The vibration spectra of crystals and the theory of their specific heats

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1. Introduction

The thermal energy of a crystalline solid may properly be identified with the energy of vibration of the atoms in it about their positions of equilibrium. The theorem in classical mechanics due to Lagrange[1] which states that a connected system of N particles has 3N normal modes of vibration enables us to go further and identify the thermal energy with the sum of the energies of these 3N vibrations, each having its own appropriate frequency. The problem thus reduces itself to that of determining the distribution in frequency of the 3N vibrations. When this is known, we have only to sum up the expressions for the average energies of the individual vibrations given by Einstein's fundamental theorem[2] to obtain the thermal energy content of the solid at any given temperature.

In the well known theories of the specific heat of solids due respectively to Debye[3] and to Born and Karman,[4] the frequency distribution is found on the basis of certain special assumptions. Following a suggestion due originally to J H Jeans,[5] these authors identify the 3N vibrations with 3N different wave-patterns filling the volume of the crystal. The 3N different frequencies which result from these assumptions make the vibration spectrum of the crystal a diffuse continuum. Lagrange's theorem, however, does not require that a system of N connected particles should necessarily possess 3N *different* frequencies. Indeed, since a crystal is an assemblage of an immense number of similar groups of particles, we should expect that they would all possess identical frequencies of internal vibration. The recognition of this led the present writer to make a fresh approach to the problem in a paper[6] which was published in these *Proceedings* eight years ago. The results of that paper furnished a simple and forthright explanation of the nature of the vibration spectra of crystals as revealed by the frequency shifts in the scattering of light by them. The theory also indicated some new and previously unsuspected features of these vibration spectra which appeared not inaccessible to observation. Experimental investigations undertaken to test the predictions of the theory have confirmed their reality. In a recent paper by the writer[7] published in these *Proceedings*, the whole of the work in this

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field has been reviewed and it has been shown that the behaviour of crystals in light-scattering completely substantiates the correctness of the approach to the subject made in the paper of 1943.

The present paper is a survey of the theoretical aspects of the subject, while the one just referred to dealt with it from the phenomenological standpoint. Its main purpose is to make it clear that the treatment of the theoretical problem given in 1943 was not only on the right lines but was also a complete and rigorous solution of it. The present paper contains also a critical examination of the premises on which the earlier theories of the subject were based. The identification of the normal modes of vibration of the atoms in a crystal with an immense number of wave-patterns comprised in its volume is shown to be an unjustifiable and wholly misconceived hypothesis. It is also shown that the consequences of that hypothesis are contradicted by the facts of observation.

2. Molecular vibrations in crystals

We shall commence by considering a simple case which approximates to the actual situation in many crystals and assume that an immense number of molecules, all of the same kind, come together and are held in a regular three-dimensional array by forces which are very weak in comparison with the forces binding the atoms together in each molecule. A substance of this kind would have a low melting point and would sublime very readily. We may cite naphthalene as an example. The molecules of the substance in the state of vapour would move, rotate and vibrate independently of each other. In the crystalline state, their translations could no longer be independent. The free rotations would also be suppressed and replaced by periodic angular oscillations. We shall at first consider here only the internal oscillations of the molecules. In the free state, the modes and frequencies of such internal oscillations would be determined by the geometric form of the molecule, the masses of the atoms comprised in it and the forces holding them together. We may ask ourselves, what would be the situation concerning these vibrations in the crystalline state?

Since by assumption, the intermolecular forces in the crystal are very weak, they could scarcely have any effect on either the modes or the frequencies of molecular vibration. The interactions, however, would have an important consequence, viz., that if any one molecule within the crystal is set in vibration, its energy would leak away to the other molecules surrounding it, and from these again to other molecules further out, and so forth, so that ultimately the energy would be dissipated through the crystal. The transfer of energy envisaged would be the slower, the weaker the intermolecular forces are, and would take a very long time before it reaches the external boundary of the crystal. It is thus evident that we are here concerned with a diffusion process and not one of wave-

propagation. From the assumptions made, it follows that the vibration spectrum of the entire crystal in the frequency region under consideration would differ but little from that of the molecules of which it is composed. In other words, it would exhibit a finite number of monochromatic frequencies.

3. The effect of coupling on the molecular vibrations

We may now remove the restriction which we laid upon ourselves for the sake of simplicity, viz., that the intermolecular forces were extremely weak. One effect of an increase of their strength would be to speed up the process of diffusion of the energy of vibration from an excited molecule to those surrounding it. Other important effects have also to be considered, viz., an increase in the frequency of the translational-*cum*-rotational oscillations of the molecules about their positions of equilibrium. The coupling between each molecule and its neighbours would also multiply the number of possible modes of their internal vibrations and alter their frequencies.

The problem which here arises was dealt with and solved in the paper of 1943 quoted in the introduction. Every normal mode must satisfy two conditions, viz., that the particles must all vibrate with the same frequency and that their phases must all be the same or opposite. A third condition is set by the nature of the problem in the case of a crystal, viz., that a normal mode should remain a normal mode, following a unit translation of the crystal along any one of the three axes of the lattice. These three conditions taken together completely determine the possible modes of vibration of the structure of the crystal. There are only two possibilities in respect of the phases of vibration in successive cells of the structure along each axis, viz., that they are the same or else alternate. Thus, in all, there are $2 \times 2 \times 2$ alternative possibilities and therefore eight species of normal modes. The $3p$ equations of motion of the p atoms in the unit cell of the structure would necessarily be different in each species. Thus we have $8 \times 3p$ or $24p$ equations of motion and the same number of solutions. Only $(24p - 3)$ solutions would represent actual vibrations, while the 3 excluded solutions would represent simple translations.

Thus, when the finiteness of the intermolecular forces is taken into account, the structure of the crystal has $(24p - 3)$ modes of vibration, each with its appropriate monochromatic frequency. These would include the translational-*cum*-rotational oscillations of the molecules which are possible by reason of their being held in a regular three-dimensional array. If we imagine the strength of the intermolecular forces to be gradually reduced, the frequency of such oscillations would diminish steadily, while the frequencies of the vibrational modes which are multiplied 8-fold in number by the coupling would converge towards the vibrational frequencies of the molecules in the free state.

4. The enumeration of wave-patterns

We turn now to the examination of the premises on which the specific heat theories of Debye and Born–Karman are based. The enumeration according to frequency or wavelength of the stationary wave-patterns within an enclosure is effected, following Rayleigh,[8] by assuming for the latter a cubical shape, and counting up the terms of a three-dimensional Fourier expansion which individually are solutions of the wave-equation valid inside the enclosure. It is essential for the argument that the waves travel freely within the enclosed space and are not subject to damping. The slightest damping of the wave during their progression would invalidate the entire procedure. We have, in fact, only to assume that the enclosure is large enough; the waves, if damped, would die away before they could traverse it from end to end and return to build up a stationary interference pattern. On the other hand, wave-propagation in material media is necessarily damped to an extent determined by the physical state of the medium and the wavelength or frequency of the vibration. Indeed, it may well happen that such damping is so enormous as altogether to preclude the possibility of wave-propagation through the medium. Hence, it follows that the identification of the normal modes of atomic vibration within material bodies with stationary wave-patterns determined by the external boundary conditions is a wholly misconceived and erroneous hypothesis.

We may illustrate the foregoing remarks by two typical examples. In the paper already cited, and again later in his book,[9] J H Jeans put forward a mathematical argument based on the Fourier analysis which claims to prove that the energy of the translatory motion of the molecules in a gas can be identified with the energy of an appropriately chosen number of sound-wave trains in it, the great majority of them having wavelengths of the same order of magnitude as the mean distance between neighbouring molecules. The proof is, however, illusory, since it overlooks the fact that sound-waves in gases are damped by viscosity. No wave-propagation is possible in a gas if the wavelength is as small as the molecular mean free path, and this is itself many times larger than the average distance between neighbouring molecules. In other words, the sound-waves proposed to be enumerated by Jeans have no physical existence!

The second example which we shall consider is that already dealt with in section 2 above. It is evident that a crystal consisting of discrete molecules having their own characteristic frequencies of vibration would present an impenetrable obstacle to the entry and propagation through the substance of "waves" having those self-same frequencies. We have only to recall in this connection the optical behaviour of a cell containing the vapour of sodium or of mercury towards the entry into it of the resonance radiations from a sodium vapour or a mercury vapour lamp respectively, or the behaviour of a rock-salt crystal towards the entry into it of infra-red radiations previously monochromatised by successive reflections at the surfaces of crystals of the same substance. Since the waves

cannot even enter the medium, it would be clearly be a fantastic procedure to identify the molecular vibrations with wave-patterns enumerated on the basis of their free propagation inside the crystal.

5. Wave propagation in periodic structures

The title of this section is the same as that of a book[10] by L Brillouin which was published a few years ago, having the sub-title "Electric filters and crystal lattices". The greater part of that book is devoted to an exposition of the ideas underlying the Debye and Born–Karman theories of crystal behaviour, and it is therefore appropriate that some reference is made to it here. Surprisingly enough, though the book concerns itself with the problem of finding the frequency spectra of crystals, one searches its pages in vain for any reference to the normal modes of vibration of the atoms in a crystal. It would seem, in fact, that Brillouin considers "waves" and "normal modes" as equivalent expressions. This is clearly a misconception. While the fundamental theorem of Lagrange enables us to enumerate the normal modes of vibration of a system, a "wave" is not a normal mode since the phase of the motion in it changes from point to point and from instant and instant, and hence one cannot, in general, enumerate waves. Only when there is perfectly undamped wave-propagation within a perfectly reflecting enclosure does the restriction of the permitted wavelengths to a specifiable but infinite sequence of values resulting therefrom enable us to regard the stationary wave-patterns as equivalent to normal modes. But as already pointed out in the preceding section, there can be no undamped wave-propagation in any material substance consisting of atoms and molecules. It follows that the contents of Brillouin's book are without significance in relation to the problems of crystal physics which it professes to deal with.

The behaviour of macroscopic systems exhibiting some sort of periodicity in their structure, e.g., a stretched string loaded at regular intervals with masses of the same or different kinds, is the theme with which most expositions of the Born–Karman theory commence. It is, therefore, necessary to examine the question whether the behaviour of crystals can at all be compared with those of mechanical models, and if so, with what limitations.

Three basic facts about crystals which we can never hope to reproduce in any artificially constructed mechanical model are, *firstly*, the immense numbers of individual particles constituting even the smallest of crystals: *secondly*, the possibility of independent movement of the atoms and molecules which reveals itself in various ways, and *thirdly*, the high frequencies of vibration which lie mostly far above the limits of validity of the classical mechanics. Besides these vital differences, it should also be pointed out that no macroscopic model can claim to represent the behaviour of a crystal unless it satisfies the conditions requisite for dynamic similarity. In other words, the linear dimensions, masses

and operative forces in the model should be so proportioned to those of the crystal that the actions taking place in the latter are reproduced in the former. If such a model were constructed—even if it be only on paper—it would immediately make it evident that its behaviour, far from supporting the Born lattice dynamics, would show its basic assumptions to be untenable.

6. Mechanical models of crystal behaviour

We shall illustrate the foregoing remarks by considering a model of a diamond crystal, enlarged in its linear dimensions by a factor of 10^7 so that the individual atoms can be conveniently observed, and slowed down in the time-rate of its actions by a factor of 10^{12} so that the movements of the atoms can be visually followed. In the actual crystal, assumed to be 1·54 millimetre in diameter, the highest characteristic frequency of atomic vibration is $1332\,cm^{-1}$ in spectroscopic units, while the highest sound velocity is 18,000 metres per second. In the model which is 15·4 kilometres in diameter, the characteristic frequency is slowed down to 40 vibrations per second, while the fastest sound wave would take 24 hours to travel from the centre of the model to its surface and return again after reflection to the centre. Let us now suppose that a group of atoms near the centre of the model is set in motion by impulses so directed that all of them move together initially in the same direction and with the same velocity. It is evident that this would result in an elastic wave which would spread outwards from the centre towards the surface of the model and return again to the centre after travelling 15·4 kilometres in 24 hours, provided, of course, that in the course of this lengthy excursion, its energy has not dissipated itself completely. Then again, let us suppose that in another experiment, the same group of atoms is excited by two simultaneous sets of impulses so directed that the atoms belonging to the two interpenetrating Bravais lattices commence moving with equal velocities in opposite directions. In this case, it is easily seen that the result of the impulses would be to set up, not a travelling wave, but a local oscillation of the two lattices with respect to each other which would gradually spread outwards. Observations during a brief period of 60 seconds would suffice for a count of 2400 complete periods of the oscillation and hence also for a precise determination of its frequency. The presence of an external boundary many kilometers away from the centre of disturbance could obviously have no influence whatever on the phenomena taking place during those 60 seconds. In other words, the nature and frequency of the oscillation excited by the impulses would depend solely on the structure of the model and on no other considerations.

We may summarise the lessons taught by our model in the following two statements. (I) *The elastic vibrations in a crystal are a consequence of the translatory movements of its volume elements and therefore also of its lattice cells; they extend through the volume of the crystal, and their frequencies are low and form*

a diffuse continuous spectrum. (II) *The characteristic vibrations in a crystal*
represent the internal oscillations of the units of its structure; they are highly
localised and their frequencies are also high and have sharply defined values
constituting a line-spectrum.

7. Born's lattice dynamics and its consequences

Whereas Debye restricted himself for the most part in his original paper to
"monoatomic" solids, in other words to crystals having relatively simple
structures, no such restriction is contemplated in the Born–Karman theory.
Indeed, the claim made on behalf of the latter is that it specifically takes into
account the lattice structure of the crystal and embraces in its scope the case of
complex structures containing many atoms per unit cell. If there be p atoms in
each cell, and N cells in the crystal, the total of $3Np$ degrees of atomic freedom of
movement are identified with the same number of wave-patterns in the crystal.
3N wave-patterns represent the "acoustic" branches of the spectrum, and the
remaining $(3p - 3)N$ wave-patterns the "optical" branches. Each wave-pattern is
identified with one of the terms in a three-dimensional Fourier expansion, and the
summation of all the terms with the totality of the possible vibrations in the
crystal.

As has already been shown earlier in the paper, the identification of normal
modes with wave-patterns is theoretically not a permissible procedure in the case
of material media, and hence the entire structure of the Born lattice dynamics falls
to the ground. It is unnecessary in these circumstances for us to consider the
question dealt with in a paper by Ledermann[11] whether the so-called "cyclic
postulate" is or is not an appropriate way of getting over the difficulty of the
unknown boundary conditions at the external surface of a crystal. On the other
hand, it might be useful to consider what the actual consequences of the Born
lattice dynamics are in relation to the nature of the vibration spectra of crystals,
so that we could proceed to compare them with the facts of experiment.

It is an immediate consequence of the Born–Karman theory that the vibration
spectrum of a crystal presents the aspect of a diffuse continuum throughout the
entire range of frequency. This is apparent from the numerous diagrams printed
in Brillouin's book and from the calculations for various cases published by Born
and his collaborators. The reason for it is also obvious. Since the wave-patterns
from a Fourier sequence, their wavelengths are crowded together as we approach
the limit where the sequence is assumed to be terminated and the wavelengths are
therefore of the same order of magnitude as the lattice spacings of the crystal. A
difference in wavelength necessarily means a change in frequency, and the
variations thus arising become large for the "optical branches" of the spectrum
near the lower limit of wavelength. Hence the frequency spectrum is spread out
very widely in this region. But the spread is far from being negligible even in the

range of greater wavelengths. Though no actual calculations have been published for the case of crystals containing ions or molecules having their own characteristic frequencies of vibration, one may feel sure that if such calculations were made, the result would not exhibit any visible resemblance to the vibration spectra of such ions or molecules as we actually know them from experimental studies.

8. The scattering of light in crystals

For reasons which can well be understood, a crystal is intensely opaque to electromagnetic radiations over a wide range of frequency on either side of its own characteristic frequencies in the infra-red. In consequence, only rather vague and fragmentary indications were available regarding the nature of the vibration spectra of crystals, until the spectroscopic study of the scattering of light introduced a new and simple as well as powerful and accurate way of exploring this field of knowledge. From the analogies presented by the case of gases, liquids and amorphous solids where the same method is equally applicable, it is obvious that the frequency shifts observed in light scattering furnish us with a straight answer to the question of the nature of the vibration spectrum of a crystal, viz., that it consists of a set of sharply-defined monochromatic frequencies in the infra-red. The general acceptance of this simple view of the case has, however, been held up by the belief in theories which were put forward at a time when there was no experimental knowledge which could set theoretical thinking on the right path. To get over the patent contradiction between those theories and the experimental facts, it was suggested that while the real vibration-spectrum is continuous, the frequency shifts observed in light-scattering represent the result of the elimination of everything except the so-called limiting frequencies of vibration with large wavelengths by a selection principle based on the idea that the mechanical waves give a coherent reflection of the incident light waves, while the rest of the spectrum is hidden away from sight by a species of optical interference.

That the way proposed for escape from the difficulties is not a reasonable one becomes evident when it is recalled that large frequency shifts are also observed in the scattering of light by the molecules of gases and of liquids. They are very properly described in these cases as the result of an incoherent scattering in which the individual molecules of the substance exchange energy with the incident radiation. If this be a correct description of the process in the cases of fluid media, there is no reason why the obviously analogous effects observed with crystals should be regarded differently and ascribed to a coherent reflection of the light waves by mechanical waves. The mere change from a fluid to the solid state cannot be claimed as a justification, for it is found that organic glasses also give sharply-defined lines as frequency shifts in light-scattering. Such glasses are solids

in every sense of the term, and since they do not possess any periodicity of structure, it is not possible in their case to invoke any selection principle which could convert a diffuse continuum into a line spectrum.

Another observed fact which is absolutely fatal to the Born lattice dynamics is the appearance in numerous cases of sharply-defined lines as frequency shifts which do not agree with the fundamental frequencies of vibration, but are overtones or summations thereof. For frequency shifts of this kind to appear, it is essential that the amplitude of the atomic oscillations should be comparable with the interatomic distances, and this again would not be possible if the energy-quantum of the particular frequency is distributed as a wave extending over the whole volume of the crystal or even any limited region inside it. Overtones and summations could appear as frequency shifts with the observed intensities only if the oscillations are highly localised, in other words, are restricted to volumes which are comparable in their dimensions to the unit cells of the crystal structure. It is clearly not possible in these circumstances for the proposed selection principle to function which would pick up a single frequency from a continuous spectrum of frequencies.

Finally, we may refer to the specially interesting cases, of which diamond is the best example, in which strongly exposed spectrograms reveal frequency shifts appearing as sharply-defined lines which are not explicable as overtones or summations of the $(3p - 3)$ normal modes in which the phase is the same in adjacent lattice cells of the crystal lattice, but which compel the $21p$ additional modes in which the phase alternates also to be considered. Diamond, for instance, exhibits besides the line with a frequency shift of 2664 cm^{-1} which is the octave of the principal frequency of 1332 cm^{-1}, also several other lines as frequency shifts which are identifiable as overtones and summations of the eight fundamental frequencies of the diamond structure. In a recent paper in these *Proceedings*, P S Narayanan[12] has described and discussed the results of his studies on the case of diamond and shown that they are altogether incompatible with the consequences of the Born lattice dynamics. It is unnecessary to re-traverse the same ground here.

Summary

The enumeration of wave-patterns within an enclosure on a scale of wavelengths or frequencies presupposes that the waves are perfectly undamped and that the enclosure is perfectly reflecting. In any material medium, however, wave-propagation is necessarily damped and such damping may be so enormous as altogether to preclude wave-propagation. It follows that it is not permissible to identify the modes of atomic vibration in crystals with wave-patterns. Since the specific heat theories of Debye and of Born–Karman are based on such identification, they cannot be sustained.

For any mechanical model to represent the dynamic behaviour of a crystal, it is necessary that it should satisfy the requirements for dynamic similarity. When these requirements are satisfied, the behaviour of the model does not support the ideas underlying the Debye and Born–Karman theories, but on the other hand agrees with the results of the theory of the dynamics of crystal lattices put forward by the writer in 1943.

The phenomena of light-scattering observed in crystals are also discussed and it is shown that the experimental facts are incompatible with the ideas underlying the Born–Karman theory.

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