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Frequency Spectrum of Crystalline Solids

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It is generally accepted that a normal crystalline solid can be pictured at absolute zero as an assembly of molecules arranged at periodically placed lattice points. Since at higher temperatures each molecule becomes a harmonic oscillator about its lattice point, in order to calculate thermodynamic properties of the crystal it is necessary to know the distribution of its internal normal modes of vibration. On the basis of the Born-von Kármán model these normal modes of vibration are roots of a secular determinant. In this paper it is shown that the $2n$ th moment of the distribution function of normal modes is proportional to the trace of the n th power of the matrix of the Born-von Kármán determinant. By expressing the dis-

tribution function as a linear combination of Legendre polynomials it is shown that the coefficient of each polynomial is a linear combination of the moments. The frequency distribution function of a two-dimensional simple cubic lattice is calculated by the above method and turns out to have two maxima. Usually the equation for a thermodynamic function $F(T)$ involves the integral of the product of the frequency distribution function $g(\nu)$ and a known function $K(T, \nu)$. We show here that when $F(T)$ is a known function of T an integral equation results with $g(\nu)$ under the integral sign. This integral equation can be solved for $g(\nu)$ by use of Fourier transforms.

I. INTRODUCTION

ONE of the failures of classical mechanics and classical statistics was their inability to explain even qualitatively the decrease in specific heat of solids with decreasing temperatures; and one of the selling points of Planck's original quantum theory had its source in the success of Einstein's¹ application of Planck's "quantized oscillators" to the lattice vibrations of a solid. By Einstein's method the vibrational factor of the partition function of a normal crystal is

$$Q = \prod_{i=1}^{3N} \frac{\exp(-h\nu_i/2kT)}{1 - \exp(-h\nu_i/kT)} \quad (1)$$

and the Einstein assumption of equal numerical value of all $3N$ frequencies of a crystal explains the observed decrease of the specific heat below the Dulong-Petit value of $3NkT$ at low temperatures. Here h = Planck's constant, k = Boltzmann's constant, T = absolute temperature, ν_i = frequency of the i th normal mode of vibration, N = number of lattice points.

Refinements in specific heat measurements in the first decade of this century demonstrated that the agreement between experiments and Einstein's theory was not quantitative at low

temperatures; and Debye² and Born and von Kármán³ pointed out that the discrepancies were probably due to the existence of a distribution of normal modes of vibration instead of a single "Einstein frequency." Thus, for example, the temperature dependent vibrational contribution per lattice point to the free energy should be written⁴

$$F_V(T) = -kT \int_0^\infty g(\nu) \log(1 - e^{-h\nu/kT}) d\nu, \quad (2)$$

where $g(\nu)d\nu$ is the fraction of normal modes with frequencies between ν and $\nu + d\nu$.

Debye's proposition to treat the solid as a continuum with the same elastic properties led to a frequency distribution proportional to ν^2 and to equations of physical quantities in terms of a parameter $\Theta = h\nu_L/k$ which theoretically should be a constant for a given crystal. The term ν_L is the largest frequency of the normal modes of vibration, and Θ is usually referred to as the Debye or characteristic temperature. Unfortunately this development which mathematically is quite simple is insufficient, for experiments

² P. Debye, *Ann. d. Physik* **39**, 789 (1912).

³ M. Born and T. von Kármán, *Physik. Zeits.* **13**, 297 (1912); **14**, 15 (1913).

⁴ For a general discussion of theory of normal solids cf. E. Schroedinger, *Handbuch der Physik* (1926), Vol. 10; M. Born and M. Göppert-Mayer, *Handbuch der Physik* (1933), Vol. 24; R. Fowler, *Statistical Mechanics* (1936), Chap. 4.

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¹ A. Einstein, *Ann. d. Physik* **22**, 180 (1906); **34**, 170 (1911).

show that Θ is not constant over a large temperature range.

The extension of Born and von Kármán of Einstein's work afforded a more accurate physical picture than that suggested by Debye. However, it led to a mathematical problem which could be solved analytically for a one-dimensional solid but which required tedious numerical calculations in two- and three-dimensional crystals. In the Born-von Kármán theory one sets up the equations of motion for a set of coupled oscillators with the same coupling and force constants as those of the crystal, and shows that the normal modes of vibration are the characteristic roots of a secular determinant of order N^3 . Actually the determinant can be factored into secular determinants of very small order, but to find $g(\nu)$ by present methods the roots of all the resulting equations (and there are $O(N^3)$ of these) must be calculated and the number of roots in every small frequency interval must be determined. Even though it seems reasonable to base the $g(\nu)$ computations on the solution of a large random sample of cubic equations, the lack of popularity of the Born-von Kármán approach is understandable.

The first part of this paper will be devoted to developing an analytical method of finding $g(\nu)$ in a Born-von Kármán crystal. This method will depend on the matrix theorem that the sum of the k th powers of the characteristic values of a matrix is equal to the trace of the k th power of the matrix. Noticing that the sum of the k th powers of the characteristic values of the Born-von Kármán matrix is proportional to the k th moment of $g(\nu)$, and that a continuous distribution function defined in a finite interval can be expanded as a linear combination of Legendre polynomials, it is apparent that the coefficients of the Legendre polynomials can be expressed as linear combinations of the moments of $g(\nu)$. This means that $g(\nu)$ can be expressed analytically as a function of the lattice constants of the crystal.

These observations will be applied in detail to a two-dimensional cubic lattice, postponing to some later date the application (which is not much more difficult) to real three-dimensional crystals.

The second part of this paper will concern the determination of $g(\nu)$ from experimental specific heat data by use of Fourier transforms.

II. $g(\nu)$ FOR THE BORN-VON KÁRMÁN MODEL

1. Mathematical Techniques

The possible frequencies of normal modes of vibration in a Born-von Kármán crystal will be shown in the next section to be roots of a secular determinant (see Eq. (17a)) and two approaches to the problem of deriving their distribution from the determinant are: (a) by calculating all or a large random sample of its roots and counting the number in each small frequency interval; (b) by evaluating the moments of the distribution function and from the moments determining the distribution.

Blackman's⁵ researches have demonstrated that the first method involves the solution of a large collection of quadratic or cubic equations and thus an enormous amount of tedious numerical work—and further, they show that the computation must be repeated for every set of lattice parameters, so method (a) cannot easily show the influence of changes in lattice parameters on changes in physical properties. Here we shall devise a technique based on the second approach which avoids tedious numerical work.

Let \mathbf{M} be the matrix of a symmetrical secular determinant whose roots are $\{\lambda_i\}$. Then

$$\mathbf{M}\psi_i = \lambda_i\psi_i, \quad (1)$$

where ψ_i is the i th characteristic vector of the matrix, and λ_i is the corresponding characteristic value. Multiplication of both sides of (1) by \mathbf{M} yields

$$\begin{aligned} \mathbf{M}^2\psi_i &= \mathbf{M}\lambda_i\psi_i = \lambda_i\mathbf{M}\psi_i \\ &= \lambda_i^2\psi_i \end{aligned}$$

and in general

$$\mathbf{M}^k\psi_i = \lambda_i^k\psi_i. \quad (2)$$

Thus λ_i^k is the characteristic value corresponding to the characteristic vector ψ_i of \mathbf{M}^k . Now it is well known⁶ that the trace of a matrix is the sum of its characteristic values, so

$$\text{Trace } \mathbf{M}^k = \sum_i \lambda_i^k. \quad (3)$$

Since the total number of characteristic values (where a characteristic value of degree of degeneracy d is counted d times) is equal to the

⁵ M. Blackman, Proc. Roy. Soc. **148**, 365, 384 (1935); **159**, 416 (1937); see also P. Fine, Phys. Rev. **56**, 355 (1939).

⁶ Cf. Rojansky, *Introductory Quantum Mechanics* (New York, 1938), p. 324.

order of the matrix, which we shall assume to be m , the average values of powers of the characteristic values of \mathbf{M} are

$$\sum \lambda_i^k / m = (\text{Trace } \mathbf{M}^k) / m. \quad (4)$$

But this is exactly the k th moment of the distribution function of the characteristic values and will be abbreviated by μ_k .

We must now find a way of expressing the distribution function $g(\lambda)$ in terms of the set of moments $\{\mu_k\}$. Let λ_s and λ_L be, respectively, the smallest and largest characteristic values of \mathbf{M} (since the matrix is finite they actually exist; also, since the matrix was assumed to be symmetrical, the λ 's are all real) and let us assume that the elements of the set $\{\lambda_i\}$ are densely distributed.

Suppose the distribution function is expanded as a linear combination of Legendre polynomials

$$g(\lambda) = \sum_{n=0}^{\infty} a_n P_n \left(\frac{2\lambda - (\lambda_L + \lambda_s)}{\lambda_L - \lambda_s} \right), \quad (5)$$

where

$$P_n(x) = \frac{1}{2^n n!} \frac{d^n}{dx^n} (x^2 - 1)^n \quad (6a)$$

and

$$\int_{-1}^1 P_k(x) P_j(x) dx = 2 \delta_{kj} / (2k + 1). \quad (6b)$$

To evaluate the coefficients $\{a_k\}$ multiply both sides of (5) by

$$P_k \left(\frac{2\lambda - \lambda_L - \lambda_s}{\lambda_L - \lambda_s} \right) d\lambda$$

and integrate from λ_s to λ_L

$$\begin{aligned} & \int_{\lambda_s}^{\lambda_L} g(\lambda) P_k \left(\frac{2\lambda - \lambda_L - \lambda_s}{\lambda_L - \lambda_s} \right) d\lambda \\ &= \sum_{n=0}^{\infty} a_n \int_{\lambda_s}^{\lambda_L} P_n \left(\frac{2\lambda - \lambda_L - \lambda_s}{\lambda_L - \lambda_s} \right) P_k \left(\frac{2\lambda - \lambda_L - \lambda_s}{\lambda_L - \lambda_s} \right) d\lambda. \end{aligned}$$

Letting $x = (2\lambda - \lambda_L - \lambda_s) / (\lambda_L - \lambda_s)$

$$\begin{aligned} & \frac{(\lambda_L - \lambda_s)}{2} \int_{-1}^1 g(\lambda) P_k(x) dx \\ &= \sum_{n=0}^{\infty} a_n \int_{-1}^1 \frac{(\lambda_L - \lambda_s)}{2} P_n(x) P_k(x) dx \\ &= a_k (\lambda_L - \lambda_s) / (2k + 1). \end{aligned}$$

Therefore

$$a_k = \frac{(2k+1)}{2} \int_{-1}^1 g \left(\frac{(1+x)\lambda_L + (1-x)\lambda_s}{2} \right) P_k(x) dx. \quad (7)$$

If we define

$$\begin{aligned} u_k &= \int_{-1}^1 x^k g(\lambda) dx \\ &= \frac{2}{(\lambda_L - \lambda_s)^{k+1}} \int_{\lambda_s}^{\lambda_L} (2\lambda - \lambda_L - \lambda_s)^k g(\lambda) d\lambda \\ &= \frac{2}{(\lambda_L - \lambda_s)^{k+1}} \int_{\lambda_s}^{\lambda_L} (\text{polynomial in } \lambda) g(\lambda) d\lambda, \quad (8) \end{aligned}$$

it is apparent that the a_k 's can be written as linear combinations of the u_k 's. Furthermore, the definition of $g(\lambda)$ implies that its moments are

$$\begin{aligned} \mu_i &= \int_{\lambda_s}^{\lambda_L} g(\lambda) \lambda^i d\lambda \\ &= (\text{Trace } \mathbf{M}^i) / m, \quad (9) \end{aligned}$$

so the u_k 's are linear combinations of μ_i 's and therefore the coefficients a_k are also linear combinations of the moments (or the traces of \mathbf{M}^i) μ_i of $g(\lambda)$.

In the theory of frequency spectrum of solids the frequencies of normal modes are proportional to the square root of the roots of the secular equation, so the smallest frequency is the negative of the largest, and the odd moments of the distribution function are zero. Considering this case in detail we have:

$$g(\lambda) = \sum_{n=0}^{\infty} a_n P_n(\lambda / \lambda_L) \quad (10a)$$

with

$$a_n = \frac{(2n+1)}{2} \int_{-1}^1 g(x\lambda_L) P_n(x) dx. \quad (10b)$$

If

$$u_k = \int_{-1}^1 g(x\lambda_L) x^k dx, \quad (11)$$

then

$$\begin{aligned} \mu_k &= \int_{-\lambda_L}^{\lambda_L} g(\lambda) \lambda^k d\lambda \\ &= \lambda_L^{k+1} u_k. \quad (12) \end{aligned}$$

Therefore

$$\begin{aligned} a_0 &= \frac{1}{2} \int_{-1}^1 g(x\lambda_L) \cdot 1 dx \\ &= \mu_0 / 2\lambda_L \\ a_1 &= \frac{3}{2} \int_{-1}^1 g(x\lambda_L) \cdot x dx \\ &= \frac{3}{2} (\mu_1 / \lambda_L^2) = 0. \end{aligned}$$

Similarly, since the odd Legendre polynomials involve only odd powers of x , and since the odd moments of $g(\lambda)$ are zero:

$$\begin{aligned} a_1 &= a_3 = \dots = a_{2n+1} = 0, \\ a_2 &= \frac{5}{2} \int_{-1}^1 g(x\lambda_L) \left(\frac{3}{2}x^2 - \frac{1}{2} \right) dx, \\ &= 5(3\mu_2 - \mu_0\lambda_L^2) / 4\lambda_L^3, \\ a_4 &= 9(35\mu_4 - 30\mu_2\lambda_L^2 + 3\mu_0\lambda_L^4) / 16\lambda_L^5, \\ a_6 &= 13(231\mu_6 - 315\mu_4\lambda_L^2 + 105\mu_2\lambda_L^4 - 5\mu_0\lambda_L^6) / 32\lambda_L^7, \end{aligned}$$

$$\begin{aligned} M\ddot{u}_{l,m} + \alpha(u_{l,m} - u_{l+1,m} + u_{l,m} - u_{l-1,m}) + \gamma(u_{l,m} + v_{l,m} - u_{l+1,m+1} - v_{l+1,m+1} + u_{l,m} + v_{l,m} \\ - u_{l-1,m-1} - v_{l-1,m-1} + u_{l,m} - v_{l,m} - u_{l+1,m+1} + v_{l+1,m-1} + u_{l,m} - v_{l,m} - u_{l-1,m+1} + v_{l-1,m+1}) = 0 \end{aligned} \quad (14a)$$

and

$$\begin{aligned} M\ddot{v}_{l,m} + \alpha(v_{l,m} - v_{l+1,m} + v_{l,m} - v_{l-1,m}) + \gamma(u_{l,m} + v_{l,m} - u_{l+1,m+1} - v_{l+1,m+1} + u_{l,m} + v_{l,m} \\ - u_{l-1,m-1} - v_{l-1,m-1} + u_{l,m} - v_{l,m} - u_{l+1,m-1} + v_{l+1,m-1} + u_{l,m} - v_{l,m} - v_{l-1,m+1} + v_{l-1,m+1}) = 0. \end{aligned} \quad (14b)$$

By assuming the periodic solutions

$$u_{l,m} = u' \exp i(2\pi\nu t + l\varphi_1 + m\varphi_2), \quad (15a)$$

$$v_{l,m} = v' \exp i(2\pi\nu t + l\varphi_1 + m\varphi_2), \quad (15b)$$

$$\varphi_1 = \pi a_1 / N; \quad \varphi_2 = \pi a_2 / N, \quad (15c)$$

where a_1 and a_2 are integers satisfying

$$-N \leq a_1, a_2 \leq N,$$

and substituting (15) into (14) one can easily show that the frequencies of the normal modes of vibration of the crystal must be roots of the characteristic equations

$$\begin{vmatrix} A(\varphi_1, \varphi_2) - 4\pi^2 M \nu^2 & B(\varphi_2, \varphi_1) \\ B(\varphi_1, \varphi_2) & A(\varphi_2, \varphi_1) - 4\pi^2 M \nu^2 \end{vmatrix} = 0, \quad (16)$$

when

$$\begin{aligned} A(\varphi_1, \varphi_2) &= 2\alpha(1 - \cos \varphi_1) + 4\gamma(1 - \cos \varphi_1 \cos \varphi_2), \\ B(\varphi_1, \varphi_2) &= 4\gamma \sin \varphi_1 \sin \varphi_2. \end{aligned}$$

and in general

$$\begin{aligned} a_{2k} &= \frac{4k+1}{(2k)! 2^{2k+1}} \int_{-1}^1 g(x\lambda_L) \left[\frac{d^{2k}}{dx^{2k}} (x^2 - 1)^{2k} \right] dx \\ &= \frac{4k+1}{(2k)! 2^{2k+1} \lambda_L} \left\{ \frac{d^{2k}}{dy^{2k}} (y^2 - 1)^{2k} \right\}_{y^k = \mu_k / \lambda_L^k}, \end{aligned} \quad (13)$$

where after the differentiation is performed in the last expression, y^k is replaced by μ_k / λ_L^k .

2. Two-Dimensional Cubic Lattice

Here we shall apply the Moment-Trace method to a two-dimensional one-component cubic lattice of the Born-von Kármán type which includes interactions between nearest and next nearest neighbors. Let α be the binding force between two nearest neighbors whose distance of separation is a and let γ be that for two next nearest neighbors whose distance of separation is $a\sqrt{2}$. If there are $2N \times 2N$ particles of mass M in our square lattice, each atom can be specified by two letters l, m ($1 \leq l, m \leq 2N$) and its displacement components along rows and columns can be represented by $u_{l,m}$ and $v_{l,m}$, respectively. The motion of the particle (l, m) is described by the simultaneous differential equations⁵

Henceforth it will be assumed that ν is measured in units of $2\pi\sqrt{M}$ so that the factor $4\pi^2 M$ can be omitted. If the matrix of the determinant (16) is represented by $M^2(a_1, a_2)$, the matrix of the entire characteristic determinant is

$$\mathbf{M}^2 = \begin{pmatrix} M^2(-N, -N) & 0 & \cdot & \cdot & \cdot & 0 & 0 \\ 0 & M^2(-N, -N+1) & \cdot & \cdot & \cdot & 0 & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & \cdot & \cdot & \cdot & M^2(N, N-1) & 0 \\ 0 & 0 & \cdot & \cdot & \cdot & 0 & M^2(N, N) \end{pmatrix} \quad (17a)$$

(the submatrices are represented as squares because the roots of their characteristic determinants are proportional to the squares of the frequencies of the normal modes of vibration). Of course:

$$\mathbf{M}^{2k} = \begin{pmatrix} M^{2k}(-N, -N) & 0 & \cdot & \cdot & \cdot & 0 & 0 \\ 0 & M^{2k}(-N, -N+1) & \cdot & \cdot & \cdot & 0 & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & \cdot & \cdot & \cdot & M^{2k}(N, N-1) & 0 \\ 0 & 0 & \cdot & \cdot & \cdot & 0 & M^{2k}(N, N) \end{pmatrix} \quad (17b)$$

Since all the small $M^2(a_1, a_2)$ matrices are of the same form, namely

$$M^2(a_1, a_2) = \begin{pmatrix} A & B \\ B & A^* \end{pmatrix} \quad (18)$$

(where $A = A(\varphi_1, \varphi_2)$; $A^* = A(\varphi_2, \varphi_1)$; $B = B(\varphi_1, \varphi_2) = B(\varphi_2, \varphi_1)$),

$$\text{Trace } \mathbf{M}^{2k} = \sum_{a_1=-N}^N \sum_{a_2=-N}^N \text{Trace } M^{2k}(a_1, a_2) \quad (19)$$

and we first need only to find traces for one general pair (a_1, a_2) . Now

$$\begin{aligned} \text{Trace } M^2(a_1, a_2) &= A(\varphi_1, \varphi_2) + A(\varphi_2, \varphi_1) \\ \text{and} \\ \text{Trace } \mathbf{M}^2 &= \sum_{a_1, a_2} [A(\pi a_1/N, \pi a_2/N) + A(\pi a_2/N, \pi a_1/N)] \\ &= 2 \sum_{a_1, a_2} A(\pi a_1/N, \pi a_2/N). \end{aligned} \quad (20a)$$

Since

$$\begin{aligned} M^4(a_1, a_2) &= M^2(a_1, a_2) \cdot M^2(a_1, a_2) \\ &= \begin{pmatrix} A & B \\ B & A^* \end{pmatrix} \begin{pmatrix} A & B \\ B & A^* \end{pmatrix} \\ &= \begin{pmatrix} A^2 + B^2 & B(A + A^*) \\ B(A + A^*) & B^2 + (A^*)^2 \end{pmatrix} \\ \text{Trace } \mathbf{M}^4 &= \sum_{a_1, a_2} [A^2 + B^2 + B^2 + (A^*)^2] \\ &= 2 \sum_{a_1, a_2} (A^2 + B^2). \end{aligned} \quad (20b)$$

Continuation of this process leads to

$$\text{Trace } \mathbf{M}^6 = 2 \sum_{a_1, a_2} (A^3 + 3AB^2), \quad (20c)$$

$$\text{Trace } \mathbf{M}^8 = 2 \sum_{a_1, a_2} (A^4 + 4A^2B^2 + 2B^2AA^* + B^4), \quad (20d)$$

$$\text{Trace } \mathbf{M}^{10} = 2 \sum_{a_1, a_2} (A^5 + 5A^3B^2 + 5A^2B^2A^* + 5AB^4). \quad (20e)$$

These Traces will be sufficient to yield a $g(\nu)$ correct to the 10th Legendre polynomial. In general the sum of the diagonal elements of the matrix

$$M^{2k}(a_1, a_2) = \underbrace{\begin{pmatrix} A & B \\ B & A^* \end{pmatrix} \begin{pmatrix} A & B \\ B & A^* \end{pmatrix} \cdots \begin{pmatrix} A & B \\ B & A^* \end{pmatrix}}_{k \text{ matrices}}$$

is $\text{Trace } M^{2k}(a_1, a_2)$.

Actually

$$\begin{aligned} \text{Trace } \mathbf{M}^2 &= 2 \sum_{a_1, a_2} \{2\alpha(1 - \cos \varphi_1) + 4\gamma(1 - \cos \varphi_1 \cos \varphi_2)\} \\ &= 2 \left\{ \sum_{a_1, a_2} (2\alpha + 4\gamma) - 4\alpha \sum_{a_1, a_2} \cos \varphi_1 - 8\gamma \left(\sum_{a_1} \cos \varphi_1 \right)^2 \right\}. \end{aligned}$$

But as shown in the appendix

$$\sum_{a_1=-N}^N \cos \varphi_1 = -1.$$

Therefore

$$\frac{\text{Trace } \mathbf{M}^2}{2(2N+1)^2} = (2\alpha + 4\gamma) + \frac{2\alpha}{(2N+1)} - \frac{4\gamma}{(2N+1)^2}.$$

Since N is very large, and since this is exactly the second moment of $g(\nu)$:

$$\mu_2 = \frac{\text{Trace } \mathbf{M}^2}{2(2N+1)^2} = (2\alpha + 4\gamma). \quad (21a)$$

To find μ_4 we must first calculate

$$\text{Trace } \mathbf{M}^4 = 2(\sum A^2 + \sum B^2).$$

For this calculation we find

$$\begin{aligned} \sum_{a_1, a_2} A^2 &= \sum_{a_1, a_2} \{4\alpha^2(1 - 2 \cos \varphi_1 + \cos^2 \varphi_2) + 16\alpha\gamma(1 - \cos \varphi_1)(1 - \cos \varphi_1 \cos \varphi_2) \\ &\quad + 16\gamma^2(1 - 2 \cos \varphi_1 \cos \varphi_2 + \cos^2 \varphi_1 \cos^2 \varphi_2)\}. \end{aligned}$$

But from the appendix:

$$\sum_{a_2} \cos^2 \varphi_2 = N+1, \quad \sum_{a_1} \cos \varphi_1 = -1,$$

so

$$\sum_{a_1, a_2} A^2 = 4\alpha^2(2N+1)^2 + 4\alpha^2(2N+1)(N+1) + 16\alpha\gamma(2N+1)^2 + 16\gamma^2(2N+1)^2 + 16\gamma^2(N+1)^2 + O(N)$$

and

$$\sum A^2 / (2N+1)^2 = 4(\alpha + 2\gamma)^2 + 2(\alpha^2 + 2\gamma^2) + O(1/N).$$

Also,

$$\sum_{a_1, a_2} B^2 = 16\gamma^2 \left(\sum_{a_1} \sin^2 \varphi_1 \right)^2,$$

but from the appendix $\sum a_1 \sin^2 \varphi_1 = N$, therefore

$$\sum B^2/(2N+1)^2 = 4\gamma^2.$$

Since

$$\mu_4 = (\text{Trace } \mathbf{M}^4)/2(2N+1)^2, \quad \mu_4 = 4(\alpha+2\gamma)^2 + 2(\alpha^2+4\gamma^2) + O(1/N). \quad (21b)$$

In a similar manner some of the higher moments can be shown to be (to within terms of order $1/N$)

$$\mu_6 = 8(\alpha+2\gamma)^3 + 12(\alpha+2\gamma)(\alpha^2+4\gamma^2), \quad (21c)$$

$$\mu_8 = 16(\alpha+2\gamma)^4 + 48(\alpha+2\gamma)^2(\alpha^2+4\gamma^2) + 6(\alpha^2+4\gamma^2)^2 + 40\alpha^2\gamma^2, \quad (21d)$$

$$\mu_{10} = 32(\alpha+2\gamma)^5 + 160(\alpha+2\gamma)^3(\alpha^2+4\gamma^2) + 120\gamma^2(\alpha+2\gamma)(7\alpha^2+8\gamma^2) + 40\alpha^2\gamma^2(\alpha+\gamma) + 60\alpha^4(\alpha+2\gamma). \quad (21e)$$

Using the results of the previous section, if we assume

$$g(\nu) = \sum_{n=0}^{\infty} a_{2n} P_{2n}(\nu/\nu_L) \quad (22)$$

(ν_L = largest frequency of a normal mode) the first few coefficients are

$$a_0 = 0.5/\nu_L,$$

$$a_2 = 5(6\alpha + 12\gamma - \nu_L^2)/4\nu_L^3,$$

$$a_4 = 9[140(\alpha+2\gamma)^2 + 70(\alpha^2+4\gamma^2) - 60(\alpha+2\gamma)\nu_L^2 + 3\nu_L^4]/16\nu_L^5.$$

The number of parameters involved in the a 's can immediately be reduced by one, for as Blackman⁵ has shown, the largest normal mode ν_L results from the 2×2 determinant in which $\varphi_1 = 0$ and $\varphi_2 = \pi$ (or vice versa, $\varphi_2 = \pi$ and $\varphi_1 = 0$); therefore by (16)

$$\nu_L^2 = 4(\alpha+2\gamma).$$

This means

$$\nu_L a_0 = \frac{1}{2},$$

$$\nu_L a_2 = \frac{5}{8},$$

$$\nu_L a_4 = 9(9\alpha^2 - 104\alpha\gamma + 36\gamma^2)/8(\alpha+2\gamma)^2, \quad \text{etc.}$$

Since the purpose of this paper is more to introduce new methods than to obtain particular results, let us limit ourselves to the special case $\gamma = 0.05\alpha$. This α, γ relationship is of special interest because it is the one used by Blackman in his detailed calculations—and may therefore give us an opportunity to compare the results of the trace-moment approach with those obtained by Blackman in his detailed root calculations. In this case $\nu_L^2 = 4.4\alpha$.

The first six even moments in the special case $\gamma = 0.05\alpha$ are⁷ (of course the odd moments are all zero)

$$\mu_0 = 1, \quad \mu_6 = 0.28150826\nu_L^6,$$

$$\mu_2 = 0.5\nu_L^2, \quad \mu_8 = 0.23560495\nu_L^8,$$

$$\mu_4 = 0.35433884\nu_L^4, \quad \mu_{10} = 0.20316225\nu_L^{10}$$

and the corresponding Legendre coefficients of (22) are

$$\nu_L a_0 = 0.5, \quad \nu_L a_6 = 0.3704,$$

$$\nu_L a_2 = 0.625, \quad \nu_L a_8 = -0.3182,$$

$$\nu_L a_4 = 0.2260, \quad \nu_L a_{10} = -0.0133.$$

⁷ The large number of significant figures is necessary because one must take differences of multiples of the μ 's in order to find the a 's.

The resulting function $\nu_L g(\nu)$ is plotted in Fig. 1. It qualitatively resembles the equivalent curve of Blackman as obtained by direct numerical computation of a random sample of normal modes. Blackman's first peak is sharper and is displaced a little more to the left. The quantitative disagreement may be the result of Blackman's smoothing process, or it may have its source in the existence of a large value for one or more of the coefficients of the higher Legendre polynomials that have been neglected here. Since our $g(\nu)$ is not quite zero at $\nu=0$ as it should be, we must be omitting some contribution of the higher polynomials.

The calculation of physical quantities from a frequency distribution of the form (22) offers no special difficulty. For example the specific heat is in general

$$C = k \int_0^{\nu_L} \frac{h^2 \nu^2 g(\nu) d\nu}{4k^2 T^2 \sinh^2 h\nu/2kT},$$

so in a low temperature region where one may expand $(\sinh^2 h\nu/2kT)^{-1}$ as an exponential series, elementary integrals of the form

$$\int_0^{\nu_L} e^{-n h \nu / k T} (\text{polynomial in } \nu) d\nu$$

are all that are involved, while at higher temperatures where it would be desirable to use a power series expansion for $(\sinh^2 h\nu/2kT)^{-1}$ one encounters only sums of integrals of the form

$$\int_0^{\nu_L} (\text{polynomials in } \nu) d\nu.$$

Before concluding this section it might be worth while reminding the reader that the expressing of $g(\nu)$ as a linear combination of Legendre polynomials is somewhat arbitrary. Any other artifice which allows one to express $g(\nu)$ as a function of the moments would be equally valid. The Legendre development merely seemed to be the most straightforward and simplest approach which occurred to the author.

III. FREQUENCY DISTRIBUTION FROM EXPERIMENTAL DATA

If in a crystal of N structureless atoms or in a complex molecule of N atoms, the frequency distribution function $g(\nu)$ is defined so that $3Ng(\nu)d\nu$ is the number of normal modes of vibration in the frequency interval ν and $\nu+d\nu$, the logarithm of the partition function (per normal mode) is given by

$$\log Z(T) = - \int_0^\infty g(\nu) \log (1 - e^{-h\nu/kT}) d\nu \quad (23a)$$

under the restriction

$$\int_0^\infty g(\nu) d\nu = 1. \quad (23b)$$

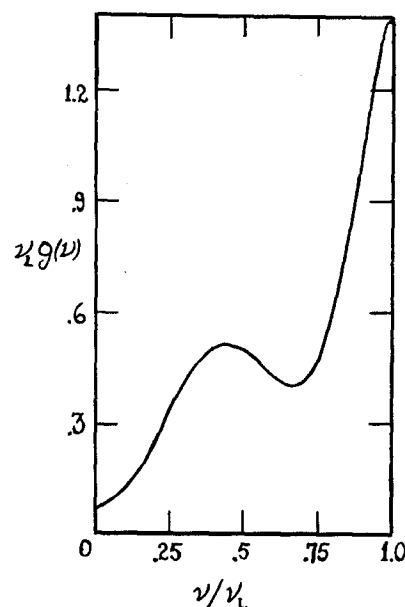


FIG. 1.

Formally a knowledge of $Z(T)$ at all temperatures permits (23a) to be regarded as an integral equation in which $g(\nu)$ occurs as the unknown function. Also, the average energy per normal mode is

$$\begin{aligned}\bar{E}(T) &= kT^2 \partial \log Z / \partial T \\ &= \int_0^\infty \frac{h\nu g(\nu) d\nu}{e^{h\nu/kT} - 1}\end{aligned}\quad (24)$$

(using for zero energy the state of lowest energy of the system including the residual energy $h\nu/2$ per normal mode) and by definition the specific heat is

$$\begin{aligned}C_v(T) &= (\partial E / \partial T)_v \\ &= k \int_0^\infty \left(\frac{h\nu}{2kT} \right)^2 \frac{g(\nu) d\nu}{\sinh^2(h\nu/2kT)}.\end{aligned}\quad (25)$$

Making the substitution $\theta = h/kT$ and writing

$$\log Z(T) = Z(\theta); \quad E(\theta) = \theta E(T/h); \quad C(\theta) = C_v(T)/k,$$

we have the three fundamental integral equations

$$Z(\theta) = - \int_0^\infty g(\nu) \log(1 - e^{-\theta\nu}) d\nu, \quad (26)$$

$$E(\theta) = \int_0^\infty g(\nu) \theta \nu d\nu / (e^{\theta\nu} - 1), \quad (27)$$

$$C(\theta) = \int_0^\infty \frac{\theta^2 \nu^2 g(\nu) d\nu}{4 \sinh^2(\theta\nu/2)},$$

all of which are of the form

$$f(\theta) = \int_0^\infty g(\nu) K(\theta\nu) d\nu. \quad (28)$$

It is quite clear that if the partition function, the internal energy or the specific heat of a given system could be found at all temperatures, and if the above integral equation could be inverted⁸ so that $g(\nu)$ would be a function of the measurable quantities it would be possible to compute $g(\nu)$ and perhaps get a better understanding of the internal structure of a given crystal or complex molecule.

As has been demonstrated in Appendix II, the formal solution of (28) is

$$g(\nu) = \frac{1}{2\pi} \int_{-\infty}^\infty \frac{du}{I(u)} \int_0^\infty f(\theta) (\nu\theta)^{iu} d\theta, \quad (29)$$

where

$$I(u) = \int_0^\infty x^{iu} K(x) dx.$$

Inasmuch as⁹

$$\int_0^\infty x^{iu} \log(1 - e^{-x}) dx = -\zeta(2 + iu) \Gamma(1 + iu)$$

⁸ Inversions of the partition function have been made before by S. Bauer, J. Chem. Phys. **6**, 403 (1938); **7**, 1097 (1939).

⁹ These integrals are easily evaluated by expanding the transcendental functions in the integrands as sums of powers of e^{-x} .

($\zeta(z)$ is the Riemann zeta-function defined by $\zeta(z) = \sum_{n=1}^{\infty} n^{-z}$)

$$\int_0^{\infty} \frac{x^{iu+1} dx}{e^x - 1} = \zeta(2+iu)\Gamma(2+iu), \quad \int_0^{\infty} \frac{x^{iu+2} dx}{4 \sinh^2 x/2} = \zeta(2+iu)\Gamma(3+iu),$$

the formal equations for $g(\nu)$ are

$$g(\nu) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{du}{\zeta(2+iu)\Gamma(1+iu)} \int_0^{\infty} Z(\theta)(\nu\theta)^{iu} d\theta, \quad (30)$$

$$g(\nu) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{du}{\zeta(2+iu)\Gamma(2+iu)} \int_0^{\infty} E(\theta)(\nu\theta)^{iu} d\theta, \quad (31)$$

$$g(\nu) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{du}{\zeta(2+iu)\Gamma(3+iu)} \int_0^{\infty} C(\theta)(\nu\theta)^{iu} d\theta. \quad (32)$$

As is to be expected, substitution of the Debye specific heat formula

$$C(\theta) = C_v(T)/NK = 3 \left(\frac{12}{\theta^3 \nu_L^3} \int_0^{\theta \nu_L} \frac{x^3 dx}{e^x - 1} - \frac{3\theta \nu_L}{e^{\theta \nu_L} - 1} \right)$$

into (32) can be shown to yield the frequency distribution

$$g(\nu) = \begin{cases} 9\nu^2/\nu_L^3 & \text{if } \nu < \nu_L \\ 0 & \text{if } \nu > \nu_L. \end{cases} \quad (33)$$

For actual calculation of $g(\nu)$ from (32) there seem to be several possible approaches. One might integrate (32) numerically after substitution of the experimental $C(\theta)$ values derived from specific heat measurements. However, since most specific heat curves are almost of the Debye form, one might divide $C(\theta)$ into a Debye and a residual portion. The Debye portion would contribute the amount (33) to $g(\nu)$ and the rest of $g(\nu)$ might be found either by numerical integration or by obtaining empirical equations for the residual $C(\theta)$. In the latter case one would attempt to fit a power series in θ to the high temperature part and a power series in $e^{-\theta}$ in the low temperature region. Then (32) could probably be integrated analytically. Another possibility would be to assume that $g(\nu)$ could be expanded in Legendre polynomials and finding the coefficients by applying the orthogonality property of the polynomials to the assumed equation (32).

In conclusion the author would like to thank Professor J. G. Kirkwood for his discussions concerning this problem.

APPENDIX I. SUMMATION FORMULA

In the main part of this paper the following trigonometric sums are needed To sum C_k and S_k it is convenient to find first

$$C_k = \sum_{a=-N}^N \cos^k \frac{\pi a}{N}; \quad S_k = \sum_{a=-N}^N \sin^k \frac{\pi a}{N}. \quad E_k = \sum_{a=-N}^N \exp(ik\pi a/N).$$

If $x = \exp(ik\pi/N) \neq 1$ when $0 < k < N$,

$$E_k = \sum_{a=-N}^N x^a = x^{-N}(1-x^{2N+1})/(1-x) \\ = e^{-i\pi k}(1-e^{2\pi i k} e^{ik\pi/N})/(1-e^{ik\pi/N}).$$

Since

$$e^{-i\pi k} = (-1)^k, \\ E_k = (-1)^k \quad \text{when } 0 < k < N.$$

Obviously $E_0 = 2N+1$.

Now

$$C_k = \frac{1}{2^k} \sum_{a=-N}^N (e^{i\pi a/N} + e^{-i\pi a/N})^k \\ = \frac{1}{2^k} \sum_{m=0}^k \frac{k!}{m!(k-m)!} \sum_{a=-N}^N e^{i\pi(2m-k)a/N}.$$

When k is odd, $2m-k$ is also odd and

$$\sum_{a=-N}^N \exp\{i\pi(2m-k)a/N\} = -1.$$

So

$$C_{k(\text{odd})} = -\frac{1}{2^k} \sum_{m=0}^k \frac{k!}{m!(k-m)!} = -1.$$

When k is even $(2m-k)$ is also even and it is zero when $k=2m$; so

$$C_{k(\text{even})} = \left\{ \sum_{m=0}^{(k/2)-1} \frac{k!}{m!(k-m)!} + \sum_{m=(k/2)+1}^k \frac{k!}{m!(k-m)!} \right. \\ \left. + \frac{(2N+1)k!}{(k/2)!(k/2)!} \right\} \\ = \frac{1}{2^k} \left\{ \sum_{m=0}^k \frac{k!}{m!(k-m)!} + \frac{2Nk!}{(k/2)!(k/2)!} \right\}$$

$$C_{k(\text{even})} = 1 + 2^{1-k} N(k!)/(k/2)!(k/2)!.$$

To find S_k we proceed in essentially the same manner:

$$S_k = \frac{1}{(2i)^k} \sum_{a=-N}^N (e^{i\pi a/N} - e^{-i\pi a/N})^k \\ = \frac{1}{(2i)^k} \sum_{a=-N}^N \frac{k!}{m!(k-m)!} \sum_{a=-N}^N (e^{i\pi a/N})^{k-m} (-e^{-i\pi a/N})^m \\ = \frac{1}{(2i)^k} \sum_{m=0}^k \frac{k!(-1)^m}{m!(k-m)!} \sum_{a=-N}^N e^{i\pi a(k-2m)/N}.$$

When k is odd $k-2m$ is odd and

$$S_{k(\text{odd})} = \frac{-1}{(2i)^k} \sum_{m=0}^k \frac{(-1)^m k!}{m!(k-m)!} \\ = -\frac{1}{(2i)^k} (1-1)^k = 0.$$

If k is even $k-2m$ is also even

$$S_{k(\text{even})} = \frac{1}{(2i)^k} \left\{ \sum_{m=0}^{k/2-1} \frac{k!(-1)^m}{m!(k-m)!} + \sum_{m=(k/2)+1}^k \frac{k!(-1)^m}{m!(k-m)!} \right. \\ \left. + \frac{(-1)^{k/2}(2N+1)k!}{(k/2)!(k/2)!} \right\} \\ = \frac{1}{(2i)^k} \left\{ \sum_{m=0}^k \frac{k!(-1)^m}{m!(k-m)!} + \frac{i^k(2N)k!}{(k/2)!(k/2)!} \right\} \\ S_{k(\text{even})} = \frac{N(k!)}{2^{k-1}(k/2)!(k/2)!}.$$

The first few C_k 's and S_k 's are

k	C_k	S_k
0	$2N+1$	$2N+1$
1	-1	0
2	$N+1$	N
3, 5, 7, 9	-1	0
4	$1+(3N/4)$	$3N/4$
6	$1+(5N/8)$	$5N/8$
8	$1+(35N/64)$	$35N/64$

APPENDIX II

Formal Solution of $f(\theta) = \int_0^\infty g(\nu) K(\theta\nu) d\nu$

Here we shall find the formal solution $g(\nu)$ of the integral equation

$$f(\theta) = \int_0^\infty g(\nu) K(\theta\nu) d\nu, \quad (\text{A})$$

when $f(\theta)$ and $K(\theta\nu)$ are assumed to be known functions. The Fourier transform method to be used is modeled on that of Payley and Wiener¹⁰ (the formal solution is also a simple consequence of some operations with Mellin transforms of f , g , and K).¹¹ Let us make the substitutions

$$\theta = e^{-\eta}, \quad \nu = e^\alpha \quad (\text{B})$$

in (A) yielding

$$e^{-\eta} f(e^{-\eta}) = \int_{-\infty}^\infty g(e^\alpha) e^{\alpha-\eta} K(e^{\alpha-\eta}) d\alpha. \quad (\text{C})$$

Multiplying by

$$e^{-i\eta\eta} d\eta / \sqrt{2\pi}$$

and integrating:

$$\frac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty e^{-\eta f(e^{-\eta})} e^{-i\eta\eta} d\eta \\ = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty g(e^\alpha) e^{-i\alpha\eta} d\alpha \int_{-\infty}^\infty e^{\alpha-\eta} e^{-i\eta(\eta-\alpha)} K(e^{\alpha-\eta}) d\eta.$$

Now let $\eta - \alpha = \beta$

$$\frac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty e^{-\eta f(e^{-\eta})} e^{-i\eta\eta} d\eta \\ = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty g(e^\alpha) e^{-i\alpha\eta} d\alpha \int_{-\infty}^\infty e^{-\beta} e^{-i\beta\eta} K(e^{-\beta}) d\beta.$$

¹⁰ R. Payley and N. Wiener, *Fourier Transforms* (New York, 1934), p. 38.

¹¹ Titchmarsh, *Theory of Fourier Transforms* (Oxford, 1937), p. 315.

Define

$$I(u) = \int_{-\infty}^{\infty} e^{-\beta(iu+1)} K(e^{-\beta}) d\beta \\ = \int_0^{\infty} x^{iu} K(x) dx.$$

Then

$$\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-\eta f(e^{-\eta})} e^{-iu\eta} d\eta = \frac{I(u)}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(e^{\alpha}) e^{-i\alpha u} d\alpha$$

and taking Fourier transforms

$$g(e^{\alpha}) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{e^{iu\alpha} du}{I(u)} \int_{-\infty}^{\infty} f(e^{-\eta}) e^{-\eta(1+iu)} d\eta.$$

By applying (B)

$$g(\nu) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{du}{I(u)} \int_0^{\infty} f(\theta) (\theta\nu)^{iu} d\theta.$$

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The Viscosity of Certain "Ferric Oxide" Hydrosols*†

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(1) The changes produced in the viscosities of "ferric oxide" hydrosols by aging, heating, and the addition of a number of electrolytes and a non-electrolyte have been studied, in some instances together with the attendant changes in the pH values and specific conductances of the systems. (2) Agreement with Poiseuille's law has been demonstrated for typical cationic and anionic hydrosols. (3) The decrease in viscosity of hydrosols on aging and heating is accompanied by an increase in specific conductance. This conductance increase in the case of cationic sols is due almost entirely to the increase in hydrogen ion activity which occurs during the reaction. This is not so for anionic hydrosols, where the conductance increase is explained by the conversion of coordinated citrate groups to citrate ions. (4) The addition of salts and acids to these hydrosols first results in a viscosity decrease, followed by an increase in viscosity at higher electrolyte concentrations. (5) The viscosity increase occurs at lower salt concentrations for those salts which are potent precipitants than for those which are weak. For cationic hydrosols, salts of both weakly and strongly coordinating anions have the same effect in depressing the viscosity; in the case of anionic hydrosols, potassium citrate is less effective in

this respect than potassium sulfate and nitrate. (6) The effects of acids in decreasing the viscosity of a sol, either cationic or anionic, was found to be the same for all acids used, when compared at the same pH values. The more powerful precipitants caused the subsequent viscosity increase to occur at lower electrolyte concentrations. (7) Acids are less effective than salts in decreasing the viscosities of cationic hydrosols. (8) Large concentrations of acetone produced a decrease in the relative viscosity of cationic hydrosols; this effect is, however, negligible in comparison with the magnitude of the changes caused by electrolytes. (9) The viscosity decrease produced by aging, heating, and the addition of electrolytes may be attributed in each case partly to the increase in electrolyte concentration of the system. (10) The viscosity resulting from these reactions is considered to be dependent also upon the micellar charge: the lower the charge, the lower the viscosity. (11) The viscosity increase at higher electrolyte concentrations may be ascribed to agglomeration of dispersed particles. (12) A mechanism based upon a Donnan equilibrium between the dispersed particle and the dispersion medium has been proposed to account for the effects observed.

INTRODUCTION

THE addition of electrolytes to hydrosols has long been known to cause changes in the viscosities of the colloidal system. Farrow¹ showed that the viscosity of hydrosols of sodium palmitate is decreased by the addition of sodium

chloride or sodium hydroxide, but passes through a minimum, increasing with further increase in electrolyte concentration. Woudstra² demonstrated that curves of similar shape were obtained upon the addition of electrolytes to ferric oxide hydrosols, and Pauli³ found electrolyte addition to lower the viscosity of ceric oxide hydrosols. In the ferric oxide system, viscosity decreases were obtained also on heating, and in the ceric, on aging. The extensive investigations of Loeb⁴ on gelatin indicated that the depression

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¹ F. D. Farrow, *J. Chem. Soc.* **101**, 347 (1912).

² H. W. Woudstra, *Kolloid Zeits.* **8**, 73 (1911).

³ W. Pauli and A. Fernau, *Kolloid Zeits.* **20**, 20 (1917).

⁴ J. Loeb, *Proteins and the Theory of Colloidal Behavior* (McGraw-Hill Book Co., 1924), second edition.