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PHYSICAL REVIEW B VOLUME 4, NUMBER 6 15 SEPTEMBER 1971

Studies of Vibrational Surface Modes. I. General Formulation*

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(Received 1 March 1971)

A general formulation is given for studies of the vibrational properties of systems which have two-dimensional periodicity and one or two surfaces. Although layered structures and other systems with interfaces fall within the scope of this formulation, the principal motivation is to provide a framework for calculating and interpreting vibrational surface properties. No assumption is made concerning crystal structure, surface orientation, the interaction between particles, or the number of particles per unit cell. Also, the treatment is applicable to reconstructed surfaces, surfaces with adsorbed impurity particles, etc., as well as unreconstructed clean surfaces, provided that the two-dimensional periodicity is preserved. A discussion is given of the properties of the vibrational modes: In general, the displacement ellipse for a given mode can have any orientation. For surfaces with "axial-inversion symmetry," however, one axis of the ellipse is always normal to the surface. If the surface has "complete reflection symmetry" with respect to a given plane, then for any two-dimensional wave vector parallel to the plane the modes will separate into two classes: one-third of the modes will be pure shear-horizontal (SH) modes, and the other two-thirds will be polarized strictly in the sagittal plane. It is possible for surface modes of one class to lie within the bulk subbands of the other class. If the crystal has either axial-inversion symmetry or a three-dimensional center of inversion, then the complex dynamical matrix can be reduced to a real, symmetric matrix of the same size. If both symmetries are present, as is the case for many surfaces of interest, then a further reduction is possible. Finally, notations are suggested for distinguishing two-dimensional vectors and for labeling symmetry points in the two-dimensional Brillouin zone associated with a surface.

I. INTRODUCTION

The study of elastic surface waves goes back almost a century, to the investigation by Lord Rayleigh in 1885 of surface waves in an isotropic elastic continuum.[1,2] In 1911, Love treated another type of surface wave which can exist when a macroscopic layer of one material is supported by a substrate of another material,[3] and in 1924 Stoneley considered a type of wave which can propagate along the interface of two materials.[4] Rayleigh waves, Love waves, Stoneley waves, and other waves in more general layered media[5] are of importance in seismology.

In the past 15 years there have been many studies of surface waves in anisotropic media.[6–13] For a surface wave in an anisotropic medium, the displacement $\vec{u}$ at the point with position vector $\vec{r} = (x, y, z)$ is given by[6]

$$\vec{u}(\vec{r}) = \sum_{n=1}^{3} c_n \vec{\eta}^n \exp[i(\vec{q}^n \cdot \vec{r} - \omega t)] \tag{1.1}$$

$$= \sum_{n=1}^{3} c_n \vec{\eta}^n \exp[i(q_z^n z + q_x x + q_y y - \omega t)] , \tag{1.2}$$

where (q_x, q_y) is the propagation vector, which is two-dimensional and parallel to the surface plane, and q_z^n is a complex number which determines the attenuation of the wave with distance from the surface. (We take the z axis to be perpendicular to the surface.) For the special case of a true Rayleigh wave in an isotropic medium, there are only two q_z^n, both of which are purely imaginary, and vibrations are limited to the sagittal plane.[14] The more general waves having the form given in Eq. (1.2) have been called "generalized Rayleigh waves."[7,8]

Very recently there has been great interest in surface waves in piezoelectric materials,[13,15,16] because of their advantages over bulk waves in acoustic-delay lines and other signal-processing applications.[17]

In contrast with the vast amount of work on surface vibrations in elastic-continuum models, there has been relatively little work on the more general problem for discrete lattices (especially in the case of monatomic materials). The continuum approximation is, of course, valid only at long wavelengths, where the microscopic discreteness of the solid is unimportant. For wavelengths of the order of a few atomic spacings, elastic-continuum theory is no longer valid and the methods of lattice dynamics are necessary.

A complete understanding of surface vibrations therefore requires detailed lattice-dynamics calculations for realistic models. One reason for the interest in such an understanding is the influence of surface vibrations on other surface properties: These vibrations affect low-energy electron-diffraction intensities in a number of ways,[18] and have an important effect on the scattering of atoms and molecules from surfaces at sufficiently low energies.[19] The vibrational spectrum also determines, in part, the surface specific heat, surface free energy, and other thermodynamic functions.[20] Moreover, the surface phonons should play an important role in determining the electron-phonon interaction in sufficiently thin films, or for electronic states localized near the surface; one effect of this electron-surface–phonon interaction is an enhancement of superconducting-transition temperatures in very thin films which apparently has been observed.[21] As a final example, the structure of the surface is in some cases dependent upon temperature, and this fact implies that the structure is affected by the lattice vibrations. Even if the structure does not change, the thermal expansion at a surface is determined by the lattice vibrations.[22]

In addition to studies of one-dimensional models[23–27] (in which wavelike surface modes are not possible, of course), there have been a number of treatments of surface modes in three-dimensional lattices[8,27–37]: Lifshitz and Rosenzweig[29] found that, in a diatomic crystal, surface modes can exist in a gap between acoustic- and optical-bulk modes, and optical-surface modes have been obtained in recent calculations for model-diatomic crystals and for ionic crystals.[30,32–35] (Surface modes in ionic crystals have apparently been observed experimentally.[38]) Gazis, Herman, and Wallis[8] have calculated the surface modes in simple force-constant models of monatomic crystals. Finally, Feuchtwang[37] has given a general formulation of the lattice-dynamics problem for a semi-infinite crystal with short-range interaction

The previous calculations of surface modes have generally been based on rather simple models. An unrealistically simple model can, of course, yield results which are unphysical. As examples, we mention the failure of the Montroll-Potts model to yield Rayleigh waves, in disagreement with elasticity theory,[39] and the fact that the qualitative features of the surface-mode spectrum are sensitive to changes in the surface force constants.[40]

It is therefore particularly important to use realistic models in the calculation of vibrational surface properties. The results of the following papers in this series,[40,41] and of earlier calculations of physical quantities at a surface,[22,42] were obtained with a model which is more realistic than previous models in being based on the consistent use of a Lennard-Jones potential

$$\phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^{6}] , \tag{1.3}$$

where ϵ and σ are potential parameters. A particle interacts with all of its neighbors, and the displacements of the particles near the surface from their positions in the bulk are taken into account. An advantage of this potential is that it yields results that depend only on the shape of the potential, and not on the potential parameters. Some other advantages are discussed elsewhere.[43] We regard this model as the best that can be used for general studies of surface vibrational properties, i.e., a more accurate interaction model would involve specializing to a particular material. Furthermore, to obtain an accurate interaction model for materials of interest (e.g., metals and materials with covalent bonding) is a matter of considerable difficulty even for the bulk, and the surface problem is much harder because of the change in electronic states and other properties near the surface.

Although Feuchtwang[37] has given a formulation of the lattice-dynamics problem for a semi-infinite crystal which can in principle be used for calculations, it is more convenient in practice to perform calculations for slab-shaped models with a finite thickness and two surfaces. The justification for using a slab-shaped model (of sufficient thickness) is that the results obtained are essentially the same as would be obtained with a semi-infinite crystal,[20,22,44] with three qualifications: (1) Since there are two surfaces, there are two nearly degenerate surface modes of each kind, which are mixtures of the modes associated with the individual surfaces. This matter is discussed in Sec. III. (2) Since there are only a finite number of layers, there are only a finite number of modes in the bulk subbands, whereas there would be an infinite number in a semi-infinite crystal. (The term "subband" is defined in Sec. II.) (3) At large wavelengths there are surface modes with large penetration depths. Such modes will be strongly affected by the truncation of the crystal at a finite thickness, and the results for a slab will therefore be quite different from the results for a semi-infinite crystal. Calculations based on slab-shaped crystals are therefore not valid in the long-wavelength limit, and in this sense are complementary to continuum calculations, which are valid *only* at long wavelengths.

The use of a slab-shaped model is, however, valid for the calculation of all surface modes except those which are deeply penetrating. It is found that (except at long wavelengths) the only important effect of increasing the thickness of the model is to populate the bulk subbands more densely. For most wave vectors, the positions of both the surface-mode frequencies and the bulk subbands do not change much beyond a thickness of about 10 layers.[20, 44]

In Paper II,[40] we give detailed numerical results for monatomic fcc crystals whose particles interact through a Lennard-Jones potential, and Paper III[41] will deal with adsorbed monolayers. In the present paper, however, we are concerned with providing a general formulation and discussion of the lattice-dynamics problem that will serve as a foundation for these papers and future work. The basic formalism is given in Sec. II, and Sec. III contains a discussion of some properties of the vibrational modes.

The material in these sections applies both to a crystal with two surfaces, which has a finite (though arbitrarily large) thickness, and to a semi-infinite crystal with one surface.[45] It is also applicable when there is reconstruction, adsorption, etc., as long as some sort of two-dimensional periodicity is preserved. Finally, no assumption is made concerning the effective interaction between particles, the number of particles per unit cell, the crystal structure, or the surface orientation. Unless explicitly stated otherwise, there are no assumptions or approximations beyond the two-dimensional periodicity, the usual adiabatic approximation, and the quasiharmonic approximation.

The main results of Secs. II and III are summarized in Sec. IV.

II. LATTICE DYNAMICS OF A CRYSTAL WITH ONE OR TWO SURFACES

If the instantaneous position of a particle (atom or ion) is represented by $\vec{\mathrm{r}}(\vec{\mathrm{l}}\kappa)$, then

$$\vec{\mathrm{r}}(\vec{\mathrm{l}}\kappa)=\vec{\mathrm{r}}_0(\vec{\mathrm{l}}\kappa)+\vec{\mathrm{u}}(\vec{\mathrm{l}}\kappa)\ , \tag{2.1}$$

where $\vec{\mathrm{r}}_0(\vec{\mathrm{l}}\kappa)$ gives the mean position of the particle and $\vec{\mathrm{u}}(\vec{\mathrm{l}}\kappa)$ is the time-dependent displacement. Here the set of numbers $\vec{\mathrm{l}}=(l_1, l_2, l_3)$ and the index κ specify a particular particle: l_3 labels a layer of particles parallel to the surface plane, l_1 and l_2 specify the points in the two-dimensional lattice (or net) which spans a plane, and κ distinguishes different particles in the unit cell associated with a particular $\vec{\mathrm{l}}$.[46] We assume that the same two-dimensional lattice can be used for all the layers, but the contents of the unit cell associated with a lattice point and a plane may differ from one layer to another.

We take the z axis to be normal to the surface and represent the unit normal by $\hat{z}$. Since two-dimensional vectors, with only x and y components, are frequently encountered in surface physics, we adopt the convention of writing such vectors with bars over roman type, e.g.,

$$\bar{\mathrm{r}}=(x, y, 0)=(x, y)\ , \quad \vec{\mathrm{r}}=(x, y, z)=\bar{\mathrm{r}}+r_z\hat{z}\ . \tag{2.2}$$

We adopt a similar convention for the set of numbers $\vec{\mathrm{l}}$:

$$\vec{\mathrm{l}}=(l_1, l_2, l_3), \qquad \bar{\mathrm{l}}=(l_1, l_2)\ . \tag{2.3}$$

We will also label symmetry points in a two-dimensional Brillouin zone by barred letters (e.g., $\bar{\Gamma}$) to distinguish them from points in a three-dimensional zone (e.g., Γ).

The position of the two-dimensional lattice point $\bar{\mathrm{l}}$ is represented by $\bar{\mathrm{r}}_0^{\bar{\mathrm{l}}}=(x_0^{\bar{\mathrm{l}}}, y_0^{\bar{\mathrm{l}}}, 0)$. In terms of the primitive lattice vectors $\bar{\mathrm{a}}_1$ and $\bar{\mathrm{a}}_2$,

$$\bar{\mathrm{r}}_0^{\bar{\mathrm{l}}}=l_1\bar{\mathrm{a}}_1+l_2\bar{\mathrm{a}}_2\ . \tag{2.4}$$

A two-dimensional reciprocal lattice vector $\bar{\mathrm{G}}$ is given by

$$\bar{\mathrm{G}}=n_1\bar{\mathrm{b}}_1+n_2\bar{\mathrm{b}}_2\ , \tag{2.5}$$

where n_1 and n_2 are integers and the primitive-reciprocal lattice vectors $\bar{\mathrm{b}}_1$ and $\bar{\mathrm{b}}_2$ are defined by

$$\bar{\mathrm{b}}_1=2\pi\frac{\bar{\mathrm{a}}_2\times\hat{z}}{\bar{\mathrm{a}}_1\cdot\bar{\mathrm{a}}_2\times\hat{z}}\ , \quad \bar{\mathrm{b}}_2=2\pi\frac{\hat{z}\times\bar{\mathrm{a}}_1}{\bar{\mathrm{a}}_2\cdot\hat{z}\times\bar{\mathrm{a}}_1}\ . \tag{2.6}$$

Equation (2.1) can be rewritten

$$\vec{\mathrm{r}}(\vec{\mathrm{l}}\kappa)=\bar{\mathrm{r}}_0^{\bar{\mathrm{l}}}+\vec{\mathrm{r}}_0(l_3\kappa)+\vec{\mathrm{u}}(\vec{\mathrm{l}}\kappa)\ . \tag{2.7}$$

Here $\vec{\mathrm{r}}_0(l_3\kappa)$ is the "basis vector" that gives the mean position of a particle (of the κth type in the l_3th layer) within the large unit cell associated with the lattice point $\bar{\mathrm{l}}$. Its projection on the xy plane is $\bar{\mathrm{r}}_0(l_3\kappa)$.

As usual, we make the adiabatic approximation and assume that the total energy of the system can be taken to be a function of the particle positions, and we expand this energy Φ in a Taylor series:

$$\Phi-(\Phi)_0=\sum_{\vec{\mathrm{l}}\kappa\alpha}\Phi_\alpha(\vec{\mathrm{l}}\kappa)u_\alpha(\vec{\mathrm{l}}\kappa)$$

$$+\frac{1}{2}\sum_{\vec{l}\kappa\alpha}\sum_{\vec{l}'\kappa'\beta}\Phi_{\alpha\beta}(\vec{l}\kappa;\vec{l}'\kappa')u_\alpha(\vec{l}\kappa)u_\beta(\vec{l}'\kappa')+\cdots\,, \tag{2.8}$$

where

$$\Phi_\alpha(\vec{l}\kappa)=\left(\frac{\partial\Phi}{\partial u_\alpha(\vec{l}\kappa)}\right)_0\,, \tag{2.9}$$

$$\Phi_{\alpha\beta}(\vec{l}\kappa;\vec{l}'\kappa')=\left(\frac{\partial^2\Phi}{\partial u_\alpha(\vec{l}\kappa)\partial u_\beta(\vec{l}'\kappa')}\right)_0\,. \tag{2.10}$$

The subscript "0" indicates that the quantities in large parens are evaluated with all particles at their mean positions.

We now make the quasiharmonic approximation, which consists of neglecting all terms but the second on the right-hand side of Eq. (2.8). The sum of the first term and the third, fourth, etc., are regarded as a "small" perturbation. In this approximation, the equations of motion are

$$M_\kappa(l_3)\frac{d^2}{dt^2}u_\alpha(\vec{l}\kappa)=-\sum_{\vec{l}\;\kappa\beta}\Phi_{\alpha\beta}(\vec{l}\kappa;\vec{l}'\kappa')u_\beta(\vec{l}'\kappa')\,. \tag{2.11}$$

Notice that in the full quasiharmonic approximation the force constants $\Phi_{\alpha\beta}(\vec{l}\kappa;\vec{l}'\kappa')$ are to be evaluated at the mean positions of the particles, with thermal expansion taken into account, rather than at the positions of static equilibrium. In the strict harmonic approximation, thermal expansion is neglected and the force constants are evaluated at the static-equilibrium positions. The first term in Eq. (2.8) then vanishes identically. Notice that even in the harmonic approximation, as defined above, the static relaxation of particles near the surface is to be taken into account.

The present formulation encompasses the following varieties of harmonic or quasiharmonic theories which have been used in studies of surface vibrations: (1) In a "partial harmonic theory" the force constants are determined for particles in the bulk (i.e., deep within the crystal) at their positions of static equilibrium. The force constants for particles near the surface are then taken to be the same as those for particles in the bulk. (2) In a "full harmonic theory" the force constants are evaluated independently for each pair of particles in the crystal, according to Eq. (2.10), with the mean positions taken to be the positions of static equilibrium. The relaxation (static displacements) of the surface particles, and the resulting changes in the force constants near the surface, are taken into account.[47] (3) In a "partial quasiharmonic theory" the force constants are evaluated according to Eq. (2.10) with the mean positions taken to be the positions corresponding to uniform thermal expansion throughout the crystal. The picture is as follows: We start with a static crystal in which the interparticle spacings near the surface are different from those in the bulk owing to static relaxation. We then allow the particles to vibrate, and the crystal will consequently expand. In this approximation we assume that the expansion is uniform, so that the spacing between any two particles in the crystal (including those near the surface) increases in proportion to the spacing between any other two particles. (4) In a "full quasiharmonic theory" the force constants are evaluated according to Eq. (2.10) without approximation. The thermal expansion is not assumed to be uniform, i.e., the "differential thermal expansion" near the surface is taken into account.

Since we want to eliminate the effect of edges and corners, we impose periodic-boundary conditions with respect to translations parallel to the surface. Then the crystal is invariant under a translation through a two-dimensional lattice vector, so that the force constants $\Phi_{\alpha\beta}(\vec{l}\kappa;\vec{l}'\kappa')$ depend only on the difference of $\bar{l}'$ and $\bar{l}$:

$$\Phi_{\alpha\beta}(\vec{l}\kappa;\vec{l}'\kappa')=\Phi_{\alpha\beta}(l_3\kappa;l_3'\kappa';\bar{l}'-\bar{l})\,. \tag{2.12}$$

This two-dimensional translational invariance of the force constants implies that the normal-mode solutions to Eq. (2.11) have the form of two-dimensional Bloch functions:

$$u_\alpha(\vec{l}\kappa)=u_\alpha(l_3\kappa)\exp[i\,(q_x x_0^{\bar{l}}+q_y y_0^{\bar{l}}-\omega t)] \tag{2.13}$$

$$=u_\alpha(l_3\kappa)\exp[i(\bar{q}\cdot\bar{r}_0^{\bar{l}}-\omega t)]\,. \tag{2.14}$$

Here $\alpha=x$, y, or z and ω is the vibrational frequency. For later convenience we write

$$u_\alpha(l_3\kappa)=[\bar{N}M_\kappa(l_3)]^{-1/2}\,Q_0\xi_\alpha(l_3\kappa)\,e^{i\bar{q}\cdot\bar{r}_0(l_3\kappa)}\,, \tag{2.15}$$

where $\bar{N}$ is the number of two-dimensional lattice points ($\bar{N}\rightarrow\infty$), $M_\kappa(l_3)$ is the mass of a particle with index κ in the l_3th plane, $\xi_\alpha(l_3\kappa)$ is normalized to unity (see below), and Q_0 gives the amplitude of vibration.

The physically distinct solutions correspond to values of the wave vector $\bar{q}$ lying in the first two-dimensional Brillouin zone (BZ) associated with the two-dimensional lattice. In Fig. 1, the Brillouin zones for the five two-dimensional lattices are depicted with the notation that we will adopt for labeling the symmetry points and lines. This notation is adapted from that given by Koster[48] for three-dimensional lattices. The distinct values of $\omega(\bar{q})$ correspond to values of $\bar{q}$ lying in the irreducible element—i.e., that part of the BZ which, under the two-dimensional symmetry operations of the crystal, can be mapped into the rest of the BZ. In Fig. 1, the irreducible element is the region within the heavy lines.

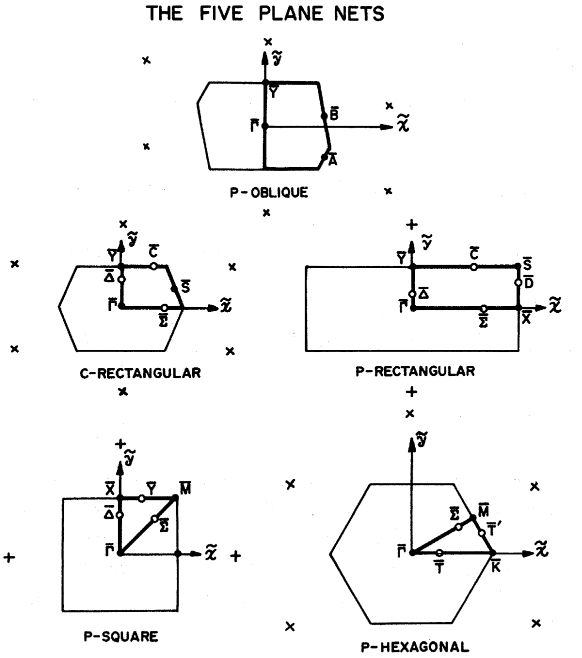

FIG. 1. Brillouin zones for the five two-dimensional lattices. The irreducible element is the area enclosed by heavy lines. The labeling of the symmetry points, and the choice of the $\tilde{x}$ and $\tilde{y}$ axes, are adapted from those of Koster (Ref. 48). The tilde is used to distinguish these axes from the x and y axes of Refs. 22, and 40–42.

If Eqs. (2.14) and (2.15) are used in Eq. (2.11), the result is

$$\sum_{l_3'\kappa'\beta} D_{\alpha\beta}(l_3\kappa; l_3'\kappa'; \bar{q})\xi_\beta(l_3'\kappa'; \bar{q}p) = \omega_p{}^2(\bar{q})\xi_\alpha(l_3\kappa; \bar{q}p) , \tag{2.16}$$

where the dynamical matrix $D_{\alpha\beta}(l_3\kappa; l_3'\kappa'; \bar{q})$ is defined by

$$D_{\alpha\beta}(l_3\kappa; l_3'\kappa'; \bar{q}) = [M_\kappa(l_3)M_{\kappa'}(l_3')]^{-1/2}\sum_{\bar{1}'} \Phi_{\alpha\beta}(\bar{1}\kappa; \bar{1}'\kappa') \times\exp\{i\bar{q}\cdot[\bar{r}_0^{\bar{1}'} + \bar{r}_0(l_3'\kappa') - \bar{r}_0^{\bar{1}} - \bar{r}_0(l_3\kappa)]\} \tag{2.17}$$

$$= [M_\kappa(l_3)M_{\kappa'}(l_3')]^{-1/2}\sum_{\bar{1}'}\Phi_{\alpha\beta}(l_3\kappa; l_3'\kappa'; \bar{1}') \times\exp\{i\bar{q}\cdot[\bar{r}_0^{\bar{1}'} + \bar{r}_0(l_3'\kappa') - \bar{r}_0(l_3\kappa)]\} , \tag{2.18}$$

and the index p is defined below. In rewriting Eq. (2.17) as Eq. (2.18), we have used Eq. (2.12) plus the fact $\bar{r}_0^{\bar{1}'-\bar{1}} = \bar{r}_0^{\bar{1}'} - \bar{r}_0^{\bar{1}}$, according to Eq. (2.4). Also, the summation over $\bar{1}'$ in Eq. (2.17) has been changed to a summation over $(\bar{1} - \bar{1}')$, and $(\bar{1} - \bar{1}')$ has been renamed $\bar{1}'$.

In Eq. (2.16), we have explicitly indicated the dependence on the wave vector $\bar{q}$, and on an index p which distinguishes the different modes corresponding to a particular $\bar{q}$. If there are $s(l_3)$ particles per unit cell in the l_3th layer [i.e., $\kappa = 1, 2, \ldots, s(l_3)$], then $p = 1, 2, \ldots, 3\mathfrak{N}$, where $\mathfrak{N} = \sum_{l_3} s(l_3)$. The eigenvectors $\xi_\alpha(l_3\kappa; \bar{q}p)$ have $3\mathfrak{N}$ components.

Since the $\xi_\alpha(l_3\kappa; \bar{q}p)$ are the eigenvectors of an Hermitian matrix, they can be taken to satisfy the usual orthogonality-normalization condition

$$\sum_{l_3\kappa\alpha} \xi_\alpha(l_3\kappa; \bar{q}p)\xi_\alpha^*(l_3\kappa; \bar{q}p') = \delta_{pp'} \tag{2.19}$$

and the completeness condition

$$\sum\nolimits_p \xi_\alpha(l_3\kappa; \bar{q}p)\xi_\beta^*(l_3'\kappa'; \bar{q}p) = \delta_{\alpha\beta}\delta_{l_3l_3'}\delta_{\kappa\kappa'} . \tag{2.20}$$

Notice that the eigenvectors are normalized to unity over the whole crystal. Also notice that if Eqs. (2.19) and (2.20) are satisfied by a given set of eigenvectors, they will automatically be satisfied for a new set defined by

$$\xi_\alpha'(l_3\kappa; \bar{q}p) = e^{i\psi(p)}\xi_\alpha(l_3\kappa; \bar{q}p) , \tag{2.21}$$

where $\psi(p)$ is a real number which is independent of α, l_3, and κ. The transformation (2.21) will thus produce an acceptable set of eigenvectors if the original set was acceptable.

According to Eqs. (2.16) and (2.18) we have

$$\omega_p(-\bar{q}) = \omega_p(\bar{q}) , \tag{2.22}$$

regardless of crystal structure, if we choose p properly. Also, we have

$$\xi_\alpha(l_3\kappa; -\bar{q}p) = e^{i\eta(p)}\xi_\alpha^*(l_3\kappa; \bar{q}p) . \tag{2.23}$$

If we redefine the eigenvectors for the wave vector $-\bar{q}$ according to Eq. (2.21), with $\psi(p) = -\eta(p)$, then the phase factor in Eq. (2.23) will disappear. We can therefore adopt the convention

$$\xi_\alpha(l_3\kappa; -\bar{q}p) = \xi_\alpha^*(l_3\kappa; \bar{q}p) . \tag{2.24}$$

In the special case of a crystal in which all the particles in a given layer are identical, the κ and κ' indices can be suppressed. Then Eq. (2.16) becomes

$$\sum_{l_3'\beta} D_{\alpha\beta}(l_3l_3'; \bar{q})\xi_\beta(l_3'; \bar{q}p) = \omega_p^2(\bar{q})\xi_\alpha(l_3; \bar{q}p) . \tag{2.25}$$

In this case, $\mathfrak{N} = N_3$, where N_3 is the number of layers in the crystal, so $p = 1, 2, \ldots, 3N_3$. Notice that the dimensionality of the dynamical matrix is the same for a monatomic crystal and a crystal in which each layer is composed of a different species of particle. Layered structures and crystals with adsorbed films are therefore, in this sense, not harder to treat computationally than monatomic crystals with surfaces.

This concludes the formulation of the lattice-dynamics problem. The procedure for calculating the vibrational modes is to determine the dynamical matrix according to Eq. (2.18), and then to determine the eigensystem by solving Eq. (2.16) numerically. In Sec. III, some properties of the vibrational modes are discussed.

III. PROPERTIES OF VIBRATIONAL MODES

A. Displacement Ellipse

The vector $\vec{\xi}(l_3\kappa;\vec{q}p)$ for a fixed l_3 and κ will be called a "polarization vector," since it gives the polarization of a particle of the κth type in the l_3th layer, i.e., it specifies the direction of motion of such a particle when the crystal is vibrating in the mode labeled by $\vec{q}$ and p. If we define a dimensionless quantity $\vec{U}(\vec{l}\kappa)$ by

$$\vec{U}(\vec{l}\kappa)\equiv \mathrm{Re}\vec{\xi}(l_3\kappa)\cos[\vec{q}\cdot\vec{r}_0(\vec{l}\kappa)-\omega t] - \mathrm{Im}\vec{\xi}(l_3\kappa)\sin[\vec{q}\cdot\vec{r}_0(\vec{l}\kappa)-\omega t]\,, \qquad (3.1)$$

then according to Eqs. (2.14) and (2.15),

$$\mathrm{Re}\vec{u}(\vec{l}\kappa)\propto\vec{U}(\vec{l}\kappa)\,. \qquad (3.2)$$

It is evident from these equations that the motion of a particle about its mean position traces out a curve which lies in the plane defined by $\mathrm{Re}\vec{\xi}(l_3\kappa)$ and $\mathrm{Im}\vec{\xi}(l_3\kappa)$. This curve is depicted in Fig. 2.

The curve can be shown to be an ellipse as follows: Let the (x', y', z')-coordinate system be defined such that $\mathrm{Re}\vec{\xi}(l_3\kappa)$ is parallel to the $x'y'$ plane and $\mathrm{Im}\vec{\xi}(l_3\kappa)$ is parallel to the x' axis. If we define

$$\theta=\vec{q}\cdot\vec{r}_0(\vec{l}\kappa)-\omega t\,, \qquad (3.3)$$

then

$$U_{x'}=\mathrm{Re}\xi_{x'}\cos\theta-\mathrm{Im}\xi_{x'}\sin\theta\,, \qquad (3.4)$$

$$U_{y'}/\mathrm{Re}\xi_{y'}=\cos\theta\,. \qquad (3.5)$$

If $\sin\theta$ in Eq. (3.4) is written as $\pm(1-\cos^2\theta)^{1/2}$ and the expression for $\cos\theta$ in Eq. (3.5) is substituted into Eq. (3.4), then one obtains after some algebraic manipulations

$$U_{x'}^2-2\,\frac{\mathrm{Re}\xi_{x'}}{\mathrm{Re}\xi_{y'}}\,U_{x'}U_{y'}+\left(\frac{(\mathrm{Re}\xi_{x'})^2+(\mathrm{Im}\xi_{x'})^2}{(\mathrm{Re}\xi_{y'})^2}\right)U_{y'}^2 =(\mathrm{Im}\xi_{x'})^2\,, \qquad (3.6)$$

which is the equation of an ellipse. We have tacitly assumed that $\mathrm{Re}\xi_{y'}\neq0$ and $\mathrm{Im}\xi_{x'}\neq0$; if either condition does not hold, the path is a straight line.

The major and minor axes of this "displacement ellipse" are given by the maxima and minima of $|\vec{U}|^2$:

$$\frac{d|\vec{U}|^2}{d\theta}=-\sin(2\theta)\left(|\mathrm{Re}\vec{\xi}|^2-|\mathrm{Im}\vec{\xi}|^2\right) -2\cos(2\theta)(\mathrm{Re}\vec{\xi})\cdot(\mathrm{Im}\vec{\xi})\,. \qquad (3.7)$$

A zero derivative occurs when

$$\theta=-\frac{1}{2}\tan^{-1}\frac{2(\mathrm{Re}\vec{\xi})\cdot(\mathrm{Im}\vec{\xi})}{|\mathrm{Re}\vec{\xi}|^2-|\mathrm{Im}\vec{\xi}|^2}\quad. \qquad (3.8)$$

Given $\vec{\xi}(l_3\kappa)$, therefore, one can determine the major and minor axes by finding the solutions to Eq. (3.8) and then substituting into the equation $\vec{U}=\mathrm{Re}\vec{\xi}\cos\theta-\mathrm{Im}\vec{\xi}\sin\theta$.

In general, the displacement ellipse can have an arbitrary orientation. However, suppose that the crystal has the following symmetry: Each particle lies on an axis, normal to the surface, such that a rotation of 180° about this axis carries every particle in the crystal into a position formerly occupied by an equivalent particle (i.e., one with the same l_3 and κ). If this condition holds, then we will say that the crystal, or surface, has "axial-inversion symmetry." We will now show that in such crystals the displacement ellipse has one axis perpendicular to the surface and the other parallel to the surface.

Consider the particle labeled by l_3 and κ for which $\bar{l}=0$. Because of the symmetry described above, for every other particle labeled by $\bar{l}'$, l_3', and κ', there is an equivalent particle labeled by $\bar{l}''$, l_3', and κ' such that

$$[\bar{r}_0^{\bar{l}''}+\bar{r}_0(l_3'\kappa')]-\bar{r}_0(l_3\kappa) =-\{[\bar{r}_0^{\bar{l}'}+\bar{r}_0(l_3'\kappa')]-\bar{r}_0(l_3\kappa)\}\,; \qquad (3.9)$$

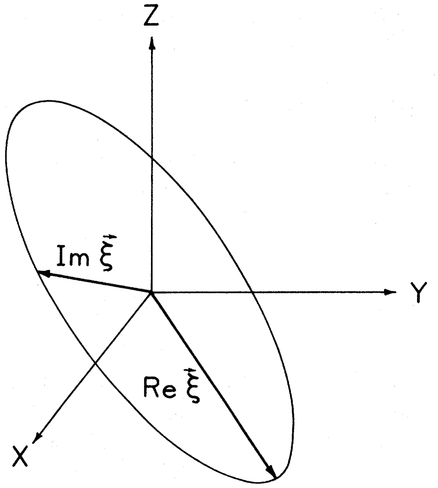

FIG. 2. Path of a particle as it moves about its mean position in a single normal mode with polarization vector $\vec{\xi}(l_3\kappa)$. The vectors from the origin are respectively proportional to $\mathrm{Re}\vec{\xi}$ and $\mathrm{Im}\vec{\xi}$. $\mathrm{Re}\vec{\xi}$ and $\mathrm{Im}\vec{\xi}$ are not necessarily perpendicular, but the path is always an ellipse. If the surface has "axial-inversion symmetry," then $\mathrm{Re}\vec{\xi}$ and $\mathrm{Im}\vec{\xi}$ are perpendicular to one another and one is perpendicular to the surface; one axis of the ellipse is then perpendicular to the surface.

i.e., the $\overline{1}'$ particle and the $\overline{1}''$ particle are the same distance from the original particle, but on opposite sides of the rotational axis which passes through it. The force constants of the $\overline{1}'$ and $\overline{1}''$ particles are related by a rotation of the coordinate system through 180° about this axis: After such a rotation, the position of the $\overline{1}'$ particle in the transformed coordinate system is equivalent to that of the $\overline{1}''$ particle in the original coordinate system. The transformed force constants for the $\overline{1}'$ particle must therefore be equal to the original force constants for the $\overline{1}''$ particle. Equation (2.10) implies that the transformed force constant $\tilde{\Phi}_{\alpha\beta}(l_3\kappa;\, l_3'\kappa';\overline{1}')$ is given by

$$\tilde{\Phi}_{\alpha\beta}(l_3\kappa;\, l_3'\kappa';\overline{1}') = \pm\,\Phi_{\alpha\beta}(l_3\kappa;\, l_3'\kappa';\overline{1}')\ , \tag{3.10}$$

where the plus sign holds if $\alpha=\beta$ or $(\alpha,\beta)=(x,y)$ or $(\alpha,\beta)=(y,x)$, and the minus sign holds otherwise. Therefore we have

$$\Phi_{\alpha\beta}(l_3\kappa;\, l_3'\kappa';\overline{1}'') = \pm\,\Phi_{\alpha\beta}(l_3\kappa;\, l_3'\kappa';\overline{1}')\ . \tag{3.11}$$

Equations (3.9) and (3.11) then imply that

$$\Phi_{\alpha\beta}(l_3\kappa;\, l_3'\kappa';\overline{1}'')\exp\{i\bar{\mathrm{q}}\cdot[\bar{\mathrm{r}}_0^{\overline{1}''}+\bar{\mathrm{r}}_0(l_3'\kappa')-\bar{\mathrm{r}}_0(l_3\kappa)]\}$$

$$=\pm\,(\Phi_{\alpha\beta}(l_3\kappa;\, l_3'\kappa';\overline{1}')$$

$$\times\ \exp\{i\bar{\mathrm{q}}\cdot[\bar{\mathrm{r}}_0^{\overline{1}'}+\bar{\mathrm{r}}_0(l_3'\kappa')-\bar{\mathrm{r}}_0(l_3\kappa)]\})^*. \tag{3.12}$$

The terms on the left- and right-hand sides of Eq. (3.12) are added together in the summation for $D_{\alpha\beta}(l_3\kappa;\, l_3'\kappa')$, according to Eq. (2.18). We thus have the following result:

$$\mathrm{Im}D_{\alpha\beta}(l_3\kappa;\, l_3'\kappa')=0,\quad \alpha=\beta \text{ or } (\alpha,\beta)=(x,y)$$

$$\text{or } (\alpha,\beta)=(y,x)\ , \tag{3.13}$$

$$\mathrm{Re}D_{\alpha\beta}(l_3\kappa;\, l_3'\kappa')=0,\quad \text{otherwise}\ . \tag{3.14}$$

This result implies that the eigenvalue equation (2.16) consists of two decoupled equations:

$$\sum_{l_3'\kappa'\beta} A_{\alpha\beta}(l_3\kappa;\, l_3'\kappa')\xi_\beta^{(i)}(l_3'\kappa';p)$$

$$=\omega_p^2\xi_\alpha^{(i)}(l_3\kappa;p)\ ,\qquad i=1,2, \tag{3.15}$$

where

$$\xi_\alpha^{(1)}(l_3\kappa;p)=\mathrm{Re}\xi_\alpha(l_3\kappa;p),\qquad \alpha=x \text{ or } y \tag{3.16}$$

$$=-\,\mathrm{Im}\xi_\alpha(l_3\kappa;p),\qquad \alpha=z \tag{3.17}$$

$$\xi_\alpha^{(2)}(l_3\kappa;p)=\mathrm{Im}\xi_\alpha(l_3\kappa;p),\qquad \alpha=x \text{ or } y \tag{3.18}$$

$$=\mathrm{Re}\xi_\alpha(l_3\kappa;p),\qquad \alpha=z \tag{3.19}$$

$$A_{\alpha\beta}(l_3\kappa;\, l_3'\kappa')$$

$$=\mathrm{Re}D_{\alpha\beta}(l_3\kappa;\, l_3'\kappa')\ ,\quad \alpha=\beta \text{ or else } \alpha\neq z \text{ and } \beta\neq z \tag{3.20}$$

$$=\mathrm{Im}D_{\alpha\beta}(l_3\kappa;\, l_3'\kappa')\ ,\qquad \beta=z \text{ and } \alpha=x \text{ or } y \tag{3.21}$$

$$=-\,\mathrm{Im}D_{\alpha\beta}(l_3\kappa;\, l_3'\kappa')\ ,\quad \alpha=z \text{ and } \beta=x \text{ or } y\ . \tag{3.22}$$

Since the original matrix with elements $D_{\alpha\beta}(l_3\kappa;\, l_3'\kappa')$ is Hermitian (see Appendix C of Ref. 22), the new matrix defined by Eqs. (3.20)–(3.22) is symmetric. Since the vectors with components $\xi_\alpha^{(1)}(l_3\kappa)$ and $\xi_\alpha^{(2)}(l_3\kappa)$ satisfy the same eigenvalue equation (3.15), they must differ by only a multiplicative constant. (In the interest of simplicity, we will assume here and throughout this section that there is no degeneracy.) Then we have either

$$\mathrm{Im}\xi_\alpha(l_3\kappa;p)=0\ ,\quad \alpha=x \text{ or } y \tag{3.23}$$

$$\mathrm{Re}\xi_\alpha(l_3\kappa;p)=0,\quad \alpha=z \tag{3.24}$$

for all l_3 and κ, or else

$$\mathrm{Re}\xi_\alpha(l_3\kappa;p)=c\,\mathrm{Im}\xi_\alpha(l_3\kappa;p),\quad \alpha=x \text{ or } y \tag{3.25}$$

$$-\,\mathrm{Im}\xi_\alpha(l_3\kappa;p)=c\,\mathrm{Re}\xi_\alpha(l_3\kappa;p),\quad \alpha=z \tag{3.26}$$

where c is a constant independent of l_3 and κ. If Eqs. (3.25) and (3.26) hold, then we can define a new set of eigenvectors with components $\xi'_\alpha(l_3\kappa;p)$ according to Eq. (2.21), with $\tan\psi(p)=c$, so that

$$\xi'_\alpha(l_3\kappa;p)=i\,\mathrm{Im}\xi_\alpha(l_3\kappa;p)/\cos\psi(p),\quad \alpha=x \text{ or } y \tag{3.27}$$

$$\xi'_\alpha(l_3\kappa;p)=\mathrm{Re}\xi_\alpha(l_3\kappa;p)/\cos\psi(p),\qquad \alpha=z\ . \tag{3.28}$$

Unless Eqs. (3.23) and (3.24) hold, therefore, we can always choose $\xi_\alpha(l_3\kappa;p)$ to be purely imaginary for $\alpha=x$ or y and purely real for $\alpha=z$. We will adopt this convention, so that we have the following result:

$$\mathrm{Im}\xi_x(l_3\kappa)=\mathrm{Im}\xi_y(l_3\kappa)=\mathrm{Re}\xi_z(l_3\kappa)=0 \tag{3.29}$$

for all l_3 and κ, or else

$$\mathrm{Re}\xi_x(l_3\kappa)=\mathrm{Re}\xi_y(l_3\kappa)=\mathrm{Im}\xi_z(l_3\kappa)=0 \tag{3.30}$$

for all l_3 and κ. In other words, either $\mathrm{Im}\vec{\xi}(l_3\kappa)$ is perpendicular to the surface and $\mathrm{Re}\vec{\xi}(l_3\kappa)$ is parallel to the surface, or else $\mathrm{Im}\vec{\xi}(l_3\kappa)$ is parallel and $\mathrm{Re}\vec{\xi}(l_3\kappa)$ perpendicular.

The assertion in the paragraph preceding Eq. (3.9) has now been proved: $\mathrm{Re}\vec{\xi}(l_3\kappa)$ and $\mathrm{Im}\vec{\xi}(l_3\kappa)$ are perpendicular to each other, so it is apparent from Eq. (3.1) that these vectors give the axes of the ellipse. Since either $\mathrm{Re}\vec{\xi}(l_3\kappa)$ or $\mathrm{Im}\vec{\xi}(l_3\kappa)$ is normal to the surface, one axis of the ellipse is normal to the surface.

As a final remark on surfaces with axial-inversion symmetry, we mention that the eigenvalue problem for such surfaces has now been considerably reduced. Suppose that we define a normalized vector $a_\alpha(l_3\kappa)$ which is a solution to

$$\sum_{l_3'\kappa'\beta} A_{\alpha\beta}(l_3\kappa;\, l_3'\kappa')a_\beta(l_3'\kappa') = \omega^2 a_\alpha(l_3\kappa)\ . \qquad (3.31)$$

Then according to Eqs. (3.16)–(3.19) and (3.29) and (3.30)

$$|a_\alpha(l_3\kappa)| = |\xi_\alpha(l_3\kappa)|\ . \qquad (3.32)$$

As long as we are interested in calculating only the vibrational frequencies ω and the magnitude of the polarization vectors,[49] the original problem expressed in Eq. (2.16) can thus be reduced to that of Eq. (3.31). In other words, we can calculate the eigensystem of a real symmetric matrix rather than that of the original complex matrix. In the Appendix, it is shown that a further reduction is possible if the crystal has a center of inversion.

B. Waves Along Symmetry Directions

Now we return to the more general problem of an arbitrary surface. We will use the term "subband" to refer to the range of allowed frequencies for a particular set of modes at a fixed value of the propagation vector $\vec{q}$.[50] A subband corresponding to a set of bulk modes will be called a "bulk subband." Any mode whose frequency lies outside the bulk subbands must be a surface mode. However, the converse is not necessarily true; i.e., it is possible for a surface mode to have a frequency lying within the bulk subbands, as we will now show.

Suppose that each particle lies on one of a set of parallel planes perpendicular to the surface, and that a reflection through any one of these planes carries every particle in the crystal into a position which was formerly occupied by an equivalent particle (i.e., one with the same l_3 and κ). We will then choose a typical such plane and say that the crystal, or surface, has "complete reflection symmetry" with respect to the typical plane.

First consider the case when the crystal has "complete reflection symmetry" with respect to the xz plane. When $q_y = 0$, it is then easy to show the following, using Eqs. (2.10) and (2.18) together with arguments like those leading up to Eq. (3.12): For every term in the summation for $D_{\alpha\beta}(l_3\kappa;\, l_3'\kappa';\, q_x0)$, there is another term which is equal to ± 1 times the first term. If $\alpha \neq \beta$ and either $\alpha = y$ or $\beta = y$, then the minus sign holds; otherwise the plus sign holds. It follows that

$$D_{\alpha\beta}(l_3\kappa;\, l_3'\kappa';\, q_x0) = 0, \quad \alpha \neq \beta \text{ and either } \alpha = y \text{ or } \beta = y\ . \qquad (3.33)$$

The eigenvalue equation (2.16) then decouples into the pair of equations

$$\sum_{\beta=x,z}\sum_{l_3'} D_{\alpha\beta}(l_3\kappa;\, l_3'\kappa';\, q_x0)\xi_\beta(l_3'\kappa';\, q_x0p) = \omega_p^2(q_x0)\xi_\alpha(l_3\kappa;\, q_x0p), \quad \alpha = x \text{ or } z \qquad (3.34)$$

$$\sum_{l_3'} D_{yy}(l_3\kappa;\, l_3'\kappa';\, q_x0)\xi_y(l_3'\kappa';\, q_x0p) = \omega_p^2(q_x0)\xi_y(l_3\kappa;\, q_x0p)\ . \qquad (3.35)$$

There will therefore be two classes of solutions—those with $\xi_y(l_3\kappa) = 0$ for all l_3 and κ, and those with $\xi_x(l_3\kappa) = \xi_z(l_3\kappa) = 0$ for all l_3 and κ. [If ξ_x, ξ_y, and ξ_z are all nonzero, then we can define two new eigenvectors, one with components $\xi_y' = 0$, $\xi_x' \neq 0$, $\xi_z' \neq 0$, and the other with components $\xi_y'' \neq 0$, $\xi_x'' = \xi_z'' = 0$, each of which satisfies Eqs. (3.34) and (3.35), so that there is degeneracy in this case.] Now suppose that the frequency $\omega_p(q_x0)$ lies within a bulk subband that is associated with bulk modes belonging to only one class. If the mode labeled by p belongs to the same class, then it should ordinarily be a mixed mode; however, if the mode labeled by p belongs to a different class, then it must be a surface mode, since there is no bulk mode of its class with frequency $\omega_p(q_x0)$.

In short, we have the following result: In some cases there will be a symmetry-induced decoupling of the eigenvalue equation which will lead to a division of the modes into two classes, with the members of one class automatically orthogonal to those of the other class. In such a case we will say that there is a "partitioning" of the modes into mutually orthogonal classes. Then any mode whose frequency lies within the bulk subbands for its class will ordinarily be a mixed mode, and any mode whose frequency lies outside the bulk subbands for its class will always be a surface mode. If there is no partitioning, a simpler statement surfices: A mode lying within the bulk subbands is ordinarily a mixed mode, and a mode lying outside the bulk subbands is always a surface mode.

We can generalize the above result for the xz plane: If the surface has "complete reflection symmetry" with respect to any given plane, then for any $\vec{q}$ which is parallel to this plane there will be a partitioning into two mutually orthogonal classes of modes. Two-thirds of the modes will belong to the first class and will be polarized strictly in the sagittal plane; i.e., $\vec{\xi}(l_3\kappa)$ will lie in the plane of $\vec{q}$ and $\hat{z}$. One-third of the modes will belong to the second class and will be pure shear-horizontal (SH) waves,[51] i.e., $\vec{\xi}(l_3\kappa)$ will be perpendicular to $\vec{q}$ and $\hat{z}$.

To prove these assertions, we translate the symmetry plane to the origin, and then rotate the coordinate system until the translated plane coincides with the $x'z$ plane in the new (x', y', z) coordinate system. Then the surface will have "complete reflection symmetry" with respect to the $x'z$ plane. Consequently, for $q_{y'} = 0$ there will be a partitioning into two classes, with $\xi_{y'} = 0$ for the first class and $\xi_{x'} = \xi_{z'} = 0$ for the second class. It is evident that $\bar{\mathrm{q}} = (q_{x'}, 0)$ is parallel to the $x'z$ plane, and thus to the original symmetry plane, and that the $\vec{\xi}$ have the polarizations described above. Finally, there are twice as many modes in the first class as in the second, since Eq. (3.34) has twice as many solutions as Eq. (3.35).

C. Slab-Shaped Crystals with a Center of Inversion

Up to this point, only two-dimensional symmetries have been discussed, and no symmetry has been assumed with respect to the third dimension. For the remainder of this section, however, we will assume that the crystal has a finite thickness and that the following is true: Consider an arbitrary particle which is labeled by κ and $(-l_3)$, which is associated with the lattice point $\bar{\mathrm{l}}$, and which has the mean position $\vec{\mathrm{r}}_0(\bar{\mathrm{l}}, -l_3, \kappa)$. Then there is some particle, identical to the first particle in its mass and other properties, which is labeled by κ and l_3, which is associated with some lattice point $\bar{\mathrm{l}}''$, and which has the mean position $\vec{\mathrm{r}}_0(\bar{\mathrm{l}}'', l_3, \kappa)$, such that

$$\vec{\mathrm{r}}_0(\bar{\mathrm{l}}'', l_3, \kappa) = -\vec{\mathrm{r}}_0(\bar{\mathrm{l}}, -l_3, \kappa) \; . \tag{3.36}$$

If this condition holds, we will say that the slab-shaped crystal has a "three-dimensional center of inversion." We will not assume any symmetries besides this one (and the two-dimensional periodicity).

According to Eqs. (2.12) and (2.17),

$$\begin{aligned} D_{\alpha\beta}(-l_3\kappa;\; -l_3'\kappa') &= [M_\kappa(l_3)M_{\kappa'}(l_3')]^{-1/2} \textstyle\sum_{l'} \Phi_{\alpha\beta}(-l_3\kappa;\, -l_3'\kappa';\, \bar{\mathrm{l}}' - \bar{\mathrm{l}}) \\ &\quad \times \exp\{i\bar{\mathrm{q}} \cdot [\bar{\mathrm{r}}_0(\bar{\mathrm{l}}', -l_3', \kappa') - \bar{\mathrm{r}}_0(\bar{\mathrm{l}}, -l_3, \kappa)]\} \; , \end{aligned} \tag{3.37}$$

since $M_\kappa(-l_3) = M_\kappa(l_3)$ according to the comments preceding Eq. (3.36). If we substitute $\bar{\mathrm{l}}'$, l_3', and κ' into Eq. (3.36), we obtain

$$\vec{\mathrm{r}}_0(\bar{\mathrm{l}}''', l_3', \kappa') = -\vec{\mathrm{r}}_0(\bar{\mathrm{l}}', -l_3', \kappa') \; , \tag{3.38}$$

where we have used $\bar{\mathrm{l}}'''$ to label the lattices point corresponding to the "partner" of the $\bar{\mathrm{l}}'$, $-l_3'$, κ' particle. Using arguments like those leading up to Eq. (3.11), one can show that

$$\Phi_{\alpha\beta}(l_3\kappa;\, l_3'\kappa';\, \bar{\mathrm{l}}''' - \bar{\mathrm{l}}'') = \Phi_{\alpha\beta}(-l_3\kappa;\, -l_3'\kappa';\, \bar{\mathrm{l}}' - \bar{\mathrm{l}}) \; , \tag{3.39}$$

in view of Eqs. (3.36) and (3.38). We also have from these equations

$$\begin{aligned} &\bar{\mathrm{r}}_0(\bar{\mathrm{l}}''', l_3', \kappa') - \bar{\mathrm{r}}_0(\bar{\mathrm{l}}'', l_3, \kappa) \\ &\qquad = -[\bar{\mathrm{r}}_0(\bar{\mathrm{l}}', -l_3', \kappa') - \bar{\mathrm{r}}_0(\bar{\mathrm{l}}, -l_3, \kappa)] \; . \end{aligned} \tag{3.40}$$

Equations (3.37), (3.39), and (3.40) give

$$\begin{aligned} D_{\alpha\beta}(-l_3\kappa;\; -l_3'\kappa') &= [M_\kappa(l_3)M_{\kappa'}(l_3')]^{-1/2} \textstyle\sum_{l'} \Phi_{\alpha\beta}(l_3\kappa;\, l_3'\kappa';\, \bar{\mathrm{l}}''' - \bar{\mathrm{l}}'') \\ &\quad \times \exp\{-i\bar{\mathrm{q}} \cdot [\bar{\mathrm{r}}_0(\bar{\mathrm{l}}''', l_3', \kappa') - \bar{\mathrm{r}}_0(\bar{\mathrm{l}}'', l_3, \kappa)]\} \; , \end{aligned} \tag{3.41}$$

where $\bar{\mathrm{l}}'''$ implicitly depends on $\bar{\mathrm{l}}'$ through Eq. (3.38). However, it makes no difference whether we sum over $\bar{\mathrm{l}}'$ or $\bar{\mathrm{l}}'''$ in Eq. (3.41), since in either case $\bar{\mathrm{l}}'''$ ranges over the complete set of lattice points. Therefore, if we change the summation in Eq. (3.41) to a summation over $\bar{\mathrm{l}}'''$, then change it again to a summation over $(\bar{\mathrm{l}}''' - \bar{\mathrm{l}}'')$, and finally rename $(\bar{\mathrm{l}}''' - \bar{\mathrm{l}}'')$ to call it $\bar{\mathrm{l}}'$, we have

$$\begin{aligned} D_{\alpha\beta}(-l_3\kappa;\; -l_3'\kappa') &= [M_\kappa(l_3)M_{\kappa'}(l_3')]^{-1/2} \textstyle\sum_{l'} \Phi_{\alpha\beta}(l_3\kappa;\, l_3'\kappa'\bar{\mathrm{l}}') \\ &\quad \times \exp\{-i\bar{\mathrm{q}} \cdot [\bar{\mathrm{r}}_0^{\bar{\mathrm{l}}'} + \bar{\mathrm{r}}_0(l_3'\kappa') - \bar{\mathrm{r}}_0(l_3\kappa)]\} \end{aligned} \tag{3.42}$$

$$= D^*_{\alpha\beta}(l_3\kappa;\, l_3'\kappa') \; , \tag{3.43}$$

according to Eq. (2.18).

From Eqs. (2.16) and (3.43), it follows that

$$\xi_\alpha(-l_3\kappa; p) = e^{i\eta(p)}\xi^*_\alpha(l_3\kappa; p) \; . \tag{3.44}$$

We can always change to a new set of eigenvectors according to Eq. (2.21) with $\psi(p) = -\frac{1}{2}\eta(p)$:

$$\xi'_\alpha(l_3\kappa; p) = e^{-i\eta(p)/2}\xi_\alpha(l_3\kappa; p) \; . \tag{3.45}$$

Then we have $\xi'_\alpha(-l_3\kappa; p) = \xi'^*_\alpha(l_3\kappa; p)$. We can thus always take

$$\xi_\alpha(-l_3\kappa; p) = \xi^*_\alpha(l_3\kappa; p) \; , \tag{3.46}$$

and we will do so.[52]

In a crystal with a three-dimensional center of inversion, all surface modes will occur in nearly degenerate pairs, provided that the thickness of the crystal is much larger than the attenuation depth of the modes in question. If the eigenvector associated with one mode has components $\xi_\alpha(l_3\kappa; p_1)$, the other mode in the pair will have an eigenvector with components

$$\xi_\alpha(l_3\kappa; p_2) \pm i\xi_\alpha(l_3\kappa; p_1) \; , \tag{3.47}$$

where the plus sign holds for $l_3 > 0$ and the minus sign for $l_3 < 0$. We will now justify these assertions.

Consider a crystal with an arbitrary, very large thickness which has a three-dimensional center of inversion; we will denote this crystal by C. Next, let S^+ and S^- denote semi-infinite crystals that coincide with C for $l_3 \geq 0$ and $l_3 < 0$, respectively. For every particle in the l_3th layer of S^+, having mean position $\vec{\mathrm{r}}_0(\vec{\mathrm{l}}\kappa)$, there is an identical particle in the layer of S^- labeled by $(-l_3)$, having mean position $-\vec{\mathrm{r}}_0(\vec{\mathrm{l}}\kappa)$, because of the inversion symmetry of C. Consequently, the following is true: Let $u_\alpha^{(+)}(\vec{\mathrm{l}}\kappa; \bar{\mathrm{q}}p)$ represent a normal mode in S^+. According to Eqs. (2.14) and (2.15) we have

$$u_\alpha^{(+)}(\vec{\mathrm{l}}\kappa; \bar{\mathrm{q}}p) = [\bar{N} M_\kappa(l_3)]^{-1/2} Q_0 \xi_\alpha^s(l_3\kappa; \bar{\mathrm{q}}p) \times \exp\{i \bar{\mathrm{q}} \cdot [\bar{\mathrm{r}}_0^{\bar{\mathrm{l}}} + \bar{\mathrm{r}}_0(l_3\kappa)] - \omega t\}, \tag{3.48}$$

where the superscript s indicates that this mode is for a semi-infinite crystal. The corresponding mode in S^-, which will be called $u_\alpha^{(-)}(\vec{\mathrm{l}}\kappa; -\bar{\mathrm{q}}p)$, is obtained by letting $\vec{\mathrm{r}}_0(\vec{\mathrm{l}}\kappa) \rightarrow -\vec{\mathrm{r}}_0(\vec{\mathrm{l}}\kappa)$, $l_3 \rightarrow -l_3$:

$$u_\alpha^{(-)}(\vec{\mathrm{l}}\kappa; -\bar{\mathrm{q}}p) = [\bar{N} M_\kappa(-l_3)]^{-1/2} Q_0 \xi_\alpha^s(-l_3\kappa; \bar{\mathrm{q}}p) \times \exp\{-i\bar{\mathrm{q}} \cdot [\bar{\mathrm{r}}_0^{\bar{\mathrm{l}}} + \bar{\mathrm{r}}_0(l_3\kappa)] - \omega t\}. \tag{3.49}$$

Equation (2.24) implies that

$$u_\alpha^{(-)}(\vec{\mathrm{l}}\kappa; \bar{\mathrm{q}}p) = [\bar{N} M_\kappa(-l_3)]^{-1/2} Q_0 \xi_\alpha^{s*}(-l_3\kappa; \bar{\mathrm{q}}p) \times \exp\{i\bar{\mathrm{q}} \cdot [\bar{\mathrm{r}}_0^{\bar{\mathrm{l}}} + \bar{\mathrm{r}}_0(l_3\kappa)] - \omega t\}, \tag{3.50}$$

and Eq. (2.22) implies that the modes in Eqs. (3.48)–(3.50) have the same frequency. Now suppose that these modes are localized at the surface and consider the following thought experiment: We cut both S^+ and S^- into two pieces, the first piece consisting of the particles for which $l_3 \geq 0$ and the second consisting of those for which $l_3 < 0$. We join the $l_3 \geq 0$ piece of S^+ to the $l_3 < 0$ piece of S^-. The resulting crystal is identical to C. Since C has an arbitrarily large thickness, the surface modes will be only infinitesimally affected by our surgery, and to an arbitarily good approximation the surface modes in Eqs. (3.48) and (3.50) will still be normal modes of C. They will also be degenerate, according to the comment following Eq. (3.50), so any linear combination

$$u_\alpha(\vec{\mathrm{l}}\kappa; \bar{\mathrm{q}}p) = [\bar{N} M_\kappa(l_3)]^{-1/2} Q_0 [a \xi_\alpha^s(l_3\kappa; \bar{\mathrm{q}}p) + b \xi_\alpha^{s*}(-l_3\kappa; \bar{\mathrm{q}}p)] \times \exp\{i\bar{\mathrm{q}} \cdot [\bar{\mathrm{r}}_0^{\bar{\mathrm{l}}} + \bar{\mathrm{r}}_0(l_3\kappa)] - \omega t\} \tag{3.51}$$

will also be a normal mode of C [In getting from Eq. (3.50) to (3.51), we have used the fact that $M_\kappa(-l_3) = M_\kappa(l_3)$ in C.]; i.e., in the normal mode for C given in Eqs. (2.14) and (2.15), we have

$$\xi_\alpha(l_3\kappa; \bar{\mathrm{q}}p) = a \xi_\alpha^s(l_3\kappa; \bar{\mathrm{q}}p) + b \xi_\alpha^{s*}(-l_3\kappa; \bar{\mathrm{q}}p). \tag{3.52}$$

We can satisfy Eq. (3.46) with the choices $a = b = 1$ or $a = -b = i$, so that the surface mode $\xi_\alpha^s(l_3\kappa; p)$ in the semi-infinite crystal leads to the degenerate pair of surface modes in C given by

$$\xi_\alpha(l_3\kappa; p_1) = \xi_\alpha^s(l_3\kappa; p) + \xi_\alpha^{s*}(-l_3\kappa; p), \tag{3.53}$$

$$\xi_\alpha(l_3\kappa; p_2) = i[\xi_\alpha^s(l_3\kappa; p) - \xi_\alpha^{s*}(-l_3\kappa; p)], \tag{3.54}$$

which are adapted to the inversion symmetry of C. Equation (3.47) follows immediately, since we can neglect the second term in Eqs. (3.53) and (3.54) for $l_3 > 0$, to an arbitrarily good approximation, and we can neglect the first term for $l_3 < 0$.

If the thickness of the crystal is not very large with respect to the attenuation depth of $\xi_\alpha^s(l_3\kappa; p)$, then the degeneracy of $\xi_\alpha(l_3\kappa; p_1)$ and $\xi_\alpha(l_3\kappa; p_2)$ is broken and Eqs. (3.47), (3.53), and (3.54) are only approximately true.

IV. CONCLUSION

The purpose of this paper was to provide a general formulation of the lattice-dynamics problem for a crystal with one or two surfaces. It should be regarded as complementary to the paper on the dynamics of a semi-infinite crystal by Feuchtwang.[37] Feuchtwang's treatment was based on a representation of the vibrational modes in terms of three-dimensional Bloch functions (with a complex k_z). Here we have not used such a representation. The present formulation is also more general in that no assumption was made concerning the range of the interaction. Feuchtwang's work, which involved a more careful treatment of the difficulties peculiar to a semi-infinite crystal, was oriented more toward formal conclusions than actual calculations, whereas one of the primary objectives of the present work was to provide a framework for calculations of vibrational surface properties. Another objective was to determine some of the properties of the vibrational modes, in order to explain the results of calculations[40] and possible future experiments.

Section II was largely devoted to establishing a serviceable notation. In particular, the convention was adopted of writing two-dimensional vectors in roman type with a superior bar (e.g., $\bar{\mathrm{r}}$) in order to distinguish them from the corresponding three-dimensional vectors (e.g., $\vec{\mathrm{r}}$). We have found this convention to be convenient and not likely to cause confusion. Also, a system of labeling the symmetry points in a two-dimensional Brillouin zone was adopted. This system was derived from that of

Koster for three-dimensional lattices. In the case of a square lattice, it is in essential agreement with the notation in a number of previous publications.

Also in Sec. II, we discussed the various versions of the quasiharmonic approximation used in studies of surface-lattice vibrations. The eigenvalue equation for the normal-mode frequencies was obtained in the usual way, with the assumption of the adiabatic approximation, the quasiharmonic approximation, and two-dimensional periodicity.

In Sec. III, the properties of the vibrational modes were considered. For an arbitrary crystal, a particle moves in an elliptical path about its mean position if the crystal is vibrating in a single normal mode. This ellipse may have any orientation in general, but if the crystal has "axial-inversion symmetry" then one axis of the ellipse is normal to the surface. [This condition holds, for example, in the case of an fcc crystal with one atom per unit cell which has a (100) or (110) surface.] For such crystals, the original dynamical matrix can always be reduced to a real symmetric matrix of the same size. If the crystal has a three-dimensional center of inversion, then the eigenvalue problem can be reduced still further; the final result is a pair of eigenvalue equations, each involving a real symmetric matrix which is (approximately) one-quarter the size of the original matrix. These reductions can be useful in calculations, since the required computer time and memory are greatly decreased.

In the case of any crystal with a finite thickness and a three-dimensional center of inversion, we can choose $\xi_\alpha(-l_3\kappa)=\xi_\alpha^*(l_3\kappa)$. The dynamical matrix for such a crystal can always be reduced to a real symmetric matrix of the same size. The surface modes will always occur in nearly degenerate pairs, if the thickness is large compared to the penetration depth of the modes.

If the crystal has "complete reflection symmetry" with respect to some plane normal to the surface, then for any wave vector $\bar{q}$ parallel to this plane the vibrational modes "partition" into two classes. The modes in one class are polarized strictly within the sagittal plane, which contains $\bar{q}$ and the normal to the surface. The modes in the other class are polarized strictly perpendicular to the sagittal plane.[53] Whenever there is such a "partitioning" into several mutually orthogonal classes of modes, it is possible for surface modes of one class to exist within the bulk subbands for another class. In fact, a mode which lies outside the bulk subbands for its class *must* be a surface mode.

Regardless of crystal symmetry or the direction of $\bar{q}$, any mode whose frequency lies above or below the bulk subbands for its $\bar{q}$, or falls in a gap between the bulk subbands, must be a surface mode.

Finally, we mention that there is no general restriction concerning the dependence of the amplitude or polarization of a vibrational mode on the distance from the surface.[54] In general, the polarization for a given mode can change from one layer to the next. For example, the particles in one layer may vibrate perpendicular to the surface while those in an adjacent layer vibrate parallel to the surface. In general, the amplitude of a surface mode need not decrease monotonically, or even regularly, with distance from the surface, and it certainly need not decrease exponentially.

APPENDIX

In this Appendix we show how the eigenvalue equation for a surface with axial-inversion symmetry can be further reduced if the crystal also has a three-dimensional center of inversion. Let us define

$$B_{\alpha\beta}(l_3\kappa;\, l_3'\kappa') = W_{\alpha\beta}(l_3\kappa;\, l_3'\kappa')\,,$$

$$(\alpha,\beta)=(x,x),\ (y,y),\ (x,y)\ \text{or}\ (y,x),\quad l_3\geq 0\,,\quad l_3'\geq 0 \tag{A1}$$

$$= W_{\alpha\beta}(l_3\kappa;\, -l_3'\kappa'),$$

$$(\alpha,\beta)=(x,z)\ \text{or}\ (y,z)\,,\qquad l_3\geq 0,\quad l_3'>0 \tag{A2}$$

$$= W_{\alpha\beta}(-l_3\kappa;\, l_3'\kappa')\,,$$

$$(\alpha,\beta)=(z,x)\ \text{or}\ (z,y)\,,\qquad l_3>0,\quad l_3'\geq 0 \tag{A3}$$

$$= W_{\alpha\beta}(-l_3\kappa;\, -l_3'\kappa'),$$

$$(\alpha,\beta)=(z,z),\qquad l_3>0,\quad l_3'>0 \tag{A4}$$

where $W_{\alpha\beta}(l_3\kappa;\, l_3'\kappa')$ was defined in Eq. (C9) of Ref. 22. We also define

$$C_{\alpha\beta}(l_3\kappa;\, l_3'\kappa') = W_{\alpha\beta}(-l_3\kappa;\, -l_3'\kappa')\,,$$

$$(\alpha,\beta)=(x,x),\ (y,y),\ (x,y),\ \text{or}\ (y,x),\qquad l_3>0,\quad l_3'>0 \tag{A5}$$

$$= W_{\alpha\beta}(-l_3\kappa;\, l_3'\kappa'),$$

$$(\alpha,\beta)=(x,z)\ \text{or}\ (y,z)\,,\qquad l_3>0,\quad l_3'\geq 0 \tag{A6}$$

$$= W_{\alpha\beta}(l_3\kappa;\, -l_3'\kappa'),$$

$$(\alpha,\beta)=(z,x)\ \text{or}\ (z,y)\,,\qquad l_3\geq 0\,,\quad l_3'>0 \tag{A7}$$

$$= W_{\alpha\beta}(l_3\kappa;\, l_3'\kappa')\,,$$

$$(\alpha,\beta)=(z,z)\,,\qquad l_3\geq 0\,,\quad l_3'\geq 0\,. \tag{A8}$$

Finally, we define

$$
\begin{aligned}
b_\alpha(l_3\kappa) &= v_\alpha(l_3\kappa), & \alpha &= x \text{ or } y, & l_3 &\geq 0 & \text{(A9)}\\
&= v_\alpha(-l_3\kappa), & \alpha &= z, & l_3 &> 0 & \text{(A10)}\\
c_\alpha(l_3\kappa) &= v_\alpha(-l_3\kappa), & \alpha &= x \text{ or } y, & l_3 &> 0 & \text{(A11)}\\
&= v_\alpha(l_3\kappa), & \alpha &= z, & l_3 &\geq 0 & \text{(A12)}
\end{aligned}
$$

where $v_\alpha(l_3\kappa)$ was defined in Ref. 22. Equations (3.13) and (3.14) of this paper, in conjunction with Eqs. (C9) and (C12) of Ref. 22, imply that

$$\sum_{\beta\kappa'} \sum_{l_3' \geq 0} B_{\alpha\beta}(l_3\kappa; l_3'\kappa') b_\beta(l_3'\kappa') = \omega^2 b_\alpha(l_3\kappa) \,, \qquad \text{(A13)}$$

$$\sum_{\beta\kappa'} \sum_{l_3' \geq 0}{}'' C_{\alpha\beta}(l_3\kappa; l_3'\kappa') c_\beta(l_3'\kappa') = \omega^2 c_\alpha(l_3\kappa) \,. \qquad \text{(A14)}$$

Here the prime on the first summation indicates that there is no $l_3'=0$ term if $\beta = z$, and the double prime on the second summation indicates that there is no $l_3'=0$ term if $\beta = x$ or y. Using Eq. (C11) of Ref. 22, one can show that

$$B_{\beta\alpha}(l_3'\kappa'; l_3\kappa) = B_{\alpha\beta}(l_3\kappa; l_3'\kappa') \,, \qquad \text{(A15)}$$

$$C_{\beta\alpha}(l_3'\kappa'; l_3\kappa) = C_{\alpha\beta}(l_3\kappa; l_3'\kappa') \,. \qquad \text{(A16)}$$

We have thus reduced the original eigenvalue problem to Eqs. (A13) and (A14), each of which involves a real symmetric matrix which is approximately one-quarter the size of the original matrix. The modes are calculated as follows: First, solve Eqs. (A13) and (A14). For each solution to Eq. (A13), construct a complete eigenvector with components $v_\alpha(l_3\kappa)$ by letting

$$
\begin{aligned}
v_\alpha(l_3\kappa) &= b_\alpha(l_3\kappa) \,, & & l_3 \geq 0 \text{ and } \alpha = x \text{ or } y & \text{(A17)}\\
&= b_\alpha(-l_3\kappa), & & l_3 < 0 \text{ and } \alpha = z & \text{(A18)}\\
&= 0 \,, & & \text{otherwise} \,. & \text{(A19)}
\end{aligned}
$$

For each solution to Eq. (A14), let

$$
\begin{aligned}
v_\alpha(l_3\kappa) &= c_\alpha(l_3\kappa), & & l_3 \geq 0 \text{ and } \alpha = z & \text{(A20)}\\
&= c_\alpha(-l_3\kappa), & & l_3 < 0 \text{ and } \alpha = x \text{ or } y & \text{(A21)}\\
&= 0 \,, & & \text{otherwise} \,. & \text{(A22)}
\end{aligned}
$$

Finally, let

$$
\begin{aligned}
\xi_\alpha(l_3\kappa) &= \tfrac{1}{2} 2^{1/2} [v_\alpha(l_3\kappa) + i v_\alpha(-l_3\kappa)] \,, & l_3 &> 0 & \text{(A23)}\\
&= v_\alpha(l_3\kappa) \,, & l_3 &= 0 & \text{(A24)}\\
&= \tfrac{1}{2} 2^{1/2} [v_\alpha(-l_3\kappa) - i v_\alpha(l_3\kappa)], & l_3 &< 0 \,. & \text{(A25)}
\end{aligned}
$$

If the eigenvectors $b_\alpha(l_3\kappa)$ and $c_\alpha(l_3\kappa)$ form complete orthonormal sets in their subspaces, then the $\xi_\alpha(l_3\kappa)$ given by Eqs. (A23)–(A25) will automatically form a complete orthonormal set satisfying Eqs. (3.29), (3.30), and (3.46).

At this point it is appropriate to make several corrections to Appendix C of Ref. 22: Equation (C13) should be replaced by Eqs. (A23)–(A25) above, and the contents of the third paragraph of Appendix C down to Eq. (C8) should be replaced by the contents of Sec. III C of this paper down to Eq. (3.46). Finally, $\vec{l}_3'$ in Eq. (C3) should be $\vec{l}'$. We also mention several other minor corrections to Ref. 22: In Eq. (3.1), the equality sign should be replaced by a proportionality sign, in Eq. (A7) the plus sign should be an equality sign, and in Ref. 6 the volume number should be 19 rather than 18. In Figs. 8 and 9, $(M\epsilon/\hbar\sigma)^{1/2}$ should be replaced by $(M\epsilon)^{1/2}/\hbar\sigma$, as in Figs. 4, 5, and 12.

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*Research sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, USAF, under Grant Nos. AFOSR-71-1973 and AFOSR-1257-67.

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[1] Lord Rayleigh, London Math. Soc. Proc. 17, 4 (1885); reprinted in *Scientific Papers by Lord Rayleigh*, Vol. 2 (Dover, New York, 1964).

[2] Elastic surface waves are vibrational waves in an elastic medium which are entirely localized at the surface, and surface modes are normal modes of vibration in a discrete lattice which are localized at the surface. Since we are here concerned only with wavelike modes, we will use the terms "wave" and "mode" interchangeably. Mixed modes (which correspond to "leaky surface waves" or "pseudo-surface-waves") are only partially localized at the surface, and bulk modes are not even partially localized.

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[45] In the case of a semi-infinte crystal, some formal precautions are needed in keeping the energy bounded, in normalizing the eigenvectors, and in specifying the boundary conditions at infinity. These matters are discussed in Ref. 37. We will not explicitly take such precautions here, since our primary motivation is calculations for crystals which have a finite thickness.

[46] Here we use the term "unit cell" to refer to the small unit cell associated with a given value of l_1, l_2, and l_3. The actual unit cell associated with a given two-dimensional lattice point (l_1, l_2) extends over all the planes of the slab—i.e., a particle within this large unit cell is specified by l_3 as well as κ.

[47] Our "full harmonic theory" is the same as Feuchtwang's "quasiharmonic theory" (see Ref. 37).

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[49] Only the magnitude $|\xi_\alpha(l_3\kappa)|$ is needed in calculating physical quantities, such as the mean-square amplitudes of vibration, and in determining the main properties of the modes—e.g., which are surface modes, how the surface modes attenuate with distance from the surface, and to what extent the modes are associated with vibrations in the x, y, and z directions. The magnitude does not, of course, give us the relative phases of the various components $\xi_\alpha(l_3\kappa)$.

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[52] It is possible to show that Eqs. (2.24), (3.29), (3.30), and (3.46) are compatible, so we can adopt all three conventions. (The last two, of course, apply only to crystals with special symmetries.)

[53] A special case of this "partitioning" was treated in Ref. 8, and a rather abbreviated discussion was given in Ref. 37.

[54] In a particular case, of course, there may be restrictions imposed by symmetry.