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Optical Properties of an Electron Gas: Further Studies of a Nonlocal Description*

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Our previous studies of the optical properties of an electron gas for which the surface scattering is specular have been extended. It is argued that to treat the quantum-mechanical effects appearing at large wave vectors properly, the nonlocal dielectric functions which appear in the expressions for the surface impedance should be finite-electron-lifetime generalizations of the Lindhard dielectric functions rather than those resulting from the Boltzmann equation. The striking anomalous absorption, due to plasmon excitation, occurring above the plasma frequency is emphasized in the discussion of the semi-infinite gas. For the case of a slab, the thickness dependence of the processes characterizing the optical properties is discussed. Electron-gas parameters representing both K and Al were used in the calculations, as were both types of dielectric functions mentioned above. A comparison of the present theory with some alternative theories, particularly that of Melnyk and Harrison, is presented.

INTRODUCTION

IN a recent study[1] of the optical properties of a semi-infinite electron gas, we showed that the surface impedance[2] Z_p for p-polarized light, incident from vacuum at an angle θ from the surface normal, is

$$Z_p=\frac{2i\Omega}{\pi}\int_0^\infty \frac{dQ_z}{Q^2}\left(\frac{Q_x^2}{\Omega^2\epsilon_l(Q,\Omega)}+\frac{Q_z^2}{\Omega^2\epsilon_t(Q,\Omega)-Q^2}\right) \tag{1}$$

when the electrons scatter specularly at the surface. In terms of the light frequency ω and the plasma frequency[3] ω_p,

$$\Omega=\omega/\omega_p\,,\quad Q_x=\Omega\sin\theta\,,\quad Q^2=Q_x^2+Q_z^2\,, \tag{2}$$

and ϵ_l and ϵ_t are the nonlocal longitudinal and transverse dielectric functions for the electron gas. This study was based upon the Boltzmann equation, and thus the expressions for ϵ_l and ϵ_t which appeared in the surface impedance were those appropriate to the Boltzmann equation, or

$$\begin{aligned}\epsilon_l^{\mathrm{Bo}}(Q,\Omega)=1&-\frac{1}{\Omega(\Omega+i\gamma)}\left(-\frac{3i\Omega}{\gamma}\right)\frac{1}{(b'Q)^2}\\&\times\left(b'Q-\frac{1}{2i}\ln\frac{1+ib'Q}{1-ib'Q}\right)\bigg/\left(bQ-\frac{1}{2i}\ln\frac{1+ib'Q}{1-ib'Q}\right),\end{aligned} \tag{3}$$

and

$$\begin{aligned}\epsilon_t^{\mathrm{Bo}}(Q,\Omega)=1&-\frac{1}{\Omega(\Omega+i\gamma)}\,\frac{3}{2}\,\frac{1}{(b'Q)^3}\\&\times\left(\frac{(b'Q)^2+1}{2i}\ln\frac{1+ib'Q}{1-ib'Q}-b'Q\right),\end{aligned} \tag{4}$$

where, with τ the mean lifetime of an electron at the Fermi surface, v the Fermi velocity, and c the velocity of light,

$$\gamma=(\omega_p\tau)^{-1}\,, \tag{5a}$$

$$b=\gamma^{-1}v/c\,, \tag{5b}$$

and

$$b'=b/(1-i\Omega/\gamma)\,. \tag{5c}$$

The reflectance R_p when the incident light is p-polarized is[1]

$$R_p=\left|\frac{\cos\theta-Z_p}{\cos\theta+Z_p}\right|^2, \tag{6}$$

and the associated absorptance is

$$A_p=1-R_p\,. \tag{7}$$

That Eq. (1) contains the longitudinal dielectric constant is due to the presence of an electric field component normal to the surface when $\theta\neq 0$. This field component induces a charge imbalance in the metal to which the system responds as it would to any charge imbalance, namely, in a fashion describable in terms of the longitudinal dielectric function. The charge imbalance manifests itself in the theory both in the structure of Eq. (1) and in the expression for ϵ_l, Eq. (3). This latter requirement, that ϵ_l should reflect the charge imbalance, precludes making the simple relaxation time approximation when solving the Boltzmann equation.

Using Eqs. (1) and (6), we reported in Ref. 1 the p-polarized optical properties of an electron gas with parameters selected to represent potassium, over the frequency range $10^{-4}\leq\Omega\leq 1$. For low frequencies, $10^{-4}\lesssim\Omega\lesssim 10^{-2}$, these equations yield a description of the ordinary anomalous skin effect identical to that obtained by Reuter and Sondheimer.[4] However, for $10^{-2}\lesssim\Omega\lesssim 1$ and $\theta\neq 0$, there is an additional absorption peak centered at $\Omega\sim 0.4$, the presence of which is not contained in the equations of Reuter and Sondheimer. This additional absorption, physically a consequence

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[1] K. L. Kliewer and R. Fuchs, Phys. Rev. **172**, 607 (1968).

[2] The definition of the surface impedance used throughout this paper and our previous papers on this subject (Refs. 1 and 5) is the usual definition multiplied by $c/4\pi$ when Gaussian units are used. c is the velocity of light. This definition is used to avoid unnecessary repetition of factors $c/4\pi$.

[3] For particles of charge e, mass m, and density n, the plasma frequency is given by $\omega_p=(4\pi ne^2/m)^{1/2}$.

[4] G. E. H. Reuter and E. H. Sondheimer, Proc. Roy. Soc. (London) **A195**, 336 (1948).

of the presence of the electric field component normal to the surface, arises in the mathematics from the longitudinal dielectric constant. In particular, it results from the occurrence in Z_p of the energy-loss function $\mathrm{Im}(-1/\epsilon_l)$, where Im denotes the imaginary part.[5]

For s polarization, a semi-infinite gas, and specular scattering we found[1] for the surface impedance Z_s

$$Z_s=\frac{2i\Omega}{\pi}\int_0^{\infty}\frac{dQ_z}{\Omega^2\epsilon_t(Q,\Omega)-Q^2}, \tag{8}$$

which, together with the expression for the reflectance R_s

$$R_s=\left|\frac{1-Z_s\cos\theta}{1+Z_s\cos\theta}\right|^2, \tag{9}$$

describes the optical properties for s-polarized fields. Equations (8) and (9) yield the ordinary anomalous skin effect but contain no structure in the frequency range $\Omega\sim 0.1$.

Equations (1) and (8) have also been generalized[6] to the case of an electron gas confined to a slab of thickness a. In this case,

$$Z_p^{(1,2)}=\frac{2i\Omega}{W}\sum_{\substack{n=-\infty\\ (\text{odd, even})}}^{\infty}\frac{1}{Q^2}\left(\frac{Q_x^2}{\Omega^2\epsilon_l(Q,\Omega)}+\frac{Q_z^2}{\Omega^2\epsilon_t(Q,\Omega)-Q^2}\right) \tag{10}$$

and

$$Z_s^{(1,2)}=\frac{2i\Omega}{W}\sum_{\substack{n=-\infty\\ (\text{odd, even})}}^{\infty}\frac{1}{\Omega^2\epsilon_t(Q,\Omega)-Q^2}, \tag{11}$$

where

$$W=\omega_p a/c\,, \tag{12a}$$

$$Q_z=n\pi/W\,, \tag{12b}$$

and $Z^{(1)}(Z^{(2)})$ is obtained by summing over all odd (even) integers n. The transmittance, reflectance, and absorptance of a slab are given by[6]

$$T=\tfrac{1}{4}|P^{(1)}-P^{(2)}|^2, \tag{13}$$

$$R=\tfrac{1}{4}|P^{(1)}+P^{(2)}|^2, \tag{14}$$

and

$$A=1-R-T\,, \tag{15}$$

where for p polarization

$$P_p^{(1,2)}=(\cos\theta-Z_p^{(1,2)})/(\cos\theta+Z_p^{(1,2)})\,, \tag{16}$$

and for s polarization

$$P_s^{(1,2)}=(1-Z_s^{(1,2)}\cos\theta)/(1+Z_s^{(1,2)}\cos\theta)\,. \tag{17}$$

These equations were investigated in Ref. 6 using electron-gas parameters representing potassium and the Boltzmann dielectric functions. The results included (1) a thickness-dependent anomalous skin effect for both s and p polarization when $10^{-4}\lesssim\Omega\lesssim 10^{-2}$, (2) for p polarization, unique absorptance structure related to the shape of $\mathrm{Im}(-1/\epsilon_l)$ when $0.1\lesssim\Omega\lesssim 1$, and (3) again for p polarization, pronounced structure[7] when $\Omega>1$ resulting from a very sharp peak in $\mathrm{Im}(-1/\epsilon_l)$ occurring along the plasmon dispersion curve where $\mathrm{Re}(\epsilon_l)=0$, Re denoting the real part.

The usual classical results can be obtained from the foregoing by replacing $\epsilon_l(Q,\Omega)$ and $\epsilon_t(Q,\Omega)$ by their $Q\rightarrow 0$ limit

$$\lim_{Q\to 0}\epsilon_l(Q,\Omega)=\lim_{Q\to 0}\epsilon_t(Q,\Omega)=\epsilon_{cl}(\Omega)=1-1/\Omega(\Omega+i\gamma)\,. \tag{18}$$

In the classical limit we can then evaluate the integrals which appear in the expressions for the surface impedances in the case of the semi-infinite electron gas. The results are

$$Z_p^{\mathrm{cl}}=(\epsilon_{\mathrm{cl}}-\sin^2\theta)^{1/2}/\epsilon_{\mathrm{cl}} \tag{19}$$

and

$$Z_s^{\mathrm{cl}}=(\epsilon_{\mathrm{cl}}-\sin^2\theta)^{-1/2}. \tag{20}$$

In the present paper we extend our previous work in the following ways. In Sec. I we argue that the dielectric functions which should appear in Eqs. (1), (8), (10), and (11) are the finite-electron-lifetime generalizations of the self-consistent-field (SCF) dielectric functions first obtained by Lindhard.[8] For the semi-infinite metal, in Sec. II, we extend the frequency range of our previous study to demonstrate the markedly nonclassical behavior of the optical properties for p polarization and $1<\Omega<(\cos\theta)^{-1}$. A relatively extensive discussion of the thickness dependence of the optical properties of a slab is presented in Sec. III. Throughout, results obtained using both the generalized Lindhard and Boltzmann dielectric functions are contrasted. In addition, electron-gas parameters representing both potassium and aluminum are used in the calculations to illustrate the role of the Fermi velocity in the results. Finally, the relation between our theory and some alternative simplified theories for the p-polarized optical structure in the frequency range $\Omega>1$ is discussed in Sec. IV.

I. DIELECTRIC FUNCTIONS

As mentioned above, the dielectric functions (3) and (4) used previously in Eqs. (1), (8), (10), and (11) were those resulting from the Boltzmann equation. However, as is clear from the derivation given in Sec. III of Ref. 1, the form of the surface-impedance expressions

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[5] Significant absorptive effects manifest themselves through the real part of the surface impedance. Hence, in Eq. (1), the presence of the multiplicative i means that the physically most important part of the term of the integrand containing ϵ_l is the imaginary part. Since all else in this portion of the integrand is real, this means that the absorptance associated with the term containing the longitudinal dielectric function is described largely by $\mathrm{Im}(1/\epsilon_l)$.

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

[7] This high-frequency structure has also been noted by A. R. Melnyk and M. J. Harrison, Phys. Rev. Letters **21**, 85 (1968).

[8] J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. **28**, No. 8 (1954).

is not a consequence of a Boltzmann equation approach. That is, any legitimate pair of dielectric functions ϵ_l and ϵ_t can be used in place of the expressions (3) and (4) in the above equations for the surface impedances.

A quantum-mechanical analysis of the anomalous skin effect problem for a semi-infinite metal, specular electron scattering, and a normally incident electromagnetic field was given by Mattis and Dresselhaus.[9] They concluded that the surface impedance was the $\theta \rightarrow 0$ limit of Eq. (1) or (8)

$$Z_{\theta=0}=\frac{2i\Omega}{\pi}\int_0^\infty \frac{dQ_z}{\Omega^2\epsilon_t(Q_z,\Omega)-Q_z^2}, \tag{21}$$

where, in the limit that all important contributions to the integral arise from $Q_z \ll k_F c/\omega_p$ (k_F is the Fermi wave number), ϵ_t was given by Eq. (4). This is precisely the result of Reuter and Sondheimer for specular scattering. However, if Mattis and Dresselhaus had not assumed that $Q_z \ll k_F c/\omega_p$, then their expression for $Z_{\theta=0}$ would still have been of the form (21), but the expression for ϵ_t would have been different. In fact, the equations of Mattis and Dresselhaus yield for ϵ_t the finite-electron-lifetime generalization of the SCF transverse dielectric constant first obtained by Lindhard in the limit $\tau \rightarrow \infty$. Now the finite-lifetime version of the expression for ϵ_t given by Lindhard has been discussed and corrected recently by the present authors[10]; the results of Ref. 10 and the equations of Mattis and Dresselhaus both give

$$\epsilon_t^{\mathrm{SCF}}(Q,\Omega)=1-[\Omega(\Omega+i\gamma)]^{-1}f_t, \tag{22}$$

where

$$f_t=\tfrac{3}{8}(z^2+u'^2+1)-\frac{3}{32z}\left([1-(z-u')^2]^2\ln\frac{z-u'+1}{z-u'-1}+[1-(z+u')^2]^2\ln\frac{z+u'+1}{z+u'-1}\right), \tag{23}$$

with

$$z=Q\omega_p/2k_F c \tag{24a}$$

and

$$u'=\frac{\Omega+i\gamma}{Qv/c}. \tag{24b}$$

Hence for normal incidence and a semi-infinite metal, a generalization of Eq. (21) with ϵ_t given by Eq. (4) is Eq. (21) with ϵ_t given by Eq. (22). Indeed, wherever ϵ_t appears in the surface-impedance equations, Eq. (22) should in general be used.[11]

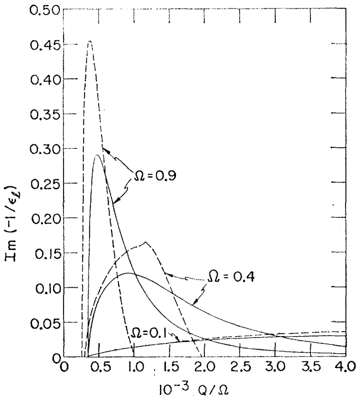

FIG. 1. Comparison of the energy-loss function $\mathrm{Im}(-1/\epsilon_l)$ calculated using the Boltzmann dielectric constant $\epsilon_l^{\mathrm{Bo}}(Q,\Omega)$ (solid lines) and the SCF dielectric constant $\epsilon_l^{\mathrm{SCF}}(Q,\Omega)$ (dashed lines), with parameters representing potassium.

When $\theta \neq 0$, the surface impedance for p-polarized fields involves the longitudinal dielectric function as well as the transverse. Based upon the above conclusion for normal incidence, an appropriate quantum-mechanical generalization of the Boltzmann equation results would be to replace ϵ_l^{Bo} by the SCF version of the longitudinal dielectric function valid for finite τ, or[12]

$$\epsilon_l^{\mathrm{SCF}}(Q,\Omega)=1+\frac{\epsilon_w-1}{1+i[Qb'-\tan^{-1}(Qb')]\gamma/Qb'\Omega}. \tag{25}$$

$\epsilon_w(Q,\Omega)$ is given by

$$\epsilon_w(Q,\Omega)=1+\frac{3(\Omega+i\gamma)}{Q^2(v/c)^2\Omega}f_l, \tag{26}$$

where

$$f_l=\frac{1}{2}+\frac{1}{8z}\left([1-(z-u')^2]\ln\frac{z-u'+1}{z-u'-1}+[1-(z+u')^2]\ln\frac{z+u'+1}{z+u'-1}\right) \tag{27}$$

and z and u' are given by Eqs. (24).

We conclude then that the quantum-mechanical expressions for the surface impedances when the electron surface scattering is specular involve the incorporation of the dielectric functions (22) and (25) into Eqs. (1), (8), (10), and (11). In discussing the results below, we shall refer to Eqs. (3) and (4) as Boltzmann dielectric

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[9] D. C. Mattis and G. Dresselhaus, Phys. Rev. **111**, 403 (1958); see Sec. IV.

[10] K. L. Kliewer and R. Fuchs, Phys. Rev. **181**, 552 (1969). The validity of the corrected version of $\epsilon_t(Q,\Omega)$ for τ finite is questionable for $Q \gtrsim k_F c/\omega_p$. However, as discussed in this reference, no physical effects are associated with ϵ_t for such large Q. See also Ref. 11.

[11] As a point of interest, the use of ϵ_t as given by Eq. (22) rather than ϵ_t as given by Eq. (4) in Eq. (21) makes no difference in the numerical value of the surface impedance, since all meaningful contributions to the integral in Eq. (21) arise when $Q \ll k_F c/\omega_p$, where Eqs. (4) and (22) are identical. The reason we are making the point here about the SCF dielectric functions is that in the case of the longitudinal dielectric function, to be discussed immediately below, the quantum-mechanical effects embodied in the SCF dielectric function yield results which differ significantly from the results obtained using the Boltzmann longitudinal dielectric function.

[12] That Eq. (25) is the appropriate finite-τ generalization of the Lindhard $\tau \rightarrow \infty$ expression is discussed in Ref. 10. The physical consequences of replacing Eq. (3) by Eq. (25) in the expressions for the surface impedance are discussed below.

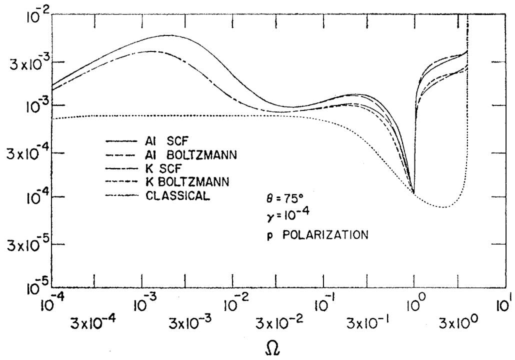

FIG. 2. Absorptance for p-polarized light incident at an angle of 75°, with $\gamma=10^{-4}$. Curves labelled Boltzmann have been calculated using the Boltzmann dielectric functions, whereas curves labeled SCF have been calculated using the SCF dielectric functions. The classical curve (for which there is no Fermi-velocity dependence) results from putting $\epsilon_l=\epsilon_t=\epsilon_{cl}$.

TABLE I. Electron-gas parameters for potassium and aluminum.

	K	Al
Fermi velocity (cm/sec)	0.85×10^{8} [a]	1.34×10^{8} [b]
Effective electron mass / Electron mass	1.0[c]	1.5[d]
Free-electron plasma frequency (rad/sec)	6.61×10^{15} [b]	1.93×10^{16} [d]

[a] Reference 14. [b] Reference 15. [c] Reference 16. [d] Reference 17.

constants, and to Eqs. (22) and (25) as SCF dielectric constants.

To what extent do we anticipate that the results using the SCF and Boltzmann dielectric functions will differ? As noted above in Ref. 10, all effects which appear as a consequence of the presence of the transverse dielectric function (such as the anomalous skin effect) will be unaffected by this change. However, differences will be seen in those effects associated with the appearance of the longitudinal dielectric constant, as is clear from the following. The Boltzmann longitudinal dielectric function ϵ_l^{Bo} is no longer valid when $Q\gtrsim k_Fc/\omega_p$, whereas the SCF longitudinal dielectric function is valid. This then means that the electron-hole pair excitation processes, which contribute significantly to $\mathrm{Im}(-1/\epsilon_l)$ for $Q\gtrsim k_Fc/\omega_p$, are not correctly described by ϵ_l^{Bo}. It is just such processes which give rise to the excess absorption in the frequency range $0.1\lesssim\Omega\lesssim1$. To illustrate this point, we have plotted in Fig. 1 $\mathrm{Im}(-1/\epsilon_l)$ for both the Boltzmann and SCF versions of ϵ_l, using parameters representing potassium (see Sec. II) with $\gamma=10^{-5}$ (a rather pure metal). The differences between the two are very evident for $\Omega\gtrsim0.4$ and these differences will manifest themselves in the optical properties. For $\Omega>1$, the optical structure for p polarization is influenced mainly by the form of the plasmon dispersion curve $\mathrm{Re}\,\epsilon_l=0$, where Re stands for the real part. Since the dispersion curves for the SCF and Boltzmann longitudinal dielectric functions differ for large Q, the optical properties in this frequency range will also reflect the difference.

Finally, we should comment on the extent to which the present surface-impedance equations, together with the SCF dielectric functions, really represent a quantum-mechanical description of the optical properties of a free-electron gas. In the derivations of Refs. 1, 6, and 10, the calculations are based upon electronic wave functions which are plane waves extending throughout all space. The fact that there is a surface (or surfaces in the case of a slab) present is taken into account by requiring the electromagnetic fields to satisfy certain symmetry conditions about a given plane (or planes in the case of a slab) in the infinite medium. These symmetry conditions give rise to a mathematical structure which does evince surface characteristics, but nonetheless the wave functions remain as plane waves.

Now we have argued above that to generalize the Boltzmann dielectric functions so as to treat large wave vectors properly, we must use the SCF dielectric functions. But it is precisely in the region of large wave

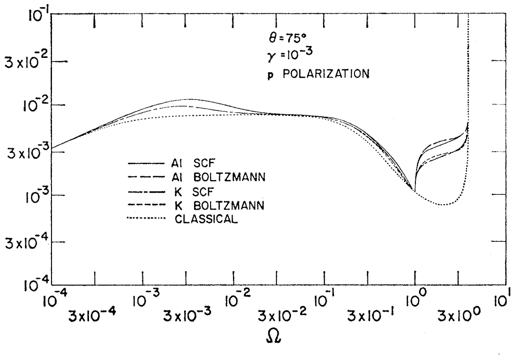

FIG. 3. Absorptance for p-polarized light incident at an angle of 75°, with $\gamma=10^{-3}$. Curves labelled Boltzmann have been calculated using the Boltzmann dielectric functions, whereas curves labeled SCF have been calculated using the SCF dielectric functions. The classical curve results from putting $\epsilon_l=\epsilon_t=\epsilon_{cl}$.

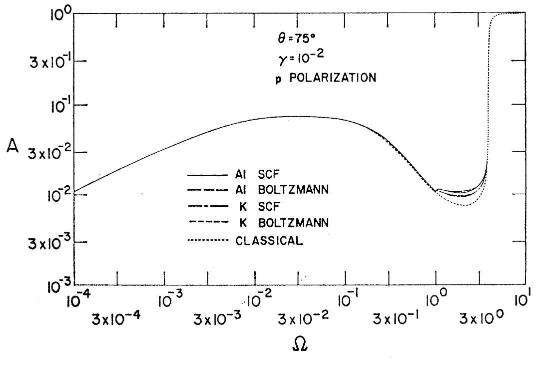

FIG. 4. Absorptance for p-polarized light incident at an angle of 75°, with $\gamma=10^{-2}$. Curves labelled Boltzmann have been calculated using the Boltzmann dielectric functions, whereas curves labeled SCF have been calculated using the SCF dielectric functions. The classical curve results from putting $\epsilon_l=\epsilon_t=\epsilon_{cl}$.

vectors that the condition which is ignored when using plane waves, namely, the condition that the wave functions be zero (or nearly so) at the surface, becomes important. That is, for distances within $\sim k_F^{-1}$ from the surface, where, in fact, much of the optical activity occurs at high frequencies, plane waves do not adequately represent the actual wave functions. Thus we must conclude that, although there is no question that the incorporation of the SCF dielectric functions does indeed represent an improvement in the theory, there remains a measure of doubt as to the validity of the results.[13]

II. SEMI-INFINITE GAS

To characterize the essentially free-electron properties of potassium and aluminum, we have utilized the parameters of Table I.[14–17]

Figures 2–4 show the absorptance for p-polarized light incident at an angle of 75°. Curves are given for both K and Al, using the Boltzmann as well as SCF dielectric functions. The values of γ selected for illustration range from 10^{-4} (pure metal) to 10^{-2} (impure metal). When $\Omega \lesssim 3\times10^{-2}$, the ordinary anomalous skin effect appears and its magnitude is seen to depend significantly upon the value of the Fermi velocity. If γ is as high as 10^{-2}, the excess absorption associated with the anomalous skin effect has faded into the background absorption, and a classical description in this frequency range is valid. It should be noted that in the region of the anomalous skin effect there is no meaningful difference between the results obtained using the Boltzmann and SCF dielectric functions. As discussed above, this indicates that the differences between the Boltzmann and SCF transverse dielectric functions are irrelevant in the present study.

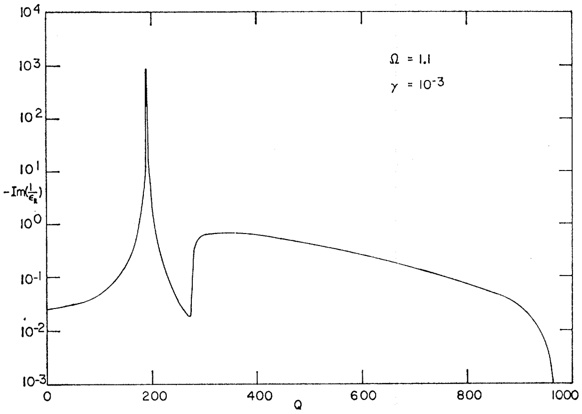

FIG. 5. Energy-loss function $\mathrm{Im}(-1/\epsilon_l)$ for potassium, using the SCF dielectric constant with $\Omega=1.1$ and $\gamma=10^{-3}$. The sharp peak is due to plasmon excitation and the broad structure is the result of single-particle excitations.

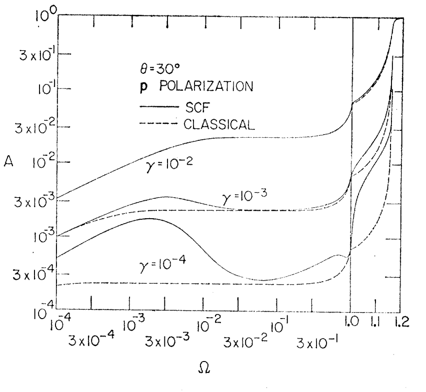

FIG. 6. Absorptance in aluminum for p-polarized light incident at an angle of 30°, with $\gamma=10^{-2}$, 10^{-3}, and 10^{-4}.

For $0.1 \lesssim \Omega < 1$, the absorptance increases significantly above the classical because of the structure in $\mathrm{Im}(-1/\epsilon_l)$ illustrated in Fig. 1. As suggested above, the absorptance is higher when the SCF version of ϵ_l is used than when the Boltzmann version of ϵ_l is used. We see also in this frequency range a rather pronounced dependence of the absorptance on the Fermi velocity.

When the value of Ω is in the range $1<\Omega<(\cos\theta)^{-1}$, Figs. 2–4 show a very dramatic deviation of the absorptance from the classical result, an effect noted previously by Forstmann.[18] This significant excess absorptance arises from a large peak in $\mathrm{Im}(-1/\epsilon_l)$ occurring when $\mathrm{Re}(\epsilon_l)=0$ and is, therefore, attributable to the excitation of plasmons. $\mathrm{Im}(-1/\epsilon_l)$ is shown in Fig. 5 for $\Omega>1$; the plasmon peak is apparent. The absorptance in this

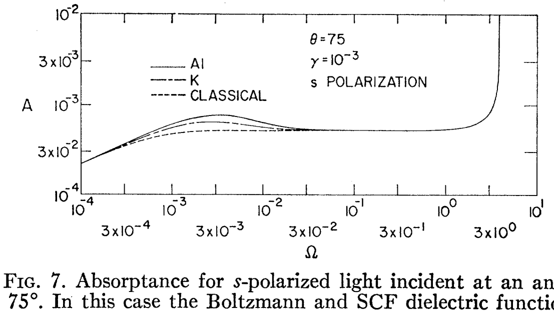

FIG. 7. Absorptance for s-polarized light incident at an angle of 75°. In this case the Boltzmann and SCF dielectric functions yield identical results.

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[13] Van Gelder has done a study in which sine functions were used for the wave functions rather than plane waves. See Phys. Letters **21**, 18 (1966).

[14] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1966), 3rd ed., p. 208.

[15] E. Fawcett, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960), p. 197.

[16] H. Mayer and B. Hietel, in *Optical Properties and Electronic Structure of Metals and Alloys*, edited by F. Abeles (North-Holland Publishing Co., Amsterdam, 1966), p. 47.

[17] H. Ehrenreich, H. R. Philipp, and B. Segall, Phys. Rev. **132**, 1918 (1963). It is indeed obvious that by using an effective electron mass which differs from the free-electron mass we are not considering Al as possessing strictly "free-electron" properties; rather, we are incorporating the effects of the band structure only insofar as they affect the optical mass of the electrons. This approximation is generally used in analyzing optical data in those regions of the spectrum for which the system evinces free-electron properties.

[18] F. Forstmann, Z. Physik **203**, 495 (1967).

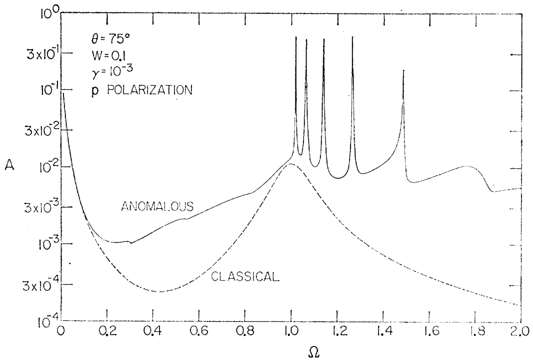

FIG. 8. Absorptance of a potassium film for *p*-polarized light incident at 75°. The film thickness is $W=0.1$ or $a=46$ Å. SCF dielectric functions have been used.

frequency range is seen to be dependent upon both the Fermi velocity and the dielectric constants employed. Since the most striking behavior occurs just at $\Omega=1$, optical measurements in this frequency range would permit an accurate determination of the plasma frequency.

The sharp absorptance increase as Ω passes through 1 has apparently been observed recently.[19] However, since the absorptance shape near $\Omega=1$ is so unique, the question arises as to why this structure has not been observed extensively. The answer is probably twofold: first, interband effects may tend to obscure this structure; second, measurements are usually not made at sufficiently large angles of incidence. This latter point is illustrated in Fig. 6, where the absorptance has been plotted for Al using the SCF dielectric functions and an incident angle of 30°. We see here that, although the deviation of the absorptance from the classical result is pronounced, excellent frequency resolution is necessary for the observation of the deviation because the absorptance is increasing so rapidly. [For $\theta=30°$, $(\cos\theta)^{-1}=1.15$.] Thus observations made with incident angles greater than about 45° are probably necessary to examine carefully the abrupt absorptance rise occurring when $\Omega=1$.

We illustrate the lackluster behavior of the absorptance for *s* polarization and an incident angle of 75° in Fig. 7. The anomalous skin effect is apparent in this figure, but for $\Omega\gtrsim4\times10^{-2}$ the absorptance is essentially classical. Results using the Boltzmann and SCF dielectric functions are the same, and since ϵ_l does not appear in the equations for *s* polarization, none of the unique effects associated with the presence of this function occur.

Finally, we would like to emphasize again, as we did in Ref. 1, that for frequencies $10^{-2}\lesssim\Omega<(\cos\theta)^{-1}$ the optical results cannot be analyzed in terms of a single frequency-dependent conductivity $\sigma_{\mathrm{cl}}(\omega)$. That is, whenever terms involving ϵ_l contribute significantly to the surface impedance for *p* polarization, the optical properties for both *s* and *p* polarization cannot be analyzed simultaneously in terms of a single frequency-dependent dielectric function $\epsilon_{\mathrm{cl}}(\omega)$ or a single frequency-dependent conductivity $\sigma_{\mathrm{cl}}(\omega)$. Rather, if such a concept is to be retained, separate expressions for $\epsilon_{\mathrm{cl}}(\omega)$ are needed in Eqs. (19) and (20) so that *s* and *p* polarization are described independently.

III. FINITE SLAB

Calculations of the optical properties of a film which were performed in Ref. 6 using Boltzmann dielectric functions have been extended using SCF dielectric functions. The parameters of Table I representing potassium were used to calculate the SCF dielectric functions [Eqs. (22) and (25)]; Eqs. (10)–(17) were then employed to find the absorptance, reflectance, and transmittance. Some of the results are shown in Figs. 8–11. The damping parameter $\gamma=10^{-3}$, the angle of incidence $\theta=75°$, and three values of the film thickness, $W=0.1$, 1.0, and 5.0, corresponding to $a=46$ Å, 460 Å, and 0.23 μ were chosen.

The sharp absorptance peaks in Fig. 8 and the corresponding reflectance anomalies in Fig. 9 which appear in the frequency range $1.0<\Omega\lesssim1.5$ are caused by the sharp maximum in $\mathrm{Im}(-1/\epsilon_l)$ associated with plasmon excitation (see Fig. 5). Sharp peaks appear neither in

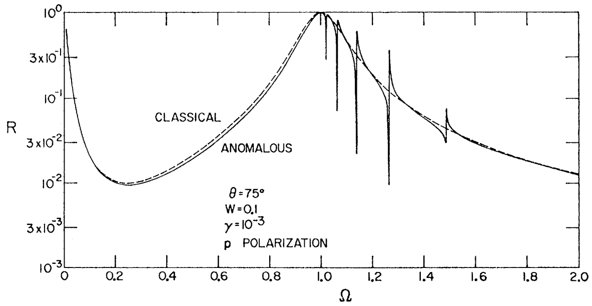

FIG. 9. Reflectance of a potassium film for *p*-polarized light incident at 75°. The film thickness is $W=0.1$ or $a=46$ Å. SCF dielectric functions have been used.

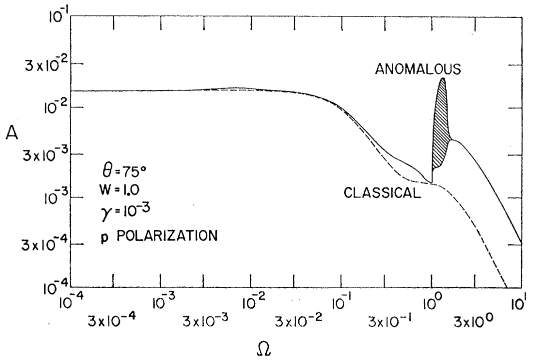

FIG. 10. Absorptance of a potassium film for *p*-polarized light incident at 75°. The film thickness is $W=1.0$ or $a=460$ Å. SCF dielectric functions have been used.

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[19] S. Yamaguchi, Bull. Am. Phys. Soc. 13, 983 (1968).

the absorptance nor in $\mathrm{Im}(-1/\epsilon_l)$ for $\Omega \gtrsim 1.5$, because in this frequency range the plasmon dispersion line has merged with the continuum of single-particle excitations, and the plasmon ceases to be a well-defined excitation. The plasmon dispersion curve and its merger with the single-particle excitation continuum is illustrated in Fig. 12. The disappearance of plasmon excitation at high frequencies is an important characteristic of the SCF longitudinal dielectric function. According to the Boltzmann dielectric function, the plasmon excitation does not merge with the single-particle excitations, and it was indeed found in the calculations using Boltzmann dielectric functions[6] that the sharp absorptance and reflectance structure persisted to much higher frequencies. This point indicates clearly the improvement in the physical content of the theory resulting from the incorporation of the SCF dielectric functions.

Absorptance structure in the frequency ranges $0.1 \lesssim \Omega < 1$ and $\Omega \gtrsim 1.5$, less pronounced than that due to plasmon excitation, is caused by the rather broad maximum in $\mathrm{Im}(-1/\epsilon_l)$ associated with single-particle excitations. The boundaries of the single-particle excitation region in the q-ω plane[20] are defined by the parabolas $\omega = vq \pm \hbar q^2/2m$. The sharp rise of $\mathrm{Im}(-1/\epsilon_l)$ as ω enters this region from above, with q fixed, is responsible for the shoulders on the high-frequency side of these broad absorptance maxima.

By comparing Fig. 8 with Fig. 1 of Ref. 6, we can see that the frequencies of corresponding absorptance peaks (for $\Omega > 1$) and shoulders (for $\Omega < 1$) are significantly raised when the Boltzmann dielectric functions are replaced by the SCF dielectric functions. This is again a consequence of the difference in excitation structure contained in the two types of longitudinal dielectric function. That is, for a fixed value of the wave vector, the frequencies of both the plasmon and the boundary of single-particle excitations are higher for the SCF dielectric function than for the Boltzmann dielectric function.

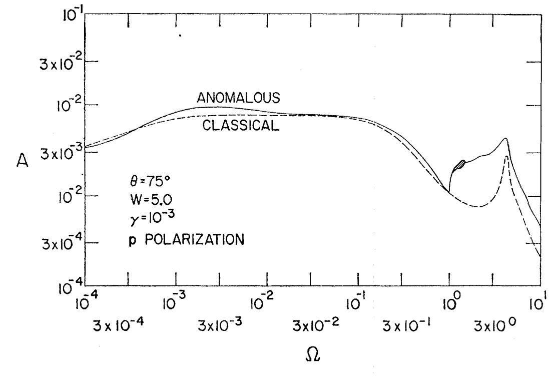

FIG. 11. Absorptance of a potassium film for p-polarized light incident at 75°. The film thickness is $W=5.0$ or $a=0.23\,\mu$. SCF dielectric functions have been used.

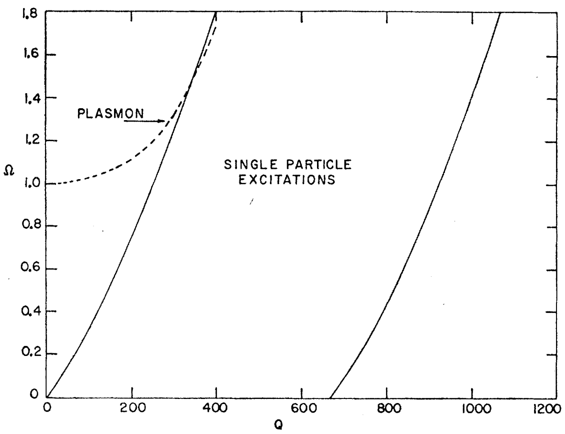

FIG. 12. Plasmon dispersion curve (dashed line) and single-particle excitation region, from the SCF longitudinal dielectric constant with parameters representing potassium.

The manner in which the structure in $\mathrm{Im}(-1/\epsilon_l)$ manifests itself in the optical properties has been discussed previously.[6] It was shown that the contributions to the absorptance arising from a given longitudinal excitation (plasmon or single-particle) appear in a thin film at $Q_z = n\pi/W$, where Q_z is the z component of the wave vector of the excitation, and $n = 1, 3, 5, \cdots$. This condition can be understood physically by considering the transfer of energy from the z component of the electric field in the film to the longitudinal excitation as the excitation is reflected back and forth between the two surfaces. The normal component of the phase velocity of the excitation is $v_z = \omega/q_z$, so that the excitation travels across the film in the time $t = aq_z/\omega$. The electric field inside the film can transfer energy to the excitation if the field goes through n half-periods of oscillation (where $n = 1, 3, 5, \cdots$) in the time t; that is, $n\pi/\omega = t = aq_z/\omega$, or $Q_z = n\pi/W$. Even integers $n = 2, 4, 6, \cdots$ are missing because in this case the energy transfer to an excitation while it traverses half the film thickness tends to cancel by symmetry the energy transfer while it traverses the remaining half.

For a thicker film ($W = 1.0$ or $a = 460$ Å) the absorptance is shown in Fig. 10. Oscillations of the absorptance in the frequency range $1.0 < \Omega \lesssim 1.5$ are so closely spaced that it is inconvenient to show individual peaks. The shaded area in this frequency range indicates the absorptance region encompassed by the oscillations. Structure in the absorptance is no longer visible in the frequency range $0.1 \lesssim \Omega < 1$, as it was for the thinnest film. The absorptance for a still thicker film ($W = 5.0$ or $a = 0.23\,\mu$) is shown in Fig. 11. Oscillations for $1.0 < \Omega \lesssim 1.5$ are still more closely spaced and have a smaller amplitude than in the thinner films. A comparison of Figs. 3 and 11 shows that there is little difference between the absorptance in a semi-infinite metal and in a film of thickness $W = 5$ for the frequency range $\Omega < (\cos\theta)^{-1} (= 3.86$ for $\theta = 75°)$. This occurs because the transmittance of the thick film for such fre-

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[20] q is the wave number.

quencies is negligible. For $\Omega > 3.86$, where the transmittance of the film increases rapidly, the absorptance reaches a maximum and then decreases rapidly with increasing frequency, whereas the absorptance of the semi-infinite metal increases monotonically toward 1.

Figures 8, 10, and 11 also show that the excess absorptance associated with the anomalous skin effect, which occurs for $\Omega \lesssim 10^{-2}$, depends upon the thickness of the film. When $W=0.1$, the anomalous skin effect is absent. As the film thickness increases, an absorptance peak first appears at a frequency near $\Omega \sim 10^{-2}$; the peak continues to grow, moves to a lower frequency, and is finally centered at $\Omega \sim 2\times10^{-3}$ for $W \gtrsim 5$. The foregoing behavior can be understood by noting that the anomalous skin effect occurs only when the film thickness a is much larger than the skin depth δ, or $a/\delta = 1.7(\Omega c/v)^{1/3}W \gg 1$.[21] If $\Omega=10^{-2}$, we find $a/\delta = 0.15$ for $W=0.1$, 1.5 for $W=1.0$, and 7.6 for $W=5.0$, which makes it plausible that the anomalous skin effect would occur at this frequency only for the thickest film, $W=5.0$. Since the ratio a/δ increases as Ω increases, with the film thickness held constant, it follows that for a film thickness such that the anomalous skin effect just begins to appear (e.g., $W=1.0$), the effect should be more pronounced at a higher frequency. This then explains why the frequency of the absorptance peak decreases as the film thickness increases from $W \simeq 1$ to $W \simeq 5$.

IV. RELATION OF PRESENT THEORY TO ALTERNATIVE THEORIES

In a semi-infinite metal, the most significant optical anomaly is the sudden increase in absorptance above the plasma frequency for p polarization, a consequence of plasmon excitation. Anomalies due to single-particle excitations are relatively less pronounced. It would therefore be of interest to have available simpler equations than those of the present theory for calculating approximately the contribution of plasmon excitation to the absorptance.

Several authors[18,22–25] have proposed theories of optical absorption in metals based on the approximation that plasmons are the only longitudinal excitations. Since such theories neglect single-particle excitations, they can be reasonable approximations only for frequencies in the range $1.0 < \Omega \lesssim 1.1$, where plasmons exist, are well-defined, and have wave vectors for which the effects of single-particle excitations are relatively unimportant (see Fig. 12). At frequencies $\Omega \gtrsim 1.1$, single-particle excitations begin to make a contribution to the optical properties significant compared with that due to plasmons.

We shall show that our general theory reduces to the theory of Melnyk and Harrison[24,25] when we make various approximations. We first neglect transverse nonlocal effects by replacing $\epsilon_t(Q,\Omega)$ by its classical limit $\epsilon_{\mathrm{cl}}(\Omega) = \lim_{Q\to0} \epsilon_t(Q,\Omega)$. This eliminates the anomalous skin effect from the theory. We also approximate the longitudinal dielectric function by

$$\epsilon_l \simeq 1 - \frac{1}{\Omega(\Omega+i\gamma)}\left(1+\frac{3}{5u'^2}\right), \qquad (28)$$

an expression valid for $|u'| \gg 1$ and $z \ll 1$ [see Eqs. (24a) and (24b)]. Single-particle excitations are thereby eliminated, so that the only nonlocal effect remaining is that associated with plasmon excitations.

The expression (1) for the surface impedance of a semi-infinite electron gas can be written

$$Z_p = Z_p{}^l + Z_p{}^t, \qquad (29)$$

where $Z_p{}^l$ and $Z_p{}^t$ are the two terms in Z_p containing ϵ_l and ϵ_t. Using the above approximations for ϵ_l and ϵ_t, we find

$$Z_p{}^l = \frac{i\sin\theta}{\epsilon_{\mathrm{cl}}} + \frac{\Omega\sin^2\theta}{\epsilon_{\mathrm{cl}}Q_a}, \qquad (30)$$

where

$$Q_a = (Q_0{}^2 - Q_x{}^2)^{1/2}, \qquad (31)$$

with

$$Q_0{}^2 = -\frac{5\,\Omega(\Omega+i\gamma)^3c^2}{3\,v^2}\epsilon_{\mathrm{cl}}. \qquad (32)$$

In addition, we have

$$Z_p{}^t = \frac{(\epsilon_{\mathrm{cl}} - \sin^2\theta)^{1/2}}{\epsilon_{\mathrm{cl}}} - \frac{i\sin\theta}{\epsilon_{\mathrm{cl}}}, \qquad (33)$$

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[21] We have used an expression for the skin depth valid in the extreme anomalous limit: $\delta = (c^2 l/3\pi\omega\beta\sigma)^{1/3}$, where l is the mean free path, σ is the dc conductivity, and $\beta = 6.9$. See G. Smith in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960), p. 185. We wish to point out that this expression for δ is appropriate for the purpose of assessing the nature of the anomalous skin effect in films of finite thickness. We are concerned only with the anomalous part of the absorptance, $A_{\mathrm{anom}} = A - A_{\mathrm{cl}}$, the excess of the total absorptance over the classical absorptance. First consider a semi-infinite medium. The anomalous absorptance is a consequence of the transfer of energy from the electric field to the electrons as they pass through the skin region. For frequencies $\Omega \lesssim 10^{-3}$, where A_{anom} is a monotonically increasing function of Ω, the "effective conductivity" theory of Pippard gives $A_{\mathrm{anom}} \sim 2\omega\delta/c \propto \omega^{2/3}$. Since δ is independent of the electron lifetime τ, A_{anom} is also independent of τ, a result which our exact calculations indicate to be approximately true. At frequencies high enough that the field goes through many oscillations during the time required for an electron to traverse the skin depth ($\omega \gg v/\delta$), the transfer of energy from the field to the electrons becomes inefficient, so that $A_{\mathrm{anom}} < 2\omega\delta/c$. Thus, as shown by the absorptivity curves, A_{anom} decreases essentially to zero as Ω increases from 3×10^{-3} to about 3×10^{-2}. Because of the relationship between A_{anom} and δ for a semi-infinite crystal, it is clear that, for a slab, A_{anom} will be essentially the semi-infinite crystal result if the slab thickness a is greater than δ, but will be reduced if a is less than δ.

[22] A. M. Fedorchenko, Zh. Tekhn. Fiz. **32**, 589 (1962) [English transl.: Soviet Phys.—Tech. Phys. **7**, 428 (1962)].

[23] A. M. Fedorchenko, Zh. Tekhn. Fiz. **36**, 1327 (1966) [English transl.: Soviet Phys.—Tech. Phys. **11**, 992 (1967)].

[24] A. R. Melnyk, Ph.D. thesis, Michigan State University, 1967 (unpublished).

[25] A. R. Melnyk and M. J. Harrison, Phys. Rev. Letters **21**, 85 (1968).

so that

$$Z_p = \frac{(\epsilon_{c1} - \sin^2\theta)^{1/2}}{\epsilon_{c1}} + \frac{\Omega \sin^2\theta}{\epsilon_{c1} Q_a} . \qquad (34)$$

The contribution of plasmon excitations to Z_p is contained entirely in the second term of Eq. (34). Note that Eq. (32) is the plasmon dispersion relation, since Q_0 is the complex wave vector satisfying $\epsilon_l(Q_0, \Omega) = 0$.

Going over to the notation of Melnyk and Harrison, we can write $(\epsilon_{c1} - \sin^2\theta)^{1/2} = \beta$, $\epsilon_{c1} \cos\theta = \alpha$, and $\Omega \sin^2\theta / \epsilon_{c1} Q_a = \gamma' / \epsilon_{c1}$,[26] so that Eqs. (34) and (6) give

$$R_p = \left| \frac{\alpha - \beta - \gamma'}{\alpha + \beta + \gamma'} \right|^2 ,$$

a result identical in form to that of Melnyk [Eq. (II.23) of Ref. 24].

Approximate equations for the optical properties of a slab when $\Omega \gtrsim 1$ can be obtained similarly by using the foregoing approximations for ϵ_t and ϵ_l in Eq. (10). The sums in Eq. (10) can then be evaluated, and the result is

$$Z_p^{(1)} \simeq -i(\beta/\epsilon_{c1}) \tan(\tfrac{1}{2}\beta W \Omega) - i(\gamma'/\epsilon_{c1}) \tan(\tfrac{1}{2} Q_0 W) \qquad (35a)$$

and

$$Z_p^{(2)} \simeq i(\beta/\epsilon_{c1}) \cot(\tfrac{1}{2}\beta W \Omega) + i(\gamma'/\epsilon_{c1}) \cot(\tfrac{1}{2} Q_0 W) . \qquad (35b)$$

Again using the notation of Melnyk and Harrison, we have $\beta W \Omega = \psi_T$ and $Q_0 W = \psi_L$. It can then be shown that the expressions for the transmittance, reflectance, and absorptance given by Eqs. (35) and Eqs. (13)–(17) are, aside from the unimportant differences in the two forms of γ' noted above, identical to Eqs. (3) of Ref. 25. The limited frequency range over which these approximate expressions are valid should be kept in mind.

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[26] We write γ' here to avoid confusion with the γ defined by Eq. (5a). In our notation, Melnyk and Harrison[24,25] give $\gamma'/\epsilon_{c1} = \Omega \sin^2\theta (1 - \epsilon_{c1}) / (\epsilon_{c1} Q_a)$, which differs from our expression by the factor $(1 - \epsilon_{c1}) = [\Omega(\Omega + i\gamma)]^{-1}$. This difference is however academic since (1) the theory of Melnyk and Harrison is quantitatively questionable for $\Omega \gtrsim 1.1$, and (2) the approximation (28), which contains the plasmon dispersion relation (32), becomes inaccurate if $\Omega \gtrsim 1.1$ and $|Q_0| \gtrsim 200$, where the conditions $|u'| \gg 1$ and $z \ll 1$ are not satisfied.

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Comparison of Dielectric Screening Methods Used in Phonon-Frequency Calculation of Normal Metals

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The various prevalent forms of the dielectric screening function relevant to a calculation of phonon frequencies of a normal metal are critically studied. Detailed calculations for sodium are carried out to investigate the variation of phonon frequencies with several dielectric screening functions. Each of these dielectric functions is used in conjunction with two forms of the electron-ion matrix element: (a) the single-OPW (orthogonalized-plane-wave) electron-ion matrix element of Vosko *et al.* and (b) Bardeen's electron-ion matrix element. When we use the single-OPW electron-ion matrix element, a systematic trend is manifest in the variation of $G(p)$ functions and phonon frequencies with the use of different dielectric functions, while no such trends are revealed if we adopt Bardeen's form of the electron-ion matrix element. It is observed that the dielectric function of Singwi ***et al.*** combined with the single-OPW electron-ion matrix element yields the best agreement with experimental phonon frequencies.

I. INTRODUCTION

A FIRST-PRINCIPLES calculation of phonon frequencies of metals hinges on a treatment of the polarizability of conduction electrons and an evaluation of the electron-ion matrix element (which we shall abbreviate as EIME). In recent years, much effort has been directed towards the understanding of both aspects of the problem. In this paper, we compare the various methods of incorporating the polarizability of electrons in calculations of lattice-vibrational frequencies of metals.

In the harmonic approximation, the angular frequencies ω of lattice vibrations of a monatomic metal are obtained from the solution of the determinantal equation

$$\det |D_{xy}(\mathbf{q}) - M\omega^2 \delta_{xy}| = 0 . \qquad (1)$$

Here, $D_{xy}(\mathbf{q})$ are the elements of the dynamical matrix, M is the mass of the ion, and $\mathbf{q}$ the phonon wave vector. The dynamical matrix is expressible as the sum of three terms:

$$D_{xy}(\mathbf{q}) = D_{xy}^{(C)}(\mathbf{q}) + D_{xy}^{(R)}(\mathbf{q}) + D_{xy}^{(E)}(\mathbf{q}) . \qquad (2)$$

The three terms on the right-hand side are contributions from three types of interactions between the ions in a metal. $D_{xy}^{(C)}(\mathbf{q})$ originates from the bare Coulomb interaction between ions, $D_{xy}^{(R)}(\mathbf{q})$ is the contribution from the exchange-overlap potential between the ions in the metal, and $D_{xy}^{(E)}(\mathbf{q})$ stems from an ion-electron-