ON THE SURFACE SPECIFIC HEAT OF A CYCLIC
CRYSTAL LATTICE

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Synopsis

A simple method is used to show that, in the harmonic approximation, the volume dependence of the specific heat, C, of a crystal lattice with cyclic boundary conditions has the form $C = AV + \mathcal{O}(V^{1/3})$, where A is volume independent, *i.e.* there is no contribution to C proportional to the surface area, and the leading-order correction to the bulk specific heat is, at most, of the order of the linear dimensions of the crystal. The proof has wider validity and gives a better upper bound for the leading-order correction term than that given by Maradudin and Wallis who gave $C = AV + \mathcal{O}(V^{5/9})$, and it is shown that the method used here is applicable to the special case treated by them.

1. *Introduction.* In the appendix to the paper by Maradudin and Wallis[1]) on a lattice-dynamical calculation of the surface specific heat of a crystal at low temperatures, there is a proof that the lattice specific heat of a crystal obeying cyclic boundary conditions contains no term proportional to the surface area of the crystal in the harmonic approximation. The proof is restricted to the low-temperature specific heats of crystals which are isotropic in the low-frequency limit. In this paper another proof of the same theorem will be given which is applicable to anisotropic crystals at arbitrary temperature.

The crystal model used by Maradudin and Wallis is a crystal of cubic symmetry and isotropic in the low-frequency limit. The allowed wave vectors, k, for the cyclic crystal then form a simple cubic lattice, and the surfaces of constant frequency in this lattice are spheres, provided one keeps to small frequencies. Maradudin and Wallis had to show that the number of normal modes with wave vectors, k, that lie inside or on a sphere centred at the point $k = 0$ has no contribution proportional to the surface area of the crystal. They prove the equivalent statement that the number of lattice points on a simple cubic lattice contained inside or on a sphere centred on one of the lattice points has no contribution proportional to the surface area of the sphere. To extend the method to anisotropic crystals and arbitrary temperature one would have to show that the number of

normal modes with wave vector lying inside or on a surface of constant frequency (now, in general, no longer a sphere) contains no term proportional to the surface area of the crystal. As Maradudin and Wallis admit, this would be difficult to do and it seems that another approach is needed if a more general result is to be obtained.

In computing the specific heat or similar quantities for a cyclic crystal one needs to perform a sum, $\sum_k f(k)$, over all allowed wave vectors, k, where $f(k)$ is some function of k. The basis of the present method is to use the Euler–Maclaurin summation formula (Whittaker and Watson[2]) to expand $\sum_k f(k)$, where $f(k)$ is assumed to have suitable analytic behaviour, in a power series in N; N^3 is the total number of unit cells in the crystal. It will be found that there is no term proportional to N^2 in such an expansion. Hence the lattice specific heat of a cyclic crystal has no contribution proportional to its surface area. The application of this result to the low-temperature lattice specific heat of the crystal model used by Maradudin and Wallis will be discussed.

2. *Proof that a cyclic crystal lattice has no contribution to its specific heat proportional to its surface area.* The cyclic crystal is defined as follows. Let the basic lattice vectors be a_1, a_2 and a_3. The crystal is made up of the totality of unit cells at positions $n_1 a_1 + n_2 a_2 + n_3 a_3$ where n_i takes all possible integral values for which $1 \leqslant n_i \leqslant N_i$, $i = 1, 2, 3$. The boundary condition is that, if $u(n)$ is the displacement for an atom in the nth unit cell, then

$$u\,(n_1 + L_1 N_1, n_2, n_3) = u\,(n_1, n_2, n_3),$$

where L_1 is an arbitrary integer, for all n_1, n_2 and n_3 with similar conditions on the dependence of $u(n)$ on n_2 and n_3. The reciprocal-lattice vectors A_1, A_2 and A_3 are defined by $a_i \cdot A_j = \delta_{ij}$. The components k_1, k_2 and k_3 of the wave vector k are given by

$$k = k_1 A_1 + k_2 A_2 + k_3 A_3.$$

The boundary condition restricts the components of k to the values $k_i = 2p\pi/N_i$ where p is integral.

It will be proved that, for a wide class of functions $f(k)$, the sum, $\sum_k f(k)$, over all the allowed wave vectors for the cyclic crystal contains no term quadratic in N_1, N_2 and N_3. It will first be shown that, for a one-dimensional cyclic crystal with N unit cells,

$$\sum_k f(k) = \frac{N}{2\pi} \int_{-\pi}^{+\pi} f(k)\,\mathrm{d}k + \mathcal{O}\left(\frac{1}{N}\right), \tag{1}$$

i.e., $\sum_k f(k)$ contains no contribution of order unity, for which the above-mentioned result for the three-dimensional crystal follows fairly easily. It is assumed that $f(k)$, as a function of the complex variable k, is analytic at all points on the real axis and that for all real k, $f(k) = f(k + 2\pi)$.

To derive eq. (1) one uses the Euler–Maclaurin summation formula[2]) in the form

$$\tfrac{1}{2}f(a) + f(a + b/N) + \cdots + f(a + b - b/N) + \tfrac{1}{2}f(a + b)$$

$$= \frac{N}{b} \int_a^{a+b} f(k) \, dk + \mathcal{O}\left(\frac{1}{N}\right), \qquad (2)$$

where $f(k)$ is analytic on the straight line joining a and $a + b$. The allowed k values for the one-dimensional cyclic crystal are

$$k = 0, \quad \pm 2p\pi/N \quad p = 1, 2, \ldots, \tfrac{1}{2}(N - 1) \quad N \quad \text{odd}$$

$$k = 0, \quad \pm 2p\pi/N, \quad \pi \quad p = 1, 2, \ldots, \tfrac{1}{2}N - 1 \quad N \quad \text{even}.$$

To derive (1) for N odd one puts $a = -\pi + \pi/N$ and $b = 2\pi$ into (2); thus

$$\tfrac{1}{2}f(-\pi + \pi/N) + f(-\pi + 3\pi/N) + \cdots + f(\pi - \pi/N) + \tfrac{1}{2}f(\pi + \pi/N)$$

$$= \frac{N}{2\pi} \int_{-\pi+\pi/N}^{+\pi+\pi/N} f(k) \, dk + \mathcal{O}\left(\frac{1}{N}\right).$$

By using the fact that $f(k) = f(k + 2\pi)$ one can adjust the limits of integration in the last equation to obtain (1) as required. The proof for N even differs only in starting with $a = -\pi$.

The sum $\sum_k f(k)$ for the three-dimensional crystal may be considered as three separate sums, $\sum_{k_1}$, $\sum_{k_2}$ and $\sum_{k_3}$ over the allowed values of the components of k, and by converting these sums into integrals by the use of (1) it will be shown that $\sum_k f(k)$ has no term quadratic in the N's. From (1)

$$\sum_{k_2} \sum_{k_1} f(k_1, k_2, k_3) = \frac{N_1}{2\pi} \int_{-\pi}^{+\pi} \left[\sum_{k_2} f(k_1, k_2, k_3)\right] dk_1 + \mathcal{O}(1)$$

$$= \frac{N_1 N_2}{(2\pi)^2} \int_{-\pi}^{+\pi} dk_1 \int_{-\pi}^{+\pi} dk_2 \, f(k) + \mathcal{O}(1),$$

and

$$\sum_k f(k) = \frac{N_1 N_2 N_3}{(2\pi)^3} \int\limits_{-\pi}^{+\pi} dk_1 \int\limits_{-\pi}^{+\pi} dk_2 \int\limits_{-\pi}^{+\pi} dk_3 f(k) + \mathcal{O}(N),$$

where by $\mathcal{O}(N)$ one means all terms of order N_i or $N_i N_j/N_k$. In the above it has been assumed that (i) $f(k)$ is invariant under translation by a reciprocal-lattice vector and (ii) if any two components of k are given arbitrary fixed real values and the third component is treated as a complex variable, then $f(k)$ is an analytic function of this third component at all points on the real axis.

Hence it has been shown that, with the restrictions (i) and (ii) on $f(k)$, $\sum_k f(k)$ for a cyclic crystal has no contribution proportional to the surface area. Therefore, if the specific heat can be expressed as such a sum $\sum_k f(k)$, it will have no contribution proportional to the surface area of the crystal; indeed, the leading-order correction to the term proportional to the volume, V, of the crystal is of order $V^{1/3}$ or smaller.

3. *Application to the crystal model used by Maradudin and Wallis.* Maradudin and Wallis write down the specific heat of an arbitrary crystal [their eq. (2.1)] as

$$C = k_B \sum_s (\tfrac{1}{2}\beta\hbar\omega_s)^2 \sinh^{-2} (\tfrac{1}{2}\beta\hbar\omega_s),$$

where ω_s are the normal-mode frequencies and β is the inverse temperature $(k_B T)^{-1}$. For the low-temperature specific heat of the crystal model the relevant frequency–wave-vector relations are

$$\omega_\nu^2 = c_\nu^2 k^2,$$

where ν is a polarization index (longitudinal or transverse) and c_ν is the appropriate sound velocity. The low-temperature specific heat written as a sum over wave vectors is

$$C = k_B \sum_\nu \sum_k B_\nu^2 k^2 \sinh^2 B_\nu(k^2)^{\frac{1}{2}},$$

where $B_\nu = \tfrac{1}{2}\beta\hbar c_\nu$. To apply the results of section 2 to the low-temperature specific heat of this crystal model it is sufficient to show that the function

$$f(k) = B (k_1^2 + k_2^2 + k_3^2) \sinh^{-2} [B (k_1^2 + k_2^2 + k_3^2)^{\frac{1}{2}}],$$

is analytic on the real axis when any one of the components of k is regarded as a complex variable and the other two have fixed real values. This is equivalent to showing that

$$g(z) = (\alpha^2 + z^2) \sinh^{-2} (\alpha^2 + z^2)^{\frac{1}{2}},$$

is analytic on the real axis for all real α where z is the complex variable. Now if $z = x + \zeta$ is a point in the neighbourhood of a point x on the real axis, then

$$g(x + \zeta) - g(x) = 2x\zeta(\sinh p - p \cosh p)\sinh^{-3} p + \mathcal{O}(\zeta^2),$$

for $p^2 = \alpha^2 + x^2 \neq 0$, so that $g(z)$ is analytic for real x except possibly at $x = 0$ when $\alpha = 0$. However, for $\alpha = 0$ one may write

$$g(z) = [z/\sinh z]^2,$$

and this is analytic for real z including $z = 0$. Hence $g(z)$ is analytic at all points on the real axis for all real α. It is therefore concluded that one can apply the theorem of section 2 to the low-temperature specific heat of the crystal model used by Maradudin and Wallis and hence the low-temperature specific heat of this crystal has volume dependence $C = AV + \mathcal{O}(V^{1/3})$ where A is volume independent, *i.e.*, there is no term proportional to surface area and the leading-order correction to the term proportional to volume is, at most, of the order of the linear dimensions of the crystal. This is a closer estimate than that given by Maradudin and Wallis who gave the upper bound of the correction term as being of order $V^{5/9}$.

One final comment on the relation between the method used here and that presented by Maradudin and Wallis is in order. They convert the sum over the wave vectors into an integral over frequency with the use of the integrated frequency spectrum. This function is discontinuous at each frequency for which there is a normal mode of the cyclic crystal. The function may be approximated by a smooth function in frequency, proportional to V, and Maradudin and Wallis show that the deviations (of which some are positive and some negative) of the exact integrated frequency spectrum from the approximate one are bounded by terms proportional to $V^{5/9}$. Even if this were the best upper bound one could obtain, it would not necessarily follow that the best upper bound to the deviation of the actual specific heat from its bulk contribution would have a volume dependence of $V^{5/9}$. Indeed, with the method presented here, in which the upper bound to the correction terms due to the replacement of a sum over the wave vectors by an integral was examined, it has been shown that the leading-order correction to the bulk specific heat is of order $V^{1/3}$ or smaller.

REFERENCES

1) Maradudin, A. A. and Wallis, R. F., Phys. Rev. **148** (1966) 945.
2) Whittaker, E. T. and Watson, G. N. Modern Analysis, Cambridge University Press, 4th ed. (Cambridge, 1927) p. 128.