Theory of surface polaritons and image potentials in polar crystals

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A quantum-mechanical derivation is presented for the dispersion of surface polaritons on polar materials. We do not assume a local dielectric function exists at the surface of the solid. We introduce quantum operators for the phonons (or excitons) and photons, and couple them in the Coulomb gauge. We derive and solve the equations of motion of these coupled oscillators. We find two solutions. One is the surface polariton that agrees with the classical result of Fuchs and Kliewer. The other is a new surface polariton that exists at the frequency of the bulk longitudinal phonon. We also prove that these are the only two solutions. We also find exactly the polarization in the solid from a static external charge, and show that it is not given by surface polaritons.

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I. INTRODUCTION

We present a derivation of surface polaritons using quantum mechanics. Surface polaritons are surface modes that are a mixture of polariztion modes of the solid and electromagnetic modes. All previous derivations are classical and derive that the surface polaritons are given by[1]

$$\kappa^2 = \frac{\omega^2}{c^2}\frac{\varepsilon(\omega)}{\varepsilon(\omega)+1}, \tag{1}$$

where $\varepsilon(\omega)$ is the dielectric function of the material and $\vec{\kappa}=(k_x,k_y,0)$ is the wave vector along the surface. When we solve for the modes using quantum mechanics, we derive the same equation for the dispersion. We also find another surface-polariton mode that exists at the frequency of the longitudinal-optical phonon. Finally, we put a fixed, static charge q outside of the surface of the polar solid. We calculate exactly the polarization induced by this charge and show it gives the classical image theory exactly. The image charge polarization is not related to surface polaritons. This conclusion disagrees with the standard belief that image charges are caused by surface polaritons.[2]

A charged particle outside of a solid surface interacts with the surface polaritons of the solid. Our solution using quantum mechanics has a different interaction than the one found using classical physics.[2–10] Although the original theory is old, it is presently used to discuss scattering of electrons in carbon and graphene when lying on a polar substrate.[11–14]

We follow the method of Hopfield,[15] who first quantized bulk polariton modes in 1958. He introduced quantum operators for both the photon field, and the phonon (or exciton) field, and solved the coupled oscillator problem. He found for bulk polaritons the dispersion,

$$k^2 = \frac{\omega^2}{c^2}\varepsilon(\omega) \tag{2}$$

which is also the equation found classically. Here $\vec{k}=(k_x,k_y,k_z)$ is the three-dimensional wave vector of the polariton. One difference between the classical and quantum derivations is that the classical derivation assumes the dielectric function $\varepsilon(\mathbf{k},\omega)$ is entirely local $\varepsilon(\omega)$ and can be applied at atomic distances. We do not make this assumption. One goal of this derivation is to derive the dispersion of surface polaritons without making any assumptions about dielectric functions. The present result is an extension of our earlier calculation.[2]

The present calculation is limited to phonons in polar insulators. That is a simple and transparent model. A similar calculation could be done for the surface plasmons in a metal but that calculation is harder since the plasma oscillations are not represented by simple harmonic oscillators. There is much interest in the energy loss of charged particles outside metal and polar surfaces, from the interaction with the modes of the solid. Some simple models for this interaction were written down years ago.[4,6–8] The present calculation shows these earlier models are not rigorous.

II. HAMILTONIAN

We start with a Hamiltonian that contains the photons, the phonons, and the phonon-photon interaction,

$$H = H_{0t} + H_{0n} + V. \tag{3}$$

We employ the Coulomb gauge.[16] We treat each of these terms in detail.

The first term is the photon Hamiltonian H_{0t} which is conventionally written in terms of raising ($a^{\dagger}_{\mathbf{k}\lambda}$) and lowering ($a_{\mathbf{k}\lambda}$) of the vector potential $A(\mathbf{r},t)$,

$$H_{0t} = \sum_{\lambda\mathbf{k}} \hbar\omega_k\left(a^{\dagger}_{\mathbf{k}\lambda}a_{\mathbf{k}\lambda}+\frac{1}{2}\right), \tag{4}$$

$$\frac{1}{c}A_{\mu}(\mathbf{r}) = \sum_{\mathbf{k}\lambda} C_{\mathbf{k}}A_{\mathbf{k}\lambda}\xi_{\mu}(\mathbf{k}\lambda)e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{5}$$

$$C_{\mathbf{k}} = \sqrt{\frac{2\pi\hbar}{\Omega\omega_k}}, \quad A_{\mathbf{k}\lambda} = a_{\mathbf{k}\lambda} + a^{\dagger}_{-\mathbf{k}\lambda}, \quad \omega_{\mathbf{k}} = ck. \tag{6}$$

The subscript $\mu=(x,y,z)$ is spatial direction while $\lambda=(1,2)$ denotes possible polarization directions of the photons. The volume of the system is Ω. We are going to treat this problem as two coupled harmonic oscillators. We need to rewrite the above results in terms of momentum and amplitude for the photon field,

$$\mathcal{A}_{\mathbf{k}\lambda} = \sqrt{\frac{\hbar}{2\omega_k}} A_{\mathbf{k}\lambda}, \tag{7}$$

$$\Pi_{\mathbf{k}\lambda} = -i\sqrt{\frac{\hbar\omega_k}{2}}(a_{\mathbf{k}\lambda} - a^\dagger_{-\mathbf{k}\lambda}), \tag{8}$$

$$[\mathcal{A}_{\mathbf{k}\lambda}, \Pi_{\mathbf{k}'\lambda'}] = i\hbar\delta_{\mathbf{k},-\mathbf{k}'}\delta_{\lambda\lambda'}, \tag{9}$$

$$H_{0t} = \frac{1}{2}\sum_{\mathbf{k}\lambda}(\Pi_{\mathbf{k}\lambda}\Pi_{-\mathbf{k}\lambda} + \omega_k^2\mathcal{A}_{\mathbf{k}\lambda}\mathcal{A}_{-\mathbf{k}\lambda}), \tag{10}$$

$$\frac{1}{c}A_\mu(\mathbf{r}) = \sqrt{\frac{4\pi}{\Omega}}\sum_{\mathbf{k}\lambda}\mathcal{A}_{\mathbf{k}\lambda}\xi_\mu(\mathbf{k}\lambda)e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{11}$$

Since $A_\mu(\mathbf{r})$ is Hermitian then $\xi_\mu(-\mathbf{k},\lambda) = \xi_\mu(\mathbf{k}\lambda)$. The phonon Hamiltonian is

$$H_{0n} = \sum_j\left(\frac{P_j^2}{2M} + \frac{K}{2}Q_j^2\right). \tag{12}$$

We assume a cubic crystal with neutral molecules. The molecule has an infrared-active phonon ω_0, which is the feature of principle interest. The phonon collective modes will be expanded in a layer geometry with operators $b_{\kappa,l}$, $b^\dagger_{-\kappa,l}$, and l labels the layer,

$$Q_{\kappa,l,\mu} = \sqrt{\frac{\hbar}{2M\omega_0}}(b_{\kappa,l,\mu} + b^\dagger_{-\kappa,l,\mu}), \tag{13}$$

$$P_{\kappa,l,\mu} = -i\sqrt{\frac{\hbar M\omega_0}{2}}(b_{\kappa,l\mu} - b^\dagger_{-\kappa,l,\mu}), \tag{14}$$

$$[Q_{\kappa,l,\mu}, P_{\kappa',l',\nu}] = i\hbar\delta_{\kappa,-\kappa'}\delta_{ll'}\delta_{\mu\nu}, \tag{15}$$

$$H_{0n} = \frac{1}{2M}\sum_{\mu,\kappa,l}[P_{\kappa,l,\mu}P_{-\kappa,l,\mu} + M^2\omega_0^2Q_{\kappa,l,\mu}Q_{-\kappa,l,\mu}]. \tag{16}$$

The surface polaritons for these phonons were originally predicted by Fuchs and Kliewer.[17,18]

There are three interaction terms. The first is from the usual $p.A$ interaction. The infrared-active mode has an effective charge of e and makes a dipole moment of $e\vec{Q}_j$. Another is an A-squared term. There is also the dipole-dipole interaction from the Coulomb interaction. The three interaction terms are

$$V_1 = -\frac{e}{Mc}\sum_j\vec{P}_j\cdot\vec{A}(\mathbf{R}_j), \tag{17}$$

$$V_2 = \frac{e^2}{2}\sum_{ij,\mu\nu}Q_{i\mu}\phi_{\mu\nu}(R_{ij})Q_{j\nu}, \tag{18}$$

$$V_3 = \frac{e^2}{2Mc^2}\sum_j A(\mathbf{R}_j)^2, \tag{19}$$

$$\phi_{\mu\nu}(\mathbf{R}) = \frac{\delta_{\mu\nu}}{R^3} - 3\frac{R_\mu R_\nu}{R^5}. \tag{20}$$

The volume of the system is $\Omega = N_{xy}LA_0$, where A_0 is the area per unit cell in the layer, N_{xy} is the number of molecules in each layer, and L is the length in the z direction. We also introduce the volume of a unit cell $\Omega_0 = A_0 a$, where a is the lattice constant between layers and the ion plasma frequency,

$$\omega_i^2 = \frac{4\pi e^2}{\Omega_0 M}. \tag{21}$$

The three-dimensional photon wave vector is $\mathbf{k} = (\vec{\kappa}, k_z)$. In terms of these new constants, the interaction terms are

$$V_1 = -\omega_i\sqrt{\frac{a}{M}}\sum_{\kappa,l}\vec{\mathcal{D}}_{\kappa,l}\cdot\vec{P}_{-\kappa,l}, \tag{22}$$

$$\mathcal{D}_{\kappa,l,\mu} = \frac{1}{\sqrt{L}}\sum_{k_z,\lambda}\xi_\mu(\mathbf{k}\lambda)\mathcal{A}_{\mathbf{k}\lambda}e^{ik_z a l}, \tag{23}$$

$$V_2 = -\frac{M\omega_i^2}{2}\sum_{\kappa,l,l',\mu\nu}Q_{\kappa,l,\mu}S_{\mu\nu}(\kappa, l-l')Q_{-\kappa,l',\nu}, \tag{24}$$

$$V_3 = \frac{\omega_i^2 a}{2}\sum_{\kappa,l}\vec{\mathcal{D}}_{\kappa,l}\cdot\vec{\mathcal{D}}_{-\kappa,l}, \tag{25}$$

$$S_{\mu\nu} = \begin{cases} l = l' & \frac{1}{3}d_{\mu\nu} \\ l \neq l' & \frac{a}{2\kappa}e^{-\kappa a|l-l'|}[q^-_\mu q^-_\nu\Theta(l-l') + q^+_\mu q^+_\nu\Theta(l'-l)] \end{cases}, \tag{26}$$

$$\theta = ak_z, \quad d_{\mu\nu} = \delta_{\mu\nu}(1-3\delta_{\mu z}), \quad q^\pm_\mu = i\kappa_\mu \pm \kappa\delta_{\mu z}, \tag{27}$$

where a is the lattice constant in the $\hat{z}$ direction. The vector $\vec{\kappa}$ is in the (x,y) plane so that κ_μ is nonzero whenever $\mu = (x,y)$. The quantity $S_{\mu\nu}$ is the two-dimensional Fourier transform of the instantaneous dipole-dipole interaction. Earlier we evaluated[2] the two-dimensional Fourier transform of the retarded dipole-dipole interaction,

$$T_{\mu\nu}(\kappa,l-l') = \begin{cases} l=l' & \frac{1}{3}d_{\mu\nu} \\ l\neq l' & \frac{a}{2p}e^{-pa|l-l'|}\left[\delta_{\mu\nu}\frac{\omega^2}{c^2}+\eta_\mu^-\eta_\nu^-\Theta(l-l')+\eta_\mu^+\eta_\nu^+\Theta(l'-l)\right] \end{cases},$$

$$p=\sqrt{\kappa^2-\omega^2/c^2}, \quad \eta_\mu^{\pm}=i\kappa_\mu \pm p\delta_{\mu z}. \tag{28}$$

The two Fourier transforms are equal if $c\to\infty$.

The phonon system has a transverse phonon (ω_T), a longitudinal phonon (ω_L), and a surface phonon (ω_S) given by

$$\omega_T^2=\omega_0^2-\frac{1}{3}\omega_i^2, \quad \omega_L^2=\omega_0^2+\frac{2}{3}\omega_i^2, \quad \omega_S^2=\omega_0^2+\frac{1}{6}\omega_i^2. \tag{29}$$

The dielectric function is

$$\varepsilon(\omega)=1+\frac{\omega_i^2}{\omega_T^2-\omega^2}=\frac{\omega_L^2-\omega^2}{\omega_T^2-\omega^2}. \tag{30}$$

Using this dielectric function in Eq. (1), the classical theory of the surface polariton has the dispersion,

$$\omega^2(\kappa)=\frac{1}{2}\left[\omega_L^2+2c^2\kappa^2-\sqrt{(\omega_L^2+2c^2\kappa^2)^2-8c^2\kappa^2\omega_S^2}\right]. \tag{31}$$

One of our quantum solutions has the same dispersion relation. The eigenfunction has the form $\exp(-\gamma a l)$, where $\gamma=\sqrt{\kappa^2-\omega^2\varepsilon(\omega)/c^2}$. Using the dispersion relation in Eq. (1), one can show

$$p^2\gamma^2=\kappa^4-\frac{\omega^2}{c^2}\left[\kappa^2(\varepsilon+1)-\frac{\omega^2}{c^2}\varepsilon\right]=\kappa^4, \tag{32}$$

$$p\gamma=\kappa^2 \tag{33}$$

which is useful later.

Another expression is the electrostatic potential outside of the crystal surface ($z<0$),

$$\phi(\mathbf{r})=\sum_j e_j\vec{Q}_j\cdot\vec{\nabla}_j\frac{1}{|\mathbf{R}_j-\mathbf{r}|} \tag{34}$$

$$=\sum_\kappa \frac{2\pi e}{A_0\kappa\sqrt{N_\perp}}e^{i\vec{\kappa}\cdot\vec{\rho}+\kappa z}\mathcal{L}, \tag{35}$$

$$\mathcal{L}=-\sum_{l,\mu}Q_{\kappa,l,\mu}q_\mu^+e^{-\kappa a l}. \tag{36}$$

This expression is useful once we determine $Q_{\kappa,l,\mu}$. A current of particles outside of the surface can also interact with the substrate through the vector potential.

III. EQUATIONS OF MOTION

Let $\mathcal{O}$ denote one of the four operators $\mathcal{A},\Pi,P,Q$. They obey an equation of motion,

$$\frac{\partial}{\partial t}\mathcal{O}=\frac{i}{\hbar}[H,\mathcal{O}] \tag{37}$$

which produces the following four equations:

$$\frac{\partial}{\partial t}\mathcal{A}_{\mathbf{k}\lambda}=\Pi_{\mathbf{k}\lambda}, \tag{38}$$

$$\frac{\partial}{\partial t}\Pi_{\mathbf{k}\lambda}=-\omega_k^2\mathcal{A}_{\mathbf{k}\lambda}+\frac{a}{\sqrt{L}}\sum_l[\hat{\xi}(\mathbf{k}\lambda)\cdot\vec{F}_{\kappa,l}]e^{-i\theta l}, \tag{39}$$

$$M\frac{\partial}{\partial t}Q_{\kappa,l,\mu}=P_{\kappa,l,\mu}-\omega_i\sqrt{Ma}\mathcal{D}_{\kappa,l,\mu}=\frac{\sqrt{Ma}}{\omega_i}F_{\kappa,l,\mu}, \tag{40}$$

$$\frac{\partial}{\partial t}P_{\kappa,l,\mu}=-M\left[\omega_0^2-\frac{\omega_i^2}{3}d_{\mu\mu}\right]Q_{\kappa,l,\mu}+M\omega_i^2\sum_{l'\neq l}S_{\mu\nu}Q_{\kappa,l',\nu}, \tag{41}$$

$$F_{\kappa,l,\mu}=\omega_i\sqrt{\frac{1}{Ma}}P_{\kappa,l,\mu}-\omega_i^2\mathcal{D}_{\kappa,l,\mu}. \tag{42}$$

Take another time derivative of Eq. (38),

$$\ddot{\mathcal{A}}_{\mathbf{k}\lambda}=\dot{\Pi}_{\mathbf{k}\lambda}=-\omega^2\mathcal{A}_{\mathbf{k}\lambda} \tag{43}$$

and combine it with Eq. (39). The first two equations can be combined to give

$$\mathcal{A}_{\mathbf{k}\lambda}=\frac{a}{\sqrt{L}}\frac{1}{\omega_k^2-\omega^2}\sum_l\hat{\xi}(\mathbf{k}\lambda)\cdot\vec{F}_{\kappa,l}e^{-ik_z a l}, \tag{44}$$

$$\mathcal{D}_{\kappa,l,\mu}=\sum_{l',\nu}G_{\mu\nu}(l-l')F_{\kappa,l',\nu}, \tag{45}$$

$$G_{\mu\nu}(l)=a\int\frac{dk_z}{2\pi c^2}e^{ik_z a l}\frac{\delta_{\mu\nu}(k_z^2+\kappa^2)-k_\mu k_\nu}{(k_z^2+p^2)(k_z^2+\kappa^2)}. \tag{46}$$

The result for $G_{\mu\nu}(l)$ is

$$G_{\mu\nu}(0)=\frac{1}{2pc^2}\left[\delta_{\mu\nu\neq z}-\frac{\kappa_\mu\kappa_\nu-\kappa^2\delta_{\mu\nu z}}{\kappa(\kappa+p)}\right], \tag{47}$$

$$G_{\mu\nu}(l)_{l\neq 0} = \frac{1}{\omega^2}[T_{\mu\nu}(l) - S_{\mu\nu}(l)]. \tag{48}$$

The equations with $l'=l$ all have a denominator with Mc^2 which makes these terms negligible. These terms are omitted. The retarded interaction from photons does not affect the dipolar interactions within a single plane. So we get

$$\mathcal{D}_{\kappa,l,\mu} = \frac{1}{\omega^2}\sum_{l'\neq l,\nu}[T_{\mu\nu}(l-l') - S_{\mu\nu}(l-l')] \times\left[\frac{\omega_i}{\sqrt{Ma}}P_{\kappa,l',\nu} - \omega_i^2\mathcal{D}_{\kappa,l',\nu}\right].$$

Take another time derivative of the above equation, and also Eq. (40) which gives

$$\frac{\dot{P}_{\kappa,l,\mu}}{M} = -\omega^2 Q_{\kappa,l,\mu} + \omega_i\sqrt{\frac{a}{M}}\dot{\mathcal{D}}_{\kappa,l,\mu}, \tag{49}$$

$$\dot{\mathcal{D}}_{\kappa,l,\mu} = \frac{1}{\omega^2}\sum_{l'\neq l,\nu}[T_{\mu\nu}(l-l') - S_{\mu\nu}(l-l')] \times\left[\frac{\omega_i}{\sqrt{Ma}}\dot{P}_{\kappa,l',\nu} - \omega_i^2\dot{\mathcal{D}}_{\kappa,l',\nu}\right]. \tag{50}$$

Substitute $\dot{P}$ from the top equation into the lower one. The factors of $\dot{\mathcal{D}}$ cancel from the right-hand side,

$$\dot{\mathcal{D}}_{\kappa,l,\mu} = -\omega_i\sqrt{\frac{M}{a}}\sum_{l'\neq l,\nu}[T_{\mu\nu}(l-l') - S_{\mu\nu}(l-l')]Q_{\kappa,l',\nu}, \tag{51}$$

$$\dot{F}_{\kappa,l,\mu} = -\omega_i\omega^2\sqrt{\frac{M}{a}}Q_{\kappa,l,\mu}. \tag{52}$$

Put this result back into Eq. (49). The resulting equation is used for the left-hand side of Eq. (41). The terms with $S_{\mu\nu}$ cancel. The final eigenvalue equation is

$$\omega^2 Q_{\kappa,l,\mu} = \left[\omega_0^2 - \frac{1}{3}\omega_i^2 d_{\mu\mu}\right]Q_{\kappa,l,\mu} - \omega_i^2\sum_{l'\neq l,\nu}T_{\mu\nu}(l-l')Q_{\kappa,l',\nu}. \tag{53}$$

The only interaction between layers is the retarded interaction $T_{\mu\nu}$.

IV. SOLUTIONS: SURFACE POLARITONS

We search for solutions to Eq. (53). Surface modes have a dependence on layer index of $\exp[-\alpha la]$, where a is a lattice constant and α is a function of $(\vec{\kappa},\omega)$. The theory seems to have three possible choices of $\alpha:\kappa,p,\gamma$. Below we prove that these are indeed the only possible choices. We start by giving the two physical solutions to Eq. (53).

A. Surface-polariton mode

The Fuchs-Kliewer surface polariton has the eigenfunction,[2,17,18]

$$Q_{\kappa,l,\mu} = Q_S\eta_\mu^- e^{-\gamma al}. \tag{54}$$

In doing the summations over l, we assume at small wave vector that

$$\sum_{l=0}^{\infty} e^{-\alpha la} = \frac{1}{1-e^{-\alpha a}} \approx \frac{1}{\alpha a}, \tag{55}$$

where α is combinations of (κ,p,γ). The summation in the eigenvalue equation gives

$$\sum_{l'\neq l,\nu} T_{\mu\nu}Q_{\kappa,l',\nu} = -Q_S\Lambda_\mu^+\frac{p}{\gamma+p}e^{-\gamma al}, \tag{56}$$

$$\Lambda_\mu^{\pm} = \left(i\kappa_\mu, \pm\frac{\kappa^2}{p}\right). \tag{57}$$

The eigenvalue equation is

$$\omega^2 Q_{\kappa,l,\mu} = \omega_0^2 Q_{\kappa,l,\mu} - \omega_i^2 Q_S e^{-\gamma al}\Xi_\mu, \tag{58}$$

$$\Xi_\mu = \frac{1}{3}d_{\mu\mu}\eta_\mu^- - \frac{p}{\gamma+p}\Lambda_\mu^+. \tag{59}$$

The expression for Ξ_μ is a bit complicated. In evaluating this expression, we assume that it is the surface polariton and therefore obeys $\Xi_\mu = C\eta_\mu^-$ The two component equations are

$$Ci\kappa_\mu = i\kappa_\mu\left(\frac{1}{3} - \frac{p}{\gamma+p}\right), \tag{60}$$

$$-Cp = \frac{2p}{3} - \frac{\kappa^2}{\gamma+p}. \tag{61}$$

A bit of algebra shows that this can only be obeyed if $p\gamma = \kappa^2$. In this case,

$$\Xi_\mu = -\frac{2p^2-\kappa^2}{3(p^2+\kappa^2)}\eta_\mu^-, \tag{62}$$

$$\omega^2 = \omega_0^2 + \frac{\omega_i^2}{3}\left(\frac{c^2\kappa^2 - 2\omega^2}{2c^2\kappa^2 - \omega^2}\right). \tag{63}$$

Solving this equation for $\omega^2(\kappa)$ does produce exactly the surface-polariton dispersion given earlier in Eq. (31). Equation (54) is the correct eigenfunction for surface polaritons. One can also solve the above equation for κ^2 and find

$$c^2\kappa^2 = \omega^2\frac{\omega_L^2 - \omega^2}{2(\omega_S^2 - \omega^2)} = \omega^2\frac{\varepsilon}{\varepsilon+1} \tag{64}$$

which is Eq. (1). This mode produces an external potential. From Eq. (36),

$$\mathcal{L} = -Q_S\frac{(\eta^-\cdot q^+)}{a(\gamma+\kappa)} = Q_S\frac{\kappa(\kappa+p)}{a(\gamma+\kappa)} = Q_S\frac{p}{a}, \tag{65}$$

where we use $\gamma p = \kappa^2$ in deriving the last identity.

B. Longitudinal surface modes

We have found another solution. There is a surface phonon with the longitudinal frequency. This result appears to be distinct. There are many longitudinal phonons in the bulk of the crystal but having one localized at the surface is unusual.

The solution starts with

$$Q_{\kappa,l,\mu} = Q_1 \xi_\mu^- e^{-\gamma al} + Q_2 \eta_\mu^- e^{-pal}, \quad \xi_\mu^- = (i\kappa_\mu, -\gamma). \tag{66}$$

The summation gives

$$2 \sum_{l' \neq l, \nu} T_{\mu\nu}(l-l') Q_{\kappa,l',\nu} = - Q_1 e^{-\gamma al}(\Lambda_\mu^+ + \Lambda_\mu^-) + e^{-pal}(Q_1 \Lambda_\mu^- - Q_2 \Lambda_\mu^+).$$

The eigenvalue equation is obtained after some algebra,

$$\omega^2 Q_{\kappa,l,\mu} = \omega_L^2 Q_{\kappa,l,\mu} + \frac{Q_T \omega_i^2}{2} e^{-pal} \Lambda_\mu^-, \tag{67}$$

$$Q_T = Q_1 + Q_2. \tag{68}$$

The only way to eliminate the term with Λ_μ^- is to set $Q_T=0$ which gives $\omega=\omega_L$. Since $\varepsilon(\omega_L)=0$ then $\gamma=\kappa$ and $\xi_\mu^- = q_\mu^-$. The longitudinal-mode eigenfunction is

$$Q_{\kappa,l,\mu} = Q_1 [q_\mu^- e^{-\kappa al} - \eta_\mu^- e^{-pal}]. \tag{69}$$

This new surface polariton is a distinct result. It also exists in a nonrelativistic solution (where $c \to \infty$). In fact, one can show that $\mathcal{D}_{\kappa,l,\mu}=0=\dot{\mathcal{D}}_{\kappa,l,\mu}$ and photons are not involved, it is truly a longitudinal solution of Maxwell's equations.

This mode has a zero potential outside of the surface. From Eq. (36), we get

$$\mathcal{L} = -\frac{Q_1}{a}\left[\frac{(q^- \cdot q^+)}{2\kappa} - \frac{(\eta^- \cdot q^+)}{p+\kappa}\right] = 0. \tag{70}$$

Earlier we showed[2] that bulk longitudinal modes also have zero field outside of the surface.

It would be interesting to try to measure this new surface polariton experimentally. Such a measurement would be difficult at long wavelength, using a probe such as Raman scattering since it is degenerate with a volume mode of the same frequency. However, this mode is a function of wave vector, and could be distinguished from the volume mode at larger values of wave vector. Note that the present derivation has been done at long wavelength and has neglected all terms of order $O(\kappa a)$. So we have not yet calculated its wave-vector dependence.

C. General solution

Next we explore other solutions by assuming a general form

$$Q_{\kappa,l,\mu} = Q t_\mu^- e^{-\alpha al}, \quad t_\mu^- = (i\kappa_\mu, -\beta), \tag{71}$$

where (α,β) need to be determined. The summation gives

$$2 \sum TQ = -\frac{p-\beta}{\alpha-p}\Lambda_\mu^- e^{-pal} - e^{-\alpha al}\left[\frac{\beta-p}{\alpha-p}\Lambda_\mu^- + \frac{\beta+p}{\alpha+p}\Lambda_\mu^+\right]. \tag{72}$$

For the moment, ignore the first term with exponent exp[$-pal$] and solve for the second term. Write it as Eqs. (58) and (59) which again gives two equations for C,

$$Ci\kappa_\mu = i\kappa_\mu\left(\frac{1}{3} - \frac{p^2-\alpha\beta}{\alpha^2-p^2}\right), \tag{73}$$

$$-C\beta = \frac{2\beta}{3} + \frac{\kappa^2(\alpha-\beta)}{\alpha^2-p^2}. \tag{74}$$

Solving these two equations gives

$$0 = (\beta-\alpha)(\kappa^2-\alpha\beta). \tag{75}$$

There are two possible solutions. The first has $\alpha=\beta$. This solution gives $\omega^2=\omega_L^2$ and is the surface polariton at the longitudinal optical frequency. In this case, $\gamma=\kappa$ so there are only two possible exponents, which combine to eliminate the term with exponent exp[$-pal$].

The other solution has $\beta=\kappa^2/\alpha$ which has an eigenvalue equation,

$$\omega^2 = \omega_0^2 - \omega_i^2\left[\frac{1}{3} - \frac{\kappa^2-p^2}{\alpha^2-p^2}\right]. \tag{76}$$

One can solve this equation for α^2 which gives that $\alpha^2=\gamma^2$ and $\beta=p$. The equation $\gamma p=\kappa^2$ is the dispersion relation for the Fuchs-Kliewer mode. When $\beta=p$, the prefactor vanishes for the term with an exponent of exp[$-pal$]. Thus, the most general solution gives only two solutions, which are the two discussed above.

Another choice for the prefactor is $t_\mu=(k_y,-k_x,0)$ which has the feature that it is perpendicular to all of the other prefactors we have used,

$$0 = t \cdot q^\pm, \quad 0 = t \cdot \eta^\pm, \quad 0 = t \cdot \Lambda^\pm. \tag{77}$$

We could not find a self-consistent solution for a surface mode with this prefactor.

V. ELECTRIC FIELD

The electric field contains the time derivative, the vector potential, which in our notation is proportional to $\Pi_{\mathbf{k}\lambda}$. Our solution gives for this quantity,

$$\Pi_{\mathbf{k}\lambda} = \frac{a}{\sqrt{L}}\frac{1}{c^2k^2-\omega^2(\kappa)}\hat{\xi}(\mathbf{k}\lambda)\cdot\left(\sum_l \vec{F}_{\kappa,l} e^{ik_z z}\right) \tag{78}$$

$$= -\frac{\omega_i\omega^2}{c^2k^2-\omega^2(\kappa)}\sqrt{\frac{aM}{L}}\hat{\xi}(\mathbf{k}\lambda)\cdot\left(\sum_l \vec{Q}_{\kappa,l} e^{ik_z z}\right), \tag{79}$$

where we used Eq. (52) to derive the last identity.

In order to discuss the electric field from a surface wave with wave vector $\vec{\kappa}$, we construct a function such as

$$\dot{\mathcal{D}}_{\kappa,\mu}(z) = \frac{1}{\sqrt{L}}\sum_{k_z,\lambda} \xi_\mu(\mathbf{k}\lambda)\Pi_{\mathbf{k}\lambda} e^{-ik_z z}. \tag{80}$$

This function is $\dot{\mathcal{D}}_{\kappa,l,\mu}$ when $z=la$. However, now our interest is outside the surface where $z<0$. Insert Eq. (79) into Eq. (80) and evaluate the summation over k_z,

$$\dot{\mathcal{D}}_{\kappa,\mu}(z) = -\omega_i\omega^2\sqrt{\frac{M}{a}}\sum_{l,\nu} G_{\mu\nu}(z-al) Q_{\kappa,l,\nu} \tag{81}$$

$$=-\omega_i\sqrt{\frac{M}{a}}\sum_{l,\nu}[T_{\mu\nu}(al-z)-S_{\mu\nu}(al-z)]Q_{\kappa,l,\nu}. \quad (82)$$

The electric field has the vector potential term and a scalar potential term. Both terms contain the factor of $S_{\mu\nu}$ and cancel. One is left with only the retarded interaction,

$$E_{\kappa\mu}(z)=\omega_i\sqrt{\frac{4\pi M}{a\Omega}}e^{i\vec{\kappa}\cdot\vec{\rho}+pz}\sum_{l,\nu}T_{\mu\nu}(al)Q_{\kappa,l,\nu}. \quad (83)$$

This interaction agrees with the classical answer. It is zero for the surface polariton at the longitudinal frequency.

VI. STATIC IMAGE POTENTIAL

Now consider the potential from a static charge q located outside the surface at the point $\mathbf{r}_q=(0,-d)$. Classical electromagnetic theory predicts the potential energy outside of the surface is

$$\phi(\mathbf{r})=q\left[\frac{1}{|\mathbf{r}-\mathbf{r}_I|}-\frac{\varepsilon-1}{\varepsilon+1}\frac{1}{|\mathbf{r}+\mathbf{r}_I|}\right]. \quad (84)$$

We wish to derive this result using our microscopic model. The first term in brackets in Eq. (84) is the source potential. Using the two-dimensional Fourier transform of the charge-dipole interaction in Eq. (36) gives an interaction potential,

$$V_q=\frac{2\pi eq}{A_0\sqrt{N_{xy}}}\sum_{\vec{\kappa},l,\mu}\frac{q_\mu^- Q_{-\kappa,l,\mu}}{\kappa}e^{i\vec{\kappa}\cdot\vec{\rho}-\kappa(d+al)}. \quad (85)$$

This term is added to the Hamiltonian. Redo the equations of motion. Since the image potential is static, all time derivatives are set equal to zero. This makes all variables except $Q_{\kappa,l,\mu}$ be zero $(0=P_{\kappa,l,\mu}=\mathcal{A}_{\mathbf{k}\lambda}=\Pi_{\mathbf{k}\lambda})$. One must then solve the equation for $Q_{\kappa,l,\mu}$ for each value of wave vector,

$$0=\frac{2\pi eq}{A_0M\kappa\sqrt{N_{xy}}}q_\mu^- e^{-\kappa(d+al)}+\left[\omega_0^2-\frac{\omega_i^2}{3}d_{\mu\mu}\right]Q_{\kappa,l,\mu} -\omega_i^2\sum_{l'\neq l}S_{\mu\nu}Q_{\kappa,l',\nu}. \quad (86)$$

Since the source term has the factor of $q_\mu^-\exp[-\kappa al]$, we try this as a solution,

$$Q_{\kappa,l,\mu}=Q_Iq_\mu^- e^{-\kappa al}. \quad (87)$$

The sum gives

$$\sum_{l',\nu}S_{\mu\nu}(l'-l)Q_{\kappa,l',\nu}=-\frac{1}{2}Q_Iq_\mu^+e^{-\kappa al}. \quad (88)$$

The terms with a prefactor of ω_i^2 are

$$-Q_I\omega_i^2e^{-\kappa al}\left[\frac{1}{3}d_{\mu\mu}q_\mu^- -\frac{1}{2}q_\mu^+\right]=\frac{q_\mu^-}{6}Q_I\omega_i^2e^{-\kappa al}. \quad (89)$$

Then Eq. (86) gives

$$0=\frac{2\pi eq}{A_0M\kappa\sqrt{N_{xy}}}q_\mu^- e^{-\kappa(d+al)}+\omega_S^2Q_Iq_\mu^- e^{-\kappa al}, \quad (90)$$

$$Q_I=-\frac{2\pi eq}{A_0M\omega_S^2\kappa\sqrt{N_{xy}}}e^{-\kappa d} \quad (91)$$

$$=-\frac{qa}{e\kappa\sqrt{N_{xy}}}\frac{\varepsilon-1}{\varepsilon+1}e^{-\kappa d}, \quad (92)$$

where the dielectric functions are evaluated at zero frequency $\varepsilon(0)=\omega_L^2/\omega_T^2$. This solution is used to calculated the potential it generates outside of the surface $(z<0)$. The quantity $\mathcal{L}$ is

$$\mathcal{L}=-Q_I\sum_{l'}(q^+\cdot q^-)e^{-2\kappa al}=\frac{\kappa}{a}Q_I, \quad (93)$$

$$\phi(\mathbf{r})=-\frac{q}{|\mathbf{r}+\mathbf{r}_I|}\left(\frac{\varepsilon-1}{\varepsilon+1}\right). \quad (94)$$

This is the correct potential term from the image charge outside of a dielectric surface.

Note that the induced polarization inside of the solid surface is given by Eq. (87). That is not the eigenfunction of a surface polariton. The idea that image potentials are caused by surface polaritons is incorrect. That idea is okay if one neglects retardation by setting the speed of light to infinity. However, when solving for the image potential using a correct relativistic formulation, as we have done here, the surface polaritons are not the polarization that induces the image potential.

VII. DISCUSSION

We have solved the quantum-mechanical problem of coupling between photon fields and phonon fields, near the surface of a polar dielectric. We have found two kinds of surface polariton. One is the Fuchs-Kliewer mode predicted many years ago.[17,18] There have been a few measurements of the dispersion of surface polaritons at very small wave vectors[19–22] using attenuated total reflection. The measurements have approximate agreement with the classical theory.

The second solution is a surface polariton at the frequency of the bulk optical phonon. This mode has not been previously predicted or discovered experimentally. It does not couple to charged particles outside of the surface and would be difficult to detect experimentally.

We have used this model to calculate the image potential induced by a fixed, static charge outside of the surface. We derived exactly the induced polarization inside of the solid surface, and found that it is not given by either surface polariton. The idea that surface polaritons cause image charges is not rigorously correct.

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