2. SOME SIMPLE FEATURES OF THE DYNAMICS OF A DEFECT ATOM IN A CRYSTAL

In this section I should like to discuss some simple features of the motion of a defect atom in a crystal as an introduction to the material to follow. Because the required calculations can be carried out analytically, I will first discuss the effects of a substitutional isotope impurity on the vibrations of a monatomic linear chain. At the end of this section the generalization of this discussion to three-dimensional crystals will be presented. For simplicity only Bravais crystals will be considered in these lectures.

The equations of motion of a monatomic linear chain of N atoms, each of which has a mass M and is coupled to its two nearest neighbors by springs of spring constant γ are

$$M\ddot{x}_n = \gamma(x_{n+1} - x_n) - \gamma(x_n - x_{n-1}) \qquad n = \frac{N}{2}+1, \ldots\ldots, \frac{N}{2}, \tag{2.1}$$

where $x_n(t)$ is the displacement of the $n^{\underline{th}}$ atom from its equilibrium position. In writing these equations we have assumed that the displacements satisfy the cyclic boundary condition,

$$x_n = x_{n+N} \tag{2.2}$$

The time independent equations of motion are obtained by making the substitution

$$x_n(t) = u_n e^{i\omega t} \tag{2.3}$$

where u_n is a time independent amplitude and ω is a frequency whose determination is one of the problems we must solve. The equations satisfied by the $\{u_n\}$ are

$$M\omega^2 u_n + \gamma(u_{n+1} - 2u_n + u_{n-1}) = 0 \qquad n = -\frac{N}{2}+1, \ldots\ldots, \frac{N}{2}. \tag{2.4}$$

It is well known that a difference equation of the type of Eq. (2.4) can be solved by setting

$$u_n = z^n, \tag{2.5}$$

provided z is related to ω by the condition

$$M\omega^2 = 2\gamma\left(1 - \frac{z + z^{-1}}{2}\right) \tag{2.6}$$

However, z cannot be arbitrary. If the cyclic boundary condition is to be satisfied we find that z must satisfy the condition

$$z^N = 1, \tag{2.7}$$

so that z is one of the N^{th} roots of unity,

$$z_s = e^{\frac{2\pi i s n}{N}} \qquad s = -\frac{N}{2}+1, \ldots\ldots, \frac{N}{2}, \tag{2.8}$$

and Eqs. (2.5) and (2.6) become

$$u_n(s) = e^{\frac{2\pi i s n}{N}} \tag{2.9a}$$

$$\omega_s^2 = \frac{2\gamma}{M}\left(1 - \cos\frac{2\pi s}{N}\right) = \omega_L^2 \sin^2\frac{\pi s}{N} \tag{2.9b}$$

where $\omega_L = (4\gamma/M)^{\frac{1}{2}}$ is the largest frequency of the chain. All the distinct solutions to this problem are thus contained in the interval $-\frac{N}{2}+1 \le s \le \frac{N}{2}$, and there are as many solutions as there are degrees of freedom in the chain. The interval $-\pi < \frac{2\pi s}{N} \le \pi$ in which all the distinct solutions lie is called the first Brillouin zone for our linear chain.

The vibration pattern described by the displacement

$$X_n(s;t) = e^{i\omega_s t + \frac{2\pi i s n}{N}} \tag{2.10}$$

is called a normal mode of the crystal, and the associated frequency

$$\omega_s = \omega_L \left|\sin\frac{\pi s}{N}\right| \tag{2.11}$$

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is called the S^{th} normal mode frequency. It should be noted that the solutions (2.10) corresponding to the frequency ω_s are doubly degenerate, that is $X_n(s;t)$ and $X_n(-s;t)$ are two linearly independent solutions of Eqs. (2.1) each corresponding to the same frequency ω_s. By taking suitable linear combinations of these solutions we can construct solutions having even or odd parity about a given atom.

With these preliminary results in hand, let us see what modifications are introduced in the vibrations of the linear chain by the introduction of defects. For this purpose it is convenient to write the time independent equations of motion of the chain in matrix form. For example, the time independent equations of motion for the perfect crystal, Eq. (2.4), can be written as

$$\underline{L}\,\underline{u} = 0 \tag{2.12}$$

where $\underline{u}$ is a column vector whose components are the $\{u_n\}$ and $\underline{L}$ is an N x N matrix whose elements are

$$L_{mn} = M\omega^2\delta_{mn} - \gamma[\delta_{m,n-1} - 2\delta_{mn} + \delta_{m,n+1}] \qquad m,n = -\tfrac{N}{2}+1, \ldots, \tfrac{N}{2} \tag{2.13}$$

The condition that the set of homogeneous equations have nontrivial solutions is that the determinant of the coefficients vanish

$$|\underline{L}| = 0 \tag{2.14}$$

and it is readily verified that the roots of this equation are given by Eq. (2.9b).

When the crystal is perturbed by the introduction of defects, the time independent equations of motion take the form

$$\sum_n L_{mn}\,u_n = \sum_k \delta L_{mk}\,u_k \tag{2.15}$$

where $\underline{\delta L}$ is the matrix which characterizes the defects. Its rank equals the number of degrees of freedom affected by the introduction of the defects. If the defects are few in number and are localized, this is a small number, and this fact is what makes the methods we are about to describe so useful in the solution of defect problems.

Let us introduce the Green's function G_{mn} by the equation

$$\sum_k L_{mk} G_{kn} = \delta_{mn} , \tag{2.16}$$

that is $\underline{G}$ is the matrix inverse to $\underline{L}$. In terms of $\underline{G}$ we can solve Eq. (2.15) to obtain

$$u_n = \sum_{lk} G_{nl} \delta L_{lk} u_k . \tag{2.17}$$

It might be objected that Eq. (2.17) can hardly be called a solution of Eq. (2.15) because the unknown displacements $\{u_n\}$ appear on both sides of this equation. What Eq. (2.17) does do is to express the displacement of any atom in the chain in terms of the displacements of the (few) atoms directly affected by the introduction of the defects. Since Eq. (2.17) gives the displacement of any atom in the crystal, it clearly gives the displacements of the atoms directly affected by the introduction of the defect. Therefore, if we let the index n on the left side of Eq. (2.17) successively take on the same values as does the index k on the right side of the same equation, we obtain a set of homogeneous equations for the determination of the displacement amplitudes directly affected by the presence of the defect. The condition that this set of equations have nontrivial solutions is that the determinant of the coefficients vanishes, and this equation gives the frequencies of the perturbed normal modes:

$$| \underline{I} - \underline{G}\,\underline{\delta L} | = 0. \tag{2.18}$$

Before we can apply the preceding results to even a simple example we need an explicit expression for the Green's function G_{mn} If we use the fact that we can express the Kronecker symbol as

$$\delta_{mn} = \frac{1}{N} \sum_{s=-\frac{N}{2}+1}^{\frac{N}{2}} e^{\frac{2\pi i s (m-n)}{N}} \tag{2.19}$$

and expand G_{mn} as

$$G_{mn} = \frac{1}{N} \sum_{s=-\frac{N}{2}+1}^{\frac{N}{2}} f_s \, e^{\frac{2\pi i s (m-n)}{N}} , \tag{2.20}$$

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then substitution of these expansions into Eq. (2.16) and the use of the explicit form for L_{mn}, Eq. (2.13) gives us

$$f_s = \left[M\omega^2 - 2\gamma \left(1 - \cos \frac{2\pi s}{N} \right) \right]^{-1} \qquad (2.21)$$

The Green's function G_{mn} is therefore given by

$$G_{mn} = \frac{1}{N} \sum_{s=-\frac{N}{2}+1}^{\frac{N}{2}} \frac{e^{\frac{2\pi i s(m-n)}{N}}}{M\omega^2 - 2\gamma + 2\gamma \cos \frac{2\pi s}{N}} \qquad (2.22)$$

From Eq. (2.22) we can easily show (by replacing s by $-s$ as a summation index) that G_{mn} depends on m and n only through the magnitude of their difference. This means that we can write the Green's function as a function of a single index, $G_l = G_{-l}$.

The special case of G_o is evaluated in Appendix D with the result

$$G_o = \frac{1}{2\gamma} \cdot \frac{\cot \frac{N\phi}{2}}{\sin \phi} \qquad (2.23)$$

where we have put

$$\omega^2 = \omega_L^2 \sin^2 \frac{\phi}{2} \qquad (2.24)$$

The general solution of Eq. (2.16) for $m \neq n$ can be written as

$$G_l = A \cos l\phi + B \sin |l| \phi . \qquad (2.25)$$

Combining this result with that given by Eq. (2.22) we find

$$G_1 = G_{-1} = G_o \cos \phi + \frac{1}{2\gamma} , \qquad (2.26)$$

so that

$$A = G_o , \quad B = \frac{1}{2\gamma \sin \phi} \qquad (2.27)$$

Combining Eqs. (2.25) and (2.27) we obtain finally

$$G_l = \frac{1}{2\gamma \sin \phi} \left[\cot \frac{N\phi}{2} \cos l\phi + \sin |l| \phi \right] \qquad (2.28)$$

We now apply the preceding results to a simple example, a substitutional isotope defect at $n = 0$. By isotope defect we mean that the impurity atom differs from the atom it replaces only in its mass. If the mass of the impurity is M', and if we define a mass defect parameter ε by

$$\varepsilon = 1 - \frac{M'}{M} \tag{2.29}$$

then the elements of the matrix $\underline{\delta L}$ are given by

$$\delta L_{mn} = \varepsilon M \omega^2 \delta_{mo} \delta_{no} \tag{2.30}$$

Only the symmetric vibration modes $(u_n = u_{-n})$ will be affected by the presence of the defect, because the antisymmetric modes $(u_n = -u_{-n})$ have a node at the position of the impurity and as a result do not feel the mass change. Equation (2.17) becomes

$$u_n = \varepsilon M \omega^2 G_n u_o , \tag{2.31}$$

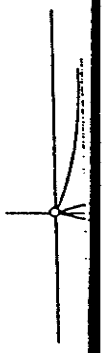
that is, the displacement of the $n^{\underline{th}}$ atom is determined entirely by the displacement of the defect atom.

The equation determining the new normal mode frequencies is obtained by setting $n = 0$ in Eq. (2.31),

$$1 = \varepsilon M \omega^2 G_o . \tag{2.32}$$

Inserting the results given by Eqs. (2.23) and (2.24) into Eq. (2.32) we find that the values of ϕ which when substituted into Eq. (2.24) give the perturbed normal mode frequencies are the roots of

$$\varepsilon \tan \frac{\phi}{2} = \tan \frac{N\phi}{2} \tag{2.33}$$



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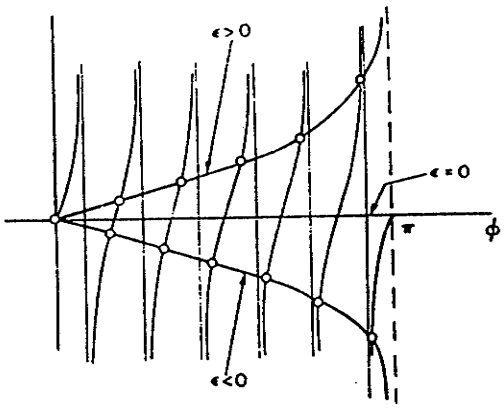

Figure 1. The graphical solution of Eq. (2.33) for the case N = 12.

We have plotted the right hand side of this equation against the left side in Fig. 1 for N = 12. From this figure we can draw some interesting conclusions. In the absence of any defect the allowed values of ϕ are given by the intersection of $\tan \frac{N\phi}{2}$ with the horizontal axis, i.e., $\phi_s^{(o)} = \frac{2\pi s}{N}$. When $\varepsilon < 0$, which corresponds to a heavy impurity, we see that the allowed values of the ϕ's are lowered relative to their unperturbed values. On the other hand, when $\varepsilon > 0$, which corresponds to a light impurity, the allowed values of the ϕ's are increased above their unperturbed values.

If we solve Eq. (2.33) by successive approximations starting from $\phi_s = \phi_s^{(o)}$, to a first approximation we have

$$\phi_s \cong \frac{2\pi s}{N} + \frac{2}{N} \tan^{-1}\left(\varepsilon \tan \frac{\pi s}{N}\right), \qquad (2.34)$$

and consequently

$$\omega_s \cong \omega_L \left| \sin \frac{\pi s}{N} \right| + \frac{\omega_L}{N} \cos \frac{\pi s}{N} \tan^{-1}\left(\varepsilon \tan \frac{\pi s}{N}\right) \qquad (2.35)$$

Because we are considering the symmetric modes, which are the only modes affected by the perturbation we can restrict ϕ_s to the interval $(0, \pi)$, since we get no new frequencies outside this interval.

The number of symmetric modes given by this restriction taken together with an equal number of unperturbed antisymmetric modes gives

the correct total number of independent normal modes for the chain.

Referring to Fig. 1 again, we note that when $\varepsilon > 0$ there is one less solution than when $\varepsilon = 0$. We appear to have lost one normal mode. This lost mode in fact corresponds to a complex value of ϕ, and has a frequency which is greater than ω_L, the maximum frequency of the unperturbed lattice. If we set

$$\phi = \pi + iz \tag{2.36}$$

in Eq. (2.33), it becomes (in the large N limit)

$$\varepsilon \coth \frac{z}{2} = \operatorname{sgn} z \tag{2.37}$$

Equation (2.37) has a solution only when $0 < \varepsilon < 1$ and this solution is

$$z = \ln \frac{1+\varepsilon}{1-\varepsilon} , \tag{2.38}$$

and corresponds to the frequency

$$\omega_o^2 = \frac{\omega_L^2}{1-\varepsilon^2} > \omega_L^2 \tag{2.39}$$

The preceding results are a special case of a general theorem due to Lord Rayleigh [6] which can be stated as: If in a dynamical system composed of an array of masses coupled to each other by Hookeian springs a single mass is reduced by δM, all frequencies are unchanged or increased, but by no more than the distance to the next unperturbed frequency. An increase of a single mass by δM leaves the frequencies unchanged or reduces them by amounts no greater than the distance to the next unperturbed frequency. The increase (decrease) of a single force constant has the same effect as the decrease (increase) of a single mass.

To conclude our discussion of this simple example we must determine the spatial dependence of the perturbed modes. This is given by

$$u_n(s) = \varepsilon M \omega_s^2 G_n(s)\, u_0(s) \tag{2.40}$$

where the index s refers to the s^{th} solution of Eq. (2.33). Our problem essentially is to determine $u_0(s)$. For this purpose we use the result of Appendix A which states that if $u_n(s)$ is to be considered as a normal mode amplitude it must be normalized according to

$$\begin{aligned} \sum_n M_n u_n^2(s) &= 1 \\ &= M\sum_n u_n^2(s) - \varepsilon M u_0^2(s) \end{aligned} \tag{2.41}$$

If we eliminate $u_n(s)$ from Eq. (2.41) with the aid of Eq. (2.40) we obtain an equation for $u_0(s)$ alone,

$$u_0^2(s) = \left\{ \varepsilon^2 M^3 \omega_s^4 \sum_n G_n^2(s) - \varepsilon M \right\}^{-1} \tag{2.42}$$

According to Eq. (2.22) we have that

$$\begin{aligned} \sum_n G_n^2 &= \frac{1}{N^2} \sum_n \sum_{s_1 s_2} \frac{e^{\frac{2\pi i (s_1 + s_2)}{N}}}{(M\omega^2 - 2\gamma + 2\gamma\cos\frac{2\pi s_1}{N})(M\omega^2 - 2\gamma + 2\gamma\cos\frac{2\pi s_2}{N})} \\ &= \frac{1}{N}\sum_s \frac{1}{(M\omega^2 - 2\gamma + 2\gamma\cos(2\pi s/N))^2} \end{aligned} \tag{2.43}$$

This sum is evaluated in Appendix D. We obtain finally

$$\sum_n G_n^2 = \frac{1}{4\gamma^2 \sin^2\phi} \frac{N}{2} \csc^2 \frac{N\phi}{2} \qquad 0 < \phi < \pi \tag{2.44a}$$

$$= \frac{2\omega^2 - \omega_L^2}{2M^2\omega^3(\omega^2 - \omega_L^2)^{3/2}} \qquad \omega > \omega_L \tag{2.44b}$$

We can simplify Eq. (2.44) somewhat if we note that it is not for an arbitrary ϕ that we want the sum, but for one of the solutions of Eq. (2.33). We therefore obtain

$$\sum_n G_n^2(s) = \frac{N}{32\gamma^2} \frac{\cos^2\frac{\phi_s}{2} + \varepsilon^2 \sin^2\frac{\phi_s}{2}}{\varepsilon^2 \sin^4\frac{\phi_s}{2}\cos^2\frac{\phi}{2}} \qquad 0 < \phi_s < \pi \tag{2.45a}$$

$$= \frac{1}{32\gamma^2} \frac{(1+\varepsilon^2)(1-\varepsilon^2)^2}{\varepsilon^3} \qquad \omega = \omega_0 > \omega_L \tag{2.45b}$$

Combining Eqs. (2.42) and (2.45) we find finally

$$u_o(s) = \left(\frac{2}{MN}\right)^{1/2} \frac{1}{(1+\varepsilon^2 \tan^2 \frac{\phi_s}{2})^{1/2}} \qquad 0 < \phi_s < \pi \tag{2.46a}$$

$$= \left(\frac{2}{M}\right)^{1/2} \left(\frac{\varepsilon}{1-\varepsilon^2}\right)^{1/2} \qquad \omega = \omega_o > \omega_L \tag{2.46b}$$

If we substitute these results into Eq. (2.4o) and use Eq. (2.28) we obtain for the displacement amplitudes

$$u_n(s) = \left(\frac{2}{MN}\right)^{1/2} \frac{1}{(1+\varepsilon^2 \tan^2 \frac{\phi_s}{2})^{1/2}} \times \tag{2.47a}$$

$$\times \left[\cos n\phi_s + \varepsilon \tan \tfrac{\phi_s}{2} \sin|n| \phi_s\right] \qquad 0 < \phi_s < \pi$$

$$= (-1)^n \left(\frac{2}{M}\right)^{1/2} \left(\frac{\varepsilon}{1-\varepsilon^2}\right)^{1/2} \left(\frac{1-\varepsilon}{1+\varepsilon}\right)^{|n|} \qquad \begin{matrix} 0 < \varepsilon < 1 \\ \omega = \omega_o > \omega_L \end{matrix} \tag{2.47b}$$

From the results given by Eq. (2.47) we see that the perturbed in-band modes are still wave-like in character, and their amplitudes are of $O(N^{-1/2})$. In contrast, in the exceptional mode of frequency $\omega_o > \omega_L$ which exists for $0 < \varepsilon < 1$ the displacements decrease exponentially with increasing distance from the impurity site, and are of $O(1)$ in magnitude. Because of the former property this exceptional mode is usually called a localized mode. In Eq. (2.47a) little error is incurred by using for the $\{\phi_s\}$ their unperturbed values.

This concludes my discussion of the simple features of the dynamics of a mass defect in a linear chain. We now turn to a look at the three dimensional problem.

In terms of the primitive translation vectors of a crystal $\bar{a}_1, \bar{a}_2, \bar{a}_3$ the position vector of the ℓ^{th} atom in a Bravais crystal is denoted by

$$\bar{x}(\ell) = \ell_1 \bar{a}_1 + \ell_2 \bar{a}_2 + \ell_3 \bar{a}_3 \tag{2.48}$$

where ℓ_1, ℓ_2, ℓ_3 are three integers which can be positive, negative, or zero, and to which we refer collectively as ℓ.

The time independent equations of motion for a perfect Bravais crystal are

$$M\omega^2 u_\alpha(\ell) - \sum_{\ell'\beta} \Phi^{(o)}_{\alpha\beta}(\ell\ell') u_\beta(\ell') = 0 . \tag{2.49}$$