# Optical Modes of Vibration in an Ionic Crystal Slab*

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The normal modes of vibration in an ionic crystal of finite thickness are found both by using lattice dynamics and by using electrodynamics, and neglecting retardation. If the wavelength is much larger than the lattice parameter, both methods give coupled integral equations involving the ionic displacements and the normal-mode frequencies. There are two classes of normal modes; those with an oscillatory spatial dependence and frequencies equal to $\nu_{TO}$ and $\nu_{LO}$, the usual transverse optical (TO) and longitudinal optical (LO) frequencies at $k\approx 0$ in an infinite crystal, and those with an exponential dependence on distance across the slab and frequencies between $\nu_{TO}$ and $\nu_{LO}$. A qualitative connection between the normal modes and optical absorption in a slab is presented.

## I. INTRODUCTION

THERE has been considerable interest of late in determining the fate of the optical frequencies in ionic crystals in the long-wavelength limit.[1–4] Rosenstock[1] concluded that in the limit $\lambda\to\infty$ the longitudinal (LO) and transverse optical (TO) frequencies should be equal, whereas Kellermann's[5] calculation agreed roughly with the Lyddane-Sachs-Teller relation.[6] Maradudin and Weiss[2] treated a finite spherical crystal of radius $R$ and argued that these results were in accord if one recognized that the limits $\mathbf{k}$ (wave vector) $\to 0$ and $R\to\infty$ could be taken in either order. Taking $\mathbf{k}\to 0$ for a crystal of fixed $R$ yielded Rosenstock's result, whereas the Lyddane-Sachs-Teller result was obtained if one took the $R\to\infty$ limit before the $\mathbf{k}\to 0$ limit.

We have examined the optical modes of vibration for an ionic crystal slab extending to infinity in the two lateral directions and of finite thickness. Since the region of greatest interest is that for which the wavelength is very long, we have examined the wavelength region $\lambda\gg r_0$ where $r_0$ is the interionic spacing. In contrast to previous work dealing with crystals which had at least one finite dimension, we have obtained the actual normal-mode distribution in this wavelength range.

Barron[4] has commented on the fact that the $\mathbf{k}\to 0$ modes should have frequencies dependent upon the geometry of the specimen due to the presence of depolarization fields. We have obtained results which differ significantly from those of Maradudin and Weiss.[2] In particular, under no conditions do the transverse and longitudinal optical frequencies coalesce as $\mathbf{k}\to 0$. This is a consequence of the fact that in the $\lambda\to\infty$ limit the surface charge distributions for the two types of vibration differ in the case of a slab.

Since the presence of a finite dimension in general precludes the use of the customary lattice dynamics approach, we discuss in Sec. II the information which can be obtained from this point of view. The actual normal-mode distribution is obtained in Sec. III both for a point-ion model and a model including electronic polarizability. Section IV includes a discussion of the optical properties of the slab in which it is shown that in the limit $\mathbf{k}\to 0$ our conclusions reduce to those of Berreman[7] who first demonstrated that optical absorption can occur at the ordinary $k\approx 0$ LO frequency.

## II. STANDARD LATTICE DYNAMICS

We investigate in this section the information which can be obtained about the normal modes of the slab from a standard lattice dynamics treatment, or the "single-cell" point of view. We denote the position vector of an ion in the static crystal by

$$\mathbf{x}(l;j)=\mathbf{x}(l)+\mathbf{x}(j), \tag{2.1}$$

where $\mathbf{x}(l)$ specifies a unit cell and is given in terms of the basis vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ by

$$\mathbf{x}(l)=n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3, \tag{2.2}$$

with $n_1$, $n_2$, and $n_3$ integers.[8] $\mathbf{x}(j)$ gives the position of the $j$th ion within the unit cell; $j=1, 2$ in the present case. Representing a displacement of the ion at $\mathbf{x}(l;j)$ by $\mathbf{u}(l;j)$, the equation of motion corresponding to the $\alpha$ component of $\mathbf{u}(l;j)$ is

$$m_j\ddot{u}_\alpha(l;j)=-\sum_{l'j'\beta}\Phi_{\alpha\beta}(l,l';j,j')u_\beta(l';j') \tag{2.3}$$

where $m_j$ is the mass of ion $j$ and $\Phi_{\alpha\beta}(l,l';j,j')$, the coupling parameter of second order, is defined by

$$\Phi_{\alpha\beta}(l,l';j,j')=\left(\frac{\partial^2\Phi}{\partial u_\alpha(l;j)\partial u_\beta(l';j')}\right)_0, \tag{2.4}$$

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[1] H. B. Rosenstock, Phys. Rev. **121**, 416 (1961).
[2] A. A. Maradudin and G. H. Weiss, Phys. Rev. **123**, 1968 (1961).
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[4] T. H. K. Barron, Phys. Rev. **123**, 1995 (1961).
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[7] D. W. Berreman, Phys. Rev. **130**, 2193 (1963).
[8] We ignore the small deviations from the equilibrium spacing near the surfaces.

where $\Phi$ is the potential function for the system and the subscript 0 denotes that the derivative is evaluated at the equilibrium position. Assuming the displacements to be of the form

$$u_\alpha(l;j)=m_j^{-1/2}w_{\alpha j}(\mathbf{k})e^{i\{\mathbf{k}\cdot\mathbf{x}(l;j)-\omega t\}}, \tag{2.5}$$

Eq. (2.3) becomes

$$\omega^2 w_{\alpha j}(\mathbf{k})=\sum_{j'\beta} C_{\alpha\beta}(\mathbf{k};j,j')w_{\beta j'}(\mathbf{k}), \tag{2.6}$$

with

$$C_{\alpha\beta}(\mathbf{k};j,j')=(m_j m_{j'})^{-1/2} \times\sum_{l'}\Phi_{\alpha\beta}(l,l';j,j')e^{-i\mathbf{k}\cdot\{\mathbf{x}(l;j)-\mathbf{x}(l';j')\}}. \tag{2.7}$$

$C_{\alpha\beta}(\mathbf{k};j,j')$ is divided into two parts, $C_{\alpha\beta}{}^e(\mathbf{k};j,j')$ corresponding to the Coulomb interactions and $C_{\alpha\beta}{}^s(\mathbf{k};j,j')$ corresponding to the short-range interactions.

The system which we are interested in is the slab of ionic crystal of the NaCl type as sketched in Fig. 1. It is immediately apparent that the $z$ direction does not possess the translational invariance of the assumed solution (2.5). However, it is precisely this point to which the discussion of the present section is directed. We restrict our attention to the long-wavelength region $\lambda\gg r_0$, where $r_0$ is the nearest-neighbor spacing in the crystal, and consider that one of the equations (2.6) for which $\mathbf{x}(l;j)=(0,0,z)$. Clearly the matrix elements $C_{\alpha\beta}{}^e(\mathbf{k};j,j')$ depend on the value of $z$; their evaluation for point ions neglecting retardation is discussed in Appendix A.

The matrix elements $C_{\alpha\beta}{}^s(\mathbf{k};j,j')$ have been determined by Kellermann for nearest-neighbor interactions only, with the result, in the limit $\lambda\gg r_0$,

$$C_{\alpha\beta}{}^s(\mathbf{k};j,j')=\frac{q_j q_{j'}\delta_{\alpha\beta}}{2r_0{}^3(m_j m_{j'})^{1/2}}(A+2B), \tag{2.8}$$

where, considering $\varphi(r)$ to be the nearest-neighbor repulsive interaction,

$$B=\frac{4r_0{}^2}{e^2}\frac{d\varphi}{dr}\bigg|_{r=r_0}, \qquad A=\frac{4r_0{}^3}{e^2}\frac{d^2\varphi}{dr^2}\bigg|_{r=r_0}. \tag{2.9}$$

Having now the matrix elements $C_{\alpha\beta}{}^e(\mathbf{k};j,j')$ and $C_{\alpha\beta}{}^s(\mathbf{k};j,j')$, we proceed in a purely formal manner to determine the "eigenvalues" $\omega^2$ in (2.6). Orienting the crystal such that the wave vector $\mathbf{k}$, here defined by $|\mathbf{k}|=2\pi/\lambda$, has components

$$k_z=k\cos\theta, \quad k_x=k\sin\theta, \quad k_y=0, \tag{2.10}$$

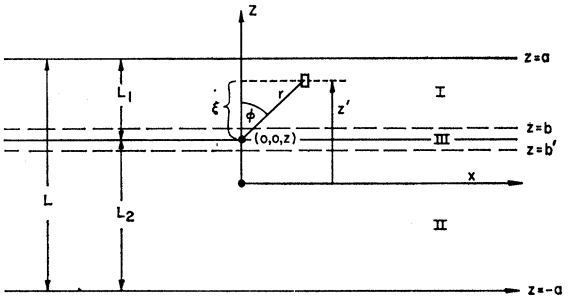


FIG. 1. Diagram of the coordinate system and various parameters used in discussing the ionic crystal slab.

the secular equation corresponding to (2.6) becomes

$$\Delta=0, \tag{2.11}$$

where the terms of $\Delta$ are displayed in Table I.

$m_+$ and $m_-$ are the cation and anion masses,

$$F=\tfrac{2}{3}(\pi e^2/r_0{}^3), \tag{2.12}$$

$$\begin{pmatrix}P\\Q\end{pmatrix}=F\sin\theta\{e^{kL_1(i\cos\theta-\sin\theta-i\theta)} \mp e^{kL_2(-i\cos\theta-\sin\theta+i\theta)}\}, \tag{2.13}$$

and

$$E=(e^2/2r_0{}^3)(A+2B). \tag{2.14}$$

Because of our coordinate system orientation, we see that that portion of the secular equation corresponding to the $y$ direction separates yielding values of $\omega^2$,

$$\omega^2=0, \quad \omega^2=\mu^{-1}(E-F), \tag{2.15}$$

where $\mu$ is the reduced mass. The former we recognize as an acoustic mode and the latter is the ordinary long-wavelength, infinite-crystal transverse frequency with the associated eigenvector

$$w\propto\begin{bmatrix}0\\0\\1\\-(m_+/m_-)^{1/2}\\0\\0\end{bmatrix}. \tag{2.16}$$

The coupled $x$-$z$ elements of the secular equation are of particular interest here. We address ourselves solely to the question of the optical modes. In the case $\theta=0$ corresponding to the wave vector normal to the slab, $P=Q=0$, the $x$-$z$ coupling ceases to exist, and we find the ordinary infinite-crystal, long-wavelength result,

$$\omega^2=(E/\mu-F/\mu), \quad w\propto\begin{bmatrix}1\\-(m_+/m_-)^{1/2}\\0\\0\\0\\0\end{bmatrix}, \tag{2.17}$$

TABLE I. Terms in the secular determinant $\Delta$ of Eq. (2.11).

| | $x_+$ | $x_-$ | $y_+$ | $y_-$ | $z_+$ | $z_-$ |
|---|---|---|---|---|---|---|
| $x_+$ | $-\omega^2-\frac{F}{m_+}(1-3\sin^2\theta)$ $-\frac{3}{2}i\frac{P}{m_+}+\frac{E}{m_+}$ | $(m_+m_-)^{-1/2}\{F(1-3\sin^2\theta)$ $+\frac{3}{2}iP-E\}$ | 0 | 0 | $\frac{1}{m_+}\{3F\sin\theta\cos\theta-\frac{3}{2}Q\}$ | $(m_+m_-)^{-1/2}\{-3F\sin\theta\cos\theta$ $+\frac{3}{2}Q\}$ |
| $x_-$ | $(m_+m_-)^{-1/2}\{F(1-3\sin^2\theta)$ $-\frac{3}{2}iP^*-E\}$ | $-\omega^2+\frac{1}{m_-}\{F(1-3\sin^2\theta)$ $-\frac{3}{2}iP+E\}$ | 0 | 0 | $(m_+m_-)^{-1/2}\{-3F\sin\theta\cos\theta$ $+\frac{3}{2}Q\}$ | $\frac{1}{m_-}\{3F\sin\theta\cos\theta-\frac{3}{2}Q\}$ |
| $y_+$ | 0 | 0 | $-\omega^2+\frac{1}{m_+}\{-F+E\}$ | $(m_+m_-)^{-1/2}\{F-E\}$ | 0 | 0 |
| $y_-$ | 0 | 0 | $(m_+m_-)^{-1/2}\{F-E\}$ | $-\omega^2+\frac{1}{m_-}\{-F+E\}$ | 0 | 0 |
| $z_+$ | $\frac{1}{m_+}\{3F\sin\theta\cos\theta-\frac{3}{2}Q^*\}$ | $(m_+m^-)^{-1/2}\{-3F\sin\theta\cos\theta$ $+\frac{3}{2}Q^*\}$ | 0 | 0 | $-\omega^2+\frac{1}{m_+}\{-F(1-3\cos^2\theta)$ $-\frac{3}{2}iP-E\}$ | $(m_+m_-)^{-1/2}\{F(1-3\cos^2\theta)$ $-\frac{3}{2}iP-E\}$ |
| $z_-$ | $(m_+m_-)^{-1/2}\{-3F\sin\theta\cos\theta$ $+\frac{3}{2}Q^*\}$ | $\frac{1}{m_-}\{3F\sin\theta\cos\theta-\frac{3}{2}Q^*\}$ | 0 | 0 | $(m_+m_-)^{-1/2}\{F(1-3\cos^2\theta)$ $+\frac{3}{2}iP^*-E\}$ | $-\omega^2+\frac{1}{m_-}\{-F(1-3\cos^2\theta)$ $-\frac{3}{2}iP-E\}$ |

the second transverse mode, and

$$\omega^2=(E/\mu+2F/\mu),$$
$$w\propto\begin{bmatrix}0\\0\\0\\0\\1\\-(m_+/m_-)^{1/2}\end{bmatrix},\tag{2.18}$$

the longitudinal mode.

Suppose we consider $\theta\neq 0$. Now the condition that must be met for the approach under discussion here to be valid is that the eigenvalues are independent of $z$. This condition can be obtained by considering $kL\gg 1$, which leads us immediately back to the situation for the infinite crystal or

$$\omega^2=E/\mu-F/\mu,\quad w\propto\begin{bmatrix}1\\-(m_+/m_-)^{1/2}\\0\\0\\-\tan\theta\\(m_+/m_-)^{1/2}\tan\theta\end{bmatrix},\tag{2.19}$$
$$\omega^2=E/\mu+2F/\mu,\quad w\propto\begin{bmatrix}1\\-(m_+/m_-)^{1/2}\\0\\0\\\cot\theta\\-(m_+/m_-)^{1/2}\cot\theta\end{bmatrix}.$$

Alternatively we can obtain $z$-independent values of $\omega$ by considering $kL\ll 1$.[9] In this case, we find

$$\omega^2=\frac{E}{\mu}+\frac{2F}{\mu}-\frac{3F}{2\mu}-kL\sin\theta,\tag{2.20}$$

with $W$ given by (2.18), and

$$\omega^2=\frac{E}{\mu}-\frac{F}{\mu}+\frac{3F}{2\mu}-kL\sin\theta,\tag{2.21}$$

with $W$ given by (2.17). Note that when $k_z\equiv 0$, the "LO" frequency (2.20) corresponds to transverse motion, and the "TO" frequency (2.21) corresponds to longitudinal motion.

These solutions will be discussed in detail in Sec. III where it will be seen that these frequencies are those which result from taking the $k_x\to 0$ limit of the general result. Thus, we conclude that ordinary lattice dynamics in the long-wavelength region provides a legitimate solution, in the present case, for arbitrary $k_z$ when $k_x=0$ and for $k\gg 1/L$ or $k\ll 1/L$ when $k_x\neq 0$. In this connection, a further point should be made. By taking $L_1=L_2$, i.e., examining the conditions corresponding to the center of the slab, one can obtain what appear to be valid expressions for the frequencies over the entire $k$ range within the long-wavelength region. That this is an invalid procedure can be seen by examining the eigenvectors. The eigenvectors are, in this case, $z$-dependent, which is not permitted since all $z$ dependence in the displacements was assumed to occur in the exponential $e^{i\mathbf{k}\cdot\mathbf{r}}$. Only in the limits $k\gg 1/L$, $k\ll 1/L$ can this $z$ dependence be ignored. Thus the apparent elimination of the $z$ dependence of the frequencies resulting from examining conditions at the center of the slab leads to invalid conclusions.

[9] The conclusion that we can obtain a generally valid solution from the single-cell point of view for normal incidence [see Eqs. (2.15)–(2.18)] would suggest that we would only have to assume $k_xL\ll 1$. That this is not the case is a consequence of the fact that the points $(0,0,z)$ and $(0,0,-z)$ are equivalent physically, but his equivalence is not manifest by our original supposition that the displacements are of the form $e^{i\mathbf{k}\cdot\mathbf{r}}$. By taking the displacements to be superpositions of $e^{\pm i\mathbf{k}\cdot\mathbf{r}}$, we would only require $k_xL\ll 1$. However, since we are investigating the ordinary lattice dynamics treatment here we persist with our original hypothesis. The conclusion [see Eqs. (2.20) and (2.21)] will be seen to correspond to the condition $k_xL\ll 1$.

## III. OPTICAL VIBRATIONAL MODES FOR THE SLAB

From the discussion of Sec. II, it is clear that the difficulty with the "single-cell" point of view is the assumption that the displacements have a $z$ dependence of the form $e^{ik_zz}$. If we replace Eq. (2.5) by the expression

$$u_\alpha(l;j)=m_j^{-1/2}w_{\alpha j}(\mathbf{k},z)e^{ik_xx(l;j)}e^{ik_yy(l;j)}e^{-i\omega t},\tag{3.1}$$

one can derive, from the lattice dynamics point of view, a set of integral equations which yield the normal modes. This derivation is sketched in Appendix B. We choose here, however, to derive this set of integral equations from the standpoint of electrodynamics.

Consider once again the ionic crystal slab sketched in Fig. 1; it extends to infinity in the $x$ and $y$ directions, and its surfaces lie on the planes $z=\pm a$. The optical modes of vibration will be found in the long-wave approximation; i.e., the displacements $\mathbf{u}^+$ and $\mathbf{u}^-$ of the positive and negative ions are slowly varying functions of position, and it is meaningful to introduce a macroscopic polarization $\mathbf{P}(\mathbf{r},t)$ and an average electric field $\mathbf{E}_{\mathrm{av}}(\mathbf{r},t)$. Thus we require that the thickness $2a$ of the slab be much larger than an interatomic distance, otherwise even the normal mode with the longest wavelength could not be treated in this approximation.

Because of translational symmetry in the $x$ and $y$ directions, the polarization $\mathbf{P}(\mathbf{r},t)$ for any normal mode contains the factor $e^{ik_xx}e^{ik_yy}$; for simplicity, imagine that the $x$ and $y$ axes have been rotated so that $k_y=0$. Then the general form of the polarization for a normal mode with frequency $\omega$ is

$$\mathbf{P}(\mathbf{r},t)=\mathbf{F}(z)e^{i(k_xx-\omega t)},\tag{3.2}$$

where $\mathbf{F}(z)$ is an unknown function. This polarization produces an electric field, which we evaluate at the site of an ion located at the point $(0,0,z)$. It is convenient to divide the crystal into three regions, marked I, II,

and III in Fig. 1. The field at the observation point is produced by the volume polarization charge $\rho=-\nabla\cdot\mathbf{P}$ in regions I and II, by the surface charge $\rho'=\mathbf{P}\cdot\mathbf{n}$ on the upper and lower surfaces of these regions and by the polarization in the thin slab III.

Break region I into infinitesimal slabs of thickness $dz'$. Each slab can be divided into uniform line charges extending in the $y$ direction, with charge density $\rho dxdz'$ per unit length. A line charge produces an electric field of magnitude $2\rho dxdz'/r$ at the observation point, where $\rho$ is of the form $\rho_0(z')e^{ik_xx}$. Therefore the total $z$ component of the field due to the slab at $z'$ is

$$dE_z=-2dz'\int_{-\infty}^{\infty}\rho_0e^{ik_xx}r^{-1}\cos\varphi dx$$

$$=-4\rho_0\xi dz'\int_0^{\infty}\frac{\cos(k_xx)}{x^2+\xi^2}dx$$

$$=-2\pi\rho_0e^{-k_x\xi}dz' \quad \text{(region I)}, \tag{3.3}$$

where

$$\xi=z'-z.$$

Similarly if the slab is in region II, below the observation point,

$$dE_z=+2\pi\rho_0e^{-k_x|\xi|}dz' \quad \text{(region II)}. \tag{3.4}$$

The total field $E_z^v$ due to the volume polarization charge is

$$E_z^v=\int_{-a}^{b'}2\pi\rho_0e^{k_x\xi}dz'-\int_b^a2\pi\rho_0e^{-k_x\xi}dz'. \tag{3.5}$$

But $\rho_0$ can be found from Eq. (3.2): $\rho(z')=\rho_0(z')e^{ik_xx}$ $=-\nabla\cdot\mathbf{P}=-[ik_xF_x+dF_z/dz']e^{ik_xx}$ at $t=0$. Thus

$$\rho_0(z')=-[ik_xF_x+dF_z/dz']$$

and

$$E_z^v=2\pi\Big[ik_x\int_b^aF_x(z')e^{-k_x(z'-z)}dz'$$

$$-ik_x\int_{-a}^{b'}F_x(z')e^{k_x(z'-z)}dz'+\int_b^a\frac{dF_z}{dz'}e^{-k_x(z'-z)}dz'$$

$$-\int_{-a}^{b'}\frac{dF_z}{dz'}e^{k_x(z'-z)}dz'\Big]$$

$$=2\pi k_x\Big[i\int_b^aF_xe^{-k_x(z'-z)}dz'-i\int_{-a}^{b'}F_xe^{k_x(z'-z)}dz'$$

$$+\int_b^aF_ze^{-k_x(z'-z)}dz'+\int_{-a}^{b'}F_ze^{k_x(z'-z)}dz'\Big]$$

$$+2\pi F_ze^{-k_x(z'-z)}\Big|_b^a-2\pi F_ze^{k_x(z'-z)}\Big|_{-a}^{b'}. \tag{3.6}$$

The surface charge density can also be broken into line charges in the $y$ direction with charge density $\rho'dx$ per unit length. $\rho'$ is also of the form $\rho'=\rho_0'e^{ik_xx}$. Therefore the contribution of a surface at $z'$ to $E_z$ is

$$E_z^s=-2\pi\rho_0'e^{-k_x(z'-z)}, \quad z'>z$$
$$=+2\pi\rho_0'e^{+k_x(z'-z)}, \quad z'<z, \tag{3.7}$$

in analogy with Eqs. (3.3) and (3.4). Since $\rho_0'e^{ik_xx}=\mathbf{P}\cdot\mathbf{n}$, $\rho_0'$ takes on the values $F_z(a)$, $-F_z(b)$, $F_z(b')$, and $-F_z(-a)$ on the surfaces at $a$, $b$, $b'$, and $-a$. The total surface contribution to $E_z$ is

$$E_z^s=2\pi[-F_z(a)e^{-k_x(a-z)}+F_z(b)e^{-k_x(b-z)}$$
$$+F_z(b')e^{k_x(b'-z)}-F_z(-a)e^{k_x(-a-z)}]. \tag{3.8}$$

This surface contribution exactly cancels the last two terms in Eq. (3.6).

Similarly, the volume contribution to $E_x$ from slabs of thickness $dz'$ in both regions I and II is

$$dE_x=-2dz'\int_{-\infty}^{\infty}\rho_0e^{ik_xx}r^{-1}\sin\varphi dx$$

$$=-2\pi i\rho_0dz'e^{-k_x|\xi|}. \tag{3.9}$$

Equation (3.9) differs from Eqs. (3.3) and (3.4) only by a factor of $i$ and by a minus sign for region II. Thus $E_x^v$ can be found simply by changing the appropriate signs in Eq. (3.6) and multiplying by $i$:

$$E_x^v=2\pi ik_x\Big[i\int_b^aF_xe^{-k_x(z'-z)}dz'+i\int_{-a}^{b'}F_xe^{k_x(z'-z)}dz'$$

$$+\int_b^aF_ze^{-k_x(z'-z)}dz'-\int_{-a}^{b'}F_ze^{k_x(z'-z)}dz'\Big]$$

$$+2\pi F_ze^{-k_x(z'-z)}\Big|_b^a+2\pi F_ze^{k_x(z'-z)}\Big|_{-a}^{b'}. \tag{3.10}$$

Similar changes of Eq. (3.8) give the surface contribution to $E_x$,

$$E_x^s=2\pi i[-F_z(a)e^{-k_x(a-z)}+F_z(b)e^{-k_x(b-z)}$$
$$-F_z(b')e^{k_x(b'-z)}+F_z(-a)e^{k_x(-a-z)}], \tag{3.11}$$

which again cancels the last two terms in Eq. (3.10). The component $P_y$ produces no polarization charge; therefore $E_y^v=E_y^s=0$.

The contribution from region III can be found in the limit as the thickness of this region approaches zero. In this limit, the variation of polarization in the $x$ direction can be disregarded, and the region can be treated as uniformly polarized slab, for which $D_z=0$ and $E_x^{av}=E_y^{av}=0$.[10] The local field at a lattice site is

$$E_z^l=E_z^{av}+4\pi P_z/3=-(4\pi P_z)+4\pi P_z/3=-(8\pi/3)P_z,$$

$$E_x^l=E_x^{av}+4\pi P_x/3=4\pi P_x/3, \tag{3.12}$$

[10] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, (Oxford University Press, London), Chap. II, Sec. 9.

and

$$E_y{}^l = E_y{}^{av} + 4\pi P_y/3 = 4\pi P_y/3.$$

Since $\mathbf{P} = \mathbf{F}(z)$ at the point $(00z)$ and at $t=0$,

$$E_z{}^l = -(8\pi/3)F_z(z), \tag{3.13}$$

$$E_x{}^l = (4\pi/3)F_x(z), \tag{3.14}$$

$$E_y{}^l = (4\pi/3)F_y(z). \tag{3.15}$$

The total local field is found by adding the three contributions given by Eqs. (3.6), (3.8), (3.13) and (3.10), (3.11), (3.14), taking the limits $b \to z$ and $b' \to z$ in the integrals over $z'$.

$$E_z = -\frac{8\pi}{3}F_z(z) + \int_{-a}^{a} G(z,z')F_z(z')dz' + i\int_{-a}^{a} G_A(z,z')F_x(z')dz', \tag{3.16}$$

$$E_x = \frac{4\pi}{3}F_x(z) - \int_{-a}^{a} G(z,z')F_x(z')dz' + i\int_{-a}^{a} G_A(z,z')F_z(z')dz', \tag{3.17}$$

$$E_y = (4\pi/3)F_y(z), \tag{3.18}$$

where

$$G(z,z') = 2\pi k_x e^{-k_x|z-z'|}, \tag{3.19}$$

and

$$G_A(z,z') = \pm 2\pi k_x e^{-k_x|z-z'|}, \tag{3.20}$$

in which the plus sign is taken for $z'>z$, and the minus sign, for $z'<z$.

In the long-wave approximation, the equations of motion of a pair of ions can be written in terms of the relative displacement $\mathbf{u}=\mathbf{u}_+-\mathbf{u}_-$ and the reduced mass $\mu$:

$$\mu\partial^2\mathbf{u}/\partial t^2 = -\mu\omega_0{}^2\mathbf{u} + q\mathbf{E}, \tag{3.21}$$

where $\omega_0$ is the optical-mode frequency which the lattice would have in the absence of Coulomb forces between the ionic charges $\pm q$.[10] Since all quantities have an $e^{-i\omega t}$ time dependence, $\partial^2\mathbf{u}/\partial t^2 = -\omega^2\mathbf{u}$. In addition, $\mathbf{u}$ is related to the polarization by

$$\mathbf{P}(\mathbf{r},t) = \mathbf{F}(z)e^{i(k_x x-\omega t)} = nq\mathbf{u}(\mathbf{r},t), \tag{3.22}$$

where $n$ is the number of ion pairs per unit volume. At $x=0$, $t=0$, $\mathbf{F}(z)=nq\mathbf{u}$. Therefore, Eq. (3.21) can be written as

$$-(\mu\omega^2/nq^2)\mathbf{F} = -\mu(\omega_0{}^2/nq^2)\mathbf{F} + \mathbf{E}. \tag{3.23}$$

If we introduce the dimensionless frequencies

$$\lambda = \mu\omega^2/nq^2, \qquad \lambda_0 = \mu\omega_0{}^2/nq^2, \tag{3.24}$$

and use Eqs. (3.16), (3.17), and (3.18) for the components of $\mathbf{E}$, Eq. (3.23) becomes

$$\left(\lambda_0 + \frac{8\pi}{3} - \lambda\right)F_z(z) = \int_{-a}^{a} G(z,z')F_z(z')dz' + i\int_{-a}^{a} G_A(z,z')F_x(z')dz', \tag{3.25}$$

$$\left(\lambda_0 - \frac{4\pi}{3} - \lambda\right)F_x(z) = -\int_{-a}^{a} G(z,z')F_x(z')dz' + i\int_{-a}^{a} G_A(z,z')F_z(z')dz', \tag{3.26}$$

$$(\lambda_0 - 4\pi/3 - \lambda)F_y(z) = 0. \tag{3.27}$$

These are the basic coupled integral equations which must be solved. Equation (3.27), which is not coupled to the other equations, can be solved immediately: The eigenvalue is $\lambda=\lambda_0-4\pi/3$, and $F_y(z)$ is an arbitrary function of $z$. This eigenvalue $\lambda_0-4\pi/3$ is equal to the usual to $k\approx 0$ frequency for an infinite crystal. Since the $y$ component of the polarization does not produce polarization charges on the surfaces, the finite slab behaves as if it were an infinite medium. All transverse polarization waves of the form $\mathbf{P}(x,z)=e^{ik_z z}e^{ik_x x}\mathbf{j}$ are solutions, and they all have the same TO frequency. Therefore, the function $F_y(z)e^{ik_x x}\mathbf{j}$ can be thought of as an arbitrary linear combination of such transverse waves, keeping $k_x$ fixed.

If we let $a \to \infty$, Eqs. (3.25) and (3.26) give the usual solutions for an infinite crystal. In this limit, the trial functions $F_x(z)=C_x e^{ik_z z}$, $F_z(z)=C_z e^{ik_z z}$ are appropriate, and Eqs. (3.25) and (3.26) become

$$\left(\lambda_0 + \frac{8\pi}{3} - \lambda\right)C_z = \frac{4\pi k_x{}^2}{k_x{}^2+k_z{}^2}C_z - \frac{4\pi k_x k_z}{k_x{}^2+k_z{}^2}C_x, \tag{3.28}$$

$$\left(\lambda_0 - \frac{4\pi}{3} - \lambda\right)C_x = -\frac{4\pi k_x{}^2}{k_x{}^2+k_z{}^2}C_x - \frac{4\pi k_x k_z}{k_x{}^2+k_z{}^2}C_z. \tag{3.29}$$

Solving the secular equation for $\lambda$, we find the TO mode,

$$\lambda = \lambda_0 - \frac{4\pi}{3}, \quad \text{with} \quad \frac{C_x}{C_z} = -\frac{k_z}{k_x}, \tag{3.30}$$

and the LO mode,

$$\lambda = \lambda_0 + \frac{8\pi}{3}, \quad \text{with} \quad \frac{C_x}{C_z} = \frac{k_x}{k_z}. \tag{3.31}$$

Before proceeding with the solution of the integral equations for a finite crystal, it is convenient to introduce dimensionless variables for distance, $\zeta=z/a$, the wave vectors, $s_x=k_x a$ and $s_z=k_z a$, and a new eigenvalue, $\gamma=(\lambda-\lambda_0)/2\pi-\frac{1}{3}$. Equations (3.25) and (3.26)

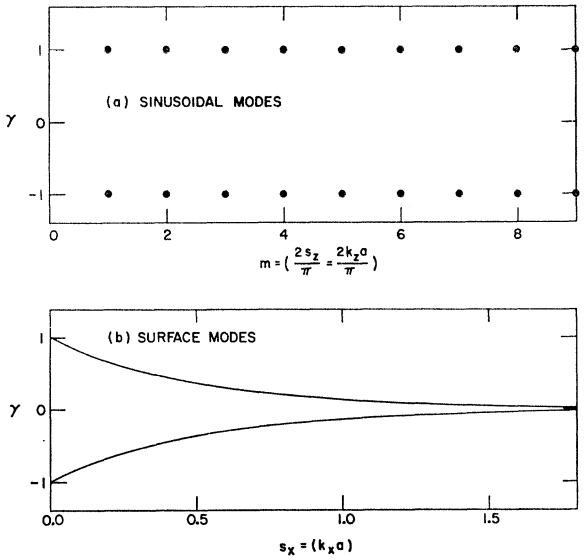


FIG. 2. Frequencies of the normal modes in a slab. The dimensionless eigenvalue $\gamma$ is related to the frequency $\omega$ by the expression $\gamma=[\mu(\omega^2-\omega_0^2)/2\pi nq^2]-\frac{1}{2}$. In Fig. 2(a), the sinusoidal modes exist only for integral values of the index $m$. Figure 2(b) shows the eigenvalues of the surface modes as a function of the $x$ component of the wave vector $s_x$.

become

$$-\gamma f_z(\zeta)=-f_z(\zeta)+\int_{-1}^{1}K(\zeta,\zeta')f_z(\zeta')d\zeta' +i\int_{-1}^{1}K_A(\zeta,\zeta')f_x(\zeta')d\zeta', \quad (3.32)$$

$$-\gamma f_x(\zeta)=f_x(\zeta)-\int_{-1}^{1}K(\zeta,\zeta')f_x(\zeta')d\zeta' +i\int_{-1}^{1}K_A(\zeta,\zeta')f_z(\zeta')d\zeta', \quad (3.33)$$

where

$$f_x(\zeta)=F_x(z), \quad f_z(\zeta)=F_z(z)$$

and

$$K(\zeta,\zeta')=s_x e^{-s_x|\zeta-\zeta'|}, \quad (3.34)$$
$$K_A(\zeta,\zeta')=\pm s_x e^{-s_x|\zeta-\zeta'|}. \begin{pmatrix}(+)\text{ for }\zeta'>\zeta\\(-)\text{ for }\zeta'<\zeta\end{pmatrix}$$

The new eigenvalue $\gamma$ has been chosen so that the infinite-crystal TO and LO modes at $\lambda=\lambda_0-(4\pi/3)$ and $\lambda=\lambda_0+(8\pi/3)$ correspond to the values $\gamma=-1$ and $\gamma=+1$.

Since the slab is symmetric with respect to the plane $\zeta=0$, it is convenient to choose the functions $f_x(\zeta)$ and $f_z(\zeta)$ to have definite parities. The kernel $K(\zeta,\zeta')$ does not change the parity of a function on which it operates, but $K_A(\zeta,\zeta')$ changes the parity. Therefore, if $f_x(\zeta)$ and $f_z(\zeta)$ satisfy the integral equations, they must be of opposite parity. It is not difficult to prove the following symmetry property of the eigenfunctions and eigenvalues: (i) If $f_x(\zeta)$ and $f_z(\zeta)$ are eigenfunctions with eigenvalue $\gamma$, then $\tilde{f}_x(\zeta)=f_z^*(\zeta)$ and $\tilde{f}_z(\zeta)=f_x^*(\zeta)$ are eigenfunctions with eigenvalue $\tilde{\gamma}=-\gamma$. Therefore, the eigenvalues occur in pairs which are symmetrically situated about $\gamma=0$. If we find an eigenvalue $\gamma$ belonging to the function $f_x$, with even parity, and $f_z$, with odd parity, for example, then we immediately know that there is another eigenvalue at $-\gamma$, and we can write down the corresponding eigenfunction.

The reality of the eigenvalues and the orthogonality of the eigenfunctions also follows from the integral equations: If $\mathbf{f}^m(\zeta)$ and $\mathbf{f}^n(\zeta)$ are two solutions belonging to different eigenvalues $\gamma^m$ and $\gamma^n$, then

$$\int_{-1}^{1}\mathbf{f}^{m*}\cdot\mathbf{f}^n d\zeta=0. \quad (3.35)$$

A partial solution to the integral equations can be found by converting them to a differential equation. We note that

$$\frac{d}{d\zeta}\int_{-1}^{1}K(\zeta,\zeta')f(\zeta')d\zeta'=s_x\int_{-1}^{1}K_A(\zeta,\zeta')f(\zeta')d\zeta' \quad (3.36)$$

and

$$\frac{d}{d\zeta}\int_{-1}^{1}K_A(\zeta,\zeta')f(\zeta')d\zeta' =s_x\left[\int_{-1}^{1}K(\zeta,\zeta')f(\zeta')d\zeta'-2f(\zeta)\right], \quad (3.37)$$

where $f(\zeta)$ is an arbitrary function. If Eq. (3.32) is differentiated once with the use of Eqs. (3.36) and (3.37), it becomes

$$-\gamma f_z'=-f_z'+s_x\int K_A f_z d\zeta'+is_x\left[\int Kf_x d\zeta'-2f_x\right]$$
$$=-f_z'+i(\gamma-1)s_x f_x$$

or

$$f_z'=-is_x f_x, \quad \text{if} \quad \gamma\neq+1. \quad (3.38)$$

Similarly, Eq. (3.33) gives

$$f_x'=is_x f_z, \quad \text{if} \quad \gamma\neq-1. \quad (3.39)$$

From Eqs. (3.38) and (3.39), we find

$$f_x''=s_x^2 f_x; \quad (3.40)$$

therefore, the general solutions are of the form

$$f_x=C_1e^{s_x\zeta}+C_2e^{-s_x\zeta}, \quad f_z=-i(C_1e^{s_x\zeta}-C_2e^{-s_x\zeta}). \quad (3.41)$$

The eigenvalue $\gamma$ and the constants $C_1$ and $C_2$ are found by requiring that $f_x(\zeta)$ and $f_z(\zeta)$ satisfy Eqs. (3.32)

TABLE II. Eigenvalues and normalized eigenfunctions for polarization waves in a slab. The normalization constants $C=(s_x/\sinh 2s_x)^{1/2}$, $h_m=(s_x^2+(\frac{1}{2}m\pi)^2)^{1/2}$ have been chosen so that $\int_{-1}^{1}(|f_x(\zeta)|^2+|f_z(\zeta)|^2)d\zeta=1$. The sinusoidal standing waves are labeled TO or LO because they can be formed by taking appropriate linear combinations of TO or LO traveling waves with $\zeta$ dependence $\exp(\pm is_x\zeta)$, where $s_z=\frac{1}{2}m\pi$.

| Type of mode | Eigenvalues $\gamma$ | Eigenfunctions $f_x(\zeta)$ | Eigenfunctions $f_z(\zeta)$ | Allowed values of $m$ |
|---|---|---|---|---|
| Surface | $-e^{-2s_x}$ | $C\cosh s_x\zeta$ | $-iC\sinh s_x\zeta$ | ⋯ |
| Surface | $+e^{-2s_x}$ | $iC\sinh s_x\zeta$ | $C\cosh s_x\zeta$ | ⋯ |
| TO | $-1$ | $-(m\pi/2h_m)\cos\frac{1}{2}m\pi\zeta$ | $i(s_x/h_m)\sin\frac{1}{2}m\pi\zeta$ | 2, 4, 6, ⋯ |
| LO | $+1$ | $-i(s_x/h_m)\sin\frac{1}{2}m\pi\zeta$ | $-(m\pi/2h_m)\cos\frac{1}{2}m\pi\zeta$ | 2, 4, 6, ⋯ |
| LO | $+1$ | $(s_x/h_m)\cos\frac{1}{2}m\pi\zeta$ | $i(m\pi/2h_m)\sin\frac{1}{2}m\pi\zeta$ | 1, 3, 5, ⋯ |
| TO | $-1$ | $-i(m\pi/2h_m)\sin\frac{1}{2}m\pi\zeta$ | $(s_x/h_m)\cos\frac{1}{2}m\pi\zeta$ | 1, 3, 5, ⋯ |

and (3.33). The results are

$$f_x=\tfrac{1}{2}C(e^{s_x\zeta}+e^{-s_x\zeta}),$$
$$f_z=-\tfrac{1}{2}iC(e^{s_x\zeta}-e^{-s_x\zeta}),\quad\text{with}\quad\gamma=-e^{-2s_x},\qquad(3.42)$$

and

$$f_x=\tfrac{1}{2}iC(e^{s_x\zeta}-e^{-s_x\zeta}),$$
$$f_z=\tfrac{1}{2}C(e^{s_x\zeta}+e^{-s_x\zeta}),\quad\text{with}\quad\gamma=+e^{-2s_x}.\qquad(3.43)$$

These eigenfunctions and eigenvalues satisfy the general symmetry requirement (i). If $s_x\gg1$, these solutions are localized at the surfaces. Therefore, they will be called surface modes, even though they extend through the entire crystal when $s_x\lesssim1$.

Equations (3.38) and (3.39) were obtained by cancelling factors of $\gamma-1$ and $\gamma+1$ which occurred on both sides of the equations. This implies that solutions exist for which $\gamma=\pm1$; accordingly, we try sinusoidal solutions of the form

$$f_x(\zeta)=C_x\cos\tfrac{1}{2}m\pi\zeta,$$
$$f_z(\zeta)=iC_z\sin\tfrac{1}{2}m\pi\zeta,\qquad(3.44)$$

where $m$ is an unknown constant. The kernels $K$ and $K_A$, when operating on these functions, yield not only the same sinusoidal functions, but in addition, exponential functions $e^{\pm s_x\zeta}$. When these trial functions are inserted into the integral equations (3.32) and (3.33), the result is

$$[C_z(\gamma-1+2s_x^2h_m^{-2})-C_xm\pi s_xh_m^{-2}]\sin\tfrac{1}{2}m\pi\zeta-V(e^{s_x\zeta}-e^{-s_x\zeta})=0,\qquad(3.45)$$

$$[C_x(\gamma+1-2s_x^2h_m^{-2})-C_zm\pi s_xh_m^{-2}]\cos\tfrac{1}{2}m\pi\zeta+V(e^{s_x\zeta}+e^{-s_x\zeta})=0,\qquad(3.46)$$

where

$$V=s_xe^{-s_x}[C_x(s_x\cos\tfrac{1}{2}m\pi-\tfrac{1}{2}m\pi\sin\tfrac{1}{2}m\pi)+C_z(\tfrac{1}{2}m\pi\cos\tfrac{1}{2}m\pi+s_x\sin\tfrac{1}{2}m\pi)]/h_m^2$$

and

$$h_m^2=s_x^2+(\tfrac{1}{2}m\pi)^2.$$

The condition $V=0$ gives

$$\frac{C_x}{C_z}=\frac{\frac{1}{2}m\pi\cos\frac{1}{2}m\pi+s_x\sin\frac{1}{2}m\pi}{\frac{1}{2}m\pi\sin\frac{1}{2}m\pi-s_x\cos\frac{1}{2}m\pi}.\qquad(3.47)$$

The condition that the coefficients of $\sin\frac{1}{2}m\pi\zeta$ and $\cos\frac{1}{2}m\pi\zeta$ vanish gives two equations involving $C_z$, $C_x$, and $\gamma$, which are of essentially the same form as Eqs. (3.28) and (3.29). The eigenvalues are the same as for the case of an infinite crystal: $\gamma=-1$, with $C_x/C_z=-m\pi/2s_x$ and $\gamma=+1$, with $C_x/C_z=2s_x/m\pi$. These ratios of $C_x/C_z$ must agree with Eq. (3.47), which gives $C_x/C_z=-m\pi/2s_x$ when $m$ is an even integer, and $C_x/C_z=2s_x/m\pi$ when $m$ is an odd integer. Therefore the eigenvalues and ratios of coefficients are

$$\gamma=-1,\quad\frac{C_x}{C_z}=-\frac{m\pi}{2s_x},\quad m=2,4,6,8,\cdots;$$
$$\gamma=+1,\quad\frac{C_x}{C_z}=\frac{2s_x}{m\pi},\quad m=1,3,5,7,\cdots.\qquad(3.48)$$

For each of these solutions, there is a related solution with eigenvalue of opposite sign, by (i). The $\zeta$ dependence of the solutions (3.44) is such that there are exactly $m$ half waves across the thickness of the slab, from $\zeta=-1$ to $\zeta=+1$. Table II summarizes the eigenvalues and normalized eigenfunctions. Figure 2(a) shows the TO and LO frequencies, which are the same as in an infinite crystal; the only effect of the finite thickness is to quantize the wave number $s_z$. The surface modes can be considered as the missing $m=0$ modes in Fig. 2(a). Figure 2(b) shows how the frequencies of the surface modes converge to a single value lying between the usual TO and LO frequencies as the slab thickness $2a$ increases, with $k_x$ constant. On the other hand, when $k_xa\to0$, the frequencies approach the usual TO and LO frequencies. In this limit, the polarization associated with the surface modes extends uniformly over the entire thickness of the slab; i.e., $f_x(\zeta)\to$ const, $f_z(\zeta)\to0$ for the low-frequency mode, and $f_x(\zeta)\to0$, $f_z(\zeta)\to$ const for the high-frequency mode.[11]

If the surface-mode eigenvalues $\gamma=\pm e^{-2s_x}$ are expanded in powers of $s_x$, the first-order approximation $\gamma\approx\pm(1-2s_x)$ agrees with Eqs. (2.20) and (2.21),

[11] R. A. Ferrell, Phys. Rev. **111**, 1214 (1958), has discussed plasmon surface modes in a thin metallic slab; these are very similar to the surface modes in ionic crystals. Ferrell's treatment, which is based on a dielectric constant $\epsilon(\omega)$, can also be used to derive the results found in this section.

obtained by conventional lattice dynamics in the limit $kL \ll 1$. The relationship between the dimensionless eigenvalue $\gamma$ and the angular frequency $\omega^2$ is

$$\omega^2=\omega_0^2+(4\pi nq^2/3\mu)(\tfrac{3}{2}\gamma+\tfrac{1}{2}) =E/\mu+(F/\mu)(\tfrac{3}{2}\gamma+\tfrac{1}{2}), \quad (3.49)$$

where $E=\mu\omega_0^2$ is the short-range force constant and $F=4\pi nq^2/3=2\pi q^2/3r_0^3$ is the Coulomb force constant. Equation (3.49) reduces to Eqs. (2.20) and (2.21) when the eigenvalues $\gamma\approx\pm(1-2s_x)=\pm(1-kL\sin\theta)$ are inserted. The "eigenfunctions" for the high-frequency mode in a thin slab ($kL\ll 1$) found by standard lattice dynamics, when expressed in terms of the polarization, are $P_z\propto e^{ik_zz}e^{ik_xx}\approx \text{const}\times e^{ik_xx}$, $P_x=0$ [Eqs. (2.5) and (2.18)]. These functions are a zero-order approximation to the true eigenfunctions for the high-frequency surface mode, $P_z\propto\cosh k_xze^{ik_xx}$, $P_x\propto\sinh k_xze^{ik_xx}$, and become identical to the true eigenfunctions when $kL\to 0$ and $k_xL\to 0$. This shows why, when $k_x>0$, the approximate eigenvalues given by (2.20) agree with the exact eigenvalues to first order in $k_x$. Similar arguments apply to the low-frequency mode.

In a thick slab ($kL\gg 1$), on the other hand, the "eigenfunctions" obtained by standard lattice dynamics are transverse or longitudinal polarization waves [Eq. (2.19)]; since they have very little overlap with the surface modes, they can be expressed primarily as linear combinations of the true sinusoidal modes, with frequencies $\nu_{TO}$ and $\nu_{LO}$. For this reason, standard lattice dynamics applied to a thick slab does not yield the surface mode frequencies.

For a slab of arbitrary thickness, the frequencies of all normal modes are either $\nu_{TO}$ or $\nu_{LO}$ when $k_x=0$. This occurs because the volume and surface contributions to the local field from the distant regions I and II vanish, leaving only the contribution from region III. Then $G(z,z')=G_A(z,z')=0$, and Eqs. (3.25) and (3.26) give the eigenvalues immediately. It is clear that the eigenvalues obtained for $k_x=0$ by standard lattice dynamics [Eqs. (2.17) and (2.18)] must be correct, since if we expand the assumed solutions with $z$-dependence $e^{ik_zz}$ in terms of the true eigenfunctions, only the frequencies $\nu_{TO}$ and $\nu_{LO}$ can enter. By setting $k_x$ (or $s_x$)$=0$ in Table II, we also see that motion in the $x$ direction involves only $\nu_{TO}$ and motion in the $z$ direction, only $\nu_{LO}$.

### Inclusion of Atomic Polarizabilities

It is not difficult to include the atomic polarizabilities $\alpha_+$ and $\alpha_-$ of the positive and negative ions, which have been neglected in the foregoing derivation of the normal modes and frequencies. $\alpha_+$ and $\alpha_-$ do not enter explicitly into Eqs. (3.2) through (3.21). When atomic polarizability is included, Eq. (3.22) becomes

$$\mathbf{P}=\mathbf{F}(z)=n(q\mathbf{u}+\alpha\mathbf{E}) \quad (3.50)$$

at $x=0$, $t=0$. $\alpha$ is the total polarizability $\alpha_++\alpha_-$, and $\mathbf{E}$ is the local field at the ionic sites. If the relative displacement $\mathbf{u}$ is eliminated from Eqs. (3.21) and (3.50), the result is

$$\left(\frac{\lambda_0-\lambda'}{1+n\alpha(\lambda_0-\lambda')}\right)\mathbf{F}=\mathbf{E}, \quad (3.51)$$

where

$$\lambda_0=\mu\omega_0^2/nq^2, \quad \lambda'=\mu\omega'^2/nq^2. \quad (3.52)$$

The primed quantities $\lambda'$ and $\omega'$ refer to this case in which polarizability is included. The only difference between Eq. (3.51) and Eq. (3.23),

$$(\lambda_0-\lambda)\mathbf{F}=\mathbf{E}, \quad (3.23')$$

is that the quantity $(\lambda_0-\lambda')/[1+n\alpha(\lambda_0-\lambda')]$ appears instead of $\lambda_0-\lambda$. The basic integral equations (3.25), (3.26), and (3.27) are modified in the same way. The equation $\lambda_0-\lambda=(\lambda_0-\lambda')/[1+n\alpha(\lambda_0-\lambda')]$ can be solved for $\lambda'$, giving

$$\lambda'=\lambda_0+[\lambda-\lambda_0]/[1+n\alpha(\lambda-\lambda_0)]. \quad (3.53)$$

If we know the eigenfunctions and eigenvalues $\lambda$ without atomic polarizability, then the eigenfunctions with polarizability are unchanged, and the new eigenvalues $\lambda'$ are given in terms of $\lambda$ by Eq. (3.53). The eigenvalues for the TO and LO modes in an infinite crystal become

$$\begin{aligned}&\text{TO: } \gamma=-1,\ \lambda-\lambda_0=-\frac{4\pi}{3},\ \lambda'=\lambda_0-\frac{4\pi/3}{1-4\pi n\alpha/3};\\ &\text{LO: } \gamma=+1,\ \lambda-\lambda_0=\frac{8\pi}{3},\quad \lambda'=\lambda_0+\frac{8\pi/3}{1+8\pi n\alpha/3}.\end{aligned} \quad (3.54)$$

The only quantitative change is that the relationship between $\gamma$ and $\lambda$, which was linear, becomes nonlinear. Thus, the eigenvalues for the surface modes in the limit of large $k_xa$, which approached $\gamma=0$ or $\lambda-\lambda_0=+2\pi/3$, a value exactly halfway between the TO and LO eigenvalues, now approach $\lambda'=\lambda_0+(2\pi/3)/[1+2\pi n\alpha/3]$, which lies nearer to the LO than the TO eigenvalue.

### Slab on a Conducting Substrate

Those normal modes in a slab of thickness $2a$ for which the polarization $F_x(z)$ or $F_y(z)$ is an odd function of $z$ are also normal modes for a slab of thickness $a$ on a perfectly conducting substrate at $z=0$. For if $F_x(z)$ and $F_y(z)$ are odd functions of $z$, then $F_z(z)$ is an even function of $z$; from Eqs. (3.16), (3.17), and (3.18), the local field components $E_x(z)$ and $E_y(z)$ are odd functions of $z$, and so are the average fields $E_x^{av}(z)$ and $E_y^{av}(z)$. Therefore, the components of the average field parallel to the conducting plane at $z=0$ vanish, as they must. Of the normal modes listed in Table II, only those on lines 2, 4, and 6 are present. It is interesting that the low-frequency surface mode is absent.

## IV. OPTICAL ABSORPTION

Let us assume that absorption of light by a crystal slab can be ascribed to the excitation of the normal

modes. If reflection and refraction at the surfaces of the slab are disregarded, so that the additional electrical field inside the slab is the same as the field of the incident wave, the absorption due to a particular normal mode is proportional to the square of the overlap integral of the field of the incident wave and the polarization for that mode. For a very thin slab, in particular, this field is essentially constant over the thickness of the slab and couples only to the "surface" modes. Equations (3.42) and (3.43) show that in the thin-slab limit ($s_x \to 0$), the $x$ polarization of the low-frequency mode is constant and the $z$ polarization is zero, whereas the reversed situation holds for the high-frequency mode. Thus when light polarized in the $x$-$z$ plane is incident normally on the slab, it excites only the low-frequency mode at $\nu_{TO}$, but if it is incident at an angle $\theta \neq 0°$, there is a component of the field in the $z$ direction which excites the high-frequency mode at $\nu_{LO}$. It follows that the absorption at $\nu_{LO}$ is proportional to $\sin^2\theta$.

This result for optical absorption in a very thin slab essentially agrees with that of Berreman.[7] He introduced a complex dielectric constant $\epsilon(\omega)$, applied Maxwell's equations with appropriate matching conditions at the surfaces, and derived expressions for the transmission and reflection coefficients. As Berreman has pointed out, since $\epsilon \to \infty$ at $\nu_{TO}$ (for no damping), there must be a normal mode with polarization perpendicular to the surface at this frequency. Also, a normal mode with polarization perpendicular to the surface at $\nu_{LO}$ is consistent with the fact that $\epsilon = 0$ at this frequency. These two modes are precisely our "surface" modes in the thin-slab limit.

The concept that the normal modes give rise to optical absorption happens to yield the correct result only for a thin slab and is actually not valid. When retardation is included, one finds that the radiative solutions to Maxwell's equations, with fields extending to infinity, are distinct from the localized solutions, with fields decreasing exponentially at infinity. Thus, the problem of transmission, absorption, and reflection of light by the slab, which involves the radiative solutions, has no immediate relation to the normal modes, which involve localized solutions. A detailed account of the effects of retardation will be published in the future.

## APPENDIX A: EVALUATION OF THE COULOMB MATRIX ELEMENTS

Starting with the Coulomb energy (we neglect retardation)

$$\Phi = \tfrac{1}{2} \sum_{\substack{ll' \\ jj'}} \frac{q_j q_{j'}}{|\mathbf{x}(l;j) + \mathbf{u}(l;j) - x(l';j') - \mathbf{u}(l';j')|}, \tag{A1}$$

it can be shown that[5]

$$C_{xy}{}^{c}(\mathbf{k};j,j) = \frac{-q_j^2}{m_j} \sum_{n \neq 0} \left[ \frac{\partial^2}{\partial x \partial y} \left\{ \frac{1}{|\mathbf{r} - \mathbf{a}_n|} \right\} \right]_{r=0} e^{i\mathbf{k}\cdot\mathbf{a}_n} \tag{A2}$$

and

$$C_{xy}{}^{c}(\mathbf{k};j,j') = \frac{-q_j q_{j'}}{(m_j m_{j'})^{1/2}} \sum_n \left[ \frac{\partial^2}{\partial x \partial y} \left\{ \frac{1}{|\mathbf{r} - \mathbf{a}_n|} \right\} \right]_{r=r_{jj'}} e^{i\mathbf{k}\cdot(\mathbf{a}_n - \mathbf{r}_{jj'})}, \tag{A3}$$

where $\mathbf{a}_n$ generates the fcc lattice of either anions or cations and $\mathbf{r}_{jj'}$ is the vector connecting the two atoms in the unit cell.[12]

In the limit $\lambda \gg r_0$, Cohen and Keffer[13] have shown that the sums in (A2) and (A3) become

$$\frac{1}{2r_0{}^3} \left( \frac{4\pi}{3} \right) \left( \delta_{ij} - \frac{3k_i k_j}{k^2} \right) \tag{A4}$$

for an infinite crystal, the coordinate directions here represented by the subscripts $i$ and $j$. The simplest way to obtain the matrix elements of interest in the present case is to subtract from (A4) the contribution to the sums from outside the slab, which means, since we are considering the equation corresponding to the position $(0,0,z)$, a subtraction of the contributions from $z > L_1$ and $z < -L_2$ (see Fig. 1). For long wavelengths, this can be accomplished by an integration over the region outside the slab. It should be noted, however, that in the small $k$ region, the same results can be obtained by a direct integration over the slab itself. Since

$$\frac{\partial^2}{\partial r_i \partial r_j} \left[ \frac{1}{|\mathbf{r} - \mathbf{a}_n|} \right]_{r=0} = \frac{3(a_n)_i (a_n)_j}{|\mathbf{a}_n|^5} - \frac{\delta_{ij}}{|\mathbf{a}_n|^3},$$

we must evaluate the integrals

$$S_n = \int_{x=-\infty}^{\infty} \int_{y=-\infty}^{\infty} \int_{z \text{ outside}} \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{|\mathbf{r}|^n} d^3r \tag{A5}$$

for $n = 3$ and 5, recognizing that the desired quantity will result from $S_5$ upon taking derivatives with respect to the components of $k$.

Consider

$$S_3 = \int_{x=-\infty}^{\infty} \int_{y=-\infty}^{\infty} \int_{z=L_1}^{\infty} \frac{e^{ik_x x} e^{ik_y y} e^{ik_z z}}{(x^2+y^2+z^2)^{3/2}} dx dy dz. \tag{A6}$$

The integrals over $x$ and $y$ can be performed using Fourier transform tables[14] with the result

$$S_3 = (2\pi k_\rho)^{1/2} \frac{\Gamma(\frac{1}{2})}{\Gamma(\frac{3}{2})} \int_{L_1}^{\infty} \frac{K_{-1/2}(k_\rho z) e^{ik_z z}}{\sqrt{z}} dz,$$

[12] There is an additional term entering (A2) which is given as $(\varphi_{\kappa\kappa}{}^{0})_{xy}$ in the paper of Kellermann (Ref. 5). This term is zero for an infinite crystal but not for a finite crystal. Since this term will, in practice, contribute to (A2) only when one is evaluating the Coulomb coefficients very near a surface, we neglect it here.

[13] M. H. Cohen and F. Keffer, Phys. Rev. **99**, 1128 (1955).

[14] See, for example, W. Magnus and F. Oberhettinger, *Formulas and Theorems for the Functions of Mathematical Physics* (Chelsea Publishing Company, New York, 1954), pp. 118–120.

where $k_\rho=(k_x^2+k_y^2)^{1/2}$ and $K_{-1/2}$ is the Bessel function of the second kind. Since

$$K_{-1/2}(x)=(\pi/2x)^{1/2}e^{-x},$$

$S_3$ becomes

$$S_3=2\pi F\{(ik_z-k_\rho),L_1\}, \tag{A7}$$

where

$$F(\xi,L_1)=\int_{L_1}^{\infty}\frac{e^{\xi z}}{\sqrt{z}}dz. \tag{A8}$$

We can evaluate $S_5$ in much the same way. The integrals over $x$ and $y$ give

$$S_5=\left(\frac{\pi}{2}\right)^{1/2}k_\rho^{3/2}\frac{\Gamma(\frac{1}{2})}{\Gamma(\frac{5}{2})}\int_{L_1}^{\infty}\frac{e^{ikz}}{z^{3/2}}K_{3/2}(k_\rho z)dz$$

and, since

$$K_{3/2}(x)=\left(\frac{\pi}{2}\right)^{1/2}\frac{(1+x)}{x^{3/2}}e^{-x},$$

$S_5$ becomes

$$S_5=e^{(ikz-k\rho)L_1}\left\{\frac{1}{2L_1^2}+\frac{(ik_z-k_\rho)}{2L_1}\right\}+\frac{(ik_z-k_\rho)^2}{2}F\{(ik_z-k_\rho),L_1\}, \tag{A9}$$

where $F(\xi,L_1)$ is defined by (A8). Adding the quantity $-\delta_{ij}S_3$ to $-3(\partial^2S_5/\partial k_i\partial k_j)$ and dividing this sum by $2r_0^3$ gives the contribution of the upper excluded region to be subtracted from (A4). It is easy to show that the contribution of the lower excluded region, from $-L_2$ to $-\infty$, to $S_3$ and $S_5$ is given by that from the upper region by replacing $L_1$ by $L_2$ and $k_z$ by $-k_z$. The evaluation of the sums, in the case where the derivatives are to be evaluated at $\mathbf{r}_{jj'}$, can be shown to yield identical results with the above case corresponding to the evaluation of the derivatives at $\mathbf{r}=0$. The results are

$$C_{xx}{}^c(\mathbf{k};j,j)=\frac{-\pi q_j^2}{r_0^3m_j}\left[\frac{2}{3}\left(1-3\frac{k_x^2}{k^2}\right)+\frac{k_x^2}{k_\rho}\left\{\frac{e^{(ikz-k\rho)L_1}}{(k_\rho-ik_z)}+\frac{e^{(-ikz-k\rho)L_2}}{(k_\rho+ik_z)}\right\}\right],$$

$$C_{yy}{}^c(\mathbf{k};j,j)=\frac{-\pi q_j^2}{r_0^3m_j}\left[\frac{2}{3}\left(1-3\frac{k_y^2}{k^2}\right)+\frac{k_y^2}{k_\rho}\left\{\frac{e^{(ikz-k\rho)L_1}}{(k_\rho-ik_z)}+\frac{e^{(-ikz-k\rho)L_2}}{(k_\rho+ik_z)}\right\}\right],$$

$$C_{zz}{}^c(\mathbf{k};j,j)=\frac{-\pi q^2}{r_0^3m_j}\left[\frac{2}{3}\left(1-3\frac{k_z^2}{k^2}\right)-k_\rho\left\{\frac{e^{(ikz-k\rho)L_1}}{(k_\rho-ik_z)}+\frac{e^{(-ikz-k\rho)L_2}}{(k_\rho+ik_z)}\right\}\right],$$

$$C_{xy}{}^c(\mathbf{k};j,j)=\frac{-\pi q_j^2k_xk_y}{r_0^3m_j}\left[\frac{-2}{k^2}+\frac{1}{k_\rho}\left\{\frac{e^{(ikz-k\rho)L_1}}{(k_\rho-ik_z)}+\frac{e^{(-ikz-k\rho)L_2}}{(k_\rho+ik_z)}\right\}\right],$$

$$C_{yz}{}^c(\mathbf{k};j,j)=\frac{-\pi q_j^2k_y}{r_0^3m_j}\left[\frac{-2k_z}{k^2}-i\left\{\frac{e^{(ikz-k\rho)L_1}}{(k_\rho-ik_z)}-\frac{e^{(-ikz-k\rho)L_2}}{(k_\rho+ik_z)}\right\}\right],$$

$$C_{zx}{}^c(\mathbf{k};j,j)=\frac{-\pi q_j^2k_x}{r_0^3m_j}\left[\frac{-2k_z}{k^2}-i\left\{\frac{e^{(ikz-k\rho)L_1}}{(k_\rho-ik_z)}-\frac{e^{(-ikz-k\rho)L_2}}{(k_\rho+ik_z)}\right\}\right],$$

$C_{xz}{}^c(\mathbf{k};j,j)=C_{zx}{}^c(\mathbf{k};j,j)^*$ and likewise for $C_{yx}(\mathbf{k};j,j)$ and $C_{zy}(\mathbf{k};j,j)$. The matrix elements $C_{\alpha\beta}{}^c(\mathbf{k};j,j')$ can be obtained from $C_{\alpha\beta}(\mathbf{k};j,j)$ by replacing $q_j^2/m_j$ by $q_jq_{j'}/(m_jm_{j'})^{1/2}$.

## APPENDIX B: INTEGRAL EQUATIONS FROM LATTICE DYNAMICS APPROACH

With the assumed displacements of the form given by Eq. (3.1) the equation analogous to (2.6) becomes

$$\omega^2w_{\alpha j}(\mathbf{k},z)=\sum_{l_z'}\sum_{j'\beta}D_{\alpha\beta}(l_z,l_z';j,j')w_{\beta j'}(\mathbf{k},z'), \tag{B1}$$

where $l_z$ is the $z$ component of lattice vector $l$,

$$D_{\alpha\beta}(l_z,l_z';j,j')=(m_jm_{j'})^{-1/2}\sum_{l_x'l_y'}\Phi_{\alpha\beta}(l,l';j,j')e^{ikx\{x_x(l';j')-x_x(l;j)\}}e^{iky\{x_y(l';j')-x_y(l;j)\}}, \tag{B2}$$

and $\Phi_{\alpha\beta}(l,l';j,j')$ is defined by (2.4). We separate $D$ into two parts, $D_{\alpha\beta}{}^c(l_z,l_z';j,j')$ corresponding to the Coulomb interactions and $D_{\alpha\beta}{}^s(l_z,l_z';j,j')$ corresponding to the short-range interactions.

Consider the case of the Coulomb interactions. For illustration, we will examine in detail the term

$$D_{\alpha\beta}{}^{c}(l_z,l_z';\,j,j)=\frac{q_j{}^2}{m_j}\sum_{\substack{l_x'l_y'\\(l'\neq l)}}\Bigg[\frac{\delta_{\alpha\beta}}{[\{x_x(l)-x_x(l')\}^2+\{x_y(l)-x_y(l')\}^2+\{x_z(l)-x_z(l')\}^2]^{3/2}}$$
$$-\frac{3\{x_\alpha(l)-x_\alpha(l')\}\{x_\beta(l)-x_\beta(l')\}}{[\{x_x(l)-x_x(l')\}^2+\{x_y(l)-x_y(l')\}+\{x_z(l)-x_z(l')\}^2]^{5/2}}\Bigg]e^{ik_x\{x_x(l')-x_x(l)\}}e^{ik_y\{x_y(l')-x_y(l)\}}. \quad \text{(B3)}$$

Since we are interested in the long-wavelength range and the sums are over all $l_x'$ and $l_y'$, we can move the origin to ion $l$ and integrate. The first term in the sum in (B3) then can be written

$$S_3=\frac{1}{2r_0{}^2}\int_{-\infty}^{\infty}e^{ik_yy}dy\int_{-\infty}^{\infty}\frac{e^{ik_xx}dx}{[x^2+y^2+\eta^2]^{3/2}}, \quad \text{(B4)}$$

where we have for convenience placed the two ions in a unit cell in the $x$-$y$ plane and

$$\eta^2=\{x_z(l)-x_z(l')\}^2\equiv\{z-z'\}^2,\quad \eta=|\xi|.$$

For $\eta\neq0$, (B4) can be integrated (see Appendix A) with the result

$$S_3=(\pi/\eta r_0{}^2)e^{-\eta k_\rho}, \quad \text{(B5)}$$

where $k_\rho=(k_x{}^2+k_y{}^2)^{1/2}$. Considering for the time being that the sum on $l_z'$ in (B1) retains its discrete character, $\eta$ will be an integral multiple of $r_0$. Thus (B5) is valid for all allowed $\eta$ except $\eta=0$.

When $\eta=0$, the condition $l'\neq l$ in (B3) means we must exclude the ion at the origin. We do this by subtracting from $S_3$ the contribution $S_3'$ from a circle of radius $\epsilon\sim r_0$ in the $x$-$y$ plane,

$$S_3'=\frac{\pi}{r_0{}^2\eta}-\frac{\pi}{r_0{}^2(\epsilon^2+\eta^2)^{1/2}}, \quad \text{(B6)}$$

so that, for $\eta=0$,

$$S_3-S_3'=(\pi/r_0{}^2\epsilon)-(\pi k_\rho/r_0{}^2). \quad \text{(B7)}$$

The second term in (B3) can be obtained by evaluating the integral

$$S_5=\frac{1}{2r_0{}^2}\int_{-\infty}^{\infty}e^{ik_yy}dy\int_{-\infty}^{\infty}\frac{e^{ik_xx}dx}{[x^2+y^2+\eta^2]^{5/2}}, \quad \text{(B8)}$$

which is equal to

$$S_5=(\pi/3r_0{}^2\eta^3)(1+\eta k_\rho)e^{-\eta k_\rho}. \quad \text{(B9)}$$

For $\eta\neq0$, we can then obtain $D_{xx}{}^{c}(l_z,l_z';\,j,j)$ by taking $3\partial^2S_5/\partial k_x{}^2$, adding (B5), and multiplying by $q_j{}^2/m_j$. Thus,

$$D_{xx}{}^{c}(l_z,l_z';\,j,j)=\frac{q_j{}^2}{m_j}\frac{\pi}{r_0{}^2}\frac{k_x{}^2}{k_\rho}e^{-\eta k_\rho}. \quad \text{(B10)}$$

For $\eta=0$ there is an additional contribution to $D$ which must be considered. That quantity which must be subtracted from $3\partial^2S_5/\partial k_x{}^2$ coming from a circle of radius $\epsilon$ about the origin is

$$3S_{5xx}{}'=\frac{3}{2r_0{}^2}\int_O\int\frac{x^2dxdy}{[x^2+y^2+\eta^2]^{5/2}}$$
$$=\frac{3\pi}{2r_0{}^2\eta}\left[\frac{-1}{(1+\epsilon^2/\eta^2)^{1/2}}+\frac{1}{3(1+\epsilon^2/\eta^2)^{3/2}}+\frac{2}{3}\right], \quad \text{(B11)}$$

so for $\eta=0$, we have

$$D_{xx}{}^{c}(l_z,l_z;\,j,j)=\frac{q_j{}^2}{m_j}\left[\frac{\pi k_x{}^2}{r_0{}^2k_\rho}-\frac{\pi}{2r_0{}^2\epsilon}\right]. \quad \text{(B12)}$$

The first term is clearly the value of (B10) for $\eta=0$. We call the second term the coplanar coefficient and denote it by $D_{xx}{}^{c'}(l_z,l_z;\,j,j)$, recognizing it to be the excess contribution to $D^c$ for $l_z=l_z'$.

The remainder of the Coulomb coefficients can be evaluated in a similar fashion with the result, valid for all $\eta$,

$$D_{yy}{}^{c}(l_z,l_z';\,j,j)=\frac{q_j{}^2}{m_j}\frac{\pi}{r_0{}^2}\frac{k_y{}^2}{k_\rho}e^{-\eta k_\rho},$$

$$D_{zz}{}^{c}(l_z,l_z';\,j,j)=\frac{-q_j{}^2}{m_j}\frac{\pi}{r_0{}^2}k_\rho e^{-\eta k_\rho},$$

$$D_{xy}{}^{c}(l_z,l_z';\,j,j)=D_{yx}{}^{c}(l_z,l_z';\,j,j)=\frac{q_j{}^2}{m_j}\frac{\pi}{r_0{}^2}\frac{k_xk_y}{k_\rho}e^{-\eta k_\rho}, \quad \text{(B13)}$$

$$D_{xz}{}^{c}(l_z,l_z';\,j,j)=D_{zx}{}^{c}(l_z,l_z';\,j,j)=\frac{q_j{}^2}{m_j}\frac{\pi i}{r_0{}^2}\frac{k_x}{\eta}(z-z')e^{-\eta k_\rho},$$

$$D_{yz}{}^{c}(l_z,l_z';\,j,j)=D_{zy}{}^{c}(l_z,l_z';\,j,j)=\frac{q_j{}^2}{m_j}\frac{\pi i}{r_0{}^2}\frac{k_y}{\eta}(z-z')e^{-\eta k_\rho}.$$

The coplanar coefficients are

$$D_{xx}{}^{c'}(l_z,l_z;\,j,j)=\frac{-q_j{}^2}{m_j}\frac{\pi}{2r_0{}^2\epsilon}=D_{yy}{}^{c'}(l_z,l_z;\,j,j), \quad \text{(B14)}$$

$$D_{zz}{}^{c'}(l_z,l_z;\,j,j)=\frac{q_j{}^2}{m_j}\frac{\pi}{r_0{}^2\epsilon},$$

all others being zero. The coefficients for $jj$ becoming $jj'$ can be obtained from (B13) and (B14) by replacing $q_j{}^2/m_j$ by $q_jq_{j'}/(m_jm_{j'})^{1/2}$.

It is a somewhat tedious though not difficult task to show that the nonzero short-range coefficients in the

long-wavelength range are[15]

$$D_{\alpha\beta}{}^{s}(l_z,l_z';\,j,j)=\delta_{l_zl_z'}\delta_{\alpha\beta}\frac{q_j^2}{m_j}\frac{(A+2B)}{2r_0{}^3},$$

$$D_{xx}{}^{s}(l_z,l_z';\,j,j')=D_{yy}{}^{s}(l_z,l_z';\,j,j')=\frac{q_jq_j'}{2r_0{}^3}\frac{1}{(m_jm_j)^{1/2}}[\delta_{l_zl_z'}(A+B)+(\tfrac{1}{2}B)(\delta_{l_z,l_z'+r_0}+\delta_{l_z,l_z'-r_0})], \tag{B15}$$

$$D_{zz}{}^{s}(l_z,l_z';\,j,j')=\frac{q_jq_j'}{(m_jm_{j'})^{1/2}}\frac{1}{2r_0{}^3}\left[2B\delta_{l_zl_z'}+\frac{A}{2}(\delta_{l_z,l_z'+r_0}+\delta_{l_z,l_z'-r_0})\right],$$

where $A$ and $B$ are given by (2.9).

We now use (B1), letting $\sum_{l_z'}\rightarrow(1/r_0)\int dz'$, and consider $\alpha=x$ and $j=+$ corresponding to a cation. The resulting equation is

$$\begin{aligned}\omega^2w_{x+}(\mathbf{k},z)=&\frac{1}{r_0}\int_{\text{slab}}dz'\Big[w_{x+}(\mathbf{k},z')\frac{e^2}{m_+}\frac{\pi}{r_0{}^2}\frac{k_x{}^2}{k_\rho}e^{-|z-z'|k_\rho}+w_{x-}(\mathbf{k},z')\frac{(-e^2)}{(m_+m_-)^{1/2}}\frac{\pi}{r_0{}^2}\frac{k_x{}^2}{k_\rho}e^{-|z-z'|k_\rho}\\&+w_{y+}(\mathbf{k},z')\frac{e^2}{m_+}\frac{\pi}{r_0{}^2}\frac{k_xk_y}{k_\rho}e^{-|z-z'|k_\rho}+w_{y-}(\mathbf{k},z')\frac{(-e^2)}{(m_+m_-)^{1/2}}\frac{\pi}{r_0{}^2}\frac{k_xk_y}{k_\rho}e^{-|z-z'|k_\rho}\\&+w_{z+}(\mathbf{k},z')\frac{e^2}{m_+}\frac{\pi ik_x}{r_0{}^2}\frac{(z-z')}{|z-z'|}e^{-|z-z'|k_\rho}+w_{z-}(\mathbf{k},z')\frac{(-e^2)}{(m_+m_-)^{1/2}}\frac{\pi ik_x}{r_0{}^2}\frac{(z-z')}{|z-z'|}e^{-|z-z'|k_\rho}\Big]\\&+\frac{e^2}{m_+}\frac{(A+2B)}{2r_0{}^3}w_{x+}(\mathbf{k},z)-\frac{e^2}{(m_+m_-)^{1/2}}\frac{1}{2r_0{}^3}(A+B)w_{x-}(\mathbf{k},z)-\frac{e^2}{4r_0{}^3}\frac{B}{(m_+m_-)^{1/2}}w_{x-}(\mathbf{k},z+r_0)\\&-\frac{e^2}{4r_0{}^3}\frac{B}{(m_+m_-)^{1/2}}w_{x-}(\mathbf{k},z-r_0)-\frac{e^2\pi}{m_+2r_0{}^2\epsilon}w_{x+}(\mathbf{k},z)+\frac{e^2}{(m_+m_-)^{1/2}}\frac{\pi}{2r_0{}^2\epsilon}w_{x-}(\mathbf{k},z),\end{aligned} \tag{B16}$$

where we have used (B13), (B14), and (B15). Expanding those terms whose arguments are $z\pm r_0$ and eliminating the anion displacements, since for optical modes

$$w_{\alpha-}(\mathbf{k},z)=-(m_+/m_-)^{1/2}w_{\alpha+}(\mathbf{k},z),$$

(B16) becomes

$$\begin{aligned}\omega^2w_{x+}(\mathbf{k},z)=&\frac{1}{r_0}\int_{\text{slab}}dz'\Big[w_{x+}(\mathbf{k},z')\frac{e^2}{\mu}\frac{\pi}{r_0{}^2}\frac{k_x{}^2}{k_\rho}e^{-|z-z'|k_\rho}+w_{y+}(\mathbf{k},z')\frac{e^2}{\mu}\frac{\pi}{r_0{}^2}\frac{k_xk_y}{k_\rho}e^{-|z-z'|k_\rho}\\&+w_{z+}(\mathbf{k},z')\frac{e^2}{\mu}\frac{\pi ik_x}{r_0{}^2}\frac{(z-z')}{|z-z'|}e^{-|z-z'|k_\rho}\Big]+\frac{e^2}{\mu}\frac{(A+2B)}{2r_0{}^3}w_{x+}(\mathbf{k},z)-\frac{e^2}{\mu}\frac{\pi}{2r_0{}^2\epsilon}w_{x+}(\mathbf{k},z),\end{aligned} \tag{B17}$$

where $\mu$ is the reduced mass. Using $E$ and $F$ defined by (2.12) and (2.14) this can be rewritten as

$$\begin{aligned}\frac{[\omega^2-E/\mu+\frac{3}{4}(r_0F/\mu\epsilon)]}{\frac{3}{2}(F/\mu)}w_{x+}(\mathbf{k},z)=&\int_{\text{slab}}dz'\Big[w_{x+}(\mathbf{k},z')\frac{k_x{}^2}{k_\rho}e^{-|z-z'|k_\rho}\\&+w_{y+}(\mathbf{k},z')\frac{k_xk_y}{k_\rho}e^{-|z-z'|k_\rho}+w_{z+}(\mathbf{k},z')ik_x\frac{(z-z')}{|z-z'|}e^{-|z-z'|k_\rho}\Big].\end{aligned} \tag{B18}$$

An additional pair of equations for $w_{y+}$ and $w_{z+}$ can be obtained in a similar manner. By considering an infinite crystal for which the eigenfrequencies are known, one can show that $\epsilon=\frac{3}{4}r_0$. Using this value of $\epsilon$ and orienting the crystal so $k_y=0$, we have finally

$$\frac{(\omega^2-E/\mu+F/\mu)}{\frac{3}{2}(F/\mu)}w_{x+}(\mathbf{k},z)=\int_{\text{slab}}dz'\left[w_{x+}(\mathbf{k},z')k_xe^{-|z-z'|k_x}+w_{z+}(\mathbf{k},z')ik_x\frac{(z-z')}{|z-z'|}e^{-|z-z'|k_x}\right], \tag{B19}$$

which is identical to Eq. (3.26).

[15] We neglect the changes in these coefficients which occur for surface ions.