PHYSICAL REVIEW B VOLUME 5, NUMBER 2 15 JANUARY 1972

Surface Polaritons and the Theory of Image Charges*

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(Received 4 May 1971)

The electric and polarization fields are solved for the case of a point charge near the interface between a dielectric and a vacuum. The solution is obtained microscopically from the point-dipole model. By knowing the position and polarizability of all of the ions, one can show how to derive the results of classical image-charge theory. Of interest is the notable contribution of surface polaritons to the image charge. They give rise to the entire polarization field if the source charge is located outside of the dielectric.

I. INTRODUCTION

If a source charge is situated near the interface between two insulating dielectrics, or a dielectric and a vacuum, the resulting potential field may be represented by a set of image charges. This well-known result follows immediately from the solution of the macroscopic Maxwell's equations. In this article we are going to derive the same results from a microscopic point of view. We confine our discussion to the interface between a semiinfinite crystal and the vacuum. The point-dipole model is adopted for the crystal: The local electric field acting at an atomic site induces polarization which can be represented as a point dipole centered on the atomic site. This microscopic viewpoint has already been applied to investigating potential fields from impurity charges inside the bulk of the material.[1,2]

The new result which emerges from the present investigation is the central importance of surface polarization modes in determining the image charges. It is now known that there are three types of long-wavelength normal modes of polarization in a dielectric.[3-8] For cubic dielectrics, to which we limit our discussion, these are the longitudinal and two transverse modes which extend throughout the bulk of the solid. The third type are the surface modes. The presence of a fixed, static source (or impurity) charge must induce in the dielectric a static polarization response. This polarization field can be represented as some linear combination of the polarization normal modes of the dielectric.

If the source charge is placed outside of the dielectric, in the vacuum region, then the surface polarization modes are the only one of the three types of normal modes which are induced. If the source charge is placed inside of the dielectric, but still near the surface, then both surface and longitudinal modes of polarization are induced. Here the surface modes again produce a polarization field equivalent to an image charge. The longitudinal modes provide the screening of the direct interaction from the source term, as they do throughout the bulk of the solid. In addition, the longitudinal modes also provide the screening of the image-charge field.

These results are only rigorously true in the limit of long-wavelength polarization modes. But it is these long-wavelength modes which produce the results equivalent to the image-charge theory of classical electrostatics. As was also true for the case of potentials in an infinite solid, there are additional interaction terms of higher multipoles. These become important in the present case when the source charge is within a few atomic distances of the surface.

In Sec. II, we discuss the case of a fixed impurity which is static in time. This problem has neither time dependence nor frequency dependence. Because of this, the modes which we find convenient to use are those which also have no frequency dependence (dispersion). These are the polarization modes calculated by ignoring retardation.[3] This is a significant distinction, since retardation affects the long-wavelength modes which are of greatest concern in the present problem. So our use of the term "surface mode" refers to those modes calculated in the absence of retardation. This does not mean that our results are in error, nor that we are neglecting retardation. Indeed, we have emphasized that there is no retardation in our static problem. Essentially we are solving a mathematical problem in which it is convenient to express the solution in terms of eigenstates (normal modes) of a certain operator. It just turns out that the eigenstates which are most convenient for our problem do not correspond to the physical set of retarded eigenstates.

II. THEORY OF IMAGE CHARGES

In Ref. 1, it was shown that a charge of q located at $\vec{R}_1$ produces a potential Φ at another point $\vec{R}_2$

given by

$$\Phi(\vec{R}_2,\vec{R}_1)=q\Big(\frac{1}{R_{12}}-\alpha\sum_{j\mu}E_\mu(\vec{R}_{2j})\,E_\mu(\vec{R}_{1j})+\alpha^2\sum_{\substack{jj'\\ \mu\nu}}E_\mu(\vec{R}_{2j})\,\Phi_{\mu\nu}(\vec{R}_{jj'})\,E_\nu(\vec{R}_{1j'})-\cdots\Big),$$

$$E_\mu(\vec{R})=R_\mu/R^3\,, \qquad (2.1)$$

$$\Phi_{\mu\nu}(\vec{R})=(\delta_{\mu\nu}-3R_\mu R_\nu/R^2)/R^3\,,$$

where $\vec{R}_j$ are the sites of the polarizable ions. For simplicity, we have assumed that all of the ions have the same isotropic polarizability α. Equation (2.1) is also valid for the present problem, as it is valid for any number of polarizable ions in any arrangement. For the surface problem it is more convenient to rewrite (2.1) in another form. Define $\vec{P}^{(1)}(\vec{R}_j)$ as the polarization of ion $\vec{R}_j$ which is induced by the charge at $\vec{R}_1$. Then we get

$$\Phi(\vec{R}_2,\vec{R}_1)=\Big(\frac{q}{R_{12}}-\sum_{\mu,j}E_\mu(\vec{R}_{2j})P_\mu^{(1)}(\vec{R}_j)\Big)\,, \qquad (2.2)$$

where the polarization obeys the equation

$$\sum_{j\nu}\,[\delta_{\mu\nu}\,\delta_{ij}+\alpha(0)\,\Phi_{\mu\nu}(\vec{R}_{ij})]\;P_\nu^{(1)}(\vec{R}_j)=q\,\alpha(0)\,E_\mu(\vec{R}_{1i})\,. \qquad (2.3)$$

The central mathematical problem is to solve Eq. (2.3) and obtain the polarization $P_\mu^{(1)}(\vec{R}_j)$. In principle, this can be accomplished by defining a Green's function $G_{\mu\nu}(\vec{R}_i,\,\vec{R}_j)$ which obeys an equation

$$\sum_{j\nu}[\delta_{\mu\nu}\delta_{ij}+\alpha(0)\,\Phi_{\mu\nu}(\vec{R}_{ij})]\;G_{\nu\lambda}(R_j,R_k)=\delta_{\mu\lambda}\,\delta_{ik}\,, \qquad (2.4)$$

and we get

$$P_\nu^{(1)}(\vec{R}_i)=q\,\alpha(0)\sum_{j\lambda}G_{\nu\lambda}(\vec{R}_i,\,\vec{R}_j)\,E_\lambda(\vec{R}_{j1})\,, \qquad (2.5)$$

$$\Phi(\vec{R}_2,\vec{R}_1)=q\,\Big(\frac{1}{R_{12}}-\alpha(0)\sum_{\substack{ij\\ \mu\nu}}E_\mu(\vec{R}_{2j})\,G_{\mu\nu}(R_j,R_i)\times E_\nu(R_{i1})\Big)\,. \qquad (2.6)$$

We have previously solved these equations in the case of the potential from an impurity charge in an infinite solid, neglecting surface effects.[1,2] Then the Green's function depended only upon the difference of its spatial variables $G_{\mu\nu}(\vec{R}_i-\vec{R}_j)$. In that case the problem could be easily solved by Fourier transforming all of the equations.

The Fourier-transform technique is less useful in surface problems. Instead, we note that the Green's function may be expressed as a sum over normal modes. Let us call ω_n the eigenfrequencies and $\Psi_\nu(\vec{R}_j;\,n)$ the eigenfunctions of the equation

$$\sum_{j,\nu}\,[\,\delta_{\mu\nu}\,\delta_{ij}+\alpha(\omega_n)\,\Phi_{\mu\nu}\,(\vec{R}_{ij})]\,\Psi_\nu(\vec{R}_j;\,n)=0\,. \qquad (2.7)$$

Then we simply get

$$G_{\mu\nu}(\vec{R}_i,\vec{R}_j)=\sum_n\frac{\Psi_\mu(\vec{R}_i;n)\,\Psi_\nu^*\,(\vec{R}_j;\,n)}{[\,1-\alpha(0)/\alpha(\omega_n)]}\,, \qquad (2.8)$$

$$\Phi(\vec{R}_2,\vec{R}_1)=q\Big(\frac{1}{R_{12}}-\alpha(0)\sum_n\frac{\Lambda^*(\vec{R}_1;\,n)\Lambda(\vec{R}_2;\,n)}{1-\alpha(0)/\alpha(\omega_n)}\Big)$$

$$\Lambda(\vec{R}_1;n)=\sum_{\nu j}E_\nu(\vec{R}_{1j})\,\Psi_\nu^*(\vec{R}_j;n)\,.$$

In the present problem, we let z be the variable normal to the surface, and $\vec{\rho}$ be the position vector parallel to the surface. The surface extends to infinity in the $\vec{\rho}$ direction, with the normal modes as plane waves in this direction. Define a two-dimensional wave vector $\vec{\kappa}$ which is confined to the Brillouin zone,

$$\Psi_\nu(\vec{R}_j;n)=e^{i\vec{\kappa}\cdot\vec{\rho}_j}\,\gamma_\nu(l;\,\vec{\kappa},m)\,,$$

where m are the additional quantum numbers needed to describe the various possible eigenstates. Since we know the form of the eigenmodes in the transverse direction, we can sum over the atom positions in these directions. In order to clarify the physics, we simplify the algebra as much as possible and assume that we have a monoatomic cubic lattice—sc, fcc, or bcc—where the z axis is the [100] direction. Then each atom position can be designated as

$$\vec{R}_j=(\vec{\rho}_j+l\vec{\rho}_0)+\hat{z}\;l\,a\,,$$

where l denotes the number of the lattice plane counting inward from the surface of the dielectric, a is the separation between planes, and $\vec{\rho}_0$ is the constant displacement in going from plane to plane. So we get

$$\Psi_\nu(\vec{R}_j\,;n)=e^{i\kappa\cdot(\vec{\rho}_j+l\vec{\rho}_0)}\,\gamma_\nu(l\,;\vec{\kappa}\,,m)\,. \qquad (2.9)$$

So the problem reduces to finding the different modes and their z dependencies. The equations we have to solve become

$$0=\sum_{l'\nu}\Big(\frac{\delta_{\mu\nu}\delta_{ll'}}{4\pi\,\bar{\alpha}(\omega_m)}+T_{\mu\nu}(\vec{\kappa}\,,l-l')\Big)\gamma_\nu(l'\,;\vec{\kappa}\,,m)\,, \qquad (2.10)$$

$$\Lambda(\vec{R}_1;\vec{\kappa}\,,m)=\sum_{l,\mu}E_\mu(\vec{\kappa}\,,l\,;\vec{R}_1)\,\gamma_u^*(l;\vec{\kappa}\,,m)\,, \qquad (2.11)$$

$$\Phi(\vec{R}_1, \vec{R}_2) = q\left[\frac{1}{R_{12}} - (4\pi\overline{\alpha}(0))\left(\frac{4\pi}{a}\right)\right.$$
$$\left.\times \sum_m \int \frac{d^2\kappa}{(2\pi)^2} \frac{\Lambda(\vec{R}_2; \vec{\kappa}, m)\Lambda^*(\vec{R}_1; \vec{\kappa}, m)}{1 - \alpha(0)/\alpha(\omega_m)}\right] \qquad (2.12)$$

where

$$\overline{\alpha} = \alpha/V_0 ,$$

$$T_{\mu\nu}(\vec{\kappa}, l - l') = \frac{V_0}{4\pi} \sum_{\rho_{j'}} e^{-i\kappa\cdot[\vec{\rho}_j - \vec{\rho}_{j'} + (l-l')\vec{\rho}_0]} \Phi_{\mu\nu}(\vec{R}_j - \vec{R}_{j'}) , \qquad (2.13)$$

$$E_\mu(\vec{\kappa}, l, \vec{R}_1) = \frac{V_0}{4\pi} \sum_{\vec{\rho}_j} e^{-i\kappa\cdot(\vec{\rho}_j + l\vec{\rho}_0)} \frac{\vec{R}_{ij}}{\vec{R}_{ij}^{\,3}} . \qquad (2.14)$$

It is shown in the Appendix that the effective interaction term at long wavelength has a short-range and long-range interaction term

$$T_{\mu\nu}(\vec{\kappa}, l - l') = T_{\mu\nu}^{\mathrm{SR}} + T_{\mu\nu}^{\mathrm{LR}} , \qquad (2.15)$$

$$T_{\mu\nu}^{\mathrm{SR}}(l - l') = v(l - l')\, d_{\mu\nu} , \qquad (2.16)$$

$$T_{\mu\nu}^{\mathrm{LR}}(\vec{\kappa}, l - l') = \tfrac{1}{2} s\, e^{-s|l-l'|} [\eta_\mu^+ \eta_\nu^+ \theta(l - l')$$
$$+ \eta_\mu^- \eta_\nu^- \theta(l' - l)] , \qquad (2.17)$$

$$s = \kappa a , \quad \eta_\mu^\pm = (\vec{\kappa}/\kappa \pm i\hat{z})_\mu , \quad d_{\mu\nu} = (\delta_{\mu\nu} - 3z_\mu z_\nu) .$$

The long-range interaction term is zero if $l = l'$. The parameters $v(l - l')$ are described in Ref. 9. They provide the local field correction in cubic dielectrics, and obey the sum rule

$$-\tfrac{1}{3} = v(0) + 2 \sum_{l=1}^{\infty} v(l) . \qquad (2.18)$$

However, they rapidly become very small as $l - l'$ increases in magnitude. The polarization vectors obey the simple multiplication rules

$$\textstyle\sum_\mu \eta_\mu^+ \eta_\mu^+ = 0 = \sum_\mu \eta_\mu^- \eta_\mu^- ,$$
$$\textstyle\sum_\mu \eta_\mu^+ \eta_\mu^- = 2 . \qquad (2.19)$$

The electric field term at long wavelength is

$$E_\mu(\vec{\kappa}, l, \vec{R}_1) = \tfrac{1}{2} ia\, e^{-i\vec{\kappa}\cdot\vec{\rho}_1} e^{-\kappa|la - z_1|}$$
$$\times [\eta_\mu^+ \theta(la - z_1) + \eta_\mu^- \theta(z_1 - la)] . \qquad (2.20)$$

The solution to Eq. (2.10) has been discussed extensively in the literature. For $\kappa \to 0$ there is only the short-range interaction (2.16). Mahan and Obermair discussed the normal modes in this case, and showed that there are no surface modes.[9] For the more complicated case of a rocksalt lattice, Tong and Maradudin showed that surface modes do exist from the short-range interaction.[6,7] The equation which results if only the long-range interaction term is retained was solved by Fuchs and Kliewer.[3] They found surface modes. Apparently no one has analytically solved the case where long-range and short-range interactions are both included.

We have not been able to obtain an exact analytical solution for the combined case of short-range and long-range interactions. We can obtain an accurate solution in the limit of long wavelength by applying perturbation theory. In this approach, we divide the short-range interaction term into two parts

$$T_{\mu\nu}^{\mathrm{SR}}(l - l') = T_{\mu\nu}^{\mathrm{SR}\,(0)}(l - l') + T_{\mu\nu}^{\mathrm{SR}\,(1)}(l - l') ,$$

where

$$T_{\mu\nu}^{\mathrm{SR}\,(0)}(l - l') = -\tfrac{1}{3}\delta_{l=l'}\, d_{\mu\nu} , \qquad (2.21)$$

$$T_{\mu\nu}^{\mathrm{SR}\,(1)}(l - l') = d_{\mu\nu}[\tfrac{1}{3}\delta_{l=l'} + v(l - l')] . \qquad (2.22)$$

First Eq. (2.10) is solved using the interaction

$$T_{\mu\nu}^{(0)} = T_{\mu\nu}^{\mathrm{SR}(0)} + T_{\mu\nu}^{\mathrm{LR}} . \qquad (2.23)$$

Then the interaction $T_{\mu\nu}^{SR(1)}$ is treated as a perturbation, and an improved solution can be obtained by first-order perturbation theory. This seems to work quite well, partly because the coefficients $v(l)$ are quite small for $l \neq 0$. In the perturbation scheme, the successive approximations produce an improved value to the "eigenvalue" $1/4\pi\overline{\alpha}$.

Now Eq. (2.10), with the interaction (2.23), is precisely the equation solved by Fuchs and Kliewer.[3] The results obtained, in the limit of a semi-infinite solid, for surface modes are

$$1/4\pi\overline{\alpha}(\omega_s) = -\tfrac{1}{6} , \qquad (2.24a)$$

$$\gamma_\mu^{(s)} = \eta_\mu^+ (s)^{1/2} e^{-sl} , \qquad (2.24b)$$

and for longitudinal modes are

$$1/4\pi\overline{\alpha}(\omega_L) = -\tfrac{2}{3} , \qquad (2.24c)$$

$$\gamma_\mu^{(L)} = (a/\pi k^2)^{1/2} \{i\kappa_\mu \sin[k_z a(l + \tfrac{1}{2})]$$
$$+ \hat{z}_\mu k_z \cos[k_z a(l + \tfrac{1}{2})]\} , \qquad (2.24d)$$

with $k^2 = \kappa^2 + k_z^2$. There is only one surface mode for each value of ω_s which satisfies (2.24a), but there is a continuum of longitudinal modes, one for each value of k_z. There are also two transverse modes of polarization in the bulk. These have an eigenvalue $1/4\pi\overline{\alpha}(\omega_T) = \frac{1}{3}$. These do not enter into the present problem, since the polarization induced by the source charge does not contain any transverse mode components.

The application of first-order perturbation theory to the surface modes produces the improved eigenvalue

$$\frac{1}{4\pi\bar{\alpha}(\omega_s)} = -\tfrac{1}{6} + \sum_{\substack{l\,l'\\ \mu\nu}} \gamma_\mu^{(s)}(\vec{\kappa}, l)^* \, T_{\mu\nu}^{SR(1)}(l-l')\, \gamma_\nu^{(s)}(\vec{\kappa}, l')$$

$$= -\tfrac{1}{6} + s\delta + O(s^2) , \qquad (2.25)$$

where

$$\delta = \sum_{l=1}^{\infty} l\, v(l) .$$

The parameter δ is easily calculated for our three lattices[9]:

Lattice	δ
sc	0.013 07
bcc	−0.070 53
fcc	−0.038 85

At long wavelengths $s = \kappa a$ is very small, so the correction term in (2.26) may be neglected. So the short-range coupling between planes of polarization has little effect upon the long-range interactions. The short-range coupling determines how the eigenstates behave in the one or two surface planes where they match to the outside vacuum. We see that the precise nature of this matching has little effect upon the eigenfrequencies. This is reasonable, since at long wavelength the surface modes extend deeply into the sample, and extend over many surface layers. A similar result was obtained in Ref. 9, where it was shown the precise matching of the one or two surface layers has little effect upon the ordinary optical properties.

The solutions (2.24) are the basis for obtaining the image-charge results. First we will do the case where both the source charge at $\vec{R}_1$ and the point $\vec{R}_2$ are outside of the surface ($z_1 < 0$, $z_2 < 0$). Then the electric field terms in 2.20 have the polarization η_μ^+. The value of $\Lambda^{(s)}$ in (2.11) from the surface modes is

$$\Lambda^{(s)}(\vec{R}, \vec{\kappa})$$

$$= +\tfrac{1}{2} ia\,(s)^{1/2} e^{-i\vec{\kappa}\cdot\vec{\rho}_1} e^{z_1\kappa} \left(\sum_{l=0}^{\infty} e^{-2sl}\right) \left(\sum_{\mu} \eta_\mu^+ \eta_\mu^-\right)$$

$$= [ia/2(s)^{1/2}]\, e^{-i\vec{\kappa}\cdot\vec{\rho}_1} e^{z_1\kappa} , \qquad (2.26)$$

which provides a contribution to the potential field in (2.12) of

$$\Phi^{(s)}$$

$$= -q \left(\frac{4\pi\bar{\alpha}}{1+\frac{4}{6}\pi\bar{\alpha}}\right) \frac{4\pi}{a} \int \frac{d^2\kappa}{(2\pi)^2} \Lambda^{(s)}(\vec{R}_2, \vec{\kappa})^* \Lambda^{(s)}(\vec{R}_1, \vec{\kappa}) .$$

Solving the integral gives

$$\Phi^{(s)} = -q\left(\frac{\epsilon - 1}{\epsilon + 1}\right) \frac{1}{R'_{12}} ,$$

where the distance from the image charge is

$$R'_{12} = [(\vec{\rho}_1 - \vec{\rho}_2)^2 + (z_1 + z_2)^2]^{1/2} .$$

Similarly, the value of $\Lambda^{(L)}$ from the longitudinal modes is

$$\Lambda^{(L)}(\vec{R}_1, \vec{\kappa}, k_z) = -\frac{a}{2}^{3/2} \frac{e^{-i\vec{\kappa}\cdot\vec{\rho}_1} e^{\kappa z_1}}{(\pi k^2)^{1/2}}$$

$$\times \sum_{l=0}^{\infty} e^{-sl} \{k_z \cos[k_z a(l+\tfrac{1}{2})] - \kappa \sin[k_z a(l+\tfrac{1}{2})]\} .$$

By evaluating the sum over l, one finds that this term is zero in the long-wavelength limit. So the longitudinal modes contribute nothing to the polarization field when the source charge is outside of the dielectric. The total polarization field is provided by the surface modes.

The other case of interest is when the source charge is located inside the dielectric. The simplest case to consider is when the source charge is at an interstitial site, so that it does not disturb the dielectric properties of the host lattice. We shall assume that the source charge is located between the L and $L+1$ lattice planes of atoms. The contribution of the surface mode is

$$\Lambda^{(s)}(\vec{R}_1, \vec{\kappa}) = ia\,(s)^{1/2} e^{-i\vec{\kappa}\cdot\vec{\rho}_1} e^{\kappa z_1} \sum_{l=L+1}^{\infty} e^{-2sl}$$

$$\cong [ia/2(s)^{1/2}]\, e^{-i\vec{\kappa}\cdot\vec{\rho}_1} e^{-\kappa z_1} .$$

By comparing with (2.26) we see that, regardless of whether z_1 is inside or outside of the dielectric, we get that

$$\Lambda^{(s)}(\vec{R}_1, \vec{\kappa}) = [ia/2(s)^{1/2}]\, e^{-i\vec{\kappa}\cdot\vec{\rho}_1} e^{-\kappa/|z_1|} .$$

So the surface modes always contribute a term to the potential of the form

$$\Phi^{(s)} = -q\left(\frac{\epsilon - 1}{\epsilon + 1}\right) [(\vec{\rho}_1 - \vec{\rho}_2)^2 + (|z_1| + |z_2|)^2]^{-1/2} .$$

The longitudinal modes only contribute if the source charge is inside of the dielectric interface. In this case we find that

$$\Lambda^{(L)}(\vec{R}_1, \vec{\kappa}, k_z) = \frac{a^{3/2} e^{-i\vec{\kappa}\cdot\vec{\rho}_1}}{2(\pi k^2)^{1/2}} \Bigg(e^{-\kappa z_1} \sum_{l=0}^{L} e^{sl}$$

$$\times [k_z \cos(k_z a(l+\tfrac{1}{2})) + \kappa \sin(k_z a(l+\tfrac{1}{2}))] - e^{\kappa z_1}$$

$$\times \sum_{l=L+1} e^{-sl} [k_z \cos(k_z a(l+\tfrac{1}{2})) - \kappa \sin(k_z a(l+\tfrac{1}{2}))]\Bigg) .$$

Both terms contribute equally at long wavelength,

$$\Lambda^{(L)}(\vec{R}_1, \vec{\kappa}, k_z) = (a/\pi k^2)^{1/2} e^{-i\vec{\kappa}\cdot\vec{\rho}_1} \sin(k_z z_1),$$

and the contribution to the potential is

$$\Phi^{(L)} = q\left(\frac{4\pi\bar{\alpha}}{1+\frac{4}{6}\pi\bar{\alpha}}\right) \frac{4\pi}{a} \int_0^{2\pi} dk_z \int \frac{d^2k}{(2\pi)^2} \Lambda^{(L)}(\vec{R}_2, \vec{\kappa}, k_z)^*$$

$$\times \Lambda^{(L)}(\vec{R}_1, \vec{\kappa}, k_z).$$

Solving the integrals gives

$$\Phi^{(L)} = -q\left(1-\frac{1}{\epsilon}\right)\left(\frac{1}{R_{12}}-\frac{1}{R'_{12}}\right).$$

Combining these contributions provides the correct macroscopic result

$$\Phi = q/R_{12} + \Phi^{(L)} + \Phi^{(s)} = \frac{q}{\epsilon}\left(\frac{1}{R_{12}} + \frac{\epsilon-1}{\epsilon+1}\,\frac{1}{R'_{12}}\right) .$$

III. DISCUSSION OF RETARDATION

The previous discussion was for a static charge, fixed in space. The important equation to be solved is (2.10), whose eigenstates are the polarization modes calculated in the absence of retardation.

The actual eigenstates of the crystal are those calculated including the influence of retardation. These modes have been calculated by Kliewer and Fuchs.[4,5] Yet even if one solves an image-charge problem which contains retardation, one does not seem to use the actual retarded polariton modes as the useful eigenstates.

For example, consider the problem of a source charge fixed in space at $\vec{R}_1$, but whose charge oscillates with a time dependence $e^{-i\Omega t}$. This problem may be solved, as we have shown before,[10] by simply replacing the instantaneous dipole interaction in (2.7) by the retarded dipole interaction. The eigenstates of this new operator are the ones which are used in the Green's function to solve (2.6). The solution proceeds just as in the instantaneous case. For example, the eigenvalue and eigenfunction of the surface mode are

$$\begin{aligned} 1/4\pi\overline{\alpha}(\omega_s) &= -\tfrac{1}{6} + \Omega^2/2(2\kappa^2c^2 - \Omega^2), \\ \gamma_\mu^{(s)} &= (ra)^{1/2}\, w_\mu^+\, e^{-ral} , \\ r &= (\kappa^2 - \Omega^2/c^2)^{1/2}, \\ w_\mu^+ &= \kappa_\mu/r + i\,\hat{z}_\mu. \end{aligned} \qquad (3.1)$$

The important aspect of (3.1) is that one now has a surface mode frequency ω_s determined as a function of $\vec{\kappa}$ and Ω.

These eigenstates (3.1) are not the retarded polariton surface states. The polariton surface states are instead given by solving (3.1) after setting both frequencies to be equal

$$1/4\pi\overline{\alpha}(\omega_s) = -\tfrac{1}{6} + \omega_s^2/2(2\kappa^2c^2 - \omega_s^2). \qquad (3.2)$$

This definition is equivalent to the more conventional definition, as for example given by Economou[8]

$$r\epsilon(\omega_s)/[\kappa^2 - \epsilon(\omega_s)\,\omega_s^2/c^2]^{1/2} = -1. \qquad (3.3)$$

By using the definition

$$\epsilon(\omega) = 1 + 4\pi\overline{\alpha}(\omega)/(1 - \tfrac{4}{3}\pi\overline{\alpha}(\omega)) ,$$

it requires only simple algebra to show that (3.2) is equivalent to (3 3)

IV. MANY-OSCILLATOR SOLUTION

The discussion of Secs. I–III treated the surface mode as if it were a single eigenstate. However, in general the polarizability $\overline{\alpha}(\omega)$ is a sum of many different oscillators

$$\overline{\alpha}(\omega) = \textstyle\sum_j \beta_j/(1 - \omega^2/\omega_j^2) \qquad (4.1)$$

from different exciton and phonon modes. In the absence of damping, each of these oscillators has a corresponding surface mode at a frequency determined by (2.24a). If we call ϵ_0 the zero-frequency dielectric constant, then the image charge

$$-q\left(\frac{\epsilon_0 - 1}{\epsilon_0 + 1}\right)$$

is really obtained by summing up the contribution from all of these surface modes. There remains, then, the question of what fraction of the image charge is contributed by each of the oscillator surface states.

That question may be answered in the following way. Let us assume that each of the oscillators in (4.1) are sufficiently separated in frequency that the dielectric function settles down to a "constant" value between each oscillators. That is, a plot of $\epsilon(\omega)$ vs ω would show dispersive regions about each oscillator frequency, and constant regions in between. Call ϵ_j the constant value in the frequency region above the oscillator labeled ω_j. So ϵ_0 is the static dielectric constant, ϵ_1 is the value above the first oscillator ω_1, etc. Then each surface oscillator contributes to the image charge the amount

$$-q\left(\frac{\epsilon_{j-1} - 1}{\epsilon_{j+1} + 1} - \frac{\epsilon_j - 1}{\epsilon_j + 1}\right) .$$

For example, in an alkali-halide crystal the dielectric function at low frequencies can be written as

$$\epsilon(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 - \omega^2/\omega_{\mathrm{TO}}^2} ,$$

where the second term is the contribution from optical phonons. One can show that the surface optical phonon contributes to the image charge the amount

$$-q\left(\frac{\epsilon_0 - 1}{\epsilon_0 + 1} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 1}\right)$$

while the remaining surface modes contribute

$$-q\left(\frac{\epsilon_\infty - 1}{\epsilon_\infty + 1}\right) .$$

Similarly, each oscillator also contributes a longitudinal mode, and each of these modes contribute

$$\frac{1}{\epsilon_j}-\frac{1}{\epsilon_{j-1}}$$

to the net screening function.

APPENDIX: LATTICE SUMS

Here we will evaluate the lattice sums in (2.13), (2.14), and (3.1). For this we use the method of planewise summation. For the static case we start with the identity which is valid for $z \neq 0$[11]:

$$U(\vec{\rho}, z, l)=\frac{v_0}{4\pi}\sum_{\vec{\rho}_j}\frac{e^{-i\vec{\kappa}\cdot(\vec{\rho}_j+l\vec{\rho}_0+\vec{\rho})}}{[(\vec{\rho}_j+l\vec{\rho}_0+\vec{\rho})^2+z^2]^{1/2}}$$

$$=\frac{v_0}{2A}\sum_{\vec{G}}\frac{e^{i\vec{G}\cdot(\vec{\rho}+l\vec{\rho}_0)}\,e^{-g|z|}}{g}, \tag{A1}$$

where $\vec{g}=\vec{\kappa}+\vec{G}$ and $\vec{\rho}$ is an arbitrary vector in the plane parallel to the surface. The reciprocal-lattice vectors $\vec{G}$ are for the two-dimensional plane of atoms, where $A=v_0/a$ is the area of the unit cell.

The result (2.14) is simply obtained from $[\vec{R}=(z, \vec{\rho})]$

$$E_\mu(\vec{\kappa}, l, \vec{R})=\frac{\partial}{\partial R_\mu}\quad e^{-i\vec{\kappa}\cdot\vec{\rho}}\,U(-\vec{\rho}, z-la, l)$$

$$=+\tfrac{1}{2}a\ e^{-i\vec{\kappa}\cdot\vec{\rho}}\sum\nolimits_{\vec{G}}e^{i\vec{G}\cdot(l\vec{\rho}_0-\vec{\rho})}\,e^{-g|z-la|}$$

$$\times[ig_\mu+g\hat{z}_\mu\,\mathrm{sgn}(z-la)]/g.$$

The most important term is $\vec{G}=0$, which provides the result listed in (2.20). This provides the long-range part of E_μ. We have omitted a short-range part of E_μ which derives from the terms with $G\neq 0$. In the limit of $\kappa\to 0$, this is

$$E_\mu^{\mathrm{SR}}(0, l, \vec{R})=(\tfrac{1}{2}a)\ e^{-i\vec{\kappa}\cdot\vec{\rho}}\sum_{\vec{G}\neq 0}e^{i\vec{G}\cdot(l\vec{\rho}_0-\vec{\rho})}\,e^{-g|z-la|}$$

$$\times[iG_\mu/G+z_\mu\,\mathrm{sgn}(z-la)].$$

For the three cubic lattices, the term G_μ is zero because of the cancellation of the terms $\pm\vec{G}$. So we only get a contribution in the $\hat{z}$ direction:

$$E_\mu^{\mathrm{SR}}(0, l, \vec{R})=+e^{-i\vec{\kappa}\cdot\vec{\rho}}\,z_\mu f(|z-la|, \vec{\rho})\,\mathrm{sgn}(z-la),$$

$$f(z, \vec{\rho})=\tfrac{1}{2}a\sum_{\vec{G}\neq 0}e^{i\vec{G}\cdot(l\vec{\rho}_0-\vec{\rho})-G|z|}.$$

This is a very short-range function of z. If z_1 is outside of the crystal, and more than a lattice constant away from the surface, this term may be neglected. If z_1 is inside the dielectric, but symmetrically located between lattice planes, this term still contributes nothing because of the cancellation for terms $z_1>la$ by those with $z_1<la$.

The result for $T_{\mu\nu}$ is obtained in a similar way from (A1):

$$T_{\mu\nu}(\vec{\kappa}, l-l')$$

$$=-\left(\frac{\partial}{\partial R_\mu}\,\frac{\partial}{\partial R_\nu}\,e^{i\vec{\kappa}\cdot\vec{\rho}}\,U(\vec{\rho}, al-al'+z, l-l')\right)_{R=0}$$

$$=-\frac{a}{2}\sum_{\vec{G}}\frac{e^{i\vec{G}\cdot\vec{\rho}_0 l}\,e^{-g|l-l'|}}{g}\,[ig_\mu-\hat{z}_\mu g\,\mathrm{sgn}(l-l')]$$

$$\times[ig_\nu-\hat{z}_\nu g\,\mathrm{sgn}(l-l')].$$

The long-range term (2.17) comes from the $\vec{G}=0$ term in the summation. The short-range term comes from the other terms with $\vec{G}\neq 0$.

It is worth noting that the lattice sums are done the same way for a retarded interactions. First consider the potential

$$V(\vec{\rho}, z, l, \Omega)=\frac{V_0}{4\pi}\sum_{\vec{\rho}_j}\frac{e^{-i\vec{\kappa}\cdot(\vec{\rho}_j+l\vec{\rho}_0+\vec{\rho})}\,e^{i(\Omega/c)x}}{x}$$

$$=\frac{a}{2}\sum_{\vec{G}}\frac{e^{i\vec{G}\cdot(\vec{\rho}+l\vec{\rho}_0)}\,e^{-r|z|}}{r},$$

$$x=[(\rho_j+l\rho_0+\rho)^2+z^2]^{1/2},$$

$$r=[g^2-\Omega^2/c^2]^{1/2}.$$

Then, for example, the retarded dipole-dipole interaction is given by

$$V_{\mu\nu}(\vec{\kappa}, l-l', \Omega)=-\left(\delta_{\mu\nu}\Omega^2/c^2+\frac{\partial}{\partial R_\mu}\,\frac{\partial}{\partial R_\nu}\right)$$

$$\times[e^{i\vec{\kappa}\cdot\vec{\rho}}\,V(\vec{\rho}, l-l'+z, l-l', \Omega)]_{\vec{R}=0}.$$

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[*] Research supported by a grant from the National Science Foundation.

[1] G. D. Mahan, Phys. Rev. 153, 983 (1967).

[2] G. D. Mahan and R. M. Mazo, Phys. Rev. 175, 1191 (1968).

[3] R. Fuchs and K. L. Kliewer, Phys. Rev. 140, A2076 (1965).

[4] K. L. Kliewer and R. Fuchs, Phys. Rev. 144, 495 (1966).

[5] R. Fuchs and K. L. Kliewer, Phys. Rev. 150, 573 (1966).

[6] S. Y. Tong and A. A. Maradudin, Phys. Rev. 181, 539 (1969).

[7] B. N. N. Achar and G. R. Maradudin, Phys. Rev. 181, 1318 (1969).

[8] E. N. Economou, Phys. Rev. 182, 539 (1969).

[9] G. D. Mahan and G. Obermair, Phys. Rev. 183, 834 (1969).

[10] G. D. Mahan, J. Chem. Phys. 43, 1569 (1965).

[11] B. R. A. Nijboer and F. W. de Wette, Physica 24, 422 (1958).