2-\omega_p^2(z)](\vec{\nabla}\times\vec{E})-\vec{\nabla}\omega_p^2(z)\times\vec{E}(\vec{r},\omega)=0. \tag{A9}$$

Now, recalling that $\vec{\nabla}\times\vec{E}=i\omega\vec{H}/c$, and for the p polarization, (plasmon case) we can rewrite Eqs. (A8) and (A9) as

$$[\omega^2-\omega_p^2(z)]n(z)+E_z(z)\frac{\partial}{\partial z}n_0(z)=0 \tag{A10}$$

and

$$\frac{\partial^2}{\partial z^2}H_y(z)-\kappa^2(z)H_y(z)+\frac{i}{c\omega}E_x(z)\frac{\partial}{\partial z}\omega_p^2(z)=0. \tag{A11}$$

In Eq. (A11) we have defined $\kappa_{(z)}^2=q^2-\omega^2\epsilon(z,\omega)/c^2$. Now, we can write Eq. (A11) as a homogeneous equation for H_y by utilizing another of Maxwell's equations. Recalling $\vec{\nabla}\times\vec{H}=-i\omega\epsilon(z,\omega)\vec{E}/c$, then

$$E_x(z)=\frac{-ic}{\omega\epsilon(z,\omega)}\frac{\partial}{\partial z}H_y(z)$$

and (A12)

$$E_z(z)=[-cq/\omega\epsilon(z,\omega)]H_y(z),$$

and hence noting that

$$\frac{\partial}{\partial z}\epsilon(z,\omega)=-\frac{1}{\omega^2}\frac{\partial}{\partial z}\omega_p^2(z)$$

we can cast Eq. (A11) as

$$H_y''(z)-\frac{\epsilon'(z,\omega)}{\epsilon(z,\omega)}H_y'(z)-\kappa_{(z)}^2H_y(z)=0, \tag{A13}$$

which is the equation solved by Guidotti *et al.*[24] for a particular choice for $n_0(z)$. We emphasize that Eq. (A13) has a regular singular point at the point on the z axis where the frequency ω equals the local plasma frequency. Hence Eq. (A13) is ill-defined for the purposes of numerical integration. One way out of this difficulty would be to add a phenomenological collision term in Euler's equation. This would add a small imaginary part to the dielectric constant and would take the singularity off the real z axis. (In fact, in Ref. 24 it was assumed that ϵ had an imaginary part.) However, this procedure was deemed meaningless by Feibelman[5] who emphasized that the coupling between the surface plasmon and the "local" bulk plasmon which originates the singularity in Eq. (A13) could only be studied by allowing for the wave-vector dependence in the dispersion relations and this means going beyond the local theory of Ref. 24. Finally, note that in the local theory the density fluctuation is obtained after solving for $H_y(z)$ by using Eqs. (A12) and (A10). In other words, Eq. (A13) is decoupled from Eq. (A10).

To close this comment on the local limit of the theory, we note that the additional branch found by Guidotti *et al.*[24] can in no way be related to the higher multipoles discussed in this paper, whose existence is due to the pressure term in Euler's equation. In fact, that additional branch was not found by Cunningham *et al.*,[36] who properly accounted for the singularity of Eq. (A11) mentioned above.

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