Dynamics of a Semi-Infinite Crystal Lattice in a Quasiharmonic Approximation. I. The Static Equilibrium Configuration of a Semi-Infinite Lattice*

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This is the first of two papers dealing with the dynamics of semi-infinite crystals. The static equilibrium structure of a semi-infinite crystal at zero temperature is considered in the first paper. The discussion of small-amplitude vibrations of the atoms about their static equilibrium positions is taken up in the second paper. The static equilibrium configuration of a semi-infinite, classical, crystal lattice at zero temperature, having a free boundary, is described in terms of a set of displacements relating the actual positions to those which the lattice particles would assume if the semi-infinite lattice were embedded in an infinite lattice. These displacements are calculated from a set of difference equations which specify the conditions of static equilibrium for the semi-infinite lattice in the absence of external forces. Several unexpected results concerning the structure of the physical boundary region were obtained. These will be shown, in a forthcoming paper, to provide a consistent interpretation of some features of low-energy electron diffraction data, which, until now, could not be interpreted. Of particular interest is the conclusion that the two-dimensional period of the semi-infinite lattice in the planes parallel to the boundary may be larger than that deduced from the bulk lattice structure. The diffraction of low-energy electrons from the surface of single crystals of Ge and Si provides a clear illustration of this effect. It is also shown that the change in the spacing of atomic planes (in the direction normal to the boundary) varies in a nonmonotonic fashion with the distance from the boundary. The effect of appreciable distortions in the surface region is considered in some detail.

I. INTRODUCTION

THE classical theory of lattice dynamics was originally formulated by Born and von Kármán[1] in terms of the so-called periodic boundary conditions. The modern elaborations of the theory, and its many applications, are discussed in great clarity and detail in the standard references, Born and Huang,[2] Liebfried,[3] Ludwig and Leibfried,[4] and Maradudin, Montroll, and Weiss.[5] The theory has great practical and aesthetic appeal because of its formal simplicity. This advantage is in no way impaired by the great practical difficulty in calculating the actual dispersion relation and frequency spectrum of any particular crystalline solids. However, one rather serious limitation of the theory is that it is inherently designed for the discussion of bulk effects, or more specifically, it applies to an infinite system. Thus, the theory does not provide a reliable conceptual framework for the analysis of phenomena occurring within the physical boundary layer whose width is of the order of 10^2 Å. Examples of such phenomena are the Mössbauer effect from a nucleus in the boundary layer and the low-energy electron diffraction and photoemission of electrons.

Recently, low-energy electron diffraction experiments have achieved a high degree of reliability and sensitivity. In principle, these experiments should enable us to study the static (equilibrium) configuration of semi-infinite crystal lattices and their dynamics (i.e., dispersion relation) with a sensitivity which is comparable to the study of the corresponding properties of infinite (bulk) crystals by means of x-ray and neutron scattering experiments. In order to utilize the available electron diffraction data, we require a formulation of the dynamics of semi-infinite crystal lattices which provides an adequate conceptual framework for the analysis of these data. That is, we require a formulation which is not necessarily ideal for *a priori* calculations, but most transparent in its formal predictions.

Several investigations of surface effects on the dynamics of crystal lattices have been reported in the literature during the last two decades. Ledermann[6] investigated the effect of boundaries on the vibrational spectrum. His work demonstrated the possible existence of vibrational states whose energy lies in an interval which is forbidden by the periodic boundary conditions. The nature of these so-called surface modes was investigated by Lifshitz,[7] using Green's-function techniques. Similar techniques were used by Maradudin and Wallis[8] in an analysis of surface contributions to the low-temperature specific heat. Wallis and co-workers[9]

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[2] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954).

[3] G. Leibfried, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. VII, Part I, p. 104.

[4] G. Leibfried and W. Ludwig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1961), Vol. 12. p. 275.

[5] A. A. Maradudin, E. W. Montroll, and G. H. Weiss, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl., Vol. 3.

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[8] A. A. Maradudin and R. F. Wallis, Phys. Rev. **148**, A962 (1966).

[9] D. C. Gazis, R. Herman, and R. F. Wallis, Phys. Rev. **119**, 533 (1960); B. C. Clark, R. Herman, and R. F. Wallis, *ibid.* **139**, A860 (1965).

have chosen a less formal approach. They considered rather restricted models to calculate explicit dispersion relations of surface modes, as well as the mean-square displacement, and mean-square velocity of atoms in the surface region. None of these investigations was concerned with the explicit equilibrium structure of the surface region of a crystal. This problem was considered by Gazis and Wallis.[10] However, Gazis and Wallis restricted themselves to the analysis of a one-dimensional monatomic model with second-neighbor interactions. It is the purpose of this paper to investigate the static equilibrium structure of a three-dimensional crystal lattice with a single free boundary. More specifically, we shall refer the actual equilibrium positions of the particles to the "nominal" equilibrium positions they would occupy if the lattice were infinite (and subject to periodic boundary conditions). We shall derive a convenient formal expression for the static displacements relating the actual positions to the "nominal" equilibrium positions of the particles in an infinite crystal lattice with periodic boundary condition. The theory is very general and involves a minimum of special assumptions concerning the nature of the effective interparticle interaction. In effect we only have to assume that the interaction has some unspecified finite range.

Following an analysis assuming small relative displacements, we also discuss the effect of anharmonicity on our results. Proceeding from our theory of the static equilibrium structure of the semi-infinite lattice, we shall develop, in a second paper,[11] a theory of the dynamics of small amplitude vibrations of particles in a semi-infinite crystal lattice, about their actual equilibrium positions. We shall derive convenient formal expressions for the normal modes of a semi-infinite crystal with a free boundary, without having to resort to Green's-function techniques. That is, we shall obtain explicit expressions, rather than integral representations of the normal modes.

The application of our theory to the analysis of low-energy electron diffraction is reasonably simple. We propose to consider this subject in our forthcoming paper.[12] In that paper we shall show that the essential characteristics of the static displacements, which specify the structure of the semi-infinite crystal, can be deduced directly from the raw diffraction data.

The model on which our theory is based is described in Sec. II. The mathematical analysis of the linearized model is taken up in Sec. III. In Sec. IV we take up the discussion of anharmonic effects. The results are summarized and discussed in Sec. V.

II. DESCRIPTION OF THE MODEL

We consider a system of atoms which, in its ground state (i.e., at $T=0$), is ordered in an approximately periodic semi-infinite lattice. We assume that the lattice is bounded by a single lattice plane, i.e., it arises from an infinite and perfect lattice by removing all "atoms" below a particular lattice plane spanned by the basis vectors $\mathbf{a}_1$, $\mathbf{a}_2$. During this operation, we freeze all of the remaining "atoms." We then release, instantaneously, all of these "atoms" and allow them to relax to the configuration which minimizes their potential energy of interaction. Thus the centers of mass of the lattice particles are located at the positions

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

Here, the vectors

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

span a semi-infinite Bravais lattice. For the following, it is essential to choose $\mathbf{a}_3$ to be orthogonal to $\mathbf{a}_1$ and $\mathbf{a}_2$. Usually this convention makes the unit cell nonprimitive.

$$\mathbf{R}(\mu),\quad \mu=1,\cdots s=\text{position of the } \mu\text{th atom}$$

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.

We shall call the vector $\mathbf{U}(\mathbf{m},\mu)$ the static displacement of the μth atom in the $\mathbf{m}$th unit cell of the infinite lattice. These static displacements are due to the creation of a free-boundary plane at $m_3=0$.

In the following we shall derive an approximate set of linear difference equations which has to be satisfied by the static displacements $\mathbf{U}(\mathbf{m},\mu)$. The nature of the solutions of these equations is then investigated with the help of the general theory of linear difference equations.

The static displacements are defined by the equilibrium conditions

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

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

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

We now make the following assumptions:

(1) The magnitude of the relative static displacements of atoms in adjacent cells is small compared to the lattice parameters. Consequently, we can approximate functions defined on the semi-infinite lattice by retaining only the lowest-order terms in their series expansion in powers of these relative displacements.

[10] Denos C. Gazis and Richard F. Wallis, J. Math. Phys. 3, 190 (1962).
[11] T. E. Feuchtwang, following paper, Phys. Rev. 155, 731 (1967).
[12] T. E. Feuchtwang, Phys. Rev. (to be published).

This is the familiar basic assumption of the harmonic approximation to lattice dynamics.[13]

(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, 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, i.e.,

$$l_3\geqslant 0. \quad (2.7)$$

It should be stressed that this assumption is rather weak, and one might even consider it reasonable to assume that the left side of Eq. (2.6) vanishes.

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

It should be stressed that assumption (3) is also valid for ionic crystals. For, as is well known from the standard treatment of the lattice dynamics of ionic crystals, the Coulombic contribution to the interionic interaction has to be decomposed into two terms. The first term represents an effective long-range interaction which is a slowly varying function of position. The second term is an effective, short-range interaction. Only the second term is included in the effective interionic interaction which enters the mechanical (microscopic) equations of motion for the ions. The long-range interaction is replaced by a macroscopic (slowly varying) effective electric field which has to satisfy the macroscopic Maxwell equations. Thus the complete dynamic problem reduces to a simultaneous solution of the mechanical equations of motion and the associated set of Maxwell equations.[2,3] We now recognize that the discussion of the equilibrium configuration of ionic and piezoelectric crystals is complicated by the necessity of making the sum of the effective interionic potential energy and of the electrostatic energy of the macroscopic field stationary. For this reason we shall explicitly exclude ionic and piezoelectric crystals from the following discussion.

We also stipulate that we wish to consider only the effect of a single free boundary. We shall therefore eliminate the effect of boundaries in the 1 and 2 dimensions. This is done by imposing periodic boundary conditions on these two (unbounded) dimensions. That is, we shall require that all functions F, defined over the lattice, have the property

$$F(m_1,m_2,m_3,\mu)=F(m_1\pm N_1,\, m_2\pm N_2,\, m_3,\, \mu), \quad (2.8)$$

where N_i, $i=1, 2$, are fixed, though arbitrary, large integers, and the limit $N_i\to\infty$ is understood.

We can use the first two assumptions listed above to approximate the vector $\mathbf{\Psi}(\mathbf{m},\mu)$ to within terms of order 2 in the relative displacements. This is achieved by considering first the Taylor expansion of $\mathbf{\Psi}(\mathbf{m},\mu)$ in terms of $\mathbf{U}$,

$$\mathbf{\Psi}(\mathbf{m},\mu)=-\mathbf{F}(\mathbf{m},\mu)$$
$$+\sum_{\mu=1}^{s}\sum_{n_3=0}^{\infty}\sum_{n_1,n_2=-\infty}^{\infty}\mathbf{\Phi}(\mathbf{m},\mu;\mathbf{n},\nu)\cdot\mathbf{U}(\mathbf{n},\nu)+O(U^2). \quad (2.9)$$

Here,

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

and,

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

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

$$\mathbf{F}(\mathbf{m},\mu)=0 \quad \text{if} \quad m_3\geqslant H_3, \quad (2.12)$$

and

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

if one or more of the following inequalities applies:

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

Our assumptions concerning the potential energy of interaction of the semi-infinite lattice imply a number of constraints on the quantities $\mathbf{F}$ and $\mathbf{\Phi}$ appearing in Eq. (2.9). These relations are stated below, and their proof is indicated in Appendix A. The relations are important for the subsequent analysis; in particular, they enable us to express Eq. (2.9) in terms of the relative static displacements.

First we note that if both m_3 and $n_3\geqslant H_3$, then the matrices $\mathbf{\Phi}(\mathbf{m},\mu;\mathbf{n},\nu)$ are identical with the coupling (or force) constants introduced in the ordinary theory of infinite lattices.[3-5] Furthermore, the forces $\mathbf{F}(\mathbf{m},\mu)$ are the unbalanced forces acting on the particles in the upper half of the infinite lattice if we remove their interaction with the particles in the lower half of the lattice, $m_3<0$.

Next we invoke the invariances of $\Phi^{(u)}$ under a translation by a lattice vector parallel to the boundary,

$$\sum_{i=1}^{2}\mathbf{a}_i m_i\to\sum_{i=1}^{2}\mathbf{a}_i(m_i+h_i), \quad h_i=\text{integer}, \quad (2.15)$$

to conclude that

$$\mathbf{F}(\mathbf{m},\mu)=\mathbf{F}(0,0,m_3,\mu)=\mathbf{F}(m_3,\mu), \quad (2.16)$$

and

$$\Phi_{ji}(\mathbf{n},\nu;\mathbf{m},\mu)=\Phi_{ij}(\mathbf{m},\mu;\mathbf{n},\nu)$$
$$=\Phi_{ij}(0,\,0,\,m_3,\,\mu;\,n_1-m_1,\,n_2-m_2,\,n_3,\,\nu);$$
$$m_3 \text{ or } n_3<H_3$$
$$=\Phi_{ij}(\mathbf{0},\,\mu;\,\mathbf{n}-\mathbf{m},\,\nu); \quad m_3 \text{ and } n_3\geqslant H_3. \quad (2.17)$$

[13] In the following we shall in fact only retain first-order terms in the relative static displacement. A nonlinear model will, however, be considered in Sec. II.

The first equation in Eq. (2.17) is a direct consequence of the definition of the Φ matrices as mixed second derivatives. The third equation in Eq. (2.17) follows from assumptions (2) and (3). We shall find it convenient to exhibit the symmetry of the Φ matrices explicitly in our notation by introducing the variable $h_i=n_i-m_i$:

$$\Phi_{ij}(\mathbf{m},\mu;\mathbf{n},\nu)$$
$$\equiv\Phi_{ij}(h_1,h_2,m_3,n_3;\mu,\nu);\quad m_3 \text{ or } n_3<H_3$$
$$\equiv\Phi_{ij}(\mathbf{h};\mu,\nu);\quad m_3 \text{ and } n_3\geqslant H_3. \tag{2.18}$$

Finally, we observe that the upper half of the infinite lattice may be viewed as a system of particles in static equilibrium with the "external" forces $\mathbf{F}(\mathbf{m},\mu)$. Hence we can deduce the following identities:

$$\sum_{\mu=1}^{s}\sum_{m_3=0}^{H_3-1}\mathbf{F}(m_3,\mu)=0, \tag{2.19}$$

and

$$\sum_{\mu=1}^{H_3-1}\sum_{m_3=0}\bar{X}_i(0,0,m_3,\mu)F_j(m_3,\mu)$$
$$-\bar{X}_j(0,0,m_3,\mu)F_i(m_3,\mu)=0, \tag{2.20}$$

where

$$\bar{X}_i(\mathbf{m},\mu)=\text{the } i\text{th component of the vector } \mathbf{R}(\mathbf{m})+\mathbf{R}(\mu).$$

These identities simply assert that the particles in the upper half of the infinite lattice experience neither a net force nor a net torque due to their interaction with the particles in the lower half of the lattice. A corresponding set of identities is imposed on the matrices $\mathbf{\Phi}(\mathbf{m},\mu;\mathbf{n},\nu)$:

$$\sum_{\mu=1}^{s}\sum_{m_3=0}^{n_3+H_3}\sum_{m_1,m_2=-\infty}^{\infty}\Phi_{ij}(\mathbf{m},\mu;\mathbf{n},\nu)=0, \tag{2.21}$$

and

$$\sum_{\mu=1}^{s}\sum_{m_3=0}^{n_3+H_3}\sum_{m_1,m_2=-\infty}^{\infty}[\bar{X}_i(\mathbf{m},\mu)\Phi_{jl}(\mathbf{m},\mu;\mathbf{n},\nu)$$
$$-\bar{X}_j(\mathbf{m},\mu)\Phi_{il}(\mathbf{m},\mu;\mathbf{n},\nu)]$$
$$=F_j(\mathbf{n},\nu)\delta_{i,l}-F_i(\mathbf{n},\nu)\delta_{j,l}. \tag{2.22}$$

If $n_3\geqslant H_3$, then these identities assume the form valid for the infinite lattice,

$$\sum_{\mu=1}^{s}\sum_{m_3=n_3-H_3}^{n_3+H_3}\sum_{m_1,m_2=-\infty}^{\infty}\Phi_{ij}(\mathbf{m},\mu;\mathbf{n},\nu)=0, \tag{2.23}$$

and

$$\sum_{\mu=1}^{s}\sum_{m_3=n_3-H_3}^{n_3+H_3}\sum_{m_1,m_2=-\infty}^{\infty}\bar{X}_i(\mathbf{m},\mu)$$
$$\times\Phi_{jl}(\mathbf{m},\mu;\mathbf{n},\nu)-\bar{X}_j(\mathbf{m},\mu)\Phi_{il}(\mathbf{m},\mu;\mathbf{n},\nu)=0. \tag{2.24}$$

It follows from Eqs. (2.13), (2.21), and (2.23) that Eq. (2.9) is in fact an expansion in powers of the relative displacements. Hence it follows that if we neglect, as a first approximation, terms of order $[\mathbf{U}(\mathbf{n},\nu)-\mathbf{U}(\mathbf{m},\mu)]^2$, then our assumptions specify the static displacements $U_i(\mathbf{m},\mu)$ as the solution of a system of $3s$ coupled linear partial difference equations with inhomogeneous boundary conditions. In the next section we shall solve these equations by means of standard methods.

At this point it might help to recapitulate the physical content of the assumptions we have made in the preceding discussion. In effect, we visualize the semi-infinite lattice to be created from an infinite lattice by means of the following thought experiment. We freeze all "atoms" in the half-space $m_3\geqslant 0$ in their static equilibrium positions. Next we remove all "atoms" from the lower half-space, $m>0$. Finally, we release, instantaneously, the remaining "atoms." These now relax, under the influence of the unbalanced forces $\mathbf{F}(\mathbf{m},\mu)$. These forces are due to the "missing" interactions of the remaining "atoms" with those that were removed.

III. THE DETERMINATION OF THE STATIC DISPLACEMENTS IN THE LINEAR APPROXIMATION

Combining Eqs. (2.3) and (2.9), we obtain the following set of difference equations:

$$\sum_{j=1}^{3}\sum_{\mu=1}^{s}\sum_{n_3=0}^{m_3+H_3}\sum_{n_1,n_2=-\infty}^{\infty}\Phi_{ij}(\mathbf{m},\mu;\mathbf{n},\nu)U_j(\mathbf{n},\nu)$$
$$=F_i(m_3,\mu),\quad m_3=0\cdots H_3-1$$
$$=0,\qquad m_3\geqslant H_3. \tag{3.1}$$

These difference equations are to be solved subject to the boundary conditions

$$\mathbf{U}(m_1,m_2,m_3,\mu)=\mathbf{U}(m_1+N_1,\,m_2+N_2,\,m_3,\,\mu), \tag{3.2}$$

and

$$\lim_{m_3\to\infty}\mathbf{U}(\mathbf{m},\mu)=0. \tag{3.3}$$

The latter condition assures that atomic arrangement characteristic of the infinite lattice is recovered at sufficiently large distances from the boundary at $m_3=0$.

We can simplify our problem considerably by taking advantage of the periodic boundary conditions, and the invariance of the problem under a translation by a lattice vector parallel to the boundary. We write

$$\mathbf{U}(\mathbf{m},\mu)=\exp\{i\mathbf{k}_\rho\cdot\mathbf{R}(\mathbf{m}_\rho)\}\mathbf{U}(m_3;\mathbf{k}_\rho), \tag{3.4}$$

where

$$\mathbf{R}(\mathbf{m}_\rho)=\sum_{i=1}^{2}\mathbf{a}_i m_i, \tag{3.5}$$

$$\mathbf{k}_\rho=2\pi\sum_{i=1}^{2}k_i\mathbf{b}_i,\quad -1<k_i=\frac{\kappa_i}{N_i}<1,$$

$$\kappa_i=\text{integer}, \tag{3.6}$$

$$\mathbf{b}_1=\frac{\mathbf{a}_2\times\mathbf{a}_3}{\mathbf{a}_1\cdot\mathbf{a}_2\times\mathbf{a}_3},\quad \mathbf{b}_2=\frac{\mathbf{a}_3\times\mathbf{a}_1}{\mathbf{a}_2\cdot\mathbf{a}_3\times\mathbf{a}_1}. \tag{3.7}$$

The rational numbers k_i, $i=1, 2$, are the components of a vector in a two-dimensional reciprocal space, which is restricted to lie in the first Brillouin zone of the two-dimensional reciprocal lattice spanned by $\{\mathbf{b}_1,\mathbf{b}_2\}$. It is clear that our choice of $\mathbf{k}_\rho$ automatically satisfies the periodic boundary conditions. It also reduces our problem to a set of $3s$ coupled ordinary difference equations of order $2H_3$,

$$\sum_{\sigma=1}^{3s}\sum_{n_3=m_3-H_3}^{m_3+H_3}\theta_{\pi\sigma}(m_3,n_3;\mathbf{k}_\rho)\times U_\sigma(n_3;\mathbf{k}_\rho)=0;\quad \pi=1,\cdots,3s\quad m_3\geqslant H_3 \tag{3.8}$$

subject to the $3sH_3$, inhomogeneous boundary conditions, at the free surface,

$$\sum_{\sigma=1}^{3s}\sum_{n_3=0}^{m_3+H_3}\theta_{\pi\sigma}(m_3,n_3;\mathbf{k}_\rho)U_\sigma(n_3;\mathbf{k}_\rho)=F_\pi(m_3)\delta_{\mathbf{k}_\rho,\mathbf{0}};\quad m_3=0\cdots H_3-1,\quad \pi=1\cdots 3s \tag{3.9}$$

and the additional condition at infinity,

$$\lim_{m_3\to\infty}U_\sigma(m_3;\mathbf{k}_\rho)=0. \tag{3.10}$$

Here, we defined the new indices

$$\pi=3(\mu-1)+i\quad \sigma=3(\nu-1)+j; \tag{3.11}$$

and the $3s$-dimensional matrices $\theta_{\pi\sigma}$,

$$\theta_{\pi\sigma}(m_3,n_3,\mathbf{k}_\rho)=\sum_{h_1,h_2=-\infty}^{\infty}\Phi_{ij}(h_1,h_2,m_3,n_3;\mu,\nu)e^{i\mathbf{k}_\rho\cdot\mathbf{R}(\mathbf{h}_\rho)}. \tag{3.12}$$

In deriving Eq. (3.9), we also used the following known relation:

$$\sum_{m_1=-N_1}^{N_1}\sum_{m_2=-N_2}^{N_2}e^{-i\mathbf{k}_\rho\cdot\mathbf{R}(\mathbf{m}_\rho)}=(2N_1+1)(2N_2+1)\delta_{\mathbf{k}_\rho,\mathbf{0}}, \tag{3.13}$$

where N_i are the integers defined by Eq. (3.2).

Equation (3.8) represents a set of $3s$ coupled difference equations which have constant coefficients if $m_3\geqslant 2H_3$. That is, using Eq. (2.18), we can rewrite Eq. (3.8) in the form

$$\sum_{\sigma=1}^{3s}\sum_{h_3=-H_3}^{H_3}\theta_{\pi\sigma}(h_3;\mathbf{k}_\rho)\times U_\sigma(m_3+h_3;\mathbf{k}_\rho)=0;\quad m_3\geqslant 2H_3. \tag{3.14}$$

The solution of difference equations with constant coefficients is significantly easier than that of the more general type. As we shall see, we can take advantage of this fact by basing our analysis on Eq. (3.14) rather than on Eq. (3.8). This we can do by means of the following trick: We define an auxiliary problem for the functions $U_\pi{}^b(\mathbf{m};\mathbf{k}_\rho)$, $m=0,\cdots,2H_3-1$, which has to satisfy the $3sH_3$ boundary conditions [Eq. (3.9)] and the $3sH_3$ equations obtained from Eq. (3.8), when $H_3\leqslant m_3\leqslant 2H_3-1$.

We furthermore impose on these functions a set of $3sH_3$ continuity or consistency relations

$$U_\pi{}^{(b)}(m_3;\mathbf{k}_\rho)=U_\pi(m_3;\mathbf{k}_\rho);\quad 2H_3\leqslant m_3\leqslant 3H_3-1,\quad \pi=1,\cdots,3s. \tag{3.15}$$

Here $U_\pi(m_3;\mathbf{k}_\rho)$ is the most general solution of Eq. (3.14) which satisfies Eq. (3.10). It is easily recognized that this procedure is equivalent to the solution of Eq. (3.8) subject to the boundary conditions, Eqs. (3.9) and (3.10). However, it is much simpler than the direct solution of these equations.

We recall that the general solution of a system of $3s$ coupled difference equations of order $2H_3$ can be viewed as a $3s$-dimensional vector. This vector can be expressed as a linear combination of a complete set of $6sH_3$, linearly independent so-called "elementary solutions" (vectors) of the system. For systems with constant coefficients, these elementary solutions are easily obtained.[14,15] Thus we find that the general $3s$-dimensional vector solution of Eq. (3.14) can, in general, be written in the form

$$\mathbf{U}(m_3;\mathbf{k}_\rho)=\sum_{g=1}^{6sH_3}c_g(\mathbf{k}_\rho)\mathbf{U}^{(g)}\times(\exp\{ik_3{}^{(g)}\};\mathbf{k}_\rho)\exp\{ik_3{}^{(g)}m_3\}, \tag{3.16}$$

where $\exp\{ik_3{}^{(g)}\}$, $g=1,\cdots,6sH_3$, are the roots of the characteristic equation

$$\det[\theta_{\pi\sigma}(\exp\{ik_3\};\mathbf{k}_\rho)]=0, \tag{3.17}$$

associated with the matrix

$$\theta_{\pi\sigma}(\exp\{ik_3\};\mathbf{k}_\rho)=\sum_{h_3=-H_3}^{H_3}e^{ik_3h_3}\theta_{\pi\sigma}(h_3;\mathbf{k}_\rho). \tag{3.18}$$

If the roots of Eq. (3.17) are all distinct, then the $3s$-dimensional vectors $\mathbf{U}^{(g)}$ are specified, within an

[14] C. Jordan, *Calculus of Finite Differences* (Chelsea Printing Company, New York, 1949), Chap. IX.

[15] Tomlinson Fort, *Finite Differences* (Clarendon Press, Oxford, England, 1948), Chaps. VII, IX.

arbitrary constant multiplier, by the matrix equation

$$\sum_{\sigma=1}^{3s} \theta_{\pi\sigma}\{ik_3^{(g)}\};\mathbf{k}_\rho)U_\sigma^{(g)} \times(\exp\{ik_3^{(g)}\};\mathbf{k}_\rho)=0;\quad \pi=1,\cdots,3s. \quad (3.19)$$

When Eq. (3.17) has a q-fold root, $\exp\{ik_3\}=\exp\{ik_3^{(g)}\}$, then Eq. (3.16) has to be modified, and we have instead

$$\mathbf{U}(m_3;\mathbf{k}_\rho)=\sum_{g\neq g_1} c_g(\mathbf{k}_\rho)\mathbf{U}^{(g)} \times(\exp\{ik_3^{(g)}\};\mathbf{k}_\rho)\exp\{ik_3^{(g)}m_3\} +\sum_{p=0}^{q-1} c_{g_1,p}(\mathbf{k}_\rho)\mathbf{U}_p^{(g_1)}(\exp\{ik_3^{(g_1)}\};\mathbf{k}_\rho) \times\binom{m_3}{p}\exp\{ik_3^{(g_1)}m_3\}. \quad (3.20)$$

Here,

$$\binom{m_3}{p}$$

is the binomial coefficient, $m_3!/p!(m_3-p)!$. The determination of the q vectors $\mathbf{U}_p^{(g)}$ associated with the q-fold root of the characteristic equation is indicated in Appendix B.

In the following we discuss only the general case, when all roots of Eq. (3.17) are simple. However, it is clear that this is no essential restriction of our analysis.

The coefficients $c_g(\mathbf{k}_\rho)$ appearing in Eq. (3.16) have to be determined from the boundary conditions imposed on the (vector) function $\mathbf{U}(m_3,\mathbf{k}_\rho)$. Before we proceed to this task, we pause to discuss some of the properties of the elementary solution vectors defined by Eqs. (3.17), (3.18), and (3.19).

We note first that Eq. (3.17) is the zero-frequency limit of the standard, implicit, definition of the dispersion relation for the infinite crystal. In the conventional notation, this relation is specified by the secular equation

$$\det[\mathbf{D}(\mathbf{k})-\mathbf{I}\omega^2]=0, \quad (3.21)$$

where the so-called dynamic matrix $\mathbf{D}(\mathbf{k})$ is the $3s$-dimensional matrix,

$$D_{\pi\sigma}(\mathbf{k})=(M_\mu M_\nu)^{-1/2}\sum_{\mathbf{h}=-\infty}^{\infty}\Phi_{ij}(\mathbf{h};\mu,\nu)e^{i\mathbf{k}\cdot\mathbf{R}(\mathbf{h})}, \quad (3.22)$$

and $\mathbf{k}$ is a vector lying in the first Brillouin zone of the reciprocal lattice spanned by $\{\mathbf{b}_1,\mathbf{b}_2,\mathbf{b}_3\}$. The novelty in our present development is that we use Eq. (3.21) or rather Eq. (3.17) to define the 3-component of the "wave vector" $\mathbf{k}$ as a function of $\mathbf{k}_\rho$. (Note that the quantity k_3 in our analysis is usually denoted $2\pi k_3$. To simplify the notation, we have suppressed the factor of 2π.)

Equation (3.17) is a polynomial of order $6sH_3$ in e^{ik_3} and has in general $6sH_3$ distinct complex roots whose absolute magnitude is different from unity. That is,

$$k_3=-i[\text{principal value of } \ln(e^{ik_3})] \quad (3.23)$$

is a complex number.

It is well known that if $\mathbf{k}_\rho=0$, Eq. (3.17) has a sixfold root, $e^{ik_3}=1$. It is also known that this is the only case in which Eq. (3.17) has roots such that k_3 is real. To this sixfold root of Eq. (3.17), $\exp\{ik_3(\mathbf{k}_\rho=0)\}=1$, there correspond the six trivial zero-frequency solutions of the dynamic equations for the infinite lattice: the three linearly independent uniform translation modes,

$$\mathbf{U}(\mathbf{m}\mu)=(U00),\ (0U0),\ (00U);\quad \text{for all } \mathbf{m},\mu,$$

and the three linearly independent infinitesimal solid-body rotations of the entire lattice.

Concerning the other solutions of Eq. (3.17) we cannot, in general, say a great deal. We can, however, easily show that complex values of k_3 have to occur in complex conjugate pairs. This follows from the observation that Eq. (2.17) implies the identities

$$[\theta_{\pi\sigma}(e^{ik_3*};\mathbf{k}_\rho)]^*=\theta_{\pi\sigma}(e^{-ik_3},-\mathbf{k}_\rho)=\theta_{\sigma\pi}(e^{ik_3},\mathbf{k}_\rho). \quad (3.24)$$

Hence

$$0=\det[\theta_{\pi\sigma}(e^{ik_3};\mathbf{k}_\rho)]\rightleftarrows\det[\theta_{\pi\sigma}(e^{ik_3*};\mathbf{k}_\rho)]=0 \quad (3.25)$$

and

$$0=\det[\theta_{\pi\sigma}(e^{ik_3};\mathbf{k}_\rho)]\rightleftarrows\det[\theta_{\pi\sigma}(e^{-ik_3};-\mathbf{k}_\rho)]=0. \quad (3.26)$$

Equation (3.25) asserts that if Eq. (3.17) has a root e^{ik_3}, then it also has a root e^{ik_3*}. This proves our previous assertion. Equation (3.26) establishes a relation between the roots of Eq. (3.17) and those of the corresponding equation obtained when $\mathbf{k}_\rho$ is replaced by $-\mathbf{k}_\rho$.

At this point we define a convention for labeling the $6sH_3$ values of k_3. We shall order the complex values of k_3 according to their absolute magnitudes. Those with positive imaginary parts are labeled by $g=1,\cdots,G$; those with negative imaginary parts are labeled by $g=G+1,\cdots,2G$. The real values are ordered according to the algebraic value of k_3 and labeled by $g=2G+1,\cdots,6sH_3$. If two complex values have the same magnitude and imaginary parts of the same sign, they are ordered according to increasing algebraic value of their real parts. In case of multiple roots of Eq. (3.17) we have to introduce a further convention for labeling these. However, this need not be spelled out at present, since it is of no particular consequence in the following.[16]

Returning to our boundary-value problem, we note that in order to satisfy Eq. (3.10), we have to restrict the summation in Eq. (3.16) to those values of k_3 which have a positive imaginary part. As we have seen,

[16] This admittedly somewhat clumsy and *ad hoc* convention is adequate for the present discussion. A more versatile though also more elaborate convention is introduced in Ref. 11, Sec. 3, Eqs. (3.26) and (3.27), in connection with the dynamic problem.

there are in general $3sH_3$ such values. In order to determine the coefficients c_g of Eq. (3.16), we now consider the following set of $9sH_3$ equations:

$$\sum_{\sigma=1}^{3s}\sum_{n_3=0}^{2H_3-1}\theta_{\pi\sigma}(m_3,n_3,\mathbf{k}_p)U_\sigma{}^b(n_3,\mathbf{k}_\rho)+\sum_{g=1}^{3sH_3}\sum_{\sigma=1}^{3s}\sum_{n_3=2H_3}^{H_3+m_3}\theta_{\pi\sigma}(m_3,n_3,\mathbf{k}_\rho)\exp\{ik_3{}^{(g)}n_3\}$$

$$\times U_\sigma(\exp\{ik_3{}^{(g)}\};\mathbf{k}_\rho)c_g(\mathbf{k}_\rho)=\left.\begin{cases}F_\pi(m_3); & m_3=0,\cdots,H_3-1\\ 0 & m_3=H_3,\cdots,3H_3-1\end{cases}\right\}\delta_{\mathbf{k}_\rho,0};\quad \pi=1,\cdots,3s. \tag{3.27}$$

In this set of equations we explicitly accounted for the continuity equations, Eqs. (3.15), and eliminated $U_\pi{}^b(m_3;\mathbf{k}_\rho)$, $m_3=2H_3,\cdots,3H_3-1$. We now introduce a new set of indices, α and γ:

$$\alpha=3sm_3+\pi,\quad 0\leqslant m_3\leqslant 3H_3-1;\quad \alpha=1,\cdots,9sH_3; \tag{3.28}$$

$$\begin{aligned}\gamma&=3sn_3+\sigma,\quad 0\leqslant n_3\leqslant 2H_3-1;\quad \gamma=1,\cdots,6sH_3,\\ &=6sH_3+g,\quad 1\leqslant g\leqslant 3sH_3;\qquad\quad =6sH_3+1,\cdots,9sH_3.\end{aligned} \tag{3.29}$$

In terms of these new indices we can rewrite Eq. (3.27) in a more concise form,

$$\sum_{\gamma=1}^{9sH_3}M_{\alpha\gamma}(\mathbf{k}_\rho)c_\gamma(\mathbf{k}_\rho)=F_\alpha\delta_{\mathbf{k}_\rho,0};\ \alpha=1,\cdots,9sH_3. \tag{3.30}$$

The $9sH_3$-dimensional matrix $M_{\alpha\gamma}$ is defined by Eqs. (3.31) and (3.32);

$$M_{\alpha\gamma}(\mathbf{k}_\rho)=\theta_{\pi\sigma}(m_3,n_3;\mathbf{k}_\rho),\quad \gamma=1,\cdots,6sH_3 \tag{3.31}$$

$$=\sum_{\sigma=1}^{3s}\sum_{n_3=2H_3}^{H_3+m_3}\theta_{\pi\sigma}(m_3,n_3;\mathbf{k}_\rho)\exp\{ik_3{}^{(g)}n_3\}U_\sigma{}^{(g)}(\exp\{ik_3{}^{(g)}\};\mathbf{k}_\rho);\quad \gamma=6sH_3+1,\cdots,9sH_3. \tag{3.32}$$

The $9sH_3$-dimensional vector c_γ is defined by Eqs. (3.33) and (3.34):

$$c_\gamma=U_\sigma{}^b(n_3;\mathbf{k}_\rho);\quad \gamma=1,\cdots,6sH_3 \tag{3.33}$$

$$=c_g(\mathbf{k}_\rho);\qquad \gamma=6sH_3+1,\cdots,9sH_3. \tag{3.34}$$

We now have to distinguish between two cases. First, if $\mathbf{k}_\rho\neq\mathbf{0}$, then Eq. (3.30) reduces to a set of $9sH_3$ linear homogeneous equations in $9sH_3$ unknowns. Hence, in this case Eq. (3.30) has a nontrivial solution if, and only if, the determinant

$$\det[M_{\alpha\gamma}(\mathbf{k}_\rho)]=0. \tag{3.35}$$

This "compatibility condition," and Eqs. (3.17) and (3.19), determine the values of $\mathbf{k}_\rho$ and the corresponding values of $\exp\{ik_3{}^{(g)}(\mathbf{k}_\rho)\}$ for which the boundary-value problem has nontrivial solutions. The physical significance of such solutions will be discussed below. Here we only note that available experimental evidence indicates that for most solids, Eqs. (3.17), (3.19), and (3.35) have no solution consistent with Eqs. (3.6) and (3.7). However, there are notable exceptions such as Si, Ge, and possible other valence crystals.[12,17] It should also be noted that if a nontrivial solution of Eqs. (3.17), (3.19), and (3.35) exists for $\mathbf{k}_\rho=\mathbf{q}_\rho$, then there must also exist such a solution for $\mathbf{k}_\rho=-\mathbf{q}_\rho$. This follows from the fact that $M_{\alpha\gamma}{}^*(\mathbf{k}_\rho)=M_{\alpha\gamma}(-\mathbf{k}_\rho)$, and from Eqs. (3.24)–(3.26). Furthermore, if the boundary plane is normal to an n-fold axis-of-rotation symmetry, then the existence of a solution of Eqs. (3.17), (3.19), and (3.35) with $\mathbf{k}_\rho=\mathbf{q}_\rho$ implies the existence of such solutions, the n distinct vectors $\mathbf{k}_\rho=R^m\mathbf{q}_\rho$ obtained by rotating $\mathbf{q}_\rho$ by $2\pi m/n$ rad about the 3 axis in reciprocal space.

The next case to consider is when $\mathbf{k}_\rho=0$. In this case Eq. (3.17) has a sixfold root $e^{ik_3}=1$. Hence, only $3sH_3-3$ roots of Eq. (3.17) lead to elementary solutions which satisfy the boundary conditions at $m_3=\infty$. Thus Eq. (3.30) represents a set of $9sH_3$ inhomogeneous linear equations in $9sH_3-3$ unknowns, and clearly has, in general, no solution. This difficulty can be eliminated by noting that Eqs. (2.19) and (2.21) imply that for $\mathbf{k}_\rho=\mathbf{0}$ only $3sH_3-3$ of the inhomogeneous equations specified by Eq. (3.9) are linearly independent. This implies that in formulating our auxiliary problem, for $\mathbf{U}^{(b)}$, we should disregard any three of the $3sH_3$ boundary conditions, Eq. (3.9). We shall drop the first three, and thus obtain instead of Eq. (3.30) the following set of $9sH_3-3$ equations in $9sH-3$ unknowns:

$$\sum_{\gamma=1}^{9sH_3-3}M_{\alpha'\gamma}(\mathbf{k}_\rho=0)c_\gamma(\mathbf{k}_\rho=0)=F_{\alpha'},$$

$$\alpha'=\alpha-3=1,\cdots,9sH_3-3. \tag{3.36}$$

The quantities appearing in Eq. (3.36) are defined by Eqs. (3.28)–(3.24). It should be noted that our labeling

[17] J. J. Lander, in *Progress in Solid-State Chemistry*, edited by H. Reiss (Pergamon Press, Inc., New York, 1965), Vol. 2, p. 26; J. J. Lander and J. Morrison, J. Appl. Phys. 34, 1403 (1963); J. Chem. Phys. 37, 729 (1962); J. J. Lander, G. W. Gobeli, and J. Morrison, J. Appl. Phys. 34, 2498 (1963).

convention for complex values of k_3 implies that, for $\mathbf{k}_\rho=\mathbf{0}$, if

$$k_3^{(\sigma)}=k_3,$$

then

$$k_3^{(\sigma-1)}=-k_3.$$

This statement follows immediately from Eqs. (3.25) and (3.26). It implies that the expansion of the static displacements in elementary solutions always includes in this case pairs of terms associated with equal, positive $\mathrm{Im}k_3$ and equal $|\mathrm{Re}k_3|$.

The solution of the set of equations specified by Eq. (3.36) is elementary. We denote the $(9sH_3-3)$-dimensional matrix of coefficients by $\mathbf{M}^{(1)}$, the set of $9sH_3-3$ unknowns c_γ by the vector $\mathbf{C}^{(1)}(\mathbf{k}_\rho=0)$, and the right side of Eq. (3.36) by the $(9sH_3-3)$-dimensional vector $\mathbf{F}^{(1)}$. Then, if

$$\det[\mathbf{M}^{(1)}]\neq 0, \tag{3.37}$$

we obtain

$$\mathbf{C}^{(1)}(\mathbf{k}_\rho=0)=[\mathbf{M}^{(1)}]^{-1}\mathbf{F}^{(1)}. \tag{3.38}$$

In principle, the rank r of $M^{(1)}$ might be less than $9sH_3-3$. In this case we find

$$\mathbf{C}^{(1)}(\mathbf{k}_\rho)=[\mathbf{M}^{(r)}]^{-1}\mathbf{F}^{(1)}+\sum_p a_p C_p^{(1)}(\mathbf{k}_\rho=0). \tag{3.39}$$

Here $\mathbf{M}^{(r)}$ is an r-dimensional, nonsingular submatrix of $\mathbf{M}^{(1)}$, and $\mathbf{F}^{(1)}$ is the associated r-dimensional component of $\mathbf{F}^{(1)}$. The $(9sH_3-3)$-dimensional vectors $C_p^{(1)}(\mathbf{k}_\rho=0)$ are $9sH_3-3-r$ linearly independent solutions of the homogeneous matrix equation,

$$\mathbf{M}^{(1)}\mathbf{C}^{(1)}(\mathbf{k}_\rho=0)=0. \tag{3.40}$$

The physical significance of the undertermined constants a_p is discussed in Sec. V.

The preceding discussion assumed throughout that Eq. (3.17) has no multiple complex roots. It is clear that this is an unessential simplifying assumption. The general treatment can be given at the expense of a somewhat more cumbersome notation.

IV. ANHARMONIC EFFECTS

A. Introductory Remarks

In the last two sections we were concerned with a linearized theory based on the assumption that the absolute magnitudes of the relative displacements of particles in adjacent unit cells were small compared to the dimensions of the unit cell. We saw that the displacements of particles more than $2H_3$ unit cells from the boundary could be expressed as linear combinations of elementary displacements, each of which depended on the distance from the boundary through a complex exponential factor. The essentially exponential decrease of the absolute displacements of particles removed by more than $2H_3$ unit cells from the surface suggests that for these particles the relative displacements of particles in adjacent cells is small. This then would justify the application of the linear theory to particles removed by more than $2H_3$ cells from the surface. More precisely, the linearized theory is self-consistent provided that the absolute displacements of particles in the region $H_3\leqslant m_3\leqslant 2H_3-1$ are small.

It is quite likely that close to the boundary ($m_3<H_3$) both absolute and relative displacements are appreciable. The preceding suggests that such displacements might be included in the analysis without drastically altering the results of the linearized analysis. Hence it is of interest to determine to what extent the results of the linear theory are modified if nonlinear terms in the static displacements of particles close to the boundary are included.

The specification of the region within which higher-order terms in the static displacements are to be explicitly included in the analysis has to be consistent with the general requirement that no net force act on the semi-infinite lattice. This consistency condition can be shown to imply that a restriction on the region in which nonlinear terms in the *relative* displacements are to be included has to be supplemented either by an *ad hoc* restriction on the derivatives of the effective potential energy of interaction, or by a restriction on the region in which nonlinear terms in the *absolute* displacements are to be included. We shall choose the second alternative.

For our purposes it is sufficient to consider the simplest extension of the linear model, namely, in the expression for the force acting on a given particle, we shall neglect all third-order terms in the relative displacements. Of the second-order terms, we only include those

$$O([U_j(\mathbf{n},\nu)-U_j(\mathbf{m},\mu)][U(\mathbf{l},\lambda)-U(\mathbf{m},\mu)]) \tag{4.1a}$$

for which one of the variables, m_3, n_3, $l_3\leqslant H_3-1$.

We shall also neglect terms,

$$O(U_i(\mathbf{m},\mu)U_j(\mathbf{n},\nu)), \quad m_3 \text{ and } n_3\geqslant H_3. \tag{4.1b}$$

In practice it is more convenient to formulate the approximation strictly in terms of the absolute static displacement. We shall thus extend the linear theory by simply including all terms

$$O(U_i(\mathbf{m};\nu)U_j(\mathbf{n};\nu)), \quad m_3 \text{ or } n_3\leqslant H_3-1 \tag{4.1c}$$

and verify that the resulting equations are the same as those derived subject to the conditions indicated by Eqs. (4.1a) and (4.1b).

The nonlinear model to be considered is specified in Sec. IV B and its preliminary analysis is given in Sec. IV C. Section IV D comprises a rather detailed analysis of the model. This detailed analysis is not essential for the understanding of the physical significance of the results which are deduced from the model, and

which are discussed at length in Sec. V. Hence Sec. IV D might be read after Sec. V.

We shall see that most of the analysis of the linear model, which was given in Sec. III, is easily adapted to the present nonlinear model, and that the essential features of the linear theory are preserved and illuminated by the following analysis.

B. Specification of the Nonlinear Model

The assumptions listed above require us to include in the expansion of the vector $\Psi(\mathbf{m},\mu)$, given by Eq. (2.9), some quadratic terms in the static displacements. The quadratic terms in the Taylor expansion of the ith component of the vector $\Psi(\mathbf{m},\mu)$ in terms of $\mathbf{U}$ are

$$\Psi_i^{(2)}(m,\mu)=\tfrac{1}{2}\sum_{j,h=1}^{3}\sum_{\mu,\lambda=1}^{s}\sum_{\substack{n_1,n_2\\ l_1,l_2\}=-\infty}}^{\infty}\sum_{n_3,l_3=0}^{\infty}[\Phi_{ijh}(\mathbf{m},\mu;\mathbf{n},\nu;\mathbf{l},\lambda)+\delta\Phi_{ijh}(\mathbf{m},\mu;\mathbf{n},\nu;\mathbf{l},\lambda)]U_j(\mathbf{n},\nu)U_h(\mathbf{l},\lambda). \tag{4.2}$$

Here

$$\Phi_{ijh}(\mathbf{m},\mu;\mathbf{n},\nu;\mathbf{l},\lambda)=\frac{\partial}{\partial\bar{X}_i(\mathbf{m},\mu)}\frac{\partial}{\partial\bar{X}_j(\mathbf{n},\nu)}\frac{\partial}{\partial\bar{X}_h(\mathbf{l},\lambda)}\Phi^{(u)}\Big|_{\{U\}=0}, \tag{4.3}$$

$$\delta\Phi_{ijh}(\mathbf{m},\mu;\mathbf{n},\nu;\mathbf{l},\lambda)=\frac{\partial}{\partial\bar{X}_i(\mathbf{m},\mu)}\frac{\partial}{\partial\bar{X}_j(\mathbf{n},\nu)}\frac{\partial}{\partial\bar{X}_h(l,\lambda)}(\Phi-\Phi^{(u)})\Big|_{\{U\}=0}, \tag{4.4}$$

and

$$\bar{X}_i(\mathbf{m},\mu)=\text{the } i\text{th component of } \mathbf{R}(\mathbf{m})+\mathbf{R}(\mu). \tag{4.5}$$

In the following we shall find it convenient to denote

$$\Phi_{ijh}(\mathbf{m},\mu;\mathbf{n},\nu;\mathbf{l},\lambda)+\delta\Phi_{ijh}(\mathbf{m},\mu;\mathbf{n},\nu;\mathbf{l},\lambda)=\tilde{\Phi}_{ijh}(\mathbf{m},\mu;\mathbf{n},\nu;\mathbf{l},\lambda). \tag{4.6}$$

The assumed finite range of the interparticle interaction implies that

$$\tilde{\Phi}_{ijh}(\mathbf{m},\mu;\mathbf{n},\nu;\mathbf{l},\lambda)=0, \tag{4.7}$$

if any one of the following inequalities applies:

$$|m_i-n_i|,\quad |m_i-l_i|,\quad |n_i-l_i|\geqslant H_i+1,\quad i=1,2,3. \tag{4.8}$$

The third-order coupling coefficients $\tilde{\Phi}_{ijh}$ satisfy identities which have a similar form to Eqs. (2.21) and (2.23), namely,

$$\sum_{\lambda=1}^{s}\sum_{l_1,l_2=-\infty}^{\infty}\sum_{l_3=0}^{\min(m_3,n_3)+H_3}\tilde{\Phi}_{ijh}(\mathbf{m},\mu;\mathbf{n},\nu;\mathbf{l},\lambda)\equiv 0,\quad m_3 \text{ and } n_3\leqslant H_3 \tag{4.9}$$

and

$$\sum_{\lambda=1}^{s}\sum_{l_1,l_2=-\infty}^{\infty}\sum_{l_3=\max(m_3,n_3)-H_3}^{\min(m_3,n_3)+H_3}\tilde{\Phi}_{ijh}(\mathbf{m},\mu;\mathbf{n},\nu;\mathbf{l},\lambda)\equiv 0,\quad m_3 \text{ or } n_3\geqslant H_3. \tag{4.10}$$

We now approximate Eq. (4.2) by dropping all terms for which n_3 and $l_3>H_3$. Thus

$$\Psi_i^{(2)}(\mathbf{m},\mu)\approx\tfrac{1}{2}\sum_{j,h=1}^{3}\sum_{\nu,\lambda=1}^{s}\sum_{\substack{n_1,n_2\\ l_1,l_2\}=-\infty}}^{\infty}\sum_{n_3,l_3=0}^{2H_3-1}\Delta(m_3,n_3,l_3)\tilde{\Phi}_{ijh}(\mathbf{m},\mu;\mathbf{n},\nu;\mathbf{l},\lambda)U_j(\mathbf{n},\nu)U_h(\mathbf{l},\lambda), \tag{4.11}$$

where

$$\begin{aligned}\Delta(m_3,n_3,l_3)&=1,\quad \text{if one of the variables } n_3,\ l_3\leqslant H_3-1 \text{ and if } m_3\leqslant 2H_3-1\\ &=0,\quad \text{otherwise.}\end{aligned} \tag{4.12}$$

It is easily checked that this approximation is consistent with the restriction

$$\sum_{\mu=1}^{s}\sum_{m_1,m_2=-\infty}^{\infty}\sum_{m_3=0}^{\infty}\Psi_i^{(2)}(\mathbf{m},\mu)\equiv 0, \tag{4.13}$$

which is imposed by the vanishing of the net force acting on the semi-infinite crystal.

Using Eqs. (4.9) and (4.10), we can also check that Eq. (4.11) implies

$$\begin{aligned}\Psi_i^{(2)}(\mathbf{m},\mu)&=0,\quad m_3\geqslant 2H_3\\ &=\tfrac{1}{2}\sum_{j,h=1}^{3}\sum_{\nu,\lambda=1}^{s}\sum_{\substack{n_1,n_2\\ l_1,l_2\}=-\infty}}^{\infty}\sum_{n_3,l_3=0}^{2H_3-1}\tilde{\Phi}_{ijh}(\mathbf{m},\mu;\mathbf{n},\nu;\mathbf{l},\lambda)\{[U_j(\mathbf{n},\nu)-U_j(\mathbf{m},\mu)]\\ &\quad\times[U_h(\mathbf{l},\lambda)-U_h(\mathbf{m},\mu)]+O(U_j(\mathbf{n};\nu)U_h(\mathbf{l};\lambda);\ n_3 \text{ and } l_3\geqslant H_3;\ m_3)\}\leqslant 2H_3-1.\end{aligned} \tag{4.14}$$

Thus our approximation indeed is equivalent to that specified by Eqs. (4.1a) and (4.1b). It is easily verified that Eq. (4.1a) has to be supplemented by a condition like that specified by Eq. (4.1b) if the approximation is to be consistent with Eq. (4.13), unless, that is, the third-order coupling constants are subjected to an additional restriction, supplementing Eqs. (4.7)–(4.10).

C. Preliminary Analysis of the Nonlinear Model

In the preceding subsection we have obtained in Eq. (4.11) a precise formulation of the nonlinearity to be considered. We now proceed to investigate its effects. Equation (4.11) clearly indicates that within our model, the displacements $\mathbf{U}(\mathbf{m},\mu)$ $m_3 \geqslant 2H_3$ are still governed by the linear difference equations discussed in Sec. III. The nonlinearity of the model can only affect the boundary values imposed on these difference equations. That is, as we shall see, the set of linear equations, Eqs. (3.27), will now be replaced by a set of nonlinear equations, to be derived below.

Following our procedure in Sec. III, we eliminate the dependence of $\Psi_i^{(2)}(\mathbf{m},\mu)$ on $\mathbf{m}_\rho$ by a Fourier transformation. That is, we write

$$\Psi_i^{(2)}(\mathbf{m},\mu)=\sum_{\mathbf{k}_\rho} e^{i\mathbf{k}_\rho\cdot\mathbf{R}(\mathbf{m}_\rho)}\Psi_\pi^{(2)}(m_3;\mathbf{k}_\rho)\,, \tag{4.15}$$

where

$$\Psi_i^{(2)}(m_3;\mathbf{k}_\rho)=\tfrac{1}{2}\sum_{\mathbf{q}_\rho}\sum_{\sigma,\eta=1}^{3s}\sum_{n_3,l_3=0}^{2H_3-1}\Delta(m_3,n_3,l_3)\tilde{\theta}_{\pi\sigma\eta}(m_3,n_3,l_3;\mathbf{q}_\rho,\mathbf{k}_\rho-\mathbf{q}_\rho)U_\sigma(n_3,\mathbf{q}_\rho)U_\eta(m_3,\mathbf{k}_\rho-\mathbf{q}_\rho)\,, \tag{4.16}$$

and

$$\tilde{\theta}_{\pi\sigma\eta}(m_3,n_3,l_3;\mathbf{q}_\rho,\mathbf{k}_\rho-\mathbf{q}_\rho)=\tilde{\theta}_{\pi\eta\sigma}(m_3,l_3,n_3;\mathbf{k}_\rho-\mathbf{q}_\rho,\mathbf{q}_\rho)$$

$$=\sum_{\substack{n_1-m_1\\ n_2-m_2}=-\infty}^{\infty}\sum_{\substack{l_1-m_1\\ l_2-m_2}=-\infty}^{\infty}\tilde{\Phi}_{ijh}(n_1-m_1,n_2-m_2,l_1-m_1,l_2-m_2;m_3,n_3,l_3;\mu,\nu,\lambda)$$

$$\times e^{i\mathbf{q}_\rho\cdot\mathbf{R}(\mathbf{n}_\rho-\mathbf{m}_\rho)}e^{i(\mathbf{k}_\rho-\mathbf{q}_\rho)\cdot\mathbf{R}(\mathbf{l}_\rho-\mathbf{m}_\rho)}\,. \tag{4.17}$$

Here, the quantities

$$\mathbf{q}_\rho=2\pi\sum_{2=1}^{2}\mathbf{b}_i q_i;\quad \mathbf{k}_\rho=2\pi\sum_{2=1}^{2}\mathbf{b}_i k_i \tag{4.18}$$

are reduced two-dimensional wave vectors, which satisfy Eqs. (3.6), (3.7), and $\mathbf{q}_\rho-\mathbf{k}_\rho$ is the reduced wave vector which is equivalent to their difference. Finally, we have used Eqs. (3.11) to define the indices σ, π, and $\eta=3(\lambda-1)+h$. Thus, within our approximation, anharmonic effects are accounted for by adding to the left side of Eq. (3.27) the term $\Psi_\pi^{(2)}(m_3;k_\rho)$. Using the compact notation introduced by Eqs. (3.28), (3.29), (3.33), and (3.34), we can write $\Psi_\pi^{(2)}(m_3;\mathbf{k}_\rho)=\Psi_\alpha^{(2)}(\mathbf{k}_\rho)$, where

$$\Psi_\alpha^{(2)}(\mathbf{k}_\rho)=(1-\tfrac{1}{2}\delta_{\mathbf{k}_\rho,0})\sum_{\gamma,\delta=1}^{6sH_3}\theta_{\alpha\gamma\delta}(\mathbf{k}_\rho,0)c_\delta(0)c_\gamma(\mathbf{k}_\rho)+\tfrac{1}{2}\sum_{\mathbf{q}_\rho\neq 0,\mathbf{k}_\rho}\sum_{\gamma,\delta=1}^{6sH_3}\theta_{\alpha\gamma\delta}(\mathbf{q}_\rho,\mathbf{k}_\rho-\mathbf{q}_\rho)c_\gamma(\mathbf{q}_\rho)c_\delta(\mathbf{k}_\rho-\mathbf{q}_\rho)\,. \tag{4.19}$$

Here,

$$\delta=3sl_3+\eta\,,$$

and

$$\theta_{\alpha\gamma\delta}(\mathbf{q}_\rho,\mathbf{k}_\rho-\mathbf{q}_\rho)=\theta_{\pi\sigma\eta}(m_3,n_3,l_3;\mathbf{q}_\rho,\mathbf{k}_\rho-\mathbf{q}_\rho)\Delta(m_3,n_3,l_3)\,.$$

Thus Eqs. (3.30) and (3.36) are replaced by the following coupled set of nonlinear equations:

$$\sum_{\gamma=1}^{9sH_3-3}M_{\alpha'\gamma}(\mathbf{0})c_\gamma(0)+\tfrac{1}{2}\sum_{\gamma,\delta=1}^{6sH_3}\theta_{\alpha'\gamma\delta}(\mathbf{0},\mathbf{0})c_\gamma(0)c_\delta(0)$$

$$=F_{\alpha'}-\sum_{\mathbf{q}_\rho>0}\sum_{\gamma,\delta=1}^{6sH_3}\theta_{\alpha'\gamma\delta}(\mathbf{q}_\rho,-\mathbf{q}_\rho)c_\gamma(\mathbf{q}_\rho)c_\delta(-\mathbf{q}_\rho);\quad \alpha'=1,\cdots,9sH_3-3;\quad \alpha'=\alpha-3. \tag{4.20}$$

Also,

$$\sum_{\gamma=1}^{9sH_3}[M_{\alpha\gamma}(\mathbf{k}_\rho)-\sum_{\delta=1}^{6sH_3}\theta_{\alpha\gamma\delta}(\mathbf{k}_\rho,0)c_\delta(0)]c_\gamma(\mathbf{k}_\rho)$$

$$=-\tfrac{1}{2}\sum_{\mathbf{q}_\rho\neq\mathbf{0},\mathbf{k}_\rho}\sum_{\gamma,\delta=1}^{6sH_3}\theta_{\alpha\gamma\delta}(\mathbf{q}_\rho,\mathbf{k}_\rho-\mathbf{q}_\rho)c_\gamma(\mathbf{q}_\rho)c_\delta(\mathbf{k}_\rho-\mathbf{q}_\rho);\quad \alpha=1,\cdots,9sH_3. \tag{4.21}$$

The nonlinear character of these equations implies that, in general, several stationary static configurations may exist. Of these, more than one might be stable, in the sense that it corresponds to a local minimum of the potential energy of interaction. In general we should expect some "simple" solutions of the form

$$c_\gamma(\mathbf{k}_\rho)=c_\gamma(\mathbf{0})\delta_{\mathbf{k}_\rho,\mathbf{0}}. \tag{4.22}$$

Another possible class of solutions has the form

$$c_\gamma(\mathbf{k}_\rho)=\sum_n \sum_{\mathbf{k}_q} c_\gamma(\mathbf{k}_\rho)\delta_{\mathbf{k}_\rho,n\mathbf{q}_\rho}, \tag{4.23}$$

where n runs over all integers such that $n\mathbf{q}_\rho$ is a reduced (two-dimensional) wave vector. According to Eqs. (4.18) and (3.6), the components q_1, q_2 of $\mathbf{q}_\rho$ are rational numbers of absolute magnitude less than unity. Thus, if q_i is a ratio of small integers, $q_i=l_i/\alpha_i$, the sum over n involves a total of $n_{\max}=\alpha_1\alpha_2$ terms. Such a solution corresponds to a configuration in which the two primitive translation vectors parallel to the boundary are increased from $\mathbf{a}_i$ to $\alpha_i\mathbf{a}_i$. There is in principle a possibility that the set $\{n\mathbf{q}_\rho\}$ includes most or all of the rational point in the first Brillouin zone. In this case the semi-infinite crystal loses its translational periodicity parallel to the boundary. This type of solution can be disregarded on physical grounds.

D. Perturbation-Theoretical Analysis of the Nonlinear Model

A complete, formal analysis of Eqs. (4.20) and (4.21) is clearly not feasible, nor is such an analysis justified in view of the limited validity of the model from which these equations were derived. The model clearly implies that the nonlinear effects are moderate. Consequently only those solutions of the nonlinear model which can be obtained by iteration of the solutions of linear model are consistent with our basic assumption. We shall, therefore, restrict our discussion to such solutions. That is, the following analysis is essentially a perturbation theory. Our results may have a larger range of validity than the normal perturbation theory, but we shall not attempt to investigate this point.

Our object is to establish two points. Firstly, the iteration of the solutions of the linear problem always leads to a solution of the form indicated by Eq. (4.22). Secondly, solutions of the form indicated by Eq. (4.23) are obtained by an iterative process if, and only if, the compatibility condition, Eq. (3.35), or one of its iterates has a solution consistent with Eqs. (3.6), (3.17), and (3.19). The physical significance of this result will be discussed in Sec. V.

In the following we shall denote the nth iterated quantities by a superscript (n). In particular, the solutions of the linear equations (3.30) and (3.36) are denoted by a superscript (0).

If the linear system has a unique solution,

$$c_\gamma{}^{(0)}(\mathbf{k}_\rho)=c_\gamma{}^{(0)}(\mathbf{0})\delta_{\mathbf{k}_\rho,\mathbf{0}}, \tag{4.24}$$

we shall define the first iterated solution by the following set of linear equations:

$$\sum_{\gamma=1}^{9sH_3-3}\Big[M_{\alpha'\gamma}(\mathbf{0})+\tfrac{1}{2}\sum_{\delta=1}^{6sH_3}\theta_{\alpha'\gamma\delta}(\mathbf{0},\mathbf{0})c_\delta{}^{(0)}(\mathbf{0})\Big]\times c_\gamma{}^{(1)}(\mathbf{0})=F_{\alpha'},\quad \alpha'=1,\cdots,9sH_3-3, \tag{4.25}$$

and

$$\sum_{\gamma=1}^{9sH_3}\Big[M_{\alpha\gamma}(\mathbf{k}_\rho)+\sum_{\delta=1}^{6sH_3}\theta_{\alpha\gamma\delta}(\mathbf{k}_\rho,\mathbf{0})c_\delta{}^{(0)}(\mathbf{0})\Big]\times c_\gamma{}^{(1)}(\mathbf{k}_\rho)=0,\quad \alpha=1,\cdots,9sH_3. \tag{4.26}$$

Equation (4.26) has a nontrivial solution if, and only if, the following compatibility condition is satisfied:

$$\det\Big[M_{\alpha\gamma}(\mathbf{k}_\rho)+\sum_{\delta=1}^{6sH_3}\theta_{\alpha\gamma\delta}(\mathbf{k}_\rho,\mathbf{0})c_\delta{}^{(0)}(\mathbf{0})\Big]=0. \tag{4.27}$$

Equation (4.27) is evidently the first iterate of Eq. (3.35). If there exists no simultaneous solution of Eqs. (4.27), (3.6), (3.17), and (3.19), then the iterative process is repeated. The nth iterated solution is obtained by replacing $c_\gamma{}^{(0)}$ by $c_\gamma{}^{(n-1)}$ and $c_\gamma{}^{(1)}$ by $c_\gamma{}^{(n)}$. It is clear that this procedure may be followed even if Eq. (3.35) or any one of its iterates has a solution which is consistent with Eqs. (3.6), (3.17), and (3.18). This is due to our freedom of choosing the trivial solution of Eq. (3.30), or its iterates, such as Eq. (4.26). In order to gain a clearer picture of the successive iterations obtained by this process it is convenient to use the more compact matrix notation, and suppress all indices.

$$C^{(0)}(\mathbf{0})=M^{-1}(\mathbf{0})F \tag{4.28}$$

and

$$C^{(1)}(\mathbf{0})=\big[1+M^{-1}(\mathbf{0})\tfrac{1}{2}\theta(\mathbf{0},\mathbf{0})M^{-1}(\mathbf{0})F\big]^{-1}M^{-1}(\mathbf{0})F. \tag{4.29}$$

If none of the eigenvalues of the matrix $M^{-1}\frac{1}{2}\theta M^{-1}F$ are of absolute magnitude ≥ 1 (this is the criterion for the convergence of perturbation theory), then the right side of Eq. (4.29) may be developed in a binomial expansion,

$$C^{(1)}(\mathbf{0})=\Big[1+\sum_{n=1}^{\infty}(-1)^n\times\big[M^{-1}(\mathbf{0})\tfrac{1}{2}\theta(\mathbf{0},\mathbf{0})M^{-1}(\mathbf{0})F\big]^nM^{-1}F. \tag{4.30}$$

Thus to first order in the third-order coupling constants θ,

$$C^{(1)}(\mathbf{0})=\big[1-M^{-1}(\mathbf{0})\tfrac{1}{2}\theta(\mathbf{0},\mathbf{0})M^{-1}(\mathbf{0})F\big]M^{-1}F. \tag{4.31}$$

This is the solution obtained in first-order perturbation theory. It is easily checked that the nth iterated solution agrees, to terms of order n in θ, with the solution obtained by nth-order perturbation theory. Hence,

assuming perturbation theory to converge, we see that we always can construct a solution of the form

$$c_\gamma(\mathbf{k}_\rho)=c_\gamma(0)\delta_{\mathbf{k}_\rho,0}\,, \tag{4.32}$$

which, in the limit of zero anharmonicity ($\theta\to 0$), reduces to the solution of the linear model.

We now turn to consider the consequences of having a nonunique nth iterated solution. This difficulty is due to the existence of a simultaneous solution of the nth iterated compatibility condition and Eqs. (3.6), (3.17), and (3.19). The discussion applies in particular to $n=0$ or 1.

If for $\mathbf{k}_\rho=\mathbf{q}_\rho$ the nth iterated compatibility condition has a solution which is consistent with Eqs. (3.6), (3.17), and (3.19), and if we choose the corresponding nontrivial solution of the nth iterate of Eq. (3.30), $c_\gamma^{(n)}(\mathbf{q}_\rho)\not\equiv 0$, then we have to modify the remaining iterated equations to account for the relevant nonlinear terms on the right side of Eqs. (4.20) and (4.21). The full set of nth iterated equations thus becomes

$$\sum_{\gamma=1}^{9sH_3}[M_{\alpha\gamma}(\pm\mathbf{q}_\rho)+\sum_{\delta=1}^{6sH_3}\theta_{\alpha\gamma\delta}(\pm\mathbf{q}_\rho,0)c^{(n-1)}(0)]c_\gamma^{(n)}(\pm\mathbf{q}_\rho)=0;\quad \alpha=1,\cdots,9sH_3 \tag{4.33}$$

$$\sum_{\gamma=1}^{9sH_3}[M_{\alpha\gamma}(\pm\mathbf{q}_\rho)+\sum_{\delta=1}^{6sH_3}\theta_{\alpha\gamma\delta}(\pm 2\mathbf{q}_\rho;0)c_\delta^{(n-1)}(0)]c_\gamma^{(n)}(\pm 2\mathbf{q}_\rho)$$
$$=-\tfrac{1}{2}\sum_{\delta=1}^{6sH_3}\theta_{\alpha\gamma\delta}(\pm\mathbf{q}_\rho,\pm\mathbf{q}_\rho)c_\gamma^{(n)}(\pm\mathbf{q}_\rho)c_\delta^{(n)}(-\mathbf{q}_\rho);\quad \alpha=1,\cdots,9sH_3 \tag{4.34}$$

$$\sum_{\gamma=1}^{9sH_3-3}[M_{\alpha'\gamma}(0)+\tfrac{1}{2}\sum_{\delta=1}^{6sH_3}\theta_{\alpha'\gamma\delta}(0,0)c_\delta^{(n-1)}(0)]c_\gamma^{(n)}(0)=F_{\alpha'}$$
$$-\sum_{\delta=1}^{6sH_3}\theta_{\alpha'\gamma\delta}(\pm\mathbf{q}_\rho,-\mathbf{q}_\rho)c_\gamma^{(n)}(\mathbf{q}_\rho)c_\gamma^{(n)}(-\mathbf{q}_\rho);\quad \alpha'=1,\cdots,9sH_3-3. \tag{4.35}$$

Now, the nontrivial null vectors $C^{(n)}(\pm\mathbf{q}_\rho)$ are only specified within a multiplicative constant $A^\pm$. This constant can be chosen, without loss of generality, to be real. Since for $\mathbf{k}_\rho=\pm\mathbf{q}_\rho$ the two null vectors are a conjugate complex pair, we then have $A^+=(A^-)^*=A^-$. Hence, we see that the complete nth-iterated solution depends on A. This dependence is rather simple, but becomes successively more complicated in the higher iterations. However, it is clear that the A dependence of the higher iterations is analytic.

In the preceding we have tacitly assumed, for the sake of simplicity, that the boundary is not normal to any m-fold axis-of-rotation symmetry. Otherwise, we should have to include also a set of equations analogous to Eqs. (4.33) and (4.34) for each one of the remaining solutions of the compatibility condition and the right-hand side of Eq. (4.35) would have to include a corresponding number of additional terms. We then would also find that our iterated solutions depend on a set of m constants A. The added complexity is only a matter of bookkeeping, and hence will not be considered further.

If we assume that the set $\{n\mathbf{q}_\rho;n=1,2,\cdots\}$ includes $n_{\max}$ distinct reduced wave vectors, then after $n_{\max}$ iterations, the solutions will have the form

$$c_\gamma^{(n_{\max})}(\mathbf{k}_\rho)=\sum_n\sum_{\mathbf{k}_\rho}c_\gamma^{(n_{\max})}(\mathbf{k}_\rho)\delta_{\mathbf{k}_\rho,n\mathbf{q}_\rho}. \tag{4.36}$$

We know that the iterative process will not converge for arbitrary values of the constant A. However, it certainly converges for $A=0$, and it may converge for some other values. In particular, if the convergence is uniform in A over some interval $I(A)$, then we know that the iterations will converge to a function which is analytic in A over a subinterval of $I(A)$.

To conclude, if one of the iterated compatibility conditions has a solution which for $\mathbf{k}_\rho=\mathbf{q}_\rho$ is consistent with Eqs. (3.6), (3.17), and (3.19), then there exists a one-parameter family of stationary configurations, that satisfy Eq. (4.23). This family may include one or more stable configurations, in which the potential energy of interaction achieves a local minimum. The static equilibrium configuration, which is associated with an absolute minimum of the potential energy, is presumably one of these stable solutions, but this is not necessary.

This concludes our iterative analysis of the nonlinear model. The physical significance of our results is discussed in the next section.

V. DISCUSSION OF THE STATIC DISPLACEMENTS

In this paper, we consider the consequences of the necessary conditions for the semi-infinite lattice to be in static equilibrium. We have considered both a linear and a nonlinear model. The two calculations agree in their general predictions though they differ in some details.

Our results can be summed up as follows: The creation of a free boundary by the removal of all particles above a given lattice plane, say $m_3=0$, leads to a spontaneous displacement of all atoms in the semi-infinite lattice from the static equilibrium positions they assume when embedded in an infinite lattice. These vector dis-

placements can in general be represented by a linear combination of "elementary displacements." The latter depend on the distance m_3 of the atom from the boundary plane $m_3=0$ through a complex exponential, $\exp\{ik_3m_3\}$, where $\mathrm{Im}k_3>0$. This implies that the magnitude of the displacement of an atom decreases, roughly exponentially, with the distance of the atom from the boundary. However, the displacements are in general not monotonic functions of m_3. This qualitative statement is in agreement with the results of Benson *et al.*,[18] who considered the effect of a free boundary on an ionic crystal with the structure of NaCl. The same conclusion was reached by Gazis and Wallis[10] on the basis of their one-dimensional model.

Our analysis suggests two further qualitative statements. First, the static displacements of atoms in the semi-infinite lattice are doubly periodic in the coordinates (m_1,m_2) parallel to the boundary. These periods may be an integer multiple of the two-dimensional unit cell spanned by $(\mathbf{a}_1,\mathbf{a}_2)$, and which characterizes the bulk, or infinite crystal. Thus

$$U_i(0,0,m_3;\mu)=U_i(m_1\alpha_1,m_2\alpha_2,m_3;\mu);\quad m_i=0,\pm1,2,\cdots;\ i=1,2. \tag{5.1}$$

In Eq. (5.1), α_i is a fixed positive integer. This integer may be larger than unity whenever Eqs. (3.17), (3.19), and (3.35) can be solved simultaneously for a set of real vectors $\{\mathbf{k}_\rho^{(f)}\}$ such that each vector has the form

$$\mathbf{k}_\rho^{(f)}=2\pi\sum_{i=1}^{2}\mathbf{b}_ik_i^{(f)}. \tag{5.2}$$

Here, in order to satisfy the periodic boundary conditions, $k_i^{(f)}$ has to be a rational number, $k_i^{(f)}=\kappa_i^{(f)}/\beta_i^{(f)}$, such that the point (k_1,k_2) lies in the first Brillouin zone of the lattice spanned by $\{\mathbf{b}_1,\mathbf{b}_2\}$. The integer α_i is less than or equal to the least-common multiple of the set $\{\beta_i^{(f)}\}$.

In the linearized theory, discussed in Secs. II and III, each vector $\mathbf{k}_\rho^{(f)}$ determines a set of static displacements to within an arbitrary multiplicative constant. The numerical values of these constants are not determined, since we have only considered the necessary conditions for static equilibrium. For the static-equilibrium configuration, these constants are determined by the requirement that the potential energy actually assumes an absolute minimum when these constants assume a particular set of numerical values. Several sets of this type may exist, and hence we may find several coexistent "domains."[19] The same comment applies to the arbitrary constants a_p in Eq. (3.39). The nonlinear theory, discussed in Sec. IV, indicates that whenever Eq. (3.35) or one of its iterates can be solved simultaneously with Eqs. (3.6), (3.17), and (3.18), for a wave vector $\mathbf{k}_\rho$, several $\mathbf{m}_\rho$-dependent sets of static displacements are coupled with each other and with the set of $\mathbf{m}_\rho$-independent displacements. The absolute magnitude of the total displacements in these stationary configurations is again undetermined. The static-equilibrium configuration is obtained by selecting among these stationary configurations the one that minimizes the potential energy of interaction.

Low-energy diffraction experiments with some valence crystals such as Ge and Si indicate that in these materials the integers α_i are definitely larger than unity.[17] Our analysis suggests that for these valence crystals, a surface structure derived from the corresponding bulk structure under the influence of the "unbalanced" forces F_α and maintaining the two-dimensional period of the atomic planes in the infinite lattice, corresponds to an unstable or possibly metastable static-equilibrium state of the semi-infinite crystal. This view is consistent with the chemical arguments proposed by Lander[20] to explain his experimental data on Ge and Si. The discussion in Sec. IV indicates furthermore the possibility that this instability may be due to an anharmonic coupling between some $\mathbf{m}_\rho$-dependent elementary displacements and the $\mathbf{m}_\rho$-independent displacements. Thus the change in the two-dimensional surface symmetry may be sensitive to external pressure, as well as to temperature, both of which affect the relative importance of anharmonic effects. In particular, it may be possible to induce "phase transformations" of the surface structure by these means. Furthermore, if the linear theory applies at low temperatures, we may find several "degenerate" configurations coexisting. This degeneracy may be lifted at elevated temperatures due to the nonlinear effects. If the surface finds itself in a metastable configuration at low temperatures, heat treatment may induce an irreversible transformation of the surface to the actual equilibrium configuration. The latter phenomenon has indeed been observed by Lander,[19] who invokes surface migration to explain his observation.

Turning to another result suggested by our analysis, suppose the static displacements of the "atoms" have the same two-dimensional period, in planes parallel to the boundary, as the bulk structure, i.e., the constants α_i in Eq. (5.1) are equal to unity. We still may find that these two-dimensional unit cells distort, such that

$$U_i(\mathbf{m},\mu_1)\neq U_i(\mathbf{m};\mu_2). \tag{5.3}$$

This phenomenon may be due either to the fact that $\mathbf{F}(m_3,\mu_1)\neq\mathbf{F}(m_3,\mu_2)$, or it may be a manifestation of an instability of the semi-infinite configuration assumed under the influence of the unbalanced forces $\mathbf{F}(m_3,\mu)$.

[18] G. C. Benson, P. I. Freeman, and Edward Dempsey, in *Advances in Chemistry*, edited by Robert F. Gould (American Chemical Society, Washington, D. C., 1961), Vol. 33, p. 26.

[19] This possibly is also suggested by J. J. Lander. See Sec. 7.6 and Fig. 31 in the first reference of Ref. 17.

[20] See first reference of Ref. 19, Sec. 7.6. Also R. Seiwatz, in *Solid Surfaces*, edited by Harry C. Gatos (North-Holland Publishing Company, Amsterdam, 1964), p. 473.

In the latter case it is necessary that one or more of the constants a_p in Eq. (3.39) be nonzero. This is, in fact, a possibility originally suggested by Molière *et al.*,[21] who investigated surface structures of ionic crystals. Unfortunately, this conclusion cannot be checked without a complete Fourier inversion of the low-energy electron diffraction data, and hence it is still rather speculative.

It is interesting to note that the instabilities of the semi-infinite configurations assumed under the influence of the unbalanced forces may be interpreted as manifestations of the existence of unstable (or zero-frequency) surface modes in the configuration considered. A change in the size of the unit cell is connected with a surface mode which has a wave vector with a nonvanishing component parallel to the surface, $\mathbf{k}_\rho \neq \mathbf{0}$. A distortion of the unit cell results from an unstable "optical" surface mode with a wave vector whose component parallel to the surface vanishes, $\mathbf{k}_\rho = \mathbf{0}$. This interpretation is analogous to the interpretation of the ferroelectric phase transition as connected with unstable (bulk) optical modes. Again, the nonlinear model suggests that the instability in the surface modes may only be latent, and manifests itself only when the $\mathbf{m}_\rho$-independent displacements have reached a sufficiently large amplitude.

In conclusion, we believe our model has great potential applicability to surface physics. Some of these applications, namely to the diffraction and the thermal diffuse scattering of low-energy electrons, will be considered in following papers,[11,12] others have yet to be explored.

APPENDIX A: PROOF OF THE SYMMETRIES OF THE UNBALANCED FORCES AND COUPLING CONSTANTS

In this Appendix, we shall briefly outline the proof of Eqs. (2.16)–(2.22). These relations are specializations of relations discussed in great length by Leibfried[3] and Ludwig and Leibfried.[4] The primary purpose of this Appendix is to make our discussion reasonably self-contained.

We start from the observation that the potential energy of interaction of any system of particles is invariant under an arbitrary infinitesimal transformation, which in turn implies a mapping,

$$O\mathbf{r}(\mathbf{m},\mu)=\mathbf{r}'(\mathbf{m},\mu)=\Omega\mathbf{r}(\mathbf{m},\mu)+\mathbf{t} =\mathbf{r}(\mathbf{m},\mu)+\omega\mathbf{r}(\mathbf{m},\mu)+\mathbf{t}, \quad \text{(A1)}$$

where Ω is an orthogonal matrix (representing a rotation) and ω is an infinitesimal skew symmetric matrix. The vector $\mathbf{r}(\mathbf{m},\mu)$ is defined by Eq. (2.5).

The invariance of the potential energy $\Phi(\{\mathbf{r}(\mathbf{l},\lambda)\})$ under the operation O implies that

$$O\Phi(\{\mathbf{r}(\mathbf{l},\lambda)\})=\Phi(\{O\mathbf{r}(\mathbf{l},\lambda)\})=\Phi(\{\mathbf{r}(\mathbf{l},\lambda)\}). \quad \text{(A2)}$$

Hence, the partial derivatives of the potential energy,

$$\Phi_{i_1\cdots i_p}(\mathbf{m}_1,\mu_1;\cdots;m_p,\mu_p) =\frac{\partial}{\partial x_{i_1}(\mathbf{m}_1,\mu_1)}\cdots\frac{\partial}{\partial x_{i_p}(\mathbf{m}_p,\mu_p)}\Phi\Big|_{\{\mathbf{r}(\mathbf{l},\lambda)\}=\{\mathbf{r}_0(\mathbf{l},\lambda)\}}, \quad \text{(A3)}$$

transform under the operation O as tensors of rank p:

$$O\Phi_{i_1\cdots i_p}(\mathbf{m}_1,\mu_1;\cdots;\mathbf{m}_p,\mu_p) =\sum_{j_1,\cdots,j_p}^{3}\Omega_{i_1j_1}\cdots\Omega_{i_pj_p}\Phi_{j_1\cdots j_p}(\mathbf{m}_1,\mu_1;\cdots;\mathbf{m}_p,\mu_p). \quad \text{(A4)}$$

Here $\{\mathbf{r}_0(\mathbf{l},\lambda)\}$ is to be interpreted as a "reference" configuration, to be specified later. If O is an infinitesimal transformation, then the transformed pth partial derivatives of Φ defined by Eq. (A3) in terms of the transformed configuration $\{O\mathbf{r}_0(\lambda,l)\}$ can be expanded in a Taylor series about the original configuration $\{\mathbf{r}_0(\lambda,l)\}$:

$$O\Phi_{i_1\cdots i_p}(\mathbf{m}_1,\mu_1;\cdots;\mathbf{m}_p,\mu_p)=\Phi_{i_1\cdots i_p}(\mathbf{m}_1,\mu_1;\cdots;\mathbf{m}_p,\mu_p)$$
$$+\sum_{i_{p+1}=1}^{3}\sum_{\mu_{p+1}=1}^{s}\sum_{\substack{m_{p+1,1}\\ m_{p+1,2}\end{subarray}=-\infty}}^{\infty}\sum_{m_{p+1,3}=0}^{\infty}\Phi_{i_1\cdots i_pi_{p+1}}(\mathbf{m}_1,\mu_1;\cdots\mathbf{m}_p,\mu_p;\mathbf{m}_{p+1},\mu_{p+1})$$
$$\times[\sum_{j=1}^{3}\omega_{i_{p+1}j}R_j(\mathbf{m}_{p+1},\mu_{p+1})+t_{i_{p+1}}]+\cdots. \quad \text{(A5)}$$

Comparing Eqs. (A4) and (A5), we obtain, for simple infinitesimal translations (i.e., when the matrix $\omega=0$),

$$\sum_{i_{p+1}=1}^{3}[\sum_{\substack{m_{p+1,1}\\ m_{p+1,2}\end{subarray}=-\infty}}^{\infty}\sum_{m_{p+1,3}=0}^{\infty}\sum_{\mu_{p+1}=1}^{s}\Phi_{i_1\cdots i_pi_{p+1}}(\mathbf{m}_1,\mu_1;\cdots;\mathbf{m}_p,\mu_p;\mathbf{m}_{p+1},\mu_{p+1})]t_{i_{p+1}}=0. \quad \text{(A6)}$$

Noting that $t_{i_{p+1}}$ is arbitrary, we conclude that the term in the square brackets has to vanish identically. Similarly,

[21] K. Molière, W. Rathje, and J. N. Stranski, Disc. Faraday Soc. 5, 21 (1949).

for an infinitesimal pure rotation (i.e., when $\mathbf{t}=0$),

$$\sum_{j,i=1}^{3}\omega_{j,i}\Big[\sum_{\mu_{p+1}=1}^{s}\sum_{\substack{m_{p+1,1}\\ m_{p+1,2}\end{subarray}}=-\infty}^{\infty}\sum_{m_{p+1,3}=0}^{\infty}(\Phi_{i_1\cdots i_p}(\mathbf{m}_1,\mu_1;\cdots\mathbf{m}_p,\mu_p;\,\mathbf{m}_{p+1},\mu_{p+1})R_j(\mathbf{m}_{p+1},\mu_{p+1}))$$

$$+\sum_{q=1}^{p}\sum_{j_q=1}^{3}\Phi_{i_1\cdots j_q\cdots i_p}(\mathbf{m}_1,\mu_1;\cdots\mathbf{m}_q,\mu_q;\cdots m_p,\mu_p)\delta_{j_q,i}\delta_{i_q,j}\Big]. \quad \text{(A7)}$$

Now, noting that ω is an arbitrary skew-symmetric infinitesimal matrix, we conclude that the term in square brackets must be symmetric in the indices i and j. Equations (A6) and (A7) apply to any semi-infinite system. In particular, if $\Phi=\Phi^{(u)}=$potential energy of interaction of the upper half of an infinite lattice, and if we define as our reference configuration $\{\mathbf{R}(\mathbf{l})+\mathbf{R}(\lambda)\}$, we obtain Eqs. (2.19) and (2.20), if $p=0$. Similarly, we obtain Eqs. (2.20)–(2.24) if $p=1$.

We now turn to consider the consequences of the invariance of the potential energy under a translation by a two-dimensional lattice vector

$$\mathbf{R}(\mathbf{m}_\rho)=\sum_{i=1}^{2}a_i m_i\rightarrow\mathbf{R}(\mathbf{m}_\rho+\mathbf{h}_\rho)=\sum_{i=1}^{2}\mathbf{a}_i(m_i+h_i);\quad h_1,\,h_2=0\pm1\cdots. \quad \text{(A8)}$$

This invariance implies that

$$\Phi_{i_1\cdots i_p}(\mathbf{m}_1,\mu_1;\cdots m_p,\mu_p)=\Phi_{i_1\cdots i_p}(\mathbf{m}_1+h_\rho,\,\mu_1;\cdots\mathbf{m}_p+\mathbf{h},\,\mu_p). \quad \text{(A9)}$$

Thus, in particular, if $\Phi=\Phi^{(u)}$, $p=0$, and $h_i=-m_i$; $i=1,\,2$, then,

$$-F_i(\mathbf{m},\mu)=\Phi_i(\mathbf{m},\mu)=\Phi_i(0,0,m_3,\mu)=-F_i(m_3,\mu). \quad \text{(A10)}$$

Similarly, if $p=1$, $h_i=-m_i$; $i=1,\,2$, then

$$\Phi_{ij}(\mathbf{m},\mu;\,\mathbf{n},\nu)=\Phi_{ij}(0,\,0,\,m_3,\,\mu;\,n_1-m_1,\,n_2-m_2,\,n_3,\,\nu). \quad \text{(A11)}$$

We also note that if in the configuration $\{\mathbf{R}(\mathbf{l})+\mathbf{R}(\lambda)\}$ each lattice point lies on an axis of rotation normal to the boundary plane $m_3=0$, then

$$F_i(\mathbf{m},\mu)=\delta_{3,i}F_3(m_3,\mu). \quad \text{(A12)}$$

This result applies in particular to alkali halides and cubic metals when the boundary plane is a (100) or a (110) plane.

APPENDIX B: THE DERIVATION OF A SET OF LINEARLY INDEPENDENT ELEMENTARY SOLUTIONS ASSOCIATED WITH A MULTIPLE ROOT OF THE CHARACTERISTIC EQUATION

In terms of the notation of Sec. III we wish to construct the q, $3s$-dimensional vectors $\mathbf{U}_p{}^{(g)}(\exp\{ik_3{}^{(g)}\};\mathbf{k}_\rho)$. We proceed by solving the $3sq$ equations

$$\sum_{p=0}^{q-1}\sum_{\sigma=1}^{3s}\sum_{h_3=-H_3}^{H_3}\theta_{\pi\sigma}(h_3;\mathbf{k}_\rho)U_{p,\sigma}(m_3+h_3,\mathbf{k}_\rho,g)=0=\sum_{p=0}^{q-1}\sum_{\sigma=1}^{3s}\sum_{l=0}^{p}\exp\{ik_3{}^{(g)}l\}$$

$$\times\binom{m_3}{p-l}\frac{1}{l!}\frac{d^l}{d(ik_3)^l}\theta_{\pi\sigma}(\exp\{ik_3{}^{(g)}\};\mathbf{k}_\rho)U_{p,\sigma}(\exp\{ik_3{}^{(g)}\};\mathbf{k}_\rho)\quad m_3=0,\cdots,q-1$$

$$\pi=1,\cdots,3s \quad \text{(B1)}$$

which can be written in matrix form,

$$\begin{bmatrix} \theta & \theta^{(1)} & \theta^{(2)} & \cdots & \dfrac{\theta^{(q-1)}}{(q-1)} \\ 0 & \theta & \theta & \cdots & \dfrac{\theta^{(q-2)}}{(q-2)} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & \cdots & \theta \end{bmatrix} \begin{bmatrix} \mathbf{U}_0 \\ y\mathbf{U}_1 \\ \cdots \\ y^{q-1}\mathbf{U}_{q-1} \end{bmatrix} = 0, \tag{B2}$$

where

$$\begin{aligned} \theta^{(l)} &= \frac{d^l}{d(ik_3)^l}\theta_{\pi\sigma}(\exp\{ik_3^{(g)}\}; \mathbf{k}_\rho), \\ y &= \exp\{ik_3^{(g)}\}, \\ \mathbf{U}_p &= U_{p,\sigma}(\exp\{ik_3^{(g)}\}; \mathbf{k}_\rho); \quad \sigma = 1, \cdots, 3s. \end{aligned} \tag{B3}$$

The q $3s$-dimensional vectors $\mathbf{U}_p$ can be determined from this matrix equation, to within q arbitrary constants, as follows: Let

$$\theta\mathbf{U} = 0, \tag{B4}$$

where the q last components of $\mathbf{U}$ are equal to one. Then,

$$\begin{aligned} \mathbf{U}_{q-1} &= \mathbf{U}, \\ \mathbf{U}_{q-2} &= \mathbf{U} + (\theta_q^{-1})\theta^{(1)}(y\mathbf{U}_{q-1}), \\ &\vdots \qquad\qquad \vdots \\ \mathbf{U}_0 &= \mathbf{U} + (\theta_q^{-1})\sum_{l=1}^{q-1}\left(\theta^{(l)}\frac{y^l}{l}\mathbf{U}_l\right), \end{aligned} \tag{B5}$$

where (θ_g) is the matrix θ with the last q rows and columns omitted, and $(\theta^{(l)}y^l\mathbf{U}_l)$ is the vector $\theta^{(l)}y^l\mathbf{U}_l$ with the last q components omitted.

The general solutions of the difference equations thus have the form

$$U_\pi(m_3; \mathbf{k}_\rho) = \sum_{g \neq g'} c_g(\mathbf{k}_\rho)U_\pi(\exp\{ik_3^{(g)}\}; \mathbf{k}_\rho)\exp\{ik_3^{(g)}m_3\} + \sum_{p=0}^{q-1} c_{g'p}(\mathbf{k}_\rho)U_{p,\pi}(\exp\{ik_3^{(g')}\}; \mathbf{k}_\rho)\binom{m_3}{p}\exp\{ik_3^{(g')}m_3\}.$$