

The specific heats of crystalline solids: Part II

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The theory of the specific heats of crystals expounded in the first part of this review is similar in its approach to that originally proposed by Einstein in the year 1907, but it fills up the lacunae left in that theory and succeeds in connecting the thermal energy of crystals with their spectroscopic behaviour, as also in explaining the facts of observation in both of these fields. It is hoped on some later occasion to set out the results following from the theory in greater detail and to illustrate them by specific examples. The present review will conclude with some comments on the theory of the specific heats of crystals put forward by Debye in the year 1912 and the closely analogous theory published by Born and Karman at about the same time. A whole generation of physicists and chemists has been persuaded to believe that these theories embody valid physico-mathematical thought and that they satisfactorily account for the facts of observation. These are circumstances which justify the inclusion in the present review of some critical remarks on those theories.

2. The fundamentals of specific heat theory

We may usefully commence our examination by recalling the ideas embodied in Einstein's paper of 1907 in the form of three distinct propositions.

- I. A crystal is an assembly in thermodynamic equilibrium of an immense number of individual oscillators which are divisible into sets, each set consisting of a great number of oscillators characterised by a common frequency of vibration.
- II. The total number of oscillators of all sorts is equal to thrice the number of atoms comprised in the crystal.
- III. The vibrational energy of each individual oscillator is quantised and its average value taken over its different possible energy states may be determined by the aid of Boltzmann's principle.

The first of these propositions finds its justification in the known physical features of crystal architecture. The second proposition follows as a logical deduction from the first taken in conjunction with the results of classical mechanics. The third proposition is a logical consequence of the principles of thermodynamics and the quantum theory when applied to the circumstances

stated in the first proposition. In the earlier part of the review, it has already been shown how these propositions enable us to deduce both the thermal and the spectroscopic behaviour of crystals.

3. The theories of Debye and Born

The basic idea underlying these other theories is that the thermal energy of a crystal may be evaluated in the same manner as the energy density of thermal radiation within a perfectly reflecting enclosure, in other words, by summing up the kinetic and potential energies of sets of wave-trains which are assumed to fill the volume of the solid and form stationary wave-patterns in its interior. J H Jeans who was the original proposer of this idea indicated in his paper of 1909 a way of escape from the more obvious difficulties which arise when it is sought to make use of it. Debye and Born who derived their inspiration from Jeans naturally also took over from his paper the special assumptions needed to put his ideas into quantitative form. These special assumptions figure prominently in both of the theories and are indeed their most characteristic feature.

The stationary wave-patterns considered by Debye were those contemplated in the classical theory of elasticity for a solid of finite volume. An enumeration on the basis of that theory shows the total number of modes of vibration to increase—without any upper limit—proportionately to the cube of the frequency up to which the enumeration is carried. To enable the enumeration thus made to form the basis of specific heat theory, Debye assumed that the enumeration is valid only up to a certain upper limit of frequency and that no modes of vibration with higher frequencies exist; the upper limiting frequency was so chosen that the number of wave-patterns is equal in number to thrice the number of atoms comprised in the crystal.

The waves considered by Born are of a more general type than those considered in the Debye theory. Whereas Debye limited himself to the consideration of crystals of comparatively simple type, viz., those containing a single species of atom and belonging to the cubic system, the theory of Born accepts no such limitation and indeed claims to be applicable to all crystals. The special assumption which figures in the Born theory is the well known "cyclic postulate" which selects the permitted wavelengths of the stationary wave-patterns filling the solid in such manner that the total number of wave-patterns is equal to thrice the number of atoms comprised in the crystal.

The questions which arise and which need to be considered are the following: Are the approaches to specific heat theory briefly summarized above logically sustainable? Are the ideas on which they are based and the conclusions to which they lead compatible with the fundamental principles of classical mechanics, thermodynamics and the quantum theory? We shall consider these questions and presently find that the answer is in each case definitely in the negative.

4. The logical fallacy

A simple calculation shows that the frequencies of vibration which determine the variation of the specific heats of crystals with temperature lie in the infra-red region of the spectrum. It follows that the oscillators which are the carriers of the thermal energy are the ultimate structural elements in the crystal. This is further confirmed by the fact that when the atoms are firmly bound together in the structural elements of the crystal, as is the case for example with diamond, the specific heats are low and the vibrational frequencies estimated from them are high; the latter inference receives direct support from spectroscopic studies. It follows from these remarks that the approach to the specific heat problem made in the theories of Debye and Born is totally misconceived. These authors concern themselves with an entirely different and irrelevant subject, namely, the vibrations of a macroscopic solid and proceed to determine and enumerate them, treating it as a boundary-value problem in wave-propagation. It is easily shown that the results thus obtained are wholly unrelated to the specific heat problem. We have only to recall that wave-motion is a kinematic concept. Hence the stationary wave-patterns inside an enclosure can be described in purely geometric terms without any reference to the question whether the material traversed by the waves does or does not possess a discrete structure. In other words, there is no nexus or connection between the stationary wave-patterns assumed to exist in the medium and the discrete structure, if any, which it possesses. It is not surprising in these circumstances that Debye and Born are obliged to introduce postulates into their theories which assume the existence of such a relationship. We have only to remark that such postulates or assumptions savour of sophistry and that theories embodying them can lay no claim to logical validity.

5. Falsity of the dynamical consequences

The theories of Debye and Born are attempts to carry over the ideas and methods of macroscopic physics into the fields of atomic dynamics, thermodynamics and quantum theory where they are inappropriate and indeed wholly out of place. The procedures they adopt naturally lead to consequences which are irreconcilable with the basic principles of these disciplines and the results following from them.

Considering the matter first from the stand-point of atomic dynamics, it is clear that we are not concerned here either with wave-propagation or with any boundary value problem. Specific heat theory rests on the determination and enumeration of the normal modes of vibration of the ultimate particles of the material, in other words, of the atoms present in the structure of the crystal. Since the range of the interatomic forces is limited and small compared with the

dimensions of any crystal of macroscopic size, these normal modes are determinable from the structure of the crystal without any reference to the size of the crystal or to the conditions at its external boundary. This also becomes evident when we compare the frequency of the atomic oscillations with the frequency of the elastic oscillations of a macroscopic crystal. The former is very great in comparison with the latter even for a crystal of colloidal dimensions. Hence the oscillations of the atoms in the interior of a crystal repeat themselves many thousands of times, thereby defining their frequency with all necessary precision, before any disturbance originating in the interior of the crystal could travel out to reach its surface and return after reflection to the place of its origin. Hence, whether the boundary is there or not makes no difference to the modes and frequencies of atomic vibration.

The fallacy of identifying the atomic vibrations with stationary wave-patterns is obvious even in such simple cases as those considered by Debye. The vast majority of the stationary wave-patterns assumed in his theory to be the carriers of the thermal energy of the crystal have wavelengths of the same order of magnitude as its lattice spacings. These are precisely the circumstances in which it is not permissible to identify the dynamical behaviour of a discrete structure with that of a medium of uniform density. The consequence of such identification is to endow the crystal with an immense number of modes of vibration with frequencies all different from each other throughout the range under consideration and thus to present a false picture of the spectroscopic behaviour of the crystal.

Though Born's theory nominally takes account of the discrete lattice structure of crystals, his "postulate of the cyclic lattice" is equivalent to assuming that the normal modes of vibration of the atoms are similar to the oscillations of the volume elements in a continuous solid having the same shape as the unit cell of the crystal but of greatly enlarged size. The stationary vibrations permitted by the postulate accordingly appear in immense numbers with wavelengths and frequencies all different from each other and with their modes wholly unrelated to the structure of the crystal. It is important to remark in this connection that Born does not restrict himself to simple lattice structures but also claims his theory to be valid for all crystals. Any one who appreciates the nature of the results following from Born's lattice theory will realize that the ideology behind his dynamics is completely false. In effect, Born endows the atoms in a crystal with a vast number of modes and frequencies of vibration which are wholly unrelated to its internal architecture and which have a continuous spectrum of frequencies, a result which is in flagrant contradiction with the facts of observation revealed by spectroscopic investigations.

6. Conflict with thermodynamics

A stationary wave-pattern is a mode of vibration in which all the volume elements of the medium oscillate with the same frequency and in the same or opposite phases and with relative amplitudes which remain invariant with time. Vibrations of this type are characteristic of a macroscopic solid and can be considered as its normal modes of vibration and determined by the methods of the classical theory of elasticity. Such vibrations can also be set up and maintained in an elastic solid artificially, as for example, by the use of a piezo-electric oscillator attached to it.

The identification of the thermal agitation in crystals with stationary wave-patterns of the nature described above which is postulated in the theories of Debye and Born is however clearly irreconcilable with the statistical concept of the nature of thermal energy in material bodies. Thermal agitation is envisaged in Boltzmann's entropy-probability principle as a chaotic and fluctuating disturbance varying in its character and intensity from instant to instant and from place to place within the material. Atomic groups of similar nature which are located in parts of the crystal not contiguous to each other may indeed vibrate with the same frequency. But there can be nothing in the nature of definite relationships either in their amplitudes or in their phases of vibration persisting in time.

The issue can also be put a little differently. A crystal is an assembly of an immense number of individual atoms which are capable of moving from their positions of equilibrium. Hence the state of the system can only be described in terms of the values of a very large number of independent variables. The interactions between neighbouring atoms would naturally influence their relative movements and determine their modes and frequencies of vibration. But we cannot in any circumstances regard the entire assembly as a single unit in the thermodynamic sense or postulate constancy of amplitude or coherence of phase in the atomic vibrations over its entire volume. A description of the thermal agitation in precisely defined terms is possible only for domains of space and periods of time which are small in comparison with macroscopic standards. In other words, the entire ideology behind the theories of Debye and Born is incompatible with the fundamental notions of the nature of thermal energy which lie at the base of the science of thermodynamics.

7. Misinterpretation of the quantum theory

As has been shown above, the theory of specific heats can be placed on a logically sustainable basis only if we recognize that the oscillators which are the carriers of the thermal energy are the structural elements in the crystal. We then obtain a picture of the thermal agitation in the solid which is consistent with the general

principles of dynamics and of thermodynamics. Necessarily, therefore, it is these same oscillators whose vibrational energies must be assumed to be quantised. Since, further, these oscillators are present in large numbers distributed over the volume of the crystal, we have a logical justification for the use of Boltzmann's principle in conjunction with the quantum hypothesis for the evaluation of the average energy of the oscillators of any particular frequency and therefrom also the evaluation of the heat capacity of the entire crystal.

To the fallacies which vitiate the Debye and Born theories we have therefore to add one more, viz., that they give a fantastic and altogether meaningless interpretation to the postulates of the quantum theory. They proceed to quantise the energy of the normal modes of vibration of a macroscopic crystal; in doing this, they ignore the fact that the theory of quanta possesses a meaning and significance only in relation to the behaviour of the physical entities which the language of determinism characteristic of macroscopic physics cannot successfully describe. For example, we can speak meaningfully of quantising the energies of rotation or vibration of a molecule of benzene; but it is patently absurd to quantise the vibrations of a tuning fork or the rotations of a flywheel.