PHYSICAL REVIEW B VOLUME 23, NUMBER 4 15 FEBRUARY 1981

Screening near a metal surface: Plasmon effects

Adolfo G. Eguiluz
Department of Physics, University of California, Irvine, California 92717
(Received 9 May 1980; revised manuscript received 15 August 1980)

We present a formulation of the problem of the screening of an electron by a metal surface in which electron-gas dispersion is fully taken into account. This is done by introducing a model Hamiltonian that treats on an equal footing the interaction of an electron with all the normal modes of a metal with a surface. The coupling functions describing this interaction are obtained in terms of general response properties of the *bounded* electron gas. As an example, we obtain explicit results for the coupling functions for a simplified model of the metal surface response, in which only collective modes (bulk and surface plasmons) contribute to the imaginary part of the density response function. We establish the plasmon-pole approximation for the *surface* problem, by showing that our model response function exactly satisfies the f-sum rule for an inhomogeneous electron gas (in the particular case of a sharp electron density profile at the surface). We present explicit results for the "image potential" acting on a charge as a function of its distance from the surface (the charge can be either outside or inside the metal). Our results stress the importance of including electron-gas dispersion (spatial dispersion) in the problem. In particular, model Hamiltonians for the electron-metal surface system that do not include electron-gas dispersion in the coupling functions, give a poor description of the screening at distances from the surface of the order of the electron screening length.

I. INTRODUCTION

There is considerable current interest in the study of screening processes near a metal surface.[1-15] In particular, it has been known for some time that the coupling of a charged particle to the surface plasmon leads to a screening self-energy that in a semiclassical approximation[7] (necessary to localize the particle) reduces to the classical image potential at distances from the surface that are large compared with the electron screening length. While this role of the surface plasmon has been repeatedly emphasized in the literature, it is noteworthy that the role of the bulk plasmon has been either ignored or (as we shall see below) treated inadequately. A rather common misconception in this context is the assumption that effects specific to the surface region arise only from the surface mode. Thus in previous theories of the screening response of a metal surface, bulk and surface modes are usually not treated explicitly on an equal footing.

The present paper aims at a description of screening near a metal surface that does treat bulk and surface modes on an equal footing. As we shall see, this can be achieved by taking into account electron-gas dispersion (spatial dispersion) consistently. Our theory, of course, resorts to approximations. It has, however, the appealing feature that the approximations are introduced in a well defined fashion, namely, at some point we must choose a model for the density response function of the bounded electron gas $\chi(\vec{q}_{\parallel}\omega|zz')$.

A convenient method for the study of the electron-metal surface interaction is the use of model Hamiltonians.[1-4,8-15] This method has the advantage of its relative simplicity. It provides a physical insight into the microscopic behavior of the system that is sometimes absent in methods intended to obtain numbers of quantitative significance (like the density functional method). A further advantage of a Hamiltonian formalism is that *dynamical* screening processes can be treated on an equal footing with static screening.

The problem is usually formulated as follows.[3,6,10-14] The external particle (e.g., an electron) is coupled to the boson field of a dispersionless surface plasmon of frequency $\omega_s=\omega_p/\sqrt{2}$ (ω_p being the bulk plasmon frequency). The Hamiltonian describing this coupling is written as[6,10]

$$H_{\rm int}^{(s)}=\hbar^{1/2}\sum_{\vec{q}_{\parallel}} e^{i\vec{q}_{\parallel}\cdot\vec{x}_{\parallel}} f_{\vec{q}_{\parallel}}^{(s)}(z)(a_{\vec{q}_{\parallel}}+a_{-\vec{q}_{\parallel}}^{\dagger}), \tag{1.1}$$

where the coupling function $f_{\vec{q}_{\parallel}}^{(s)}(z)$ is given by[12,13]

$$[f_{\vec{q}_{\parallel}}^{(s)}(z)]^2=\frac{\pi e^2\omega_p^2}{2A}\frac{1}{q_{\parallel}\omega_s}e^{-2q_{\parallel}|z|}. \tag{1.2}$$

Here $\vec{q}_{\parallel}$ is the surface plasmon wave vector, z is the coordinate perpendicular to the jellium surface (the jellium occupying the half-space $z<0$), and A is the surface area. As mentioned above,[7(a)] this model leads to a description of the external charge-surface interaction given by the classical image potential $-e^2/4z$. Obviously, if the external charge is near the surface, $z\to 0$, Eq. (1.2) cannot properly describe its screening by the surface plasmon.

Another shortcoming of the above model is the following. Equation (1.2) implies that the interaction under consideration is the same, whether

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the external charge is outside or inside the metal. We note that in this model the density fluctuation corresponding to the surface plasmon is a delta function localized at the surface, and its associated scalar potential satisfies Laplace's equation for both $z>0$ and $z<0$; hence the factor $\exp(-2q_{\parallel}|z|)$ in Eq. (1.2). Now in a real metal, the electron screening length λ is finite (not zero, as in the above model), and the density fluctuation that corresponds to the surface plasmon acquires a finite spread (of the order of λ) into the metal. Its associated potential must then satisfy *Poisson's* equation for $z<0$, and the coupling function must reflect this fact. Thus, Eq. (1.2) is not qualitatively correct for $z<0$. We note that it has been suggested[14] that spatial dispersion ($\lambda \neq 0$) can be accounted for by simply letting ω_s in Eq. (1.2) become $\omega_s(q_{\parallel})$, the dispersive surface plasmon frequency. The above argument suggests that this is not correct for $z<0$. (In Sec. III we show this to be incorrect for $z>0$ also.)

Related to the preceding remarks is the fact that the coupling to the bulk modes[9-13] has not, in general, been treated adequately. The root of this problem is the following. In the absence of electron-gas dispersion[7] ($\lambda=0$), the scalar potential φ_B due to the bulk modes happens to vanish at the surface, $z=0$. Since outside the surface $\nabla^2\varphi_B=0$, it follows from potential theory that $\varphi_B\equiv 0$ outside the surface. Hence, a charge at position $z>0$ would not interact with the bulk plasmons. Thus, the Hamiltonian for the coupling to the bulk modes is usually written as follows[9-13]:

$$H_{\rm int}^{(B)}=\hbar^{1/2}\sum_{\vec{q}_{\parallel};q_z} e^{i\vec{q}_{\parallel}\cdot\vec{x}_{\parallel}} f^{(B)}_{\vec{q}_{\parallel};q_z}(z)(a_{\vec{q}}+a^{\dagger}_{-\vec{q}}), \qquad (1.3)$$

where $\vec{q}=(\vec{q}_{\parallel};q_z\hat{z})$ and the coupling function $f^{(B)}_{\vec{q}_{\parallel};q_z}(z)$ is given by[15]

$$[f^{(B)}_{\vec{q}_{\parallel};q_z}(z)]^2=\frac{2\pi e^2\omega_p}{\Omega}\frac{1}{q^2}(1-\cos 2q_z z)\Theta(-z), \qquad (1.4)$$

Ω being the volume of the system. (Here $q_z=n\pi/d$; $\Omega=Ad$, $n=1,2,3,\ldots$)

Now a more realistic description of screening ($\lambda\neq 0$) immediately invalidates the result that $\varphi_B=0$ at $z=0$. (This fact has been ignored even in papers whose purpose is to include the effects of electron-gas dispersion[9]). Thus, an external charge can interact with the bulk modes for $z>0$.[16,17] It has been estimated[16,18] that the bulk modes account for 30% of the "image potential" V felt by a charge localized at $z=0$ [whereas the above model gives no contribution to $V(z\geq 0)$]. Furthermore, a continuity argument suggests that when the external charge penetrates the surface ($z<0$) its screening by the bulk modes will not be properly given by (1.4) for $|z|<\lambda$.

In this paper we present a description of screening near a metal surface which is conceptually simple and at the same time is free from the objections posed above on earlier theories. Of the processes that contribute to the dressing of an electron in the surface region we isolate those due to the screening response of the electron gas. In Sec. II we introduce a Hamiltonian for such processes. We note that in this paper we do not discuss the Hartree-Fock self-energy at all. We obtain general expressions for the coupling functions that generalize Eqs. (1.2) and (1.4) in terms of general properties of the *bounded* electron gas. In Sec. III we evaluate those coupling functions for a model of the bounded electron-gas response[17] in which only collective modes contribute to the imaginary part of the density response function. We explicitly show that our choice of response function exactly satisfies the important f-sum rule[19] in both its "local" and "global" forms.[20] Thus, the model of Sec. III establishes the *surface* counterpart of the rather popular plasmon-pole approximation first proposed by Lundqvist[21] for the *homogeneous* electron gas.[22] Note that for large wave vectors this approximation effectively takes into account the electron-hole pair contribution to screening in an "average" sense.[22] Now the model of Sec. III assumes a sharp electron density profile at the surface. This is known to be a crude approximation to the actual density profile at a metal surface. However, the generalization of the theory of Sec. III to more complicated (if not entirely realistic) density profiles[23] is straightforward. While we hope to report on this extension of our work in a future publication, we believe that our present approach and results merit separate presentation. The analytical results of Secs. III and IV display rather clearly the role of the collective modes of a metal with a surface in the screening response of such a surface. Furthermore, because our approximate model satisfies basic requirements like the local conservation of charge (f-sum rule), it is free from the objections we have raised on the existing theories, and the fact that we obtain physically reasonable image potentials in the vicinity of the surface, we expect our results to be of qualitative significance in a variety of surface problems[1-15] dealing with the electron-plasmon interaction near a surface. In Sec. IV we obtain a result for the electron self-energy that generalizes an earlier result of Feibelman *et al.*[7(a)] by the inclusion of electron-gas dispersion in the aforementioned coupling functions. In order to show explicitly the consequences of electron-gas dispersion, we consider a simple

semiclassical approximation in which the self-energy becomes a local function of position. We are thus led to an "image potential."

We present explicit results for the image potential as a function of distance from the surface, for an external charge either outside or inside the metal. When compared with previous work[7(b),9,11] our results show differences brought about by electron-gas dispersion (spatial dispersion). These differences should be directly observable in experiments like the measurement of relaxation energies[6] as a function of the distance of the photoemitting atom from the surface. A summary and critique of our results is given in Sec. V. Finally, in Appendix A we briefly quote some formal results from the many-body theory of the (inhomogeneous) electron gas which are used in Sec. II, and in Appendix B we obtain an explicit result for the imaginary part of the density response function of a semi-infinite metal which we utilize in Sec. III. (We note that Appendix B constitutes a useful extension of the work reported in Ref. 17.)

II. MODEL HAMILTONIAN

Consider a metal described by a jellium background occupying the half-space $z<0$, and an electron gas that is characterized by a ground-state density profile $n_0(z)$, such that the system as a whole is neutral. An "external" electron moving in the surface region will couple, via its Coulomb field, with the normal modes of such a metal. We can study this coupling by considering the electron self-energy $\Sigma(\vec{x}\vec{x}'|tt')$.[8,24,25] In Appendix A we recall that, from the exact electron self-energy for the full electron Hamiltonian we can extract a contribution, $\Sigma_{nn}(\vec{x}\vec{x}'|tt')$, that arises from the collective (screening) response of the electron gas. For the geometry of the present problem, we Fourier transform Eq. (A5) according to

$$\Sigma_{nn}(\vec{x}\vec{x}'|\Omega_n)=\frac{1}{A}\sum_{\vec{k}_\parallel} e^{i\vec{k}_\parallel\cdot(\vec{x}_\parallel-\vec{x}'_\parallel)}\Sigma_{nn}(\vec{k}_\parallel\Omega_n|zz'), \quad (2.1)$$

(where $\vec{x}_\parallel$ is the component of the vector position $\vec{x}$ on the plane of the surface) and obtain the result

$$\Sigma_{nn}(\vec{k}_\parallel\Omega_n|zz')=-\frac{1}{\beta_T\hbar}\frac{1}{A}\sum_{\vec{q}_\parallel}\sum_{\Omega_m}\int_{-\infty}^{+\infty}dz_1\int_{-\infty}^{+\infty}dz_2 v_{\vec{q}_\parallel}(z-z_1)v_{\vec{q}_\parallel}(z'-z_2)G_{\vec{k}_\parallel-\vec{q}_\parallel}(zz'|\Omega_n-\Omega_m)\chi^{(\mathcal{T})}_{nn}(\vec{q}_\parallel\Omega_m|z_1z_2), \quad (2.2)$$

Here $\beta_T=1/k_BT$ and the frequencies Ω_n and Ω_m are defined in Eq. (A6). In this paper $\vec{k}_\parallel$ and $\vec{q}_\parallel$ are two-dimensional wave vectors in the plane of the jellium surface (the plane $z=0$). In Eq. (2.2) there appears (the frequency Fourier transform of) the electron Green's function $G_{\vec{k}_\parallel}(zz'|tt')$ defined by

$$G_{\vec{k}_\parallel}(zz'|t,t')=(-i)\langle\mathcal{T}(c_{\vec{k}_\parallel}(z,t)c^\dagger_{\vec{k}_\parallel}(z',t'))\rangle, \quad (2.3)$$

where $\mathcal{T}$ is the Wick imaginary time-ordering operator.[26] Also:

$$v_{\vec{q}_\parallel}(z-z_1)=\frac{2\pi e^2}{q_\parallel}e^{-q_\parallel|z-z_1|} \quad (2.4)$$

is the two-dimensional Fourier transform of the Coulomb potential energy and $\chi^{(\mathcal{T})}_{nn}(\vec{q}_\parallel\Omega_m|zz')$ is the two-dimensional Fourier transform of the time-ordered density response function $\chi^{(\mathcal{T})}_{nn}(\vec{x}\vec{x}'|\Omega_m)$, defined in Eq. (A4). We note that the latter has the spectral representation (A7), which can be Fourier transformed [according to Eq. (2.1)] to give a spectral representation for $\chi^{(\mathcal{T})}_{nn}(\vec{q}_\parallel\Omega_m|zz')$, namely

$$\chi^{(\mathcal{T})}_{nn}(\vec{q}_\parallel\Omega_m|zz')=\frac{1}{\pi}\int_0^\infty d\omega\frac{2\omega}{\Omega_m^2-\omega^2}\mathrm{Im}\chi^{(R)}(\vec{q}_\parallel\omega|zz'), \quad (2.5)$$

where

$$\mathrm{Im}\chi^{(R)}(\vec{q}_\parallel\omega|zz')=\frac{1}{2\hbar}\int_{-\infty}^{+\infty}dt\,e^{i\omega(t-t')}\times\langle[\hat{n}_{\vec{q}_\parallel}(z,t),\hat{n}_{-\vec{q}_\parallel}(z',t')]_-\rangle \quad (2.6)$$

is the imaginary part of the "retarded" density response function $\chi^{(R)}(\vec{q}_\parallel\omega|zz')$. Now from Eq. (2.6) and the symmetry property:

$$\mathrm{Im}\chi^{(R)}(-\vec{q}_\parallel\omega|z'z)=\mathrm{Im}\chi^{(R)}(\vec{q}_\parallel\omega|zz'), \quad (2.7)$$

which follows from the corresponding result for $\mathrm{Im}\chi^{(R)}(\vec{x}\vec{x}'|\omega)$ [see Eq. (A11)], we can show the following result[27]:

$$\mathrm{Im}\chi^{(R)}(\vec{q}_\parallel\omega|zz')=\mathrm{sgn}\omega\sum_n W^{(n)}_{\vec{q}_\parallel}(zz')\delta(\omega^2-\omega_n^2(q_\parallel)), \quad (2.8)$$

where the "weights" $W^{(n)}_{\vec{q}_\parallel}(zz')$ are given by ($T=0$ K)

$$W^{(n)}_{\vec{q}_\parallel}(zz')=\frac{2\pi}{\hbar}\omega_n(q_\parallel)\langle0|\hat{n}_{\vec{q}_\parallel}(z)|n\rangle\langle n|\hat{n}_{-\vec{q}_\parallel}(z')|0\rangle, \quad (2.9)$$

and the frequencies $\omega_n(q_\parallel)$ give the poles of the retarded density response function as a function of $|\vec{q}_\parallel|$. We stress that the sum over n runs over

both collective and single-particle modes (involving single-pair and multipair excitations[19]), i.e., over the excited states $|n\rangle$ coupled to the ground state $|0\rangle$ by the density fluctuation operator $\hat{n}_{\vec{q}_\parallel}(z)$.

Substituting Eq. (2.8) into Eq. (2.5) and the resulting equation into Eq. (2.2), we obtain the result that

$$\Sigma_{nn}(\vec{k}_\parallel\Omega_n|zz') = -\frac{1}{\pi A}\frac{1}{\beta_T\hbar}\sum_n\sum_{\vec{q}_\parallel}\sum_{\Omega_m}\int_{-\infty}^{+\infty}dz_1\int_{-\infty}^{+\infty}dz_2\, v_{\vec{q}_\parallel}(z-z_1) \times v_{\vec{q}_\parallel}(z'-z_2)W^{(n)}_{\vec{q}_\parallel}(z_1z_2)\frac{1}{\Omega_m^2-\omega_n^2(\vec{q}_\parallel)}G_{\vec{k}_\parallel-\vec{q}_\parallel}(zz'|\Omega_n-\Omega_m)\,. \quad (2.10)$$

Equation (2.10) is an exact consequence of Eq. (2.2). However, it is too formal a result. Its physical meaning can be most clearly understood by introducing a model Hamiltonian. We noted before that the purpose of this paper is to describe the dressing of an electron by the screening response of the normal modes of a metal with a surface. We thus consider the following electron-boson Hamiltonian (note that both plasmon and electron-hole-pair-type excitations obey boson statistics):

$$H = H_e + H_b + H_{e\text{-}b}\,. \quad (2.11)$$

Here H_e, the free-electron Hamiltonian is given by

$$H_e = \frac{\hbar^2}{2m}\sum_{\vec{k}_\parallel}\int_{-\infty}^{+\infty}dz\, c^\dagger_{\vec{k}_\parallel}(z,t)\left(k_\parallel^2 - \frac{d^2}{dz^2}\right)c_{\vec{k}_\parallel}(z,t)\,, \quad (2.12)$$

while H_b, the free-boson Hamiltonian is defined by

$$H_b = \sum_n\sum_{\vec{q}_\parallel}\hbar\omega_{q_\parallel n}[a^\dagger_{\vec{q}_\parallel n}(t)a_{\vec{q}_\parallel n}(t) + \tfrac{1}{2}]\,, \quad (2.13)$$

and $H_{e\text{-}b}$, the Hamiltonian for the electron-boson interaction is given by

$$H_{e\text{-}b} = \sum_n\sum_{\vec{k}_\parallel,\vec{q}_\parallel}\hbar^{1/2}\int_{-\infty}^{+\infty}dz\, g^{(n)}_{\vec{q}_\parallel}(z)c^\dagger_{\vec{k}_\parallel}(z,t)c_{\vec{k}_\parallel-\vec{q}_\parallel}(z,t) \times[a_{\vec{q}_\parallel n}(t) + a^\dagger_{-\vec{q}_\parallel n}(t)]\,. \quad (2.14)$$

Here the operator $c^\dagger_{\vec{k}_\parallel}(z,t)$ creates an electron with momentum $\hbar\vec{k}_\parallel$ at position z and time t. Similarly, the operator $a^\dagger_{\vec{q}_\parallel n}(t)$ creates an n-channel boson with momentum $\hbar\vec{q}_\parallel$ at time t. (Note that none of the normal modes of a metal with a surface carries a momentum perpendicular to the surface.)

In Eq. (2.14) we have introduced the (unknown) coupling functions $g^{(n)}_{\vec{q}_\parallel}(z)$. They provide a measure of the strength of a process in which an electron at position z and with momentum $\hbar(\vec{k}_\parallel - \vec{q}_\parallel)$ is scattered via the destruction (creation) of an n-channel boson of momentum $\hbar\vec{q}_\parallel(-\hbar\vec{q}_\parallel)$. We remark that prior to this work the coupling functions have only been obtained ignoring electron-gas dispersion[13] which, as indicated in the Introduction, is not satisfactory. One possible approach to the present problem is the canonical quantization method.[16] This method treats the external electron classically. Moreover, it requires the knowledge of the frequencies $\omega_{q_\parallel n}$ *a priori*. Thus, one must start out by solving some dynamical equations of motion explicitly, and this can only be done for very simple models.[28] Another approach[29] is provided by the paper of Feibelman *et al.*,[7(a)] which starts out in a general fashion, but appears to be difficult to use except in the simplest case that, again, neglects electron-gas dispersion. Other methods, like that of Gersten and Tzoar[9] do not treat bulk and surface modes on an equal footing (or, equivalently, electron-gas dispersion is not adequately included, see Secs. III and IV).

At this stage our method for obtaining the coupling functions rather suggests itself.[30] We require that, to second order in the coupling functions, the electron self-energy for our model Hamiltonian be the same as that given by Eq. (2.10). To second order in g, the self-energy $\Sigma_{\vec{k}_\parallel}(zz'|\Omega_n)$ corresponding to Eqs. (2.11)–(2.14), can be obtained in a rather straightforward fashion.[24] The result is given by

$$\Sigma_{\vec{k}_\parallel}(zz'|\Omega_n) = \frac{(-1)}{\beta_T\hbar}\sum_n\sum_{\vec{q}_\parallel}\sum_{\Omega_m} g^{(n)}_{\vec{q}_\parallel}(z)g^{(n)}_{\vec{q}_\parallel}(z') \times G_{\vec{k}_\parallel-\vec{q}_\parallel}(zz'|\Omega_n-\Omega_m) \times D^{(n)}(\vec{q}_\parallel;\Omega_m)\,, \quad (2.15)$$

where

$$D^{(n)}(\vec{q}_\parallel;\Omega_m) = \frac{2\omega_{q_\parallel n}}{\Omega_m^2 - \omega^2_{q_\parallel n}}\,, \quad (2.16)$$

is the bare n-channel boson propagator. The physical meaning of Eq. (2.15) is clear: An electron at position z' with momentum $\hbar\vec{k}_\parallel$ creates, via the electron-boson interaction g, a virtual n-channel boson with momentum $\hbar\vec{q}_\parallel$. The electron then propagates (via G) to position z, where it destroys the boson (which propagated via its own propagator $D^{(n)}$). We emphasize that Eq. (2.15) provides a normal-mode expression for the self-energy in which bulk and surface modes are treated on an equal footing.

At this point we make the *definition* [see Eq. (2.13)]

$$\omega_{q_\parallel n} \equiv \omega_n(q_\parallel)\,, \quad (2.17)$$

and as indicated above, we require that Eq. (2.15) be the same as Eq. (2.10). This leads to the fol-

lowing result for the coupling functions $g^{(n)}_{\vec{q}_\parallel}(z)$:

$$[g^{(n)}_{\vec{q}_\parallel}(z)]^2=\frac{1}{2\pi A\omega_n(q_\parallel)}\int_{-\infty}^{+\infty}dz_1\int_{-\infty}^{+\infty}dz_2 v_{\vec{q}_\parallel}(z-z_1) \times v_{\vec{q}_\parallel}(z-z_2)W^{(n)}_{\vec{q}_\parallel}(z_1z_2)\,. \tag{2.18}$$

Our theory, up to this point, is general. In order to proceed forward, we must introduce a model for the bounded electron-gas response that provides us with the weights $W^{(n)}_{\vec{q}_\parallel}(zz')$. That is the subject of the next section (where, of course, we circumvent the problem of finding the complete set $\{|n\rangle\}$).

III. A MODEL FOR THE COUPLING FUNCTIONS

In order to apply the method presented in Sec. II to specific problems, we must introduce a model for the dynamical response of an electron gas whose ground-state density profile is $n_0(z)$. According to Eqs. (2.8) and (2.18), this in turn will provide us with a model for the coupling functions $g^{(n)}_{\vec{q}_\parallel}(z)$.

A. Plasmon-pole approximation for $\chi(\vec{q}_\parallel\omega|zz')$

The exact $\chi(\vec{q}_\parallel\omega|zz')$ (Ref. 31) for a self-consistent $n_0(z)$ is not known. In fact, it is not known even in the much simpler case of the homogeneous electron gas, in which χ depends on the *difference* $z-z'$, and the relevant quantity is the Fourier coefficient $\chi(\vec{q};\omega)\equiv\chi(\vec{q}_\parallel,q_z;\omega)$. We note that the theory of Sec. II is fully microscopic and it would indeed be desirable to utilize a microscopic density response function. Unfortunately, the explicit form of $\chi(\vec{q}_\parallel\omega|zz')$ is not known for any microscopic theory (except in the $\omega\to\infty$ limit[7(a)]). To date, the only microscopic calculations of the density response function[32-34] treat the dynamics of the electron gas in the random-phase approximation and assume the presence of an *infinite* potential barrier to confine the electrons to the metal interior (of course, in reality the barrier is finite; furthermore in a self-consistent calculation the barrier is not an *external* potential). In particular, Zaremba and Griffin[33] obtained the Fourier coefficients $\chi(\vec{q}_\parallel\omega|q_zq_z')$ of a double cosine Fourier series for $\chi(\vec{q}_\parallel\omega|zz')$. Thus, a double integration (that must be done numerically) separates their results from $\chi(\vec{q}_\parallel\omega|zz')$ which is what we need. At this point we recall that, as suggested in the Introduction, a model Hamiltonian (like that of Sec. II) is meant to give a qualitative picture of what to expect from a more elaborate calculation. Hence, introducing an *approximate* model for the response function that will require rather extensive numerical calculations, while eventually unavoidable, does not seem ideal in a first application of the theory. Thus, in what follows we will adopt the explicit result for $\chi(\vec{q}_\parallel\omega|zz')$ obtained in Ref. 17 (hereafter referred to as I) for a macroscopic (hydrodynamic) model of the bounded electron gas. In this model, the only modes that partake in the screening response are collective modes (plasmons). From the point of view of the above, this is a choice born of necessity. However, it allows us to obtain a qualitative picture of collective effects in the electron-metal surface interaction that is expected to be useful as a guideline for a more complete calculation. In this connection we recall that, as emphasized by Hedin and Lundqvist[25] for the case of the infinite electron gas, the dominant effect in the screening response of the electron gas is given by the singular nature of the electron-plasmon coupling in the long-wavelength limit. Furthermore, provided the f-sum rule is satisfied,[25] meaningful qualitative results for the electron self-energy are obtained, ignoring the detailed structure of the electron-hole pair contribution to $\chi(\vec{q};\omega)$ (plasmon-pole approximation[21]). Our model for $\chi(\vec{q}_\parallel\omega|zz')$ provides the plasmon-pole approximation for the *surface* problem. We show below that our $\chi(\vec{q}_\parallel\omega|zz')$ exactly satisfies the f-sum rule and thus, in an "average sense",[22] the electron-hole pair contribution to screening is taken into account.

In I, the hydrodynamic density response function $\chi(\vec{q}_\parallel\omega|zz')$ was obtained for a jellium slab of width $2L$, assuming that the electron density profile exactly replicates the jellium background ("sharp" density profile). The close relation between the model of I and the (microscopic) semiclassical RPA (Ref. 33) is analyzed in detail in I. In Appendix B we outline the steps necessary to take the (rather tricky) $L\to\infty$ limit (half-space problem). In this limit, the series of delta-function lines that compose the bulk plasmon spectrum of a thin film [Eq. (3.18) of I] merge into a continuous structure. Our model for $\mathrm{Im}\chi(\vec{q}_\parallel\omega|zz')$ is, then:

$$\mathrm{Im}\chi(\vec{q}_\parallel\omega|zz')=\frac{\omega_p^2}{4e^2}\,\mathrm{sgn}\omega\,\Theta(-z)\Theta(-z')\left[\frac{q_\parallel\hat{\gamma}_s(\hat{\gamma}_s+q_\parallel)^2}{(\hat{\gamma}_s+\frac{1}{2}q_\parallel)}e^{\hat{\gamma}_s(z+z')}\delta(\omega^2-\omega_s^2(q_\parallel))\right.$$
$$\left.+\frac{2}{\pi}\int_0^\infty dp\left((q_\parallel^2+p^2)\cos pz\cos pz'+\frac{B(\vec{q}_\parallel;p|zz')}{p^4+p^2\left(q_\parallel^2+\frac{\omega_p^2}{\beta^2}\right)+\frac{\omega_p^4}{4\beta^4}}\right)\delta(\omega^2-\omega_B^2(q_\parallel;p))\right], \tag{3.1}$$

which consists of a sharp (delta-function) surface plasmon peak and a (very narrow) bulk plasmon peak at $\omega \cong \omega_p$.[35]

In Eq. (3.1), $\Theta(z)$ is the unit step function and we have defined

$$B(\vec{q}_{\parallel}; p\,|zz') = -\frac{\omega_p^4}{4\beta^4} q_{\parallel}^2 \cos p(z+z') + \frac{\omega_p^2}{2\beta^4} q_{\parallel} p \nu^2 \sin p(z+z'), \tag{3.2}$$

where

$$\nu^2(q_{\parallel}, p) = \frac{\omega_p^2}{2} + \beta^2(q_{\parallel}^2 + p^2), \tag{3.3}$$

with $\beta^2 = \frac{3}{5} v_F^2$ (v_F being the Fermi velocity). Note that in the present model the parameter β accounts for the finite screening length of the electron gas.[36] We have also defined

$$\omega_B^2(q_{\parallel}; p) = \omega_p^2 + \beta^2(q_{\parallel}^2 + p^2), \tag{3.4}$$

the dispersion relation for the bulk plasmon continuum and

$$\omega_s^2(q_{\parallel}) = \frac{\omega_p^2}{2} + \beta q_{\parallel}\left(\frac{\omega_p^2}{2} + \frac{\beta^2 q_{\parallel}^2}{4}\right)^{1/2} + \frac{\beta^2 q_{\parallel}^2}{2}, \tag{3.5}$$

the surface plasmon dispersion relation. Finally, we have called $\hat{\gamma}_s(q_{\parallel})$ the inverse decay length (into the metal) of the surface plasmon charge fluctuation. It satisfies the quadratic equation (B21).

Of course, the integration over p in Eq. (3.1) is trivially done noting that, for $\omega^2 \geq \omega_p^2 + \beta^2 q_{\parallel}^2$:

$$\delta(\omega^2 - \omega_B^2(q_{\parallel}; p)) = \frac{1}{2\beta^2 p_B}\,\delta(p - p_B), \tag{3.6}$$

with

$$p_B = \left(\frac{\omega^2 - \omega_p^2}{\beta^2} - q_{\parallel}^2\right)^{1/2}. \tag{3.7}$$

Here, however, we will only utilize the form (3.1) for $\mathrm{Im}\chi$ (which form is convenient both to make contact with the theory of Sec. II and to verify that the f-sum rule is satisfied. We consider first the latter question).

We note that the *exact* $\chi(\vec{q}_{\parallel}\omega\,|zz')$ satisfies the following result[37] (which is the f-sum rule in the case of an inhomogeneous electron gas with ground-state density profile $n_0(z)$]:

$$\int_{-\infty}^{+\infty} \frac{d\omega}{\pi}\,\omega\,\mathrm{Im}\chi(\vec{q}_{\parallel}\omega\,|zz') = \frac{1}{m}\left(q_{\parallel}^2 + \frac{\partial^2}{\partial z\,\partial z'}\right) n_0(z)\,\delta(z - z'), \tag{3.8}$$

where z and z' lie inside the metal. Note that for the *homogeneous* electron gas we can Fourier transform Eq. (3.8) and obtain ($q^2 \equiv q_{\parallel}^2 + q_z^2$):

$$\int_{-\infty}^{+\infty} \frac{d\omega}{\pi}\,\omega\,\mathrm{Im}\chi(\vec{q};\omega) = \frac{n_0}{m} q^2, \tag{3.9}$$

the "usual" form of the f-sum rule.[19] We note that, as stressed by Griffin and Harris,[20] Eq. (3.8) provides a "strong" (or "local") form of the f-sum rule which has a "global" counterpart of the form (3.9) in terms of the dynamic structure factor $S(\vec{q};\omega)$ of the inhomogeneous electron gas.[17] We emphasize that both local and global versions of the sum rule apply in the case of the *inhomogeneous* electron gas, the former version being more restrictive than the latter one. It is noteworthy that except for the work of Griffin and Harris[20] and Wikborg and Inglesfield,[34] no attempt appears to have been made in the past to examine the various models put forth for the response of a metal surface in the light of Eq. (3.8) which, as remarked above, is an important constraint[25] (related to charge conservation[19]) on any approximate density response function.

With the result for $\mathrm{Im}\chi(\vec{q}_{\parallel}\omega\,|zz')$ given by Eq. (3.1), we can show the result that (the intermediate steps are omitted for brevity)

$$\int_{-\infty}^{+\infty} \frac{d\omega}{\pi}\,\omega\,\mathrm{Im}\chi(\vec{q}_{\parallel}\omega\,|zz') = \frac{\omega_p^2}{4\pi e^2}\Theta(-z)\Theta(-z')\left[\frac{\omega_p^2}{2\beta^2}\frac{q_{\parallel}(\hat{\gamma}_s + q_{\parallel})}{(\hat{\gamma}_s + \frac{1}{2}q_{\parallel})} e^{\hat{\gamma}_s(z+z')} + \left(q_{\parallel}^2 + \frac{\partial}{\partial z}\frac{\partial}{\partial z'}\right)\delta(z - z') - \frac{\omega_p^2}{2\beta^2}\frac{q_{\parallel}(\hat{\gamma}_s + q_{\parallel})}{(\hat{\gamma}_s + \frac{1}{2}q_{\parallel})} e^{\hat{\gamma}_s(z+z')}\right] \tag{3.10a}$$

$$= \frac{n_0}{m}\Theta(-z)\Theta(-z')\left(q_{\parallel}^2 + \frac{\partial^2}{\partial z\,\partial z'}\right)\delta(z - z'), \tag{3.10b}$$

and since here $n_0(z) = n_0\Theta(-z)$, Eq. (3.10b) agrees with Eq. (3.8) [recall that in Eq. (3.8), z and z' lie inside the metal]. We note that the *surface* plasmon peak in $\mathrm{Im}\chi$ gives rise to the first term in Eq. (3.10a), while the *bulk* modes account for the remaining two terms, the last of which (manifestly a surface-induced contribution) exactly cancels the surface plasmon term. Our theory thus indicates the importance of treating the response of the bulk and surface modes on an equal footing if one is to have a theory of surface response consistent with the local f-sum rule (3.8). Finally,

we note that it was indeed to be expected for our result (3.1) to satisfy Eq. (3.8), since local charge conservation is built into it from the beginning.[17]

B. The coupling functions for a semi-infinite metal

Having put forth a model for $\mathrm{Im}\chi(\vec{q}_{\parallel}\omega\,|\,zz')$, we can obtain explicit results for the coupling functions $g^{(n)}_{\vec{q}_{\parallel}}(z)$. Comparing Eqs. (2.8) and (3.1) we can read off the following results for the weights $W^{(n)}_{\vec{q}_{\parallel}}(zz')$:

$$W^{(s)}_{\vec{q}_{\parallel}}(zz')=\frac{\omega_p^2}{4e^2}\frac{q_{\parallel}\hat{\gamma}_s(\hat{\gamma}_s+q_{\parallel})^2}{(\hat{\gamma}_s+\frac{1}{2}q_{\parallel})}\Theta(-z)\Theta(-z')e^{\hat{\gamma}_s(z+z')}, \tag{3.11}$$

for the surface plasmon channel, and

$$W^{(B)}_{\vec{q}_{\parallel};p}(zz')=\frac{\omega_p^2}{2\pi e^2}\Theta(-z)\Theta(-z')\times\left((q_{\parallel}^2+p^2)\cos pz\cos pz'+\frac{B(\vec{q}_{\parallel};p\,|\,zz')}{p^4+p^2\left(q_{\parallel}^2+\frac{\omega_p^2}{\beta^2}\right)+\frac{\omega_p^4}{4\beta^4}}\right), \tag{3.12}$$

for the bulk plasmon channels (labeled by the continuous variable p, $0\leq p<\infty$). We next substitute Eqs. (3.11) and (3.12) into the general result (2.18). Note that in Eq. (2.18) z can be either positive or negative, depending on whether the electron is outside or inside the metal, respectively. We consider both cases separately.

(a) Electron outside the metal ($z>0$). This is the simpler case. A little algebra yields the results:

$$[g^{(s)}_{\vec{q}_{\parallel}}(z)]^2=\frac{\pi e^2\omega_p^2}{2A}\frac{1}{q_{\parallel}\omega_s(q_{\parallel})}\frac{\hat{\gamma}_s(q_{\parallel})}{\hat{\gamma}_s(q_{\parallel})+\frac{1}{2}q_{\parallel}}e^{-2q_{\parallel}z}, \tag{3.13}$$

and

$$[g^{(B)}_{\vec{q}_{\parallel};p}(z)]^2=\frac{e^2\omega_p^2}{A}\frac{1}{\omega_B(q_{\parallel};p)}\frac{p^2}{p^4+p^2\left(q_{\parallel}^2+\frac{\omega_p^2}{\beta^2}\right)+\frac{\omega_p^4}{4\beta^4}}e^{-2q_{\parallel}z}. \tag{3.14}$$

Consider first Eq. (3.13). We note that setting $\beta=0$, i.e., dropping electron-gas dispersion, it reduces to Eq. (1.2) [as $\beta\to 0$, $\hat{\gamma}_s\sim\beta^{-1}$, see Eq. (B21)]. Another limit in which both results agree is $q_{\parallel}\to 0$. Then, since for large z the factor $\exp(-2q_{\parallel}z)$ strongly favors the coupling to the $q_{\parallel}\to 0$ part of the dispersion curve, we conclude that (as expected) when the electron is far from the surface, its coupling to the surface plasmon is adequately given by models that ignore electron-gas dispersion.[6] However, as the electron moves closer to the surface, it can couple to a surface plasmon with a finite $\vec{q}_{\parallel}$, for which the factor

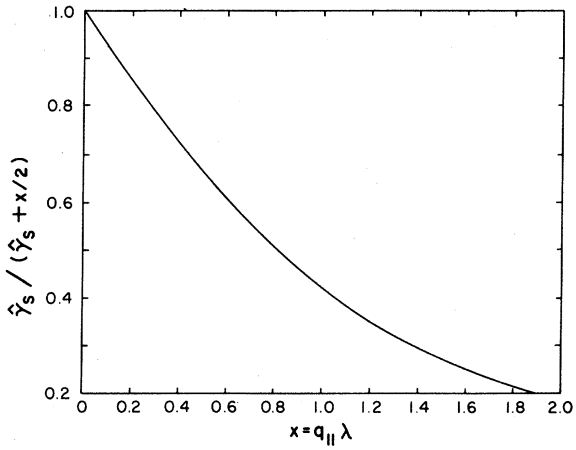

FIG. 1. The ratio $\hat{\gamma}_S(q_{\parallel})/(\hat{\gamma}_S(q_{\parallel})+q_{\parallel}/2)$. According to Eqs. (3.13) and (1.2), this ratio gives the effect of electron-gas dispersion in the coupling function $g^{(s)}_{\vec{q}_{\parallel}}(z)$ for an electron outside the surface. Note that the interaction is effectively cut off at large wave vectors. (In the absence of electron-gas dispersion the above ratio equals unity for all wave vectors.) (Note: $\lambda=\beta/\omega_p$ is the electron screening length).

$\hat{\gamma}_s(q_{\parallel})/[\hat{\gamma}_s(q_{\parallel})+q_{\parallel}/2]$ deviates from unity [its value in Eq. (1.2)]. This ratio is plotted in Fig. 1, which clearly shows that the coupling to the surface channel is substantially reduced, for $q_{\parallel}\neq 0$, from what it would be were the plasmon dispersionless. We stress that, since the interaction is effectively cutoff for large values of $q_{\parallel}$, the electron self-energy will be *finite* for $z\to 0$. Finally, note that in terms of the distance from the surface, Fig. 1 implies that the coupling is reduced appreciably for values of z that are not necessarily small compared to $\lambda=\beta/\omega_p$.

We now turn to Eq. (3.14). We note that the right-hand side vanishes if $\beta\to 0$. Thus, when the electron is outside the surface, its coupling to the bulk modes is (as argued in the Introduction) entirely due to electron-gas dispersion.[16] We notice that the factor $\exp(-2q_{\parallel}z)$ is also present in Eq. (3.14) (as it should be). This, again, favors the coupling to small-$\vec{q}_{\parallel}$ modes. However, whereas $g^{(s)}$ is *singular* at small wave vectors ($g^{(s)}\sim q_{\parallel}^{-1/2}$), $g^{(B)}$ is *analytic* in that limit. Thus, unlike the case of the surface mode, the coupling to the bulk modes is of short range. Note that at small distances from the surface (e.g., distances of interest in the grazing scattering of, say, fast ions from surfaces[38] and/or chemisorption problems[8]) the relative importance of the coupling to both channels is not obvious *a priori* (see Sec. IV).

(b) Electron inside the metal ($z<0$). Equations (3.11), (3.12), and (2.18) lead to the following results:

$$[g^{(s)}_{\vec{q}_\parallel}(z)]^2 = \frac{\pi e^2 \omega_p^2}{2A} \frac{1}{q_\parallel \omega_s(q_\parallel)} \frac{\hat{\gamma}_s[(\hat{\gamma}_s + q_\parallel)e^{q_\parallel z} - 2q_\parallel e^{\hat{\gamma}_s z}]^2}{(\hat{\gamma}_s + \frac{1}{2}q_\parallel)(\hat{\gamma}_s - q_\parallel)^2} \tag{3.15}$$

and

$$[g^{(B)}_{\vec{q}_\parallel;p}(z)]^2 = [g_\infty(\vec{q}_\parallel;p)]^2 + \frac{4e^2\omega_p^2}{A\beta^4} \frac{1}{\omega_B(q_\parallel;p)} \frac{p^2}{(q_\parallel^2+p^2)^2} \frac{G(\vec{q}_\parallel;p\,|z)}{p^4 + p^2\left(q_\parallel^2 + \frac{\omega_p^4}{\beta^2}\right) + \frac{\omega_p^4}{4\beta^4}}, \tag{3.16}$$

where

$$[g_\infty(\vec{q}_\parallel;p)]^2 = \frac{2e^2\omega_p^2}{A} \frac{1}{(q_\parallel^2+p^2)\omega_B(q_\parallel;p)} \tag{3.17}$$

and

$$G(\vec{q}_\parallel;p\,|z) = \frac{\omega_B^4}{4} e^{2q_\parallel z} - \omega_B^2 e^{q_\parallel z}\left(\nu^2 \cos pz + \frac{\omega_p^2}{2}\frac{q_\parallel}{p}\sin pz\right) + \frac{1}{2p^2}\left[\left(p^2\nu^4 - \frac{\omega_p^4}{4}q_\parallel^2\right)\cos 2pz + \omega_p^2\nu^2 q_\parallel p \sin 2pz\right]. \tag{3.18}$$

Consider Eq. (3.15). As suggested in the Introduction, Eq. (3.15) is *not* obtained from Eq. (3.13) by setting $z \to -z$. This reflection symmetry holds only for $q_\parallel \to 0$, that is, for values of $|z|$ large enough that the finite spread of the surface plasmon charge fluctuation is irrelevant. Note that in both cases the coupling is singular for $q_\parallel \to 0$. Thus the surface plasmon also gives rise to a long range screening interaction *inside* the metal.

We note that in Eq. (3.16) we have explicitly separated out the function g_∞ [see Eq. (3.17)], giving the coupling to the bulk plasmon deep inside the metal. Equation (3.17) agrees, for $\beta \to 0$, with the first term in Eq. (1.4). The second term in Eq. (3.16) gives the effect on $g^{(B)}$ brought about by the presence of the surface. Because of electron-gas dispersion, this term differs *qualitatively* from the corresponding term in Eq. (1.4). Now the first term in Eq. (3.18) obviously vanishes for $z \to -\infty$. That the remaining terms in that equation give a vanishing contribution to screening deep inside the metal, is a consequence of the fact that the poles of Eq. (3.16) occur on the imaginary axis. Finally, we note that a major qualitative change that Eq. (3.16) presents with respect to Eq. (3.14) is that now the coupling to the bulk modes is singular for $q^2 = (q_\parallel^2 + p^2) \to 0$. Thus, the associated screening of the electron is *long ranged*.

The coupling functions obtained above lead us to the following picture of the electron-metal surface interaction. For an electron far outside the metal surface, the screening is dominated by the surface plasmon channel. For an electron deep inside the metal, the bulk plasmon channel is the dominant one. In the surface region both channels are expected to be relevant. In Sec. IV we shall give an approximate measure of the relative importance of both channels in the particular case of the static screening of a charge in the surface region.

Finally, it seems appropriate that we compare the results of this section with those of Gersten and Tzoar,[9] who first addressed the question of how to describe the coupling of an electron to the bulk and surface plasmons in the presence of electron-gas dispersion. Their method, however, fails to treat bulk and surface modes on an equal footing. In particular, the method of Ref. 9 hinges on an expression for the scalar potential due to the normal modes of a metal with a surface [Eq. (2.13) of Ref. 9] whose *form* is valid only in the absence of electron-gas dispersion (see the Introduction). Furthermore, Gersten and Tzoar's derivation of (in our notation) $g^{(B)}$ is made assuming the medium will respond like an *infinite*, homogeneous electron gas. The results of Ref. 9 for the coupling functions can be written as follows:

$$[g^{(B)}_{GT}(\vec{q}_\parallel;p\,|z)]^2 = \frac{2e^2\omega_p}{A}\frac{1}{(q_\parallel^2+p^2)} \times \left(\frac{\epsilon(\vec{q};0)-1}{\epsilon(\vec{q};0)}\right)^{1/2}(1-\cos 2pz)\Theta(-z) \tag{3.19}$$

and

$$[g^{(s)}_{GT}(\vec{q}_\parallel\,|z)]^2 = \frac{\pi e^2\omega_p}{\sqrt{2}A}\frac{1}{q_\parallel}\left(\frac{1-\bar{\epsilon}(\vec{q}_\parallel;0)}{1+\bar{\epsilon}(\vec{q}_\parallel;0)}\right)^{1/2} e^{-2q_\parallel|z|}. \tag{3.20}$$

In Eq. (3.19), $\epsilon(\vec{q};0)$ is the static dielectric function of the *homogeneous* electron gas. In Eq. (3.20), $\bar{\epsilon}(\vec{q}_\parallel;0)$ is the static limit of the "surface" dielectric function[9,32,39] $\bar{\epsilon}(\vec{q}_\parallel;\omega)$, namely:

$$\bar{\epsilon}(\vec{q}_\parallel;0) = \frac{q_\parallel}{\pi}\int_{-\infty}^{+\infty} dq_z \frac{1}{(q_\parallel^2+q_z^2)\epsilon(\vec{q};0)}. \tag{3.21}$$

Now, utilizing the "hydrodynamic" approximation[19] for $\epsilon(\vec{q};\omega)$, namely[40]:

$$\epsilon(\vec{q};\omega) = \frac{\omega^2 - \omega_p^2 - \beta^2 q^2}{\omega^2 - \beta^2 q^2}, \tag{3.22}$$

Eq. (3.21) gives the result that

$$\bar{\epsilon}(\vec{q}_\parallel;0) = \frac{q_\parallel}{\left(q_\parallel^2 + \frac{\omega_p^2}{\beta^2}\right)^{1/2}}. \tag{3.23}$$

Equations (3.22) (rather, its $\omega = 0$ limit) and (3.23) agree qualitatively with the corresponding expressions utilized in Ref. 9 (see Figs. 1 and 2 of Ref. 9). Substituting Eqs. (3.22) and (3.23) into Eqs.

(3.19) and (3.20) yields, respectively;

$$[g_{\mathrm{GT}}^{(B)}(\vec{q}_{\parallel};p\,|z]^2=\frac{2e^2\omega_p^2}{A}\frac{1}{(q_{\parallel}^2+p^2)\omega_B(q_{\parallel};p)}\times(1-\cos 2pz)\Theta(-z) \tag{3.24}$$

and

$$[g_{\mathrm{GT}}^{(s)}(\vec{q}_{\parallel}\,|z)]^2=\frac{\pi e^2\omega_p}{\sqrt{2}A}\frac{1}{q_{\parallel}}\frac{\beta}{\omega_p}\left[\left(q_{\parallel}^2+\frac{\omega_p^2}{\beta^2}\right)^{1/2}-q_{\parallel}\right]e^{-2q_{\parallel}|z|}. \tag{3.25}$$

Comparing Eq. (3.24) with Eqs. (3.14) and (3.16) and Eq. (3.25) with Eqs. (3.13) and (3.15), we are led to the following conclusions. For an electron outside the metal surface, Eq. (3.25) is qualitatively similar to Eq. (3.13). As expected, however, for an electron inside the metal, the coupling functions (3.24) and (3.25) agree with the ones obtained in the present work only in the (rather trivial) limit that $z\to-\infty$. Thus, in an actual calculation of a screening self-energy in the surface region, we expect our coupling functions to yield different results from what would obtain by using Eqs. (3.24) and (3.25). In Sec. IV we argue that this should lead to observable results.

IV. THE ELECTRON SELF-ENERGY: RESULTS FOR THE IMAGE POTENTIAL

Equations (2.15) and (2.18) give the self-energy of an electron that results from its coupling to the normal modes of a metal with a surface (or, equivalently, the self-energy due to the collective response of the metal). Since the Green's function G is a functional of the self-energy Σ, Eq. (2.15) is really an integral equation for Σ. Formally, Eq. (2.15) can be solved by iteration. Here we shall follow common practice[25] and keep the "zeroth-order" iteration only, i.e., we set $G=G^{(0)}$ in Eq. (2.15). The bare-electron Green's function $G^{(0)}$ satisfies the differential equation

$$\left[\frac{d^2}{dz^2}+\left(\frac{2m}{\hbar}\Omega_n-k_{\parallel}^2\right)\right]G_{\vec{k}_{\parallel}}^{(0)}(zz'\,|\Omega_n)=\frac{2m}{\hbar}\delta(z-z'). \tag{4.1}$$

It is convenient to consider the solution to Eq. (4.1) in its Fourier representation, namely:

$$G_{\vec{k}_{\parallel}}^{(0)}(zz'\,|\Omega_n)=\frac{2m}{\hbar}\int_{-\infty}^{+\infty}\frac{dk_z}{2\pi}\frac{e^{ik_z(z-z')}}{\frac{2m}{\hbar}\Omega_n-(k_{\parallel}^2+k_z^2)}. \tag{4.2}$$

Substituting Eqs. (2.16) and (4.2) into Eq. (2.15) gives

$$\Sigma_{\vec{k}_{\parallel}}(zz'\,|\Omega_n)=\sum_n\sum_{\vec{q}_{\parallel}}g_{\vec{q}_{\parallel}}^{(n)}(z)g_{\vec{q}_{\parallel}}^{(n)}(z')\times\int_{-\infty}^{+\infty}\frac{dk_z}{2\pi}e^{ik_z(z-z')}S_{\vec{k}_{\parallel};\vec{q}_{\parallel}}^{(n)}(k_z;\Omega_n), \tag{4.3}$$

where we have called

$$S_{\vec{k}_{\parallel};\vec{q}_{\parallel}}^{(n)}(k_z;\Omega_n)=\frac{1}{\beta_T\hbar}\sum_{\Omega_m}\frac{1}{\Omega_m-\Omega_n+\frac{\hbar}{2m}[(\vec{k}_{\parallel}-\vec{q}_{\parallel})^2+k_z^2]}\times\frac{2\omega_n(q_{\parallel})}{\Omega_m^2-\omega_n^2(q_{\parallel})}. \tag{4.4}$$

The sum over the frequencies Ω_m [defined in Eq. (A6)] can be carried out in the usual way.[24] Upon substituting its value into Eq. (4.3), we analytically continue the self-energy to frequencies just above the real axis (i.e., $\Omega_n\to\omega+i\eta$, $\eta\to0+$). This gives us the self-energy for the retarded Green's function.[41] Finally, we take the $T=0$ K limit. We thus obtain the following result for the self-energy (ω real):

$$\Sigma_{\vec{k}_{\parallel}}(zz'\,|\,\omega)=\sum_n\sum_{\vec{q}_{\parallel}}g_{\vec{q}_{\parallel}}^{(n)}(z)g_{\vec{q}_{\parallel}}^{(n)}(z')\mathcal{G}_{\vec{k}_{\parallel},\vec{q}_{\parallel}}^{(n)}(z-z'\,|\,\omega), \tag{4.5}$$

where we have called

$$\mathcal{G}_{\vec{k}_{\parallel},\vec{q}_{\parallel}}^{(n)}(z-z'\,|\,\omega)=\left(\frac{m}{\hbar}\right)\frac{e^{i\alpha_{\vec{k}_{\parallel},\vec{q}_{\parallel}}^{(n)}(\omega)|z-z'|}}{i\alpha_{\vec{k}_{\parallel},\vec{q}_{\parallel}}^{(n)}(\omega)}, \tag{4.6}$$

with

$$\alpha_{\vec{k}_{\parallel},\vec{q}_{\parallel}}^{(n)}(\omega)=\left(\frac{2m}{\hbar}\right)^{1/2}\left[\omega-\left(\omega_n(q_{\parallel})+\frac{\hbar}{2m}(\vec{k}_{\parallel}-\vec{q}_{\parallel})^2\right)+i\eta\right]^{1/2}. \tag{4.7}$$

Equation (4.5) generalizes a result of Feibelman *et al.*[7] by including the effects of electron-gas dispersion in the electron-metal surface interaction. The self-energy given by Eq. (4.5) is, obviously, a nonlocal function of position. The contribution to Eq. (4.5) from each channel becomes complex ($\alpha^{(n)}$ real) above the threshold for emission of the corresponding excitation. Of course, the spatial range of the various channels is determined by the coupling functions $g_{\vec{q}_{\parallel}}^{(n)}(z)$. For the bulk (surface) plasmon channel, the self-energy is always real for $\omega<\omega_p$ ($\omega<\omega_p/\sqrt{2}$). Note that if the single-particle channels were included explicitly in Eq. (4.5), they would provide decay channels at small frequencies.

Now, both the nonlocality and dissipative character of the self-energy (4.5) are essentially determined by the "propagator" $\mathcal{G}^{(n)}$. Hence, in both regards the analysis of Ref. 7(a) applies qualitatively here. The major difference that Eq. (4.5) presents with respect to Ref. 7 is brought in by the coupling functions $g_{\vec{q}_{\parallel}}^{(n)}(z)$. Thus, in order to illustrate the effects of electron-gas dispersion in a clear fashion, we now consider the semiclassical approximation $m\to\infty$, in which

$$g^{(n)}_{\vec{k}_\parallel,\vec{q}_\parallel}(z-z'\,|\,\omega)\xrightarrow[m\to\infty]{}\frac{\delta(z-z')}{\omega-\omega_n(q_\parallel)+i\eta} \tag{4.8}$$

[Eq. (4.8) can be proved, for example, by Fourier-transforming Eq. (4.6)]. Then, defining the "potential energy" $V(z)$ such that

$$\Sigma_{\vec{k}_\parallel=0}(zz'\,|\,\omega=0)=\delta(z-z')V(z)\,, \tag{4.9}$$

we have the result that

$$V(z)=-\sum_n\sum_{\vec{q}_\parallel}\frac{1}{\omega_n(q_\parallel)}[g^{(n)}_{\vec{q}_\parallel}(z)]^2\,. \tag{4.10}$$

Thus, in the present semiclassical approximation, the self-energy becomes a local function of position.[7] Note that in Eq. (4.9) we have set $\vec{k}_\parallel=0$, $\omega=0$ in order to localize the massive particle. (Obviously, in this limit the particle whose self-energy we are considering is no longer an "electron", but rather a heavy ion).

We stress that the above approximation for Σ is useful not only to quantify the effects of electron-gas dispersion in the electron-metal surface interaction, but also because of the widespread use of the image-potential concept in surface physics. Equation (4.10) generalizes the classical image potential $-e^2/4z$, by taking into account electron-gas dispersion in the response of the metal surface.

A final reason why Eq. (4.10) is of interest is found in a related physical problem. It is possible to show that (the magnitude of) $V(z)$ gives the "relaxation energy"[1,6,8] of a deep core level of an atom located in the surface region. Equation (4.10) generalizes Eq. (16) of Ref. 6 by including the effects of electron-gas dispersion in the hole-metal surface interaction. Thus, measuring the relaxation energy[6] as a function of the position of the hole left behind by the photoemitted electron, one could obtain useful information about screening processes in the surface region.

We note that no assumption has been made in deriving Eq. (4.10) with regards to the form of the coupling functions $g^{(n)}_{\vec{q}_\parallel}(z)$. In what follows we utilize the coupling functions we obtained in Sec. III. Our program is then to substitute Eqs. (3.13) and (3.14) (for $z>0$), and Eqs. (3.15) and (3.16) (for $z<0$), into Eq. (4.10) and carry out the required integrals. In both cases it is convenient to define the separate contributions to the image potential $V(z)$ from the surface and bulk channels, $V_S(z)$ and $V_B(z)$, respectively. Then

$$V(z)=V_S(z)+V_B(z)\,. \tag{4.11}$$

(a) Image potential for $z>0$. Proceeding as just indicated, we obtain the results that

$$V_S(z)=-\frac{e^2\omega_p^2}{4}\int_0^\infty dq_\parallel e^{-2q_\parallel z}\frac{1}{\omega_s^2(q_\parallel)}\frac{\hat{\gamma}_s(q_\parallel)}{\hat{\gamma}_s(q_\parallel)+\frac{1}{2}q_\parallel}\,, \tag{4.12}$$

and (upon performing the integral over p by contour integration)

$$V_B(z)=-\frac{e^2\beta^2}{\omega_p^2}\int_0^\infty dq_\parallel q_\parallel e^{-2q_\parallel z}\left[-\left(q_\parallel^2+\frac{\omega_p^2}{\beta^2}\right)^{1/2}+\frac{1}{2}\frac{\left(q_\parallel^2+\frac{3}{2}\frac{\omega_p^2}{\beta^2}\right)}{\left(\frac{q_\parallel^2}{4}+\frac{\omega_p^2}{2\beta^2}\right)^{1/2}}\right]. \tag{4.13}$$

From Eqs. (4.11)–(4.13) we can show the result that

$$V(z)=-\frac{e^2\beta^2}{\omega_p^2}\int_0^\infty dq_\parallel e^{-2q_\parallel z}\left[\frac{1}{2}\left(2q_\parallel^2+\frac{\omega_p^2}{\beta^2}\right)-q_\parallel\left(q_\parallel^2+\frac{\omega_p^2}{\beta^2}\right)^{1/2}\right]. \tag{4.14}$$

Equation (4.14) agrees with the result first obtained by Newns[42] in a purely classical calculation of the image potential [note that with the approach of Ref. 42 the role played by the normal modes of themetal goes unnoticed]. Equations (4.12) and (4.13) agree with the results of Barton,[16] who used the canonical quantization method to study the coupling of the external charge and the metal surface.

It is, in fact, possible to evaluate the integrals in Eqs. (4.12)–(4.14) in terms of known functions, namely, the Struve and Neumann functions of order zero and one.[43] We shall not display the resulting expressions, however. (They are useful to obtain the limits for large and small values of z/λ given in Ref. 44). For intermediate values of z/λ it is more illuminating to give a plot of the image potentials obtained above. This is done in Fig. 2. Note that, as mentioned in the Introduction, $(V_B/V)_{z=0}\cong 0.3$. We stress that the classical-image potential

$$V_{\text{image}}(z)=-\frac{e^2}{4z}\,, \tag{4.15}$$

is obtained from Eq. (4.10) if we use Eq. (1.2) for $g^{(s)}_{\vec{q}_\parallel}(z)$. Figure 2 shows that approximation for the coupling function $g^{(s)}$ to be totally inadequate for $z\sim\lambda$. (This was anticipated on more general grounds in Sec. III B). The main conclusion to be drawn from Fig. 2 is that, provided $g^{(s)}$ is given by Eq. (3.13) [and *not* by Eq. (1.2)], the surface

channel by itself gives a sufficiently accurate description of the screening for $z \gtrsim \lambda$. For small values of z/λ and, as we shall see below, for $z<0$, it is important to include on an equal footing the contribution to screening from the bulk channels.

(b) Image potential for $z<0$. Equations (4.10), (3.15), and (3.16) yield the results

$$V_S(z) = -\frac{e^2\omega_p^2}{4}\int_0^\infty dq_\parallel \frac{1}{\omega_s^2(q_\parallel)} \frac{\hat{\gamma}_s[(\hat{\gamma}_s+q_\parallel)e^{q_\parallel z} - 2q_\parallel e^{\hat{\gamma}_s z}]^2}{(\hat{\gamma}_s+\frac{1}{2}q_\parallel)(\hat{\gamma}_s-q_\parallel)^2}, \tag{4.16}$$

and (after carrying out the p integral by contour integration)

$$V_B(z) = -\frac{e^2}{2\lambda} + e^2\int_0^\infty dq_\parallel \left\{ \frac{\beta^2}{2\omega_p^2} \frac{q_\parallel}{\left(q_\parallel^2+\frac{\omega_p^2}{\beta^2}\right)^{1/2}} \left[q_\parallel - \left(q_\parallel^2+\frac{\omega_p^2}{\beta^2}\right)^{1/2}\right]^2 \exp\left[2\left(q_\parallel^2+\frac{\omega_p^2}{\beta^2}\right)^{1/2} z\right] - \left(1+\frac{\omega_p^2}{4\beta^2}\frac{(\hat{\gamma}_s+q_\parallel)}{(\hat{\gamma}_s+\frac{1}{2}q_\parallel)(\hat{\gamma}_s+2q_\parallel)^2}\right)e^{2q_\parallel z} \right.$$
$$- \frac{2}{(q_\parallel-\hat{\gamma}_s)^2}\left[\frac{q_\parallel\hat{\gamma}_s}{(\hat{\gamma}_s+\frac{1}{2}q_\parallel)(\hat{\gamma}_s+q_\parallel)}\left(\frac{\omega_p^2}{2\beta^2}e^{(\hat{\gamma}_s+q_\parallel)z} - \hat{\gamma}_s q_\parallel e^{2\hat{\gamma}_s z}\right)\right.$$
$$\left.\left. - \frac{1}{(\hat{\gamma}_s+2q_\parallel)^2}\left(2q_\parallel^4 - \frac{3}{4}q_\parallel^2\frac{\omega_p^2}{\beta^2} + \frac{\omega_p^4}{4\beta^4}\right)e^{2q_\parallel z}\right]\right\}. \tag{4.17}$$

We note that $V_B(z=-\infty) = -e^2/2\lambda$, is the screening energy due to the bulk plasmon in the case of an infinite, homogeneous electron gas. The integral in Eq. (4.17) gives the surface-induced contribution to $V_B(z)$ (it consists of terms that vanish as $z \to -\infty$). From Eqs. (4.16) and (4.17) we can show that, for $|z| \gg \lambda$:

$$V_S(z) \to -\frac{e^2}{4|z|}, \quad V_B(z) \to -\frac{e^2}{2\lambda} + \frac{e^2}{4|z|}. \tag{4.18}$$

Thus, for $|z| \gg \lambda$:

$$V(z) \to -\frac{e^2}{2\lambda} + O\left(\frac{\lambda}{z}\right)^2. \tag{4.19}$$

Hence, deep inside the metal, the surface-induced contribution to $V_B(z)$ exactly cancels the image potential due to the surface plasmon. Now, the cancellation leading to the absence of the z^{-1} term in Eq. (4.19) is a general feature of our results. In effect, it is possible to show that the last three lines in Eq. (4.17) exactly cancel Eq. (4.16) (the algebra involved in the proof is lengthy, so we omit it). Thus we have the result that

$$V(z) = -\frac{e^2}{2\lambda} + \frac{e^2\beta^2}{2\omega_p^2}\int_0^\infty dq_\parallel \frac{q_\parallel}{\left(q_\parallel^2+\frac{\omega_p^2}{\beta^2}\right)^{1/2}} \times \left[q_\parallel - \left(q_\parallel^2+\frac{\omega_p^2}{\beta^2}\right)^{1/2}\right]^2 \times \exp\left[2\left(q_\parallel^2+\frac{\omega_p^2}{\beta^2}\right)^{1/2} z\right]. \tag{4.20}$$

We emphasize that Eq. (4.20) shows that the total image potential *monotonically* decreases from its value at $z=0$ $[V(0) = -e^2/3\lambda]$ to its value at $z=-\infty$ $[V(-\infty) = -e^2/2\lambda]$. Also, our demonstration stresses the importance of treating bulk and surface modes on an equal footing (this point was also emphasized in Sec. III A in connection with the f-sum rule).

In Fig. 3 we present plots of $V_S(z)$, $V_B(z)$, and $V(z)$ throughout the surface region. Note that whereas the total potential reaches its bulk value for $|z| \sim \lambda$, the separate contributions to it, namely $V_S(z)$ and $V_B(z)$ have a more complicated behavior, reaching their asymptotic values only after several electron screening lengths.

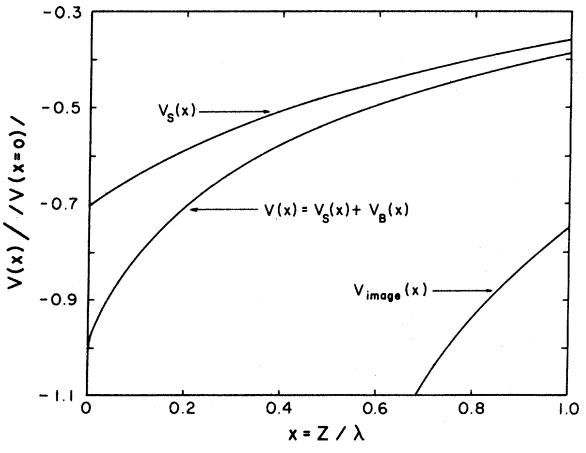

FIG. 2. The "image potential" $V(z)$ [see Eq. (4.14)] acting on a charge localized at a distance $x=z/\lambda$ outside a metal surface. Here λ is the electron screening length. $V_S(z)$ is the contribution to $V(z)$ from the surface plasmon channel (the difference $V-V_S$ being due to the bulk plasmon channels). Also shown is the classical image potential, $V_{\text{image}} = -e^2/4z$. [Note: $V(0) = -e^2/3\lambda$].

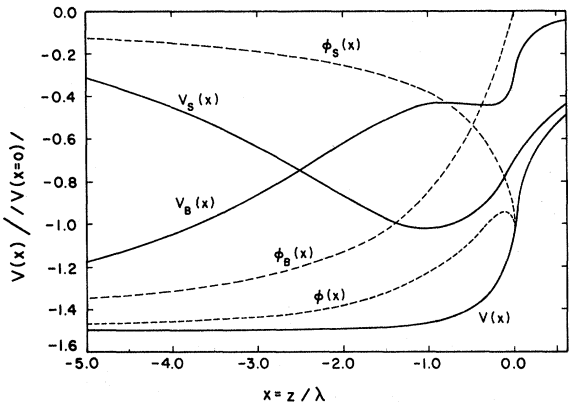

FIG. 3. Plots of $V(z)$, $V_S(z)$, and $V_B(z)$ in the surface region. Note that whereas the total potential gives a smooth potential barrier that reaches its bulk value for $|z| \sim\lambda$, its separate components $V_S(z)$ and $V_B(z)$ have a more complicate behavior. These potentials reach their asymptotic values $V_S(-\infty)=0$ and $V_B(-\infty)=-e^2/2\lambda$, respectively, rather deep into the metal. [Note: $V(-\infty) = -1.5\,|V(0)|$]. Also shown are the potentials $\phi_S(x)$, $\phi_B(x)$, and $\phi(x)\,[=\phi_S(x)+\phi_B(x)]$ obtained from Eq. (4.10) with the coupling functions given by Eqs. (3.24) and (3.25). Note that $\phi(x)$ equals $V(x)$ for $x>0$.

We note that in the absence of spatial dispersion[7(b),11] [i.e., utilizing the coupling functions given by Eqs. (1.2) and (1.4)], the surface-induced contribution to the image potential from the bulk modes exactly cancels (for all $z<0$) the classical-image potential $(-e^2/4|z|)$ due to the surface plasmon. [This can be proved, e.g., from Eq. (4.20) with $\beta\to 0$]. The remaining (bulk) term, $-e^2/2\lambda$ is, in this approximation, infinite ($\lambda\sim\beta$). Thus the smooth "barrier" $V(z)$ of Fig. 3 is entirely due to spatial dispersion.

This new feature of our results could be directly observable in surface-sensitive photoelectron measurements of relaxation energies[6] and is in marked contrast with, for example, the results of dispersionless theories like those of Barrera and Duke[7(b)] and Chang and Langreth.[11] The former authors obtained an image potential [Eq. (28) of Ref. 7(b)] that is a (cutoff-dependent) *constant* for all $z<0$. For $z>0$ it gives the classical-image potential (4.15). Chang and Langreth[11] calculated (for $z<0$) the relaxation energy $\Delta E=-V(z)$ of a deep core level. These authors utilized the coupling functions (1.2) and (1.4). They obtained a finite (see above paragraph) and z-dependent result via the use of a cutoff in their integrals over $q_\parallel$. Their results for $V(z)$ show an absolute minimum at a finite value of $|z|$, which is absent from Fig. 3 of the present work [see Eq. (4.20)]. Finally, we consider the results obtained by substituting in Eq. (4.10) the coupling functions obtained by Gersten and Tzoar[9] [see Eqs. (3.24) and (3.25)]. This is shown in Fig. 3 where, for convenience, we have called ϕ_S, ϕ_B, and $\phi(\equiv\phi_S+\phi_B)$ the corresponding image potentials. For $z>0$, it is found that $\phi(z)[\equiv\phi_S(z)]$ exactly agrees with $V(z)$ [note that $\phi_B(z)\equiv 0$ in this region]. For $z<0$, agreement between the various potentials is found only for $z\ll-\lambda$. We note that the curve for $\phi(x)$ shows a small local minimum just inside the surface. (This is reminiscent of a similar feature of a calculation of Evans and Mills[15,45] of the surface polaron binding energy). Such a minimum is not present in our result for $V(z)$, that is, the minimum disappears with a proper inclusion of electron-gas dispersion effects. We note that the difference between our method and that of Ref. 9 is expected to be even more pronounced in *dynamical* problems, since then the bulk and surface channels can manifest themselves separately.

V. SYNOPSIS AND CRITIQUE

We have presented a theory of the screening of an electron by a metal surface in which a key role is played by the functions coupling the electron to the normal modes of a metal with a surface. Explicit results for the coupling functions were obtained in Sec. III within the surface plasmon-pole approximation. We can summarize the new results of Secs. II and III with the statement that the coupling functions given by Eqs. (3.13)–(3.18) are free of the qualitative shortcomings that, as noted in the Introduction, apply to local (or nondispersive) theories of electron conduction ($\lambda=0$), and to some extent, to more general theories[9] that, in the presence of spatial dispersion, fail to treat bulk and surface modes on an equal footing. While the detailed functional forms of our coupling functions are surely dependent on, e.g., our assumption (Sec. III) of a sharp electron density profile at the surface, some of our conclusions are expected to be more generally valid. Among these: (a) our explicit result that the coupling to the bulk modes, while finite outside the metal surface, is of short range ($g^{(B)}$ analytic as $q_\parallel\to 0$); (b) the fact that the coupling to surface plasmons with $q_\parallel\neq 0$ (this coupling is *absent* in theories with $\lambda=0$) leads to an interaction that is already strongly reduced (with respect to those $\lambda=0$ or "bare-image" theories) for $z\sim\lambda$, suggests that the detailed electron-hole pair structure of the true response function is important for $z\ll\lambda$ only. This is in agreement with earlier numerical results of Gadzuk[46]; (c) our results for the coupling functions for $z<0$ are qualitatively different from, and *a priori* more realistic than those from previous theories.

As a first application of our results for the

coupling functions, we obtained in Sec. IV, explicit results for the image potential. While the very concept of a local image potential is an idealization of the actual self-energy of a finite-mass particle like an electron, these results are nonetheless of direct interest to the study of the relaxation energies of deep core levels of atoms near the surface of a simple metal (e.g., aluminum). In fact, the measurement of these relaxation energies[6] as a function of the distance of the photoemitting atom from the surface should provide (especially for $z<0$) a good experimental test of our new results and their differences with previous work in the area. Finally, as noted above (and for the same reason), we expect that the detailed electron-hole pair structure of a real metal should affect our results for $V(z)$ for $z \ll \lambda$ only. (Recall that the single-particle response is considered only in an average sense in the plasmon-pole approximation.) For example, it is possible to show that the slope of $V(z)$ has a logarithmic singularity at $z=0$. Also, our result for $V(z)$ does not (as expected) show Friedel oscillations (see Fig. 3). Both deficiencies of our results would, of course, be absent in a more complete theory. Given the difficulties inherent in such a theory, our simpler results should be useful as an average representation (which is the spirit of the plasmon-pole approximation) of the screening for $|z| \lesssim \lambda$.

Finally, we note that the coupling functions considered in this paper can be utilized in calculations other than the static screening results of Sec. IV. This is, in fact, one of our reasons for centering our theory around them. For example, we can consider the case of a hole in a deep core level of an atom in the surface region. The functions coupling the hole and the normal modes of the metal, $\lambda^{(n)}_{H;\vec{q}_\parallel}$, are found to be given by [47]

$$\lambda^{(n)}_{H;\vec{q}_\parallel} = \int d^3x\, e^{i\vec{q}_\parallel\cdot\vec{x}_\parallel} \left|\varphi(\vec{x})\right|^2 g^{(n)}_{q_\parallel}(z)\,, \tag{5.1}$$

where $\varphi(\vec{x})$ is the wave function of the core level. The coupling functions (5.1) can be utilized in the study of photoemission problems.[47]

ACKNOWLEDGMENTS

This work was begun (and a good part of it carried out) at the University of Toronto. The kind hospitality of the members of the Solid State Group is gratefully acknowledged. I thank Professor A. Griffin for useful discussions and Dr. H. Kranz for an early copy of his thesis (Ref. 8), which I found very motivating. I would like to acknowledge support by the NRC of Canada and the National Science Foundation Grant No. DM-7809430. I also thank Professor A. A. Maradudin for a reading of the manuscript and Professor D. L. Mills for useful comments.

APPENDIX A: ELECTRON SELF-ENERGY

From chapters 5 and 12 of the book by Kadanoff and Baym[24] (see also Ref. 25), we can obtain an *exact* equation for the electron self-energy for the full electron Hamiltonian, namely:

$$\Sigma(1;1') = \delta(1-1')\int d2\, v(1-2)\langle\hat{n}(2)\rangle + M(1;1')\,, \tag{A1}$$

where

$$M(1;1') = i\int d2 \int d3\, v(1-2)G(1;3)\Gamma(3,1';2) + \Sigma_{nn}(1;1') \tag{A2}$$

and

$$\Sigma_{nn}(1;1') = i\int d2\int d3\int d4\int d5\, v(1-2)v(4-5)G(1;3) \times \Gamma(3,1';4)\chi^{(T)}_{nn}(5;2). \tag{A3}$$

Here $1 \equiv (\vec{x}_1, t_1)$, $2 \equiv (\vec{x}_2, t_2)$, etc., and the integrals run over all of configuration space and over the time interval $[0, -i\beta_T\hbar]$, $(\beta_T = 1/k_B T)$. In Eq. (A1), $\hat{n}(2) = \psi^\dagger(2)\psi(2)$ is the density operator and $v(1-2) = v(\vec{x}_1 - \vec{x}_2)\delta(t_1 - t_2)$ is the Coulomb interaction. In Eqs. (A2) and (A3), $\Gamma(1,2;3)$ is the so-called "vertex function," defined, e.g., in Eq. (13.18) of Ref. 25. We note that the first terms in Eqs. (A1) and (A2) are, respectively, the usual Hartree term and a generalized exchange term (the latter reduces to the more conventional Fock term if $G \to G_0$, the bare-electron Green's function and $\Gamma \to 1$). Finally, $\Sigma_{nn}(1;1')$ represents the contribution to the total self-energy arising from the collective response of the electron gas. It is a functional of the *time-ordered* density response function of the electron gas, $\chi^{(T)}_{nn}(1;2)$, defined by

$$\chi^{(T)}_{nn}(1;2) \equiv \left(\frac{\delta\langle\hat{n}(1)\rangle}{\delta U(2)}\right)_{U=0}. \tag{A4}$$

We note that $U(\vec{x};t)$ is an auxiliary scalar potential that is introduced[24] to relate the two-particle Green's function and the one-particle Green's function (through the latter's functional derivative with respect to U). It is set equal to zero at the end [see Eq. (A4)].

In this paper we are only concerned with Σ_{nn}, which we now consider in the usual approximation of neglecting "vertex corrections." This approximation (which is hard to justify *a priori*[25]) here means $\Gamma(1,2;3) \to \delta(1-3)\delta(1-2)$. Then, noting that G and Σ_{nn} satisfy (on the imaginary time axis)

the periodic boundary condition[24] appropriate for fermions whereas $\chi_{nn}^{(T)}$ satisfies that appropriate for bosons, we Fourier transform Eq. (A3) and obtain

$$\Sigma_{nn}(\vec{x}\vec{x}'\,|\,\Omega_n) = -\frac{1}{\beta_T\hbar}\sum_{\Omega_m}\int d^3x_1\int d^3x_2 v(\vec{x}-\vec{x}_1)v(\vec{x}'-\vec{x}_2) \times G(\vec{x}\vec{x}'\,|\,\Omega_n-\Omega_m) \times \chi_{nn}^{(T)}(\vec{x}_1\vec{x}_2\,|\,\Omega_m)\,, \tag{A5}$$

where

$$\hbar\Omega_n = \mu - \frac{n\pi}{i\beta_T}\,, \quad \hbar\Omega_m = -\frac{m\pi}{i\beta_T}\,, \tag{A6}$$

$n(m)$ being an odd (even) integer. Note that here the chemical potential of the electron gas μ appears in the fermion but not the boson frequencies because the density operator does not create or destroy particles.

Equation (A5) is used in Sec. II for the special case of the surface problem in which $\Sigma_{nn}(\vec{x}\vec{x}'\,|\,\Omega_n) = \Sigma_{nn}(\vec{x}_\parallel - \vec{x}_\parallel'; zz'\,|\,\Omega_n)$.

We close this appendix by noting some results for the time-ordered density response function that we shall need in Sec. II. (These results are more commonly found in the literature in the simpler case of the homogeneous electron gas[19].) We first note the following spectral representation:

$$\chi_{nn}^{(T)}(\vec{x}\vec{x}'\,|\,\Omega_m) = \frac{1}{\pi}\int_0^\infty d\omega \frac{2\omega}{\Omega_m^2-\omega^2}\,\mathrm{Im}\chi_{nn}^{(R)}(\vec{x}\vec{x}'\,|\,\omega)\,, \tag{A7}$$

where

$$\mathrm{Im}\chi_{nn}^{(R)}(\vec{x}\vec{x}'\,|\,\omega) \equiv \frac{1}{2\hbar}\int_{-\infty}^{+\infty} dt\, e^{i\omega(t-t')} \times \langle[\hat{n}(\vec{x}t), \hat{n}(\vec{x}'t')]_-\rangle \tag{A8}$$

is the imaginary part of the *retarded* density response function, i.e., the physical response to an external scalar potential φ_{ext}. Specifically,[17]

$$n(\vec{x};\omega) = \int d^3x'\,\chi_{nn}^{(R)}(\vec{x}\vec{x}'\,|\,\omega)\varphi_{\mathrm{ext}}(\vec{x}';\omega) \tag{A9}$$

gives the fluctuation in the electron-number density produced by $\varphi_{\mathrm{ext}}(\vec{x};\omega)$.

We emphasize that the proof of Eq. (A7) makes explicit use of the following property:

$$\mathrm{Im}\chi_{nn}^{(R)}(\vec{x}\vec{x}'\,|\,-\omega) = -\mathrm{Im}\chi_{nn}^{(R)}(\vec{x}\vec{x}'\,|\,\omega)\,, \tag{A10}$$

which can be proved[48] starting from Eq. (A8) and noting that the Hermitian operator $\hat{n}(\vec{x}t)$ has a definite signature under time reversal (+1). [In the simpler case of the translationally invariant system, the definition (A8) suffices to prove (A10) (Ref. 19)]. Other useful symmetry properties that follow from time-reversal considerations are[48]

$$\mathrm{Im}\chi_{nn}^{(R)}(\vec{x}'\vec{x}\,|\,\omega) = \mathrm{Im}\chi_{nn}^{(R)}(\vec{x}\vec{x}'\,|\,\omega) \tag{A11}$$

(which we shall refer to in Sec. II), and

$$[\mathrm{Im}\chi_{nn}^{(R)}(\vec{x}\vec{x}'\,|\,\omega)]^* = \mathrm{Im}\chi_{nn}^{(R)}(\vec{x}\vec{x}'\,|\,\omega)\,. \tag{A12}$$

APPENDIX B: $\mathrm{Im}\,\chi(\vec{q}_\parallel\omega\,|zz')$ FOR A SEMI-INFINITE METAL

In this appendix we briefly indicate how to obtain the half-space limit of the imaginary part of the density response function obtained in I for a metal slab of thickness $2L$ [Eqs. (3.18) and (3.26) of I].

Taking the limit $L\to\infty$ of $\mathrm{Im}\chi(\vec{q}_\parallel\omega\,|zz')$ is trivial in the frequency region below ω_p, but it requires a careful treatment of the bulk plasmon continuum ($\omega > \omega_p$). We start out by changing variables (with respect to I) according to $z\to z+L$, $z'\to z+L$. This sets the origin of coordinates on the right-hand edge of the film. Note that now $L\to\infty$ means that the slab is *semi*-infinite (half-space limit). For frequencies $\omega > \omega_p$, $\mathrm{Im}\chi(\vec{q}_\parallel\omega\,|zz')$ is given by Eq. (3.18) of I which, for brevity, we do not reproduce here. We must consider the $L\to\infty$ limit of the products:

$$\cos\gamma_{sn}(z+L)\cos\gamma_{sn}(z'+L) \tag{B1}$$

and

$$\sin\gamma_{an}(z+L)\sin\gamma_{an}(z'+L)\,, \tag{B2}$$

where $\gamma_{sn}(q_\parallel)$ and $\gamma_{an}(q_\parallel)$ are the solutions to the eigenvalue equations

$$\begin{matrix}\tan\gamma L \\ \cot\gamma L\end{matrix} = \mp\frac{q_\parallel}{\gamma}\frac{\omega_\pm^2(q_\parallel)}{\omega_\mp^2(q_\parallel)+\beta^2(q_\parallel^2+\gamma^2)}\,, \tag{B3}$$

with

$$\omega_\pm^2(q_\parallel) = \frac{\omega_p^2}{2}(1\mp e^{-2q_\parallel L})\,. \tag{B4}$$

Utilizing simple trigonometric identities for $\cos\gamma_{sn}(z+L)$ and $\sin\gamma_{an}(z+L)$ in conjunction with Eq. (B3), we can write

$$\cos\gamma_{sn}(z+L) = \frac{\cos\gamma_{sn}L\{\gamma_{sn}[\omega_-^2+\beta^2(q_\parallel^2+\gamma_{sn}^2)]\cos\gamma_{sn}z + q_\parallel\omega_+^2\sin\gamma_{sn}z\}}{\gamma_{sn}[\omega_-^2+\beta^2(q_\parallel^2+\gamma_{sn}^2)]} \tag{B5}$$

and

$$\sin\gamma_{an}(z+L) = \frac{\sin\gamma_{an}L\{\gamma_{an}[\omega_+^2+\beta^2(q_\parallel^2+\gamma_{an}^2)]\cos\gamma_{an}z + q_\parallel\omega_-^2\sin\gamma_{an}z\}}{\gamma_{an}[\omega_+^2+\beta^2(q_\parallel^2+\gamma_{an}^2)]}\,. \tag{B6}$$

We next introduce the "phase shifts" δ according to

$$\gamma_{sn}(q_\parallel)=\frac{1}{L}[n\pi-\delta_{sn}(q_\parallel)]\,, \tag{B7}$$

$$\gamma_{an}(q_\parallel)=\frac{1}{L}[(n+\tfrac{1}{2})\pi-\delta_{an}(q_\parallel)]\,, \tag{B8}$$

where $n=1,2,3,\ldots$.[17] Note that the phase shifts represent the difference between the solutions of the eigenvalue equations (B3) and the values of the "standing-wave" wave vectors $n\pi/L$ and $(2n+1)\pi/2L$ that are sometimes used as effective wave vectors for the (symmetric and antisymmetric) normal modes of a metal film. From Eqs. (B7) and (B8) it follows that

$$\cos\gamma_{sn}L=(-1)^n\cos\delta_{sn}(q_\parallel) \tag{B9}$$

and

$$\sin\gamma_{an}L=(-1)^n\cos\delta_{an}(q_\parallel)\,. \tag{B10}$$

Equations (B9) and (B10) are to be substituted into Eqs. (B5) and (B6), respectively.

The above holds for arbitrary values of L. We next note that Eq. (3.18) of I has an overall factor of L^{-1}. It is then possible to show that, in the limit $L\to\infty$, only the first term in a Euler-Maclaurin series of the form[43]

$$\sum_{n=1}^{\infty}F_n=\int_1^{\infty}dn\,F(n)+\tfrac{1}{2}F(n=1)-\frac{1}{12}\left(\frac{dF(n)}{dn}\right)_{n=1}+\cdots \tag{B11}$$

contributes to Eq. (3.18) of I. Furthermore, the integrand in that term is to be taken to *zeroth order* in L^{-1}.

Consider then Eq. (B7). Setting $p=n\pi/L$ (notice that now p is a continuous variable running from $p=0$ to $p=\infty$), we have

$$\gamma_{sn}(q_\parallel)\underset{L\to\infty}{\longrightarrow}\gamma(q_\parallel;p)=p-\frac{1}{L}\delta(q_\parallel;p)\,, \tag{B12}$$

and, to zeroth order in L^{-1}, $\cos\gamma_{sn}z=\cos pz$ and $\sin\gamma_{sn}z=\sin pz$. Thus

$$\lim_{L\to\infty}\cos\gamma_{sn}(z+L)=(-1)^n\cos\delta(q_\parallel;p)\,\frac{(p\nu^2\cos pz+\frac{1}{2}q_\parallel\omega_p^2\sin pz)}{p\nu^2}\,, \tag{B13}$$

where we have called

$$\nu^2(q_\parallel;p)=\frac{\omega_p^2}{2}+\beta^2(q_\parallel^2+p^2)\,. \tag{B14}$$

We next note that $\tan\gamma_{sn}L=-\tan\delta_{sn}$ and thus for $L\to\infty$, recalling the identity $\cos^2\delta=1/(1+\tan^2\delta)$, we obtain the result

$$\cos^2\delta(q_\parallel;p)=\frac{1}{\beta^4}\,\frac{p^2}{(q_\parallel^2+p^2)}\,\frac{\nu^4(q_\parallel;p)}{p^4+p^2\left(q_\parallel^2+\frac{\omega_p^2}{\beta^2}\right)+\frac{\omega_p^4}{4\beta^4}}\,. \tag{B15}$$

Utilizing Eqs. (B13) and (B15) leads to the result

$$\lim_{L\to\infty}\cos\gamma_{sn}(z+L)\cos\gamma_{sn}(z'+L)=\cos pz\cos pz'+\frac{B(\vec{q}_\parallel;p|zz')}{(q_\parallel^2+p^2)\left[p^4+p^2\left(q_\parallel^2+\frac{\omega_p^2}{\beta^2}\right)+\frac{\omega_p^4}{4\beta^4}\right]}\,, \tag{B16}$$

where we have defined

$$B(\vec{q}_\parallel;p|zz')=-\frac{\omega_p^4}{4\beta^4}q_\parallel^2\cos p(z+z')+\frac{\omega_p^2}{2\beta^4}q_\parallel p\nu^2\sin p(z+z')\,. \tag{B17}$$

We note that Eq. (B16) was cast in a way convenient in connection with the f-sum rule (see Sec. III). We finally note that it is straightforward to show that the product (B2) equals the result (B16) in the limit $L\to\infty$. This ensures that (as it should be) the symmetric and antisymmetric modes of a slab contribute equally to the $L\to\infty$ result (B18).

As mentioned above, the $\lim L\to\infty$ of $\mathrm{Im}\chi(q_\parallel\omega|zz')$ in the frequency region $\omega<\omega_p$ [see Eq. (3.27) of I], is straightforward (recall that we must set $z\to z+L$, $z'\to z'+L$ before taking the limit). Here we only give the final result. The preceding discussion leads us to the following expression for the imaginary part of the density response function for a hydrodynamic model of a semi-infinite electron gas that occupies the half-space $z<0$:

$$\mathrm{Im}\chi(q_\parallel\omega|zz')=\frac{\omega_p^2}{4e^2}\,\mathrm{sgn}\omega\,\Theta(-z)\Theta(-z')\left[\frac{2}{\pi}\int_0^{\infty}dp\left((q_\parallel^2+p^2)\cos pz\cos pz'+\frac{B(\vec{q}_\parallel;p|zz')}{p^4+p^2\left(q_\parallel^2+\frac{\omega_p^2}{\beta^2}\right)+\frac{\omega_p^4}{4\beta^4}}\right)\delta(\omega^2-\omega_B^2(q_\parallel;p))\right.$$
$$\left.+\frac{q_\parallel\hat{\gamma}_s(\hat{\gamma}_s+q_\parallel)^2}{(\hat{\gamma}_s+\frac{1}{2}q_\parallel)}\,e^{\hat{\gamma}_s(z+z')}\delta(\omega^2-\omega_s^2(q_\parallel))\right]\,. \tag{B18}$$

In Eq. (B18) we have defined

$$\omega_B^2(q_\parallel;p)=\omega_p^2+\beta^2(q_\parallel^2+p^2)\,, \tag{B19}$$

the "bulk-plasmon" dispersion relation, and

$$\omega_s^2(q_\parallel)=\omega_p^2+\beta^2[q_\parallel^2-\hat{\gamma}_s^2(q_\parallel)]\,, \tag{B20}$$

the surface plasmon dispersion relation, where $\hat{\gamma}_s$ is the inverse decay length of the surface plasmon charge fluctuation $[n(z)\sim\exp(\hat{\gamma}_s z)]$, satisfying the (very useful) relation

$$\frac{\omega_p^2}{2\beta^2}=\hat{\gamma}_s(\hat{\gamma}_s+q_\parallel)\,. \tag{B21}$$

Note that Eq. (3.5) is obtained by substituting the solution of Eq. (B21) into Eq. (B20).

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[27]Equation (2.8) holds for $T=0$ K. For finite T, the single sum over n is replaced by a double summation (because of transitions involving states other than the ground state). In order to simplify the notation, and since eventually we set $T=0$ K, we ignore this formal inconsistency of Eq. (2.8).
[28]We note that from the work of Barton (Ref. 16), one could extract for $z>0$ the coupling functions (3.13) and (3.14) of the present paper.
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[36]See the discussion of Sec. II B of Ref. 17 in connection with the definition of this parameter for the surface problem.
[37]Given two operators $A(t)$ and $B(t)$, and defining the spectral weight function $\rho_{AB}(\omega)$ by

$$\rho_{AB}(\omega)=\int_{-\infty}^{+\infty}dt\;e^{i\omega t}[\langle A(t)B(0)\rangle\mp\langle B(0)A(t)\rangle]\,,$$

where the upper (lower) sign applies for bosons (fermions) we can show the general result that (Ref. 41)

$$\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\,\omega\,\rho_{AB}(\omega)=\frac{1}{\hbar}\langle[[A,H],B]_\mp\rangle\,.$$

In the particular case that $A(t)\to\hat{n}(\vec{x},t)$ and $B(t')\to\hat{n}(\vec{x}',t')$ and noting that $\rho_{nn}(\vec{x}\vec{x}'|\omega)$, the above re-

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[44]For $z/\lambda \gg 1$ we have that

$$V_S(z) \to -(e^2/4z)\,[1-(3/\sqrt{8})\lambda/z+\cdots],$$

$$V_B(z) \to -(e^2/4z)\,[(-1+3/\sqrt{8})\lambda/z+\cdots],$$

and

$$V(z) \to -(e^2/4z)(1-\lambda/z+\cdots).$$

For $z/\lambda=0$ we have that $V_S(0) = -e^2/3\sqrt{2}\lambda$, $V_B(0) = -(e^2/3\lambda)(1-1/\sqrt{2})$, and $V(0) = -e^2/3\lambda$.

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