Response of Metal Surfaces to Static and Moving Point Charges and to Polarizable Charge Distributions

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A phenomenological dielectric approximation is proposed for studying the response of metal surfaces to external charge distributions and is illustrated by detailed calculations using the Thomas-Fermi model. The procedure is based on the replacement of the dielectric-response kernel in a constitutive relation by its asymptotic expression in the bulk region. It represents an alternative to the classical step-density approximation, where the nonuniform density profile near the surface is replaced by the bulk electron density up to an abrupt termination. While the two procedures are equivalent for a local solid, they are quite different in general because of the different nature of the quantitites being approximated by bulk expressions. Detailed applications include the calculation of the image-potential interaction and of the induced surface dipole for static point charges external to the metal surface, the study of the corresponding quantities for charges embedded in the surface, and, finally, the calculation of the effective polarizability of an adsorbed atom and of the image potential and induced surface dipole for a polarizable ion. Comparison with self-consistent surface-model calculations indicates that for charges external to the surface the results for the above-mentioned dielectric approximation are much more realistic than those for the step-density approximation. However, for the case of embedded charges far away from the surface the step-density approximation yields a more accurate result for the surface dipole. A final section is devoted to the generalization of the step-density treatment to time-dependent response problems, assuming specular reflection of electrons at the surface. Some necessary general formulas are derived in a first part, which is then followed by a detailed study of the image-potential interaction for point charges moving uniformly along various prescribed trajectories. Explicit calculations for a local dielectric function indicate a strong dependence of the instantaneous interaction on the past trajectory of the external charge, as well as strong deviations from the quasistatic image potential in some cases. These modifications arise from real and virtual excitation of surface plasmons for particles moving outside the metal, and from both surface- and bulk-plasmon excitation for particles moving inside the metal.

I. INTRODUCTION

The dielectric response of a metal surface to external perturbing charge distributions is of direct interest for a number of phenomena. In particular, the image-potential interaction between a static point charge and a metal surface plays an important role in the study of the Schottky effect,[1] of the tunneling between two metal electrodes separated by an insulating barrier[2] as well as in field-evaporation,[3] field-desorption,[4,5] field-emission,[6] and low-energy-electron-scattering[7] problems. It must also be taken into account in the detailed interpretation of chemisorption energies for atoms which are partially ionized in the adsorbed state.[8] On the other hand, an adsorbed ion and its induced screening charge constitute a dipole p normal to the surface, which is responsible for the initial decrease of the work function of the metal[9,10] as a function of adsorbate concentration. This change in the work function Φ is given by

$$\frac{d\Phi}{dN} = -4\pi|p|, \quad N \to 0 \tag{1.1}$$

where N is the density of adsorbed atoms.

The modifications of the response arising when the external point charge is replaced by a polarizable ion or atom may also be significant, as indicated by measurements of the dielectric constant of adsorbed layers.[11] For example, a large enhancement of the polarizability of Xe atoms adsorbed on a Pd surface has recently been found by studying the work function as a function of coverage.[12]

According to classical electrostatics the interaction energy W between a static point charge of strength q and a perfect conductor is determined by the potential of a hypothetical charge $-q$, placed at the image point with respect to the surface:

$$W = -q^2/4\eta|z_0| , \tag{1.2}$$

where $|z_0|$ is the distance of the charge from the metal surface and η is the static dielectric constant of the bounding medium. On the other hand, since for an ideal conductor the screening charge induced in the metal is located on the surface, the dipole formed by the external and induced charges is given by

$$p = -q|z_0| , \tag{1.3}$$

and is directed normal to the surface.

The above expressions are valid only for distances $|z_0|$ large compared to the actual screening

length λ_s ($\lambda_s = 0$ for a perfect conductor) of the metal electron gas. For quantitative analyses it is very important to know in what way the divergence of (1.2) as one approaches the surface is removed by the effect of finite screening. Also, because of the long range of the image potential, it is important to determine the asymptotic multipolar corrections to the $1/|z_0|$ behavior. On the other hand, for $\lambda_s \neq 0$ the charge induced in the metal extends over a surface layer of finite thickness, a feature which may lead to deviations from the classical value (1.3) for the induced surface dipole.

In the case of moving external charges one expects the existence of dynamical corrections to the image potential (1.2), in addition to the static corrections considered above. Two kinds of dynamical effects may arise. First, if the velocity v of the external charge is comparable to velocities of metallic electrons, the screening response of the electrons is no longer adiabatic. This leads to corrections to (1.2) which depend on the ratio v/v_F, where v_F is the Fermi velocity. Second, a sufficiently fast particle may excite surface- and bulk-plasmon oscillations in the electron gas,[13] which will manifest themselves through additional corrections to the quasistatic image potential.

One of the objects of the present paper is to discuss results which are based on a simple phenomenological treatment of the response of metal surfaces to external charge distributions. This procedure, which will be referred to as a dielectric approximation (DA), is an alternative to a well-known procedure of a similar nature, which may be called the classical step-density approximation (SDA). The basic idea in both procedures is that instead of treating the metal response in a completely self-consistent way from first principles, one tries to simplify the problem by describing a certain part of it phenomenologically; the remaining part of the problem is then treated in a self-consistent way. Such procedures are useful not only for studying problems which may be too complicated to be handled satisfactorily from first principles (such as responses to polarizable charge distributions or to various dynamic perturbations), but also because they provide a simple understanding of the basic aspects of the response of metal surfaces. A number of self-consistent calculations of metal-surface responses have recently been carried out in the framework of the uniform background model for the ions (jellium model). Using various approximations, Lang and Kohn[14] and Hamann and Appelbaum[15] have calculated the image potential, whereas Ying, Smith, and Kohn[16] have studied screening charges and induced surface dipoles from such a point of view. Comparison with these results will enable us to assess the reliability of the phenomenological procedures in their detailed predictions. Before introducing the DA it is useful to discuss briefly the infinite-barrier model for a metal surface, as well as its quasiclassical version which is just the SDA mentioned above.

In the infinite-barrier model for a jellium system the bulk one-electron potential is assumed to be terminated at the surface by an infinite-potential step, which prevents the electron distribution from extending into the vacuum. Such a model was first introduced by Bardeen[17] for the study of work functions. In particular, Bardeen calculated the nonuniform electron density in the surface region, where it drops continuously from its bulk value to zero. He showed that the requirement of charge neutrality in the metal is satisfied if the jellium discontinuity is placed at a distance $u = 3\pi/8k_F$ (k_F is the Fermi wave number) below the surface. The response of the infinite-barrier model to point charges has recently been studied in the random-phase approximation (RPA) by Beck and Celli[18] and by Newns[19] and a number of related studies have also appeared.[20-26] In this case the induced charge-density fluctuation, like the unperturbed electron density, vanishes at the infinite-potential step. Beck and Celli[18] have also analyzed the quasiclassical limit of the infinite-barrier model. In this limit the unperturbed electron density is uniform right up to the surface where it then drops abruptly from its bulk value to zero. This is the SDA mentioned earlier, which has been applied to a variety of static-[20,21,24,25] and dynamic-response problems in recent years. In particular, the induced charge density no longer vanishes at the surface in this case. Beck and Celli find that the quasiclassical limit is obtained by neglecting the quantum-mechanical interference between incoming electrons and electrons reflected from the infinite barrier. They also point out that since in this approximation the electron density does not vanish at the surface, it describes a system whose true physical surface lies above the effective surface of discontinuity. The physical surface is defined by the infinite-potential step where the electron density vanishes. As discussed above, its position is chosen such that charge neutrality is satisfied in the quantum-mechanical treatment. Note that if one imposes charge neutrality within the quasiclassical limit, one is led to place the effective surface at the jellium background edge. It is important to emphasize the phenomenological nature of the quasiclassical SDA. Indeed, as discussed by Beck and Celli, this approximation cannot be fully justified in terms of a model for the surface since in general the interference terms may not be neglected. On the other hand, since it allows for some loss of coherence at the surface, one might expect it to be more realistic than the fully quantum-mechanical model of an

infinite potential barrier.[18] It is well known, however, that the detailed results for the SDA[18–20] differ quite strongly from those of the self-consistent calculations of the image potential[14,15] and of induced surface dipoles.[16]

On the contrary the DA, to which we now turn, leads to much more satisfactory results both for the image potential and for induced surface dipoles. This procedure is of a similar phenomenological nature as the quasiclassical SDA but it is not based on the infinite-barrier model, nor does it use a uniform-density approximation. Instead of starting directly from a density-response equation characterizing the surface in infinite-barrier[18,19] and self-consistent[14,16] treatments, we consider the equivalent nonlocal constitutive relation which relates the displacement and electric fields inside the bounded system. In this case the true surface is located at a point outside the jellium background where the total electron density has dropped to a sufficiently small value. In a spirit of neglecting the microscopic variations which are specific to the surface region, we replace the dielectric kernel in the constitutive relation everywhere by its known asymptotic form in the bulk. This approximation parallels closely the one of replacing the actual unperturbed electron-density profile by the average bulk density, as done in the SDA for the infinite-barrier model.[18] The DA and SDA must therefore be placed on similar footings and it is not possible, *a priori*, to discriminate in favor of one of them. We note that the two approximations are equivalent for systems described by a local dielectric constant, as may be the case for dielectrics, or for metals in an approximate high-frequency-response treatment. For nonlocal systems the two approximations are different and lead generally to quite different results. Just as in the SDA, we are led to introduce an effective surface at which the electron density is nonzero and such that the dielectric kernel has the bulk form in the interior and the empty-space form in the outside region. This effective surface must therefore be chosen to lie below the physical surface at which the electron density vanishes for a true surface model. On the other hand, since the region above it is assumed to be empty it cannot be placed inside the jellium background.

As in classical electrostatics,[27] the absence of a precise prescription for the position of the effective surface in the above approximations is related to the fact that the jellium background does not enter explicitly in the detailed description. Therefore the validity of such treatments is restricted to perturbing charges whose distance from the surface is large compared to the range of the electron-density variation near the jellium edge.

In Sec. II we formulate our DA in detail and illustrate it by calculating the response to static point charges in the Thomas–Fermi approximation. For comparison we also give a parallel discussion of the Thomas–Fermi theory in the SDA both in Sec. II and in Sec. III, which is devoted to detailed applications. Since various aspects of the Thomas–Fermi response of metal surfaces in the SDA have not been emphasized before,[20,21,18] we believe that the present study provides a more complete discussion for this case as well. In Sec. III we consider successively the calculation of the image potential, of the induced surface dipole, and of the corresponding quantities for point charges embedded in a metal surface. As a further illustration we study the response to polarizable charge distributions[28] and calculate various quantities of interest such as the effective polarizability, the induced surface dipole, and the image interaction for adsorbed ions.

In order to discuss the image-potential interaction for oscillating or moving external charges it is necessary to formulate the response of the metal surface for the case of dynamic perturbations. This generalization is discussed in the first part of Sec. IV, using the SDA and assuming specular reflection of electrons at the surface. In this treatment the instantaneous electrostatic potential and induced charge density are expressed in terms of a general dielectric function and depend, in addition, on the past trajectory of the external charge. The first part of Sec. IV concludes with some useful expressions for a "surface dielectric function" first introduced by Newns.[19] In a second part the general results are applied to the study of the dynamic image potential for charges moving uniformly along various prescribed trajectories. A general summary is given in Sec. V.

II. THOMAS-FERMI RESPONSE TO STATIC CHARGE DISTRIBUTIONS

A. Formulation of Procedures

We consider a bounded electron gas occupying the half-space $z>0$ and assume, for simplicity, that the half-space $z<0$ is unoccupied. The extension of the following discussion to the case of a bounding medium having a dielectric constant $\eta \neq 1$ is trivial. The response of the metal surface to a static external charge density $n_{\text{ext}}(\vec{r})$ is obtained by solving Maxwell's equations in the whole space. The bounded electron gas is described by a nonlocal constitutive relation giving the displacement field $\vec{D}(\vec{r})$ as a function of the total electric field $\vec{E}(\vec{r})$. Equivalently, one may characterize it by a density-response equation determining the induced charge-density fluctuation $\delta n(\vec{r})$ in terms of the electrostatic potential $V(\vec{r})$. Depending on whether one introduces $\vec{D}(\vec{r})$ or $\delta n(\vec{r})$ one has to solve either

$$\vec{\nabla}\cdot\vec{D}(\vec{r}) = 4\pi n_{\text{ext}}(\vec{r}) , \tag{2.1}$$

or Poisson's equation

$$\nabla^2 V(\vec{r}) = -4\pi[\delta n(\vec{r}) + n_{\text{ext}}(\vec{r})] , \tag{2.2}$$

with

$$\vec{E}(\vec{r}) = -\vec{\nabla} V(\vec{r}) . \tag{2.3}$$

Because of translational invariance parallel to the surface $z=0$ it is convenient to define Fourier components $f(z, k_\parallel)$ of the charge density and of the field components by

$$f(\vec{r}) = \frac{1}{(2\pi)^2} \int d\vec{k}_\parallel \, e^{i\vec{k}_\parallel \vec{\rho}} f(z, \vec{k}_\parallel) , \tag{2.4}$$

where $\vec{\rho} \equiv (x, y)$ and $\vec{k}_\parallel$ is a two-dimensional wave vector parallel to the surface. Since the problem is separable with respect to components of the fields parallel and perpendicular to the surface we introduce the vector notations $\vec{F}(z, \vec{k}_\parallel) \equiv [\vec{F}_\parallel(z), F_z(z)]$ and $E_\parallel(z) = \vec{E}_\parallel(z) \cdot \vec{k}_\parallel / k_\parallel$. We shall discuss the constitutive relations which are obtained in the phenomenological SDA and DA introduced in Sec. I. While a general discussion is deferred to Sec. IV, we restrict ourselves here to a linearized Thomas–Fermi treatment in view of the applications and because the differences between the two approximations are conveniently illustrated in this case.

In the SDA the true unperturbed electron density profile $n_0(\vec{r})$ for an infinite-barrier model is replaced by an abrupt step at an effective surface, which terminates a bulk electron gas of constant average density n_0. The linearized Thomas–Fermi density-response equation is then of the same form as for a homogeneous bulk system:

$$\delta n(\vec{r}) = -\frac{k_s^2}{4\pi} V(\vec{r}), \quad z>0 \tag{2.5}$$

where $\lambda_s = k_s^{-1}$ is the Thomas–Fermi screening length defined by

$$k_s^2 = 6\pi n_0 e^2 / \epsilon_F , \tag{2.6}$$

and ϵ_F is the Fermi energy for the homogeneous electron gas. Substitution in (2.2) and Fourier transformation then yields a closed equation for $V(z, k_\parallel) \equiv V(z)$:

$$\frac{d^2V(z)}{dz^2} - \alpha^2 V(z) = -4\pi n_{\text{ext}}(z, k_\parallel), \quad z>0 \tag{2.7}$$

where

$$\alpha = (k_\parallel^2 + k_s^2)^{1/2} . \tag{2.8}$$

The boundary conditions which follow from (2.2) are that $V(z)$ and $dV(z)/dz$ must be continuous in all space. The complete solution is then obtained by matching the bounded solution of (2.7) and its derivative, to the corresponding expressions in the vacuum region (which may be obtained by letting $k_s \to 0$).

On the other hand, in formulating the new DA we postulate the existence of an explicit form for the density-response equation between $\delta n(z, k_\parallel)$ and $V(z, k_\parallel)$ as derived, for example, in self-consistent or infinite-barrier treatments. We then assume that this equation has been transformed into an equivalent constitutive relation of the form

$$\vec{D}(z, \vec{k}_\parallel) = \theta(-z)\vec{E}(z, \vec{k}_\parallel) + \theta(z) \int_0^\infty dz' \epsilon(z, z', \vec{k}_\parallel)\vec{E}(z', \vec{k}_\parallel) , \tag{2.9}$$

which together with (2.1) and (2.3) determines $V(z, k_\parallel)$ and $\delta n(z, k_\parallel)$. The surface $z=0$ which is introduced in this expression is assumed to be placed a sufficient distance away from the jellium edge, such that the electron density in the region $z<0$ is negligible. The inhomogeneous kernel $\epsilon(z, z', \vec{k}_\parallel)$ is characteristic of the surface model and reduces asymptotically to the Fourier transform $\epsilon(z-z', \vec{k}_\parallel)$ of the bulk dielectric function for z and z' sufficiently far away from the surface. Our DA then amounts to introduce an effective sharp surface such that inside this surface the kernel $\epsilon(z, z', \vec{k}_\parallel)$ is replaced everywhere by its bulk expression $\epsilon(z-z', \vec{k}_\parallel)$, whereas outside of it it takes the empty-space form $\delta(z-z')$. As discussed in Sec. I, this effective surface is defined in a similar way as an effective surface in the SDA for the infinite-barrier model. Assuming now for convenience that the true surface is shifted towards the region $z<0$ such that our effective surface coincides with $z=0$, we thus approximate (2.9) by

$$\vec{D}(z, \vec{k}_\parallel) \simeq \theta(-z)\vec{E}(z, \vec{k}_\parallel) + \theta(z) \int_0^\infty dz' \epsilon(z-z', \vec{k}_\parallel)\vec{E}(z', \vec{k}_\parallel) . \tag{2.10}$$

We note that the screening charge obtained by solving (2.1) and (2.10) will generally include a surface charge contribution of a similar nature as the charge fluctuations which are found in elementary electrostatics[27] or in local studies of dynamic problems.[29] This is not surprising in view of the phenomenological nature of all these treatments. We also note that a dynamic version of the present DA has recently been applied by the author in a study of surface plasmons.[30]

It is clear that in the framework of a density-matrix formulation and for a given model of the surface the actual derivation of a constitutive relation of the form (2.9) will be even more involved than the derivation of the corresponding density-response equation. However, such a derivation would not be very helpful as far as the justification of the DA, Eq. (2.10), is concerned. Indeed, from the fact that the SDA cannot be viewed as a true approximation in the quantum treatment of an infinite-barrier model[18] one is led to suspect that, similarly, the DA cannot be fully justified in terms of a detailed model for the surface.

The Thomas–Fermi dielectric function is $\epsilon(k) = 1 + k_s^2 k^{-2}$, so that

$$\epsilon(z, k_\parallel) = \delta(z) + \frac{k_s^2}{2k_\parallel} e^{-k_\parallel |z|} , \qquad (2.11)$$

and from the Fourier transform of (2.1) and (2.3), combined with (2.10) and (2.11), we obtain the following integrodifferential equation:

$$\frac{d^2 E_\parallel(z)}{dz^2} - k_\parallel^2 E_\parallel(z) = -i \frac{k_s^2 k_\parallel}{2} \left[i \int_0^\infty dz' \, e^{-k_\parallel |z-z'|} E_\parallel(z') + \int_0^\infty dz' \, \mathrm{sgn}(z'-z) e^{-k_\parallel |z-z'|} E_z(z') \right] + 4\pi i k_\parallel n_{\mathrm{ext}}(z, k_\parallel), \quad z>0 . \qquad (2.12)$$

We may simplify the right-hand side of this equation by means of integrations by parts, using (2.3), and rewrite it in terms of the potential

$$V(z) = (i/k_\parallel) E_\parallel(z) . \qquad (2.13)$$

The final form of (2.12) is then

$$\frac{d^2 V(z)}{dz^2} - \alpha^2 V(z) = -\tfrac{1}{2} k_s^2 V(0^+) e^{-k_\parallel z} - 4\pi n_{\mathrm{ext}}(z, k_\parallel), \quad z>0 \qquad (2.14)$$

which depends parametrically on the value of the potential just inside the metal, and shows explicitly the difference between the DA and the SDA as characterized by (2.7).

Consistently with the use of a constitutive relation and of Eq. (2.1), one has to require that $D_z(z, k_\parallel)$ rather than $dV(z)/dz$ be continuous at the surface ($z=0$) if no external surface charges are present. This is also found to be necessary in the simple phenomenological treatment of surface plasmons based on a local high-frequency approximation for the dielectric constant.[29]

B. Static Point-Charge Perturbations

In the case of a static point charge of strength q placed at $z=z_0$ on the z axis we have

$$n_{\mathrm{ext}}(z, k_\parallel) = q\,\delta(z - z_0) .$$

We consider both the case where the charge is external to the metal surface ($z_0 < 0$) and where it is embedded in the surface ($z_0 > 0$). Furthermore, for the purpose of later discussion we present explicit expressions for the potential $V(z, k_\parallel)$ as well as for the induced bulk and surface screening charges. The bulk density fluctuation $\delta n(z, k_\parallel)$ is defined through Poisson's equation (2.2):

$$\delta n(z, k_\parallel) = -\frac{1}{4\pi} \left(\frac{d^2 V(z, k_\parallel)}{dz^2} - k_\parallel^2 V(z, k_\parallel) \right) - q\,\delta(z - z_0), \quad z>0 \qquad (2.15)$$

and from Gauss's theorem the surface charge fluctuation $\sigma(k_\parallel)$ is

$$4\pi\sigma(k_\parallel) = \left(\frac{dV(z, k_\parallel)}{dz} \right)_{z=0^-} - \left(\frac{dV(z, k_\parallel)}{dz} \right)_{z=0^+} . \qquad (2.16)$$

Here 0^+ and 0^- denote points just outside and just inside the metal surface.

In the SDA a straightforward solution of (2.7), by the method of variation of constants, and the matching of $V(z, k_\parallel)$ and $dV(z, k_\parallel)/dz$ to the vacuum solutions at $z=0$ yield the explicit expressions

$$V(z, k_\parallel) = V_i(z, k_\parallel) + V_0(z, k_\parallel) , \qquad (2.17)$$

where the direct term

$$V_0(z, k_\parallel) = 2\pi q \left[\frac{1}{\alpha} e^{-\alpha |z-z_0|} \theta(z)\theta(z_0) + \frac{1}{k_\parallel} e^{-k_\parallel |z-z_0|} \theta(-z)\theta(-z_0) \right] , \qquad (2.18)$$

is the potential of an external charge in homogeneous infinite media and $V_i(z, k_\parallel)$ is the induced potential which is due to the presence of the interface:

$$V_i(z, k_\parallel) = \frac{2\pi q}{\alpha + k_\parallel} \left[\frac{\alpha - k_\parallel}{\alpha} e^{-\alpha(z+z_0)} \theta(z_0) + 2e^{k_\parallel z_0} e^{-\alpha z} \theta(-z_0) \right] , \quad z>0 \qquad (2.19a)$$

$$= \frac{2\pi q}{\alpha + k_\parallel} \left[2e^{-\alpha z_0} e^{k_\parallel z} \theta(z_0) - \frac{\alpha - k_\parallel}{k_\parallel} e^{k_\parallel (z+z_0)} \theta(-z_0) \right] , \quad z<0 . \qquad (2.19b)$$

The bulk density fluctuation is given by

$$\delta n(z, k_\parallel) = -q k_s^2 \left[\frac{1}{2\alpha} \left(\frac{\alpha - k_\parallel}{\alpha + k_\parallel} e^{-\alpha(z+z_0)} + e^{-\alpha |z-z_0|} \right) \theta(z_0) + \frac{1}{\alpha + k_\parallel} e^{k_\parallel z_0} e^{-\alpha z} \theta(-z_0) \right] \theta(z) , \qquad (2.20)$$

and the surface charge obviously vanishes in this case. In these expressions we have combined the results for charges embedded in the metal and for charges external to it, $\theta(z)$ being the unit step function, $\theta(z) = 1$ for $z>0$, $\theta(z) = 0$ for $z<0$. The characteristic features of the above expressions at long wavelengths are the rapid decay of the induced potential and of the induced density fluctuation inside

the metal, and the slow decay of the induced potential in the vacuum region. Note that the second term in (2.20) for an embedded charge is just the fluctuation which would be induced in a homogeneous electron gas.

Turning to the DA, we find that the potential inside the metal as obtained by solving (2.14) is of the form (2.17), where $V_0(z, k_\parallel)$ is given by (2.18) and

$$V_i(z, k_\parallel) = ae^{-\alpha z} + \tfrac{1}{2} V(0^+, k_\parallel) e^{-k_\parallel z}, \quad z > 0 . \quad (2.21)$$

Here $V(0^+, k_\parallel)$ may be readily expressed in terms of the arbitrary constant a. We also require the explicit form of $D_z(z, k_\parallel)$ in the metal region, which is obtained from (2.10) and (2.11) by substituting $E_z(z, k_\parallel)$ as given by (2.3), (2.17), (2.18), and (2.21). After some straightforward calculations we get

$$D_z(z, k_\parallel) = \frac{k_\parallel}{2}\left\{\frac{k_s^2}{k_\parallel^2}\,\frac{\alpha}{\alpha - k_\parallel}\,a + V(0^+, k_\parallel)\left[1 + \frac{k_s^2}{2k_\parallel}\left(z + \frac{1}{2k_\parallel}\right)\right]\right\} e^{-k_\parallel z}$$
$$+ 2\pi q \frac{\alpha}{k_\parallel}\left(e^{-k_\parallel |z - z_0|} - \frac{k_s^2}{2\alpha(\alpha + k_\parallel)}\, e^{-\alpha z_0} e^{-k_\parallel z}\right) \operatorname{sgn}(z - z_0)\,\theta(z_0), \quad z > 0 . \quad (2.22)$$

In the vacuum region we have

$$V(z, k_\parallel) = be^{k_\parallel z} + \frac{2\pi q}{k_\parallel} e^{-k_\parallel |z - z_0|}\,\theta(-z_0), \quad z < 0 \quad (2.23)$$

and by matching $V(z, k_\parallel)$ and $D_z(z, k_\parallel)$ at $z = 0$ we determine the constants a and b. The final results are

$$V_i(z, k_\parallel) = 2\pi q \left\{\frac{e^{-\alpha z_0}}{\alpha}\left[e^{-k_\parallel z} - \frac{\Delta'}{\Delta}\,(e^{-\alpha z} + e^{-k_\parallel z})\right]\theta(z_0) + \frac{2e^{k_\parallel z_0}}{k_\parallel \Delta}(e^{-\alpha z} + e^{-k_\parallel z})\,\theta(-z_0)\right\}, \quad z > 0 \quad (2.24a)$$

$$V_i(z, k_\parallel) = 2\pi q \left[\frac{2}{\alpha}\, e^{-\alpha z_0}\left(1 - \frac{\Delta'}{\Delta}\right)e^{k_\parallel z}\,\theta(z_0) + \frac{1}{2k_\parallel \Delta}\left(1 - \frac{3}{2}\frac{k_s^2}{k_\parallel^2} - \frac{\alpha}{k_\parallel}\right)e^{k_\parallel (z + z_0)}\,\theta(-z_0)\right], \quad z < 0 \quad (2.24b)$$

where

$$\Delta = \frac{1}{2}\left(7 + \frac{3}{2}\frac{k_s^2}{k_\parallel^2} + \frac{\alpha}{k_\parallel}\right) , \quad (2.25)$$

$$\Delta' = \frac{1}{2}\left(7 + \frac{3}{2}\frac{k_s^2}{k_\parallel^2} - \frac{\alpha}{k_\parallel}\right) - \frac{\alpha^2}{k_\parallel^2}\, e^{(\alpha - k_\parallel) z_0} . \quad (2.26)$$

The density fluctuations (2.15) and (2.16) are then given by

$$\delta n(z, k_\parallel) = -q k_s^2 \left[\frac{1}{2\alpha}\left(e^{-\alpha |z - z_0|} - \frac{\Delta'}{\Delta}\, e^{-\alpha (z + z_0)}\right)\theta(z_0) + \frac{1}{k_\parallel \Delta}\, e^{k_\parallel z_0} e^{-\alpha z}\,\theta(-z_0)\right]\theta(z) , \quad (2.27)$$

$$\sigma(k_\parallel) = -\frac{q}{2}\left[\frac{e^{-\alpha z_0}}{\alpha}\left((\alpha + 3k_\parallel)\frac{\Delta'}{\Delta} + \alpha - 3k_\parallel\right)\theta(z_0) + \frac{e^{k_\parallel z_0}}{\Delta}\left(1 + \frac{3}{2}\frac{k_s^2}{k_\parallel^2} - \frac{\alpha}{k_\parallel}\right)\theta(-z_0)\right] . \quad (2.28)$$

As seen from (2.24a), the potential inside the metal has now additional slowly decaying components at long wavelengths. This indicates that the screening is less efficient in the DA than in the SDA. Another difference lies in the fact that for an embedded charge the potential (2.24a) and the induced screening charge (2.27) contain a term which is independent of the distance $|z_0|$ in the limit $k_\parallel \to 0$. This term arises from the last term in (2.26), which in turn is due to the first term in the second bracket of (2.22). Finally, we note that in the limit $\lambda_s = k_s^{-1} \to 0$ and for a charge external to the surface the induced potentials (2.19b) and (2.24b) reduce to the vacuum potentials of a charge $-q$ placed at $-z_0$. This is precisely the potential of the classical image charge in a perfect conductor.

III. DETAILED APPLICATIONS

In our discussion of point charges we are mainly interested in the electrostatic potential $V(\vec{r}) \equiv V(z, \vec{\rho})$ and in the surface dipole $\vec{p} = (0, 0, p)$ constituted by the external charge and the induced screening charge. Using (2.4), we have

$$V(z, \vec{\rho}) = \frac{1}{2\pi}\int_0^\infty dk_\parallel J_0(k_\parallel \rho) k_\parallel V(z, k_\parallel) , \quad (3.1)$$

where $J_0(x)$ is the Bessel function of the first kind, and we note that $J_0(0) = 1$. In particular, the interaction energy W between the charge q placed at

$\vec{r} = (0, 0, z_0)$ and the metal surface is given by

$$W = \frac{q}{4\pi} \int_0^\infty dk_\parallel k_\parallel V_i(z_0, k_\parallel) . \quad (3.2)$$

For a charge external to the surface this represents the so-called image potential interaction. Using the charge neutrality condition

$$\int_{0^-}^\infty dz[\delta n(z, k_\parallel = 0) + \delta(z)\sigma(k_\parallel = 0)] = -q , \quad (3.3)$$

which may be checked explicitly from (2.20) and (2.27) and (2.28), the induced surface dipole is given by

$$p = q\left(z_0 - \int_0^\infty dz \frac{z\delta n(z, k_\parallel = 0)}{-q}\right) . \quad (3.4)$$

This quantity measures the distance between the external charge and the center of mass of the bulk screening charge averaged over x and y. We shall now discuss successively the image potential, the surface dipole and the corresponding quantities for charges embedded near the surface. Finally we shall analyze some properties in the case where the external point charge is replaced by a polarizable atom or ion adsorbed on the surface.

A. Image Potential

Using (2.19b) and (2.24b) the explicit expressions for the interaction energy (3.2) for a charge outside the surface are

$$W_{sda} = -\frac{q^2 k_s}{2} \int_0^\infty dx\, e^{-2k_s|z_0|x} (x - \sqrt{1+x^2})^2 , \quad (3.5)$$

in the SDA, and

$$W_{da} = -\frac{q^2 k_s}{2} \int_0^\infty dx\ e^{-2k_s|z_0|x} \times \frac{3 - 2x[x - (1+x^2)^{1/2}]}{3 + 2x[7x + (1+x^2)^{1/2}]} , \quad (3.6)$$

in the DA. The image potential (3.5) has been derived previously by Newns[20] and an equivalent expression has been given by Sidyakin.[21] One may easily verify that both (3.5) and (3.6) lead to a finite result in the limit $z_0 \to 0$ and that they coincide with the classical expression (1.2) for an ideal conductor ($\lambda_s = 0$). This shows that the finite screening effect removes the $1/|z_0|$ divergence of the classical image potential. Because of the long range of the image potential it is of interest to examine the asymptotic corrections to the classical expression for $2k_s|z_0| \gg 1$, i.e., for distances large compared to the screening length. In this limit we obtain from (3.5) and (3.6)

$$W_{sda} = -\frac{q^2}{4|z_0|}\left(1 - \frac{1}{k_s|z_0|} + \frac{1}{k_s^2|z_0|^2} + \cdots\right) , \quad (3.7)$$

$$W_{da} = -\frac{q^2}{4|z_0|}\left(1 - \frac{8}{3k_s^2|z_0|^2} + \frac{8}{3k_s^3|z_0|^3} + \cdots\right) . \quad (3.8)$$

An important difference between these two expressions is the absence of a term of $O(k_s^{-1}|z_0|^{-1})$ in W_{da}.

We now observe that (3.7) and (3.8) may be rewritten in the form

$$W_{sda} = -\frac{q^2}{4(|z_0| + k_s^{-1})} + O(k_s^{-4}|z_0|^{-4}) \quad (3.9)$$

and

$$W_{da} = -\frac{q^2}{4|z_0|} + O(k_s^{-3}|z_0|^{-3}) . \quad (3.10)$$

This shows that to lowest order in the asymptotic corrections the classical image potential is unchanged in the DA. On the other hand, the classical image potential remains also valid in the SDA if instead of measuring distances from the electron density step one now measures them from a new effective surface which is shifted by a screening length, $\lambda_s = k_s^{-1}$, towards the interior of the metal. In order to clarify the meaning of the new effective surface we calculate the position of the center of mass of the screening charge. Since this center of mass lies on the z axis it is given by

$$z_1 = \frac{1}{-q} \int_{0^-}^\infty dz\, z \int d\vec{\rho}[\delta n(z, \vec{\rho}) + \sigma(\vec{\rho})\delta(z)] ,$$

$$= \frac{1}{-q} \int_{0^-}^\infty dz\, z\delta n(z, k_\parallel = 0) . \quad (3.11)$$

Substitution of (2.20), (2.27), and (2.28) then yields

$$z_1 = k_s^{-1} \quad \text{for the SDA,} \quad (3.12)$$

$$z_1 = 0 \quad \text{for the DA,} \quad (3.13)$$

where (3.13) is a direct consequence of the fact that the average over $\vec{\rho}$ of the bulk density (2.27) vanishes for all z. This shows that the effective reference surfaces in the pseudoclassical image potentials (3.9) and (3.10) lie at the centers of mass of the induced density fluctuation. Furthermore, the fact that (3.9) and (3.10) contain no terms proportional to the inverse square of the distance to the center of mass means that an expansion of the image potential into a multipole series includes no dipole contributions. Finally we mention the work of Lang and Kohn for a self-consistent surface model.[14] These authors have shown that in this case the classical image potential is also valid in first approximation if the distance of the external charge from the surface is interpreted as being the distance of this charge from the center of mass of the induced charge density. This is in complete agreement with the present conclusions.

A precise comparison of the results for the image

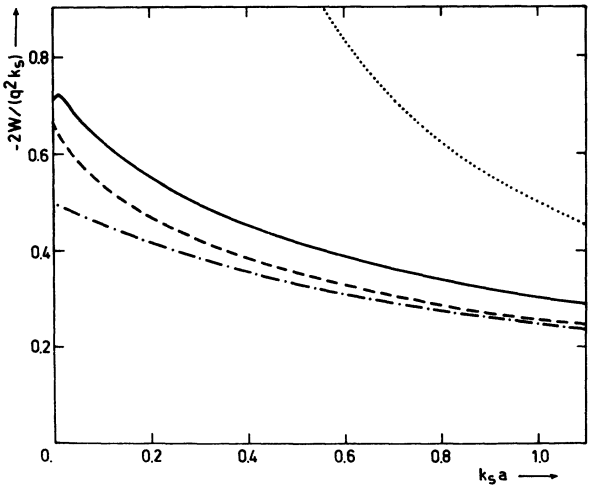

FIG. 1. Image attraction energy W versus distance $a \equiv |z_0|$ from surface. Classical result, assuming $k_s \to \infty$ (dotted curve); dielectric approximation Thomas–Fermi result (full curve); step-density approximation Thomas–Fermi result (dashed curve); Gomer–Swanson formula (dashed-dotted curve).

potential obtained in various treatments of the jellium model is difficult because of the differences in the models for the surface and in the approximations used. However, if the jellium discontinuity is used as a common reference to fix the distance $|z_0|$, one finds that the effective surface for the classical image potential is outside the jellium for the self-consistent results[14,15] while, according to (3.9) and (3.10), it is inside the jellium for the SDA and at the jellium edge for the DA. In this regard the DA is thus much more satisfactory than the SDA, especially since for the DA one might actually place the effective surface slightly outside the jellium background (see Sec. I). We also note that in the quantum-mechanical treatment of the infinite-barrier model[18,19] the effective classical surface is placed even further below the jellium edge than in the SDA.

At short distances the integrals in (3.5) and (3.6) must be computed numerically, although we note that (3.5) may be expressed in terms of several tabulated functions.[21] The results as a function of $k_s|z_0|$ are plotted in Fig. 1 and are compared to the classical expression (1.2), as well as to the phenomenological interaction

$$W = -\frac{q^2}{4(|z_0| + k_s^{-1})}, \tag{3.14}$$

introduced by Gomer and Swanson[4,20] for the interpretation of field desorption data. It follows that at short distances the difference between W_{da} and W_{sda} is rather small compared to the differences with the classical expression. As expected, W_{sda} agrees better with (3.14) than W_{da}. However, it must be recalled that the Thomas–Fermi approximation becomes inaccurate in the range of distances $|z_0| < k_s^{-1}$, where the short-wavelength behavior of $\epsilon(k)$ plays an important role.

It is interesting to reinterpret the image potential in the DA in order to separate the contributions of surface and bulk screening charges, respectively. The image interaction energy may be written in the general form

$$W = \tfrac{1}{2}\int_{0^-}^{\infty} dz \int d\vec{\rho}\, V_0(z, \vec{\rho})\, \delta\rho(z, \vec{\rho}), \tag{3.15}$$

where $V_0(z, \vec{\rho})$ is the vacuum potential of the external charge and $\delta\rho(z, \vec{\rho})$ denotes the sum of the induced bulk and surface charge fluctuations $\delta n(z, \vec{\rho})$ and $\sigma(\vec{\rho})$. Thus by using the definition (2.4) of Fourier transforms we obtain for the case of an external charge placed on the z axis

$$W = W^S + W^B, \tag{3.16}$$

$$W^S = \frac{1}{4\pi}\int_0^{\infty} dk_{\parallel}\, k_{\parallel}\, V_0(z=0, k_{\parallel})\sigma(k_{\parallel}), \tag{3.17}$$

$$W^B = \frac{1}{4\pi}\int_0^{\infty} dz \int_0^{\infty} dk_{\parallel}\, k_{\parallel}\, V_0(z, k_{\parallel})\delta n(z, k_{\parallel}), \tag{3.18}$$

where $V_0(z, k_{\parallel})$ is given by the second term in (2.18). In the case of the SDA, where the screening charge includes only bulk charge, one may easily verify from (2.18) and (2.20) that (3.18) reduces to the explicit expression (3.5). Turning to the DA, we obtain from (2.27) and (2.28)

$$W^S_{da} = -\frac{q^2 k_s}{2}\int_0^{\infty} dx\, \frac{3 + 2x[x - (1+x^2)^{1/2}]}{3 + 2x[7x + (1+x^2)^{1/2}]}\, e^{-2k_s|z_0|x}, \tag{3.19}$$

$$W^B_{da} = \frac{q^2 k_s}{2}\int_0^{\infty} dx\, \frac{4x[x - (1+x^2)^{1/2}]}{3 + 2x[7x + (1+x^2)^{1/2}]}\, e^{-2k_s|z_0|x}. \tag{3.20}$$

The sum of these two contributions coincides with (3.6). The asymptotic expressions for $2k_s|z_0| \gg 1$ are

$$W^S_{da} = -\frac{q^2}{4|z_0|}\left(1 - \frac{2}{3k_s|z_0|} + \frac{34}{9k_s^2|z_0|^2} + \cdots\right), \tag{3.21}$$

$$W^B_{da} = -\frac{q^2 k_s}{6}\left(\frac{1}{k_s^2|z_0|^2} - \frac{5}{3k_s^3|z_0|^3} + \cdots\right). \tag{3.22}$$

This shows that in the DA the classical image-potential term arises from an induced surface charge, just like in the classical electrostatic treatment.[27] Furthermore, the absence of a dipole term of $O(|z_0|^{-2})$ in the asymptotic expression of W_{da} is seen to be due to an exact cancellation of terms of this order between surface and bulk charge contributions. Finally, the actual corrections to the classical image

potential may be interpreted as due to deviations of the induced surface charge from its uniform value, and to variations of the induced bulk charge about its zero average value.

B. Surface Dipole

According to (3.4), (3.12), and (3.13), the surface dipoles constituted by the external charge placed at z_0 and the induced charge fluctuations are given by

$$p_{\mathrm{sda}} = -q(|z_0| + k_s^{-1}) , \tag{3.23}$$

$$p_{\mathrm{da}} = -q|z_0| , \tag{3.24}$$

where the first expression is similar to one obtained by Newns.[19,20] The minus sign indicates that the induced dipole points out of the surface for $q>0$ and towards the inside for $q<0$. Thus we find that in the Thomas–Fermi treatment for the DA the classical expression (1.3) for the induced surface dipole remains unchanged.

On the other hand, self-consistent calculations by Ying, Smith, and Kohn[16] have shown that the induced surface dipole vanishes in the Thomas–Fermi approximation when the external charge is moved through the surface region. In this case the center of mass of the screening charge remains located at the position of the external charge, which is also the reason why such a calculation does not allow one to recover the classical image potential. In later work[31] Kohn and co-workers have shown that by including the first gradient correction to the linearized Thomas–Fermi equation in a self-consistent scheme, one is able to obtain a surface dipole which varies with $|z_0|$, as well as to recover the image potential.

The effect of the gradient of the density fluctuation in the self-consistent response equation is similar to that of an effective surface of discontinuity for the electrons, in that it keeps the center of mass of the induced charge away from the position of the external charge.[32] In this sense the results for the SDA and the DA in the Thomas–Fermi case are more general than those of a self-consistent Thomas–Fermi treatment,[16] since in the latter the c.m. of the induced charge is not delocalized with respect to the external charge. In particular, this suggests that it is appropriate to regard the corrections to the classical dipole (1.3), rather than the total dipoles themselves, as the analog of the self-consistent dipoles calculated by Kohn *et al.*[16] Such a comparison shows that the present DA is superior to the SDA since it leads to a vanishing correction to the classical surface dipole in the Thomas–Fermi approximation.

As pointed out by Newns,[19] there is some evidence for the existence of a correction to the classical dipole (1.3), based on work function changes as a result of adsorption of Cs atoms on tungsten at low coverage. However, these considerations rely on field emission data by Sidorski, Pelley, and Gomer,[9] where there are some problems related to the determination of the coverage values. More recent data by Lee, Blott, and Hopkins[10] lead to the value $|p| \simeq 2.06\, e$Å for Cs on W(110) and earlier data by Schmidt and Gomer[9] give $|p| \simeq 1.64e$ Å for K on W(110). These values are based on the assumption that the charge of the adsorbed ion is just minus one unit of electron charge, $|q| = e$. We observe that these results agree to better than 20% with Eq. (3.24) if we take for $|z_0|$ the ionic radii,[33] $R_{\mathrm{Cs}^+} = 1.69$ Å and $R_{\mathrm{K}^+} = 1.33$ Å, which seems to be a reasonable choice for the case of adsorption on a closely packed crystal face.

C. Charges Embedded in Metal Surface

The interaction energy of the embedded charge ($z_0>0$) with the metal surface is obtained from (2.19a), (2.24a), and (3.2). We find

$$W_{\mathrm{sda}} = \frac{q^2}{2k_s^2}\int_0^\infty dk_{\parallel}\frac{k_{\parallel}}{\alpha}(\alpha - k_{\parallel})^2 e^{-2\alpha z_0} \tag{3.25}$$

in the SDA and

$$W_{\mathrm{da}} = -\frac{q^2}{2}\int_0^\infty dk_{\parallel}\frac{k_{\parallel}}{\alpha}\left[\frac{14k_{\parallel}^2 + 3k_s^2 - 2\alpha k_{\parallel} - 4\alpha^2 e^{(\alpha - k_{\parallel})z_0}}{14k_{\parallel}^2 + 3k_s^2 + 2\alpha k_{\parallel}} \times (e^{-\alpha z_0} + e^{-k_{\parallel} z_0}) - e^{-k_{\parallel} z_0}\right] e^{-\alpha z_0} \tag{3.26}$$

in the DA. At large distances these expressions take the form

$$W_{\mathrm{sda}} = \frac{q^2}{4z_0}\left[1 - \left(\frac{\pi}{k_s z_0}\right)^{1/2} + \cdots\right] e^{-2k_s z_0} , \tag{3.27}$$

$$W_{\mathrm{da}} = \frac{q^2}{6k_s z_0^2}\left(1 - \frac{2}{3k_s z_0} + \cdots\right) , \tag{3.28}$$

which verifies that in the classical limit of a perfect conductor the interaction vanishes for both approximations. Two characteristic features are the repulsive nature of the interaction and the fact that W_{sda} is much more localized than W_{da}. It is also instructive to study the induced surface dipole, although for an embedded charge this dipole is not directly connected to a measurable quantity. By substituting (2.20) and (2.27) in (3.4), we obtain successively

$$p_{\mathrm{sda}} = -\frac{q}{k_s} e^{-k_s z_0} , \tag{3.29}$$

$$p_{\mathrm{da}} = -\frac{2}{3}\frac{q}{k_s} . \tag{3.30}$$

We note that these dipoles vanish in the classical limit, as expected. In comparing the results for the case where the charge is external to the surface and where it is embedded in it, we observe

that terms of the same form as those which have disappeared in (3.8) and (3.24), as compared to (3.7) and (3.23), appear now in the corresponding expressions when the charge is inside the metal.

The differences in the form of the interactions (3.27) and (3.28) and of the induced dipoles (3.29) and (3.30) may be interpreted as follows.

In the SDA the induced potential and charge (2.19a) and (2.20) are nonzero only because the surface lies at a finite distance from the embedded charge q. Therefore we identify the interaction (3.27) and the dipole (3.29) as typical finite-size effects. On the other hand, the contributions (3.28) and (3.30) arise from terms in (2.24a) and (2.27) which do not vary with the distance z_0 in the limit $k_{\parallel} \to 0$. One might therefore interpret them as describing true surface effects, as opposed to finite-size effects.

We observe that for an embedded charge far away from the surface the induced surface dipole vanishes in the SDA, as it does in the self-consistent Thomas–Fermi treatment of Kohn and co-workers.[16] Thus in this limit the SDA yields a more accurate result for the surface dipole than the DA. However, at very small distances, where both (3.29) and (3.30) are inaccurate, the DA gives a slightly better result. Unfortunately it is not possible to make a more detailed comparison of the above treatments with self-consistent calculations since, as emphasized before, they cannot be fully justified in terms of a true surface model. Finally, we note that the significance of the above results for charges embedded in the surface is probably rather questionable because of the role of nonlinear screening effects in this case.

D. Polarizable Charge Distributions

We now turn to some aspects of the response of metal surfaces to real ions or atoms located outside the metal. In the case of an ion, the point-charge interaction energy and induced surface dipole will be modified if one allows for the finite polarizability of the ion. Furthermore, it is known experimentally[11,12] that the polarizability of an adsorbed ion or atom may be strongly enhanced relative to its free-space value. In the following we study these effects in the framework of a Thomas–Fermi treatment, using the DA of Sec. II. A similar analysis for the SDA has recently been given by Antoniewicz[28] and we shall briefly review his results for comparison.

In order to calculate the effective polarizability α of an adsorbed atom we assume the presence of a uniform electric field E_0 normal to the surface, which induces a point dipole of the same direction on the atom. First we recall the expression for α in classical electrostatics. The dipole moment $\vec{\mu}$ which is induced on the atom is given by

$$\vec{\mu} = (0,\ 0,\ \mu)\,, \quad \mu = \alpha_0(E_0 + E_d)\,, \tag{3.31}$$

where α_0 is the polarizability of the free atom and E_d is the field at the ion position z_0 ($z_0 < 0$) due to the image dipole induced in the metal:

$$E_d \equiv E_d^{\text{class}} = 2\mu/(2|z_0|)^3\,. \tag{3.32}$$

In this approximation, the effective polarizability of the atom is thus

$$\alpha \equiv \frac{\mu}{E_0} = \frac{\alpha_0}{1 - \alpha_0/4|z_0|^3}\,, \tag{3.33}$$

and for a dipole normal to the surface the dipole-image dipole interaction U is given by

$$U \equiv U^{\text{class}} = -\mu^2/(2|z_0|)^3\,. \tag{3.34}$$

In (3.31) we have neglected the effects associated with the charge density induced by the external field in the absence of the adsorbed atom. Since the corresponding induced field may be represented by the image field of an external charge placed a large distance away from the surface it is negligible compared to the field of the image of the point dipole induced on the atom. If the perturbing system is an ion, the point-charge image force acts as an external field which polarizes the ion and thus leads to a charge-dipole interaction and to an additional contribution to the induced surface dipoles. Since, in particular, the denominator of (3.33) is singular as one approaches the surface it is of interest to study the modifications of these results due to a finite electron screening length.

Following Antoniewicz,[28] we observe that the induced potential $V_i^d(z, \vec{\rho})$ created by a dipole $(0, 0, \mu)$ at $z_0 < 0$ may be obtained from the superposition of potentials of the form (2.24b) and (2.19b) of two point charges q and $-q$ placed at z_0 and $z_0 + \Delta z_0$, respectively. Indeed, this represents the induced potential for a dipole if we take the limit $q \to \infty$, $\Delta z_0 \to 0$ while keeping the dipole moment $\mu = -q\Delta z_0$ finite. In this way we get

$$V_i^d(z, \vec{\rho}) = -\mu k_s^2 \int_0^\infty dx\, J_0(k_s\rho x)\, x\, f e^{k_s(z+z_0)x}, \qquad z < 0 \tag{3.35}$$

$$f = [x - (1 + x^2)^{1/2}]^2 \tag{3.36}$$

in the SDA, and

$$V_i^d(z, \vec{\rho}) = -\mu k_s^2 \int_0^\infty dx\, J_0(k_s\rho x)\, x g(x) e^{k_s(z+z_0)x}, \qquad z < 0 \tag{3.37}$$

$$g(x) = \frac{3 - 2x[x - (1 + x^2)^{1/2}]}{3 + 2x[7x + (1 + x^2)^{1/2}]} \tag{3.38}$$

in the DA. The field of the image dipole at the position of the ion is defined by

$$E_d(z = z_0, \vec{\rho} = 0) \equiv -\left(\frac{\partial V_i^d(z, \vec{\rho} = 0)}{\partial z}\right)_{z=z_0} = \gamma E_d^{\text{class}}\,, \tag{3.39}$$

and is normal to the surface. The dimensionless quantity γ is then given by

$$\gamma \equiv \gamma_{sda} = 4(k_s|z_0|)^3 \int_0^\infty dx\, x^2 f(x) e^{2k_s z_0 x} , \quad (3.40)$$

$$\gamma \equiv \gamma_{da} = 4(k_s|z_0|^3) \int_0^\infty dx\, x^2 g(x) e^{2k_s z_0 x} , \quad (3.41)$$

in the SDA and DA, respectively. Using (3.31), (3.39), and (3.32) the effective polarizability is found to be

$$\alpha = \frac{\alpha_0}{1 - \gamma\alpha_0/4|z_0|^3} . \quad (3.42)$$

The quantity γ, which describes the finite screening effect, is equal to one in the classical case and is plotted numerically in Fig. 2 as a function of $k_s|z_0|$. The curve for γ_{sda} has been taken from the work of Antoniewicz.[28] An important effect of a finite screening length in the present case is to remove the divergence for $z_0 \to 0$ in the denominator of the classical expression for the effective polarizability. The asymptotic forms for γ are

$$\gamma_{sda} = 1 - \frac{3}{k_s|z_0|} + \frac{6}{k_s^2|z_0|^2} + \cdots , \quad (3.43)$$

$$\gamma_{da} = 1 - \frac{16}{k_s^2|z_0|^2} + \cdots , \quad (3.44)$$

and we note that, just like the lowest corrections to the image potential, this quantity may be interpreted as an effective shift of the image plane[28] in the classical expression (3.33). The order of magnitude of the enhancement factor in α depends critically on the distance of the atom from the surface. In the case of an adsorbed ion this distance might be identified with the ionic radius, in which case the classical correction ($\gamma = 1$) to α amounts typically to 15% for a Cs^+ ion.

We now consider the effect of the polarizability of an ion of charge q on its interaction with a metal surface. In this case the field E of the induced image charge acts to polarize the ion, just like an applied external field. According to (2.19b), (2.24b), and (3.1) E is given by

$$E \equiv E_{sda}(z = z_0, \vec{\rho} = 0) = q k_s^2 \int_0^\infty dx\, x f(x) e^{2k_s z_0 x} , \quad (3.45)$$

$$E \equiv E_{da}(z = z_0, \vec{\rho} = 0) = q k_s^2 \int_0^\infty dx\, x g(x) e^{2k_s z_0 x} , \quad (3.46)$$

whose asymptotic expressions are

$$E_{sda}(z_0, 0) = \frac{q}{(2|z_0|)^2}\left(1 - \frac{2}{k_s|z_0|} + \frac{3}{k_s^2|z_0|^2} + \cdots\right) , \quad (3.47)$$

$$E_{da}(z_0, 0) = \frac{q}{(2|z_0|)^2}\left(1 - \frac{8}{k_s^2|z_0|^2} + \frac{32}{3k_s^3|z_0|^3} + \cdots\right) . \quad (3.48)$$

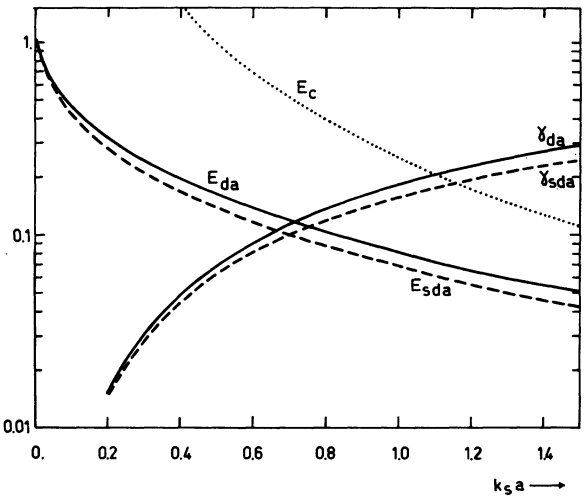

FIG. 2. Parameter γ determining the effective polarizability of an ion, and point-charge image field E acting on the ion [in units of (charge) $\times k_s^2$], versus distance $a \equiv |z_0|$ from the surface. Dielectric approximation Thomas–Fermi results (full curves); step-density approximation Thomas–Fermi results (dashed curves); classical values: $\gamma_c = 1$ and E_c (dotted curve).

In Fig. 2 we have plotted the image charge fields (3.45) and (3.46) for small $|z_0|$ and compared them with the classical result. Equation (3.45) coincides with the result of Antoniewicz, who expressed the integral in terms of tabulated functions but did not plot it numerically. This leads to an effective induced charge-dipole interaction energy

$$W_1 = -\tfrac{1}{2}\alpha E^2 , \quad (3.49)$$

which, in the first approximation, is simply to be added to the point-charge interactions (3.5) and (3.6). In the classical case,

$$W_1 \equiv W_1^{class} = -\alpha q^2/2(2|z_0|)^4 .$$

Finally, a rather more significant effect is the influence of the polarizability on the induced surface dipole for an adsorbed ion. In first approximation the surface dipole for a polarizable ion is given by a point-charge contribution of the form (3.23) or (3.24) plus twice the effective point dipole due to the field of the image charge:

$$p_{sda} = -q(|z_0| + k_s^{-1}) + 2\alpha E_{sda}(z_0, 0) , \quad (3.50)$$

$$p_{da} = -q|z_0| + 2\alpha E_{da}(z_0, 0) . \quad (3.51)$$

The factor 2 comes from the effect of the image point dipole. By putting numbers in these expressions we find that the finite polarizability reduces the induced surface dipole by as much as 20% to 30% for alkali ions.[34] This effect reduces appre-

ciably the agreement between experimental and theoretical values for induced surface dipoles which was discussed earlier using Eq. (3.24). Finally, on the basis of our previous discussion for point charges we expect the results of the DA to be more accurate than those of the SDA for the present case.

IV. RESPONSE TO TIME-DEPENDENT CHARGE DISTRIBUTIONS

A. Formulation

In this section we consider the response of metal surfaces to time-dependent external charge distributions, using a rather general description in terms of the dielectric function $\epsilon(k, \omega)$ of a homogeneous electron gas. Such a treatment could be applied to study dynamical corrections to the various effects which have been analyzed in Sec. III, as well as to discuss static responses more accurately. However, since in most cases such studies will require extensive numerical calculations we restrict ourselves here to the simplest illustrative examples.

First we mention very briefly the extension of the treatment for the DA of Sec. II to the case where the external charge distribution $n_{ext}(\vec{r}, t)$ is time dependent. If one neglects retardation effects, the response is still defined by equations of the form of (2.1), (2.3), and (2.10). However, since the fields are now time dependent one introduces Fourier components $f(z, \vec{k}_{\parallel}, \omega)$ which oscillate as $e^{-i\omega t}$, instead of (2.4), and one replaces the integral kernel in (2.10) by $\epsilon(z, \vec{k}_{\parallel}, \omega)$, the Fourier transform of $\epsilon(k, \omega)$. In this case, however, the solution cannot be developed more explicitly without specifying the detailed form of $\epsilon(k, \omega)$. This approach will therefore not be discussed further.

The remainder of this subsection deals with a dynamic generalization of the quasiclassical SDA. The method which we employ is a simple extension of the one introduced by Ritchie and Marusak[35] in the study of surface plasmons for specular reflection. One of its advantages is that all the quantities of interest are expressed explicitly in terms of $\epsilon(k, \omega)$. For a Thomas–Fermi dielectric function our analysis reduces to the one of Sec. II in the SDA. In addition, our final expressions, which are valid for moving charges, contain as special cases some results for a fixed oscillating charge derived previously by Newns[19] and by Peuckert,[25] using quite different methods. As a byproduct we also obtain explicit expressions for a "surface dielectric function" first introduced by Newns.[19]

In the framework of a classical SDA treatment of the dynamical response one may construct approximations for the constitutive relation for a bounded system by making simple assumptions about the reflection properties of the surface. In particular, one knows that the assumption of specular reflection of electrons at the surface is equivalent to defining the displacement field in the metal half-space through the constitutive relation

$$\vec{D}(z, \vec{k}_{\parallel}, \omega) = \int_{-\infty}^{\infty} dz' \epsilon(z - z', \vec{k}_{\parallel}, \omega) \vec{E}'(z', \vec{k}_{\parallel}, \omega), \quad z > 0 \qquad (4.1)$$

where $\vec{E}'(z, \vec{k}_{\parallel}, \omega)$ is a symmetric field which is defined in terms of the true electric field in the metal region:

$$\vec{E}'(z, \vec{k}_{\parallel}, \omega) \equiv \vec{E}'(z) = \theta(z) \begin{pmatrix} \vec{E}_{\parallel}(z) \\ E_z(z) \end{pmatrix} + \theta(-z) \begin{pmatrix} \vec{E}_{\parallel}(-z) \\ -E_z(-z) \end{pmatrix} . \qquad (4.2)$$

Since (4.1) is equivalent to the constitutive relation for a fictitious infinite medium in which the electric field is symmetric about $z = 0$, the net electric current across this plane of the medium is zero at any time. As a consequence the current vanishes also at the surface of the true semi-infinite electron gas described by (4.1) and bounded by vacuum. This becomes completely clear by noting the following features. Firstly, electrons are not allowed to cross the real surface. Secondly, in order to establish a symmetric field of the form (4.2) one has to place a charge sheet at $z = 0$ which then acts to screen out charge fluctuations in such a way that electrons are moving independently in the two halves of the fictitious medium. This phenomenological argument demonstrates that (4.1) corresponds to specular reflection in a classical picture.

Before discussing the dynamical response in detail it is useful to make the connection between a treatment based on (4.1) and the Thomas–Fermi response treatment in the SDA for the static case. Using (4.2), we rewrite (4.1) in the form of Eq. (2.9) with

$$\epsilon(z, z', \vec{k}_{\parallel}, \omega) = \epsilon(z - z', \vec{k}_{\parallel}, \omega) \pm \epsilon(z + z', \vec{k}_{\parallel}, \omega), \qquad (4.3)$$

where the plus sign enters the constitutive relation between the parallel components, and the minus sign that corresponding to the z components of the fields. By combining (2.9), using (2.11), (4.3), and (2.13), with the Fourier transform of Maxwell's equations (2.1) and (2.3) we get the following equation for the potential in the region $z > 0$:

$$\frac{d^2 V(z, k_{\parallel})}{dz^2} - k_{\parallel}^2 V(z, k_{\parallel}) = -4\pi n_{ext}(z, k_{\parallel}) + \frac{k_s^2}{2} \left[k_{\parallel} \int_0^{\infty} dz' \left(e^{-k_{\parallel}|z-z'|} + e^{-k_{\parallel}|z+z'|} \right) V(z', k_{\parallel}) \right.$$

$$-\int_0^\infty dz'\ (e^{-k_\parallel|z-z'|}\,\mathrm{sgn}(z'-z)+e^{-k_\parallel|z+z'|})\ \frac{dV(z',k_\parallel)}{dz'}\Big] \quad . \quad (4.4)$$

This equation reduces exactly to the form (2.7) by means of integrations by parts. In addition, one may verify that in this case the matching conditions $D_z(0^+, k_\parallel) = D_z(0^-, k_\parallel)$ and $E_z(0^+, k_\parallel) = E_z(0^-, k_\parallel)$ are consequences of one another. This establishes the complete equivalence between the linearized Thomas–Fermi equation in the SDA and the constitutive relations (4.1) and (4.2) expressed with the Thomas-Fermi dielectric function (2.11). We note that without an explicit proof of the connection of (4.1) to an actual density response equation, the meaning of this relation would be somewhat unclear in the static case. Indeed, in a classical treatment the concept of reflection at the surface is meaningful only if the electron trajectories are specified as functions of time in the first place. Such a description is of course embodied in a time-dependent treatment.

In the dynamical treatment we restrict ourselves to point charge perturbations, and more specifically to charges moving along the z axis with a prescribed time dependence $z_0(t)$. Furthermore, in order to incorporate in our discussion the special case of a fixed oscillating charge

$$q(t) = qe^{-i\omega_0 t}\ , \quad (4.5)$$

we shall let the strength of the charge be an implicit function of time as well. A symmetric field of the form (4.2) may be generated by a fictitious dynamic charge sheet of density $\rho_s(x, y, t)\delta(z)$, supplemented by symmetrically placed external charges if such charges are present in the real metal half-space. The associated screened potential $V'(z, k_\parallel, \omega)$ in the fictitious infinite medium described by (4.1) is then obtained from Maxwell's equations (for $c \to \infty$) using as sources $\rho_s(x, y, t)\delta(z)$ and, eventually, two symmetrically located charges at $z_0(t)$ and $-z_0(t)$. The true electrostatic potential in the metal half-space, which coincides with $V'(z, k_\parallel, \omega)$ for $z > 0$, is then given by

$$V(z, k_\parallel, \omega) = 2\rho_s(k_\parallel, \omega)\int_{-\infty}^{\infty} dk_z\ \frac{e^{ik_z z}}{k^2\epsilon(k,\omega)} + 4\int_{-\infty}^{\infty} dt' e^{i\omega t'} q(t')\theta(z_0(t')) \times \int_{-\infty}^{\infty} dk_z \frac{e^{ik_z z}}{k^2\epsilon(k,\omega)}\cos k_z z_0(t')\ , \quad z > 0 \quad (4.6)$$

where

$$k^2 = k_z^2 + k_\parallel^2\ . \quad (4.7)$$

This expression generalizes the ones obtained by Beck and Celli[18] for static charges and by Ritchie and Marusak[35] in the absence of external charges. On the other hand, the solution of Poisson's equation for the vacuum region is

$$V(z, k_\parallel, \omega) = ae^{k_\parallel z} + \frac{2\pi}{k_\parallel}\int_{-\infty}^{\infty} dt' e^{i\omega t'} q(t') \times \theta(-z_0(t'))e^{-k_\parallel|z-z_0(t')|}, \quad z < 0. \quad (4.8)$$

The fictitious surface charge $\rho_s(k_\parallel, \omega)$ and the constant a are determined by matching $V(z, k_\parallel, \omega)$ and $D_z(z, k_\parallel, \omega)$ at the interface $z = 0$.

From (4.1 and 4.2) and (4.6) we obtain

$$D_z(z, k_\parallel, \omega) = -2i\Big[\rho_s(k_\parallel, \omega)\int_{-\infty}^{\infty} dk_z\ \frac{k_z e^{ik_z z}}{k^2} + 2\int_{-\infty}^{\infty} dt' e^{i\omega t'} q(t')\theta(z_0(t')) \times \int_{-\infty}^{\infty} dk_z\ \frac{k_z e^{ik_z z}}{k^2}\cos k_z z_0(t')\Big], \quad z > 0 \quad (4.9)$$

and, for $z < 0$, $D_z = E_z = -dV/dz$. The final solutions of the matching conditions are

$$\rho_s(k_\parallel, \omega) = \frac{2}{\Delta}\int_{-\infty}^{\infty} dt' e^{i\omega t'} q(t')\Big[\theta(-z_0(t'))\, e^{k_\parallel z_0(t')} - \theta(z_0(t'))\frac{k_\parallel}{\pi}\int_{-\infty}^{\infty} dk_z\ \frac{\cos k_z z_0(t')}{k^2\epsilon(k,\omega)}\Big]\ , \quad (4.10)$$

$$a = \frac{2}{\Delta}\int_{-\infty}^{\infty} dt' e^{i\omega t'} q(t')\Big[\frac{\pi}{k_\parallel}\,\theta(-z_0(t'))\, e^{k_\parallel z_0(t')} \times \Big(\frac{k_\parallel}{\pi}\int_{-\infty}^{\infty}\frac{dk_z}{k^2\epsilon(k,\omega)} - 1\Big) + 2\theta(z_0(t'))\int_{-\infty}^{\infty} dk_z\ \frac{\cos k_z z_0(t')}{k^2\epsilon(k,\omega)}\Big], \quad (4.11)$$

where

$$\Delta = \frac{k_\parallel}{\pi}\int_{-\infty}^{\infty}\frac{dk_z}{k^2\epsilon(k,\omega)} + 1\ . \quad (4.12)$$

Incidentally, the equation

$$\Delta = 0 \quad (4.13)$$

is the condition for the existence of solutions to the homogeneous parts of the matching equations and determines the dispersion relation for surface plasmons in the present model. This formula is well known and was first derived by Ritchie and Marusak[35] and by Wagner.[36]

The total electrostatic potential at $(\vec{r}, t) \equiv (z, \vec{\rho}, t)$ in the presence of a moving charge $q(t)$ at $(0, 0, z_0(t))$ is then

$$V(z, \vec{\rho}, t) = \frac{1}{(2\pi)^2}\int_{-\infty}^{\infty} d\omega\, e^{-i\omega t} \times \int_0^{\infty} dk_{\parallel} k_{\parallel} J_0(k_{\parallel}\rho)\, V(z, k_{\parallel}, \omega). \quad (4.14)$$

The instantaneous interaction energy between the charge $q(t)$ and the metal surface is given by

$$W = \tfrac{1}{2} q(t)\, V_i(z_0(t), \vec{\rho} = 0, t) \ ,$$

where $V_i(z, \vec{\rho}, t)$ denotes the total electrostatic potential minus the potential which the charge $q(t)$ would create if the medium where it is placed would have infinite extent. This homogeneous medium potential is given by the second term in (4.8) for the case where the charge is in vacuum, and by that contribution in the second term of (4.6) which arises from the term $\frac{1}{2}e^{-ik_z z_0(t')}$ of the cosine for the case of a charge inside the metal. For a charge whose trajectory lies outside the metal, the combination of (4.11) and (4.8) yields

$$W = \frac{q(t)}{4\pi}\int_{-\infty}^{\infty} d\omega\, e^{-i\omega t}\int_0^{\infty} dk_{\parallel} \times \int_{-\infty}^{\infty} dt'\, e^{i\omega t'} q(t')\, e^{k_{\parallel}[z_0(t)+z_0(t')]}\, \frac{1-\epsilon_s(k_{\parallel},\omega)}{1+\epsilon_s(k_{\parallel},\omega)} \ , \qquad z_0(t) < 0 \quad (4.16)$$

where

$$\epsilon_s(k_{\parallel}, \omega) = \left[\frac{k_{\parallel}}{\pi}\int_{-\infty}^{\infty} \frac{dk_z}{k^2 \epsilon(k, \omega)}\right]^{-1} \ . \quad (4.17)$$

On the other hand, for a charge whose motion is confined to the interior of the metal the interaction energy (4.15) is given by

$$W = \frac{q(t)}{(2\pi)^2}\int_{-\infty}^{\infty} d\omega\, e^{-i\omega t}\int_0^{\infty} dk_{\parallel} k_{\parallel}\int_{-\infty}^{\infty} dk_z\, \frac{e^{ik_z z_0(t)}}{k^2 \epsilon(k, \omega)} \times \left[\rho_s(k_{\parallel}, \omega) + \int_{-\infty}^{\infty} dt'\, e^{ik_z z_0(t')}\right], \qquad z_0(t) > 0 \ . \quad (4.18)$$

Finally, the bulk screening charge density $\delta n(z, k_{\parallel}, \omega)$ may be easily written down explicitly, using the definition

$$\delta n(z, k_{\parallel}, \omega) = -\frac{1}{4\pi}\left[\frac{d^2 V(z, k_{\parallel}, \omega)}{dz^2} - k_{\parallel}^2 V(z, k_{\parallel}, \omega)\right] - \int_{-\infty}^{\infty} dt\, e^{i\omega t} q(t)\, \delta(z - z_0(t)) \ , \qquad z > 0 \quad (4.19)$$

and substituting (4.6) and (4.10).[37]

In the special case of a fixed oscillating charge of the form (4.5) the image potential interaction (4.16) reduces to

$$W = \frac{1}{2} q^2(t)\int_0^{\infty} dk_{\parallel}\, e^{-2k_{\parallel}|z_0|}\, \frac{1-\epsilon_s(k_{\parallel}, \omega_0)}{1+\epsilon_s(k_{\parallel}, \omega_0)} \ , \quad (4.20)$$

which coincides essentially with an expression obtained by Peuckert[25] in a quite different way. The present expression (4.20) is similar to a more general one derived by Newns[19] in terms of a "surface dielectric function," which here takes the special form (4.17). In particular, (4.20) generalizes the formula (3.5) which is valid in the Thomas–Fermi theory for the SDA. Note that in the case where the half-space is a dielectric medium of dielectric constant ϵ_0 we obtain from (4.8), (4.11), and (4.14)

$$V(z, \vec{\rho}, t) = \frac{q}{\{\rho^2 + [z - z_0(t)]^2\}^{1/2}} - \frac{\epsilon_0 - 1}{\epsilon_0 + 1}\, \frac{q}{\{\rho^2 + [z + z_0(t)]^2\}^{1/2}} \ , \qquad z_0(t) < 0 \quad (4.21)$$

and for the image interaction energy

$$W = -\frac{1}{4}\, \frac{\epsilon_0 - 1}{\epsilon_0 + 1}\, \frac{q^2}{|z_0(t)|} \ , \quad z_0(t) < 0 \ . \quad (4.22)$$

These quasistatic expressions are well known in ordinary electrostatics.[27] Of course, the corresponding expressions for a charge moving inside the dielectric medium may also be recovered, using (4.6), (4.14), and (4.18).

The comparison of (4.16) and (4.22) shows that the introduction of a surface dielectric function establishes a close formal similarity between the Fourier components in (4.16) and the reduction factor $(\epsilon_0 - 1)/(\epsilon_0 + 1)$ of the image charge in the case of a dielectric. On the other hand, with the definition (4.17) one may view (4.13) as a special case of a condition expressing that the sum of the surface dielectric functions of the media on both sides of the interface is zero. This is the nonlocal generalization of a similar condition for the bulk dielectric functions obtained in a local description. These remarks emphasize the usefulness of the concept of a surface dielectric function.

For the sake of completeness we shall display some useful model expressions for the surface dielectric function (4.17). A simple form for the bulk dielectric function of an electron gas, which interpolates between the high-frequency and static Thomas–Fermi limits, is the hydrodynamic expression

$$\epsilon(k, \omega) = 1 - \frac{\omega_p^2}{(\omega + i/2\tau)^2 - \beta^2 k^2} \quad (4.23)$$

where $\beta^2 = v_F^2/3$ and τ is a phenomenological relaxation time.[38] Substitution of this expression in (4.17) and evaluation of the integral yields

$$\epsilon_s(k_\parallel, \omega) = \frac{\omega^2 - \omega_p^2}{\omega^2 - \gamma^{-1} k_\parallel \omega_p^2} \quad , \quad \gamma^2 > 0, \ \tau \to \infty \qquad (4.24)$$

where

$$\gamma = \left(k_\parallel^2 + \frac{\omega_p^2 - \omega^2}{\beta^2} \right)^{1/2} . \qquad (4.25)$$

In the static limit, this expression takes the form

$$\epsilon_s(k_\parallel, 0) = \frac{(k_\parallel^2 + k_s^2)^{1/2}}{k_\parallel} \quad , \quad k_s^2 = \frac{\omega_p^2}{\beta^2} \quad , \qquad (4.26)$$

which has been discussed by Newns.[19] The substitution of (4.26) in (4.20) leads, in fact, directly to the image interaction (3.5) for the SDA Thomas–Fermi theory. On the other hand, we may obtain the form of the static surface dielectric function in the Thomas–Fermi treatment of the DA by rewriting (3.6) in the form of (4.20). The result is

$$\epsilon_s(k_\parallel, 0) = \frac{1}{4} \left[3 + \frac{3}{2} \frac{k_s^2}{k_\parallel^2} + \left(1 + \frac{k_s^2}{k_\parallel^2} \right)^{1/2} \right] . \qquad (4.27)$$

B. Dynamic Corrections to the Image Potential

In this subsection we illustrate Eqs. (4.16) and (4.18) for specific forms of the trajectory $z_0(t)$. In particular, we discuss dynamical corrections to the classical image potential (1.2) which result from the finite velocity of the external charge q. Whereas (4.16) and (4.18) are restricted to situations where the trajectory is confined to one side of the metal surface, we shall later discuss an important case where the trajectory actually crosses the interface. Incidentally, since in our treatment the time dependence of the external charges is *a priori* specified, we are ignoring any recoil effects which may be important at small velocities and whose study requires a different formalism.[39] For simplicity we restrict the following discussion to the case of a local dielectric function of the form

$$\epsilon(k, \omega) \equiv \epsilon(\omega) = 1 - \frac{\omega_p^2}{(\omega + i/2\tau)^2} \quad . \qquad (4.28)$$

Since the SDA and DA are equivalent in this case, one is describing a system where both the unperturbed electron density and the dielectric response kernel are replaced by bulk expressions. Indeed, the constitutive relations of the form of (2.10) and (4.1) and (4.2) coincide for a local $\epsilon(\omega)$. Also, since for a local system the screening charge may only have the form of a surface charge, a phenomenological response treatment for this case is meaningful only if one makes D_z rather than E_z continuous at the surface. The continuity of D_z expresses that no external charges exist on the surface, while the continuity of E_z would mean that neither induced nor external surface charges are present.[27]

First we consider the case of a charge q moving outside the metal surface. By substituting (4.28) and (4.17) in (4.16) and carrying out the integrations over $k_\parallel$ and ω we get, for $\tau \to \infty$,

$$W = -\frac{q^2 \omega_s}{2} \int_{-\infty}^{t} dt' \, \frac{\sin \omega_s (t' - t)}{z_0(t) + z_0(t')} \quad , \quad z_0(t) < 0 \qquad (4.29)$$

where $\omega_s = \omega_p/\sqrt{2}$ is the surface-plasmon frequency. It is seen that (4.29) satisfies causality requirements as a consequence of the fact that the zeros of (4.28) lie in the lower half of the complex-frequency plane. The dependence of the instantaneous interaction energy on the past trajectory of the external charge is a consequence of the retardation with which the surface experiences the effect of the time-dependent perturbation. This leads to a reduction of the interaction for a uniformly moving charge which is approaching the surface sufficiently slowly. At this point we specialize further to the case of a particle moving with a constant velocity v, for which (4.29) may be easily evaluated. We shall discuss successively three different situations.

Case (1). Particle moving uniformly from $-\infty$ towards the surface:

$$z_0(t) = vt \ , \ t \in [-\infty, 0] \ . \qquad (4.30)$$

In this case (4.29) yields the exact result

$$W = -\frac{q^2 \omega_s}{2v} f\left(\frac{2\omega_s |z_0(t)|}{v} \right) \qquad (4.31)$$

where[40]

$$f(x) = \mathrm{Ci}(x) \sin x - \mathrm{si}(x) \cos x \ , \qquad (4.32)$$

$$\mathrm{Ci}(x) = -\int_x^\infty \frac{\cos t}{t} \, dt,$$

$$\mathrm{si}(x) = -\int_x^\infty \frac{\sin t}{t} \, dt \ . \qquad (4.33)$$

The interaction energy (4.31) vanishes for large velocities as a result of the fact that the electrons cannot follow the motion of the external charge in this case. At distances such that $2\omega_s v^{-1} |z_0(t)| \gg 1$ the use of the asymptotic expression[40] of $f(x)$ leads to

$$W = -\frac{q^2}{4|z_0|} \left(1 - \frac{v^2}{2\omega_s^2 |z_0|^2} + \frac{3v^4}{2\omega_s^4 |z_0|^4} - \cdots \right) , \qquad (4.34)$$

where the first term is the usual quasistatic image potential. At short distances the dynamic effects lead to a saturation of the interaction energy, whereas the classical result (1.2) becomes singular

in this case. Indeed, from (4.31) and (4.32) we obtain for $|z_0(t)| \to 0^+$

$$W(0^+) = -\frac{\pi}{4}\frac{q^2\omega_s}{v} \quad . \tag{4.35}$$

In this regard the dynamic effect plays a role similar to that of finite static screening studied in Secs. II and III. This is not surprising since it also corresponds to an imperfect screening mechanism, which is due in this case to the retardation of the response of the electron gas to the variable external perturbation.

In general, the interaction energy (4.29) includes contributions due to the polarization of the electron gas at the surface (which may be described in terms of virtual excitations) as well as to the creation of real surface plasmons. These two contributions may be separated by going back to Eq. (4.16) and performing the integration over t' before those over ω and $k_{\parallel}$, using (4.30). In this way one may verify that the interaction energy (4.31) arises purely from surface polarization, just like the classical image potential itself. We note that asymptotic corrections similar to those which are present in (4.34) have been obtained previously by Takimoto[41] for a particle moving parallel to the surface at a constant velocity.

Case (2). Particle created at the surface at $t=0$ and moving away from it with constant initial velocity. Since in this case

$$z_0(t) = -vt\ ,\quad t\in[0,\infty]\ , \tag{4.36}$$

the integration over the past trajectory in (4.29) extends only from 0 to t, and we find

$$W = -\frac{q^2\omega_s}{2v}\left[f\left(\frac{2\omega_s|z_0|}{v}\right) - f\left(\frac{\omega_s|z_0|}{v}\right)\cos\frac{\omega_s|z_0|}{v} + g\left(\frac{\omega_s|z_0|}{v}\right)\sin\frac{\omega_s|z_0|}{v}\right], \tag{4.37}$$

where

$$g(x) = -\mathrm{Ci}(x)\cos x - \mathrm{si}(x)\sin x\ . \tag{4.38}$$

Using the asymptotic expressions[40] for $f(x)$ and $g(x)$, we obtain, for $\omega_s v^{-1}|z_0| \gg 1$,

$$W = -\frac{q^2}{4|z_0|}\left[\left(1-\frac{v^2}{2\omega_s^2|z_0|^2}+\cdots\right) - 2\left(1-\frac{2v^2}{\omega_s^2|z_0|^2}+\cdots\right)\cos\frac{\omega_s|z_0|}{v} + \frac{2v}{\omega_s|z_0|}\left(1-\frac{6v^2}{\omega_s^2|z_0|^2}+\cdots\right)\sin\frac{\omega_s|z_0|}{v}\right], \tag{4.39}$$

while for $|z_0| \to 0$ we get

$$W(0^+) = 0\ . \tag{4.40}$$

In the present case the dynamical effects are particularly striking since at large distances they are of the same order of magnitude as the classical interaction itself. Moreover, the interaction (4.39) alternates in sign as a function of $|z_0|$. Following the procedure indicated in case (1), one may verify that while the first term in (4.37) is due to surface polarization, the last two terms correspond to real surface-plasmon excitation. At short distances the polarization effect tends to be cancelled by the contribution of real surface plasmon excitation, as shown by (4.40).

In fact, the last two terms in (4.37) are directly associated with the sudden creation of the charge q with initial velocity v at the surface at $t=0$. On the one hand, the absence of such terms when the the charge is created at infinity [case (1)] rules out their connection with the motion itself, while, on the other hand, the sudden creation of the charge q near the surface is the only process available for real surface plasmon excitation at low velocities. Finally, in the case of a fixed oscillating charge, one may verify explicitly that similar terms do arise when the charge is switched on suddenly at $t=0$, $z=z_0$, while being absent when the switching is performed adiabatically.

Case (3). Uniformly moving particle which is elastically reflected at the surface.

For this situation we have

$$z_0(t) = -v|t|,\quad t\in[-\infty,\infty]\ , \tag{4.41}$$

and from (4.29) we obtain

$$W = -\frac{q^2\omega_s}{2v}\left[f\left(\frac{2\omega_s|z_0|}{v}\right) + 2\theta(t)g\left(\frac{\omega_s|z_0|}{v}\right)\sin\frac{\omega_s|z_0|}{v}\right], \tag{4.42}$$

whose limiting expressions are

$$W = -\frac{q^2}{4|z_0|}\left[\left(1-\frac{v^2}{2\omega_s^2|z_0|^2}+\cdots\right) + \frac{4v\theta(t)}{\omega_s|z_0|}\left(1-\frac{6v^2}{\omega_s^2|z_0|^2}+\cdots\right)\sin\frac{\omega_s|z_0|}{v}\right], \quad \omega_s v^{-1}|z_0| \gg 1 \tag{4.43}$$

$$W(0^+) = -\frac{\pi}{4}\frac{q^2\omega_s}{v}\ . \tag{4.44}$$

Again, the first term in (4.42) arises from surface polarization and the second term corresponds to surface-plasmon losses.

It is also of interest to study the interaction for a charge q whose trajectory stays inside the metal surface. Using the local approximation (4.28) and performing successively the integrations over $k_{\parallel}$ and ω in (4.18), using (4.10) and (4.12), we get

$$W=\frac{q^2}{2}\int_{-\infty}^{t}dt'\ \frac{\omega_p\sin\omega_p(t-t')-\omega_s\sin\omega_s(t-t')}{z_0(t)+z_0(t')}\ , \tag{4.45}$$

For the case

$$z_0(t)=vt,\quad t\in[0,\infty]\ , \tag{4.46}$$

which corresponds to a particle created at the surface at $t=0$ and accelerated suddenly to a constant velocity v, we thus obtain

$$W=\frac{q^2}{2v}\left[\omega_p f\left(\frac{2\omega_p z_0}{v}\right)-\omega_s f\left(\frac{2\omega_s z_0}{v}\right)\right.$$
$$-\omega_p f\left(\frac{\omega_p z_0}{v}\right)\cos\frac{\omega_p z_0}{v}+\omega_s f\left(\frac{\omega_s z_0}{v}\right)\cos\frac{\omega_s z_0}{v}$$
$$\left.+\omega_p g\left(\frac{\omega_p z_0}{v}\right)\sin\frac{\omega_p z_0}{v}-\omega_s g\left(\frac{\omega_s z_0}{v}\right)\sin\frac{\omega_s z_0}{v}\right]. \tag{4.47}$$

As before, the origin of the various contributions may be seen by substituting the trajectory equation (4.46) directly in (4.18) and (4.10) and performing the integrations over t' first. This shows that the first two terms in (4.47) are associated with polarization of the surface and the remaining ones with surface and bulk plasmon excitation. In fact, the difference between (4.47) and (4.37) lies in the terms describing the effect of virtual and real excitation of bulk plasmons. These bulk plasmon terms, which are associated with the presence of the surface, correspond to the effect of the finite size of the system on bulk plasmon excitation. A similar finite-size effect is well known in the study of energy losses due to bulk plasmon or phonon excitation in fast-electron transmission through thin films.[42]

In practice, as well as for comparison with the above results, it is useful to study the image-potential interaction in cases where the particle crosses the vacuum-metal interface. We restrict ourselves to the simplest situation, namely that of a charge moving along the z axis with a uniform velocity,

$$z_0(t)=vt,\quad t\in[-\infty,\infty]\ , \tag{4.48}$$

and assume the electron gas to be described by the local dielectric function (4.28). Similar cases are usually discussed in analyses of energy losses in fast-electron transmission experiments,[13] as well as in studies of the emission of transition radiation[43] by charges moving across an interface. Unfortunately the general formulas for W discussed above are not applicable in the present case, since in applying the boundary conditions at $z=0$ we have assumed explicitly that the particle trajectory is confined to one side of the surface. Using the Fourier transform $(q/v)e^{i(\omega/v)z}$ of the external source charge density $q\delta(x)\delta(y)(z-vt)$, it is straightforward to calculate the components $V(z,k_{\parallel},\omega)$ of the electrostatic potential by solving Maxwell's equations, neglecting retardation. The result is

$$V(z,k_{\parallel},\omega)=\frac{4\pi q}{v(k_{\parallel}^2+\omega^2/v^2)}$$
$$\times\left[\frac{1}{\epsilon(\omega)}\left(\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}\,e^{-k_{\parallel}z}+e^{i(\omega/v)z}\right)\theta(z)\right.$$
$$\left.-\left(\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}\,e^{k_{\parallel}z}-e^{i(\omega/v)z}\right)\theta(-z)\right]. \tag{4.49}$$

Note that with the Fourier representation for the external charge density one avoids having to specify the position of the trajectory with respect to the surface when applying the boundary conditions. As usual, we have imposed continuity of $E_{\parallel}(z,k_{\parallel},\omega)$ and of $D_z(z,k_{\parallel},\omega)$ at $z=0$. The interaction of the charge q with the surface is determined by the exponentially decaying terms in (4.49), and by using (4.14) and (4.15) we get

$$W=-\frac{q^2\omega_p^2}{2}\int_0^{\infty}dk_{\parallel}\left[\frac{e^{2k_{\parallel}vt}}{2(k_{\parallel}^2v^2+\omega_s^2)}\,\theta(-t)-k_{\parallel}ve^{-k_{\parallel}vt}\right.$$
$$\times\left(\frac{k_{\parallel}ve^{-k_{\parallel}vt}}{2(k_{\parallel}^2v^2+\omega_p^2)(k_{\parallel}^2v^2+\omega_s^2)}-\frac{\sin\omega_s t}{\omega_s(k_{\parallel}^2v^2+\omega_s^2)}\right.$$
$$\left.\left.+\frac{2\sin\omega_p t}{\omega_p(k_{\parallel}^2v^2+\omega_p^2)}\right)\theta(t)\right]\ . \tag{4.50}$$

The remaining integrals may be expressed in terms of known functions,[44] and with the definitions (4.32) and (4.38) we finally have

$$W=-\frac{q^2}{2v}\left\{\omega_s f\left(\frac{2\omega_s|z_0|}{v}\right)-\theta(z_0(t))\left[\omega_p f\left(\frac{2\omega_p z_0}{v}\right)\right.\right.$$
$$+2\omega_p g\left(\frac{\omega_p z_0}{v}\right)\sin\frac{\omega_p z_0}{v}$$
$$\left.\left.-2\omega_s g\left(\frac{\omega_s z_0}{v}\right)\sin\frac{\omega_s z_0}{v}\right]\right\}\ . \tag{4.51}$$

This expression is to be compared with Eq. (4.42) for the case of a specularly reflected charge, which shows that, as expected, the difference lies only in the effect of bulk plasmons. The limiting forms of (4.51) when the particle is just outside or inside the metal surface are

$$W(0^-)=-\frac{\pi}{4}\frac{q^2\omega_s}{v}\ , \tag{4.52a}$$

$$W(0^+)=\frac{\pi}{4}(\sqrt{2}-1)\frac{q^2\omega_s}{v}\ . \tag{4.52b}$$

For $\omega_p v^{-1}|z_0|\gg 1$, W is given by (4.34) when the charge is outside the surface, and by

$$W=\frac{q^2v}{2\omega_p|z_0|^2}\left[\frac{v}{4\omega_p|z_0|}+\left(1-\frac{6v^2}{\omega_p^2|z_0|^2}\right)\sin\frac{\omega_p|z_0|}{v}\right.$$

$$-\sqrt{2}\left(1-\frac{6v^2}{\omega_s^2|z_0|^2}\right)\sin\frac{\omega_s|z_0|}{v}+O(|z_0|^{-3})\Big] , \tag{4.53}$$

when it is embedded in the surface. The absence of a long-range term of $O(|z_0|^{-1})$ in (4.53) is a consequence of the combination of bulk and surface plasmon effects in the polarization terms in (4.51).

The above results show that the instantaneous image-potential interaction for a moving point charge depends quite sensitively on the nature of the past trajectory of the charge. The dynamical image force resulting from (4.51) could be used to calculate the surface energy loss experienced by a fast electron transmitted through a metal-vacuum interface. Indeed, this energy loss may be viewed as the work done on the electron by the electric field of the charge disturbance which is induced in the metal surface. The case of a charged particle created at the surface with some initial velocity is relevant to the photoelectric and field-emission effects. In the above calculations we have ignored the acceleration and deceleration of the external charge by the image force which is acting on it. As is well known[43] this effect provides a mechanism for the emission of transition radiation when a charge is moving uniformly across a vacuum-metal interface.

V. SUMMARY

In Secs. II and III we have analyzed the electrostatic response of a metal surface to various external charge distributions. We have outlined a simple dielectric approximation as an alternative to the familiar quasiclassical step-density approximation for this problem. Since the two procedures are quite similar in spirit one has the possibility of selecting the one giving the most accurate results for each particular problem. In this sense the DA and SDA may be regarded as complementary to one another. However, neither of these approximations can be fully justified in terms of a self-consistent first-principles treatment of the surface.

Applying our DA in a Thomas–Fermi treatment we have obtained explicit results for the image potential interaction and for the surface dipole constituted by the external charge and the induced screening charge in the metal. We have calculated similar quantities for the case of charges embedded in the metal surface. Finally, we have studied the enhancement of the polarizability of an atom or a molecule placed a short distance outside a metal surface and, furthermore, we have considered the effect of the atomic polarizability on the image-potential interaction and on the surface dipole associated with an adsorbed ion. In all cases we have compared our detailed results with those obtained by previous authors, using the quasiclassical SDA.

To the extent that a comparison of these results with self-consistent calculations is meaningful, we find that the DA yields much better results than the SDA for point charges external to the surface. However, this is not so in the case of point charges embedded deep in the metal, at least as far as the induced surface dipole is concerned.

In Sec. IV we have extended the response treatment to dynamic situations and for a general description of a bulk electron gas in terms of the dielectric function. We have given a detailed discussion in the framework of the SDA and for specular reflection of electrons at the surface. In this case we have derived general expressions for the image-potential interaction for charges moving along prescribed trajectories. We have applied the results to a detailed study of the dynamical image potential for a uniformly moving charge. We have considered trajectories both inside and outside the metal surface, as well as trajectories crossing the interface. Using a local dielectric function we have found a strong dependence of the instantaneous interaction on the past trajectory of the moving charge. We have interpreted the various contributions in the dynamical image interaction in terms of polarization of the surface and of surface and bulk plasmon creation. A study of some applications of these results is under way.

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$$\delta n(z, k_\parallel, \omega) = q \int_{-\infty}^{\infty} \frac{dk_z}{\epsilon(k, \omega)} \left([1-\epsilon(k, \omega)] \times \cos k_z (z - z_0) + \cos k_z (z + z_0) - \frac{2\cos k_z z}{1+\epsilon_s^{-1}(k_\parallel, \omega)} \int_{-\infty}^{\infty} \frac{dk'_z}{\pi} \frac{k_\parallel}{k_\parallel^2 + k_z'^2} \frac{\cos k'_z z_0}{\epsilon(k_\parallel, k'_z, \omega)} \right) \times \delta(\omega - \omega_0), \; z_0 > 0, \; z > 0,$$

instead of Peuckert's Eq. (39). In the present formulation, which is quite different from the one used by Peuckert, one would recover this author's expression by subtracting in the right-hand side of (4.19) both the fictituous surface charge density $\rho_s(k_\parallel, \omega)\delta(z)$ and the image of the embedded charge q. Such an expression, of course, does not define the true induced charge density.
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Thermoelectric Effects in Pure and V-Doped Ti_2O_3 Single Crystals*

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The Seebeck coefficient α for pure and V-doped Ti_2O_3 single crystals has been measured between 54 and 500 K. A very strong peak in α near 75 K for Ti_2O_3 is interpreted as arising from phonon-drag effects; this peak is missing for the V-doped specimens. Between 150 and 350 K the variation of α with temperature T could be interpreted in terms of a standard model for mixed conduction in a semiconductor. For $T > 350$ K, α diminished rapidly with increasing T, which reflects the semiconductor-semimetal transition that has been reported in the literature on the basis of conductivity studies. The effect of doping on thermoelectric phenomena has been investigated in detail and is found closely to parallel the effects encountered in conductivity measurements. An explanation is offered as to why V-doped Ti_2O_3 exhibits p-type characteristics. Values of relevant band parameters have been determined.

I. INTRODUCTION

There has been considerable interest in the electrical properties of Ti_2O_3; most of this work, which is largely confined to electrical conductivity studies, is summarized in several review articles.[1-4] Attention has been focused primarily on the electrical transition which occurs between approximately 400 and 600 K, in which range the material changes from a semiconductor to a semi-