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Polaritons in a spatially dispersive medium: Surface effects. I

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The effects of surface distortion are included in a microscopic model of a spatially dispersive dielectric. An exactly soluble model (soluble within the refractive-index approximation) is discussed from which the Hopfield-Thomas reflectivity anomaly for normally incident light is recovered as a long-wavelength limit. The form of the additional boundary condition $[P(x)+\lambda P'(x)=0]$ at the surface of the dielectric is also considered.

I. INTRODUCTION

Dielectric media may exhibit anomalous optical properties in the vicinity of a narrow-excitation band, as a consequence of the exciton's ability to transport energy within the crystal. This additional channel for energy transport gives rise to the phenomenon known as spatial dispersion which has received considerable attention[1-10] since it requires the existence of two propagating waves (with unique dielectric constants) in contrast to the classical theory in which only one wave can exist. As a consequence of this additional wave, the boundary conditions as deduced from Maxwell's equations for continuum electrodynamics are not sufficient to determine the amplitudes of the electromagnetic waves at the surface of a spatially dispersive medium. Thus the determination of the additional boundary condition (ABC) represents a problem of considerable importance.

Early theoretical investigations by Pekar[1] concluded that the required ABC was $\vec{P}=0$ ($\vec{P}$ being the polarization vector). Hopfield and Thomas[2] (HT) provided experimental evidence that this could not, in general, be the case. Using a one-dimensional exciton model and continuum electromagnetic theory they showed that the exclusion of the bulk exciton from the surface region was required to explain the experimentally observed results.

More recently, theoretical efforts have employed semiclassical radiation theory[6, 11] and the refractive-index approximation (RIA)[3] to develop a microscopic theory of spatially dispersive media. In addition to providing a "first-principles" understanding of this phenomena, this approach has the advantage of being able to "derive" the ABC. By taking explicit account of the three-dimension character of the lattice Philpott[5] has been able to extend the range of the microscopic theory to include non-normal incidence. While these theories have given a rather clear understanding of the phenomenon, their derivations of the "appropriate" ABC are somewhat suspect since they uniformly neglect the nonuniformity of the crystal near the surface. Even more significant, however, is the fact that an anomaly in the reflectivity spectrum for normally incident light near the longitudinal frequency [frequency at which the "new" dielectric function $\epsilon_2(\omega)$ vanishes] observed by HT and as alluded to above, cited by those authors as contradictory to the $P=0$ ABC is absent in these theories. It is the aim of this preliminary work to show how the microscopic theory should be modified to remove this discrepancy. In doing so the deformation of the crystal near the surface will be considered explicitly thereby enabling us to obtain additional insight into the ABC required in the continuum theory. Section II discusses the modifications of the microscopic theory and presents a simple model, soluble within the RIA which reproduced the experimentally observed phenomenon missing from the usual microscopic models. Section III concludes and points the direction for future investigations.

II. MICROSCOPIC MODEL

A. General considerations

We imagine the crystal to be a discrete half space of parallel planes with the $(l, l+1)$ planes separated by a distance a_l. To allow for the effects of surface distortion neither the configuration of the atoms within the planes nor the a_l are assumed constant within this quasi-one-dimensional model (that is we will restrict ourselves to the case of normal incidence). However, as l increases ($l=1$ labels the first plane) $a_l \rightarrow a$ and the atomic planes approach their bulk configuration. As a consequence of these changes in crystal structure the excitation energy $\epsilon(l)$ of excitons near the surface will differ from those of the bulk. It is possible to develop a detailed microscopic theory of the electronic structure of these excitons.[12] From such an analysis one expects $\epsilon(l)$ will increase with respect to its "bulk" value as $l\rightarrow 1$. Even within this quasi-one-dimensional model interplane (dispersive) interactions, the result of exciton interactions other than dipole-dipole, will exist and in general must be l dependent. (In a full three-dimensional treatment, Philpott[5] has shown that an additional dispersive interaction which decays exponentially results from the dipole-dipole terms.)

Within the semiclassical theory[3,6,11] this mechanical system can be described in terms of the two interactions outlined above, $\epsilon(l)$ the exciton energy (referred to its bulk value) and $\upsilon(l,l')$ the interplane coupling interaction such that the interaction of the mechanical system and the radiation field of frequency ω (near ω_0, the exciton frequency) is described by a Maxwell equation [Eq. (2.1)] and a constitutive relation [Eq. (2.2)]. Specifically

$$\frac{\partial^2}{\partial x^2}E(x)=-\frac{\omega^2}{C^2}\left[E(x)+4\pi P(x)\right], \qquad (2.1)$$

$$\left((\omega_0^2-\omega^2)-\frac{2\omega_0}{h}\left[\upsilon(l)-\hat{U}(l)\right]\right)P(l)=\alpha_0\omega_0^2E(x=x_l), \qquad (2.2)$$

where

$$P(x)=\sum_l\delta(x-x_l)P(l), \qquad (2.3)$$

$$\hat{\upsilon}(l)P(l)\equiv\sum_{l'}\upsilon(l,l')P(l'), \qquad (2.4)$$

$$\hat{U}(l)P(l)=\epsilon(l)P(l). \qquad (2.5)$$

Here we note again that it is possible to give sufficient conditions for the validity of these phenomenological equations based on a microscopic model Hamiltonian for the crystal and semiclassical radiation theory[6] (the Hartree-Fock limit of quantum electrodynamics).[11] We assume that these conditions are met and refer the reader to the literature for details.

We now consider the solution of the above equations in light of the preceding discussion. Solving Eq. (2.1) and inserting the result into Eq. (2.2) gives

$$\left((\omega_0^2-\omega^2)-\frac{2\omega_0}{h}\left[\hat{\upsilon}(l)-\epsilon(l)\right]\right)P(l)=\alpha_0\omega_0^2\left(E_0e^{i\omega al/c}+\frac{2\pi\omega ai}{c}\sum_{l'=1}^{\infty}e^{i\omega a|l-l'|/c}P(l')\right), \qquad (2.6)$$

where E_0 is the strength of the incident electric field and for convenience we have set $a_l\equiv a$, but retained the nonuniformity in $\epsilon(l)$ and $\hat{\upsilon}(l)$. It will be useful to have the analogous equation for a continuum dielectric, that being

$$\left((\omega_0^2-\omega^2)-\hat{V}(x)+\frac{2\omega_0}{h}\epsilon(x)\right)P(x)=\alpha_0\omega_0^2\left(E_0e^{i\omega x/c}+\frac{2\pi\omega i}{c}\int_0^{\infty}e^{i\omega|x-x'|/c}P(x')dx'\right), \qquad (2.7)$$

where $\hat{V}(x)$ is some differential operator which for small-wave-vector excitations can be taken as

$$\hat{V}(x)=\frac{h\omega_0}{m^*}\frac{\partial^2}{\partial x^2}, \qquad (2.8)$$

where m^* is the reduced mass of the exciton.

From the preceding discussion we expect $\epsilon(l)=0$ for $l>L$, where L loosely speaking defines the range of the surface region. The behavior of $\epsilon(l)$ for $l\leq L$ (i.e., in the surface region) is not known precisely, but it is not unreasonable to expect $\epsilon(l)>\epsilon(l+j)$ for $j>0$. Further, since the principal origin of the dispersive interaction is the electronic excitation, this interaction is expected to be reduced in this region.

The particular form of $\hat{\upsilon}(l)$ is crucial for this problem since it determines the number of refractive indices required to solve Eq. (2.6)[3,5,6] (and see below). However in the continuum limit given by Eqs. (2.7) and (2.8) exactly two refractive indices (the remaining Maxwell's equations and one unknown boundary condition) are required to determine the relevant electromagnetic fields. There are two choices of $\hat{\upsilon}(l)$ which in the "homogeneous" case result in a two-refractive-index solution of Eq. (2.6): (a) The exponential model (exp) and (b) nearest-neighbor (nn) model. In (a)

$$\frac{2\omega_0}{h}\hat{\upsilon}_{\exp}(l)f(l)=J_E\sum_{l'}e^{-Ka|l-l'|}f(l'), \qquad (2.9)$$

while in (b)

$$(2\omega_0/h)\hat{\upsilon}_{nn}(l)f(l)=J(D^+-2D^0+D^-)f(l)$$
$$\equiv J[f(l+1)-2f(l)+f(l-1)], \qquad (2.10a)$$

or more generally,

$$(2\omega_0/h)\upsilon_{nn}(l)f(l)=J_1(l)f(l+1)+J_{-1}(l)f(l-1)-2J_0(l)f(l). \qquad (2.10b)$$

In this work we will treat variants of both these models. Note that Eq. (2.10a) can be viewed as representing the discretization of Eq. (2.7). Alternatively, it may be viewed as arising from a harmonic interaction between nearest-neighbor planes with force constant J {so that the dispersive force on $P(l)$ is $J[P(l+1)-P(l)]-J[P(l)-P(l-1)]$}. This later interpretation will prove useful in discussing the ABC.

B. Soluble model

Before discussing Eq. (2.6) in its full generality, we describe an approximate model which contains the essential physics, in that it reproduces the experimental observations, while having the advantage of being exactly soluble within the RIA. The model[2] (which was motivated by the discussion of HT)[2] replaces $\epsilon(l)$ described above by a step function

$$\epsilon(l)=0,\quad l\geqslant L+1 \qquad \epsilon(l)=U,\quad l\leqslant L \tag{2.11}$$

(for the nearest-neighbor interaction this approximation will be relaxed somewhat, see below). Further, since the surface region is expected to exhibit reduced dispersion, $\hat{\mathfrak{v}}(l)$ is approximated in this region by $\hat{\mathfrak{v}}(l)=0$. This later assumption is not necessary to obtain a model soluble within the RIA. However, it does reduce the algebra enormously rendering the physics more transparent. The definition of $\hat{\mathfrak{v}}_{\exp}(l)$ is completed by restricting the summation in Eq. (2.10) to $l'\geqslant L+1$ so that there is no dispersive coupling between the two regions. A similar constraint will be placed on $\hat{\mathfrak{v}}_{\mathrm{nn}}(l)$. For Eq. (2.9b) this amounts to setting $J_{-1}(L+1)=0$. This point will be discussed further below.

Within the RIA a trial solution of Eq. (2.6) in the form

$$P(l)=\sum_\alpha C^\alpha e^{i\omega n^\alpha a l/c}\Theta(l-(L+1)) + C^+ e^{-i\omega n a l/c}\Theta(L-l) + C^- e^{-i\omega n a l/c}\Theta(L-l)\,, \tag{2.12}$$

is sought where the refractive indices n^α, n and the amplitudes C^α, C^+, C^- are to be determined and

$$\Theta(l)=\begin{cases}1, & l\geqslant 0\\ 0, & l<0\,.\end{cases} \tag{2.13}$$

The n^α must be selected so that $P(l)$ describes a wave propagating to the right in the bulk. The unknown refractive indices and amplitudes are deduced by inserting Eq. (2.12) into Eq. (2.6) and performing the required lattice sums (which become geometric series).

We consider the case of exponential coupling first. For $l<L+1$, we find

$$\begin{aligned}&[\omega_0^2-\omega^2+(2\omega_0/h)U](C^+e^{in\phi l}+C^-e^{-in\phi l})\\ &=\alpha_0\omega_0^2\left\{E_0e^{i\phi l}+2\pi\phi i\left[\sum_\alpha C^\alpha e^{-i\phi l}\frac{e^{i\phi(n^\alpha+1)L}}{e^{-i\phi(n^\alpha+1)}-1}+C^+\left(\frac{e^{i\phi l}}{e^{-i(n-1)\phi}-1}+e^{i\phi nl}\frac{i\sin\phi}{\cos n\phi-\cos\phi}-e^{-i\phi l}\frac{e^{i\phi(n+1)L}}{e^{-i\phi(n+1)}-1}\right)\right.\right.\\ &\left.\left.\qquad+C^-\left(\frac{e^{+i\phi l}}{e^{i\phi(n+1)}-1}+e^{-i\phi l}\frac{i\sin\phi}{\cos n\phi-\cos\phi}-e^{-i\phi l}\frac{e^{-i\phi(n-1)L}}{e^{i\phi(n-1)}-1}\right)\right]\right\},\end{aligned} \tag{2.14}$$

where $\phi=(\omega/c)a$, while for $l\geqslant L+1$ we have

$$\begin{aligned}&\sum_\alpha\left((\omega_0^2-\omega^2)e^{in^\alpha\phi l}-J_E\frac{e^{-Kal}e^{(i\phi n^\alpha+Ka)L}}{e^{-(i\phi n^\alpha+Ka)}-1}+J_Ee^{in^\alpha\phi l}\frac{\sinh Ka}{\cos n^\alpha\phi-\cosh Ka}\right)C^\alpha\\ &=\alpha_0\omega_0^2\left[E_0e^{i\phi l}+2\pi\phi i\left(\sum_\alpha C^\alpha e^{i\phi l}\frac{e^{i\phi(n^\alpha-1)L}}{e^{-i\phi(n^\alpha-1)}-1}+e^{i\phi n^\alpha l}\frac{i\sin\phi}{\cos n^\alpha\phi-\cos\phi}\right.\right.\\ &\left.\left.\qquad+C^+e^{i\phi l}\frac{1-e^{i\phi(n-1)L}}{e^{-i\phi(n-1)}-1}+C^-e^{i\phi l}\frac{1-e^{-i\phi(n+1)L}}{e^{i\phi(n+1)}-1}\right)\right].\end{aligned} \tag{2.15a}$$

The requisite amplitudes and refractive indices are now determined as follows

(i) Setting the coefficient of $e^{in^\alpha\phi l}$ equal to zero in Eq. (2.15a) gives a single dispersion relation for n^α

$$(\omega_0^2-\omega^2)-\frac{J_E\sinh Ka}{2(\sinh^2\tfrac{1}{2}Ka+\sin^2\tfrac{1}{2}n^\alpha\phi)}=+\frac{\pi\phi\sin\phi}{\sin^2\tfrac{1}{2}n^\alpha\phi-\sin^2\tfrac{1}{2}\phi}. \tag{2.16a}$$

It is sufficient for the present discussion to point out that this equation is quadratic in $\sin^2\frac{1}{2}n\phi$ and will therefore yield two n^α corresponding to waves propagating to the right as promised. Equation (2.16a) is discussed in detail by Sipe and Van Kronendonk[6] who first proposed the exponential model.

(ii) Setting the coefficient of $e^{+i\phi nl}$ equal to zero in Eq. (2.14) gives the dispersion relation for n

$$\left(\omega_0^2-\omega^2+\frac{2\omega_0 U}{h}\right)=\alpha_0\omega_0^2\frac{\pi\phi\sin\phi}{\sin^2\frac{1}{2}n\phi-\sin^2\frac{1}{2}\phi}. \quad (2.17)$$

This is the usual dispersion relation for a non-spatially dispersive medium (with a shift in the absorption line) and yields a unique value of n.

There are four equations to be determined to fix the four amplitudes.

(iii) Setting the coefficient of $e^{i\phi l}$ equal to zero in Eqs. (2.14) and (2.15a) gives, respectively,

$$-E_0=2\pi\phi i\left(\frac{C^+}{e^{-i(n-1)\phi}-1}+\frac{C^-}{e^{i\phi(n+1)}-1}\right), \quad (2.18)$$

$$-E_0=2\pi\phi i\left(\sum_\alpha C^\alpha\frac{e^{i\phi(n^\alpha-1)L}}{e^{i\phi(n^\alpha-1)}-1}+C^+\frac{1-e^{i\phi(n-1)L}}{e^{-i\phi(n-1)}-1}+C^-\frac{e^{-i\phi(n-1)L}}{e^{i\phi n-1}-1}\right). \quad (2.19)$$

We shall refer to Eq. (2.18) as the first extinction theorem[13] since it shows that in the surface region the incident electric field with propagation vector ω/c is annihilated and replaced by a wave with propagation vector $n(\omega/c)$. Equation (2.19) represents a second extinction theorem. This can be seen more readily by using Eq. (2.18) in Eq. (2.19) to yield

$$\sum_\alpha C^\alpha\frac{e^{i\phi(n^\alpha-1)L}}{e^{-i\phi(n^\alpha-1)}-1}=C^+\frac{e^{i\phi(n-1)L}}{e^{-i\phi(n-1)}-1}+C^-\frac{e^{-i\phi(n+1)L}}{e^{i\phi(n+1)}-1}. \quad (2.20)$$

As in Eq. (2.18) this equation represents the destruction of the wave with propagation vector $(n\omega/c)$ in the bulk.

The two equations that remain to be determined are obtained by

(iv) Setting to zero the coefficient of $e^{-i\phi l}$ in Eq. (2.14) to give

$$\sum_\alpha C^\alpha\frac{e^{i\phi n^\alpha L}}{e^{-i\phi(n^\alpha+1)}-1}=C^+\frac{e^{i\phi nL}}{e^{-i\phi(n+1)}-1}+C^-\frac{e^{-i\phi nL}}{e^{i\phi(n-1)}-1}, \quad (2.21)$$

and (v) that of e^{-Kal} in Eq. (2.15a) giving

$$\sum_\alpha\left(\frac{1}{e^{-(i\phi n^\alpha+Ka)}-1}e^{in^\alpha\phi L}\right)C^\alpha=0. \quad (2.22a)$$

We defer discussion of these final two equations until after examination of the *nn* model to which we now turn.

For the nearest-neighbor model we must consider three regions of space (a) the surface region $l<L+1$, (b) the bulk region $l>L+1$, and (c) the interfacial "region" $l=L+1$. For $l<L+1$ we again find Eq. (2.14), while for $l>L+1$ Eq. (2.15a) is replaced by an equation whose right-hand side is the same as that in Eq. (2.15a), but those left-hand side is replaced by

$$\sum_\alpha[(\omega_0^2-\omega^2)-(2J_1\cos n^\alpha\phi+J_0)]C^\alpha e^{in^\alpha\phi l}. \quad (2.23)$$

We shall refer to the equation just described as Eq. (2.15b) without writing it out explicitly. Note that in deriving this equation we have used Eq. (2.10b) with $J_{\pm1}(l)=J_1$ and $J_0(l)=J_0$, to describe the nearest-neighbor dispersion.

The dispersion relations for n^α and n as well as three of the four equations for the amplitudes C^+, C^-, and C^α can now be deduced for the nearest-neighbor interaction using Eqs. (2.14) and (2.15b) in conjunction with steps (i)–(iv) described above. Doing this we recover the dispersion relation for n, Eq. (2.17), the extinction theorems Eqs. (2.18) and (2.19), and Eq. (2.21). The dispersion relation for n^α [Eq. (2.16a)], however, is replaced by

$$[\omega_0^2-\omega^2-(2J_1+J_0)]+4J_1\sin^2\tfrac{1}{2}n^\alpha\phi=\frac{\pi\phi\sin\phi}{\sin^2\frac{1}{2}n^\alpha\phi-\sin^2\frac{1}{2}\phi}. \quad (2.16b)$$

As was the case for Eq. (2.16a), it suffices for our purposes to observe that Eq. (2.16b) yields two n^α and the reader is referred to the literature for a more detailed discussion of the equation.[3]

To derive the analog of the fourth equation for the amplitudes Eq. (2.22a) we must consider the form of Eq. (2.6) for $l=L+1$ (the interfacial plane). As a first approximation we might, as indicated previously, take $\epsilon(L+1)=J_{-1}(L+1)=0$ and retain $J_1(L+1)=J_1$ and $J_0(L+1)=J_0$ (their bulk values). Doing this we obtain

$$\sum_\alpha e^{i\phi n^\alpha L}C^\alpha=0. \quad (2.22b)$$

However, if one thinks in terms of the harmonic model for nearest-neighbor interactions [Eq. (2.10a)] (which goes over to the usual continuum equation in the $a\to0$ limit) it is more appropriate to think of "cutting the left-hand spring" at the boundary so that $J_1(L+1)=J$, $J_0(L+1)=-J$ (rather than its bulk value of $-2J$), and $J_{-1}(L+1)=0$. Further the assumption of a step-function-like change in $\epsilon(l)$ was overly restrictive. We can relax this assumption somewhat by allowing $\epsilon(l)$ to assume some intermediate value say U_1, where $0<U_1<U$. In this case Eq. (2.6) reduces to

$$\sum_\alpha [(U_1-J)e^{in^\alpha\phi}+J]e^{i\phi n^\alpha L}C^\alpha=0\,. \tag{2.22c}$$

Clearly, Eq. (2.22b) is a special case of Eq. (2.22c).

We are now in a position to address the two central points of this work (a) the reflectivity anomaly, and (b) the ABC. We begin with a discussion of the reflectivity anomaly, that is the additional feature (peak) in the Drude tail of the reflectivity observed by HT.

The reflection coefficient r is defined

$$r=R/E_0\,,$$

where R is the reflected electric field. The total electric field $E(l)$ is given by [see Eq. (2.1)]

$$E(l)=E_0e^{i\phi l}+2\pi\phi i\sum_{l'=1}^{\infty}e^{i\phi|l-l'|}P(l')\,. \tag{2.24}$$

Inserting Eq. (2.12) into Eq. (2.24) evaluated in the limit $l\to-\infty$ gives for R

$$R=\sum_\alpha C^\alpha\frac{e^{i\phi(n^\alpha+1)L}}{e^{-i\phi(n^\alpha+1)}-1}+C^+\frac{1-e^{i\phi(n+1)L}}{e^{-i\phi(n+1)}-1}+C^-\frac{1-e^{-i\phi(n-1)L}}{e^{i\phi(n-1)}-1}\,. \tag{2.25}$$

The reflectivity therefore becomes

$$-r=\frac{(e^{-i\phi(n-1)}-1)(e^{i\phi(n+1)}-1)}{(e^{i\phi(n+1)}-1)(e^{i\phi(n-1)}-1)}\times\left[\frac{(e^{i\phi(n-1)}-1)+\gamma(e^{-i\phi(n+1)}-1)}{(e^{i\phi(n+1)}-1)+\gamma(e^{-i\phi(n-1)}-1)}\right], \tag{2.26}$$

where $\gamma=C^-/C^+$ and Eqs. (2.18) and (2.21) have been used to simplify the result. Note that Eq. (2.26) expresses the reflectivity in terms of the waves existing in the surface region alone. To determine γ Eq. (2.21) is divided by Eq. (2.20) to give, after some straightforward algebra

$$-\gamma e^{i\phi 2nL}=\frac{(e^{i\phi(n+1)}-1)(e^{i\phi(n-1)}-1)}{(e^{-i\phi(n-1)}-1)(e^{-i\phi(n+1)}-1)}\times\left[\frac{(e^{-i\phi(n-1)}-1)-r^*(e^{-i\phi(n+1)}-1)}{(e^{i\phi(n+1)}-1)-r^*(e^{i\phi(n-1)}-1)}\right], \tag{2.27}$$

where

$$r^*=\frac{(e^{-i\phi(n_1-1)}-1)(e^{-i\phi(n_2-1)}-1)}{(e^{-i\phi(n_1-1)}-1)(e^{-i\phi(n_2+1)}-1)}b(n_1,n_2,\phi)\,, \tag{2.28}$$

$$b(n_1,n_2,\phi)=\frac{(e^{-i\phi(n_2+1)}-1)-\lambda(e^{-i\phi(n_1+1)}-1)}{(e^{-i\phi(n_2-1)}-1)-\lambda(e^{-i\phi(n_1-1)}-1)}\,, \tag{2.29}$$

$$\lambda=-C_2/C_1e^{i\phi(n_2-n_1)L}\,, \tag{2.30}$$

and n_1, n_2 are the two values of n^α obtained from the solution of Eq. (2.15). Finally λ is calculated from one of Eqs. (2.22). These equations have the general form

$$\sum_\alpha V(\alpha,\phi)e^{in^\alpha\phi L}C^\alpha=0\,, \tag{2.22d}$$

so that

$$\lambda=V(1,\phi)/V(2,\phi)\,. \tag{2.31}$$

Equations (2.26)–(2.31) represent the general solution for r within the microscopic model presented here. It is important to make the connection between this model and the continuum theory. To this end we return to Eq. (2.22) in its various guises. Equation (2.22c) can be expanded as

$$0=\sum_{\alpha,j}\left((U_1-J)\frac{(in^\alpha\phi)^j}{j!}+J\right)e^{i\phi n^\alpha L}C^\alpha\,,$$

$$0=\sum_{\alpha,j=1}\left(U_1+(U_1-J)\frac{1}{j!}\frac{\partial^j}{\partial(la)^j}\right)C^\alpha e^{(in^\alpha\omega/c)al}\bigg|_{l=L}\,. \tag{2.32}$$

Similarly Eq. (2.22a) becomes

$$0=\sum_{\alpha,m,j}\frac{(i\phi n^\alpha m)^j}{j!}e^{-Kam}C^\alpha e^{in^\alpha\phi L}=\sum_{\alpha,j=0}\left(S_j(K)\frac{1}{j!}\frac{\partial^j}{\partial(la)^j}\right)C^\alpha e^{(in^\alpha\omega/c)al}\bigg|_{l=L}\,, \tag{2.33}$$

where

$$S_j(K)=\sum_{m=1}^{\infty}m^je^{-Kam}\,. \tag{2.34}$$

Thus we see that in the continuum limit Eqs. (2.22) reduce to various ABC's on the bulk polarization at the surface-bulk interface. For example, in the extreme long-wavelength limit Eqs. (2.32) and (2.33) may be expanded to zeroth order in $n^\alpha\phi$ to give a Dirichlet condition on the polarization ($P=0$) while expanding to first order in $n^\alpha\phi$ gives the Robin or mixed condition ($b_1P+b_2\,\partial P/\partial x=0$). Finally note that for the form of the nearest-neighbor interaction considered in Eq. (2.10a) expansion to first order in $n^\alpha\phi$ gives the Neumann condition $[\partial P(x)/\partial x=0]$ rather than the Robin condition.

Equation (2.32) or (2.33) can be used in conjunction with similar expansions of Eqs. (2.26)–(2.30) to obtain approximate solutions for the reflection coefficient r. For example, expanding to Eq. (2.22) 0th order and Eqs. (2.26)–(2.32) to first-order in $n^\alpha\phi$ gives

$$r=\frac{n(1-\gamma)-(1+\gamma)}{n(1-\gamma)+(1+\gamma)}\quad\text{for }\gamma=\gamma_0\,, \tag{2.35}$$

where

$$\frac{1+\gamma_0}{1-\gamma_0}=\frac{(n+n^+)e^{-i2\phi nL}+(n-n^+)}{(n+n^+)e^{-i2\phi nL}+(n-n^+)} \tag{2.36}$$

and

$$n^+=(n_1n_2+1)/(n_1+n_2)\,. \tag{2.37}$$

This "Dirichlet" limit of the microscopic theory, that is Eqs. (2.35) and (2.37), together with Eq. (2.15b) was first derived, with slight modifications to include the contribution of the nonresonant electronic states to the crystal dielectric constant, by HT[2] from continuum electromagnetic theory in order to explain their reflectivity data. Thus, their explanation of the reflectivity anomaly is thus seen to be a zeroth-first-order approximation to a suitably modified microscopic theory, as advertised.

Of course, other limits of the microscopic theory are possible. The next step would be to retain terms of order $n^\alpha\phi$ in Eq. (2.22) as well as Eqs. (2.26)–(2.30), yielding the "mixing boundary condition" limit. Using the general form of Eq. (2.32) ($U_1\neq J$) for concreteness, the reflectivity is given in this approximation by Eq. (2.35) evaluated at $\gamma=\gamma_1$, where

$$\gamma_1 e^{-2i\phi nL}=\frac{n(1-r^*)-(1+r^*)}{n(1-r^*)+(1+r^*)}\,, \tag{2.38}$$

$$r^*=cr(n_1)cr(n_2)b_1(n_1,n_2,\phi)\,, \tag{2.39}$$

$$cr(n^\alpha)=\frac{n^\alpha-1}{n^\alpha-1}\,, \tag{2.40}$$

$$b_1(n_1,n_2,\phi)$$
$$=\frac{[(1+\nu)+\nu i n_2\phi](n_2+1)-[(1+\nu)+\nu i n_1\phi](n_1+1)}{[(1+\nu)+\nu i n^2\phi](n_2-1)-[(1+\nu)+\nu i n_2\phi](n_1-1)}\,, \tag{2.41}$$

and

$$\nu=(U_1-J)/J\,. \tag{2.42}$$

Note that for the nearest-neighbor interaction described by Eq. (2.10a), the Neuman limit, r follows from Eqs. (2.35), (2.38)–(2.41) with $\nu=1$.

Finally we note that including the change in refractive index is crucial in explaining the experimentally observed spectrum. If this effect is omitted, we find $r=r^*$ which fails to show the reflection anomaly regardless of the form of Eq. (2.22).

We now return briefly to the problem of the ABC for the continuum theory. We have already seen, for the nearest-neighbor interaction, how a change in the energy at the exciton at an interface can change the ABC from a Dirichlet [Eq. (2.22b)], to a mixed [Eq. (2.22c)], $U_1\neq J$), to a Neumann condition [Eq. (2.22c), $U=J$] condition. However in order to obtain a model which is exactly soluble (within the RIA) the continuous variation of $\epsilon(l)$ in the surface region was replaced by a rather abrupt variation [Eq. (2.11)]. (Spatial dispersion was also neglected in this region but as indicated, this omission was merely a convenience.) This approximation precludes a more definitive conclusion regarding the ABC than that mentioned above. To include the variation in $\epsilon(l)$ properly would necessitate replacing nl by $n(l)$. We intend to give a more detailed account of this important problem in a future publication which includes both the spatial variation in $n(l)$ and the effect of spatial dispersion. Finally we note that using Eqs. (2.18) and (2.27) will determine a value of P at the surface. This value, however, has little relation to the ABC as a consequence of the insertion of the boundary layer at $l=L+1$ and the omission of spatial dispersion from the boundary region.

III. CONCLUSION

In this work we have taken the initial step toward the inclusion of surface effects in a microscopic theory of spatially dispersive media. Using a model which takes into account, in a simple manner, the variation of refractive index near the surface the results of Hopfield and Thomas were obtained as a particular limit of a microscopic theory. Although the model presented here is too simplistic to assess precisely the role of the change in refractive index on the ABC required in a continuum theory, we were able to make some general remarks concerning this effect. In a future publication we hope to present a more detailed discussion of this important problem.

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