that

$$\frac{c_s^{\mathrm{el}}}{\gamma T}=\frac{1+\alpha}{1-\alpha}(T/T_0)^{2\alpha/(1-\alpha)}.$$

The dashed curves in Fig. 5 are plots of this equation for two different values of α. It may be seen that the niobium data do not fit any of the α curves, so that it may be concluded that there is as yet no theory of the heat capacity of superconductors which is in satisfactory agreement with these experiments.

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The Vibrational Spectrum and Specific Heat of Sodium

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The frequency spectrum of the normal vibrations of a body-centered cubic crystal lattice is derived by a method suggested by Houston, in which the secular equation is solved along three lines in the reciprocal lattice and the result is interpolated by means of suitably chosen spherical harmonics. Some corrections are applied to the high-frequency part of the spectrum, and the lattice part of the specific heat of metallic sodium is calculated as a function of temperature.

I. THE PROBLEM

In the theory of ideal metals one considers effectively free conduction electrons moving in the field of a lattice of positive ions. These conduction electrons move very fast compared with the ions of the lattice, and are relatively weakly coupled to them, so that an "adiabatic" separation is always made as follows. In considering properties of the conduction electrons one regards the ions as at rest or at most vibrating as a perturbation (to give the thermal part of the resistivity); conversely, in the study of lattice properties such as the specific heat at intermediate temperatures and a large part of the elastic constants, the lattice is regarded as held together by the "smeared-out" field of the electrons.

Here we are interested in calculating the specific heat of metallic sodium at moderately low temperatures, i.e., between about 10°K and 100°K, and in this region the only effective contribution comes from the lattice of ions. At extremely low temperatures, the electronic contribution to the specific heat becomes important, while at high temperatures the specific heat has approximately the value predicted by classical equipartition, but with some disturbing effects believed to be due to the large amplitude of the lattice vibrations and consequent anharmonicity and also due to the electrons. There is an additional disturbing effect in the case of sodium giving a peak in the specific heat at about 7°K.[1] Such effects are known to occur in a number of the crystal. Then, to get physical results, we apply substances: they may arise because of changes in crystal structure, but in any case they cannot be accounted for in terms of lattice vibrations.

To calculate the specific heat we just have a statistical knowledge of the degrees of freedom of the ions. For this purpose it is convenient to regard the ions as making up a lattice and to study the frequency spectrum of the lattice vibrations, which are the normal modes of the system. The reason for doing this statistically is that in a macroscopic crystal there are $\sim 10^{23}$ ions, i.e. $\sim 3\times 10^{23}$ degrees of freedom.

The best method that has been developed so far for obtaining the frequency spectrum is that of Born and v. Karman,[2] who set up the classical equations of motion of an ion interacting with its close neighbors, with given force constants as parameters. These parameters are to be determined from the elastic constants of the lattice. With the use of Born's cyclic boundary conditions, the condition that the equations of motion have a nonvanishing solution corresponding to small harmonic vibrations of the ions about their equilibrium positions gives the secular equations. Thus, if there are N atoms in a three-dimensional lattice, there are N distinct 3×3 secular determinants in the simplest case; these have $3N$ roots, the frequencies of the normal modes of vibration. We are interested in finding the frequency spectrum of these $3N$ vibrations, i.e., finding how many of them lie in any given frequency range. This frequency distribution is obtained by solving a suitable number of the $N(\sim 10^{23})$ secular equations.

Thus we obtain a frequency spectrum by setting up classical equations of motion in terms of certain force constants which are related to the elastic properties of

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[1] G. L. Pickard and F. E. Simon, Proc. Phys. Soc. (London) **61**, 1 (1948). The specific heat of sodium up to 300°K has been measured by F. E. Simon and W. Zeidler, Z. physik. Chem. **B123**, 383 (1926).

[2] M. Born and T. v. Karman, Physik. Z. **13**, 297 (1912); **14**, 15 (1913).

Bose-Einstein statistics to the frequency spectrum obtained in this way, and thus get the specific heat.

II. METHODS OF SOLUTION

The central technical problem is solving a sufficient number of the N secular determinants to get a frequency spectrum, without too much labor. Several methods have been given: there are methods which depend on solving a suitably chosen random sample of the N secular equations;[3] also, there is an elegant method developed by Montroll,[4] which depends on obtaining the frequency spectrum in terms of moments of various powers of the vibration frequencies. This method unfortunately suffers from the severe practical limitation that in the lower approximations the spectrum is given more accurately at high than at low frequencies, and at low temperatures, where the specific heat deviates markedly from the classical value, it is just the low-frequency part of the spectrum which is of importance. Leighton[5] has derived the frequency spectrum of some face-centered cubic lattices by a mechanical-analog method.

Houston[6] has described a method of deriving the frequency spectrum of any lattice by solving the secular equation analytically along a certain number of directions in the reciprocal lattice, and interpolating by means of suitably chosen spherical harmonics. This method is extremely simple in computation, and is satisfactory at low frequencies. However, Nakamura[7] has examined the method closely for the case of a square two-dimensional lattice, which has been solved exactly by Montroll,[8] and comes to the conclusion that the method of Houston fails at large frequencies. Also Van Hove[9] has examined the nature of the singularities of the frequency spectrum of general lattices, and finds that the infinite peaks characteristic of Houston's method are not given by the exact theory. It ought to be mentioned that Houston in his original article realized (or at least implied) these drawbacks of his method.

In this work the Houston's method is used, together with some modifications suggested by Nakamura's criticism. The reason for this is that for actual thermal properties one is interested not so much in the detailed shape of the frequency spectrum, but in various integrals including the spectrum as a weighting function, so that perhaps the errors in the shape of the high-frequency part of the spectrum may not be too serious in this connection.

III. SEPARATION OF THE ELASTIC CONSTANTS

We are considering the case of sodium, a monatomic metal with a body-centered cubic lattice, in which the conduction electrons are effectively free[10] so that the adiabatic separation into an ionic lattice and free electrons should be relatively satisfactory. However, sodium is extremely anisotropic as far as its crystal properties are concerned. In principal axes, its three independent elastic constants, c_{11}, c_{12}, c_{44}, in Voigt's notation are given in Table I, where the measurements of Bender[11] and of Quimby and Siegel[12] at 90°K are given, as well as the calculations of Fuchs[13] for absolute zero. The measurements are very difficult, and this accounts for the relatively large spread of the experimental results.

It is usual, in applications of the theory of Born and v. Karman,[2] to consider all the interactions in the lattice to be central, and to take into account the interaction of each ion with its nearest and second-nearest neighbors; the force constants for these interactions are denoted respectively by α and γ, and are measured in units of dynes/cm. The simplest over-all picture of a cubic crystal like sodium is obtained by assuming, as do Fuchs[13] and Leighton,[5] that the conduction electrons form a fluid in that their energy depends only on the volume and is therefore not affected by a pure shear deformation of the crystal; thus the electrons contribute one independent elastic constant. The lattice of ions has cubic symmetry and is regarded as defined by two independent elastic constants because one supposes that the ions interact with central forces.[14] Thus, if the

TABLE I. The elastic constants of metallic sodium (in units of 10^{11} dynes/cm^2).[a]

	c_{11}	c_{12}	c_{44}	$c_{11}-c_{12}$
Experimental data (90°K): Bender[b]	0.945	0.779	0.618	0.166
Quimby and Siegel[c]	0.603	0.459	0.586	0.144
Calculation (0°K): Fuchs[d]	0.972	0.831	0.580	0.141

[a] The data actually used are those of Fuchs; for the separation of Eq. (1) the data on c_{44}, and $c_{11}-c_{12}$ are the significant ones.
[b] See reference 11.
[c] See reference 12.
[d] See reference 13.

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[3] M. Blackman, Repts. Progr. Phys. **8**, 11 (1941) (Blackman has done much work on different aspects of the problem); P. C. Fine, Phys. Rev. **56**, 355 (1939): body-centered cubic lattice, applied to tungsten.

[4] E. W. Montroll, J. Chem. Phys. **10**, 218 (1942); **11**, 481 (1943); E. W. Montroll and D. C. Peaslee, J. Chem. Phys. **12**, 98 (1944): body-centered cubic lattice. See also H. Thirring, Phys. Z. **14**, 867 (1913); **15**, 127, 180 (1914).

[5] R. B. Leighton, Revs. Modern Phys. **20**, 165 (1948): application to silver.

[6] W. V. Houston, Revs. Modern Phys. **20**, 161 (1948).

[7] T. Nakamura, Progr. Theoret. Phys. **5**, 213 (1950).

[8] E. W. Montroll, J. Chem. Phys. **15**, 575 (1948).

[9] L. Van Hove, Phys. Rev. **89**, 1189 (1953). I am indebted to Dr. Van Hove for sending me a copy of this article prior to publication.

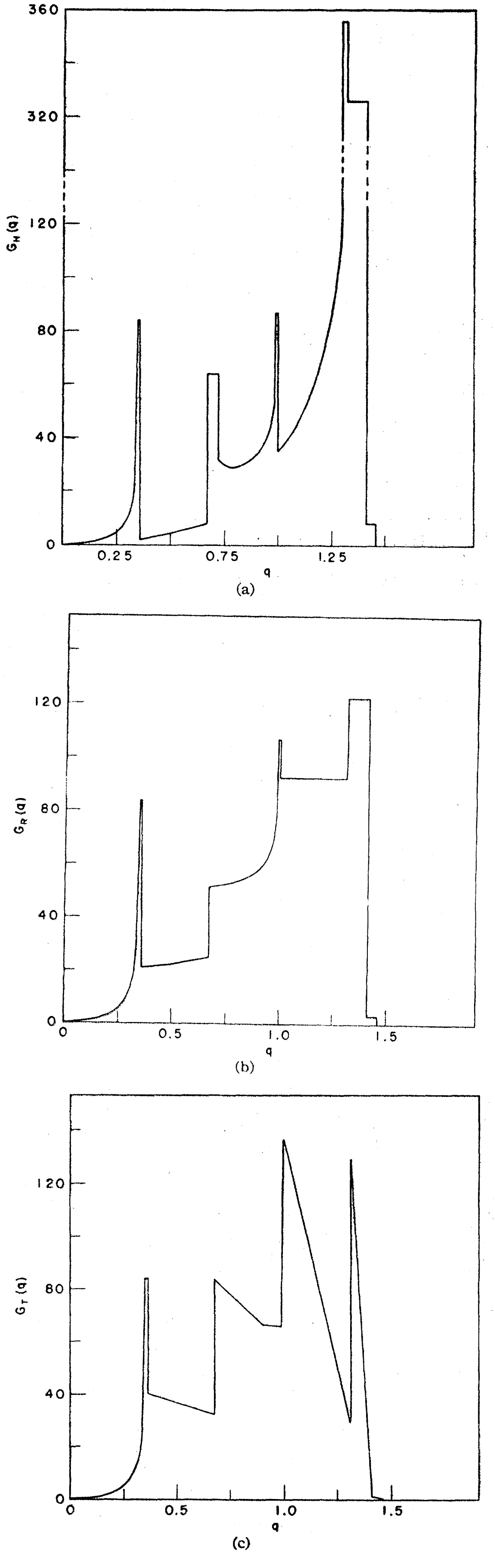
[10] The effective mass of the conduction electrons in sodium is 0.94 m (in the Bloch approximation); see F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 354; also N. F. Mott and H. Jones, *Theory of Metals and Alloys* (Oxford University Press, London, 1936).

[11] O. Bender, Ann. Physik **34**, 359 (1939).

[12] S. L. Quimby and S. Siegel, Phys. Rev. **54**, 293 (1938).

[13] K. Fuchs, Proc. Roy. Soc. (London) **A153**, 622 (1935); **A157**, 444 (1936).

[14] For a cubic crystal with only central forces between the atoms we have the Cauchy conditions, $c_{12}=c_{44}$, so that there are only two independent elastic constants. An isotropic medium has only two independent elastic constants, because $c_{11}=c_{12}+2c_{44}$. For an isotropic solid with central forces between the atoms there is only one independent elastic constant, because $c_{12}=c_{44}=\frac{1}{3}c_{11}$. See L. Brillouin, *Les Tenseurs* (Dover Publications, New York, 1946), Chap. X.



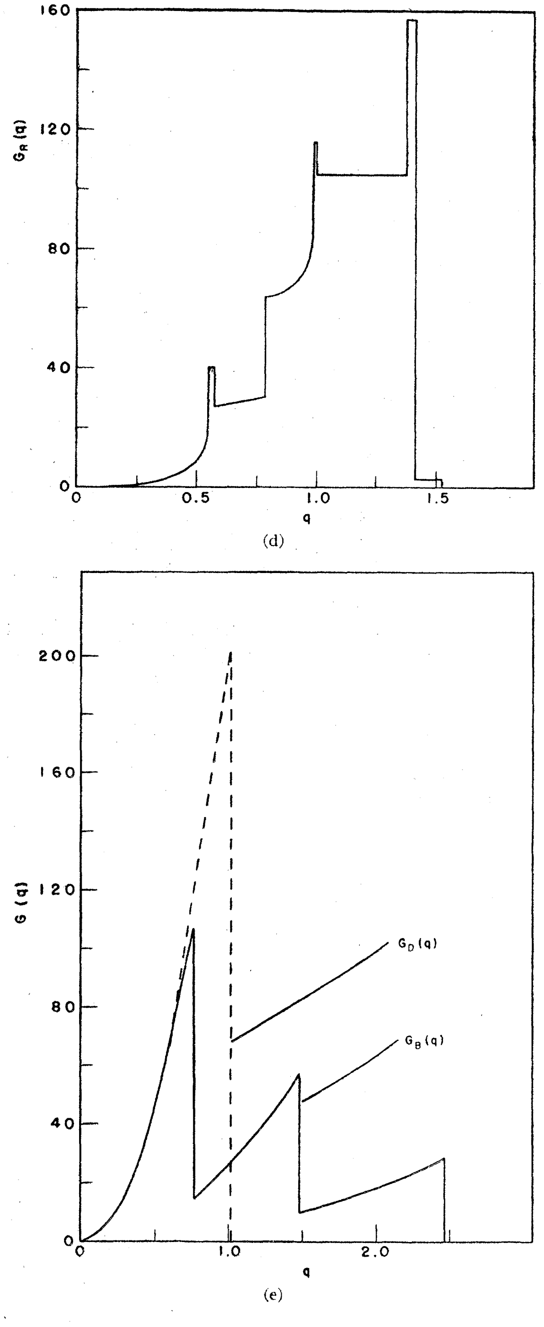


FIG. 1. The frequency spectrum of a body-centered cubic lattice for various models. (For convenience in the calculation, all infinite peaks have been replaced by finite ones of equal area.) The separability condition (1) is used everywhere except in Fig. 1(d), so that $g=\frac{1}{8}$ except in Fig. 1(d), where $g=\frac{1}{3}$. (a) The spectrum $G_H(q)$ given by Houston's original method; (b) The spectrum $G_R(q)$ given by the R approximation to Houston's method; (c) The spectrum $G_T(q)$ given by the T approximation; (d) The spectrum $G_R(q)$ for $g=\frac{1}{3}$; (e) The spectra given by Debye's theory, $G_D(q)$, and by Brillouin's modification, $G_B(q)$, both for the case $g=\frac{1}{8}$.

electron contribution to c_{ij} is c_{ij}^E and the lattice contributes c_{ij}^L, then the total elastic constants are supposed, in this approximation, to be just the sum of electron and lattice terms. Hence we have

$$\begin{gathered} c_{11}=c_{11}^L+c_{11}^E, \quad c_{12}=c_{12}^L+c_{12}^E, \quad c_{44}=c_{44}^L, \\ c_{44}^E=0, \quad c_{11}^E=c_{12}^E; \quad c_{12}^L=c_{44}^L. \end{gathered} \tag{1}$$

This separation of electron and lattice contributions to the elastic constants is very attractive, but one may perhaps question whether it is legitimate. To test the hypothesis some calculations have also been made without assuming the separation. In this case, if we still regard our lattice as defined by two elastic constants, it is reasonable to say that

$$c_{11}^L=c_{11}; \quad c_{44}\leqslant c_{12}^L=c_{44}^L\leqslant c_{12}. \tag{1'}$$

Calculations with the lower limit for c_{44}^L coincide approximately with those made with the separation (1); some calculations with the upper limit, $c_{44}^L=c_{12}$, are also reported. The results with the separation (1) show much better agreement with experiment than those with $c_{44}^L=c_{12}$.

IV. BRILLOUIN'S MODEL FOR THE SPECIFIC HEAT

It is of interest to see how the present calculations compare with those of simpler theories. The two obvious theories available are Debye's well-known theory which treats a lattice as a homogeneous continuum with a maximum frequency cutoff, and a modification due to Brillouin[15] which has a cutoff in wavelength. The reason for Brillouin's modification is that for an isotropic medium it gives the correct number of longitudinal and transverse modes, unlike Debye's theory, which merely gives the correct total number of modes.

The calculation for the present anisotropic case is discussed in Appendix A; the results for the specific heat using the separability condition (1) are given in Fig. 2, which shows the effective Debye temperature Θ as a function of the absolute temperature T for a number of models. According to Debye's theory, the specific heat at constant volume C_v is a function of Θ/T, where Θ is independent of the temperature; it is then usual to express the experimental C_v data at any given T by a value of Θ which is unique, but does in general depend on T.[16]

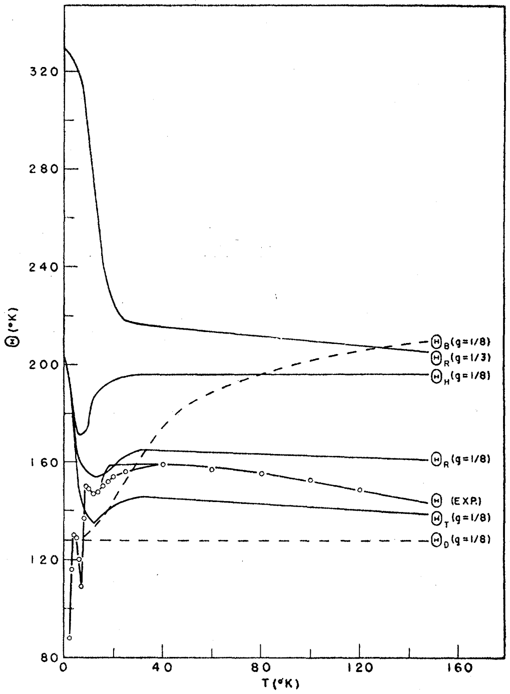


FIG. 2. The effective Debye temperature Θ for sodium, as a function of the absolute temperature T. The Θ's calculated from the spectra of Fig. 1 are compared with the experimental data. (See references 1 and 17.)

All these calculations of the Debye and Brillouin models are based on the lattice elastic constants obtained with the separability condition (1). Using the experimental elastic constants and defining a Debye temperature in terms of them, one gets results which differ very little from the present ones. The reason for this comes from the averaging over velocities used in calculating the Debye temperature.

V. THE SECULAR EQUATION AND ITS ROOTS

A derivation of the secular equation for a body-centered cubic lattice has been given by Fine[3] and by Montroll and Peaslee.[4] It is rather special, and accordingly a method of derivation which may be applied also to noncubic lattices is outlined in Appendix B. The secular equation is the following:

$$\begin{vmatrix} 1-\cos x\cos y\cos z+g\sin^2 x-q^2 & \sin x\sin y\cos z & \sin x\sin z\cos y \\ \sin x\sin y\cos z & 1-\cos x\cos y\cos z+g\sin^2 y-q^2 & \sin y\sin z\cos x \\ \sin x\sin z\cos y & \sin y\sin z\cos x & 1-\cos x\cos y\cos z+g\sin^2 z-q^2 \end{vmatrix}=0, \tag{2}$$

where (x, y, z) are coordinates in the reciprocal lattice, i.e., in the space of wave numbers, and

$$g=\gamma/2\alpha, \quad q^2=(M/8\alpha)\omega^2. \tag{3}$$

M is the mass of an ion, ω the angular frequency of a normal mode, and α and γ are force constants for nearest and second-nearest neighbor interactions. The

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[15] L. Brillouin, *Wave Propagation in Periodic Structures* (McGraw-Hill Book Company, Inc., New York, 1946), article 39.

[16] F. M. Kelly and D. K. C. MacDonald, Can. J. Phys. **31**, 147 (1953).

force constants are connected with the elastic constants of the lattice by the relations

$$c_{11}{}^{L}=(\alpha+\gamma)/a;\quad c_{12}{}^{L}=c_{44}{}^{L}=\alpha/a, \tag{4}$$

where $2a$ is the length of the side of the unit cube; $2a=4.24\times10^{-8}$ cm. The separation of Eq. (1) together with the experimental data for sodium (see Table I) corresponds to $g=\frac{1}{8}$; the condition (1′) gives the limits $\frac{1}{10}\leqslant g\leqslant\frac{1}{3}$. The calculation has been done with $g=\frac{1}{8}$ throughout unless stated otherwise.

Houston's method of calculation[6] is to solve the secular equation (2) along three lines in the reciprocal lattice, denoted by $L.1$, $L.2$, $L.3$:

$$\begin{aligned} L.1:&\quad \mathbf{r}=(0,0,r),\\ L.2:&\quad \mathbf{r}=(0,s,s),\\ L.3:&\quad \mathbf{r}=(t,t,t). \end{aligned} \tag{5}$$

Along each line there are three roots: we denote those along $L.1$ by a, b, c; those along $L.2$ by d, e, f; and those along $L.3$ by g, h, k. The detailed form of these roots is discussed in Appendix C. The solution as a whole has three branches (I, II, III) corresponding to the one longitudinal and two transverse branches in an isotropic medium, and the branches link up the roots as follows:

$$\begin{array}{rccccc} & L.1 & & L.2 & & L.3\\ \text{Branch I:} & a & \text{and} & f & \text{and} & g\\ \text{II:} & b & \text{and} & d & \text{and} & h\\ \text{III:} & c & \text{and} & e & \text{and} & k. \end{array} \tag{6}$$

The detail of the linking is discussed in Appendix C.

VI. THE FREQUENCY SPECTRUM

Along a given line in the reciprocal lattice, the number of modes of vibration in a frequency range, q to $q+dq$, is proportional to the corresponding volume of phase space, that is, to

$$r^2(dr/dq)dq,$$

where $r=r(q)$ is the wave number along the line corresponding to the frequency q. For the total lattice there are $G(q)dq$ modes of vibration in this frequency range, and, apart from a normalization factor, $G(q)$ is given by the expression[17]

$$\begin{aligned} G(q)&=\Sigma_{\Lambda}G^{\Lambda}(q),\\ G^{\Lambda}(q)&=0.359r^2(dr/dq)|_{\Lambda}+1.624s^2(ds/dq)|_{\Lambda}\\ &\qquad+1.679t^2(dt/dq)|_{\Lambda}, \end{aligned} \tag{7}$$

where $\Lambda=$ I, II, III, and

$$\begin{aligned} &r^2(dr/dq)|_{\text{I}}=r^2(dr/dq) \text{ for root } a,\\ &r^2(dr/dq)|_{\text{II}}=r^2(dr/dq) \text{ for root } b, \text{ and so on;}\\ &t^2(dt/dq)|_{\text{III}}=t^2(dt/dq) \text{ for root } k. \end{aligned}$$

The $G^{\Lambda}(q)$ are the contributions of the three branches I, II, III to the distribution function $G(q)$. The reason for considering the branches separately is to make the corrections suggested by Nakamura. The detailed expressions for $r^2(dr/dq)$, etc., are given in Appendix C.

Now we can immediately derive the frequency spectrum $G_H(q)$ according to Houston's original procedure. In general each $G_H{}^{\Lambda}(q)$ will have three singularities corresponding to the maximum frequencies along the three lines $L.1$–$L.3$. Two or more of these critical frequencies may coincide, and root g is anomalous. The result for $G_H(q)$ is given in Fig. 1(a).

Nakamura[7] has given a detailed examination of Houston's method for the case of a square two-dimensional lattice which has been solved exactly by Montroll. He finds that in this case Houston's method gives the low-frequency behavior correctly for each branch, deviates somewhat in the shape of $G(q)$ at the first peak (i.e., the peak of lowest frequency) on each branch, and is completely wrong above the first peak on each branch, in fact, the frequency spectrum falls off continuously above the first peak to zero at the maximum frequency predicted by Houston's method.

These features are probably fairly characteristic of the method. If one is interested only in properties like the specific heat the method seems usable, because here one is most concerned with the detailed behavior of $G(q)$ at low frequencies, and apart from this one may be satisfied with a knowledge of the location of the discontinuities in $G(q)$ and in the total number of modes between the discontinuities. This area is given correctly by Houston's method, being just composed of terms of the form

$$\int_{q_1}^{q_2} r^2\frac{dr}{dq}dq=\tfrac{1}{3}(r_2{}^3-r_1{}^3).$$

The method used here is the following. We study each branch Λ (I, II, III) separately. Consider a branch Λ with the roots α, β, γ (e.g., the roots b, d, h along branch II). Let root α have a singularity in $r^2(dr/dq)$ at $q=q_\alpha$, and similarly, let β, γ have singularities at q_β, q_γ where $q_\alpha<q\beta<q_\gamma$ (the generalization to any other case, such as root g of branch I, is immediate). Then Houston's method gives the following properties at least approximately correctly:

(1) $G^{\Lambda}(q)$ for $0\leqslant q\leqslant q\alpha$;
(2) the positions of q_β, q_γ; and
(3) the areas

$$A_{\beta\alpha}=\int_{q_\alpha}^{q_\beta}G_\beta{}^{\Lambda}(q)dq;\quad A_{\gamma\alpha}=\int_{q_\alpha}^{q_\gamma}G_\gamma{}^{\Lambda}(q)dq,$$

where $G_\beta{}^{\Lambda}(q)$ is the contribution to $G^{\Lambda}(q)$ due to root β, etc.; thus

$$G^{\Lambda}(q)=G_\alpha{}^{\Lambda}(q)+G_\beta{}^{\Lambda}(q)+G_\gamma{}^{\Lambda}(q),$$

i.e., $G_\alpha{}^{\text{I}}(q)=0.359r^2(dr/dq)$ for root a (of branch I).

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[17] Equation (7) is essentially Houston's Eq. (11) (reference 6). I am indebted to Dr. Houston for sending me a list of corrections to his article.

By analogy with Montroll's and Nakamura's results, we represent $G^{\Lambda}(q)$ for $q>q_{\alpha}$ by functions without singularities at q_{β}, q_{γ} but having the properties (2), (3) given by Houston's solution. In particular, we use two simple forms which appear fairly plausible by analogy with Nakamura's work.

Approximation R (rectangle): replace $G_{\beta}{}^{\Lambda}(q)$ by a rectangle of area $A_{\beta\alpha}$ lying between q_{α} and q_{β}, and similarly for $G_{\gamma}{}^{\Lambda}(q)$.

Approximation T (triangle): replace $G_{\beta}{}^{\Lambda}(q)$ by a triangle of area $A_{\beta\alpha}$ lying between q_{α} and q_{β}, such that its peak is at q_{α}, i.e., its height is $2A_{\beta\alpha}/(q_{\beta}-q_{\alpha})$ at q_{α} and zero at q_{β}; and a similar expression for $q_{\gamma}{}^{\Lambda}(q)$.

The results for $G_R(q)$ and for $G_T(q)$ are given in Figs. 1(b) and 1(c). They may be compared with $G_H(q)$ given by the original calculation by Houston's method. For convenience in calculation the infinite peaks in $G(q)$ have been replaced by finite ones having the same area. The curves in Figs. 1(a)–1(c) refer to $g=\frac{1}{8}$, corresponding to the assumption of separability of electron and lattice contributions to the elastic constants, as implied in Eq. (1).

VII. THE SPECIFIC HEAT

In giving the specific heat at constant volume C_v as a function of the absolute temperature T, it is usual to plot an effective Debye temperature Θ, which depends on T, as a function of T, because this Debye temperature is a sensitive criterion, and one of some physical significance, at least for $\Theta\gtrsim T$. The results, based on the separability condition (1), are given in Fig. 2 for a number of models. We give first the Debye temperature obtained from measurements of the specific heat.[1] Then the effective Θ of Debye's and Brillouin's models, as predicted from the elastic constants, are given (see Sec. IV and Appendix A). Also there are three Θ's coming from the three approximations used here, namely Θ_H, Θ_R, Θ_T, resulting from $G_H(q)$ [i.e., Houston's original picture—see Fig. 1(a)], from $G_R(q)$ [Fig. 1(b)] and from $G_T(q)$ [Fig. 1(c)], respectively. From the shapes of the $G(q)$ it is clear that we must have $\Theta_H\geqslant\Theta_R\geqslant\Theta_T$, and by comparison with Nakamura's discussion one would expect the exact $G(q)$ to lie somewhere between $G_R(q)$ and $G_T(q)$, and hence one would also expect the exact Θ to lie somewhere between Θ_R and Θ_T.

All the calculations discussed above refer to the case where the separation of elastic constants into ionic (lattice) and electronic terms is made as suggested by Fuchs[13] and Leighton;[5] thus, $g=\frac{1}{8}$. To test the validity of this separation, we proceed as suggested in Sec. III. If we still wish to describe the lattice by two elastic constants, $c_{11}{}^L$ and $c_{12}{}^L=c_{44}{}^L$, but without assuming the separability condition of Eq. (1), then we have to take the limits of Eq. (1′), which give $\frac{1}{10}\leqslant g\leqslant\frac{1}{3}$. The frequency spectrum calculated on the R approximation with $g=\frac{1}{3}$ is given in Fig. 1(d), and the corresponding specific heat, or rather Θ_R, is given in Fig. 2. We see there, by comparison with the experimental Θ, that $g=\frac{1}{8}$ gives a much more satisfactory result than $g=\frac{1}{3}$, so that there is certainly no evidence against the separation of Eq. (1).

One feature of the theory which is mentioned by Nakamura[18] is that if one puts $g=0$, i.e., considers only interactions of an ion with its nearest neighbors, then Houston's method does not give a very good frequency spectrum because there are too many modes of zero frequency; in fact, the frequency of the first peak in $G(q)$ is proportional to $g^{\frac{1}{2}}$. There is no reason to suppose that this feature is peculiar to Houston's method of evaluation; in fact, if one considers only nearest-neighbor interactions there are many modes of zero frequency, as can be seen by examining the secular equation. From physical reasoning it would seem that the case $g=0$ might be taken to correspond to a liquid, as representing only extreme short-range order; and it might perhaps be possible to use this kind of treatment in discussing some properties of liquids. In this picture the physical meaning of the modes of zero frequency is that they correspond to flow rather than to vibrational motion.

The precise meaning of the results given in Fig. 2 has to be discussed in some detail. As was pointed out in Sec. I, only the range 10°K $\leqslant T\leqslant$ 100°K is strictly relevant for comparison with experiment. C_v has a peak at 7°K, and also it exceeds the classical value $3Nk$ above 206°K, and the fall in Θ above 100°K is due to this. Besides, for $T=120$°K, C_v is already 5.5 cal/M degree, so that a very small error in C_v introduces a large but not particularly significant error in Θ. From the admissible region between 10° and 100°K it is clear that $g=\frac{1}{8}$ gives better reults than $g=\frac{1}{3}$, and that the experimental Θ value lies between Θ_R and $\&_T$ as one might expect, in particular, Θ_R (which comes from $G_R(q)$, which is actually the simplest function to use) gives the best approximation.

In general, one is particularly interested in the character of the lattice specific heat corresponding to temperatures of less than 10°K in the present case, because this is where the specific form of the frequency spectrum is most important. The general features of the frequency spectrum shown in all the models used here are the same, and are of the character usually found in calculations of this type. Generally these give $G(q)$ proportional to q^2 at low frequencies as in the simple Debye theory, but with a number of peaks at higher frequencies. In consequence of this the present curves of Θ *vs* T are similar to other such calculations,[3,5,6] with a relatively high value near $T=0$, then a minimum, and finally a rise to a constant value. For $g=\frac{1}{8}$ there are slight falls in Θ_R, Θ_T above 30°K, but these are probably not particularly significant.

It is clear[7,9] that Houston's method, even with modifications like those used here, does not give a particularly accurate expression for the frequency

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[18] S. Huzinaga, Busseiron Kenkyu (Japanese report of chemical physics in Japanese) No. **20**, 117 (1949).

spectrum. However, the R approximation to $G(q)$ in particular gives a fairly satisfactory approximation to the Born-v. Karman frequency spectrum, with considerably less computational work than any other comparable method suggested so far, and this feature may make it suitable for various other applications. For instance, in the present case the elastic constants of sodium are not known very accurately, and also it seemed desirable to check the validity of the separability condition (1). Again, in many applications like the present, the deviations of the frequency spectrum from the simple Debye form give only a small correction to most observable effects, so that a fairly simple correction like the present one might be quite useful. Further, an approximation like the present one can be improved with relatively little work if the secular equation is solved along more than three lines in the reciprocal lattice.

I should like to thank Dr. D. K. C. MacDonald, who suggested this problem to me, Dr. W. Kohn, Dr. E. W. Montroll, and Dr. T. Y. Wu for helpful discussions.

APPENDIX A. BRILLOUIN'S MODEL FOR THE SPECIFIC HEAT

Given a mode Λ with sound velocity v_Λ, we may obtain the corresponding characteristic temperature Θ_Λ by

$$\Theta_\Lambda = v_\Lambda \cdot \frac{h}{k} \cdot \left(\frac{3N}{4\pi V}\right)^{\frac{1}{3}}, \tag{A.1}$$

if there are N atoms in a volume V. By Debye's theory there is a single characteristic temperature Θ_D determined by a mean velocity $\bar{v}$ defined by

$$\frac{1}{\bar{v}^3} = \frac{1}{3}\left(\frac{1}{v_{\mathrm{long}}^3} + \frac{2}{v_{\mathrm{trans}}^3}\right); \quad \text{or} \quad = \frac{1}{3}\cdot\frac{1}{4\pi}\sum_{\Lambda=\mathrm{I}}^{\mathrm{III}} \int \frac{d\Omega}{v_\Lambda^3}. \tag{A.2}$$

Thus, if the Debye function for the specific heat of N atoms is $C_v(\Theta_D/T)$, then Brillouin's formula for the specific heat of an isotropic medium is

$$C_v(\Theta_B/T) = \tfrac{1}{3}C_v(\Theta_{\mathrm{long}}/T) + \tfrac{2}{3}C_v(\Theta_{\mathrm{trans}}/T), \tag{A.3}$$

where Θ_{long}, Θ_{trans} are defined in terms of the velocities of the longitudinal and transverse vibrations. In general, Θ_B as defined by Eq. (A.3) will change with temperature.

The procedure used here is the following. From the secular equation we can calculate the velocities $v(\Lambda; Lj)$ for all three branches $\Lambda = \mathrm{I}, \mathrm{II}, \mathrm{III}$, along the lines $L.1$–$L.3$ of Eq. (5). Then we define mean velocities v_Λ by the relations

$$\frac{1}{v_\Lambda^3} = \frac{0.286}{[v(\Lambda; L.1)]^3} + \frac{0.457}{[v(\Lambda; L.2)]^3} + \frac{0.257}{[v(\Lambda; L.3)]^3}. \tag{A.4}$$

The coefficients are derived from Houston's analysis; they are the same as those for the corresponding r^2dr/dq [see Eq. (7)—the difference in the numerical factors arises because $r = \sqrt{2}s = \sqrt{3}t$]. From the v_Λ we get the corresponding Θ_Λ by using Eq. (A.1), and then

$$C_v(\Theta_B/T) = \tfrac{1}{3}\sum_{\Lambda=\mathrm{I}}^{\mathrm{III}} C_v(\Theta_\Lambda/T). \tag{A.5}$$

With the lattice elastic constants determined by the separability condition (1), one finds that $\Theta_{\mathrm{I}} = 304$°K, $\Theta_{\mathrm{II}} = 181$°K, $\Theta_{\mathrm{III}} = 93.5$°K. Defining Θ_D by means of v_D, where

$$\frac{1}{v_D^3} = \frac{1}{3}\sum_{\Lambda=\mathrm{I}}^{\mathrm{III}} \frac{1}{v_\Lambda^3},$$

we find that $\Theta_D = 128$°K. The frequency spectrum corresponding to the Debye and Brillouin models is given in Fig. 1(e), with the same normalization as for the other $G(q)$; the corresponding values of Θ_D, Θ_B are given in Fig. 2.

APPENDIX B. DERIVATION OF THE SECULAR EQUATION

For a substance containing only one kind of atom it is frequently possible to find a lattice with a unit cell containing only one atom on the average. Such a lattice is called a Bravais lattice. Physically this means that we have a lattice made up of unit cells each having just three degrees of freedom. In a crystal these three degrees of freedom are the so-called acoustic vibration: they correspond to the translational motion of the individual atoms in the gas phase. If there are two atoms in a unit cell, then of the six degrees of freedom, three are acoustic, corresponding to motion of the unit cell as a whole, while the remaining three specify the motion of one of the two atoms in the cell with respect to the other. This corresponds to the internal molecular rotation and vibration of the molecule in the gas phase. It contributes the "optic" branch of the lattice vibrations. (The extension to more than two atoms per unit cell is trivial.) In general, simple monatomic lattices have only an acoustic vibration, just as simple monatomic gases have only translational degrees of freedom.

It seems desirable to keep the above basic fact in mind. In a simple cubic lattice the unit cube is just the unit cell of the Bravais lattice, but in a body-centered cubic lattice, if one takes the elementary cube as basis one again, the unit cell contains two atoms. If the cyclic boundary conditions are applied to this cube, one obtains a 6×6 secular equation which may be factored into two (essentially equivalent) 3×3 determinants. This is basically the procedure adopted by Fine[3] and by Montroll and Peaslee[4] in their derivation of the secular equation of a body-centered cubic lattice.[19] The derivation is correct, but it is not clear how it should

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[19] They made use of the fact that a body-centered cubic lattice may be made up of two interpenetrating simple cubic lattices. By applying the cyclic boundary conditions independently to each of these simple cubic lattices, they got a 6×6 secular determinant.

be generalized to a noncubic crystal structure. This generalization is immediate if one imposes the cyclic conditions on a minimal (i.e., Bravais) unit cell.

Consider a body-centered cubic lattice with cube length $2a$, and take an ion at the point $a(l, m, n)$ as central, where l, m, n are integers. The nearest neighbors of the central ion are at $a(l\pm 1, m\pm 1, n\pm 1)$ (for any choice of the ± signs), and its second-nearest neighbors are at $a(l\pm 2\, m, n)$; $a(l, m\pm 2, n)$; $a(l, m, n\pm 2)$. This description in terms of the conventional unit cube may be called the C system; the unit cell contains two atoms. The Bravais or minimal unit cell (in the B system) is defined by the central ion and any three of its eight nearest neighbors. Let

$$\boldsymbol{\tau}^1=a(-1, 1, 1), \quad \boldsymbol{\tau}^2=a(1, -1, 1), \quad \boldsymbol{\tau}^3=a(1, 1, -1),$$

be the unit vectors defining the B system. Then, in the B system the position of a point is defined by the relation

$$a(\lambda, \mu, \nu)=\lambda\boldsymbol{\tau}^1+\mu\boldsymbol{\tau}^2+\nu\boldsymbol{\tau}^3.$$

The detailed correspondence between the naming in the C and the B system is given in Table II. With the uniform notation given there, if we use a shorthand notation of the type

$$u(a-2)=u(a)+u(\bar{a})-2u(0), \quad \text{etc.},$$

the equations of motion are

$$\begin{aligned}F_x(0)&=\alpha u_x(a+b+c+d-8)+\gamma u_x(e-2)\\&\quad+\kappa u_y(-a-b+c+d)+\kappa u_z(-a+b-c+d),\\F_y(0)&=\alpha u_y(a+b+c+d-8)+\gamma u_y(f-2)\\&\quad+\kappa u_z(a-b-c+d)+\kappa u_x(-a-b+c+d),\\F_z(0)&=\alpha u_z(a+b+c+d-8)+\gamma u_z(g-2)\\&\quad+\kappa u_x(-a+b-c+d)+\kappa u_y(a-b-c+d).\end{aligned} \tag{A.6}$$

These are just Eq. (4) of Montroll and Peaslee,[4] apart from the notation; the Cauchy condition will give $\kappa=\alpha$.

The classical macroscopic equations of motion are

$$\rho\ddot{u}_x=c_{11}\frac{\partial^2 u_x}{\partial x^2}+c_{44}\left(\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)u_x$$
$$+(c_{12}+c_{44})\left(\frac{\partial^2 u_y}{\partial x_y}+\frac{\partial^2 u_z}{\partial x_z}\right),$$

etc., and if we identify these u's, which are small but macroscopic displacements, with the previous $u(0)$, $u(a)$, $\cdots$, which are displacements of individual lattice points, and use results of the kind

$$du/dx=(1/a)[u(l+1, m, n)-u(l, m, n)],$$

then we get the identification

$$c_{11}{}^L=(\alpha+\gamma)/a; \quad c_{12}{}^L=c_{44}{}^L=\alpha/a=\kappa/a. \tag{4}$$

TABLE II. Correspondence between the labeling of lattice points in C (cube) and B (Bravais) systems.

C system	Uniform notation	B system
Central lattice point:		
(l, m, n)	0	(λ, μ, ν)
Nearest neighbors:		
$(l\mp 1, m\pm 1, n\pm 1)$	$a, \bar{a}$	$(\lambda\pm 1, \mu, \nu)$
$(l\pm 1, m\mp 1, n\pm 1)$	$b, \bar{b}$	$(\lambda, \mu\pm 1, \nu)$
$(l\pm 1, m\pm 1, n\mp 1)$	$c, \bar{c}$	$(\lambda, \mu, \nu\pm 1)$
$(l\pm 1, m\pm 1, n\pm 1)$	$d, \bar{d}$	$(\lambda\pm 1, \mu\pm 1, \nu\pm 1)$
Second-nearest neighbors:		
$(l\pm 2, m, n)$	$e, \bar{e}$	$(\lambda, \mu\pm 1, \nu\pm 1)$
$(l, m\pm 2, n)$	$f, \bar{f}$	$(\lambda\pm 1, \mu, \nu\pm 1)$
$(l, m, n\pm 2)$	$g, \bar{g}$	$(\lambda\pm 1, \mu\pm 1, \nu)$

Now we apply the cyclic boundary conditions as follows:

$$\begin{aligned}&u(\lambda, \mu, \nu)=u(0, 0, 0)\exp[i(\lambda\chi^1+\mu\chi^2+\nu\chi^3)],\\&\chi^j=\pi\lambda^j/L^j;\ \lambda^j\ \text{integers}:\ -L^j\leqslant\lambda^j\leqslant L^j;\ j=1, 2, 3;\end{aligned} \tag{A.7}$$

considering a macroscopic tetrahedron with L^j ions in the $\boldsymbol{\tau}^j$ direction. The (χ^j) are vectors in a space reciprocal to the B system. In terms of them,

$$\begin{aligned}u(a)&=u(0)\exp(i\chi^1),\\u(a-2)&=-2u(0)(1-\cos\chi^1), \quad \text{etc.}\end{aligned}$$

One now transforms the (χ^j) into (x, y, z), which form a vector in a space reciprocal to the C system. Using the relation

$$\begin{bmatrix}x\\y\\z\end{bmatrix}=\tfrac{1}{2}\begin{bmatrix}0&1&1\\1&0&1\\1&1&0\end{bmatrix}\cdot\begin{bmatrix}\chi^1\\\chi_2\\\chi^3\end{bmatrix},$$

and the condition

$$\ddot{u}=-\omega^2 u$$

for harmonic vibrations, one obtains the secular Eq. (2), which is just Montroll and Peaslee's Eq. (11a).

The derivation sketched here can readily be adapted to other lattices; in particular, Leighton's expression for a face-centered cubic lattice[5] can be derived quite similarly, whereas the method of Montroll and Peaslee[4,19] would entail setting up a 12×12 secular determinant, which can then be factored into four 3×3 determinants.

APPENDIX C. THE ROOTS OF THE SECULAR EQ. (2)

(C.1) We wish to solve the secular equation along the three lines $L.1$–$L.3$ of Eq. (5). Along $L.1$, the secular Eq. (2) is

$$\begin{vmatrix}1-\cos r-q^2&0&0\\0&1-\cos r-q^2&0\\0&0&1-\cos r+g\sin^2 r-q^2\end{vmatrix}=0,$$

because $x=y=0$, $z=r$, along $L.1$.

The third factor along the diagonal gives the single root (a),

$$\cos r=(Q-1)/2g: \quad Q^2=(1+2g)^2-4gq^2,$$

and the other two factors give a double root, denoted by (*b*) and (*c*),

$$q/\sqrt{2}=\sin(r/2).$$

Along *L*.2 we find, similarly, three roots (*d*), (*e*), (*f*),

root (*d*): $q=\sin s.$

root (*e*): $q/\sqrt{g}=\sin s.$

root (*f*): $q/(2+g)^{\frac{1}{2}}=\sin s.$

Along *L*.3 we have to solve a cubic equation. By putting

$$x=1-\cos^3 t+g\sin^2 t-q^2;\quad A=\sin^2 t\cos t,$$

the secular equation reduces to the form

$$\begin{vmatrix} x & A & A \\ A & x & A \\ A & A & x \end{vmatrix}=0$$

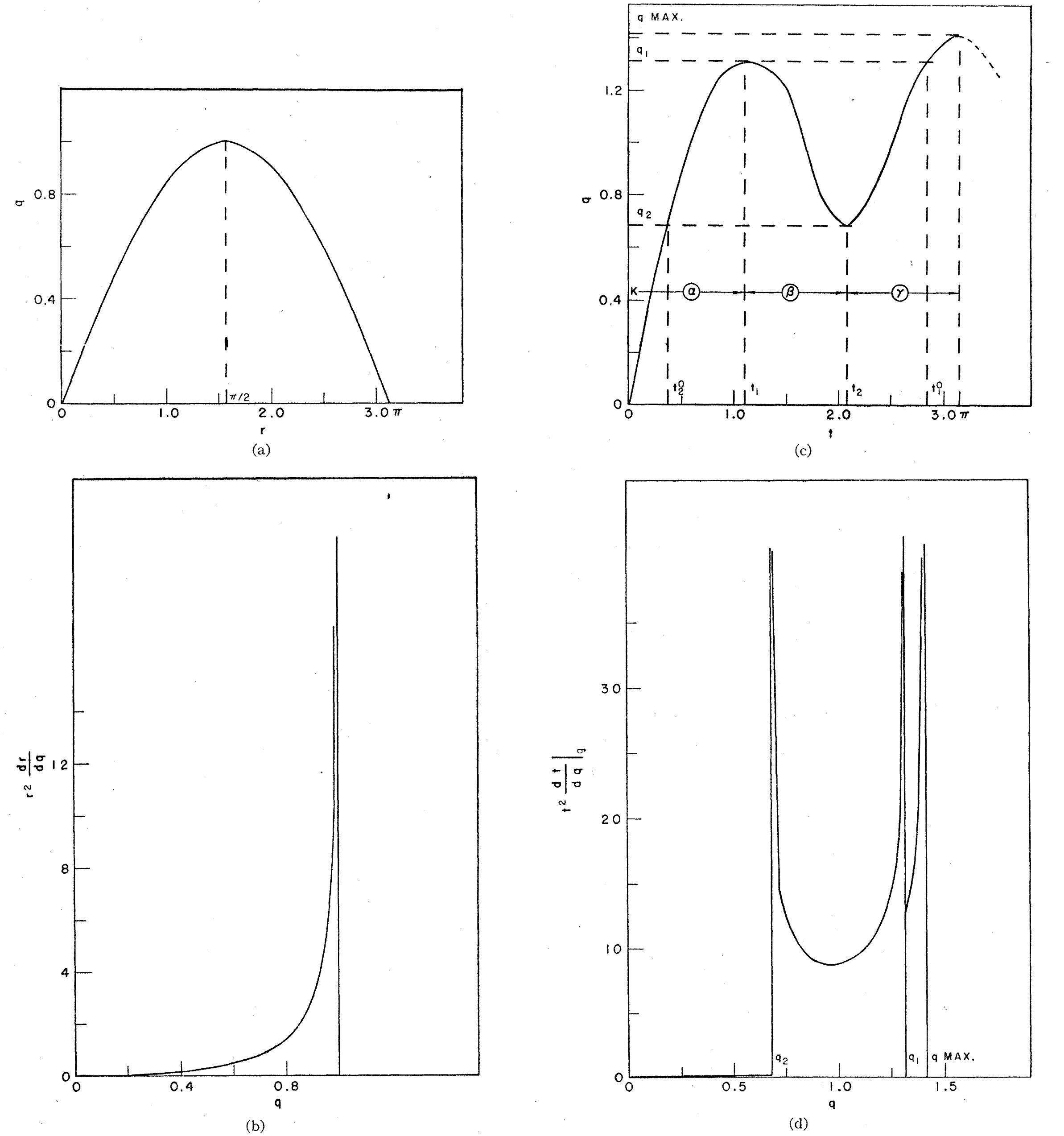

FIG. 3. The roots of the secular equation. (a) Frequency q as a function of wave number r for root (*d*), actually any root of type (1) or (2) of Appendix C shows similar behavior; (b) the density function r^2dr/dq as a function of q for root (*d*); (c) frequency q as a function of wave number t for root (*g*); and (d) the density function t^2dt/dq as a function of q for root (*g*).

which has the single root (g), $x=-2A$, and the double root (h), (k) given by $x=A$. Explicitly,

$$q^2=1+g+2\cos t-g\cos^2 t-3\cos^3 t$$

for root (g); this is rather a curious function. For roots (h) and (k),

$$\cos t=(Q-1)/2g;$$

[see root (a), above].

(C.2) Now we must link up the nine roots $(a)\cdots(k)$ into three branches I, II, III. To link up the solutions along $L.1$ with those along $L.2$, we solve the secular equation in the plane

$$(0,ak,k):\quad 0\leqslant a\leqslant 1;\quad k\text{ small.}$$

In this plane, $\cos x=1$; $\sin x=0$; $\cos y=1-\tfrac{1}{2}a^2k^2$; $\sin y=ak$; etc., so the secular Eq. (2) becomes

$$\begin{vmatrix} \tfrac{1}{2}(1+a^2)-q^2/k^2 & 0 & 0 \\ 0 & \tfrac{1}{2}(1+a^2)+ga^2-q^2/k^2 & a \\ 0 & a & \tfrac{1}{2}(1+a^2)+g-q^2/k^2 \end{vmatrix}=0. \qquad \text{(A.8)}$$

Consider the single root of Eq. (A.8)

$$q=k[\tfrac{1}{2}(1+a^2)]^{\frac{1}{2}}.$$

Along $L.1$, $k=r$, $a=0$; $q=r/\sqrt{2}$ —root (b) or (c).

Along $L.2$, $k=s$, $a=1$; $q=s$ —root (d).

One proceeds similarly for the other two roots of (A.8), and also for the planes defined by $L.2$ and $L.3$, and $L.3$ and $L.1$. This method of linking up roots is justified because all three branches of the solution are regular near the origin. The final result is displayed in Eq. (6); the labeling of the branches I, II, III is of course arbitrary.

(C.3) The character of most of the roots is very simple, namely, (See Table I)

Type (1): $q/A=\sin(Br)$,

$$\frac{r^2dr}{dq}=\frac{[\sin^{-1}(q/A)]^2}{B^3A[1-(q/A)^2]^{\frac{1}{2}}},$$

TABLE III. The roots of the secular Eq. (2), for the case $g=1/8$.

Root	a	$b=c$	d	e	f	g	$h=k$
Branch	I	II, III	II	III	I	I	II, III
Type	(ii)	(i)	(i)	(i)	(i)	*	(ii)
q(max)	$\sqrt{2}$	$\sqrt{2}$	1	0.3535	1.458	$\sqrt{2}$	$\sqrt{2}$

* Root g is anomalous: see Figs. 3(c) and 3(d). For $g=1/8$, $q_2=0.683$; $q_1=1.314$; $t_1=1.095$; $t_2=2.08$; $t_2{}^0=0.36$; $t_1{}^0=2.81$.

for roots (b), (c), (d), (e), (f); and

Type (2): $\cos r=(Q-1)/2g$,

$$\frac{r^2dr}{dq}=\frac{2q\cdot\{\cos^{-1}[(Q-1)/2g]\}^2}{Q\{1-[(Q-1)/2g]^2\}^{\frac{1}{2}}},$$

for roots (a), (h), (k).

For roots of type (1) or (2), q increases monotonically with r up to a maximum value which corresponds to $r=\pi/2B$ for type (1), and to $r=\pi$ for type (2); beyond this maximum the whole curve of $q=q(r)$ is just repeated with a suitable inversion. The general form of $q(r)$ and of r^2dr/dq for this case is shown in Figs. 3(a) and (b); the area under the curve of r^2dr/dq is, of course, just $\tfrac{1}{3}r_{\max}{}^3$.

The behavior of root (g) is peculiar: $q(t)$ is shown in Fig. 3(c), and t^2dt/dq is shown in Fig. 3(d). Explicitly, t^2dt/dq is given by the following expression:

$$t^2dt/dq=\begin{cases} t^2dt/dq\,|_\alpha\ [\text{read: } t^2dt/dq \text{ in the region } \alpha \text{ of Fig. } 3\text{(d)}] \text{ for } 0\leqslant q\leqslant q_2;\ 0\leqslant t\leqslant t_2{}^0. \\ t^2dt/dq\,|_\alpha+t^2dt/dq\,|_\beta+t^2dt/dq\,|_\gamma \text{ for } q_2\leqslant q\leqslant q_1;\ t_2{}^0<t<t_1{}^0. \\ t^2dt/dq\,|_\gamma \text{ for } q_1\leqslant q\leqslant q_{\max};\ t_1{}^0\leqslant t\leqslant\pi. \end{cases}$$

Along $L.1$, the turning point of $q(r)$ is $r=\pi$; along $L.2$, it is $s=\pi/2$, and along $L.3$, $t=\pi$. The turning point must of course be the same for all roots along a given line; it may be identified with the boundary of the first Brillouin zone along the line in question. The curves of q as a function of r are just the usual ones of frequency as a function of wave number.