Theory of Surface Modes of Vibration in Two- and Three-Dimensional Crystal Lattices*

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Theoretical expressions have been developed for the frequencies and displacements of the normal modes of vibration for two- and three-dimensional alternating diatomic lattices with free boundaries. Only square and cubic lattices are considered. Nearest-neighbor Hooke's law forces having both longitudinal and transverse components are assumed. The results have been obtained both by a perturbation method in which the ratio of the transverse and longitudinal force constants is treated as a small quantity and by a Green's function method. The use of the free boundary condition leads to the existence of surface modes of vibration in which the displacement amplitude is relatively large for a light atom on a boundary and decreases roughly exponentially toward the interior of the lattice. A band of surface mode frequencies lies in the "forbidden" gap between the acoustical and optical branches.

I. INTRODUCTION

AN understanding of the effects of free surfaces on the normal modes of vibration of crystal lattices is important in the investigation of such subjects as the infrared lattice vibration spectra of crystals and the specific heats of very fine powders. In a previous paper[1] it has been shown that one-dimensional diatomic lattices with free ends and nearest neighbor Hooke's law interactions may possess one or possibly two "surface" modes of vibration, i.e., modes in which the displacement amplitudes are relatively large at one or both ends of the lattice and decrease roughly exponentially toward the interior of the lattice. The frequencies for these surface modes lie in the "forbidden" gap between the acoustical and optical branches. If all the atomic masses are made equal so that a monatomic lattice results, the surface modes pass over into ordinary wave-like modes.

In the present paper an investigation is given of surface modes in finite square and cubic lattices of the sodium chloride type using the model discussed by Rosenstock and Newell[2] and by Montroll and Potts.[3] It is assumed that each atom interacts only with its nearest neighbors according to a Hooke's law force. This interaction contains both central and noncentral components. Instead of the usual cyclic boundary condition, the free boundary condition is employed in which atoms on the surface are assumed to interact only with their nearest neighbors on the interior of the lattice and are otherwise free.

II. THE ROSENSTOCK-NEWELL MODEL

The equations of motion for the atoms in the Rosenstock-Newell model of the diatomic square lattice with free boundaries can be written as

$$m_\alpha \ddot{u}_{jk}=\tau(u_{j,k-1}-u_{jk})(1-\delta_{k,1})+\sigma(u_{j-1,k}-u_{jk})(1-\delta_{j,1})+\sigma(u_{j+1,k}-u_{jk})(1-\delta_{j,2N})+\tau(u_{j,k+1}-u_{jk})(1-\delta_{k,2N}),\quad 1\leqslant j\leqslant 2N,\quad 1\leqslant k\leqslant 2N,\quad \text{(1a)}$$

$$m_\alpha \ddot{v}_{jk}=\tau(v_{j-1,k}-v_{jk})(1-\delta_{j,1})+\sigma(v_{j,k-1}-v_{jk})(1-\delta_{k,1})+\sigma(v_{j,k+1}-v_{jk})(1-\delta_{k,2N})+\tau(v_{j+1,k}-v_{jk})(1-\delta_{j,2N}),\quad 1\leqslant j\leqslant 2N,\quad 1\leqslant k\leqslant 2N,\quad \text{(1b)}$$

where u and v are the x and y components of the displacement of an atom from equilibrium and the quantities j and k are integers specifying the position of an atom in the lattice. The mass m_α has the value m_1 if $j+k$ is even and the value m_2 if $j+k$ is odd. The quantities σ and τ are the Hooke's law force constants for the central and noncentral interactions, respectively. The Kronecker δ's in Eqs. (1a) and (1b) are introduced to take into account the free boundaries at the edges $j=1$, $2N$ and $k=1$, $2N$. Equations (1a) and (1b) may be easily generalized to give the equations of motion for the diatomic cubic lattice of the NaCl type with free boundaries.

The Rosenstock-Newell model has a number of realistic features. For example, it possesses resistance to shear in contrast to a model with only nearest neighbor central forces. A great advantage of the Rosenstock-Newell model is its mathematical simplicity which permits one to carry out a fairly complete analysis without excessive labor. On the other hand, the Rosenstock-Newell model has a number of drawbacks. The equations of motion show an unrealistic lack of coupling between the displacements in the x direction and those in the y and z directions. The presence of only two force constants implies a relationship between the three elastic constants c_{11}, c_{12}, and c_{44} which is not necessarily satisfied by real cubic crystals. Furthermore, the Rosenstock-Newell model does not possess rotational invariance.

* A preliminary account of this work was given at the Chicago Meeting of the American Physical Society, March 27–29, 1958 [Bull. Am. Phys. Soc. Ser. II, 3, 110 (1958)].

[1] R. F. Wallis, Phys. Rev. **105**, 540 (1957).

[2] H. B. Rosenstock and G. F. Newell, J. Chem. Phys. **21**, 1607 (1953).

[3] E. W. Montroll and R. B. Potts, Phys. Rev. **100**, 525 (1955); **102**, 72 (1956).

In spite of these difficulties, however, it is felt that an investigation of the Rosenstock-Newell model can yield qualitatively correct information concerning certain types of surface modes of vibration.

A. Monatomic Simple Square and Simple Cubic Lattices

Exact expressions can be obtained for the normal mode frequencies of the Rosenstock-Newell model in the monatomic cases. Taking $m_\alpha=m_1=m_2=m$ in Eqs. (1a) and (1b), the normal mode frequencies for the monatomic simple square lattice are specified by

$$\omega^2=\frac{4\sigma}{m}\left\{\sin^2(\varphi_1/2)+\frac{\tau}{\sigma}\sin^2(\varphi_2/2)\right\}, \tag{2a}$$

where

$$\varphi_1=n_1\pi/2N, \quad 0\leqslant n_1\leqslant 2N-1 \tag{2b}$$

$$\varphi_2=n_2\pi/2N, \quad 0\leqslant n_2\leqslant 2N-1. \tag{2c}$$

The corresponding displacement amplitudes associated with the normal modes can be written as

$$u_{jk}=U\cos(j-\tfrac{1}{2})\varphi_1\cos(k-\tfrac{1}{2})\varphi_2\exp(i\omega t), \tag{3a}$$

$$v_{jk}=0, \tag{3b}$$

and

$$u_{jk}=0, \tag{4a}$$

$$v_{jk}=V\cos(j-\tfrac{1}{2})\varphi_2\cos(k-\tfrac{1}{2})\varphi_1\exp(i\omega t), \tag{4b}$$

where U and V are arbitrary constants.

One sees from Eqs. (2) that all normal mode frequencies lie in a band of width $2[(\sigma+\tau)/m]^{\frac{1}{2}}$. It is clear from Eqs. (3) and (4) that all normal vibrations are wave-like in character and that none have the exponential drop-off with distance from the boundary characteristic of surface modes. This result has been previously noted by Kaplan.[4]

The preceding results can readily be generalized to the simple cubic monatomic lattice using the Rosenstock-Newell model. One again finds that all modes are wave-like in character and that there are no surface modes.

B. Diatomic Simple Square Lattice

The problem of finding exact solutions to the equations of motion for the finite diatomic simple square and simple cubic lattices is considerably more difficult than for the monatomic case. So far we have been unable to find exact solutions for the finite diatomic lattices and have been forced to make use of other methods of attack. One method is to treat the ratio τ/σ as a small quantity and use perturbation theory. A second procedure is to regard the surface as a "defect" in an otherwise perfect lattice and employ the Green's function method of Montroll and Potts[3] to investigate the localized modes which arise. The perturbation treatment has the advantage of being applicable to lattices which are finite in all dimensions, but it is valid only if τ/σ is small. The Green's function method, on the other hand, is not restricted to small values of τ/σ, but the calculations can be carried through in detail only if the lattice is finite in one dimension and infinite in all other dimensions.

a. Perturbation Theory

From Eqs. (1a) and (1b) one sees that the motions in the x and y directions are not coupled. One can therefore restrict one's efforts to the x direction and obtain the motion in the y direction by inspection from that in the x direction.

By making the substitutions

$$u_{jk}=Um_1^{-\frac{1}{2}}A_{jk}\exp(i\omega t), \quad j+k \text{ even} \tag{5a}$$

$$u_{jk}=Um_2^{-\frac{1}{2}}A_{jk}\exp(i\omega t), \quad j+k \text{ odd} \tag{5b}$$

where the A_{jk} are time-independent amplitudes and U is an arbitrary constant, the solution of Eqs. (1a) becomes equivalent to the diagonalization of a matrix M called the dynamical matrix, whose dimensions are $4N^2\times 4N^2$ and whose eigenvalues are the values of ω^2. The quantities A_{jk} form the elements of the normalized eigenvectors of M.

The matrix M can be written as

$$M=M_0+(\tau/\sigma)M_1, \tag{6}$$

where M_0 and M_1 are independent of τ/σ. The matrix M_0 consists of $2N\times 2N$ dimensional matrices along the main diagonal with all other elements zero. Each $2N\times 2N$ matrix is the matrix which must be diagonalized to obtain the normal mode frequencies of the linear diatomic chain with nearest neighbor Hooke's law interactions. One can verify this by observing that if τ/σ is zero, Eqs. (1a) reduce to the equations of motion for $2N$ independent linear diatomic chains of $2N$ atoms each. Since exact solutions to the linear diatomic chain problem have been given in previous work,[1] the exact eigenvalues and eigenvectors of M_0 can be written down immediately.

There are $2N$ eigenvectors of M_0 which correspond to surface modes of the $2N$ linear diatomic chains. The elements for N of these eigenvectors may be written as

$$A_{2j-1,q}{}^0(s,q')=cm_1^{\frac{1}{2}}(-1)^{j-1}(m_1/m_2)^{j-1}\delta_{qq'}, \tag{7a}$$

$$A_{2j,q}{}^0(s,q')=cm_2^{\frac{1}{2}}(-1)^{j}(m_1/m_2)^{j}\delta_{qq'}, \quad 1\leqslant j\leqslant N, \tag{7b}$$

where q' is an odd integer in the range $1\leqslant q'\leqslant 2N$. The normalizing constant c is given by

$$c=\{[m_1m_2/(m_2-m_1)][1-(m_1/m_2)^{2N}]\}^{-\frac{1}{2}}. \tag{7c}$$

For the remaining N eigenvectors, q' is an even integer in the range $1\leqslant q'\leqslant 2N$ and the masses m_1 and m_2 should be interchanged in Eqs. (7). The eigenvalue of M_0

[4] H. Kaplan, Bull. Am. Phys. Soc. **2**, 147 (1957).

corresponding to each of the $2N$ surface-mode eigenvectors of M_0 is

$$\omega_s^2=\sigma(m_1+m_2)/m_1m_2. \tag{8}$$

There are also $2N(2N-2)$ eigenvectors of M_0 which correspond to wave-like modes. Their elements are given by

$$A_{2j-1,q}{}^0(\varphi,q')=c'm_1^{\frac{1}{2}}\{\sin(2j-1)\varphi - x\sin(2j-2)\varphi\}\delta_{qq'}, \tag{9a}$$

$$A_{2j,q}{}^0(\varphi,q')=c'm_2^{\frac{1}{2}}\{x^{-1}\sin 2j\varphi-\sin(2j-1)\varphi\}\delta_{qq'}, \quad 1\leqslant j\leqslant N, \tag{9b}$$

$$c'=(2/N)^{\frac{1}{2}}\{m_1[1-2x\cos\varphi+x^2] +m_2[1-2x^{-1}\cos\varphi+x^{-2}]\}^{-\frac{1}{2}}. \tag{9c}$$

for q' odd and similar expressions with m_1 and m_2 interchanged for q' even. The corresponding frequencies are given by

$$\omega_\varphi^2=\omega_s^2\left\{1\pm\left[\cos^2\varphi+\left(\frac{m_2-m_1}{m_2+m_1}\right)^2\sin^2\varphi\right]^{\frac{1}{2}}\right\}, \tag{10}$$

and the quantities x and φ are

$$x=\left(\frac{m_2\omega_\varphi^2-2\sigma}{m_1\omega_\varphi^2-2\sigma}\right)^{\frac{1}{2}} \tag{11a}$$

and

$$\varphi=n\pi/2N, \tag{11b}$$

where the integer n lies in the range $1\leqslant n\leqslant N-1$ for the acoustical branch [lower sign in Eq. (10)] and in the range $N+1\leqslant n\leqslant 2N-1$ for the optical branch [upper sign in Eq. (10)].

Finally, there are $2N$ eigenvectors of M_0 corresponding to translational modes of zero frequency. The elements of the eigenvectors are given by

$$A_{2j-1,q}{}^0(t,q')=m_1^{\frac{1}{2}}[N(m_1+m_2)]^{-\frac{1}{2}}\delta_{qq'}, \tag{12a}$$

$$A_{2j,q}{}^0(t,q')=m_2^{\frac{1}{2}}[N(m_1+m_2)]^{-\frac{1}{2}}\delta_{qq'} \tag{12b}$$

for q' odd and by Eqs. (12) with m_1 and m_2 interchanged for q' even.

The eigenvalues of M correct to first order in τ/σ are readily calculated by degenerate perturbation theory. Let us first consider the $2N$ eigenvalues and eigenvectors of M_0 which correspond to the surface modes with frequency ω_s given by Eq. (8). The corrected eigenvalues obtained by first-order perturbation theory can be grouped into several classes. For the first class the frequencies are specified by

$$\omega^2=\omega_s^2+\tau(G-F\cos\gamma), \tag{13a}$$

where

$$F=4N(m_2-m_1)(m_1m_2)^{N-1}/[m_2^{2N}-m_1^{2N}], \tag{13b}$$

and

$$G=2(m_1^2+m_2^2)/[m_1m_2(m_1+m_2)]. \tag{13c}$$

The values of γ are determined by solving the transcendental equation[5]

$$F/G=\cos(N-\tfrac{1}{2})\gamma/\cos(N+\tfrac{1}{2})\gamma. \tag{14}$$

There are N independent values of γ arising from Eq. (14) which can be chosen to lie in the range $0\leqslant\gamma\leqslant\pi$. For each value of γ there is a set of displacements given by

$$u_{pq}=Um_\alpha^{-\frac{1}{2}}\textstyle\sum_{q'}A_{pq}{}^0(s,q') \times\cos(N+\tfrac{1}{2}-q')\gamma\exp(i\omega t), \tag{15}$$

with ω given by Eq. (13a), $A_{pq}{}^0(s,q')$ by Eqs. (7a) and (7b) and $m_\alpha=m_1$ or m_2 depending on whether $p+q$ is even or odd, respectively.

We note from the form of the $A_{pq}{}^0$ given by Eqs. (7a) and (7b) that light atoms on opposite edges have relatively large maximum displacements and that the displacements decrease exponentially toward the interior of the lattice. Since the largest displacements are perpendicular to the edges along which they occur, we shall refer to these modes as transverse edge modes. Examination of the quantity $f_1(q')=\cos(N+\frac{1}{2}-q')\gamma$ in Eq. (15) reveals that $f_1(q')=f_1(2N+1-q')$. Consequently, we further classify the modes under discussion as symmetric transverse edge modes. The displacements for a typical symmetric transverse edge mode are shown in Fig. 1.

A second class of transverse edge modes has frequencies given by Eq. (13a), but the values of γ are determined by the equation

$$F/G=\sin(N-\tfrac{1}{2})\gamma/\sin(N+\tfrac{1}{2})\gamma. \tag{16}$$

If $(F/G)\geqslant(N-\frac{1}{2})/(N+\frac{1}{2})$, there are N independent values of γ satisfying Eq. (16), whereas if $(F/G)<(N-\frac{1}{2})/(N+\frac{1}{2})$, there are only $N-1$ independent values. For each value of γ there is a set of displace-

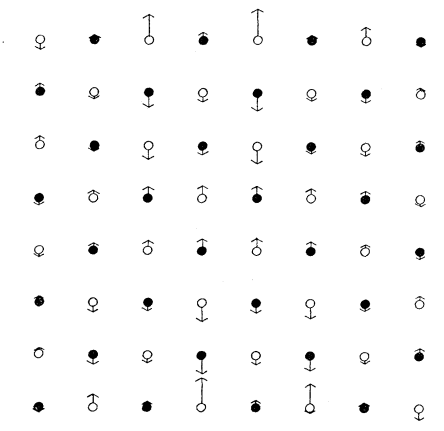

FIG. 1. Displacements for a typical symmetric transverse edge mode. The open circles represent the lighter atoms and the solid circles the heavier atoms.

[5] See K. F. Herzfeld, J. Chem. Phys. **10**, 508 (1942).

ments given by

$$u_{pq}=Um_\alpha^{-\frac{1}{2}}\sum_{q'}A_{pq}{}^0(s,q')\times\sin(N+\tfrac{1}{2}-q')\gamma\exp(i\omega t). \quad (17)$$

Letting $f_2(q')=\sin(N+\frac{1}{2}-q')\gamma$, we observe that $f_2(q')=-f_2(2N+1-q')$. Consequently, the modes specified by Eqs. (13a), (16), and (17) will be referred to as antisymmetric transverse edge modes.

Another type of surface mode occurring in the diatomic square lattice is the corner mode. To first order in perturbation theory the frequencies of the corner modes are given by

$$\omega^2=\omega_s{}^2+\tau(G-F\cosh\gamma). \quad (18)$$

For the symmetric corner mode the value of γ is determined by the equation

$$F/G=\cosh(N-\tfrac{1}{2})\gamma/\cosh(N+\tfrac{1}{2})\gamma, \quad (18a)$$

and the displacements can be written as

$$u_{pq}=Um_\alpha^{-\frac{1}{2}}\sum_{q'}A_{pq}{}^0(s,q')\times\cosh(N+\tfrac{1}{2}-q')\gamma\exp(i\omega t), \quad (18b)$$

with ω given by Eq. (18). The displacements for a typical symmetric corner mode are shown in Fig. 2.

For the antisymmetric corner mode the value of γ is determined by

$$F/G=\sinh(N-\tfrac{1}{2})\gamma/\sinh(N+\tfrac{1}{2})\gamma, \quad (18c)$$

and the displacements can be written as

$$u_{pq}=Um_\alpha^{-\frac{1}{2}}\sum_{q'}A_{pq}{}^0(s,q')\times\sinh(N+\tfrac{1}{2}-q')\gamma\exp(i\omega t). \quad (18d)$$

There is a symmetric corner mode for all physical values of F and G provided $m_1\neq m_2$, but an antisymmetric corner mode exists only if $(F/G)<(N-\frac{1}{2})/(N+\frac{1}{2})$. If the latter condition is not satisfied, the antisymmetric corner mode passes over into an antisymmetric transverse edge mode. In the limit $N\to\infty$, $F/G\to 0$ so that there will be two corner modes for all but very small crystals.

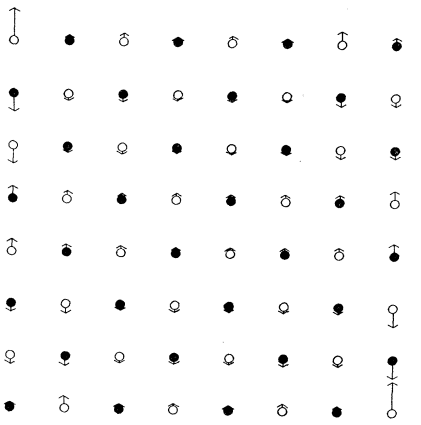

FIG. 2. Displacements for a typical symmetric corner mode. The open circles represent the lighter atoms and the solid circles the heavier atoms.

Let us now carry out the first-order perturbation calculation using the $2N$ eigenvectors of M_0 specified by Eqs. (9) and corresponding to a given value of φ. One obtains a set of $N-1$ symmetric wave-like modes for each value of φ with frequencies given by

$$\omega^2=\omega_\varphi{}^2+\tau(g-f\cos\gamma), \quad (19)$$

where $\omega_\varphi{}^2$ is given by Eq. (10),

$$f=\frac{4[2-(x+x^{-1})\cos\varphi]}{m_1(1-2x\cos\varphi+x^2)+m_2(1-2x^{-1}\cos\varphi+x^{-2})}, \quad (19a)$$

and

$$g=\frac{2[2-2(x+x^{-1})\cos\varphi+x^2+x^{-2}]}{m_1(1-2x\cos\varphi+x^2)+m_2(1-2x^{-1}\cos\varphi+x^{-2})}. \quad (19b)$$

The values of γ are determined by

$$f/g=\cos(N-\tfrac{1}{2})\gamma/\cos(N+\tfrac{1}{2})\gamma, \quad (19c)$$

and the displacements are given by

$$u_{pq}=Um_\alpha^{-\frac{1}{2}}\sum_{q'}A_{pq}{}^0(\varphi,q')\times\cos(N+\tfrac{1}{2}-q')\gamma\exp(i\omega t), \quad (19d)$$

where ω is given by Eq. (19).

One also obtains a set of antisymmetric wave-like modes for each value of φ. The frequencies are given by Eq. (19) with γ values determined by

$$f/g=\sin(N-\tfrac{1}{2})\gamma/\sin(N+\tfrac{1}{2})\gamma. \quad (20)$$

The displacements are obtained from Eq. (19d) by replacing $\cos(N+\frac{1}{2}-q')\gamma$ by $\sin(N+\frac{1}{2}-q')\gamma$. There are $N-1$ antisymmetric wave-like modes for each value of φ if $(f/g)<(N-\frac{1}{2})/(N+\frac{1}{2})$ and N modes if $(f/g)\geq(N-\frac{1}{2})/(N+\frac{1}{2})$.

For each value φ there is one symmetric surface mode and one antisymmetric surface mode, provided $(f/g)<(N-\frac{1}{2})/(N+\frac{1}{2})$, with frequencies given by

$$\omega^2=\omega_\varphi{}^2+\tau(g-f\cosh\gamma), \quad (21a)$$

and the values of γ determined by

$$f/g=\cosh(N-\tfrac{1}{2})\gamma/\cosh(N+\tfrac{1}{2})\gamma \quad (21b)$$

for the symmetric surface mode, and by

$$f/g=\sinh(N-\tfrac{1}{2})\gamma/\sinh(N+\tfrac{1}{2})\gamma \quad (21c)$$

for the antisymmetric surface mode. The corresponding displacements are obtained from Eq. (19d) by replacing the quantity $\cos(N+\frac{1}{2}-q')\gamma$ by $\cosh(N+\frac{1}{2}-q')\gamma$ or $\sinh(N+\frac{1}{2}-q')\gamma$ for the symmetric and antisymmetric surface modes, respectively. Since the largest displacements occur along two opposite edges and are parallel to these edges, we shall refer to these modes as longitudinal edge modes. If the condition $(f/g)<(N-\frac{1}{2})/(N+\frac{1}{2})$ is not satisfied, the antisymmetric longitudinal edge mode passes over into a wave-like mode.

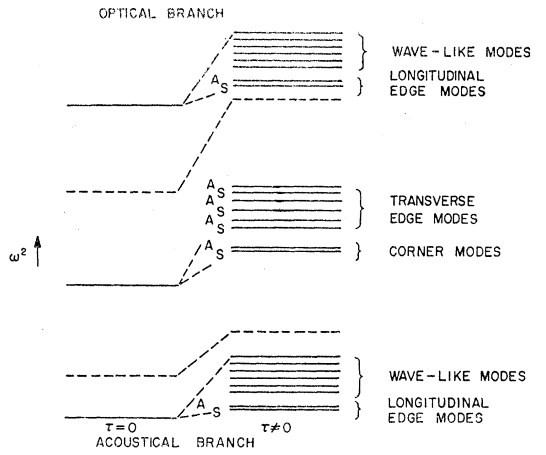

FIG. 3. Diagram of the squares of the normal mode frequencies for a finite diatomic square lattice. The symbols S and A designate symmetric and antisymmetric modes, respectively.

A first-order perturbation calculation has also been made using the translational eigenvectors of M_0 given by Eqs. (12). One obtains a set of wave-like modes but no surface modes.

A diagram of the normal mode frequencies for the Rosenstock-Newell model of a diatomic square lattice with 8 atoms on an edge is given in Fig. 3 for the cases $\tau=0$ and $\tau\neq0$. It is assumed that $(N-\frac{1}{2})/(N+\frac{1}{2})$ is greater than both f/g and F/G. This condition is generally satisfied unless the crystal is very small. All frequencies are doubly degenerate because of the independence of the motions in the x and y directions. These motions would in general be coupled in a model having interactions more complicated than those of the Rosenstock-Newell model. The double degeneracy would then be resolved.

Of the modes with frequencies in the optical and acoustical branches only those are shown in Fig. 3 which lie closest to the forbidden gap when $\tau=0$. The transverse edge mode frequencies lie in the "forbidden" gap and form a band of width $2\tau F$ (in terms of ω^2). From the expression for F given in Eq. (13b), one sees that the width approaches zero as $N\rightarrow\infty$. The transverse edge modes are alternately symmetric and antisymmetric. Split off below the transverse edge mode frequencies are the frequencies for the corner modes, the symmetric corner mode frequency lying lower than the antisymmetric.

The modes with frequencies in either the acoustical or optical branches and which correspond to a given value of φ yield a band of wave-like mode frequencies having a width of $2\tau f$ in terms of ω^2. The longitudinal edge mode frequencies are split off below the band of wave-like modes with the symmetric mode having the lower frequency.

It may be noted that the first order perturbation treatment of the modes with frequencies in the acoustical or optical branches is probably not valid unless N is small or τ/σ is very small. If N is not small, the splittings due to the τ/σ perturbation may become comparable to or greater than the frequency separations corresponding to different values of φ. Higher orders of perturbation theory would then be required to take into account the contributions of modes with different φ values. This difficulty does not, however, occur for modes with frequencies in the "forbidden" gap, provided the gap is not too narrow.

b. Green's Function Method

Let us consider a diatomic square lattice with $2N$ atoms along each edge and with cyclic boundary conditions applied. The equilibrium positions of the atoms may be designated by pairs of integers (p,q). If the interactions of the Rosenstock-Newell model are employed, a "surface" may be introduced by setting the interactions between atoms $(0,q)$ and $(1,q)$ equal to zero where the integer q may take on any value in the range $-N\leqslant q\leqslant N$. Treating the interactions set equal to zero as a "defect," we have evaluated the frequencies for the transverse edge modes with frequencies in the "forbidden" gap. The nature of the assumed model excludes the possibility of corner modes. The calculation is based on a straightforward application of the method of Montroll and Potts[3] which, however, in its original form does not permit the investigation of longitudinal edge modes with frequencies in the acoustical or optical branches. The evaluation of the required Green's function is conveniently done only in the limit $N\rightarrow\infty$ so that the results apply to a semi-infinite lattice.

The frequencies in the "forbidden" gap are determined by the transcendental equation

$$2[\zeta^2-(1-\eta)h]\cos(\theta/2)=\zeta[4(1-\eta)+h]\sin(\theta/2), \quad (22a)$$

where

$$\zeta=\{[2+2z-(1+\rho)y][(1+1/\rho)y-2-2z]\}^{\frac{1}{2}}, \quad (22b)$$

$$h=(2+\rho+1/\rho)y-4-4z, \quad (22c)$$

$$\eta=(\tau/\sigma)\cos\psi, \quad (22d)$$

$$\theta=\arctan(\eta\zeta/|1+\tfrac{1}{4}\zeta^2-\eta^2|), \quad (22e)$$

$$\rho=m_1/m_2, \quad (22f)$$

$$y=(\omega/\omega_s)^2, \quad (22g)$$

$$z=\tau/\sigma. \quad (22h)$$

The quantity ψ is 2π times the reciprocal wavelength describing propagation of the surface waves parallel to the edge of the lattice. The physical range of interest for ψ can be taken to be $-\pi/2\leqslant\psi\leqslant\pi/2$.

If z is small compared to unity, one can obtain a solution of Eq. (22a) in powers of z. The result to second order in z is

$$y=1+2\frac{(1+\rho^2)}{(1+\rho)^2}z+4\frac{\rho(1-\rho)^2}{(1+\rho)^4}(1+\cos^2\psi)z^2. \quad (23)$$

To first order in z, the transverse edge modes all have the same frequency. This result agrees with that obtained by perturbation theory in the limit $N \rightarrow \infty$. The degeneracy is resolved in second order so that a band of frequencies results.

Exact numerical solutions to Eq. (23) have been obtained for $\rho=0.5$ and $z=0.1$, 0.5, and 1.0 using the IBM-704 computer at the Research Laboratories of the General Motors Corporation. I am indebted to Dr. Robert Herman through whom the computer was made available for this problem and to Dr. Harold Willis Milnes who supervised the programming. The results are shown in Fig. 4 where y is plotted against ψ. The total variation in y for $z=0.1$ is only 0.001 which is not evident in the figure. It is interesting to note that the exact results are rather well fitted by values calculated from Eq. (23) even for $z=1.0$.

For the semi-infinite lattice under consideration one can discuss the distribution of surface mode frequencies. Since the frequency distribution function is proportional to $d\psi/d\omega$, it possesses infinities at the smallest and largest frequencies of the transverse surface mode band.

c. *Diatomic Simple Cubic Lattice*

The Rosenstock-Newell model for the diatomic simple cubic lattice has been treated by both perturbation and Green's function methods. The results of the first order perturbation calculation are presented schematically in Fig. 5. There are a number of surface modes which may be classified as transverse face modes, transverse edge modes, corner modes, longitudinal face modes, and longitudinal edge modes. To illustrate the analogy with the two-dimensional results, we shall give expressions for the frequencies and displacements for some of the transverse face modes in a crystal containing

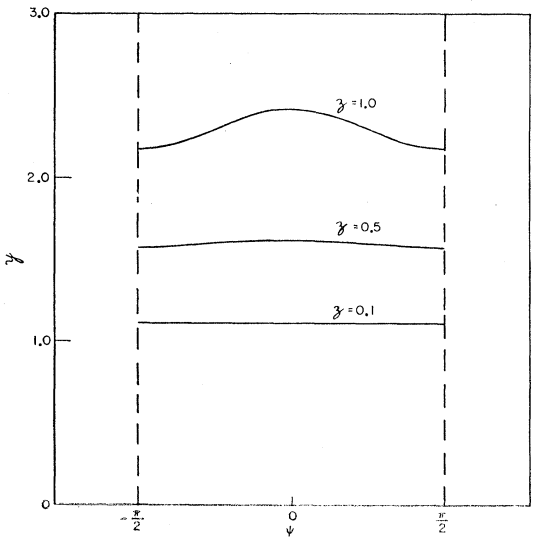

FIG. 4. The frequency squared plotted as a function of propagation constant for the transverse edge modes of the semi-infinite diatomic square lattice. The mass ratio is one-half.

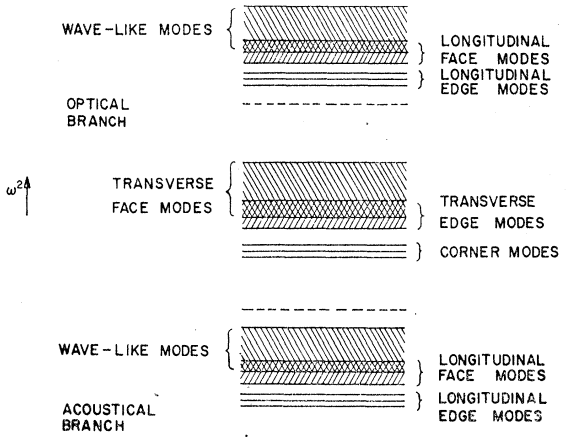

FIG. 5. Diagram of the squares of the normal mode frequencies for a finite diatomic cubic lattice. The symbols S and A designate symmetric and antisymmetric modes, respectively.

$8N^3$ atoms. The frequencies are given by

$$\omega^2=\omega_s^2+\tau[2G-F(\cos\gamma_1+\cos\gamma_2)], \qquad (24)$$

where F and G are the same as in Eqs. (13b) and (13c), and γ_1 and γ_2 are each solutions of Eq. (14). The x components of the displacements are given by

$$u_{pqr}=Um_\alpha^{-\frac{1}{2}}\sum_{q'}\sum_{r'}A_{pqr}{}^0(s,q',r')\cos(N+\tfrac{1}{2}-q')\gamma_1 \times\cos(N+\tfrac{1}{2}-r')\gamma_2\exp(i\omega t), \qquad (25a)$$

where $m_\alpha=m_1$ or m_2 according to whether $p+q+r$ is odd or even. The quantities $A_{pqr}{}^0(s,q',r')$ are given by

$$A_{2j-1,\,q,\,r}{}^0(s,q',r')=cm_1^{\frac{1}{2}}(-1)^{j-1}(m_1/m_2)^{j-1}\delta_{qq'}\delta_{rr'}, \qquad (25b)$$

$$A_{2j,\,q,\,r}{}^0(s,q',r')=cm_2^{\frac{1}{2}}(-1)^{j}(m_1/m_2)^{j}\delta_{qq'}\delta_{rr'}, \quad 1\leqslant j\leqslant N, \qquad (25c)$$

where c is given by Eq. (7c), q' and r' are integers in the range between unity and $2N$ inclusive and $q'+r'$ is even. For $q'+r'$ odd, the masses m_1 and m_2 are interchanged in Eqs. (25b) and (25c).

For other transverse face modes one or both of the cosine factors in Eq. (25a) are replaced by sines. The γ's involved in the sine factors are then determined by Eq. (16). Transverse edge modes arise if one of the cosine terms in Eq. (24) is replaced by the hyperbolic cosine and the corresponding cosine factor in Eq. (25a) is replaced by either a hyperbolic cosine or hyperbolic sine. The γ associated with the hyperbolic function is determined by either Eq. (18a) or (18c). Corner modes are obtained by replacing both cosine terms in Eq. (24) by hyperbolic cosines and the cosine factors in Eq. (25a) by hyperbolic cosines or hyperbolic sines.

If $(F/G)<(N-\frac{1}{2})/(N+\frac{1}{2})$, there are $4(N-1)^2$ transverse face modes, $8(N-1)$ transverse edge modes and 4 corner modes, while if F/G does not satisfy this condition, there are $(4N^2-4N+1)$ transverse face modes, $(4N-2)$ transverse edge modes and one corner mode.

The transverse face mode frequencies form a band in the "forbidden" gap. The transverse edge mode frequencies also form a band which may be entirely below the band for the face modes or may overlap the lower portion. The corner modes frequencies in general lie below the face and edge mode bands. All frequencies are threefold degenerate because of the independence of the motions in the x, y, and z directions.

The Green's function calculation of the surface mode frequencies for the diatomic simple cubic lattice in the limit $N \rightarrow \infty$ again leads to an equation of the form of Eq. (22a) except that z is to be redefined as $2(\tau/\sigma)$ and η as $(\tau/\sigma)(\cos\psi_1+\cos\psi_2)$. A power series solution to second order in z is given by

$$y=1+4\frac{(1+\rho^2)}{(1+\rho)^2}z + 16\frac{\rho(1-\rho)^2}{(1+\rho)^4}[1+\tfrac{1}{4}(\cos\psi_1+\cos\psi_2)^2]z^2, \quad (26)$$

where y and ρ have been defined previously.

III. DISCUSSION

Surface modes of vibration in crystal lattices have been discussed previously by Lifshitz and Rosenzweig.[6] Using a technique rather similar to that of Montroll and Potts,[3] Lifshitz and Rosenzweig have found that two types of surface modes may exist in diatomic crystals, one type being analogous to the Rayleigh waves of continuum theory and a second type being derived from the optical branch and having no analog in continuum theory. The paper of Lifshitz and Rosenzweig gives only general results which are applicable only to semi-infinite lattices, so that edge and corner modes are not discussed. Unfortunately, we have not been able to obtain a more detailed treatment given by Rosenzweig.[7]

From the fact that the Rosenstock-Newell model of the monatomic simple cubic lattice does not possess surface modes, we may conclude that the Rayleigh-type[8] surface modes do not exist for this model. The surface modes found for the diatomic lattices are therefore not analogous to Rayleigh waves since in the continuum limit there is no distinction between monatomic and diatomic lattices. It is possible that the surface modes for the diatomic lattices correspond to the "optical" surface modes of Lifshitz and Rosenzweig.

The absence of Rayleigh-type surface modes in the Rosenstock-Newell model is probably a consequence of the particular nature of the model. Stoneley[9] has investigated the continuum theory of surface waves in cubic materials and found that Rayleigh-type waves do not exist for all possible values of the elastic constants c_{11}, c_{12}, and c_{44}. For the Rosenstock-Newell model in the continuum limit the relation $c_{12}=0$ is satisfied. The elastic constants consequently may not lie in the range of values for which Rayleigh-type waves exist. Another possible reason for the nonexistence of Rayleigh-type waves in the Rosenstock-Newell model is the lack of coupling in the latter between the displacements in the x, y, and z directions. A detailed investigation of these points is currently underway.

IV. ACKNOWLEDGMENTS

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