

## NOTE ON THE VIBRATION SPECTRUM OF A CRYSTAL

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The purpose of this note is to present a simple proof of the rule usually given for obtaining the spectrum of normal frequencies of a crystal. The rule is that the distribution of frequencies is the same as those of a hypothetical crystal satisfying the 'cyclic boundary condition'. We shall in the following refer to the hypothetical case as the 'mathematical crystal'.

Arguments for this rule have been given in many contexts, the most complete proof being probably that given by Ledermann (1944) but, in view of the fact that there is still some controversy about it, it may be useful to give yet another proof, based on a more physical reasoning.

For our purpose 'spectrum' refers merely to the position of the characteristic frequencies. No statement is implied about their occurrence in the emission, absorption or scattering of light.

The rule must be understood with the following limitations: (a) it is not claimed that the normal *modes* of the mathematical crystal are identical with those of the real crystal. (b) It is not claimed that the exact values of the frequencies are the same in both cases, but merely that the distribution, i.e. the average number in a frequency interval  $\Delta\omega$  large enough to contain many frequencies is the same in the two cases to the leading order in  $N$ , where  $N$  is the linear dimension of the crystal in terms of the lattice spacing. Our argument will be formulated to cover three dimensions and the presence of several atoms in the unit cell. This will make our notation somewhat cumbersome; to avoid adding to the formal complications we assume the lattice to be of cubic symmetry and take a unit cell of cubic shape. We also assume the crystal to be a cube with its edges along the crystal axes. The argument could easily be freed also from these restrictions, at the expense of some slight further complexity of notation.

The idea of the proof is to show a connection between the frequency distribution and the propagation of disturbances through the crystal. In particular, from the knowledge of the propagation of disturbances over times up to a certain time  $\tau$ , we can uniquely determine the frequency distribution except for its fine structure which concerns frequency intervals less than  $1/\tau$ . Now for a disturbance starting from a point distant  $l$  from the nearest surface, the propagation will be the same as in an infinite crystal for a time less than  $l/c$ , where  $c$  is the maximum velocity of sound. Hence, for a crystal dimension of 1 cm., and with  $c \sim 10^5$ ,  $l/c$  will be of the order of  $10^{-5}$  sec., and larger than say,  $10^{-10}$  sec., for practically all the crystal. It follows therefore that over such times the propagation of disturbances is the same in the mathematical and the real crystal, and hence that the frequency distribution for the two is the same except for oscillations in frequency intervals of the order of  $10^{10}$  sec.<sup>-1</sup>, (corresponding in spectroscopic terminology to about  $\cdot 05$  cm.<sup>-1</sup>).

A very similar reasoning was used in an earlier paper (Peierls, 1936) concerned with justifying the cyclic boundary condition in the derivation of the equation of state of a relativistic gas. There are, however, some minor differences between the two problems, the crystal problem being, on the whole, the simpler one, and it is

therefore easiest to explain the method anew, rather than to rely on the results of the earlier paper.

We assume our crystal to be a cube, each side containing  $N$  cells, so that each cell can be enumerated by three integers,

$$1 \leq n_1, n_2, n_3 \leq N. \quad \dots \quad \dots \quad \dots \quad \dots \quad (1)$$

We label the position of an atom within the cell by  $s$ ,

$$1 \leq s \leq p \quad \dots \quad \dots \quad \dots \quad \dots \quad (2)$$

The three co-ordinates will be distinguished by a suffix  $\rho$

$$\rho = x, y, z \quad \dots \quad \dots \quad \dots \quad \dots \quad (3)$$

Then, if the  $\rho$ -th co-ordinate of the  $s$ -th atom in cell  $\underline{n}$  at time  $t$  is denoted by  $x_{\rho s}(\underline{n}, t)$ , a normal vibration is given by

$$x_{\rho s}(\underline{n}, t) = a_{\rho s}^\alpha(\underline{n}) \cos(\omega_\alpha t - \gamma_\alpha) \quad \dots \quad \dots \quad \dots \quad (4)$$

Here  $\alpha$  labels the normal modes

$$1 \leq \alpha \leq 3pN \quad \dots \quad \dots \quad \dots \quad \dots \quad (5)$$

$\omega_\alpha$  is the corresponding (circular) frequency;  $\gamma_\alpha$  is a phase. The coefficients and the frequencies are, in principle, to be found from the equations of motion and the boundary conditions.

It is known from general theory that the amplitudes  $a$  are orthogonal in the sense that

$$\sum_\rho \sum_s \sum_{\underline{n}} a_{\rho s}^\alpha(\underline{n}) a_{\rho s}^\beta(\underline{n}) m_s = 0, \quad \alpha \neq \beta$$

$m_s$  being the mass of the  $s$ -th atom. They can be normalized so as to make the sum equal to unity when  $\alpha = \beta$ ; with that convention we have

$$\sum_\rho \sum_s \sum_{\underline{n}} a_{\rho s}^\alpha(\underline{n}) a_{\rho s}^\beta(\underline{n}) m_s = \delta_{\alpha\beta} \quad \dots \quad \dots \quad \dots \quad (6)$$

$\delta_{\alpha\beta}$  being the Kronecker symbol, as usual.

Conversely it follows that

$$\sum_\alpha a_{\rho s}^\alpha(\underline{n}) a_{\rho' s'}^\alpha(\underline{n}') = \frac{1}{m_s} \delta_{\rho\rho'} \delta_{ss'} \delta_{\underline{n}\underline{n}'} \quad \dots \quad \dots \quad \dots \quad (7)$$

We now want to consider the distribution of frequencies  $\omega_\alpha$ . To find the number of frequencies within the interval  $\omega + \frac{1}{2}\Delta$ ,  $\omega - \frac{1}{2}\Delta$ , we should obtain the quantity

$$F(\omega) = \sum_\alpha D(\omega_\alpha - \omega) \quad \dots \quad \dots \quad \dots \quad (8)$$

where

$$D(x) = \begin{cases} 1, & |x| < \frac{\Delta}{2} \\ 0, & |x| > \frac{\Delta}{2} \end{cases}$$

However, this definition is not convenient, because of the discontinuity, which means that whether a certain frequency is counted or not depends on its precise value. It is therefore more convenient to use a smooth weight function for  $D$  to which we give the following properties :

$$\int_{-\infty}^{\infty} D(x) dx = \Delta \quad \dots \quad \dots \quad \dots \quad (9)$$

$$D(x) \ll 1 \text{ if } x \gg \Delta \quad \dots \quad \dots \quad \dots \quad (10)$$

In addition,  $D(x)$  is to be a smooth function so that its Fourier transform converges rapidly ; if

$$g(\tau) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\tau\omega} D(\omega) d\omega; D(\omega) = \int_{-\infty}^{\infty} e^{+i\tau\omega} g(\tau) d\tau \dots \quad (11)$$

the condition

$$g(\tau) \ll \Delta \text{ if } \tau \gg \frac{1}{\Delta} \quad \dots \quad \dots \quad \dots \quad (12)$$

is compatible with (9) and (10). For instance, a possible choice of  $D$  is

$$D(x) = \frac{1}{\sqrt{2\pi}} e^{-x^2/2\Delta^2}; g(\tau) = \frac{\Delta}{2\pi} e^{-\Delta^2\tau^2/2}$$

It is clear that, with this definition of  $D$ , the expression (8) represents the spectrum of vibrations except for the fine structure, provided  $\Delta$  is small compared to the maximum frequency  $\omega_{max}$ .

It will be convenient in the following to replace  $F(\omega)$  by

$$\begin{aligned} G(\omega) &= F(\omega) + F(-\omega) \\ &= \sum_{\alpha} [D(\omega_{\alpha} - \omega) + D(\omega_{\alpha} + \omega)] \quad \dots \quad \dots \quad \dots \quad (13) \end{aligned}$$

Because of (10) the extra term vanishes in fact, unless we are concerned with the very low-frequency end of the spectrum, where  $\omega \sim \Delta$ , otherwise, since the  $\omega_{\alpha}$  are positive,  $\omega + \omega_{\alpha}$  will certainly appreciably exceed  $\Delta$ .

Now insert the Fourier transform (11)

$$\begin{aligned} G(\omega) &= \sum_{\alpha} \int d\tau g(\tau) [e^{i\omega_{\alpha}\tau} e^{-i\omega\tau} + e^{i\omega_{\alpha}\tau} e^{+i\omega\tau}] \\ &= \int d\tau 2g(\tau) \cos \omega\tau \sum_{\alpha} e^{i\omega_{\alpha}\tau} \quad \dots \quad \dots \quad \dots \quad (14) \end{aligned}$$

If  $D(x)$  is an even function,  $g(\tau)$  will also be even, so that (14) can also be written as

$$G(\omega) = 4 \int_0^{\infty} d\tau g(\tau) \cos \omega\tau \sum_{\alpha} \cos \omega_{\alpha}\tau \quad \dots \quad \dots \quad \dots \quad (15)$$

However, because of (12) it is sufficient to include Fourier components belonging to values of  $\tau$  not much greater than  $1/\Delta$ , say up to  $\epsilon/\Delta$ , where  $\epsilon$  is a numerical constant. We write

$$G(\omega) = 4 \int_0^{\epsilon/\Delta} d\tau g(\tau) \cos \omega\tau \Phi(\tau) \quad \dots \quad (16)$$

where

$$\Phi(\tau) = \sum_{\alpha} \cos \omega_{\alpha}\tau, \quad \tau < \epsilon/\Delta \quad \dots \quad (17)$$

Now we show that  $\Phi(\tau)$  has a simple physical significance. For this purpose use the identity (6) to write (17) as

$$\begin{aligned} \Phi(\tau) &= \sum_{\alpha} \sum_{\rho, s, \underline{n}} m_s a_{\rho s}^{\alpha}(\underline{n}) a_{\rho s}^{\alpha}(\underline{n}) \cos \omega_{\alpha}\tau \\ &= \sum_{\rho s \underline{n}} \phi_{\rho s \underline{n}}(\tau) \quad \dots \quad (18) \end{aligned}$$

with

$$\phi_{\rho s \underline{n}}(\tau) = \sum_{\alpha} m_s a_{\rho s}^{\alpha}(\underline{n}) a_{\rho s}^{\alpha}(\underline{n}) \cos \omega_{\alpha}\tau \quad \dots \quad (19)$$

This quantity has the following meaning: Let at  $t=0$  all atoms be in their equilibrium positions except that the  $s$ -th atom in cell  $\underline{n}$  is displaced by an infinitesimal amount  $\delta$  in the  $\rho$  direction, and is there released from rest. Then the value of the  $\rho$ -th co-ordinate of this atom at time  $\tau$  is exactly  $\delta \cdot \phi_{\rho s \underline{n}}(\tau)$ .

To see this, remember that the general solution of the equation of the motion is given by

$$x_{\rho s}(\underline{n}, t) = \sum_{\alpha} c_{\alpha} a_{\rho s}^{\alpha}(\underline{n}) \cos(\omega_{\alpha}t - \gamma_{\alpha}) \quad \dots \quad (20)$$

the  $c_{\alpha}$  and  $\gamma_{\alpha}$  being arbitrary.

We require that solution for which all atoms are at rest at  $t=0$ , which requires that all  $\gamma_{\alpha} = 0$ .

Furthermore, to satisfy given initial values  $x_{\rho s}(\underline{n}, 0)$

$$x_{\rho s}(\underline{n}, 0) = \sum_{\alpha} c_{\alpha} a_{\rho s}^{\alpha}(\underline{n}) \quad \dots \quad (21)$$

We can solve this for  $c_{\alpha}$  in the usual way using the orthogonality relation (6). Multiply (21) by a particular  $a_{\rho s}^{\alpha}(\underline{n})$  and by  $m_s$  and sum:

$$c_{\alpha} = \sum_{\rho, s} \sum_{\underline{n}} m_s a_{\rho s}^{\alpha}(\underline{n}) x_{\rho s}(\underline{n}, 0) \quad \dots \quad (22)$$

Insert in (20)

$$x_{\rho s}(\underline{n}, t) = \sum_{\rho' s' \underline{n}'} x_{\rho' s'}(\underline{n}', 0) \sum_{\alpha} m_{s'} a_{\rho s}^{\alpha}(\underline{n}) a_{\rho' s'}^{\alpha}(\underline{n}') \cos \omega_{\alpha}t \quad \dots \quad (23)$$

(23) expresses generally the co-ordinates of any atom at time  $t$  in terms of those of all atoms at time 0. If at time 0 only one co-ordinate is disturbed, the sum on the right contains only one term, and the same co-ordinate at time  $t$  becomes then

$$x_{\rho\sigma}(\underline{n}, t) = x_{\rho\sigma}(\underline{n}, 0) \sum_{\alpha} m_{\sigma} a_{\rho\sigma}^{\alpha}(\underline{n}) a_{\rho\sigma}^{\alpha}(\underline{n}) \cos \omega_{\alpha} t$$

which by comparison with (19) is

$$x_{\rho\sigma}(\underline{n}, 0) \phi_{\rho\sigma\underline{n}}(t)$$

This proves our statement about the  $\phi_{\rho\sigma\underline{n}}$ .

Now it is known that a disturbance will propagate in the main with the group velocity, and that at time  $t$  a disturbance starting from cell  $\underline{n}$  will be negligible at all points in the lattice distant more than  $ct$  from  $\underline{n}$ , where  $c$  is the greatest value of the group velocity (for either the 'acoustic' or 'optical' branches). Its order of magnitude is the same as that of ordinary sound velocity.

To be precise one should remember that in a dispersive medium there exist 'precursor' signals preceding the main front, which advances with maximum group velocity. However, their amplitude diminishes exponentially with the distance from the front.

Now compare the value of  $\phi_{\rho\sigma\underline{n}}(t)$  with the same quantity for an infinite crystal. Let the distance of cell from the boundary of the actual crystal be  $l_n$ . Then the solution of the time-dependent equations for the infinite crystal will almost satisfy the boundary conditions if  $l_n > ct$ . The amplitude at the boundary will depend exponentially on  $l_n$ . To satisfy the boundary conditions exactly we must add a reflected wave of similar amplitude, and its amplitude at cell  $\underline{n}$  will, in fact, vary exponentially with  $2l_n - ct$ . Hence the difference between  $\phi$  and  $\phi^{\infty}$  decreases exponentially with  $2l_n - ct$ .

Now divide the crystal into an interior and a surface part, the 'surface' part extending to a depth  $\beta N$ , where  $\beta$  is a suitable small number. The total contribution from the 'surface' terms to the sum (18) is then of the order of  $6\beta N^3$  compared to a total of  $N^3$  and their omission represents a relative error of the order  $6\beta$ . On the other hand, the remaining 'internal' terms belong to points distant from the surface by more than  $\beta N$  atoms and their contribution is therefore equal to those of an infinite crystal except for corrections decreasing exponentially with

$$2 \beta N a - ct \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (24)$$

Except for these errors, the  $\phi$  functions are the same as for an infinite crystal and also the same as for the 'mathematical' crystal with the cyclic boundary condition for which it is easy to write down the spectrum explicitly.

(It is equally easy to write down expressions for the  $\phi_{\rho\sigma}^{\infty}(\underline{n})$  for the infinite crystal directly and thus evaluate the spectrum of a finite crystal without using the cyclic boundary condition at all; the answer is, of course, just the same.)

To illustrate the quantitative side, assume a crystal of 1 cm. thickness ( $N \sim 10^8$ ). Choose  $\beta = 10^{-4}$  and  $\tau = 10^{-10}$  sec. assuming  $c$  to be about  $10^6$  cm./sec.

Then the omission of surface atoms in the sum (18) causes a relative error of  $6\beta \sim .06\%$ . The boundary correction for the  $\phi$  for an internal point is an exponential function of (24) in which the positive term is at least  $10^{-4}$  and the negative at most  $10^{-5}$ . Hence we get an exponential function of an argument  $10^{-4}$  cm. or  $10^4$  lattice constants. Both these errors are therefore negligible for practical purposes.

On the other hand, our choice of  $\tau$  means that in the Fourier integral (16) we lose components with  $\tau > 10^{-10}$  sec. and therefore the fine structure of the spectrum  $G(\omega)$  over frequency ranges less than  $\Delta \sim \frac{1}{\tau} \sim 10^{10}$  sec.<sup>-1</sup>. In spectroscopic language this corresponds to about  $10^{10}/2\pi c_L \sim \cdot 05$  cm.<sup>-1</sup>, ( $c_L$  being the light velocity) a fine structure which would not normally be resolved if it existed. Clearly these numbers represent generous limits and much closer estimates could be obtained.

## REFERENCES

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