Dynamics of a Semi-Infinite Crystal Lattice in a Quasiharmonic Approximation. II. The Normal-Mode Analysis of a Semi-Infinite Lattice*

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This is the second of two papers dealing with the dynamics of semi-infinite crystal lattices. The present paper is concerned with the small-amplitude vibrations of the atoms in a semi-infinite crystal lattice, with a free boundary, about their actual static equilibrium positions. The static equilibrium configuration (at zero temperature) of such a lattice was discussed in the first paper. The normal modes of the semi-infinite lattice are derived in a harmonic approximation. These modes are represented as linear combinations of elementary bulk modes and elementary surface waves, the latter having a wave vector whose component normal to the surface is complex. All the elementary modes which specify a given normal mode have the same frequency, and the same two-dimensional reduced wave vector $\mathbf{k}_\rho$. The normal modes are again classified into "bulk modes" and "surface modes." The latter represent a vibrational state, consistent with a free boundary, in which the displacements decrease essentially exponentially with the distance from the free boundary. The dispersion relation of the surface modes is discussed in some detail. The theory is developed in terms of the complex vibrational energy-band structure. The approach is related to Heine's analysis of generalized Bloch functions in terms of the complex electronic energy-band structure.

I. INTRODUCTION

THIS is the second in a series of two papers dealing with the dynamics of semi-infinite crystal lattices. In the first paper[1] we considered the static equilibrium configuration of such a lattice. In the present paper we consider the dynamics of small-amplitude vibrations of the lattice particles about their static equilibrium configuration in a semi-infinite lattice with a free boundary.

In the last few years there has been a considerable increase in the interest in surface phenomena in crystalline solids. Among these there are some which are ideally suited to study the equlibrium configuration of the physical boundary layer and its effect on the vibrational spectrum of the crystal. Examples of such phenomena are the diffraction and thermal diffuse scattering of low-energy electrons from a single crystal and the Mössbauer effect from a nucleus in the boundary layer. In order to extract from these experiments as much information as possible concerning the surface structure and its vibrational effects, we need a formulation of the dynamics of semi-infinite crystal lattices which is conceptually simple, and most transparent in its formal conclusions. It is, however, not necessary that this formulation be particularly suitable for *a priori* calculations.

The classical theory of lattice dynamics was formulated by Born and von Kármán,[2] and extended by Born and Huang,[3] Leibfried,[4] Ludwig and Leibfried,[5] and Maradudin, Montroll, and Weiss.[6] An outstanding advantage of this theory is its formal simplicity. This feature of the theory follows primarily from the imposition of the so-called periodic boundary conditions on the lattice, which in effect restrict the theory to infinite crystals; hence it can only apply to the analysis of bulk effects.

The effect of surfaces on the dynamics of solids was first investigated by means of the elastic-continuum model. These investigations were primarily extensions of Rayleigh's original work on surface waves in anisotropic elastic medium.[7] During the last two decades, several investigations of the surface effects on the dynamics of crystal lattices have been reported in the literature. Ledermann established that vibrational states with energy in intervals which are forbidden by periodic boundary conditions may exist.[8] The nature of these so-called surface modes was examined in considerable detail by Lifshitz,[9] who used Green's-function techniques, originally developed for the discussion of localized-impurity–induced vibrational modes. Similar techniques were used by Maradudin and Wallis in their analysis of surface contributions to the low-temperature

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specific heat.[10] Wallis and co-workers have used a less formal approach to calculate explicit dispersion relations for surface modes. Those workers used rather simple explicit models which they analyzed numerically.[11] This work was discussed by Maradudin in a comprehensive review article.[12] All of this work explicitly neglects the fact that the harmonic approximation for the vibrational states of the semi-infinite solid refers explicitly to small-amplitude vibrations about the equilibrium configuration of the semi-infinite lattice. More precisely it is assumed that the latter does not differ significantly from the corresponding configuration for the infinite lattice. In fact, only recently has there been any attempt to consider the equilibrium structure of the free surface of a semi-infinite lattice. This investigation was based, however, on a one-dimensional monatomic model.[13] In the present paper we wish to formulate the harmonic approximation for the semi-infinite lattice on the basis of our analysis of the static equilibrium configuration of this system, which was made in the first paper of this series.[14] The theory is kept as general as possible, and involves only the assumption that the effective interparticle interaction has some unspecified finite range. We propose to derive convenient formal expressions for the normal modes of the semi-infinite crystal lattice with a free boundary, without having to resort to Green's-function techniques. That is, we obtain explicit expressions for these modes, rather than their integral representation. The advantage of this formulation is manifest. We shall also consider in some detail the formal structure of the dispersion relations for surface modes, a problem which has not yet received sufficient attention.

In a forthcoming paper we propose to apply our results to a theory of the thermal diffuse scattering of low-energy electrons.

The model on which our theory is based is described in detail in the first paper of the series.[1] In Sec. II, we shall therefore restrict ourselves to a brief statement of our assumptions. We then proceed to formulate the harmonic approximation for the semi-infinite lattice. Special attention is given to the proper boundary conditions to be imposed at an infinite distance from the free boundary. In Sec. III we go through a preliminary analysis of the model. In Sec. IV we determine the normal modes of the semi-infinite crystal lattice. The results are summarized and discussed in Sec. V.

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[14] In the following we shall refer to this paper (Ref. 1) as I.

II. FORMULATION OF THE HARMONIC APPROXIMATION FOR SEMI-INFINITE CRYSTAL LATTICES

In this section we wish to formulate the harmonic approximation for the semi-infinite lattice. That is, we are concerned with low-energy excitations of the semi-infinite crystal lattice, characterized by the fact that the atoms undergo small, time-dependent displacements $\mathbf{u}(\mathbf{m},\mu)$ from their static equilibrium positions, $\mathbf{R}(\mathbf{m},\mu)$.

The static-equilibrium positions were discussed in I. However, in order to make the present paper reasonably self-contained, we shall explain briefly the notation which was introduced in Sec. II of Paper I, and restate the basic assumptions of our model of the semi-infinite crystal lattice.

We write the static equilibrium positions $\mathbf{R}(\mathbf{m},\mu)$ in the following form:

$$\mathbf{R}(\mathbf{m},\mu)=\mathbf{R}(\mathbf{m})+\mathbf{R}(\mu)+\mathbf{U}(\mathbf{m},\mu)\,, \tag{2.1}$$

where

$$\mathbf{R}(\mathbf{m})=\sum_{i=1}^{3}\mathbf{a}_i m_i\,,\quad m_1,m_2=0,\pm1,\pm2\,,\quad m_3=0,1,2\,. \tag{2.2}$$

The basis vectors $\mathbf{a}_1,\mathbf{a}_2$ are the primitive translation vectors for the planes parallel to the boundary. The third basis vector $\mathbf{a}_3$ is orthogonal to $\mathbf{a}_1$ and $\mathbf{a}_2$ (that is, $\mathbf{a}_3$ is normal to the boundary surface). Usually this convention makes the unit cell spanned by $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ nonprimitive.

$\mathbf{R}(\mu)$, where $\mu=1,\cdots,s$, refers to the position of the μth atom in that unit cell of the infinite lattice which includes the point $\mathbf{R}(0,0,0)$. The mass of this atom is M_μ. The vector $\mathbf{U}(\mathbf{m},\mu)$ is the static displacement of the μth atom in the $\mathbf{m}$th unit cell of the infinite lattice, which occurs upon the creation of a free boundary at $m_3=0$.

These static displacements are defined by the equilibrium conditions,

$$\begin{aligned}&\Psi(\mathbf{m},\mu)=\nabla_{\mathbf{r}(\mathbf{m},\mu)}\Phi\big|_{\{\mathbf{r}(\mathbf{l},\lambda)\}=\{\mathbf{R}(\mathbf{l},\lambda)\}}=0\,,\\ &m_1,m_2=0\pm1,\pm2,\cdots,\\ &m_3=0,2,3,\cdots,\\ &\mu=1,\cdots,s\,,\end{aligned} \tag{2.3}$$

where

$$\mathbf{r}(\mathbf{l},\lambda)=\mathbf{R}(\mathbf{l},\lambda)+\mathbf{u}(\mathbf{l},\lambda)\,, \tag{2.4}$$

and $\Phi(\{\mathbf{r}(\mathbf{l},\lambda)\})$ is the potential energy of interaction of the semi-infinite lattice in the configuration:

$$\{\mathbf{r}(\mathbf{l},\lambda);\ l_1,l_2=0\pm1,\pm2,\cdots;\ l_3=0,1,2,\cdots;\ \mu=1,\cdots,s\}\,. \tag{2.5}$$

We make the following assumptions:

(1) The magnitude of the relative static displace-

ments of the atoms in adjacent cells is small compared to the dimension of the unit cell.

(2) The potential energy of interaction of the semi-infinite lattice in the nonequilibrium configuration, $\{\mathbf{U}(\mathbf{l},\lambda)\}=0$, differs from the potential energy of interaction of the particles in the upper half of the infinite lattice ($m_3 \geqslant 0$), in the same configuration, by terms of the third order in the relative static displacements; that is, we assume,

$$\Phi(\{\mathbf{U}(\mathbf{l},\lambda)\}=0)-\Phi^{(u)}(\{\mathbf{R}(\mathbf{l})+\mathbf{R}(\lambda)\})=O((\Delta U)^3). \quad (2.6)$$

Here $\Phi^{(u)}(\{\mathbf{R}(\mathbf{l})+\mathbf{R}(\lambda)\})$ is the potential energy of interaction of the particles in the upper half of the infinite lattice, $l_3 \geqslant 0$.

(3) The range of the effective interatomic interactions is finite. The precise mathematical formulation of this assumption is given below.

The small displacements $\mathbf{u}(\mathbf{l},\lambda)$ of the atoms from their static-equilibrium positions lead to an increase of the potential energy of interaction above the value it assumes in the static equilibrium configuration. In the harmonic approximation, we assume that this change in the potential energy of interaction is a bilinear form in the displacements, which can be written in the form

$$\Phi(\{\mathbf{r}(\mathbf{l},\lambda)\})-\Phi_0$$
$$=\tfrac{1}{2}\sum_{\substack{m_1,m_2=-\infty\\ n_1,n_2}}^{\infty}\sum_{m_3,n_3=0}^{\infty}\sum_{\nu,\mu=1}^{s}\sum_{i,j=1}^{3}\Psi_{ij}(\mathbf{m},\mu;\mathbf{n},\nu)\times(u_i(\mathbf{m},\mu)-u_j(\mathbf{n},\nu))^2. \quad (2.7)$$

Here $\mathbf{r}$ and $\mathbf{u}$ are defined by Eqs. (2.1), (2.2), and (2.4). The matrix

$$\mathbf{\Psi}(\mathbf{m},\mu;\mathbf{n},\nu)=\nabla_{\mathbf{r}(\mathbf{m},\mu)}\nabla_{\mathbf{r}(\mathbf{n},\nu)}\Phi\,|_{\{r(\mathbf{l},\lambda)\}=\{R(\mathbf{l},\lambda)\}}=\mathbf{\Psi}^T(\mathbf{n},\nu;\mathbf{m},\mu), \quad (2.8)$$

and we have explicitly used the equilibrium conditions Eq. (2.3). We shall use Eq. (2.7) to derive the equations of motion for the semi-infinite lattice. This will be done in Sec. III. The rest of this section is devoted to a discussion of the matrices $\mathbf{\Psi}(\mathbf{m},\mu;\mathbf{n},\nu)$ entering Eq. (2.7), and to a derivation of the boundary conditions to be imposed on the displacements $\mathbf{u}(\mathbf{m},\mu)$.

It is clear that the multiple infinite series in Eq. (2.7) is purely formal. In fact, since Eq. (2.7) represents a term in the potential energy of a many-particle system, it is proportional to the number of particles and hence it diverges. We are, however, only interested in the dependence of the potential energy on the quantities $u_i(\mathbf{m},\mu)$, and not with the numerical value of the series; hence we may impose a summation convention using exponential convergence factors of the form

$$\exp\{-\sum_{i=1}^{3}\epsilon_i|m_i|\},\ \exp\{-\sum_{i=1}^{3}\eta_i|n_i|\},$$

where $0<\epsilon_i,\eta_i\ll 1$; $i=1, 2, 3$ are arbitrary small positive numbers. It will be understood that these factors are absorbed in the functions $u_i(\mathbf{m},\mu)$ and $u_j(\mathbf{n},\nu)$. Also, we shall require the limit $\epsilon_i, \eta_i \to 0^+$ to be taken at the end of any calculation involving the series in Eq. (2.7). This limit is trivial as far as Eq. (2.8) is concerned: $-\Phi_{ij}(\mathbf{m},\mu;\mathbf{n},\nu)$ represents the ith component of the force acting on the particle located at $\mathbf{R}(\mathbf{m},\mu)$ due to a unit displacement, along the j axis, of the particle located at $\mathbf{R}(\mathbf{n},\nu)$, and thus is a manifestly finite and well-defined quantity. A similar comment obviously applies to Eq. (2.9) and all other infinite series in the following discussion. These series always represent the net finite force acting on a particular particle.

In order to proceed, we shall assume that $\Phi(\{\mathbf{r}(\mathbf{l},\lambda)\})$ satisfies the three assumptions listed above. We can therefore expand the matrices $\mathbf{\Psi}$ in a formal power series in the set of static displacement $\mathbf{U}(\mathbf{l},\lambda)$.

Thus,

$$\mathbf{\Psi}(\mathbf{m},\mu;\mathbf{n},\nu)=\mathbf{\Phi}(\mathbf{m},\mu;\mathbf{n},\nu)+\sum_{l_1,l_2=-\infty}^{\infty}\sum_{l_3=0}^{\infty}\sum_{\lambda=1}^{s}[\mathbf{\Phi}(\mathbf{m},\mu;\mathbf{n},\nu;\mathbf{l},\lambda)+\delta\mathbf{\Phi}(\mathbf{m},\mu;\mathbf{n},\nu;\mathbf{l},\lambda)]\mathbf{U}(\mathbf{l},\lambda)+\cdots. \quad (2.9)$$

Here,

$$\mathbf{\Psi}(\mathbf{m},\mu;\mathbf{n},\nu)=\nabla_{\mathbf{R}(\mathbf{m},\mu)}\nabla_{\mathbf{R}(\mathbf{n},\nu)}\Phi^{(u)}\,|_{\{\mathbf{U}(\mathbf{l},\lambda)\}=0}, \quad (2.10)$$

$$\mathbf{\Phi}(\mathbf{m},\mu;\mathbf{n},\nu;\mathbf{l},\lambda)=\nabla_{\mathbf{R}(\mathbf{m},\mu)}\nabla_{\mathbf{R}(\mathbf{n},\nu)}\nabla_{\mathbf{R}(\mathbf{l},\lambda)}\Phi^{(u)}\,|_{\{\mathbf{U}(\mathbf{l},\lambda)\}=0}, \quad (2.11)$$

$$\delta\mathbf{\Phi}(\mathbf{m},\mu;\mathbf{n},\nu;\mathbf{l},\lambda)=\nabla_{\mathbf{R}(\mathbf{m},\mu)}\nabla_{\mathbf{R}(\mathbf{n},\nu)}\nabla_{\mathbf{R}(\mathbf{l},\lambda)}(\Phi-\Phi^{(u)})\,|_{\{\mathbf{U}(\mathbf{l},\lambda)\}=0}. \quad (2.12)$$

We now can make more precise our assumption (3), concerning the finite range of the effective interatomic interaction. We shall assume that

$$\mathbf{\Phi}(\mathbf{m},\mu;\mathbf{n},\nu)=0, \quad (2.13)$$

if one of the following inequalities applies:

$$|m_i-n_i|\geq H_i+1;\quad i=1, 2, 3. \quad (2.14)$$

Also,

$$\mathbf{\Phi}(\mathbf{m},\mu;\mathbf{n},\nu;\mathbf{l},\lambda)=0=\delta\mathbf{\Phi}(\mathbf{m},\mu;\mathbf{n},\nu;\mathbf{l},\lambda), \quad (2.15)$$

if one of the following inequalities applies:

$$|m_i-n_i|,|m_i-l_i|,|n_i-l_i|\geq H_i+1;\quad i=1, 2, 3. \quad (2.16)$$

Our assumptions concerning the potential energy of interaction imply a number of constraints on the quantities $\mathbf{\Phi}(\mathbf{m},\mu;\mathbf{n},\nu)$, $\mathbf{\Phi}(\mathbf{m},\mu;\mathbf{n},\nu;\mathbf{l},\lambda)$, and $\delta\mathbf{\Phi}(\mathbf{m},\mu;\mathbf{n},\nu;\mathbf{l},\lambda)$. Some of these relations are listed below. The proof of these relations is given in Appendix A of I.

We note that if m_3 and $n_3 \geq H_3$, then the matrices $\mathbf{\Phi}(\mathbf{m},\mu;\mathbf{n},\nu)$ are the harmonic coupling (or force) constants introduced in the ordinary theory of infinite crystal lattices.[4-6] Similarly, if m_3, n_3, and l_3 are all $\geq 2H_3$, then the quantities $\mathbf{\Phi}(\mathbf{m},\mu;\mathbf{n},\nu;\mathbf{l},\lambda)$ are the ordinary third-order (harmonic) constants of the in-

finite lattice. If, however, one of the indices m_3, n_3, $l_3<H_3$, then these anharmonic constants differ from those in the infinite lattice.

We shall rewrite Eq. (2.9) in the form

$$\Psi(\mathbf{m},\mu;\,\mathbf{n},\nu)=\Phi(\mathbf{m},\mu;\,\mathbf{n},\nu)+\delta\Phi(\mathbf{m},\mu;\,\mathbf{n},\nu). \quad (2.17)$$

The matrices $\delta\Phi$ account for two related, though distinct, boundary effects. Both effects are due to the relaxation of the atoms from their static-equilibrium positions in the infinite lattice. First we have an anharmonic effect involving the coupling constant $\Phi(\mathbf{m},\mu;\,\mathbf{n},\nu;\,\mathbf{l},\lambda)$. Next we have to account for the possibility that the dependence of Φ on the atomic positions may be affected by the creation of a free boundary. According to assumption (2), above, $\Phi-\Phi^{(u)}=O((\Delta U)^3)$, and consequently the coefficients $\delta\Phi(\mathbf{m},\mu;\,\mathbf{n},\nu;\,\mathbf{l},\lambda)$ do not necessarily vanish. If we invoke the assumed finite range of the interatomic interaction, we may expect these coefficients to have an appreciable value only if at least two of the indices m_3, n_3, l_3 are less than H_3. We showed in I that the static displacements $\mathbf{U}$ decrease roughly exponentially with the distance from the free boundary, hence we shall make the "working approximation"

$$\delta\Phi(\mathbf{m},\mu;\,\mathbf{n},\nu)=0, \quad \text{if} \quad m_3 \quad \text{or} \quad n_3\geq 2H_3. \quad (2.18)$$

This assumption is convenient, though not essential. It can be weakened by including the effect of $\delta\Phi$ if m_3 or $n_3\leq pH_3-1$, where $p=\text{integer}\geq 2$.

We next note that

$$\begin{aligned}\Phi_{ij}(\mathbf{m},\mu;\,\mathbf{n},\nu)&=\Phi_{ij}(\mathbf{n},\nu;\,\mathbf{m},\mu)\\&=\Phi_{ij}(0,0,m_3,\mu;\,n_1-m_1,\,n_2-m_2,\,n_2,\,\nu);\\&\qquad\qquad m_3 \quad \text{or} \quad n_3<H_3\\&=\Phi_{ij}(\mathbf{0},\mu;\,\mathbf{n}-\mathbf{m},\nu); \qquad m_3 \quad \text{and} \quad n_3\geq H_3. \quad (2.19)\end{aligned}$$

The first equation in Eq. (2.19) follows from the definition of the matrices Φ as mixed second derivatives. The second equation follows from assumptions (2) and (3) above, and the invariance of the function $\Phi^{(u)}$ under a translation by a lattice vector $\mathbf{R}(\mathbf{m})$ parallel to the boundary plane. We shall find it convenient to exhibit the symmetry of the matrices Φ explicitly in our notation, by introducing the variables $h_i=n_i-m_i$,

$$\begin{aligned}\Phi_{ij}(\mathbf{m},\mu;\,\mathbf{n},\nu)&\equiv\Phi_{ij}(h_1,h_2,m_3,n_3;\,\mu,\nu);\\&\qquad\qquad m_3 \quad \text{or} \quad n_3<H_3\\&\equiv\Phi_{ij}(\mathbf{h};\,\mu,\nu); \qquad m_3 \quad \text{and} \quad n_3\geq H_3. \quad (2.20)\end{aligned}$$

Turning to the matrices $\delta\Phi(\mathbf{m},\mu;\,\mathbf{n},\nu)$, we see that because of the form of the static displacements, discussed in the first paper, we have

$$\begin{aligned}&\delta\Phi(\alpha_1m_1,\alpha_2m_2,m_3,\mu;\,\alpha_1n_1,\alpha_2n_2,n_3,\nu)\\&\quad=\delta\Phi(0,0,m_3,\mu;\,\alpha_1h_1,\alpha_2h_2,n_3,\nu)\\&\qquad\equiv\delta\Phi(\alpha_1h_1,\alpha_2h_2;\,m_3,m_3+h_3;\,\mu,\nu), \quad (2.21)\end{aligned}$$

where

$$h_i=n_i-m_i; \quad i=1,\,2,$$

and the static displacements have the symmetry,

$$\begin{aligned}&\mathbf{U}(0,0,m_3;\,\mu)=\mathbf{U}(\alpha_1m_1,\alpha_2m_2,m_3;\,\mu);\\&\qquad m_i=0,\,\pm1,\,\cdots,\,\alpha_i=\text{integer}\geq 1. \quad (2.22)\end{aligned}$$

If $\alpha_i>1$, e.g., for Ge and Si, it is convenient to relabel the functions defined on the semi-infinite lattice by introducing the larger two-dimensional unit cell spanned by $\{\alpha_1\mathbf{a}_1,\alpha_2\mathbf{a}_2\}$ having $(\alpha_1\alpha_2 s)$ atoms per unit cell. We shall, in this case, use the convention that the new function F' is related to the old function F by the relation

$$\begin{aligned}&F'(m_1,\,m_2,\,m_3,\,\mu=\mu'+p_1+p_2)\\&\qquad=F(m_1+p_1m_2+p_2,\,m_3,\,\mu'), \quad (2.23)\end{aligned}$$

where

$$0\leq p_i=\text{integer}\leq\alpha_i-1; \quad i=1,\,2 \quad (2.24)$$

$$\mu'=1\cdots s',$$

$$\mu=1\cdots\alpha_1\alpha_2s'=s. \quad (2.25)$$

In the following we shall assume such a relabeling to have been performed whenever necessary. It should be noted that whenever α_1 and α_2 are both equal to unity, the neglect of the matrices $\delta\Phi$ in Eq. (2.17) should not lead to serious errors. However, whenever one or both of the α's is larger than unity, the neglect of the matrices $\delta\Phi$ should lead to qualitatively wrong results, because of the fact that quasiharmonic force constants $\Psi(\mathbf{m},\mu;\,\mathbf{n},\nu)$ are not invariant under the full two-dimensional translation (symmetry) group of the harmonic force constants $\Phi(\mathbf{m},\mu;\,\mathbf{n},\nu)$.[15]

In order to complete the formulation of the harmonic approximation for the dynamics of the semi-infinite crystal lattice, we have to specify the boundary conditions to be imposed on the displacements $\mathbf{u}(\mathbf{m},\mu)$. In order to eliminate the effect of boundaries in the two unbounded dimensions, 1 and 2, we impose the conventional periodic boundary conditions on the dependence of $\mathbf{u}$ on the variables m_1,m_2. At the boundary plane $m_3=0$ we shall impose free-boundary conditions. That is, we shall assume that there are no external forces acting on any particle. The mathematical statement of these conditions will be given in the next section. The only boundary conditions that require some discussion are thus seen to be those to be imposed at an infinite distance from the free boundary, i.e., when $m_3\rightarrow\infty$.

In general, the choice of boundary conditions is dictated by the use to be made of the results, and the ease of obtaining a formal solution of the problem posed. Our principal concern is the effect of a single free boundary in modifying the functional form of the vibrational modes characteristic of the infinite lattice subject to periodic boundary conditions. This suggests that we

[15] The matrices $\Psi(\mathbf{m},\mu;\,\mathbf{n},\nu)$ are the harmonic force constants of the semi-infinite lattice. However, when they are expressed in terms of the force constants of the infinite lattice, they include anharmonic contributions, hence the designation quasiharmonic, as distinguished from the matrices $\Phi(\mathbf{m},\mu;\,\mathbf{n},\nu)$ which are essentially the harmonic force constants of the infinite lattice.

impose on the semi-infinite lattice the following set of "quasiperiodic" boundary conditions:

$$\mathbf{u}(\mathbf{m},\mu)=\mathbf{v}(\mathbf{m},\mu)+\mathbf{w}(\mathbf{m},\mu);\quad m_3\geq 2H_3, \tag{2.26}$$

where $\mathbf{v}$ satisfies the periodic boundary conditions,

$$\mathbf{v}(m_1, m_2, m_3+N_3, \mu)=\mathbf{v}(m_1,m_2,m_3,\mu), \tag{2.27}$$

with N_3 an arbitrary, though fixed, large positive integer, and the limit $N_3\rightarrow\infty$ is understood.

On $\mathbf{w}$ we impose the condition

$$\lim_{m_3\rightarrow\infty}|w_i(m_1,m_2,m_3,\mu)|=0 \quad \text{if} \quad \mathbf{v}\equiv 0,$$
$$=M<\infty \quad \text{if} \quad \mathbf{v}\not\equiv 0. \tag{2.28}$$

When $v\not\equiv 0$, it is a plane wave with a group velocity whose 3-component is $v_{g,3}(\mathbf{v}(\mathbf{m},\mu))$. In this case we impose on $\mathbf{w}$ the additional condition that $\lim_{m_3\rightarrow\infty}\mathbf{w}$ is to be a sum of plane waves, such that the sign of the 3-component of the group velocity of each wave is $-\mathrm{sgn}v_{g,3}(\mathbf{v}(\mathbf{m},\mu))$. We include here the case where $v_{g,3}(\mathbf{v}(\mathbf{m},\mu))=0$. Thus we see that $\mathbf{w}$ may be thought of as the scattered wave associated with the incident wave $\mathbf{v}$.

Physically, the preceding boundary conditions reflect the interpretation of the semi-infinite lattice as an infinite lattice (subject to periodic boundary conditions) into which a free boundary is introduced by means of the thought experiment outlined in Sec. II of Paper I. The modifications of the modes, $\mathbf{v}$, of the periodic lattice by means of the free boundary is completely specified by the scattered wave $\mathbf{w}$.

Mathematically, the quasiperiodic boundary conditions are a device to select a countable subset from the continuous spectrum associated with the standard homogenous boundary condition for unbounded domains, i.e., the requirement that the vibrational modes be bounded at infinity. Such a restriction of the spectrum is essential in view of the physical requirement that the vibrational spectrum of a discrete system, consisting of a countable number of particles, be a countable set.

We shall see that, in practice, quasiperiodic boundary conditions are readily imposed. Furthermore, the discreteness of the spectrum may in general be ignored, a situation familiar from the conventional dynamics of infinite lattices, subject to periodic boundary conditions. In conclusion we note that the boundary conditions explicitly allow for the occurrence of vibrational modes which have no counterpart in the infinite lattice; namely, nontrivial solutions for which $\mathbf{v}\equiv 0$, and for which

$$\lim_{m_3\rightarrow\infty} w_i(m_1,m_2,m_3,\mu)=0=\lim_{m_3\rightarrow\infty} u_i(m_1,m_2,m_3,\mu).$$

These solutions are, in the terminology of scattering theory, states bound at the boundary; that is, they represent surface waves.

III. PRELIMINARY ANALYSIS OF THE EQUATIONS OF MOTION

A. The Equations of Motion

Using Eqs. (2.7), (2.8), (2.17), and (2.18) we can now write the time-Fourier transformation of the classical equations of motion for the semi-infinite lattice as a set of partial-differencee quations for the s three-dimensional vectors $\mathbf{u}(\mathbf{m},\mu;\omega^2)$,

$$M_\mu\mathbf{u}(\mathbf{m},\mu;\omega^2)\omega^2=\sum_{\nu=1}^{s}\sum_{n_1,n_2=-\infty}^{\infty}\sum_{n_3=0}^{m_3+H_3}[\mathbf{\Phi}(\mathbf{m},\mu;\mathbf{n},\nu)$$
$$+\delta\mathbf{\Phi}(\mathbf{m},\mu;\mathbf{n},\nu)]\mathbf{u}(\mathbf{n},\nu;\omega^2), \tag{3.1}$$
$$m_3=\geq H_3.$$

The boundary conditions imposed on this set are, at the free boundary,

$$M_\mu\mathbf{u}(\mathbf{m},\mu;\omega^2)\omega^2=\sum_{\nu=1}^{s}\sum_{n_1,n_2=-\infty}^{\infty}\sum_{n_3=0}^{m_3+H_3}[\mathbf{\Phi}(\mathbf{m},\mu;\mathbf{n},\nu)$$
$$+\delta\mathbf{\Phi}(\mathbf{m},\mu;\mathbf{n},\nu)]\mathbf{u}(\mathbf{n},\nu;\omega^2), \tag{3.2}$$
$$m_3=0,\ \cdots,\ H_3-1.$$

At an infinite distance from the free boundary, we impose quasiperiodic conditions,

$$\mathbf{u}(\mathbf{m},\mu;\omega^2)=\mathbf{v}(\mathbf{m},\mu;\omega^2)+\mathbf{w}(\mathbf{m},\mu,\omega^2),\ m_3\geq 2H_3,$$
$$\mathbf{v}(m_1,m_2,m_3,\mu;\omega^2)=\mathbf{v}(m_1,m_2,m_3+N_3,\mu;\omega^2),$$
$$\lim_{m_3\rightarrow\infty}|w_i(m_1,m_2,m_3,\mu)|=0, \qquad \mathbf{v}\equiv 0$$
$$=M<\infty,\ \mathbf{v}\not\equiv 0. \tag{3.3}$$

Here, N_3 is an arbitrary but very large integer, and the limit $N_3\rightarrow\infty$ is understood. When $\mathbf{v}\not\equiv 0$, then $\lim_{m_3\rightarrow\infty}\mathbf{w}$ is a sum of plane waves. The group velocity of each of these waves has a 3-component whose sign is the negative of the sign of the 3-component of the group velocity of $\mathbf{v}$.

Finally, we impose periodic boundary conditions in the two unbounded, 1 and 2, dimensions:

$$\mathbf{u}(m_1,m_2,m_3\mu;\omega^2)=\mathbf{u}(m_1+N_1, m_2+N_2, m_3, \mu;\omega^2), \tag{3.4}$$

where N_1 and N_2 are arbitrary though fixed integers, and the limit $N_i\rightarrow\infty$ is understood.

We now take advantage of the invariance of the boundary-value problem under a translation by a lattice vector parallel to the boundary; that is, when

$$\mathbf{R}(\mathbf{m}_\rho)=\sum_{i=1}^{2}\alpha_i\mathbf{a}_i m_i\rightarrow\sum_{i=1}^{2}\alpha_i\mathbf{a}_i(m_i+h_i)$$
$$=\mathbf{R}(\mathbf{m}_\rho+\mathbf{h}_\rho);\ h_i=0,\ 1,\ \cdots. \tag{3.5}$$

Hence, we write

$$M_\mu{}^{1/2}\mathbf{u}(\mathbf{m},\mu;\omega^2)=e^{i\mathbf{k}_\rho\cdot\mathbf{R}(\mathbf{m}_\rho)}\mathbf{u}(m_3,\mu;\omega^2,\mathbf{k}_\rho), \tag{3.6}$$

where

$$\mathbf{k}_\rho = 2\pi \sum_{i=1}^{2} \frac{1}{\alpha_i}\mathbf{b}_i k_i,$$

$$-1 < k_i = \frac{\kappa_i}{N_i} < 1, \quad \kappa_i = \text{integer}, \tag{3.7}$$

and

$$\mathbf{b}_1 = \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}, \quad \mathbf{b}_2 = \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot \mathbf{a}_3 \times \mathbf{a}_1}. \tag{3.8}$$

The rational numbers k_1, k_2 are the components of a vector in a two-dimensional reciprocal space. This vector is restricted to lie within the first Brillouin zone of the two-dimensional reciprocal lattice spanned by $\{\alpha_1^{-1}\mathbf{b}_1, \alpha_2^{-1}\mathbf{b}_2\}$.

The substitution indicated by Eq. (3.6) reduces Eq. (3.1) to a set of $3s$-coupled ordinary difference equations

$$\sum_{\sigma=1}^{3s} \sum_{n_3=m_3-H_3}^{m_3+H_3} [\theta_{\pi\sigma}(m_3,n_3;\omega^2,\mathbf{k}_\rho) + \delta\theta_{\pi\sigma}(m_3,n_3;\mathbf{k}_\rho)] u_\sigma(m_3;\omega^2,\mathbf{k}_\rho) = 0; \tag{3.9}$$
$$m_3 \geq H_3, \ \pi = 1, \cdots, 3s.$$

These equations are subject to the following boundary conditions:

$$\sum_{\sigma=1}^{3s} \sum_{n_3=0}^{m_3+H_3} [\theta_{\pi\sigma}(m_3,n_3;\omega^2,\mathbf{k}_\rho) + \delta\theta_{\pi\sigma}(m_3,n_3;\mathbf{k}_\rho)] u_\sigma(n_3;\omega^2,\mathbf{k}_\rho) = 0, \tag{3.10}$$
$$m_3 = 0, \cdots, H_3 - 1, \ \pi = 1, \cdots, 3s,$$

and the quasiperiodic conditions

$$u_\pi(m_3;\omega^2,\mathbf{k}_\rho) = v_\pi(m_3;\omega^2,\mathbf{k}_\rho) + w_\pi(m_3;\omega^2,\mathbf{k}_k), \quad m_3 \geq 2H_3,$$

$$v_\pi(m_3+N_3;\omega^2,\mathbf{k}_\rho) = v_\pi(m_3;\omega^2,\mathbf{k}_\rho),$$

and

$$\lim_{m_3\to\infty} |w_\pi(m_3;\omega^2,\mathbf{k}_\rho)| = 0, \qquad \mathbf{v} \equiv 0$$
$$= M < \infty, \ \mathbf{v} \not\equiv 0. \tag{3.11}$$

When $\mathbf{v} \not\equiv 0$, then $\lim_{m_3\to\infty} w_\pi$ is a sum of plane waves. The group velocity of each wave has a 3-component whose sign is the negative of the sign of the 3-component of the group velocity of $\mathbf{v}$.

The indices π, σ are defined as follows:

$$\pi = 3(\mu-1)+i, \quad \sigma = 3(\nu-1)+j. \tag{3.12}$$

The matrices $\boldsymbol{\theta}$ and $\delta\boldsymbol{\theta}$ are defined, using Eqs. (2.12) and (2.22), by Eqs. (3.13) and (3.14):

$$\theta_{\pi\sigma}(m_3,n_3;\omega^2,\mathbf{k}_\rho) = (M_\mu M_\nu)^{-1/2} \sum_{h_1,h_2=-\infty}^{\infty} [\Phi_{ij}(h_1,h_2,m_3,n_3;\mu,\nu) \times e^{i\mathbf{k}_\rho\cdot\mathbf{R}(\mathbf{h}_\rho)} - \delta_{i,j}\delta_{\mu,\nu}\delta_{m_3,n_3}\omega^2], \tag{3.13}$$

$$\delta\theta_{\pi\sigma}(m_3,n_3;\mathbf{k}_\rho) = (M_\mu M_\nu)^{-1/2} \sum_{h_1,h_2=-\infty}^{\infty} \delta\Phi_{ij}(h_1,h_2,m_3,n_3;\mu,\nu) e^{i\mathbf{k}_\rho\cdot\mathbf{R}(\mathbf{h}_\rho)}. \tag{3.14}$$

Equations (3.9) and (3.10) are manifestly similar to Eqs. (3.8) and (3.9) of Paper I. This suggests that the dynamical equations be analyzed by the technique applied in I to the static equations. Following the procedure described in Sec. III of I, we extract from Eq. (2.8) a set of difference equations with constant coefficients,

$$\sum_{\sigma=1}^{3s} \sum_{h_3=-H_3}^{H_3} \theta_{\pi\sigma}(h_3;\omega^2,\mathbf{k}_\rho) u_\sigma(m_3+h_3;\omega^2,\mathbf{k}_\rho) = 0; \quad m_3 \geq 2H_3, \ \pi = 1, \cdots, 3s. \tag{3.15}$$

We can write the general solution of this set of equations as a linear combination of a set of $6sH_3$ linearly independent elementary solutions,[16,17] i.e.,

$$u_\pi(m_3;\omega^2,\mathbf{k}_\rho) = \sum_g \sum_{p=0}^{q(g)-1} c_{g,p}(\omega^2,\mathbf{k}_\rho) u_{p,\pi}{}^{(g)} \times (\exp\{2\pi i k_3{}^{(g)}\};\omega^2,\mathbf{k}_\rho) \binom{m_3}{p} \exp\{2\pi i k_3{}^{(g)} m_3\}, \tag{3.16}$$

where $q(g)$ is the multiplicity of the root $\exp\{2\pi i k_3{}^{(g)}\}$ of the characteristic equation,

$$\det[\theta_{\pi\sigma}(e^{2\pi i k_3};\omega^2,\mathbf{k}_\rho)] = 0, \tag{3.17}$$

and g now runs only over distinct roots of Eq. (3.17). The matrix $\boldsymbol{\theta}$ in Eq. (3.17) is defined by the relation

$$\theta_{\pi\sigma}(e^{2\pi i k_3};\omega^2,\mathbf{k}_\rho) = \sum_{h_3=-H_3}^{H_3} \theta_{\pi\sigma}(h_3;\omega^2,\mathbf{k}_\rho) e^{2\pi i k_3 h_3}. \tag{3.18}$$

If $\exp\{2\pi i k_3{}^{(g)}\}$ is a simple root of Eq. (3.17) then the $3s$-dimensional vector $\mathbf{u}^{(g)}$ is the null vector of the matrix $\boldsymbol{\theta}(\exp\{2\pi i k_3{}^{(g)}\};\omega^2,\mathbf{k}_\rho)$, i.e.,

$$\sum_{\sigma=1}^{3s} \theta_{\pi\sigma}(\exp\{2\pi i k_3{}^{(g)}\};\omega^2,\mathbf{k}_\rho) u_\sigma{}^{(g)} \times (\exp\{2\pi i k_3{}^{(g)}\};\omega^2,\mathbf{k}_\rho) = 0; \quad \pi = 1, \cdots, 3s. \tag{3.19}$$

The determination of the q linearly independent vectors $\mathbf{u}_p{}^{(g)}$ associated with a q-fold root of Eq. (3.17) is indicated in Appendix B of I.

To simplify our notation, we shall in the following suppress the factor 2π in the exponentials. We shall also restrict ourselves to the general case where Eq. (3.17)

[16] Charles Jordan, *Calculus of Finite Differences* (Chelsea Publishing Company, New York, 1949), Chap. IX.

[17] Tomlinson Fort, *Finite Differences* (Clarendon Press, Oxford, England, 1948); J. J. Lander, *Progress in Solid State Chemistry* (Pergamon Press, Inc., New York, 1965), Vol. 2, p. 26.

has only simple roots. The effect and significance of multiple roots will be discussed separately.

The coefficients $c_g(\omega^2,\mathbf{k}_\rho)$ appearing in Eq. (3.16) have to be determined from the boundary conditions, Eq. (3.11), and an auxiliary problem to be discussed in Sec. IV. Before we proceed to this problem we shall briefly indicate some general properties of the characteristic equation (3.17), and of the elementary solutions of Eq. (3.15).

B. General Properties of the Elementary Solutions of Eq. (3.15)

The symmetry of the matrices $\boldsymbol{\theta}$, indicated by Eq. (2.19), implies that

$$[\theta_{\pi\sigma}(e^{ik_3*};\omega^2,\mathbf{k}_\rho)]^*=\theta_{\sigma\pi}(e^{ik_3};\omega^2,\mathbf{k}_\rho)=\theta_{\pi\sigma}(e^{-ik_3};\omega^2-\mathbf{k}_\rho). \quad (3.20)$$

Thus the generalization of Eqs. (3.25) and (3.26) of Paper I is

$$\det[\theta_{\pi\sigma}(e^{ik_3};\omega^2,\mathbf{k}_\rho)]=0\leftrightarrow\det[\theta_{\pi\sigma}(e^{ik_3*};\omega^2,\mathbf{k}_\rho)]=0, \quad (3.21)$$

and

$$\det[\theta_{\pi\sigma}(e^{ik_3};\omega^2,\mathbf{k}_\rho)]=0\leftrightarrow\det[\theta_{\pi\sigma}(e^{-ik_3};\omega^2,-\mathbf{k}_\rho)]=0. \quad (3.22)$$

Thus, we conclude that complex values of $k_3(\omega^2;\mathbf{k}_\rho)$ occur in conjugate complex pairs. We also note that Eqs. (3.21) and (3.22) imply that

$$0=\det[\theta_{\pi\sigma}(e^{ik_3};\omega^2,\mathbf{k}_\rho)]\leftrightarrow\det[\theta_{\pi\sigma}(e^{-ik_3*};\omega^2,-\mathbf{k}_\rho)]=0. \quad (3.23)$$

This is a statement of the time-reversal invariance of the full (time-dependent) dynamic problem. We note that Eq. (3.17) is an unconventional way of defining the dispersion relation for the infinite crystal, usually written in the form

$$\det[D_{\pi\sigma}(\mathbf{k})-\delta_{\pi\sigma}\omega^2]=0. \quad (3.24)$$

In fact, Eq. (3.22) is the generalization of the known result,

$$\omega(\mathbf{k})=\omega(-\mathbf{k}), \quad (3.25)$$

to include complex values of k_3.

At this point it should be noted that Eq. (3.17) defines the complex, $6sH_3$-valued algebraic function $\exp\{ik_3(\omega^2;\mathbf{k}_\rho)\}$ of the complex variable ω^2 and the pair of real parameters k_1, k_2. This rather obvious remark may be used as a point of departure for an analysis analogous to the discussion of generalized Bloch functions given by Heine[18] and Blount.[19] This analysis, though somewhat tedious, sheds considerable light on the analytic structure of the phonon energy function for the infinite crystal. Another important consequence of this analysis is the elucidation of the analytic dependence of the elementary solutions of Eq. (3.15) on the parameter ω^2. This is an important result for the derivation of the Green's (matrix) function for the semi-infinite lattice. The details of the above analysis will be given in another publication. Here we only wish to list the main results which will be used below.

The $6sH_3$ branches of the algebraic function $\exp\{ik_3(\omega^2;\mathbf{k}_\rho)\}$ can be defined in such a way that if $\omega^2\geq 0$, then

$$\mathrm{Im}k_3^{(g)}\gtreqless 0 \quad \text{for} \quad g=\mp 3sH_3\cdots\mp 1, \quad (3.26)$$

and

$$\left[\frac{\partial k_3^{(g)}}{\tau\omega}\right]^{-1}\gtreqless 0 \quad \text{for} \quad g=\mp 3sH_3\cdots\mp 1, \quad (3.27)$$

if

$$\mathrm{Im}k_3^{(g)}=0.$$

These statements can be conveniently visualized in terms of one-dimensional sections of the (complex) $3s$-valued phonon energy function:

$$\omega=\omega_n(k_3;\mathbf{k}_\rho=\text{const}), \quad n=1,\cdots,3s.$$

This algebraic function is the inverse of the $6sH_3$-valued function $\exp\{ik_3(\omega^2;\mathbf{k}_\rho)\}$. The constant value of $\mathbf{k}_\rho$ is chosen so as to satisfy Eq. (3.7), and ik_3 is defined as the principal value of $\ln[e^{ik_3}(\omega^2;\mathbf{k}_\rho)]$.

As ω ranges along the real axis from 0 to infinity, the gth branch of $k_3(\omega^2;\mathbf{k}_\rho)$ may assume real values over one or more ω intervals. Over such an interval, $k_3^{(g)}$ traces out a portion of the one-dimensional section of the energy function, which is bounded by two extrema, at which

$$\frac{\partial(\omega^2)}{\partial(\exp\{ik_3\})}=2i\omega\exp\{-ik_3\}\frac{\partial\omega}{\partial k_3}=0. \quad (3.28)$$

If the gth branch of k_3 assumes real values over two disconnected, real, ω intervals, then it joins two branches of the phonon energy function $\omega(k_3;\mathbf{k}_\rho=\text{const})$ along a path in the complex k_3 plane. Along this path, ω assumes real values.

It is not necessary that every branch of $k_3(\omega^2;\mathbf{k}_\rho=\text{const})$ assume real values over some real ω interval. Furthermore, it is possible that for some particular value of $\mathbf{k}_\rho$, $\mathbf{k}_\rho=\mathbf{k}_\rho^{(1)}$, no branch of $k_3(\omega^2;\mathbf{k}_\rho^{(1)})$ assumes real values as ω ranges over some given ω interval, although some or all branches will assume real values over the same ω interval when $\mathbf{k}_\rho=\mathbf{k}_\rho^{(2)}$. An example of this is provided by the acoustic bands of a solid. Here, if $\mathbf{k}_\rho=\mathbf{0}$, several (namely six) branches of $k_3(\omega^2;\mathbf{0})$ assume real values over an interval extending to $\omega=0$. However, for any other value of $\mathbf{k}_\rho$, there is always a frequency $\omega_l(\mathbf{k}_\rho)>0$ such that over the interval $[0,\omega_l(\mathbf{k}_\rho)]$ no branch of $k_3(\omega;\mathbf{k}_\rho)$ assumes real values. Stated differently, there is no normal mode of the infinite lattice which has a frequency $<\omega_l(\mathbf{k}_\rho)$ and a component of the

[18] V. Heine, Proc. Phys. Soc. (London) **81**, 300 (1963).

[19] E. I. Blount, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1962), Vol. 13, Appendix C.

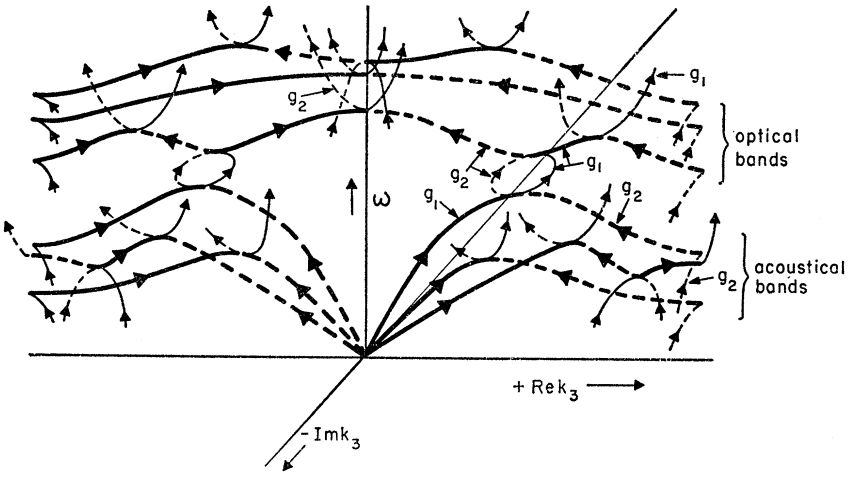

FIG. 1. Hypothetical one-dimensional section of a phonon-energy function for $\mathbf{k}_\rho=0$. Solid lines indicate branches of $k_3^{(g)}(\omega^2;\mathbf{k}_\rho)$ with index $g<0$. Dashed lines indicate branches of $k_3^{(g)}(\omega^2;\mathbf{k}_\rho)$ with index $g>0$. Heavy lines are in the plane k_3 real, ω real, light lines are out of this plane. For light dashed lines, $\mathrm{Im}k_3^{(g)}<0$, for light solid lines, $\mathrm{Im}k_3^{(g)}>0$. Arrows identify the sense in which the several portions of the one-dimensional sections of the allowed phonon energy bands are traced out by $k_3^{(g)}(\omega;\mathbf{k}_\rho)$. $k_3^{(g_1)}$ and $k_3^{(g_2)}$ join an acoustical and an optical band, along a path on which $\mathrm{Im}k_3^{(g)}\neq 0$. Note that since $\mathbf{k}_\rho=0$, $\omega(k_3)=\omega(-k_3)$.

wave vector parallel to the surface, which is equal to $\mathbf{k}_\rho$. This can be seen from the fact that for this case, the dispersion relation can be approximated by

$$\omega^2(\mathbf{k})=c_n^2(\mathbf{k}_\rho/|\mathbf{k}_\rho|)|\mathbf{k}|^2,\quad n=1,2,3,$$
$$c_n=\text{velocity of sound},\qquad (3.29)$$

or

$$|\mathbf{b}_3|k_3=\pm\left[\frac{\omega^2}{c_n^2(\mathbf{k}_\rho/|\mathbf{k}_\rho|)}-|\mathbf{k}_\rho|^2\right]^{1/2}. \qquad (3.30)$$

Hence,

$$\omega_l(\mathbf{k}_\rho)=\text{smallest of the three numbers}$$
$$c_n(\mathbf{k}_\rho/|\mathbf{k}_\rho|)|\mathbf{k}_\rho|,\quad n=1,2,3.$$

It can also be shown that for a fixed value of $\mathbf{k}_\rho$, each energy band is traced out by an even number of branches of the function $k_3(\omega^2,\mathbf{k}_\rho=\text{const})$, half of which are characterized by $[\partial k_3^{(g)}/\partial\omega]^{-1}\geq 0$. That is, the group velocities of the elementary solutions (which are equal to the normal modes of the infinite lattice) corresponding to these values of $k_3(\omega^2;\mathbf{k}_\rho)$ have a positive 3-component.

Figures 1 and 2 illustrate the preceding remarks with the help of a hypothetical dispersion relation. Such plots were obtained numerically by Gazis and Wallis for a one-dimensional diatomic lattice.[20]

Finally we remark that Eq. (3.20) implies that the roots of the characteristic equations,

$$\det[\theta_{\pi\sigma}(\exp\{ik_3\};\omega^2,\pm\mathbf{k}_\rho)]=0, \qquad (3.31)$$

are connected by the relation

$$\exp\{ik_3^{(g_1)}(\omega^2;-\mathbf{k}_\rho)\}=\exp\{i-[k_3^{(g_2)}(\omega^2;\mathbf{k}_\rho)]^*\}, \qquad (3.32)$$

where, in general, $g_1\neq g_2$. Hence, if these roots are simple, we also have

$$u_\sigma(\exp\{ik_3^{(g_2)}(\omega^2;\mathbf{k}_\rho)\};\omega^2,\mathbf{k}_\rho)$$
$$=[u_\sigma(\exp\{-ik[_3^{(g_2)}(\omega^2;\mathbf{k}_\rho)]\}^*;\omega^2,-\mathbf{k}_\rho)]^*$$
$$=[u_\sigma(\exp\{ik_3^{(g_1)}(\omega^2;-\mathbf{k}_\rho)\};\omega^2,-\mathbf{k}_\rho)]^*. \qquad (3.33)$$

[20] See the third paper in Ref. 11.

The analog of this relation for the periodic factor in the Bloch function is well known, at least for real values of k_3.

IV. DETERMINATION OF THE NORMAL MODES OF THE SEMI-INFINITE LATTICE

Referring to our discussion in Sec. III B, we shall distinguish three cases:

(*i*) *"Bulk" modes.* In this case, the frequency ω lies in one of the allowed bands of the one dimensional section of the phonon-energy function specified by $\mathbf{k}_\rho$. Here we may assume that the infinite lattice with periodic boundary conditions has a vibrational mode characterized by the given values of ω and $\mathbf{k}_\rho$, or, stated differently, $(2\pi)^{-1}k_3(\omega;\mathbf{k}_\rho)$ has at least two real values, one of which is equal to a rational number in the interval $(-\frac{1}{2},\frac{1}{2})$. As a matter of convenience we restrict ourselves to the general case where all of the real values of $k_3(\omega^2;\mathbf{k}_\rho)$ are distinct. We also assume no accidental degeneracy of the modes of the lattice with periodic boundary conditions, i.e., only one value of k_3 equals 2π times a rational number.[20a] We shall see that in this case we can construct a vibrational mode of the semi-infinite lattice which, at large distances from the free surface, reduces to a sum of plane waves. We call such modes "bulk" modes.

(*ii*) *"Surface" modes.* In this case the frequency ω lies in a forbidden band of the one-dimensional section of the phonon-energy function specified by $\mathbf{k}_\rho$. The frequency ω may in fact lie in an absolutely forbidden band, but this is not necessary. In this case all values of $k_3(\omega^2,\mathbf{k}_\rho)$ are complex, and we shall see that surface modes may exist for such frequencies.

(*iii*) *Frequencies at which $k_3(\omega^2;\mathbf{k}_\rho)$ has real multiple values.* Here we are concerned only with multiple values associated with extrema in the allowed bands of the one-

[20a] *Note added in proof.* This simplifying assumption will be dropped in the latter part of the discussion.

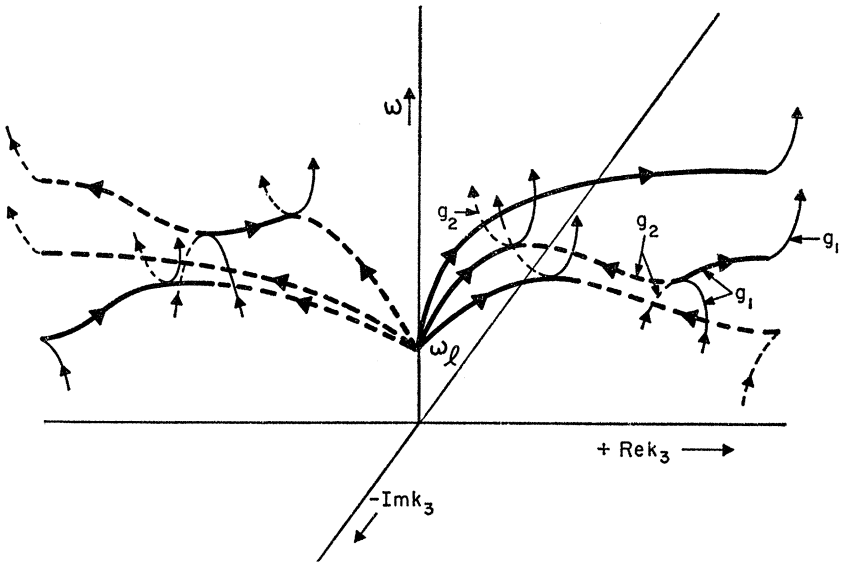

FIG. 2. Hypothetical one-dimensional section of a phonon energy function for $\mathbf{k}_\rho \neq 0$, hence $\omega(k_3; \mathbf{k}_\rho) \neq \omega(-k_3; \mathbf{k}_\rho)$. For $\omega < \omega_l$ all branches of $k_3(\omega^2; \mathbf{k}_\rho)$ are complex. See the caption for Fig. 1 for additional comments.

dimensional section of the phonon-energy function. We shall see that, in general, if the infinite lattice, with periodic boundary conditions, has a vibrational mode at such an extremal frequency, then the semi-infinite lattice does not have a mode at that frequency.

A. Bulk Modes

Suppose that for some given set of values $\{\omega^2, \mathbf{k}_\rho\}$, $2p$ branches of $k_3(\omega^2; \mathbf{k}_\rho)$ assume real values. Suppose further that one of these $2p$ values of $(2\pi)^{-1}k_3(\omega^2; \mathbf{k}_\rho)$, say the gth, is a rational number in the interval $(-\frac{1}{2}, \frac{1}{2})$, and that according to our labeling convention, Eqs. (3.26) and (3.27), $g > 0$. Then we can clearly satisfy the quasiperiodic boundary conditions with

$$u_\pi(m_3; \omega^2, \mathbf{k}_\rho, g) = N_g(\omega^2, \mathbf{k}_\rho)[u_\pi{}^{(g)}(\exp\{ik_3{}^{(g)}\}; \omega^2, \mathbf{k}_\rho) \times \exp\{ik_3{}^{(g)}m_3\} + \sum_{g'=-3sH_3}^{-1} R_{gg'}(\omega^2, \mathbf{k}_\rho)u_\pi{}^{(g')} \times (\exp\{ik_3{}^{(g')}\}; \omega^2, \mathbf{k}_\rho)\exp\{ik_3{}^{(g')}m_3\}]; \; m_3 \geq 2H_3. \tag{4.1}$$

If $g < 0$, then the sum with respect to g' in Eq. (4.1) runs over the $3sH_3 - p$ negative indices which label complex values of k_3 (with positive imaginary parts) and the p-positive indices labeling real values of k_3.

In Eq. (4.1), $N_g(\omega^2, \mathbf{k}_\rho)$ is a normalization constant, to be discussed below. The coefficients $R_{gg'}(\omega^2, \mathbf{k}_\rho)$ have to be determined from the continuity conditions

$$u_\pi(m_3; \omega^2, \mathbf{k}_\rho, g) = u_\pi{}^B(m_3; \omega^2, \mathbf{k}_\rho, g); \quad m = 2H_3, \cdots, 3H_3 - 1, \quad \pi = 1, \cdots, 3s. \tag{4.2}$$

The functions $u_\pi{}^B(m_3; \omega^2, \mathbf{k}_\rho, g)$ are solutions of the auxiliary problem specified by Eq. (3.10) and the $3sH_3$ equations obtained from Eq. (3.9) when $H_3 \leq m_3 \leq 2H_3 - 1$. Proceeding as in Sec. III of paper I, it is a simple matter to derive a set of $9sH_3$ linear equations for the $9sH_3$ unknowns:

$$\{u_\pi{}^B(m_3; \omega^2, \mathbf{k}_\rho, g); \quad m_3 = 0, \cdots, 2H_3 - 1, \quad \pi = 1, \cdots, 3s\},$$

and

$$\{R_{gg'}(\omega^2, \mathbf{k}_\rho); \quad g' = -3sH_3, \cdots, -1\}.$$

Here, and in the following, we restrict ourselves, for the sake of economy in notation, to the case where $g > 0$.

Introducing a more compact notation, we obtain the following set of equations:

$$\sum_{\gamma=1}^{9sH_3} M_{\alpha\gamma}(\omega^2, \mathbf{k}_\rho)R_{g\gamma}(\omega^2, \mathbf{k}_\rho) = u_\alpha(\omega^2, \mathbf{k}_\rho, g); \; \alpha = 1, \cdots, 9sH_3. \tag{4.3}$$

Here,

$$\alpha = 3sm_3 + \pi; \quad 0 \leq m_3 \leq 3H_3 - 1, \quad \alpha = 1, \cdots, 9sH_3; \tag{4.4}$$

$$\gamma = 3sn_3 + \sigma; \quad 0 \leq n_3 \leq 2H_3 - 1, \quad \gamma = 1, \cdots, 6sH_3,$$
$$= g' + 9sH_3 + 1; \quad \gamma = 6sH_3 + 1, \cdots, 9sH_3. \tag{4.5}$$

(If $g < 0$, we require a similar, though more complicated, mapping of the $3sH_3$ indices g' onto

$$\gamma = 6sH_3 + 1 \cdots 9sH_3.)$$

The $9sH_3$-dimensional matrix $M_{\alpha\gamma}$ is defined by Eqs. (4.6) and (4.7): For $\gamma = 1, \cdots, 6sH_3$,

$$M_{\alpha\gamma}(\omega^2, \mathbf{k}_\rho) = \theta_{\pi\sigma}(m_3, n_3; \omega^2, \mathbf{k}_\rho) + \delta\theta_{\pi\sigma}(m_3, n_3; \mathbf{k}_\rho); \tag{4.6}$$

For $\gamma = 6sH_3 + 1, \cdots, 9sH_3$,

$$M_{\alpha\gamma}(\omega^2, \mathbf{k}_\rho) = 0; \; \alpha = 1, \cdots, 3sH_3$$
$$= \sum_{\sigma=1}^{3s} \sum_{n_3=2H_3}^{m_3+H_3} \theta_{\pi\sigma}(n_3 - m_3)\exp\{ik_3{}^{(g')}n_3\}u_\sigma{}^{(g')} \times (\exp\{ik_3{}^{(g')}\}; \omega^2, \mathbf{k}_\rho); \; \alpha = 3sH_3 + 1, \cdots, 9sH_3. \tag{4.7}$$

The $9sH_3$-dimensional vector $R_{g\gamma}(\omega^2,\mathbf{k}_\rho)$ is defined by Eq. (4.8):

$$R_{g\gamma}(\omega^2,\mathbf{k}_\rho)=u_\pi{}^B(m_3;\,\omega^2,\mathbf{k}_\rho,g);\quad \gamma=1,\,\cdots,\,6sH_3$$
$$=N_g(\omega^2,\mathbf{k}_\rho)R_{gg'}(\omega^2,\mathbf{k}_\rho);\quad \gamma=6sH_3+1\cdots 9sH_3. \quad (4.8)$$

Finally,

$$u_\alpha(\omega^2,\mathbf{k}_\rho)=0;\ \alpha=1,\,\cdots,\,3sH_3$$
$$=-N_g(\omega^2;\,\mathbf{k}_\rho)\sum_{\sigma=1}^{3s}\sum_{n_3=2H_3}^{H_3+m_3}\theta_{\pi\sigma}(n_3-m_3;\,\omega^2,\mathbf{k}_\rho)$$
$$\times\exp\{ik_3{}^{(g)}n_3\}u_\sigma{}^{(g)}(\exp\{ik_3{}^{(g)}\};\,\omega^2,\mathbf{k}_\rho);$$
$$\alpha=3sH_3+1,\,\cdots,\,9sH_3. \quad (4.9)$$

Here we recall that

$$\theta_{\pi\sigma}(m_3,n_3;\,\omega^2,\mathbf{k}_\rho)+\delta\theta_{\pi\sigma}(m_3,n_3;\,\mathbf{k}_\rho)=\theta_{\pi\sigma}(n_3-m_3;\,\omega^2,\mathbf{k}_\rho)$$

if both m_3 and $n_3\geq H_3$. In general,

$$\det[M_{\alpha\gamma}(\omega^2,\mathbf{k}_\rho)]\neq 0; \quad (4.10)$$

hence,

$$N_g(\omega^2,\mathbf{k}_\rho)R_{gg'}(\omega^2,\mathbf{k}_\rho)=\sum_{\alpha=3sH_3}^{9sH_3}(M^{-1})_{\gamma\alpha}u_\alpha(\omega^2,\mathbf{k}_\rho). \quad (4,11)$$

If, for some particular choice of $\mathbf{k}_\rho$,

$$\det[M_{\alpha\gamma}(\omega^2,\mathbf{k}_\rho)]=0, \quad (4.12)$$

then the homogenous matrix equation

$$\sum_{\gamma=1}^{9sH_3}M_{\alpha\gamma}(\omega^2,\mathbf{k}_\rho)R_{g\gamma}(\omega^2,\mathbf{k}_\rho)=0 \quad (4.13)$$

has a nontrivial solution, which implies that there exists a nontrivial solution of Eqs. (3.9) and (3.10) having the form

$$u_\pi(m_3;\,\omega^2,\mathbf{k}_\rho)=\sum_{g'=-3sH_3}^{-1}c_{g'}(\omega^2,\mathbf{k}_\rho)$$
$$\times\exp\{ik_3{}^{(g')}m_3\}u_\sigma{}^{(g')}(\exp\{ik_3{}^{(g')}\};\,\omega^2,\mathbf{k}_\rho)\mathbf{h} \quad (4.14)$$

This solution violates the quasiperiodic boundary conditions unless all $3sH_3$ values of $k_3(\omega^2;\,\mathbf{k}_\rho)$ entering the sum with respect to g' are complex. In this case Eq. (4.14) represents one of the surface waves to be discussed below.

Physically, the exclusion of solutions of the form indicated by Eq. (4.14) is based on the fact that if the sum with respect to g' includes real values of $k_3(\omega^2;\,\mathbf{k}_\rho)$, then these solutions imply a steady transport of energy to infinity, and hence cannot represent stationary free vibrations of the lattice. This objection does not apply when the real values of $k_3(\omega^2;\,\mathbf{k}_\rho)$ are such that $[\partial k_3{}^{(g')}/\partial\omega(\omega^2;\,\mathbf{k}_\rho)]^{-1}=0$. As we shall see below, this represents the limiting case of an "unlocalized" surface wave.

The discrete index g in Eq. (4.1) is redundant unless the infinite lattice with periodic boundary conditions exhibits an accidental degeneracy at $\{\omega^2,\mathbf{k}_\rho\}$; i.e., more than one branch of the function $k_3(\omega^2;\,\mathbf{k}_\rho)$ satisfies the equation

$$(2\pi)^{-1}k_3{}^{(g)}(\omega^2;\,\mathbf{k}_\rho)=r;\ r=\text{rational number},$$
$$-\tfrac{1}{2}<r\leq\tfrac{1}{2}. \quad (4.15)$$

In that case a symmetric orthogonalization process leads to the functions

$$u_\pi(m_3;\omega^2,\mathbf{k}_\rho,g)$$
$$=N_g(\omega^2,\mathbf{k}_\rho)[u_\pi{}^{(g)}(\exp\{ik_3{}^{(g)}\};\omega^2,\mathbf{k}_\rho)\exp\{ik_3{}^{(g)}m_3\}$$
$$\times\exp\{ik_3{}^{(g)}m_3\}+\sum_{g\neq g'}R_{gg'}(\omega^2,\mathbf{k}_\rho)u_\pi{}^{(g')}$$
$$\times(\exp\{ik_3{}^{(g')}\};\,\omega^2,\mathbf{k}_\rho)\exp\{ik_3{}^{(g')}m_3\}];$$
$$m_3\geq 2H_3. \quad (4.16)$$

Here g' ranges only over values for which

$$\mathrm{Im}[k_3{}^{(g')}(\omega^2,\mathbf{k}_\rho)]\geq 0,$$

and we impose the orthonormalization conditions

$$\lim_{\epsilon\to 0^+}\sum_{\pi=1}^{3s}\sum_{m_3=0}^{\infty}e^{-\epsilon m_3}[u_\pi(m_3;\,\omega^2,\mathbf{k}_\rho,g)]^*$$
$$\times u_\pi(m_3;\,\omega'^2,\mathbf{k}_\rho,g')=\delta(\omega^2-\omega'^2)\delta_{g,g'}. \quad (4.17)$$

The orthogonality of vibrational modes associated with different values of ω^2 is proven in Appendix A. Thus, in general, Eq. (4.17) just fixes the normalization constant $N_g(\omega^2,\mathbf{k}_\rho)$. However, in case of accidental degeneracy of the periodic solutions of the infinite lattice, it provides a subsidiary set of relations, which together with Eq. (4.3) suffice to determine the coefficients in Eq. (4.16).

The Zero-Frequency Limit

In the preceding we explicitly excluded the zero-frequency limit. This limit will now be considered. It is physically obvious that there exist trivial zero-frequency modes, namely the three linearly independent translations, and the three linearly independent infinitesimal solid-body rotations. This result follows immediately from the invariance of the force acting on a given particle under an arbitrary infinitesmial translation and/or infinitesimal rotation of the entire lattice.[21] The six trivial zero-frequency modes are the only "vibrational" modes of the infinite lattice which are unaffected by the free boundary. These modes are the elementary solutions of Eq. (3.15) belonging to the sixfold root, $\exp\{ik_3(\omega^2=0,\,\mathbf{k}_\rho=0\}=1$, of the characteristic equation (3.17). All other zero-frequency roots of Eq. (3.17) correspond to complex values of k_3. Hence any nontrivial zero-frequency mode would represent a static

[21] An analysis of this invariance is given in Appendix A of Paper I.

displacement of the type considered in Sec. III of I. However, in the present case, the deformation has to be out of the true static equilibrium configuration of the semi-infinite lattice and hence, could only occur under the influence of an appropriate set of external forces. This argument demonstrates that the semi-infinite lattice with a free boundary cannot exhibit non-trivial zero-frequency modes. This is in fact a general restriction to be imposed on any force-constant model. This conclusion is equivalent with the requirement that the zero-frequency limit of any lattice dynamics must correspond to the elastic theory for an appropriate continuous, anistropic medium with corresponding boundary conditions.

B. Surface Modes

If for a given set of values $\{\omega^2,\mathbf{k}_\rho\}$ all of the $6sH_3$ branches of $k_3(\omega^2;\mathbf{k}_\rho)$ are complex, then the function $\mathbf{v}(m,\mu)$ appearing in Eq. (3.11) vanishes identically. We now can satisfy the quasiperiodic boundary conditions with

$$u_\pi(m_3;\omega^2,\mathbf{k}_\rho)=\sum_{g=-3sH_3}^{-1} c_g(\omega^2,\mathbf{k}_\rho)u_\pi{}^{(g)} \times(\exp\{ik_3{}^{(g)}\};\omega^2,\mathbf{k}_\rho)\exp\{ik_3{}^{(g)}m_3\};\ m_3\geq 2H_3, \quad (4.18)$$

where the coefficients c_g have to be determined by a set of continuity conditions, such as Eq. (4.2). Proceeding as before, we obtain a set of $9sH_3$ linear homogeneous equations of the form

$$\sum_{\gamma=1}^{9sH_3} M_{\alpha\gamma}(\omega^2;\mathbf{k}_\rho)c_\gamma(\omega^2,\mathbf{k}_\rho)=0. \quad (4.19)$$

The matrix $M_{\alpha\gamma}$ has been defined by Eqs. (4.6) and (4.7). The $9sH_3$-dimensional vector c_γ is defined by Eq. (4.20):

$$\begin{aligned} c_\gamma(\omega^2,\mathbf{k}_\rho)&=u_\pi{}^B(m_3;\omega^2,\mathbf{k}_\rho);\quad \gamma=1,\cdots,6sH_3\\ &=c_g(\omega^2,\mathbf{k}_\rho);\quad \gamma=6sH_3+1,\cdots,9sH_3. \end{aligned} \quad (4.20)$$

Equation (4.19) has a nontrivial solution if, and only if,

$$\det[M_{\alpha\gamma}(\omega^2,\mathbf{k}_\rho)]=0. \quad (4.21)$$

Thus we have to find a simultaneous solution of Eqs. (3.17), (3.18), (3.19), and (4.21). This gives us a consistent set of values of $\omega^2,\mathbf{k}_\rho$ and $k_3{}^{(g)}(\omega^2;\mathbf{k}_\rho)$ along with the corresponding elementary solutions $u_\pi(\exp\{ik_3{}^{(g)}m_3\})$ of Eq. (3.15). Whenever these sets of values are such that $\omega^2=\omega_s{}^2\geq 0$, $\mathbf{k}_\rho$ satisfies Eq. (3.7), and all values of $k_3(\omega^2;\mathbf{k}_\rho)$ are complex, we can construct a solution of our boundary-value problem in the form indicated by Eq. (4.18). We do this by choosing $\{c_\gamma\}$ to be a null vector of the matrix $M_{\alpha\gamma}(\omega^2,\mathbf{k}_\rho)$, i.e.,

$$\sum_{\gamma=1}^{9sH_3} M_{\alpha\gamma}(\omega_s{}^2,\mathbf{k}_\rho)c_\gamma(\omega_s{}^2,\mathbf{k}_\rho)=0;\ \gamma=1,\cdots,9sH_3 \quad (4.22)$$

where $\omega^2=\omega_s{}^2$ and $\mathbf{k}_\rho$ area set of simultaneous solutions of Eqs. (3.17), (3.19), and (4.21). The characteristic feature of the vibrational modes having the form indicated by Eq. (4.18) is that the amplitude of the displacement of lattice particles from their static equilibrium positions decreases, essentially exponentially, with the distance m_3 from the boundary. Hence we can consider the vibration to be localized or bound at the surface. It is, however, important to realize that, in general, the dependence of $\mathbf{u}$ on m_3 is neither a simple exponential, nor even monotonic: There is no general restriction on the real part of the functions $k_3{}^{(g)}(\omega_s{}^2(\mathbf{k}_\rho);\mathbf{k}_\rho)$ which can, in fact, assume any value in the interval $(-\pi,\pi]$.

The surface modes are square summable, and we impose on them the orthonormalization

$$\sum_{\pi=1}^{3s}\sum_{m_3=0}^{\infty}[u_\pi(m_3;\omega_s{}^2(\mathbf{k}_\rho),\mathbf{k}_\rho)]^* \times u_\pi(m_3;\omega_{s'}{}^2(\mathbf{k}_\rho),\mathbf{k}_\rho)=\delta_{\omega_s{}^2,\omega_{s'}{}^2}. \quad (4.23)$$

Since, for a fixed value of $\mathbf{k}_\rho$, no surface-mode frequency ω_s can lie in one of the $3s$ intervals, $\omega_n(\mathbf{k}_\rho)$, in which the bulk mode frequencies lie, the surface and bulk modes are mutually orthogonal, i.e.,

$$\sum_{\pi=1}^{3s}\sum_{m_3=0}^{\infty}[u_\pi(m_3;\omega_s{}^2(\mathbf{k}_\rho),\mathbf{k}_\rho)]^*u_\pi(m_3;\omega^2,\mathbf{k}_\rho,g)=0. \quad (4.24)$$

We now turn to a brief discussion of some features of the dispersion relation of the surface modes.

In Sec. III B we considered k_3 to be an algebraic function of the variable ω^2 and the fixed pair of real parameters $\mathbf{k}_\rho=2\pi\sum_{i=1}{}^2\alpha_i{}^{-1}\mathbf{b}_ik_i$. It is now convenient to extend our definition of k_3, by treating $\exp\{2\pi ik_i\}$; $i=1,2$ as two independent variables, ranging over the entire complex plane. This involves a process of analytic continuation starting with the functions

$$k_3{}^{(g)}(\omega^2;\exp\{2\pi ik_1\}=c_1,\exp\{2\pi ik_2\}=c_2)$$

and continuing them first over the $\exp\{2\pi ik_1\}$ plane and then over the $\exp\{2\pi ik_2\}$ plane. We need not be concerned with the actual tedious process since we are only concerned with the formal result. Next we note that the vectors $u_\pi{}^{(g)}(\exp\{ik_3{}^{(g)}\};\omega^2,\mathbf{k}_\rho)$ are, by construction, polynomials in the variables $\exp\{ik_3{}^{(g)}\},\omega^2$, $\exp\{2\pi ik_1\}$, and $\exp\{2\pi ik_2\}$. Hence we find that the determinant, $\det[M_{\alpha\gamma}(\omega^2,\mathbf{k}_\rho)]$, can be considered a polynomial in the variables:

$$\omega^2,\exp\{2\pi ik_1\},\exp\{2\pi ik_2\},\exp\{2\pi ik_3{}^{(g)}(\omega^2;\exp\{2\pi ik_1\},\exp\{2\pi ik_2\})\};\ g=-3sH_3,\cdots,-1.$$

This suggests that we interpret Eqs. (3.17), (3.18), and (4.21) as the implicit definition of the algebraic function $\omega_s{}^2$ of the two complex variables $\exp\{2\pi ik_1\}$ and $\exp\{2\pi ik_2\}$. In particular we may consider the one-dimensional sections of this function

$$\omega_s{}^2(\exp\{2\pi ik_1\};\exp\{2\pi ik_2\}=c_2),$$

and its inverse $\exp[2\pi i k_1^{(s)}(\omega^2; \exp\{2\pi i k_2\}=c_2)]$. These can be discussed in a manner similar to that outlined in Sec. III B. We are primarily concerned with those values of

$$k_1^{(s)} = (2\pi i)^{-1} \text{ principal values of } \ln[\exp\{2\pi i k_1^{(s)}\}], \tag{4.25}$$

which lie on a line segment contained in the first Brillouin zone, and for which at least one branch of the function $\omega_s^2[\exp\{2\pi i k_1\}; \exp\{2\pi i k_2\}=c_2]$ is positive, and for which all branches of $k_3^{(g)}(\omega_s^2>0; \mathbf{k}_\rho)$ assume complex values. The analyticity of all these functions implies that such values of k_1 cannot in general be isolated points, i.e., that all k_1 on a subinterval of the above-mentioned segment have to satisfy our requirement. Clearly the preceding applies also to the case where we fix k_1 and consider k_2 a variable. We also note that, as a function of frequency, a given branch of $k_1^{(s)}$ assumes real values on intervals on the real ω axis, which are bounded by frequencies for which

$$\left[\frac{\partial[\exp(2\pi i k_1^{(s)})]}{\partial(\omega^2)}\right]^{-1}_{k_2=\text{const}} = \frac{\omega}{\pi i} \times \exp\{-2\pi i k_1^{(s)}\}\left[\frac{\partial k_1^{(s)}}{\partial\omega}\right]^{-1}_{k_2=\text{const}} = 0. \tag{4.26}$$

Now,

$$0=\left[\frac{\partial k_1^{(s)}}{\partial\omega}\right]^{-1} = \left[\sum_{g=-3sH_3}^{-1} \frac{\partial k_1^{(s)}}{\partial k_3^{(g)}}\frac{\partial k_3^{(g)}}{\partial\omega}\right]^{-1} \tag{4.27}$$

implies that at least one term in the summation on the right of Eq. (4.27) is infinite, i.e., for example,

$$\left[\frac{\partial k_1^{(s)}}{\partial k_3^{(g)}}\frac{\partial k_3^{(g)}}{\partial\omega}\right]^{-1}_{k_2=\text{const}} = 0.$$

Hence, at least two branches of k_3 have the same value. This multiple value of k_3 may be real, in which case we have the limiting case of an unlocalized surface mode, mentioned in our discussion of Eq. (4.14). This type of solution of the dynamic problem is analogous to a zero-energy scattering resonance. We now recall that only a dense subset of the points $\mathbf{k}_\rho$ in the first Brillouin zone of the two-dimensional reciprocal lattice, spanned by $\{\alpha_1^{-1}\mathbf{b}_1, \alpha_2^{-1}\mathbf{b}_2\}$, are consistent with the periodic boundary conditions imposed in the 1 and 2 dimensions. We thus conclude from the preceding that the spectrum of the surface modes is a dense subset of a set of ω intervals (surface bands). Unlike the bulk-energy bands, the surface bands are defined only over subregions of the first Brillouin zone. The preceding remark has to be further qualified: If the two-dimensional Brillouin zone has lines of symmetry, then it is possible that surface modes are associated with a dense set of points along such lines, but not with any points in a sector of the zone including this line. This is because for this case the dynamical problem separates into two uncoupled sets of difference equations, one consisting of s equations, the other of $2s$ equations. A particular example of such a case is considered by Gazis *et al.*[22] Finally, we note that according to Eq. (4.26), the point $k_1=0=k_2, \omega=0$ is a lower boundary of a surface band. More precisely, the zero-frequency modes may also be interpreted as the zero-frequency limit of surface modes (Rayleigh waves). Here, as in the case of the unlocalized surface modes, the imaginary part of at least one value of k_3 tends to zero at the band edge of the surface modes in question. This is not generally necessary.

C. Real Multiple Value of $k_3(\omega^2; k_\rho)$

We know from the theory of algebraic functions that a real multiple value $k_{3,0}$ of the function $k_3(\omega^2, k_\rho)$ occurs either if

$$\left.\frac{\partial(\omega_n^2)}{\partial(\exp\{ik_3\})}\right|_{k_3=k_{3,0}} = -2\omega_n \exp\{-ik_3\}\left.\frac{\partial\omega_n}{\partial k_3}\right|_{k_3=k_{3,0}} = 0, \tag{4.28}$$

or if the derivative on the left side of Eq. (4.28) is undefined.[23] Here $\omega_n^2(\exp\{ik_3\}; \mathbf{k}_\rho)$ is one of the $3s$ branches of the inverse of the function $\exp\{ik_3(\omega^2, \mathbf{k}_\rho)\}$.

In the first case an allowed band of the one-dimensional section of the phonon-energy function has an extremum, i.e.,

$$\partial\omega_n/\partial k_3|_{k_3=k_{3,0}} = 0. \tag{4.29}$$

In the second case one or more bands have a common point at $(k_{3,0}; \mathbf{k}_\rho)$. The nature of this point, i.e., the way the bands diverge from a point of degeneracy can be investigated by means of standard techniques discussed in the theory of algebraic functions. Such degeneracies arise if the point $(k_{3,0}; \mathbf{k}_\rho)$ lies on a line of symmetry of the first Brillouin zone of the three-dimensional reciprocal lattice. For an arbitrary point $(k_{3,0}; \mathbf{k}_\rho)$ such degeneracies are vanishingly probable, in the sense of Herring.[24] We shall not consider the degeneracy problem any further, since it is a rather specialized problem requiring considerable and tedious analytic work.

Turning to the case where Eq. (4.29) applies, we shall consider first the case where $\omega_n(k_3; \mathbf{k}_\rho)$ has an extremum at a frequency ω_0, at which there exists a mode of the infinite lattice with periodic boundary conditions. This implies that the extremum ω_0 of $\omega_n(k_3; \mathbf{k}_\rho)$ is assumed at a rational value r of $(2\pi)^{-1}k_3$. We may assume that r is a double value of $k_3(\omega^2; \mathbf{k}_\rho)$. In this case the quasi-periodic boundary conditions can be satisfied if, and only if,

$$(\partial k_3^{(g)}/\partial\omega)^{-1}|_{\omega=\omega_0} = 0, \tag{4.30}$$

[22] See the first paper in Ref. 11.

[23] See K. Knopp, *Theory of Functions* (Dover Publications, Inc., New York, 1947), Part II, Chaps. 5 and 6.

[24] C. Herring, Phys. Rev. **52**, 365 (1937).

for all real-valued branches of k_3, and

$$\det[M_{\alpha\gamma}(\omega^2,\mathbf{k}_\rho)]=0. \tag{4.31}$$

Here the matrix $M_{\alpha\gamma}$ is defined by Eq. (4.7). Thus we see that if the semi-infinite lattice has a vibrational mode of frequency ω_0, then this mode must be an unlocalized surface mode. Furthermore, according to Eq. (4.30) this is possible only of ω_0 is an absolute extremum of $\omega_n(k_3;\mathbf{k}_\rho)$, and if it is a boundary point of an interval on the real ω axis on which no branch of k_3 has real values. A completely different situation arises if $\omega_n(k_3=2\pi r;\mathbf{k}_\rho)=\omega_0$ and ω_0 is an extremum of $\omega_n(k_3;\mathbf{k}_\rho)$, which, however, is assumed at some irrational value of $2\pi^{-1}k_3$. In this case there exists at ω_0 a bulk mode, which can be found by means of the normal procedure, i.e., Eqs. (4.3)–(4.9).

V. CONCLUSIONS AND DISCUSSION

It was stressed in the Introduction that our principal concern is the formal characterization of the functional form of the normal vibrational modes of a semi-infinite crystal lattice. This result is of considerable interest in the study of surface effects. As a particular example, we may mention the thermal diffuse scattering of low-energy electrons.

The vibrational states of the semi-infinite lattice were subjected to quasiperiodic boundary conditions at an infinite distance from the free boundary. These boundary conditions were discussed in Sec. II, where it was shown that they emphasize the relation of the semi-infinite lattice to the infinite lattice with periodic boundary conditions. It was shown that the vibrational modes of the semi-infinite lattice fall into two classes.

(1) The bulk modes can be expressed as a sum of a plane-wave mode of the infinite lattice with periodic boundary conditions, and a "scattered" wave. This scattered wave reduces, at an infinite distance from the boundary, to a finite sum of plane waves which do not satisfy periodic boundary conditions. The group velocities of these plane waves all have a component normal to the boundary which has a sign opposite to the sign of the corresponding component of the group velocity of the plane wave satisfying periodic boundary conditions.

Such a bulk mode exists for each frequency at which the infinite lattice has a plane-wave vibrational mode, provided this wave has a group velocity with a nonvanishing component normal to the boundary. In general, no "bulk" mode exists at a frequency at which the plane wave, satisfying periodic boundary conditions, has a group velocity with a vanishing component normal to the boundary. The exception to this rule is when the bulk mode reduces to a so-called unlocalized surface mode. These modes reduce, at an infinite distance from the boundary, to a set of plane waves, each of which has a group velocity with a vanishing component normal to the boundary.

(2) The second class of modes are the surface modes. These modes have a vanishing amplitude at an infinite distance from the boundary. They consist of a sum of plane waves whose wave vector has a complex component normal to the boundary. The imaginary part of this component of the wave-vector is positive. No general restriction is imposed on the real part of this component of $\mathbf{k}$. It was shown that the surface modes have frequencies which form a dense subset of continuous intervals or surface bands. The dispersion relation, i.e., the dependence of the frequency of the surface modes on the transverse wave vectors $\mathbf{k}_\rho$, was considered. It was shown that for a fixed-transverse wave vector $\mathbf{k}_\rho$ the frequencies of the surface modes lie in intervals which have at most their endpoint in common with the intervals in which there exist frequencies of bulk modes with the same value of $\mathbf{k}_\rho$. A somewhat more complete study of the dispersion of the bulk modes was undertaken. This study was based on the interpretation of the phonon-energy function at a fixed value of $\mathbf{k}_\rho$, as an algebraic function of the complex variable $\exp\{ik_3\}$. This procedure follows a similar analysis, by Heine, of the energy bands of Bloch electrons.

The entire analysis assumed a finite, though arbitrary, range of the effective interparticle interaction and hence the results are rather generally valid. However, there is considerable scope for further analysis of the analytic properties of the dispersion relations of the two classes of modes. This holds in particular for the surface modes. Another problem being investigated is the use of the thermal diffuse scattering of low-energy electrons to study the dispersion relation of the surface modes.

APPENDIX: PROOF OF THE ORTHOGONALITY OF THE NORMAL MODES [EQ. (4.59)]

In this Appendix we shall prove the orthogonality of those solutions of Eqs. (3.9), (3.10), and (3.11) which correspond to different values of ω^2. This result follows from the symmetry of the equations of motion, or more precisely, from the Hermitian character of the boundary-value problem.

Consider the expression

$$S(\epsilon_3,\eta_3)=\sum_{n_3,m_3=0}^{\infty}\sum_{\pi,\sigma=1}^{3s} e^{-\epsilon_3 m_3}[u_\pi(m_3;\omega'^2,\mathbf{k}_\rho)]^* \times\Phi_{\pi\sigma}(m_3,n_3;\mathbf{k}_\rho)e^{-\eta_3 n_3}u_\sigma(n_3;\omega^2,\mathbf{k}_\rho), \tag{A1}$$

where

$$\Phi_{\pi\sigma}(m_3,n_3;\mathbf{k}_\rho)=\sum_{h_1h_2=-\infty}^{\infty}\Phi_{ij}(\mathbf{m},\mu;\mathbf{n},\nu)\exp\{i\mathbf{k}_\rho\cdot\mathbf{R}(\mathbf{h}_\rho)\}. \tag{A2}$$

The matrices $\Phi_{ij}(\mathbf{m},\mu;\mathbf{n},\nu)$ are defined by Eq. (2.11). $u_\pi(m_3;\omega'^2,\mathbf{k}_\rho)$ and $u_\sigma(n_3;\omega^2,\mathbf{k}_\rho)$ are solutions of the boundary-value problem belonging to different values of ω^2. $0<\epsilon_3,\eta_3\ll 1$, are arbitrary but fixed small, positive numbers.

The exponential convergence factors ensure the absolute convergence of the two infinite sums over n_3 and m_3. Hence, the order of these sums is immaterial. Summing first over n_3 and σ, we may safely set $\eta_3=0$, for the series is convergent. Hence, we obtain

$$S(\epsilon_3,0)=\sum_{\pi=1}^{3s}\sum_{m_3=0}^{\infty} e^{-\epsilon_3 m_3}[u_\pi(m_3;\omega'^2,\mathbf{k}_\rho)]^* \times[\omega^2 u_\pi(m_3;\omega^2,\mathbf{k}_\rho)]. \quad \text{(A3)}$$

Similarly, if we sum first over m_3 and π, we obtain

$$S(0,\eta_3)=\sum_{\sigma=1}^{3s}\sum_{n_3=0}^{\infty} e^{-\eta_3 n_3}u_\sigma(n_3;\omega^2,\mathbf{k}_\rho) \times[\omega'^2 u_\sigma(n_3;\omega'^2,\mathbf{k}_\rho)]^*, \quad \text{(A4)}$$

but the dummy variable η_3,n_3,σ can clearly be replaced by ϵ_3,m_3,π. Furthermore, ω'^2 is real. Hence, Eq. (A4) reduces to

$$S(0,\epsilon_3)=\omega'^2\sum_{\pi=1}^{3s}\sum_{m_3=0}^{\infty} e^{-\epsilon_3 m_3}[u_\pi(m_3;\omega'^2,\mathbf{k}_\rho)]^* \times u_\pi(m_3;\omega^2,\mathbf{k}_\rho). \quad \text{(A5)}$$

On the other hand, we can check directly that we require in (A1) only one convergence factor. That is,

$$S(\epsilon_3,\eta_3)=S(\epsilon_3,0)=S(0,\epsilon_3). \quad \text{(A6)}$$

Hence subtracting Eq. (A.3) from Eq. (A.4), we obtain

$$0=(\omega'^2-\omega^2)\sum_{\pi=1}^{3s}\sum_{m_3=0}^{\infty} e^{-\epsilon_3 m_3}[u_\pi(m_3;\omega'^2,\mathbf{k}_\rho)]^* \times u_\pi(m_3,\omega^2;\mathbf{k}_\rho) \quad \text{(A7)}$$

or

$$\sum_{\pi=1}^{3s}\sum_{m_3=0}^{\infty} e^{-\epsilon_3 m_3}[u_\pi(m_3,\omega'^2,\mathbf{k}_\rho)]^* u_\pi(m_3;\omega^2,\mathbf{k}_\rho)=0$$

if

$$\omega^2\neq\omega'^2, \quad \text{(A8)}$$

and, since ϵ_3 is arbitrary, we can now go to the limit $\epsilon_3\to 0^+$. This proves Eq. (4.17) for $\omega^2\neq\omega'^2$. A similar analysis leads to the proof of the Dirac delta-function normalization indicated in Eq. (4.17). We note here that the entire limiting procedure can be dispensed with when $\mathbf{u}$ is a surface mode, for then the u's themselves are exponentially bounded.

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Current Saturation and Trap-Controlled Electron Drift Mobility in Photoconductive CdS†

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Current saturation due to acoustic oscillations in CdS is observed, both in a transverse mode and in a longitudinal mode. The most pronounced saturation occurred in the transverse mode, although the applied dc field was parallel to the c axis, and one should expect saturation mainly in the longitudinal mode. A method for determining the threshold field for oscillation, utilizing the buildup time for current saturation under applied pulsed dc electric field, is discussed. The threshold field is used to determine the electron drift mobility for photoconducting CdS in the temperature range from 204 to 438°K. The temperature dependence of the mobility can be described as a combination of scattering from lattice vibration and trapping from two impurity levels, $\epsilon_1=0.02$ eV with density $N_1=6\times10^{17}$ cm^{-3} and $\epsilon_2=0.1$ eV with density $N_2=8\times10^{16}$ cm^{-3}, and is given by

$$\mu_d=\frac{1.28\times10^6 T^{-3/2}}{1+1420T^{-3/2}e^{0.02/kT}+189T^{-3/2}e^{0.1/kT}}\ \text{cm}^2/\text{V sec}.$$

I. INTRODUCTION

IN their theoretical analysis of acoustoelectric amplification in piezoelectric semiconductors, Hutson and White[1,2] indicated that trapped charge could have a large influence on the propagation constants, but made no use of this concept in their experimental verification of acoustoelectric amplification in CdS.[3] Several authors[4–6] have ignored this effect, while others have given the effect an extensive treatment.[7–10] Moore and Smith[9] have considered the effect of traps on acoustoelectric current saturation in CdS, and have shown that the

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