Effect of Free Ends on the Vibration Frequencies of One-Dimensional Lattices*

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Vibration frequencies have been calculated for finite one-dimensional lattices in which the point masses alternately have the values m_α and m_β, $m_\alpha<m_\beta$. Only nearest neighbor Hooke's law interactions are considered. The end atoms are assumed to interact only with their nearest neighbors on the interior of the lattice and are otherwise free. If the numbers of atoms having masses m_α and m_β are equal, there exists a single mode whose frequency squared lies at the middle of the "forbidden" gap between the optical and acoustical branches. For this "surface" mode the displacements of the atoms from their equilibrium positions decrease roughly exponentially from the end having the lighter atom. For the case of N atoms of mass m_β and $N+1$ atoms of mass m_α there exist two modes whose frequencies lie in the "forbidden" gap provided $(m_\alpha/m_\beta)<N/(N+1)$. These modes correspond to symmetric and antisymmetric displacements. The displacements are largest for the end atoms and decrease roughly exponentially toward the center of the lattice.

I. INTRODUCTION

THE calculation of the vibration frequencies of crystal lattices has generally made use of the so-called "cyclic" or "periodic" boundary condition. The cyclic condition has the advantage that it introduces considerable simplification into the calculations of the vibration frequencies. Born[1] has investigated two types of one-dimensional lattice and has concluded that one obtains the same frequency distribution function, $g(\nu)$, using the cyclic condition as one obtains by assuming the lattices to have free ends. Accordingly it appears that the cyclic condition leads to correct results for properties determined by the frequency distribution such as the specific heat of large crystals.

The cyclic condition has the disadvantage that its use prevents one from investigating surface effects. In addition it has recently been shown by Rosenstock[2] that the details of the infrared absorption spectrum of an ionic lattice may not be correctly given when the cyclic condition is used. This discrepancy appears to arise from differences in the phases of the atomic displacements for a cyclic lattice compared to a lattice with free ends.

The vibration frequencies of monatomic one-dimensional lattices with free ends and nearest neighbor Hooke's law interactions have been discussed by Born[1] and by Halford.[3] All modes of vibration are wave-like in character, and all frequencies lie in a single band. Approximately one-half the frequencies have exactly the same values as those found when the cyclic condition is used. The remaining frequencies have values smaller by a quantity of order $\sim 1/N$ from the values given by the cyclic condition where N is the number of point masses in the lattice. The limiting frequency distribution function as $N\to\infty$ is the same for both cyclic and free boundaries.

The vibration frequencies of a diatomic one-dimensional lattice with free ends and nearest neighbor Hooke's law interactions have been studied by Born.[1] The number of point masses—i.e., atoms—having the lighter mass was taken to be the same as the number having the heavier mass. The atoms were arranged in an alternating array. According to Born all modes are wave-like in character with frequencies in either the optical branch or the acoustical branch. However, it appears that two of the solutions—i.e., those for which the variable φ has the value π—are trivial with the atomic displacements all zero. One of these solutions may be replaced by the solution having zero frequency corresponding to translation of the lattice. The nature of the remaining solution forms part of the subject matter of the present paper. Aside from a possible set of frequencies of measure zero, the frequency distribution function in the limit of infinitely many atoms is the same as that obtained using the cyclic boundary condition.

The present paper is a report on calculations of the vibration frequencies of finite one-dimensional lattices. The atoms composing a given lattice may have either of two different masses and are arranged in an alternating array. Only nearest neighbor Hooke's law interactions are considered. The cyclic boundary condition is not used. It is assumed that the end atoms interact only with their nearest neighbors on the interior of the lattice and are otherwise free. The end atoms constitute what may be called the "surface" of the lattice. Only longitudinal vibrations are considered; i.e., the displacements of the atoms are parallel to the axis of the lattice. Two lattices are considered, one with end atoms not alike and one with end atoms alike.

II. FINITE DIATOMIC LATTICE WITH END ATOMS NOT ALIKE

In this section we consider the vibration frequencies of a diatomic one-dimensional lattice consisting of N atoms of mass m_α and N atoms of mass m_β, with $m_\alpha<m_\beta$. The atoms are assumed to be arranged in an

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[1] M. Born, Proc. Phys. Soc. (London) **54**, 362 (1942).
[2] H. B. Rosenstock, J. Chem. Phys. **23**, 2415 (1955).
[3] J. O. Halford, J. Chem. Phys. **19**, 1375 (1951).

alternating array so that the end atoms have different masses. The nearest neighbor Hooke's law force constant is denoted by k.

The equations of motion for the atoms of the lattice are given by

$$m_\alpha d^2\xi_1/dt^2 = k(\xi_2 - \xi_1), \tag{1.1}$$

$$m_\beta d^2\xi_{2j}/dt^2 = -k(\xi_{2j} - \xi_{2j-1}) + k(\xi_{2j+1} - \xi_{2j}), \quad 1 \leq j \leq N-1, \tag{1.2j}$$

$$m_\alpha d^2\xi_{2j-1}/dt^2 = -k(\xi_{2j-1} - \xi_{2j-2}) + k(\xi_{2j} - \xi_{2j-1}), \quad 2 \leq j \leq N, \tag{1.2$j-1$}$$

$$m_\beta d^2\xi_{2N}/dt^2 = -k(\xi_{2N} - \xi_{2N-1}), \tag{1.2N}$$

where ξ is the displacement of an atom from its equilibrium position and the subscripts $2j-1$ and $2j$ specify the positions of light and heavy atoms, respectively, in the lattice. If one makes the substitutions

$$\xi_{2j-1} = A_{2j-1}\exp(i\omega t), \tag{2.2$j-1$}$$

$$\xi_{2j} = A_{2j}\exp(i\omega t), \tag{2.2j}$$

the equations of motion are transformed to a system of linear homogeneous algebraic equations. If $q_\alpha = k/m_\alpha$ and $q_\beta = k/m_\beta$, the secular equation can be written in the form

$$D_{2N}(u,v) = 0, \tag{3}$$

where

$$D_{2N}(u,v) = \begin{vmatrix} u+1 & 1 & & & & & & \\ 1 & v & 1 & & & & & \\ & 1 & u & 1 & & & & \\ & & \cdot & \cdot & \cdot & & & \\ & & & \cdot & \cdot & \cdot & & \\ & & & & 1 & v & 1 & \\ & & & & & 1 & u & 1 \\ & & & & & & 1 & v+1 \end{vmatrix}_{2N}, \tag{4.1}$$

$$u = (\omega^2/q_\alpha) - 2, \tag{4.2}$$

$$v = (\omega^2/q_\beta) - 2, \tag{4.3}$$

and the subscript $2N$ denotes the size of the determinant.

The evaluation of the determinant $D_{2N}(u,v)$ has been given by Rutherford.[4,5] If one introduces the quantity θ defined by

$$(uv)^{\frac{1}{2}} = -2\cos\theta, \tag{5.1}$$

the determinant $D_{2N}(u,v)$ can be written as

$$D_{2N}(u,v) = (uv+u+v)\sin 2N\theta/\sin 2\theta. \tag{5.2}$$

Solutions to the secular equation, Eq. (3), may then be obtained from the solutions to the equations

$$\sin 2N\theta/\sin 2\theta = 0, \tag{5.3}$$

$$uv+u+v = 0. \tag{5.4}$$

[4] D. E. Rutherford, Proc. Roy. Soc. (Edinburgh) **A62**, 229 (1947).

[5] D. E. Rutherford, Proc. Roy. Soc. (Edinburgh) **A63**, 232 (1951).

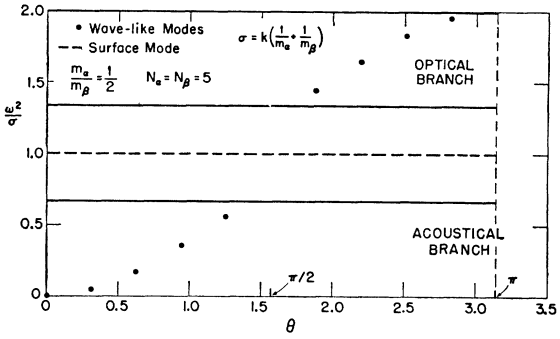

FIG. 1. The square of the frequency as a function of θ when the end atoms are not alike.

The relationship between the frequency ω and the variable θ can be found by substituting Eqs. (4.2) and (4.3) into Eq. (5.1) and solving for ω^2. The result is

$$\omega^2 = \sigma\{1 \pm (\cos^2\theta + \epsilon^2\sin^2\theta)^{\frac{1}{2}}\}, \tag{6.1}$$

where

$$\sigma = q_\alpha + q_\beta, \tag{6.2}$$

$$\epsilon = (m_\beta - m_\alpha)/(m_\beta + m_\alpha). \tag{6.3}$$

The solutions to Eq. (5.3) which yield independent values of ω are given by

$$\theta = n\pi/2N, \quad 1 \leq n \leq N-1, \tag{7.1}$$

where n is an integer. There are $2N-2$ frequency values specified by Eqs. (6.1) and (7.1).

The solutions of Eq. (5.4) are

$$\omega^2 = 0, \tag{7.2}$$

$$\omega^2 = \sigma. \tag{7.3}$$

The zero frequency corresponds to translation of the lattice. The frequency given by Eq. (7.3) lies in the region between the acoustical and optical branches which contains no frequencies if the cyclic condition is used. The value of θ corresponding to Eq. (7.3) is complex and is given by

$$\theta = (\pi/2) + i\sinh^{-1}(p/2), \tag{7.4}$$

where

$$p^2 = (m_\beta - m_\alpha)^2/m_\alpha m_\beta. \tag{7.5}$$

It will be seen later that the mode with frequency given by Eq. (7.3) is a "surface" mode; i.e., the maximum displacements of the atoms decrease roughly exponentially from the end having the lighter atom. All other modes are wave-like in character with the parameter θ playing the role of a reciprocal wavelength.

The frequencies for the $2N$ degrees of freedom have now been accounted for. In Fig. 1 the square of the frequency measured in units of σ is plotted as a function of θ for a mass ratio $m_\alpha/m_\beta = \frac{1}{2}$ and $N = 5$. The extended zone scheme is used in this figure so that the acoustical branch corresponds to $0 \leq n \leq N-1$ and the optical branch to $N+1 \leq n \leq 2N-1$. The boundaries of the

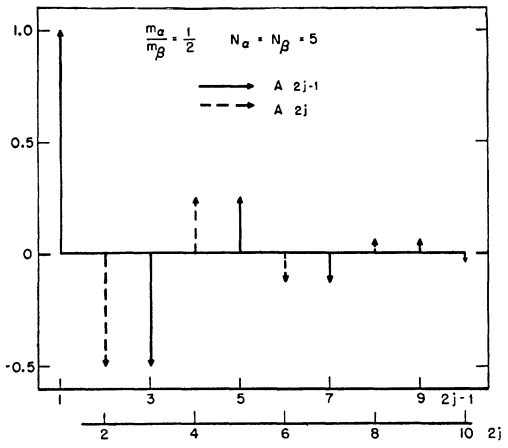

FIG. 2. The maximum atomic displacement as a function of position in the lattice for the surface mode when the end atoms are not alike.

gap between the acoustical and optical branches are specified by $\omega^2/\sigma=1+\epsilon$ and $\omega^2/\sigma=1-\epsilon$. The frequency squared for the surface mode is indicated by a dashed line because the θ value is complex. Alternate frequencies starting with the zero frequency have values identical with those given by the cyclic condition. The remaining frequencies in the acoustical and optical branches are smaller by a quantity $\sim 1/N$ than their counterparts for the cyclic lattice. The frequency for the surface mode passes into the optical branch when one imposes the cyclic condition.

It may be verified by substitution into the equations of motion that the maximum displacements for the mode with frequency in the "forbidden" gap between the optical and acoustical branches are given by

$$A_{2j-1}=c'(-1)^{j-1}(m_\alpha/m_\beta)^{j-1}, \tag{8.1}$$

$$A_{2j}=c'(-1)^{j}(m_\alpha/m_\beta)^{j}, \tag{8.2}$$

where the normalization constant c' satisfies the equation

$$\sum_{j=1}^{N}(m_\alpha A_{2j-1}^2+m_\beta A_{2j}^2)=1, \tag{9}$$

and is given by

$$c'=\{[m_\alpha m_\beta/(m_\beta-m_\alpha)][1-(m_\alpha/m_\beta)^{2N}]\}^{-\frac{1}{2}}. \tag{10}$$

In Fig. 2 the maximum displacements specified by Eqs. (8.1) and (8.2) with $c'=1$ are plotted as a function of position of the atoms in the lattice for $m_\alpha/m_\beta=\frac{1}{2}$ and $N=5$. It is to be emphasized that this figure is a graph and not a physical diagram. The actual displacements are parallel to the axis of the lattice. The displacement of the lighter end atom is relatively large. The adjacent heavy atom has a displacement smaller in the inverse ratio of the masses. Certain pairs of adjacent light and heavy atoms have the same displacement so that no force acts between such atoms during the motion. The displacements of atoms having a given mass decrease exponentially from the end having the lighter atom. It seems reasonable, therefore, to designate this mode as a surface mode. In the limit as the mass ratio tends to unity the magnitudes of the displacements become equal, and the surface mode passes into a wave-like mode. The monatomic lattice accordingly has no surface mode in agreement with previous results.

III. FINITE DIATOMIC LATTICE WITH END ATOMS ALIKE

The case in which the end atoms are alike and have the lighter of the two masses will now be considered. The number of atoms with mass m_α is $N+1$; the number with mass m_β is N. The equations of motion for interior atoms of the lattice are given by Eqs. $(1.2j)$ with $1\leq j\leq N$ and Eqs. $(1.2j-1)$ with $2\leq j\leq N$. The equations of motion for the end atoms are

$$m_\alpha d^2\xi_1/dt^2=k(\xi_2-\xi_1), \tag{11.1}$$

$$m_\alpha d^2\xi_{2N+1}/dt^2=-k(\xi_{2N+1}-\xi_{2N}). \tag{11.2N+1}$$

We consider first the case in which N is even so that the central atom is light.

In solving the secular equation it is convenient to make use of the presence of a center of symmetry in the lattice under consideration. Inversion at the center of symmetry is accomplished mathematically by replacing j by $N-j+2$ and $N-j+1$ in the quantities $2j-1$ and $2j$, respectively, which appear as subscripts on ξ and A. This operation leaves the equations of motion invariant. Let us introduce the symmetry displacements defined by

$$A_{\alpha j}{}^{+}=\tfrac{1}{2}[A_{2j-1}+A_{2(N-j+2)-1}], \tag{12.1j}$$

$$A_{\beta j}{}^{+}=\tfrac{1}{2}[A_{2j}+A_{2(N-j+1)}], \tag{12.2j}$$

$$A_{\alpha j}{}^{-}=\tfrac{1}{2}[A_{2j-1}-A_{2(N-j+2)-1}], \tag{12.3j}$$

$$A_{\beta j}{}^{-}=\tfrac{1}{2}[A_{2j}-A_{2(N-j+1)}], \tag{12.4j}$$

for $1\leq j\leq N/2$, and

$$A_{\alpha j}{}^{+}=A_{2j-1} \tag{12.5}$$

for $j=(N/2)+1$. The quantities $A_{\alpha j}{}^{+}$ and $A_{\beta j}{}^{+}$ remain unchanged on inversion at the center of symmetry, while the quantities $A_{\alpha j}{}^{-}$ and $A_{\beta j}{}^{-}$ change sign. One finds that the $A_{\alpha j}{}^{+}$ and $A_{\beta j}{}^{+}$ satisfy a set of linear homogeneous algebraic equations involving only the $A_{\alpha j}{}^{+}$ and $A_{\beta j}{}^{+}$ as variables. The solutions to this set of equations lead to a set of vibrational modes which will be called symmetric. The quantities $A_{\alpha j}{}^{-}$ and $A_{\beta j}{}^{-}$ similarly satisfy a set of equations involving only $A_{\alpha j}{}^{-}$ and $A_{\beta j}{}^{-}$. The corresponding solutions lead to a set of modes which will be called antisymmetric.

Using the methods of Rutherford[4,5] one can write the secular equation for the symmetric modes in the rather simple form

$$X=Y, \tag{13.1}$$

where

$$X=(u/v)^{\frac{1}{2}}\cos(N+1)\theta, \tag{13.2}$$

$$Y=\cos N\theta, \tag{13.3}$$

and θ is defined in Eq. (5.1). The positive value of $(u/v)^{\frac{1}{2}}$ in Eq. (13.2) is appropriate to the extended zone scheme in which the acoustical branch corresponds to $0\leq\theta\leq\pi/2$ and the optical branch to $\pi/2\leq\theta\leq\pi$.

The solutions to Eq. (13.1) can be obtained graphically. One finds in general that there are $(N/2)+1$ real values of θ is the range $0\leq\theta\leq\pi/2$ which satisfy Eq. (13.1) provided the mass ratio m_α/m_β satisfies the condition

$$N/(N+1)\leq m_\alpha/m_\beta\leq 1. \tag{14.1}$$

These $(N/2)+1$ solutions correspond to the symmetric modes of the acoustical branch. If the mass ratio does not satisfy Eq. (14.1) so that

$$0<m_\alpha/m_\beta<N/(N+1), \tag{14.2}$$

one finds that there are only $N/2$ real values of θ in the acoustical branch which satisfy Eq. (13.1).

For the case where the numbers of light and heavy atoms are equal, a solution to the secular equation exists having θ complex. This suggests that a solution to Eq. (13.1) with θ complex may exist when the mass ratio satisfies Eq. (14.2). One finds that this is indeed the case. For θ having the form $\theta=(\pi/2)+i\psi$, a solution to Eq. (13.1) exists if the mass ratio satisfies Eq. (14.2) but not if it satisfies Eq. (14.1).

For the optical branch, Eq. (13.1) possesses $N/2$ solutions with real values of θ in the range $\pi/2\leq\theta\leq\pi$ for all mass ratios between zero and unity. These solutions correspond to the symmetric modes of the optical branch.

We now turn to the antisymmetric solutions which are obtained from the equations specifying the quantities $A_{\alpha j}^{-}$ and $A_{\beta j}^{-}$. Using the results of Rutherford,[4,5] one can rewrite the secular equation as

$$X'=Y', \tag{15.1}$$

where

$$X'=(v/u)^{\frac{1}{2}}(\sin N\theta)/(\sin\theta), \tag{15.2}$$

$$Y'=[\sin(N+1)\theta]/(\sin\theta). \tag{15.3}$$

The positive value of $(v/u)^{\frac{1}{2}}$ in Eq. (15.2) is appropriate for the extended zone scheme.

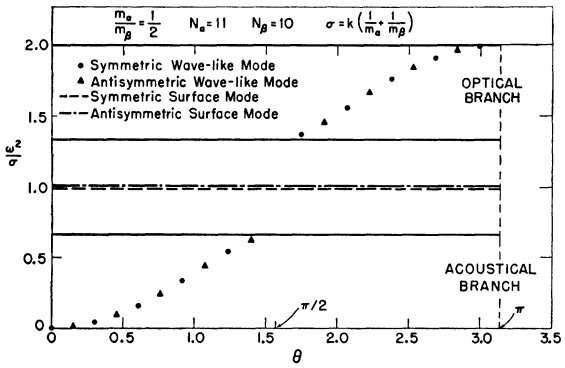

FIG. 3. The square of the frequency as a function of θ for mass ratio one-half with ten heavy atoms and eleven light atoms.

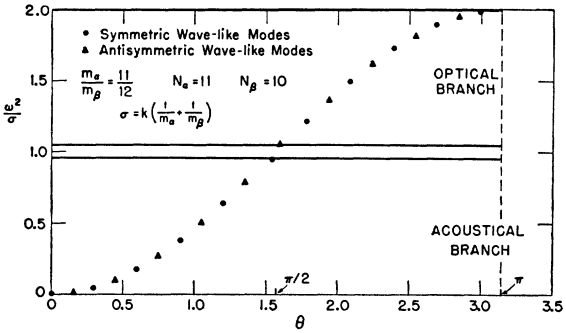

FIG. 4. The square of the frequency as a function of θ for mass ratio eleven-twelfths with ten heavy atoms and eleven light atoms.

The solutions to Eq. (15.1) may be found graphically. In the acoustical branch with θ a real number in the range $0\leq\theta\leq\pi/2$, there are $N/2$ solutions for any mass ratio between zero and unity. These solutions correspond to the antisymmetric modes of the acoustical branch.

In the optical branch with θ real in the range $\pi/2\leq\theta\leq\pi$, Eq. (15.1) possesses $N/2$ solutions provided the mass ratio satisfies Eq. (14.1). These solutions correspond to the antisymmetric modes in the optical branch. All $2N+1$ modes of vibration have now been accounted for when the mass ratio is greater than or equal to the critical value $N/(N+1)$.

When the mass ratio is less than the critical value $N/(N+1)$, Eq. (15.1) possesses only $(N/2)-1$ solutions in the optical branch for real values of θ. The remaining solution to Eq. (15.1) corresponds to a complex value of θ of the form $\theta=(\pi/2)-i\psi$.

In Fig. 3 the square of the frequency in units of σ is plotted as a function of θ for $m_\alpha/m_\beta=\frac{1}{2}$ with eleven light atoms and ten heavy atoms. All modes except two are wave-like in character and have frequencies in either the acoustical or optical branches.

The two modes with complex values of θ have frequencies lying in the "forbidden" gap between the optical and acoustical branches. These modes are surface modes, one being symmetric and the other antisymmetric.

In Fig. 4 the square of the frequency in units of σ is plotted as a function of θ for $m_\alpha/m_\beta=11/12$ with eleven light atoms and ten heavy atoms. The mass ratio for this case does not satisfy the criterion for the existence of surface modes given by Eq. (14.2). All modes are wave-like in character with frequencies in either the acoustical or optical branch. The gap between the optical and acoustical branches is quite narrow and in fact vanishes for mass ratio unity.

For the case under discussion in which both end atoms have the lighter mass and in which the number of heavy atoms is even, the symmetry displacements defined by Eqs. (12) may be taken proportional to the cofactors of the corresponding elements in the first row of the

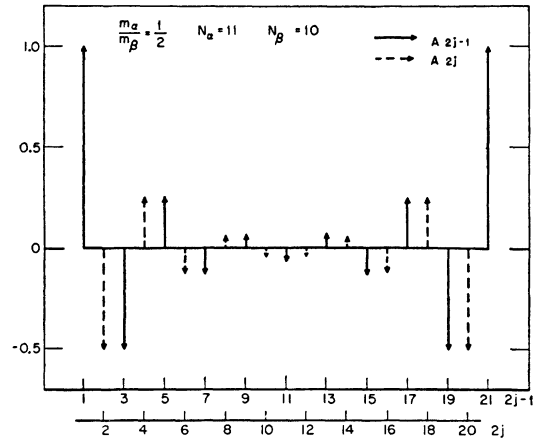

FIG. 5. The maximum atomic displacement as a function of position in the lattice for the symmetric surface mode when the end atoms are alike.

appropriate secular determinant. For the symmetric modes the quantities $A_{\alpha j}^-$ and $A_{\beta j}^-$ are all zero, while for the antisymmetric modes the quantities $A_{\alpha j}^+$ and $A_{\beta j}^+$ are all zero.

One finds that the maximum displacements A_{2j-1} and A_{2j} for the symmetric wave-like modes are given by the equations

$$A_{2j-1}=c_s[\cos(N-2j+2)\theta]/[\cos N\theta], \tag{16.1}$$

$$A_{2j}=c_s[\cos(N-2j+1)\theta]/[\cos(N+1)\theta], \tag{16.2}$$

where the normalization constant c_s is chosen so that

$$\sum_{j=1}^{N+1} m_\alpha A_{2j-1}^2+\sum_{j=1}^{N} m_\beta A_{2j}^2=1, \tag{16.3}$$

and is given by

$$c_s=\sqrt{2}\left\{\frac{m_\alpha}{\cos^2 N\theta}\left[(N+1)+\frac{\sin 2(N+1)\theta}{\sin 2\theta}\right]+\frac{m_\beta}{\cos^2(N+1)\theta}\left[N+\frac{\sin 2N\theta}{\sin 2\theta}\right]\right\}^{-\frac{1}{2}}. \tag{16.4}$$

For the antisymmetric wave-like modes the maximum displacements A_{2j-1} and A_{2j} are given by

$$A_{2j-1}=c_a[\sin(N-2j+2)\theta]/[\sin N\theta], \tag{17.1}$$

$$A_{2j}=c_a[\sin(N-2j+1)\theta]/[\sin(N+1)\theta], \tag{17.2}$$

where the normalization constant is again chosen so that Eq. (16.3) is satisfied and is given by

$$c_a=\sqrt{2}\left\{\frac{m_\alpha}{\sin^2 N\theta}\left[(N+1)-\frac{\sin 2(N+1)\theta}{\sin 2\theta}\right]+\frac{m_\beta}{\sin^2(N+1)\theta}\left[N-\frac{\sin 2N\theta}{\sin 2\theta}\right]\right\}^{-\frac{1}{2}}. \tag{17.3}$$

Expressions for the maximum displacements for the symmetric surface mode may be obtained by replacing θ by $(\pi/2)+i\psi$ in Eqs. (16.1), (16.2), and (16.4). Similarly, the maximum displacements for the antisymmetric surface mode can be obtained by replacing θ by $(\pi/2)-i\psi$ in Eqs. (17.1), (17.2), and (17.3).

In Fig. 5 the maximum displacements are plotted as a function of positions of the atoms in the lattice for the symmetric surface mode when $m_\alpha/m_\beta=\frac{1}{2}$, the number of light atoms is eleven and the number of heavy atoms is ten. The normalization constant was chosen so that $A_1=1$. The end atoms, which are light, have very large relative displacements. As one proceeds toward the center of the lattice from either end, the maximum displacements decrease roughly exponentially. Adjacent light and heavy atoms do not have equal displacements in contrast to the case where the end atoms have different masses.

For the case in which $m_\alpha/m_\beta=11/12$, with eleven light atoms and ten heavy atoms, the maximum displacements are plotted in Fig. 6 as a function of positions of the atoms for the symmetric mode with the highest frequency in the acoustical branch. This mode passes into the mode shown in Fig. 5 when the mass ratio changes from 11/12 to 1/2. In Fig. 6 the displacements of the light atoms increase slightly as one approaches the center of the lattice from either end. Accordingly, for mass ratio 11/12, this mode is not conveniently described as a surface mode.

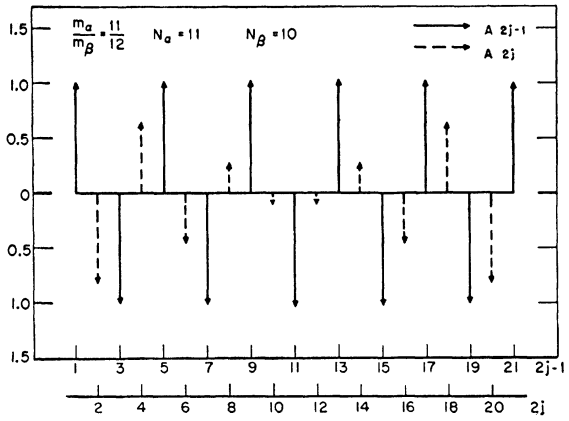

FIG. 6. The maximum atomic displacement as a function of position in the lattice for the symmetric mode with the highest frequency in the acoustical branch when no surface modes exist.

The discussion so far given in this section has been restricted to the case in which the number of heavy atoms is an even integer. If the number of heavy atoms is odd, so that the central atom is heavy, one finds that for a mass ratio satisfying Eq. (14.1) all modes are wave-like in character with frequencies in either the acoustical or optical branches. If the mass ratio satisfies Eq. (14.2), two modes are surface modes having frequencies in the "forbidden" gap between the acoustical and optical

branches. The situation is illustrated in Fig. 7 which indicates the frequencies and the symmetries of the modes. When surface modes exist, the surface modes of lower and higher frequencies are, respectively, antisymmetric and symmetric in contrast with the case where the number of heavy atoms is even.

If both end atoms are heavy so that the number of heavy atoms exceeds the number of light atoms by one, all modes are found to be wave-like and no surface modes exist.

IV. DISCUSSION

The principal result contained in the present paper is that an alternating diatomic one-dimensional lattice with nearest neighbor Hooke's law interactions and free ends may possess surface modes of vibration with frequencies in the "forbidden" gap between the optical and acoustical branches. A rather general criterion can be given for the existence of surface modes; namely, the total mass of the light atoms must be less than the total mass of the heavy atoms. If surface modes exist,

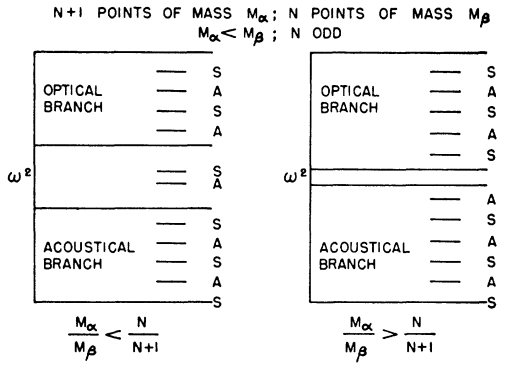

FIG. 7. Frequencies and symmetries of the normal modes when the end atoms are both light and the central atom is heavy.

the number of surface modes is equal to the number of ends of the lattice which have light atoms.

When one end atom is light and the other heavy, the criterion for the existence of surface modes is satisfied for any mass ratio less than unity. When both end atoms are light, the criterion is satisfied only if the mass ratio is less than the number of heavy atoms divided by the number of light atoms. When both end atoms are heavy, the criterion is not satisfied for any mass ratio.

The surface modes of vibration are in some respects similar to the "localized" modes in lattices containing defects which have been investigated by Montroll and Potts[6] and by Mazur, Montroll, and Potts.[7] These authors have found that under proper conditions lattices containing defects may possess vibrational modes having frequencies in ranges not ordinarily permitted. In addition, the displacements of the atoms decrease exponentially as the distance from the defect increases.

The surface of a crystal can in fact be regarded as a special type of defect. Consider, for example, the alternating diatomic lattice with equal numbers of light and heavy atoms and with the cyclic boundary condition imposed. By letting one force constant go to zero, this case is converted into an alternating diatomic lattice with free ends. The zero force constant constitutes the defect.

A general discussion of surface modes of vibration of lattices has been given by Lifshitz and Pekar.[8] These authors appear to use a Green's function method similar to that developed by Montroll and Potts.[6] Lifshitz and Pekar conclude that under suitable conditions surface vibrational modes, having frequencies not lying in the acoustical or optical branches, exist for two- and three-dimensional lattices as well as one-dimensional lattices.

The surface modes discussed in the present paper are analogous to the electronic surface states in crystals investigated by Tamm[9] and by Goodwin.[10] An electron in a surface state is localized near the surface of the crystal and has an energy lying in a "forbidden" band.

The differences in the modes of vibration obtained when one uses the free boundary condition rather than the cyclic condition may manifest themselves in a number of ways. The specific heat of very finely powdered crystals may show deviations from the corresponding value for a large crystal. Preliminary calculations indicate that the surface mode may lead to an observable though very small peak in the infrared absorption of finely powdered ionic crystals. The surface modes may be of interest in the theoretical investigation of surface phenomena such as adsorption and heterogeneous catalysis.

V. ACKNOWLEDGMENTS

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