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Dielectric continuum theory of the electronic structure of interfaces

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General expressions for the density-density and potential-potential response functions, ground-state (i.e., surface) energy, and one-electron optical potential are derived for a model of planar interfaces between two media, each of which is described by a local frequency-dependent dielectric function. These expressions are utilized to evaluate the surface energies characteristic of interfaces between semiconductors (insulators) described by the uniform dielectic function $\epsilon_S(\omega) = 1 + \omega_p^2(\Delta^2 - \omega^2 - i\omega/\tau)^{-1}$, metals described by $\epsilon_M(\omega) = 1 - \omega_p^2/\omega(\omega + i/\tau)$, and the vacuum $[\epsilon_V(\omega) \equiv 1]$. Plasmon damping (i.e., nonzero τ^{-1}) is shown to limit the range of nonlocality of the one-electron optical potential to $\lambda \sim (2\hbar\tau/m)^{1/2}$ and to decrease the surface energy. The surface energy of semiconductor interfaces is found to diminish monotonically with increases in the band-gap parameter $E_g = \hbar\Delta$. The conventional expressions for the surface energy of metals as a function of their density, $n = m\omega_p^2/4\pi e^2$, are recovered in the $\tau \rightarrow \infty$ limit, although errors in some previous derivations of these expressions are displayed. Finally, the structure and limitations of local models of surface properties are examined critically, and the well-known hydrodynamic and step-density random-phase-approximation models of metal-vacuum interfaces are shown to be elementary consequences of classical electrostatics in the limit that $\epsilon_M(\omega) = 1 - \omega_p^2/\omega^2$.

I. INTRODUCTION

In this paper we construct a dielectric model of the electronic structure of interfaces between two continuous media each of which is described by a simple frequency-dependent dielectric function $\epsilon_i(\omega)$. Planar interfaces are examined for convenience, although the extension to other geometries is a routine, if tedious, exercise in classical electrostatics,[1] as is the generalization[2] to nonuniform but local, dielectric media described by $\epsilon_i(\vec{r}, \omega)$. Our most significant result is the demonstration that within the confines of this model, quantum-theoretical properties like the surface energy and optical potential can be derived from classical electrostatics in an elementary, almost trivial, fashion. While attempts to construct such derivations have been made before[3] (especially within the context of studies of inhomogeneous dielectrics in the derivation of expressions for the van der Waals force in the three-medium case), they proved less successful because they failed to obtain closed-form expressions for the ground-state energy like that[4] utilized herein. Moreover, we find unexpected errors in[5] and limitations on[5–10] earlier model calculations of the surface energy of metals.

The main thrust of the work reported herein is the demonstration of the simple, transparent structure of a dielectric continuum model of interface properties and the application of the resulting expressions for the surface energy and optical potential to examine general features of and trends in surface properties as functionals of specific materials parameters (e.g., the energy gap of semiconductors and plasmon lifetime). Our expressions for the surface energy and optical potential reduce to those obtained earlier by many others in the special case of metal-vacuum interfaces, as will be noted as appropriate in the text of the paper.

Although the dielectric continuum model does not lead to a quantitative description of surface properties, as has been demonstrated explicitly for the vacuum-"jellium" interface,[11–13] considerable insight into the structure of dielectric models of surface properties can be obtained because of the simple structure of its predictions. As an illustration of this fact, the consequences of various model dielectric functions which have been proposed for insulators,[14–18] are displayed explicitly within the context of refining Phillips' considerations[19] of the energetics of metal-semiconductor contacts. We expect, however, the model to be of most use because of its analytical simplicity and elegance, rather than as a reliable indicator of the properties of "real" solids.

We proceed by displaying in Sec. II the derivation, via classical electrostatics, of the retarded correlation functions, the surface energy, and the one-electron optical potential obtained from the dielectric continuum model. Comparison of these model predictions with those obtained by other authors also is presented in this section. Section III contains a discussion of the surface energies of metal-vacuum, semiconductor-vacuum, metal-metal, and metal-semiconductor interfaces. Finally, we present a synopsis of our results, and their consequences for models of electron-solid

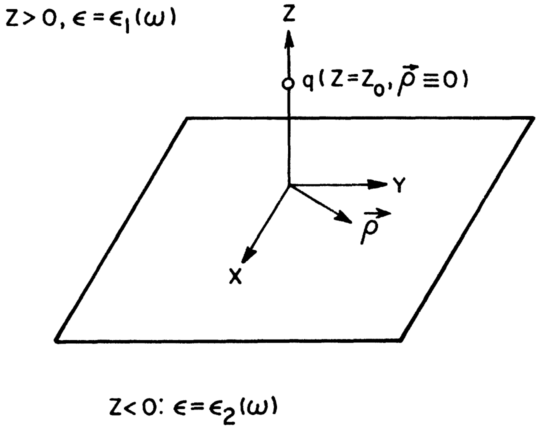

FIG. 1. Schematic diagram of the interface which shows the choice of the coordinate system and the location of the charge q.

scattering[20] and metal-semiconductor interfaces[21–23] in Sec. IV.

II. PLANAR INTERFACE BETWEEN TWO DIELECTRIC CONTINUA: GENERAL ANALYSIS

A. Model

Our initial task is the evaluation of the electrostatic fields of a point charge in the vicinity of a planar boundary between two dissimilar dielectric media provided that each medium is characterized by a local dielectric function $\epsilon(\vec{r}, \omega)$ dependent on position $\vec{r}$ and angular frequency ω. This computation is a routine exercise in classical electrostatics[1] once the dielectric functions of the adjoining media have been specified. A schematic diagram of the interface is shown in Fig. 1. We consider the special case that both media are dielectric continua characterized by $\epsilon_1(\omega)$ $(z>0)$ and $\epsilon_2(\omega)$ $(z<0)$, respectively.

Since we are concerned with *local* media, the most general form for $\epsilon_1(\omega)$ is[21]

$$\epsilon_i(\omega)=1+\omega_p^2\sum_\gamma \frac{f_\gamma}{\omega_\gamma^2-\omega^2}\ , \tag{1a}$$

$$\omega_p^2=4\pi n e^2/m\ , \tag{1b}$$

$$\sum_\gamma f_\gamma=1\ , \tag{1c}$$

in which n is the electron density in the solid, the ω_γ are resonance frequencies, and Eq. (1c) is the well-known[21] "f-sum rule." In the case of metals, it is conventional to select all of the ω_γ equal to zero in which case Eq. (1) yields

$$\epsilon_M(\omega)=1-\omega_p^2/\omega^2\ . \tag{2}$$

In the case of insulators, several diverse models of $\epsilon(\omega)$ have been proposed.[14–18] Those due to Hermanson[17] and Inkson[18] both reduce to the same form in the local limit, i.e.,

$$\epsilon_S(\omega)=1+\omega_p^2/(\Delta^2-\omega^2)\ . \tag{3a}$$

Moreover, Eq. (3a) evidently satisfies the f-sum rule, and reduces to $\epsilon_M(\omega)$ in the limit that $\Delta\to 0$.

A common practice in the study of semiconductor structures is the parameterization of the static dielectric function $\epsilon(0)$ by variables of chemical significance. For example, in the Phillips–Van Vechten model, we would write

$$E_g=\hbar\Delta=(E_h^2+C^2)^{1/2}\ , \tag{3b}$$

in which E_h is the homopolar band gap (obtained from diamond, silicon, and a bond-length scaling formula) and C is the ionic band gap obtained from the measured value of $\epsilon(0)$. It is important to stress that such models will prove appropriate for surface energy calculations only if the f-sum rule is satisfied [i.e., Eq. (3a) contains only one free parameter Δ]. Thus models like that of Wemple and DiDomenico,[15] in which Eq. (1a) is fit to experimental data using a single oscillator for which $f_\gamma\neq 1$, cannot be utilized in our analysis even though they might provide an adequate description of $\epsilon_S(\omega)$ over the range $\omega<\Delta$ (see Sec. II C).

In Eqs. (1), the imaginary part of $\epsilon(\omega)=\epsilon'+i\epsilon''$ is obtained by setting $\omega\to\omega+i\delta$ and taking $\delta\to 0^+$ following integrations over ω. An important point, established by plasmon spectroscopy via inelastic low-energy electron diffraction[24,25] is that surface collective excitations (plasmons), defined via

$$\epsilon_1(\Omega_s)+\epsilon_2(\Omega_s)=0 \tag{4a}$$

in our local two-medium model, occur at complex frequencies $\hbar\Omega_s=\hbar\omega_s+i\Gamma_s$, $\Gamma_s/\hbar\omega_s\sim 0.2$. A similar result is well known[26] to hold for bulk collective excitations (plasmons) defined by

$$\epsilon(\Omega_b)=0 \tag{4b}$$

in the local model. Although the observed magnitude of the plasmon lifetimes is not well understood,[25] their existance is readily incorporated into our model by use of the dielectric functions

$$\epsilon_M(\omega)=1-\omega_p^2/\omega(\omega+i/\tau)\ , \tag{5a}$$

$$\epsilon_S(\omega)=1+\omega_p^2/(\Delta^2-\omega^2-i\omega/\tau)\ . \tag{5b}$$

Equations (5) provide a three-parameter (ω_p, Δ, τ) description of each of two dielectric media comprising an interface. Since all of these parameters may be obtained directly from bulk optical-absorption and electron energy-loss spectra, the dielectric continuum model constitutes the simplest uniquely specified model of interface properties as functionals of known bulk spectra which we could construct. While our study of this model was undertaken merely as a prelude to that of a more adequate nonlocal dielectric model [i.e., $\epsilon = \epsilon(\vec{q}, \omega)$], the elegant simplicity of our final results and the insight which they afford into the structure of dielectric models of interface properties seemed to us to merit separate presentation. Moreover, they afford the opportunity to examine the general consequences of the large values of τ implied by electron scattering experiments.

B. Electrostatic potential-potential propagator

The electrostatic field, $\vec{E}(\vec{r}, t) = \vec{E}(\vec{r}, \omega)e^{i\omega t}$, associated with a charge $q(\vec{r}, t) = e\delta(\vec{r} - \vec{r}_0)e^{i\omega t}$ in the vicinity of a planar interface between the two local dielectric media indicated schematically in Fig. 1, may be obtained from any electrostatics text to be given by[1] $\vec{E}(\vec{r}, \omega) = -\nabla\phi(\vec{r}, \omega)$, with

$$\phi(\vec{r}, \vec{r}_0; \omega) = \begin{cases} \dfrac{e}{\epsilon_1(\omega)}\left[\dfrac{1}{[\rho^2 + (z - z_0)^2]^{1/2}} + \left(\dfrac{\epsilon_1(\omega) - \epsilon_2(\omega)}{\epsilon_1(\omega) + \epsilon_2(\omega)}\right)\dfrac{1}{[\rho^2 + (z + z_0)^2]^{1/2}}\right], & z > 0, \\ \dfrac{2e}{[\epsilon_1(\omega) + \epsilon_2(\omega)]}\,\dfrac{1}{[\rho^2 + (z - z_0)^2]^{1/2}}, & z < 0 \end{cases} \tag{6a}$$

if $z_0 > 0$, and

$$\phi(\vec{r}, \vec{r}_0; \omega) = \begin{cases} \dfrac{2e}{[\epsilon_1(\omega) + \epsilon_2(\omega)]}\,\dfrac{1}{[\rho^2 + (z - z_0)^2]^{1/2}}, & z < 0, \\ \dfrac{e}{\epsilon_2(\omega)}\left[\dfrac{1}{[\rho^2 + (z - z_0)^2]^{1/2}} + \left(\dfrac{\epsilon_2(\omega) - \epsilon_1(\omega)}{\epsilon_2(\omega) + \epsilon_1(\omega)}\right)\dfrac{1}{[\rho^2 + (z + z_0)^2]^{1/2}}\right], & z < 0 \end{cases} \tag{6b}$$

if $z_0 < 0$. In this subsection we demonstrate how this result alone leads immediately to the zero-wave-vector plasmon propagators predicted by random-phase approximation (RPA) and hydrodynamic models[27] and to a formula for the surface energy originally derived by Craig[5] to within a factor of 2 (and subsequently rederived in a different formalism by Barrera and Gerlach[4]).

The quantity used in quantum field theories of electron-solid interactions to describe the propagation of the electrostatic interaction through an inhomogeneous dielectric from position $\vec{r}$ to $\vec{r}'$ is the retarded particle-hole spectral-density propagator $\Lambda(\vec{r}, \vec{r}', \omega)$.[27,28] In classical models, this propagator is simply the electrostatic energy of an electron at $\vec{r}'$ associated with the polarization of the dielectric medium created by an electronic charge oscillating with frequency ω at position $\vec{r}$. Moreover, for the planar geometry indicated in Fig. 1, the complete propagator may be Fourier analyzed for motion parallel to the surface, i.e.,

$$\Lambda(\vec{r}', \vec{r}; \omega) = \int \frac{d^2q}{(2\pi)^2}\, e^{i\vec{q}\cdot(\vec{\rho}' - \vec{\rho})}\Lambda(z', z; \vec{q}, \omega), \tag{7}$$

where $\vec{q}$ is a two-dimensional vector on a plane parallel to the interface. Use of the spectral representation

$$\frac{1}{r} = \frac{1}{2\pi^2}\int d^3k\, \frac{e^{i\vec{k}\cdot\vec{r}}}{k^2}, \tag{8}$$

and subtraction of the field of the electron in the absence of the dielectric (i.e., $e/[\rho^2 + (z - z_0)^2]^{1/2}$) in Eqs. (6) to obtain the induced fields transmitted by the medium, leads to

$$\begin{aligned} \Lambda(z', z; \vec{q}, \omega) \equiv{}& \int d^2\rho'\, e^{-i\vec{q}\cdot\vec{\rho}'}\left(e\phi(\vec{\rho}' + z'\hat{k}, z\hat{k}; \omega) - \frac{e}{[\rho'^2 + (z' - z)^2]^{1/2}}\right) = \frac{2\pi e^2}{q}\left[\left(\frac{1}{\epsilon_1(\omega)} - 1\right)e^{-q|z-z'|}\right. \\ &\left. + \frac{1}{\epsilon_1(\omega)}\left(\frac{\epsilon_1(\omega) - \epsilon_2(\omega)}{\epsilon_1(\omega) + \epsilon_2(\omega)}\right)e^{-q(|z|+|z'|)}\right]\Theta(z)\Theta(z') + \frac{2\pi e^2}{q}\left(\frac{2}{\epsilon_1(\omega) + \epsilon_2(\omega)} - 1\right) \\ &\times e^{-q(|z|+|z'|)}[\Theta(z)\Theta(-z') + \Theta(-z)\Theta(z')] + \frac{2\pi e^2}{q}\left[\left(\frac{1}{\epsilon_2(\omega)} - 1\right)e^{-q|z-z'|}\right. \\ &\left. + \frac{1}{\epsilon_2(\omega)}\left(\frac{\epsilon_2(\omega) - \epsilon_1(\omega)}{\epsilon_2(\omega) + \epsilon_1(\omega)}\right)e^{-q(|z|+|z'|)}\right]\Theta(-z)\Theta(-z'). \end{aligned} \tag{9}$$

The $\exp(-q|z - z'|)$ terms in Eq. (9) arise from the transmission of bulk polarization fields through one component of the interface shown in Fig. 1, whereas the $\exp[-q(|z| + |z'|)]$ terms arise from the surface charge induced at the interface. The symbol $\Theta(z)$ designates the step function

$$\Theta(z)=\begin{cases}1, & z>0\ ,\\ \tfrac{1}{2}, & z=0\ ,\\ 0, & z<0\ .\end{cases} \tag{10}$$

Equation (9) is not yet in the form used by Duke *et al.*[27,28] because the surface-charge terms exhibit poles at the frequencies of bulk collective oscillations, Eq. (4b), as well as at those of the surface collective oscillations, Eq. (4a). In order to obtain the bulk and surface plasmon propagators in the form used by Duke *et al.*, these two sets of singularities are readily separated to give

$$\Lambda(z',z;\vec{q},\omega)=\frac{2\pi e^2}{q}\left(\frac{2}{\epsilon_1(\omega)+\epsilon_2(\omega)}-1\right)e^{-q(|z|+|z'|)}+\frac{2\pi e^2}{q}\left(\frac{1}{\epsilon_1(\omega)}-1\right)\left(e^{-q|z-z'|}-e^{-q(|z|+|z'|)}\right)\Theta(z)\Theta(z')$$
$$+\frac{2\pi e^2}{q}\left(\frac{1}{\epsilon_2(\omega)}-1\right)\left(e^{-q|z-z'|}-e^{-q(|z|+|z'|)}\right)\Theta(-z)\Theta(-z')\ . \tag{11}$$

The results given in Refs. 27 and 28 for the metal-vacuum interface are obtained by inserting into Eq. (11) the metal dielectric function given by Eq. (2) and $\epsilon_1(\omega)\equiv 1$ for the vacuum. We obtain

$$\frac{1}{\epsilon_2(\omega)}-1=\frac{(\omega_p/\omega)^2}{1-(\omega_p/\omega)^2} \tag{12a}$$

and

$$\frac{2}{\epsilon_1(\omega)+\epsilon_2(\omega)}-1=\frac{1-\epsilon_2(\omega)}{1+\epsilon_2(\omega)}=\frac{\omega_p^2/2\omega^2}{1-\omega_p^2/2\omega^2}\ , \tag{12b}$$

which upon utilization in Eq. (11) yields directly the surface-plasmon propagator indicated in Eqs. (64) and (94)–(96) of Ref. 27. In this reference, the form of Eq. (11) was derived by demonstrating that the surface and bulk plasmons correspond to orthogonal eigenfunctions of a Hermitian operator. The analysis presented above reveals that from the perspective of a classical dielectric function formalism, however, Eq. (11) is the elementary consequence of a partial-fraction expansion of the classical induced surface-charge field into components associated with the bulk and surface spectral densities, i.e., $1/\epsilon_i(\omega)-1$ and $2/[\epsilon_1(\omega)+\epsilon_2(\omega)]-1$, respectively. Moreover, it is evident from our treatment that in the only case for which the RPA orthonormalcy relations for bulk and surface plasmons can be worked out explicitly (i.e., the high-frequency step-density model[27]) they amount to a complicated restatement of the consequences of classical electrostatics. It is also clear that the RPA orthonormalcy relations cannot be extended immediately to include the effects of plasmon damping.

A discussion of the difficulties inherent in attempting to extend the RPA analysis to more complicated surface charge densities may be found both in Ref. 27 and in a host of more recent works on this topic.[11–13,29–35] Our analysis reveals that in the local limit the RPA may be obtained simply from Eq. (2) plus classical electrostatics. It also suggests that even in the nonlocal case[11–13,29–35] the direct use of electrostatics plus a model dielectric function may prove a more convenient and transparent approach to the computation of the electrostatic propagator associated with multilayer media.

C. Density-density propagator and surface energy

The quantities needed to calculate the surface energy are the diagonal matrix elements of the retarded density-density (i.e., polarization) propagator.[4] Consequently, in the subsection we first review the definition of this propagator and its relationship to the electrostatic propagator evaluated in Sec. II B. Then we give explicit forms for the polarization propagator and the surface energy obtained in our dielectric continuum model. We conclude the subsection by comparing our expression for the surface energy with those obtained by other authors.

The electrostatic polarization propagator is defined by[36]

$$\Lambda(\vec{r}\,',\vec{r};t'-t)=-i\Theta(t'-t)\langle[e\hat{\phi}(\vec{r}\,',t'),e\hat{\phi}(\vec{r},t)]\rangle\ . \tag{13}$$

The quantity $\phi(\vec{r},t)$ is the electrostatic field operator. The propagator or interest in surface energy calculations, i.e., $\alpha(\vec{r},\vec{r};t'-t)$, is defined via

$$\alpha(\vec{r}\,',\vec{r};t'-t)=\delta\rho(\vec{r}\,',t')/\delta\rho_{\text{ext}}(\vec{r},t)\ , \tag{14}$$

where $\delta\rho$ and $\delta\rho_{\text{ext}}$ are the induced and external electron densities respectively. Alternatively, α is defined by

$$\alpha(\vec{r}\,',\vec{r};t'-t)=-i\Theta(t'-t)\int d^3r''$$
$$\times\langle[\hat{\rho}(\vec{r}\,',t'),\hat{\rho}(\vec{r}\,'',t)]\rangle V(\vec{r}\,''-\vec{r})\ , \tag{15}$$

where $\hat{\rho}(\vec{r},t)$ is the electron density operator and $V(\vec{r}-\vec{r}\,')$ is the bare Coulomb potential. Using Eqs. (7), (13), and (15) it is straightforward to show that

$$\Lambda(z',z;\vec{q},\omega)=-\frac{2\pi e^2}{q}\int_{-\infty}^{\infty}dz''\{\alpha_{++}(z',z'';\vec{q},\omega)\times\Theta(z')\Theta(z)+\alpha_{--}(z',z'';\vec{q},\omega)\Theta(-z')\Theta(-z)+\alpha_{+-}(z',z'';\vec{q},\omega)[\Theta(z)\Theta(-z')+\Theta(-z)\Theta(z')]\}e^{-q|z''-z|}\ . \tag{16}$$

Inserting Eq. (16) into Eq. (11) to obtain the polarization propagator yields

$$\alpha_{++}(z',z;\vec{q},\omega)=\delta(z)e^{-qz'}\frac{1}{\epsilon_1(\omega)}\left(\frac{\epsilon_2(\omega)-\epsilon_1(\omega)}{\epsilon_1(\omega)+\epsilon_2(\omega)}\right)+\delta(z'-z)\left(1-\frac{1}{\epsilon_1(\omega)}\right)\ , \tag{17a}$$

$$\alpha_{--}(z',z;\vec{q},\omega)=\delta(z)e^{qz'}\frac{1}{\epsilon_2(\omega)}\left(\frac{\epsilon_1(\omega)-\epsilon_2(\omega)}{\epsilon_1(\omega)+\epsilon_2(\omega)}\right)+\delta(z-z')\left(1-\frac{1}{\epsilon_2(\omega)}\right)\ , \tag{17b}$$

$$\alpha_{+-}(z',z;\vec{q},\omega)=\delta(z)e^{-q|z'|}\left(\frac{2}{\epsilon_1(\omega)+\epsilon_2(\omega)}-1\right)\ . \tag{17c}$$

The terms containing $\delta(z)$ emanate from charge induced on the surface. Thus, we can define the surface contributions to the diagonal density-density response function $\alpha(z,z;\vec{q},\omega)$ via collecting these terms in Eqs. (17a)–(17c) to yield

$$\alpha_s(z,z;\vec{q},\omega)=\frac{\delta(z)}{2}\left[\left(\frac{1}{\epsilon_1(\omega)}-\frac{1}{\epsilon_2(\omega)}\right)\left(\frac{\epsilon_2(\omega)-\epsilon_1(\omega)}{\epsilon_2(\omega)+\epsilon_1(\omega)}\right)\right]\ , \tag{18}$$

noting that $\Theta^2(z)=\Theta(z)$ and $\Theta(z\to 0)=\frac{1}{2}$. At zero temperature the surface energy γ may be written in terms of $\alpha_s(z,z;\vec{q},\omega)$ via[4]

$$\gamma=\int_0^{e^2}\frac{dg}{g}\int\frac{d^2q}{(2\pi)^2}\int_0^{\infty}\hbar\frac{d\omega}{2\pi}\times\int_{-\infty}^{\infty}dz\ \mathrm{Im}\alpha_s(z,z;\vec{q},\omega)\ , \tag{19}$$

which in our case of a planar interface becomes

$$\gamma=\frac{\hbar}{2}\int_0^{e^2}\frac{dg}{g}\int\frac{d^2q}{(2\pi)^2}\int_0^{\infty}\frac{d\omega}{2\pi}\times\mathrm{Im}\left(\frac{[\epsilon_1(\omega)-\epsilon_2(\omega)]^2}{\epsilon_1(\omega)\epsilon_2(\omega)[\epsilon_1(\omega)+\epsilon_2(\omega)]}\right)\ . \tag{20}$$

In Eqs. (19) and (20) the square of the electronic charge e^2 is replaced by g in the expressions for $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ under the integral. The ω integral is taken over the cut of the bracketed expression which extends from $\omega=0$ to infinity.

Equation (19) is precisely twice the corresponding result given in Eq. (3.12) of Ref. 5 although we have written it in terms of the retarded dielectric functions $\epsilon_1(\omega+i\delta;\ \delta\to 0^+)$ rather than the Matsubara frequency sums used by Craig.

In the special case of a metal-vacuum interface [e.g., that specified by Eqs. (12)], Eq. (20) may be compared with the results of several authors.[4–8] While differing from Craig's general formula, Eq. (3.12) in Ref. 5, by the factor of 2 noted above, it is identical to the zero-point energy utilized by Schmit and Lucas[7] and by Feibelman.[8] Indeed, we now see that these authors' expressions for the surface energy differ from that of Craig[5] *both* by the factor of 2 inherent in Eq. (19) *and* by an additional factor of three caused by introducing an e^2-dependent cutoff on the q integration *prior to* (rather than after) performing the coupling constant (g) integral. This conclusion is contrary to Craig's claim[6] that the inversion of the order of the q and g integrations gives the entire factor of 6. We note, moreover, that in a proper theory the coupling constant integral *must be performed first*, giving the surface energy as a *difference* of particle-hole excitation energies at $g=e^2$ and $g=0$.[12,37–39] Not only does the occurrence of this difference have the technical consequence that the collective mode contribution to the surface energy is reduced[12,13] but more important it introduces the large wave-vector (q) cutoff into the expression for the surface energy.[12,37,38] Therefore the use of a wave-vector cutoff which depends on e^2 *prior* to the coupling constant (g) integration in Eqs. (19) or (20) is conceptually incorrect as well as technically inaccurate.

A further interesting consequence of Eq. (20) is its apparent independence of the shape of the electron density profile in the vicinity of the interface. This surprising result may be proved explicitly for the metal-vacuum interface by use of Barrera and Gerlach's form[4] for the $\alpha_s(z,z;\vec{q},\omega)$ i.e.,

$$\alpha_s(z,z;\vec{q},\omega)=-\frac{(\omega_p^2/\omega^2)(dn/dz)}{2[1-\omega_p^2 n(z)/\omega^2]^2}\left(\frac{\omega_p^2/2\omega^2}{1-\omega_p^2/2\omega^2}\right) \tag{21}$$

to evaluate the integral over z in Eq. (19). In Eq. (21) the symbol $n(z)$ designates a normalized density profile, $n(-\infty)=1$ and $n(\infty)=0$. The integral over z in Eq. (21) is performed easily giving

$$\int_{-\infty}^{\infty}dz\ \alpha_s(z,z;\vec{q},\omega)=\frac{1}{2}\left(\frac{1}{1-\omega_p^2/\omega^2}-1\right)\left(\frac{\omega_p^2/2\omega^2}{1-\omega_p^2/2\omega^2}\right)=\frac{1}{2}\left(\frac{1}{\epsilon_M(\omega)}-1\right)\left(\frac{1-\epsilon_M(\omega)}{1+\epsilon_M(\omega)}\right)\ , \tag{22}$$

which is precisely the result given by Eq. (20) for the planar, semiclassical interface between a metal and a vacuum.

In conclusion, it is noteworthy that the polarization propagator α and hence the surface energy can be calculated directly via classical electrostatics. Equation (14) indicates that $\alpha(\vec{r}', \vec{r}; \omega)$ is simply the induced electron density at $\vec{r}'$, produced by an external point charge at $\vec{r}$ oscillating with frequency ω. In the case of a planar geometry the electron-density induced, which corresponds to α, can be calculated electrostatically from Eqs. (16) to give Eqs. (17), which lead to Eq. (20) for the surface energy.

D. One-electron optical potential

In this subsection we apply our simple local dielectric formalism to calculate the electron-solid optical potential for high-energy electrons. The one-electron optical potential recently has been used to describe the electron-solid scattering in model calculations of low-energy electron diffraction (LEED) intensities[20] and photoemission studies.[40] Here we calculate that part of the optical potential which accounts for the absorption and emission of bulk and surface plasmons following the procedure of Ref. 27. For simplicity, we confine our attention to the solid-vacuum interface because our important conclusions will result from the large value of τ in Eqs. (5), independent of the value of Δ.

The optical potential can be described[41,42] by the coordinate representation of the retarded proper self-energy $\Sigma(\vec{r}', \vec{r}; \omega)$. In the case of high-energy electrons ($E \gtrsim 100$ eV), used, e.g., in LEED, the relevant contribution to $\Sigma(\vec{r}', \vec{r}; \omega)$, in the zero-temperature limit, is given by [see Eq. (114b) of Ref. 27].

$$\Sigma(\vec{r}', \vec{r}; \omega) = -\frac{\hbar}{\pi} \int_0^\infty dx\, G(\vec{r}', \vec{r}; \omega - x)\, \mathrm{Im}\Lambda(\vec{r}, \vec{r}'; x), \tag{23}$$

in which $G(\vec{r}', \vec{r}; \omega)$ is the retarded electron propagator. In our model of planar interfaces Eq. (23) can be Fourier analyzed along the surface to give

$$\Sigma(z', z; \vec{q}, \omega) = -\frac{\hbar}{\pi} \int_0^\infty dx \int \frac{d^2q'}{(2\pi)^2} \times G(z', z; \vec{q}+\vec{q}', \omega - x)\, \mathrm{Im}\Lambda(z, z'; \vec{q}', x). \tag{24}$$

For the purpose of estimating the optical potential for high-energy electrons one can use[27] (a plane-wave basis for G)

$$G(z', z; \vec{q}, \omega) = \int_{-\infty}^{\infty} \frac{dk_\perp}{2\pi} \frac{e^{ik_\perp(z'-z)}}{\hbar\omega - (\hbar^2/2m)(q^2 + k_\perp^2)}, \tag{25}$$

in which $k_\perp$ is the component of the wave vector in the direction perpendicular to the interface.

In order to calculate Σ from Eq. (24) we use for G the expression given by Eq. (25) and for Λ the expression given by Eq. (11) with the model dielectric function of Eq. (5b). We obtain

$$\Sigma(z', z; \vec{q}, \omega) = -\frac{\hbar}{\pi} \sum_{i=p,s} \int \frac{d^2q'}{(2\pi)^2} \frac{2\pi e^2}{q'} \omega_i^2 F_i(z', z; q') \int_{-\infty}^{\infty} \frac{dk_\perp}{2\pi} e^{ik_\perp(z'-z)} \times \int_0^\infty dx \left(\hbar(\omega - x) - \frac{\hbar^2}{2m} (|\vec{q}+\vec{q}'|^2 + k_\perp^2)\right)^{-1} \mathrm{Im}\left(x^2 + \frac{ix}{\tau} - (\omega_i^2 + \Delta^2)\right)^{-1}, \tag{26a}$$

where

$$F_i(z', z; q') = \begin{cases} (e^{-q'|z'-z|} - e^{-q'(|z|+|z'|)})\, \Theta(-z)\Theta(-z'); & i = p, \\ e^{-q'(|z|+|z'|)}, & i = s. \end{cases} \tag{26b}$$

The subindex p and s refer to the bulk and the surface contributions to the optical potential, respectively.

The x integral can be performed analytically to give

$$\Sigma(z', z; \vec{q}, \omega) = \frac{1}{2\pi} \sum_{i=p,s} \int \frac{d^2q'}{(2\pi)^2} \frac{2\pi e^2}{q'} \frac{\omega_i^2}{\Omega_i} F_i(z', z; q') \int_{-\infty}^{\infty} \frac{dk_\perp}{2\pi} e^{ik_\perp(z'-z)} \left[\pi\, \mathrm{Re}\left(\frac{1}{x_0 - \Omega_i + i/2\tau}\right) - \mathrm{Re}\left(\frac{1}{x_0 - \Omega_i + i/2\tau} + \frac{1}{x_0 + \Omega_i + i/2\tau}\right) \tan^{-1}\frac{1}{2\Omega_i\tau} + \mathrm{Im}\left(\frac{1}{x_0 - \Omega_i + i/2\tau} - \frac{1}{x_0 + \Omega_i + 1/2\tau}\right) \times \left(i\pi\Theta(x_0) - \ln_{10} \left|\frac{x_0}{(\omega_i^2 + \Delta^2)^{1/2}}\right|\right)\right], \tag{27a}$$

$$\Omega_i^2 = \omega_i^2 + \Delta^2 - (1/2\tau)^2, \tag{27b}$$

$$x_0 = \omega - (\hbar/2m)(|\vec{q}+\vec{q}'|^2 + k_\perp^2). \tag{27c}$$

Before analyzing the effects of plasmon damping on the optical potential, we note that one can obtain the classical image potential as a limiting case provided we take the semiclassical limit ($m \to \infty$) of Eq. (27) at zero frequency and impose a cutoff wave vector q_c in the evaluation of the q' integral. We find that in the limit $q_c^{-1} \ll |z|, |z'|$ the self-energy becomes

$$\Sigma(z', z; \vec{q}, 0) = \delta(z' - z)\left[-\frac{e^2 q_c}{2}\left(1 - \frac{1}{\epsilon(0)}\right)\Theta(-z') - \frac{e^2}{4|z|}\left(\frac{e(0)-1}{e(0)+1}\right)\Theta(z')\right] . \tag{28}$$

Hence, we recover the classical local image potential as expected. Here $e(0) = 1 + \omega_p^2/\Delta^2$ is the static dielectric constant corresponding to our model dielectric function of Eq. (5b). In the metallic limit ($\Delta \to 0$) we recover the results of Ref. 27.

Since $\omega_i^2 + \Delta^2 \gg 1/2\tau$, the dominant terms in the $k_\perp$ integral of Eq. (27a) are

$$\int_{-\infty}^{\infty} \frac{dk_\perp}{2\pi}\, e^{ik_\perp(z'-z)}\left[\pi \operatorname{Re}\left(\frac{1}{x_0 - \Omega_i + i/2\tau}\right) + i\pi\Theta(x_0)\operatorname{Im}\left(\frac{1}{x_0 - \Omega_i + i/2\tau}\right)\right] , \tag{29}$$

which can be approximated by

$$\int_{-\infty}^{\infty} \frac{dk_\perp}{2\pi}\, e^{ik_\perp(z'-z)}\left(\frac{\pi}{x_0 - \Omega_i + i/2\tau}\right) . \tag{30}$$

This integral can be performed in the complex $k_\perp$ plane yielding

$$\Sigma(z', z; \vec{q}, \omega) \approx -\frac{\mu}{4}\sum_{i=p,s}\int \frac{d^2q'}{(2\pi)^2}\,\frac{2\pi e^2}{q'}\,\frac{\omega_i^2}{\Omega_i}\,F_i(z', z; q')\,\frac{\exp[-\mu(\gamma_i + i\delta_i)|z'-z|]}{\gamma_i + i\delta_i} , \tag{31a}$$

$$\mu = (2m/\hbar)^{1/2} , \tag{31b}$$

$$\gamma_i = (1/\sqrt{2})\{-(\omega - \nu_i) + [(\omega - \nu_i)^2 + (1/2\tau)^2]^{1/2}\}^{1/2} , \tag{31c}$$

$$\delta_i = (1/\sqrt{2})\{(\omega - \nu_i) + [(\omega - \nu_i)^2 + (1/2\tau)^2]^{1/2}\}^{1/2} , \tag{31d}$$

and

$$\nu_i = \Omega_i + (\hbar/2m)|\vec{q} + \vec{q}\,'|^2 . \tag{31e}$$

It can now easily be seen that due to the finite plasmon lifetime the range of nonlocality of the optical potential is always finite at all frequencies. The shortest range of nonlocality is when $\omega \to 0$. The range increases as ω increases being limited by a length $\lambda \sim [\mu/(2\tau)^{1/2}]^{-1} = (\hbar\tau/m)^{1/2}$ as $\omega \to \nu_i$.

If we now take the $\tau \to \infty$ limit in Eq. (31) it can easily be shown that for $\omega > (\omega_i^2 + \Delta^2)^{1/2}$ the range of the nonlocality is not well defined owing to the appearance of the factors $e^{-i\mu\delta_i}$ in the q' integral recovering, in this way, the metallic-limit ($\Delta \to 0$) results discussed in Ref. 27. Thus, we obtain the important result that the approximate validity of local models of the optical potential, whose use is essentially universal in the theory of LEED[20] and photoemission,[40] is a direct consequence of plasmon damping which itself is most probably a result of imperfections in the samples being studied.

III. SURFACE ENERGY OF INTERFACES

In this section we analyze the effects of plasmon damping on the surface energy γ and evaluate the surface energy of various interfaces using Eq. (20) derived in Sec. IIC. We proceed by recalling from Sec. IIC that the coupling constant (g) integration in Eq. (20) must be performed prior to the ω and q integrations. For any model *local* dielectric function which satisfies the f-sum rule [e.g., Eq. (1c)] the g integration can be performed in closed form leaving a general expression for γ as an integral over ω and q. Using this expression we first analyze the effects of plasmon damping on the surface energy γ examining, for simplicity, the metal-vacuum (*MV*) and the semiconductor-vacuum (*SV*) interfaces. In particular, we show that plasmon lifetime has a strong effect in decreasing the surface energy, the effect being stronger for metals than for semiconductors. Next, we calculate the surface energy of a two-dielectric interface as a function of the material parameters ω_{pi} and Δ_i, in order to establish the general features of the behavior of γ as a function of these parameters. Thus, in this calculation we utilize the model dielectric functions given by Eq. (3a) in which plasmon damping is neglected. Specifically, we analyze the behavior of γ for semiconductor-semiconductor (*SS*), semiconductor-metal (*SM*), and metal-metal (*MM*) interfaces in turn, and conclude with some general observations about the energetics of interfaces.

Starting from Eq. (20) we perform first the coupling constant (g) integration. From Eqs. (1) we see that the g dependence of any model local dielectric function which obeys the f-sum rule is given by

$$\epsilon_i(\omega;g)-1=g\left(\omega_p^2\sum_\gamma\frac{f_\gamma}{\omega_r^2-\omega^2}\right)\quad. \tag{32}$$

Insertion of Eq. (32) into Eq. (20) and integration over g from 0 to 1 yields

$$\gamma=\frac{\hbar}{2}\int\frac{d^2q}{(2\pi)^2}\int_0^\infty\frac{d\omega}{2\pi}\ln[f(i\omega)], \tag{33a}$$

$$f(\omega)=\{\tfrac{1}{2}[\epsilon_1(\omega)+\epsilon_2(\omega)]\}^2/\epsilon_1(\omega)\epsilon_2(\omega)\quad. \tag{33b}$$

In Eqs. (33) $\epsilon_i(\omega)\equiv\epsilon_i(\omega;g=1)$ and the analytic properties of $f(\omega)$ were exploited in order to convert the ω integral along the real axis into an integral along the imaginary axis.

Since our model local dielectric functions given by Eqs. (5) satisfy the f-sum rule we are able to analyze the effects of a finite plasmon lifetime on the surface energy by computing γ for the *SV* interface via use of

$$\epsilon_1(\omega)=1, \tag{34a}$$

$$\epsilon_2(\omega)=1+\omega_p^2/(\Delta^2-\omega^2-i\omega/\tau). \tag{34b}$$

While such an analysis is not directly applicable to real solids because of the nonlocality (i.e., $\vec{q}$ dependence) of the dielectric function, nevertheless it reveals the structure of a *local* dielectric theory. Inserting Eqs. (34) into Eqs. (33) and considering that $\omega_i\tau\gg1$ (for the plasmons to be well-defined excitations) yields

For $\Delta<1/2\tau\ll\omega_i$,

$$\gamma_{SV}=\frac{\hbar q_c^2}{16\pi}\left(2\Omega_s-\Omega_p-\frac{2}{\pi}\left\{2\Omega_s\tan^{-1}\frac{1}{2\Omega_s\tau}-\Omega_p\tan^{-1}\frac{1}{2\Omega_p\tau}+\frac{1}{2}\left[\left(\frac{1}{2\tau}\right)^2-\Delta^2\right]^{1/2}\ln\left(\frac{1/2\tau-[(1/2\tau)^2-\Delta^2]^{1/2}}{1/2\tau+[(1/2\tau)^2-\Delta^2]^{1/2}}\right)\right.\right.$$
$$\left.\left.+\frac{1}{2\tau}\ln\left(\frac{\omega_s^2+\Delta^2}{\Delta[\omega_p^2+\Delta^2]^{1/2}}\right)\right\}\right)\quad. \tag{35a}$$

For $1/2\tau<\Delta$ and $1/2\tau\ll\omega_i$,

$$\gamma_{SV}=\frac{\hbar q_c^2}{16\pi}\left\{2\Omega_s-\Omega_p-\left[\Delta^2-\left(\frac{1}{2\tau}\right)^2\right]^{1/2}-\frac{2}{\pi}\left[2\Omega_s\tan^{-1}\frac{1}{2\Omega_s\tau}-\Omega_p\tan^{-1}\frac{1}{2\Omega_p\tau}-\left[\Delta^2-\left(\frac{1}{2\tau}\right)^2\right]^{1/2}\right.\right.$$
$$\left.\left.\times\tan^{-1}\left(\frac{1}{2\tau[\Delta^2-(1/2\tau)^2]^{1/2}}\right)+\frac{1}{2\tau}\ln\left(\frac{\omega_s^2+\Delta^2}{\Delta(\omega_p^2+\Delta^2)^{1/2}}\right)\right]\right\}, \tag{35b}$$

where

$$\Omega_i^2=\omega_i^2+\Delta^2-(1/2\tau)^2 \tag{27b}$$

and q_c is the familiar cutoff wave vector introduced in the otherwise divergent q integral which assumes the existence of dispersionless plasmons only for wave numbers less than q_c. A better description of the dispersion of the plasmon frequency or the inclusion of particle-hole excitation modes lie beyond *any* local treatment.

When $\Delta\rightarrow0$ in Eq. (35a) the surface energy of the *MV* interface is obtained to be

$$\gamma_{MV}=\frac{q_c^2\hbar\omega_p}{16\pi}\left(\left[2-\left(\frac{1}{\omega_p\tau}\right)^2\right]^{1/2}-\left[1-\left(\frac{1}{2\omega_p\tau}\right)^2\right]^{1/2}-\frac{2}{\pi}\left\{\left[2-\left(\frac{1}{\omega_p\tau}\right)^2\right]^{1/2}\tan^{-1}\left(\frac{1}{\omega_p\tau[2-(1/\omega_p\tau)^2]^{1/2}}\right)\right.\right.$$
$$\left.\left.-\left[1-\left(\frac{1}{2\omega_p\tau}\right)^2\right]^{1/2}\tan^{-1}\left(\frac{1}{2\omega_p\tau[1-(1/2\omega_p\tau)^2]^{1/2}}\right)+\frac{1}{2\omega_p\tau}\ln\left(\frac{\omega_p\tau}{2}\right)\right\}\right). \tag{36}$$

Furthermore, as $\tau\rightarrow\infty$ we obtain

$$\gamma_{MV}=(q_c^2\hbar\omega_p/16\pi)\,(\sqrt{2}-1)\quad, \tag{37}$$

which is simply the Schmit and Lucas result[7] for the *MV* interface derived from the changes in the number of modes and the corresponding change in the zero-point energies of longitudinal and transverse *undamped* plasma oscillations.

To examine the influence of finite τ^{-1} on the surface energy in Fig. 2 we plot Eq. (36) for γ_{MV} as a function of the plasmon lifetime $1/\omega_p\tau$. It is evident from this figure that the strong plasmon damping observed in metals[24,25] reduces the surface energy by a considerable amount with respect to its undamped ($\tau\rightarrow\infty$) value given by Eq. (37). For example, in the case of aluminum, for which $1/\omega_p\tau\simeq0.1$,[24,25] γ is reduced by about 20%. This significant decrease in the surface energy due to plasmon damping negates the validity of the quantitative claims of Ref. 7 even though these claims have already been criticized[11–13] for different reasons, mainly the effects of nonlocality on the dielectric function in the jellium-vacuum interface.

For semiconductors (Δ finite) the consequences of plasmon damping on the surface energy in turn depend strongly on the value of the band-gap parameter Δ. First we take in Eq. (35b) the $\tau \rightarrow \infty$limit to obtain

$$\gamma_{SV} = (q_c^2 \hbar \omega_p / 16\pi) \{ [2 + (2\Delta/\omega_p)^2]^{1/2} - [1 + (\Delta/\omega_p)^2]^{1/2} - \Delta \}. \quad (38)$$

This result reveals, as illustrated in Fig. 3, that the surface energy drops markedly, with respect to its metallic limit ($\Delta \rightarrow 0$), as the band gap increases. For a semiconductor with $\Delta/\omega_p = 0.5$ the surface energy decreases by 70% with respect to the corresponding one of a metal with the same plasma frequency ω_p.

To examine the effect of plasmon lifetime on γ_{SV} we also show in Fig. 3 the surface energy γ_{SV} as a function of the semiconductor band gap Δ/ω_p for different values of the plasmon lifetime $z \equiv 1/\omega_p\tau$ as given by Eqs. (35). Evidently, the decrease in the surface energy with increasing τ^{-1} becomes less important as the value of the band gap increases. For small-gap semiconductors, i.e.,

$$\Delta/\omega_p \simeq 0.05 \quad (39a)$$

and

$$1/\omega_p\tau \simeq 0.1 \ , \quad (39b)$$

the decrease on the surface energy is of about 18% while for large-gap insulators, i.e., $\Delta/\omega_p \simeq 0.8$ and $1/\omega_p\tau \simeq 0.1$, the corresponding reduction of γ_{SV} is of only 1%.

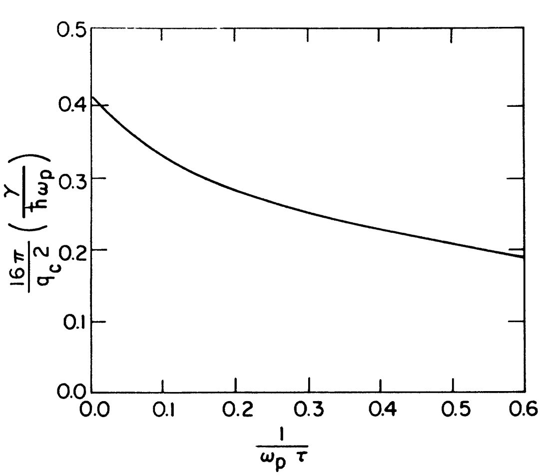

FIG. 2. Surface energy γ of a metal-vacuum interface as a function of $1/\omega_p\tau$.

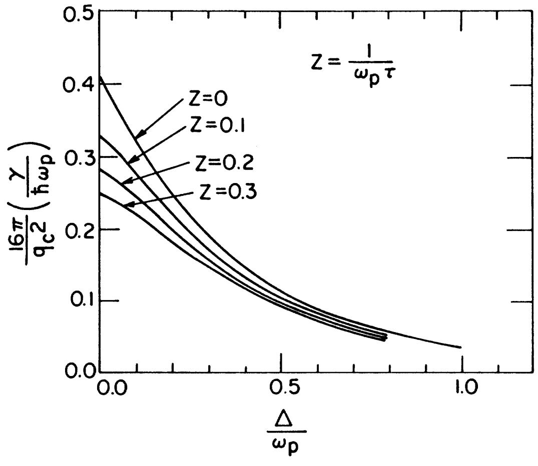

FIG. 3. Surface energy γ of the semiconductor-vacuum interface as a function of the semiconductor band gap Δ/ω_p for different values $z = 1/\omega_p\tau$ of the plasmon lifetime. The curve $z = 0$ is the surface energy of the metal-vacumm interface corresponding to undamped plasmons.

Given Eqs. (33), we can cast our results into a form which relates γ to changes in plasmon zero-point energies for the special case in which $\epsilon_i(\omega)$ is a meromorphic function of ω with poles and zeros only on the real axis. In this case the function $f(\omega)$ which appears in Eq. (33) is also meromorphic in ω and with poles and zeros only on the real axis. Therefore an integration by parts of the ω integral of Eq. (33) is possible and with an appropriate change of integration contour Eq. (33) becomes

$$\gamma = -\frac{\hbar}{2} \int \frac{d^2q}{(2\pi)^2} \int_C \frac{d\omega}{2\pi i} \, \omega \, \frac{\partial}{\partial\omega} \ln [f(\omega)] \ , \quad (40)$$

where the contour C is a half circle in the right-half ω plane, and it has been assumed that $f(\omega) \sim 1/\omega^2$, when $\omega \rightarrow \infty$. Integration of Eq. (40) through a well-known integration theorem[43] shows that the surface energy can be written

$$\gamma = \frac{\hbar}{4} \int \frac{d^2q}{(2\pi)^2} \left(2 \sum_S \omega_S - \omega_{b1} - \omega_{b2} - \omega_{T1} - \omega_{T2} \right) , \quad (41)$$

i.e., as a sum of plasmon normal modes. Here $\epsilon_1(\omega_S) + \epsilon_2(\omega_S) = 0$ defines the surface-plasmon mode, $\epsilon_i(\omega_{bi}) = 0$ defines the bulk-plasmon mode, and $\epsilon_i^{-1}(\omega_{Ti}) = 0$ defines the bulk-transverse-excitation mode.

Equation (41) admits the obvious interpretation that in a local dielectric theory the surface energy is simply the change in plasmon zero-point energy upon the formation of an interface. Therefore in the case of the MV interface with $\epsilon_M = 1 - \omega_p^2/\omega^2$, Eq. (41) evidently reduces to the Schmit and Lucas[7] surface energy formula derived from changes in the number of normal modes of the system when the surface is introduced. In the case of nonlocal dielectric models, the zero-point energy formulas are more complex because of particle-hole states, but the general structure of the theory probably also can be cast into a form analogous to Eq. (41), as shown in a special case by Griffin *et al.*[12]

Next, it is instructive to calculate the surface energy γ_{SS} of the *SS* interface using Eq. (41) directly and the model dielectric function of Eq. (3a) in which plasmon damping is neglected. The surface energies of the *SM* and *MM* interfaces are obtained directly from γ_{SS} as limiting cases. The *SS* interface is characterized by

$$\epsilon_1(\omega) = 1 + \omega_{p1}^2/(\Delta_1^2 - \omega^2)\ , \tag{42a}$$

$$\epsilon_2(\omega) = 1 + \omega_{p}^2{}_2/(\Delta_2^2 - \omega^2). \tag{42b}$$

Substituting Eqs. (42) into Eq. (41), and introducing a cutoff wave vector q_c on the q integration, we obtain after some algebra

$$\begin{aligned}(16\pi/q_c^2)(\gamma_{SS}/\hbar\omega_{p2}) = {} & [((1+x^2+2y_1^2+2y_2^2)+\{(1+x^2+2y_1^2+2y_2^2)^2-8[(1+y_2^2)y_1^2+(x^2+y_1^2)y_2^2]\}^{1/2})^{1/2} \\ & +((1+x^2+2y_1^2+2y_2^2)-\{(1+x^2+2y_1^2+2y_2^2)^2-8[(1+y_2^2)y_1^2+(x^2+y_1^2)y_2^2]\}^{1/2})^{1/2}]_S-[(x^2+y_1^2)^{1/2} \\ & +(1+y_2^2)^{1/2}]_b-(y_1+y_2)_T ,\end{aligned} \tag{43a}$$

$$x = \omega_{p1}/\omega_{p2}, \tag{43b}$$

$$y_1 = \Delta_1/\omega_{p2}, \tag{43c}$$

$$y_2 = \Delta_2/\omega_{p2}, \tag{43d}$$

and the subindices S, b, and T, refer to the contributions of the surface, bulk, and transverse-excitation modes, respectively. From Eqs. (43) we can obtain the surface energy, γ_{SM} for the *SM* interface by setting $y_1 = \Delta_1/\omega_{p2} = 0$ in Eqs. (43). In Fig. 4 we display a graph of γ_{SM} as a function of the semiconductor band gap Δ_2/ω_{p2} for different ratios $x = \omega_{p1}/\omega_{p2}$ of the plasma frequencies. The curve $x = 0$ is a limiting case which corresponds to the surface energy γ_{SV} of the *SV* interface given already in Eq. (38) while the value of the curves at $\Delta_2/\omega_{p2} = 0$ gives the surface energy γ_{MM} of the *MM* interface for metals with plasma frequencies ω_{p2} and ω_{p1}. The general behavior of γ_{MM} as a function of $x = \omega_{p1}/\omega_{p2}$ is obtained by setting $y_1 = y_2 = 0$ in Eq. (43) and is displayed in Fig. 5. The value of γ_{MM} at $x = 0$ corresponds to the surface energy γ_{MV} at the metal-vacuum interface [see Eq. (37)] and from there it decreases to zero at $x = 1$ where the two metals are identical and consequently no surface exists.

In order to illustrate the behavior of γ_{SS} as a function of the material parameters we show in Fig. 6 its functional dependence with $y_2 = \Delta_2/\omega_{p2}$ and different $x = \omega_{p1}/\omega_{p2}$ plasma frequency ratios choosing, as an example, $y_1 = \Delta_1/\omega_{p2} = 0.5$. In this case for $x = 1.0$ the surface energy goes to zero at $\Delta_2/\omega_{p2} = 0.5$ which is the point at which both semiconductors are identical. Evidently, γ is a monotonically decreasing function of the gap parameter only of the higher density semiconductor.

Our final topic in this section is a brief interpretation of the results derived using Eqs. (5) and (33) and illustrated in Figs. 2–6. First, the reduction in surface energy caused by increasing plasmon damping has the obvious origin of simulating, as best one can in a local dielectric model, the reduction of the zero-point energy associated with collective branches of the excitation spectrum.[12,37,38] It is noteworthy that this transfer at $\vec{q} = 0$ occurs *in addition to* that obtained for $\vec{q} \neq 0$ plasmons by Griffin *et al.*[12] Second, the general reduction in γ with increasing Δ for semiconductor-vacuum contacts also exhibits the obvious interpretation, stressed earlier within the context of local-density models,[22] that it is a result of decreasing the difference in the valence-electron surface charge density between the solid and the vacuum. A similar comment obviously describes the behavior of surface energies in bimetallic contacts (Fig. 5). Thus, the only really "novel" results of our analyses are those obtained for metal-

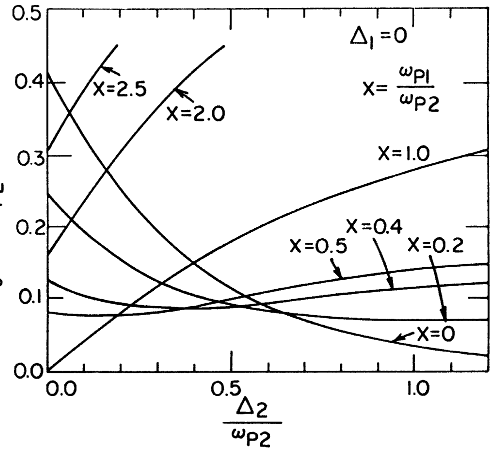

FIG. 4. Surface energy γ of the semiconductor-metal interface as a function of the semiconductor band gap Δ_2/ω_{p2} for different ratios $x = \omega_{p1}/\omega_{p2}$ of the plasma frequencies. The curve $x = 0$ corresponds to the semiconductor-vacuum interface.

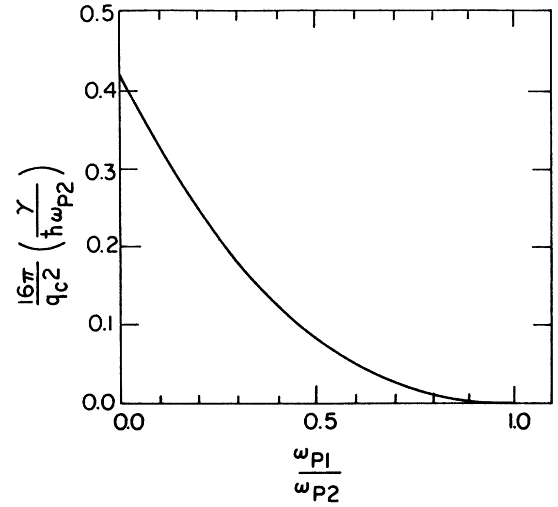

FIG. 5. Surface energy γ of the metal-metal interface for metals with plasma frequencies ω_{p1} and ω_{p2} as a function of a function of the ratio $x = \omega_{p1}/\omega_{p2}$. The values at $x = 0$ corresponds to the metal-vacuum interface.

semiconductor (Fig. 4) and semiconductor-semiconductor (Fig. 6) interfaces.

Since Phillips has invoked a qualitative version of our analysis to describe the energetics of metal-semiconductor contacts, let us conclude by relating our results to his.[19] He argues that to obtain a charge transfer excitation leading to the formation of a dipole charge layer capable of "pinning" the Fermi-level at a metal-semiconductor contact, an energy of $\frac{1}{2}E_g = \frac{1}{2}\hbar\Delta$ per surface atom is required, where E_g is related to $\epsilon(\omega = 0)$ via Eqs. (3). He then argues that the gain in surface energy, in our notation

$$\Delta\gamma = \gamma_S + \gamma_M - \gamma_{SM}, \tag{44}$$

is the source of energy for this transition. Thus if

$$\Delta\gamma \cdot a_S > \tfrac{1}{2}\hbar\Delta, \tag{45a}$$

a charge transfer excitation occurs and the Fermi level is pinned at the interface ("covalent semiconductors") whereas if

$$\Delta\gamma \cdot a_S < \tfrac{1}{2}\hbar\Delta, \tag{45b}$$

such a transfer cannot occur and the barrier height at the metal-semiconductor interface scales as the difference in electron affinity of the semiconductor and work function of the metal ("ionic semiconductors"). In Eqs. (45) a_S designates the surface area per surface atom. In the case that he considers, i.e., $\omega_{p1} = \omega_{p2}$, $q_{c1} = q_{c2}$, we see immediately from Figs. 3 and 4 that $\Delta\gamma a_S$ is a monatonically decreasing function of Δ. Therefore a critical value Δ_c of Δ will exist such that $\Delta\gamma(\Delta_c)a_S = \frac{1}{2}\hbar\Delta_c$ and for $\Delta > \Delta_c$ inequality (45b) is satisfied, whereas for $\Delta < \Delta_c$ (45a) is satisfied. Thus, the model does predict qualitatively that small-gap semiconductors should exhibit Fermi-level pinning but large-gap semiconductors should not, although this qualitative prediction is not unique to the dielectric continuum model.[22] Unfortunately, however, Phillips' numerics[19] are incorrect because he failed to note that $\gamma_{SV} < \gamma_{MV}$, neglected to subtract out γ_{SM}, and implicitly presumed that $a_S q_c^2/16\pi \equiv 1$. In fact, all of these approximations conspire to render his calculated values of $\Delta\gamma a_S$ substantially larger than we would expect to be reasonable, so that in fact the model predicts a critical value of $\epsilon(0)$ well above ten, in disagreement with the data presented in Ref. 19.

IV. SYNOPSIS

The objective of the work reported in this paper is the explicit demonstration of how far toward the computation of quantum-theory surface properties, in particular surface energies and optical potentials, one can go solely on the basis of classical electrostatic models of local dielectric media. Our main analytical results are the derivation of explicit, closed-form expressions for the surface energy [Eqs. (19) and (20)] and one-electron optical potential [Eq. (27)] as functionals of the parameters occurring in dielectric-continuum models of the frequency-dependent dielectric functions of metals and insulators [Eqs. (5)]. The extension of our results to dielectric functions locally varying in space as well as frequency are possible, but are rather messy algebraically and un-

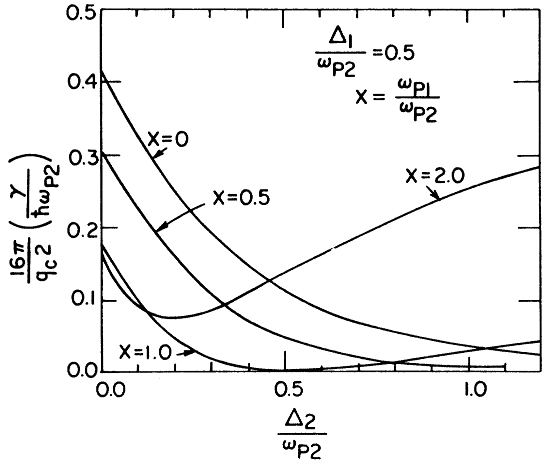

FIG. 6. Surface energy γ of the semiconductor-semiconductor interface as a function of the band gap Δ_2/ω_{p2} of one of them for different $x = \omega_{p1}/\omega_{p2}$ plasma frequency ratios.

illuminating.[2] Their extension to nonlocal dielectric media has been considered in part by numerous authors,[27,44–50] with the result that the detailed predictions of the various models depend on (imperfectly known) boundary conditions in the vicinity of the interfaces of such dielectrics.

The motion of a charged particle in the presence of a local dielectric medium has, of course, been examined several times over the years.[51–55] Our analysis differs from these earlier ones by virtue of evaluating not only the electrostatic fields (Sec. II B), but also the surface energies (Sec. II C) and one-electron optical potential (Sec. II D). Thus, as emphasized earlier, the major new feature of our approach lies in the use of the well-known electrostatic results presented in Sec. II B to derive the quantum-field-theoretic results presented in Secs. II C and II D. Some of these results had been obtained earlier in special cases[4–13,27,28,49,50,56] (most particularly that of the metal-vacuum interface), but only by the use of far more complicated analytical methodologies than the simple application of classical electrostatics described herein. Thus, we view our main contribution as being the explicit demonstration that for local dielectric media classical electrostatics leads in a simple and transparent fashion directly to the host of quantum-field-theoretic expressions for the optical potential[27,28,33,49,50,56] and surface energy[4–13] which have appeared in the literature.

While it is presumptuous to regard so simple a model as appropriate for the description of actual interfaces, the dielectric continuum formulas derived herein nevertheless lead to two further ancillary conclusions about the surface electronic properties of solids. First, they display how surface-plasmon damping dramatically reduces the range of the nonlocality in the high-energy, one-electron optical potential of relevance in the models of low-energy electron diffraction (LEED) from solids: a result which underlies a modern surface-structure determination via LEED intensity analysis.[20] Second, an immediate consequence of this model is the demonstration that even for local media, charge transfer excitations[19] do not afford a natural interpretation of the different behavior of metal contacts on "covalent" and "ionic" tetrahedrally coordinated semiconductors.

ACKNOWLEDGMENTS

The authors are indebted to Professor G. D. Mahan for bringing Ref. 44 to their attention and to Ms. L. Kennedy for assistance.

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