PHYSICAL REVIEW B VOLUME 9, NUMBER 12 15 JUNE 1974

Microscopic calculation of surface-plasmon dispersion and damping*

Peter J. Feibelman
Physics Department, State University of New York at Stony Brook, Stony Brook, New York 11790
(Received 16 November 1973)

Exact calculations of the linear coefficient of surface-plasmon dispersion and damping $\alpha = \alpha_1 + i\alpha_2 \equiv \lim_{q\to 0} q^{-1}[\omega_s(q)/\omega_s(0) - 1]$, using the random-phase-approximation dynamical equation, for a jellium-vacuum interface characterized by a smooth, finite, surface potential barrier are described in detail. α is shown to be markedly sensitive to the shape of this barrier, casting doubt on the reliability of using non-self-consistent potential barriers to determine surface plasmon properties. For the case of an Al-density ($r_s = 2$) substrate, the sensitivity of α to barrier shape should manifest itself through a rather strong increase of α_1 with alkali-impurity adsorption.

I. INTRODUCTION

The properties of surface plasmons have recently become the object of much experimental[1–4] and theoretical[5–18] investigation, stimulated by the hope that the measurement of the surface-plasmon dispersion relation will yield information concerning the electronic structure of free-electron-metal surfaces,[5,16] and also by the knowledge that the force law, which determines the trajectory of a fast electron impinging on such a surface, is in large part a manifestation of (real and virtual) surface-plasmon excitation.[18] As a result of recent inelastic-low-energy-electron-diffraction (ILEED) experiments,[1] the first values are now available of the parameters of the surface-plasmon dispersion relation for a characterized, single-crystal [clean Al(111)] surface, and measurements of the variation of these parameters with alkali (Na and Cs) adsorption can be expected in the not too distant future.[19] On the theoretical side, in the last two years, the first microscopic calculations of surface-plasmon properties have been reported.[6–9,16,17] These calculations, all based on the random-phase-approximation (RPA) equation of motion,[13] have been increasingly realistic in their descriptions of the static free-electron-metal surfaces at which surface plasma oscillations occur. My own calculations, which are the most recent, are the first in which the static metal surface is described by a smooth finite (and, in principle, self-consistent) surface potential barrier. In two rather brief reports of these calculations,[16,17] I have presented numerical results that show (a) that the surface-plasmon dispersion relation is quite sensitive to the assumed shape of this potential barrier,[16] and (b) that one should expect marked changes of the dispersion relation as a function of alkali coverage, for an Al-density substrate.[17] The present paper is devoted to a detailed exposition of the calculations which led to these conclusions. Specifically, in Sec. II, the algebraic reduction of the RPA dynamical equation is presented, which I found to be convenient for the calculation of the long-wavelength slope of the surface plasmon dispersion relation. In addition, I show that my reduction of the RPA equation leads to a formal expression for this slope, which is equivalent to the formal result found earlier by Harris and Griffin.[10] In Sec. III, the details of my numerical work are described; in addition to discussing methods of integration, mesh sizes, and so forth, I explain how I reduced the RPA integral equation approximately to a *finite* set of linear algebraic equations, i.e., a set which I could solve numerically. (This reduction involves knowing the asymptotic form of the charge fluctuation associated with a long-wavelength surface plasmon, deep inside the metal which is supporting the plasmon. This asymptotic form is derived in Appendix B; Appendix A is also devoted to the evaluation of asymptotic properties of certain important integrals.)

In Sec. IV, the results of the calculations are reviewed, and, in particular, the sensitivity of the surface-plasmon dispersion relation to barrier shape and to alkali adsorption is shown. Finally, in Sec. V, directions are discussed for future theoretical work on surface plasmons. The reader who is not interested in following all of the technical details of the calculation reported in this paper should skip over the material between Eqs. (2.35) and (2.51), and all of Sec. III.

II. RPA THEORY OF SURFACE PLASMON DISPERSION AND DAMPING

For a variety of materials (Al, Mg, ...), the frequency of long-wavelength surface plasmons[20] is found to be approximately equal to $\omega_p/\sqrt{2}$, the semiclassical value for a jellium-vacuum interface.[21] Thus, the RPA dynamical equation, which predicts precisely this value for the infinite-wavelength surface plasmon frequency,[14] seems a useful starting point for the microscopic calculation of the surface plasmon dispersion relation $\omega = \omega_s(q)$.

In all RPA surface-plasmon calculations that have been reported to date,[6–9,16,17] the solid surface has been taken to be flat,[22] and the single-electron potential energy (which should, in principle, contain the effects of the periodic ionic lattice as well as those of the self-consistent distribution of electrons) to be spatially constant apart from a discontinuous step at a "surface plane," say, $z=0$. In the present work I have retained the restriction to a jellium model, translationally invariant in planes parallel to the surface, but have gone beyond previous efforts in allowing for a surface potential barrier $V(z)$ of essentially arbitrary form. By virtue of this generalization, it has been possible for me to study the sensitivity of surface-plasmon properties to the model shape of $V(z)$,[16] and, in particular, to the changes in $V(z)$ that might be expected as a result of alkali adsorption on a free-electron-metal surface.[17] The results of these studies are further discussed in Sec. IV. Since the very definition of the jellium model involves averaging out short-wavelength properties of a solid, its use forces one to focus attention on the solid's response to long-wavelength fields. However, the infinite-wavelength surface-plasmon frequency, within the RPA at least,[14] is equal to $\omega_p/\sqrt{2}$, irrespective of the details of surface structure. Thus, within the RPA this frequency is uninteresting as a surface diagnostic property, and, expanding the surface plasmon dispersion relation in powers of the wave vector $\vec{q}$ in the form

$$\omega_s(q)=(\omega_p/\sqrt{2})[1+(\alpha_1+i\alpha_2)q+(\beta_1+i\beta_2)q^2+\cdots], \tag{2.1}$$

it is rather the coefficients $\alpha_1, \alpha_2, \beta_1, \beta_2, \ldots$ whose relation to surface structure one is led to study. In what follows, the RPA dynamical equation is cast into a form which permits the direct evaluation of α_1 and α_2, i.e., in which the fact that $\omega_s(0)=\omega_p/\sqrt{2}$ is accounted for exactly; this form of the RPA equation thereby greatly facilitates the numerical computation of the α's.

For a semi-infinite solid which is translationally invariant in two dimensions, the surface plasmon is entirely characterized by a wave vector $\vec{q}$ directed along the surface, and a (complex) frequency $\omega=\omega_s(q)$. In this geometry, therefore, the RPA equation for the fluctuating electric potential $\phi_{q\omega}(z)$, associated with a surface plasmon is an integral equation in one variable, namely, z, the coordinate normal to the surface. This equation takes the form[13]

$$\phi_{q\omega}(z)=\int\frac{d^2k}{(2\pi)^2}\int_0^\infty\frac{2d\kappa}{\pi}\,2\theta_{k\kappa}\int dz'\,dz'' \times\frac{2\pi e^2}{q}\,e^{-q|z-z'|}\,\psi_\kappa(z') \times\mathcal{G}^{+}_{k,\kappa,q,\omega}(z',z'')\,\psi_\kappa(z'')\phi_{q\omega}(z'') \tag{2.2}$$

In Eq. (2.2), the $\psi_\kappa(z)$ are electron wave functions corresponding to the assumed surface potential barrier $V(z)$; that is, they satisfy the Schrödinger equation (with $\hbar=1$)

$$h\psi_\kappa(z)\equiv\left(-\frac{1}{2m}\frac{d^2}{dz^2}+V(z)\right)\psi_\kappa(z)=\omega_\kappa\psi_\kappa(z)\ . \tag{2.3}$$

Assuming $V(z)$ to have the asymptotic behavior

$$V(z)\to\begin{cases}0\,, & z\to-\infty\\ -(\Phi+\epsilon_F)\,, & z\to+\infty\end{cases}\ , \tag{2.4}$$

where Φ and ϵ_F are, respectively, the work function and Fermi energy of the metal in question, it follows that

$$\omega_\kappa=\kappa^2/2m-\Phi-\epsilon_F\ . \tag{2.5}$$

Thus, in Eq. (2.2), the zero-temperature Fermi function $\theta_{k\kappa}$ is given by

$$\theta_{k\kappa}=\Theta(\epsilon_F-(1/2m)(k^2+\kappa^2))\ . \tag{2.6}$$

The function $(2\pi e^2/q)e^{-q|z-z'|}$, in Eq. (2.2), is the $\vec{q}$th Fourier component of the Coulomb potential $e^2/[x^2+y^2+(z-z')^2]^{1/2}$. Finally, the quantity $\mathcal{G}^{+}_{k,\kappa,q,\omega}(z',z'')$ is defined by the expression

$$\mathcal{G}^{\pm}_{k,\kappa,q,\omega}(z',z'') =G^{+}\left(z',z'';\,\omega+\frac{k^2-(\vec{k}+\vec{q})^2}{2m}+\omega_\kappa\right) \pm G^{-}\left(z',z'';\,-\omega+\frac{k^2-(\vec{k}+\vec{q})^2}{2m}+\omega_\kappa\right), \tag{2.7}$$

in which $G^{\pm}(z',z'';\epsilon)$ are, respectively, the outgoing and incoming Green's functions corresponding to $V(z)$. These functions satisfy the equation

$$(\epsilon-h)\,G^{\pm}(z,z';\epsilon)=\left(\epsilon+\frac{1}{2m}\frac{d^2}{dz^2}-V(z)\right)\times G^{\pm}(z,z';\epsilon)=\delta(z'-z'') \tag{2.8}$$

and have the spectral representations

$$G^{\pm}(z',z'';\epsilon)=\int_\kappa\frac{\psi_\kappa(z')\psi^*_\kappa(z'')}{\epsilon\pm i\delta-\omega_\kappa}\ , \tag{2.9}$$

where the integral on κ runs over the complete set of solutions to Eq. (2.3). The substitution of Eqs. (2.9) and (2.7) into Eq. (2.2) leads back to a more familiar looking form of the RPA equation for $\phi_{q\omega}(z)$.[13]

It should be recognized that, as it stands, Eq. (2.2) has branches of solutions other than the one which corresponds to surface plasmons. In particular, it has bulk-plasmon solutions, which are characterized by the sinusoidal oscillation of $\phi_{q\omega}(z)$ as $z\to\infty$, and by $\mathrm{Re}\,\omega>\omega_p$. It may also have solutions corresponding to "higher-order" surface-plasma modes.[5,18] Thus, in order to use Eq. (2.2) to calculate the ordinary surface-plasmon dispersion relation, one must seek a means of focusing only on that branch of solutions to Eq. (2.2) which emerges from the frequency $\omega_p/\sqrt{2}$ at $q=0$.

The study of Eq. (2.2) at $q=0$, however, is complicated by the presence of the factor q^{-1} in its kernel. In order to overcome the difficulty, one makes use of the following identity:

$$\mathcal{G}^{+}_{k,\kappa,q,\omega}(z',z'')=\left(\frac{1}{2m}(q^2+2\vec{k}\cdot\vec{q})-\omega_\kappa+V(z)-\frac{1}{2m}\frac{d^2}{dz^2}\right)\mathcal{G}^{-}_{k,\kappa,q,\omega}(z',z'')\ , \tag{2.10}$$

which is a trivial consequence of the definitions of $\mathcal{G}^{\pm}$ [Eq. (2.7)] and of the equations of motion for the $G^{\pm}$ [Eq. (2.8)]. Using Eq. (2.10) to substitute for $\mathcal{G}^{\pm}$ in Eq. (2.2), integrating by parts on z', and using the fact that $\psi_\kappa(z')$ is a solution to Eq. (2.3), one may rewrite Eq. (2.2) in the form

$$\phi_{q\omega}(z)=\frac{2\pi e^2}{m\omega}\int\frac{d^2k}{(2\pi)^2}\int_0^\infty\frac{2d\kappa}{\pi}\,2\theta_{k\kappa}\int dz''\,dz'\left[e^{-q|z-z'|}\left(\vec{k}\cdot\hat{q}\psi_\kappa(z')-\operatorname{sgn}(z-z')\frac{d\psi_\kappa}{dz'}+\psi_\kappa(z)\delta(z-z')\right)\times\mathcal{G}^{-}_{k,\kappa,q,\omega}(z',z'')\right]\psi_\kappa(z'')\phi_{q\omega}(z'')\ , \tag{2.11}$$

in which $\hat{q}=\vec{q}/q$. In this form there is no hindrance to the examination of the $q=0$ limit, and indeed it is straightforward to show that at $q=0$, Eq. (2.11) has the solution[14]

$$\phi_{0\omega}(z)=\text{const}=1\ , \tag{2.12}$$

$$\omega=\omega_p/\sqrt{2} \tag{2.13}$$

The proof that Eqs. (2.12) and (2.13) solve Eq. (2.11) proceeds via the identity

$$\int dz''\,\mathcal{G}^{-}_{k,\kappa,q,\omega}(z',z'')\psi_\kappa(z'')=\frac{2\omega}{\omega^2-[(2\vec{k}\cdot\vec{q}+q^2)/2m]^2}\,\psi_\kappa(z')\ , \tag{2.14}$$

which is a consequence of Eqs. (2.7) and (2.9). Substituting Eq. (2.12) into (2.11) (at $q=0$), and using Eq. (2.14) to perform the z'' integrals, one discovers that $\phi_{0\omega}(z)=1$ is a solution to Eq. (2.11) if, and only if, the equation

$$1=\frac{4\pi e^2}{m\omega^2}\int\frac{d^2k}{(2\pi)^2}\int_0^\infty\frac{2d\kappa}{\pi}\,2\theta_{k\kappa}\times\left(-\int dz'\operatorname{sgn}(z-z')\psi_\kappa(z')\frac{d\psi_\kappa}{dz'}+\psi_\kappa^2(z)\right) \tag{2.15}$$

holds for all values of z.

Equation (2.15) may be simplified through the recognition that the quantity $n_0(z)$ defined by

$$n_0(z)\equiv\int\frac{d^2k}{(2\pi)^2}\int_0^\infty\frac{2d\kappa}{\pi}\,2\theta_{k\kappa}\,|\psi_\kappa(z)|^2\ , \tag{2.16}$$

represents the unperturbed Jellium electron number density, as a function of z. Substitution of Eq. (2.16) into (2.15), and integration by parts on z', reduces Eq. (2.15) to the form

$$1=(2\pi e^2/m\omega^2)[n_0(z\to\infty)+n_0(z\to-\infty)]\ . \tag{2.17}$$

Far out into the vacuum, i.e., as $z\to-\infty$, the electron density vanishes. Thus Eq. (2.17) is equivalent to

$$\omega^2=(2\pi e^2/m)\,n_0(z\to\infty)=\tfrac{1}{2}\omega_p^2\ , \tag{2.18}$$

as was claimed [cf. Eq. (2.13)].

In what follows, the knowledge that Eqs. (2.12) and (2.13) solve Eq. (2.11) at $q=0$ is used to extend the possibility of solving the latter for the surface-plasmon frequency at values of q slightly different than zero. The method used is an adaptation of one which suggests itself naturally if $V(z)$ is taken to be an infinite square step potential.[7,18]

The quantity $\sigma_{q\omega}$, which may be thought of as being proportional to the surface charge fluctuation associated with a plasma oscillation, is defined by the equation

$$\sigma_{q\omega}\equiv\frac{2\pi e^2}{m\omega}\int\frac{d^2k}{(2\pi)^2}\int_0^\infty\frac{2d\kappa}{\pi}\,2\theta_{k\kappa}\times dz'\,dz''\,\frac{d\psi_\kappa}{dz'}\,\mathcal{G}^{-}_{k,\kappa,q,\omega}(z',z'')\times\psi_\kappa(z'')\phi_{q\omega}(z'')\ . \tag{2.19}$$

Note that at $q=0$, substituting for $\phi_{0\omega}(z)$ from Eq. (2.12), and using Eqs. (2.14) and (2.16), $\sigma_{0\omega}$ is given by

$$\sigma_{0\omega}(\phi_{0\omega}(z)=1)=-\frac{2\pi e^2 n_0(z\to\infty)}{m\omega^2}=-\frac{\omega_p^2}{2\omega^2}\ . \tag{2.20}$$

With this result in mind, let

$$\nu_{0\omega}(z)\equiv(1-\omega_p^2/\omega^2)\phi_{q\omega}(z)-\sigma_{q\omega}\ . \tag{2.21}$$

At $q=0$, since $\phi_{0\omega}(z)$ is constant in space, then

$$\nu_{0\omega}(z)=(\text{const})\times(1-\omega_p^2/2\omega^2)=0\ , \tag{2.22}$$

where the last equality in Eq. (2.22) follows from Eq. (2.13). Thus, for small, but finite, values of q, $\nu_{q\omega}(z)$ is a quantity of $O(q)$; and by converting Eq. (2.11) from an equation for $\phi_{q\omega}(z)$ to one for $\nu_{q\omega}(z)$, one may expect that its $q=0$ solution will be explicitly extracted.

The conversion of Eq. (2.11) is accomplished by substituting Eq. (2.22) into it, and by using Eqs. (2.19) and (2.14). After straightforward manipulation, one finds the following equation for $\nu_{q\omega}(z)$ in terms of $\sigma_{q\omega}$:

$$\nu_{q\omega}(z)=\nu^{(0)}_{q\omega}(z)+\frac{\omega_p^2}{2\omega n_\infty}\int\frac{d^2k}{(2\pi)^2}\int_0^\infty\frac{2d\kappa}{\pi}\times\int dz'\,dz''\,2\theta_{k\kappa}L_{\vec{k},\kappa,\vec{q}}(z,z')\times\mathcal{G}^-_{k,\kappa,q,\omega}(z'z'')\psi_\kappa(z'')\nu_{q\omega}(z'')\ . \qquad (2.23)$$

In Eq. (2.23), the quantity n_∞ is equal to $n_0(z\to\infty)$, the kernel $L_{\vec{k},\kappa,\vec{q}}(z,z')$ is defined by

$$L_{\vec{k},\kappa,\vec{q}}(z,z')\equiv[\vec{k}\cdot\hat{q}+\delta(z-z')]e^{-q|z-z'|}\psi_\kappa(z')+[\mathrm{sgn}(z'-z)e^{-q|z-z'|}+1]\frac{d\psi_\kappa}{dz'}\ , \qquad (2.24)$$

and the inhomogeneous term $\nu^{(0)}_{q\omega}(z)$ is given by

$$\nu^{(0)}_{q\omega}(z)=\frac{\omega_p^2\sigma_{q\omega}}{\omega^2}\left[\left(\frac{1}{n_\infty}\int\frac{d^2k}{(2\pi)^2}\int_0^\infty\frac{2dk}{\pi}\int dz'\,2\theta_{k\kappa}L_{\vec{k},\kappa,\vec{q}}(z,z')\psi_\kappa(z')\ \frac{1}{1-[(2\vec{k}\cdot\vec{q}+q^2)/2m\omega]^2}\right)-1\right] \qquad (2.25)$$

In order to complete the conversion to the new unknown function $\nu_{q\omega}(z)$, it is also necessary to eliminate $\phi_{q\omega}(z)$ in the definition of $\sigma_{q\omega}$ [Eq. (2.19)]. Substitution of Eq. (2.23) into (2.19), and the use of Eq. (2.14) yields the expression for $\sigma_{q\omega}$ as a quadrature over $\nu_{q\omega}(z)$,

$$\sigma_{q\omega}\left(1-\frac{\omega_p^2}{\omega^2}+\frac{\omega_p^2}{2n_\infty\omega^2}\int\frac{d^2k}{(2\pi)^2}\int_0^\infty\frac{2d\kappa}{\pi}\ 2\theta_{k\kappa}\int dz'\ \frac{d}{dz'}\,[\psi_\kappa^2(z')]\ \frac{1}{1-[(2\vec{k}\cdot\vec{q}+q^2)/2m\omega]^2}\right)$$
$$=-\frac{\omega_p^2}{2\omega n_\infty}\int\frac{d^2k}{(2\pi)^2}\int_0^\infty\frac{2d\kappa}{\pi}\ 2\theta_{k\kappa}\int dz'dz''\ \frac{d\psi_\kappa}{dz'}\ \mathcal{G}^-_{k,\kappa,q,\omega}(z',z'')\psi_\kappa(z'')\nu_{q\omega}(z'')\ . \qquad (2.26)$$

Equations (2.23) and (2.26) for $\nu_{q\omega}(z)$ and $\sigma_{q\omega}$ are together completely equivalent to the RPA equation for $\phi_{q\omega}(z)$ [Eq. (2.11)]. The advantage of using the new pair of equations is revealed in the limit of small values of q. In this limit, assuming that the important values of $|z-z'|$ are always small compared to q^{-1}, one may Taylor expand $e^{-q|z-z'|}$ in Eq. (2.23), thereby finding, through terms of $O(z)$, that $\nu_{q\omega}(z)$ satisfies the equation

$$\nu_{q\omega}(z)=\frac{q\sigma_{q\omega}}{n_\infty}\int dz'(z-z')\ \frac{dn_0}{dz'}+\int dz''K_\omega(z,z'')\nu_{q\omega}(z'')\ , \qquad (2.27)$$

where $K_\omega(z,z'')$ is given by

$$K_\omega(z,z'')\equiv\frac{\omega}{n_\infty}\int\frac{d^2k}{(2\pi)^2}\int_0^\infty\frac{2d\kappa}{\pi}\ 2\theta_{k\kappa}\int dz'\left(2\theta(z'-z)\ \frac{d\psi_\kappa}{dz'}+\delta(z'-z)\psi_\kappa(z')\right)\mathcal{G}^-_{k,\kappa,0,\omega}(z'z'')\psi_\kappa(z'')\ . \qquad (2.28)$$

Equation (2.27) directly shows that $\nu_{q\omega}(z)/\sigma_{q\omega}$ is a quantity of $O(q)$ as $q\to 0$, as expected [cf., Eq. (2.20)]. Thus, Eq. (2.26), which in the $q\to 0$ limit assumes the form

$$\omega^2=\frac{\omega_p^2}{2}\left[1-\frac{\omega}{n_\infty}\int\frac{d^2k}{(2\pi)^2}\int_0^\infty\frac{2d\kappa}{\pi}\ 2\theta_{k\kappa}\int dz'dz''\ \frac{d\psi_\kappa}{dz'}\ \mathcal{G}^-_{k,\kappa,0,\omega}(z',z'')\ \psi_\kappa(z'')\left(\frac{\nu_{q\omega}(z'')}{\sigma_{q\omega}}\right)+O(q^2)\right]\ , \qquad (2.29)$$

permits the direct calculation of the departure of ω from $\omega_p/\sqrt{2}$ through terms of $O(q)$, once Eq. (2.27) has been solved for $\nu_{q\omega}(z)/\sigma_{q\omega}$. It is essentially via the numerical solution of Eqs. (2.27) and (2.29), then, that I have obtained values of α_1 and α_2 for different potential barriers $V(z)$.

However, before proceeding to a discussion of the numerical analysis, it is necessary to resolve two issues. First, one must show that the fact that the inhomogeneous term of Eq. (2.27) behaves as z in the limit $z\to+\infty$ is *not* an indication that the response of the electron gas deep inside the metal is important in determining $\omega_s(q)$. Thus, one will have justified the q expansion of $e^{-q|z-z'|}$, which leads from Eq. (2.23) to (2.27). Second, one should check whether the expression for the coefficient of q in Eq. (2.29) is identical to the formal expression for the linear coefficient of surface plasmon dispersion and damping which has been given by Harris and Griffin.[10] The remainder of this section is devoted to these tasks.

In order to show that it is only values of z near the surface that are important in solving for $\omega_s(q)$ to $O(q)$, one replaces $\nu_{q\omega}(z)$ by a new unknown function $\Delta_{q\omega}(z)$ defined by

$$\Delta_{q\omega}(z) \equiv \frac{1}{q\sigma_{q\omega}}\,\nu_{q\omega}(z) + \frac{1}{n_\infty}\int dz'(z-z')\,\frac{dn_0}{dz'} - \frac{1}{m\omega^2}\,\frac{dV}{dz}\,. \tag{2.30}$$

where $V(z)$ is the static potential barrier. Using Eq. (2.30) to substitute for $\nu_{q\omega}(z)/\sigma_{q\omega}$ in Eq. (2.27), the latter assumes the form

$$\Delta_{q\omega}(z) = \Delta^{(0)}_{q\omega}(z) + \int dz''K_\omega(z,z'')\Delta_{q\omega}(z'')\ , \tag{2.31}$$

where $K_\omega(z,z'')$ is defined in Eq. (2.28), and where, using Eq. (2.14) at $q=0$, $\Delta^{(0)}_{q\omega}(z)$ may be written

$$\Delta^{(0)}_{q\omega}(z) = -\frac{1}{m\omega^2}\,\frac{dV}{dz} + 2z - \int_z^\infty dz''K_\omega(z,z'')\left(z'' - \frac{1}{m\omega^2}\,\frac{dV}{dz''}\right)\,. \tag{2.32}$$

In what follows, the remaining integral on the right-hand side of Eq. (2.32) is evaluated, leading to the surprisingly simple expression for $\Delta^{(0)}_{q\omega}(z)$,

$$\Delta^{(0)}_{q\omega}(z) = -\frac{1}{m\omega^2}\,\frac{dV}{dz} - 2\int_z^\infty dz'\left(1 - \frac{n_0(z')}{n_\infty}\right). \tag{2.33}$$

According to Eq. (2.33), $\Delta^{(0)}_{q\omega}(z)$ has the asymptotic behavior

$$\Delta^{(0)}_{q\omega}(z) \to \begin{cases} \sin(2k_F z+\delta)/z^2\ , & z\to\infty \quad (2.34\text{a}) \\ 2z, & z\to-\infty\ , \quad (2.34\text{b}) \end{cases}$$

where the phase shift δ, a constant, depends on $V(z)$. Equation (2.34a) indicates that $\Delta^{(0)}_{q\omega}(z)$ is small for values of z appreciably inside the metal. On the basis of this behavior one can easily show that the important values of z and z'' in Eq. (2.31) are only those near the surface, as is necessary.

It is also demonstrated below that the subsitution of Eq. (2.30) into (2.29) leads to the expression for ω^2 in terms of $\Delta_{q\omega}(z)$,

$$\omega^2 = \frac{\omega_p^2}{2}\left[1 - \frac{q}{n_\infty}\left(\int dz'\frac{dn_0}{dz'}\,\Delta_{q\omega}(z') - \int\frac{d^2k}{(2\pi)^2}\,\frac{2d\kappa}{\pi}\,2\theta_{k\kappa}\int dz'dz''\psi_\kappa(z') \times \frac{dV}{dz'}\,\mathcal{G}^+_{k\kappa 0\omega}(z',z'')\psi_\kappa(z'')\Delta_{q\omega}(z'')\right)\right]. \tag{2.35}$$

On the basis of Eq. (2.35) it is easy to see that ω^2 is completely determined by values of $\Delta_{q\omega}(z)$ in the surface region of the metal and not the deep interior. [At a first reading, one may wish to skip the text from this point to the beginning of the paragraph containing Eq. (2.51).]

The proofs of these statements follow from the asymptotic properties of the functions $I^\pm_{n,n'}(z', z''; \omega)$ defined by

$$I^\pm_{n,n'}(z',z'';\omega) \equiv \frac{\omega}{n_\infty}\int\frac{d^2k}{(2\pi)^2}\int_0^\infty\frac{2d\kappa}{\pi}\,2\theta_{k\kappa} \times\left[\left(\frac{d}{dz'}\right)^n\psi_\kappa(z')\right]\left(\frac{d}{dz'}\right)^{n'}\mathcal{G}^\pm_{k\kappa 0\omega}(z',z'')\psi_\kappa(z'')\ , \tag{2.36}$$

in terms of which $K_\omega(z,z'')$ may be written

$$K_\omega(z,z'') = 2\int_z^\infty dz'\,I^-_{1,0}(z',z'',\omega) + I^-_{0,0}(z,z'';\omega)\ . \tag{2.37}$$

In Appendix A it is shown for sufficiently well-behaved potential barriers[23] $V(z)$, that the integrals $I^\pm_{n,n'}(z',z'';\omega)$ approach zero as sinusoidal functions of z'' times z''^{-2}, as $z''\to\infty$ with z' held fixed, and it is shown that the kernel $K_\omega(z,z'')$ therefore approaches zero in a similar fashion, if z (or z'') is held fixed and z'' (or z) approaches ∞. [In the limits z' or $z''\to-\infty$, i.e., far outside the metal, it is clear that the $I_{n,n'}$ approach zero exponentially, because of the exponential decay of the functions of $\psi_\kappa(z)$ as $z\to-\infty$, for $\kappa<k_F$. Thus [cf., Eq. (2.38)], $K_\omega(z,z'')$ approaches zero exponentially for $z''\to-\infty$ with z held fixed, while it approaches a constant as $z\to-\infty$ with z'' held fixed.]

In order to evaluate the integral on the right-hand side of Eq. (2.32), one considers the quantity $J^+_n(z',\omega)$ given by

$$J^+_n(z',\omega) \equiv \frac{\omega}{n_\infty}\int\frac{d^2k}{(2\pi)^2}\int_0^\infty\frac{2d\kappa}{\pi}\,2\theta_{k\kappa} \times\left[\left(\frac{d}{dz'}\right)^n\psi_\kappa(z')\right]\int dz''\left[(\omega-h'') \times\bar{\mathcal{G}}^+_{k\kappa 0\omega}(z',z'')\right]z''\psi_\kappa(z'')\ , \tag{2.38}$$

in which

$$h'' \equiv -\frac{1}{2m}\,\frac{d^2}{dz''^2} + V(z'')\ . \tag{2.39}$$

According to Eqs. (2.7) and (2.8), $J^+_n(z';\omega)$ may be rewritten

$$J^+_n(z';\omega) = \frac{\omega}{n_\infty}\int\frac{d^2k}{(2\pi)^2}\int_0^\infty\frac{2d\kappa}{\pi}\,2\theta_{k\kappa}\left[\left(\frac{d}{dz'}\right)^n\psi_\kappa(z')\right] \times\left(2z'\psi_\kappa(z') - \omega\int dz''\,\mathcal{G}^-_{k\kappa 0\omega}(z',z'')z''\psi_\kappa(z'')\right). \tag{2.40}$$

However, thanks to the asymptotic properties of the $I^{\pm}_{n,n'}$, which guarantee that the integrand of Eq. (2.38) is decreasing as z''^{-1} times a sinusoid at $z''\to\infty$ and exponentially as $z''\to-\infty$, one may obtain another expression for $J_n^+(z',\omega)$, integrating by parts on z'' and dropping the boundary terms at $z''=\pm\infty$. This expression is

$$J_n^+(z',\omega)=\frac{\omega}{n_\infty}\int\frac{d^2k}{(2\pi)^2}\times\int_0^\infty\frac{2d\kappa}{\pi}\,2\theta_{k\kappa}\left[\left(\frac{d}{dz'}\right)^n\psi_\kappa(z')\right]\times\int dz''\mathcal{G}^+_{k\kappa0\omega}(z',z'')\,\frac{1}{m}\,\frac{d\psi_\kappa}{dz''}\,. \quad (2.41)$$

Thus, comparing Eq. (2.41) and (2.40), one has for use within the $\vec{k}$ and κ integrals (which, cf. Appendix A, permit the integration by parts) the identity

$$\omega\int dz''\,\mathcal{G}^-_{k\kappa0\omega}(z',z'')z''\psi_\kappa(z'')=2z'\psi_\kappa(z')-\int dz''\,\mathcal{G}^+_{k\kappa0\omega}(z',z'')\,\frac{1}{m}\,\frac{d\psi_\kappa}{dz''}\,. \quad (2.42)$$

Similarly, considering the quantity $K_n^-(z',\omega)$, defined by

$$K_n^-(z',\omega)=\frac{\omega}{n_\infty}\int\frac{d^2k}{(2\pi)^2}\times\int_0^\infty\frac{2d\kappa}{\pi}\,2\theta_{k\kappa}\left[\left(\frac{d}{dz'}\right)^n\psi_\kappa(z')\right]\times\int dz''(\omega_\kappa-h'')\,\mathcal{G}^-_{k\kappa0\omega}(z',z'')\,\frac{d\psi_\kappa}{dz''}\,, \quad (2.43)$$

one proves (again for use within the $\vec{k}$ and κ integrals) the identity

$$\omega\int dz''\,\mathcal{G}^+_{k\kappa0\omega}(z',z'')\,\frac{d\psi_\kappa}{dz''}=\int dz''\,\mathcal{G}^-_{k\kappa0\omega}(z',z'')\,\frac{dV}{dz''}\,\psi_\kappa(z'')\,, \quad (2.44)$$

which when combined with Eq. (2.47) yields

$$\int dz''\mathcal{G}^-_{k\kappa0\omega}(z',z'')\left(z''-\frac{1}{m\omega^2}\,\frac{dV}{dz''}\right)\psi_\kappa(z'')=\frac{2}{\omega}\,z'\psi_\kappa(z')\,. \quad (2.45)$$

Equation (2.33) can now be derived from Eq. (2.32), via the substitution of Eqs. (2.28) and (2.45) in the latter, followed by the use of Eq. (2.16), and the recognition of the identity

$$\int_z^\infty dz'\,(z'-z)\,\frac{dn_0}{dz'}\equiv\int_z^\infty dz'\,[n_\infty-n_0(z')]\,. \quad (2.46)$$

Similarly, one can derive Eq. (2.35) from Eq. (2.29) by substituting Eq. (2.30) into the latter, by making use of Eqs. (2.14) and (2.45), and finally by using the identity

$$\int dz'\,\mathcal{G}^-_{k\kappa0\omega}(z',z'')\,\frac{d\psi_\kappa}{dz''}=\frac{2}{\omega}\,\frac{d\psi_\kappa}{dz'}-\frac{1}{\omega}\int dz''\,\mathcal{G}^+_{k\kappa0\omega}(z',z'')\,\frac{dV}{dz''}\,\psi_\kappa(z'')\,, \quad (2.47)$$

whose proof is analogous to that of Eq. (2.44) [one starts with $K_n^+(z',\omega)$ instead of $K_n^-(z',\omega)$].

Having established the validity of Eq. (2.35), which may be written in the form

$$\omega^2=\frac{\omega_p^2}{2}\left(1-\frac{q}{n_\infty}\int dz'\,\frac{dn_0}{dz'}\,\Delta_{q\omega}(z')-\frac{q}{\omega}\int dz'dz''\,\frac{dV}{dz'}\,I^+_{0,0}(z',z'';\omega)\Delta_{q\omega}(z'')\right), \quad (2.48)$$

one sees the fact that ω^2 is determined entirely by values of $\Delta_{q\omega}(z)$ in the surface region to follow from the asymptotic falloff of $I^+_{0,0}(z,z'';\omega)$ as $z''\to\pm\infty$ (see above, cf. also Appendix A), and from the fact that dn_0/dz' and dV/dz' are only nonzero near the surface.

Knowing that ω^2 is determined by $\Delta_{q\omega}(z)$ in the surface region, one now asks whether the values of $\Delta_{q\omega}(z)$ there are themselves determined [via Eq. (2.31)] entirely in terms of the electronic response in that region. This question is answered by considering the iterates $\Delta^{(n)}_{q\omega}(z)$ of Eq. (2.31), for example,

$$\Delta^{(1)}_{q\omega}(z)\equiv\int dz''\,K_\omega(z,z'')\,\Delta^{(0)}_{q\omega}(z'')\,. \quad (2.49)$$

Note that since $K_\omega(z,z'')$ and $\Delta^{(0)}_{q\omega}$ both fall off as z''^{-2} for $z''\to\infty$, and since $K_\omega(z,z'')$ approaches zero exponentially as $z''\to-\infty$, while $\Delta^{(0)}_{q\omega}$ diverges only linearly in that limit, the variable z'' in the integral of Eq. (2.49) is confined to the surface region. Thus the asymptotic properties of $\Delta^{(1)}_{q\omega}(z)$ are just those of $K_\omega(z,z'')$ as a function of z, for z'' fixed, namely (cf. above), that

$$\Delta^{(1)}_{q\omega}(z)\to\begin{cases}\text{a constant,} & \text{as } z\to-\infty\\ \text{a sinusoid times } z^{-2}, & \text{as } z\to+\infty\,.\end{cases} \quad (2.50)$$

Using Eq. (2.50), one shows similarly that $\Delta^{(2)}_{q\omega}(z)$ and, iteratively, that $\Delta^{(n)}_{q\omega}(z)$, for any $n>1$, has the same general asymptotic behavior as $\Delta^{(1)}_{q\omega}(z)$. Thus the values of all of the iterates of Eq. (2.31) are completely determined by values of previous iterates in the surface region. Therefore the important values of $\Delta_{q\omega}(z)$ itself are entirely determined in the surface region, and one concludes that the q expansion of $e^{-q|z-z'|}$ in Eq. (2.23) is asymptotically valid to $O(q)$.

Since one can now believe that Eqs. (2.31) and (2.35) provide a correct basis for the evaluation of $\omega_s(q)$ to $O(q)$, it is relevant to ask whether Eq.

(2.35) agrees with the formal result of Harris and Griffin,[10] which relates $\omega_s(q)$, to this order, to the fluctuating electron number density $\delta n_{q\omega}(z)$ associated with a surface plasmon. Harris and Griffin's formula for $\omega_s(q)$ is

$$\omega_s^2(q) = \frac{\omega_p^2}{2}\left[1 + q\left(\int dz\, z\,\delta n_{q\omega}(z) \Big/ \int dz\, \delta n_{q\omega}(z) + \int dz\, \rho(z)\right) + O(q^2)\right] , \qquad (2.51)$$

in which

$$\rho(z) \equiv n_0(z)/n_\infty - \Theta(z) , \qquad (2.52)$$

where $\Theta(z)$ is the ordinary step function. The remainder of this section is devoted to a demonstration that Eqs. (2.35) and (2.51) do in fact agree.

The demonstration makes use of the fact that the fluctuating potential associated with a surface plasmon $\phi_{q\omega}(z)$ is related to $\delta n_{q\omega}(z)$ by Poisson's equation[13]

$$\phi_{q\omega}(z) = \frac{2\pi e^2}{q} \int dz'\, e^{-q|z-z'|}\, \delta n_{q\omega}(z') , \qquad (2.53)$$

which, by virtue of the fact that $q|z-z'|$ is always small in the evaluation of $\omega_s(q)$, may be expanded as

$$\phi_{q\omega}(z) \approx \frac{2\pi e^2}{q} \int dz' (1 - q|z-z'| + \cdots)\, \delta n_{q\omega}(z') . \qquad (2.54)$$

One proceeds by noting that Eqs. (2.31), (2.28), and (2.47), together with the fact that $I^-_{0,0}(z,z';\omega) \to 0$ as $z \to -\infty$, permit Eq. (2.35) to be rewritten in the simple form

$$\omega^2 \equiv \omega_s^2(q) = \frac{\omega_p^2}{2}\left(1 - \frac{q}{2} \lim_{z\to-\infty} [\Delta_{q\omega}(z) - \Delta^{(0)}_{q\omega}(z)]\right) . \qquad (2.55)$$

The function $\Delta^{(0)}_{q\omega}(z)$ is given explicitly in Eq. (2.33). Making use of Eq. (2.52), this formula for $\Delta^{(0)}_{q\omega}(z)$ can be rewritten in the form

$$\Delta^{(0)}_{q\omega}(z) = -\frac{1}{m\omega^2}\frac{dV}{dz} + 2\int_z^\infty dz'\, \rho(z') + 2z\theta(-z) . \qquad (2.56)$$

The function $\Delta_{q\omega}(z)$ is related to $\phi_{q\omega}(z)$ by Eqs. (2.30) and (2.21). Using these equations, one finds that

$$\Delta_{q\omega}(z) = \frac{1}{q}\left[\left(1 - \frac{\omega_p^2}{\omega^2}\right)\frac{\phi_{q\omega}(z)}{\sigma_{q\omega}} - 1\right] + z - \frac{1}{n_\infty}\int dz'\, z' \frac{dn_0}{dz'} - \frac{1}{m\omega^2}\frac{dV}{dz} . \qquad (2.57)$$

One now wishes to eliminate $\phi_{q\omega}(z)$ and $\sigma_{q\omega}$ from Eq. (2.57) in favor of $\delta_{q\omega}(z)$. Of course $\phi_{q\omega}(z)$ can easily be eliminated using Eq. (2.54). It is less straightforward, however, to see how to dispose of $\sigma_{q\omega}$. The trick, in this regard, is to make use of the fact that by virtue of the asymptotic falloff of $\Delta^{(0)}_{q\omega}(z)$, as $z \to \infty$, and of the similar behavior (discussed above) of all of the iterates of Eq. (2.31), the function $\Delta_{q\omega}(z) \to 0$ as $z \to \infty$. [Indeed (cf. Appendix B), it can be shown that $\Delta_{q\omega}(z)$ approaches zero as z^{-2} times a sinusoidal function of z, in this limit.] According to Eq. (2.57), this behavior of $\Delta_{q\omega}(z)$ requires $\phi_{q\omega}(z)$ to have the asymptotic form

$$\phi_{q\omega}(z\to\infty) = \frac{\sigma_{q\omega}}{1 - \omega_p^2/\omega^2}\left(1 - qz + \frac{q}{n_\infty}\int dz'\, z' \frac{dn_0}{dz'}\right) . \qquad (2.58)$$

However, in the same limit, Eq. (2.54) requires $\phi_{q\omega}(z\to\infty)$ to be of the form

$$\phi_{q\omega}(z\to\infty) = \frac{2\pi e^2}{q}\int dz'\, \delta n_{q\omega}(z')(1 - q(z-z') + \cdots) . \qquad (2.59)$$

Comparison of Eqs. (2.59) and (2.58) yields an expression for $\sigma_{q\omega}$ in terms of $\delta n_{q\omega}(z')$, which when substituted into Eq. (2.57) results in the formula

$$\Delta_{q\omega}(z) = \frac{1}{q}\left[\frac{q}{2\pi e^2}\left(\left(\phi_{q\omega}(z) \Big/ \int dz'\, \delta n_{q\omega}(z)\right)\left(1 + \frac{q}{n_\infty}\int dz'\, z' \frac{dn_0}{dz'} - q\int dz'\, z' \delta n_{q\omega}(z') \Big/ \int dz'\, \delta n_{q\omega}(z') + O(q^2)\right) - 1\right] + z - \frac{1}{n_\infty}\int dz'\, z' \frac{dn_0}{dz'} - \frac{1}{m\omega^2}\frac{dV}{dz} . \qquad (2.60)$$

One substitutes for $\phi_{q\omega}(z)$ in Eq. (2.60) using Eq. (2.54). The resulting formula together with Eq. (2.56) may then be combined to yield to $O(q)$, as $z \to -\infty$, the expression

$$\Delta_{q\omega}(z\to-\infty) - \Delta^{(0)}_{q\omega}(z\to-\infty) = -2\left[\left(\int dz'\, z'\, \delta n_{q\omega}(z') \Big/ \int dz'\, \delta n_{q\omega}(z')\right) - \frac{1}{n_\infty}\int dz'\, z' \frac{dn_0}{dz'}\right] . \qquad (2.61)$$

Using Eq. (2.52) to convert the last integral in Eq. (2.61) to $\int dz'\, \rho(z')$, and substituting Eq. (2.61) into Eq. (2.55), it is seen that the latter is identical to the Harris-Griffin formula (2.51), which was to be shown.

In conclusion, it should be noted that despite its appealing look of simplicity, Eq. (2.51) does not lend itself to particularly straightforward physical interpretation. The main difficulties in interpreting it are (a) that $\delta n_{q\omega}(z)$ is a complex number and thus not an observable quantity and (b) that the dynamical equation, e.g., Eq. (2.31), gives no obvious clue as to the relation between $\delta n_{q\omega}(z)$ and simple structural features of the surface. It is presumably for these reasons that Eq. (2.51) has never been applied.

III. NUMERICAL EVALUATION OF $\omega_s(q)$

Of the equivalent forms of the RPA dynamical equation, the pair of equations involving $\Delta_{q\omega}(z)$, Eqs. (2.31) and (2.55) is best suited for computing, because these equations present the least difficulty in the region of large positive values of z. In this section I discuss the reduction of Eq. (2.31) to an integral equation on a compact domain of the z axis,[24] and I present some of the technical details associated with its numerical solution. (The reader who does not wish to follow all of the technical details of the calculation reported in this paper may skip this section.)

In order to evaluate the function $\Delta_{q\omega}(z)$ numerically, one would like to convert Eq. (2.31) to a matrix equation on a sufficiently finely spaced mesh of values of z, of the form

$$\Delta_{q\omega}(z_j)=\Delta^{(0)}_{q\omega}(z_j)+\sum_{j''} w_{j''}K_\omega(z_j,\, z_{j''})\,\Delta_{q\omega}(z_{j''})\ , \qquad (3.1)$$

where the w_j are appropriately chosen weights. One would then solve for $\Delta_{q\omega}(z_j)$ by inverting the matrix $\delta_{jj''}-w_{j''}K_\omega(z_j,z_{j''})$. ($\delta_{jj''}$ is Kronecker δ function.) However, since the domain of integration in Eq. (2.31) is $-\infty<z''<\infty$, the matrix one needs to invert is apparently an infinite one, not amenable to inversion on the computer. In order to proceed therefore, one requires a method for reducing the z'' integration of Eq. (2.31), effectively, to an integration over only a compact domain of z''s about the jellium surface.

On the vacuum side of the surface, $z''\to-\infty$, this problem is not a severe one, because of the fact (cf. Sec. II) that $K_\omega(z,z'')$ falls exponentially to zero as $z''\to-\infty$. This fact permits one, with negligible error, to replace the lower limit of the z'' integral in Eq. (2.31) [and thus the lowermost value of $z_{j''}$ in the j'' sum of Eq. (3.1)] by a finite value, $-Z_m$, with Z_m sufficiently large and positive. Clearly, the value chosen for Z_m should not affect the computed values of $\Delta_{q\omega}(z)$ and $\omega_s(q)$. In practice, I found, by trying a variety of values of Z_m for a given $V(z)$, that it was easy to find a range of acceptable values of Z_m, by this standard.

Unfortunately, the integration limit $z''\to+\infty$ cannot simply be replaced by a cutoff. The problem is that the larger the value of z, the larger is the value of z'' at which the function $K_\omega(z,z'')$ begins to fall off: or in other words, $K_\omega(z,z'')$ has matrix elements of non-negligible magnitude along (but not necessarily on) its diagonal, for arbitrarily large z and z''.

One therefore adopts a different method for handling the large z'' region in Eq. (2.31), based on knowing the asymptotic form of $\Delta_{q\omega}(z'')$ as $z''\to\infty$. Suppose, as is shown in Appendix B to be true, that for z'' sufficiently large, $\Delta_{q\omega}(z'')$ is of the form

$$\Delta_{q\omega}(z'')\approx z''^{-2}\sum_{l=1}^{L} c_l e^{ik_l z''}\ , \qquad (3.2)$$

where the $\{k_l\}$ are a finite set of known wave vectors, and the $\{c_l\}$ are constants to be determined. If Eq. (3.2) holds for z'' larger than some large value Z_M, then Eq. (2.31) can be written in the form

$$\Delta_{q\omega}(z)\approx\Delta^{(0)}_{q\omega}(z)+\int_{-Z_m}^{Z_M}dz''\,K_\omega(z,z'')\Delta_{q\omega}(z'')+\sum_{l=1}^{L}c_l F_{l,\omega}(z)\ , \qquad (3.3)$$

where

$$F_{l,\omega}(z)\equiv\int_{Z_M}^{\infty}dz''\,K_\omega(z,z'')\,\frac{e^{ik_l z''}}{z''^2}\ . \qquad (3.4)$$

Equation (3.3) will be useful if one can obtain simple expressions for the functions $F_{l,\omega}(z)$, and if the the $\{c_l\}$ can be related to values of $\Delta_{q\omega}(z'')$ corresponding to $z''\subset[-Z_m, Z_M]$.

The evaluation of the $F_{l,\omega}(z)$ is further discussed below. In order to relate the c_l to values of $\Delta_{q\omega}(z'')$ with $z''\subset[-Z_m,Z_M]$, one assumes that for values of z'' smaller than but near to Z_M, the, asymptotic form of $\Delta_{q\omega}(z'')$, Eq. (3.2) is still valid. For L such values of z'', $\{Z_1,\ldots,Z_L\}$, one therefore has

$$\Delta_{q\omega}(Z_{l'})=Z_{l'}^{-2}\sum_{l=1}^{L}c_l e^{ik_l Z_{l'}}\ ,\quad l'=1,L\ , \qquad (3.5)$$

a set of L equations which can be inverted to yield

$$c_l=\sum_{l'=1}^{L}\mathfrak{M}^{-1}_{ll'}\,\Delta_{q\omega}(Z_{l'})\ ,\quad l=1,L\ , \qquad (3.6)$$

in which $\mathfrak{M}^{-1}_{ll'}$ is the inverse of the matrix

$$\mathfrak{M}_{ll'}\equiv Z_{l'}^{-2}e^{ik_l Z_{l'}}\ . \qquad (3.7)$$

One now returns to Eq. (3.3), approximating the z'' integral by a sum over a mesh of points $\{z_j;\,j=1,J\}$ such that $z_1=-Z_m$ and $z_J=Z_M$, and choosing the $Z_1,\ldots,Z_L$, for example, to equal

$\{z_J - L+1, \ldots, z_J\}$. One thus converts Eq. (3.3) to the approximate finite-dimensional matrix equation

$$\Delta_{q\omega}(z_j) = \Delta^{(0)}_{q\omega}(z_j) + \sum_{j''=1}^{L} K_\omega(z_j, z_{j''}) w_{j''} \Delta_{q\omega}(z_{j''}) + \sum_{l=1}^{L} F_{l,\omega}(z_j) \sum_{l'=1}^{L} \mathfrak{M}^{-1}_{ll'} \Delta_{q\omega}(z_{J-L+l'}) . \quad (3.8)$$

All of the numerical results reported in Sec. IV were obtained by solving Eq. (2.31) in the approximate form of Eq. (3.8). In what follows, the preliminaries to the numerical solution of Eq. (4.8) are presented. The kernel $K_\omega(z,z'')$ is rewritten in a form which is better suited for computation than that of Eq. (2.28), and the functions $F_{l,\omega}(z)$ are evaluated to leading order in Z_M^{-1}. This section concludes with a description of the details of my numerical calculations: integration methods mesh sizes, etc.

An essential element of the numerical solution of Eq. (3.8) is obviously the evaluation of the kernel $K_\omega(z,z'')$. This evaluation is greatly facilitated by the replacement of the z' integral in Eq. (2.28), for $K_\omega(z,z'')$, with an integral over only the surface region, via the use of an identity similar to Eq. (2.47), viz.,

$$\int_z^\infty dz' \frac{d\psi_\kappa}{dz'} \mathcal{G}^-_{\vec{k}\kappa 0\omega}(z',z'') = \frac{2}{\omega}\frac{d\psi_\kappa}{dz} + \frac{1}{2m\omega}\left(\frac{d\psi_\kappa}{dz}\frac{d}{dz} - \frac{d^2\psi_\kappa}{dz^2}\right)\mathcal{G}^+_{\vec{k}\kappa 0\omega}(z,z'') - \frac{1}{\omega}\int_z^\infty dz' \psi_\kappa(z')\frac{dV}{dz'}\mathcal{G}^+_{\vec{k}\kappa 0\omega}(z',z'') . \quad (3.9)$$

Equation (3.9) is proven by the same method as was used for Eq. (2.47), and is valid, as were the previous such identities, only within $\vec{k}$ and κ integrals that permit the dropping of boundary term at $z'=\infty$ (in integrating by parts). Substituting Eq. (3.9) into Eq. (2.28), one obtains an expression for $K_\omega(z,z'')$, which is easily evaluated numerically, viz.,

$$K_\omega(z,z'') = \frac{2}{n_\infty}\frac{dn_0}{dz''}\theta(z''-z) + \frac{1}{m\omega}[I^+_{1,1}(z,z'';\omega) - I^+_{2,0}(z,z'';\omega)] + I^-_{0,0}(z,z'';\omega) - \frac{1}{\omega}\int_z^\infty dz'\frac{dV}{dz'} I^+_{0,0}(z',z'';\omega) , \quad (3.10)$$

where the $I^\pm_{n,n'}(z,z'';\omega)$ are defined in Eq. (2.36). It is this expression for $K_\omega(z,z'')$ which I used for computation.

In order to compute values of the functions $F_{l,\omega}(z)$ of Eq. (3.4), it is desirable [cf. Eqs. (3.4), (3.10), and (2.36)] to be able to evaluate the integrals

$$\int_{Z_M}^\infty dz''\, G^\pm(z,z'';\pm\omega+\omega_\kappa)\psi_\kappa(z'')e^{ik_lz''}/z''^2 , \quad (3.11)$$

in closed form, or at least to be able to convert them to integrals over a compact domain. {Note, by the way [cf. Eq. (3.3)], that one only needs the $F_{l,\omega}(z)$, and therefore the integrals of (3.11), for values of $z \le Z_M$.} Assume that Z_M has been chosen sufficiently large $z'' \ge Z_M \ge z$, the Green's functions $G^\pm(z,z'';\pm\omega+\omega_\kappa)$ assume the forms [cf. Eqs. (A2) and (A5) of Appendix A]

$$\frac{1}{w(\omega+\omega_\kappa)}\psi^-(z;\omega+\omega_\kappa)\exp[i(2m\omega+\kappa^2)^{1/2}z''] \quad (3.12)$$

and[25]

$$\left(\frac{1}{w(\omega+\omega_\kappa)}\psi^-(z;\omega_\kappa-\omega)\right)^* \exp[-i(\kappa^2-2m\omega)^{1/2}z''] ,$$

and the evaluation of the integrals of (3.11) is reduced to the evaluation of the function $\mathcal{I}_p(z)$, defined by

$$\mathcal{I}_p(z) \equiv \int_z^\infty dz''\, z''^{-2} e^{ipz''} \quad (3.13)$$

for appropriate values of p, and $z = Z_M$.

In order to calculate $\mathcal{I}_p(Z_M)$ for p real and $|pZ_M| > 1$, I used a simple Padé approximant,[26] which is accurate to one part in 10^7. For $\mathrm{Im}\,p > 0$, I approximated $\mathcal{I}_p(z)$ by the asymptotic form

$$\mathcal{I}_p(z) \xrightarrow[pz\to\infty]{} \frac{1}{ipz^2} e^{ipz} . \quad (3.14)$$

Finally, for p real with $|pZ_M| < 1$, I used the identities

$$\int_z^\infty dz''\, z''^{-2}\cos(pz'') = z^{-1} - \tfrac{1}{2}\pi|p| + p\int_0^{pz} d\nu\, \nu^{-2}\sin^2\nu , \quad (3.15a)$$

$$\int_z^\infty dz''\, z''^{-2}\sin(pz'') = p\left[1 - C + \ln\left(1+\frac{1}{|p|z}\right)\right] - \int_0^{|p|z} d\nu\, \nu^{-1}\left(\frac{\sin\nu}{\nu} - \frac{1}{1+\nu}\right), \quad (3.15b)$$

where C is Euler's constant. The use of these identities permits one to integrate accurately over the point $p=0$ when the occasion arises (and it does, cf. Appendix B, all too often).

The remainder of this section is devoted to a description of some of the details of my computations. In order to obtain the functions $\psi_\kappa(z)$, and the functions $\psi^\pm(z;\pm\omega+\omega_\kappa)$, in terms of which [cf. Eq. (A2) of Appendix A] one may express the Green's functions $G^\pm(z,z'';\pm\omega+\omega_\kappa)$, I integrated the Schrödinger equation [Eq. (2.3) or Eq. (A3)] using the Noumerov method[27] which is highly accurate. As a result the mesh of z's on which these functions were known consisted of equally spaced values of z; therefore all necessary z integrations were performed using the Newton-Cotes method.[28] On the other hand, κ integrals were performed by Gaussian integration. The matrix inversions required to obtain $\mathfrak{M}_{ll'}^{-1}$, cf. Eq. (3.6), and to solve Eq. (3.8) were performed using the standard matrix inversion package on the S.U.N.Y., Stony Brook, IBM 370-155 computer system.

Typically, a mesh of 32 values of κ gave a sufficiently accurate set of values of $K_\omega(z, z'')$ and $F_{l,\omega}(z)$. The accuracy of the κ integration was verified by making the mesh finer. A mesh of on the order of 30 or 35 equally spaced values of z_j was generally used in solving Eq. (3.8). The fineness of the mesh was again judged to be sufficient by increasing the density of points and observing little change in the results.

In order to test the validity of a choice Z_m, I imposed two criteria. First I required, for any single choice Z_m, that the quantity $\Delta_{q\omega}(z) - \Delta_{q\omega}^{(0)}(z)$ be the same at $z = Z_m$ as at mesh points z adjacent to Z_m. The satisfaction of this requirement (of which an illustration is given in Fig. 1) guarantees that the value chosen for Z_m is sufficiently far into the vacuum that $\Delta_{q\omega}(z) - \Delta_{q\omega}^{(0)}(z)$ is behaving asymptotically there, and therefore, that the value obtained for α via the equation [cf. Eq. (2.55)]

$$\alpha = -\tfrac{1}{4}[\Delta_{q\omega}(Z_m) - \Delta_{q\omega}^{(0)}(Z_m)] \tag{3.16}$$

is not explicitly dependent on Z_m. Second in order to check that α was not implicitly dependent on Z_m, I verified, for selected cases, that if $\Delta_{q\omega}(z) - \Delta_{q\omega}^{(0)}(z)$ was independent of z, for z near Z_m, then the "re"-solution of Eq. (3.8) with a value of Z_m farther out into the vacuum yielded the same value of α as did the first calculation.

I checked that α was independent of Z_M similarly, by determining a value of α with one value of Z_M and then verifying that for a larger Z_m, I would find the same value of α. My choice of which z_j's to use as $Z_1, \ldots, Z_L$ [cf. the sentence following Eq. (3.7)] was not always $\{z_{J-L+1}, \ldots, z_J\}$. In certain cases I found it useful to choose the values $\{z_{J-2L+2}, z_{J-2L+4}, \ldots, z_J\}$ in order to eliminate numerical noise in solving for $\Delta_{q\omega}(z)$.

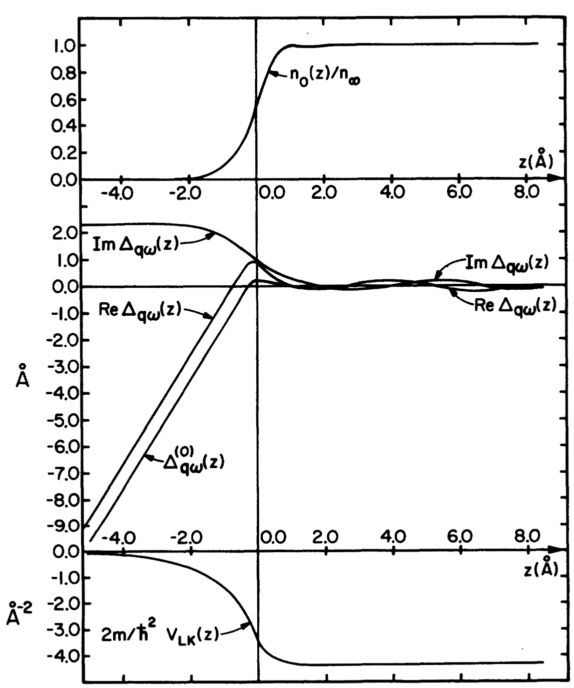

FIG. 1. Calculated values of electron density $n_0(z)/n_\infty$ (in upper panel), and of $\Delta_{q\omega}^{(0)}(z)$ and $\Delta_{q\omega}(z)$ (center panel), using the Lang-Kohn potential barrier $V_{LK}(z)$ for $r_s = 2$, shown in the lower panel. Note that $\Delta_{q\omega}(z) - \Delta_{q\omega}^{(0)}(z)$ approaches a constant as $z \to -\infty$. This constant [cf. Eqs. (2.55) and (2.1)] equals $-4(\alpha_1 + i\alpha_2)$.

IV. SENSITIVITY OF SURFACE-PLASMON DISPERSION AND DAMPING TO BARRIER SHAPE, AND TO IMPURITY ADSORPTION

As I stated at the outset, the motivation for the present study of surface-plasmon dispersion and damping has been to gain insight into the relation between surface electronic structure and surface plasmon properties. The first steps in this direction, reviewed in this section[29] have been exploratory ones. I have solved Eq. (3.8) numerically, and using Eq. (2.55) have obtained values of the linear coefficient of surface plasmon dispersion and damping α for a variety of choices of the potential barrier $V(z)$. [Within the RPA, as described above, the specification of $V(z)$ is equivalent to the specification of all static surface electronic structural properties.]

In order to explore the sensitivity of α to the shape of $V(z)$, for a given bulk jellium conduction-electron density, I have evaluated α using the Lang-Kohn self-consistent potential barrier[30] for that density $V_{LK}(z)$, and also using model barriers of the form

$$V(z;\, a, \Phi) = -(\epsilon_F + \Phi)\left\{1 + \exp\left[-\left(\frac{z}{a} + \frac{bz^3}{a^3}\right)\right]\right\}^{-1}, \tag{4.1}$$

with various values of the surface diffuseness and work function parameters, a and Φ [and with $b = \frac{1}{125}$ (see Ref. 31)]. Results, for conduction electron densities corresponding to electron gas radii r_s between 2 and 6, are presented in Figs. 2 and 3.

One notes in these figures that both α_1 and α_2 show a marked sensitivity to the shape of $V(z)$. For example, in Fig. 2 it is seen that the computed values of α_1 and α_2 vs r_s are systematically only about $\frac{1}{2}$ as large for the asymmetric (i.e., mostly concave downwards) Lang-Kohn barriers as they are for symmetric model barriers, of the

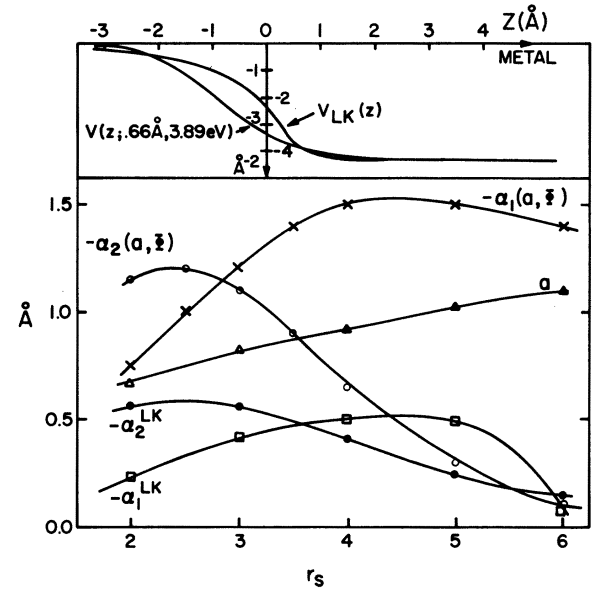

FIG. 2. Dependence of α_1 and α_2 on r_s. The curves labeled $-\alpha_1^{LK}$ and $-\alpha_2^{LK}$ were calculated using the Lang-Kohn potentials. The curves labeled $-\alpha_1(a, \Phi)$ and $-\alpha_2(a, \Phi)$ were calculated using $V(z; a, \Phi)$ with the values of a that are shown, and values of taken from Ref. 30. Upper panel: comparison, for $r_s = 2$, of $(2m/\hbar^2)V_{LK}(z)$ and $(2m/\hbar^2)V(z;\ 0.66\ \text{Å},\ 3.89\ \text{eV})$. The units are Å^{-2}.

form given in Eq. (4.1), of comparable surface diffuseness. One also notes that the values of α_1 and α_2 for the Lang-Kohn barrier at Al density ($r_s \approx 2$) are about three times as large as the values -0.07 and -0.21 Å, respectively, reported by Beck and Celli[6] for a step-function barrier. In Fig. 3, this difference is put in perspective, in that α_1 and α_2 are shown to be quite rapidly varying functions of a, the diffuseness parameter of $V(z;\ a, \Phi)$, which equals zero for Beck and Celli's potential.

The curves in Fig. 2 were calculated using values of Φ obtained self-consistently by Lang and Kohn before "lattice corrections,"[30] and using values of a chosen by requiring $V(z;\ a, \Phi)$ to equal $V_{LK}(z)$ at the two points where its values are $10\%(\epsilon_F + \Phi)$ and $90\%(\epsilon_F + \Phi)$ below the vacuum level. The values of a that were used are given in Fig. 2. The upper panel of this figure is a comparison of the Lang-Kohn barrier $V_{LK}(z)$ and $V(z;\ 0.66\ \text{Å},\ 3.89\ \text{ev})$, for $r_s = 2$.

It is worth noting in Fig. 2 that α_1 is in general negative, despite the strong sensitivity of the α's to the shape of $V(z)$. It was the observation of negative values of α_1, by keV electron transmission through Mg films[4] (polycrystalline, with uncharacterized surface geometry and purity), and later by inelastic low-energy-electron diffraction on an Al(111) surface[32] that provoked much of the recent theoretical work on surface plasmon properties. Bennett[5] first showed that the unexpected sign of α_1 could be understood within a hydrodynamic model of an electron fluid surface. His results were subsequently corroborated by Beck and Celli[6] for a square-step ($a = 0$) potential, and are corroborated again by the present results for a variety of barrier shapes.

In Fig. 3, for Al density ($r_s = 2.07$), I show the dependence of α_1 and α_2 on ϕ and a. Note in the upper panel (A) that the α's depend rather weakly on Φ, at least on the scale of work function changes that one might expect for different single-crystal surfaces. On the other hand, in the lower panel (B) one sees that the variation of the α's with a is quite rapid. The values of α_1 and α_2 decrease in magnitude by factors of ~4 and ~5, respectively between the values of $a = 0.67$ Å for which (cf. upper panel of Fig. 2) $V(z;\ 0.67\ \text{Å},\ 3.86\ \text{eV})$ and $V_{LK}(z)$ are of comparable surface diffuseness, and $a = 0.335$ Å, which is $\frac{1}{2}$ this approximately self-consistent diffuseness. The trend of the α's with decreasing a does appear to be in the direction of Beck and Celli's $a = 0$ variational result, lending credence to the validity of the variational method. However, the rapid variation of the α's with a also forces one to conclude that the agreement of their value of $\alpha_1(a = 0)$ and experiment[32] is accidental.

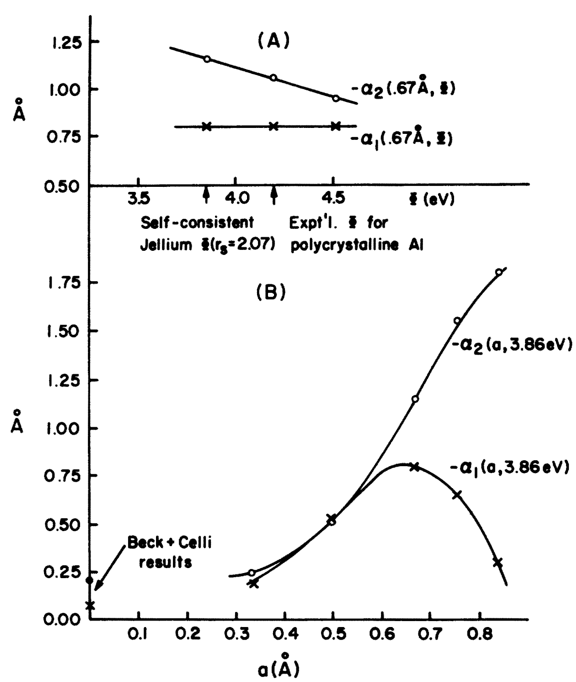

FIG. 3. (a) Dependence of $\alpha_1(0.67\ \text{Å},\ \Phi)$ and $\alpha_2(0.67\ \text{Å},\ \Phi)$ on Φ, for $r_s = 2.07$. (b) Dependence of $\alpha_1(a,\ 3.86\ \text{eV})$ and $\alpha_2(a,\ 3.86\ \text{eV})$ on a for $r_s = 2.07$. Beck and Celli's variational results for $a = 0$ (Ref. 6) are also shown.

Incidentally, this conclusion is supported by the fact that in more recent experiments the values of α_1 for Al and Mg no longer appear to be negative.[1,2]

The fact that the α's vary rapidly with potential barrier shape makes it natural to suppose that, in particular, they will be sensitive to the changes in this barrier which result from impurity adsorption. The ILEED experiments of Porteus should soon provide experimental information in this regard, for the cases of Cs and Na adsorption on an Al(111) substrate.[19] In the meantime, I have attempted to estimate the magnitude of this effect theoretically,[17] using the self-consistent potential barriers provided by Lang's calculations[33] of work-function changes versus alkali adsorption on an Al density ($r_s = 2$) jellium substrate. Lang's potential barriers $V_L(z)$ each correspond to the adsorption, on the $r_s = 2$ substrate, of a fixed number per unit area of a certain species of alkali atoms. For each of these potential barriers, I have solved for the corresponding values of α_1 and α_2, using Eqs. (3.8) and (2.55). I present the results of these calculations in Fig. 4.

Lang and Kohn originally showed[30] that the use of a step-function model of the ionic (positive) charge distribution at a clean free-electron-metal surface leads to self-consistent electron density profiles which account reasonably well for measured surface energies and work functions. On the basis of this success, Lang has generalized the Lang-Kohn jellium model to one for alkali-covered surfaces,[33] in which the positive background charge-density drops to zero in two steps from its value in the substrate. The second step represents the ionic charge of the adlayer. Its width d (see Fig. 4, inset) is set equal to the distance between the most closely packed planes of bulk crystals of the alkali species being adsorbed. The volume density of the adlayer positive charge n^{Ad} is taken to equal the fractional coverage θ times the average ionic density of the akali metal in its bulk form n_∞^{Ad}. Thus, at $\theta = 1$, which is referred to in Fig. 4 as "full coverage" (and in Ref. 17 as "monolayer coverage"), the adlayer ionic charge is that of one close-packed layer of alkali adatoms. This prescription for choosing values of n^{Ad} and d, to correspond to a given experimental adlayer coverage, leads to fairly good agreement with experimental work function versus alkali coverage data; I have therefore also used it in preparing Fig. 4.

Because the results shown in Fig. 4 correspond to a jellium model of both the substrate and adsorbate ionic charge, it seems reasonable to focus attention on their qualitative rather than on their quantitative features. The most striking aspect of the results is that α_1, the dispersion coefficient, is rather strongly sensitive to alkali adsorption (on the $r_s = 2$ substrate) while α_2, the damping coefficient, is less so. The values of α_1 and α_2 are plotted in Fig. 4 vs $N^{\mathrm{Ad}} = dn^{\mathrm{Ad}}$, the number of alkali atoms adsorbed per unit area. Note that α_1 rises roughly linearly with coverage, and that for a given value of N^{Ad}, α_1 is rather insensitive to which alkali species is being adsorbed (i.e., to what value of d has been chosen). On the other hand $\alpha_2(N^{\mathrm{Ad}}, d)$ does seem to depend on d, and thus on alkali species, for fixed N^{Ad}. (The solid curves in Fig. 4 are drawn in solely as guides to the eye.)

The sign change of α_1 at $N^{\mathrm{Ad}} \approx 0.2 \times 10^{15}$ atoms/cm^2, in Fig. 4, is a "quantitive" feature of the results, in that there could obviously not be such a sign change if $\alpha_1(N^{\mathrm{Ad}} = 0)$ had not turned out to be negative. According to the latest ILEED experiments on a clean Al(111) surface, it is now believed that $\alpha_1(N^{\mathrm{Ad}} = 0)$ is in fact positive (the "best fit"[1] is $\alpha_1 = 0.2$ Å $\pm$ 0.1 Å). This result, if true,

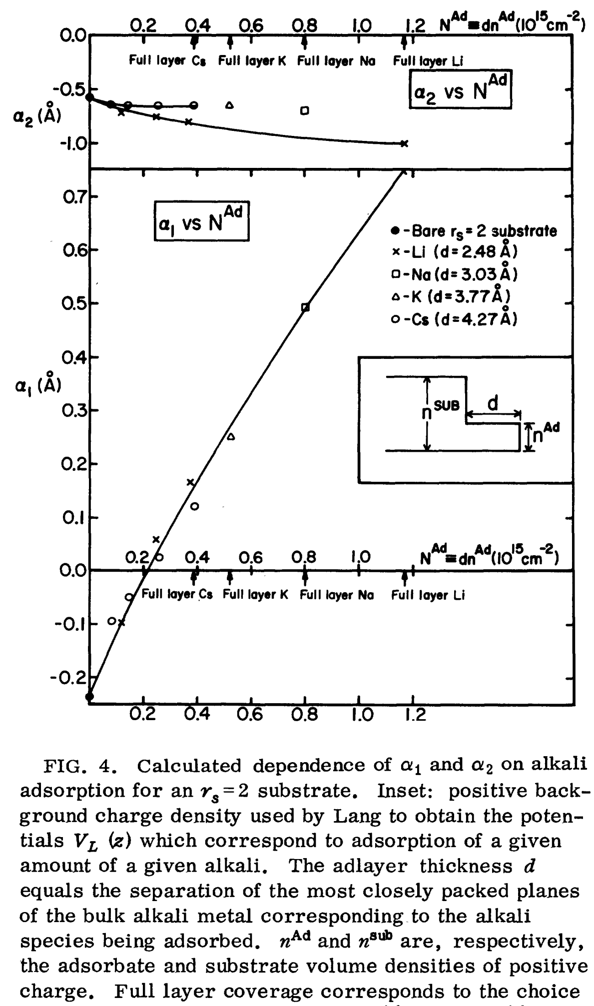

FIG. 4. Calculated dependence of α_1 and α_2 on alkali adsorption for an $r_s = 2$ substrate. Inset: positive background charge density used by Lang to obtain the potentials $V_L(z)$ which correspond to adsorption of a given amount of a given alkali. The adlayer thickness d equals the separation of the most closely packed planes of the bulk alkali metal corresponding to the alkali species being adsorbed. n^{Ad} and n^{sub} are, respectively, the adsorbate and substrate volume densities of positive charge. Full layer coverage corresponds to the choice of positive adlayer charge density n^{Ad} equal to n_∞^{Ad}, the bulk-charge density of the corresponding bulk alkali metal. $N^{\mathrm{Ad}} \equiv dn^{\mathrm{Ad}}$, is the number of alkali atoms adsorbed per unit area.

precludes the observation of a sign change in α_1 with coverage; it also suggests that one will have to go beyond the jellium model if one is to have a quantitative theory of surface-plasmon dispersion. The question of going beyond the jellium model, to calculate α_1 and α_2, is discussed below in Sec. V.

V. DISCUSSION: DIRECTIONS FOR FUTURE THEORETICAL STUDIES OF SURFACE PLASMON PROPERTIES

The results presented in Figs. 2–4 give a qualitative indication of the sensitivity of α_1 and α_2 to the shape of the surface potential barrier $V(z)$. However, they represent only a first step in clarifying the nature of the physical relation between the α's and $V(z)$, which remains obscure because of the complicated form of Eqs. (2.31) and (2.55).

There are two lines along which one would hope to be able to make further progress. First, by making an extensive study of the values of α_1 and α_2 for some sort of "complete set" of potential barriers $V(z)$, one might hope to be able to detect empirically those aspects of $V(z)$ which cause α_1 and α_2 to vary. For example, one might learn what aspects of $V_{\rm LK}(z)$ and of potentials of comparable surface diffuseness $V(z\,;\,a,\Phi)$, cause the values of α_1 and α_2 to which they lead to differ by factors of ~2, or to learn what aspects of Lang's potentials for alkali adsorbates render $\alpha_1(N^{\rm Ad},d)$ essentially independent of d.

Second, by developing a means for incorporating the effects of lattice periodicity into the theory of surface plasmon dispersion and damping, one would presumably be able to test calculations of the α's against experimental measurements. The present jellium calculations do not permit such a test.

In calculating work functions, Lang argues[33] that the approximate validity of the use of a jellium model stems from the fact that a work function is a quantity whose definition, as the energy given up in removing an electron from a metal to α, involves an average (of the surface dipole) over the entire metal surface. More generally, one would argue the discreteness of a metal's ionic charge should not play an important role in determining the magnitude of any of its long-wavelength surface properties. And indeed it is this argument which leads one to suppose that Lang's potentials should provide a basis for calculating long-wavelength surface plasmon dispersion and damping.

However, this argument neglects the fact that surface plasma oscillation is a high-frequency phenomenon, whose dispersion relation reflects the selection rules which govern surface-plasmon decay, while a work function is a static surface property, in which such selection rules play no role. In the absence of departures from two-dimensional translation invariance, whether due to lattice periodicity or to some other form of "surface roughness,"[34] it is known, in general, that $q=0$ surface plasmons are undamped,[14] or in other words, that

$$\mathrm{Im}\,\omega_s(q=0)=0\ . \tag{5.1}$$

Thus, the experimental (ILEED) observation that

$$|\mathrm{Im}\,\omega_s(q=0)/\mathrm{Re}\,\omega_s(q=0)|\approx 18\%\ , \tag{5.2}$$

for an Al(111) surface, is a good indication that departures from two-dimensional translation invariance not only can but actually do play a significant role in determining $\omega_s(q)$ for small values of q.

One may estimate the scale of length which characterizes the relevant departures from surface "flatness" by assuming that their effect is to couple initially undamped infinite wavelength surface plasmons to surface plasmons of shorter wavelength, whose damping, for the sake of the estimate, can be assumed to be governed by the linear damping law [cf. Eq. (2.1)]

$$\mathrm{Im}\,\omega_s(q)=\omega_s(0)\alpha_2 q\ . \tag{5.3}$$

Using the value $\alpha_2=-0.57$ Å calculated for a clean $r_s=2$ substrate [using $V_{\rm LK}(z)$], it is seen that in order to explain the experimental damping ratio of Eq. (5.2), one must assume the important departures from surface flatness couple the $q=0$ surface plasmon to modes of wave-vector $\approx(0.18/0.57$ Å$^{-1})$. Thus the length scale which characterizes these departures is of the order of $(0.57/0.18)$ Å $\approx$ a few Å, which makes it seem likely that they are associated with lattice periodicity (as opposed to surface "imperfections," i.e., steps, kinks, ...). I hope to be able to incorporate lattice periodicity effects, into the theory of surface plasmons, perturbatively, for free-electron metals.

ACKNOWLEDGMENT

I am grateful to N.D. Lang for providing me with computer cards containing his self-consistent potentials, and for many useful discussions.

APPENDIX A

In this appendix, I derive the asymptotic falloff behavior of integrals of the form $I^{\pm}_{n,n'}(z',z'';\omega)$, cf. Eq. (2.36), which enter into the calculation of the kernel $K_\omega(z,z'')$, cf. Eq. (2.37). The first step in the derivation is the recognition that $\mathcal{G}^{\pm}_{k\kappa 0\omega}(z',z'')$ is independent of $\vec{k}$, by virtue of Eq. (2.7), and therefore that the $I^{\pm}_{n,n'}$ can be written

$$I^{\pm}_{n,n'}(z',z'';\omega)=\frac{\omega}{\pi^2 n_\infty}\int_0^{k_F}d\kappa\,(k_F^2-\kappa^2)\left(\frac{d}{dz'}\right)^n\psi_\kappa(z')\left(\frac{d}{dz'}\right)^{n'}\times\mathcal{G}^{\pm}_{k\kappa 0\omega}(z',z'')\,\psi_\kappa(z')\ . \tag{A1}$$

Note in Eq. (A1) that the factor $(k_F^2-\kappa^2)$ vanishes at the upper limit of integration. For potential barriers $V(z)$ which do not have a solution at $\kappa=0$ (that is, a $\kappa=0$ resonance), the integrand of Eq. (A1) also vanishes at the lower integration limit. It is argued below that by virtue of this behavior at the limits of integration, the integrals $I^{\pm}_{n,n'}$ fall off as z''^{-2} times a sinusoidal function of z'', as $z''\to\infty$ (with z' held fixed).

The proof is simplified by the fact that the Green's functions whose sum or difference equals $\mathcal{G}^{\pm}_{k\kappa 0\omega}(z',z'')$ have the closed representations

$$G^+(z',z'';E)=[1/w(E)]\times[\theta(z'-z'')\psi^+(z';E)\psi^-(z';E)+\theta(z''-z')\psi^+(z'';E)\psi^-(z';E)]\,, \tag{A2a}$$

$$G^-(z',z'';E)=[G^+(z',z'';E)]^*\,, \tag{A2b}$$

where the $\psi^{\pm}(z;E)$ are the solutions to the equation

$$\left(-\frac{1}{2m}\frac{d^2}{dz^2}+V(z)\right)\psi^{\pm}(z;E)=E\psi^{\pm}(z;E)\,, \tag{A3}$$

which obey, respectively, as $z\to\pm\infty$, an outgoing wave boundary condition, and where the Wronskian $w(E)$ is given by

$$w(E)=\frac{1}{2m}\left(\frac{d\psi^+}{dz}(z;E)\psi^-(z;E)-\psi^+(z;E)\frac{d\psi^-(z;E)}{dz}\right)\,. \tag{A4}$$

Using Eqs. (A3) and (2.4), it is clear that as $z''\to\infty$, the wave function $\psi^+(z'';\pm\omega+\omega_\kappa)$ has the dependence

$$\psi^+(z'';\pm\omega-\omega_\kappa)\to\exp[i(\pm 2m\omega+\kappa^2)^{1/2}z'']\,, \tag{A5}$$

where for the minus sign the square root is to be interpreted as $i(2m\omega-\kappa^2)^{1/2}$ if $\kappa^2<2m\omega$. At the same time, the wave functions $\psi_\kappa(z)$ have the asymptotic form as $z\to\infty$,

$$\psi_\kappa(z)\to\sin(\kappa z+\delta_\kappa)\,, \tag{A6}$$

where δ_κ is a phase shift independent of z. The assumption that $V(z)$ has no $\kappa=0$ state implies[35] that

$$\delta_{\kappa=0}=0\,. \tag{A7}$$

Consider first the term in $I^{\pm}_{n,n'}$ corresponding to $G^+(z',z'';\omega+\omega_\kappa)$. In the limit $z''\to\infty$, this term approaches

$$\int_0^{k_F}d\kappa\,(\kappa_F^2-\kappa^2)f_{n,n'}(z',\kappa,\omega)\times\exp[i(2m\omega+\kappa^2)^{1/2}z'']\sin(\kappa z''+\delta_\kappa)\,, \tag{A8}$$

where

$$f_{n,n'}(z',\kappa,\omega)\equiv\frac{\omega}{\pi^2 n_\infty}\left[\left(\frac{d}{dz'}\right)^n\psi_\kappa(z')\right]\times\left[\left(\frac{d}{dz'}\right)^{n'}\psi^-(z';\omega+\omega_\kappa)\right]\frac{1}{w(\omega+\omega_\kappa)}\,. \tag{A9}$$

By virtue of Eqs. (A3) and (2.3), the quantity $f_{n,n'}(z',\kappa,\omega)$ is an analytic function of κ along the line $0\le\kappa\le k_F$. Moreover, since $V(z)$ has no state at $\kappa=0$, one has

$$\psi_\kappa(z)\xrightarrow[\kappa\to 0]{}0\,,\quad\forall z\,, \tag{A10}$$

and thus one obtains

$$f_{n,n'}(z',0,\omega)=0\,, \tag{A11}$$

One uses these facts to integrate by parts in the expression of (A8), after rewriting it in the form

$$\frac{1}{2i}\int_0^{k_F}d\kappa(k_F^2-\kappa^2)f_{n,n'}(z',\kappa,\omega)\left(\frac{e^{i\delta_\kappa}(2m\omega+\kappa^2)^{1/2}}{iz''[(2m\omega+\kappa^2)^{1/2}+\kappa]}\frac{d}{d\kappa}(\exp\{i[(2m\omega+\kappa^2)^{1/2}+\kappa]z''\})+\frac{e^{-i\delta_\kappa}(2m\omega+\kappa^2)^{1/2}}{iz''[(2m\omega+\kappa^2)^{1/2}-\kappa]}\frac{d}{d\kappa}(\exp\{i[(2m\omega+\kappa^2)^{1/2}-\kappa]z''\})\right). \tag{A12}$$

The crucial point is the vanishing of the boundary terms, due to Eq. (A11), and to the fact that $k_F^2-\kappa^2=0$ at $\kappa=k_F$. Because the boundary terms vanish, the expression of (A12) is equivalent to the expression

$$+\frac{1}{2z''}\int_0^{k_F}d\kappa\left[\exp\{i[(2m\omega+\kappa^2)^{1/2}+\kappa]z''\}\frac{d}{d\kappa}\left((k_F^2-\kappa^2)f_{n,n'}(z',\kappa,\omega)\frac{e^{i\delta_\kappa}(2m\omega+\kappa^2)^{1/2}}{(2m\omega+\kappa^2)^{1/2}-\kappa}\right)+\exp\{i[(2m\omega+\kappa^2)^{1/2}-\kappa]z''\}\frac{d}{d\kappa}\left((k_F^2-\kappa^2)f_{n,n'}(z',\kappa,\omega)\frac{e^{-i\delta_\kappa}(2m\omega+\kappa^2)^{1/2}}{(2m\omega+\kappa^2)^{1/2}-\kappa}\right)\right]\,. \tag{A13}$$

According to the Riemann-Lebesgue lemma[36] the integrand of (A13) vanishes as a sinusoid times z''^{-1}, as $z''\to\infty$, and thus the entire expression vanishes as z''^{-2} times the sinusoid, as desired. One may verify this fact directly, of course, integrating by parts once again in (A13). One thereby finds it to have the asymptotic behavior as $z''\to\infty$,

$$(A\exp\{i[(2m\omega+k_F^2)^{1/2}+k_F]z''\}+B\exp\{i[(2m\omega+k_F^2)^{1/2}-k_F]z''\})/z''^2\,, \tag{A14}$$

where A and B depend on n, n', and z' (and in which, incidentally, the integration limit $\kappa = 0$ contributes nothing).

It remains to verify that the term in $I^{\pm}_{n,n'}(z', z''; \omega)$ containing $G^-(z', z''; -\omega+\omega_\kappa)$ instead of $G^+(z', z''; \omega+\omega_\kappa)$ has a similar or faster falloff behavior as $z'' \to \infty$. There are two cases.

(i) If $k_F^2 < 2m\omega$, then for all κ between 0 and k_F, one has

$$\psi^+(z''; -\omega+\omega_\kappa) \xrightarrow[z''\to\infty]{} \exp[-(2m\omega-\kappa^2)^{1/2} z''] . \tag{A15}$$

Thus the falloff of the $G^-(z, z''; -\omega+\omega_\kappa)$ term in $I^{\pm}_{n,n'}$ is exponential as $z'' \to \infty$, and the over-all asymptotic behavior of $I^{\pm}_{n,n'}$ is of the form shown in (A14).

(ii) If $k_F^2 > 2m\omega$, which is true for sufficiently dense jellium (e.g., at Al density), then the G^- contribution of $I^{\pm}_{n,n'}$ takes the form

$$\begin{aligned}&\int_0^{(2m\omega)^{1/2}} d\kappa\,(k_F^2-\kappa^2) f^*_{n,n'}(z', \kappa, -\omega)\\ &\quad\times \exp[-(2m\omega-\kappa^2) z''] \sin(\kappa z''+\delta_\kappa)\\ &\quad+\int_{(2m\omega)^{1/2}}^{k_F} d\kappa\,(k_F^2-\kappa^2) f^*_{n,n'}(z', \kappa, -\omega)\\ &\quad\times \exp[-i(\kappa^2-2m\omega)^{1/2} z''] \sin(\kappa z''+\delta_\kappa).\end{aligned} \tag{A16}$$

One may easily carry out an integration by parts in each of the integrals of (A16), analogous to that performed for the integral of (A8). One finds that boundary terms at $\kappa = (2m\omega)^{1/2}$ contribute nothing to the asymptotic value of the expression of (A16) as $z'' \to \infty$, but that the boundary term at $\kappa = k_F$ does contribute, yielding for $I^{\pm}_{n,n'}(z', z'')$ terms with the asymptotic dependence on z'',

$$\begin{aligned}&(C \exp\{i[(k_F^2-2m\omega)^{1/2}+k_F] z''\}\\ &\quad+ D \exp\{i[(k_F^2-2m\omega)^{1/2}-k_F] z''\})/z''^2 .\end{aligned} \tag{A17}$$

Thus in either case, the integrals $I^{\pm}_{n,n'}(z'z'')$ behave as z''^{-2} times a sinusoid as $z'' \to \infty$, as was originally claimed.

APPENDIX B

In this appendix, I show that, asymptotically as $z \to \infty$, $\Delta_{q\omega}(z)$ assumes the form

$$\Delta_{q\omega}(z\to\infty) \approx z^{-2} \sum_{l=1}^{L} c_l e^{ik_l z} \tag{B1}$$

to leading order. The c_l are a set of constants, to be determined by solving Eq. (3.8). The k_l are determined below; there turn out to be a finite number, L, of them, where $L=6$ if $k_F^2 < 2m\omega$ and $L=10$ if $k_F^2 > 2m\omega$.[37]

By virtue of Eq. (2.31), the asymptotic behavior of $\Delta_{q\omega}(z)$ is governed by that of $\Delta^{(0)}_{q\omega}(z)$, given in Eq. (2.34), as well as (self-consistently) by that of

$$\int dz'' K_\omega(z, z'') \Delta_{q\omega}(z'') . \tag{B2}$$

In order to determine the behavior of this integral, one studies the functions $M_{n,n'}(z; \omega)$ defined by

$$\begin{aligned}M^{\pm}_{n,n'}(z; \omega) \equiv{}& \frac{\omega}{\pi^2 n_\infty} \int_0^{\kappa_F} d\kappa\,(k_F^2-\kappa^2)\\ &\times\left[\left(\frac{d}{dz}\right)^n \psi_\kappa(z)\right]\left(\frac{d}{dz}\right)^{n'}\\ &\times\int dz''\, G^{\pm}(z, z''; \pm\omega+\omega_\kappa)\psi_\kappa(z'')\Delta_{q\omega}(z'') .\end{aligned} \tag{B3}$$

[It is easy to express the integral of (B2) in terms of the $M^{\pm}_{n,n'}(z, \omega)$, using Eqs. (3.10), (2.36), and (2.7).]

One attempts to determine a set of wave-vectors $\{k_l\}$, such that Eq. (B1) is self-consistent, i.e., such that the use of Eq. (B1) in evaluating the $M^{\pm}_{n,n'}(z; \omega)$ will lead to the result that $M^{\pm}_{n,n'}(z\to\infty; \omega)$ varies as z^{-2} times a linear combination of the same set of plane waves $e^{ik_l z}$. For example, consider $M^+_{0,0}(z; \omega)$ which [cf. Eqs. (A2) and (A4)] may be expressed as

$$\begin{aligned}M^+_{0,0}(z; \omega) ={}& \frac{\omega}{\pi^2 n_\infty} \int_0^{k_F} d\kappa\,(k_F-\kappa^2) \frac{1}{w(\omega+\omega_\kappa)} \psi_\kappa(z)\\ &\times\Big(\psi^+(z; \omega+\omega_\kappa) \int_{-\infty}^{z} dz''\, \psi^-(z''; \omega+\omega_\kappa)\\ &\times\psi_\kappa(z'')\Delta_{q\omega}(z'') + \psi^-(z; \omega+\omega_\kappa)\\ &\times\int_z^{\infty} dz''\, \psi^+(z''; \omega+\omega_\kappa)\psi_\kappa(z'')\Delta_{q\omega}(z'')\Big).\end{aligned} \tag{B4}$$

Because $\psi_\kappa(z''\to-\infty)$ is proportional to $\exp[z''(2m\Phi+k_F^2-\kappa^2)^{1/2}]$, the z'' integral from $-\infty$ to z in Eq. (B4) is a differentiable function of κ, in the region $[0, k_F]$. For this reason the term in Eq. (B4) involving this z'' integral can be evaluated asymptotically, using the method of integration by parts. One breaks the integration from $-\infty$ to z into the two parts, from $-\infty$ to a point Z, and from Z to z, where the point Z is chosen to be sufficiently deep inside the metal, that for $z'' > Z$ one may replace the functions $\psi^-(z''; \omega+\omega_\kappa)$, and $\Delta_{q\omega}(z'')$ by their asymptotic forms.

As $z \to \infty$, using Eqs. (A5) and (A6), the contribution to $M^+_{0,0}(z; \omega)$ from the integral over $(-\infty, Z)$ can be written in the form

$$\int_0^{k_F} d\kappa\,(k_F^2-\kappa^2) \sin(\kappa z+\delta_\kappa) \exp[i(2m\omega+\kappa^2)^{1/2} z] A_\omega(\kappa) , \tag{B5}$$

where $A_\omega(\kappa)$, as explained, is a differentiable function of κ, and where by virtue of Eq. (A9), $\delta_0 = 0$ and $A_\omega(0) = 0$. As a result, using methods identical to those of Appendix A, one finds that the expression of (B5) behaves, as $z \to \infty$, as a linear combination of

$$z^{-2} \exp\{iz[(2m\omega+k_F^2)^{1/2} \pm k_F]\} , \tag{B6}$$

or in other words, that two of set of k_l must be $(2m\omega + k_F^2)^{1/2} \pm k_F$.

The contribution to $M^{+}_{0,0}(z\,;\,\omega)$ from the integral over (Z, z) is somewhat less straightforwardly evaluated. In the limit $z \to \infty$, using Eqs. (A5) and (A6) and the fact that

$$\psi^{-}(z\to\infty\,;\,\omega+\omega_\kappa) \simeq \exp[-iz(2m\omega+\kappa^2)^{1/2}] + r(\omega+\omega_\kappa)\exp[iz(2m\omega+\kappa^2)^{1/2}]\,, \qquad \text{(B7)}$$

where $r(\omega+\omega_\kappa)$ is a reflection coefficient, this contribution is proportional to the difference of the integrals, $J_\pm$, which are defined by

$$J_\pm \equiv \int_0^{k_F} d\kappa (k_F^2-\kappa^2)\,\frac{e^{\pm i\delta_\kappa}}{(\kappa^2+2m\omega)^{1/2}} \times \exp\{iz[(2m\omega+\kappa^2)^{1/2}\pm\kappa]\}\,B(\kappa,z)\,, \qquad \text{(B8)}$$

where

$$B(\kappa,z) \equiv \int_Z^z dz'\, z'^{-2}\Big(\sum_l c_l e^{ik_l z'}\Big) \times \sin(\kappa z'+\delta_\kappa)\{\exp[-iz(2m\omega+\kappa^2)^{1/2}] + r(\omega+\omega_\kappa)\exp[iz(2m\omega+\kappa^2)^{1/2}]\}\,. \qquad \text{(B9)}$$

Let

$$g_\pm(\kappa\,;\,\omega) \equiv (2m\omega+\kappa^2)^{1/2} \pm \kappa\,. \qquad \text{(B10)}$$

Then, using the differentiability of $B(\kappa, z)$, and twice integrating by parts on κ, one obtains the expression for $J_\pm$,

$$J_\pm = \frac{e^{izg_\pm(\kappa;\,\omega)}}{z^2 g'_\pm(\kappa\,;\,\omega)}\,\frac{d}{d\kappa}\left(\frac{(k_F^2-\kappa^2)\,e^{\pm i\delta_\kappa}}{(\kappa^2+2m\omega)^{1/2} g'_\pm(\kappa\,;\,\omega)}\,B(\kappa,z)\right)\Bigg|_0^{k_F} - \frac{1}{z^2}\int d\kappa\, e^{izg_\pm(\kappa;\,\omega)}\,\frac{d}{d\kappa}\left[\frac{1}{g'_\pm(\kappa\,;\,\omega)}\,\frac{d}{d\kappa}\left(\frac{k_F^2-\kappa^2}{(\kappa^2+2m\omega)^{1/2}}\,\frac{e^{\pm i\delta_\kappa}}{g'_\pm(\kappa,\omega)}\,B(\kappa,z)\right)\right]\,. \qquad \text{(B11)}$$

In the boundary term of Eq. (B11), the limit k_F only contributes if the $d/d\kappa$ operates on $(k_F^2-\kappa^2)$, while the contributions from the limit $\kappa=0$ are equal in J_+ and J_-, and therefore cancel when one evaluates $J_+ - J_-$. Thus, the z dependence contributed to $M^{\pm}_{0,0}(z\,;\,\omega)$ by the boundary terms of $J_\pm$ is of the form

$$z^{-2}\exp\{iz[(2m\omega+k_F^2)^{1/2}\pm k_F]\}\,B(k_F,z)\,. \qquad \text{(B12)}$$

In order to determine the asymptotic behavior of $B(k_F, z)$, one needs to evaluate the limiting form of integrals such as

$$\int_Z^z dz'\, z'^{-2}\exp\{iz'[\pm(2m\omega+k_F^2)^{1/2}\pm k_F + k_l]\}\,. \qquad \text{(B13)}$$

There are two possibilities: (a) If k_l is such that the argument of the exponential is zero, then an integral such as (B13) equals $(Z^{-1}-z^{-1})$, which as $z\to\infty$, behaves as a constant. Thus the asymptotic dependence of (B12) adds nothing new; it is the same as was given in (B6). (b) If the argument of the exponential of (B13) does not vanish, then the integral behaves asymptotically as

$$\{iZ^{-2}[\pm(2m\omega+k_F^2)^{1/2}\pm k_F+k_l]\}^{-1} \times \exp\{iZ[\pm(2m\omega+k_F^2)^{1/2}\pm k_F+k_l]\} + O(1/z^2)\,, \qquad \text{(B14)}$$

in which case one also obtains the asymptotic behavior given in (B6), for $M^{\pm}_{0,0}(z\,;\,\omega)$.

Next one examines the integral on κ remaining in Eq. (B11). Note that this integral is premultiplied by z^{-2}. As a result, one only need consider the term in this integral, in which both $d/d\kappa$ operators act on $B(\kappa, z)$. [The proof of this statement follows from the fact that integrals of the form,

$$\int_Z^z dz'\, z'^{-2} e^{ipz'}$$

and

$$\int_Z^z dz'\, z'^{-1} e^{ipz'}\,,$$

are bounded, respectively, by Z^{-1} and $\ln(z/Z)$, and the use of the Riemann-Lebesgue lemma.] However, the evaluation of $d^2B(\kappa,z)/d\kappa^2$ is easy, because the two κ derivatives bring down two factors of z' from the various sinusoids. Thus one finds that the integral term in (B11) contributes asymptotic z dependences of the form

$$\frac{1}{z^2}\int_0^{k_F} d\kappa\, e^{izg_\pm(\kappa;\,\omega)}F(\kappa) \times (\exp\{iz[\pm(2m\omega+\kappa^2)^{1/2}\pm\kappa+k_l]\} - \exp\{iZ[\pm(2m\omega+\kappa^2)^{1/2}\pm\kappa+k_l]\})\,, \qquad \text{(B15)}$$

where $F(\kappa)$ is a smooth function of κ.

In this expression, the term involving Z falls to zero, as $z\to\infty$, at least as fast as z^{-3}, by virtue of the Riemann-Lebesgue lemma. The same is true of the term involving

$$\exp\{iz[\pm(2m\omega+\kappa^2)^{1/2}\pm\kappa+k_l]\}\,,$$

unless the equation

$$g_\pm(\kappa,\omega) \pm (2m\omega+\kappa^2)^{1/2}\pm\kappa = 0 \qquad \text{(B16)}$$

is satisfied. In this case, the integral of (B15) behaves asymptotically as

$$z^{-2}e^{ik_l z}\,. \qquad \text{(B17)}$$

Thus, collecting results, the assumption that $\Delta_{q\omega}(z)$ behaves asymptotically as in Eq. (B1) leads to the conclusion that $M^{+}_{0,0}(z\,;\,\omega)$ contains in its asymptotic behavior, a linear combination of terms of the form $z^{-2}e^{ik_l z}$, where the set of k_l's includes $\pm 2k_F$ [from $\Delta^{(0)}_{q\omega}(z)$] and $(2m\omega + k_F^2)^{1/2} \pm k_F$.

In order to complete the study of the asymptotic properties of $M^{+}_{0,0}(z\,;\,\omega)$, one must now consider the contribution of the term [cf. Eq. (B4)] involving the z'' integral from z to ∞.

As $z \to \infty$, using Eqs. (A5), (A6), and (B7), this contribution can be seen to behave as

$$\int_0^{k_F} d\kappa\,(k_F^2 - \kappa^2)\;\frac{\sin(\kappa z + \delta_\kappa)}{(2m\omega + \kappa^2)^{1/2}}$$
$$\times\{\exp[-i(2m\omega + \kappa^2)^{1/2} z] + r(\omega + \omega_\kappa)$$
$$\times \exp[i(2m\omega + \kappa^2)^{1/2}]z\}$$
$$\times \sum_{l=1}^{L} c_l[e^{i\delta_\kappa} S_l^{+}(z, \kappa, \omega) - e^{-i\delta_\kappa} S_l^{+}(z, -\kappa, \omega)]\,, \tag{B18}$$

where the functions $S_l^{\pm}$ are defined by

$$S_l^{\pm}(z, \kappa, \omega) \equiv \int_z^\infty dz'\,z'^{-2} \exp\{iz'[k_l \pm (2m\omega + \kappa^2) + \kappa]\}\;. \tag{B19}$$

Consider first the term involving $S_l^{+}(z, +\kappa, \omega)$ in Eq. (B18). If the equation

$$k_l + (2m\omega + \kappa^2)^{1/2} + \kappa = 0 \tag{B20}$$

cannot be satisfied for $0 < \kappa < k_F$, then $S_l(z, \kappa, \omega)$ can be replaced in (B18) by the asymptotic expression

$$S_l^{+}(z \to \infty, \kappa, \omega) = \{-iz^2[k_l + (2m\omega + \kappa^2)^{1/2} + \kappa]\}^{-1}$$
$$\times \exp\{iz[k_l + (2m\omega + \kappa^2)^{1/2} + \kappa]\}$$
$$+ O(1/z^3)\;. \tag{B21}$$

Substituting Eq. (B21) into (B18), one then finds that the $S_l^{+}(z, \kappa, \omega)$ term of (B18) varies asymptotically as z^{-2} times a linear combination of the $e^{ik_l z}$, plus terms which die off more rapidly as $z \to \infty$. One obtains a similar result for the $S_l^{+}(z, -\kappa, \omega)$ term, under the assumption that

$$k_l + (2m\omega + \kappa^2)^{1/2} - \kappa = 0 \tag{B22}$$

cannot be satisfied for $0 < \kappa < k_F$.

However, it should be noted that Eqs. (B20) and (B22) *can* have solutions for $0 < \kappa < k_F$, for various of the k_l's that one already knows must be included in $\{k_l\}$. For example, if $k_l = -2k_F$, then Eq. (B20) has a solution at $\kappa = k_F - m\omega/2k_F$. (See Table I for more examples.) In this case the replacement of $S^{+}(z \to \infty, \kappa, \omega)$ in (B18) by Eq. (B21) is not a correct procedure, as is evidenced by the fact that the denominator in Eq. (B21) can equal zero, and one must take explicit account of the fact that $S_l^{+}(z, \kappa, \omega)$ is not analytic at $\kappa = k_F - m\omega/2k_F$.

In order to solve this problem quite generally, one considers integrals of the form

$$I(z) = \int_0^{k_F} d\kappa\, C(\kappa)\, e^{if(\kappa)z} \int_z^\infty dz'\,\frac{e^{ig(\kappa)z'}}{z'^2}\,, \tag{B23}$$

in which $C(\kappa)$, $f(\kappa)$, and $g(\kappa)$ are assumed to be smooth functions of κ, and in which $g(\kappa)$ is assumed to have a zero at a point $\kappa = k_0$, with $0 < k_0 < k_F$.

The asymptotic behavior of $I(z)$ as $z \to \infty$ can be obtained by breaking the κ integration of Eq. (B23) into four integrations over the domains $[0, k_0 - \Lambda z^{-p}]$, $[k_0 - \Lambda z^{-p}, k_0]$, $[k_0, k_0 + \Lambda z^{-p}]$, and $[k_0 + \Lambda z^{-p}, k_F]$, where Λ is an arbitrary constant and p is a constant satisfying $\frac{1}{2} < p < 1$. Consider first, the integral over the third of these domains, which I call $I_3(z)$. Since κ is restricted, in this integral, to be arbitrarily near to k_0 (as z becomes arbitrarily large), the functions $C(\kappa)$, $f(\kappa)$, $g(\kappa)$ in $I_3(z)$ may be Taylor expanded about $\kappa = k_0$; the expansion yields

$$f(\kappa) = f(k_0) + (\kappa - k_0) f'(k_0) + \tfrac{1}{2}(\kappa - k_0)^2 f''(k_0) + \cdots\,, \tag{B24a}$$

$$g(\kappa) = (\kappa - k_0)\, g'(k_0) + \tfrac{1}{2}(\kappa - k_0)^2 g''(k_0) + \cdots\,, \tag{B24b}$$

$$C(\kappa) = C(k_0) + \cdots\,, \tag{B24c}$$

where in Eq. (B24b), the constant $g(k_0)$ has, by assumption, been set equal to zero. Using Eqs. (B24), one may write $I_3(z)$ for $z \to \infty$ in the form

$$I_3(z) \approx C(k_0)\, e^{if(k_0)z} \int_{k_0}^{k_0 + \Lambda z^{-p}} d\kappa \int_z^\infty dz'\,z'^{-2} \exp\{i[(\kappa - k_0)(zf'(k_0) + z'g'(k_0)) + \tfrac{1}{2}(\kappa - k_0)^2(zf''(k_0) + z'g''(k_0)) + \cdots\} \tag{B25}$$

or, changing variables, as

$$I_3(z) = C(k_0)\, e^{if(k_0)z}\, \Lambda z^{-(1+p)} \int_0^1 d\gamma \int_1^\infty d\nu\, \nu^{-2} \exp\{i\Lambda z^{1-p}\gamma[f'(k_0) + \nu g'(k_0)] + \tfrac{1}{2} i\Lambda^2 z^{1-2p}\gamma^2[f''(k_0) + \nu g''(k_0)] + \cdots\}\;. \tag{B26}$$

However, by virtue of the choice $p > \frac{1}{2}$, the term in the exponential, in Eq. (B26), which is proportional to z^{1-2p}, is negligible in the limit $z \to \infty$. Dropping this term therefore, and interchanging orders of integration one may reduce Eq. (B26) to the form

$$I_3(z) = C(k_0)\, e^{if(k_0)z}\, \frac{1}{iz^2} \int_1^\infty \frac{d\nu}{\nu^2}\, \frac{\exp\{i\Lambda z^{1-p}[f'(k_0)+\nu g'(k_0)]\}-1}{f'(k_0)+\nu g'(k_0)} \quad , \tag{B27}$$

which can easily be asymptotically estimated as $z\to\infty$, since p has been chosen smaller than unity. Similarly, the integral $I_2(z)$ which corresponds to the second domain of κ, viz., $[k_0-\Lambda z^{-p}, k_0]$, may be written

$$I_2(z) \simeq C(k_0)\, e^{if(k_0)z}\, \frac{1}{iz^2} \int_1^\infty \frac{d\nu}{\nu^2}\, \frac{1-\exp\{-i\Lambda z^{1-p}[f'(k_0)+\nu g'(k_0)]\}}{f'(k_0)+\nu g'(k_0)} \quad . \tag{B28}$$

In order to evaluate $I_2(z)+I_3(z)$ (which is the quantity actually needed), one uses the method of contour distortion, thereby finding the expression

$$I_2(z)+I_3(z) = 2C(k_0)\,\mathrm{sgn}[g'(k_0)]\,e^{if(k_0)z}z^{-2} \times \int_0^\infty d\nu\, \mathrm{Re}\left(\frac{\exp\{i\Lambda z^{1-p}[f'(k_0)+g'(k_0)]-\nu\Lambda z^{1-p}|g'(k_0)|\}-1}{(1+i\nu)^2[f'(k_0)+g'(k_0)+i\nu g'(k_0)]}\right) \quad . \tag{B29}$$

As $z\to\infty$, the term in the integrand of Eq. (B29) involving the exponential yields a contribution to I_2+I_3 which dies off as z^{-3+p}, and which therefore can be neglected. The term which comes from the 1 in the numerator, however, gives rise to a term in I_2+I_3 which behaves as $z^{-2}\exp[if(k_0)z]$.[38] This term must be retained.

It remains to evaluate $I_1(z)$ and $I_4(z)$, the κ integrals corresponding to the domains $[0, k_0-\Lambda z^{-p}]$ and $[k_0+\Lambda z^{-p}, k_F]$, for example, $I_1(z)$, which may be written in the form

$$I_1(z) = \frac{1}{z}\int_0^{k_0-\Lambda z^{-p}} d\kappa\, C(\kappa)\, e^{if(\kappa)z} \int_1^\infty d\nu\, \frac{e^{ig(\kappa)z\nu}}{\nu^2} \quad . \tag{B30}$$

By virtue of the fact that κ does not get closer to k_0 than $k_0-\Lambda z^{-p}$ in Eq. (B30), the argument of the exponential in the ν integral is always at least of order $g'(k_0)\Lambda z^{1-p}$, which is arbitrarily large as $z\to\infty$, $I_1(z)$ takes the form

$$I_1(z\to\infty) = \frac{1}{iz^2}\int_0^{k_0-\Lambda z^{-p}} d\kappa\, C(\kappa)\, \frac{e^{i[f(\kappa)+g(\kappa)]z}}{g(\kappa)} \quad . \tag{B31}$$

Similarly, as $z\to\infty$, the integral $I_4(z)$ is of the form

$$I_4(z\to\infty) = \frac{1}{iz^2}\int_{k_0+\Lambda z^{-p}}^{k_F} d\kappa\, C(\kappa)\, \frac{\exp\{i[f(\kappa)+g(\kappa)]z\}}{g(\kappa)} \quad . \tag{B32}$$

There are now two possibilities: either $f(\kappa)+g(\kappa)$ is constant in κ {this situation occurs [cf. (B18)] when $g(\kappa)=(\kappa^2+2m\omega)^{1/2}+\kappa+k_l$ and $f(\kappa)=-(\kappa^2+2m\omega)^{1/2}-\kappa$}, or otherwise, $f(\kappa)+g(\kappa)$ is a smoothly varying function of κ of nonzero derivative. In the first case,

$$f(\kappa)+g(\kappa)=k_l \;, \tag{B33}$$

the integral $I_1(z)$ takes the form

$$I_1(z\to\infty) = \frac{e^{ik_l z}}{iz^2}\int_0^{k_0-\Lambda z^{-p}} d\kappa\, \frac{C(\kappa)}{g(\kappa)} \quad . \tag{B34}$$

In order to take advantage of the facts that $g(\kappa)$ is smooth and that $g(k_0)=0$, one defines the function $\tilde{g}(\kappa)$ by the equation

$$g(\kappa)=(\kappa-k_0)\tilde{g}(\kappa) \;. \tag{B35}$$

Note that

$$g'(k_0)=\tilde{g}(k_0)\neq 0 \;. \tag{B36}$$

One substitutes Eq. (B35) into (B34) and integrates by parts, obtaining the result

$$I_1(z\to\infty) \simeq \frac{e^{ik_l z}}{iz^2}\left(\frac{C(k_0)}{\tilde{g}(k_0)}\ln\Lambda z^{-p} - \frac{C(0)}{\tilde{g}(0)}\ln k_0\right) - \frac{e^{ik_l z}}{iz^2}\int_0^{k_0-\Lambda z^{-p}} d\kappa\, \ln(k_0-\kappa)\, \frac{d}{d\kappa}\left(\frac{C(\kappa)}{\tilde{g}(\kappa)}\right) \quad . \tag{B37}$$

As $z\to\infty$, it can be seen upon a further integration by parts that the integral term in Eq. (B37) vanishes as $z^{-(2+p)}\ln z\, e^{ik_l z}$, which can be neglected. Similarly, if Eq. (B33) holds, the integral $I_4(z\to\infty)$ may be shown to behave as

$$I_4(z\to\infty) = \frac{e^{ik_l z}}{iz^2}\left(\frac{C(k_F)}{\tilde{g}(k_F)}\ln(k_F-k_0) - \frac{C(k_0)}{\tilde{g}(k_0)}\ln\Lambda z^{-p}\right) + \cdots \quad . \tag{B38}$$

Thus the sum $I_1(z\to\infty)+I_4(z\to\infty)$ behaves asymptotically according to

$$I_1(z\to\infty)+I_4(z\to\infty)=\frac{e^{ik_lz}}{iz^2}\,\frac{C(\kappa)}{\tilde{g}(\kappa)}\,\ln|\kappa-k_0|\Big|_0^{k_F}+\cdots\ . \tag{B39}$$

In the second case, in which $f(\kappa)+g(\kappa)$ is a smoothly varying function of κ, of nonzero derivative, the integral $I_1(z)$ may be converted (integrating by parts) to the form

$$I_1(z\to\infty)=-\frac{1}{z^3}\,\frac{C(\kappa)\,e^{i[f(\kappa)+g(\kappa)]z}}{g(\kappa)[f'(\kappa)+g'(\kappa)]}\Big|_0^{k_0-\Lambda z^{-p}}+\frac{1}{z^3}\int_0^{k_0-\Lambda z^{-p}}d\kappa\,e^{i[f(\kappa)+g(\kappa)]z}\,\frac{d}{d\kappa}\left(\frac{C(\kappa)}{g(\kappa)[f'(\kappa)+g'(\kappa)]}\right). \tag{B40}$$

In the boundary term of Eq. (B40), the contribution at $\kappa=k_0-\Lambda z^{-p}$ behaves asymptotically as $z^{-(3-p)}$, cf. Eq. (B24b), while the contribution at $\kappa=0$ is of $O(z^{-3})$; the boundary term is therefore negligible in the limit $z\to\infty$. The asymptotic behavior of the integral term in Eq. (B40) is dominated by the fact that $g(\kappa)$ vanishes at $\kappa=k_0$. One may obtain a bound on the asymptotic value of this integral term by allowing the $d/d\kappa$ operator to act on $[g(\kappa)]^{-1}$, and by replacing the resulting $[g(\kappa)]^{-2}$ in the integrand by the largest value it assumes within the domain of integration, namely, $[g'(k_0)z^{-p}]^{-2}$. Making this replacement, and using the Riemann-Lebesgue lemma,[36] one then finds the integral term to be of order $z^{-(4-2p)}$ as $z\to\infty$, which again may be dropped in comparison with terms of $O(z^{-2})$.

TABLE I. Compilation of the results of searching for those values of $\kappa\subset[0,k_F]$ at which the functions $S^{\pm}(z,\pm\kappa,\omega)$ are not analytic. The nonanalyticities occur for values of κ which solve any of the equations in the first column, producing asymptotic behavior of $\Delta_{q\omega}(z)$ governed by wave vectors given in the fourth column. Note that the set of k_l's in the table is closed, in the sense that the same finite set of k_l's appears in the second and fourth columns.

Condition for nonanalyticity of $S_l^{\pm}(z,\pm\kappa,\omega)$, Eq. (B19)	k_l	Value of κ at which nonanalyticity occurs	Plane-wave wave-vectors generated by nonanalyticity
For $S_l^+(z,+\kappa,\omega)$:	$-2k_F$	$k_F-m\omega/2k_F$	$\pm 2k_F,\ \pm m\omega/k_F$
$(2m\omega+\kappa^2)^{1/2}+\kappa+k_l=0$	$-m\omega/k_F$	$-k_F+m\omega/2k_F$	a
(which has solutions only if $k_l<0$)	$-(k_F^2-2m\omega)^{1/2}-k_F$	$(k_F^2-2m\omega)^{1/2},\ k_F^2>2m\omega$	$-(k_F^2-2m\omega)^{1/2}\pm k_F,\ (k_F^2-2m\omega)^{1/2}\pm k_F$
	$(k_F^2-2m\omega)^{1/2}-k_F$	$-(k_F^2-2m\omega)^{1/2},\ k_F^2>2m\omega$	b
For $S_l^+(z,-\kappa,\omega)$:	$-2k_F$	$-k_F+m\omega/2k_F$	a
$(2m\omega+\kappa^2)^{1/2}-\kappa+k_l=0$	$-m\omega/k_F$	$k_F-m\omega/2k_F$	$\pm 2k_F,\ \pm m\omega/k_F$
(which has solutions only if $k_l<0$)	$-(k_F^2-2m\omega)^{1/2}-k_F$	$(k_F^2-2m\omega)^{1/2},\ k_F^2>2m\omega$	b
	$(k_F^2-2m\omega)^{1/2}-k_F$	$(k_F^2-2m\omega)^{1/2}$	$-(k_F^2-2m\omega)^{1/2}\pm k_F,\ (k_F^2-2m\omega)^{1/2}\pm k_F$
For $S_l^-(z,\kappa,-\omega)$, $k_F^2>2m\omega$:	$-2k_F$	$k_F+m\omega/2k_F,\ m\omega>2k_F^2$	c
$-(\kappa^2-2m\omega)^{1/2}+\kappa+k_l=0$	$-m\omega/k_F$	$k_F+m\omega/2k_F,\ 2k_F^2>m\omega$	c
[which has solutions only if $0>k_l>-(2m\omega)^{1/2}$ (assuming $\kappa>0$)].	$-(k_F^2-2m\omega)^{1/2}-k_F$	No solution, $k_l<-(2m\omega)^{1/2}$	...
	$(k_F^2-2m\omega)^{1/2}-k_F$	k_F	d
	$2k_F$	$k_F+m\omega/2k_F,\ 2k_F^2>m\omega$	c
For $S_l^-(z,-\kappa,-\omega)$, $k_F^2>2m\omega$	$m\omega/k_F$	$k_F+m\omega/2k_F,\ m\omega>2k_F^2$	c
$-(\kappa^2-2m\omega)^{1/2}-\kappa+k_l=0$	$-(k_F^2-2m\omega)^{1/2}+k_F$	No solution, $k_l<(2m\omega)^{1/2}$	...
[which has solutions only if $k_l>(2m\omega)^{1/2}$ (assuming $\kappa>0$)]	$(k_F^2-2m\omega)^{1/2}+k_F$	k_F	d
	$(k_F^2+2m\omega)^{1/2}+k_F$	$(k_F^2+2m\omega)^{1/2}$	c
	$(k_F^2+2m\omega)^{1/2}-k_F$	No solution, $k_l<2m\omega$	...

[a] Irrelevant for physical values of r_s, for which $-k_F+m\omega/2k_F<0$.
[b] Irrelevant because this value of κ is smaller than 0.
[c] Irrelevant because this value of κ is larger than k_F.
[d] Irrelevant because this nonanalyticity gives rise to an asymptotic falloff of $O(z^{-3}\ln Z)$.

Thus, finally, in the case, $f(\kappa)+g(\kappa)\neq a$ constant in κ, the integral $I_1(z)$ is negligible as $z\to\infty$. A similar argument holds for $I_4(z)$.

Collecting results at this point, one has shown that the asymptotic behavior of the integral $I(z)$, of Eq. (B23), is given by

$$I(z) \xrightarrow[z\to\infty]{} (\text{const.})\, z^{-2} e^{izf(k_0)} \quad , \tag{B41}$$

where by assumption, $g(k_0)=0$. Thus returning to the integral of (B18) [which is a sum of integrals of the form of $I(z)$], one has shown that it behaves asymptotically as a linear combination of terms of the form

$$z^{-2}\exp[\pm i(2m\omega+k_0^2)^{1/2}\pm k_0] \ , \tag{B42}$$

where k_0 is any value of κ in $(0, k_F)$, such that

$$(2m\omega+k_0^2)^{1/2}\pm k_0+k_l=0 \ . \tag{B43}$$

It has previously been shown, cf. the paragraph following (B17), that the set of k_l's governing the asymptotic behavior of $M^+_{0,0}(z,\omega)$ includes $\pm 2k_F$ and $(2m\omega+k_F^2)^{1/2}\pm k_F$. To this set, one must now add $\pm(2m\omega+k_0^2)^{1/2}\pm k_0$, for each k_0 that solves Eq. (B43), and with k_l being any of the totality of k_l's. For example, take $k_l=-2k_F$ in Eq. (B43). One finds then, that the equation

$$(2m\omega+k_0^2)^{1/2}+k_0-2k_F=0 \tag{B44}$$

has the solution $k_0=k_F-m\omega/2k_F$, and that the set of k_l's therefore be supplemented by

$$\pm\left[2m\omega+\left(k_F-\frac{m\omega}{2k_F}\right)^2\right]^{1/2}\pm\left(k_F-\frac{m\omega}{2k_F}\right)=\pm\frac{m\omega}{k_F},\ \pm 2k_F \tag{B45}$$

The values $\pm 2k_F$ of (B45) are of course not new, but the values $\pm m\omega/k_F$ are, and thus the set $\{k_l\}$ must be at least

$$\{\pm 2k_F,\ (2m\omega+k_F^2)^{1/2}\pm k_F,\ \pm m\omega/k_F\} \ . \tag{B46}$$

Proceeding in the same manner, one finds that the equations

$$(2m\omega+k_0^2)^{1/2}-k_0-2k_F=0$$
$$(2m\omega+k_0^2)^{1/2}\pm k_0+(2m\omega+k_F^2)^{1/2}\pm k_F=0 \ , \tag{B47}$$
$$(2m\omega+k_0^2)^{1/2}+k_0+m\omega/2k_F=0$$

have no solutions for k_0 such that $0<k_0<k_F$.[39] The only other equation of the form of Eq. (B40) that does have such a solution is

$$(2m\omega+k_0^2)^{1/2}-k_0-m\omega/2k_F=0 \ , \tag{B48}$$

which is solved by

$$k_0=k_F-m\omega/2k_F \ , \tag{B49}$$

which, cf, Eq. (B42), implies that the set $\{k_l\}$ must include

$$\pm\left[2m\omega\ \pm\left(k_F-\frac{m\omega}{2k_F}\right)^2\right]^{1/2}\pm\left(k_F-\frac{m\omega}{2k_F}\right)=\pm\frac{m\omega}{k_F},\ \pm 2k_F \tag{B50}$$

just as in (B45). Thus, the fact that Eq. (B49) solves (B48) leads to no new values of k_l; and one concludes that if $\Delta_{q\omega}(z)$ is given asymptotically by Eq. (B1) with k_l in the set given in (B46), then $M^+_{0,0}(z\,;\omega)$ will also behave asymptotically as a linear combination of $z^{-2}e^{ik_lz}$, where k_l is in this same set.

The question which remains is whether the contributions of the other $M^\pm_{n,n'}(z\,;\omega)$ to

$$\int dz''K_\omega(z,z'')\Delta_{q\omega}(z'') \ ,$$

cf. Eqs. (B2) and (B3), require the inclusion of any additional k_l's. The answer to this question depends on the sign of $k_F^2-2m\omega$. In any case it is clear that the arguments which have been used to this point to evaluate $M^+_{0,0}(z\to\infty\,;\omega)$ apply equally well to $M^-_{n,n'}(z\to\infty\,;\omega)$.

Consider, for example, $M^-_{0,0}(z\,;\omega)$, which [cf. Eqs. (B3), (A2), and (A4)] may be expressed as

$$M^-_{0,0}(z\,;\omega)=\frac{\omega}{\pi^2 n_\infty}\int_0^{k_F}d\kappa\,(k_F^2-\kappa^2)\,\frac{1}{w^*(\omega_\kappa-\omega)}\,\psi_\kappa(z)\Big(\psi^{+*}(z\,;\omega_\kappa-\omega)\times\int_{-\infty}^{z}dz''\psi^{-*}(z''\,;\omega_\kappa-\omega)\psi_\kappa(z'')\Delta_{q\omega}(z'')+\psi^{-*}(z\,;\omega_\kappa-\omega)\int_z^\infty dz''\psi^{+*}(z''\,;\omega_\kappa-\omega)\psi_\kappa(z'')\Delta_{q\omega}(z'')\Big) \ . \tag{B51}$$

In the limit $z\to\infty$, the wave functions $\psi^\pm(z\,;\omega_\kappa-\omega)$ behave according to

$$\psi^+(z\to\infty\,;\omega_\kappa-\omega)=\exp[-z(2m\omega-\kappa^2)^{1/2}] \ , \tag{B52a}$$

and

$$\psi^-(z\to\infty\,;\omega_\kappa-\omega)=\exp[-z(2m\omega-\kappa^2)^{1/2}]+r(\omega_\kappa-\omega)\exp[+z(2m\omega-\kappa^2)^{1/2}] \ , \tag{B52b}$$

where $r(\omega_\kappa-\omega)$ is a reflection coefficient. Thus if the inequality

$$k_F^2<2m\omega \tag{B53}$$

holds, the $\psi^\pm(z\to\infty\,;\omega_\kappa-\omega)$ are non-oscillating for $0<\kappa<k_F$. This fact permits the expression (B51) for $M^-_{0,0}$ to be evaluated easily.

The integral $I(z)$ defined by

$$I(z)\equiv\int_z^\infty dz''\psi^{+*}(z''\,;\omega_\kappa-\omega)\psi_\kappa(z'')\Delta_{q\omega}(z'') \ , \tag{B54}$$

may be asymptotically expanded using Eqs. (B52a), (A6), and (B1), leading to the result

$$I(z\to\infty)=z^{-2}\sum_l c_l \exp\{[ik_l-(2m\omega-\kappa^2)^{1/2}]z\} \times \frac{1}{2i}\left(\frac{e^{i(\kappa z+\delta_\kappa)}}{(2m\omega-\kappa^2)^{1/2}-i(k_l+\kappa)} - \frac{e^{-i(\kappa z+\delta_\kappa)}}{(2m\omega-\kappa^2)^{1/2}-i(k_l-\kappa)}\right) . \quad \text{(B55)}$$

Substituting Eq. (B55) into Eq. (B51), one finds that the z'' integral over (z,∞) contributes to the asymptotic value of $M^-_{0,0}(z;\omega)$ the term

$$-\frac{m\omega}{\pi^2 n_\infty}\frac{1}{2iz^2}\sum_l c_l e^{ik_l z} \times\int_0^{k_F} d\kappa\,(k_F^2-\kappa^2)\frac{\sin(\kappa z+\delta_\kappa)}{(2m\omega-\kappa^2)^{1/2}} \times\left(\frac{e^{i(\kappa z+\delta_\kappa)}}{(2m\omega-\kappa^2)^{1/2}-i(k_l+\kappa)} - \frac{e^{-i(\kappa z+\delta_\kappa)}}{(2m\omega-\kappa^2)^{1/2}-i(k_l-\kappa)}\right) \quad \text{(B56)}$$

plus terms that fall off exponentially as $z\to\infty$. According to the Riemann-Lebesgue lemma the integral in (B56) equals a constant plus terms that fall off as z^{-1}, and which when premultiplied by z^{-2} can therefore be neglected.

The z'' integral over $(-\infty,z)$ in Eq. (B51) can similarly be shown to behave asymptotically as z^{-2} times a linear combination of $e^{ik_l z}$ where the k_l are just those which have been assumed to play a role in the asymptotic expression for $\Delta_{q\omega}(z)$. Thus, as long as Eq. (B53) is satisfied, neither $M^-_{0,0}(z\to\infty;\omega)$, nor, by virtue of a similar argument, any of the $M^-_{n,n'}(z\to\infty;\omega)$ requires the addition of any new values of k_l to the set given in (B46). [Thus for $k_F^2<2m\omega$, $L=6$ as was stated below Eq. (B1).]

If on the other hand the inequality

$$k_F^2>2m\omega \quad \text{(B57)}$$

holds, then the asymptotic behavior of $\psi^\pm(z;\omega_\kappa-\omega)$ is oscillatory, for $2m\omega<\kappa^2<k_F$. In this case therefore, one might expect the asymptotic properties of $M^-_{0,0}(z;\omega)$ to be as complex as those of $M^+_{0,0}(z,)$, and indeed, in this case it is found that the set $\{k_l\}$ must contain four more elements.

As in the case of $M^+_{0,0}(z,\omega)$, for $k_F^2<2m\omega$ one breaks the contribution to $M^-_{0,0}(z;\omega)$ of the z'' integral over $(-\infty,z)$ into two parts, one from the integration region $(-\infty,Z)$ and the other from (Z,z), where Z is taken to be sufficiently large that for $z''>Z$, $\psi^-(z'';\omega_\kappa-\omega)$, $\psi_\kappa(z'')$, $\Delta_{q\omega}(z'')$ may be represented by their asymptotic forms. Proceeding exactly as for $M^+_{0,0}$, one then finds that the z'' integral over $(-\infty,Z)$ contributes asymptotic terms to $M^-_{0,0}(z\to\infty;\omega)$ of the form[40]

$$z^{-2}\exp\{-iz[(k_F^2-2m\omega)^{1/2}\pm k_F]\} . \quad \text{(B58)}$$

One also finds, in analogy to the case of $M^+_{0,0}$, that the z'' integral over (Z,z) contributes terms of the form of (B58), as well as terms of the form $z^{-2}\times e^{ik_l z}$. Finally, one investigates the contributions of the z'' integral over (z,∞) in Eq. (B51), for $k_F^2>2m\omega$. One finds that these contributions include terms of the form $z^{-2}e^{ik_l z}$ (which add nothing new to $\{k_l\}$), and that if one of the equations

$$-(k_0^2-2m\omega)^{1/2}\pm k_0+k_l=0 , \quad \text{(B59)}$$

can be satisfied with k_0 between $(2m\omega)^{1/2}$ and k_F, then they also include terms of the form

$$z^{-2}\exp\{iz[\pm(k_0^2-2m\omega)^{1/2}\pm k_0]\} . \quad \text{(B60)}$$

Collecting these results for $M^-_{0,0}(z;\omega<k_F^2/2m)$, one sees that the set of k_l's must be expanded to include

$$-(k_F^2-2m\omega)^{1/2}\pm k_F . \quad \text{(B61)}$$

It must also include the values

$$\pm(k_0^2-2m\omega)^{1/2}\pm k_0 , \quad \text{(B62)}$$

where k_0 is any solution to Eqs. (B59), as well as the values

$$\pm(k_0^2+2m\omega)^{1/2}\pm k_0 , \quad \text{(B63)}$$

where k_0 is any solution to Eqs. (B43) for a new value of k_l.

It is easy to verify, and the verification is illustrated in Table I, that these new possibilities, for $k_F^2>2m\omega$, require the set of k_l to be[37]

$$\{\pm 2k_F,\ (2m\omega+k_F^2)^{1/2}\pm k_F,\ \pm m\omega/k_F,\ \pm(k_F^2-2m\omega)^{1/2}\pm k_F\} . \quad \text{(B64)}$$

Two of the new values of k_l [cf. Eq. (B58)] come directly from the z'' integral over $(-\infty,z)$ in Eq. (B51). The other two values of k_l, namely, $+(k_F^2-2m\omega)^{1/2}\pm k_F$ arise from the fact that the equation

$$(2m\omega+\kappa^2)^{1/2}+\kappa-(k_F^2-2m\omega)^{1/2}-k_F=0 \quad \text{(B65)}$$

has the solution

$$\kappa=(k_F^2-2m\omega)^{1/2} . \quad \text{(B66)}$$

With these results, the study of the contributions of $M^-_{0,0}(z;\omega)$ to the asymptotic behavior of $\Delta_{q\omega}(z)$ is complete. It is easy to see that the other $M^-_{n,n'}(z;\omega)$ in $K_\omega(z,z'')$ contribute no further new values of k_l. The asymptotic form of $\Delta_{q\omega}(z)$ is correctly given by Eq. (B1), where the set $\{k_l\}$ has six elements for $k_F^2<2m\omega$, given in (B46), while it has ten elements for $k_F^2>2m\omega$, given in (B64).

*Work supported in part by National Science Foundation Grants Nos. GU3850 and H039314.

[1]J. O. Porteus and W. N. Faith, Phys. Rev. B 8, 491 (1973); C. B. Duke and U. Landman, *ibid.* 8, 505 (1973).

[2]T. Kloos and H. Raether, Phys. Lett. A 44, 157 (1973).

[3]S. Andersson, B. I. Lundqvist, G. Srinivasan, and E. Wikborg, Solid State Commun. 11, 1405 (1972).

[4]C. Kunz, Z. Phys. 196, 311 (1966).

[5]A. J. Bennett, Phys. Rev. B 1, 203 (1970).

[6]D. E. Beck and V. Celli, Phys. Rev. Lett. 28, 1124 (1972).

[7]D. E. Beck, Phys. Rev. B 4, 1555 (1971).

[8]C. H. Heger and D. Wagner, Z. Phys. 244, 499 (1971).

[9]J. E. Inglesfeld and E. Wikborg, J. Phys. C 6, L158 (1973).

[10]J. Harris and A. Griffin, Phys. Lett. A 34, 51 (1971); Can. J. Phys. 48, 2592 (1970).

[11]L. Kleinman, Phys. Rev. B 7, 2258 (1973).

[12]J. Heinrichs, Phys. Rev. B 7, 3487 (1973).

[13]P. J. Feibelman, Phys. Rev. 176, 551 (1968).

[14]P. J. Feibelman, Phys. Rev. B 2, 220 (1970).

[15]P. J. Feibelman, Phys. Rev. B 2, 2974 (1970).

[16]P. J. Feibelman, Phys. Rev. Lett. 30, 975 (1973).

[17]P. J. Feibelman, Surf. Sci. 40, 102 (1973).

[18]P. J. Feibelman, C. B. Duke, and A. Bagchi, Phys. Rev. B 5, 2436 (1972).

[19]J. O. Porteus (private communication).

[20]By long-wavelength I mean long on an atomic scale but short compared to c/ω_p.

[21]R. H. Ritchie, Phys. Rev. 106, 874 (1957).

[22]That is, translationally invariant in two dimensions.

[23]"Sufficiently well-behaved barriers" are those which do not have a "zero-energy resonance," i.e., for which Eq. (2.3) has no solution for $\omega_k = -(\Phi + \epsilon_F)$ that decays asymptotically to zero as $z \to -\infty$ and which behaves no worse than as a constant as $z \to +\infty$. For such a potential, $\psi_k(z)$ is identically zero if $\kappa = 0$, and is an analytic function of κ at that point.

[24]This reduction will permit the approximate conversion of Eq. (2.31) to a *finite* matrix equation.

[25]For $\kappa^2 < 2m\omega$, $(\kappa^2 - 2m\omega)^{1/2}$ is taken to equal $-i(2m\omega - \kappa^2)^{1/2}$.

[26]C. Hastings, Jr., assisted by J. T. Hayward and J. P. Wong, Jr., *Approximations for Digital Computers* (Princeton U.P., Princeton, N.J., 1955).

[27]J. M. Blatt, J. Comp. Phys. 1, 382 (1967).

[28]M. Abramowitz and I. Steegun, *Handbook of Mathematical Functions* (Dover, New York, 1965), p. 886.

[29]Many of the results given in this section have already been reported briefly, in Refs. 16 and 17.

[30]N. D. Lang and W. Kohn, Phys. Rev. B 1, 4555 (1970); 3, 1215 (1971).

[31]The inclusion of the z^3 term in the exponential facilitates computation. By choosing $b = \frac{1}{125}$, I ensured that the value of b would have no effect on my results for α_1 and α_2.

[32]A. Bagchi, C. B. Duke, P. J. Feibelman, and J. O. Porteus, Phys. Rev. Lett. 27, 998 (1971); C. B. Duke and A. Bagchi, J. Vac. Sci. Tech. 9, 738 (1972).

[33]N. D. Lang, Phys. Rev. B 4, 4234 (1971).

[34]Such as steps, kinks, dislocations, etc.

[35]Otherwise one would have $\psi_{\kappa=0}(z) = \sin\delta_{\kappa=0}$, which violates the assumption that $\psi_{\kappa=0}(z)$ is identically zero.

[36]See, e.g., M. J. Lighthill, *Introduction to Fourier Analysis and Generalized Functions* (Cambridge U.P., Cambridge, England, 1962).

[37]In Ref. 16, it was incorrectly stated that $L = 8$ for $k_F^2 > 2m\omega$. I have verified that the oversight that led to this misstatement, namely, neglect of two values of k_l (cf. Table I), $(k_F^2 - 2m\omega)^{1/2} \pm k_F$, in fitting $\Delta_{q\omega}(z \to \infty)$ had no quantitative effect on the values of α_1 and α_2 reported in Refs. 16 and 17.

[38]If $f'(k_0) + g'(k_0) = 0$, the divergence of the 1 term at $\nu = 0$ is cancelled by that of the exponential term.

[39]Since the κ integrals of Eq. (B3) are from $\kappa = 0$ to $\kappa = k_F$ values of k_0 matter which are in the interval $(0, k_F]$.

[40]The proof does require that the apparent nonanalyticity of the integrand of Eq. (B48) at $\kappa = (2m\omega)^{1/2}$ not contribute; the fact that it does not follows from the analyticity of $G^{\pm}(z, z'; E)$ at $E = -\Phi - \epsilon_F$, or in other words from the assumption (cf. Ref. 23) that $V(z)$ has no zero-energy resonance.