Dielectric Response of a Semi-Infinite Degenerate Electron Gas*†

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The dielectric response at frequency ω (neglecting retardation) of an idealized metal with two plane parallel surfaces is calculated in the Hartree approximation, with special emphasis on the limit of infinite thickness. It is assumed that the unperturbed system may be regarded as consisting of free particles confined between plane parallel boundaries. The validity of this approximation is discussed. The response is expressed in terms of the perturbing source potential in Fourier representation, and involves the inverse of an infinite matrix $\mathbf{E}$; $\mathbf{E}$ is calculated in the limit of infinite interfacial separation at $\omega=0$ and at $\omega\neq 0$ for one-dimensional potentials. A dielectric function $\epsilon_{\mathbf{Q}}(\omega)$, where $\mathbf{Q}$ is a wave vector parallel to the surface, is introduced, which is inversely proportional to the sum of all elements in $\mathbf{E}^{-1}$. The surface-plasmon dispersion relation is given implicitly by $\epsilon_{\mathbf{Q}}(\omega)+1=0$. The classical image theorem for a semi-infinite dielectric medium is obeyed at a given $\mathbf{Q}$ and ω if $\epsilon_{\mathbf{Q}}(\omega)$ replaces the classical dielectric constant. The Fermi-Thomas approximation, the lowest-order correction to it, and the classical (high-frequency) approximation are derived. In agreement with earlier work, the corrections to the classical approximation, which relate to the damping and dispersion of surface plasmons, are found to be linear in the wave vector. Numerical results are obtained for a uniform static electric field normal to the surface. The calculated screening length d is well approximated by $d\simeq\lambda^{-1}+\frac{1}{8}\lambda_F$, where λ^{-1} is the Fermi-Thomas screening length and λ_F the Fermi wavelength, the second term representing the lowest quantum correction; this result is 2–3 times λ^{-1} in the metallic density range, owing almost entirely to the low electron density in the surface region. The results are compared with experiment. The long-range Friedel oscillations are discussed in an appendix.

I. INTRODUCTION

THE dielectric response of a metal surface to some perturbing potential, which may be time dependent, plays an important role in a number of surface phenomena. Thus the interaction energy between an ion a short distance outside the surface and the induced charged density contributes to the energy of ionic and polar chemisorption,[1] and enters the energetics of field evaporation,[2] and desorption.[3,4] The adsorbate ions and their induced charge constitute a dipole layer which produces a change in work function.[1,5] The dielectric response of the metal surface is fundamental to the weaker interaction of physical adsorption,[6] and in addition this response should be included in treatments of the rather complex problem of covalent chemisorption.[7,8] Essentially macroscopic theories of optical reflectivity[9] and surface plasmon excitation[10,11] are usually valid under normal long-wavelength conditions, but we shall find that microscopic characteristics enter into the Landau damping of surface plasmons. We shall here restrict ourselves to the linear dielectric response, although nonlinear effects may play a subsidiary role in some of the problems mentioned above.

The random phase approximation (RPA)[12] provides a quite successful model of the linear bulk dielectric response of a simple metal, in which scattering by the ion cores may be neglected. The metal may then be replaced by a "jellium" model in which the cores are spread out into a uniform distribution of positive charge. The RPA dielectric function may also be derived from the time-dependent Hartree approximation,[13] and it is this formulation which we shall employ; the success of static Hartree theory in treating nonuniform systems such as atoms suggests the applicability of this approach to the present problem. The jellium approximation will also be invoked, so that translational symmetry is retained in directions parallel to the surface. The equivalent of the unperturbed plane-wave eigenstates which form the starting point for treating the bulk electron gas will now be the set of one-particle eigenstates belonging to the effective one-electron Hamiltonian of the semi-infinite metal. This Hamiltonian includes the appropriately defined self-consistent potential at the idealized jellium surface.

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[8] D. M. Edwards and D. M. Newns, Phys. Letters **24A**, 236 (1967); Phys. Rev. **178**, 1123 (1969).

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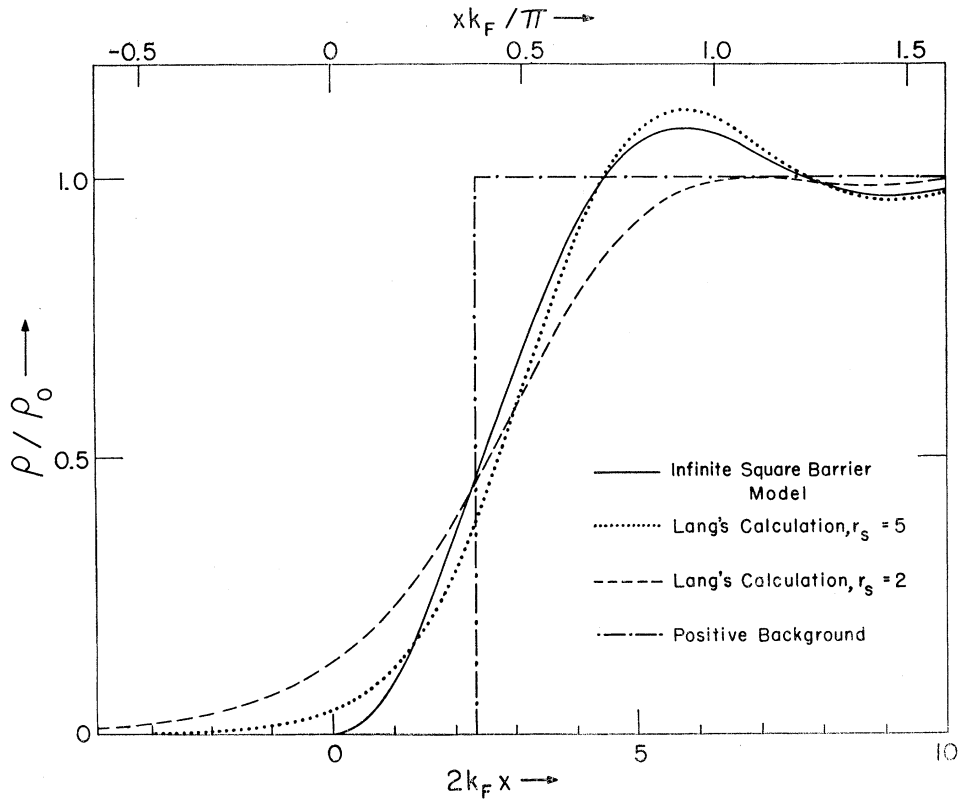

FIG. 1. Charge density of electron gas at metal surface. Solid line refers to infinite square barrier in region $x<0$, assuming free electrons, and remaining curves to self-consistent calculations of Lang (see text for details). ρ_0 is density in interior of metal. Unit π/k_F equals one half-Fermi wavelength.

We shall, in the following, adopt the simplest approximation to the unperturbed wave functions in assuming the potential to form an infinite square barrier at the surface. If the surface is formed by the $x=0$ plane, we take $V(x)=\infty$ for $x<0$ and $V(x)=0$ for $x>0$. The eigenstates now take the well-known form $\psi(\mathbf{x}) \propto \exp[i(k_y y+k_z z)] \sin k_x x$, and the unperturbed charge density is easily shown to be[14,15]

$$\rho(x')=\rho_0[1+3\cos x'/x'^2-3\sin x'/x'^3], \qquad (1)$$

where

$$x'=2k_F x,$$

k_F is the Fermi wave vector $k_F=(3\pi^2 n_0)^{1/3}$, and $n_0=\rho_0/e$ is the electron density in the interior of the metal. Equation (1) is illustrated by the full curve in Fig. 1, from which it is evident that the charge density deviates significantly from its bulk value only within a distance of about $\frac{1}{2}$-Fermi wavelength from the surface.

In fact a more realistic representation of the electron distribution at the surface of a simple metal is provided by the semi-infinite jellium model, in which the positive charge distribution is taken as a step function at the surface. The electronic wave functions and the self-consistent potential may in this case be obtained from the solution of the Hartree-Fock equations, with some allowance for correlation, as approximately carried out by Bardeen.[15] Recent calculations include those of Bennett and Duke,[16] Smith[17] (employing a semiclassical method), and Lang.[18] Now it was shown by Bardeen[15] that on addition of the step-function charge distribution

$$\rho_+(x)=-\rho_0, \quad x>3\pi/8k_F$$
$$=0, \quad x<3\pi/8k_F$$

to Eq. (1), the resulting distribution satisfies the requirement of charge neutrality in the interior of the metal, a result readily derived from the phase-shift sum rule of Sugiyama.[19] Hence it is appropriate to compare the charge distribution (1) with self-consistent calculations made from the semi-infinite jellium model provided the step-function jellium distribution is taken as lying in the region $x>3\pi/8k_F$. Such a comparison with the calculations of Lang[18] is shown in Fig. 1. The charge distribution at $r_s=5$ is similar to that of

[14] R. Berg and L. Wilets, Proc. Phys. Soc. (London) A68, 229 (1955).
[15] J. Bardeen, Phys. Rev. 49, 653 (1936).
[16] A. J. Bennett and C. B. Duke, Phys. Rev. 160, 541 (1967); A. J. Bennett (private communication).
[17] J. R. Smith, Phys. Rev. 181, 522 (1969).
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Eq. (1) except for the presence of a tail at $x<0$, a conclusion also arrived at by Bardeen in his work at $r_s=4$. At $r_s=2$ the distribution is in much poorer agreement with the infinite barrier model. It may be argued that the behavior of the wave functions should resemble that of the charge distributions. If the surface potential barrier sufficiently exceeds the Fermi energy, then at large enough x for the potential to be negligible the wave functions will take the form

$$\psi(x) \propto \exp[i(k_y y+k_z z)] \sin k_x(x+a),$$

where the scattering length a is approximately independent of k_x. The requirement of charge neutrality demands that $a\simeq 0$ so that in the region where $V(x)\simeq 0$ (i.e., for $x\gtrsim 3\pi/8k_F$ at $r_s=5$) [18] the wave functions will be similar to those in the infinite barrier model. Continuity will ensure that this similarity remains for some distance into the barrier, though breaking down in the tail region. Since the high barrier limit seems to be approached in Lang's $r_s=5$ calculation, the infinite square barrier model should represent a fair approximation to semi-infinite jellium at $r_s=4$–5 if the contribution to the dielectric response from the tail region is small; the latter will in any case be subject to modification in the presence of adsorbed atoms. It should however be noted that the validity of the RPA is itself questionable in this density region. At $r_s\sim 2$ the infinite barrier model may represent a poor approximation to semi-infinite jellium, and the applicability of semiclassical methods[17] here might be worth investigating.

It is worth discussing qualitatively the main effects distinguishing the response of the semi-infinite gas from the bulk response. The first stage in the Hartree calculation is the determination of the one-particle response, in which the Coulomb interactions between the electrons are neglected. It is desired to find the change in charge density $\delta\rho(\mathbf{x})$ due to a small perturbing potential $V(\mathbf{x})$. The one-particle response to a static and spatially homogeneous potential V may be obtained by differentiating (1) with respect to the Fermi level, the result being

$$\delta\rho(x)=\frac{Vk_F}{\pi^2 r_B}\left(1-\frac{\sin x'}{x'}\right), \qquad (2)$$

where r_B is the Bohr radius. Equation (2) is plotted as the dotted curve in Fig. 3, in which the response $\delta\rho$ is seen to deviate markedly from spatial homogeneity near the surface, where it necessarily satisfies the condition $\delta\rho=0$. If we express $V(\mathbf{x})$ and $\delta\rho(\mathbf{x})$ in terms of their Fourier components $V_\mathbf{q}$ and $\delta\rho_\mathbf{q}$, then we may say that the single component V_0 of potential gives rise to a range of charge density components $\delta\rho_\mathbf{q}$. Conservation of momentum $\mathbf{q}$ equally fails for other components $V_\mathbf{q}$ of potential. This is in contrast with the case of the homogeneous electron gas, where conservation of momentum greatly simplifies the treatment; in particular, it is possible to define a response function $R_\mathbf{q}=\delta\rho_\mathbf{q}/V_\mathbf{q}$. In the present case the response function must unavoidably be generalized to a response matrix.

Once the relation between $\delta\rho(\mathbf{x})$ and $V(\mathbf{x})$ is known, it becomes necessary, in order to achieve self-consistency, to calculate the electrostatic potential of the charge density $\delta\rho$. The consequent introduction of electrostatic boundary conditions at the surface of the system constitutes the second modification to the problem of the homogeneous electron gas. An important and well-known physical consequence of the boundary conditions, which introduce the vacuum half-space into the problem, is that a static exterior charge is not screened in directions parallel to the surface. As is intuitively reasonable, the Fermi-Thomas[20,21] approximation is found below to be valid at sufficiently high electron densities; this approximation correctly includes the boundary conditions just mentioned, while neglecting nondiagonality of the response matrix. It is shown below that the nondiagonal elements are responsible for the lowest order correction to the Fermi-Thomas approximation, which arises from the requirement that the charge density be zero at the surface.

A number of papers treating the dielectric response of the semi-infinite electron gas are available,[20–27] excluding purely classical calculations, references to which may be found in Ref. 27. The work of Fedders[22] on the infinite square barrier model is based on the equation of motion for the two-particle Green's function within the RPA, from which a complicated integral equation for the response functions is at length derived; on putting the coulomb interaction equal to zero a free-electron response matrix is obtained which is essentially identical to that calculated below. Fedders finds the dispersion and damping corrections to the classical surface plasmon frequency to be linear in wave vector, a result also obtained by Guernsey[25] for a semi-infinite classical plasma, although the coefficients of these corrections are not calculated. Ritchie and Marusak[27] had earlier determined both the linear behavior and the coefficients by neglecting the nondiagonal elements of the response matrix, but the justification for this approximation is not very clear. The work of Gerlach[20] and Gadzuk[23] on the infinite barrier model is in some respects closer to the self-consistent field approach discussed below. Gerlach[20] however significantly departs from the methods of Fedders, Gadzuk, and the present author in choosing sine rather than cosine Fourier transforms, a choice

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which permits scattering out of the discrete set of allowed momenta normal to the surface (assuming slab geometry). Gerlach concludes that the Lindhard dielectric function may still be employed at the surface, a result in disagreement with the present work; in particular we find that the major contributions both to the screening length and the amplitude of the one-dimensional Friedel oscillations derives from the nondiagonal rather than the diagonal or Lindhard part of the response matrix. The neglect of nondiagonality is also a defect in the treatment of Gadzuk,[23] in addition to which the imaging theorem employed by this author in solving the self-consistency problem would appear to be correct only for one-dimensional potentials. Feibelman[24] gives a quantum derivation of what is essentially the time Fourier transform of Laplace's equation for a nonuniform dielectric, the local dielectric function being $\epsilon=1-\omega_p^2/\omega^2$, where the plasma frequency ω_p depends on the local electron density n_0 via $\omega_p^2=4\pi n_0 e^2/m$. The validity of this is presumably confined to density variations of longer wavelength than that of the plasmon—a serious limitation. Feibelman then goes on to develop an interesting perturbation treatment of Landau damping, the coefficient of the linear variation of damping with wave vector being calculated. The corresponding coefficient of dispersion is however found to be zero. In comparing this with other work, Feibelman's assumption of a step-function electron density distribution at the surface should be borne in mind.

The present paper begins by recalculating Fedder's free-electron-response matrix by a related method, though making an initial separation of the potential into symmetric and antisymmetric parts. The matrix is then calculated in special cases (Sec. II and Appendix A). The self-consistency problem is formally solved in Sec. III, by a straightforward application of the differential equations of electrostatics rather than Fedder's difficult integral-equation approach. The results appear in a form simply related to the classical electrostatics of a semi-infinite dielectric. Explicit calculation requires inversion of a matrix trivially related to the one-electron-response matrix, this being simplest in the static case when the matrix is real. Two limiting cases are discussed in Sec. IV A and IV B, and a one-dimensional static calculation is carried out numerically in Sec. IV C. A suggestion is also made concerning the calculation of corrections to the classical (high-frequency) limiting formula; we are in agreement with Fedders in finding these to be linear in wave number. The results are discussed, and compared with the rather limited experimental data, in Sec. V.

II. INDEPENDENT PARTICLE RESPONSE

We begin by calculating the linear response of the system to a perturbing potential $V(\mathbf{x},t)$ in the Hamiltonian, assuming the electrons to be noninteracting, and subsequently impose the Hartree self-consistency requirement. Let the change in electron density of the noninteracting system be $\delta n(\mathbf{x},t)$. The self-consistency condition is then

$$U(\mathbf{x},t)+\varphi(\mathbf{x},t)=V(\mathbf{x},t), \tag{3}$$

where φ is the potential due to the charge density $\delta\rho=e\delta n$, and U the source potential which may be assumed to arise from some external source charge distribution.

The response $\delta\rho$ may be obtained from the expression[28]

$$\delta\rho(\mathbf{x},t)=\int_0^t dt' \int d^3x' R(\mathbf{x},t,\mathbf{x}',t')V(\mathbf{x}',t') \tag{4}$$

where (employing $\hbar=1$ units) the response function R is defined by

$$R(\mathbf{x},t,\mathbf{x}',t')=ie^2\sum_{\sigma,\sigma'}\langle\phi_0|[\rho_\sigma(\mathbf{x}',t'),\rho_{\sigma'}(\mathbf{x},t)]|\phi_0\rangle, \tag{5}$$

$$\rho_\sigma(\mathbf{x},t)=\sum_{i,j}C_{i\sigma}^\dagger(t)C_{j\sigma}(t)\varphi_i^*(\mathbf{x})\varphi_j(\mathbf{x}). \tag{6}$$

The perturbation is assumed to be switched on at $t=0$. The density operator ρ_σ for spin σ is defined in terms of the creation and destruction operators $C_{i\sigma}^\dagger$, $C_{i\sigma}$ corresponding to the one-particle wave functions $\varphi_i(\mathbf{x})$ of the unperturbed system, these operators being all in the interaction representation. $|\phi_0\rangle$ is the time-independent Heisenberg ground state of the unperturbed system.

In the absence of the interparticle interactions

$$C_{i\sigma}(t)=e^{-i\omega_i t}C_{i\sigma}, \tag{7}$$

where $\hbar\omega_i=\epsilon_i$ is the energy eigenvalue of φ_i. The time dependence may then be factored out of the commutator in (5). Now

$$\langle\phi_0|[C_{i\sigma}^\dagger C_{j\sigma},C_{k\sigma}^\dagger C_{l\sigma}]|\phi_0\rangle=[f(i)-f(j)]\delta_{il}\delta_{jk}\delta_{\sigma\sigma'}, \tag{8}$$

where, assuming $T=0$,

$$f(i)=1, \quad \epsilon_i<\epsilon_F$$
$$=0, \quad \epsilon_i>\epsilon_F.$$

From (4), (7), and (8),

$$R(\mathbf{x},\mathbf{x}',t-t')=2ie^2\sum_{ij}[f(i)-f(j)]e^{i(w_i-w_j)(t'-t)}\times\varphi_i^*(\mathbf{x}')\varphi_j(\mathbf{x}')\varphi_j^*(\mathbf{x})\varphi_i(\mathbf{x}). \tag{9}$$

The Fourier transform of a function $f(\tau)$ of time is defined as

$$f(\omega)=\int_0^\infty e^{iw\tau}f(\tau)d\tau. \tag{10}$$

Hence, in Fourier representation

$$\delta\rho(\mathbf{x},\omega)=\int d^3x'\, R(\mathbf{x},\mathbf{x}',\omega)V(\mathbf{x}',\omega), \tag{11}$$

$$R(\mathbf{x},\mathbf{x}',\omega)=2e^2\sum_{ij}\frac{f(i)-f(j)}{\omega_j-\omega_i+\omega-i\alpha}\times\varphi_i^*(\mathbf{x}')\varphi_j(\mathbf{x}')\varphi_j^*(\mathbf{x})\varphi_i(\mathbf{x}), \tag{12}$$

[28] R. Kubo, J. Phys. Soc. Japan 12, 570 (1957).

where α is an infinitesimal positive constant. Equations (11) and (12) give the linear response of any large system of noninteracting fermions.

Let the physical surfaces of the electron gas form the planes $x=0$ and $x=l$ of a Cartesian coordinate system. The potential will be assumed zero within the metal and infinite outside it,

$$\begin{aligned} V(x)&=0, \quad 0<x<l \\ &=\infty, \quad x<0, x>l. \end{aligned} \tag{13}$$

The remaining boundaries are taken to be the planes $y=\pm L$, $z=\pm L$, at which the boundary conditions are assumed periodic. The normalized eigenfunctions are

$$\begin{aligned} |\mathbf{K},k\rangle &= (2L^3)^{-1/2} e^{i\mathbf{K}\cdot\mathbf{x}} \sin kx, \\ k_i &= (m_i\pi/l), \quad m_i=1,2,3,\ldots, \quad i=x \\ &= (m_i\pi/L), \quad m_i=0,\pm1,\pm2,\ldots, \quad i=y,z \\ \langle \mathbf{K},k|\mathbf{K}'k'\rangle &= \delta_{\mathbf{K}\mathbf{K}'}\delta_{kk'}. \end{aligned} \tag{14}$$

We here adopt the convention

$$\begin{aligned} \mathbf{K} &\equiv (k_y,k_z), \\ k &\equiv k_x, \\ \mathbf{X} &\equiv (y,z), \end{aligned} \tag{15}$$

so that $\mathbf{k}\equiv(k_x,k_y,k_z)=(\mathbf{K},k)$, and $\mathbf{x}\equiv(x,y,z)=(\mathbf{X},x)$. From (12) and (14)

$$R(\mathbf{x},\mathbf{x}',\omega)=\frac{e^2}{2L^4l^2}\sum_{\mathbf{K}\mathbf{K}'}\sum_{k,k'>0}\frac{f(\mathbf{K},k)-f(\mathbf{K}',k')}{\omega(\mathbf{K}',k')-\omega(\mathbf{K},k)+\omega-i\alpha} \times e^{i(\mathbf{K}-\mathbf{K}')\cdot(\mathbf{X}-\mathbf{X}')}\sin kx'\sin k'x'\sin kx\sin k'x. \tag{16}$$

This is the basic linear response function in the $\mathbf{x}$ representation for the noninteracting electron gas bounded by two parallel planes.

The self-consistency problem is in general more tractable when expressed in Fourier representation than in $\mathbf{x}$ representation. The space Fourier transform of a function $u(\mathbf{x})$ may be defined as follows:

$$u_{\mathbf{q}}=\int_v d^3x e^{i\mathbf{Q}\cdot\mathbf{x}}\cos qx\, u(\mathbf{x}), \tag{17}$$

where v is the volume of the $l\times2L\times2L$ system. The choice of the $\cos qx$ transform in (17) leads to rational momenta in the response function, as is not the case for sine or exponential transforms, a result previously found by Fedders[22] and by Gadzuk.[23] For simplicity we shall in the following confine ourselves to odd functions $u(x)=-u(l-x)$, since the parity of the potential is not important when $l\to\infty$ and the perturbation is localized near the surfaces. More general potentials are considered in Sec. III. The inverse transform is then

$$u(\mathbf{x})=\frac{1}{2L^2l}\sum_{\mathbf{Q}}\sum_{q>0}e^{-i\mathbf{Q}\cdot\mathbf{x}}\cos qx\, u_{\mathbf{q}}. \tag{18a}$$

In (18a) and in the following $q=(2n+1)\pi/l$, $n=0,1,2\ldots$. Thus

$$u(\mathbf{x})\underset{l\to\infty}{=}\frac{1}{4\pi^3}\int d^3q e^{-i\mathbf{Q}\cdot\mathbf{x}}\cos qx\, u_{\mathbf{q}}. \tag{18b}$$

The integration in (18b) being over the $q>0$ half-space.

Using (17) and (18) together with the expression (11) for $\delta\rho(\mathbf{x})$ and the definition (12) of $R(\mathbf{x},\mathbf{x}',\omega)$, we have

$$\delta\rho_{\mathbf{q}}(\omega)=\sum_{q'}R_{\mathbf{Q},q,q'}(\omega)V_{\mathbf{Q},q'}(\omega), \tag{19a}$$

$$=\frac{l}{2\pi}\int dq' R_{\mathbf{Q},q,q'}V_{\mathbf{Q},q'}(\omega), \tag{19b}$$

with the definition (17) of the Fourier transforms $\delta\rho_{\mathbf{q}}$ and $V_{\mathbf{q}}$. $R_{\mathbf{Q},q,q'}$ is given by

$$R_{\mathbf{Q},q,q'}(\omega)=\frac{2}{l}\int d^2(X-X')dxdx'e^{i\mathbf{Q}\cdot(\mathbf{X}-\mathbf{X}')} \times\cos qx\cos q'x'R(\mathbf{x},\mathbf{x}',\omega). \tag{20}$$

The factor $2/l$ is here introduced for convenience. In order to evaluate (20), we shall find it a considerable simplification to remove the restriction that k and k' take only positive values in the summation (16), thus introducing a factor $\frac{1}{4}$ into (16). However, we shall continue to require that $q>0$, $q'>0$. We also adopt the abbreviation

$$F(\mathbf{K},k,\mathbf{K}',k')=\frac{f(\mathbf{K},k)-f(\mathbf{K}',k')}{\omega(\mathbf{K}',k')-\omega(\mathbf{K},k)+\omega-i\alpha}. \tag{21}$$

On substituting (16) into (20), and using the relations

$$\int_0^l dx\sin k'x\sin kx\cos qx$$

$$=\tfrac{1}{4}l(\delta_{k',k+q}+\delta_{k',k-q}-\delta_{k',-k-q}-\delta_{k',-k+q}), \tag{22a}$$

$$\int d^2X e^{i(\mathbf{K}-\mathbf{K}')\cdot\mathbf{x}}=4L^2\delta_{\mathbf{K},\mathbf{K}'}, \tag{22b}$$

where the second integration is over the basic $2L\times2L$ area in the $\mathbf{X}$ plane, then we find

$$\begin{aligned} R_{\mathbf{Q},q,q'}=\frac{e^2}{16L^2l}\sum_{\mathbf{K},k,k'}&F(\mathbf{K},k,\mathbf{K}+\mathbf{Q},k') \\ &\times[\delta_{k',k+q}-\delta_{k',-k-q}-\delta_{k',q-k}+\delta_{k',k-q}] \\ &\times[\delta_{k',k+q'}-\delta_{k',-k-q'}-\delta_{k',q'-k}+\delta_{k',k-q'}]. \end{aligned} \tag{23}$$

On using the property that the function F depends only on the moduli of its arguments (23) may be

simplified to the expression

$$R_{\mathbf{Q},q,q'}=\frac{e^2}{4L^2l}\sum_{\mathbf{K}}\{\sum_{k=-\infty}^{\infty}F(\mathbf{K},k,\mathbf{K}+\mathbf{Q},k+q)\delta_{qq'}$$
$$-F[\mathbf{K},\tfrac{1}{2}(q'+q),\mathbf{K}+\mathbf{Q},\tfrac{1}{2}(q-q')]$$
$$-F(\mathbf{K},\tfrac{1}{2}(q'-q),\mathbf{K}+\mathbf{Q},\tfrac{1}{2}(q+q')]\}. \quad (24)$$

Impermissible terms requiring $q<0$ or $q'<0$ have been omitted.

It is convenient to write (24) in the form

$$\mathbf{R}_{\mathbf{Q},q,q'}=D_{\mathbf{Q},q}\delta_{qq'}-A_{\mathbf{Q},q,q'}, \quad (25)$$

where in the limits $L\to\infty$ and $l\to\infty$

$$D_{\mathbf{Q},q}(\omega)=\frac{e^2}{4\pi^3}\int\frac{f(\mathbf{k})-f(\mathbf{k}+\mathbf{q})}{\omega(\mathbf{k}+\mathbf{q})-\omega(\mathbf{k})+\omega-i\alpha}d^3k\equiv D_{\mathbf{q}}(\omega), \quad (26)$$

$$A_{\mathbf{Q},q,q'}(\omega)=\frac{e^2}{4\pi^2l}\int\{F[\mathbf{K},\tfrac{1}{2}(q+q'),\mathbf{K}+\mathbf{Q},\tfrac{1}{2}(q-q')]$$
$$+F[\mathbf{K},\tfrac{1}{2}(q'-q),\mathbf{K}+\mathbf{Q},\tfrac{1}{2}(q+q')]\}d^2K, \quad (27)$$

the integral (26) being over all $\mathbf{k}$ space. If $L\to\infty$ but l is kept finite, in which case the theory applies to an infinite film of thickness l, $\mathbf{A}$ is still defined by (27) whereas $\int dk$ is replaced by $\pi l^{-1}\sum_{k=-\infty}^{\infty}$ in Eq. (26), [or D may be defined by (30) below]. Equations (25)–(27) had been earlier obtained by Fedders,[22] who does not, however, separate the symmetric and antisymmetric parts of V. Fedders differs in subtracting off $A_{\mathbf{Q},q,q}$, an error which vanishes as $l\to\infty$.

The response matrix is seen to consist of a diagonal part D and a nondiagonal part $\mathbf{A}$, which is symmetric in q and q'. The diagonal part is seen from (26) to be identical with the well-known response function of a noninteracting Fermi gas subject to periodic boundary conditions. If this were not so then the effect of the boundary conditions would be to modify the response deep within the gas, which is not to be expected even in the absence of any Coulomb interaction between the particles. The nondiagonal terms should give rise to a contribution to the response localized near the planes $x=0$ and $x=l$.

The response $\delta\rho$ must be zero at $x=0$ for each component $V_{\mathbf{P},p}$ of potential. If $V_{\mathbf{P},p}$ is the only nonzero component of the perturbation, then from (19a) and (18b)

$$\delta\rho_{\mathbf{Q}}(x)\equiv\frac{2}{l}\sum_{q}\cos qx\,\delta\rho_{\mathbf{q}}$$
$$=\frac{2}{l}\delta_{\mathbf{P},\mathbf{Q}}V_{\mathbf{P},p}\sum_{q}R_{\mathbf{P},q,p}\cos qx, \quad (28)$$

so that

$$\delta\rho_{\mathbf{P}}(0)=2l^{-1}V_{\mathbf{P},p}\sum_{q}R_{\mathbf{P},q,p}. \quad (29)$$

Hence if (29) is to be zero, then from (25)

$$\sum_{q'}A_{\mathbf{Q},q,q'}=D_{\mathbf{Q},q}. \quad (30)$$

Now on substituting $k=-\frac{1}{2}(q+q')$ in the first term and $k=\frac{1}{2}(q-q')$ in the second it is evident that

$$\sum_{q>0}F[\mathbf{K},\tfrac{1}{2}(q+q'),\mathbf{K}+\mathbf{Q},\tfrac{1}{2}(q-q')]$$
$$+\sum_{q>0}F[\mathbf{K},\tfrac{1}{2}(q'-q),\mathbf{K}+\mathbf{Q},\tfrac{1}{2}(q+q')]$$
$$=\sum_{k=-\infty}^{\infty}F(\mathbf{K},k,\mathbf{K}+\mathbf{Q},k+q').$$

Multiplying this equation by $e^2/4\pi^2l$, and integrating over $\mathbf{K}$, we see that on referring to (26) and (27) the sum rule (30) is verified. Equation (30) will later prove to be useful. $A_{\mathbf{Q},q,q'}$ may be written explicitly as

$$A_{\mathbf{Q},q,q'}=\frac{2e^2}{8\pi^2l}\int d^2K\Big(\frac{f[\mathbf{K},\tfrac{1}{2}(q+q')]-f[\mathbf{K}+\mathbf{Q},\tfrac{1}{2}(q-q')]}{\omega[\mathbf{K}+\mathbf{Q},\tfrac{1}{2}(q-q')]-\omega[\mathbf{K},\tfrac{1}{2}(q+q')]+\omega-i\alpha}$$
$$+\frac{f[\mathbf{K},\tfrac{1}{2}(q-q')]-f[\mathbf{K}+\mathbf{Q},\tfrac{1}{2}(q+q')]}{\omega[\mathbf{K}+\mathbf{Q},\tfrac{1}{2}(q+q')]-\omega[\mathbf{K},\tfrac{1}{2}(q-q')]+\omega-i\alpha}\Big) \quad (31)$$

which may be rewritten

$$A_{\mathbf{Q},q,q'}{}^{(1)}=\frac{2e^2}{4\pi^2l}P\int d^2K\frac{\{f[\mathbf{K},\tfrac{1}{2}(q-q')]-f[\mathbf{K}+\mathbf{Q},\tfrac{1}{2}(q+q')]\}\{\omega[\mathbf{K}+\mathbf{Q},\tfrac{1}{2}(q+q')]-\omega[\mathbf{K},\tfrac{1}{2}(q-q')]\}}{\{\omega[\mathbf{K}+\mathbf{Q},\tfrac{1}{2}(q+q')]-\omega[\mathbf{K},\tfrac{1}{2}(q-q')]\}^2-\omega^2}, \quad (32)$$

$$A_{\mathbf{Q},q,q'}{}^{(2)}=\frac{2e^2}{8\pi l}\int d^2K\{f[\mathbf{K},\tfrac{1}{2}(q-q')]-f[\mathbf{K}+\mathbf{Q},\tfrac{1}{2}(q+q')]\}$$
$$\times\delta\{\omega+\omega[\mathbf{K}+\mathbf{Q},\tfrac{1}{2}(q+q')]-\omega[\mathbf{K},\tfrac{1}{2}(q-q')]\}+\delta\{\omega-\omega[\mathbf{K}+\mathbf{Q},\tfrac{1}{2}(q+q')]+\omega[\mathbf{K},\tfrac{1}{2}(q-q')]\}, \quad (33)$$

where $\mathbf{A}^{(1)}$ and $\mathbf{A}^{(2)}$ are the real and imaginary parts of $\mathbf{A}$, respectively.

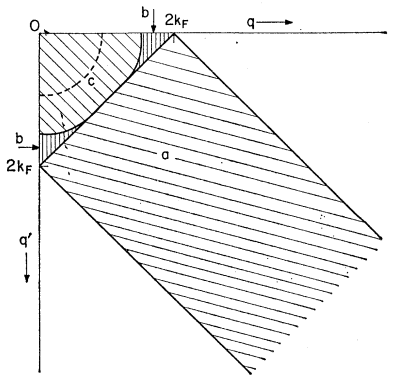

FIG. 2. Nondiagonal part **A** of one-electron response matrix. Elements of **A** in regions *a*, *b*, and *c* are given by Eqs. (35a)–(36c), respectively, and are zero in unshaded region. Broken curve shows alternative boundary between *b* and *c*.

The integrals (32) and (33) are straightforward, the results being somewhat complex for $\omega\neq 0$. Expressions for D and **A** in the special case of zero frequency are given below, and for $Q=0$ and nonzero ω in Appendix A. It is convenient to write

$$b=q/2k_F, \quad b'=q'/2k_F,$$
$$\mathbf{B}=\mathbf{Q}/2k_F.$$

Then

$$D_{\mathbf{b}}(0)=\frac{\lambda^2}{4\pi}\left(\tfrac{1}{2}+\frac{(1-|\mathbf{b}|^2)}{4|\mathbf{b}|}\ln\left|\frac{1+|\mathbf{b}|}{1-|\mathbf{b}|}\right|\right). \quad (34)$$

For $b<b'$ then, $A_{\mathbf{B},b,b'}$ is given by the following:

If $b'>1+b$,

$A_{\mathbf{B},b,b'}=0$.

If $1-b<b'<1+b$,

$$A_{\mathbf{B},b,b'}=\frac{\lambda^2}{8k_F l B^2}$$
$$\times\{B^2+bb'-[b^2b'^2+B^2(b^2+b'^2+B^2-1)]^{1/2}\}. \quad (35a)$$

If

$$\tfrac{1}{2}-\mathrm{Re}(\tfrac{1}{4}-B^2)^{1/2}<b<1-b'$$

or

$$b'<\mathrm{Re}B[(1-b'^2-B^2)/(b'^2+B^2)]^{1/2},$$

$$A_{\mathbf{B},b,b'}=\lambda^2/4k_F l. \quad (35b)$$

If

$$b<\tfrac{1}{2}-\mathrm{Re}(\tfrac{1}{4}-B^2)^{1/2}$$

and

$$\mathrm{Re}B[(1-b'^2-B^2)/(b'^2+B^2)]^{1/2}<b'<1-b,$$

$$A_{\mathbf{B},b,b'}=\frac{\lambda^2}{4k_F l B^2}$$
$$\times\{B^2-[b^2b'^2+B^2(b^2+b'^2+B^2-1)]^{1/2}\}. \quad (35c)$$

If $b>b'$, $A_{\mathbf{B},b,b'}=A_{\mathbf{B},b',b}$. Here λ is the Fermi-Thomas screening wave number given by

$$\lambda^2=4\pi e^2N(\epsilon_F)=4k_F/\pi r_B, \quad (36)$$

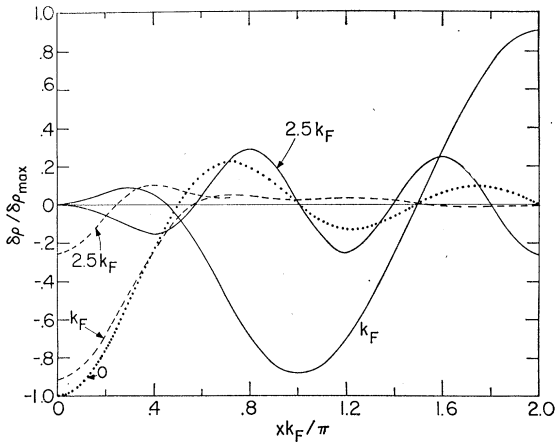

FIG. 3. Response in surface region to a perturbation $V\cos qx$ neglecting interelectronic interactions, for the cases $q=0$, k_F, and $2k_F$. Solid lines give the total change in charge density $\delta\rho$, and dashed and dotted curves the surface or nondiagonal contribution to $\delta\rho$. $\delta\rho_{\max}=\lambda^2V/4\pi$ is the limiting response at large distances from surface when $q=0$.

where $N(\epsilon_F)$ is the density of states at the Fermi level, and r_B the Bohr radius.

The matrix **A** is sketched in Fig. 2 for the case $\omega=0$. When $q+q'>2k_F$, $A_{qq'}$ is given by (35a) near the diagonal, but is zero if $|q-q'|>2k_F$. Referring to (19), it will be clear that this implies that an external perturbation $V_{Q,q}$ cannot give rise to Fourier components of $\delta\rho_{Q,q'}$ outside the range $q-2k_F<q'<q+2k_F$. This is to be expected since the highest Fourier component of charge density behaves like $\cos 2k_Fx$. The region $q+q'<2k_F$ is divided into two parts when $0<Q<k_F$, with the area in which $A_{Q,q,q'}$ is a constant given by (35b) increasing as Q decreases and occupying the whole region at $Q=0$.

In the one-dimensional case $Q=0$ the matrix elements at zero frequency are given by the simple relations

$$A_{bb'}(0)=\frac{\lambda^2}{4lk_F}, \quad \text{for } b+b'<1 \quad (37a)$$

$$=\left(\frac{\lambda^2}{16lk_F}\right)\frac{[1-(b-b')^2]}{bb'},$$

$$b+b'>1 \text{ and } |b-b'|<1 \quad (37b)$$

$$=0, \quad |b-b'|>1. \quad (37c)$$

From (35) the zero frequency matrix elements may be shown to lie in the range

$$0<A_{\mathbf{B},b,b'}(0)<\lambda^2/4lk_F. \quad (38)$$

The sum rule (30) provides a check on (35).

The response to a static one-dimensional potential

$$V(\mathbf{x})=V\cos qx$$

affords a simple illustration of the one-electron response.

$\delta\rho(x)$ may be calculated from (28) and (37), the results in the limit $l\to\infty$ being given for several values of q in Fig. 3. The response differs significantly from that of a homogeneous electron gas only within a distance $\sim k_F^{-1}$ from the surface, as is to be expected. If $q\to 0$ we obtain the simple analytical result

$$\delta\rho = V\lambda^2(4\pi)^{-1}[1-(\sin 2k_F x)/2k_F x]$$

which was derived by an elementary method above [see Eq. (2)].

III. SELF-CONSISTENCY

The self-consistent response may now be calculated by introducing Eq. (3) connecting the self-consistent potential V with the source potential U due to an external charge. Retardation effects will be neglected in the following. The explicit dependence on ω will frequently be omitted. From (3) and (10) we have

$$U(\mathbf{x},\omega)+\varphi(\mathbf{x},\omega)=V(\mathbf{x},\omega). \tag{39}$$

We now operate on this with $e^{i\mathbf{Q}\cdot\mathbf{x}}\cos qx\nabla^2$ and integrate over the $l\times 2L\times 2L$ volume v of the electron gas. Applying Green's theorem to the right-hand side we obtain

$$\begin{aligned}\int_v e^{i\mathbf{Q}\cdot\mathbf{x}}\cos qx(\nabla^2 U+\nabla^2\varphi)\,d^3\mathbf{x}&\\ =\int_v V\nabla^2(\cos qx e^{i\mathbf{Q}\cdot\mathbf{x}})\,d^3\mathbf{x}&\\ +\int_S \cos qx e^{i\mathbf{Q}\cdot\mathbf{x}}\nabla V\cdot d\mathbf{S}&\\ -\int_S V\nabla(\cos qx e^{i\mathbf{Q}\cdot\mathbf{x}})\,d\mathbf{S}.&\end{aligned} \tag{40}$$

S is the surface of the system, which consists of the planes $x=0$ and $x=l$. The second surface integral vanishes at these planes. Introducing the source charge distribution $s(\mathbf{x})$, and using Poisson's equation, we have

$$\begin{aligned}4\pi(s_{\mathbf{q}}+\delta\rho_{\mathbf{q}})=-|\mathbf{q}|^2V_{\mathbf{q}}+\int e^{i\mathbf{Q}\cdot\mathbf{x}}\left[-\frac{\partial V}{\partial x}\right]_{x=0}d^2X&\\ -\int e^{i\mathbf{Q}\cdot\mathbf{x}}\left[\frac{\partial V}{\partial x}\right]_{x=l}d^2X,&\end{aligned} \tag{41}$$

employing the definition (17); or, using the presumed antisymmetry of the potential

$$4\pi s_{\mathbf{q}}=-|\mathbf{q}|^2V_{\mathbf{q}}-4\pi\delta\rho_{\mathbf{q}}-2V_{\mathbf{Q}}'(0), \tag{42}$$

where here and in the following we introduce the mixed representation $V_{\mathbf{Q}}(x)$ by

$$V_{\mathbf{Q}}(x)=\int e^{i\mathbf{Q}\cdot\mathbf{x}}V(\mathbf{x})d^2X \tag{43}$$

and the prime in (42) denotes differentiation with respect to x. Substituting (19) for $\delta\rho_{\mathbf{q}}$ we obtain

$$4\pi s_{\mathbf{q}}=-2V_{\mathbf{Q}}'(0)-\sum_{q'}[|\mathbf{q}|^2\delta_{qq'}+4\pi R_{\mathbf{Q},q,q'}]V_{\mathbf{Q},q'}, \tag{44}$$

$$=-2V_{\mathbf{Q}}'(0)-\sum_{q'}E_{\mathbf{Q},q,q'}V_{\mathbf{Q},q'}, \tag{45}$$

where

$$E_{\mathbf{Q},q,q'}=|\mathbf{q}|^2\delta_{qq'}+4\pi R_{\mathbf{Q},q,q'}. \tag{46}$$

The matrix $\mathbf{E}$ is related to the dielectric matrix, which would be obtained on dividing (46) by $|\mathbf{q}|^2$. In fact we wish to express V in terms of the source perturbation, whence on multiplying (45) by the inverse $\mathbf{E}^{-1}$

$$V_{\mathbf{Q},q}=-\sum_{q'}E_{\mathbf{Q},q,q'}^{-1}[4\pi s_{\mathbf{Q},q'}+2V_{\mathbf{Q}}'(0)]. \tag{47}$$

If the source charge is far from the surface we may omit the term $2V_{\mathbf{Q}}'(0)$ and neglect the nondiagonal elements of $\mathbf{E}$, when (47) becomes identical with the well-known result for the homogeneous electron gas,

$$V_{\mathbf{q}}=U_{\mathbf{q}}/\epsilon_{\mathrm{RPA}}(\mathbf{q},\omega), \tag{48a}$$

where neglecting surface contributions

$$U_{\mathbf{q}}=4\pi s_{\mathbf{q}}/|\mathbf{q}|^2$$

and the RPA dielectric function is given by

$$\epsilon_{\mathrm{RPA}}(\mathbf{q},\omega)=1+4\pi D_{\mathbf{q}}(\omega)/|\mathbf{q}|^2. \tag{48b}$$

In the present problem $V_{\mathbf{Q}}'(0)$ must be determined from the boundary conditions at the surface. Let us first restrict ourselves to one-dimensional potentials, when $Q=0$. If the electric field is required to be zero far outside the metal then

$$V'(0)\equiv\left[\frac{\partial V}{\partial x}\right]_{x=0}=4\pi\int_{-\infty}^{0}\sigma(x)dx, \tag{49}$$

where $\sigma(x)$ is the source charge at x per unit area. Evidently $\sigma(x)$ must be antisymmetric, i.e., $\sigma(l-x)=-\sigma(x)$. Now $V_{\mathbf{Q}}'(0)=4L^2V'(0)$, whence dividing (47) by $4L^2$

$$V_q=-\sum_{q'}E_{0,q,q'}^{-1}[4\pi\sigma_{q'}+2V'(0)] \tag{50}$$

in which $V'(0)$ is given by (49) and, in general, f_q is related to $f(x)$ by

$$f_q=\int_0^l dx\cos qx f(x), \tag{51a}$$

$$f(x)=\frac{2}{l}\sum_q\cos qx f_q. \tag{51b}$$

Combining (50) and the inverse transform (51b) we

have for $x>0$

$$V(x) \underset{x>0}{=} -\frac{l}{\pi^2}\int dq \cos qx \times \int dq' E_{0,q,q'}^{-1}[2\pi\sigma_{q'}+V'(0)], \quad (52)$$

where the limit $l\to\infty$ has been taken. Continuation of the solution into the $x<0$ region then gives

$$V(x) \underset{x<0}{=} 4\pi x\int_{-\infty}^{x}\sigma(x')dx' - 4\pi\int_0^x x'\sigma(x')dx'+V(0), \quad (53)$$

where $V(0)$ is to be obtained from (52). The result for $x>l$ is then obtained from the antisymmetry of V about $x=\frac{1}{2}l$. Equations (52) and (53) give the formal solution to the one-dimensional problem.

We now turn to the general case $Q\neq 0$. Let the regions $x<0$, $0<x<l$, and $x>l$ be denoted, respectively, by I, II, and III. Further let U^{I}, U^{II}, and U^{III} denote the potentials due to that part of the source charge lying in the appropriate regions. In the regions outside the metal it is convenient to work in the mixed $(\mathbf{Q},x)$ representation which may be defined for any function by (43) and its inverse Fourier transform [see Eq. (64) below]. Now in region I the source potentials $U_{\mathbf{Q}}^{\mathrm{II}}(x)$ and $U_{\mathbf{Q}}^{\mathrm{III}}(x)$ together with the potential $\varphi_{\mathbf{Q}}(x)$ of the response charge density obey Laplaces's equation, e.g.,

$$\frac{d^2}{dx^2}U_{\mathbf{Q}}^{\mathrm{II}}(x)=Q^2U_{\mathbf{Q}}^{\mathrm{II}}(x), \quad (54)$$

whereas $U_{\mathbf{Q}}^{\mathrm{I}}(x)$ obeys Poisson's equation in this region

$$\left[\frac{d^2}{dx^2}-Q^2\right]U_{\mathbf{Q}}^{\mathrm{I}}(x)=4\pi s_{\mathbf{Q}}(x). \quad (55)$$

The solutions of these equations in the region $x<0$ are

$$\varphi_{\mathbf{Q}}(x)=e^{Qx}\varphi_{\mathbf{Q}}(0), \quad (56a)$$

$$U_{\mathbf{Q}}^{\mathrm{II}}(x)=e^{Qx}U_{\mathbf{Q}}^{\mathrm{II}}(0), \quad (56b)$$

$$U_{\mathbf{Q}}^{\mathrm{III}}(x)=e^{Qx}U_{\mathbf{Q}}^{\mathrm{III}}(0), \quad (56c)$$

$$U_{\mathbf{Q}}^{\mathrm{I}}(x)=\frac{2\pi}{Q}\left\{e^{Qx}\int_0^x e^{-Qx'}s_{\mathbf{Q}}(x')dx' - e^{-Qx}\int_{-\infty}^{x}e^{Qx'}s_{\mathbf{Q}}(x')dx'\right\}. \quad (56d)$$

From (39) and (56),

$$V_{\mathbf{Q}}'(0)=Q[U_{\mathbf{Q}}^{\mathrm{II}}(0)+U_{\mathbf{Q}}^{\mathrm{III}}(0)+\varphi_{\mathbf{Q}}(0)]-QU_{\mathbf{Q}}^{\mathrm{I}}(0) =QV_{\mathbf{Q}}(0)-2QU_{\mathbf{Q}}^{\mathrm{I}}(0). \quad (57)$$

Now, applying (18b) to (47) we have

$$V_{\mathbf{Q}}(0)=-\frac{2}{l}\sum_{q,q'}E_{\mathbf{Q},q,q'}^{-1}[4\pi s_{\mathbf{Q},q'}+2V_{\mathbf{Q}}'(0)]. \quad (58)$$

Combining (57) and (58) and solving for $V_{\mathbf{Q}}(0)$,

$$V_{\mathbf{Q}}(0,\omega) =\left[2U_{\mathbf{Q}}^{\mathrm{I}}(0,\omega)-\frac{8\pi}{l}\epsilon_{\mathbf{Q}}(\omega)\sum_{q,q'}E_{\mathbf{Q},q,q'}^{-1}(\omega)s_{\mathbf{Q},q}(\omega)\right]\Big/ [1+\epsilon_{\mathbf{Q}}(\omega)], \quad (59)$$

where

$$\epsilon_{\mathbf{Q}}(\omega)\equiv\left[\frac{4Q}{l}\sum_{q,q'}E_{\mathbf{Q},q,q'}^{-1}(\omega)\right]^{-1}. \quad (60)$$

The dependence on ω has here been explicitly restored. From (56d) $U_{\mathbf{Q}}^{\mathrm{I}}(0,\omega)$ is given by

$$U_{\mathbf{Q}}^{\mathrm{I}}(0,\omega)=-\frac{2\pi}{Q}\int_{-\infty}^{0}e^{Qx'}s_{\mathbf{Q}}(x',\omega)dx'. \quad (61)$$

Equation (59) is a significant result, since it gives the potential at the surface of the metal in terms of the source charge distribution. It should be noted that the first term in the numerator of (59) depends only on the exterior part of the source charge, and the second only on the interior part.

From (18), (47), and (57)

$$V_{\mathbf{Q}}(x,\omega)\underset{x<0}{=}-\frac{4}{l}\sum_{q,q'}\cos qxE_{\mathbf{Q},q,q'}^{-1}(\omega) \times[2\pi s_{\mathbf{Q},q'}(\omega)+QV_{\mathbf{Q}}(0,\omega)-2QU_{\mathbf{Q}}^{\mathrm{I}}(0,\omega)]. \quad (62)$$

The potential in region I is, from (56) and (39),

$$V_{\mathbf{Q}}(x,\omega)\underset{x<0}{=}e^{Qx}[V_{\mathbf{Q}}(0,\omega)-U_{\mathbf{Q}}^{\mathrm{I}}(0,\omega)]+U_{\mathbf{Q}}^{\mathrm{I}}(x,\omega), \quad (63)$$

where $U_{\mathbf{Q}}^{\mathrm{I}}(x,\omega)$ is given by (56d) and $V_{\mathbf{Q}}(0,\omega)$ by (59). $V(\mathbf{x})$ is obtained from (62) or (63) by

$$V(\mathbf{x})=\frac{1}{4\pi^2}\int d^2\mathbf{Q}e^{-i\mathbf{Q}\cdot\mathbf{x}}V_{\mathbf{Q}}(x). \quad (64)$$

The potential in region III is obtained from (63) by symmetry. The solution is given in principle by (62) and (63) for any extended source distribution in the surface region.

An important special case arises if there is no source charge within the metal, when $s_q(\omega)$ vanishes and (59) becomes

$$V_{\mathbf{Q}}(0,\omega)=2U_{\mathbf{Q}}^{\mathrm{I}}(0,\omega)/[1+\epsilon_{\mathbf{Q}}(\omega)]; \quad (65)$$

hence from (63),

$$V_{\mathbf{Q}}(x,\omega)\underset{x<0}{=}U_{\mathbf{Q}}^{\mathrm{I}}(x,\omega)+U_{\mathbf{Q}}^{\mathrm{I}}(0,\omega)e^{Qx}\left(\frac{1-\epsilon_{\mathbf{Q}}(\omega)}{1+\epsilon_{\mathbf{Q}}(\omega)}\right). \quad (66)$$

Now in the region $x>0$ the potential U^{I} takes the form

$$U_{\mathbf{Q}}{}^{\mathrm{I}}(x,\omega) \underset{x>0}{=} U_{\mathbf{Q}}{}^{\mathrm{I}}(0,\omega)e^{-Qx}. \tag{67}$$

With the aid of (67), Eq. (66) may be written

$$V_{\mathbf{Q}}(x,\omega) \underset{x<0}{=} U_{\mathbf{Q}}{}^{\mathrm{I}}(x,\omega)+U_{\mathbf{Q}}{}^{\mathrm{I}}(-x,\omega)\left(\frac{1-\epsilon_{\mathbf{Q}}(\omega)}{1+\epsilon_{\mathbf{Q}}(\omega)}\right). \tag{68}$$

Equation (68) is simply the classical image theorem for a semi-infinite dielectric medium; this states that if there is a source charge distribution outside the dielectric, then in the external region the induced potential is equal to the reflection of the source potential in the surface multiplied by the factor $(1-\epsilon)/(1+\epsilon)$, where ϵ is the dielectric constant of the medium. Evidently $\epsilon_{\mathbf{Q}}$ plays the role of the classical dielectric constant, although because of its Q dependence in the present problem (68) is valid only for each parallel Fourier component $\mathbf{Q}$. It should be noted that (68) remains valid for the antisymmetric potentials considered here even for a film of finite thickness, the effects of finite l being incorporated into $\epsilon_{\mathbf{Q}}$ in the present formalism. A practical consequence of Eq. (68) is that any problem involving only exterior sources may be solved with the relatively restricted information embodied in $\epsilon_{\mathbf{Q}}(\omega)$, which is a function of only two variables, ω and Q. In more general problems it is necessary to work with the entire matrix $\mathbf{E}^{-1}$. The calculation of $\epsilon_{\mathbf{Q}}(\omega)$ *a priori* according to the present formalism itself requires inversion of the $\mathbf{E}$ matrix; nevertheless it is an advantage that the results may for many purposes be presented in the concise form (60).

The inversion of the $\mathbf{E}$ matrix is the central problem in applying the formalism developed here. It is sometimes convenient to express $\mathbf{E}^{-1}$ as an iteration series. We define

$$E_{\mathbf{Q},q,q'}=4\pi[\Delta_{\mathbf{Q},q'}\delta_{qq'}-A_{\mathbf{Q},q,q'}], \tag{69}$$

where from (46)

$$\Delta_{\mathbf{Q},q}=(4\pi)^{-1}(Q^2+q^2)+D_{\mathbf{Q},q}. \tag{70}$$

$\Delta_{\mathbf{q}}$ is related to the dielectric function of the homogeneous electron gas by $\Delta_{\mathbf{q}}=|\mathbf{q}|^2\epsilon_{\mathrm{RPA}}(\mathbf{q},\omega)/4\pi$ [see Eq. (48b)]. Now

$$\mathbf{E}^{-1}=(4\pi)^{-1}[\mathbf{\Delta}^{-1}+\mathbf{\Delta}^{-1}\mathbf{A}\mathbf{\Delta}^{-1}+\mathbf{\Delta}^{-1}(\mathbf{A}\mathbf{\Delta}^{-1})^2+\cdots] \tag{71}$$

or

$$E_{qq'}{}^{-1}=(4\pi)^{-1}\left(\frac{\delta_{qq'}}{\Delta_q}+\frac{A_{qq'}}{\Delta_q\Delta_{q'}}+\sum_{q''}\frac{A_{qq''}A_{q''q'}}{\Delta_q\Delta_{q''}\Delta_{q'}}+\cdots\right), \tag{72}$$

where the suffix $\mathbf{Q}$ has been omitted for convenience. All terms of (72) are of the same order in l, as can be seen by referring to (30). From the above results (34) and (38) we see that $D_{\mathbf{Q},q}$ and $A_{\mathbf{Q},q,q'}$ are always positive at zero frequency. Hence all the terms in (72) are positive in this case so that

$$E_{\mathbf{Q},q,q'}{}^{-1}>\delta_{qq'}/4\pi\Delta_q, \qquad \omega=0 \tag{73}$$

or

$$0<\epsilon_{\mathbf{Q}}(0)<\left(\frac{Q}{2\pi^2}\int_0^\infty\frac{dq}{\Delta_{\mathbf{Q},q}}\right)^{-1}, \quad \omega=0. \tag{74}$$

Thus the effect of including the nondiagonal elements of $\mathbf{E}$ is always to decrease the static dielectric function seen by a charge outside the metal.

From (59) we note that $\epsilon_{\mathbf{Q}}(\omega)$ plays an important role even when interior source charges exist, since the condition for the potentials $\pm V_{\mathbf{Q}}(0)$ at the surfaces to be infinite is

$$\epsilon_{\mathbf{Q}}(\omega)+1=0, \tag{75}$$

independent of the mode of excitation. Equation (75) gives implicitly the dispersion relation for the antisymmetric surface plasmon modes of a film of thickness l or, on taking the limit $l\rightarrow\infty$, the modes of a single surface. A similar result applies to the symmetric modes if the definition of $\epsilon_{\mathbf{Q}}$ is modified as described below. It should be noted that retardation is neglected in (75), which is therefore inapplicable when $Q\lesssim\omega/c$, where c is the velocity of light.

For simplicity only charge densities and potentials antisymmetric about the plane $x=\frac{1}{2}l$ have been considered so far. Since any potential may be expressed as a linear combination of even and odd potentials, extension of the above results to symmetric potentials completes in principle the solution for finite l. When the function $u(x)$ is symmetric in $x-\frac{1}{2}l$, the Fourier series (18a) takes the form

$$u(\mathbf{x})=\frac{1}{2L^2l}\sum_{\mathbf{Q}}\sum_{q\geq0}e^{-i\mathbf{Q}\cdot\mathbf{x}}\cos qx\,u_q\eta_q,$$

where $q=2n\pi/l$; $n=0, 1, 2, \ldots$, and the discontinuous factor η_q is given by $\eta_q=\frac{1}{2}$ when $q=0$ and $\eta_q=1$ for $q>0$. A similar modification applies to $f(x)$ in (51b), and a factor η_p, where p is the summation variable, is also introduced into Eqs. (19a), (29), the sum rule (30), and (45). The changed parity leads to the following changes in the principle equations. Thus a factor $1/\eta_q$ appears in the diagonal term of (24), and hence $D_{\mathbf{Q},q}$ is replaced by $D_{\mathbf{Q}q}/\eta_q$ in (25). The last term in (41) changes sign, leaving (42) unaffected. On replacing the definition (46) of $\mathbf{E}$ by

$$E_{\mathbf{Q},q,q'}=q^2\delta_{qq'}/\eta_q+4\pi R_{\mathbf{Q},q,q'}$$

and introducing a factor $1/\eta_q$ into the definition (69) of Δ_q, Eqs. (58)–(75) remain unchanged. In the following it is to be assumed that the potentials are antisymmetric unless otherwise stated.

IV. APPLICATIONS

Two special cases, the Fermi-Thomas and classical limits, are of interest as they will be shown to require

consideration of only the leading term in the series (72). In addition we shall derive below the lowest-order correction to the potential in the Fermi-Thomas approximation, which is smaller than the Fermi-Thomas term by the factor $(\lambda r_B)^{-1}$. It should be noted that the first correction to the Fermi-Thomas approximation in the case of the homogeneous electron gas is of order $(\lambda r_B)^{-2}$; the lower-order correction in the present problem arises from the large oscillations in $\delta\rho$ in the surface region due to the requirement that $\delta\rho$ be zero at the surface itself. In the case of the classical approximation, valid at small wave vector Q and finite frequency, the calculation of appropriate corrections unfortunately proves difficult beyond general observations as to their form.

In order to extend our results into the region of metallic electron densities, the matrix $\mathbf{E}$ was inverted numerically for the case of a static one-dimensional potential. No internal sources were included, so that the metal surface could be regarded as forming one plate of a parallel plate condensor. The one-dimensional solutions may be related to the change in work function due to a layer of charges lying outisde the surface, an experimentally measurable quantity. An interesting finding is that the calculated screening length agrees rather accurately with the corrected Fermi-Thomas approximation mentioned above.

A. Fermi-Thomas Limit

The Fermi-Thomas approximation is valid at zero frequency in the limit of high electron density, which implies that

$$\lambda \ll k_F \quad \text{or} \quad \lambda \gg r_B^{-1}. \tag{76}$$

The potential V is then a solution of the Fermi-Thomas equation $\nabla^2 V = \lambda^2 V$ in source-free regions of the homogeneous electron gas.

Let us first consider, from a simple physical standpoint, the case of the semi-infinite high-density electron gas subject to a one-dimensional potential such that the normal electric field $V'(0)$ at the surface is fixed, there being no internal sources. In the Fermi-Thomas approximation the potential and charge density $\delta\rho(x)$ per unit surface area are

$$V(x) = V(0)e^{-\lambda x}, \quad \delta\rho(x) = \lambda^2 V(0) e^{-\lambda x}/4\pi, \tag{77}$$

where $V(0) = -V'(0)/\lambda$.

We now make use of the one-dimensional free-electron response matrix given in Eq. (37). The Fourier component $\delta\rho_0$ of charge density for $q \to 0$ may be defined in the limit $l \to \infty$. From (19), (34), and (37), $\delta\rho_0$ is given by

$$\delta\rho_0 = \frac{\lambda^2}{4\pi}\left(V_0 - \frac{1}{2k_F}\int_0^{2k_F} V_q dq\right).$$

According to (17), $\frac{1}{2}\delta\rho_0$ is the induced charge associated with a single surface, and may thus be equated to $V'(0)/4\pi$, where $V'(0)$ is the normal electric field at the surface. Hence multiplying the last equation by $\frac{1}{2}$, and converting to x representation by (17), we have

$$V'(0) \underset{l\to\infty}{=} -\lambda^2 \int_0^{l/2} V(x)\left(1 - \frac{\sin 2k_F x}{2k_F x}\right)dx.$$

Here integration over the potential at one surface in the limit $l \to \infty$ is implied. This equation is exact; it may also be obtained from the sum rule of Sugiyama[19] on evaluating the phase shift in Born approximation. Now deviations from Eq. (77) should take the form of quantum oscillations in $\delta\rho(x)$ of large amplitude [since $\delta\rho(0)$ must equal zero] but also large wave vector $\sim 2k_F$. From Poisson's equation $V(x)$ will be insensitive to these oscillations and should be well approximated by $V(x) = V(0)\exp(-\lambda x)$. Inserting this ansatz into the last equation we obtain

$$V'(0) = -\lambda^2 V(0) \int_0^{l/2} e^{-\lambda x}\left(1 - \frac{\sin 2k_F x}{2k_F x}\right)dx \tag{78a}$$

which should be valid at high electron density. We might plausibly regard Eq. (78a) as an integration over the charge density

$$\delta\rho(x) = V(0)\lambda^2 e^{-\lambda x}[1 - (\sin 2k_F x)/2k_F x]/4\pi,$$

which decays exponentially with superimposed quantum oscillations such that $\delta\rho(0) = 0$. This charge density is what would be expected if Eq. (2) giving the response in the long-wavelength limit were applicable locally with $V = V(0)\exp(-\lambda x)$. In the high-density limit this is at least reasonable in the region $0 < x \ll \lambda^{-1}$, where $V(x) \simeq V(0)$.

The exact integral of (78a) is not as significant as the evaluation to lowest order in λ/k_F, from which we obtain

$$V(0) = -V'(0)\lambda^{-1}[1 + \pi\lambda/4k_F] + O(\lambda^2/k_F^2). \tag{78b}$$

Equation (78b) gives the lowest-order correction to the potential in the Fermi-Thomas approximation.

We now turn to the series (72) for the inverse response matrix $\mathbf{E}^{-1}$. In addition to (76) it will be assumed that

$$Q \ll r_B^{-1} \quad \text{or} \quad Q \ll k_F. \tag{79}$$

The second inequality follows from the first and (76). Now $1/\Delta_q$ is large when $q \leq (\lambda^2 + Q^2)^{1/2}$ but tends to zero as q^{-2} at large q. Further, according to (38) and (35b), $A_{qq'}$ has its maximum value (35b) when q and q' are small provided that $Q < k_F$. The nth term in the series (72) is a multiple summation over a function which is, therefore, large only when all the q suffixes lie in the range $q \leq (\lambda^2 + Q^2)^{1/2}$, i.e., $q \ll k_F$ in the present limit. A and Δ may then be approximated by their values in the region of small q

$$\Delta_q \simeq (4\pi)^{-1}(Q^2 + q^2 + \lambda^2 - \lambda^2 q^2/12k_F^2 + \cdots), \tag{80a}$$

$$A_{qq'} = \lambda^2/4lk_F = 1/\pi l r_B. \tag{80b}$$

If λ and Q are sufficiently small the nth term will therefore approach the value

$$[E_{qq'}^{-1}]^{(1)}\simeq\delta_{qq'}/(\lambda^2+Q^2+q^2),$$

$$[E_{qq'}^{-1}]^{(n)}\simeq\frac{4}{lr_B(\lambda^2+Q^2+q^2)(\lambda^2+Q^2+q'^2)}\times\left(\sum_{q''}\frac{4}{lr_B(\lambda^2+Q^2+q''^2)}\right)^{n-2},\quad n>1. \tag{81}$$

Let us confine ourselves to calculating $\epsilon_{\mathbf{Q}}$, defined by (60), for the case $l\to\infty$. Summing (81) over q, q' and converting all summations to integrations we then obtain

$$[\epsilon_{\mathbf{Q}}^{-1}]^{(1)}\simeq Q/(Q^2+\lambda^2)^{1/2},$$

$$[\epsilon_{\mathbf{Q}}^{-1}]^{(n)}\simeq\frac{Q}{r_B(\lambda^2+Q^2)}\left(\frac{1}{r_B(\lambda^2+Q^2)^{1/2}}\right)^{n-2},\quad n>1. \tag{82}$$

The limiting values (82) of the term $[\epsilon_{\mathbf{Q}}^{-1}]^{(n)}$ are of order $[r_B(\lambda^2+Q^2)^{1/2}]^{1-n}$. It is reasonable to assume that the nth term may be expanded in powers of r_B^{-1}, an expansion of which the first term is given by (82). Now a collection of all terms in r_B^{-r} from $[\epsilon_{\mathbf{Q}}^{-1}]^{(1)}\cdots[\epsilon_{\mathbf{Q}}^{-1}]^{(r+1)}$ could in principle be used to form the $(r+1)$th term of an expansion of $\epsilon_{\mathbf{Q}}^{-1}$ in powers of r_B^{-1}. It will be assumed that such an expansion converges, at least asymptotically.

We shall calculate only the terms up to $r=1$ of the series for $\epsilon_{\mathbf{Q}}^{-1}$, which requires knowledge only of $[\epsilon_{\mathbf{Q}}^{-1}]^{(1)}$ and $[\epsilon_{\mathbf{Q}}^{-1}]^{(2)}$. From (72) and (80a), $[\epsilon_{\mathbf{Q}}^{-1}]^{(1)}$ is found to contribute the $r=0$ term, given in (82), but no linear term. The linear term is thus found by setting $n=2$ in (82). Adding these terms we obtain

$$\epsilon_{\mathbf{Q}}^{-1}=Q(Q^2+\lambda^2)^{-1/2}\times[1+r_B^{-1}(Q^2+\lambda^2)^{-1/2}+0(\lambda^2/k_F^2)]. \tag{83}$$

On inserting (83) into (65), and substituting (61) for $U_{\mathbf{Q}}^{\text{ext}}(0)$, then our previous one-dimensional result (78b) is retrieved on taking the limit $Q\to 0$. In principle higher-order corrections could be obtained by an extension of this procedure.

For completeness we give the general solution of the Fermi-Thomas equation for a semi-infinite metal ($l\to\infty$), assuming only exterior source charge. If only the first term in parenthesis in (83) is included, then from (66)

$$V_{\mathbf{Q}}(x)\underset{x<0}{=}U_{\mathbf{Q}}^{\mathrm{I}}(x)-U_{\mathbf{Q}}^{\mathrm{I}}(0)e^{Qx}\lambda^{-2}[Q-(\lambda^2+Q^2)^{1/2}]^2. \tag{84a}$$

Similarly, neglecting the last term in parentheses in (80a), and taking only the first term in the iteration series (72), we obtain on insertion into (62)

$$V_{\mathbf{Q}}(x)\underset{x>0}{=}-2Q\lambda^{-2}U_{\mathbf{Q}}^{\mathrm{I}}(0)[Q-(Q^2+\lambda^2)^{1/2}]\times\exp[-(Q^2+\lambda^2)^{1/2}x]. \tag{84b}$$

It is seen from (84b) that the potential in the metal is screened at least as rapidly as $\exp(-\lambda x)$ in the direction normal to the surface.

B. Classical Limit

The classical approximation to the dielectric function $\epsilon_{\mathrm{RPA}}(\mathbf{q},\omega)$ of the homogeneous electron gas is valid in the region $\omega\gg qv_F$, where v_F is the Fermi velocity. ϵ_{RPA} may then be approximated by[12]

$$\epsilon_{\mathrm{RPA}}=1-\omega_p^2/\omega^2-3\omega_p^2v_F^2|\mathbf{q}|^2/5\omega^4+\cdots, \tag{85}$$

where ω_p is the bulk plasma frequency given by $\omega_p^2=4\pi n_0e^2/m$. This may be regarded as an expansion in powers of $|\mathbf{q}|$ at nonzero ω. Correspondingly the classical approximation to the surface dielectric response results from expanding the inverse of the matrix $\mathbf{E}$ in powers of Q when $\omega\neq 0$. Consider the expression (60) for $\epsilon_{\mathbf{Q}}$, which on using (72) may be written (suppressing the suffix $\mathbf{Q}$ on the right for convenience)

$$\epsilon_{\mathbf{Q}}^{-1}=\frac{Q}{\pi l}\left(\sum_q\frac{1}{\Delta_q}+\sum_{q,q'}\frac{A_{qq'}}{\Delta_q\Delta_{q'}}+\sum_{q,q'',q'}\frac{A_{qq''}A_{q''q'}}{\Delta_q\Delta_{q''}\Delta_{q'}}+\cdots\right). \tag{86}$$

Let us concern ourselves with only the first two terms in the expansion

$$\epsilon_{\mathbf{Q}}^{-1}=a_0+a_1Q+\cdots a_nQ^n+\cdots. \tag{87}$$

Evidently $a_0=0$ unless the series in braces in (86) possesses a singularity at $Q=0$, whereas a_1 is obtained from the Q-independent term in the series. Accordingly we let $Q\to 0$ in the expression in braces in (86), and examine the series for singularities. Since $A_{\mathbf{Q},q,q'}$ is well behaved when $Q\to 0$, and is confined to the numerators in (86), the limit $Q=0$ may be taken in this function (see Appendix A). The relevant singularities in the summations of (86) arise from the behavior of the summands in the region of small q; hence we may employ (85), which is valid when $Q\to 0$ and $q\to 0$, together with the relation $\Delta_q(\omega)=|\mathbf{q}|^2\epsilon_{\mathrm{RPA}}(\mathbf{q},\omega)/4\pi$, as an approximation to Δ near the singularities. Then the behavior of the summand of the nth term in the series (86) when $Q\to 0$ and all arguments $q_i\to 0$ may be written as

$$1/\Delta_{\mathbf{Q},q_0}\sim 1/(Q^2+q_0^2),\quad n=1$$
$$A_{q_0q_1}A_{q_1q_2}\cdots A_{q_{n-2}q_{n-1}}/(\Delta_{q_0}\Delta_{q_1}\cdots\times\Delta_{q_{n-2}}\Delta_{q_{n-1}})\sim(q_1q_2\cdots q_{n-2})^2,\quad n>1. \tag{88}$$

It is evident that only the first term is singular and

contributes to a_0. Using (85) and taking the limit $l\to\infty$

$$a_0=\frac{2Q}{\pi(1-\omega_p^2/\omega^2)}\int_0^\infty\frac{dq}{Q^2+q^2}=\left(1-\frac{\omega_p^2}{\omega^2}\right)^{-1}. \quad (89)$$

Hence using (87),

$$\epsilon_Q(\omega)=1-\omega_p^2/\omega^2-a_1Q/a_0^2. \quad (90)$$

We thus find that when $Q\to 0$ the surface dielectric function $\epsilon_Q(\omega)$ approaches the value of the bulk dielectric function $\epsilon_{\mathrm{RPA}}(\mathbf{q},\omega)$ in the region $|\mathbf{q}|\to 0$, provided ω is finite. This result, which is used widely in, for example, the theory of optical reflectance,[9] is of more general validity than suggested by the present derivation.

From (75) and (90) the surface plasmon frequency is given by

$$\omega_s=2^{-1/2}\omega_p(1+\tfrac{1}{4}a_1Q), \quad (91)$$

hence at sufficiently small Q, $\omega_s\to 2^{-1/2}\omega_p$, which is the well-known classical result.

The complex coefficient a_1, which gives rise to a correction in (90) of first order in Q, arises partly from a more accurate evaluation of the first term in (86) than the approximation (89), and partly from the remaining terms in the series, in which Q may be set equal to zero. The latter terms, whose structure is too complex to discuss here, certainly do not vanish, and we shall assume they do not mutually cancel. Ritchie[26] has calculated a_1 by considering only the first term, and Ritchie and Marusak[27] have derived corrections of higher order in Q from this term. The present formalism does not however seem to offer any simple justification for this approximation, and a rigorous calculation of a_1 might therefore be of interest. This calculation could be of some importance, since the real part of a_1 enters (91) as a linear correction to the dispersion law for surface plasmons and the imaginary part gives rise to a damping factor proportional to Q, which might be experimentally observable. In the absence of any dissipative effects in the model, the damping is evidently of the Landau type, originating in the decay of a surface plasmon into a particle-hole pair. This process is not severely restricted by momentum conservation as in the case of bulk plasmons. In principle a_1 might be calculated numerically on putting $\omega=2^{-1/2}\omega_p$ and using the identity

$$+\pi\mathbf{E}^{-1}=\mathbf{\Delta}^{-1}+(\mathbf{\Delta}-\mathbf{\Delta}\mathbf{A}^{-1}\mathbf{\Delta})^{-1},$$

where the first term on the right-hand side gives the correction of Ritchie and Marusak[27] and the second may be inverted numerically after putting $Q=0$ everywhere (see Appendix A).

The surface plasmon dispersion law for a film may also be derived from the present formalism. For antisymmetric modes, (89) becomes

$$a_0{}^u=\frac{4Ql}{\pi^2(1-\omega_p^2/\omega^2)}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2+l^2Q^2/\pi^2}$$
$$=(1-\omega_p^2/\omega^2)^{-1}\tanh\tfrac{1}{2}Ql. \quad (92)$$

Similarly, for the symmetric modes we have from the results given at the end of Sec. III

$$a_0{}^g=\frac{4Ql}{\pi^2(1-\omega_p^2/\omega^2)}\sum_{n=0}^{\infty}\frac{\eta_n}{4n^2+l^2Q^2/\pi^2}$$
$$=(1-\omega_p^2/\omega^2)^{-1}\coth\tfrac{1}{2}Ql, \quad (93)$$

hence, neglecting a_1 and using (75), the plasmon frequencies are given by

$$\omega_u{}^2=\omega_p^2/(1+\tanh\tfrac{1}{2}Ql), \quad (94a)$$

$$\omega_g{}^2=\omega_p^2/(1+\coth\tfrac{1}{2}Ql), \quad (94b)$$

where ω_u and ω_g denote the frequencies of odd and even modes, respectively. The simple classical results (94) are significantly modified by including retardation effects[29]; they have also been obtained as a limiting case in Fedder's work.[22]

C. Numerical Calculations

Numerical inversion of the matrix $\mathbf{E}$ was used to obtain results applicable to the metallic range of densities ($2<r_s<6$). For simplicity, calculations have been limited to the case of static antisymmetric one-dimensional potentials ($Q=0$) with no interior sources. The relevant equations are, from (50), (51b), and (42), together with the condition $s_q=0$,

$$V(x)=\frac{-4V'(0)}{l}\sum_{q,q'}E_{qq'}{}^{-1}\cos qx, \quad (95)$$

$$\delta\rho(x)=\frac{V'(0)}{\pi l}\sum_q\left[q^2\sum_{q'}E_{qq'}{}^{-1}-1\right]\cos qx. \quad (96)$$

The electric field at the surface $V'(0)$ is assumed to be given. Since $q=(2n+1)\pi/l$, where n is an integer, the requirement that the $E_{qq'}$ form a discrete matrix implies that l be finite. From (46), (25), and (30), the elements of $\mathbf{E}$ are

$$E_{qq'}=-4\pi A_{qq'},\quad q\neq q' \quad (97a)$$

$$E_{qq}=4\pi\left[q^2+\sum_{q'\neq q}A_{qq'}\right], \quad (97b)$$

where $A_{qq'}$ is given by (37).

The infinite matrix $\mathbf{E}$ may be truncated at $q=q_0$, $q'=q_0$ for the purpose of calculation. By using the sum rule (30) it is not difficult to show that truncation is permissible provided that

$$q_0{}^2\gg D(q_0)^2 \quad (98)$$

[29] E. Economou, Phys. Rev. **182**, 539 (1969).

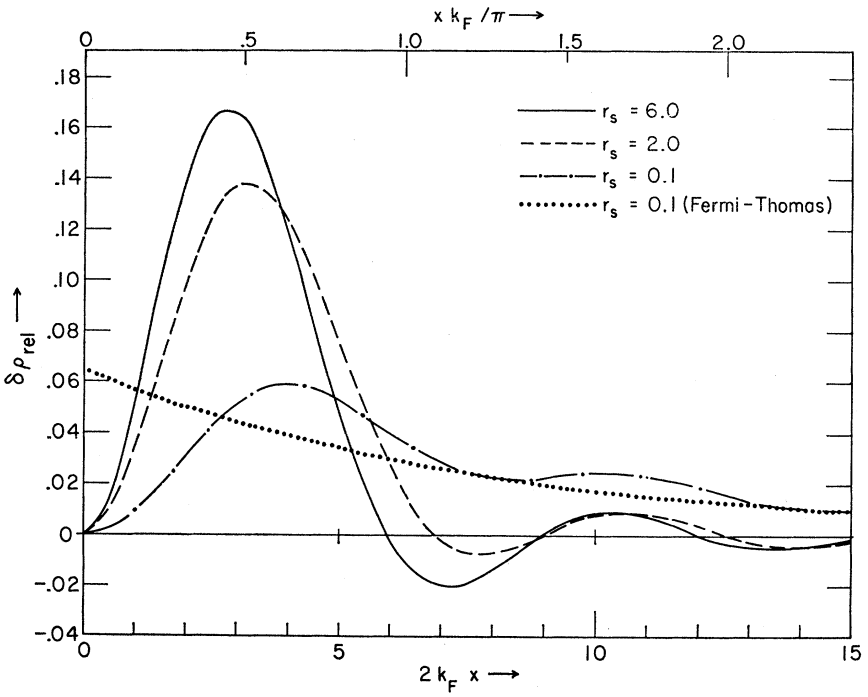

FIG. 4. Relative change in charge density $\delta\rho_{\rm rel}$ for a one-dimensional perturbing potential due to an external source as a function of distance x from surface. Absolute perturbed charge density $\delta\rho(x)$ per unit area is given by

$$\delta\rho = k_F V'(0)\delta\rho_{\rm rel}/\pi.$$

for q_0 sufficiently large. A sufficient condition for (98) is that $q_0^2 \gg \lambda^2$; if N is the order of the truncated matrix $\mathbf{E}$, so that $q_0 = (2N+1)\pi/l$, this may be written $N^2 \gg (\lambda l)^2$. In fact in the range of densities studied the effect of truncation was found to be entirely negligible for $q_0 \geq 4k_F$. Errors due to the choice of a finite value of l exceed those due to truncation but are nevertheless remarkably small in the range of densities studied. The reason for this lies in the exactness of the present approach for antisymmetric potentials at finite l, so that when $\lambda l \gg 1$ the mutual interaction of the two surfaces should be screened out except for the effects of the long-range oscillatory component of $\delta\rho$, which is manifested by a very small oscillatory variation in the

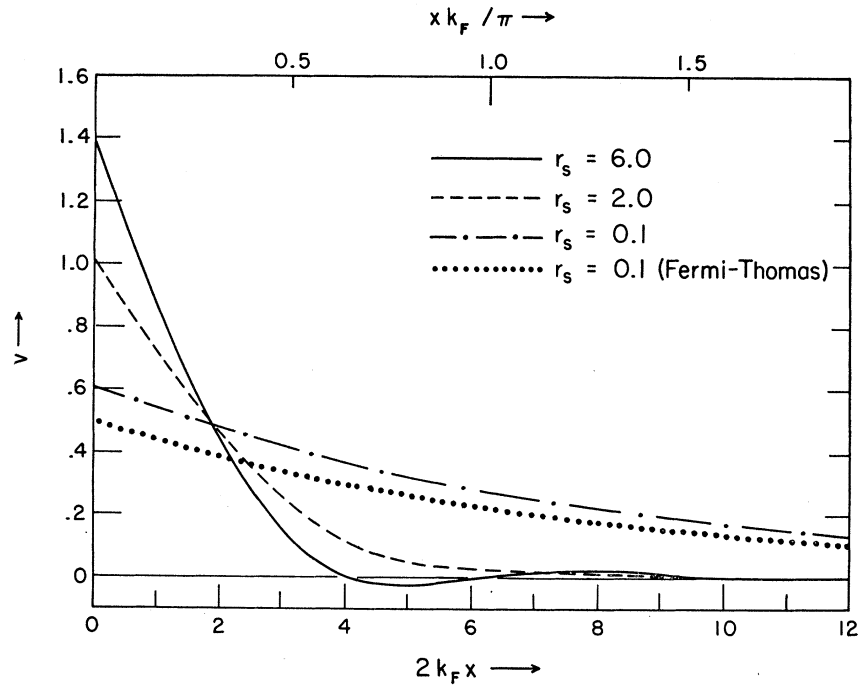

FIG. 5. Relative electrostatic potential v within metal for a one-dimensional perturbing potential due to an external source as a function of distance x from surface. Absolute potential $V(x)$ is given by $V = 2V'(0)v/\lambda$.

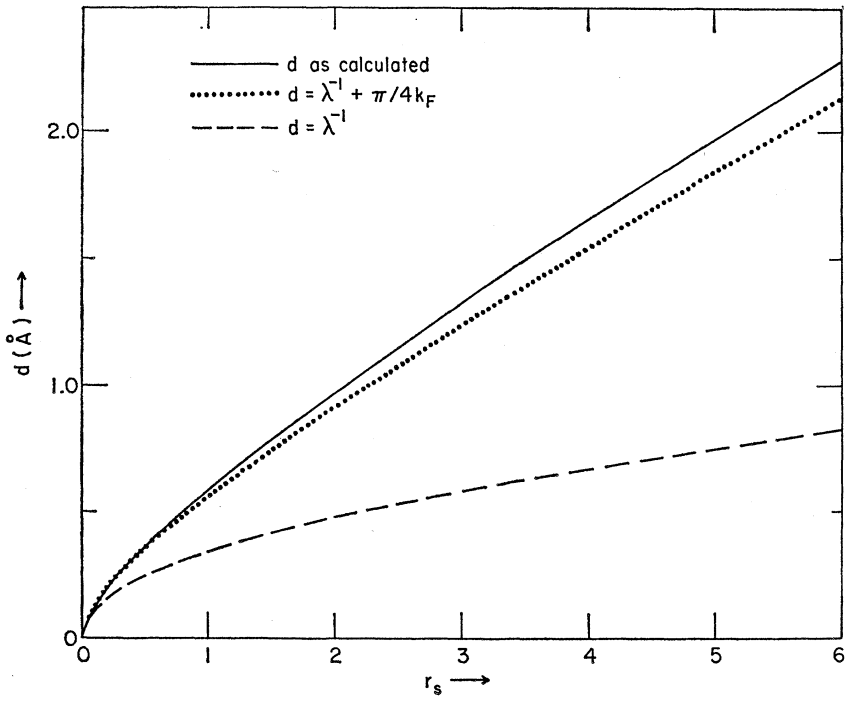

FIG. 6. Screening length d, defined as $d=V(0)/V'(0)$, as a function of r_s. d is shown as calculated and in the Fermi-Thomas and corrected Fermi-Thomas approximations.

calculated quantities as functions of l. Combination of $\lambda l \gg 1$ with the requirement for truncation gives the condition $N \gg 1$. In practice, if $q_0 \simeq 4k_F$ and $n \geq 40$, results corresponding to the limit $l \to \infty$ may be obtained with an error derived from the convergence as N and q_0 are increased to be less than $\sim 0.2\%$.

A standard computer program was used to perform the inversion, the remaining manipulations in (95) and (96) being straightforward. The results are shown in Figs. 4–7. At the highest electron density studied, $r_s=0.1$, the perturbed charge density is seen from Fig. 4 to approximate the Fermi-Thomas charge density given by Eq. (77). The principal deviation from the Fermi-Thomas charge density takes the form of quantum oscillations arising from the requirement $\delta\rho(0)=0$,

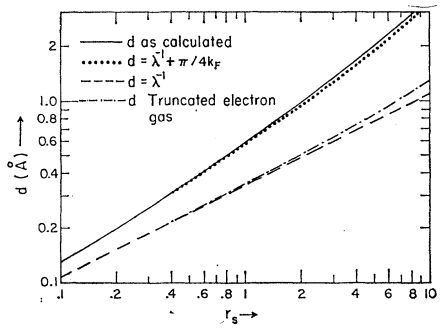

FIG. 7. Plot of log$d$ versus logr_s. Screening length d is shown as calculated and in Fermi-Thomas and corrected Fermi-Thomas approximations. Curve marked "Truncated electron gas" refers to calculation neglecting nondiagonal matrix elements (see text).

as already discussed in Sec. IV A. At electron densities corresponding to $r_s=2$ and $r_s=6$, which are approximately upper and lower bounds to the range of metallic densities, the Fermi wavelength and Fermi-Thomas screening length λ^{-1} are comparable and the charge density $\delta\rho$ decays to a low value after only one or two oscillations. The magnitude and phase of the residual oscillatory part of $\delta\rho$ at large x may be calculated from first principles [see Eq. (B6)], and is found to be in approximate agreement with these numerical results. It should be noted that the maximum value of $\delta\rho$ in fact decreases with r_s at a fixed $V'(0)$, although this is masked by the choice of units in Fig. 4. The self-consistent potential $V(x)$ is seen from Fig. 5 to be insensitive to the oscillations in $\delta\rho$, as expected from Poisson's equation. At $r_s=0.1$, $V(x)$ is thus of approximately exponential form, in agreement with the approximation embodied in Eq. (78a).

It is convenient to introduce the screening length d, a quantity of some experimental significance, by

$$d=V(0)/V'(0). \tag{99}$$

The screening length is the value of x at which the external potential $V=V'(0)x+V(0)$ would cross the x axis on continuation into the metal; it is zero for a perfect conductor and equal to λ^{-1} in the Fermi-Thomas approximation. Let us suppose there is an adsorbed layer of ions of charge q at a distance a from the surface. Then the resulting change in work function $\Delta\varphi$ is

$$\Delta\varphi=4\pi nq(a+d), \tag{100}$$

where n is the surface concentration of ions. Equation (100) is exact, because the potential difference due to the adsorbate layer depends only on the $Q=0$ component of charge in the layer, not on its local distribution.[18] In addition, the dipole moment of a single charge q is given by $\mu=2q(a+d)$.

The calculated screening length is shown as a function of r_s in Figs. 6 and 7. Figure 7 shows that d approaches its high-density limiting value of λ^{-1} rather slowly. However, on combining (78b), which includes the lowest-order correction to the Fermi-Thomas approximation, with (99), we obtain

$$d=\lambda^{-1}+\pi/4k_F. \tag{101}$$

As may be seen from Figs. 6 and 7, Eq. (101) is a remarkably accurate approximation to the calculated screening length, the error being only $\sim 7\%$ at $r_s=6$.

In Fig. 7 we also show the results of a very simple calculation in which the nondiagonal elements of $\mathbf{E}$ were neglected. The electron gas is thus assumed to retain its bulk properties right up to the surface, a situation which is not, in fact, possible. This calculation is actually equivalent to that for an infinite electron gas with source charge distribution $V'(0)\delta(x)/2\pi$ per unit surface area, i.e., the one-dimensional version of Langer and Vosko's[30] work on the screening of a point charge. In this case the screening length is at most $\sim 10\%$ greater than λ^{-1}, showing the Lindhard screening correction to be small compared with the nondiagonal correction.

V. DISCUSSION OF RESULTS

Before comparing the screening length calculation of the last section with the rather limited experimental data, it is of interest to consider briefly the relation between the high-density formula (101) for d and earlier treatments of the inhomogeneous electron gas. The established procedures[31,32] for correcting the Fermi-Thomas approximation have been based on expansions in powers of a small parameter (e.g. $\hbar$), within the Hartree-Fock approximation. This method has proved rather successful in calculating metallic work functions[17] and total atomic energies,[32] but less so for other atomic properties.[33] The method fails to reproduce the quantum oscillations associated for example with the atomic-shell structure. In studying the power series expansion for an exactly soluble one-dimensional free-electron model, Payne[34] points out that important terms of an oscillatory nature are not included. More recently in the work of Kohn and Sham[35] on the nonuniform free-electron gas in one dimension, a quite different approach, in which the Fermi-Thomas approximation is supplemented with oscillatory terms arising from the classical turning points, was found to be remarkably successful. Now from the derivation in the first part of Sec. IV A, it will be clear that the correction to the Fermi-Thomas approximation embodied in (101) is closely connected with the inclusion of quantum oscillations in the charge density associated with the requirement $\delta\rho(0)=0$, and we may conclude that the quantum corrections of Refs. 31 and 32 are not relevant here. A generic relation between the methods of Kohn and Sham and the correction (101) seems therefore evident, although the present calculation involves the Hartree linear response and a stepwise discontinuity in potential rather than a linear turning point.

Experimental determinations of the screening length d for the metal-vacuum interface at present depend on measuring the change in work function due to a layer of adsorbed ions, whose surface concentration n, charge q, and radius a must be known. The change in work function $\Delta\varphi$ is then related to d by Eq. (100). An artifact in this technique arises from the expected penetration by the ion into the outer exponential tail of the electronic charge density, which should lead to smaller d than calculated by assuming the ion to rest on the $x=0$ plane of the infinite square barrier charge density. The surfaces of constant electron density at a real metal surface will tend to some extent to follow the underlying atomic structure of the crystal plane. If, as seems likely, the ion is adsorbed on concave regions of the surface, this represents an additional penetration mechanism, further reducing d.

Additional complications may arise from nonlinear effects due to the rather strong electric fields of the adsorbed ions. Some idea of the magnitude of the nonlinearity may be gained from calculations based on the full Fermi-Thomas model, of which (77) represents only the linearized approximation. Such calculations for one-dimensional potentials have been made numerically by Ku and Ullman,[36] who report significant nonlinearities only for normal fields $V'(0)$ "near 10^9 V cm^{-1}," and by Tsong and Müller,[37] who have obtained the lowest-order nonlinear corrections analytically. From the formulas of the latter authors, the maximum error in d in the case of a Cs^+ ion, for which $V'(0)\simeq 5.3$ V/Å, may be estimated as $\sim 15\%$ at $r_s=4$ and $\sim 3\%$ at $r_s=2$. Somewhat larger corrections are expected for actual metal surfaces because the larger screening lengths predicted above imply larger potentials at a given field, and because the "local" electron density near the surface is less than in the bulk. Nonlinearities will also be greater for other alkali atoms, whose radius is less than that of Cs^+. It should be recalled however

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TABLE I. Experimental screening lengths on tungsten in Å.

Surface	(110)	(211)	(100)	(111)
δ [a]	3.0,3.5	1.9,2.4	1.7,1.9	1.3,1.8
d [a,b]	1.35,1.85	0.25,0.75	···,0.25	···,0.15

[a] First value quoted is from Gavrilyuk, Naumovets, and Fedorus (Ref. 5), the second from Sidorski, Pelley, and Gomer (Ref. 1).
[b] Based on $R_{Cs}=1.65$ Å. Only positive d values given.

that linear methods are often employed[30] in treating the screening of charged bulk impurities, where the potential diverges. Qualitatively we expect a positive ion to increase the electron density near the surface, thus promoting the efficiency of screening and reducing d, with the opposite effect for a negative species.

Measurements of $\delta=d+a$ have been made on tungsten by Gauvilyuk, Naumovets, and Fedorus,[5] and by Sidorski, Pelley, and Gomer,[1] using Cs^+ ions. Results derived from $\partial\varphi/\partial n$ at $n=0$, assuming the charge on Cs^+ to be unity, are given in Table I. The δ of Sidorski, Pelley, and Gomer are generally larger than the values of Gauvilyuk, Naumovets, and Fedorus, but the same trend is reported by the two groups, the decrease in calculated δ from left to right in Table I being usually interpreted[1,5] as a decrease in q. Reasons for this are: (a) Work function of the bare metal surface also decreases from left to right in Table I, so that the occupancy of the virtual $6s$ state of Cs will increase in this direction, and (b) overlap of the Cs and metal wave functions should be least for the more closely packed surfaces, such as (110), for which the virtual state width should be minimal; this effect acts to reduce the $6s$ occupancy on close-packed surfaces. In addition, penetration of the surface by the Cs^+ ion due to nonplanarity should be greater for the more loosely packed surfaces, but this should result in only a small reduction in δ due to the large Cs^+ radius. This interpretation suggests that the closely packed (110) face yields the most reliable value for δ. Taking 1.64 Å for the Cs^+ radius leads to screening lengths of $d=1.35$ Å (Gauvilyuk, Naumovets, and Fedorus) and 1.85 Å (Sidorski, Pelley, and Gomer).

The band structure of tungsten as calculated by Mattheiss[38] shows the presence of a very broad $5d$ band, which can be regarded only very crudely as a tight-binding-like one, and an sp band strongly hybridized with it. If the d wave functions could be regarded as completely corelike it would be appropriate to consider screening by the sp band alone, which should contain about one electron per atom since the d bands appear to be approximately half-filled. The hybridization should not have too serious an effect at the short wavelengths important in the present calculation (see for example Phillip's[39] estimates of screening in semiconductors) and as a first approximation the effective value $r_s\simeq 3.0$ derived from the sp electron density may be used in calculating d. From Fig. 6 this is seen to predict $d\simeq 1.3$ Å, which is as close to the experimental results as can be expected from this crude argument. In the opposite extreme r_s could be determined from the full electron density of six electrons per atom, which is the point of view taken by Smith,[17] but the author feels that the nonideality of the energy bands, presumably associated with highly anisotropic charge densities, renders such an approximation suspect.

The comparison which we have made with experiment must appear rather inconclusive, largely, due to the complicated electronic structure of the substrate metal which was studied. Nevertheless it has been argued above that the experimental artifacts all act in the direction of reducing d, and thus the observed values of $d\sim 1.35$–1.85 Å greatly in excess of any likely Fermi-Thomas screening length definitely suggest the existence of a quantum correction similar to that discussed in this paper.

Calculations have in this paper been confined to one-dimensional potentials. An important three-dimensional case is the external point charge, which represents approximately the perturbation due to an ion outside the surface. The image energy W of a charge q at $\mathbf{b}=(b,0,0)$, where $b<0$, is given by $W=\frac{1}{2}q^2\varphi(\mathbf{b})$ [21] in a linear response theory. Using (66), (61), and (64) the image energy may then be expressed as

$$W=\tfrac{1}{2}q^2\int_0^\infty dQ e^{2Qb}\left(\frac{1-\epsilon_Q}{1+\epsilon_Q}\right), \tag{102}$$

this being a generalization of Eq. (22) of Ref. 21, which applied only in the Fermi-Thomas approximation. In view of the success of the approximate form (101) for d, the use of the equivalent approximation (83) in (102) suggests itself. Unfortunately the resulting expression for W diverges at small $\mathbf{b}$; at large $\mathbf{b}$ it approaches the expression[3,21]

$$W=-q^2/4(b+d), \tag{103}$$

where d is given by (101). In the absence of a numerical evaluation of (102), Eq. (103) may possibly be used as an extrapolation formula down to values of b where use of (83) is invalid.

VI. CONCLUSIONS

The principal results of the present investigation are as follows:

(i) The assumptions underlying this work, namely, the use of Hartree approximation and the choice of "particle in a box" wave functions to describe the unperturbed ground state, are believed to be approximately valid at $r_s\sim 4$.

(ii) The dielectric response is expressed in Fourier representation (most generally for slab geometry) and reduced essentially to the inversion of an infinite matrix $\mathbf{E}$. A dielectric function $\epsilon_{\mathbf{Q}}$ may be defined, de-

[38] L. F. Mattheiss, Phys. Rev. **139**, A1893 (1965).
[39] J. C. Phillips, Phys. Rev. Letters **20**, 550 (1968).

pending on frequency and on a two-dimensional wave vector $\mathbf{Q}$ parallel to the surface. The free oscillations of the system (surface plasmons) occur at the solutions of $\epsilon_Q+1=0$. In addition, for source charges outside the metal, the classical image theorem for a semi-infinite dielectric medium is valid at given values of $\mathbf{Q}$ and frequency, provided ϵ_Q replaces the classical dielectric constant of the medium.

(iii) The Fermi-Thomas approximation, the lowest-order correction to it, and the classical (high-frequency) limit may be derived from the present formalism. Corrections to the classical approximation, which give the dispersion and damping of surface plasmons, are found to be of the same form as in some previous work.

(iv) Numerical results are obtained for a static electric field normal to the surface. The screening length is found to be more than twice its Fermi-Thomas value λ^{-1} in the range of metallic densities, but to be well approximated by the expression $d=\lambda^{-1}+\pi/4k_F$, in which $\pi/4k_F$ is the lowest-order quantum correction. The large deviations of d from λ^{-1} originate almost entirely in the nondiagonal elements of the dielectric matrix, and should thus be attributed to the abnormally low electron density near the surface.

Comparison of the experimental results on tungsten with the present theory is difficult owing to the complicated electronic structure of this metal. Nevertheless the observed screening length is compatible with a free-electron model if $r_s\sim 3$–4.

(v) For one-dimensional perturbing potentials, the induced charge density within the metal at large distances from the surface falls off as $\delta\sim c(\sin 2k_F x)/x^2$. The constant $c=V'(0)/8\pi k_F$ at high electron densities, if the perturbation is a normal electric field $V'(0)$.

Note added in proof. L. I. Schiff[41] has recently treated the static one-dimensional surface screening problem by a method which avoids the assumption of an infinite square potential barrier. Qualitatively similar results are obtained. It is worth noting that the relation obtained by Herring[42] between surface screening and the electric field just outside a nonuniformly strained metal specimen (which in fact motivated Schiff's work) might make possible an experimental determination of a precisely defined surface screening parameter.

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APPENDIX A: DYNAMIC RESPONSE MATRIX

In the one-dimensional case $B=0$, at nonzero frequency, the matrix elements are given below.

Let $b=q/2k_F$ and $u=\omega/4\epsilon_F$. Then

$$D_b^{(1)}(u)=\frac{\lambda^2}{8\pi}\left\{1+\frac{1}{4b}\left[1-\left(b+\frac{u}{b}\right)^2\right]\ln\left|\frac{1+(b+u/b)}{1-(b+u/b)}\right|-\frac{1}{4b}\left[1-\left(b-\frac{u}{b}\right)^2\right]\ln\left|\frac{1-(b-u/b)}{1+(b-u/b)}\right|\right\}, \quad \text{(A1)}$$

$$\begin{aligned}D_b^{(2)}(u)&=0, \quad \text{for } u>b^2+b\\&=0, \quad \text{for } b>1 \text{ and } u<b^2-b\\&=\frac{\lambda^2 u}{8b}, \quad \text{for } b<1 \text{ and } |u|<|b^2-b|\\&=\frac{\lambda^2}{32b}[1-(b-u/b)^2]\\&\qquad\qquad \text{for } |b^2-b|<|u|<|b^2+b|. \quad \text{(A2)}\end{aligned}$$

Equations (A1) and (A2) are essentially the well-known results of Lindhardt.[13] The nondiagonal matrix elements are

$$\begin{aligned}A_{bb'}^{(1)}(u)&=0, \quad \text{for } |b-b'|>1\\&=\frac{\lambda^2}{8lk_F}\frac{b^2b'^2}{b^2b'^2-u^2}, \quad \text{for } b+b'<1\\&=\frac{\lambda^2}{32lk_F}\frac{bb'[1-(b-b')^2]}{b^2b'^2-u^2},\\&\qquad\qquad \text{for } b+b'>1 \text{ and } |b-b'|<1 \quad \text{(A3)}\end{aligned}$$

$$\begin{aligned}A_{bb'}^{(2)}(u)&=0, \quad \text{for } |b-b'|>1\\&=\frac{\pi\lambda^2 bb'}{16lk_F}[\delta(u-bb')-\delta(u+bb')],\\&\qquad\qquad \text{for } b+b'<1\\&=\frac{\pi\lambda^2 bb'}{64lk_F}[1-(b-b')^2][\delta(u-bb')-\delta(u+bb')],\\&\qquad\qquad \text{for } b+b'>1 \text{ and } |b-b'|<1. \quad \text{(A4)}\end{aligned}$$

APPENDIX B: FRIEDEL OSCILLATIONS

In this appendix we discuss the long-range oscillations in charge density associated with a static perturbation localized near the surface. For simplicity the discussion is confined to one-dimensional potentials, although the

[40] M. J. Lighthill, *Fourier Analysis and Generalized Functions* (Cambridge University Press, Cambridge, 1958).
[41] L. I. Schiff (private communication).
[42] C. Herring, Phys. Rev. **171**, 1361 (1968).

present methods should be capable of extension to the three-dimensional case. We assume $l\to\infty$.

From Eq. (19a) the Fourier transform of the charge distribution is

$$\delta\rho_q=D_qV_q-\frac{l}{2\pi}\int A_{qq'}V_{q'}dq'. \tag{B1}$$

Using (18b), $\delta\rho(x)$ is then

$$\delta\rho(x)=\frac{1}{\pi}\int dqD_qV_q\cos qx-\frac{l}{2\pi^2}\int dq(\cos qx)\times\int dq'A_{qq'}V_{q'}. \tag{B2}$$

Now in the limit $x\to\infty$ the main contribution to the integrals in (B2) comes from the singularities in the integrands. In the first term the only singularity is the well-known logarithmic singularity in D_q [given by Eq. (34)] at $q=2k_F$. The function $A_{qq'}$ has singularities along the straight lines shown in Fig. 2 (the curved boundaries refer only to $Q\neq0$). Because, in general, these are singularities only in derivative, it is easily shown that they give contributions to $\delta\rho$ only of order x^{-3} or higher. The points $(0,2k_F)$ and $(2k_F,0)$ where the singular lines intersect represent more serious singularities. The singularity at $q=0$, $q'=2k_F$ does not however contribute to lowest order because $\sin qx$ is zero at this point. Hence the major contribution in the second term of (B2) derives from $q=2k_F$, $q'=0$. We therefore put $V_q=V_{2k_F}$ in the first term, and $V_{q'}=V_0$ in the second term of (B2), which becomes

$$\delta\rho(x)\underset{x\to\infty}{=}\frac{1}{\pi}\int dq\cos qx\left[V_{2k_F}D_q-V_0\frac{l}{2\pi^2}\int dq'A_{qq'}\right].$$

Using the sum rule (30) this may be written

$$\delta\rho(x)\underset{x\to\infty}{=}\frac{2k_F}{\pi}[V_{2k_F}-V_0]\int_{1-\gamma}^{1+\gamma}dbD_b\cos bx', \tag{B3}$$

where $x'=2k_Fx$, $b=q/2k_F$, and $\gamma=0^+$. Referring to (34) we see that the singular part of D_b is $D_b=-\lambda^2(1-b)\times\ln|1-b|/8\pi$ near $b=1$. Putting $y=b-1$ we have

$$\delta\rho(x)\underset{x\to\infty}{=}\frac{\lambda^2k_F}{4\pi^2}(V_{2k_F}-V_0)\times[\cos x'\,\mathrm{Re}f(x')-\sin x'\,\mathrm{Im}f(x')], \tag{B4}$$

where

$$f(x')=\int_{-\gamma}^{\gamma}dye^{ix'y}y\ln|y|=-i\pi x'^{-2}+O(x'^{-3}) \tag{B5}$$

(for the last step, see, e.g., Lighthill[40]). Combining these results, we have

$$\delta\rho(x)=-\frac{1}{4\pi^2r_Bx^2}[V_0-V_{2k_F}]\sin2k_Fx. \tag{B6}$$

Equation (B6) relates the asymptotic Friedel oscillations to the Fourier components of the self-consistent potential V, which are given by (50). Note that from the definition (17) the V_q are twice the normal cosine transforms of the potential at one surface. Since at all densities down to those found in metals we find that $V_0\gg V_{2k_F}$, the Friedel oscillations are dominated by the V_0 term which originates in the nondiagonal matrix elements and thus in the nonuniform surface electron density. Equation (B6) is found to be in approximate agreement with the calculations of Sec. IV C.

At sufficiently high electron densities we may neglect V_{2k_F} and employ the Fermi-Thomas approximation (77) in calculating V_0, hence (B6) becomes

$$\delta\rho_{\mathrm{osc}}(x)=-\frac{V'(0)}{8\pi k_F}\frac{\sin2k_Fx}{x^2}, \tag{B7}$$

where we have also assumed the source to be purely the normal external field $V'(0)$. According to (B7) the Friedel oscillations should be the same for all curves in Fig. 4, in which $\delta\rho$ is plotted in units of $V'(0)k_F/\pi$; this is seen to be roughly true. A much better approximation to (B6) is obtained on multiplying the right-hand side of (B7) by the factor $1+\pi\lambda/4k_F$).