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The Theory of the One-Dimensional Lattice Defects

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Abstract A general method of calculating the frequency shift due to lattice defects is developed for a one dimensional lattice with an arbitrary number of lattice points.

The method is based on the Fourier transform of the equation of motion. It is shown that the frequency spectrum is determined by the roots of 5×5 secular equation, the coefficients of which depend on defects in the mass and the force constant as well as the number of the lattice points. For the limiting case of infinite lattice, the dimension of the secular equation reduces to three and the result agrees with that of Montroll and Potts.

Introduction

The frequency distribution for the normal modes of vibration of a lattice with defects (impurities, holes and interstitials etc.) exhibits a discrete spectra in addition to the band spectra as shown schematically in Fig. 1. The

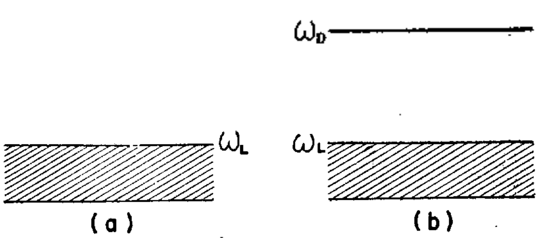


Fig. 1. Frequency spectrum of
(a) Perfect lattice
(b) lattice with defect
W_L=Maximum frequency
W_D=Discrete frequency for localized mode

frequency shift due to lattice defects in the band is small and can be calculated by the perturbation method. However, this is not applicable for the localized frequency shift.

Lax and Smith[1] calculated the frequency shift by using the method developed by Koster and Slater[2] in the calculation of electronic energy levels in a metal with defects. Later, Montroll and Potts [3,4,5] developed a theory by which one can calculate the localized frequency as well as the self energy of a defect and the interaction energy between defects. This theory gives a simple algebraic equation for the localized frequency in the case of an infinite lattice but a series expansion formula in the case of a finite lattice[5].

In the present work, we shall derive a simple algebraic equation for the localized and non-localized frequencies for a one dimensional finite lattice with defects. This kind of problem arises for example, in the calculation of normal mode frequencies of a linear hydrocarbon with a double bond or a subtituent, for these could be considered as defects in the corresponding normal hydrocarbon.

The frequency distribution of a defected lattice in one dimension. Consider the small vibration of a one dimensional lattice on N atoms with the same mass M and the same harmonic force constant γ except for the s-th atom which has the mass $M+\Delta M$ and the force constant $\gamma+\Delta\gamma$. With the assumptions of the nearest neighbour harmonic approximation and the free boundary condition, the Lagrangean L of the system may be written as,

$$L=\frac{1}{2}M\sum_{i=1}^{N}\dot{x}_i^2+\frac{1}{2}\Delta M\dot{x}_s^2 -\frac{1}{2}\gamma\sum_{i=1}^{N-1}(x_{i+1}-x_i)^2 -\frac{1}{2}\Delta\gamma[(x_s-x_{s-1})^2+(x_{s+1}-x_s)^2] \qquad (1)$$

where x_i is the displacement of the i-th atom from its equilibrium position. The equation of motion is given by

$$-M\ddot{x}_j+\gamma(x_{j+1}-2x_j+x_{j-1})=\Delta\gamma(x_{s-1}-x_s)\delta_{j,s-1} + [\Delta M\ddot{x}_s-\Delta\gamma(x_{s+1}-2x_s+x_{s-1})]\delta_{j,s} + \Delta\gamma(x_{s+1}-x_s)\delta_{j,s+1} \qquad (2)$$

$$j=1, 2, \cdots\cdots\cdots N$$

with the free boundary conditions

$$x_0=x_1, \qquad x_N=x_{N+1}$$

In eq. (2), $\delta_{j,s}$ is the Kronecker delta defined by

$$\delta_{j,s}=\begin{cases}1 & j=s\\ 0 & j\neq s\end{cases}$$

As usual, we put

$$x_j=u_je^{-i\omega t}, \quad i=\sqrt{-1}$$

Then eq. (2) becomes

$$Mw^2u_j+\gamma(u_{j+1}-2u_j+u_{j-1}) =\Delta\gamma(u_{s-1}-u_s)\delta_{j,s-1} -[\Delta Mw^2u_s+\Delta\gamma(u_{s+1}-2u_s+u_{s-1})]\delta_{j,s} +\Delta\gamma(u_{s+1}-u_s)\delta_{j,s+1} \qquad (3)$$

where

$$j=1, 2, \cdots\cdots\cdots\cdots N \text{ and}$$

$$u_0=u_1, \qquad u_N=u_{N+1}$$

In order to simplify the set of differential equations, we introduce the Fourier transform of u_j by

$$U=\sum_{j=1}^{N}u_je^{-ij\varphi} \qquad (4)$$

Then, eq. (3) takes the form

$$[Mw^2+2\gamma(\cos\varphi-1)]U =\gamma u_1(1-e^{-i\varphi}) +\gamma u_N(e^{-i(N+1)\varphi}-e^{-iN\varphi}) +\Delta\gamma(u_{s+1}-u_s)e^{-i(s-1)\varphi} +[\Delta Mw^2u_s+\Delta\gamma(u_{s+1}-2u_s+u_{s-1})]e^{-is\varphi} +\Delta\gamma(u_{s+1}-u_s)e^{-i(s+1)\varphi} \qquad (5)$$

where we have assumed $s\neq 1$, N in order to eliminate the boundary condition. It is a simple matter to solve separately the case where $s=1$ or N.

We note here that on the right hand side of eq. (5) there appears only u_1, u_{s-1}, u_s, u_{s+1}, u_N.

In order to obtain u_j, we use the Fourier inversion,

$$u_j=\frac{1}{2\pi}\int_0^{2\pi}Ue^{ij\varphi}d\varphi \qquad (6)$$

Then, from eq. (5)

$$u_j=u_1(I_j-I_{j-1}+u_N(I_{N-j+1}-I_{N-j}) +\frac{\Delta\gamma}{\gamma}u_{s-1}(I_{s-j-1}-I_{s-j})$$

$$+u_s\left[\frac{\Delta M}{\gamma}w^2 I_{s-j} + \frac{\Delta\gamma}{\gamma}(I_{s-j-1}-2I_{s-j}+I_{s-j+1})\right]\Bigg]$$
$$+\frac{\Delta\gamma}{\gamma}u_{s+1}(I_{s-j+1}-I_{s-j}) \qquad (7)$$

where

$$I_\nu=\frac{\gamma}{2\pi}\int_0^{2\pi}\frac{e^{i\nu\varphi}}{Mw^2+2\gamma(\cos\varphi-1)}d\varphi \qquad (8)$$

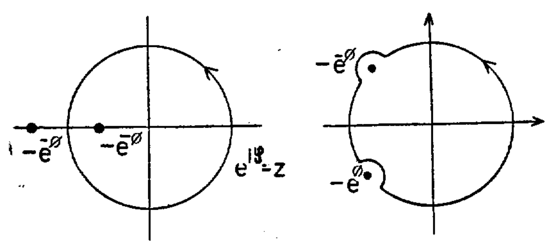
Obviously $I_\nu=I_{-\nu}$. The integration may be carried out by the contour integral,

$$I_\nu=\frac{1}{2\pi i}\oint_c\frac{z^{|\nu|}dz}{(z+e^{\phi})(z+e^{-\phi})}$$
$$=\frac{(-e^{-\phi})^{|\nu|}}{2\sinh\phi} \qquad (9)$$

where the contour c is given in Fig. (2) and ϕ is defined by

$$\frac{Mw^2}{2\gamma}-1=\cosh\phi\begin{cases}\geqq 1 & \phi\geqq 0\\ <1 & \phi=\text{immaginary}\end{cases} \qquad (10)$$

We shall see later that the real ϕ describes the localized frequency. It may be worthwhile to discuss how to determine the contour C. When ϕ is real, there is no difficulty in defining the contour C. When ϕ is immaginary, however, there exist four ways of drawing the



(i) Real Ø (ii) Imaginary Ø

Fig 2. The contours C on Z-plane

contour. It turns out that only the contour defined in Fig. (2) yields the analytical continuation of the case where ϕ is real. The result thus obtained is also the physically meaningful one.

Now eq. (7) may be written in the form

$$u_j=A_{j1}u_1+A_{jN}u_N+A_{j,s-1}u_{s-1}$$
$$+A_{j,s}u_s+A_{j,s+1}u_{s+1} \qquad (11)$$

where the coefficients $A_{j,s}$ are defined by the corresponding terms of eq. (7). In order to simplify the explicit forms of $A_{j,\nu}$, we put

$$x=-C^{-\phi} \qquad (12)$$

Then

$$I_\nu=x^{1+|\nu|}/(x^2-1) \qquad (13)$$

Thus we obtain for $A_{j,\nu}$

$$A_{j,\nu}=a_{j,\nu}/(x+1) \qquad (14)$$

where $a_{j,\nu}$ is given by

$$a_{j1}=x^j,$$
$$a_{j,N}=x^{N-j+1},$$

$$a_{j,s-1}=\begin{cases}-kx^{s-j} & \text{for } s>j\\ kx^{j-s+1} & \text{for } s\leqq j,\end{cases}$$
$$a_{j,s}=\begin{cases}(m-k)x^{s-j}(x-1) & \text{for } s>j\\ (m-2k)x-m & \text{for } s=j\\ (m-k)x^{j-s}(x-1) & \text{for } s<j\end{cases}$$
$$a_{j,s+1}=\begin{cases}kx^{s-j+1} & \text{for } s\geqq j\\ -kx^{j-s} & \text{for } s<j\end{cases}$$

and here

$$m=\Delta M/M,\quad k=\Delta\gamma/\gamma$$

We may write eq. (10) as follows

$$(x+1)u_j=\sum_{\nu} a_{j,\nu}u_\nu;\quad \nu=1,\ s-1,\ s,\ s+1,\ N \tag{15}$$

where j runs from 1 to N as before. If we restrict $j=1,\ s-1,\ s,\ s+1,\ N,$ then $\{a_{j\nu}\}$ become a 5×5 square matrix given by

$$a=\begin{Bmatrix} x & x^N & -kx^{s-1} & (m-k)x^{s-1}(x-1) & kx^s \\ x^N & x & kx^{N-s+1} & (m-k)x^{N-s}(x-1) & -kx^{N-s} \\ x^{s-1} & x^{N-s+2} & -kx & (m-k)x(x-1) & kx^2 \\ x^s & x^{N-s+1} & kx & (m-2k)x-m & kx \\ x^{s+1} & x^{N-s} & kx^2 & (m-k)x(x-1) & -kx \end{Bmatrix} \tag{16}$$

To obtain the condition for eq. (15) to have a non trivial solution for μ_ν, the coefficients must satisfy the following secular equation,

$$\det|\boldsymbol{a}-(x+1)\boldsymbol{I}|=0 \tag{17}$$

where $\boldsymbol{I}$ is a unit matrix. This is the algebraic equation of x which we are looking for. This may be written explicitely as follows,

$$\begin{vmatrix} -1 & x^N & -kx^{s-1} & (m-k)x^{s-1}(x-1) & kx^2 \\ x^N & -1 & kx^{N-s+1} & (m-k)x^{N-s}(x-1) & -kx^{n-s} \\ x^{s-1} & x^{N-s+s} & -(k+1)x-1 & (m-k)x(x-1) & kx^2 \\ x^s & x^{N-s+1} & kx & (m-2h-1)x-(m+1) & kx \\ x^{s+1} & x^{N-s} & kx^2 & (m-k)x(x-1) & -(k+1)x-1 \end{vmatrix}=0 \tag{18}$$

Once we solve this equation for x, then the frequency w is given from eqs. (10) and (12) as follows

$$w^2=-\frac{\gamma}{M}\cdot\frac{(x-1)^2}{x} \tag{19}$$

For the localized mode, we have from eq. (10)

$$\left(\frac{w}{w_L}\right)^2=\cosh^2\phi/2>1;\quad w_L^2=\frac{4\gamma}{M} \tag{20}$$

so that ϕ must be real and positive. This means that $|x|<1$ from eq. (12). Accordingly for a large N we could use an iteration method to solve eq. (18) starting from $x^N=0$. When N is small, obviously there is no difficulty in solving the equation.

In the following, we shall apply Eq. (18) for two special cases:

1) The perfect lattice; $(m=k=0)$,

$$\det|\boldsymbol{a}-(x+1)\boldsymbol{I}|=(x+1)^3\begin{vmatrix} -1 & x^N \\ x^N & -1 \end{vmatrix}=0 \tag{21}$$

The roots from the factor $(x+1)^3$ are redundant. These are introduced from the transformation $a_{j,\nu}=A_{j,\nu}(x+1)$. Accordingly

$$x^{2N}=1$$

which yields the well known frequency distribution of one dimensional lattice with free boundary condition [3]

$$w^2=\frac{2\gamma}{M}\left(1+\cos\frac{n\pi}{N}\right),\ n=1,2,\ N \tag{22}$$

ii) The localized mode of infinite lattice

Since $x^N\to0$, as $N\to\infty$, eq. (18) reduces to the following after a trivial simplification,

$$\begin{vmatrix} -(k+1)x-1 & (m-k)x(x-1) & kx^2 \\ kx & (m-2k-1)x-(m+1) & kx \\ kx^2 & (m-k)x(x-1) & -(k+1)x-1 \end{vmatrix}=0 \tag{23}$$

which is the equation first derived by Montroll and Potts [5].

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