PHYSICAL REVIEW B VOLUME 19, NUMBER 4 15 FEBRUARY 1979

Density response function and the dynamic structure factor of thin metal films: Nonlocal effects

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(Received 14 July 1978)

We use the hydrodynamic model of the bounded electron gas to evaluate the density response function of a thin film, including the effects of electron-gas dispersion (nonlocal effects). We obtain the contribution from the complete spectrum of plasma modes to the inelastic differential scattering cross section for keV electrons. Our results are for a sharp electron-density profile at the slab surfaces. Because of nonlocal effects, the spectrum is composed of a series of distinct bulk plasmons, in addition to the two surface plasmons of a thin film. We present a detailed analysis of the dynamic structure factor of a thin film in the small-wave-vector limit. We show that for sufficiently thin films, the limits $\beta \rightarrow 0$ (which defines the local limit) and $q_{\parallel} L \rightarrow 0$ (where $q_{\parallel}$ is the wave vector of the plasmon and L is half the film thickness) are not interchangable in our expression for the differential cross section. Thus the local-approximation result of Ritchie for the transmission probability of a fast electron through a thin film is recovered in the $\beta \rightarrow 0$ limit only for $q_{\parallel} L > 1$. We also show the close relationship between the hydrodynamic density response function and the density response function obtained in the semiclassical random-phase approximation with classical specular scattering at the boundaries.

I. INTRODUCTION

Previous studies[1-6] of the problem of the interaction of an external charge and a thin metal film, have been mainly based on a local response of the electron gas. In this paper we use the hydrodynamic model of the inhomogeneous electron gas[7-13] to evaluate the density response function of a thin film, including spatially dispersive (nonlocal) effects. With this model we obtain, for the first time, in an explicit way, the contribution from the complete spectrum of plasma modes to the inelastic differential scattering cross section for an electron impinging on a metal film.

The reflection symmetry about the midplane of a film allows us to classify the normal modes as symmetric and antisymmetric under this reflection operation. The complete spectrum of normal modes (of each parity) consists of a surface plasmon and of a set of bulk plasmons. The dispersion relation of the surface plasmons of thin metal films has been measured by electron-transmission experiments.[14,15] The bulk plasmons have only been detected in a different type of experiment, namely, in the measurements of "anomalous" optical absorption in thin silver films by Lindau and Nilsson.[16] [The anomalous structure in the absorptance[17,18] can be approximately explained in terms of the peaks in $\mathrm{Im}(1/\epsilon_l)$, which occur where $\mathrm{Re}\epsilon_l(\vec{k}, \omega) = 0$, $\epsilon_l(\vec{k}, \omega)$ being the longitudinal dielectric function of the homogeneous electron gas.] In this paper we obtain the dynamic structure factor of a thin metal film, which generalizes to the *bounded* system the "loss function" appropriate to an infinite system. We are thus able to study the excitation of bulk (and surface) plasmons of a thin film by high-energy electrons. Under optimum conditions, i.e., very thin, free-electron-like metal films, the dispersion relation of the bulk plasmons could be obtained from electron-transmission experiments.

This paper is organized as follows. In Sec. II, we define the response of the electron system in a thin film to an external charge distribution (the so-called "dielectric response function") and to an external longitudinal field (the "density response function"). We evaluate both response functions within a hydrodynamic approximation.[7-13] We only consider the simplest model for the ground-state electron density profile, in which the electron density exactly replicates the (jellium) background profile. In a future publication we hope to study the contribution to the response functions from the "higher multipole" surface plasmons, whose existence is predicted by nonlocal theories[9,11,12,19] for sufficiently diffuse electron density profiles. In Sec. II we also make contact with the microscopic calculation of Griffin and Zaremba[20,21] [random-phase-approximation (RPA) dynamics plus the assumption of classical specular scattering at the boundaries]. We show that both theories give the same *form* for the Fourier coefficients of the density response function in a double-cosine Fourier representation. These coefficients depend on the properties of the electron system only through the infinite-medium response function. We show that, in fact, in this representation, the hydrodynamic density response function is obtained by replacing the RPA infinite-medium dielectric function by its hydrodynamic counterpart. A consequence of this result is that the parameter β which enters Euler's equation must be the same in the (sharp-) surface problem as in the bulk problem. Ambiguity concerning this point has been an unsatisfactory aspect[22,23] of the hydrodynamic theory in its application to surface problems.

In Sec. III we evaluate the imaginary part of the density response function. This requires a discussion of the dispersion relations of the plasma modes of a metal film. From a knowledge of the imaginary part of the density response function we proceed, in Sec. IV, to obtain the dynamic structure factor of a thin metal film and the differential scattering cross section for processes in which an external (fast) electron creates a collective mode of the electron system. We note that the hydrodynamic theory does not include the contribution to the response function from the electron-hole pair excitations. The δ-function peaks in the cross section would be broadened in a theory (like RPA) that included Landau damping.

In Sec. V, we present a detailed analysis of the dynamic structure factor in the limit $q_{\parallel}L \to 0$, where $q_{\parallel}$ is the component of the wave-vector transfer in the plane of the slab surfaces and L is one-half the film width. We give numerical results for the dynamic structure factor as a function of film thickness for forward transmission of keV electrons. One interesting result that emerges from Sec. V is that the limits $q_{\parallel}L \to 0$ and $\beta \to 0$ (where $\beta \to 0$ defines the local limit) are not interchangeable in our general expression for the dynamic structure factor. Thus, although the well-known expression for the differential cross section due to Ritchie[1] is obtained on setting $\beta = 0$ in Eq. (4.3) (see Appendix A), this procedure is valid for $q_{\parallel}L > 1$ only. (This condition is *always* satisfied in the half-space problem, in which $L \to \infty$). We show in Sec. V that when $q_{\parallel}L < 1$ the dynamic structure factor of the nonlocal theory does not reduce to the one obtained with the local theory ($\beta = 0$) upon taking the limit $\beta \to 0$. This unexpected behavior of the dynamic structure factor is a reflection of a similar feature of the dispersion relations (of which the former quantity is a functional): the limits $q_{\parallel}L \to 0$ and $\beta \to 0$ cannot be interchanged in the dispersion relations of the antisymmetric (bulk and surface) modes. Although nonlocal effects enter the dispersion relations in terms of a small parameter, the fact that this parameter is *finite* is critical in the case of the antisymmetric modes. In fact, in the limit $q_{\parallel}L \to 0$, the dispersion relation of the antisymmetric modes is not an analytic function of β at $\beta = 0$. We remark that the low-frequency response in which the symmetric surface plasmon is involved, is correctly described by the local theory.

We close this Introduction by noting that it is usually stated (see, e.g., Ref. 6 and, in a different physical case, Ref. 24) that an external charge does not interact with the bulk plasmons. This statement is based on the argument that the bulk plasmons do not give rise to a potential *outside* the solid. This is not the case in the nonlocal theory.[13] In Appendix B we write down the expression for the scalar potential, outside the film, due to the bulk plasmons of both reflection symmetries. Finally, in Appendix C we briefly discuss the influence of retardation effects.

II. DENSITY RESPONSE FUNCTION OF A THIN FILM

A. Hydrodynamic approximation

In this paper we consider a solid with a slab geometry. The ionic background is represented by a jellium model. The ensuing translational symmetry in the plane of the surfaces of the jellium slab is explicitly taken into account in defining the so-called "dielectric response function" $D(\vec{q}_{\parallel}\omega\,|zz')$ by the equation

$$n_1(\vec{q}_{\parallel}\omega\,|z) = \int_{-\infty}^{+\infty} dz'\, D(\vec{q}_{\parallel}\omega\,|zz')n_{\text{ext}}(\vec{q}_{\parallel}\omega\,|z')\,. \tag{2.1}$$

Here $n_1(\vec{q}_{\parallel}\omega\,|z)$ denotes the fluctuation in the electron number density induced by an external charge density

$$\rho_{\text{ext}}(\vec{q}_{\parallel}\omega\,|z) = |e|\,n_{\text{ext}}(\vec{q}_{\parallel}\omega\,|z)\,, \tag{2.2}$$

and we have called z the coordinate normal to the jellium surfaces (taken for convenience to be at planes $z = \pm L$). The wave vector $\vec{q}_{\parallel}$ is a two-dimensional vector in a plane parallel to those surfaces.

We start out by evaluating $D(\vec{q}_{\parallel}\omega\,|zz')$ for a hydrodynamic model of the bounded electron gas, an often used approximation.[7-13] Assuming that the total energy of the system can be expressed as a functional of the density $n(\vec{x},t)$,[7,10-12] we can deduce (via Hamilton's equations) the equations of hydrodynamics:

$$\frac{\partial}{\partial t} n + \vec{\nabla}\cdot\vec{J} = 0 \tag{2.3}$$

and

$$mn\frac{d}{dt}\vec{v} = -|e|\,n(\vec{E} - \vec{\nabla}V_{\text{back}}) - n\vec{\nabla}\frac{\delta}{\delta n}G\{n\}\,. \tag{2.4}$$

In Eq. (2.4) we have neglected retardation effects by formally setting the speed of light $c = \infty$. The total longitudinal field satisfies Poisson's equation:

$$\vec{\nabla}\cdot\vec{E}=4\pi|e|[N_+-n(\vec{x},t)+n_{\text{ext}}(\vec{x},t)]. \qquad (2.5)$$

We recall that the functional $G\{n\}$, whose functional derivative enters the "pressure term" in Eq. (2.4) represents the exchange, correlation, and internal kinetic energies of the electron system.

We next linearize the equations of motion in the usual way,[12] obtaining the following differential equation for the induced density fluctuation:

$$\beta^2\nabla^2 n_1(\vec{x},\omega)+(\omega^2-\omega_p^2)n_1(\vec{x},\omega)=-\omega_p^2 n_{\text{ext}}(\vec{x},\omega), \qquad (2.6)$$

where $\omega_p^2\equiv 4\pi n_0 e^2/m$. Here we have made two approximations. First, we have assumed[25] that the ground-state electron number density $n_0(z)$ is given by

$$n_0(z)=n_0[\Theta(z+L)-\Theta(z-L)], \qquad (2.7)$$

n_0 being equal to the background number density N_+. The second approximation consists in keeping only the "Thomas-Fermi" contribution to the density functional G. In this case, we have[11]

$$n_0\vec{\nabla}\left(\frac{\delta G}{\delta n}\right)_1=m\beta^2\vec{\nabla}n_1(\vec{x},\omega), \qquad (2.8)$$

with $\beta^2=1/3v_F^2$. We shall, however, consider β as a parameter to be determined by comparison with microscopic theory (see below).

We emphasize that the nonlocal parameter β^2 multiplies the highest derivative of the differential equation for the density fluctuations [Eq. (2.6)]. Thus, in the local theory ($\beta^2=0$) the mathematical description of the response of the electron system is completely altered. This point is eventually responsible for our result (Sec. V) that, when $q_\parallel L<1$, the $\beta\to 0$ limit of the results of the nonlocal theory can be different from what is obtained from a local theory [Eq. (2.6) with $\beta^2=0$].

Fourier transforming Eq. (2.6) and substituting Eq. (2.1) into the resulting equation leads to the differential equation for the dielectric response function $D(\vec{q}_\parallel\omega|zz')$:

$$\left(\beta^2\frac{d^2}{dz^2}+(\omega^2-\omega_p^2-\beta^2q_\parallel^2)\right)D(\vec{q}_\parallel\omega|zz')=-\omega_p^2\delta(z-z'). \qquad (2.9)$$

Here $|z|<L$, whereas $-\infty<z'<+\infty$. Thus the differential equation is homogeneous when the external charge is outside the solid. Its presence will then be reflected only in the boundary conditions. Equation (2.9) is to be solved with the boundary condition that the z component of the current fluctuation must vanish at $z=\pm L$. This condition can be stated as

$$-n_0|e|\left(\frac{d}{dz}\phi_1(\vec{q}_\parallel\omega|zz')\right)_{z=\pm L}+m\beta^2\left(\frac{d}{dz}D(\vec{q}_\parallel\omega|zz')\right)_{z=\pm L}=0, \qquad (2.10)$$

where

$$\phi_1(\vec{q}_\parallel\omega|zz')=\frac{2\pi|e|}{q_\parallel}e^{-q_\parallel|z-z'|}-\frac{2\pi|e|}{q_\parallel}\int_{-\infty}^{+\infty}dz''\,e^{-q_\parallel|z-z''|}D(\vec{q}_\parallel\omega|z''z'). \qquad (2.11)$$

We remark that since the scalar potential is given in terms of an *integral* over the density fluctuations, the usual electromagnetic boundary conditions are automatically satisfied by our solution.

Solving Eqs. (2.9)–(2.11) involves rather lengthy but straightforward algebra. Here we shall simply give the final result. We note, however, the result

$$\left(\frac{d^2}{dz}+\gamma^2\right)\frac{\sin\gamma|z-z'|}{2\gamma}=\delta(z-z'), \qquad (2.12)$$

which immediately provides a particular solution of the inhomogeneous equation (2.9) for $|z'|<L$. Here [and with reference to Eq. (2.9)] we have made the definition

$$\gamma=(+)[(\omega^2-\omega_p^2)/\beta^2-q_\parallel^2]^{1/2}, \qquad (2.13)$$

which takes the branch of the square root such that γ is positive definite.

The result for $D(\vec{q}_\parallel\omega|zz')$ can be expressed as follows:

$$D(\vec{q}_\parallel\omega|zz')=\Theta(L-|z|)\{\Theta(z'+L)\Theta(L-z')f_1(q_\parallel\omega|zz')+[\Theta(z'-L)+\Theta(-z'-L)]f_2(q_\parallel\omega|zz')\}, \qquad (2.14)$$

where

$$f_1(q_\parallel\omega|zz')=\frac{\omega_p^2}{2\beta^2\gamma}\left[-\sin\gamma|z-z'|+\frac{\cos\gamma z}{\Delta^{(s)}(q_\parallel,\omega)}\left(\frac{2\omega^2}{\omega_p^2}\frac{\gamma}{q_\parallel}e^{-q_\parallel L}\cosh q_\parallel z'-G^{(s)}(q_\parallel,\omega)\cos\gamma z'\right)-\frac{\sin\gamma z}{\Delta^{(a)}(q_\parallel,\omega)}\left(\frac{2\omega^2}{\omega_p^2}\frac{\gamma}{q_\parallel}e^{-q_\parallel L}\sinh q_\parallel z'+G^{(a)}(q_\parallel\omega)\sin\gamma z'\right)\right] \qquad (2.15)$$

and

$$f_2(q_\parallel \omega|zz') = \frac{\omega_p^2-\omega^2}{\beta^2 q_\parallel}\left(\frac{\cos\gamma z}{\Delta^{(s)}(q_\parallel,\omega)}\sinh q_\parallel L \mp \frac{\sin\gamma z}{\Delta^{(a)}(q_\parallel,\omega)}\cosh q_\parallel L\right)e^{-q_\parallel|z'|}. \quad (2.16)$$

In Eq. (2.16) the upper (lower) sign applies when $z'>L$ ($z'<-L$). Here we have introduced the functions

$$\Delta^{(s)}(q_\parallel,\omega) \equiv \cos\gamma L + \frac{2\omega^2-\omega_p^2}{\omega_p^2}\frac{\gamma}{q_\parallel}\sin\gamma L - e^{-2q_\parallel L}[\cos\gamma L-(\gamma/q_\parallel)\sin\gamma L], \quad (2.17)$$

$$\Delta^{(a)}(q_\parallel,\omega) \equiv -\sin\gamma L + \frac{2\omega^2-\omega_p^2}{\omega_p^2}\frac{\gamma}{q_\parallel}\cos\gamma L - e^{-2q_\parallel L}[\sin\gamma L+(\gamma/q_\parallel)\cos\gamma L], \quad (2.18)$$

$$G^{(s)}(q_\parallel,\omega) \equiv \Delta^{(a)}(q_\parallel,\omega) + 2e^{-2q_\parallel L} \times [\sin\gamma L+(\gamma/q_\parallel)\cos\gamma L], \quad (2.19)$$

and

$$-G^{(a)}(q_\parallel,\omega) \equiv \Delta^{(s)}(q_\parallel,\omega) + 2e^{-2q_\parallel L} \times [\cos\gamma L+(\gamma/q_\parallel)\sin\gamma L]. \quad (2.20)$$

Now, the dielectric response function D was introduced in this paper because it arises most naturally in the hydrodynamic theory. Our main concern, however, is the density response function $\chi(\vec{q}_\parallel\omega|zz')$, defined by

$$n_1(\vec{q}_\parallel\omega|z) = \int_{-\infty}^{+\infty} dz'\,\chi(\vec{q}_\parallel\omega|zz')U_{\text{ext}}(\vec{q}_\parallel\omega|z'). \quad (2.21)$$

Here U_{ext} is the potential energy of an electron in a longitudinal field. It is related to n_{ext} through Poisson's equation, which can be used to obtain χ in terms of D (that is, in terms of f_1 and f_2). Carrying out the required algebra we obtain the following result for χ:

$$\begin{aligned}\chi(\vec{q}_\parallel\omega|zz') = {} & \Theta(L-|z|)\Theta(L-|z'|)\\ & \times\left[-\frac{1}{4\pi e^2}\frac{\omega_p^2}{\beta^2}\delta(z-z') + \frac{1}{4\pi e^2}\frac{\omega_p^2(\omega^2-\omega_p^2)}{2\beta^4\gamma}\left(\sin\gamma|z-z'| + \frac{G^{(s)}(q_\parallel,\omega)}{\Delta^{(s)}(q_\parallel,\omega)}\cos\gamma z\cos\gamma z' + \frac{G^{(a)}(q_\parallel,\omega)}{\Delta^{(a)}(q_\parallel,\omega)}\sin\gamma z\sin\gamma z'\right)\right]\\ & + \frac{1}{4\pi e^2}\frac{\omega_p^2}{2\beta^2}\Theta(L-|z|)[\delta(z'+L)F(q_\parallel\omega|z) + \delta(z'-L)F(q_\parallel\omega|-z)], \end{aligned} \quad (2.22)$$

where

$$\begin{aligned}F(q_\parallel\omega|z) \equiv {} & \cos\gamma(z+L) - [2e^{-q_\parallel L}\sinh q_\parallel L + G^{(s)}(q_\parallel,\omega)\sin\gamma L][\cos\gamma z/\Delta^{(s)}(q_\parallel,\omega)]\\ & -[2e^{-q_\parallel L}\cosh q_\parallel L + G^{(a)}(q_\parallel,\omega)\cos\gamma L][\sin\gamma z/\Delta^{(a)}(q_\parallel,\omega)]. \end{aligned} \quad (2.23)$$

We note that χ becomes singular as $\beta\to 0$ [see comment below Eq. (2.8)]. In Sec. III we evaluate Imχ, which in Sec. IV is used to calculate the dynamic structure factor of a thin film. Thus Eq. (2.22) is the basis of the rest of our analysis.

B. Comparison with the microscopic theory

It is of interest to establish whether the response function in our hydrodynamic theory represents a well-defined approximation to the corresponding response function provided by the microscopic (RPA) theory.[20,21] In order to answer this question we first express our hydrodynamic response function in the double-cosine Fourier representation in which the "semiclassical" RPA response function is known[20,21] in closed form. For this purpose, we shift the origin $z=0$ such that it now lies on the left-hand edge of the film (whose width is $d=2L$) and introduce the Fourier components $\chi(\vec{q}_\parallel\omega|kk')$ such that

$$\chi(\vec{q}_\parallel\omega|zz') = \frac{1}{(d)^2}\sum_{k,k'}\cos kz\cos k'z'\,\chi(\vec{q}_\parallel\omega|kk'). \quad (2.24)$$

From the theory of Fourier series, we know that $k=n\pi/d$, $k'=n'\pi/d$, and n and n' take on values $0, \pm1, \pm2, \ldots$. The inverse transformation is

$$\chi(\vec{q}_\parallel\omega|kk') = \int_0^d dz\int_0^d dz'\cos kz\cos k'z'\,\chi(\vec{q}_\parallel\omega|zz'). \quad (2.25)$$

We note that the inversion symmetry about the midplane of the slab [which is apparent in the representation (2.22) for χ] leads to the restriction that k and k' must have the same parity (that is, n and n' must be both even or both odd integers).

Our program is then to substitute Eq. (2.22) (after making the change of variables $z \to L+z$, $z' \to L+z'$) into the right-hand side of Eq. (2.25) and carry out the required integrals. The ensuing algebra is lengthy and here we only display the answer. [It may be worth remarking that the terms that include $\delta(z' \pm L)$ in Eq. (2.22) do not contribute to the final expression (2.27)]. Recalling that

$$\chi_B(\vec{q}, \omega) \equiv \chi(\vec{q}_{\parallel}, q_z; \omega) = \frac{\omega_p^2}{4\pi e^2} \frac{q^2}{\omega^2 - \omega_p^2 - \beta^2 q^2} \tag{2.26}$$

(with $q^2 = q_{\parallel}^2 + q_z^2$) is the hydrodynamic density response function in the case of the infinite, homogeneous electron gas,[26] we cast the result for $\chi(\vec{q}_{\parallel}\omega|kk')$ as follows:

$$\begin{aligned}\chi(\vec{q}_{\parallel}\omega|kk') &= \chi_B(\vec{q}, \omega)\tfrac{1}{2}d(\delta_{k',k} + \delta_{k',-k}) \\ &\quad - \frac{2q_{\parallel}}{4\pi e^2}\frac{v(\vec{q})\chi_B(\vec{q}, \omega)v(\vec{q}')\chi_B(\vec{q}', \omega)}{D^{(s,a)}(q_{\parallel}, \omega)},\end{aligned} \tag{2.27}$$

where $\vec{q} = (\vec{q}_{\parallel}, k)$, $\vec{q}' = (\vec{q}_{\parallel}, k')$,

$$v(\vec{q}) = 4\pi e^2/(q_{\parallel}^2 + k^2), \tag{2.28}$$

and we have made the definitions

$$\frac{1}{D^{(s)}(q_{\parallel}, \omega)} = \frac{2(\omega^2 - \omega_p^2)}{\omega_p^2}\frac{\gamma}{q_{\parallel}} e^{-q_{\parallel}L}\frac{\sinh q_{\parallel}L \sin\gamma L}{\Delta^{(s)}(q_{\parallel}\omega)} \tag{2.29a}$$

and

$$\frac{1}{D^{(a)}(q_{\parallel}, \omega)} = \frac{2(\omega^2 - \omega_p^2)}{\omega_p^2}\frac{\gamma}{q_{\parallel}} e^{-q_{\parallel}L}\frac{\cosh q_{\parallel}L \cos\gamma L}{\Delta^{(a)}(q_{\parallel}\omega)}. \tag{2.29b}$$

We recall that $\Delta^{(s)}(q_{\parallel}, \omega)$ and $\Delta^{(a)}(q_{\parallel}, \omega)$ are given by Eqs. (2.17) and (2.18), respectively. In Eq. (2.27) it is understood that when n and n' are even (odd) integers, the denominator of the "surface term" is $D^{(s)}(q_{\parallel}, \omega)$ $[D^{(a)}(q_{\parallel}, \omega)]$.

Equation (2.27) has exactly the same *form* as the corresponding RPA result[20,21] which, we recall, is derived with the assumption of classical specular scattering at the jellium surfaces [which results in a ground-state electron density of the form (2.7)]. In that case, $\chi_B(\vec{q}, \omega)$ is the RPA bulk density response function and the definition that corresponds to Eqs. (2.29) is

$$D_{\mathrm{RPA}}^{(s,a)}(q_{\parallel}, \omega) = 1 + \frac{1}{d}\sum_{k\,\binom{\text{even}}{\text{odd}}}\frac{2q_{\parallel}}{q_{\parallel}^2 + k^2}\frac{1}{\epsilon_B(\vec{q}_{\parallel}, k; \omega)}, \tag{2.30}$$

where $\epsilon_B(\vec{q}, \omega)$ is the RPA bulk dielectric function.[26] In Eq. (2.30) the sum over even (odd) values of m defines $D_{\mathrm{RPA}}^{(s)}(q_{\parallel}, \omega)$ $[D_{\mathrm{RPA}}^{(a)}(q_{\parallel}, \omega)]$.

The formal identity between the hydrodynamic and the RPA results for $\chi(\vec{q}_{\parallel}\omega|kk')$ suggests that the hydrodynamic model gives a well-defined approximation to the RPA in *surface* problems as well as in the *bulk* problem. To establish the relation between both models uniquely, all we have to do is investigate whether substituting the bulk RPA dielectric function by its hydrodynamic analogue in Eq. (2.30), we recover Eq. (2.29). This is, in fact, the case. The proof of this assertion makes use of the following result ($z_n = in\pi/d$):

$$\sum_n \frac{\omega^2 - \beta^2 q_{\parallel}^2 + \beta^2 z_n^2}{(q_{\parallel}^2 - z_n^2)(\gamma^2 + z_n^2)} = \frac{d}{2}\frac{\omega^2}{(\omega^2 - \omega_p^2)}\begin{cases}\dfrac{\omega^2}{q_{\parallel}}\coth q_{\parallel}L + \dfrac{\omega_p^2}{\gamma}\cot\gamma L & (2.31\text{a})\\[2ex] \dfrac{\omega^2}{q_{\parallel}}\tanh q_{\parallel}L - \dfrac{\omega_p^2}{\gamma}\tan\gamma L\,. & (2.31\text{b})\end{cases}$$

The upper (lower) equation obtains when the sum runs over all even (odd) integers n. The result (2.31) can be obtained by the method employed in the theory of finite-temperature Green's functions to evaluate frequency sums.[27]

An obvious corollary to this result (i.e., in the double-cosine Fourier representation the hydrodynamic density response function of a thin film is obtained from the corresponding RPA response function by replacing the RPA bulk dielectric function by its hydrodynamic counterpart), is that the value of β^2 that is implicit in Eq. (2.27) [and hence the value of β^2 in Eq. (2.22)] is fixed by considerations pertaining to the theory of the *infinite* electron gas.[28] Since this point has given rise to some controversy in the literature[5,22,23] we now consider it in some detail. We recall that in the case of the uniform electron gas, the choice[8] $\beta^2 = 3/5v_F^2$ ensures that the bulk-plasmon dispersion relation given by hydrodynamics agrees, to lowest order in q^2/k_F^2, with that obtained in the RPA. The above corollary requires that we use *the same* value of β in determining the surface-plasmon dispersion relation. The dispersion relation so obtained [see Eq. (3.25)] agrees, to $O(q_{\parallel})$ with that first obtained microscopically by Wagner.[29]

We noted before that the Thomas-Fermi approximation gives $\beta^2 = 1/3v_F^2$. Thus we still lack the "correct" functional at high frequencies. We emphasize that what we have proved in this section is that the introduction of a (sharp) surface does not add any *new* inconsistencies in the hydrodynamic theory (contrary to what is implied in Ref. 22). If we had a first-principles reason why the

Thomas-Fermi $G\{n\}$ for the *uniform* electron gas should be multiplied by $\frac{5}{9}$ at $\omega \sim \omega_p$, we would immediately have a theory for the *bounded* system with the same degree of validity.

Further insight into this discussion can be gained by referring to the explicit solution of the semiclassical collisionless Boltzmann equation obtained by Griffin and Zaremba.[20] In their analysis, the dynamics of the electron gas enters only through the semiclassical density response function of a uniform, free-electron gas, $\pi_0(\vec{q}, \omega)$, given by

$$\pi_0(\vec{q}, \omega) = -\int \frac{d^3p}{(2\pi)^3} \frac{\vec{q}\cdot\vec{\nabla}_p f(\epsilon_p)}{\omega - \vec{q}\cdot\vec{p}/m}\,. \tag{2.32}$$

However, an explicit expression of π_0 is *not* needed in solving the self-consistent equation for the Fourier coefficients $n_1(\vec{q}_{\parallel}\omega|k_z)$ [Eq. (2.22) of Ref. 20]. Solving that equation and noting that

$$\epsilon(\vec{q}, \omega) = 1 - v(\vec{q})\pi_0(\vec{q}, \omega)\,, \tag{2.33}$$

gives Eqs. (2.27) and (2.30). The analysis of Griffin and Zaremba[20] shows that once one makes some approximation to the bulk Lindhard function, the self-consistent-field (SCF) theory leads to a consistent theory for the *surface* as well as *bulk* dynamics. Within this context, it is clear that the derivation of Ref. 20, with

$$\pi_0(\vec{q}, \omega) = (n_0/m)\,q^2/(\omega^2 - \beta^2 q^2) \tag{2.34}$$

would yield the same $\chi(\vec{q}_{\parallel}\omega|zz')$ given by the hydrodynamic model based on Eqs. (2.6) and (2.7).

The shortcomings of the hydrodynamic theory of the uniform electron gas are clearly seen from Eqs. (2.32) and (2.34): the analytic structure of the Lindhard function (2.32) cannot be completely described by the single-pole approximation (2.34). In fact, this statement provides a concise way of viewing Harris'[22] criticism of the hydrodynamic theory. However, we note that, Eqs. (2.32) and (2.34) are identical, up to order q^4, with the choice $\beta^2 = 3/5v_F^2$. Choosing this as the "correct" value of β, this parameter is fixed, once and for all, for *both* bulk and surface phenomena.

Utilizing the identity of Eqs. (2.32) and (2.34) for small values of $q = (q_{\parallel}^2 + k^2)^{1/2}$, it is possible to show that, when $q_{\parallel} \to 0$, the dispersion relations of the normal modes of a thin film that are characterized by small values of k (i.e., the surface plasmons and the first few bulk plasmons; see Secs. III–V and Ref. 20) are the same in both the SCF microscopic theory and in the hydrodynamical model.

We summarize the preceding discussion by stating that, at small values of $q_{\parallel}$, the hydrodynamic theory of the bounded electron gas is a good approximation to the microscopic SCF theory of the electronic collective modes of a metal slab. The advantage of the hydrodynamic theory is that the calculations are simple enough that quantities of importance, like the dynamic structure factor, may be obtained in closed form.

III. IMAGINARY PART OF THE DENSITY RESPONSE FUNCTION

The density response function obtained in Sec. II can be used as the basis for the study of a variety of phenomena dealing with the interaction of external charges and the electronic collective modes of a thin film. In Secs. IV and V, we shall use it to evaluate the loss spectrum of a fast electron transmitted through a metal film. There we shall only need the imaginary part of $\chi(\vec{q}_{\parallel}\omega|zz')$, whose explicit expression we now obtain. From the structure of Eq. (2.22) it is clear that the poles of $\chi(\vec{q}_{\parallel}\omega|zz')$ are given by the zeros of $\Delta^{(s)}(q_{\parallel}, \omega)$ and $\Delta^{(a)}(q_{\parallel}, \omega)$. (It may be easily checked that the zeros of γ do not give rise to poles of the response function.) It is convenient to analyze the pole structure of $\chi(\vec{q}_{\parallel}\omega|zz')$ (and hence its imaginary part) separately in the regions of the $(\omega, q_{\parallel})$ plane where γ is real and where it is imaginary.

A. γ real: "Bulk-plasmon region"

From the zeros of $\Delta^{(s,a)}(q_{\parallel}, \omega)$ we can establish the following eigenvalue equations for $\gamma(q_{\parallel})$:

$$\gamma \tan\gamma L = -q_{\parallel}\, \frac{\omega_+^2(q_{\parallel})}{\omega_-^2(q_{\parallel}) + \beta^2(q_{\parallel}^2 + \gamma^2)} \quad \text{(symmetric)} \tag{3.1}$$

and

$$\gamma \cot\gamma L = q_{\parallel}\, \frac{\omega_-^2(q_{\parallel})}{\omega_+^2(q_{\parallel}) + \beta^2(q_{\parallel}^2 + \gamma^2)} \quad \text{(antisymmetric)}\,, \tag{3.2}$$

where we have introduced the frequencies

$$\omega_{\pm}^2(q_{\parallel}) \equiv \tfrac{1}{2}\omega_p^2(1 \mp e^{-2q_{\parallel}L})\,. \tag{3.3}$$

We shall refer to the solutions of Eqs. (3.1) and (3.2) as $\gamma_{s,n}(q_{\parallel})$ and $\gamma_{a,n}(q_{\parallel})$, respectively. It is useful to recast the eigenvalue equations as follows:

$$\gamma_{s,n}(q_{\parallel}) = (1/L)(n\pi - \delta_{s,n})\,, \tag{3.4}$$

where $n = 1, 2, 3, \ldots$ and

$$\gamma_{a,n}(q_{\parallel}) = (1/L)[(n + \tfrac{1}{2})\pi - \delta_{a,n}]\,, \tag{3.5}$$

where $n = 0, 1, 2, 3, \ldots$. Here

$$\delta_{s,n} \equiv \arctan\left(\frac{q_{\parallel}}{\gamma_{s,n}}\, \frac{\omega_+^2(q_{\parallel})}{\omega_-^2(q_{\parallel}) + \beta^2(q_{\parallel}^2 + \gamma_{s,n}^2)}\right) \tag{3.6}$$

and

$$\delta_{a,n} \equiv \arctan\left(\frac{q_{\parallel}}{\gamma_{a,n}}\, \frac{\omega_-^2(q_{\parallel})}{\omega_+^2(q_{\parallel}) + \beta^2(q_{\parallel}^2 + \gamma_{a,n}^2)}\right). \tag{3.7}$$

In Eqs. (3.6) and (3.7), we take the principal branch of the arctan. We note that in Eq. (3.4), the value $n=0$ is not allowed because γ is positive definite. On the other hand, in the case of Eq. (3.5), some care is required to determine whether the value $n=0$ is allowed or not. In the limit $q_\parallel L \to 0$ this is simple, however, because $\delta_{a,n} \to 0$ and hence $\gamma_{a,n=0} \simeq \pi/2L$, $n=0$ being thus allowed. For finite values of $q_\parallel L$, Eq. (3.7) is really an eigenvalue equation for $\delta_{a,n}$ and this question has to be settled along different lines. This is discussed below and in Sec. V.

We emphasize that the "phase shifts" $\delta_{s,n}$ and $\delta_{a,n}$ represent the difference between the solutions of the eigenvalue equations (3.1) and (3.2) and the values of the "effective wave vectors" that arise in a standing-wave analysis of the modes of a metal film.[16] Considering $\delta_{s,n}$ and $\delta_{a,n}$ as functions of γ for fixed $q_\parallel$, we see that as $\gamma \to \infty$, both $\delta_{s,n}$ and $\delta_{a,n} \to 0$; as $\gamma \to 0$, both $\delta_{s,n}$ and $\delta_{a,n} \to \frac{1}{2}\pi$. The phase shifts are evaluated in the small-wave-vector limit in Sec. V.

A graphical solution of Eqs. (3.1) and (3.2) helps to visualize the preceding discussion. In Fig. 1, we present the graphical solution of Eq. (3.1); the intersections in the lower half plane correspond to the roots $\gamma_{s,n}(q_\parallel)$. Clearly, the value $n=0$ is excluded. In Fig. 2 we give the graphical solution of Eq. (3.2): the intersections in the upper half plane define the roots $\gamma_{a,n}(q_\parallel)$. For definiteness, in both figures, we used parameters appropriate to a 40-Å-thick potassium film. However, the qualitative features are quite general. In the case of Fig. 2, it is possible to show that the existence of the mode corresponding to $n=0$ depends on whether the curve corresponding to the right-hand side of Eq. (3.2) intersects the vertical axis *below* unity. This condition can be expressed as

$$q_\parallel L\left(\frac{1+e^{-2q_\parallel L}}{1-e^{-2q_\parallel L}+\Lambda(q_\parallel L)^2}\right)<1\,, \tag{3.8}$$

where the (dimensionless) parameter Λ is defined as

$$\Lambda \equiv 2\beta^2/\omega_p^2 L^2\,. \tag{3.9}$$

It can also be shown that there is a critical wave vector $q_\parallel^c$ given by

$$q_\parallel^c L \simeq \tfrac{3}{2}\Lambda\,, \tag{3.10}$$

such that the inequality (3.8) is satisfied for $q_\parallel < q_\parallel^c$. Thus, for $q_\parallel > q_\parallel^c$, the $n=0$ antisymmetric bulk mode is absent. For the parameters of Fig. 2, we find $q_\parallel^c L \simeq 0.008$. Thus this mode is present only for the curve corresponding to $q_\parallel L = 0.001$. Finally, it may be worth mentioning here that the "disappearance" of the $n=0$ *bulk* antisymmetric mode for $q_\parallel > q_\parallel^c$ is accompanied by the "appearance" of the antisymmetric *surface* mode.[30]

The frequencies associated with $\gamma_{s,n}$ and $\gamma_{a,n}$ are given by [see Eq. (2.13)]:

$$\omega_{s,n}^2(q_\parallel) = \omega_p^2 + \beta^2 q_\parallel^2 + \beta^2\gamma_{s,n}^2(q_\parallel) \tag{3.11}$$

and

$$\omega_{a,n}^2(q_\parallel) = \omega_p^2 + \beta^2 q_\parallel^2 + \beta^2\gamma_{a,n}^2(q_\parallel)\,. \tag{3.12}$$

It can be shown (see Appendix B) that $\omega_{s,n}$ and $\omega_{a,n}$ are the frequencies at which normal modes of the form

$$n(q_\parallel\omega|z) \sim \begin{cases}\cos\gamma_{s,n}z & \text{(symmetric)}\\ \sin\gamma_{a,n}z & \text{(antisymmetric)}\end{cases} \tag{3.13}$$

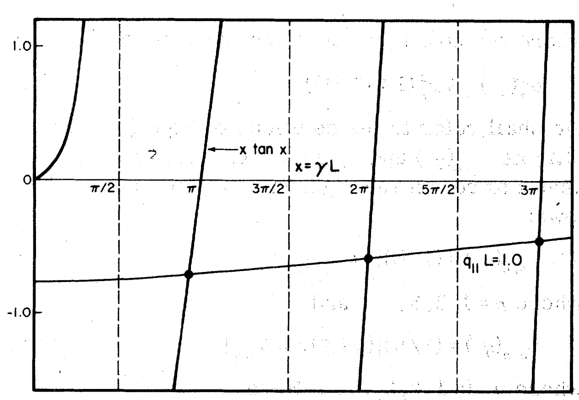

FIG. 1. Graphical solution of Eq. (3.1) for parameters appropriate to a potassium film ($r_s = 4.86$) for thickness $d = 2L = 40$ Å (we use the same parameters in Figs. 2–4; qualitatively, these figures apply to thicker films). The graph of the right-hand side of Eq. (3.1) for $q_\parallel L = 1.0$ is shown. For small values of $q_\parallel L$, this curve becomes indistinguishable with the x axis.

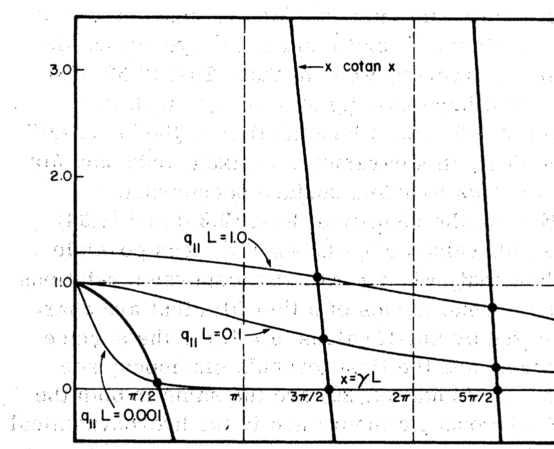

FIG. 2. Graphical solution of Eq. (3.2). The curve that represents the right-hand side of Eq. (3.2) for $q_\parallel L = 0.001$ (0.1) intersects the vertical axis slightly below (above) unity. We note that here $q_\parallel^c L \doteq 0.008$ (see text). The horizontal line (it lies slightly above unity) represents the right-hand side of Eq. (C9).

can exist in a thin film. These density fluctuations are, respectively, the symmetric and antisymmetric bulk plasmons of the metal film.

We next turn to calculating the imaginary part of $\chi(\vec{q}_\parallel\omega|zz')$ in the bulk-plasmon region. For brevity, in the remainder of this subsection, we refer explicitly to the symmetric modes only. The counterparts of Eqs. (3.14)–(3.17) and (3.19) for the antisymmetric modes are obtained substituting $\omega_{s,n}\to\omega_{a,n}$, $\gamma_{s,n}\to\gamma_{a,n}$, $\omega_+\to\omega_-$, and $\sin\gamma_{s,n}L\to\cos\gamma_{a,n}L$ in the appropriate equations.

We note that $\Delta^{(s)}$ depends on the frequency ω only through its square, ω^2. Thus we can write (with a slight inconsistency in the notation):

$$\Delta^{(s)}(q_\parallel,(\omega-i\eta)^2) \simeq \Delta^{(s)}(q_\parallel,\omega^2)-2i\omega\eta\frac{d}{d\omega^2}\Delta^{(s)}(q_\parallel,\omega^2) \qquad (3.14)$$

to first order in η. Now, noting that

$$\Delta^{(s)}(q_\parallel,\omega^2_{s,n}(q_\parallel))=0 \qquad (3.15)$$

and utilizing well-known properties of the δ function, we can show that

$$\operatorname{Im}1/\Delta^{(s)}(q_\parallel,\omega^2) = \pi\,\mathrm{sgn}\omega\sum_{n=1}^{\infty}\left(\frac{d}{d\omega^2}\Delta^{(s)}(q_\parallel,\omega^2)\right)^{-1}_{\omega^2=\omega^2_{s,n}}\times\delta(\omega^2-\omega^2_{s,n}(q_\parallel)). \qquad (3.16)$$

We note that $G^{(s)}$ also depends on ω through its square only [see Eq. (2.19)]. We can then show the surprisingly simple result

$$G^{(s)}(q_\parallel,\omega^2=\omega^2_{s,n}(q_\parallel))=-2\frac{\omega_+^2(q_\parallel)}{\omega_p^2}\frac{1}{\sin\gamma_{s,n}L}. \qquad (3.17)$$

We note that from Eq. (3.17) and the identity $f(x)\delta(x-a)=f(a)\delta(x-a)$, it follows that the imaginary part of $F(q_\parallel\omega|z)$ [see Eq. (2.22)] vanishes.

We have now all the elements to obtain the imaginary part of $\chi(\vec{q}_\parallel\omega|zz')$ in the bulk-plasmon region. The final result is conveniently written

$$\operatorname{Im}\chi(\vec{q}_\parallel\omega|zz')=-\frac{\omega_p^2}{4e^2}\frac{\mathrm{sgn}\omega}{\beta^2L}\Theta(L-|z|)\Theta(L-|z'|)\left(\sum_{n=1}^{\infty}\frac{1}{D^{(+)}_{B,n}(q_\parallel)}\cos\gamma_{s,n}z\cos\gamma_{s,n}z'\,\delta(\omega^2-\omega^2_{s,n}(q_\parallel))+\sum_{n=0}^{\infty}\frac{1}{D^{(-)}_{B,n}(q_\parallel)}\sin\gamma_{a,n}z\sin\gamma_{a,n}z'\,\delta(\omega^2-\omega^2_{a,n}(q_\parallel))\right), \qquad (3.18)$$

where we have defined

$$D^{(+)}_{B,n}(q_\parallel)\equiv\frac{1}{\omega^2_{s,n}(q_\parallel)-\omega_p^2}\left[-1+\frac{\sin^2\gamma_{s,n}L}{q_\parallel L}\left(\frac{3\omega^2_{s,n}(q_\parallel)-[2\omega_p^2+\omega_+^2(q_\parallel)]-2\beta^2q_\parallel^2}{\omega_+^2(q_\parallel)}\right)\right] \qquad (3.19)$$

and $D^{(-)}_{B,n}$ is obtained from $D^{(+)}_{B,n}$ via the substitutions indicated above Eq. (3.14). It is understood that the $n=0$ term in Eq. (3.18) is included for $q_\parallel<q_\parallel^c$ only.

B. γ imaginary: "Surface-plasmon" region

With the substitution $\gamma\to i\hat{\gamma}$, the equations $\Delta^{(s,a)}(q_\parallel,\omega)=0$ are conveniently expressed as eigenvalue equations for $\hat{\gamma}(q_\parallel)$:

$$\hat{\gamma}\tanh\hat{\gamma}L=q_\parallel\frac{\omega_+^2(q_\parallel)}{\omega_-^2(q_\parallel)+\beta^2q_\parallel^2-\beta^2\hat{\gamma}^2} \qquad (3.20)$$

and

$$\hat{\gamma}\coth\hat{\gamma}L=q_\parallel\frac{\omega_-^2(q_\parallel)}{\omega_+^2(q_\parallel)+\beta^2q_\parallel^2-\beta^2\hat{\gamma}^2}, \qquad (3.21)$$

respectively. The frequencies $\omega_\pm(q_\parallel)$ [defined in Eq. (3.2)] are the frequencies corresponding to density fluctuations of the form

$$n(q_\parallel,\omega_\pm(q_\parallel)|z)\sim\delta(z+L)\pm\delta(z-L), \qquad (3.22)$$

which are the symmetric and antisymmetric "surface" plasmons of the thin film in the local theory.[5] (Note that $\hat{\gamma}\sim\beta^{-1}$ as $\beta\to0$.)

We now discuss the graphical solution of Eqs. (3.20) and (3.21). It is easy to verify that $\hat{\gamma}=q_\parallel$ is a solution to both equations, but this root is spurious, since density fluctuations of the form $\cosh q_\parallel z$ or $\sinh q_\parallel z$ do not give $J_z(q_\parallel\omega|z=\pm L)=0$.

As illustrated in Figs. 3 and 4, there is a second solution to each of Eqs. (3.20) and (3.21). We shall call it $\hat{\gamma}_s(q_\parallel)$ and $\hat{\gamma}_a(q_\parallel)$, respectively. From Fig. 3 it is obvious that the root $\hat{\gamma}_s(q_\parallel)$ exists for all $q_\parallel$, whereas the presence of the root $\hat{\gamma}_a(q_\parallel)$ (Fig. 4) depends on whether the curve representing the right-hand side of Eq. (3.21) intersects the vertical axis *above* unity. It is easy to show that this condition corresponds to the opposite of the inequality (3.8). We thus conclude that the antisymmetric surface mode only exists for $q_\parallel>q_\parallel^c$ [given by (3.10)].[31] The total number of normal modes is, of course, independent of $q_\parallel$, since for $q_\parallel>q_\parallel^c$, the $n=0$ antisymmetric bulk mode ceases to exist.

The frequencies associated with $\hat{\gamma}_{a,s}(q_\parallel)$ are given by

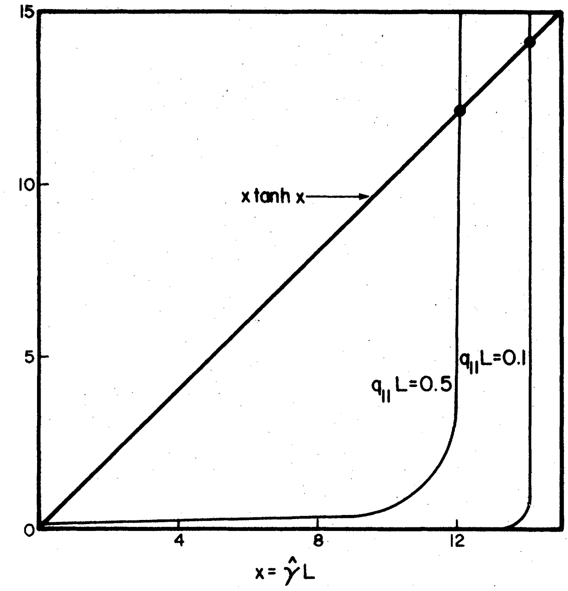

FIG. 3. Graphical solution of Eq. (3.20) for two values of the product $q_\parallel L$. The parameters of the system are the same as those of Figs. 1 and 2.

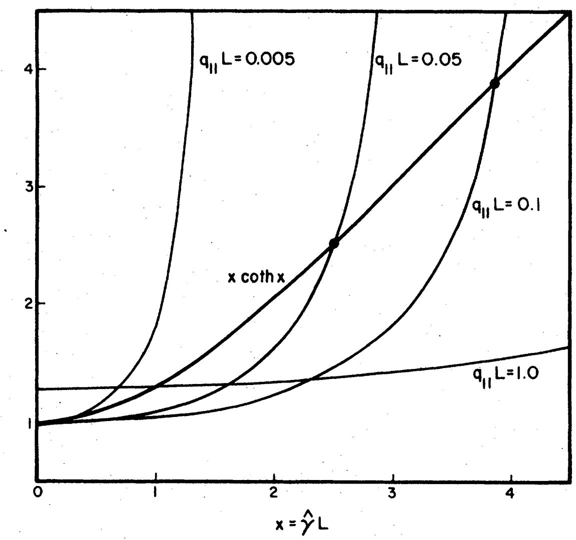

FIG. 4. Graphical solution of Eq. (3.21) for four values of $q_\parallel L$. The curve for $q_\parallel L = 0.005$ intersects the vertical axis slightly below unity (this does not show in the scale of the figure). We recall that here $q_\parallel^c L = 0.008$.

$$\omega^2_{s,a}(q_\parallel) = \omega_p^2 + \beta^2 q_\parallel^2 - \beta^2 \hat{\gamma}_{s,a}(q_\parallel) . \tag{3.23}$$

It can be shown (see Appendix B) that $\omega_s(q_\parallel)$ and $\omega_a(q_\parallel)$ are the frequencies at which normal modes of the form

$$n(q_\parallel \omega \,|z) \sim \begin{cases} \cosh\hat{\gamma}_s z \text{ (symmetric)}, \\ \sinh\hat{\gamma}_a z \text{ (antisymmetric)} \end{cases} \tag{3.24}$$

can exist in the thin film. These modes are respectively, the symmetric and antisymmetric "surface" plasmons in the nonlocal theory. It is straightforward to show that in the limit $q_\parallel L \gg 1$ both $\omega_s(q_\parallel)$ and $\omega_a(q_\parallel)$ approach the well-known expression for the surface plasmon in the hydrodynamic theory, namely,[5]

$$\omega^2_{\mathrm{SP}} = \tfrac{1}{2}\left[\omega_p^2 + \beta q_\parallel (2\omega_p^2 + \beta^2 q_\parallel^2)^{1/2} + \beta^2 q_\parallel^2\right] . \tag{3.25}$$

We can now evaluate the imaginary part of $\chi(\vec{q}_\parallel \omega | zz')$ in the surface-plasmon region. Noting that

$$\Delta^{(s,a)}(q_\parallel, \omega_{s,a}(q_\parallel)) = 0 , \tag{3.26}$$

we can establish the counterparts of Eqs. (3.16)–(3.19). This leads to the result

$$\mathrm{Im}\chi(\vec{q}_\parallel \omega | zz') = \frac{\omega_p^2}{4e^2}\,\frac{\mathrm{sgn}\,\omega}{\beta^2 L}\,\Theta(L - |z|)\Theta(L - |z'|)\left(\frac{1}{D^{(+)}_{\mathrm{sur}}(q_\parallel)} \cosh\hat{\gamma}_s z \cosh\hat{\gamma}_s z' \,\delta(\omega^2 - \omega_s^2(q_\parallel)) + \frac{1}{D^{(-)}_{\mathrm{sur}}(q_\parallel)} \sinh\hat{\gamma}_a z \sinh\hat{\gamma}_a z' \,\delta(\omega^2 - \omega_a^2(q_\parallel))\right) \tag{3.27}$$

where

$$D^{(+)}_{\mathrm{sur}}(q_\parallel) \equiv \frac{1}{\omega_s^2(q_\parallel) - \omega_p^2}\left[1 + \frac{\sinh^2\hat{\gamma}_s L}{q_\parallel L}\left(\frac{3\omega_s^2(q_\parallel) - [2\omega_p^2 + \omega_+^2(q_\parallel)] - 2\beta^2 q_\parallel^2}{\omega_+^2(q_\parallel)}\right)\right] \tag{3.28}$$

and $D^{(-)}_{\mathrm{sur}}$ is obtained from $D^{(+)}_{\mathrm{sur}}$ with the substitutions $\omega_s \to \omega_a$, $\omega_+ \to \omega_-$, $\sinh\hat{\gamma}_s L \to \cosh\gamma_a L$, plus the change $1 \to -1$ in the first term inside the large parentheses in Eq. (3.28). We recall that the contribution to Eq. (3.27) from the antisymmetric surface mode is valid for $q_\parallel > q_\parallel^c$ only. In Sec. IV we utilize this result for $\mathrm{Im}\chi$ to evaluate the dynamic structure factor of a thin metal film.

IV. DYNAMIC STRUCTURE FACTOR OF A THIN FILM

The dyanmic structure factor[26] embodies the maximum information one can deduce from an electron inelastic scattering experiment. That information is obtained by measuring the angular distribution (i.e., momentum transfer) of inelastically scattered electrons. We recall that, in the first Born approximation (which is valid for sufficiently high incident electron energies), the differential cross section is given by the Van Hove expression

$$\frac{d^2\sigma}{d\Omega\, dE} = \frac{m^2}{(2\pi)^3\hbar^5}\,\frac{k_f}{k_0}\,v^2(\vec{q})S(\vec{q},\omega)\,, \tag{4.1}$$

where $S(\vec{q},\omega)$ is the dynamic structure factor of the solid, $\hbar\omega$ and $\hbar\vec{q}=\hbar(\vec{k}_f-\vec{k}_0)$ are, respectively, the energy and momentum transferred to the solid by the external particle (here a keV electron) and $v(\vec{q})=4\pi e^2/q^2$. We note that $\vec{q}$ is a three-dimensional vector of components $(\vec{q}_\parallel; q_z)$. For the film geometry considered in this paper, we can express the relation between $S(\vec{q},\omega)$ and the imaginary part of the density response function as follows[20] $(\omega\neq 0)$:

$$S(\vec{q},\omega)=\frac{2\hbar}{1-e^{-\beta_T\hbar\omega}}\,A\int_{-\infty}^{+\infty}dz\int_{-\infty}^{+\infty}dz'\,e^{-iq_z(z-z')}\times \mathrm{Im}\chi(\vec{q}_\parallel;\omega-i\eta|zz')\,, \tag{4.2}$$

where $\beta_T=1/k_BT$, A is the surface area of the film, and $\eta\to 0^+$. We note that the elastic peak $(\omega=0)$ has been excluded from Eq. (4.2) since it is of no interest in this paper.

A nice feature of the hydrodynamic model of a bounded electron gas is that the spatial dependence of $\mathrm{Im}\chi(\vec{q}_\parallel\omega|zz')$ is simple enough that the double integral required in Eq. (4.2) can be performed without difficulty. We find

$$\begin{aligned}S(\vec{q},\omega)=-\frac{2\hbar}{1-e^{-\beta_T\hbar\omega}}\,\frac{A}{L}\,\frac{\omega_p^2}{e^2}\,\beta^2\,\mathrm{sgn}\omega\Bigg(&\sum_{n=1}^{\infty}\frac{A^{(+)}_{B,n}(q_\parallel)}{D^{(+)}_{B,n}(q_\parallel)}\,\delta(\omega^2-\omega^2_{s,n}(q_\parallel))+\sum_{n=1}^{\infty}\frac{A^{(-)}_{B,n}(q_\parallel)}{D^{(-)}_{B,n}(q_\parallel)}\,\delta(\omega^2-\omega^2_{a,n}(q_\parallel))\\ &-\frac{A^{(+)}_{\mathrm{sur}}(q_\parallel)}{D^{(+)}_{\mathrm{sur}}(q_\parallel)}\,\delta(\omega^2-\omega_s^2(q_\parallel))-\Theta(q_\parallel-q_\parallel^c)\,\frac{A^{(-)}_{\mathrm{sur}}(q_\parallel)}{D^{(-)}_{\mathrm{sur}}(q_\parallel)}\,\delta(\omega^2-\omega_a^2(q_\parallel))\\ &+\Theta(q_\parallel^c-q_\parallel)\,\frac{A^{(-)}_{B,0}(q_\parallel)}{D^{(-)}_{B,0}(q_\parallel)}\,\delta(\omega^2-\omega^2_{a,n=0}(q_\parallel))\Bigg)\,.\end{aligned} \tag{4.3}$$

Here, we have defined

$$A^{(+)}_{B,n}(q_\parallel)=\left(\frac{q_z\cos\gamma_{s,n}L\,\sin q_zL-\gamma_{s,n}\sin\gamma_{s,n}L\,\cos q_zL}{\omega_p^2-\omega^2_{s,n}(q_\parallel)+\beta^2q^2}\right)^2, \tag{4.4}$$

$$A^{(-)}_{B,n}(q_\parallel)=\left(\frac{q_z\sin\gamma_{a,n}L\,\cos q_zL-\gamma_{a,n}\cos\gamma_{a,n}L\,\sin q_zL}{\omega_p^2-\omega^2_{a,n}(q_\parallel)+\beta^2q^2}\right)^2, \tag{4.5}$$

$$A^{(+)}_{\mathrm{sur}}(q_\parallel)=\left(\frac{q_z\cosh\hat{\gamma}_sL\,\sin q_zL+\hat{\gamma}_s\sinh\hat{\gamma}_sL\,\cos q_zL}{\omega_p^2-\omega_s^2(q_\parallel)+\beta^2q^2}\right)^2, \tag{4.6}$$

and

$$A^{(-)}_{\mathrm{sur}}(q_\parallel)=\left(\frac{q_z\sinh\hat{\gamma}_aL\,\cos q_zL-\hat{\gamma}_a\cosh\hat{\gamma}_aL\,\sin q_zL}{\omega_p^2-\omega_a^2(q_\parallel)+\beta^2q^2}\right)^2, \tag{4.7}$$

where $q^2=q_\parallel^2+q_z^2$. Thus, for a given value of the momentum transfer parallel to the plane of the slab surfaces, the dynamic structure factor of the metal film [and hence the differential scattering cross section (4.1)] has peaks at the frequencies of the collective modes discussed in Sec. III. The first two terms within the large parentheses of Eq. (4.3) give, respectively, the peaks due to the $n=1,2,3,\ldots$ symmetric and antisymmetric bulk plasmons; the third term corresponds to the symmetric surface plasmon; and the last two terms correspond to the antisymmetric surface mode (for $q_\parallel>q_\parallel^c$) and the antisymmetric $n=0$ bulk mode (for $q_\parallel<q_\parallel^c$). It is possible to show that the "weight" and frequency of the $n=0$ bulk mode turn smoothly into the corresponding quantities for the antisymmetric surface mode on letting $q_\parallel$ approach $q_\parallel^c$ from below.[32]

It will be shown in Sec. V that the weights of the bulk modes are rapidly decreasing functions of n. The spacing between the lines decreases with increasing film thickness. Thus, even for moderately thick samples (d of the order of a few hundred angstroms), the bulk plasmons give rise, in effect, to just one narrow peak at $\omega\sim\omega_p(q_\parallel)$ with $q_z\simeq 0$.

We note that q_z, the z component of the momentum transfer, is taken up by the center of mass of the film (the normal modes of the thin film do not carry momentum along the z axis). It can be expressed in terms of $q_\parallel$ and ω, through the laws of conservation of energy and momentum in the scattering process. Furthermore, the delta functions in Eq. (4.3) require that ω be equal to one of the eigenfrequencies $\omega(q_\parallel)$ for the given value of $q_\parallel$. Thus the equation that determines $q_z(q_\parallel)$ is

$$q_z^2+2\vec{k}_0\cdot\vec{q}_z+(q_\parallel^2+2\vec{k}_0\cdot\vec{q}_\parallel)-(2m/\hbar)\omega(q_\parallel)=0\,. \tag{4.8}$$

Note that $\vec{q}_{\parallel}$ is the only independent variable in Eqs. (4.4)–(4.7).

Since the hydrodynamic approximation leaves out the contribution to the spectrum of charge fluctuations from the electron-hole excitations, Landau damping is absent and the peaks in $S(\vec{q}, \omega)$ are infinitely sharp. Nonetheless at small values of $q_{\parallel}$ (see Sec. V), these peaks are expected to be sufficiently narrow even when Landau damping is included.

In Sec. V, we present a detailed analysis of the dynamic structure factor (4.3) in the limit $q_{\parallel}L \ll 1$. In Appendix A we show that in the limit $\beta = 0$ our expression (4.3) for $S(\vec{q}, \omega)$ reduces to an expression equivalent to the classic Ritchie formula[1] for the transmission probability for an electron incident on a metal film. However, this conclusion is valid for $q_{\parallel}L \gtrsim 1$ only. In effect, we show in Sec. V and Appendix A that

$$\lim_{\beta\to 0}\lim_{q_{\parallel}L\to 0} S(\vec{q}, \omega) \neq \lim_{q_{\parallel}L\to 0}\lim_{\beta\to 0} S(\vec{q}, \omega) . \tag{4.9}$$

V. APPLICATION TO NEARLY FORWARD SCATTERING

In this section we consider the $q_{\parallel}L \to 0$ limit of Eq. (4.3). This corresponds to the study of nearly forward transmission of keV electrons through thin metal films. We note that (for example) in the case of normal incidence, the momentum transfer to the plasma modes of the film can be approximated by

$$q_{\parallel} \simeq k_0\theta \simeq (E_0^{1/2}/24\pi)\theta , \tag{5.1}$$

where E_0 (the energy of the incident beam) is measured in eV and $q_{\parallel}$ is measured in Å^{-1}.[33] Then, with scattering angles of the order of 10^{-4} rad,[14] we conclude that the condition $q_{\parallel}L \ll 1$ is indeed fulfilled for all relevant energies over a substantial range of film thicknesses. For example, with $E_0 = 20$ keV, taking $d = 2L = 200$ Å, we obtain $q_{\parallel}L \simeq 0.018$.

The dynamic structure factor (4.3) is a functional of the dispersion relations of the bulk and surface plasmons of the metal film. Thus we must begin by finding the explicit solutions of the dispersion relations of Sec. III in the limit $q_{\parallel}L \to 0$.

A. Bulk plasmons

Expanding both sides of Eqs. (3.1) and (3.2) in powers of $(q_{\parallel}L)$ and equating the coefficients of like powers on both sides of the respective equations we obtain, to lowest order,

$$\gamma_{s,n}(q_{\parallel}) \simeq \frac{n\pi}{L} - q_{\parallel}^2 \frac{L}{n\pi} \frac{\omega_p^2}{\omega_p^2 + \beta^2(n\pi/L)^2} , \tag{5.2}$$

with $n = 1, 2, 3, \ldots$ and

$$\gamma_{a,n}(q_{\parallel}) \simeq \left(n + \frac{1}{2}\right)\frac{\pi}{L} - q_{\parallel}\frac{\omega_p^2 L^2}{\beta^2}\frac{1}{(n+\frac{1}{2})^3\pi^3} , \tag{5.3}$$

where $n = 0, 1, 2, 3, \ldots$. In Eq. (5.2), the value $n = 0$ is excluded because γ is positive definite. We note that a comparison of Eqs. (5.2) and (5.3) with Eqs. (3.4) and (3.5) yields the values of the phase shifts $\delta_{s,n}$ and $\delta_{a,n}$ to lowest order in $(q_{\parallel}L)$. The frequencies corresponding to Eqs. (5.2) and (5.3) are given by

$$\omega_{s,n}^2(q_{\parallel}) \simeq \omega_p^2 + \beta^2\left(\frac{n\pi}{L}\right)^2 + \beta^2 q_{\parallel}^2\left(1 - \frac{2\omega_p^2}{\omega_p^2 + \beta^2(n\pi/L)^2}\right) \tag{5.4}$$

and

$$\omega_{a,n}^2(q_{\parallel}) \simeq \omega_p^2 + \beta^2\left(n + \frac{1}{2}\right)^2\frac{\pi^2}{L^2} - q_{\parallel}L\frac{2\omega_p^2}{(n+\frac{1}{2})^2\pi^2} . \tag{5.5}$$

An interesting feature of these results is that, in the limit $\beta \to 0$, the frequencies of the symmetric modes reduce identically to ω_p (as one would have expected) but the frequencies of the antisymmetric modes do not. This is because the second term in the expansion (5.3) is proportional to β^{-2}. In fact, the next term in that expansion is proportional to β^{-4}, so that the quadratic term in the expansion (5.5) is proportional to β^{-2}. Thus, the dispersion relation for the antisymmetric bulk modes in the region $q_{\parallel}L < 1$ is not an analytic function of β at $\beta = 0$. We note that, since β is indeed finite in any physical system, there is no real divergence here. The point is, however, that (as it will be emphasized below) the local theory[1-6] does not represent the "local limit" of the nonlocal theory when the wave vectors of interest are such that $q_{\parallel}L < 1$. The reason for this unexpected feature of the nonlocal theory can be found in Eq. (3.2). For finite β, the right-hand side of Eq. (3.2) behaves like $q_{\parallel}\beta^{-2}$ in the $q_{\parallel}L \ll 1$ limit. If, however, we were to use a local theory from the beginning,[1-6] we have $\beta = 0$ and the right-hand side of Eq. (3.2) would tend to L^{-1} as $q_{\parallel}L \to 0$. Thus, the two limits are not interchangeable.[34]

We can summarize the preceding discussion in the following way. Writing down Eqs. (3.1) and (3.2) in dimensionless form, we notice that nonlocal effects enter only through the parameter Λ, defined in Eq. (3.9). Now, for physically realizable values of L and r_s (the Wigner-Seitz radius) in the metallic range, Λ is small compared to unity (even for a potassium film 40-Å thick, $\Lambda \simeq 0.005$). However, the fact that Λ is *finite* (β finite) accounts for the limits $q_{\parallel} \to 0$, $\beta \to 0$ not being interchangeable for the antisymmetric modes.

B. Surface plasmons

In this case, it is best to make use of the method of Appendix B, to which we refer the reader for details. For the symmetric mode we find, to first order in $(q_\parallel L)$,

$$\hat{\gamma}_s(q_\parallel) \simeq (\omega_p/\beta)(1 - \tfrac{1}{2} q_\parallel L) \tag{5.6}$$

and

$$\omega_s^2(q_\parallel) \simeq \omega_p^2 q_\parallel L \,. \tag{5.7}$$

We note that in the small-wave-vector limit, the right-hand side of Eq. (3.21) has a pole at the value of $\hat{\gamma}_s(q_\parallel)$ given by Eq. (5.6). (This poses no restriction on the method of Appendix B.) An alternative method of obtaining the result (5.6) is to equate to zero the expression (2.18) and solve to lowest order.

With regard to $\hat{\gamma}_a(q_\parallel)$, we find that for $q_\parallel L \to 0$ it vanishes identically. This is a reflection of the fact (encountered in Sec. III) that for $q_\parallel = 0$, the antisymmetric surface mode does not exist.

We now proceed to take the $q_\parallel L \to 0$ limit of Eq. (4.3). Performing the required algebra we find, *to lowest order in* $q_\parallel L$

$$\begin{aligned} S(\vec{q}, \omega) \underset{q_\parallel L \to 0}{\simeq} \frac{2\hbar}{1 - e^{-\beta_T \hbar\omega}} \frac{A}{L} \frac{\omega_p^2}{e^2} \operatorname{sgn}\omega \Bigg(\sum_{n=1}^{\infty} \Bigg\{ & \frac{(n\pi/L)^2}{[(q_{z0}^2)^2 - (n\pi/L)^2]^2} \left[1 + (q_\parallel L)^2 a_n^{(+)} \left(\frac{d^2}{dq_\parallel^2} \gamma_{s,n}(q_\parallel) \right)_{q_\parallel = 0} \right] \\ & \times q_{z0}^2 \sin^2 q_{z0} L \, \delta(\omega^2 - \omega_{s,n}^2(q_\parallel)) \Bigg\} \\ + \sum_{n=1}^{\infty} \Bigg\{ & \frac{(n+\frac{1}{2})^2 \pi^2/L^2}{[q_{z0}^2 - (n+1/2)^2 \pi^2/L^2]^2} \left[1 + (q_\parallel L) a_n^{(-)} \left(\frac{d}{dq_\parallel} \gamma_{a,n}(q_\parallel) \right)_{q_\parallel = 0} \right] \\ & \times q_{z0}^2 \cos^2 q_{z0} L \, \delta(\omega^2 - \omega_{a,n}^2(q_\parallel)) \Bigg\} \\ + \tfrac{1}{2} & (q_\parallel L)^2 \cos^2 q_{z0} L \, \delta(\omega^2 - \omega_s^2(q_\parallel)) \\ + & \frac{(\pi/2L)^2}{(q_{z0}^2 - \pi^2/4L^2)^2} \left[1 + (q_\parallel L) a_{n=0}^{(-)} \left(\frac{d}{dq_\parallel} \gamma_{a,n=0} \right)_{q_\parallel = 0} \right] \\ \times & q_{z0}^2 \cos^2 q_{z0} L \, \delta(\omega^2 - \omega_{a,n=0}^2(q_\parallel)) \Bigg) \,. \end{aligned} \tag{5.8}$$

The frequencies that specify the location of the δ-function peaks in Eq. (5.8) are given by Eqs. (5.4), (5.5), and (5.7), respectively. We have denoted by q_{z0} the value of q_z that corresponds to each of those peaks for $q_\parallel = 0$ (see below). The derivatives of $\gamma_{s,n}(q_\parallel)$ and $\gamma_{a,n}(q_\parallel)$ that enter Eq. (5.8) are readily obtained from Eqs. (5.2) and (5.3). We emphasize that, at $q_\parallel = 0$, $d\gamma_{a,n}/dq_\parallel$ is proportional to β^{-2}. The coefficients $a_n^{(+)}$ and $a_n^{(-)}$ have rather lengthy expressions and for brevity they are not displayed here. Suffice it to state that both sets of coefficients are functions of β with a well-defined $\beta = 0$ limit. Thus, the contribution to the differential cross section from the antisymmetric modes $(n = 0, 1, 2, \ldots)$ would blow up if we were to take the limit $\beta = 0$ of Eq. (5.8).

In Appendix A we derive an expression for the dynamic structure factor within the framework of the local theory[1] ($\beta = 0$ from the start). Consider the $q_\parallel L \to 0$ limit of $S(\vec{q}_\parallel, \omega)$ as given by Eq. (A4); comparing that result with Eq. (5.8) leads to the conclusion that, at small scattering angles, the differential scattering cross section provided by the local theory[1] *does not* represent the "local limit" ($\beta \to 0$) of the corresponding quantity as given by the nonlocal theory. We do not believe this point has been noted before in the literature. We remark that the limit $q_\parallel L \to 0$ can always be realized (even for very thick films) by letting $q_\parallel \to 0$. In a nearly-forward-transmission experiment, the values of L for which the above conclusion about the "local limit" is relevant are restricted by the condition $q_\parallel L < 1$, $q_\parallel$ being given by Eq. (5.1) (for the case of normal incidence) with $\theta \sim 10^{-4}$ rad.[14] Still, this condition allows for fairly thick samples.[35] Finally, we note that the symmetric surface-plasmon peak [the third term on the right-hand side of Eq. (5.8)] is correctly given by the local theory of Appendix A.[36]

In Figs. 5 and 6, we represent Eq. (5.8) for the case of a potassium film ($r_s = 4.86$) of various thicknesses, for $q_\parallel = 0$. For definiteness, we took $E_0 = 40$ keV and confined ourselves to normal incidence of the incoming electron beam. The position of the bulk-plasmon peaks at $q_\parallel = 0$ is obtained from Eqs. (5.4) and (5.5). The symmetric surface plasmon occurs at $\omega = 0$; its weight vanishes at $q_\parallel = 0$.[37] The rapid decrease of the weights of the successive bulk-plasmon peaks is easily explained as follows. Neglecting the "recoil term", Eq. (4.8)

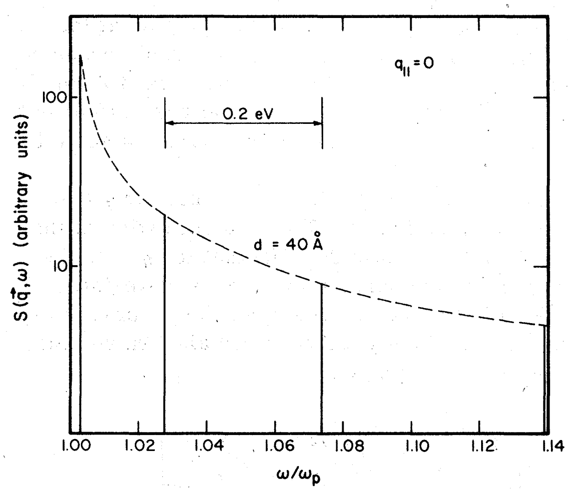

FIG. 5. Dynamic structure factor for a film: $r_s = 4.86$, $d = 40$ Å, and $q_{\parallel} = 0$. The incident beam energy is $E_0 = 40$ keV. The height of the vertical lines gives the strength of the corresponding δ-function peaks in Eq. (5.8). For the parameters of this figure, the weights of the symmetric bulk modes are negligible ($\sin q_{z0}L \simeq 0$).

gives $q_{z0} = m\,\omega(q_{\parallel})/\hbar k_0$, which can be expressed as[33]

$$q_{z0} = B\alpha_n^{(s,a)}, \tag{5.9}$$

with

$$B = 22.7\, r_s^{-3/2}/E_0^{1/2}\ \text{Å}^{-1}, \tag{5.10}$$

and

$$\alpha_n^{(s)} = (1 + \tfrac{1}{2}\Lambda\pi^2 n^2)^{1/2} \tag{5.11a}$$

for the symmetric modes ($n = 1, 2, 3, \ldots$) while

$$\alpha_n^{(a)} = [1 + \tfrac{1}{2}\Lambda\pi^2(n+\tfrac{1}{2})^2]^{1/2} \tag{5.11b}$$

for the antisymmetric modes ($n = 0, 1, 2, \ldots$). Substituting Eqs. (5.9)–(5.11) into Eq. (5.8) leads to the result that the weights of the symmetric modes decrease like n^{-2} from a maximum value for $n = 1$ and the weights of the antisymmetric modes decrease like $(2n+1)^{-2}$ from a maximum value for $n = 0$.

In Fig. 5 we show the contribution to $S(\vec{q}, \omega)$ from the antisymmetric modes for $d = 40$ Å. For this value of the film thickness, the weights of the symmetric modes are negligible ($\sin q_{z0}L \simeq 0$) and thus the plot really represents the full dynamic structure factor. We note that, for this particular value of d, the spacing between the lines is greater than the optimum present-day energy resolution ($\sim$30 meV). Thus, they could be resolved in a forward-scattering experiment.[38] Since the relative intensity of the lines becomes very small as n increases, we expect that only the first few bulk-plasmon peaks would be observable.

According to Refs. 16–18, when particle-hole excitations are included in the theory,[39] Landau

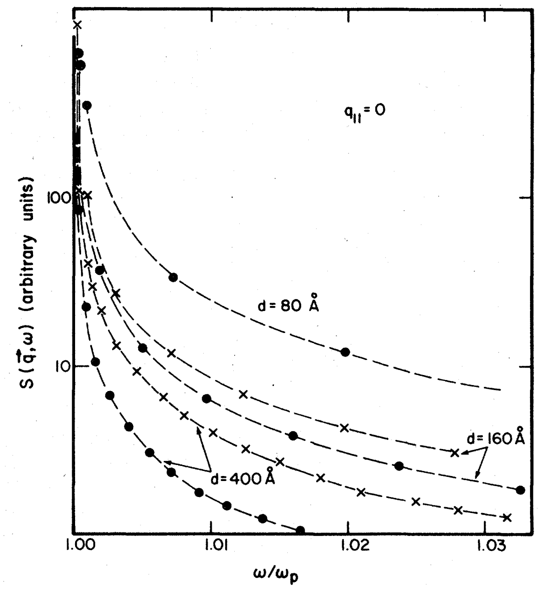

FIG. 6. Dynamic structure factor of a potassium film at $q_{\parallel} = 0$, for three values of the thickness d, with E_0 140 keV. We show the envelopes of the weights of the bulk plasmons of both parities. The dots and crosses indicate the frequencies and strengths of the corresponding peaks. For $d = 80$ Å, the weights of the symmetric modes are still very small compared to those of the antisymmetric modes (cf. Fig. 5).

damping sets in (at small wave vectors $q_{\parallel}$) for $\omega \gtrsim 1.1\omega_p$, being negligible for $\omega \lesssim 1.1\omega_p$ (and very strong for $\omega \gtrsim 1.5\omega_p$). As Figs. 5 and 6 illustrate the relevant peaks in $S(\vec{q}, \omega)$ occur precisely where Landau damping is small.[40] It is straightforward to include collisonal damping via an effective collision time in Euler's equation, but this gives rise to a negligible broadening of the lines in pure samples at low temperatures.

In Fig. 6, we illustrate the dependence of $S(\vec{q}, \omega)$ on film thickness. As d increases, the lines becomes more closely spaced and the relevant ones lie closer to $\omega = \omega_p$. For convenience we show the separate contributions from the symmetric and antisymmetric modes for each value of d (for clarity, we only show the intersection of the actual lines with the envelope of the weights). We remark that, in the case of Fig. 6, the spacing between the lines is too small for these to be resolved. However, it may be possible to observe the change in the "half-width" of the envelope function as d increases from, say, 40 to 400 Å.

A comment on how the explicit results of this section would be modified at larger values of $q_{\parallel}L$ (e.g., $q_{\parallel}L \gtrsim 1$) appears appropriate here. The main qualitative change is that both symmetric and antisymmetric surface plasmons can be excited, giving rise to peaks below ω_p (at frequencies close to those given by the local theory,

$\omega \simeq \omega_\pm$). The peak due to the $n=0$ antisymmetric bulk mode is now absent. We note that the basic input in Eq. (5.8) is the set of values of $\gamma_{s,n}$ and $\gamma_{a,n}$. As Figs. 1 and 2 make clear, only the first few roots are appreciably modified from the values that obtain at $q_{\parallel}L=0$. The main qualitative feature of Figs. 5 and 6, namely, the rapid decrease of the weights with n, remains unchanged. Of course, for a given value of $q_{\parallel}L$, the spacing between the plasmon lines decreases as the film thickness increases.

ACKNOWLEDGMENTS

I would like to thank Professor A. Griffin for suggesting this problem and for helpful discussions. I would like to acknowledge support by the National Research Council of Canada.

APPENDIX A: THE LOCAL LIMIT OF $S(\vec{q}, \omega)$

In this appendix we take the $\beta=0$ limit of Eq. (4.3) and obtain an expression [Eq. (A4)] equivalent to Ritchie's formula[1] for the transmission probability for an electron incident on a thin metal film. We emphasize that in so doing we are overlooking the result shown in Sec. V, that the limits $q_{\parallel}L \to 0$ and $\beta \to 0$ cannot be interchanged in Eq. (4.3). With this premise in mind, then, we set $\beta=0$ in Eq. (4.3) and after little algebra, we obtain

$$S(\vec{q}, \omega) \underset{(\beta=0)}{=} -\frac{2\hbar}{1-e^{-\beta_T\hbar\omega}} \frac{A}{L} \frac{\omega_p^2}{e^2} \operatorname{sgn}\omega \left\{ \sum_{n=1}^{\infty} \left[\beta^2 \left(\frac{A_{B,n}^{(+)}(q_{\parallel})}{D_{B,n}^{(+)}(q_{\parallel})} + \frac{A_{B,n}^{(-)}(q_{\parallel})}{D_{B,n}^{(-)}(q_{\parallel})} \right) \right]_{\beta=0} \delta(\omega^2-\omega_p^2) - \frac{1}{2} q_{\parallel}L \left(\frac{\omega_+^2(q_{\parallel})}{\omega_-^2(q_{\parallel})} \cos^2 q_z L\, \delta(\omega^2-\omega_+^2(q_{\parallel})) + \frac{\omega_-^2(q_{\parallel})}{\omega_+^2(q_{\parallel})} \sin^2 q_z L\, \delta(\omega^2-\omega_-^2(q_{\parallel})) \right) \right\}, \tag{A1}$$

where the $\beta=0$ limit of the coefficients in the infinite sums is understood. We note that in this case the bulk plasmons are degenerate, giving one peak at $\omega=\omega_p$. We can evaluate the total weight of this peak by making use of the f-sum rule (that our theory must satisfy, since charge conservation is built into it from the beginning) which can be stated[20]

$$\int_{-\infty}^{+\infty} \frac{d\omega}{\pi}\, \omega S(\vec{q}, \omega) = \hbar q^2 \frac{N}{m}. \tag{A2}$$

Substituting Eq. (A1) into Eq. (A2) and utilizing the identity

$$\int_{-\infty}^{+\infty} d\omega \frac{\omega}{1-e^{-\beta_T\hbar\omega}} \operatorname{sgn}\omega\, \delta(\omega^2-\omega_0^2) = \frac{1}{2} \tag{A3}$$

[ω_0 being any of the frequencies relevant to Eq, (A1)], we find

$$S(\vec{q}, \omega) \underset{\beta=0}{\to} \frac{2\hbar}{1-e^{-\beta_T\hbar\omega}} V \frac{\omega_p^2}{v(q)} \pi \operatorname{sgn}\omega \left\{ \left[1 - \frac{q_{\parallel}}{q^2 L} \left(\frac{\omega_+^2(q_{\parallel})}{\omega_-^2(q_{\parallel})} \cos^2 q_z L + \frac{\omega_-^2(q_{\parallel})}{\omega_+^2(q_{\parallel})} \sin^2 q_z L \right) \right] \delta(\omega^2-\omega_p^2) + \frac{q_{\parallel}}{q^2 L} \left(\frac{\omega_+^2(q_{\parallel})}{\omega_-^2(q_{\parallel})} \cos^2 q_z L\, \delta(\omega^2-\omega_+^2(q_{\parallel})) + \frac{\omega_-^2(q_{\parallel})}{\omega_+^2(q_{\parallel})} \sin^2 q_z L\, \delta(\omega^2-\omega_-^2(q_{\parallel})) \right) \right\}, \tag{A4}$$

where $V=2LA$. Substituting Eq. (A4) into Eq. (4.1) and doing some algebra, the differential cross section we obtain agrees with Eq. (23) of Ritchie's paper. It should be noted that agreement is found after correcting for a misprint in Ritchie's equation: the second $(\epsilon-1)$ factor in the numerator must be squared. In addition, the reduction in the weight of the bulk-plasmon peak in Eq. (A4), due to the presence of the film surfaces, can be shown to agree with Eq. (106a) of Ref. 5 after some misprints in this equation are corrected.

APPENDIX B: DISPERSION RELATIONS FOR SMALL WAVE VECTORS

In this appendix we outline a general method for obtaining the dispersion relations at small wavevectors. This procedure provides an independent derivation of Eqs. (5.2), (5.3), and (5.6) [and the result that $\hat{\gamma}_a(q_{\parallel})$ vanishes identically for $q_{\parallel}L \to 0$] which seems of interest given the anomalous dependence on β of some of the results discussed in Sec. V.

The normal modes of the thin film correspond (in the model of Sec. II) to density fluctuations $n_1(q_\parallel\omega|z)$ that satisfy the homogeneous version of Eq. (2.9), with the boundary condition $J_z(q_\parallel\omega|z=\pm L)=0$. Defining

$$F(q_\parallel,\gamma)=\beta^2\left(\frac{d}{dz}\,n_1(q_\parallel\omega|z)\right)_{z=\pm L} \mp\frac{\omega_p^2}{2}\,e^{-q_\parallel L}\int_{-L}^{L}dz\,e^{+q_\parallel z}n_1(q_\parallel\omega|z)\,, \tag{B1}$$

the above boundary condition can be stated as the equation

$$F(q_\parallel,\gamma_n(q_\parallel))=0\,, \tag{B2}$$

whose solutions $\gamma_n(q_\parallel)$ give the allowed values of γ for both bulk and surface modes (of each parity), according to whether n_1 is given by Eqs. (3.13) or (3.24), respectively. Here we are interested in the solutions to Eq. (B2) in the limit $q_\parallel L\to 0$, in which case it is convenient to make a Taylor series expansion:

$$F(q_\parallel,\gamma_n(q_\parallel))=[F(q_\parallel,\gamma_n(q_\parallel))]_{q_\parallel=0}+\left(\frac{d}{dq_\parallel}\,F(q_\parallel,\gamma_n(q_\parallel))\right)_{q_\parallel=0}q_\parallel+\cdots. \tag{B3}$$

In order for Eq. (B2) to be satisfied identically, we must impose that each term of the series (B3) vanish. By this method we are able to identify the coefficients in the expansion

$$\gamma_n(q_\parallel)=\gamma_n(q_\parallel=0)+\left(\frac{d}{dq_\parallel}\,\gamma_n\right)_{q_\parallel=0}q_\parallel+\frac{1}{2}\left(\frac{d^2}{dq_\parallel^2}\,\gamma_n\right)_{q_\parallel=0}q_\parallel^2+\cdots, \tag{B4}$$

and this leads to the results (5.2), (5.3), and (5.6). We also find that $\hat{\gamma}_a$ and its derivatives vanish at $q_\parallel=0$.

We close this appendix by recording the expressions for the scalar potential due to the *bulk* plasmons of the thin film *outside* the system. Measuring the coordinate z from the right-hand edge of the film we obtain, for $z>0$

$$\phi_{s,n}(q_\parallel\omega|z)=\beta^2N^{(+)}\,\frac{4\pi}{\omega_p^2}\,\frac{\gamma_{s,n}}{q_\parallel}\,\sin\gamma_{s,n}L\,e^{-q_\parallel z} \tag{B5}$$

for the symmetric modes, and

$$\phi_{a,n}(q_\parallel\omega|z)=-\beta^2N^{(-)}\,\frac{4\pi}{\omega_p^2}\,\frac{\gamma_{a,n}}{q_\parallel}\,\cos\gamma_{a,n}L\,e^{-q_\parallel z} \tag{B6}$$

for the antisymmetric modes. In the derivation of Eqs. (B5) and (B6), use was made of the eigenvalue relations (3.1) and (3.2), respectively. The potentials (B5) and (B6) remain finite in the half-space limit, $q_\parallel L\gg 1$. This is a purely nonlocal effect. We also note that if we let $\beta\to 0$, both potentials would appear to vanish for all wave vectors, in accordance with the usual statement[5,6] that bulk modes do not generate an electric field outside the solid. At small wave vectors, however, care must be exercised in the case of the antisymmetric modes. For $q_\parallel L<1$ we must first substitute Eq. (5.3) into (B6). This leads to

$$\phi_{a,n}(q_\parallel\omega|z)=(-1)^{n+1}N^{(-)}\,\frac{4\pi}{(n+\frac{1}{2})^2\pi^2/L^2}+O(q_\parallel L)\,. \tag{B7}$$

We emphasize that the first term in Eq. (B7) is *independent* of β. Furthermore, the term of $O(q_\parallel L)$ turns out to be proportional to β^{-2}. This result is another manifestation of the fact that whenever "size effects" are relevant, the results of the local theory may not follow from those of the nonlocal theory upon taking the "local limit" $\beta\to 0$ at the end. Currently under investigation is a detailed analysis of the influence of this effect in the problem of a charge located outside a metal film.

APPENDIX C: EFFECT OF RETARDATION

In this appendix, we briefly discuss the plasmon dispersion relations of a thin film when retardation effects are included. We find that the $n=1,2,3,\ldots$ bulk modes (of both parities) are not affected very much by retardation in that, near the "light line", their frequencies are close to the values obtained in the electrostatic theory of Sec. V. The major effect of retardation is to allow for the existence of the antisymmetric surface mode for all wave vectors $q_\parallel$. Its dispersion relation becomes (as in the case of the local theory) photonlike for $q_\parallel\to 0$.

In the presence of retardation, the linearized Euler equation is an inhomogeneous integro-differential equation[41] for the current fluctuation $\vec{J}(\vec{q}_\parallel\omega|z)$ associated with the plasmons of the thin film. The corresponding density fluctuation is still given by the solution to the homogeneous version of Eq. (2.9). It is convenient to transform the z component of Euler's equation into a differential equation by appropriate differentiation. We can then express J_z as

$$J_z(\vec{q}_\parallel\omega|z)=i\omega\left(1-\frac{\beta^2}{c^2}\right)\int_{-L}^{L}dz'\,G(q_\parallel\omega|zz')\,\frac{d}{dz'}\,n(\vec{q}_\parallel\omega|z')\,, \tag{C1}$$

where $|z|<L$, c is the speed of light, and the function $G(q_\parallel\omega|zz')$ satisfies the equation

$$\left(\frac{d^2}{dz^2} - \kappa^2\right) G(q_\parallel\omega|zz') = \delta(z - z') , \quad \text{(C2)}$$

with the boundary condition

$$G(q_\parallel\omega|z = \pm L;\ z') = 0 . \quad \text{(C3)}$$

In Eq. (C2), both $|z|$ and $|z'| \le L$. The condition (C3) ensures that $J_z(q_\parallel \omega|z = \pm L) = 0$. The usual electromagnetic boundary conditions are satisfied by our solution, since the electromagnetic field is given everywhere in terms of *integrals* over the charge and current density fluctuations. In Eq. (C2) we have defined

$$\kappa^2 = (1/c^2)(\omega_p^2 - \omega^2) + q_\parallel^2 , \quad \text{(C4)}$$

and we have assumed $q_\parallel > \omega/c$. This requirement guarantees that the modes we are seeking do not radiate.

Substituting the solutions for $G(q_\parallel\omega|zz')$ and $n(q_\parallel\omega|z)$ into Eq. (C1), the dispersion relations are obtained by imposing that the resulting expression for $J_z(q_\parallel\omega|z)$ satisfy the original integrodifferential equation. The following results are obtained:

(a) *Bulk modes*. The eigenvalue equations for γ are

$$\gamma \tan\gamma L = -q_\parallel^2 \frac{\omega_p^2}{\alpha(\omega^2 - \omega_p^2) + \omega^2\kappa \coth\kappa L} \quad \text{(C5)}$$

for the symmetric modes, and

$$\gamma \cot\gamma L = q_\parallel^2 \frac{\omega_p^2}{\alpha(\omega^2 - \omega_p^2) + \omega^2\kappa \tanh\kappa L} \quad \text{(C6)}$$

for the antisymmetric modes. Here

$$\alpha^2 \equiv q_\parallel^2 - \omega^2/c^2 > 0 . \quad \text{(C7)}$$

It is easy to verify that, setting $c = \infty$, Eqs. (C5) and (C6) reduce to Eqs. (3.1) and (3.2), respectively.

In what follows, we only consider the limit $\alpha \to 0$ of Eqs. (C5) and (C6). Then:

$$\gamma \tan\gamma L = -\frac{\omega_p}{c} \tanh \frac{\omega_p L}{c} \ \text{(symmetric)} \quad \text{(C8)}$$

and

$$\gamma \cot\gamma L = \frac{\omega_p}{c} \coth \frac{\omega_p L}{c} \ \text{(antisymmetric)} \quad \text{(C9)}$$

From Eqs. (C8) and (C9) we can obtain the *intersections* of the dispersion relations with the light line $\omega = cq_\parallel$. These intersections occur very close to the frequencies of the corresponding electrostatic modes at $q_\parallel = 0$. This is illustrated by Figs. 1 and 2: the points where the graphs of the left-hand side of Eqs. (C8) and (C9) intersect the horizontal line corresponding to the right-hand side of the equations, give the solutions to the respective equations. In the case of Fig. 1, the right-hand side is indistinguishable from the x axis. In the case of Fig. 2, we note that since $x \coth x > 1$ for $x > 0$, the $n = 0$ antisymmetric bulk mode is never an allowed solution (contrary to the case of the electrostatic theory, where it exists for $q_\parallel < q_\parallel^c$).

(b) *Surface modes*. The dispersion relations are obtain simply by substituting $\gamma \to i\hat{\gamma}$ in Eqs. (C5) and (C6). In both cases it can be shown that the dispersion relations do not intersect the light line at a finite frequency. The only solution as $\alpha \to 0$ is, for each parity, $\omega \simeq cq_\parallel$. Thus in the case of the antisymmetric surface mode, the effect of retardation is indeed drastic. Note that this mode is now allowed for all wavevectors.

In conclusion, we infer that the electrostatic theory of Sec. VI should be a good first approximation to a more complete calculation of the cross section that included retardation effects. The only exception is that the lowest antisymmetric mode is strongly altered at small wave vectors, as discussed above.

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[1]R. H. Ritchie, Phys. Rev. 106, 874 (1957).
[2]E. A. Stern and R. A. Ferrell, Phys. Rev. 120, 130 (1960).
[3]E. N. Economou and K. L. Ngai, Adv. Chem. Phys. 27, 265 (1975).
[4]A. A. Lucas, in *Elementary Excitations in Solids, Molecules and Atoms*, edited by J. T. Devreese, A. B. Kunz, and T. C. Collins (Plenum, London, 1974), P. A, p. 65.
[5]P. J. Feibelman, C. B. Duke, and A. Bagchi, Phys. Rev. B 5, 2436 (1972).
[6]G. D. Mahan, in *Elementary Excitations in Solids, Molecules and Atoms*, edited by J. T. Devreese, A. B. Kunz, and T. C. Collins (Plenum, London, 1974), P. B, p. 93.
[7]F. Bloch, Z. Phys. 81, 363 (1933); Helv. Phys. Acta 7, 385 (1934).
[8]R. H. Ritchie, Prog. Theor. Phys. (Kyoto) 29, 607 (1963); R. H. Ritchie and A. L. Marusak, Surf. Sci. 4, 234 (1966); R. H. Ritchie and R. E. Wilems, Phys. Rev. 178, 372 (1969); F. Forstmann, Z. Phys. 203, 495 (1967); K. Sturm, *ibid.* 209, 329 (1968). More recent references include A. Fetter, Ann. Phys. (N.Y.) 81, 367 (1973); J. Heinrichs, Phys. Rev. B 8, 1346 (1973); A. D. Boardman, B. V. Paranjape, and R. Teshima, Surf. Sci. 49, 275 (1975), A. D. Boardman and E. D. Isaac, Phys. Lett. A 53, 399 (1975); F. Forstmann and H. Stenschke, Phys. Rev. B 17, 1489 (1978).
[9]A. J. Bennett, Phys. Rev. B 1, 203 (1970).
[10]S. C. Ying, Nuovo Cimento B 23, 270 (1974). See also the article by N. H. March in Ref. 4, p. 97.
[11]A. Eguiluz, S. C. Ying, and J. J. Quinn, Phys. Rev. B 11, 2118 (1975).
[12]A. Eguiluz and J. J. Quinn, Phys. Rev. B 14, 1347

(1976); 13, 4299 (1976).

[13]G. Barton (unpublished).

[14]P. Schmüser, Solid State Commun. 2, 41 (1964); and Z. Phys. 180, 105 (1964).

[15]H. Raether, Surf. Sci. 8, 233 (1967); K. J. Kane and H. Raether, Phys. Rev. Lett. 37, 1355 (1976).

[16]I. Lindau and P. O. Nilsson, Phys. Scr. 3, 87 (1971).

[17]W. E. Jones, K. L. Kliewer and R. Fuchs, Phys. Rev. 178, 1201 (1969).

[18]R. Fuchs and K. L. Kliewer, Phys. Rev. 185, 905 (1969).

[19]J. E. Inglesfield and E. Wikborg, J. Phys. F 5, 1706 (1975).

[20]A. Griffin and E. Zaremba, Phys. Rev. A 8, 486 (1973).

[21]A. Griffin and J. Harris, Can. J. Phys. 54, 1396 (1976).

[22]J. Harris, Phys. Rev. B 4, 1022 (1971).

[23]L. Kleinman, Phys. Rev. B 7, 2288 (1973).

[24]E. Evans and D. L. Mills, Phys. Rev. B 8, 4004 (1973).

[25]Although the combination of spatially dispersive effects ($\beta \neq 0$) with the use of a more realistic diffuse density profile is expected to add structure to the density response function [by introducing new poles due to the higher multipole surface plasmons (Refs. 9, 11, 12, and 19)], here we only discuss the influence of spatial dispersion with a sharp-surface model of the electron density in a thin film.

[26]D. Pines and P. Nozières, *The Theory of Quantum Liquids* (Benjamin, New York, 1966).

[27]L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (Benjamin, Menlo Park, 1962).

[28]We emphasize that this result has been obtained for a metal film with a sharp electron density profile, Eq. (2.7). Although it is, in principle, straightforward to obtain a more general hydrodynamic responce function (e.g., for a two-step model of the slab surfaces), there is not available at the present time, a microscopic response function more general than that of Refs. 20 and 21. It would indeed be of interest to establish the relations between both theories in such a case.

[29]D. Wagner, Z. Naturforsch. A 21, 634 (1966).

[30]A similar effect was found in Ref. 20 for the case of a system of fermions interacting through a short-range Yukawa potential.

[31]The value of $q_{\parallel}^c$ given by Eq. (3.10) is small enough that the influence of retardation effects should be investigated. In Appendix C, we show that, when retardation is allowed for, the antisymmetric surface plasmon does exist for all wave vectors, down to $q_{\parallel} = 0$. The $n=0$ antisymmetric bulk mode is then always absent.

[32]This result allows us to make a Taylor series expansion of Eq. (4.3) in powers of $q_{\parallel}$ (Sec. V) with a radius of convergence greater than $q_{\parallel}^c$. We note that in transmission experiments, typical values of $q_{\parallel}$ are indeed greater than $q_{\parallel}^c$.

[33]N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart, and Winston, New York, 1976), p. 365.

[34]In Appendix B we indicate a different derivation of Eqs. (5.2) and (5.3). This corroborates the conclusions drawn below Eq. (5.5).

[35]Of course, the expression (5.8) for $S(\vec{q},\omega)$ is valid for $q_{\parallel} L \ll 1$ only. The less restrictive condition $q_{\parallel} L < 1$ (for an expansion in powers of $q_{\parallel} L$ to be approximately given by a few terms) would require more terms in the expansion (5.8), but our conclusion about the local limit remains the same [see comments below Eq. (5.5)]. Note that with $E_0 = 20$ keV and $\theta \simeq 10^{-4}$ rad, $q_{\parallel} L$ reaches the value of unity for $L \simeq 5000$ Å.

[36]We also note that the value of $\omega_{a,\,n=0}$ that enters the last term in Eq. (5.8) is numerically very close to the frequency of the antisymmetric surface plasmon of the local theory, $\omega_-(q_{\parallel}) \simeq \omega_p (1 - q_{\parallel} L)^{1/2}$. The corresponding weights, however, are qualitatively different.

[37]Of course, in practice, the incoming beam has a finite angular width, so that even in this limit, there is coupling to the low-frequency surface plasmon.

[38]Admittedly, the bulk-plasmon losses can only be resolved for films which are quite thin, as our examples suggest. This, however, is a question unrelated to the point made in Ref. 35.

[39]The effect of Landau damping can be studied quantitatively (Ref. 20) by evaluating explicitly Eq. (2.30).

[40]This is consistent with the statement made at the end of Sec. II B, that for $q_{\parallel} \to 0$ the dispersion relations of the bulk plasmons characterized by the first few values of n, are the same in the hydrodynamic model as in the RPA theory.

[41]See, e.g., the first of Ref. 12, Eqs. (3.2)–(3.5).