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Normal modes of oscillations of lattices

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Abstract. Polynomial equations are obtained for the solutions of the vibrational frequencies of a simple cubic, primitive orthorhombic and tetragonal Bravais lattices of finite size with particles connected to their nearest neighbours through both central and non-central forces, but with arbitrary forces connecting the surface atoms to the rigid walls. The exact expressions of the different normal modes of oscillations and the amplitudes of vibration of different particles in various modes are obtained by solving three decoupled partial difference equations.

Keyword. Lattice oscillations.

1. Introduction

Normal modes of oscillations of a simple cubic lattice have been investigated by a number of authors. Montroll and Potts (1955 *a*, 1955 *b*), Koster (1954), Koster and Slater (1954), Matthias, Geballe and Compton (1963) made detailed study on the effect of lattice defects on lattice vibration by using the cyclic boundary conditions. However, it has been pointed out that the cyclic boundary conditions may not give the correct results since in a real crystal the presence of a boundary surface influence the physical properties of the atoms of the crystal, especially those in the vicinity of the surface.

Using one-dimensional lattice with free ends Rosenstock (1955) has shown that the cyclic boundary conditions may not give correct results for the surface effects of a thin film and the infrared absorption spectrum of an ionic lattice. Recently Puszkarski (1973) has solved the problem of vibrations of a finite linear chain with arbitrary asymmetrical boundary conditions. Maradudin, Montroll and Weiss (1963) have discussed the effects of surfaces on the vibrations of three dimensional crystal lattice when the ratio of surface area to volume of the crystal is not negligible. They have shown that surface effects may alter the temperature dependence of thermodynamic functions and give rise to distinct size effects. MacRae and Germer (1962) have observed that the vibrational amplitudes of the surface atoms become more important than those in the interior of the crystal in the phenomenon of diffraction of low-energy electrons by the surface of nickel crystal. The behaviour of specific heat of the lattice at low temperature has been interpreted in terms of the vibrations of the surface atoms (Dupuis, Mazo and Onsager 1960). Many authors (Wallis and Gazis 1962, Rich 1963, Maradudin and Mehngailis 1964, Ashkin 1964) have studied the Mossbauer effect for

a crystal with a free surface and have found a strong dependence of the mean-square amplitude and Doppler shift on the position of the resonant nucleus relative to the surface. Ashkin (1964) has studied the vibrational frequencies of the localized modes due to mass defect. The surface effect of the crystal is taken into account by creating mathematically a pair of boundary surfaces by setting to zero all interatomic forces which cross a given plane. Maradudin and Melngailis (1964) represented the surface as an extended defect. Thus in order to find the finite size effect of the crystal on various physical phenomena one has to treat the surface atoms in a different manner from the atoms in the interior of the crystal.

In a previous paper (Chaudhuri 1974, hereafter this paper will be referred as I) we discussed the problem of vibration of one-dimensional monoatomic and diatomic lattices with arbitrary end forces. The present paper extends the discussion to the case of three-dimensional lattices. Our model uses nearest-neighbour harmonic central and non-central forces. The technique developed here is applicable to the vibrations of simple cubic, primitive orthorhombic and tetragonal Bravais lattices. The macroscopic crystal has the shape of rectangular prism whose edges are parallel to the edges of the crystallographic unit cell. This choice as shown by Payton and Visscher (1967) affords the simplification that the motions in each Cartesian direction are independent. We assume that the surface atoms are connected to the rigid walls by arbitrary forces. The amplitudes of vibration of different particles in normal modes of oscillations satisfy three decoupled partial difference equations. We solve the partial difference equation by a method which is analogous to the method of separation of variables applied to partial differential equations. We obtain a set of polynomial equations for the allowed frequencies of vibration of the lattice. We also obtain the exact expressions for the amplitudes of the different particles in the various vibration modes. As special cases of our problem we have considered the effects of different end springs on the vibrational frequencies and the amplitudes of vibration.

2. Three-dimensional monoatomic lattices

We consider a simple L × M × N 3-dimensional lattice of L × M × N identical particles each of mass μ. Each particle in the lattice is coupled to its nearest neighbours through both central and non-central forces, whereas the particles on the surfaces of the crystal are connected to rigid walls with arbitrary force constants. The co-ordinate axes are chosen to be parallel to the crystal cell edges $\boldsymbol{a}$, $\boldsymbol{b}$ and $\boldsymbol{c}$ where $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$ are the three primitive translation vectors of the crystal. We shall denote the positions of the lattice points (l, m, n) by the set (x_{lmn}, y_{lmn}, z_{lmn}) which are the components of the displacements of atoms parallel to the cell edges. The force constant matrix for adjacent atoms referred with respect to $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$ as the basis is taken to be diagonal. In that case the motions in the x, y and z directions are independent of each other (Payton and Visscher, 1967) and therefore we need only analyze the behaviour of a lattice with one degree of freedom per lattice point. The equations of motion for small vibrations may be written as

$$\mu \ddot{x}_{lmn} = k_{1x}\,[x_{l+1\,mn} - 2x_{lmn} + x_{l-1\,mn}$$
$$- (S_{1x}\,x_{lmn} + x_{l-1\,mn})\,\delta_{1l}$$
$$- (S'_{1x}\,x_{lmn} + x_{l+1\,mn})\,\delta_{Ll}]$$
$$+ k_{2x}\,[x_{l\,m+1\,n} - 2x_{lmn} + x_{l\,m-1\,n}$$
$$- (S_{2x}\,x_{lmn} + x_{l\,m-1\,n})\,\delta_{1m}$$
$$- (S'_{2x}\,x_{lmn} + x_{l\,m+1\,n})\,\delta_{Mm}]$$
$$+ k_{3x}\,[x_{lm\,n+1} - 2x_{lmn} + x_{lm\,n-1}$$
$$- (S_{3x}\,x_{lmn} + x_{lm\,n-1})\,\delta_{1n}$$
$$- (S'_{3x}\,x_{lmn} + x_{lm\,n+1})\,\delta_{Nn}]$$
$$l = 1, 2, \ldots, L$$
$$m = 1, 2, \ldots, M$$
$$n = 1, 2, \ldots, N \qquad (1)$$

where

$$S_{ix} = K_{ix}/k_{ix} - 1, \quad S'_{ix} = K'_{ix}/k_{ix} - 1$$
$$i = 1, 2, 3.$$

Here k_{1x} represents the central force constant and k_{2x} and k_{3x} are the non-central force constants for vibrations in the x-direction. K_{1x} and K'_{1x} are the force constants at the boundary surfaces at $l = 1$ and $l = L$, K_{2x}, K'_{2x}, K_{3x} and K'_{3x} are the similar quantities at the boundary surfaces $m = 1$, $m = M$, $n = 1$, and $n = N$ respectively, the conditions $S_{ix} = S'_{ix} = -1$ $(i = 1, 2, 3)$ correspond to free surfaces of the lattice. Equations similar to (1) exist for the y- and z-directions of vibrations of the lattice points.

We seek normal mode solutions of (1) having the form

$$x_{lmn} = a_{lmn} \cos(\omega t + \delta) \qquad (2)$$

where a_{lmn} is the amplitude of vibration of the (l, m, n)th particle of the lattice and ω is the angular frequency of the normal vibration. The system of second order differential equations (1) is then transformed into a partial difference equation:

$$(-\mu\omega^2 + 2k_{1x})\,a_{lmn} - k_{1x}\,(a_{l+1\,mn} + a_{l-1\,mn})$$
$$= k_{2x}\,(a_{l\,m+1\,n} - 2a_{l\,mn} + a_{l\,m-1\,n})$$
$$+ k_{3x}\,(a_{lm\,n+1} - 2a_{lmn} + a_{lm\,n-1}) \qquad (3)$$

with the end conditions

$$a_{0mn} = -S_{1x}\,a_{1mn} \qquad (4\,a)$$
$$a_{l0n} = -S_{2x}\,a_{l1n} \qquad (4\,b)$$
$$a_{lm0} = -S_{3x}\,a_{lm1} \qquad (4\,c)$$
$$a_{L+1\,mn} = -S'_{1x}\,a_{Lmn} \qquad (4\,d)$$

$$a_{l\,M+1\,n} = -S'_{2x}\, a_{lMn} \tag{4e}$$

$$a_{lm\,N+1} = -S'_{3x}\, a_{lmN}\,. \tag{4f}$$

It should be mentioned that there is no particle for $l = 0$, $l = L + 1$, $m = 0$, etc. The additional quantities $\{a_{0mn}\}$, $\{a_{L+1\,mn}\}$, etc. occurring in (4) are introduced purely formally so that equations arising due to the "end atoms" ($l = 1$, $l = L$, etc.) acquires the same form as exists for $l = 2, 3, \ldots, L - 1$, etc. Consequently (3) holds for $l = 1, \ldots, L$; $m = 1, \ldots, M$; $n = 1, \ldots, N$.

3. Solutions of the partial difference equation and allowed angular frequencies

There are $L \times M \times N$ number of a_{lmn} and from (3) and (4) one can see that there are $L \times M \times N$ linear equations connecting all these amplitudes. For the existence of the solution of the system of equations it is necessary that the determinant of order $L \times M \times N$ whose elements are the coefficients of a_{lmn} should vanish. It immediately shows that there are $L \times M \times N$ allowed values of ω^2. In this paper a simple method of finding all the allowed frequencies is suggested.

It is well known that a partial differential equation can be transformed into a partial difference equation (Morse and Feshbach 1953). A partial differential equation can be solved in some cases by the method of sepration of variables. An equivalent method for the case of partial difference equation is discussed here.

Due to its simple structure, the partial difference equation in (3) can be broken into three decoupled (ordinary) difference equations if one writes

$$a_{lmn} = A(l)\, B(m)\, C(n). \tag{5}$$

Equation (3) now becomes

$$\begin{aligned}
&\frac{1}{A(l)}\left[(-\mu\omega^2 + 2k_{1x})\, A(l) - k_{1x}\{A(l+1) + A(l-1)\}\right] \\
&\quad = \frac{1}{B(m)\, C(n)}\left[k_{2x}\, C(n)\{B(m+1) - 2B(m) + B(m-1)\}\right. \\
&\quad \left. + k_{3x}\, B(m)\{C(n+1) - 2C(n) + C(n-1)\}\right] \\
&\quad = -\alpha_1.
\end{aligned} \tag{6}$$

Left hand side of (6) is a function of l only and it is equal to some quantities which are functions of m and n, and therefore they must be equal to some constant $-\alpha_1$, thus the l-equation becomes

$$(-\mu\omega^2 + 2k_{1x} + \alpha_1)\, A(l) - k_{1x}\{A(l+1) + A(l-1)\} = 0. \tag{7}$$

The allowed values of α_1 will be determined by imposing the end condition (4). Equation (7) is a difference equation in one index l only. So this method is analogous to the method of separation of variables applied to partial differential equations.

The method of solution of a second order difference equation in one variable has been discussed in detail in I. We have from (7)

$$A(l) = f_l(\beta_1)\, A(1) - f_{l-1}(\beta_1)\, A(0) \tag{8}$$

where

$$\beta_1 = (-\mu\omega^2 + 2k_{1a} + \alpha_1)/k_{1a} \tag{9}$$

$$f_l(\beta_1) = 2^{-l+1} \sum_{r=0}^{P} \binom{l}{2r+1} \beta_1^{\,l-2r-1} (\beta_1^{\,2} - 4)^r \tag{10}$$

with $P = l/2$ or $(l-1)/2$ whichever is an integer. The properties of the polynomial $f_l(\beta_1)$ are discussed in the previous paper I. If we apply the end condition (4 *a*) the eq. (8) becomes

$$A(l) = F(l, \beta_1, S_{1a})\, A(1) \tag{11}$$

where

$$F(l, \beta_1, S_{1a}) = f_l(\beta_1) + S_{1a} f_{l-1}(\beta_1). \tag{12}$$

B (m) and C (n) can be solved from (6) in exactly the same manner by separating the variables m and n:

$$\frac{1}{B(m)} [(\alpha_1 - 2k_{2a})\, B(m) + k_{2a} \{B(m+1) + B(m-1)\}]$$

$$= \frac{1}{C(n)} [2k_{3a} C(n) - k_{3a} \{C(n+1) + C(n-1)\}]$$

$$= -\alpha_2. \tag{13}$$

where α_2 is some constant independent of m and n. Equations (13) have the following solutions

$$B(m) = F(m, \beta_2, S_{2a})\, B(1) \tag{14}$$

$$C(n) = F(n, \beta_3, S_{3a})\, C(1) \tag{15}$$

where the end conditions (4 *b*) and (4 *c*) have been used and

$$\beta_2 = (2k_{2a} - \alpha_1 - \alpha_2)/k_{2a} \tag{16}$$

$$\beta_3 = (2k_{3a} + \alpha_2)/k_{3a}. \tag{17}$$

The allowed values of β_1, β_2 and β_3 are obtained by imposing the end conditions (4 *d*), (4 *e*) and (4*f*):

$$F(L+1, \beta_1, S_{1a}) + S'_{1a} F(L, \beta_1, S_{1a}) = 0 \tag{18}$$

$$F(M+1, \beta_2, S_{2a}) + S'_{2a} F(M, \beta_2, S_{2a}) = 0 \tag{19}$$

$$F(N+1, \beta_3, S_{3a}) + S'_{3a} F(N, \beta_3, S_{3a}) = 0. \tag{20}$$

Equation (18) is a polynomial equation in β_1 of degree L having L values of β_1. Therefore by solving (18)–(20) we will get L values of β_1, M values of β_2 and N values of β_3. It is evident from (9), (16) and (17) that corresponding to one

value of β_3 or α_2, there are M values of β_2 or α_1 and corresponding to each of α_1, there are L values of β_1 or ω^2. Therefore the system of polynomial equations (18)–(20) admits $L \times M \times N$ values of frequencies given by

$$\mu\omega^2 = \sum_{j=1}^{3} k_{jx}(2 - \beta_j). \tag{21}$$

If we define

$$\lambda_j = \tfrac{1}{2}[\beta_j + (\beta_j^2 - 4)^{1/2}] = \exp(i\phi_j)$$

then the allowed frequencies can be expressed as

$$\mu\omega^2 = 4 \sum_{j=1}^{3} k_{jx} \sin^2(\phi_j/2). \tag{22}$$

The amplitudes of vibrations of the lattice points are also exactly determined by this method:

$$a_{lmn} = a_{111} F(l, \beta_1, S_{1x}) F(m, \beta_2, S_{2x}) F(n, \beta_3, S_{3x}). \tag{23}$$

Let us consider some of the special cases:

(i) *Free end conditions* $S_{ix} = S'_{ix} = -1 \quad (i = 1, 2, 3)$.

The frequencies are given by (22) with the following values of ϕ_j

$$\phi_1 = (r_1 - 1)\pi/L \qquad r_1 = 1, 2, \ldots, L$$

$$\phi_2 = (r_2 - 1)\pi/M \qquad r_2 = 1, 2, \ldots, M$$

$$\phi_3 = (r_3 - 1)\pi/N \qquad r_3 = 1, 2, \ldots, N$$

The amplitudes a_{lmn} are expressed as

$$a_{lmn} = a_{111} \cos(l - \tfrac{1}{2})\phi_1 \cos(m - \tfrac{1}{2})\phi_2 \cos(n - \tfrac{1}{2})\phi_3 /$$
$$(\cos\phi_1/2 \cos\phi_2/2 \cos\phi_3/2).$$

It should be noted that for $r_1 = r_2 = r_3 = 1$, $\omega^2 = 0$ and a_{lmn} a_{111} which correspond to the translation of lattice.

(ii) $S_{ix} = S'_{ix} = 0 \quad (i = 1, 2, 3)$

In this case the force constants at the boundary surfaces are same as the interatomic forces. Now the allowed values of ϕ_1, ϕ_2 and ϕ_3 are the following:

$$\phi_1 = r_1\pi/(L + 1) \qquad r_1 = 1, 2, \ldots, L$$

$$\phi_2 = r_2\pi/(M + 1) \qquad r_2 = 1, 2, \ldots, M$$

$$\phi_3 = r_3\pi/(N + 1) \qquad r_3 = 1, 2, \ldots, N$$

The amplitudes of vibrations are

$$a_{lmn} = a_{111} \sin l\phi_1 \sin m\phi_2 \sin n\phi_3/(\sin\phi_1 \sin\phi_2 \sin\phi_3)$$

(iii) $S_{iz} = S'_{iz} = 1$ $(i = 1, 2, 3)$

In this special case ϕ_1, ϕ_2 and ϕ_3 have the following allowed values:

$$\phi_1 = r_1\pi/L \qquad r_1 = 1, 2, \ldots, L$$

$$\phi_2 = r_2\pi/M \qquad r_2 = 1, 2, \ldots, M$$

$$\phi_3 = r_3\pi/N \qquad r_3 = 1, 2, \ldots, N$$

and the amplitudes take the following simple form

$$a_{lmn} = a_{111} \sin(l - \tfrac{1}{2})\phi_1 \sin(m - \tfrac{1}{2})\phi_2 \sin(n - \tfrac{1}{2})\phi_3 /$$

$$(\sin\phi_1/2 \sin\phi_2/2 \sin\phi_3/2).$$

If we consider all the real values of λ_i, *i.e.*, $\phi_i = \phi_2 = \phi_3 = \pi$ the frequency and the amplitudes are given by

$$\mu\omega^2 = 4(k_{1z} + k_{2z} + k_{3z})$$

and

$$a_{lmn} = a_{111}(-1)^{l+m+n+1}.$$

This mode of vibration is quite unusual. The mgnitude of maximum x-displacements of all the particles are same, but any two adjacent atoms have displacements in two opposite directions.

For the vibration in the y- and z-directions we can write equations similar to (1) in which the force constants k_{1x}, k_{2x} and k_{3x} for the crystal lattice and K_{iz} and K'_{iz} $(i = 1, 2, 3)$ at the boundary surfaces have to be changed. In a real crystal some of the force constants depending on the symmetry of the crystal may be same, but here we may discuss the problem in general. We can follow the method discussed above step by step and ultimately obtain the allowed frequency conditions and the exact expressions for the amplitudes $\{l_{lmn}\}$ and $\{c_{lmn}\}$ for the vibrations in the y- and z-directions in terms of l_{111} and c_{111} respectively. In this way we may obtain true three-dimensional motions of the crystal.

4. Discussion

We have obtained a method of solving a partial difference equation, which is similar to the well-known method of separation of variables applied to partial differential equations. This technique gives us the exact expressions of the different normal modes of oscillations of a lattice with nearest neighbour interactions and arbitrary surface forces. Polynomial equations are obtained for the solutions of the vibrational frequencies. In case of mass defect the method of separation of variables is not applicable and therefore one has to develop a perturbation technique or some other method for solving the problem of vibrations of the defective lattice with arbitrary boundary conditions. In our simple procedure we obtain exact expressions for the amplitudes of the different particles in the various vibration modes. With the help of these amplitudes one may obtain the mean square velocities and displacements for different particles which are useful

in many problems of solid state theory. Finite size effect of the crystal on various physical phenomena can be studied in our simple model.

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