THEORY OF THE VIBRATION OF SIMPLE CUBIC LATTICES WITH NEAREST NEIGHBOR INTERACTIONS

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1. Introduction

A crystalline solid is generally considered to be an assembly of almost periodically-spaced atoms or molecules. A set of periodic atomic equilibrium positions is postulated to exist such that no net force acts on any atom when all are at their equilibrium positions. Thermal excitation (or quantum mechanical zero point energy at low temperatures) causes the atoms to vibrate about these equilibrium positions.

The atoms interact with each other through the much-studied interatomic forces so that, if a single atom is displaced from its equilibrium position, a force acts on the others (and indeed a restoring force acts on the displaced atom). The magnitude of this force decreases rapidly with an increase in the interatomic distance. It is generally assumed that the displacements of atoms from their equilibrium positions are so small that the interatomic forces between a pair of atoms is proportional to the deviation of their separation distance from its equilibrium value. The force constant is largest for nearest neighbor pairs in the crystalline lattice, and becomes very small for more distant neighbors. In view of this Hooke's law approximation to interatomic forces, a crystal can be visualized as a periodic array of coupled springs and masses. Such a system of coupled oscillators has a set of normal modes of vibration in terms of which all motions of the system can be described.

The theory of lattice vibrations has become of considerable importance for several reasons. The thermodynamic properties of a crystal depend on the manner in which its lattice vibrations are excited by its thermal energy. The optical properties of ionic crystals are determined by the character of the excitation of lattice vibrations by electromagnetic waves. The electrical properties of superconductors and semiconductors seem to be influenced by lattice vibrations.

In the past few years considerable progress has been made in the detailed understanding of lattice vibrations through the investigation of simplified models and general topological theorems [1] through [6]. We shall concern ourselves here with the analysis of a model of a simple cubic lattice with interactions between nearest neighbors only; "cubes" of 1, 2, 3 and a very large number of dimensions will be discussed. It is well known that noncentral forces must be included in this model if it is to be stable against shear. The distribution function of the vibrational frequen-

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cies of normal modes of oscillation of this model has been investigated by Rosenstock and Newell [6] who revived interest in the model. This model has the undesirable property that displacements of atoms in the directions of the various coordinate axes are independent of each other. It has the advantage that most of its interesting properties can be described in relatively simple analytical forms, a feature that is difficult to duplicate in more complicated models.

The first problem to be considered here is the determination of the number of normal modes in a given frequency interval. This quantity is required in the calculation of the thermodynamic properties of a crystal.

The second problem discussed is the distribution function of the location of a given atom with respect to its equilibrium position. This problem has been examined by Peierls [7], and briefly by Wigner [8]. We shall show that this distribution function is Gaussian, and find analytical expressions for the dispersion in terms of dimensionality, temperature, and interatomic forces. In the early days of X-ray crystallography, Debye [9] investigated the effect of this Gaussian distribution on the broadening of X-ray spots or lines.

The third problem to be mentioned is the effect of local disturbances, such as impurities, holes, etc., on lattice vibrations. A method will be outlined for handling these situations.

Finally we shall give a brief calculation of the quantum mechanical zero point energy of our lattice model.

Many of the mathematical problems discussed here also appear in the theory of random walks on discrete lattices and in the theory of the tight binding approximation of electrons in solids.

Since, in our model the x, y, and z vibrations are independent, we can obtain our required results by considering the vibrations of lattices with one degree of freedom associated with each lattice point.

2. Normal modes, Slater's sum and thermodynamic quantities

Let us consider a set of identical particles of unit mass (the mass can be inserted in final formula to make the units come out correctly), each having one degree of freedom and each being coupled to its nearest neighbors on a n-dimensional simple "cubic" lattice with $(N + 2)$ particles along each edge of the n dimensional cube. We choose all the force constants in a direction parallel to a given "cube" axis to have the same value and postulate the potential energy of interaction to be

$$\Phi = \tfrac{1}{2}\gamma_1 \sum_{m_1, m_2, \cdots = 0}^{N} (u_{m_1, m_2, m_3, \cdots} - u_{m_1+1, m_2, \cdots})^2 \tag{2.1}$$

$$+ \tfrac{1}{2}\gamma_2 \sum_{m_1, m_2, \cdots = 0}^{N} (u_{m_1, m_2, m_3, \cdots} - u_{m_1, m_2+1, \cdots})^2 + \cdots .$$

The constant γ_1 will generally be used to represent the central force constant, and the other γ_j's the noncentral ones which are generally smaller in value. We have chosen $u_{m_1, m_2, m_3, \cdots}$ to be the deviation of the configuration of the particle at the $(m_1, m_2, \cdots, m_n)$-th lattice point from its equilibrium value. We shall choose the boundary conditions to be such that all particles on the cube faces are fixed:

(2.2a) $$u_{0,m_2,m_3,\cdots} = u_{N+1,m_2,m_3,\cdots} = 0 ,$$

(2.2b) $$u_{m_1,0,m_3,\cdots} = u_{m_1,N+1,m_3,\cdots} = 0 , \quad \text{etc.}$$

All u's with a subscript 0 or $N + 1$ are chosen to be zero. We shall be interested in systems in which N is very large, say, $0(10^{23})$, and in the limit as $N \to \infty$.

Since the kinetic energy of our system of particles is

(2.3) $$T = \tfrac{1}{2} \sum \dot{u}^2_{m_1,m_2,m_3,\cdots} ,$$

the Hamiltonian $H = T + V$ and the Lagrangian $L = T - V$ are quadratic forms. They can be diagonalized through the introduction of the normal coordinates $\eta_{s_1,s_2,s_3,\cdots}$ which are defined so that

(2.4) $$u_{m_1,m_2,\cdots} = \left(\frac{2}{N+1}\right)^{n/2} \sum_{s_1,s_2,\cdots=1}^{N} \eta_{s_1 s_2 \cdots} \sin \frac{\pi m_1 s_1}{N+1} \sin \frac{\pi m_2 s_2}{N+1} \cdots .$$

If we write

(2.5) $$S_j = \sum_{m_1,m_2,\cdots=0}^{N} (u_{m_1,m_2,\cdots,m_j,\cdots} - u_{m_1,m_2,\cdots,m_j+1,\cdots})^2 ,$$

and use the fact that

(2.6) $$\sum_{m=0}^{N} \sin \frac{\pi m s}{N+1} \sin \frac{\pi m s'}{N+1} = \sum_{m=0}^{N} \cos \frac{\pi m s}{N+1} \cos \frac{\pi m s'}{N+1} = \frac{1}{2}(N+1)\, \delta_{ss'} ,$$

and

(2.7) $$\sum_{m=0}^{N} \cos \frac{\pi m s}{N+1} \sin \frac{\pi m s'}{N+1} = 0 ,$$

we see that

(2.8) $$S_j = 2 \sum_{s_1,s_2,\cdots=1}^{N} \left(1 - \cos \frac{\pi s_j}{N+1}\right) \eta^2_{s_1 s_2 \cdots}$$

and hence that

(2.9) $$\Phi = \frac{1}{2} \sum_{s_1,s_2,\cdots=1}^{N} \omega^2_{s_1 s_2 \cdots} \, \eta^2_{s_1 s_2 \cdots} ,$$

where

(2.10) $$\omega^2_{s_1 s_2 \cdots} = 2 \sum_{j=1}^{N} \gamma_j \left(1 - \cos \frac{\pi s_j}{N+1}\right) .$$

Frequently we let

(2.11) $$\phi_j = \pi s_j/(N+1) , \qquad s_j = 1, 2, \cdots, N .$$

The largest value of ω^2 is

(2.12) $$\omega_L^2 = 4(\gamma_1 + \gamma_2 + \cdots + \gamma_n) .$$

The Hamiltonian of our system is, in normal coordinates

$$(2.13)\qquad H = \frac{1}{2} \sum_{s_1 s_2 \cdots = 1}^{N} [\dot{\eta}^2_{s_1 s_2 \cdots} + \omega^2_{s_1 s_2 \cdots} \eta^2_{s_1 s_2 \cdots}] .$$

This Hamiltonian leads to the Schroedinger equation

$$(2.14)\qquad \sum_{s_1 s_2 \cdots = 1}^{N} \left\{ \hbar^2 \frac{\partial^2 \Psi}{\partial \eta^2_{s_1 s_2 \cdots}} + (2E_{s_1 s_2 \cdots} - \omega^2_{s_1 s_2 \cdots} \eta^2_{s_1 s_2 \cdots})\Psi \right\} = 0$$

with

$$(2.15)\qquad E = \sum_{s_1 s_2 \cdots = 1}^{N} E_{s_1 s_2 \cdots} .$$

The variables separate. A typical wave function with its associated energy level is

$$(2.16a)\qquad \Psi_{\{n_{s_1 s_2 \cdots}\}}(\{\eta_{s_1 s_2 \cdots}\}) = \sum_{s_1 s_2 \cdots = 1}^{N} \Psi_{n_{s_1 s_2 \cdots}}(x_{s_1 s_2 \cdots})$$

$$(2.16b)\qquad E_{\{n_{s_1 s_2 \cdots}\}} = \sum_{s_1 s_2 \cdots = 1}^{N} \hbar\, \omega_{s_1 s_2 \cdots}(n_{s_1 s_2 \cdots} + \frac{1}{2})$$

with

$$(2.16c)\qquad x^2_{s_1 s_2 \cdots} = \omega_{s_1 s_2 \cdots} \eta^2_{s_1 s_2 \cdots}/\hbar .$$

The brackets $\{n_{s_1 s_2 \cdots}\}$ and $\{\eta_{s_1 s_2 \cdots}\}$ represent the sets of all n's and η's which refer to all states and coordinates of particles. The function $\Psi_n(x)$ is defined as

$$(2.17)\qquad \Psi_n(x) = \frac{e^{-1/2 x^2/2} H_n(x)}{(2^n n! \pi^{1/2})^{1/2}} ,$$

$H_n(x)$ being the nth Hermite polynomial.

The position distribution function of a system of particles at equilibrium at temperature T is proportional to the Slater sum

$$(2.18)\qquad S(u) = \sum_n |\Psi_n(u)|^2 \exp(-E_n/kT) ,$$

where $\{\Psi_n(u)\}$ is the set of wave functions of our lattice and $\{E_n\}$ the set of associated energy levels. The Slater sum of our system of interest is the product of N^n factors of which the $(s_1, s_2, \cdots)$-th is

$$(2.19)\qquad S_{s_1, s_2, \cdots}(x_{s_1 s_2 \cdots}) = \sum_{n=0}^{\infty} \Psi^2_n(x_{s_1 s_2 \cdots}) \exp\{-(n + \tfrac{1}{2})\hbar\omega_{s_1 s_2 \cdots}/kT\}$$

$$= \left[2\pi \sinh \frac{\hbar\omega_{s_1 s_2 \cdots}}{kT}\right]^{-1/2} \exp\left\{-\omega_{s_1 s_2 \cdots} \eta^2_{s_1 s_2 \cdots} \hbar^{-1} \tanh\left(\frac{1}{2} \frac{\hbar\omega_{s_1 s_2 \cdots}}{kT}\right)\right\}$$

(this summation is given by Titchmarsh [10]). This expression was derived in an interesting manner by Bloch [11].

The logarithm of the partition function of our system of particles, being the logarithm of the integral of the Slater sum, is

$$\log Z = \sum_{s_1 s_2 \cdots = 1}^{N} \log \frac{1}{2}\left\{ \operatorname{csch} \frac{1}{2} \frac{\hbar\omega_{s_1 s_2 \cdots}}{kT} \right\}. \tag{2.20}$$

The various thermodynamic properties of our system can be derived from log Z. When the number of degrees of freedom becomes large the frequencies become dense and one can introduce a frequency distribution function, or frequency spectrum, $g(\nu)$ (where $2\pi\nu = \omega$) with the property that $\int_{\nu_1}^{\nu_2} g(\nu)d\nu$ is the number of frequencies between ν_1 and ν_2. The log Z is expressed in terms of $g(\nu)$ as

$$\log Z = \int_0^{\nu_L} g(\nu) \log\left\{\frac{1}{2} \operatorname{sech}\left(\frac{1}{2}\frac{h\nu}{kT}\right)\right\} d\nu \tag{2.21}$$

where ν_L is the largest frequency.

The first statistical problem associated with lattice vibrations that we shall consider here is the determination of the distribution of frequencies, or frequency spectrum of our model.

3. Frequency spectrum

We have found the circular frequencies $\omega_{s_1 s_2 \cdots}$ of our model to be given by[1]

$$\omega^2_{s_1 s_2 \cdots} = 2 \sum_{j=1}^{n} \gamma_j \left(1 - \cos \frac{\pi s_j}{N+1}\right) = 4 \sum \gamma_j \sin^2 \tfrac{1}{2}\phi_j \tag{3.1}$$

with $s_j = 1, 2, \cdots, N$ and $j = 1, 2, \cdots, N$.

The values of ω^2 are finite in number, but as N becomes large, the random variable ω^2 has a limiting density G_n. That is, if we let $H_n^N(a)$ be the number of choices of s, such that $\omega^2_{s_1 s_2 \cdots} \leqq a$, then

$$\lim_{N\to\infty} \frac{1}{N^n} H_n^N(a) = \int_{-\infty}^{a} G_n(x)dx . \tag{3.2}$$

The density G_n can be computed by the method of characteristic functions. Consider $(1/N^n)H_n^N$ as a cumulative distribution function. Then the characteristic function

$$\begin{aligned} f_n^N(\alpha) &= E(e^{i\alpha\omega^2}) \\ &= \frac{1}{N^n} \sum_{s_1 s_2 \cdots = 1}^{N} \exp\{2i\alpha \textstyle\sum \gamma_j(1 - \cos \pi s_j/[N+1])\} . \end{aligned} \tag{3.3}$$

In the limit as $N \to \infty$, this sum reduces to the integral

$$f_n(\alpha) = \pi^{-n} \int \cdot \overset{\pi}{\underset{0}{\vdots}} \cdot \int \exp\left\{2i\alpha \sum_{j=1}^{n} \gamma_j(1 - \cos\phi_j)\right\} d\phi_1 \cdots d\phi_n . \tag{3.4}$$

We have considered the set of all frequencies generated by (3.1) to represent a

[1] The energy levels of electrons in simple cubic lattices also satisfy this formula when one uses the tight binding approximation and considers only interactions between nearest neighbors. Hence $G_n(E)$ represents the energy distribution function.

population in which each set of s_j's has the same probability of occurring. The function $G_n(\omega^2)$ is the probability density function of a "large number" of squares of circular frequencies chosen at random from our population.

The function $G_n(\omega^2)$ is related to the $g(\nu)$ defined above (2.21) by

$$g(\nu) = 4\pi\omega N^n G(\omega^2) \ . \tag{3.5}$$

Since the Bessel function $J_0(x)$ has the integral representation

$$J_0(x) = \pi^{-1}\int_0^{\pi} e^{-ix\cos\phi}\, d\phi \ , \tag{3.6}$$

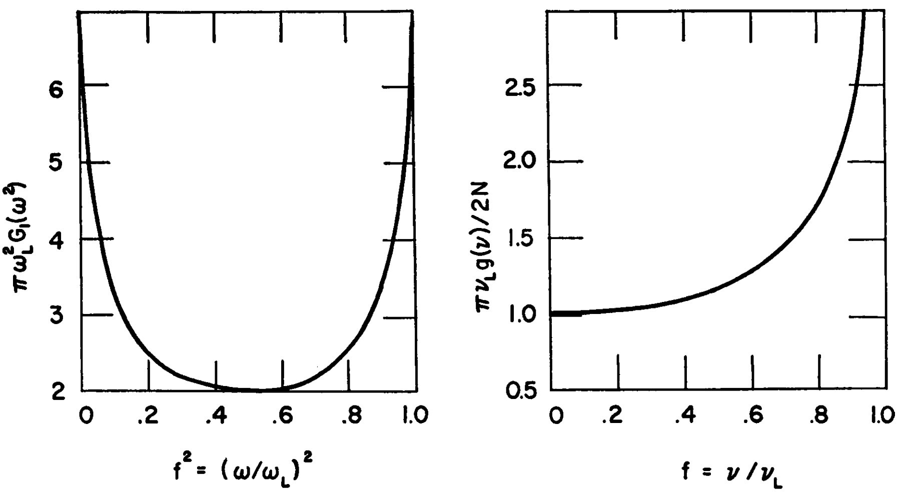


FIGURE 1
Frequency spectrum of a 1-D lattice

we can rewrite (3.4) as

$$f_n(\alpha) = \prod_{j=1}^{n} \exp(2i\alpha\gamma_j) J_0(2\alpha\gamma_j) \ . \tag{3.7}$$

Hence (see also [12])

$$G_n(\omega^2) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\alpha\omega^2} \prod_{j=1}^{n} \{J_0(2\alpha\gamma_j) e^{2i\alpha\gamma_j}\}\, d\alpha \ . \tag{3.8}$$

The largest frequency corresponds to $\phi_1 = \phi_2 = \cdots = \pi$ and has the value

$$\omega_L^2 = 4(\gamma_1 + \gamma_2 + \cdots + \gamma_n) \ , \tag{3.9}$$

where we define β_j by

$$n\beta_j = \gamma_1^j + \gamma_2^j + \cdots + \gamma_n^j \ . \tag{3.10}$$

We see that

$$G(\omega^2) = 0 \quad \text{if} \quad \omega^2 > \omega_L^2 = 4n\beta \ , \qquad \text{or} \quad \omega^2 < 0 \ . \tag{3.11}$$

We shall now find explicit analytical expressions for $G_n(\omega^2)$ when $n = 1, 2$, and 3, and an asymptotic form for large n. We abbreviate the phrase n-dimensional by $n - D$ and the words frequency spectrum by FS.

(a) $n = 1$. The $1 - D$ expression for (3.5) is

$$G_1(\omega^2) = (2\pi)^{-1} \int_{-\infty}^{\infty} \exp[-i\alpha(\omega^2 - 2\gamma_1)] J_0(2\alpha\gamma_1) d\alpha \tag{3.12}$$

$$= \begin{cases} 1/\pi\omega(\omega_L^2 - \omega^2)^{1/2} & \text{if } \omega^2 < \omega_L^2 \\ 0 & \text{if } \omega^2 > \omega_L^2 . \end{cases}$$

Equation (3.5) implies the following FS (see figure 1)

$$\nu_L g(\nu) = 2N\pi^{-1}(1 - f^2)^{-1/2} \quad with \quad f = \nu/\nu_L , \tag{3.13}$$

where, if we admit a nonunit mass M,

$$\nu_L = (2\pi)^{-1}(4\gamma_1/M)^{1/2} . \tag{3.14}$$

At low frequencies

$$g(\nu) \sim 2N(M/\gamma_1)^{1/2} . \tag{3.15}$$

(b) $n = 2$. The 2-D frequency density function is

$$G_2(\omega^2) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\alpha(\omega^2 - 2\gamma_1 - 2\gamma_2)} J_0(2\alpha\gamma_1) J_0(2\alpha\gamma_2) d\alpha . \tag{3.16}$$

When

$$J_0(2x\gamma_1)\, J_0(2x\gamma_2) = \frac{1}{\pi} \int_0^{\pi} J_0(2x[\gamma_1^2 + \gamma_2^2 - 2\gamma_1\gamma_2 \cos\theta]^{1/2}) d\theta \tag{3.17}$$

is substituted into (3.16) and the formula

$$\int_0^{\infty} J_0(at) \cos bt\, dt = \begin{cases} (a_2 - b^2)^{-1/2} & \text{if } a > b \\ 0 & \text{if } a < b \end{cases} \tag{3.18}$$

is applied, it is found that

$$G_2(\omega^2) = \begin{cases} \dfrac{1}{\pi^2} \displaystyle\int_0^{\pi} \frac{d\theta}{[\omega^2(\omega_L^2 - \omega^2) - 16\gamma_1\gamma_2 \cos^2 \frac{1}{2}\theta]^{1/2}} & \text{if } \omega^2(\omega_L^2 - \omega^2) > 16\gamma_1\gamma_2 \\ \dfrac{1}{\pi^2} \displaystyle\int_{\theta_0}^{\pi} \frac{d\theta}{[\omega^2(\omega_L^2 - \omega^2) - 16\gamma_1\gamma_2 \cos^2 \frac{1}{2}\theta]^{1/2}} & \text{if } \omega^2(\omega_L^2 - \omega^2) < 16\gamma_1\gamma_2 \end{cases} \tag{3.19}$$

where

$$\cos^2 \tfrac{1}{2}\theta_0 = \omega^2(\omega_L^2 - \omega^2)/16\gamma_1\gamma_2 . \tag{3.20}$$

$G_2(\omega^2)$ is immediately expressible as a complete elliptic integral of the first kind in both ranges. We have

$$G_2(\omega^2) = \frac{2}{\omega\pi^2(\omega_L^2 - \omega^2)^{1/2}} K\left(\frac{4(\gamma_1\gamma_2)^{1/2}}{\omega(\omega_L^2 - \omega^2)^{1/2}}\right) \quad \text{if} \quad \omega^2(\omega_L^2 - \omega^2) > 16\gamma_1\gamma_2 , \tag{3.21}$$

$$G_2(\omega^2) = \frac{1}{2\pi^2(\gamma_1\gamma_2)^{1/2}} K\left(\frac{\omega(\omega_L^2 - \omega^2)^{1/2}}{4(\gamma_1\gamma_2)^{1/2}}\right) \quad \text{if} \quad 0 < \omega^2(\omega_L^2 - \omega^2) < 16\gamma_1\gamma_2 . \tag{3.22}$$

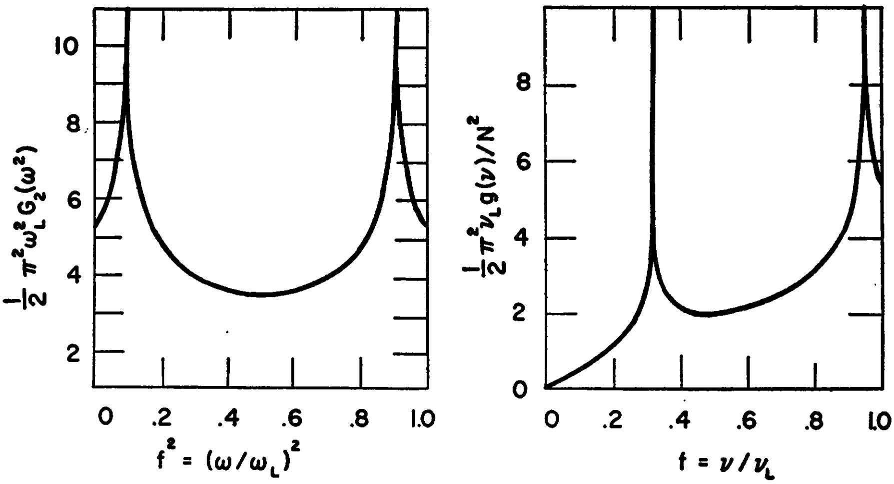


FIGURE 2

Frequency spectrum of a 2-E lattice with $\gamma_2/\gamma_1 = 1/9$. Logarithmic singularities occur at $f = 0.316$ and 0.948.

The inequality associated with (3.21) is equivalent to $(\omega^2 - 4\gamma_1)(\omega^2 - 4\gamma_2) \leqq 0$. Hence (3.21) is valid when $4\gamma_2 < \omega^2 < 4\gamma_1$ (we assume $\gamma_2 < \gamma_1$). Similarly (3.22) is valid when $\omega^2 > 4\gamma_1$ or $\omega^2 < 4\gamma_2$. It is to be noted that in the limit as $\gamma_2 \to 0$, equation (3.21) approaches the one-dimensional result (3.12). We have plotted $G_2(\omega^2)$ and $g(\nu)$ in figure 2. As $\omega \to 0$ (3.22) becomes $G_2(\omega^2) \sim [4\pi(\gamma_1\gamma_2)^{1/2}]^{-1}$ so that

$$g(\nu) \sim 2\pi\nu N^2(M^2/\gamma_1\gamma_2)^{1/2} . \tag{3.23}$$

$G_3(\omega^2)$ has a logarithmic singularity at $\omega^2 = 4\gamma_2$ and one at $\omega^2 = 4\gamma_1$.

(c) $n = 3$. The 3-*D* frequency density function is

$$G_3(\omega^2) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\alpha(\omega^2-2\gamma_1-2\gamma_2-2\gamma_3)} J_0(2\alpha\gamma_1)J_0(2\alpha\gamma_2)J_0(2\alpha\gamma_3)d\alpha . \tag{3.24}$$

The function $G_3(\omega^2)$ was first computed by Bowers and Rosenstock [2] for the case $\gamma_1 = \gamma_2 = \gamma_3$. Other cases have been given by Rosenstock and Newell [6]. The integral can be expressed in terms of generalized hypergeometric functions of three variables, which in the range of convergence has the series representation

$$(3.25)\qquad F_3(a;\beta_1,\beta_2,\beta_3;\gamma_1,\gamma_2,\gamma_3;z_1,z_2,z_3)$$

$$= \sum_{m_1 m_2 \cdots} \frac{(a)_{m_1+m_2+m_3}(\beta_1)_{m_1}(\beta_2)_{m_2}(\beta_3)_{m_3}}{(\gamma_1)_{m_1}(\gamma_2)_{m_2}(\gamma_3)_{m_3}\, m_1!m_2!m_3!} z_1^{m_1} z_2^{m_2} z_3^{m_3} .$$

Here $(a)_\nu = \Gamma(a+\nu)/\Gamma(a)$. We use the formula (see [13])

$$(3.26)\qquad \int_0^\infty e^{-p\alpha} J_0(\alpha\gamma_1)J_0(\alpha\gamma_2)J_0(\alpha\gamma_3)d\alpha$$

$$= \frac{1}{p+\frac{1}{2}i\omega_L^2} F_3\left(1;\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2};1,1,1;\frac{2i\gamma_1}{p+\frac{1}{2}i\omega_L^2},\frac{2i\gamma_2}{p+\frac{1}{2}i\omega_L^2},\frac{2i\gamma_3}{p+\frac{1}{2}i\omega_L^2}\right)$$

to obtain

$$(3.27)\qquad G_3(\omega^2) = \frac{1}{2\pi i\omega^2} F_3(1;\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2};1,1,1;2\gamma_1\omega^{-2},2\gamma_2\omega^{-2},2\gamma_3\omega^{-2})$$

$$+\frac{1}{2\pi i(\omega_L^2-\omega^2)} F_3(1;\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2};1,1,1;2\gamma_1(\omega_L^2-\omega^2)^{-1},2\gamma_2(\omega_L^2-\omega^2)^{-1},2\gamma_3(\omega_L^2-\omega^2)^{-1}) .$$

Hence $G_3(\omega^2)$ is symmetrical with respect to $\omega^2 = \frac{1}{2}\omega_L^2$. Since the required properties of these F_3 functions have never been discussed we shall find it more instructive to analyze our frequency spectrum from a slightly different point of view.

We apply Parseval's theorem to the integration of (3.24). It is to be recalled that if

$$(3.28)\qquad f(y) = \frac{1}{(2\pi)^{1/2}}\int_{-\infty}^{\infty} F(\alpha)e^{i\alpha y}d\alpha \quad\text{and}\quad g(y) = \frac{1}{(2\pi)^{1/2}}\int_{-\infty}^{\infty} G(\alpha)e^{i\alpha y}d\alpha ,$$

then

$$(3.29)\qquad \int_{-\infty}^{\infty} F(\alpha)G^*(\alpha)d\alpha = \int_{-\infty}^{\infty} f(y)g^*(y)dy .$$

Hence, if we let

$$(3.30)\qquad G(\alpha) = J_0(2\alpha\gamma_1)\exp i\alpha(\omega^2-2\gamma_1-2\gamma_2-2\gamma_3)$$

and

$$(3.31)\qquad F(\alpha) = J_0(2\alpha\gamma_2)J_0(2\alpha\gamma_3) ,$$

we find

$$(3.32)\qquad G_3(\omega^2) = \frac{1}{2\pi}\int_{-\infty}^{\infty} f(y)g^*(y)dy ,$$

where $f(y)$ and $g(y)$ are determined as follows.

We have

$$g(y) = (2\pi)^{-1/2} \int_{-\infty}^{\infty} J_0(2\alpha\gamma_1) \exp [i\alpha(y + \omega^2 - 2\gamma_1 - 2\gamma_2 - 2\gamma_3)]d\alpha . \tag{3.33}$$

This integral is of the same form as that of the 1-D frequency density function and has the value

$$g(y) = \begin{cases} (2/\pi)^{1/2}[(y + \omega^2 - \omega_3^2)(\omega_L^2 - \omega_3^2 - \omega^2 - y)]^{-1/2} \\ \qquad\qquad \text{if } \omega_3^2 - \omega^2 < y < \omega_L^2 - \omega^2 - \omega_3^2 \\ 0 \qquad \text{if } (y + \omega^2 - \omega_L^2 + \omega_3^2)(y + \omega^2 - \omega_3^2) > 0 , \end{cases} \tag{3.34}$$

where

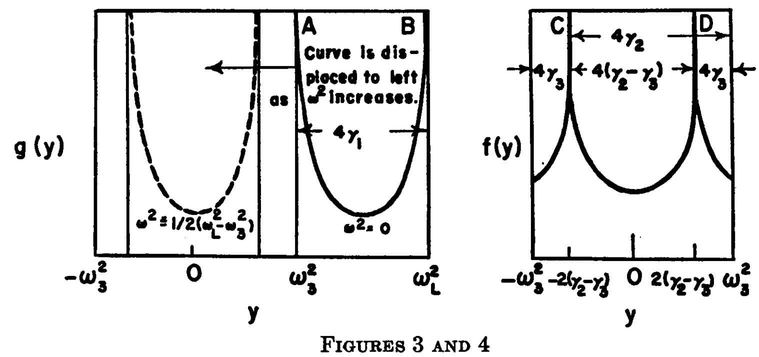
$$\omega_1^2 = 2(\gamma_1 + \gamma_2) , \quad \omega_2^2 = 2(\gamma_1 + \gamma_3) , \quad \text{and} \quad \omega_3^2 = 2(\gamma_2 + \gamma_3) . \tag{3.35}$$

We postulate $\gamma_1 \geqq \gamma_2 \geqq \gamma_3$ so that $\omega_1 \geqq \omega_2 \geqq \omega_3$.

We find $f(y)$ in the same manner that the frequency spectrum of a 2-D lattice was determined:

$$f(y) = \begin{cases} 0 \qquad \text{if } y^2 > \omega_3^4 , \\ \tfrac{1}{2}(2/\pi^3\gamma_2\gamma_3)^{1/2}K(\tfrac{1}{4}[(\omega_3^4 - y^2)/\gamma_2\gamma_3]^{1/2}) \\ \qquad \text{if } 4(\gamma_2 - \gamma_3)^2 < y^2 < \omega_3^4 , \\ (2/\pi)^{3/2}(\omega_3^4 - y^2)^{-1/2}K(4[\gamma_3\gamma_2/(\omega_3^4 - y^2)]^{1/2}) \\ \qquad \text{if } y^2 < 4(\gamma_2 - \gamma_3)^2 . \end{cases} \tag{3.36}$$

The function $g(y)$ is sketched for a typical value of ω in figure 3 while $f(y)$ is sketched in figure 4. Since the integral $G_3(\omega^2)$ is the integral of the product of these



FIGURES 3 AND 4

The 3-D frequency spectrum is proportional to the integral of the product of $g(y)$ and $f(y)$. The functions $f(y)$ and $g(y)$ are sketched here. $f(y)$ is independent of ω while $g(y)$ moves to the left as ω^2 increases.

two functions, only that range of y for which neither $f(y)$ nor $g(y)$ vanish contributes to G_3. Notice that the nonvanishing range of $g(y)$ is to the right of ω_3^2 when $\omega^2 \leqq 0$, and is to the left of $-\omega_3^2$ when $\omega^2 \geqq \omega_L^2$. Hence $G_3 = 0$ when $\omega^2 \leqq 0$ or $\geqq \omega_L^2$ as is required by equation (3.11).

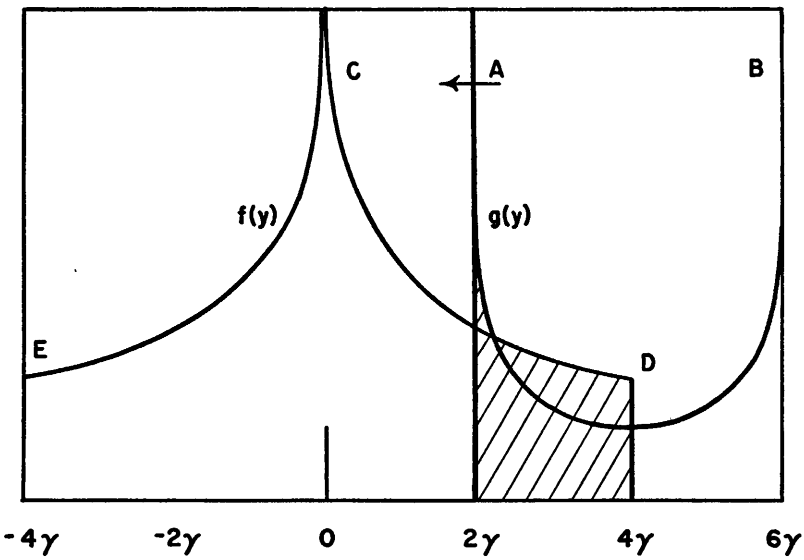


FIGURE 5
The shaded area in this figure represents an example of the overlap of $f(y)$ and $g(y)$ when $\gamma_1 = \gamma_2 = \gamma_3 = \gamma$.

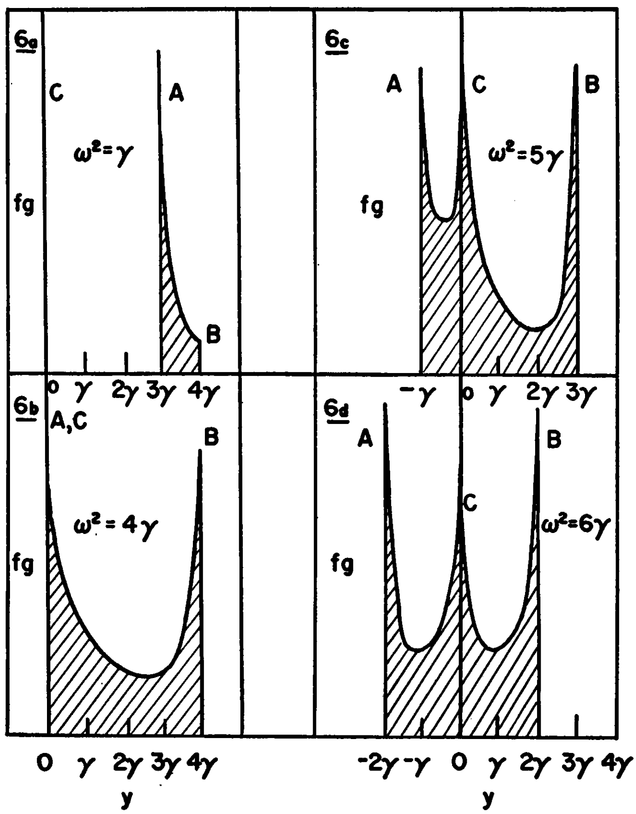


FIGURE 6
Variations in $f(y)g(y)$ with ω^2. The area under the various fg curves is proportional to the frequency distribution which corresponds to the appropriate value of ω^2.

When ω^2 is very small a slight nonvanishing overlap of $f(y)$ and $g(y)$ occurs in the neighborhood of $y = \omega_3^2$. The main contribution to $G_3(\omega^2)$ then comes from the 1-*D* type of peak in $g(y)$ at $y = \omega_3^2 - \omega^2$. Hence in the limit as $\omega \to 0$ we replace the elliptic integral (3.36) by its asymptotic value $\frac{1}{2}\pi$ and we replace the factor $(\omega_L^2 - \omega_3^2 - \omega^2 - y)$ in (3.34) by $\omega_L^2 - 2\omega_3^2 = 4\gamma_1$ to find

$$G_3(\omega^2) \sim [8\pi^2(\gamma_1\gamma_2\gamma_3)^{1/2}]^{-1} \int_{\omega_3^2-\omega^2}^{\omega_3^2} dy/(y + \omega^2 - \omega_3^2)^{1/2} \tag{3.37}$$

$$= \omega/4\pi^2(\gamma_1\gamma_2\gamma_3)^{1/2} .$$

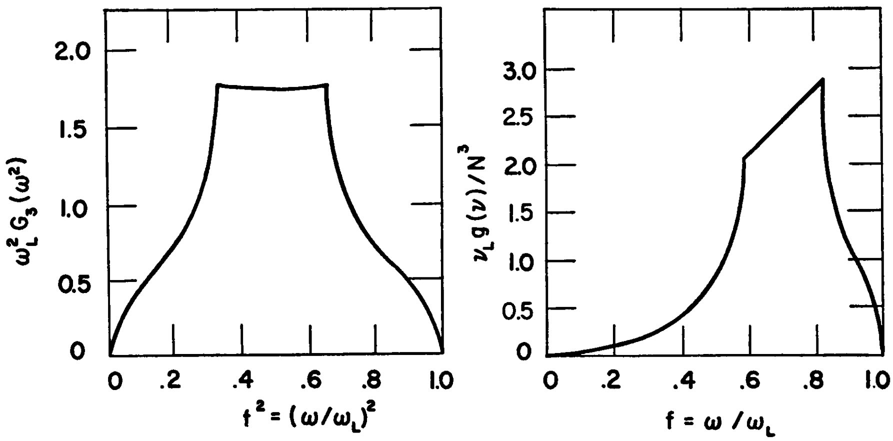


FIGURE 7
Frequency spectrum of a 3-*D* lattice with $\gamma_1 = \gamma_2 = \gamma_3 = \gamma$. Here $\omega_L^2 = 12\gamma$.

Hence the frequency distribution function approaches [see equation (3.8)]

$$g(\nu) \sim 4\pi\nu^2 N^3(M^3/\gamma_1\gamma_2\gamma_3)^{1/2} \quad \text{as} \quad \nu \to 0 . \tag{3.38}$$

Since $G_3(\omega^2) = G_3(\omega_L^2 - \omega^2)$ in our model, we also have

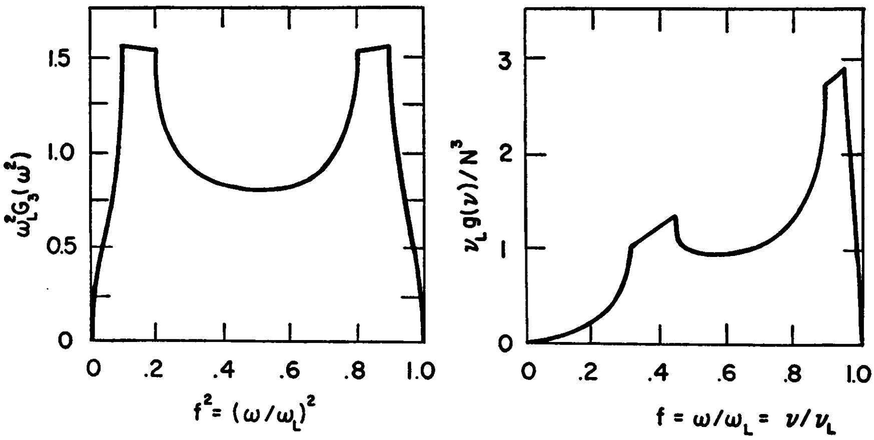
$$g(\nu) \sim 8\nu_L^2\pi N^3(M^3/\gamma_1\gamma_2\gamma_3)^{1/2}[1 - (\nu/\nu_L)^2]^{1/2} \quad \text{as} \quad \nu \to \nu_L . \tag{3.39}$$

This shows that $g(\nu)$ has a vertical tangent at $\nu = \nu_L$ as has been predicted by van Hove [4].

In order to get a qualitative picture of the entire *FS* let us first consider the case $\gamma_1 = \gamma_2 = \gamma_3 = \gamma$. Then the two peaks in figure 4 coincide at $y = 0$ (see figure 5). If we slide $g(y)$ to the left along the y axis (this corresponds to increasing ω^2) as sketched in figure 5 the nonvanishing range of y in the product fg increases (see figures 6a and 6b) and hence $G_3(\omega^2)$ increases. Furthermore, the peaks A and C come together so that $G_3(\omega^2)$ increases very rapidly. This rapid rise stops abruptly at $\omega^2 = 4\gamma$ for two reasons. First, the end of the nonvanishing part of $g(y)$ passes the end of $f(y)$ at 4γ. Hence the total length of the nonvanishing y range of $f(y)g(y)$ stops increasing linearly with ω^2 and remains constant. Secondly, the peaks A and C no longer reinforce each other. As a moves further to the left (figure 6c) the decrease in the contribution of values of y in the neighborhood of A is compensated by an increase from the neighborhood of B [B gets multiplied by the rising part of $f(y)$]. On this basis $G_3(\omega^2)$ remains quite constant until the point B passes C (when $\omega^2 = 8\gamma$) and A passes E. Then both the effective range in y starts to decrease and the reinforcement of B and C diminishes. Hence $G_3(\omega^2)$ drops rapidly at $\omega^2 = 8\gamma$.

The complete $G_3(\omega^2)$ curve is plotted in figure 7a, while that of $g(\nu)$ is given in figure 7b.

The above argument is immediately generalized to the case $\gamma_3 = \gamma_2 < \gamma_1$. Here the distance between A and B in $g(y)$, being $4\gamma_1$, exceeds that between C and D in $f(y)$, $4\gamma_3$. Hence although the $G_3(\omega^2)$ curve flattens abruptly at $\omega^2 = \omega_3^2$ when A and C coincide, it drops suddenly when B passes D (at $\omega^2 = 4\gamma_1$) only to rise to a new peak when B comes in contact with C at $\omega^2 = \omega_L^2 - \omega_3^2$. The second peak is a reflection of the first about the line $\omega^2 = \frac{1}{2}\omega_L^2$. Hence the final $G_3(\omega^2)$ curve is of the form given in figure 8a with the corresponding FS given in figure 8b.



FIGURES 8a AND 8b
Frequency spectrum of a 3-D spectrum with $\gamma_2 = \gamma_3 = \gamma$ and $\gamma_1 = 8\gamma$

When $\gamma_3 < \gamma_2 = \gamma_1$ the 2-D type factor $f(y)$ has two peaks instead of one as in figure 4 and the reader can easily verify that the $G_3(\omega^2)$ curve is of the form given in figure 9. In the most general cases $\gamma_3 < \gamma_2 < \gamma_1$, singularities occur at $\omega^2 = \omega_1^2$, ω_2^2, ω_3^2, $\omega_L^2 - \omega_1^2$, $\omega_L^2 - \omega_2^2$, and $\omega_L^2 - \omega_3^2$. However, the detailed shape of $G_3(\omega^2)$ depends on various other inequalities which might exist between the γ's.

The procedure described above can be generalized for the deduction of a 4-D frequency density function from a 3-D one. The main result is that a new set of corners appear and that the angles of approach to corners need not be so steep. This increase in the number of corners persists as n becomes larger, until in the limit as $n \to \infty$, $G_n(\omega^2)$ becomes Gaussian under a wide set of conditions on the force constants.

The function $(1/N^n)H_n^N$ can be considered as the distribution of the sum of n independent random variables. Hence G_n is the density of the sum of n independent random variables and in general

$$G_{n+1}(\omega^2) = \int_{-\infty}^{\infty} G_n(y)G_1(\omega^2 - y)dy \,. \tag{3.40}$$

Since G_n is symmetric about $\frac{1}{2}\omega_{L,n}^2 = 2(\gamma_1 + \cdots + \gamma_n)$, this becomes

$$G_{n+1}(\omega^2) = \int_{-\infty}^{\infty} G_n(\omega_{L,n}^2 - y)G_1(\omega^2 - y)dy \tag{3.41}$$

$$= \int_{-\infty}^{\infty} G_n(y + \tfrac{1}{2}\omega_{L,n}^2)G_1(y + \omega^2 - \tfrac{1}{2}\omega_{L,n}^2)dy .$$

(*d*) *n very large.* We shall now give a set of conditions under which $G(\omega^2)$ be-

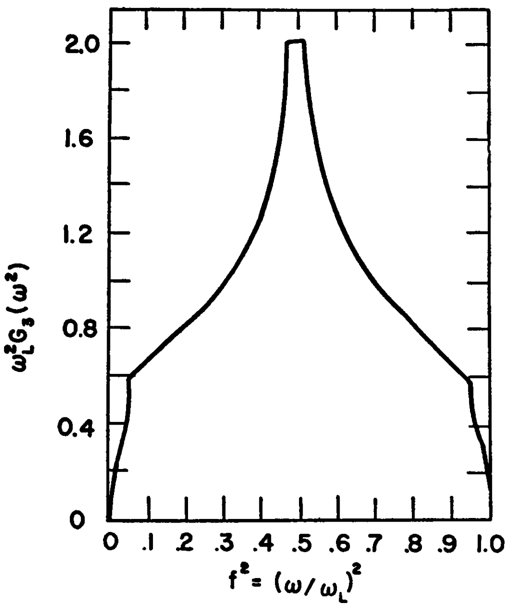


FIGURE 9

The frequency spectrum in a 3-*D* lattice with $\gamma_1 = \gamma_2 = 9\gamma$ and $\gamma_3 = \gamma_1$

comes Gaussian in the limit of large *n*. The deviations of the square of the normal mode frequencies from their average value is

$$\omega^2 - 2(\gamma_1 + \gamma_2 + \cdots + \gamma_n) = -2 \sum_{j=1}^{n} \gamma_j \cos \theta_j . \tag{3.42}$$

This quantity can be considered as a sum of random variables $x_j = -2\gamma_j \cos \theta_j$, $j = 1, 2, \cdots, n$; with first and second moments

$$E(x_j) = -(2\gamma_j/\pi) \int_0^{\pi} \cos \theta_j \, d\theta_j = 0 , \tag{3.43}$$

$$E(x_j^2) = (4\gamma_j^2/\pi) \int_0^{\pi} \cos^2 \theta_j \, d\theta_j = 2\gamma_j^2 . \tag{3.44}$$

Since the x_j's are independent, the dispersion of ω^2 from its mean value is

$$B_n = E[(\omega^2 - 2n\beta_1)^2] = \sum_{j=1}^{n} 2\gamma_j^2 = 2n\beta_2 . \tag{3.45}$$

We can now find a set of conditions under which G_n is approximately Gaussian for large n. By the Lindeberg-Lévy form of the central limit theorem [14], if $E = \max_{j=1,\cdots,n}(2\gamma_j/\sqrt{2n\beta_2})$, then the difference between G_n and the Gaussian distribution is small in the sense that

$$\left| \int_{-\infty}^{a} G_n(\omega^2)d\omega^2 - \int_{-\infty}^{a} \Phi(\omega^2)d\omega^2 \right| < 6E^{1/4} \tag{3.46}$$

where Φ is the density of the normal distribution with the same mean dispersion as G_n.

In the special case $\gamma_1 = \gamma_2 = \cdots = \gamma_n = \gamma$, $\beta_2 = \gamma^2$ and $\omega_L^2 = 4n\gamma$ so that

$$G_n(\omega^2) = \frac{1}{2\gamma[\pi n]^{1/2}} \exp\left[-4n(f^2 - \tfrac{1}{2})^2\right], \qquad (f = \omega/\omega_L = \nu/\nu_L)\ , \tag{3.47}$$

which means that the frequency density function approaches a δ-function with its peak at $f^2 = \frac{1}{2}$ as $n \to \infty$. The frequency spectrum becomes

$$\nu_L g(\nu) = 4(n/\pi)^{1/2} f N^n \exp\left[-4n(f^2 - \tfrac{1}{2})^2\right]. \tag{3.48}$$

The behavior of $G_n(\omega^2)$ for very small values of ω can be determined by noting that small values of $\omega_{s_1,s_2,\cdots}$ are associated with small values of $\phi_1, \phi_2, \cdots$ so that $\omega^2_{s_1 s_2 \cdots} \sim [\pi/(N+1)]^2 \sum \gamma_j s_j^2$. The fraction of frequencies with $\omega_{s_1,\cdots} < \omega$ (ω small) is then proportional to 2^{-n} times the volume of the ellipsoid $\sum (s_j/a_j)^2 = \omega^2$, with $a_j = [(N+1)/\pi]\gamma_j^{-1/2}$ or

$$\left(\frac{N+1}{2\pi}\right)^2 \frac{[\Gamma(\frac{1}{2})]^2}{\Gamma(1+\frac{1}{2}n)} \frac{(\omega^2)^{\frac{1}{2}n}}{(\gamma_1\gamma_2\cdots\gamma_n)^{1/2}}.$$

The proportionality constant is $(\pi/N+1)^2$, the volume of one unit cell in the lattice whose lattice points are $\{\pi s_j/N+1\}$. Hence the frequency density function becomes

$$G_n(\omega^2) \sim \frac{n(\frac{1}{2}\pi^{-1/2})^n(\omega^2)^{\frac{1}{2}n-1}}{2\Gamma(1+\frac{1}{2}n)(\gamma_1\gamma_2\cdots\gamma_n)^{1/2}} \quad \text{as} \quad \omega^2 \to 0\ . \tag{3.49}$$

The reader can easily verify that this checks with the special case $n = 1, 2, 3$ examined above. Since $G_n(\omega^2) = G_n(\omega_L^2 - \omega^2)$ we also have

$$G_n(\omega^2) \sim \frac{n}{2} \frac{(\frac{1}{2}\pi^{-1/2})^n(\omega_L^2 - \omega^2)^{\frac{1}{2}n-1}}{\Gamma(1+\frac{1}{2}n)(\gamma_1\gamma_2\cdots\gamma_n)^{1/2}} \quad \text{as} \quad \omega^2 \to \omega_L^2\ . \tag{3.50}$$

We close this section with a few remarks about the distribution of characteristic values of the n-dimensional Laplace difference operator D^2. When $n = 1$, D^2 is defined by $D^2 u_m = u_{m+1} - 2u_m + u_{m-1}$. The characteristic values λ which satisfy $D^2 u + \lambda u = 0$ under the boundary conditions (2.2) are given by (2.10) with $\gamma_1 = \gamma_2 = \cdots = 1$:

$$\lambda_{s_1,s_2,\cdots} = 2\sum_{j=1}^{N}\left(1 - \cos\frac{\pi s_j}{N+1}\right), \qquad s_j = 1, 2, \cdots, N\ , \tag{3.51}$$

whereas those of the corresponding differential operator ∇^2 with $\nabla^2 u + \lambda u = 0$ are

$$\lambda_{s_1 s_2 \cdots} = (\pi^2/L^2)(s_1^2 + s_2^2 + \cdots + s_n^2), \qquad s_j = 1, 2, 3, \cdots, \tag{3.52}$$

if u vanishes on the boundary of an n dimensional cube with sides of length L.

It is well known that the number of characteristic values $\lambda_{s}\ldots$ between λ and $\lambda + d\lambda$ is $\lambda^{-1+n/2}d\lambda$. In our discrete problem, in the limit as $N \to \infty$ this number is $N^n G_n(\lambda)$ with $G_n(\lambda)$ being given by (3.8) and with $\gamma_1 = \gamma_2 = \gamma_3 = 1$. As has been discussed above various peaks and singularities occur.

The manner in which the distribution function of the discrete lattice degenerates into that of the continuum is clear if we let $N = aL$ in (3.51), a being the lattice spacing, and rewrite $Du + \lambda u = 0$ as $a^{-2}D^2u + \lambda u = 0$. Then (3.51) becomes

$$\lambda_{s_1 s_2 \cdots} = a^{-2} \sum_{j=1}^{N} \left(1 - \cos \frac{\pi a s_j}{L}\right). \tag{3.53}$$

The largest value of λ, $2/a^2$ approaches infinity as $a \to 0$. The characteristic value which corresponds to a fixed set of s_j's approaches (3.52) in this limit. All the peaks and singularities recede to infinity as $a \to \infty$ so that the density function has its continuum form proportional to $\lambda^{-1+n/2}$ in any preassigned finite region. Of course, in the limit as $a \to 0$, $a^{-2}D^2 \to \nabla^2$.

4. Localizability of particles on a lattice

We shall now determine the distribution function of a given particle about its equilibrium position in our lattice. If the dispersion becomes large compared with a lattice spacing, we can no longer associate a particle with a given lattice point and therefore cannot consider a periodic lattice to exist. This question of dispersion due to heat energy in a crystal was first considered by Debye [9] who asked if the general character of an X-ray diffraction pattern of a crystal was affected by lattice vibrations.

We can express the characteristic function of the displacement $u_{m_1 m_2 \cdots}$ of the $(m_1, m_2, \cdots)$-th lattice point from equilibrium as the following integral over the Slater sum:

$$H_{m_1 m_2 \cdots}(\alpha) = \frac{\int \cdot \overset{\infty}{\underset{-\infty}{\vdots}} \cdot \int e^{i\alpha u_{m_1 m_2 \cdots}} \prod_{s_1 s_2 \cdots = 1}^{N} S_{s_1 s_2 \cdots}(u_{s_1 s_2 \cdots}) du_{s_1 s_2 \cdots}}{\int \cdot \overset{\infty}{\underset{-\infty}{\vdots}} \cdot \int \prod_{s_1 s_2 \cdots = 1}^{N} S_{s_1 s_2 \cdots}(u_{s_1 s_2 \cdots}) du_{s_1 s_2}}. \tag{4.1}$$

In view of (2.4), (2.19), and the formula

$$\int_{-\infty}^{\infty} e^{ib\eta} e^{-a\eta^2} d\eta = (\pi/a)^{\frac{1}{2}} \exp(-b^2/4a), \tag{4.2}$$

we find that $u_{m_1 m_2 \cdots}$ has a Gaussian characteristic function

$$H_{m_1 m_2 \cdots}(\alpha) = \exp(\tfrac{1}{2}\sigma^2_{m_1 m_2 \cdots}\alpha^2), \tag{4.3}$$

and hence the Gaussian probability density function

$$(4.4) \qquad F_{m_1m_2\cdots}(u) = (2\pi\sigma^2_{m_1m_2\cdots})^{-\frac{1}{2}} \exp(-u^2/2\sigma^2_{m_1m_2\cdots})$$

where

$$(4.5) \qquad \sigma^2_{m_1m_2\cdots} = \hbar N^{-n} \sum_{s_1s_2\cdots s_n=1}^{N} \frac{\sin^2 \frac{\pi s_1 m_1}{N+1} \sin^2 \frac{\pi s_2 m_2}{N+1} \cdots \sin^2 \frac{\pi s_n m_n}{N+1}}{\omega_{s_1s_2\cdots} \tanh \frac{1}{2} \frac{\hbar\omega_{s_1s_2\cdots}}{kT}}.$$

Since we are concerned only with limit results that are appropriate for very large lattices we let $N \to \infty$ and find the following integral representation for $\sigma^2_{m_1m_2\cdots}$:

$$(4.6) \qquad \sigma^2_{m_1m_2\cdots} = \frac{\hbar}{\pi^n} \int_0^{\pi} \cdots \int \frac{\prod_{j=1}^{n} \sin^2 \phi_j m_j \, d\phi_1 \cdots d\phi_n}{\omega(\phi_1 \cdots \phi_n) \tanh\left(\frac{1}{2} \frac{\hbar\omega(\phi_1 \cdots \phi_n)}{kT}\right)}.$$

The author has been unable to express this multiple integral as a simple function. However, high and low temperature expansions are obtainable without too much difficulty.

(a) *High temperature expansion.* When x is small ($x < \pi$),

$$(4.7) \qquad \coth x = \frac{1}{x}\left(1 + \frac{1}{3}x^2 - \frac{1}{45}x^4 + \frac{2x^6}{945} - \cdots\right).$$

Hence at high temperatures with $h\nu_L/2kT < \pi$,

$$(4.8) \quad \sigma^2_{m_1m_2\cdots} = 2kT\left[S^{(0)}_{m_1m_2\cdots} + \frac{1}{3}\left(\frac{\hbar}{2kT}\right)^2 S^{(2)}_{m_1m_2\cdots} - \frac{1}{45}\left(\frac{\hbar}{2kT}\right)^4 S^{(4)}_{m_1m_2} + \cdots\right],$$

where

$$(4.9) \quad S^{(0)}_{m_1m_2\cdots} = \pi^{-n} \int_0^{\pi} \cdots \int \frac{\sin^2 \phi_1 m_1 \sin^2 \phi_2 m_2 \cdots \sin^2 \phi_n m_n}{2 \sum \gamma_j (1 - \cos \phi_j)} d\phi_1 d\phi_2 \cdots d\phi_n,$$

$$(4.10) \quad S^{(2)}_{m_1m_2\cdots} = \pi^{-n} \int_0^{\pi} \cdots \int \sin^2 \phi_1 m_1 \sin^2 \phi_2 m_2 \cdots \sin^2 \phi_n m_n d\phi_1 \cdots d\phi_n = (\tfrac{1}{2})^n,$$

$$(4.11) \quad S^{(4)}_{m_1m_2\cdots} = 2\pi^{-n} \int_0^{\pi} \cdots \int \sin^2 \phi_1 m_1 \sin^2 \phi_2 m_2 \cdots \sin^2 \phi_n m_n \cdot \left\{\sum_{j=1}^{n} \gamma_j (1 - \cos \phi_j)\right\} d\phi_1 \cdots d\phi_n$$

$$= 2\pi^{-n} (\tfrac{1}{2}\pi)^{n-1} \sum_{j=1}^{n} \gamma_j \int_0^{\pi} (1 - \cos \phi) \sin^2 m\phi d\phi$$

$$= (\tfrac{1}{2})^{n-1} \sum_{j=1}^{n} \gamma_j = (\tfrac{1}{2})^{n+1} \omega_L^2, \quad \text{etc.}$$

The integral $S^{(0)}_{m_1m_2}\cdots$ can be reduced to quadratures by noting that $Z^{-1}=\int_0^\infty e^{-Zx}\,dx$ so that it can be written as

$$S^{(0)}_{m_1m_2}\cdots = \frac{1}{2\pi^n}\int_0^\infty dx \prod_{j=1}^{n}\int_0^\pi \sin^2 \phi_j m_j\, e^{-x\gamma_j(1-\cos\phi_j)}\,d\phi_j\,. \tag{4.12}$$

Since

$$\int_0^\pi \sin^2 m\phi \exp(x\gamma\cos\phi)d\phi = \frac{1}{2}\int_0^\pi (1-\cos 2m\phi)\exp(x\gamma\cos\phi)d\phi = \frac{\pi}{2}[I_0(x\gamma)-I_{2m}(\gamma x)]\,, \tag{4.13}$$

we have

$$S^{(0)}_{m_1m_2}\cdots = 2^{-(n+1)}\int_0^\infty e^{-x\Sigma\gamma_j}\prod_{j=1}^{n}\{I_0(x\gamma_j)-I_{2m_j}(x\gamma_j)\}dx\,. \tag{4.14}$$

The form of these integrals is so sensitive to the value of n that we shall not write a general expression for $S^{(0)}$ (even though one can be written in terms of generalized hypergeometric functions). We shall rather find $S^{(0)}$ when $n = 1, 2, 3$.

(i) *Linear chains*, $n = 1$. Here

$$\begin{aligned} S^{(0)}_m &= \frac{1}{4}\int_0^\infty e^{-x\gamma}[I_0(x\gamma)-I_{2m}(x\gamma)]dx \\ &= \frac{1}{4\gamma}\lim_{p\to 1}\left[\int_0^\infty e^{-px}I_0(x)dx - \int_0^\infty e^{-px}I_{2m}(x)dx\right] \\ &= \frac{1}{4\gamma}\lim_{p\to 1}(p^2-1)^{-\frac{1}{2}}[1-(p+\sqrt{p^2-1})^{-2m}] \\ &= m/2\gamma\,. \end{aligned} \tag{4.15}$$

Hence the one-dimensional high temperature expansion for σ_m^2 for a particle of mass M is

$$\sigma_m^2 = \frac{kT}{4\pi^2 M\nu_L^2}\left[4m + \frac{1}{3}\left(\frac{h\nu_L}{2kT}\right)^2 - \frac{1}{90}\left(\frac{h\nu_L}{2kT}\right)^4 + \cdots\right]. \tag{4.16}$$

This series converges when $h\nu_L/2kT < \pi$. If we choose m to be larger than 10^4 all temperature dependent terms in the bracket can be neglected and

$$\sigma_m^2 = \frac{mkT}{M\pi^2\nu_L^2} \qquad \text{if} \quad h\nu_L/2kT < \pi\,. \tag{4.17}$$

(ii) *Square lattice*, $n = 2$. Here

$$S^{(0)}_{m_1m_2}\cdots = \frac{1}{8}\int_0^\infty e^{-x(\gamma_1+\gamma_2)}[I_0(x\gamma_1)-I_{2m_1}(x\gamma_1)][I_0(x\gamma_2)-I_{2m_2}(x\gamma_2)]dx\,. \tag{4.18}$$

The formula (see [13])

$$(4.19)\qquad I_{\mu,\nu} = \int_0^\infty e^{-px} I_{2\mu}(x\gamma_1)I_{2\mu}(x\gamma_2)dx$$

$$= \frac{\gamma_1^{2\mu}\gamma_2^{2\nu}\Gamma(\frac{1}{2}+\mu+\nu)\Gamma(1+\mu+\nu)}{\pi^{1/2}p^{1+2\mu+2\nu}\Gamma(1+2\mu)\Gamma(1+2\nu)} \mathfrak{F}_4(\tfrac{1}{2}+\mu+\nu,\ 1+\mu+\nu,\ 2\mu+1,\ 2\nu+1,\ \gamma_1^2/p^2,\ \gamma_2^2/p^2)$$

where $\mathfrak{F}_4$ is a generalized hypergeometric function

$$(4.20)\qquad \mathfrak{F}_4(\alpha, \beta; \gamma, \gamma'; x, y) = \sum \frac{(\alpha)_{m+n}(\beta)_{m+n}}{(\gamma)_m(\gamma')_n m!n!} x^m y^n$$

with $(a)_n = \Gamma(a + n)/\Gamma(a)$ allows us to write

$$(4.21)\qquad S_{m_1m_2}^{(0)} = \frac{1}{8}\{I_{0,0} - I_{0,2m_2} - I_{2m_1,0} + I_{2m_1,2m_2}\} .$$

Since asymptotic formulas for generalized hypergeometric functions in the limit of large μ and ν have not been discussed in the literature, we shall write $S_{m_1m_2}^{(0)}$ as a form more appropriate for the range of large m_1 and m_2. We can determine the qualitative behavior of $\sigma_{m_1m_2}^2$ for points far from the boundaries of our square lattice by letting $m_1 = m_2 = m$. Then

$$(4.22)\qquad S_{m,m}^{(0)} = \frac{1}{8}\left\{\int_0^\infty e^{-x(\gamma_1+\gamma_2)}[I_0(x\gamma_1)I_0(x\gamma_2) - I_{2m}(x\gamma_1)I_{2m}(x\gamma_2)]dx\right.$$
$$+ \int_0^\infty e^{-x(\gamma_1+\gamma_2)} I_{2m}(x\gamma_1)[I_{2m}(x\gamma_2) - I_0(x\gamma_2)]dx$$
$$\left. + \int_0^\infty e^{-x(\gamma_1+\gamma_2)} I_{2m}(x\gamma_2)[I_{2m}(x\gamma_1) - I_0(x\gamma_2)]dx\right\} .$$

The asymptotic behavior of the second two integrals is discussed in appendix I where it is shown that they are negligible compared with the first when m is large. The first integral converges but if it is separated into the difference of two integrals each of those does not. However, if we introduce the integrating factor exp $(-\gamma\epsilon)$ both converge. Then we have as the value of the difference (see [13])

$$(4.23)\qquad \lim_{\epsilon\to 0}\left\{\int_0^\infty e^{-x(\gamma_1+\gamma_2+\epsilon)} I_0(x\gamma_1)I_0(x\gamma_2)dx - \int_0^\infty e^{-x(\gamma_1+\gamma_2+\epsilon)} I_{2m}(x\gamma_1)I_{2m}(x\gamma_2)dx\right\}$$

$$= \lim_{\epsilon\to 0}\frac{1}{\pi(\gamma_1\gamma_2)^{1/2}}\left[Q_{-\frac{1}{2}}\left(\frac{(\gamma_1+\gamma_2+\epsilon)^2-\gamma_1^2-\gamma_2^2}{2\gamma_1\gamma_2}\right) - Q_{2m-\frac{1}{2}}\left(\frac{(\gamma_1+\gamma_2+\epsilon)^2-\gamma_1^2-\gamma_2^2}{2\gamma_1\gamma_2}\right)\right]$$

where the Q's are Legendre functions of the second kind. Since (see [15]) $Q_\nu(Z) \sim -\frac{1}{2}\log(\frac{1}{2}\epsilon) - \gamma - \Psi(\nu + 1)$, where $Z = 1 + \epsilon$ and $\epsilon \to 0$, $\gamma = 0.57721$, and $\Psi(n + x) - \Psi(x) = 1/x + 1/(x + 1) + \cdots + 1/(x + n - 1)$, our integral becomes

$$(4.24)\qquad \frac{2}{\pi(\gamma_1\gamma_2)^{1/2}}\left\{1 + \frac{1}{3} + \frac{1}{5} + \cdots + \frac{1}{2m-1}\right\} \sim \frac{1}{\pi(\gamma_1\gamma_2)^{1/2}}\log 2m .$$

Hence as $m \to \infty$

$$(4.25) \qquad S^{(0)}_{m,m} \sim [8\pi(\gamma_1\gamma_2)^{1/2}]^{-1} \log 2m \ .$$

If we introduce a mass M for the particles, the term $(\gamma_1\gamma_2)^{1/2}$ becomes $(\gamma_1\gamma_2/M^2)^{1/2}$, $\nu_L^2 = (\gamma_1 + \gamma_2)/\pi^2 M$ and our desired dispersion becomes

$$(4.26) \quad \sigma^2_{m,m} \sim \frac{kT}{2M\nu_L^2}\left\{\frac{1}{2\pi^3}\left[\frac{(\gamma_1+\gamma_2)^2}{\gamma_1\gamma_2}\right]^{\frac{1}{2}} \log 2m + \frac{1}{3}\left(\frac{h\nu_L}{2kT}\right)^2 - \frac{1}{90}\left(\frac{h\nu_L}{2kT}\right)^4 + \cdots\right\}$$

where the series converges if $h\nu_L/2kT < \pi$. Hence as long as $\log 2m \gg \pi$ $(m \gg 12)$ we can neglect the temperature dependent terms in the bracket to find

$$(4.27) \qquad \sigma^2_{m,m} \sim \frac{kT}{4\pi(\gamma_1\gamma_2)^{1/2}} \log 2m \quad \text{if} \quad h\nu_L/2kT < m \ .$$

(iii) *Simple cubic lattice*, $n = 3$. In this case $S^{(0)}_{m_1m_2m_3}$ is a sum of four integrals over products of the Bessel functions [see equation (4.14)]. In the limit of large m_1, m_2, m_3 (lattice points far from the boundaries of the cube) one can apply the asymptotic results of Appendix III (equation III–6) to find that those terms with at least one large subscript become negligibly small. Then one finds

$$(4.28) \qquad S^{(0)}_{m_1m_2m_3} \rightarrow 2^{-4}\int_0^\infty e^{-x(\gamma_1+\gamma_2+\gamma_3)}\, I_0(x\gamma_1)I_0(x\gamma_2)I_0(x\gamma_3)dx = S^{(0)}$$

as m_1, m_2, $m_3 \rightarrow \infty$. The case of main physical interest is one with two of the γ's equal, say $\gamma_2 = \gamma_3$. Then one finds from equation II-20 and equation II-17 that $S_{m_1m_2m_3}$ is independent of the m_j's as they become large and that

$$(4.29) \qquad \begin{aligned} S^{(0)} &= S^{(0)}_{m_1m_2m_3} = \frac{1}{4\pi^2(\gamma_1\gamma_2)^{1/2}}\{(1+\gamma)^{\frac{1}{2}} - (\gamma - 1)^{\frac{1}{2}}\}K(k_3)K'(k_3) \\ &= \frac{1}{16\gamma_2} I([\gamma_1/\gamma_2]^{1/2}) \end{aligned}$$

where $\gamma = (3\gamma_1 + 4\gamma_2)/\gamma_1$, $k_3 = \frac{1}{2}[(\gamma - 1)^{1/2} - (\gamma - 3)^{1/2}][(\gamma + 1)^{1/2} - (\gamma - 1)^{1/2}]$, and $K(k_3)$ corresponds as usual to the elliptic function of the second kind and $K'(k_3) = K([1 - k_3^2]^{1/2})$. The integral $I(\alpha)$ is discussed in Appendix II and plotted in figure 13.

When noncentral forces are weak (when $\gamma_1 \gg \gamma_2$), equation (4.29) simplifies to

$$(4.30) \qquad S^{(0)}_{m_1m_2m_3} \sim \frac{(2 - 2^{1/2})}{4\pi^2(\gamma_1\gamma_2)^{1/2}} K^2(2^{1/2} - 1) \qquad \text{as} \quad \gamma_1/\gamma_2 \rightarrow 0 \ .$$

This result, being independent of (m_1, m_2, m_3), implies that at all lattice points far from the boundaries of our cube

$$(4.31) \quad \sigma^2 = \frac{kT}{8\pi^2\nu_L^2 M}\left\{[(\gamma_1+2\gamma_2)/\gamma_2]I(\gamma_1/\gamma_2) + \frac{1}{6}(h\nu_L/2kT)^2 - \frac{1}{180}(h\nu_L/2kT)^4 + \cdots\right\}.$$

This expression differs from the analogous 1-D and 2-D results in that it depends only on the temperature, particle masses and force constants.

We now proceed with the

(b) *Low temperature expansion*. When x is large $\coth x = 1 + 2e^{-2x} + 2e^{-4x} + 2e^{-6x} + \cdots$ so that

$$(4.32)\quad \sigma^2_{m_1m_2\cdots} = \frac{\hbar}{\pi^n}\int_0^\pi\cdots\int \omega^{-1}\left[1+2\sum_{j=1}^{\infty}\exp\left(-j\frac{\hbar\omega}{kT}\right)\right]\prod_1^n \sin^2\phi_j m_j d\phi_1\cdots d\phi_n.$$

The asymptotic low temperature limit can be reduced to quadratures through the introduction of

$$(4.33)\qquad z^{-\frac{1}{2}} = (2/\pi^{1/2})\int_0^\infty e^{-zx^2}\,dx$$

and a repetition of the argument used in the derivation of (4.14). We then have

$$(4.34)\qquad \sigma^2_{m_1m_2\cdots} \sim \frac{\hbar(\pi)^{-\frac{1}{2}}}{2^{n+\frac{1}{2}}}\int_0^\infty x^{-\frac{1}{2}}e^{-x\Sigma\gamma_j}\prod_{j=1}^n \{I_0(x\gamma_j) - I_{2m_j}(x\gamma_j)\}\,dx$$

where, as before, $I_m(x)$ is the nth Bessel function of purely imaginary argument.

We shall now find $\sigma^2_{m_1,m_2,\cdots}$ for 1, 2, and 3 dimensions.

(i) $n = 1$, *one-dimensional lattice.*

$$(4.35)\qquad \sigma^2_m \sim \frac{1}{4}\hbar\left(\frac{2}{\pi}\right)^{\frac{1}{2}}\int_0^\infty x^{-\frac{1}{2}}e^{-x\gamma}[I_0(x\gamma) - I_{2m}(x\gamma)]dx$$

$$= \frac{\hbar 2^{1/2}}{4(\pi\gamma)^{1/2}}\lim_{p\to 1}\left\{\int_0^\infty x^{-\frac{1}{2}}e^{-px}I_0(x)dx - \int_0^\infty x^{-\frac{1}{2}}e^{-px}I_{2m}(x)dx\right\}$$

$$= \frac{\hbar\gamma^{-\frac{1}{2}}}{2\pi}\lim_{p\to 1}\{Q_{-\frac{1}{2}}(p) - Q_{2m-\frac{1}{2}}(p)\}$$

where $Q_n(x)$ is the nth Legendre function of the second kind. It has a singularity at $x = 1$. The asymptotic expression in the neighborhood of $x = 1$ is (see [15])

$$(4.36)\qquad Q_\nu(x) \sim -\tfrac{1}{2}\log(x-1)/2 - \gamma - \Psi(1+\nu) + O(x-1)$$

where γ is Euler's constant 0.57721... and where for integral n

$$(4.37)\qquad \Psi(Z+n) - \Psi(Z) = \frac{1}{Z} + \frac{1}{Z+1} + \cdots + \frac{1}{Z+n-1}\,.$$

We finally obtain the low temperature limit

$$(4.38)\qquad \sigma^2_m = \frac{\hbar}{2\pi\gamma^{1/2}}[\Psi(2m+\tfrac{1}{2}) - \Psi(\tfrac{1}{2})]\hbar/(2\pi\gamma^{\frac{1}{2}})$$

$$= \frac{\hbar}{\pi\gamma^{1/2}}\left[1 + \frac{1}{3} + \frac{1}{5} + \cdots + \frac{1}{4m-1}\right].$$

The sum has the asymptotic value $\frac{1}{2}\log m$ when m is large. We can introduce the particle mass M and use this asymptotic relation to find

$$(4.39)\qquad \sigma^2_m = \tfrac{1}{2}(\hbar/M\nu_L\pi^2)\log m\,.$$

(ii) $n = 2$, *square lattice.*

We apply (4.34) with $n = 2$ to obtain

$$(4.40)\quad \sigma^2_{m_1m_2} = \frac{2^{\frac{1}{2}}}{8}\hbar\pi^{-\frac{1}{2}}\{F_{00}(\gamma_1,\gamma_2) - F_{0,2m_2}(\gamma_1,\gamma_2) - F_{2m_1,0}(\gamma_1,\gamma_2) + F_{2m_1,2m_2}(\gamma_1,\gamma_2)\}$$

where (see [13])

$$(4.41)\qquad F_{\alpha,\beta}(\gamma_1,\gamma_2) = \int_0^\infty x^{-\frac{1}{2}} e^{-x(\gamma_1+\gamma_2)} I_\alpha(x\gamma_1) I_\beta(x\gamma_1)dx$$
$$= (\gamma_1\gamma_2)^{-1/4}\,\Gamma(\alpha+\beta+\tfrac{1}{2}) P^{-\alpha}_{\beta-\frac{1}{2}}(\Gamma_2) P^{-\beta}_{\alpha-\frac{1}{2}}(\Gamma_1)\ ,$$

$$(4.42)\qquad \Gamma_j = [(\gamma_1+\gamma_2)/\gamma_j]^{1/2}, \qquad j = 1, 2;$$

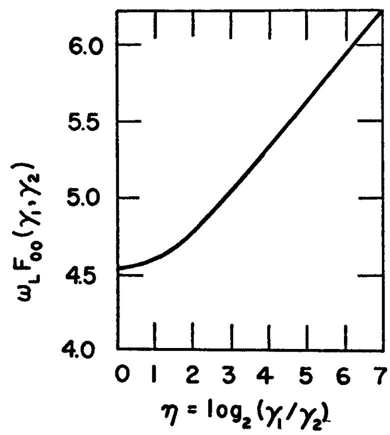


FIGURE 10

Variation of the integral $\omega_L F_{00}$ $(\gamma_1\gamma_2)$; (see equation 4.41) with $(\gamma_1/\gamma_2) = 2^n$.

and $P^\nu_\mu(Z)$ is the Legendre function of the first kind. In the special case $\alpha = \beta = 0$, we have

$$(4.43)\qquad F_{00}(\gamma_1,\gamma_2)$$
$$= \frac{8}{\pi^{3/2}(\gamma_1\gamma_2)^{1/4}} \frac{1}{[(\Gamma_1+1)(\Gamma_2+1)]^{1/2}} K\,[(\Gamma_2-1)(\gamma_2/\gamma_1)^{\frac{1}{2}}] K[(\Gamma_1-1)(\gamma_1/\gamma_2)^{\frac{1}{2}}]\ ,$$

where as usual $K(k)$ is a complete elliptic integral of the first kind. We have plotted this function in figure 10.

It is shown in Appendix IV that when $\gamma_1^{-1}m_1^2 + \gamma_2^{-1}m_2^2$ is large

$$(4.44)\qquad F_{2m_1,2m_2}(\gamma_1,\gamma_2) = \frac{1}{4}\left(\frac{2}{\gamma_1\gamma_2\pi}\right)^{\frac{1}{2}} / (\gamma_1^{-1}m_1^2 + \gamma_2^{-1}m_2^2)^{\frac{1}{2}}\ .$$

Hence as m_1 and $m_2 \to \infty$,

$$(4.45)\qquad \sigma^2_{m_1,m_2} \sim \frac{2^{\frac{1}{2}}}{8}\frac{\hbar\pi^{-\frac{1}{2}}}{M^{\frac{1}{2}}} F_{00}(\gamma_1,\gamma_2)\ ,$$

independently of m_1 and m_2. Furthermore when $\gamma_2 \ll \gamma_1$, F_{00} has the asymptotic form

$$(4.46)\qquad F_{00}(\gamma_1,\gamma_2) \sim (2\pi\gamma_1)^{-\frac{1}{2}} \log(64\gamma_1/\gamma_2)\ .$$

Hence the dispersion gets large as $\gamma_2 \to 0$.

(iii) *3-D lattices.*

The 3-D expression for the low temperature σ^2 which is analogous to (4.40) contains six integrals of products of three Bessel functions. Those integrals with Bessel functions of order m_1, m_2, or m_3 can be expected to approach zero with increasing m_1, m_2, and m_3 even faster than those of products of two Bessel functions. Hence for those atoms far from the boundaries, we have the asymptotic low temperature dispersion (see equation (4.34))

$$\sigma_0^2 = \frac{2^{\frac{1}{2}}\hbar}{16\pi^{\frac{1}{2}}}\int_0^\infty x^{-\frac{1}{2}}\, e^{-x(\gamma_1+\gamma_2+\gamma_3)} I_0(x\gamma_1)I_0(x\gamma_2)I_0(x\gamma_3)dx\ . \tag{4.47}$$

A series expansion can easily be obtained for this integral when $\gamma_2 = \gamma_3$ (it is to be recalled that $\gamma_2 \ll \gamma_1$ in interesting physical cases). We have

$$\sigma_0^2 = \frac{\hbar 2^{\frac{1}{2}}}{16\pi^{\frac{1}{2}}}\int_0^\infty x^{-\frac{1}{2}}\, e^{-x(\gamma_1+2\gamma_2)} I_0(x\gamma_1) \sum_{m=0}^{\infty} \frac{(\frac{1}{2}x\gamma_2)^{2m}\Gamma(2m+1)}{m![\Gamma(1+m)]^3}\, dx\ . \tag{4.48}$$

After interchanging the order of integration and summation and applying a formula on p. 196 of Tables of Integral Transforms [13] we find

$$\sigma_0^2 = \frac{\hbar}{16[\gamma_2(\gamma_1+\gamma_2)]^{1/4}M^{1/2}}\left\{P_{-\frac{1}{2}}(Z)+\sum_{m=1}^{\infty}2^{-8m}\left(\frac{\gamma_2}{\gamma_1+\gamma_2}\right)^m\frac{\Gamma(4m+1)}{[\Gamma(m+1)]^4}P_{2m-\frac{1}{2}}(Z)\right\} \tag{4.49}$$

$$Z = \tfrac{1}{2}(\gamma_1 + 2\gamma_2)/[\gamma_2(\gamma_1+\gamma_2)]^{1/2} \tag{4.50}$$

where $P_n(Z)$ represents the nth order Legendre polynomial. When m is large (see [16])

$$P_{2m-\frac{1}{2}}\left(\frac{\gamma_1+2\gamma_2}{2[\gamma_2(\gamma_1+\gamma_2)]^{\frac{1}{2}}}\right) \sim \frac{1}{(\pi\gamma_1)^{\frac{1}{2}}(4m-1)^{\frac{1}{2}}}\left(\frac{\gamma_1+\gamma_2}{\gamma_2}\right)^m[\gamma_2(\gamma_1+\gamma_2)]^{1/4} \tag{4.51}$$

and

$$\Gamma(4m)/[\Gamma(m+1)]^4 \sim \frac{(2\pi)^{1/2}2^{8m}}{8\pi^2 m^{5/2}}\ . \tag{4.52}$$

Hence the mth term approaches

$$\frac{[\gamma_2(\gamma_1+\gamma_2)]^{1/4}}{2\pi^2 m^2(2\gamma_1)^{1/2}} \tag{4.53}$$

so that the series can be expected to converge fairly rapidly.

A good approximation can be obtained for σ^2 by using (4.53) when $m \geqq 4$ and using the exact terms when $m < 4$. We have

$$\sum_4^\infty m^{-2} = (\pi^2/6) - (49/36) \tag{4.54}$$

and

$$P_{-\frac{1}{2}}\left(\frac{\gamma_1+2\gamma_2}{2[\gamma_2(\gamma_1+\gamma_2)]^{\frac{1}{2}}}\right) = \frac{4}{\pi\gamma_1}[(\gamma_1+\gamma_2)^{\frac{1}{2}}-\gamma_2^{\frac{1}{2}}][\gamma_2(\gamma_1+\gamma_2)]^{1/4}K([(\gamma_1+\gamma_2)^{\frac{1}{2}}-\gamma_2^{\frac{1}{2}}]^2/\gamma_1) \tag{4.55}$$

$$P_{\frac{1}{2}}\left(\frac{\gamma_1+2\gamma_2}{2[\gamma_2(\gamma_1+\gamma_2)]^{\frac{1}{2}}}\right) = \frac{2}{\pi}\left(\frac{\gamma_1+\gamma_2}{\gamma_2}\right)^{1/4}E(\{\gamma_1/[\gamma_1+\gamma_2]\}^{\frac{1}{2}})\ , \tag{4.56}$$

where K and E are elliptic integrals of the first and second kind. The Legendre functions $P_{3/2}$, $P_{7/2}$, and $P_{11/2}$ can be expressed as

$$P_{3/2}(Z) = \frac{4}{3} ZP_{1/2}(Z) - \frac{1}{3} P_{-\frac{1}{2}}(Z) \tag{4.57}$$

$$P_{7/2}(Z) = \frac{1}{105} (384Z^3 - 208Z)P_{1/2}(Z) - \frac{1}{105} (96Z^2 - 25)P_{-\frac{1}{2}}(Z) \tag{4.58}$$

$$P_{11/2}(Z) = \frac{1}{10395} \{(122{,}880Z^5 - 129{,}024Z^3 + 25{,}668Z)P_{1/2}(Z) - (30{,}720Z^4 - 23{,}616Z^2 + 2025)P_{-\frac{1}{2}}(Z)\} . \tag{4.59}$$

We have plotted the asymptotic value of $\sigma_0^2 M^{1/2}\sigma_1^{1/2}/\hbar$ as a function of γ_2/γ_1 in figure 11 as the temperature approaches 0°K.

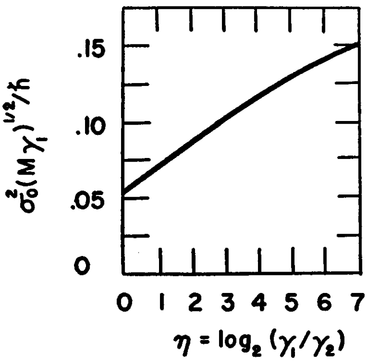


FIGURE 11

Variation of the dispersion σ_0^2 of a given atom (in a 3-D lattice) from its equilibrium position at absolute zero temperature as a function of the ratio of central to noncentral force constants (γ_1/γ_2). The parameter n is chosen so that $\gamma_1/\gamma_2 = 2^n$.

In the limit as $\gamma_2/\gamma_1 \rightarrow 0$, the parameter Z [see (4.50)] approaches $\frac{1}{2}(\gamma_2/\gamma_1)^{1/2}$ so that (see [15])

$$P_{2m-\frac{1}{2}}(Z) \sim \frac{\Gamma(2m)(\gamma_1/\gamma_2)^{m-1/4}}{\frac{1}{2}\Gamma(2m + \frac{1}{2})} \tag{4.60}$$

so that the series in (4.43) becomes

$$\pi^{-\frac{1}{2}}(\gamma_2/\gamma_1)^{1/4}\sum_{m=1}^{\infty} 2^{-8m} \frac{\Gamma(2m)\Gamma(4m+1)}{\Gamma(2m+\frac{1}{2})[\Gamma(m+1)]^4} = 0.0666\,(\gamma_2/\gamma_1)^{1/4} \tag{4.61}$$

while $P_{-1/2}(Z)$ becomes $\frac{1}{\pi}\left(\frac{\gamma_2}{\gamma_1}\right)^{1/4} \log(16\,\gamma_1/\gamma_2)$. Hence, in the limit as $\gamma_1/\gamma_2 \rightarrow \infty$ and $T \rightarrow 0$

$$\sigma_0^2 \sim \frac{\hbar}{16\pi(\gamma_1 M)^{1/2}} \log(16\gamma_1/\gamma_2) . \tag{4.62}$$

This differs from the corresponding 2–D expression (4.46) by having the factor 16 rather than 64 in the logarithmic term.

A good approximation to the first temperature dependent term in the expansion of σ^2 [see equation (4.32)] as a power series in (kT) can be obtained as follows.

In the limit as $T \to 0$ the main contribution of the integrand of

$$(4.63) \qquad \pi^{-3} \iiint_0^{\pi} \omega^{-1} \sum_{j=1}^{\infty} \exp\,(-j\hbar\omega/kT) d\phi_1 d\phi_2 d\phi_3$$

comes at small value of ω. However, the relation between ω and the ϕ's in this range is $\omega^2 \sim \sum_{j=1}^{3} \gamma_j \phi_j^2$. Since each of the exponentials is a rapidly decreasing Gaussian function in this approximation, the upper limits of integration can be extended to ∞ and one can introduce spherical polar coordinates (after letting $x = \phi_1 \gamma_1^{1/2}$, etc.). Then the integral becomes

$$4.64) \qquad \frac{1}{\pi^3(\gamma_1\gamma_2\gamma_3)^{1/2}} \sum_{j=1}^{\infty} \int_0^{\infty} \frac{4\pi\omega^2}{\omega} \exp\,(-j\hbar\omega/kT) d\omega = \frac{4(kT)^2}{\pi^2\hbar^2(\gamma_1\gamma_2\gamma_3)^{1/2}} \sum j^{-2} = \frac{2}{3} \frac{(kT/\hbar)^2}{(\gamma_1\gamma_2\gamma_3)^{1/2}}\,.$$

The first two terms in a low temperature expansion of the dispersion is (in the symmetrical lattice with $\gamma_2 = \gamma_3$)

$$(4.65) \qquad \sigma^2 \sim \sigma_0^2 + \frac{2\hbar}{3(\gamma_1 M)^{1/2}} \left(\frac{kT}{h\nu_L}\right)^2 \left(\frac{\gamma_1 + 2\gamma_2}{\gamma_2}\right) + \cdots .$$

We see that as the effect of noncentral forces diminishes (that is, as $\gamma_2/\gamma_1 \to 0$) the zero point dispersion increases and the temperature dependent dispersion becomes effective at lower temperatures. The next order terms in the expansion would come from the ϕ^4 terms in the expansion of ω^2.

The dispersion can be obtained from an integration over the frequency distribution function at all temperatures

$$(4.66) \qquad \sigma^2 = \frac{\hbar}{16\pi^4 N^3} \int_0^{\nu_L} \frac{g(\nu) d\nu}{\nu \tanh\left(\frac{1}{2}\frac{h\nu}{kT}\right)}\,.$$

We can summarize the results of this section as follows. Every particle in our lattice has a Gaussian distribution about its equilibrium position. The value of σ^2 in the distribution depends on temperatures, force constants, and dimensionality.

In a linear chain σ^2 is proportional at high temperatures to the distance of the particle of interest from a fixed end of the chain; at low temperatures, to the logarithm of that distance. Hence those atoms far from the ends of a long chain might vibrate over distances long compared with the lattice spacings.

A particle on a 2-D lattice has a σ^2 which is independent of its equilibrium position at low temperatures provided that it is far away from lattice boundaries. At high temperatures σ^2 is proportional to kT times the logarithm of its distance from the boundaries. Hence, at low temperatures a particle is localized at a given unit cell, while in a system of a sufficiently large number of particles a particle sufficiently far from a boundary may at high temperatures lose its localization.

The particles in a three-dimensional lattice with harmonic forces are localized at all temperatures. We have plotted σ^2 (figure 12) as a function of temperature for typical particles far from boundaries. Curves are given for various values of γ_2/γ_1.

As is to be expected the dispersion increases as the strength of the noncentral force constant diminishes.

It is to be recalled that in our nearest neighbor interaction model the above-discussed values of σ^2 correspond to the components of displacements from equilibrium in the direction of only one of the crystal axes. The total dispersion is the sum of that over all three directions. When more distant neighbor interactions are included the displacements in different directions are correlated. In a highly anisotropic lattice the dispersions from equilibrium are greatest in the direction of weakest intermolecular forces.

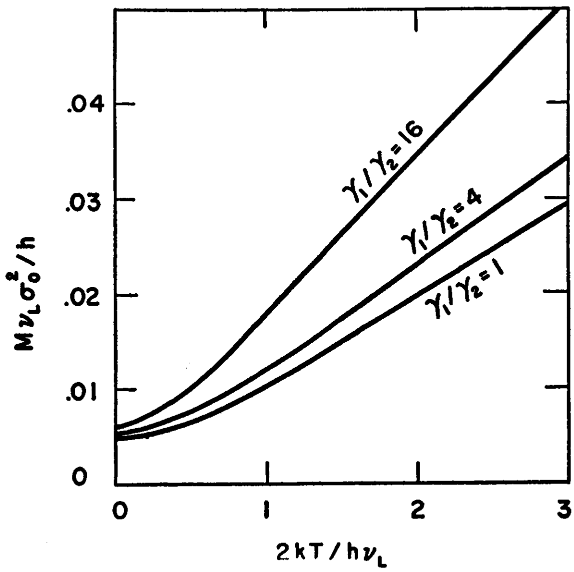


FIGURE 12

Variation of the dispersion σ^2 with temperature in a 3-D lattice

The joint distribution function of the displacements of a pair of particles from equilibrium is the double Fourier transform of the characteristic function

$$(4.67)\qquad G(\{m\},\ \{m+\mu\};\alpha_1,\alpha_2) = E(\exp -i[\alpha_1 u_{m_1,m_2,\cdots} + \alpha_2 u_{m_1+\mu_1,\cdots}])\ .$$

Here $\{m\} \equiv (m_1, m_2, \cdots, m_n)$ represents the coordinates of one of the particles, and $\{m+\mu\}$ those of the other. Various values of the displacements are weighted by the Slater sum. One finds the characteristic function (4.67) to be Gaussian with the formula

$$(4.68)\qquad \exp\left[-\tfrac{1}{2}(\sigma_m^2\alpha_1^2 + 2r\alpha_1\alpha_2\sigma_m\sigma_{m+\mu} + \alpha_2^2\sigma_{m+\mu}^2)\right]$$

where the σ's are given by (4.6) and

$$(4.69)\qquad r\sigma_m\sigma_{m+\mu} = \frac{\hbar}{(2\pi)^n}\int_0^\pi\cdots\int \frac{\prod_1^n\{\cos\phi_j\mu_j - \cos\phi_j(2m_j+\mu_j)\}}{\omega\tanh\left(\frac{1}{2}\frac{\hbar\omega}{kT}\right)}d\phi_1\cdots d\phi_n\ .$$

Here r is the correlation coefficient between particles separated by the vector μ. Since the characteristic function (4.68) is Gaussian, its Fourier transform is also Gaussian and the joint distribution function is

$$(4.70)\qquad F(u_m, u_{m+\mu}) = \frac{1}{2\pi\sigma_m\sigma_{m+\mu}(1-r^2)^{1/2}} \exp\left\{-\frac{1}{2(1-r^2)}\left[\left(\frac{u_m}{\sigma_m}\right)^2 - 2r\frac{u_m}{\sigma_m}\frac{u_{m+\mu}}{\sigma_{m+\mu}} + \left(\frac{u_{m+\mu}}{\sigma_{m+\mu}}\right)^2\right]\right\}.$$

High and low temperature limits of r (defined in (4.69)) are obtained in the same way as they were found in the discussion of σ. We shall merely list these results for the 1-D case and high temperature asymptotic results for the 3-D lattice.

In the 1-D case the high temperature limit of (4.69) is

$$(4.71)\qquad r\sigma_m\sigma_{m+\mu} = mkT/\pi^2 M\nu_L^2 .$$

This equation combined with (4.16) yields

$$(4.72)\qquad r = [1 + (\mu/m)]^{-1/2}.$$

Hence, as $\mu \to \infty$ for fixed m, the correlation coefficient vanishes. At low temperatures (and finally large values of μ for fixed m)

$$(4.73)\qquad r\sigma_m\sigma_{m+\mu} = (\hbar/M\nu_L\pi^2)\left\{\frac{1}{2\mu+1} + \frac{1}{2\mu+3} + \cdots + \frac{1}{2\mu+(4m-1)}\right\}$$

$$\sim (\hbar/2\pi^2 M\nu_L)\log(1 + 2m\mu^{-1}) \sim \hbar m/\pi^2 M\mu\nu_L .$$

We combine this with (4.39) to obtain the asymptotic result as $\mu \to \infty$ for fixed m,

$$(4.74)\qquad r \sim 2(m/\mu)/[(\log m)(\log \mu)]^{1/2}.$$

A direct application of equation III-2 in Appendix III gives the 3-D high temperature result (which is independent of m) when μ and m are large

$$(4.75)\qquad r\sigma_m\sigma_{m+\mu} = \frac{kT}{8\pi(\gamma_1\gamma_2\gamma_3)^{1/2}s^{1/2}M}\ ;\quad s^2 = \mu_1^2\gamma_1^{-1} + \mu_2^2\gamma_2^{-1} + \mu_3^2\gamma_3^{-1} .$$

Since σ_m and $\sigma_{m+\mu}$ are both proportional to $(kT)^{1/2}$, we find that r is proportional to $s^{-1/2}$. The value of the proportionality constant depends on the particle mass and force constants but not on the temperature.

A quantity of importance in X-ray diffraction is the distribution function of $(u_{m+\mu} - u_m)$. This is obtained from the characteristic function (4.67) when $\alpha_1 = -\alpha_2 = \alpha$. Hence (4.68) reduces to

$$(4.76)\qquad \exp[-\tfrac{1}{2}\alpha^2(\sigma_m^2 - 2r\sigma_m\sigma_{m+\mu} + \sigma_{m+\mu}^2)] .$$

Hence our required distribution is Gaussian with a dispersion

$$\sigma_{m+\mu,m}^2 = \sigma_m^2 - 2r\sigma_m\sigma_{m+\mu} + \sigma_{m+\mu}^2 .$$

In three-dimensional lattices $2r\sigma_m\sigma_{m+\mu}$ vanishes for large values of μ and $\sigma_m \cong \sigma_{m+\mu}$ so that in this range $\sigma_{m+\mu,m}^2 \sim 2\sigma_m^2$. However, in one-dimensional lattices $2r\sigma_m\sigma_{m+\mu}$ might become large. In this case we have

(4.77) $$\sigma^2_{m+\mu,m} = \mu kT/\pi^2 M\nu_L^2$$

at high temperatures, and

(4.78) $$\sigma^2_{m+\mu,m} \sim \frac{\hbar}{2\pi^2 M\nu_L} \log \mu$$

at low.

5. Effect of local disturbances on lattice vibrations

In this section we shall outline a procedure which can be used to discuss the effect of local disturbances in a lattice on its lattice vibrations. By a local disturbance we mean a foreign atom at a lattice point, a hole, etc. We shall restrict our analysis to 3-D lattices but the method is applicable to those of any number of dimensions.

The difference equations from which we obtained the characteristic frequencies of our normal modes ω^2 in section 2 are

(5.1) $$\begin{aligned} &\gamma_1[u_{m_1+1,m_2,m_3} - 2u_{m_1,m_2,m_3} + u_{m_1-1,m_2,m_3}] \\ &+ \gamma_2[u_{m_1,m_2+1,m_3} - 2u_{m_1,m_2,m_3} + u_{m_1,m_2-1,m_3}] \\ &+ \gamma_3[u_{m_1,m_2,m_3+1} - 2u_{m_1,m_2,m_3} + u_{m_1,m_2,m_3-1}] + M\omega^2 u_{m_1m_2m_3} = 0 \,. \end{aligned}$$

Here m_1, m_2, m_3 range through 1, 2, $\cdots$, N. For convenience we shall change our notation to let the m's range from $-N/2$ to $N/2$. When the boundary conditions (2.2) are chosen the normal mode frequencies (2.10) result. Now suppose that some masses or force constants are different from the others. Then the coefficients of the certain u's are different from those given above. Indeed, if we let D represent the difference operator which acts on u_{m,m_2,m_3} to yield the above equations, that is, if

(5.2) $$Du_{m_1m_2m_3} = 0 \,,$$

then our new equation, which would show the effect of local disturbances, would be (the total displacement of an atom from its equilibrium position is the sum of the original unperturbed displacement plus the solution of the following)

(5.3) $$Du_{m_1m_2m_3} = \sum_{j,k,l} w^{j,k,l}(m_1 + j,\ m_2 + k,\ m_3 + l)u_{m_1+j,m_2+k,m_3+l}$$

$$m_1,\ m_2,\ m_3 = 0,\ \pm 1,\ \pm 2,\ \cdots,\ \pm N/2 \,,$$

where the functions $w^{j,k,l}(m_1 + j,\ m_2 + k,\ m_3 + l)$ would characterize the disturbance. For example, if we merely change the mass of the particle at (a, b, c) to M' and leave all force constants fixed

(5.4) $$w^{j,k,l}(m_1 + j,\ m_2 + k,\ m_3 + l) \equiv 0$$

unless j, k and l are zero and $m_1 = a$, $m_2 = b$ and $m_3 = c$. Then

(5.5) $$w^{0,0,0}(a, b, c) = (M - M')\omega^2 \,.$$

If the force constants between a single atom at (a, b, c) and its neighbors are changed all w's would be zero except $w^{\pm 1,0,0}(a \pm 1, b, c)$; $w^{0,\pm 1,0}(a, b \pm 1, c)$; $w^{0,0,\pm 1}(a, b, c \pm 1)$; $w^{0,0,0}(a, b, c)$.

The set of equations (5.3) can be solved through the use of Green's functions. We shall follow the ideas used in the paper of R. T. Duffin on discrete potential theory [17]. Since we are interested only in local disturbances let $N \to \infty$ and first consider the Green's function $g(m_1, m_2, m_3)$ which is the solution of

$$Dg = 1 \quad \text{for} \quad m_1 = m_2 = m_3 = 0 \tag{5.6a}$$

$$Dg = 0 \quad \text{otherwise} \tag{5.6b}$$

$$g \to 0 \quad \text{as} \quad m_1^2 + m_2^2 + m_3^2 \to \infty . \tag{5.6c}$$

The Green's function can easily be verified to be

$$\begin{aligned} g(m_1, m_2, m_3) &= \frac{1}{(2\pi)^3} \iiint_{-\pi}^{\pi} \frac{e^{i(\phi_1 m_1 + \phi_2 m_2 + \phi_3 m_3)} d\phi_1 d\phi_2 d\phi_3}{M\omega^2 - 2\gamma_1(1-\cos\phi_1) - 2\gamma_2(1-\cos\phi_2) - 2\gamma_3(1-\cos\phi_3)} \\ &= \int_0^\infty e^{-\alpha[M\omega^2 - 2(\gamma_1+\gamma_2+\gamma_3)]}\, d\alpha \prod_{j=1}^{3} \left\{ \frac{1}{2\pi} \int_{-\pi}^{\pi} e^{i\phi_j m_j}\, e^{-2\gamma_j \cos\phi_j}\, d\phi_j \right\} \\ &= \int_0^\infty e^{-\alpha M\omega^2} \prod_{j=1}^{3} \left\{ i^{m_j}\, e^{2\alpha\gamma_j}\, J_{m_j}(2\alpha i \gamma_j) \right\} d\alpha \end{aligned} \tag{5.7}$$

where as usual $J_m(i\alpha)$ is a Bessel function of imaginary argument. This integral converges when $M\omega^2 > 4 \sum \gamma_j = M\omega_L^2$ or $M\omega^2 < 0$. It can be represented as a generalized hypergeometric function of three variables (see equation (3.27) of this article and [13], p. 184). The function $g(0, 0, 0)$ has been tabulated by M. Tikson [18] when $\gamma_1 = \gamma_2 = \gamma_3$. Since these integrals occur in many problems in which cubic lattices appear (ferromagnetism, electrons in metals, random walks on lattices, etc.) their tabulation would be a worthwhile project. Asymptotic expressions for large m's are easily obtained by following the method discussed in appendix III.

Now that the Green's function is known, it is easily verified that

$$u_{m_1 m_2 m_3} = \sum_{jkl} \sum_{m_1 m_2 m_3} g(m_1 + j - n_1,\, m_2 + k - n_2,\, m_3 + l - n_3) \cdot w^{jkl}(n_1, n_2, n_3) u_{n_1 n_2 n_3} . \tag{5.8}$$

The application of the D operator and the use of (5.6) immediately yield (5.3). An important feature of this result is that it is exact (no perturbation calculation is made). A similar result has been obtained by Slater and Koster [19] in their application of Wannier electronic wave functions to the problem of an impurity in a semiconductor. It has also been discussed by Lax [23]. The effect of holes on lattice vibrations has been treated by perturbation theory by Stripp and Kirkwood [20].

Although several detailed applications of (5.8) will be discussed in another paper we shall indicate the approach to the simple problem of a change of mass of a single atom without the change in force constants. This will give the spirit of the method of using (5.8). Suppose the impurity atom is at the origin so that $w^{000}(0, 0, 0) = (M - M')\omega^2$ and all other w's are zero. Then,

$$u_{m_1 m_2 m_3} = g(m_1 m_2 m_3)\omega^2(M - M')u_{000} . \tag{5.9}$$

The new normal mode frequency ω^2 would be determined by setting $m_1, m_2, m_3 = 0$ and solving the transcendental equation

$$\frac{1}{\omega^2(M - M')} = g(0, 0, 0) \tag{5.10}$$

for ω^2. When $\gamma_1 = \gamma_2 = \gamma_3$, Tikson's tables are very helpful in obtaining the solution. This value of ω^2 lies outside the continuum of frequencies which we discussed in section 3. With this value of ω^2, the vanishing of the disturbance to the normal lattice vibrations with increasing distance from the impurity can be discussed through (5.9).

In cases of more complicated sources of disturbance one sometimes has to solve a set of simultaneous equations to find u_{m_1,m_2,m_3} and the impurity frequencies ω^2.

6. Zero point energy

We finish this report with a brief discussion of the quantum mechanical zero point energy of our model

$$\begin{aligned} E_0 &= \tfrac{1}{2}\hbar \sum_i \omega_i \\ &= \frac{1}{(2M)^{1/2}} \hbar (N/\pi)^n \int_0^\pi \cdots \int \left\{ \sum \gamma_j (1 - \cos \phi_j) \right\}^{1/2} d\phi_1 \cdots d\phi_n . \end{aligned} \tag{6.1}$$

This expression can be reduced to quadratures by employing the following representation of $x^{1/2}$:

$$x^{1/2} = \frac{1}{2\pi^{1/2}} \int_{-\infty}^{\infty} \left(\frac{1 - e^{-x a^2}}{a^2} \right) da . \tag{6.2}$$

Then

$$\begin{aligned} E_0 &= \frac{\hbar}{2(2\pi M)^{1/2}} \left(\frac{N}{\pi}\right)^n \int_0^\infty a^{-2}\, da \int_0^\pi \cdots \int [1 - e^{-a^2 \Sigma \gamma_j (1 - \cos \phi_j)}]\, d\phi_1 \cdots d\phi_n \\ &= \frac{\hbar N^n}{4(2\pi M)^{1/2}} \int_0^\infty b^{-3/2} \left[1 - \prod_{j=1}^n \{ e^{-b\gamma_j} I_0(b\gamma_j) \} \right] db . \end{aligned} \tag{6.3}$$

An integration by parts finally yields

$$\begin{aligned} E_0 = \frac{\hbar N^n}{2(2\pi M)^{1/2}} \sum_{j=1}^n \gamma_j \int_0^\infty b^{-1/2} e^{-b\Sigma\gamma_j} [I_0(b\gamma_1) \cdots I_0(b\gamma_n)] \\ \cdot [I_0(b\gamma_j) - I_1(b\gamma_j)]/I_0(b\gamma_j) db . \end{aligned} \tag{6.4}$$

The zero point energy of a 1-D lattice is [see discussion under (4.34)]

$$\begin{aligned} E_0 &= \frac{\hbar N \gamma}{2(2\pi M)^{1/2}} \int_0^\infty b^{-1/2} e^{-b\gamma} [I_0(b\gamma) - I_1(b\gamma)] db \\ &= \frac{\hbar N \gamma}{2\pi (M\gamma)^{1/2}} [\Psi(3/2) - \Psi(1/2)] = \frac{\hbar N}{\pi} \left(\frac{\gamma}{M}\right)^{1/2} . \end{aligned} \tag{6.5}$$

Since the zero point energy of 2-D and 3-D lattices involves four and six integrals, respectively, we shall not write them down explicitly here. We merely point out that each of these integrals is of the form dealt with in the discussion of the asymptotic low temperature expression of σ^2 [see (4.34)].

APPENDIX I. ON THE INTEGRATION OF

$$\text{(I-1)} \qquad \int_0^\infty \exp\left[-x(\gamma_1 + \gamma_2)\right]\{I_{m_1}(x\gamma_1)I_{m_2}(x\gamma_2) - I_{m_3}(x\gamma_1)I_{m_4}(x\gamma_2)\}dx$$

WHEN

$$k_1^2 = m_1^2\gamma_1^{-1/2} + m_2^2\gamma_2^{-1/2} \quad \text{and} \quad k_2^2 = m_3^2\gamma_1^{-1/2} + m_4^2\gamma_2^{-1/2}$$

ARE BOTH LARGE

This integral appears in equation (3.23). We shall show that it can be neglected when compared to one in which one of the k's is small. For this purpose it is desirable to go backwards and rewrite the required integral as (we shall be interested only in the case of even values of m)

$$\text{(I-2)} \qquad \frac{1}{4\pi^2}\iint_{-\pi}^{\pi} \frac{e^{i(m_1\phi_1+m_2\phi_2)} - e^{i(m_3\phi_1+m_4\phi_2)}}{\gamma_1 + \gamma_2 - \gamma_1\cos\phi_1 - \gamma_2\cos\phi_2}\, d\phi_1 d\phi_2\,.$$

We shall not be too rigorous in the following, but this as well as several integrations of later appendices can be put on a more rigorous basis by following a method developed by Duffin [17]. When the m's are large the integrand in the neighborhood of $(\phi_1, \phi_2) = 0$ gives the main contribution to the integral. Hence if we introduce the factor $J_0(\alpha R)$ with α very small and $R = i\phi_1\gamma_1^{1/2} + j\phi_2\gamma_2^{1/2}$ or $R^2 = \phi_1^2\gamma_1 + \phi_2^2\gamma_2$, replace the denominator of the integrand by $\frac{1}{2}\gamma_1\phi_1^2 + \frac{1}{2}\gamma_2\phi_2^2$, allow the integration to extend over the entire real (ϕ_1, ϕ_2) space, and transform to polar coordinates, our integral becomes

$$\text{(I-3)} \qquad \frac{1}{2\pi^2(\gamma_1\gamma_2)^{1/2}}\int_0^\infty \frac{2RJ_0(\alpha R)}{R^2}\, dR \left[\int_0^\pi e^{iRk\cos\theta}\, d\theta - \int_0^\pi e^{iRk'\cos\theta'}\, d\theta'\right]$$

where k and k' are the vectors

$$k = m_1\gamma_1^{-1/2}\, i + m_2\gamma_2^{-1/2}\, j\,, \quad k' = m_3\gamma_1^{-1/2}\, i + m_4\gamma_2^{-1/2}\, j\,,$$

and θ and θ' are the polar angles between the vectors R and k and R and k'. The integrals with respect to θ are again Bessel functions of order zero. The desired expression becomes

$$\text{(I-4)} \quad \frac{1}{\pi(\gamma_1\gamma_2)^{1/2}}\int_0^\infty \frac{J_0(\alpha R)}{R}\,[J_0(kR) - J_0(k'R)]dR$$

$$= \frac{1}{\pi(\gamma_1\gamma_2)^{1/2}}\left\{\int_0^\infty \frac{J_0(\alpha R)}{R}\,[1 - J_0(Rk')]dR - \int_0^\infty \frac{J_0(\alpha R)}{R}\,[1 - J_0(Rk)]dR\right\}.$$

Since both of the integrals in the bracket are "Bateman integrals" (see Watson [22]), the entire expression becomes

$$\text{(I-5)} \qquad = \frac{1}{\pi(\gamma_1\gamma_2)^{1/2}}\,[\log k'/\alpha - \log k/\alpha] = \frac{1}{\pi(\gamma_1\gamma_2)^{1/2}}\log(k'/k)$$

$$= \frac{1}{\pi(\gamma_1\gamma_2)^{1/2}}\log\left(\frac{\gamma_2 m_3^2 + \gamma_2 m_4^2}{\gamma_2 m_1^2 + \gamma_1 m_2^2}\right),$$

a result independent of the value of the small number α which was introduced in the integrating factor $J_0(\alpha R)$.

The case of interest for equation (3.24) in the text is $m_1 = m_2 = m_3 = 2m$ and $m_4 = 0$. Our required integral reduces to

$$\text{(I-6)} \qquad \frac{1}{\pi(\gamma_1\gamma_2)^{1/2}} \log \left(\frac{\gamma_2}{\gamma_2 + \gamma_3}\right),$$

which for fixed γ_1 and γ_2 is small compared to $[\pi(\gamma_1\gamma_2)^{1/2}]^{-1} \log 2m$ as $m \to \infty$.

APPENDIX II. GENERALIZATION OF AN INTEGRAL OF WATSON

Let

$$\text{(II-1a)} \qquad I(\alpha) = \pi^{-3} \iiint_0^{\pi} \frac{d\phi_1 d\phi_2 \phi d_3}{(2 + \alpha^2) - \cos\phi_1 - \cos\phi_2 - \alpha^2 \cos\phi_3}$$

$$\text{(II-1b)} \qquad = \frac{1}{2\pi^3} \iiint_0^{\pi} \frac{d\phi_1 d\phi_2 d\phi_3}{\sin^2 \frac{1}{2}\phi_1 + \sin^2 \frac{1}{2}\phi_2 + \alpha^2 \sin^2 \frac{1}{2}\phi_3}.$$

The special case $\alpha = 1$ has been discussed by Watson [21]. We shall follow his technique here. If one introduces a set of Cartesian variables $x_1 = \tan \frac{1}{2}\phi_1$, $x_2 = \tan \frac{1}{2}\phi_2$, and $x_3 = \alpha \tan \frac{1}{2}\phi_3$, then transforms these to spherical polar coordinates, and finally replaces the angle ϕ by $\phi = \frac{1}{2}\Psi$, the integral (II-1b) reduces to

$$\text{(II-2)} \quad I(\alpha) = \frac{4\alpha}{\pi^3}\int_0^{\frac{1}{2}\pi}\int_0^{\frac{1}{2}\pi}\int_0^{\infty} \frac{\sin\theta \, dr d\theta d\Psi}{\alpha^2 + r^2\sin^2\theta[\frac{1}{2}\alpha^2\sin^2\theta\sin^2\Psi + (1+\alpha^2)\cos^2\theta] + \frac{1}{4}r^4(2+\alpha^2)\sin^4\theta\cos^2\theta\sin^2\Psi}.$$

The integration with respect to θ can be carried out in an elementary manner if r is replaced by a new variable t which is defined as $t2^{1/2} = r \sin\theta$ (for fixed θ) and the order of integration is interchanged. Then

$$\text{(II-3)} \quad I(\alpha) = \frac{4\alpha\sqrt{2}}{\pi^3}\int_0^{\infty} dt \int_0^{\frac{1}{2}\pi} d\Psi \int_0^{\frac{1}{2}\pi} \frac{d\theta}{\alpha^2 + t^2[\alpha^2\sin^2\theta\sin^2\Psi + 2(1+\alpha^2)\cos^2\theta] + (2+\alpha^2)t^4\cos^2\theta\sin^2\Psi}$$

$$= \frac{2\sqrt{2}}{\pi^2}\int_0^{\infty}\int_0^{\pi/2} \frac{dt d\Psi}{\sqrt{(1+t^2\sin^2\Psi)[\alpha^2 + 2t^2(1+\alpha^2) + (2+\alpha^2)t^4 \sin^2\Psi]}}.$$

The integral over t can be reduced to an elliptic integral if we replace Ψ by a new variable ζ which we define by $\tan\Psi = \zeta/(1 + t^2)^{1/2}$.

Again we interchange the order of integration. We find

(II-4) $I(\alpha)$

$$= 2^{3/2}\pi^{-2}\int_0^\infty \frac{d\zeta}{(1+\zeta^2)^{1/2}}\int_0^\infty \frac{dt}{\{(1+t^2)[\alpha^2(1+\zeta^2)+t^2(\zeta^2(2+\alpha^2)+2(1+\alpha^2))]\}^{1/2}}$$

$$= \frac{2^{3/2}}{\pi^2}\int_0^\infty \frac{d\zeta}{(1+\zeta)^{1/2}[\zeta^2(2+\alpha^2)+2(1+\alpha^2)]^{1/2}} K'\left(\alpha\left[\frac{1+\zeta^2}{\zeta^2(2+\alpha^2)+2(1+\alpha^2)}\right]^{1/2}\right).$$

The transformation $\zeta = \tan\chi$ leads to

$$\text{(II-5)}\quad I(\alpha) = \frac{2^{3/2}}{\alpha\pi^2}\int_0^{\frac{1}{2}\pi} \frac{d\chi}{\left[\frac{2(1+\alpha^2)}{\alpha^2} - \sin^2\chi\right]^{1/2}} K'\left(\frac{1}{\left[\frac{2(1+\alpha^2)}{\alpha^2} - \sin^2\chi\right]^{1/2}}\right).$$

If we substitute

$$\text{(II-6)}\qquad 2\pi K'(k) = -\left[\frac{d}{d\epsilon}\sum_{n=0}^{\infty}\frac{\Gamma^2(n+\frac{1}{2}+\epsilon)k^{2n+2\epsilon}}{n!\,\Gamma(n+1+2\epsilon)}\right]_{\epsilon=0}$$

into (II-5) and interchange the order of integration and summation, we find

$$\text{(II-7)}\quad I(\alpha) = -\frac{2^{1/2}}{\alpha\pi^3}\left[\frac{d}{d\epsilon}\sum_{n=0}^{\infty}\frac{\Gamma^2(n+\frac{1}{2}+\epsilon)}{n!\,\Gamma(n+1+2\epsilon)}\int_0^\infty \frac{d\chi}{[2(1+\alpha^2)\alpha^{-2}-\sin^2\chi]^{n+1/2+\epsilon}}\right]_{\epsilon=0}.$$

We perform this last integration by choosing c to be the smallest root of

$$\text{(II-8)}\qquad c^2 - 2\gamma c + 1 = 0$$

with

$$\text{(II-9)}\qquad \gamma = (4 + 3\alpha^2)/\alpha^2\,.$$

Then

$$\text{(II-10)}\qquad 4c\left\{\frac{2(1+\alpha^2)}{\alpha^2} - \sin^2\chi\right\} = (1 + ce^{2i\chi})(1 + ce^{-2i\chi})\,.$$

If we substitute this expression into (II-7) and expand the integral in a power series in c we find

$$\text{(II-11)}\qquad \int_0^{\pi/2}[2(1+\alpha^2)\alpha^{-2} - \sin^2\chi]^{-n-1/2-\epsilon}\,d\chi$$

$$= \tfrac{1}{2}\pi(4c)^{n+1/2+\epsilon}\;{}_2F_1\,(n+\tfrac{1}{2}+\epsilon, n+\tfrac{1}{2}+\epsilon; 1; c^2)$$

where ${}_2F_1$ is the hypergeometric function of the four arguments given in the parentheses.

The integral (II-7) can be expressed in terms of a hypergeometric function of two variables if (II-11) is substituted into (II-7) and the definition of $\mathfrak{F}_4$ is applied. We obtain

$$\text{(II-12)}\quad I(\alpha) = -\frac{1}{2^{1/2}\alpha\pi^2}\left\{\frac{d}{d\epsilon}[(4c)^{1/2+\epsilon}\frac{\Gamma^2(\frac{1}{2}+\epsilon)}{\Gamma(1+2\epsilon)}\mathfrak{F}_4(\tfrac{1}{2}+\epsilon, \tfrac{1}{2}+\epsilon; 1+2\epsilon, 1; 4c,c^2)]\right\}_{\epsilon=0}$$

where $\mathfrak{F}_4$ denotes the fourth kind of Appell's hypergeometric function of two variables [see equation (4.20)]. It has been shown by Bailey that $\mathfrak{F}_4$ can be factored into a product of two ordinary hypergeometric functions of one variable (see also p. 238, [15])

$$\text{(II-13)} \qquad \mathfrak{F}_4[u, v + v' - u - 1; v, v'; x(1 - y), y(1 - x)]$$

$$= {}_2F_1(u, v + v' - u - 1; v; x)\, {}_2F_1(u, v + v' - u - 1; v'; y)$$

provided that $x + y < 1$ and

$$\text{(II-14)} \qquad \{|x(1 - y)|\}^{1/2} + \{|y(1 - x)|\}^{1/2} < 1 .$$

The values of the significant parameters in our case are

$$\text{(II-15)} \qquad u = \tfrac{1}{2} + \epsilon$$

$$\text{(II-16)} \qquad v = 1 + 2\epsilon, v' = 1$$

$$\text{(II-17)} \qquad v + v' - u - 1 = \tfrac{1}{2} + \epsilon = \alpha$$

$$\text{(II-18)} \qquad x(1 - y) = 4c \quad \text{while} \quad y(1 - x) = c^2.$$

The explicit values of x and y are the roots of this pair of equations for which (II-14) is satisfied. The value of c, the positive root of (II-8), is

$$\text{(II-19)} \qquad c = \gamma - (\gamma^2 - 1)^{1/2} .$$

Since the square root of c is

$$\text{(II-20)} \qquad c^{1/2} = 2^{-1/2}\{(\gamma + 1)^{1/2} - (\gamma - 1)^{1/2}\}$$

we see that

$$\text{(II-21)} \qquad \{|x(1 - y)|\}^{1/2} + \{|y(1 - x)|\}^{1/2} - 1 = 2c^{1/2} + c - 1$$

$$= 2^{1/2}\{(\gamma + 1)^{1/2} - (\gamma - 1)^{1/2}\} + (\gamma - 1)^{1/2}\{(\gamma - 1)^{1/2} - (\gamma + 1)^{1/2}\}$$

$$= -[(\gamma - 1)^{1/2} - 2^{1/2}][(\gamma + 1)^{1/2} - (\gamma - 1)^{1/2}].$$

As long as α is real [see equation (II-9)] $\gamma = 3 + 4\alpha^{-2} > 3$, and (II-21) is negative as is required by (II-14).

The roots of (II-18) with the property $x + y < 1$ are $x = 1 - k_3^2 = (k_3')^2$ and $y = k_2^2 = 1 - (k_2')^2$, where

$$\text{(II-22)} \qquad k_3 = \tfrac{1}{2}[(\gamma - 1)^{1/2} + (\gamma - 3)^{1/2}][(\gamma + 1)^{1/2} - (\gamma - 1)^{1/2}]$$

$$\text{(II-23)} \qquad k_2 = \tfrac{1}{2}[(\gamma - 1)^{1/2} - (\gamma - 3)^{1/2}][(\gamma + 1)^{1/2} - (\gamma - 1)^{1/2}] .$$

Our required integral then takes the form

$$\text{(II-24)} \quad I(\alpha) = -\frac{1}{2^{1/2}\alpha\pi^2}$$

$$\cdot \left\{\frac{d}{d\epsilon}\left[(4c)^{1/2+\epsilon}\frac{\Gamma^2(\frac{1}{2}+\epsilon)}{\Gamma(1+2\epsilon)} F(\tfrac{1}{2}+\epsilon, \tfrac{1}{2}+\epsilon, 1+2\epsilon, k_3'^2) F(\tfrac{1}{2}+\epsilon, \tfrac{1}{2}+\epsilon, 1, k_2^2)\right]\right\}_{\epsilon=0} .$$

The quantity inside the bracket is of the same general form as the corresponding quantity treated by Watson in his analysis of (II-1) with $\alpha = 1$. We employ his result and find

(II-25) $$I(\alpha) = 2^{3/2}k_2'k_3'K(k_2)K(k_3)/\alpha\pi^2$$

where $K(k)$ is the complete elliptic integral of the second kind. Various relations are easily shown to exist between k_2, k_3, k_2', and k_3'. For example,

(II-26)
$$k_2'k_3' = 2(k_2k_3)^{1/2}$$
$$(k_3/k_2) = \tfrac{1}{2}(\sqrt{\gamma - 3} + \sqrt{\gamma - 1})^2 .$$

Equation (II-13) reduces to Watson's result when $\alpha = 1$ (and hence $\gamma = 7$) for then k_2 and k_3 agree with Watson's value for these quantities.

Equation (II-25) can also be written as

(II-27) $$I(\alpha) = 4[(\gamma + 1)^{1/2} - (\gamma - 1)^{1/2}]\pi^{-2}\alpha^{-1}K(k_2)K(k_3) .$$

Two limiting forms exist for $I(\alpha)$ in the range of very small and large α. As $\alpha \rightarrow 0$,

(II-28) $$I(\alpha) \sim \frac{1}{\pi} \log (2^{5/2} \alpha^{-1}) ,$$

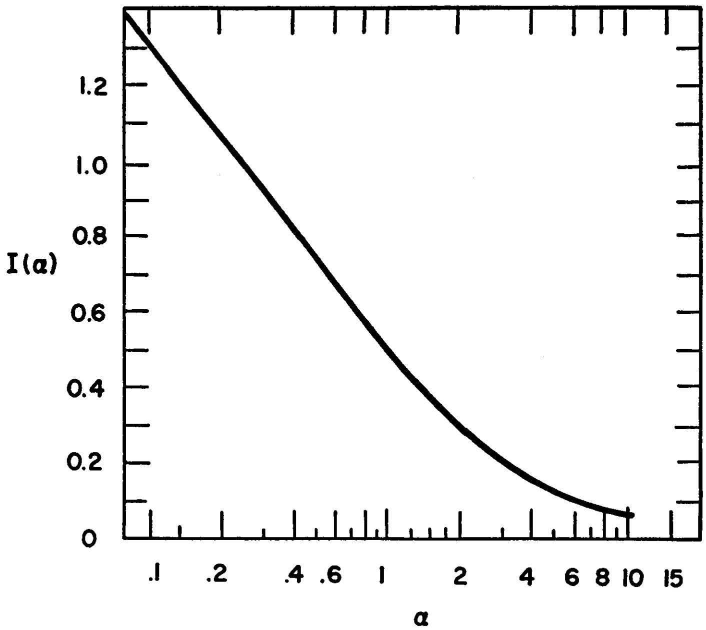


FIGURE 13
Variation of the generalized Watson integral (equation II-1a) with α. The Watson value 0.505 corresponds to $\alpha = 1$.

while as $\alpha \rightarrow \infty$

(II-29) $$I(\alpha) \sim \frac{2^{5/2}(2^{1/2} - 1)}{\pi^2\alpha} \{K(2^{1/2} - 1)\}^2 = 0.633\alpha^{-1} .$$

We have plotted $I(\alpha)$ as a function of α in figure 13.

The function $I(\alpha)$ is related to the integral (4.28) through

$$\text{(II-30)} \quad \int_0^\infty e^{-(2\gamma_2+\gamma_1)x} I_0(x\gamma_1)[I_0(x\gamma_2)]^2 dx$$

$$= \frac{1}{\pi^3} \iiint_0^\pi \frac{d\phi_1 d\phi_2 d\phi_3}{(2\gamma_2+\gamma_1)-\gamma_1 \cos\phi_1-\gamma_2\cos\phi_2-\gamma_2\cos\phi_3} = \gamma_2^{-1} I([\gamma_1/\gamma_2]^{1/2}) .$$

APPENDIX III. ASYMPTOTIC FORM OF

$$\text{(III-1)} \qquad \frac{1}{\pi^3} \iiint_0^\pi \frac{e^{i(m_1\phi_1+m_2\phi_2+m_3\phi_3)}\, d\phi_1 d\phi_2 d\phi_3}{\sum_1^3 \gamma_j(1 - \cos\phi_j)}$$

AS

$$s^2 = m_1^2\gamma_1^{-1} + m_2^2\gamma_2^{-1} + m_3^2\gamma_3^{-1} \to \infty$$

This type of integral has been evaluated by Duffin [17] when $\gamma_1 = \gamma_2 = \gamma_3$. We note that when k is large the main contribution comes in the range of small values of the ϕ's. The integration can, without significant change, be extended over the entire range of positive ϕ's. One introduces a radius vector $R = i\phi_1\gamma_1^{1/2} + j\phi_2\gamma_2^{1/2} + k\phi_3\gamma_3^{1/2}$ so that the polar coordinate representation of the integral becomes

$$\text{(III-2)} \qquad \frac{1}{8} \cdot \frac{2}{\pi^3(\gamma_1\gamma_2\gamma_3)^{1/2}} \int_0^\infty \int_0^\pi 2\pi e^{isR\cos\theta} \sin\theta dR d\theta ,$$

where s is the vector $s = im_1\gamma_1^{-1/2} + jm_2\gamma_2^{-1/2} + km_3\gamma_3^{-1/2}$, and θ is the polar angle between R and s. After integration with respect to θ we have

$$\text{(III-3)} \qquad \frac{1}{\pi^2(\gamma_1\gamma_2\gamma_3)^{1/2}} \int_0^\infty \frac{\sin Rs}{Rs} dR = \frac{1}{2\pi s(\gamma_1\gamma_2\gamma_3)^{1/2}}$$

with

$$\text{III-4)} \qquad s = (m_1^2\gamma_1^{-1} + m_2^2\gamma_2^{-1} + m_3^2\gamma_3^{-1})^{1/2} .$$

This asymptotic form to (III-1) is equivalent to

$$\text{(III-5)} \qquad \int_0^\infty e^{-(\gamma_1+\gamma_2+\gamma_3)x} I_{m_1}(x\gamma_1) I_{m_2}(x\gamma_2) I_{m_3}(x\gamma_3) dx \sim \frac{1}{2\pi s(\gamma_1\gamma_2\gamma_3)^{1/2}}$$

as $s \to \infty$. Here the I's are Bessel functions of purely imaginary argument.

APPENDIX IV. ON THE INTEGRATION OF

$$\text{IV-1)} \qquad F_{\alpha,\beta}(\gamma_1, \gamma_2) = \int_0^\infty x^{-1/2} e^{-x(\gamma_1+\gamma_2)} I_\alpha(x\gamma_1) I_\beta(x\gamma_2) dx$$

AS

$$(\alpha^2\gamma_1^{-1} + \beta^2\gamma_2^{-1}) \to \infty$$

We use the double integral representation of F

$$\text{(IV-2)} \qquad \frac{1}{4\pi^{3/2}} \iint_{-\pi}^{\pi} \frac{e^{i(\alpha\phi_1 + \beta\phi_2)}\, d\phi_1 d\phi_2}{[\gamma_1(1 - \cos\phi_1) + \gamma_2(1 - \cos\phi_2)]^{1/2}} .$$

When α and β are large the main contribution to the integral comes from the region of small ϕ_1 and ϕ_2. Hence if we introduce the integrating factor exp $(-\mu R)$ (here μ is small number), with $R^2 = \gamma_1\phi_1^2 + \gamma_2\phi_2^2$, we can extend the range of integration over the entire real plane. We then have, after a reduction to polar coordinates,

$$\text{(IV-4)} \qquad F_{\alpha,\beta}(\gamma_1, \gamma_2) \sim \frac{[2/\gamma_1\gamma_2]^{1/2}}{4\pi^{3/2}} \int_0^\infty \int_0^\pi R^{-1}\{\exp(-\mu R + ikR\cos\theta)\}\, 2R dR d\theta ,$$

where $k^2 = \alpha^2\gamma_1^{-1} + \beta^2\gamma_2^{-1}$.

Hence

$$\text{(IV-4)} \qquad F_{\alpha,\beta}(\gamma_1, \gamma_2) \sim \frac{1}{2}\left(\frac{1}{\pi\gamma_1\gamma_2}\right)^{1/2} \int_0^\infty e^{-\mu R} J_0(kR) dR = (2\pi\gamma_1\gamma_2)^{-1/2}(\mu^2 + k^2)^{-1/2} .$$

In the limit of large k and small μ we find

$$\text{(IV-5)} \qquad F_{\alpha,\beta}(\gamma_1, \gamma_2) \sim (2\pi)^{-1/2}(\alpha^2\gamma_2 + \beta^2\gamma_1)^{-1/2} .$$

This result could also have been obtained by applying various asymptotic forms for Legendre functions to (4.41).

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REFERENCES

[1] E. W. Montroll, "Dynamics of a square lattice," *Jour. of Chemical Physics*, Vol. 15 (1947) pp. 575–591.

[2] W. A. Bowers and H. B. Rosenstock, "On the vibrational spectra of crystals," *Jour. of Chemical Physics*, Vol. 18 (1950), pp. 1056–1062.

[3] M. Smollett, "The frequency spectrum of a two dimensional ionic lattice," *Proc. of the Phys. Soc.*, Sec. A, Vol. 65 (1952), 109–115.

[4] L. Van Hove, "The occurrence of singularities in the elastic frequency distribution of a crystal," *Physical Review*, Vol. 89 (1953), pp. 1189–1193.

[5] G. F. Newell, "Vibrational spectrum of a simple cubic lattice," *Jour. of Chemical Physics*, Vol. 21 (1953), pp. 1877–1883.

[6] H. B. Rosenstock and G. F. Newell, "Vibrations of a simple cubic lattice I," *Jour. of Chemical Physics*, Vol. 21 (1953), pp. 1607–1608.

[7] R. E. Peierls, "Quelques propriétés typiques des corps solides," *Ann. de l'Inst. Henri Poincaré*, Vol. 5 (1935), pp. 177–222.

[8] E. Wigner, *Lecture Notes on Solid State Physics*, Princeton University (1948).

[9] P. Debye, "Interferenz von Röntgenstrahlen und Wärmebewegung," *Ann. der Physik*, Vol. 43 (1914), pp. 49–95.

[10] E. C. Titchmarsh, *Introduction to the Theory of Fourier Integrals*, Oxford, Oxford University Press, 1937, p. 78.

[11] F. von Bloch, "Zur Theorie des Austauschproblems und der Remanenzerscheinung der Ferromagnetika," *Zeitschrift für Physik*, Vol. 74 (1932), p. 309.

[12] E. W. MONTROLL, "Frequency spectrum of vibrations of a crystal lattice," *Amer. Math. Monthly*, Vol. 61 (supplement to No. 7), (1954), pp. 46–73.

[13] A. ERDÉLYI, W. MAGNUS, F. OBERHETTINGER, F. TRICOMI, *Tables of Integral Transforms*, Vol. I, New York, McGraw-Hill Book Co., 1954.

[14] P. LÉVY, *Théorie de l'Addition des Variables Aléatoires*, Paris, Gauthier-Villars, 1937.

[15] A. ERDÉLYI, W. MAGNUS, F. OBERHETTINGER, F. TRICOMI, *Higher Transcendental Functions*, New York, McGraw-Hill Book Co., 1953, p. 163.

[16] G. PÓLYA and G. SZEGÖ, "*Aufgaben und Lehrsätze aus der Analysis*, Vol. I, Berlin, J. Springer, 1925, p. 79.

[17] R. J. DUFFIN, "Discrete potential theory," *Duke Math. Jour.*, Vol. 20 (1953), pp. 233–251.

[18] M. TIKSON, "Tabulation of an integral arising in the theory of cooperative phenomena," *Jour. Res. Nat. Bureau of Standards*, Vol. 50 (1953), pp. 177–178.

[19] G. F. KOSTER and J. C. SLATER, "Wave functions for impurity levels, *Physical Review*, Vol. 95 (1954), pp. 1167–1176.

[20] K. F. STRIPP and J. G. KIRKWOOD, "Lattice vibrational spectrum of imperfect crystals," *Jour. of Chemical Physics*, Vol. 22 (1954), pp. 1579–1586.

[21] G. N. WATSON, "Three triple integrals," *Quarterly Jour. of Math.* (Oxford), Vol. 10 (1939), pp. 266–276.

[22] ———, *A Treatise on the Theory of Bessel Functions*, Cambridge, The University Press, 1944, p. 406.

[23] M. LAX, "Localized Perturbations," *Physical Review*, Vol. 94 (1954), p. 1391.