Nonlocal corrections to Fresnel optics: How to extend *d*-parameter theory beyond jellium models

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The *d*-parameter theory for describing the corrections to Fresnel optics of an interface is generalized to include local-field effects arising from discrete atomic structure. The derivation focuses on what effective matching conditions must be applied to macroscopic fields at the interface. These matching conditions on one hand determine reflection and transmission amplitudes that can be measured by experiments, and, on the other hand, they may be parametrized by the elements of a 3×3 d tensor, which can be calculated by theory. The derivation shows that the d elements completely characterize the first-order corrections to Fresnel optics and indicates when and how different elements may be related by symmetries.

I. INTRODUCTION

There has been interest for a long time in describing possible corrections to the Fresnel formulas for surface reflection and transmission amplitudes. The effects we have in mind arise from intrinsic surface or interface phenomena that cannot be treated within the simple picture of a sharp boundary between two distinct, homogeneous media. Diffuseness of the interface region plus the common need for a nonlocal spatial response can combine to produce a loss of bulk symmetries and a gain of surface specific excitations. We seek a theory that can tractably incorporate all of these possibilities.

A formal approach to this task that dates back to the previous century[1,2] exploits the following simplification. A perturbation theory of the corrections can be devised whose expansion parameter is the ratio r of two length scales. The larger length in the denominator is of the order of the wavelength of a macroscopic, transverse electromagnetic wave in bulk, while the smaller length in the numerator characterizes the effective spatial width of the interface response. For many systems over wide ranges of frequency the ratio of two such lengths is much less than unity, which implies that a series expansion in the ratio may quickly converge. We shall make use of this idea by first formulating our theory so that it yields, at zeroth order, the sharp-surface Fresnel answers and by then retaining carefully only first-order corrections to it. Our aim is to exhibit both what needs to be calculated in a theory of these corrections and what may be determined by an experiment to observe these corrections. In other words, we present a way to parametrize the corrections that is hopefully useful and adaptable for both theory and experiment.

Of course, similar goals have been the aim of many previous efforts.[1-39] Our scheme is more general than most of these, retaining its formal validity for a wide range of physical systems. Still, there are other theories[22,28,32,35,38] which in their final equations are essentially equivalent to ours, but which present their derivation and results in a different form.

Our derivation may be more transparent since it avoids explicit reference to Green's functions of the Maxwell equations and since it remains close in form to the matching problem that yields the standard Fresnel formulas. Furthermore, because the separation and neglect of higher-order terms in the expansion are largely based on qualitative arguments, it is useful to see the same results finally emerge from different approaches. We do have several model calculations in progress that illustrate numerically both the content and limitations of the theory,[40] but we wish to present now only a theoretical overview of our approach separated from the many practical approximations required by detailed computations. This mode of presentation also serves to emphasize the number of quantities that one can hope to determine with optical probes of an interface, without confusing the issue with the various parameters of particular theoretical model systems.

Our theory is a generalization of the *d*-parameter formulation developed by Feibelman and others[11,23-25,34] which was originally derived to describe nonlocal corrections to Fresnel optics for jellium models of metal surfaces. These models are characterized by allowing spatial inhomogeneity to exist only along the surface normal and only near the surface. From this starting point the formalism proves that the first-order corrections to Fresnel optics in the long-wavelength limit can be completely parametrized by two complex valued functions with the dimension of length, the d parameters $d_\perp$ and $d_\parallel$. Let us show explicitly how these appear in the earlier theories since it allows us to introduce our notation and gives one a point of reference for the basic nature of the theory and of the generalizations that will be derived.

We consider a flat interface between two bulk media and have in mind a matching problem involving different electromagnetic plane-wave solutions on the different sides. Each of these plane waves is chosen to have a common frequency ω and a common wave-vector projection parallel to the surface $\mathbf{Q}$. We align our Cartesian coordinate system with these waves, using the surface normal to define the x axis, $\hat{\mathbf{Q}}$ to define a second axis, and $\hat{\mathbf{t}}=\hat{\mathbf{x}}\times\hat{\mathbf{Q}}$ the third axis, which is perpendicular to the plane of incidence. Assume for now that the macroscopic Maxwell equations are characterized by an isotropic dielectric function[41] that depends only on ω and allow on each side only one relevant solution (to within a sign) for the normal component of the wave vector in a plane wave with fixed ω and $\hat{\mathbf{Q}}$. For instance, a p-polarized electric field in one of the bulk media may be written as the real part of

$$\mathbf{E}^0(\mathbf{x},t)=\gamma e^{i(\mathbf{Q}\cdot\mathbf{X}-\omega t)}(Q,\mp p,0)e^{\pm ipx} . \tag{1}$$

Here, γ sets the overall amplitude while the triplet of numbers in the parentheses describes the relative components of $\mathbf{E}^0$ along the $\hat{\mathbf{x}}$, $\hat{\mathbf{Q}}$, and $\hat{\mathbf{t}}$ axes. The normal component of the wave vector p is determined by

$$p^2=\frac{\omega^2}{c^2}\epsilon(\omega)-Q^2 , \tag{2}$$

where $\epsilon(\omega)$ is the bulk dielectric function and we use the sign convention that p lies in the first quadrant of the complex plane. The $\pm$ signs in (1) determine whether the wave is "traveling" towards or away from the interface. From the above $\mathbf{E}^0$ one can easily construct $\mathbf{D}^0$ and $\mathbf{B}^0=\mathbf{H}^0$. We refer to such solutions as bulk partial waves. In standard Fresnel optics these are the only allowed functional forms since ϵ is constant in space except for a discontinuity across $x=0$. From them one forms linear combinations on each side consistent with the physical conditions for $x\rightarrow\pm\infty$; e.g., an incident and reflected wave on the left and a transmitted wave on the right.

The coefficients that set the relative weights of these partial waves are determined by imposing boundary conditions across $x=0$. The standard Fresnel conditions are continuity of $\mathbf{E}_{\parallel}$, $D_{\perp}$, $\mathbf{H}_{\parallel}$, and $B_{\perp}$, where $\perp$ means along the surface normal and $\parallel$ means within the surface plane. We write these as

$$\Delta D_x^0=0 , \tag{3a}$$

$$\Delta E_Q^0=0 , \tag{3b}$$

$$\Delta E_t^0=0 , \tag{3c}$$

$$\Delta B_x^0=0 , \tag{3d}$$

$$\Delta H_Q^0=0 , \tag{3e}$$

$$\Delta H_t^0=0 , \tag{3f}$$

where ΔD_x^0 is the jump in the x component of $\mathbf{D}^0$ across $x=0$, etc. When one chooses either s or p polarization then three of these six conditions are trivially satisfied, while one of the remaining three is mathematically redundant. This leaves two independent constraints to determine, say, the reflection and transmission amplitudes in response to an incident wave.

The above is an outline of the textbook procedure of Fresnel optics. The extension of this prescription that has been derived by the d-parameter theory is at the macroscopic level rather slight. One still works with fields of the form (1), but now acknowledges that they can only represent asymptotic behavior well outside the surface region. Yet, if the effective width of the latter is small compared to c/ω, $1/Q$, $1/p$, etc., the amplitudes of the bulk partial waves are only slightly changed and may be determined for jellium models to first order by the revised boundary conditions

$$\Delta D_x^0\simeq -iQd_{\parallel}(\epsilon_a-\epsilon_b)E_Q^0 , \tag{4a}$$

$$\Delta E_Q^0\simeq +iQd_{\perp}(1/\epsilon_a-1/\epsilon_b)D_x^0 , \tag{4b}$$

$$\Delta E_t^0\simeq 0 , \tag{4c}$$

$$\Delta B_x^0\simeq 0 , \tag{4d}$$

$$\Delta H_Q^0\simeq -i\frac{\omega}{c}d_{\parallel}(\epsilon_a-\epsilon_b)E_t^0 , \tag{4e}$$

$$\Delta H_t^0\simeq +i\frac{\omega}{c}d_{\parallel}(\epsilon_a-\epsilon_b)E_Q^0 , \tag{4f}$$

where a and b label the different bulk media. As with Eqs. (3), only two of the above equations are independent and nontrivial once one specifies the polarization as either s or p. Also note that these modified equations are only sensible for a perturbative evaluation since the discontinuities in field components on the left-hand sides are determined by the surface values of the same fields on the right-hand sides. The equations allow one to find the corrections to Fresnel formulas to first order in the d's, but no further. Examples of their solution for reflection and transmission amplitudes are given in Appendix A. Here we simply stress that the d's which depend only on ω, completely characterize the influence of the interface to first order in r. The other quantities appearing in (4) were all defined at the level of Fresnel optics. Hence, from an experimental point of view, varying $\mathbf{Q}$ by varying, say, the angle of incidence, does not involve any new physics. Indeed, data from one angle of incidence imply explicit constraints on results at the same ω for other angles of incidence.[42]

On the theoretical side, the jellium theory also provides a prescription for calculating the d's. In the absence of extrinsic damping, $d_{\parallel}$ is real valued and independent of ω. In fact, for a suitable choice of the origin of x (at the jellium edge), $d_{\parallel}$ can be set to zero. On the other hand, $d_{\perp}$ is complex valued and frequency dependent, but can be found from the "center of mass" of the induced screening charge density due to a long-wavelength perturbation:

$$d_{\perp}(\omega)=\int dx\, x\,\delta\rho(x,\omega)\Big/\int dx\,\delta\rho(x,\omega) . \tag{5}$$

Here, $\delta\rho$ is the screening charge density, which may be computed with the speed of light set to infinity (i.e., by doing a nonretarded calculation). This simplification, which like the whole theory is valid because the width of the region of screening is assumed small compared to transverse wavelengths, i.e., $r\ll 1$, lies behind the recent progress in calculations of $d_{\perp}$.[42–52] These papers use a variety of computational methods but their results are in reasonable agreement[53] with each other and with the pioneering calculations of Feibelman.[54] However, none of them include the effects of discrete atomic structure, which restricts their experimental relevance.

In the rest of this paper we derive a generalization of d-parameter theory that removes many of the limitations imposed by the jellium models. Specifically, we allow for three-dimensional local-field effects in both the interface and bulk regions. Formal matching conditions are obtained in Sec. II and their parametrization with d's is treated in Sec. III. The final results are quite similar to Eqs. (5) [see Eqs. (31)]. More d parameters are necessary in order to describe the reduced symmetry, but they retain the attractive feature of being independent of $|\mathbf{Q}|$, which simplifies their measurement, and independent of c, which simplifies their calculation.[40]

II. DERIVATION OF MATCHING CONDITIONS

The line of argument that we choose to generalize was developed in Refs. 15, 24, 34, and 55. In brief, it is based on formal comparisons between the exact and what we call reference fields. The latter are defined to agree with the exact fields when one is far from the interface and then they are extrapolated towards a matching plane within the interface. The discontinuities in various components of the macroscopic pieces of these reference fields can be expressed in terms of integrals over the differences between the exact and reference fields, which in turn can be parametrized by d's. Our approach is to follow the spirit of the earlier derivations, but to make suitable allowances for the presence of local-field effects.

We start by considering a single homogeneous crystalline medium with no boundary. The microscopic Maxwell equations for an excitation at frequency ω in such a medium are written as[41]

$$\begin{aligned} &\nabla\cdot\mathbf{D}=0, \quad \nabla\times\mathbf{E}=+\frac{i\omega}{c}\mathbf{B}\,, \\ &\nabla\cdot\mathbf{B}=0, \quad \nabla\times\mathbf{H}=-\frac{i\omega}{c}\mathbf{D}\,, \end{aligned} \tag{6}$$

Here,

$$\mathbf{D}=\mathbf{E}+4\pi\mathbf{P} \tag{7}$$

with

$$\mathbf{P}=i\mathbf{J}/\omega\,, \tag{8}$$

so from the equation of continuity,

$$-\nabla\cdot\mathbf{P}=-i\nabla\cdot\mathbf{J}/\omega=\delta\rho\,. \tag{9}$$

The primary quantities are **E**, **B**, and **J**, while the others are simply defined in terms of them. The current density **J** describes the full microscopic response and is linearly, but not locally, related to **E**. From **J** one can easily obtain the polarization **P** and the induced charge density $\delta\rho$. The assumed microscopic periodicity allows us to use Bloch's theorem in writing out the solution of Maxwell's equations. For an electric field of frequency ω and wave vector **q** (within the first Brillouin zone)

$$\mathbf{E}_{\mathbf{q}\omega}(\mathbf{x},t)=e^{i(\mathbf{q}\cdot\mathbf{x}-\omega t)}\left[\mathbf{E}_0+\sum_{\mathbf{G}\neq 0}\mathbf{E}_{\mathbf{G}}e^{i\mathbf{G}\cdot\mathbf{x}}\right]\,, \tag{10}$$

where the **G** are reciprocal lattice vectors and both ω/c and $|\mathbf{q}|$ are much smaller than any nonzero $|\mathbf{G}|$ for the ω we consider. This field generalizes the bulk partial wave considered in the Introduction.

In a macroscopic theory one tried to avoid explicit reference to the $\mathbf{E}_{\mathbf{G}}$ amplitudes when seeking the macroscopic field amplitude $\mathbf{E}_0$ and dispersion relation $\omega=\omega(\mathbf{q})$. This is accomplished by rearranging (and approximating) the full set of Maxwell equations so that a modified constituitive relation between the long-wavelength parts of **D** and **E** is obtained in the form

$$\mathbf{D}_0=\overleftrightarrow{\epsilon}_M\cdot\mathbf{E}_0\,, \tag{11}$$

where $\mathbf{D}_0$ is the analogue of $\mathbf{E}_0$ in the microscopic equation for $\mathbf{D}_{\mathbf{q}\omega}(\mathbf{x},t)$ and $\overleftrightarrow{\epsilon}_M$ is the so-called macroscopic dielectric tensor. We do not wish to describe the details of this analysis further; see Ref. 35 for an illustration and a list of papers that develop and apply it. For us it is sufficient to note two facts.

First, the reduction from a microscopic to a macroscopic description of **E** can in bulk be simply accomplished by projecting out all nonzero **G** contributions from the exact field. The dielectric functions that appear in the Fresnel formulas are determined by $\overleftrightarrow{\epsilon}_M$. We shall assume that $\overleftrightarrow{\epsilon}_M$ depends only on frequency and is isotropic. This assumption does not omit local-field effects, as evidenced by the model of point-dipole-polarizable entities on a cubic lattice, which leads to the Clausius-Mossotti dielectric function.[56] We make this assumption to simplify the analysis and because in the systems of interest to use the anisotropy will be a surface, rather than bulk effect.

The second useful fact is that the reduction from microscopic to macroscopic fields envisioned here can be inverted if one knows the full Hamiltonian. To be specific, the $\mathbf{E}_{\mathbf{G}}$ of (10) are implicitly known once $\mathbf{E}_0$ is specified. This is an important point in any practical calculation, but for now we note it merely as a reminder of the one-to-one relation between macroscopic and microscopic fields. A theory need only find the $\mathbf{E}_0$'s in different media to determine formally the full asymptotic solution.

Now consider an interface between two media of the sort described above. We assume that the interface is flat (on average) and that one can find a Bravais net for which both of the bulk media and the interface have a common two-dimensional translational symmetry.[57] Of course such symmetry does not exist in the third direction, orthogonal to the interface. As before, we use this normal to define $\hat{\mathbf{x}}$. Near the interface the exact fields can no longer vary as simply as (10). Still they must reduce to linear combinations of such bulk partial waves as one moves away from the interface and in optical experiments it is only this asymptotic behavior that can be directly detected. We define reference fields as linear combinations of bulk partial waves whose relative weights make them match the exact field far from the interface, but which do not change their functional form until one crosses a matching plane at $x=x_0$ in the interface region. We write, for example,

$$\mathbf{E}^0(\mathbf{x},t)=\Theta(x-x_0)\mathbf{E}^>(\mathbf{x},t)+\Theta(x_0-x)\mathbf{E}^<(\mathbf{x},t)\,, \tag{12}$$

where $\Theta(y)=1$ for $y>0$ and zero otherwise, and where the exact field $\mathbf{E}(\mathbf{x},t)$ obeys

$$\begin{aligned} \mathbf{E}(\mathbf{x},t) &\underset{x\gg x_0}{\longrightarrow} \mathbf{E}^>(\mathbf{x},t) \\ &\underset{x\ll x_0}{\longrightarrow} \mathbf{E}^<(\mathbf{x},t)\,. \end{aligned} \tag{13}$$

Each $\mathbf{E}^{\lessgtr}$ is a linear combination of $\mathbf{E}_{q\omega}$ of the form (10). The reference fields obey the Maxwell equations (6) almost everywhere if all fields and sources are written as in (12). The only necessary correction terms are due to x derivatives of the Θ functions in (12), always yielding $\delta(x-x_0)$ contributions; e.g.,

$$\nabla\cdot\mathbf{D}^0=\Delta D_x^0\delta(x-x_0)\ , \tag{14}$$

where

$$\Delta D_x^0=\hat{\mathbf{x}}\cdot[\mathbf{D}^{>}(x_0,\mathbf{X},t)-\mathbf{D}^{<}(x_0,\mathbf{X},t)]\ . \tag{15}$$

Now form the difference between the exact and reference fields and keep only the pieces that vary slowly parallel to the interface. The latter process is denoted by $\mathbf{E}\rightarrow\langle\mathbf{E}\rangle_{\parallel}$. Our assumptions about the system's translational symmetry imply that what remains can vary at fixed x only as $e^{i\mathbf{Q}\cdot\mathbf{X}}$, where $\mathbf{Q}$ is the (common) surface projection of each macroscopic wave vector and $\mathbf{X}$ lies in the surface plane. Hence any gradients parallel to the interface can be replaced with factors of $i\mathbf{Q}$. Again we use a Cartesian-coordinate system based on $\hat{\mathbf{x}}$, $\hat{\mathbf{Q}}$, and $\hat{\mathbf{t}}=\hat{\mathbf{x}}\times\hat{\mathbf{Q}}$. The sequence of algebra that comes next is best illustrated by example. Begin with

$$\nabla\cdot\langle\mathbf{D}-\mathbf{D}^0\rangle_{\parallel}=-\langle\Delta D_x^0\rangle_{\parallel}\delta(x-x_0)$$

or (16)

$$=iQ\langle D_Q-D_Q^0\rangle_{\parallel}+\frac{\partial}{\partial x}\langle D_x-D_x^0\rangle_{\parallel}\ .$$

Equating the two versions of the right-hand sides and integrating over x from deep in the bulk on one side of the interface to deep in the bulk on the other we obtain using an analogue of (13)

$$\langle\Delta D_x^0(x_0)\rangle_{\parallel}=-iQ\int dx\,\langle D_Q-D_Q^0\rangle_{\parallel}\ . \tag{17a}$$

A similar process can be repeated for each one of the Maxwell equations in which an x derivative appears. We find

$$\langle\Delta B_x^0(x_0)\rangle_{\parallel}=-iQ\int dx\,\langle B_Q-B_Q^0\rangle_{\parallel}\ , \tag{17b}$$

$$\langle\Delta E_Q^0(x_0)\rangle_{\parallel}=+iQ\int dx\,\langle E_x-E_x^0\rangle_{\parallel}+i\frac{\omega}{c}\int dx\,\langle B_t-B_t^0\rangle_{\parallel}\ , \tag{17c}$$

$$\langle\Delta H_Q(x_0)\rangle_{\parallel}=+iQ\int dx\,\langle H_x-H_x^0\rangle_{\parallel}-i\frac{\omega}{c}\int dx\,\langle D_t-D_t^0\rangle_{\parallel}\ , \tag{17d}$$

$$\langle\Delta E_t^0(x_0)\rangle_{\parallel}=-i\frac{\omega}{c}\int dx\,\langle B_Q-B_Q^0\rangle_{\parallel}\ , \tag{17e}$$

$$\langle\Delta H_t^0(x_0)\rangle_{\parallel}=+\frac{i\omega}{c}\int dx\,\langle D_Q-D_Q^0\rangle_{\parallel}\ . \tag{17f}$$

Equations (17) express the discontinuities in various reference field components across the plane $x=x_0$ in terms of integrals through the interface of parallel averaged differences of other field components. The x_0 dependence on the right sides of (17) is hidden in the definition of the reference fields, see (12). Note that the six field components (out of the twelve total $\mathbf{E}$, $\mathbf{D}$, $\mathbf{B}$, $\mathbf{H}$) that appear on the left hand sides do not appear on the right hand sides and vice versa.

Equations (17) are exact but not all of the integrals are of the same size. We next discard those that are second order (or higher) in the presumed small parameter r of effective interface width times any macroscopic, transverse wave-vector component.[58] These all involve moments of components of $\mathbf{B}=\mathbf{H}$, which in Fresnel optics would be continuous. The mathematics involves an integration by parts

$$\int dxG=(x-x_0)G-\int dx\,(x-x_0)\frac{\partial G}{\partial x}\ , \tag{18}$$

where the surface term may be dropped and the derivative in the transformed integral is replaced using a Maxwell equation. We use three versions of this manipulation:

$$\int dx\,\langle B_x-B_x^0\rangle_{\parallel}=+iQ\int dx(x-x_0)\langle B_Q-B_Q^0\rangle_{\parallel}\ , \tag{19a}$$

$$\int dx\,\langle H_Q-H_Q^0\rangle_{\parallel}=-iQ\int dx(x-x_0)\langle H_x-H_x^0\rangle_{\parallel}+i\frac{\omega}{c}\int dx\,(x-x_0)\langle D_t-D_t^0\rangle_{\parallel}\ , \tag{19b}$$

$$\int dx\,\langle H_t-H_t^0\rangle_{\parallel}=-i\frac{\omega}{c}\int dx\,(x-x_0)\langle D_Q-D_Q^0\rangle_{\parallel}\ . \tag{19c}$$

If we now assume that the relative sizes of the field components do not depend on r, substitute (19) back into (17), and drop all terms formally of order r^2 or smaller, we obtain

$$\langle\Delta D_x^0(x_0)\rangle_{\parallel}\cong-iQ\int dx\,\langle D_Q-D_Q^0\rangle_{\parallel}\ , \tag{20a}$$

$$\langle\Delta E_Q^0(x_0)\rangle_{\parallel}\cong+iQ\int dx\,\langle E_x-E_x^0\rangle_{\parallel}\ , \tag{20b}$$

$$\langle\Delta E_t^0(x_0)\rangle_{\parallel}\cong 0\ , \tag{20c}$$

$$\langle\Delta B_x^0(x_0)\rangle_{\parallel}\cong 0\ , \tag{20d}$$

$$\langle\Delta H_Q^0(x_0)\rangle_{\parallel}\cong-i\frac{\omega}{c}\int dx\,\langle D_t-D_t^0\rangle_{\parallel}\ , \tag{20e}$$

$$\langle\Delta H_t^0(x_0)\rangle_{\parallel}\cong+i\frac{\omega}{c}\int dx\,\langle D_Q-D_Q^0\rangle_{\parallel}\ , \tag{20f}$$

in which the structure of (4) is becoming evident.

Indeed, for jellium models at this stage one can usefully define d parameters to characterize the integrals in (20). However, for more general systems the dependence on x_0 is inconvenient. The problem is that for systems with bulk variations on an atomic scale, the location of the matching plane with the unit cell is numerically important. Both the reference fields on the right of (20) and the discontinuities on the left of (20) can depend sensitively on the choice of x_0. We suppress this sensitivity by averaging the x_0 dependence in (20) over the depth of the unit cell for the bulk periodicity along $\hat{\mathbf{x}}$.[59] The integrals in (20) over components of the parallel averaged exact fields are unaffected by this process since they are independent of x_0. The reference fields on the right sides of (20) are changed only because the Θ functions in (12) are changed; e.g.,

$$\Theta(x-x_0)\to\bar{\Theta}(x-x_0)=\int_{-a/2}^{a/2}\frac{dx'}{a}\Theta(x-(x_0+x'))\ , \tag{21}$$

where a is the spatial period along $\hat{\mathbf{x}}$ in bulk. We add an overbar to reference fields defined with $\bar{\Theta}$'s instead of Θ's. Finally, the result of the average of x_0 over a for each field component contributing to the Δ terms in (20)–see (15)–is to isolate from each bulk partial wave within it the macroscopic amplitude. The latter quantities are precisely what one needs in order to discuss the Fresnel results and their corrections. In the long-wavelength limit these amplitudes have a negligible variation with x_0. They become in fact, the same quantities used on the right sides of (4), so we write them almost in the same way by dropping the x_0 dependence and the $\|$ subscripts. Incorporating all these changes, (20) becomes

$$\langle \Delta D_x^0\rangle \cong -iQ\int dx\,\langle D_Q-\bar{D}_Q^{\,0}\rangle_{\|}\ , \tag{22a}$$

$$\langle \Delta E_Q^0\rangle \cong +iQ\int dx\,\langle E_x-\bar{E}_x^{\,0}\rangle_{\|}\ , \tag{22b}$$

$$\langle \Delta E_t^0\rangle \cong 0\ , \tag{22c}$$

$$\langle \Delta B_x^0\rangle \cong 0\ , \tag{22d}$$

$$\langle \Delta H_Q^0\rangle \cong -i\frac{\omega}{c}\int dx\,\langle D_t-\bar{D}_t^{\,0}\rangle_{\|}\ , \tag{22e}$$

$$\langle \Delta H_t^0\rangle \cong +i\frac{\omega}{c}\int dx\,\langle D_Q-\bar{D}_Q^{\,0}\rangle_{\|}\ . \tag{22f}$$

These equations relate discontinuities in the macroscopic field amplitudes across a matching plane in the interface region to integrals of the difference between an exact field component and the same component of a reference field. The derivation has assumed that these two field components only differ over a region that is small compared to macroscopic transverse wavelengths and omitted higher-order corrections. Within the same approximation the integrals can be reexpressed in several ways, as shown in Appendix B. However, all these equations basically represent consistency relations in that information about the exact fields of a particular configuration are apparently needed on both sides of the equations. The arguments out of this impasse are developed in the next section.

III. *d* PARAMETERS

The various field components whose difference moments appear on the right sides of (22) are all components which in the Fresnel picture would have a discontinuity across the dielectric boundary. For the exact fields these discontinuities are of course absent, but the spatial scale over which they are removed is narrow compared to a macroscopic transverse wavelength. In this limit it is not unreasonable to assume that the interpolation form of the exact field between its asymptotic variation depends on very few details of that asymptotic behavior. The charges and currents responsible for the interpolation form lie in the interface region and their distinct response is induced by the slow fields of more distant charges and currents. We shall assume that the only relevant details are the differences in the asymptotic macroscopic field components.

To express this mathematically, introduce two vectors $\mathbf{M}$ and $\mathcal{E}$ whose components are, respectively,

$$M_x=\int dx\,\langle E_x-\bar{E}_x^{\,0}\rangle_{\|}\ , \tag{23a}$$

$$M_Q=\int dx\,\langle D_Q-\bar{D}_Q^{\,0}\rangle_{\|}\ , \tag{23b}$$

$$M_t=\int dx\,\langle D_t-\bar{D}_t^{\,0}\rangle_{\|}\ , \tag{23c}$$

and

$$\mathcal{E}_x=(1/\epsilon_a-1/\epsilon_b)\langle D_x^0\rangle\ , \tag{24a}$$

$$\mathcal{E}_Q=(\epsilon_a-\epsilon_b)\langle E_Q^0\rangle\ , \tag{24b}$$

$$\mathcal{E}_t=(\epsilon_a-\epsilon_b)\langle E_t^0\rangle\ . \tag{24c}$$

Here, a and b label the different bulk media and the integrals run from deep in medium a to deep in medium b. The field components on the right-hand side of (24) are macroscopic and are the ones that are essentially constant through the interface region. The prefactors with different ϵ's convert them to the differences of the macroscopic field components which are discontinuous in the Fresnel limit. Our assumption is that

$$\mathbf{M}=\overleftrightarrow{\mathrm{d}}\cdot\mathcal{E} \tag{25}$$

where the 3×3 matrix of d parameters describe the intrinsic response of the interface and are independent of the magnitude of the asymptotic fields. They may possibly depend on the direction of $\hat{\mathbf{Q}}$, but if $r\ll1$, they should not depend on $|\mathbf{Q}|$ as long as the surface component of phase velocity of the electromagnetic disturbance, $\omega/|\mathbf{Q}|$, does not become comparable to a characteristic speed of material excitations. This latter constraint implies that one can calculate the response assuming $|\mathbf{Q}|\to0$. Furthermore, the relative narrowness of the interface region allows one to neglect retardation effects across it.

An explicit, but purely formal, representation of the various d-parameter elements in terms of effective dielectric functions is given in Appendix B. The arguments there give additional support to the factorization in (25).

The final technical point about definitions (23)–(25) that we discuss concerns the dependence on x_0.[60] The vector $\mathcal{E}$ is independent of x_0 in the long-wavelength limit, while $\mathbf{M}$ depends on x_0 through the reference fields it contains. Imagine changing $x_0\to x_0+b$. This should be equivalent to moving the physical system by $-b$. The changes in $\mathbf{M}$ are determined by integrals of the form

$$f(b)=\int_{-\infty}^{\infty}dx\int_{-a/2}^{a/2}\frac{dx'}{a}[\Theta(x-x_0-b-x')-\Theta(x-x_0-x')]e^{ikx}\ . \tag{26}$$

The factor e^{ikx} comes from a bulk partial wave with

$$k = p + G \ , \tag{27}$$

where p is the normal component of a $\mathbf{q}$ such as in (10) and G is an integer times $2\pi/a$. Reversing the order of integration yields

$$f(b) = -\int_{-a/2}^{a/2} \frac{dx'}{a} \int_{x_0+x'}^{x_0+b+x'} dx e^{ikx} = \frac{i}{k}(e^{ikb}-1)e^{ikx_0}\frac{\sin(ka/2)}{(ka/2)} \ . \tag{28}$$

In the long-wavelength limit,[60] $a,b,x_0 \ll 1/p$, so $f(b)$ is dominated by

$$f(b) \cong -b\delta_{G,0} \ . \tag{29}$$

This implies in turn that when $x_0 \to x_0 + b$

$$\mathbf{M} \to \mathbf{M} - b\mathcal{E} \tag{30}$$

so each of the diagonal elements of the d-tensor shifts by $-b$, while the off-diagonal elements are unchanged. The normalization of $\mathcal{E}$ has in fact been chosen[23] so that this translation property of the d's is so simple. One can then say that part of the information carried by the diagonal d's is the location of the interface on an absolute scale and should expect that properties that are independent of absolute interface location can involve diagonal d's only via differences.

Now use (25) to reexpress (22);

$$\langle \Delta D_x^0 \rangle \cong -iQ(\epsilon_a - \epsilon_b)(d_{QQ}\langle E_Q^0 \rangle + d_{Qt}\langle E_t^0 \rangle - d_{Qx}\langle D_x^0 \rangle / \epsilon_a \epsilon_b) \ , \tag{31a}$$

$$\langle \Delta E_Q^0 \rangle \cong +iQ(\epsilon_a - \epsilon_b)(-d_{xx}\langle D_x^0 \rangle / \epsilon_a \epsilon_b + d_{xQ}\langle E_Q^0 \rangle + d_{xt}\langle E_t^0 \rangle) \ , \tag{31b}$$

$$\langle \Delta E_t^0 \rangle \cong 0 \ , \tag{31c}$$

$$\langle \Delta B_x^0 \rangle \cong 0 \ , \tag{31d}$$

$$\langle \Delta H_Q^0 \rangle \cong -i\frac{\omega}{c}(\epsilon_a - \epsilon_b)(d_{tt}\langle E_t^0 \rangle + d_{tQ}\langle E_Q^0 \rangle - d_{tx}\langle D_x^0 \rangle / \epsilon_a \epsilon_b) \ , \tag{31e}$$

$$\langle \Delta H_t^0 \rangle \cong -\frac{\omega}{Qc}\langle \Delta D_x^0 \rangle \ , \tag{31f}$$

which should be compared to Eqs. (4). To develop an explicit solution of such equations, one needs to specify what macroscopic fields exist as $x \to \pm\infty$. In Appendix A we derive solutions of (31) for which an incident wave of either pure s or pure p polarization approaches the interface from medium a. If one only wants the first-order corrections to reflection coefficients for such a situation, then the d elements that couple different polarization $(d_{xt}, d_{tx}, d_{Qt}, d_{tQ})$ may be neglected. Further, if the equilibrium system obeys time-reversal invariance, the Onsager symmetries[61] between the remaining off-diagonal d elements (d_{xQ}, d_{Qx}) are such that they do not appear in the answers for the reflection amplitudes. We invoke these simplifications here, which allow us to write the reflection amplitudes as

$$r_s \cong \frac{1 - \dfrac{p_b}{p_a} - i\dfrac{\omega^2/c^2}{p_a}(\epsilon_b - \epsilon_a)d_{tt}}{1 + \dfrac{p_b}{p_a} + i\dfrac{\omega^2/c^2}{p_a}(\epsilon_b - \epsilon_a)d_{tt}} \ , \tag{32}$$

$$r_p \cong \frac{\dfrac{\epsilon_b}{\epsilon_a} - \dfrac{p_b}{p_a} + i\left[\dfrac{\epsilon_b - \epsilon_a}{\epsilon_a}\right][p_b d_{QQ} - (Q^2/p_a)d_{xx}]}{\dfrac{\epsilon_b}{\epsilon_a} + \dfrac{p_b}{p_a} + i\left[\dfrac{\epsilon_b - \epsilon_a}{\epsilon_a}\right][p_b d_{QQ} + (Q^2/p_a)d_{xx}]} \ , \tag{33}$$

where the p's are from (2).

If we completely ignore the d's, these equations become the Fresnel formulas for r_s^0, r_p^0, i.e., solutions of (3). If we replace d_{xx} with $d_\perp$ and both d_{QQ} and d_{tt} with $d_\parallel$, they represent the solutions of (4). Away from possible zeroes of the denominators, we can further expand (32) and (33) to

$$r_s \cong r_s^0(1 + 2ip_a d_{tt} + \cdots) \ , \tag{34}$$

$$r_p \cong r_p^0\left[1 + 2ip_a\left[d_{QQ} - \frac{Q^2\epsilon_b/\epsilon_a}{(\epsilon_b/\epsilon_a)p_a^2 - Q^2}(d_{xx} - d_{QQ})\right] + \cdots\right] \ , \tag{35}$$

where we stress that the dependence on the angle of incidence, θ_a, appears only in $Q = (\omega/c)\ (\epsilon_a)^{1/2}\sin\theta_a$ and $p_a = (\epsilon_a\omega^2/c^2 - Q^2)^{1/2}$. At normal incidence $\theta_a = 0 = Q$ and $r_s^0 = -r_p^0$, so the first-order difference between $|r_s|^2$ and $|r_p|^2$ which is measured in reflection difference spectroscopies,[62,63] is determined by the difference between the imaginary parts of d_{tt} and d_{QQ}. These do vary with azimuthal angle because their formal definition ties them to the direction of $\mathbf{Q}$. However, for a system with Onsager symmetries we can relate them to d elements defined with respect to the principal axes of the interface plane. If the latter are given by the orthogonal directions $\hat{\mathbf{y}}$ and $\hat{\mathbf{z}}$, then

$$d_{QQ} = d_{yy}\cos^2\gamma + d_{zz}\sin^2\gamma \ , \tag{36}$$

$$d_{tt} = d_{yy}\sin^2\gamma + d_{zz}\cos^2\gamma \ , \tag{37}$$

where γ is the angle between $\hat{\mathbf{Q}}$ and $\hat{\mathbf{y}}$.

Equations (32)–(37) indicate how the d's enter experimentally accessible quantities, subject to the idealizations invoked here. This is also the limit in which our equations match those of earlier theories.[22,28,32,35,38] Further illustrations are given in Appendix A, including transmission amplitudes and an indication how the off-diagonal d elements can be detected. Here we turn to theoretical questions about the d elements. Although we cannot obtain so simple a result as (5) in the general case, one can, from the analysis of Appendix B, reduce the formal calculation of the diagonal d elements to finding

$$d_{xx} = -\int dx \langle P_x - \bar{P}_x^0 \rangle_{\parallel} / \langle \Delta P_x^0 \rangle ,$$
$$d_{QQ} = -\int dx \langle P_Q - \bar{P}_Q^0 \rangle_{\parallel} / \langle \Delta P_Q^0 \rangle , \qquad (38)$$
$$d_{tt} = -\int dx \langle P_t - \bar{P}_t^0 \rangle_{\parallel} / \langle \Delta P_t^0 \rangle ,$$

which express them as a normalized excess of interface polarization. The numerical evaluation for realistic model systems of Eqs. (38)—or definitions (23)–(25) or the dielectric function formulas of Appendix B—requires a major computational effort.[40,64,65] However, relatively simple calculations can be done for lattices of point-dipole-polarizable entities[66,67] that allow one to illustrate results from the opposite extreme of the jellium model calculations.

We have used such simple model calculations to explore the content and limitations of the basic theory.[40] This is a useful exercise because the derivation presented here has only extracted results to first order in the presumed small parameter of the problem. Higher-order corrections have been discarded at several stages and even the small parameter is not unambiguously defined.

The qualitative interpretation of the d's that results from these calculations is in essential agreement with that summarized by Feibelman for the jellium models.[25] The only limitation of the theory that we discuss here arises near the threshold of a bulk polariton; e.g., at the edge of a plasmon, optical phonon, or exciton band. Our derivation which assumes only one bulk solution of the Maxwell equations at each ω and $\mathbf{Q}$ would appear to fail badly when additional excitations are possible. However, the keys to our formal analysis are that only one bulk excitation be considered in defining the reference fields and that it alone be described on a macroscopic level by, say (1,2) with p small. This can often be done in the presence of several bulk excitations, especially if they have different symmetries which forbid a distortion of their separate dispersion relations. For instance, the predictions of the d-parameter theory near the onset of a longitudinal bulk polariton compare quite well with the exact results (of very simple models) once a weak extrinsic damping is included.[40,68] Such comparisons are, however, much less favorable near transverse bulk polariton bands. Here, the spatial dispersion effects on the bulk partial waves cannot be ignored unless strong extrinsic damping processes are present, too.

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APPENDIX A

We derive here the first-order solution of the approximate matching equations (31). Note that these only refer to the macroscopic amplitudes of the fields and almost separate into two distinct sets for different polarizations. For s waves, $\langle B_x^0 \rangle$, $\langle H_Q^0 \rangle$, and $\langle E_t^0 \rangle$ are nonzero and if in one medium

$$\langle \mathbf{B}^0 \rangle \sim e^{i(\mathbf{Q}\cdot\mathbf{X}-\omega t)} (Q, \mp p, 0) e^{\pm ipx} \qquad (A1)$$

then $\langle \mathbf{H}^0 \rangle = \langle \mathbf{B}^0 \rangle$ and

$$\langle \mathbf{E}^0 \rangle \sim e^{i(\mathbf{Q}\cdot\mathbf{X}-\omega t)} \left[0, 0, \frac{\omega}{c} \right] e^{\pm ipx} . \qquad (A2)$$

Comparing these we see that

$$\langle B_x^0 \rangle = \frac{Qc}{\omega} \langle E_t^0 \rangle \qquad (A3)$$

for either direction of the bulk partial wave motion along $\hat{\mathbf{x}}$ and for either bulk medium. This implies that (31c) and (31d) are redundant. For p waves, $\langle D_x^0 \rangle$, $\langle E_Q^0 \rangle$, and $\langle H_t^0 \rangle$ are nonzero and if in one medium

$$\langle \mathbf{E}^0 \rangle \sim e^{i(\mathbf{Q}\cdot\mathbf{X}-\omega t)} (Q, \mp p, 0) e^{\pm ipx} \qquad (A4)$$

then $\langle \mathbf{D}^0 \rangle = \epsilon \langle \mathbf{E}^0 \rangle$ and

$$\langle \mathbf{B}^0 \rangle \sim e^{i(\mathbf{Q}\cdot\mathbf{X}-\omega t)} \left[0, 0, -\epsilon \frac{\omega}{c} \right] e^{\pm ipx} . \qquad (A5)$$

Comparing these we see that[41]

$$\langle D_x^0 \rangle = -\frac{Qc}{\omega} \langle H_t^0 \rangle \qquad (A6)$$

for either direction of the bulk partial wave motion along $\hat{\mathbf{x}}$ and for either bulk medium. This implies that (31a) and (31f) are redundant.

Now consider an incident p wave from medium a which lies in $x < x_0$. Neglecting for now the coupling between polarizations we write

$$\langle \mathbf{E}^0 \rangle = e^{i(\mathbf{Q}\cdot\mathbf{X}-\omega t)} \begin{cases} \alpha_p (Q, -p_a, 0) e^{ip_a x} + r_p (Q, p_a, 0) e^{-ip_a x}, & x < 0 \\ t_p (Q, -p_b, 0) e^{ip_b x}, & 0 < x \end{cases} \qquad (A7)$$

where we place the origin at the matching plane and use α_p to set the amplitude of the incident wave. The two unknowns r_p and t_p are determined from the two independent nontrivial equations (31a) and (31b):

$$\epsilon_b t_p Q - \epsilon_a [Q(\alpha_p + r_p)] = -iQM_t = -iQ(\epsilon_a - \epsilon_b)[d_{QQ}(-t_p p_b) - d_{Qx}(t_p Q)/\epsilon_a] , \qquad (A8)$$

$$-t_p p_b - [-p_a(\alpha_p - r_p)] = +iQM_x = iQ(\epsilon_a - \epsilon_b)[-d_{xx}(t_p Q)/\epsilon_a + d_{xQ}(-t_p p_b)] . \qquad (A9)$$

Here we have written the required components of **M** in terms of field components on the b side of the interface. This is the simplest algebraic procedure, but to first order in the d's we could also have used field components on the a side, or any linear combination of the two whose two weights sum to unity. The solution of (A8) and (A9) yields

$$t_p/\alpha_p = \frac{2}{\frac{\epsilon_b}{\epsilon_a}+\frac{p_b}{p_a}+i\left[\frac{\epsilon_b-\epsilon_a}{\epsilon_a}\right][d_{QQ}p_b+d_{xx}Q^2/p_a+Q(d_{Qx}/\epsilon_a+\epsilon_a d_{xQ}p_b/p_a)]}, \tag{A10}$$

$$r_p/\alpha_p = \frac{\frac{\epsilon_b}{\epsilon_a}-\frac{p_b}{p_a}+i\left[\frac{\epsilon_b-\epsilon_a}{\epsilon_a}\right][d_{QQ}p_b-d_{xx}Q^2/p_a+Q(d_{Qx}/\epsilon_a-\epsilon_a d_{xQ}p_b/p_a)]}{\frac{\epsilon_b}{\epsilon_a}+\frac{p_b}{p_a}+i\left[\frac{\epsilon_b-\epsilon_a}{\epsilon_a}\right][d_{QQ}p_b+d_{xx}Q^2/p_a+Q(d_{Qx}/\epsilon_a+\epsilon_a d_{xQ}p_b/p_a)]}, \tag{A11}$$

which when expanded to first order in d's gives

$$t_p/\alpha_p = t_p^0\left[1-ip_a\left[\frac{\epsilon_b-\epsilon_a}{\epsilon_b p_a+\epsilon_a p_b}\right][d_{QQ}p_b+d_{xx}Q^2/p_a+Q(d_{Qx}/\epsilon_a+\epsilon_a d_{xQ}p_b/p_a)]\right], \tag{A12}$$

$$r_p/\alpha_p = r_p^0\left[1+2ip_a\left[d_{QQ}+\frac{Q\epsilon_b/\epsilon_a}{\frac{\epsilon_b}{\epsilon_a}p_a^2-Q^2}[Q(d_{QQ}-d_{xx})+(d_{Qx}/\epsilon_b-\epsilon_a d_{xQ})]\right]\right]. \tag{A13}$$

To further simplify this result we assume time-reversal invariance, which in turn implies the symmetry[61] of the following moments from Appendix B:

$$\langle(\hat{\epsilon}_{xx})^{-1}\cdot\hat{\epsilon}_{xQ}\rangle = \langle\hat{\epsilon}_{Qx}\cdot(\hat{\epsilon}_{xx})^{-1}\rangle, \tag{A14}$$

where the dielectric functions defined here are to be integrated over all position dependence. The equality (A14), together with the form of Eqs. (B8) and definitions (23)–(25), lead to

$$d_{Qx}=\epsilon_a\epsilon_b d_{xQ}, \tag{A15}$$

which reduces (A13) to (35) if we set $\alpha_p=1$.

Note that even with (A15) the influence of the off-diagonal d_{xQ} remains in the result (A12) for the transmission amplitude. It also appears to remain in the denominators of (A10) and (A11), whose vanishing describes a surface mode. However, the d_{xQ} that appears there is with (A15) multiplied by $(\epsilon_b/\epsilon_a+p_b/p_a)$, which is the zeroth-order Fresnel denominator. We conclude that the influence of d_{xQ} on the dispersion of surface modes is a second-order effect when (A15) holds and hence is irrelevant in our first-order theory.

Matters are much less complicated when one considers an incident s wave. Letting it approach the interface from medium a and again neglecting the small coupling between polarizations we write

$$\langle \mathbf{B}^0\rangle = e^{i(\mathbf{Q}\cdot\mathbf{X}-\omega t)}\begin{cases}\alpha_s(Q,-p_a,0)e^{ip_a x}\\ +r_s(Q,p_a,0)e^{-ip_a x}, & x<0\\ t_s(Q,-p_b,0)e^{ip_b x}, & 0<x\end{cases} \tag{A16}$$

where $x_0=0$ and α_s sets the amplitude of the incident wave. The two unknown r_s and t_s are determined from the two independent nontrivial equations (31d) and (31e):

$$t_sQ-[Q(\alpha_s+r_s)]=0, \tag{A17}$$

$$\begin{aligned}-t_sp_b-[-p_a(\alpha_s-r_s)] &= -i\frac{\omega}{c}M_t,\\ &= -i\frac{\omega}{c}(\epsilon_a-\epsilon_b)d_{tt}t_s(\omega/c).\end{aligned} \tag{A18}$$

The solution of these equations is

$$t_s/\alpha_s = t_s^0\left[1+i\frac{\omega^2}{c^2}\left[\frac{\epsilon_a-\epsilon_b}{p_a+p_b}\right]d_{tt}\right], \tag{A19}$$

$$r_s/\alpha_s = r_s^0(1+2ip_a d_{tt}), \tag{A20}$$

where we have expanded about the Fresnel results. Equation (A20) becomes (32) when we set $\alpha_s=1$.

Let us repeat that both the results (A12),(A13) and (A19),(A20) have been obtained by neglecting d_{xt}, d_{tx}, d_{tQ}, and d_{Qt}. These d elements are responsible for coupling between the different polarizations. As long as we imagine that only a pure s or p-polarized wave is incident, then the reflection and transmission *amplitudes* for p- or s-polarized waves, respectively, are proportional to these d elements alone and hence the reflection and transmission *coefficients* for p- or s-polarized waves, respectively, are second-order, negligible effects. However, if we let the incident wave be a coherent mixture of s and p-polarized waves, as in an ellipsometric measurement, then the reflected and refracted waves will both have a zeroth-order, Fresnel contribution as well as linear corrections determined by all of the d's. We do not write out the formulas here, but remark that time-reversal invariance suppresses the appearance of d_{xQ} and d_{Qx} in the reflection amplitude, as we have shown above, but does not remove the influence of the other two pairs of off-diagonal d elements which are related under this symmetry by

$$d_{tx}=\epsilon_a\epsilon_b d_{xt} \ , \tag{A21}$$

$$d_{tQ}=d_{Qt} \ . \tag{A22}$$

Finally we note the changes required to treat various simple "inversions" of the problems solved here. We have assumed the medium a lies in $x<x_0$ and medium b in $x_0<x$. If one switches the location of the bulk media, then all d elements change sign. If instead one keeps the bulk media in place but allows the incident wave to come from medium b, then the equations for the reflection and transmission amplitudes have the same form as those found here except that the a and b subscripts must be switched and all d elements multiplied by -1. Doing both of the above "inversions" of course leads to no change in the reflection and transmission amplitudes.

APPENDIX B

We develop here several alternate formal ways to write the integrals appearing in (20). The first change uses identity (7) to introduce the polarization differences and manipulation (16) to eliminate at first order all other field components. For instance,

$$\int dx\langle D_Q-D_Q^0\rangle_\parallel=4\pi\int dx\langle P_Q-P_Q^0\rangle_\parallel + \int dx\langle E_Q-E_Q^0\rangle_\parallel \tag{B1}$$

and the second integral may be dropped because

$$\int dx\langle E_Q-E_Q^0\rangle_\parallel=-iQ\int dx(x-x_0)\langle E_x-E_x^0\rangle_\parallel - i\frac{\omega}{c}\int dx(x-x_0)\langle B_t-B_t^0\rangle_\parallel \tag{B2}$$

is second order in the small parameter r. Similarly,

$$\int dx\langle E_x-E_x^0\rangle_\parallel=\int dx\langle D_x-D_x^0\rangle_\parallel - 4\pi\int dx\langle P_x-P_x^0\rangle_\parallel \tag{B3}$$

can be simplified because

$$\int dx\langle D_x-D_x^0\rangle_\parallel=+iQ\int dx(x-x_0)\langle D_Q-D_Q^0\rangle_\parallel \tag{B4}$$

is negligible. With such changes, (22) becomes

$$\langle\Delta D_x^0\rangle\cong-4\pi iQ\int dx\langle P_Q-\bar{P}_Q^0\rangle_\parallel \ , \tag{B5a}$$

$$\langle\Delta D_Q^0\rangle\cong-4\pi iQ\int dx\langle P_x-\bar{P}_x^0\rangle_\parallel \ , \tag{B5b}$$

$$\langle\Delta E_t^0\rangle\cong 0 \ , \tag{B5c}$$

$$\langle\Delta B_x^0\rangle\cong 0 \ , \tag{B5d}$$

$$\langle\Delta H_Q^0\rangle\cong-4\pi i\frac{\omega}{c}\int dx\langle P_t-\bar{P}_t^0\rangle_\parallel \ , \tag{B5e}$$

$$\langle\Delta H_t^0\rangle\cong+4\pi i\frac{\omega}{c}\int dx\langle P_Q-\bar{P}_Q^0\rangle_\parallel \ . \tag{B5f}$$

From the point of view of (B5) the first corrections to Fresnel optics all arise from excess surface polarization. With $\mathbf{J}=-i\omega\mathbf{P}$ one could also easily write all the integrals as measures of excess surface current densities.

We next express the integrals in (22) in terms of nonlocal, anisotropic dielectric functions. Our primary motivation is to make formal contact with earlier work; the direct evaluation of the formulas below may not be the most practical path to follow. The analysis starts by writing

$$\langle\mathbf{D}(x)\rangle_\parallel=\int d\mathbf{x}'\overleftrightarrow{\epsilon}(x,x')\langle\mathbf{E}(x')\rangle_\parallel \ , \tag{B6}$$

a linear relation between the exact, parallel averaged displacement and electric fields. In the long-wavelength limit, the implicit dependence in (B6) of the one-dimensional effective dielectric function on the common surface projected macroscopic wave vector $\mathbf{Q}$ is negligible. Using an operator notation to imply the integrals over x' we rewrite (B6) as

$$\langle D_x\rangle_\parallel=\hat{\epsilon}_{xx}\cdot\langle E_x\rangle_\parallel+\hat{\epsilon}_{xQ}\cdot\langle E_Q\rangle_\parallel+\hat{\epsilon}_{xt}\cdot\langle E_t\rangle_\parallel \tag{B7a}$$

$$\langle D_Q\rangle_\parallel=\hat{\epsilon}_{Qx}\cdot\langle E_x\rangle_\parallel+\hat{\epsilon}_{QQ}\cdot\langle E_Q\rangle_\parallel+\hat{\epsilon}_{Qt}\cdot\langle E_t\rangle_\parallel \tag{B7b}$$

$$\langle D_t\rangle_\parallel=\hat{\epsilon}_{tx}\cdot\langle E_x\rangle_\parallel+\hat{\epsilon}_{tQ}\cdot\langle E_Q\rangle_\parallel+\hat{\epsilon}_{tt}\cdot\langle E_t\rangle_\parallel \tag{B7c}$$

Formally solving (B7a) for $\langle E_x\rangle_\parallel$ and substituting in (B7b) and (B7c) yields

$$\langle E_x\rangle_\parallel=(\hat{\epsilon}_{xx})^{-1}\cdot\langle D_x\rangle_\parallel-(\hat{\epsilon}_{xx})^{-1}\cdot\hat{\epsilon}_{xQ}\cdot\langle E_Q\rangle_\parallel - (\hat{\epsilon}_{xx})^{-1}\cdot\hat{\epsilon}_{xt}\cdot\langle E_t\rangle_\parallel \ , \tag{B8a}$$

$$\langle D_Q\rangle_\parallel=\hat{\epsilon}_{Qx}\cdot(\hat{\epsilon}_{xx})^{-1}\cdot\langle D_x\rangle_\parallel + [\hat{\epsilon}_{QQ}-\hat{\epsilon}_{Qx}\cdot(\hat{\epsilon}_{xx})^{-1}\cdot\hat{\epsilon}_{xQ}]\cdot\langle E_Q\rangle_\parallel + [\hat{\epsilon}_{Qt}-\hat{\epsilon}_{Qx}\cdot(\hat{\epsilon}_{xx})^{-1}\cdot\hat{\epsilon}_{xt}]\cdot\langle E_t\rangle_\parallel \ , \tag{B8b}$$

$$\langle D_t\rangle_\parallel=\hat{\epsilon}_{tx}\cdot(\hat{\epsilon}_{xx})^{-1}\cdot\langle D_x\rangle_\parallel + [\hat{\epsilon}_{tQ}-\hat{\epsilon}_{tx}\cdot(\hat{\epsilon}_{xx})^{-1}\cdot\hat{\epsilon}_{xQ}]\cdot\langle E_Q\rangle_\parallel + [\hat{\epsilon}_{tt}-\hat{\epsilon}_{tx}\cdot(\hat{\epsilon}_{xx})^{-1}\cdot\hat{\epsilon}_{xt}]\cdot\langle E_t\rangle_\parallel \ . \tag{B8c}$$

Our rewriting of (B7) has arranged that the parallel averaged field components that appear on the right sides of (B8) are the ones that are constant through the interface to lowest order in r, and hence can be taken outside the integrals. A similar reduction can be done for $\langle\mathbf{D}^{\lessgtr}\rangle_\parallel$ and $\langle\mathbf{E}^{\gtrless}\rangle_\parallel$, from which one can build reference forms of the combinations appearing in (B8), with the same field components factoring out. By our assumptions on bulk symmetry, only dielectric functions with diagonal subscripts will be nonzero in these results. Finally, the differences required in (22) can be formed to yield

$$\langle\Delta D_x^0\rangle\cong-iQ\{\hat{\epsilon}_{Qx}\cdot(\hat{\epsilon}_{xx})^{-1}\cdot\langle D_x^0\rangle + [\delta\hat{\epsilon}_{QQ}-\hat{\epsilon}_{Qx}\cdot(\hat{\epsilon}_{xx})^{-1}\cdot\hat{\epsilon}_{xQ}]\cdot\langle E_Q^0\rangle + [\hat{\epsilon}_{Qt}-\hat{\epsilon}_{Qx}(\hat{\epsilon}_{xx})^{-1}\cdot\hat{\epsilon}_{xt}]\cdot\langle E_t^0\rangle\} \ , \tag{B9a}$$

$$\langle\Delta E_Q^0\rangle\cong iQ[\delta(\hat{\epsilon}_{xx})^{-1}\cdot\langle D_x^0\rangle-(\hat{\epsilon}_{xx})^{-1}\cdot\hat{\epsilon}_{xQ}\cdot\langle E_Q^0\rangle - (\hat{\epsilon}_{xx})^{-1}\cdot\hat{\epsilon}_{xt}\cdot\langle E_t^0\rangle] \ , \tag{B9b}$$

$$\langle\Delta E_t^0\rangle\cong 0 \ , \tag{B9c}$$

$$\langle\Delta B_x^0\rangle\cong 0 \ , \tag{B9d}$$

$$\langle \Delta H_Q^0 \rangle \cong -i\frac{\omega}{c}\{\hat{\epsilon}_{tx}\cdot(\hat{\epsilon}_{xx})^{-1}\cdot\langle D_x^0\rangle + [\hat{\epsilon}_{tQ}-\hat{\epsilon}_{tx}\cdot(\hat{\epsilon}_{xx})^{-1}\cdot\hat{\epsilon}_{xQ}]\cdot\langle E_Q^0\rangle + [\delta\hat{\epsilon}_{tt}-\hat{\epsilon}_{tx}\cdot(\hat{\epsilon}_{xx})^{-1}\cdot\hat{\epsilon}_{xt}]\cdot\langle E_t^0\rangle\}\ , \tag{B9e}$$

$$\langle \Delta H_t^0 \rangle \cong -\frac{\omega}{cQ}\langle \Delta D_x^0\rangle\ , \tag{B9f}$$

where δ implies the difference between exact and reference functions. We have used here the notation of (24) for the surface values of the macroscopic field components of the right hand sides. The functional form of (B9) serves as a formal justification for our introduction of the d parameters in (25). The same combination of $\hat{\epsilon}$'s as in (B9) also appears in the theories of Refs. 17, 22, 28, 30, 31, and 38, but the $\delta\hat{\epsilon}$'s here can differ from theirs because of a different choice of effective reference fields. No one has yet done model calculations that retain the full nonlocal, asymmetric structure implied by the above, but there has been progress in this direction.[64–67]

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[1]P. Drude, *The Theory of Optics* (Dover, New York, 1959), p. 290.
[2]For earlier references, see J. W. S. Rayleigh, Proc. R. Soc. London **86**, 207 (1912).
[3]C. Strachan, Proc. Cambridge Philos. Soc. **29**, 116 (1933).
[4]D. V. Sivukhin, Zh. Eksp. Teor. Fiz. **30**, 374 (1956) [Sov. Phys.—JETP **3**, 269 (1956)].
[5]G. A. Bootsma and F. Meyer, Surf. Sci. **14**, 52 (1969).
[6]P. W. Atkins and A. D. Wilson, Surf. Sci. **22**, 433 (1970).
[7]J. D. E. McIntyre and D. E. Aspnes, Surf. Sci. **24**, 417 (1971).
[8]M. J. Dignam and M. Moskovits, J. Chem. Soc. Faraday Trans. 2 **69**, 56 (1973).
[9]M. Nakayama, J. Phys. Soc. Jpn. **39**, 265 (1974).
[10]J. D. E. McIntyre, in *Optical Properties of Solids–New Developments*, edited by B. O. Seraphin (North-Holland, New York, 1976), p. 555.
[11]P. J. Feibelman, Phys. Rev. B **14**, 762 (1976).
[12]S. F. Timashev and M. A. Krykin, Phys. Status Solidi B **76**, 67 (1976).
[13]M. J. Dignam and J. Fedyk, J. Phys. (Paris) Colloq. **38**, C5-57 (1977).
[14]W. Plieth and K. Naegele, Surf. Sci. **64**, 484 (1977).
[15]G. Mukhopadhyay and S. Lundqvist, Phys. Scr. **17**, 69 (1978).
[16]A. Bagchi, R. G. Barrera, and A. K. Rajagopal, Phys. Rev. **20**, 4824 (1979).
[17]J. E. Sipe, Phys. Rev. B **22**, 1589 (1980).
[18]A. M. Brodsky and M. I. Urbakh, Surf. Sci. **94**, 369 (1980).
[19]F. H. P. M. Habraken, D. L. J. Gijzeman, and G. A. Bootsma, Surf. Sci. **96**, 482 (1980).
[20]B. B. Dasgupta and R. Fuchs, Phys. Rev. B **23**, 3710 (1981).
[21]R. G. Barrera and A. Bagchi, Phys. Rev. B **24**, 1612 (1981).
[22]R. Del Sole, Solid State Commun. **37**, 537 (1981).
[23]P. J. Feibelman, Phys. Rev. B **23**, 2629 (1981).
[24]P. Apell, Phys. Scr. **24**, 795 (1981).
[25]P. J. Feibelman, Prog. Surf. Sci. **12**, 287 (1982).
[26]J. Lekner, Physica A **112**, 544 (1982).
[27]J. Lekner, Physica A **113**, 506 (1982).
[28]W. L. Mochan, R. Fuchs, and R. G. Barrera, Phys. Rev. B **27**, 771 (1983).
[29]P. Apell, A. Lyungbert, and S. Lundqvist, Phys. Scr. **30**, 367 (1984).
[30]A. M. Brodsky, L. I. Daikhin, and M. I. Urbakh, J. Electroanal. Chem. **171**, 1 (1984).
[31]A. M. Brodsky and M. I. Urbakh, Prog. Surf. Sci. **15**, 121 (1984).
[32]R. Del Sole and E. Fiorino, Phys. Rev. B **29**, 4631 (1984).
[33]J. Lekner, Physica A **128**, 229 (1984).
[34]K. Kempa and R. R. Gerhardts, Surf. Sci. **150**, 157 (1985).
[35]W. L. Mochan and R. G. Barrera, Phys. Rev. B **32**, 4984 (1985); **32**, 4989 (1985).
[36]F. Forstmann and R. R. Gerhardts, *Optical Optics Near the Plasma Frequency* (Springer, Berlin, 1986).
[37]R. Del Sole, in *Electromagnetic Surface Excitations,* edited by R. F. Wallis and G. I. Stegeman (Springer, New York, 1986).
[38]A. Muramatsu and W. Hanke, in *Structure and Dynamics of Surfaces II,* Vol. 43 of *Topics in Current Physics,* edited by W. Schommers and P. von Blanckenhagen (Springer, New York, 1987).
[39]J. Lekner, *The Theory of Reflection of Electromagnetic and Particle Waves* (Nijhoff, Dordrecht, 1987).
[40]W. Chen and W. L. Schaich (unpublished).
[41]We treat the magnetic permeability $\mu(\omega)$ as identically 1, so $\mathbf{B}\equiv\mathbf{H}$.
[42]W. L. Schaich, Phys. Rev. B **37**, 6193 (1988).
[43]R. R. Gerhardts and K. Kempa, Phys. Rev. B **30**, 5704 (1984).
[44]K. Kempa and W. L. Schaich, Phys. Rev. B **32**, 8375 (1985).
[45]P. Gies and R. R. Gerhardts, Europhys. Lett. **1**, 513 (1986).
[46]K. Kempa and W. L. Schaich, Phys. Rev. B **34**, 547 (1986).
[47]P. Gies, R. R. Gerhardts, and T. Maniv, Phys. Rev. B **35**, 458 (1987).
[48]K. Kempa and W. L. Schaich, Solid State Commun. **61**, 357 (1987).
[49]P. Gies and R. R. Gerhardts, J. Vac. Sci. Technol. A **5**, 936 (1987).
[50]W. L. Schaich and K. Kempa, Phys. Scr. **35**, 204 (1987).
[51]A. Liebsch, Phys. Rev. B **36**, 7378 (1987).
[52]K. Kempa and W. L. Schaich, Phys. Rev. B **37**, 6711 (1988).
[53]K. Kempa, A. Liebsch, and W. L. Schaich, Phys. Rev. B **38**, 12 645 (1988).
[54]P. J. Feibelman, Phys. Rev. B **12**, 1319 (1975).
[55]F. Garcia-Moliner and F. Flores, *Introduction to the Theory of Solid Surfaces* (Cambridge University Press, New York, 1979), p. 56.
[56]J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1975), p. 152.
[57]In all calculations to date, whenever one allows only a discrete translational symmetry in one bulk medium the other bulk medium has been vacuum.
[58]See Refs. 26, 27, 33, 34, and 39 for theories that go beyond this first-order approximation, but use simpler model systems. An explicit proof of when $r \ll 1$ requires detailed consideration of one's specific microscopic model; see Ref. 40 for several examples.
[59]We assume this period is the same in both bulk media. See Ref. 57.
[60]We assume that the origin for x and the location of x_0 both lie

in the interface region.
[61]L. E. Reichl, *A Modern Course in Statistical Physics* (University of Texas Press, Austin, 1980), p. 507.
[62]D. E. Aspnes, J. Vac. Sci. Technol. B **3**, 1498 (1985).
[63]S. Selci, F. Ciccacci, G. Chiarotti, P. Chiaradia, and A. Crescenti, J. Vac. Sci. Technol. A **5**, 327 (1987).
[64]R. Del Sole and A. Selloni, Phys. Rev. B **30**, 883 (1984).
[65]A. Sellone, P. Marsella, and R. Del Sole, Phys. Rev. B **33**, 8885 (1986).
[66]W. L. Mochan and R. G. Barrera, Phys. Rev. Lett. **55**, 1192 (1985).
[67]W. L. Mochan and R. G. Barrera, Phys. Rev. Lett. **56**, 2221 (1986).
[68]K. Kempa and W. L. Schaich, Phys. Rev. B (to be published).