

Remarks on the Vibrations of Diatomic Lattices*

A. A. MARADUDIN, P. MAZUR, E. W. MONTROLL, AND G. H. WEISS

University of Maryland, College Park, Maryland

I. INTRODUCTION

ALTHOUGH the modern theory of lattice vibrations originated in the work of Born and von Karman,¹ Lord Kelvin had, in the 1880's, already made certain remarks relevant to the behavior of diatomic lattices and monatomic lattices with impurities. He had found the separation of the frequency spectrum into two bands in diatomic (one-dimensional) lattices, and had shown that waves driven with a frequency not included in the bands are not propagated through a lattice and damp out in a distance that depends on the difference between the driven frequency and the band edges. Many of Kelvin's ideas on wave propagation in periodic media were discussed in his famous Baltimore lectures² of 1884. It is well known that these lectures were the "official" statement of the status of physics at the end of the 19th century, and that they included a clear description of the unsolved problems of the time. However, it is not generally realized that the papyrographed edition of these lectures was probably the first of the long line of "preprints" through which much of contemporary physics has first been unveiled to the fraternity. The papyrograph was a precursor of the modern ditto machine. The two specimens of the preprints seen by one of the authors (E. W. M.) have a fresh and well-preserved appearance. The published copy of the lectures appeared in 1904 after some of the galley proofs rested uncorrected for many years in Kelvin's files.

The theory of lattice vibrations has progressed a long way since the days of Kelvin, but direct experimental determinations of the frequency spectrum and the phase relations which associate frequencies with particular points in the reciprocal lattice are a very recent addition to the subject. The application of the x-ray and neutron scattering techniques used in these experiments have been described elsewhere in the proceedings of this conference. The theory of lattice vibrations has been developing from two general points of view: the first is concerned with careful investigations of the lattice vibrations of particular materials and the second has been the mathematical exploration of qualitative features of the frequency spectrum and of the dispersion relations and of the effect of various perturbations (point defects, disorder, etc.) on these quantities.

The main purpose of this paper is to follow the latter point of view and to discuss aspects of the frequency spectrum of diatomic lattices through the aid of a model of the simple cubic lattice with nearest neighbor interactions³⁻⁶ (central and noncentral), and some general mathematical theorems. The remainder of this introduction is a review of properties of the spectrum of a monatomic lattice. The more systematic theory as it has been applied to real crystals is discussed in the book of Born and Huang⁷ and in the *Handbuch* article of Blackman⁸ (who was the first to realize the inadequacy of the Debye spectrum).

The x , y , and z components of the displacement of an atom in a simple cubic lattice are conveniently independent of each other. The equations of motion are those of a lattice with one degree of freedom per lattice point. We let the displacement of the (l, m, n) th particle from equilibrium in the x direction be $x_{l, m, n}$. Then the equations of motion of the lattice are

$$M\ddot{x}_{l, m, n} = \gamma_1(x_{l+1, m, n} - 2x_{l, m, n} + x_{l-1, m, n}) + \gamma_2(x_{l, m+1, n} - 2x_{l, m, n} + x_{l, m-1, n}) + \gamma_3(x_{l, m, n+1} - 2x_{l, m, n} + x_{l, m, n-1}), \quad (\text{I.1})$$

where γ_1 is the central force constant and γ_2 and γ_3 the noncentral force constants between nearest neighbors. Two similar sets of equations exist for y and z displacements.

It is customary to express the motions of particles in the lattice as linear combinations of the normal modes,

$$x_{l, m, n} = \exp\{i(\omega t + l\varphi_1 + m\varphi_2 + n\varphi_3)\}, \quad (\text{I.2})$$

the φ 's being chosen as

$$\varphi_j = 2\pi s_j/N, \quad s_j = 0, 1, 2, \dots, N-1, \quad (\text{I.3})$$

so that the x 's satisfy periodic boundary conditions

$$x_{l, m, n} = x_{l+N, m, n}, \text{ etc.}, \quad (\text{I.4})$$

N being the number of lattice points in each direction in the lattice. The points $(\varphi_1, \varphi_2, \varphi_3)$ are points on the

³ H. B. Rosenstock and G. F. Newell, *J. Chem. Phys.* **21**, 1607 (1953).

⁴ W. A. Bowers and H. B. Rosenstock, *J. Chem. Phys.* **18**, 1056 (1950).

⁵ E. W. Montroll, *Am. Math. Monthly* **LXI**, 46 (1954).

⁶ E. W. Montroll, *Proceedings of the Third Berkeley Symposium on Mathematical Statistics and Probability*, Vol. III, p. 209 (1956).

⁷ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954).

⁸ M. Blackman, *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. VII.

* This research was supported by the U. S. Air Force through the Air Force Office of Scientific Research, Air Research and Development Command under Contract No. AF18(600)1315.

¹ M. Born and T. v. Karman, *Physik. Z.* **13**, 297 (1912).

² W. Thompson and Lord Kelvin, *Baltimore Lectures*, 1904.

reciprocal lattice. The normal mode frequencies are found to be the function $\omega(\varphi_1, \varphi_2, \varphi_3)$ defined by

$$M\omega^2 = \sum_1^3 2\gamma_j(1 - \cos \varphi_j), \quad (I.5)$$

which is triply periodic in reciprocal space.

It is clear that $G(\omega^2)$, the distribution function of ω^2 , is simply related to that of

$$X = \sum_{j=1}^n \gamma_j \cos \varphi_j \quad (I.6)$$

where each φ_j is a random variable which (as $N \rightarrow \infty$) is uniformly distributed in the interval $(0, 2\pi)$. It is not surprising that the grand master of small vibrations, Lord Rayleigh, should have been the first to discuss such distribution functions even though his analysis appeared in his theory of random walks⁹ rather than in the *Theory of Sound*.¹⁰

The function X is merely the x displacement of a random walker who takes a step of length γ_1 at an angle φ_1 relative to the x axis, then takes another of length γ_2 at an angle φ_2 relative to the same axis, then a third of length γ_3 at an angle φ_3 , etc. The distribution function was found for small values of n and it was shown that as $n \rightarrow \infty$ it becomes Gaussian when $\gamma_1 = \gamma_2 = \gamma_3 = \dots$. Rayleigh pointed out that certain points existed at which the distribution functions changed their character. The values of ω^2 are finite in number but as N becomes large the random variable ω^2 has a limiting density $G(\omega^2)$. The frequency distribution $G(\omega^2)$ is the Fourier transform of its characteristic function

$$f(\alpha) = E\{\exp i\alpha\omega^2\} = \int_0^\infty G(\omega^2) \exp(i\alpha\omega^2) d\omega^2. \quad (I.7)$$

Then for an n -dimensional lattice⁶

$$\begin{aligned} f_n(\alpha) &= \frac{1}{N^n} \sum_{s_1, s_2, \dots, s_n=0}^{N-1} \exp\left\{\frac{2i\alpha}{M} \sum_{j=1}^n \gamma_j \left(1 - \cos \frac{2\pi s_j}{N}\right)\right\} \\ &= \prod_{j=1}^n N^{-1} \sum_{s_j=0}^{N-1} \exp\left\{\frac{2i\alpha}{M} \gamma_j \left(1 - \cos \frac{2\pi s_j}{N}\right)\right\} \\ &\sim \prod_{j=1}^n \frac{1}{2\pi} \int_0^{2\pi} e^{2i\alpha\gamma_j/M} \exp(-2i\alpha\gamma_j M^{-1} \cos \varphi_j) d\varphi_j \\ &= \prod_{j=1}^n e^{2i\alpha\gamma_j/M} J_0(2\alpha\gamma_j/M), \end{aligned} \quad (I.8)$$

as $N \rightarrow \infty$, $J_0(x)$ being the Bessel function of order zero.

⁹ Lord Rayleigh, *Phil. Mag.* **10**, 73 (1880).

¹⁰ Lord Rayleigh, *The Theory of Sound* (Dover Publications, New York, 1945), second edition.

The frequency spectrum of an n -dimensional lattice is then

$$G_n(\omega^2) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(-i\alpha\omega^2) \times \prod_{j=1}^n \left\{ J_0\left(\frac{2\alpha\gamma_j}{M}\right) e^{2i\alpha\gamma_j/M} \right\} d\alpha. \quad (I.9)$$

The square of the largest frequency, ω_L^2 , is

$$M\omega_L^2 = 4(\gamma_1 + \gamma_2 + \dots + \gamma_n). \quad (I.10)$$

Since $J_0(x)$ is an even function, only the real part of the exponential contributes to $G_n(\omega^2)$. One finds (in this special model)

$$G_n(\omega^2) = G_n(\omega_L^2 - \omega^2), \quad (I.11)$$

so that $G_n(\omega^2)$ is symmetrical with respect to $\frac{1}{2}\omega_L^2$.

The details of the calculation of $G_n(\omega^2)$ from (I.9) are given in reference 6. The frequency spectra for lattices of 1, 2, 3 and a very large number of dimensions are sketched in Fig. 1.

The singular points of $G(\omega^2)$ were first noticed by one of the authors¹¹ (although they appear in another context in the Rayleigh random walk theory mentioned above) in the investigation of the spectrum of a square lattice with nearest and next nearest neighbor interactions where it was found that two logarithmic singularities appear in contrast to the linearity in ω of $g(\omega) = 2\omega G(\omega^2)$ obtained from the Debye theory. A similar result was obtained by Bowers and Rosenstock⁴ for the transverse vibrations of a two-dimensional square lattice. In 1952 Smollett¹² studied the in-plane vibrations of a two-dimensional ionic lattice and found that the two infinities found by Montroll and Bowers and Rosenstock assuming short-range interactions also exist in the ionic lattice.

Since $G(\omega^2)d\omega^2$ is the fraction of frequencies between ω^2 and $\omega^2 + d\omega^2$ it is clear that $G(\omega^2)$ is proportional to the rate at which $(\varphi_1, \varphi_2, \varphi_3)$ space is swept out by a

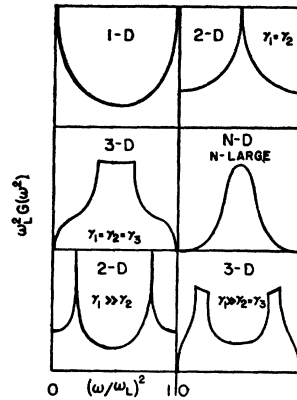


FIG. 1. Sketch of distribution function of squares of normal mode frequencies in linear square and simple cubic lattices with nearest neighbor interactions. The N -dimensional case approaches a gaussian as $N \rightarrow \infty$. The upper four figures correspond to equal central and noncentral force constants; the lower two to weak noncentral force constants.

¹¹ E. W. Montroll, *J. Chem. Phys.* **15**, 575 (1947).

¹² M. Smollett, *Proc. Phys. Soc. (London)* **A65**, 109 (1952).

surface of constant frequency as the frequency increases. The distribution function $g(\omega)$ can then be expressed (for a single branch of the spectrum) as the volume integral¹¹

$$g(\omega) = \frac{1}{8\pi^3} \frac{\partial}{\partial \omega} \iiint_{\omega=\omega(\varphi_1, \varphi_2, \varphi_3)} d\varphi_1 d\varphi_2 d\varphi_3 \quad (\text{I.12a})$$

or the surface integral¹³

$$g(\omega) = \frac{1}{(2\pi)^3} \iint \frac{dS}{|\text{grad}\omega|}, \quad (\text{I.12b})$$

where the integration proceeds over the entire surface $\omega = \text{constant}$. Smollett noticed that singularities in the frequency spectrum are related to the saddle points in the surfaces of constant frequency in the $(\varphi_1, \varphi_2, \varphi_3)$ space. $\text{grad } \omega = 0$ at saddle points as well as at minima and maxima which characterize band edges.

In 1953 Van Hove¹³ generalized Smollett's arguments and explicitly calculated out the possible types of singularities $g(\omega)$ might have in the two- and three-dimensional lattices and associated them with the character of the second-order terms in the Taylor expansions of ω about the points in $(\varphi_1, \varphi_2, \varphi_3)$ space where all first-order derivatives of ω jointly vanish—the so-called “critical points” of the frequency. Using the critical point theory of the calculus of variations in the large (developed by M. Morse)^{14,15} he showed that these critical points are a direct consequence of the periodicity of a crystal lattice and not of the detailed character of the atomic force constants.

We give a qualitative analysis of one of Morse's theorems in two dimensions.⁵ Let $G(\varphi_1, \varphi_2)$ be a continuous doubly periodic function of φ_1 and φ_2 with continuous first and second derivatives, the derivatives vanishing only at isolated points. Then Morse's theorem states that G has at least two saddle points. Now a doubly periodic function is equivalent to a function defined on a torus; hence this theorem is equivalent to the statement that a function $G(\varphi_1, \varphi_2)$ with the properties postulated above and defined on a torus has at least two saddle points.

Since G has been chosen to be continuous it must have at least one maximum and one minimum point in each of its periods. Let the location of one of these maxima be denoted by an X in each period in Fig. 2 and let the location of one set of equivalent minima be represented by heavy dots (points D , E , etc.).

If the maxima A and B are connected by a curve such as 1 in Fig. 2, there is at least one point on the curve where G has a smaller value than at neighboring points on the curve. G also achieves a smallest value along

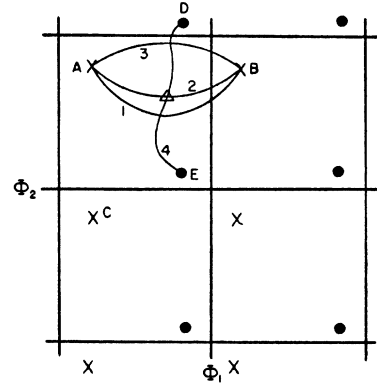


FIG. 2. Curves connecting maxima and minima of functions defined on a doubly periodic space.

any other curves, for example on 2 and 3, which connect A and B . The locus of these points forms a continuous curve which passes through E and D . G must achieve a largest value somewhere along this locus of smallest values. Let this be accomplished at the point represented by the small triangle in Fig. 2. This point must be a saddle point because as one passes along 4 from E to D it is a relative maximum, and as one passes from A to B it is a relative minimum.

The same argument could be applied by the examination of paths which connect A and C . Hence the function G has at least two saddle points. It is easy to trace out the same proof when one period of (φ_1, φ_2) space is wrapped into a torus. The number of saddle points of a function defined at all points on the surface of a N - D manifold is at least equal to the maximum number of closed paths $[(N-1)-D]$ manifolds which cannot be transformed into each other or into a point by a continuous deformation of the paths. This number is known as the Betti number of the surface.

The fact that there might be two saddle points in our reciprocal (φ_1, φ_2) space does not guarantee the existence of two logarithmic singularities in $g(\omega)$. The value of $\omega(\varphi_1, \varphi_2)$ at the two saddle points may correspond to the same frequency. This is the case when a square lattice is elastically symmetrical.

Van Hove also discussed the number of critical points that could be expected in a three-dimensional lattice. He showed that, while in general there will be no infinities in $g(\omega)$ for three-dimensional lattices, $dg(\omega)/d\omega$ has at least two infinite discontinuities and has the value $-\infty$ at the high-frequency end of the spectrum. This is in agreement with Fig. 1 for our simple cubic model. In connection with the numerical estimation of $g(\omega)$ he argued that “great attention has to be paid to location and shape of the critical points of $\omega(\varphi_1, \varphi_2, \varphi_3)$. This information can be obtained from the shape of the contours of constant frequency in reciprocal space, as was done by Smollett for a two-dimensional ionic lattice.”¹³ It should be noted, however, that knowledge of the critical points of $\omega(\varphi_1, \varphi_2, \varphi_3)$ determines only the shape of $g(\omega)$ about the critical frequencies ω_c but leaves the magnitude of $g(\omega_c)$ undetermined, necessitat-

¹³ L. Van Hove, Phys. Rev. 89, 1189 (1953).

¹⁴ M. Morse, *Functional Topology and Abstract Variational Theory* (Gauthier-Villars, Paris, 1939), Fascicule 92.

¹⁵ H. Seifert and W. Threlfall, *Variationsrechnung im Grossen* (Chelsea Publishing Company, New York).

ing some kind of interpolation scheme to fill in the spectrum between these frequencies. However, a greater difficulty exists in that no method is available for locating *all* the critical points, knowledge of the location and nature of these being necessary for a complete description of the frequency spectrum. In 1955 Rosenstock¹⁶ presented an algebraic-topological method for locating critical points for the three primitive cubic lattices but it is not clear whether the method is capable of locating all of the critical points exactly or of assuring that all of them have, in fact, been found. Golovin¹⁷ has also studied the problem of determining all the critical points for the three primitive cubic lattices via purely algebraic arguments, but again it is not clear that all possible critical points have been found.

The foregoing discussion applies only to the case that the critical points in the surfaces of constant frequency in $(\varphi_1, \varphi_2, \varphi_3)$ space are analytic. Recently Phillips¹⁸ with the aid of topological arguments has extended Van Hove's treatment to the case where nonanalytic critical points occur as well. He has determined the nature of the singularities occurring in $g(\omega)$ due to such critical points and has set up formulas which relate the number of critical points of different kinds of an n -dimensional manifold to the Betti numbers for the manifold.

II. THE FREQUENCY SPECTRUM FOR A SIMPLE CUBIC LATTICE WITH TWO DIFFERENT MASSES AND NEAREST NEIGHBOR INTERACTIONS ONLY

We now proceed to study the effect of the introduction of a second atomic species into a simple cubic lattice. First we consider an ordered diatomic lattice of the NaCl type.

We identify a typical lattice point by the triple (m_1, m_2, m_3) . The masses M_1 and M_2 will be located at alternate positions on our simple cubic lattice. The heavier mass M_1 is associated with lattice points with $(m_1 + m_2 + m_3)$ even and the lighter M_2 with $(m_1 + m_2 + m_3)$ odd. The x , y , and z components of the motion of a given atom in a simple cubic lattice with nearest neighbor interactions only are independent of each other. Hence, we need only consider the equations of motion of the x component and deduce the behavior of the y and z components by symmetry.

The equations of motion for particles on the even points are

$$\begin{aligned} M_1 \ddot{x}(m_1, m_2, m_3) &= \sum_{\substack{\epsilon_j=0,1 \\ \epsilon_1+\epsilon_2+\epsilon_3=1}} [x(m_1+\epsilon_1, m_2+\epsilon_2, m_3+\epsilon_3) \\ &\quad - 2x(m_1, m_2, m_3) + x(m_1-\epsilon_1, m_2-\epsilon_2, m_3-\epsilon_3)] \\ &\quad \times [\epsilon_1\gamma_1 + \epsilon_2\gamma_2 + \epsilon_3\gamma_3]; \quad (\text{II.1a}) \end{aligned}$$

for $(m_1 + m_2 + m_3)$ odd

$$\begin{aligned} M_2 \ddot{x}(m_1, m_2, m_3) &= \sum_{\substack{\epsilon_j=0,1 \\ \epsilon_1+\epsilon_2+\epsilon_3=1}} [x(m_1+\epsilon_1, m_2+\epsilon_2, m_3+\epsilon_3) \\ &\quad - 2x(m_1, m_2, m_3) + x(m_1-\epsilon_1, m_2-\epsilon_2, m_3-\epsilon_3)] \\ &\quad \times [\epsilon_1\gamma_1 + \epsilon_2\gamma_2 + \epsilon_3\gamma_3]. \quad (\text{II.1b}) \end{aligned}$$

Here γ_1 is the central force constant between a pair of nearest neighbors in the same x , y plane, and γ_2 and γ_3 are respectively the noncentral force constants associated with a pair of particles in the same x , y plane and with a pair in adjacent x , y planes.

We assume solutions of the form

$$x(m_1, m_2, m_3) = e^{i\omega t} u(m_1, m_2, m_3), \quad (\text{II.2})$$

where u is a function of position only and impose the cyclic boundary condition in a cube with $2N$ particles on each side. If we substitute this expression into (II.1a) and (II.1b) we obtain a pair of sets of equations for the u 's. These can be reduced to the more compact single set

$$\begin{aligned} M^* \omega^2 v(m_1, m_2, m_3) &+ \sum_{\substack{\epsilon_j=0,1 \\ \epsilon_1+\epsilon_2+\epsilon_3=1}} [v(m_1+\epsilon_1, m_2+\epsilon_2, m_3+\epsilon_3) \\ &\quad - 2v(m_1, m_2, m_3) + v(m_1-\epsilon_1, m_2-\epsilon_2, m_3-\epsilon_3)] \\ &\quad \times [\epsilon_1\gamma_1 + \epsilon_2\gamma_2 + \epsilon_3\gamma_3] = 0, \quad (\text{II.3}) \end{aligned}$$

which is valid for all (m_1, m_2, m_3) regardless of the parity of $(m_1 + m_2 + m_3)$ if we define M^* and $v(m_1, m_2, m_3)$ by¹⁹

$$\begin{aligned} M^* \omega^2 - (2\gamma_1 + 2\gamma_2 + 2\gamma_3) &= [M_1 \omega^2 - (2\gamma_1 + 2\gamma_2 + 2\gamma_3)]^{\frac{1}{2}} \\ &\quad \times [M_2 \omega^2 - (2\gamma_1 + 2\gamma_2 + 2\gamma_3)]^{\frac{1}{2}}, \quad (\text{II.4}) \end{aligned}$$

$$v(m_1, m_2, m_3) = \begin{cases} [M_1 \omega^2 - (2\gamma_1 + 2\gamma_2 + 2\gamma_3)]^{\frac{1}{2}} u(m_1, m_2, m_3) & \sum_j m_j \text{ even} \\ [M_2 \omega^2 - (2\gamma_1 + 2\gamma_2 + 2\gamma_3)]^{\frac{1}{2}} u(m_1, m_2, m_3) & \sum_j m_j \text{ odd.} \end{cases} \quad (\text{II.5})$$

In all expressions where square roots appear we adopt the convention that the positive sign for the square root is the appropriate one.

The set of equations (II.3) is just that for the vibrations of a monatomic crystal with atomic mass M^* .

¹⁶ H. B. Rosenstock, Phys. Rev. **97**, 290 (1955).

¹⁷ N. E. Golovin (private communication).

¹⁸ J. C. Phillips, Phys. Rev. **104**, 1263 (1956).

¹⁹ E. W. Montroll and R. B. Potts, Phys. Rev. **100**, 525 (1955); **102**, 72 (1956).

Hence the normal mode frequencies are roots of [see Eq. (I.5)]

$$M^*\omega^2 = 2\sum_j 1^3 \gamma_j (1 - \cos \varphi_j) \quad \varphi_j = 2\pi s_j / N, \quad (\text{II.6})$$

where the s_j are integers which range from 1 to $2N$ (or from $-N+1$ to N). Substitution of Eq. (II.4) into Eq. (II.6) implies that when

$$M_1\omega^2 > M_2\omega^2 \geq 2\gamma_1 + 2\gamma_2 + 2\gamma_3 \quad (\text{II.7})$$

then

$$\begin{aligned} [M_1\omega^2 - 2(\gamma_1 + \gamma_2 + \gamma_3)]^{\frac{1}{2}} \\ \times [M_2\omega^2 - 2(\gamma_1 + \gamma_2 + \gamma_3)]^{\frac{1}{2}} \\ = -2\sum_j 1^3 \gamma_j \cos \varphi_j. \end{aligned} \quad (\text{II.8})$$

In view of our sign convention for the square root the sum on the right of this equation must be negative. This limits the possible values of the s_j for which Eq. (II.8) is satisfied. Hence when

$$\sum_j 1^3 \gamma_j \cos \varphi_j < 0$$

Eqs. (II.7) and (II.8) give us

$$\begin{aligned} M_1 M_2 \omega_+^2 = (\gamma_1 + \gamma_2 + \gamma_3)(M_1 + M_2) \\ + [(\gamma_1 + \gamma_2 + \gamma_3)^2 (M_1 - M_2)^2 \\ + 4M_1 M_2 (\sum_j 1^3 \gamma_j \cos \varphi_j)^2]^{\frac{1}{2}}. \end{aligned} \quad (\text{II.9})$$

In a similar manner we find that, when

$$M_2\omega^2 < M_1\omega^2 \leq 2\gamma_1 + 2\gamma_2 + 2\gamma_3, \quad (\text{II.10})$$

then

$$\begin{aligned} [(2\gamma_1 + 2\gamma_2 + 2\gamma_3) - M_1\omega^2]^{\frac{1}{2}} \\ \times [(2\gamma_1 + 2\gamma_2 + 2\gamma_3) - M_2\omega^2]^{\frac{1}{2}} \\ = 2\sum_j 1^3 \gamma_j \cos \varphi_j. \end{aligned} \quad (\text{II.11})$$

In view of our sign convention for square roots this implies that

$$\sum_j 1^3 \gamma_j \cos \varphi_j > 0.$$

In this case we find from Eqs. (II.10) and (II.11) that

$$\begin{aligned} M_1 M_2 \omega_-^2 = (\gamma_1 + \gamma_2 + \gamma_3)(M_1 + M_2) \\ - [(\gamma_1 + \gamma_2 + \gamma_3)^2 (M_1 - M_2)^2 \\ + 4M_1 M_2 (\sum_j 1^3 \gamma_j \cos \varphi_j)^2]^{\frac{1}{2}}. \end{aligned} \quad (\text{II.12})$$

The frequencies given by Eq. (II.9) are limited between

$$\begin{aligned} \omega_-^2 = \frac{2}{M_2}(\gamma_1 + \gamma_2 + \gamma_3) \leq \omega_+^2 \\ \leq 2(\gamma_1 + \gamma_2 + \gamma_3) \left(\frac{1}{M_1} + \frac{1}{M_2} \right) = \omega_3^2 \end{aligned} \quad (\text{II.13})$$

and represent the optical band. The frequencies given by Eq. (II.12) are limited between

$$0 \leq \omega_-^2 \leq \frac{2}{M_1}(\gamma_1 + \gamma_2 + \gamma_3) = \omega_1^2 \quad (\text{II.14})$$

and represent the acoustical band. It is not difficult to verify that the total number of normal mode frequencies for the x component of motion is equal to $8N^3$, the total number of degrees of freedom in the x direction.

Each set of frequencies is a monotonic function of the variable

$$X = \sum_j 1^3 \gamma_j \cos \varphi_j. \quad (\text{II.15})$$

Then (II.9) and (II.12) can be written more compactly as

$$\omega_+^2 = \frac{1}{2}(\omega_1^2 + \omega_2^2) + \frac{1}{2} \left[(\omega_2^2 - \omega_1^2)^2 + \frac{16X^2}{M_1 M_2} \right]^{\frac{1}{2}} \quad (\text{II.16a})$$

$$\omega_-^2 = \frac{1}{2}(\omega_1^2 + \omega_2^2) - \frac{1}{2} \left[(\omega_2^2 - \omega_1^2)^2 + \frac{16X^2}{M_1 M_2} \right]^{\frac{1}{2}}. \quad (\text{II.16b})$$

The variable X can be considered as a random variable whose distribution function might be determined by selecting a large number of sets $(\varphi_1, \varphi_2, \varphi_3)$ at random from the range $(0, 2\pi)$ of each φ and computing the value of the sum

$$\sum_j 1^3 \gamma_j \cos \varphi_j$$

for each selection. The frequency distribution function associated with each branch can then be determined from that of X .

Let

$$F_3(x) dx = \text{prob}\{x \leq X \leq x + dx\}, \quad (\text{II.17})$$

as obtained through our random selection of φ 's. Then it is well known that

$$F_3(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f_3(\alpha) e^{-i\alpha x} d\alpha,$$

where, proceeding as we did in the derivation of Eq. (I.8),

$$f_3(\alpha) = \prod_1^3 J_0(\alpha \gamma_j).$$

Hence

$$F_3(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\alpha x} \prod_1^3 J_0(\alpha \gamma_j) d\alpha. \quad (\text{II.18})$$

When $\gamma_1 > \gamma_2 = \gamma_3$ the function $F_3(x)$ has the form given in Fig. 1 but with a displacement in the x axis which makes F_3 symmetrical with respect to the origin.

The frequencies ω_+ are a monotone increasing function of X for $X > 0$ [Eq. (II.16a)]. Hence the

distribution function $G_+(\omega^2)$ defined by

$$G_+(\omega^2)d\omega^2 = \text{prob}\{\omega^2 \leq \omega_+^2 \leq \omega^2 + d\omega^2\} \quad (\text{II.19})$$

is related to $F(x)$ by

$$G_+(\omega^2) = F(x)(dx/d\omega^2). \quad (\text{II.20})$$

This relation is deduced by the following well-known argument. Let U be a positive function of ω^2 and hence of X . Then the average value of U is

$$\begin{aligned} E(U) &= \int_{\omega_1^2}^{\omega_3^2} U(\omega^2)G_+(\omega^2)d\omega^2 \\ &= \int_0^{X_1} U(x)G_+(x)\frac{d\omega^2}{dx}dx \end{aligned} \quad (\text{II.21})$$

(with $X_1 = \gamma_1 + \gamma_2 + \gamma_3$). On the other hand $E(U)$ can be computed directly by averaging over x :

$$E(U) = \int_0^{X_1} U(x)F(x)dx. \quad (\text{II.22})$$

Since both expressions for $E(U)$ are valid for all $U(X)$, (II.20) follows.

Now (II.16a) implies

$$\frac{d\omega^2_+}{dx} = \frac{2}{(M_1M_2)^{\frac{1}{2}}} \frac{[(\omega^2 - \omega_1^2)(\omega^2 - \omega_2^2)]^{\frac{1}{2}}}{[\omega^2 - \frac{1}{2}(\omega_1^2 + \omega_2^2)]} \quad (\text{II.23})$$

so that

$$\begin{aligned} G_+(\omega^2) &= \frac{(M_1M_2)^{\frac{1}{2}}}{2} \frac{[\omega^2 - \frac{1}{2}(\omega_1^2 + \omega_2^2)]}{[(\omega^2 - \omega_1^2)(\omega^2 - \omega_2^2)]^{\frac{1}{2}}} \\ &\times F\left(\frac{(M_1M_2)^{\frac{1}{2}}}{2} \frac{[(\omega^2 - \omega_1^2)(\omega^2 - \omega_2^2)]^{\frac{1}{2}}}{[\omega^2 - \frac{1}{2}(\omega_1^2 + \omega_2^2)]}\right). \end{aligned} \quad (\text{II.24})$$

In a similar manner it is easily shown that $G_-(\omega^2)$, the distribution function of ω_-^2 , the acoustical band is given by

$$\begin{aligned} G_-(\omega^2) &= \frac{(M_1M_2)^{\frac{1}{2}}}{2} \frac{[\frac{1}{2}(\omega_1^2 + \omega_2^2) - \omega^2]}{[(\omega_1^2 - \omega^2)(\omega_2^2 - \omega^2)]^{\frac{1}{2}}} \\ &\times F\left(\frac{(M_1M_2)^{\frac{1}{2}}}{2} \frac{[\frac{1}{2}(\omega_1^2 + \omega_2^2) - \omega^2]}{[(\omega_1^2 - \omega^2)(\omega_2^2 - \omega^2)]^{\frac{1}{2}}}\right). \end{aligned} \quad (\text{II.25})$$

As $M_1 \rightarrow M_2 = M$, $\omega_1^2 \rightarrow \omega_2^2 \rightarrow \frac{1}{2}\omega_L^2$ and

$$G_+(\omega^2) = \frac{1}{2}MF\left(\frac{M}{2}[\omega^2 - \frac{1}{2}\omega_L^2]\right) \quad \text{for } \frac{1}{2}\omega_L^2 < \omega^2 < \omega_L^2$$

$$G_-(\omega^2) = \frac{1}{2}MF\left(\frac{M}{2}[\frac{1}{2}\omega_L^2 - \omega^2]\right) \quad \text{for } 0 < \omega^2 < \frac{1}{2}\omega_L^2,$$

the well-known result for a monatomic lattice.

Since

$$F_3(0) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \prod_1^3 J_0(\alpha\gamma_j) d\alpha$$

is not zero we see that as $\omega^2 \rightarrow \omega_1^2$ in $G_-(\omega^2)$ and $\omega^2 \rightarrow \omega_2^2$ in $G_+(\omega^2)$ infinities of the one-dimensional type exists at the band edges [the one-dimensional $G(\omega^2)$ is proportional to $(\omega_L^2 - \omega^2)^{-\frac{1}{2}}$]. We have plotted the total frequency spectrum $G_+(\omega^2) + G_-(\omega^2)$ as a function of ω^2 in Fig. 3.

Returning now to Van Hove's work, we mentioned that he showed that infinities would not appear in the frequency spectra of three-dimensional lattices. This is correct when the critical points are isolated. However, in the present nearest neighbor approximation the whole surface $2\gamma_1 \cos \varphi_1 + 2\gamma_2 \cos \varphi_2 + 2\gamma_3 \cos \varphi_3 = 0$ turns out to be a critical surface; hence the square root singularities in $G(\omega^2)$ at the corresponding value of ω^2 . Mazur²⁰ has calculated the frequency spectrum for a three-dimensional simple cubic alternating diatomic lattice with second neighbor interactions included and finds that in this case the square root infinities at the gap edges disappear and are replaced by large but finite peaks. The results of this calculation are shown in Fig. 4. The calculations are a generalization of those made by Newell²¹ in his analysis of a one-component simple cubic lattice with nearest and next nearest neighbor interactions.

Independently, T. A. Hoffman²² has used similar methods to obtain the density of electronic states in the linear combinations of atomic orbitals approximation for two- and three-dimensional monatomic and diatomic lattices. His results qualitatively resemble

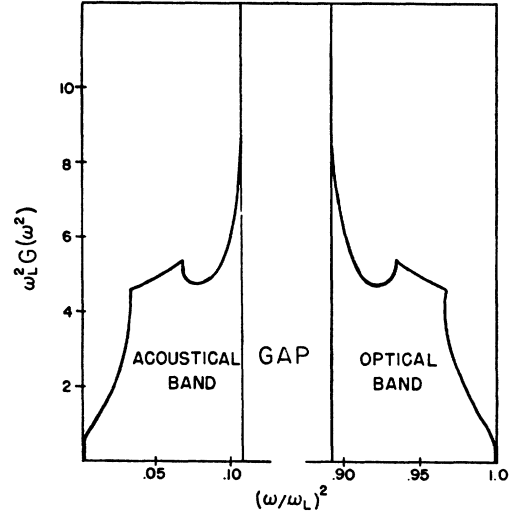


FIG. 3. Distribution of ω^2 for diatomic lattice with $M = 8m$ and $\gamma_1/\gamma_2 = 8$.

²⁰ P. Mazur, Ph.D. thesis, University of Maryland (1957).

²¹ G. F. Newell, J. Chem. Phys. 21, 1877 (1953).

²² T. A. Hoffman, Acta Phys. Acad. Sci. Hung. 1, 175 (1951).

those given here for the corresponding vibrational frequency spectra.

III. LOCALIZED DEFECT MODES IN A CRYSTAL

Various types of disordered two-component lattices can exist. Three extreme cases are

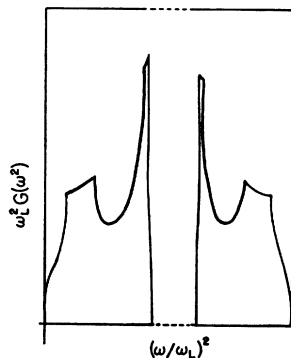
- (a) small number of *B* atoms in a matrix of *A* atoms,
- (b) slightly disordered lattices of *A* and *B* atoms,
- (c) completely disordered lattices of *A* and *B* atoms.

The influence of cases (a) and (b) on lattice vibrations can be discussed at considerable length while many unsolved problems exist in connection with (c). We discuss some aspects of (a) and (b) in this section.

As was mentioned in Sec. II, if one attempts to drive a crystal at a frequency outside the band of normal mode frequencies the driven wave is attenuated in a short distance, the effective distance diminishing as the displacement of a frequency from band edges increases. Hence, if the existence of a localized defect introduces a new isolated frequency into the frequency spectrum, the associated normal mode of vibration must be localized around the defect since the defect is a source of waves whose frequency is such as to insure attenuation. Such localized modes are analogous to bound states of electrons around impurity centers in semiconductors.

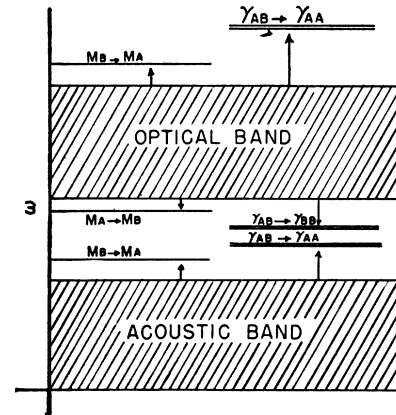
A detailed analysis of the effect of constraints and variations of parameters on dynamical systems undergoing small vibrations was made by Rayleigh¹⁰ and Routh²³ many years ago. Several of their results show qualitatively how defects force frequencies out of the bands and hence how localized defect modes develop in crystal lattices. The separation of adjacent levels in a given frequency band is of order $1/N$, N being the number of atoms in the lattice (except near band edges and singularities in the spectrum). The density of levels becomes continuous as $N \rightarrow \infty$ and the band gap has a finite value in this limit. It was shown by Rayleigh that if a single mass is reduced by δM all frequencies are increased, but by no more than the

FIG. 4. Sketch of the distribution function of the square of normal mode frequencies in a diatomic simple cubic lattice with nearest and next nearest neighbor interactions. Notice that the infinities at the inner band edges have become finite peaks. The distribution function has lost its symmetry.



²³ E. J. Routh, *Dynamics of a System of Rigid Bodies* (Dover Publications, New York, 1955).

FIG. 5. Sketch of localized mode frequencies in a diatomic lattice which result from a disordered pair of atoms. $M_B \rightarrow M_A$ is used to identify the mode that results from replacing the mass of an atom of kind *B* by that of one of kind *A*. $M_A < M_B$.



distance to the next higher unperturbed frequency. Hence, as $N \rightarrow \infty$ in our lattice all frequencies suffer a change of at most $O(1/N)$ except those associated with the upper edge of each band. These are raised by amounts at most proportional to δM (when δM is small) but independent of N as $N \rightarrow \infty$. These frequencies, being displaced out of the band, are those of localized modes. An increase of a single mass by δM reduces all frequencies by amounts no greater than the distance to adjacent lower unperturbed frequencies. Since the lowest frequency is only of order $1/N^\alpha$ from zero (α being a constant > 0 which depends on the dimensionality of the lattice) the only localized mode which can develop is that associated with the displacement of the lower optical band edge frequency. The increase (decrease) of a single force constant has the same effect as a reduction (enhancement) of a single mass. We have given a more detailed discussion of Rayleigh's theorem in Appendix A.

The change in the frequency spectrum due to interchanging *A* and *B* atoms in an ordered *AB* lattice can be seen from a consideration of Rayleigh's theorem. Let the mass of an *A* atom be M_A and that of the *B* atom be M_B with $M_A < M_B$. Then the act of replacing a heavy *B* atom by a lighter *A* atom causes a localized mode to emerge from the top of the optical and another from the top of the acoustical band. The completion of the interchange by replacing the light *A* with a heavier *B* causes a mode to emerge from the bottom of the optical band. Similar remarks can be made about the influence of a change in force constants. The various frequencies of the localized modes and their sources are sketched in Fig. 5 for the case of $\gamma_{AA} > \gamma_{AB}$ and $\gamma_{BB} < \gamma_{AB}$. The diagram corresponds to our simple cubic lattice model which possesses one degree of freedom per lattice point. All degrees of freedom are taken into account by multiplying each mode by a degeneracy factor of three. This degeneracy is split by considering next nearest neighbor interactions. If two force constants are changed at widely separated points in a lattice the associated localized mode frequencies are degenerate. The degeneracy is split as the two anomalous

force constants are brought closer together. If it is assumed that only central force constants are changed when an A atom is replaced by a B atom in our ordered diatomic lattice two new force constants are associated with the substituted B atom. The pairs of closely lying frequencies in Fig. 5 are drawn to correspond to the resulting splitting of pairs of anomalous force constant localized mode frequencies.

Some of the localized modes shown in Fig. 5 might be suppressed for the following reason. Suppose a small decrease in a mass is made so that frequencies barely rise from the bands. A large decrease in the force constants which reduce all frequencies might return these modes to the bands. This interplay between changes of masses and force constants has been discussed for one-dimensional systems elsewhere.¹⁹ Situations exist in which a frequency does not emerge from the bands until a parameter is changed by more than a certain critical amount.

The systematic theory of the analysis of localized modes has been made by Lifshitz²⁴ and his collaborators, by Montroll and Potts¹⁹ (the corresponding analysis of electron levels has been made by Koster and Slater²⁵), and by Montroll, Maradudin, and Weiss.²⁶ We sketch the latter work below and then apply it to several examples.

Let the normal mode frequencies of our crystal be $\omega_1, \omega_2, \omega_3, \dots$. Then we consider additive functions of the frequencies

$$S = \sum_j f(\omega_j). \quad (\text{III.1})$$

For example, the zero point energy of the crystal is given by (III.1) with $f(z) = (\frac{1}{2})\hbar z$, while $f(\alpha)$, the characteristic function of the squares of the frequencies, corresponds to $f(z) = N^{-1} \exp(i\alpha z^2)$. The distribution function of the squares of the frequencies $G(\omega^2)$ is the Fourier transform of $f(\alpha)$. Furthermore, most thermodynamic functions are additive functions of the frequencies.

Let us suppose the ω_j 's to be the zeros of the secular determinant corresponding to a matrix M , i.e., $\det M(\omega_j) = 0$. Then we may write for S ,

$$S = \frac{1}{2\pi i} \int_C f(z) d\{\log \det M(z)\}, \quad (\text{III.2})$$

where the closed contour C extends in a counterclockwise direction around the relevant zeros of $\det M(z)$ and where it is assumed that $f(z)$ has no poles inside or on the boundary of C . Certain corrections are necessary when the latter condition is not satisfied.

²⁴ I. M. Lifshitz, *Nuovo cimento*, Suppl. A1, 3, 591 (1956).

²⁵ C. F. Koster and J. C. Slater, *Phys. Rev.* 95, 1167 (1954); G. F. Koster, *Phys. Rev.* 95, 1436 (1954); M. Lax, *ibid.* 95, 1391 (1954).

²⁶ Montroll, Maradudin, and Weiss, *Proceedings of the Many-Body Conference* (Interscience Publishers Inc., New York, 1958).

Now suppose the matrix M to be the sum of two matrices

$$M = M_0 + \delta M = M_0(I + M_0^{-1}\delta M). \quad (\text{III.3})$$

Here M_0 is to be associated with a perfect lattice and δM is to contain variations from the perfect lattice. We represent the elements of M_0 , M_0^{-1} , and δM by $\{a_{ij}\}$, $\{a_{ij}^{(-1)}\}$, and $\{\epsilon_{ij}\}$, respectively, and define a matrix Δ by $\Delta = I + M_0^{-1}\delta M$. Then $\det M = (\det M_0)(\det \Delta)$. Substitution of this factorization into (III.2) leads us to an expression for the change in S , ΔS , due to the insertion of defects:

$$\Delta S = \frac{1}{2\pi i} \int_C f(z) d\{\log \det \Delta(z)\}. \quad (\text{III.4})$$

Since the elements of the matrix $M_0^{-1}\delta M$ are

$$(M_0^{-1}\delta M)_{ij} = \sum_k a_{ik}^{(-1)} \epsilon_{kj}, \quad (\text{III.5})$$

those of Δ are

$$\Delta_{ij} = \delta_{ij} + \sum_k a_{ik}^{(-1)} \epsilon_{kj}. \quad (\text{III.6})$$

The matrix $\Delta(\omega)$ is of fundamental importance in the present theory. It is basic to the calculation of ΔS . Furthermore from Eq. (III.4) we see that the roots of

$$\det \Delta(z) = 0 \quad (\text{III.7})$$

give the normal mode frequencies of the lattice containing defects, while Montroll and Potts¹⁹ have shown that the eigenvectors of the matrix $D(\omega) = \Delta(\omega) - I$ describe the normal mode motion of the particles directly affected by the presence of the defect.

The determinant Δ is easily constructed when only a small number of nonvanishing ϵ_{kj} 's exist. For example, suppose only one element of M_0 is perturbed, *viz.*, $\epsilon_{\alpha\alpha} \neq 0$ while all other ϵ 's vanish. Then $\epsilon_{kj} = \epsilon_{\alpha\alpha} \delta_{k\alpha} \delta_{\alpha j}$ and

$$\Delta_{ij} = \delta_{ij} + a_{i\alpha}^{(-1)} \delta_{\alpha j} \epsilon_{\alpha\alpha}. \quad (\text{III.8})$$

Hence we have

$$\det \Delta = \det \Delta_{ij} = 1 + a_{\alpha\alpha}^{(-1)} \epsilon_{\alpha\alpha}. \quad (\text{III.9})$$

As a slightly more complicated example we consider the change in M_0 due to the substitution of an impurity for a normal atom in a three-dimensional simple cubic lattice of N^3 identical atoms of mass M connected by springs with a central force constant γ_1 and noncentral force constant γ_2 . The matrix M_0 has elements

$$\begin{aligned} & (M_0)_{m_1 m_2 m_3; m_1' m_2' m_3'} \\ &= (M\omega^2 - 2\gamma_1 - 4\gamma_2) \delta_{m_1 m_2 m_3; m_1' m_2' m_3'} + \gamma_1 (\delta_{m_1 m_2 m_3; m_1'+1, m_2', m_3'} \\ &+ \delta_{m_1 m_2 m_3; m_1'-1, m_2', m_3'} + \gamma_2 (\delta_{m_1 m_2 m_3; m_1', m_2'+1, m_3'} \\ &+ \delta_{m_1 m_2 m_3; m_1', m_2'-1, m_3'} + \delta_{m_1 m_2 m_3; m_1', m_2', m_3'+1} \\ &+ \delta_{m_1 m_2 m_3; m_1', m_2', m_3'-1}), \quad (\text{III.10}) \end{aligned}$$

where

$$\delta_{ijk^{i',j',k'}} = \begin{cases} 1 & \text{when } i=i', j=j', k=k' \\ 0 & \text{otherwise.} \end{cases} \quad (\text{III.10a})$$

The matrix M_0 can be written in a two-dimensional form by, say, making the mappings $(1,1,1) \rightarrow 1$, $(1,1,2) \rightarrow 2$, \dots , $(1,1,N) \rightarrow N$, $(1,2,1) \rightarrow N+1$, $(1,2,2) \rightarrow N+2$, \dots . The frequencies of the localized modes can be found by solving the equation

$$\det \Delta = 0. \quad (\text{III.11a})$$

An immediate generalization of the one-dimensional analysis of reference 26 or a rewriting of an equation

$$g(n_1, n_2, n_3) = N^{-3} \sum_{s_1 s_2 s_3=1}^N \frac{\exp[(2\pi i/N)(s_1 n_1 + s_2 n_2 + s_3 n_3)]}{M\omega^2 - (2\gamma_1 + 4\gamma_2) + 2\gamma_1 \cos(2\pi s_1/N) + 2\gamma_2 \cos(2\pi s_2/N) + 2\gamma_2 \cos(2\pi s_3/N)} \quad (\text{III.12})$$

$$= \frac{1}{\pi^3} \int_0^\pi \int_0^\pi \int_0^\pi \frac{\cos n_1 \varphi_1 \cos n_2 \varphi_2 \cos n_3 \varphi_3 d\varphi_1 d\varphi_2 d\varphi_3}{M\omega^2 - (2\gamma_1 + 4\gamma_2) + 2\gamma_1 \cos \varphi_1 + 2\gamma_2 \cos \varphi_2 + 2\gamma_2 \cos \varphi_3}$$

as $N \rightarrow \infty$. These Green functions are merely the elements of the inverse of M_0 :

$$(M_0^{-1})_{m_1 m_2 m_3; m_1' m_2' m_3'} = g(m_1 - m_1', m_2 - m_2', m_3 - m_3'). \quad (\text{III.13})$$

Tables of the three-dimensional Green's functions have been prepared and will be published elsewhere. The solutions of (III.11a) for the frequencies that come out of the top of the band of allowed frequencies when an impurity atom is inserted in a lattice are plotted in Fig. 6 for various masses and force constants.

As a second example we consider the effect of a localized defect on an ordered diatomic lattice and give a quantitative confirmation to some of the remarks made at the beginning of this section on the application of Rayleigh's theorem to localized modes due to a disordered pair. The papers by Montroll and Potts¹⁹ and Mazur *et al.*²⁷⁻²⁹ contain discussions of the effect of a single impurity on a diatomic lattice.

We now consider a one-dimensional diatomic lattice of atoms of alternating masses M_1 and M_2 , with $M_1 > M_2$ and with force constant γ . Equations of motion can be set up as they were in Sec. II. We let $u(n)$ be the time-independent factor of the displacement of the n th atom from equilibrium. Then after letting

$$v(2n) = (M_1 \omega^2 - 2\gamma)^{1/2} u(2n) \quad (\text{III.14a})$$

$$v(2n+1) = (M_2 \omega^2 - 2\gamma)^{1/2} u(2n+1) \quad (\text{III.14b})$$

$$M^* \omega^2 - 2\gamma = [(M_1 \omega^2 - 2\gamma)(M_2 \omega^2 - 2\gamma)]^{1/2} \quad (\text{III.14c})$$

we follow Sec. II to obtain

$$\gamma v(n-1) + (M^* \omega^2 - 2\gamma)v(n) + \gamma v(n+1) = 0. \quad (\text{III.15})$$

²⁷ Mazur, Montroll, and Potts, J. Wash. Acad. Sci. **46**, 2 (1956).

²⁸ R. L. Bjork, Phys. Rev. **105**, 456 (1957).

²⁹ J. Hori and T. Asahi, Progr. Theoret. Phys. **17**, 523 (1957).

in reference 19 shows that $\det \Delta$ can be written in the form

$$\det \Delta = \{1 + M^{-1}(\gamma_1' - \gamma_1)[g(0,0,0) - g(2,0,0)]\} \\ \times \left\{ 1 + [g(0,0,0) - 2g(1,0,0) + g(2,0,0)](2,0,0) \right. \\ \times (\gamma_1' - \gamma_1)M^{-1} - 2[g(0,0,0) - g(1,0,0)] \\ \left. \times \left(\frac{\gamma_1}{M} - \frac{\gamma_1'}{M'} \right) \right\}, \quad (\text{III.11b})$$

where $g(n_1, n_2, n_3)$ is the three-dimensional Green's function

We denote by M_0 the matrix of the coefficients of the v 's in Eq. (III.15). The elements of the inverse matrix M_0^{-1} we denote by $a_{j, j+k}^{(-1)} \equiv g(k)$, and they are given by^{19,26}

$$g(k) = \frac{1}{\pi} \int_0^\pi \frac{\cos k \varphi d\varphi}{M^* \omega^2 - 2\gamma + 2\gamma \cos \varphi} \\ = \frac{1}{2\gamma\pi} \int_0^\pi \frac{\cos k \varphi d\varphi}{\{[(\omega^2/\omega_1^2) - 1][(\omega^2/\omega_2^2) - 1]\}^{1/2} + \cos \varphi}, \quad (\text{III.16})$$

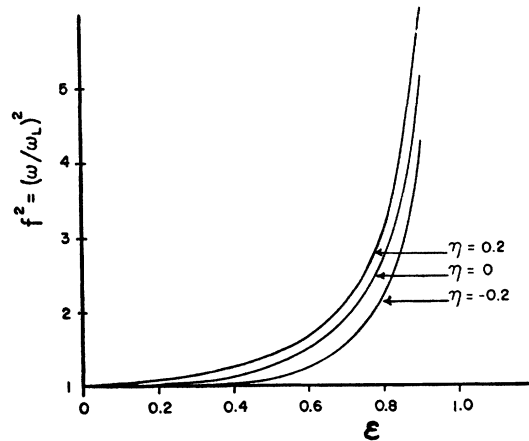


FIG. 6. Localized mode frequency in a three-dimensional simple cubic lattice resulting from an impurity atom with mass M' and central force spring constant γ_1' . Here $\epsilon = (M'/M - 1)$ and $\eta = (\gamma_1' - \gamma_1)/\gamma_1$. The ratio $\gamma_1/\gamma_2 = 8$.

where

$$\omega_1^2 = 2\gamma/M_1, \quad \omega_2^2 = 2\gamma/M_2, \quad (\omega_1^2 + \omega_2^2 = \omega_L^2) \quad (\text{III.17})$$

are the top of the acoustical band and bottom of the optical band, respectively. The elements $g(k)$ have a different form depending on whether we are interested in the frequencies that emerge from the top of the optical band ($\omega^2 > \omega_L^2$) or in the frequencies which enter the gap between the bands ($\omega_1^2 < \omega^2 < \omega_2^2$).

When $\omega^2 > \omega_L^2$ we readily find that

$$g(k) = \frac{(-1)^k \omega_1 \omega_2}{2\gamma} \times \frac{[(\omega^2 - \omega_1^2)^{\frac{1}{2}}(\omega^2 - \omega_2^2)^{\frac{1}{2}} - \omega(\omega^2 - \omega_L^2)^{\frac{1}{2}}]^{k|k|}}{\omega(\omega^2 - \omega_L^2)^{\frac{1}{2}}(\omega_1 \omega_2)^{|k|}} \quad (\text{III.18a})$$

while for $\omega_1^2 < \omega^2 < \omega_2^2$

$$g(k) = -i(-1)^{|k|} \frac{\omega_1 \omega_2}{2\gamma} \times \frac{[\omega(\omega_L^2 - \omega^2)^{\frac{1}{2}} - (\omega^2 - \omega_1^2)^{\frac{1}{2}}(\omega_2^2 - \omega^2)^{\frac{1}{2}}]^{k|k|}}{\omega(\omega_L^2 - \omega^2)(\omega_1 \omega_2)^{|k|}}. \quad (\text{III.18b})$$

We assume that the particle at $k=0$ exchanges its site with the particle at $k=2n+1$. The set of equations (III.15) is unaffected by this interchange except for the following two equations (written in terms of u 's)

$$\gamma u(-1) + (M_1 \omega^2 - 2\gamma)u(0) + (M_2 - M_1)\omega^2 \times u(0) + \gamma u(1) = 0, \quad (\text{III.19a})$$

$$\gamma u(2n) + (M_2 \omega^2 - 2\gamma)u(2n+1) + (M_1 - M_2)\omega^2 \times u(2n+1) + \gamma u(2n+2) = 0. \quad (\text{III.19b})$$

If we transform these equations according to Eq. (III.14), we obtain

$$\gamma v(-1) + (M^* \omega^2 - 2\gamma)v(0) + (M_2 - M_1)\omega^2 \times \frac{(M_2 \omega^2 - 2\gamma)^{\frac{1}{2}}}{(M_1 \omega^2 - 2\gamma)^{\frac{1}{2}}} v(0) + \gamma v(1) = 0,$$

$$\gamma v(2n) + (M^* \omega^2 - 2\gamma)v(2n+1) + (M_1 - M_2)\omega^2 \times \frac{(M_1 \omega^2 - 2\gamma)^{\frac{1}{2}}}{(M_2 \omega^2 - 2\gamma)^{\frac{1}{2}}} v(2n+1) + \gamma v(2n+2) = 0.$$

Thus the elements of the defect matrix δM are

$$(\delta M)_{ij} = (M_2 - M_1)\omega^2 \frac{(M_2 \omega^2 - 2\gamma)^{\frac{1}{2}}}{(M_1 \omega^2 - 2\gamma)^{\frac{1}{2}}} \delta_{i,0} \delta_{j,0} + (M_1 - M_2)\omega^2 \frac{(M_1 \omega^2 - 2\gamma)^{\frac{1}{2}}}{(M_2 \omega^2 - 2\gamma)^{\frac{1}{2}}} \delta_{i,2n+1} \delta_{j,2n+1}. \quad (\text{III.20})$$

In the present case the matrix of the determinant $|\Delta|$ is

$$\Delta = \begin{pmatrix} 1 + g(0)(M_2 - M_1)\omega^2 \epsilon_1 & g(2n+1)(M_1 - M_2)\omega^2 \epsilon_2 \\ g(2n+1)(M_2 - M_1)\omega^2 \epsilon_1 & 1 + g(0)(M_1 - M_2)\omega^2 \epsilon_2 \end{pmatrix}, \quad (\text{III.21a})$$

where

$$\epsilon_1 = \epsilon_2^{-1} = \frac{(M_2 \omega^2 - 2\gamma)^{\frac{1}{2}}}{(M_1 \omega^2 - 2\gamma)^{\frac{1}{2}}}. \quad (\text{III.21b})$$

The determinant $|\Delta|$ becomes

$$|\Delta| = 1 + (M_1 - M_2)^2 \omega^4 \left\{ \frac{g(0)}{(M_1 \omega^2 - 2\gamma)^{\frac{1}{2}}(M_2 \omega^2 - 2\gamma)^{\frac{1}{2}}} - g^2(0) + g^2(2n+1) \right\}. \quad (\text{III.22})$$

This has two different forms depending on whether $\omega^2 > \omega_L^2$ or $\omega_1^2 < \omega^2 < \omega_2^2$. Thus if we substitute Eq. (III.18a) into Eq. (III.22) we obtain

$$\omega^2 > \omega_L^2: \quad |\Delta| = 1 + \frac{(\omega_2^2 - \omega_1^2)^2}{\omega_1^2 \omega_2^2} \frac{\omega^2}{\omega^2 - \omega_L^2} \times \left\{ \frac{\omega(\omega^2 - \omega_L^2)^{\frac{1}{2}} - (\omega^2 - \omega_1^2)^{\frac{1}{2}}(\omega^2 - \omega_2^2)^{\frac{1}{2}}}{(\omega^2 - \omega_1^2)^{\frac{1}{2}}(\omega^2 - \omega_2^2)^{\frac{1}{2}}} + \frac{[(\omega^2 - \omega_1^2)^{\frac{1}{2}}(\omega^2 - \omega_2^2)^{\frac{1}{2}} - \omega(\omega^2 - \omega_L^2)^{\frac{1}{2}}]^{2k}}{(\omega_1 \omega_2)^{2k}} \right\}; \quad (\text{III.23a})$$

while if we substitute Eq. (III.18b) into Eq. (III.22) we obtain ($\omega_1^2 < \omega^2 < \omega_2^2$)

$$|\Delta| = 1 + \frac{(\omega_2^2 - \omega_1^2)^2}{\omega_1^2 \omega_2^2} \frac{\omega^2}{\omega_L^2 - \omega^2} \times \left\{ \frac{(\omega^2 - \omega_1^2)^{\frac{1}{2}}(\omega^2 - \omega_2^2)^{\frac{1}{2}} - \omega(\omega_L^2 - \omega^2)^{\frac{1}{2}}}{(\omega^2 - \omega_1^2)^{\frac{1}{2}}(\omega^2 - \omega_2^2)^{\frac{1}{2}}} + \frac{[\omega(\omega_L^2 - \omega^2)^{\frac{1}{2}} - (\omega^2 - \omega_1^2)^{\frac{1}{2}}(\omega_2^2 - \omega^2)^{\frac{1}{2}}]^{2k}}{(\omega_1 \omega_2)^{2k}} \right\}, \quad (\text{III.23b})$$

where for convenience we have put $k=2n+1$.

The frequencies of the localized defect modes are the roots of $|\Delta|=0$. In general the equations cannot be solved analytically and recourse must be made to numerical methods. However, since the off-diagonal terms in the matrix Δ decrease exponentially with increasing k , i.e., with increasing separation between the interchanged masses, in the limit that $k \rightarrow \infty$ the equation $|\Delta|=0$ factors into two equations

$$(M_1 - M_2)\omega^2 \epsilon_1 g(0) = 1, \quad (\text{III.24a})$$

$$(M_2 - M_1)\omega^2 \epsilon_2 g(0) = 1. \quad (\text{III.24b})$$

In the case that $\omega^2 > \omega_L^2$ this pair of equations becomes

$$\alpha\omega(\omega^2 - \omega_2^2)^{\frac{1}{2}} = (\omega^2 - \omega_1^2)^{\frac{1}{2}}(\omega^2 - \omega_L^2)^{\frac{1}{2}}, \quad (\text{III.25a})$$

$$-\beta\omega(\omega^2 - \omega_1^2)^{\frac{1}{2}} = (\omega^2 - \omega_2^2)^{\frac{1}{2}}(\omega^2 - \omega_L^2)^{\frac{1}{2}}, \quad (\text{III.25b})$$

where

$$\alpha = 1 - (\omega_1^2/\omega_2^2), \quad \beta = (\omega_2^2/\omega_1^2) - 1. \quad (\text{III.26})$$

Only the first of Eqs. (III.25) has a solution for $\omega^2 > \omega_L^2$:

$$\omega^2 = \frac{1}{2}\omega_2^2 + \frac{1}{1-\alpha^2} \left\{ \omega_1^2 + \frac{1}{2}[(1-\alpha^2)^2\omega_2^4 + 4\alpha^2\omega_1^4]^{\frac{1}{2}} \right\}. \quad (\text{III.27})$$

When $\omega_1^2 < \omega^2 < \omega_2^2$ Eqs. (III.24) become

$$\alpha\omega(\omega_2^2 - \omega^2)^{\frac{1}{2}} = (\omega^2 - \omega_1^2)^{\frac{1}{2}}(\omega_L^2 - \omega^2)^{\frac{1}{2}} \quad (\text{III.28a})$$

$$\beta\omega(\omega^2 - \omega_1^2)^{\frac{1}{2}} = (\omega_2^2 - \omega^2)^{\frac{1}{2}}(\omega_L^2 - \omega^2)^{\frac{1}{2}}. \quad (\text{III.28b})$$

Both of these equations have solutions corresponding to frequencies in the gap between the optical and acoustical bands:

$$\omega_A^2 = \frac{1}{2}\omega_2^2 + \frac{1}{1-\alpha^2} \left\{ \omega_1^2 - \frac{1}{2}[4\alpha^2\omega_1^4 + (1-\alpha^2)^2\omega_2^4]^{\frac{1}{2}} \right\} \quad (\text{III.29a})$$

$$\omega_0^2 = \frac{1}{2}\omega_1^2 + \frac{1}{1-\beta^2} \left\{ \omega_2^2 - \frac{1}{2}[4\beta^2\omega_2^4 + (1-\beta^2)^2\omega_1^4]^{\frac{1}{2}} \right\}. \quad (\text{III.29b})$$

ω_A^2 is the frequency which for $M_1/M_2 \sim 1$ emerges from the top of the acoustical band while ω_0^2 is the frequency which at the same time drops out of the bottom of the optical band. The frequencies given by Eqs. (III.27) and (III.29) are plotted as a function of M_1/M_2 in Fig. 7. It will be noted that ω_A^2 and ω_0^2 cross when $M_1/M_2 \cong 3.75$. Furthermore as $M_1/M_2 \rightarrow \infty$, $\omega_A^2 \rightarrow \frac{1}{2}\omega_L^2$ while $\omega_0^2 \rightarrow \omega_1^2$.

When k is small, however, a new feature appears. We have solved Eqs. (III.23) numerically for several values of k and the ratio M_1/M_2 . In Fig. 7 we have plotted as the dotted curves the values of ω_0^2 and ω_A^2 and the frequency which comes out of the top of the optical band for the special value $k=1$. The two sets of curves for $k=1$ and $k=\infty$ are the envelopes of the family of curves which is obtained by letting k assume successively the values 1, 3, 5, \dots . We see that for $k < \infty$ the two frequencies ω_A^2 and ω_0^2 no longer intersect but remain separated for all values of $M_1/M_2 > 1$.

To obtain more information about the variation of the various defect frequencies with the separation between the interchanged particles we must solve Eqs. (III.23) as a function of k . If we introduce the following notations,

$$\omega^2 = x\omega_1^2 \quad \omega_2^2 = \lambda\omega_1^2 \quad \omega_L^2 = (1+\lambda)\omega_1^2, \quad (\text{III.30})$$

we see from Eqs. (III.23) that the defect frequencies

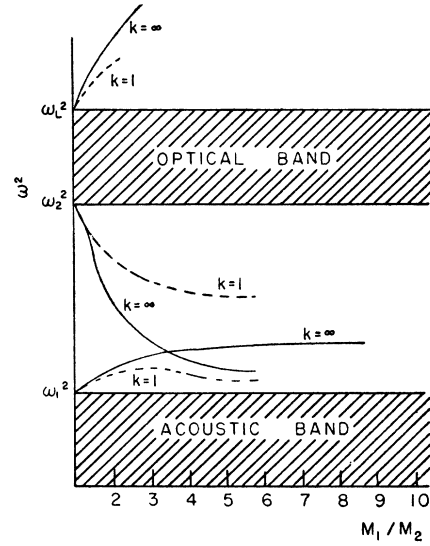


FIG. 7. The variation with mass ratios and separation of the localized frequencies which arise on interchanging the positions of two unlike atoms in a diatomic linear chain. For any finite separation of interchanged atoms ($k < \infty$) the curves representing the frequencies which come into the gap can come arbitrarily close to the curves corresponding to infinite separation, but they never touch each other.

are given by the solutions of

$$\frac{\lambda}{(\lambda-1)^2} \frac{x-\lambda-1}{x} = \frac{(x-1)^{\frac{1}{2}}(x-\lambda)^{\frac{1}{2}} - x^{\frac{1}{2}}(x-\lambda-1)^{\frac{1}{2}}}{(x-1)^{\frac{1}{2}}(x-\lambda)^{\frac{1}{2}}}, \quad (\text{III.31a})$$

$$\frac{[(x-1)^{\frac{1}{2}}(x-\lambda)^{\frac{1}{2}} - x^{\frac{1}{2}}(x-\lambda-1)^{\frac{1}{2}}]^{2k}}{\lambda^k}, \quad x > 1 + \lambda$$

$$\frac{\lambda}{(\lambda-1)^2} \frac{1+\lambda-x}{x} = \frac{x^{\frac{1}{2}}(1+\lambda-x)^{\frac{1}{2}} - (x-1)^{\frac{1}{2}}(\lambda-x)^{\frac{1}{2}}}{(x-1)^{\frac{1}{2}}(\lambda-x)^{\frac{1}{2}}}, \quad 1 < x < \lambda \quad (\text{III.31b})$$

$$\frac{[x^{\frac{1}{2}}(1+\lambda-x)^{\frac{1}{2}} - (x-1)^{\frac{1}{2}}(\lambda-x)^{\frac{1}{2}}]^{2k}}{\lambda^k}.$$

This form for the equations is useful for their numerical solution, but also allows us to obtain approximate analytic solutions for them as follows. Both equations are of the form

$$A(x) = B(x) - [C(x)]^k. \quad (\text{III.32})$$

From the numerical solution we know that the solution

for $k=1$ does not differ greatly from the solution for $k=\infty$ particularly for $M_1/M_2 \sim 1$ or $M_1/M_2 \gg 1$, and this suggests that we express the solution to Eq. (III.32) as

$$x = x_0 + \epsilon, \quad (\text{III.33})$$

where x_0 satisfies

$$A(x_0) = B(x_0) \quad (\text{III.34})$$

and ϵ is assumed to be small. Substituting Eq. (III.33) into Eq. (III.32) and making use of Eq. (III.34) we obtain finally the following expression for ϵ correct to first order:

$$\epsilon \cong - \frac{[C(x_0)]^k}{A'(x_0) - B'(x_0) + kC'(x_0)[C(x_0)]^{k-1}} \sim - \frac{[C(x_0)]^k}{A'(x_0) - B'(x_0)}, \quad (\text{III.35})$$

where the primes denote differentiation with respect to the argument, and the second expression in Eq. (III.35) is valid for large k . This method of solution is an application of Newton's method for the solution of equations involving differentiable functions. The x_0 's appropriate to the three out of the band frequencies are obtained from Eqs. (III.27) and (III.29).

With this result we can make some qualitative comments about the broadening of the defect frequency levels due to the distribution of separations between the pair of interchanged particles. Equations (III.30), (III.33), (III.35) imply that each of the three defect frequencies can be expressed generally as

$$\omega_k^2 = (\omega_\infty)^2 [1 - \gamma(\delta)^k + \dots] \quad 0 < \delta < 1. \quad (\text{III.36})$$

For example for the case $M_1 = (3/2)M_2$, the expansion for the frequency which comes out of the top of the optical band is

$$\omega^2 = \omega_\infty^2 \left[1 - \frac{(0.3086)^k}{8.1322} + \dots \right], \quad (\text{III.37a})$$

while the frequencies which come out of the top of the acoustic band and the bottom of the optical band, respectively, can be expanded as

$$\omega_A^2 = \omega_\infty^2 \left[1 - \frac{(0.8123)^k}{115.74} + \dots \right] \quad (\text{III.37b})$$

and

$$\omega_0^2 = \omega_\infty^2 \left[1 + \frac{(0.7082)^k}{33.845} + \dots \right], \quad (\text{III.37c})$$

where the ω_∞ 's appearing in Eqs. (III.37) are different in each case. Thus as the separation between the two interchanged particles decreases the frequencies which come out of the top of the acoustic and optical bands are depressed while the frequency which drops out of the bottom of the optical band is raised. This behavior

is just what would be expected from arguments based on Rayleigh's theorems.¹⁰

We have seen that point defects might lead to localized modes and that when several identical defects are introduced the defect frequency splits by an amount that depends on the separation distance of defects. Large numbers of point defects may appear in a random manner or may be regularly spaced as they would be in a screw dislocation or at a stacking fault. In the random case we would expect the formation of a defect band which would be a diffuse broadening of the defect frequency. In the regular case we would expect the defect spectrum to have the characteristics of that of a periodic system of the appropriate dimensionality. A screw dislocation might have localized modes with a typical spectrum of a one-dimensional lattice with more than nearest neighbor interaction. The indirect coupling between more distant parts of the dislocation would be related to the Green's function of the normal lattice in which the dislocation is imbedded.

We shall discuss the line shape of randomly distributed defects in the next section.

IV. LATTICE VIBRATIONS OF DISORDERED LATTICES

The problem of determining the vibrational properties of a randomly disordered many-component lattice has received much attention recently and has stimulated a great deal of ingenious mathematical thought. The interest in this problem is due in part to the light it throws on such properties of many-component lattices as the vibrational contribution to the thermodynamic functions of binary alloys and the separation of isotropic mixtures into separate phases at very low temperatures. This model has in addition a direct application to the evaluation of electronic energy levels in disordered alloys as well as to certain aspects of the spin wave theory of magnetism.

In the earliest paper on the subject Dyson³⁰ obtained an explicit expression for the frequency spectrum of any disordered linear chain. This expression is given in terms of the solution to a certain linear, homogeneous integral equation. He presented a solution in closed form to this equation only for a simple but physically unrealistic model of a chain, in which the masses and spring constants take on any positive values subject to a certain probability distribution. In the physically more interesting case where two types of particles are randomly distributed over the lattice sites (with no correlations between the position of the particles) the subsidiary integral equation reduces to a functional equation. However, he did not attempt a solution of this equation and indeed seems to have underestimated the difficulty of a numerical solution. Dyson's technique, moreover, cannot be generalized for use in higher dimensions.

³⁰ F. J. Dyson, Phys. Rev. **92**, 1331 (1953).

Prigogine, Bingen, and Jeener³¹ studied precisely this latter model in connection with the evaluation of the zero-point energy of isotopic mixtures. Their method, a perturbation calculation, is not restricted to the one dimensional case as is Dyson's. They use an exact frequency spectrum for the unperturbed lattice in the one-dimensional case, but in two and three dimensions they use a Debye spectrum. As is frequently the case in perturbation calculations, the authors did not discuss the convergence of the resulting series. This point is of some interest because certain results found by Maradudin and Weiss³² cast light on the question of convergence, and in particular seem to suggest that in certain cases the perturbation series of Prigogine, Bingen, and Jeener do not converge.

Lifshitz and Stepanova³³ presented a formal method for calculating the frequency spectrum and Helmholtz free energy of a random lattice. Their paper uses linear operator theory developed previously by Lifshitz,²⁴ and is based on an expansion of the various functions in powers of the concentration of one type of atom in a lattice composed of atoms of a second type. Although the method can be used in any number of dimensions, no detailed calculations are made. The Lifshitz-Stepanova treatment of this problem seems to be the most difficult to apply for computational purposes.

Schmidt³⁴ has presented a very elegant theory for the one-dimensional chain. His method, like that of Dyson, depends upon the fact that the characteristic matrix is a Jacobi matrix. This limits the use of his method to one dimension only. Schmidt derives a functional equation satisfied by the distribution function together with a convergent iterative procedure for determining this function. His paper actually presents an approximate expression for the frequency distribution function under the assumption of low impurity concentration although Schmidt does not calculate averages of any functions of frequency using this distribution function.

Asahi and Hori²⁹ have presented a method of solution for the one-dimensional problem which is probably the simplest way yet devised to solve for the in-band frequencies. Unfortunately the method cannot be extended to higher dimensions.

We begin our discussion of the effects of disorder by outlining several methods that are useful when the concentration of defects in a monatomic lattice is low. The following presentation follows that of Montroll, Maradudin, and Weiss.²⁶

If two identical widely separated point defects exist in a lattice each is the source of a localized mode of the same frequency. As the distance between the two is diminished the frequency degeneracy is split,

at first symmetrically about the original frequencies. At separations greater than several lattice spacings the splitting depends only on the distance between the two defects (at smaller separations the direction of the line of centers relative to the crystal axes become important). Hence all defect levels are broadened in a system with a small but finite concentration of randomly distributed defects. The line width at low concentrations can be estimated by weighting a given frequency separation by the number of nearest neighbor defect pairs whose distance leads to that splitting. Interactions between more distant neighbors can be neglected at low concentrations.

Let $\Omega = f(r)$ be the level spacing appropriate to a pair of defects separated by a distance r . Furthermore, let $W(r)dr$ be the probability that the nearest neighbor to a given defect be between r and $r+dr$. Then the fraction of levels split into a pair with separation less than Ω

$$N(\Omega) = - \int_0^{\Omega} W(r) \left(\frac{dr}{d\Omega} \right) d\Omega. \quad (\text{IV.1})$$

The distribution of nearest neighbor distance between random points was derived by Paul Hertz (see also Chandrasekhar³⁵). If ρ is the average number of points per unit volume (unit length in one dimension and unit area in two), the distribution function is

$$W(r) = \begin{cases} 2\rho e^{-2\rho r} & \text{one dimension} \\ 2\pi r \rho \exp(-\pi\rho r^2) & \text{two dimensions} \\ 4\pi r^2 \rho \exp(-\frac{4}{3}\pi\rho r^3) & \text{three dimensions.} \end{cases} \quad (\text{IV.2})$$

It is known that the splitting due to a pair of defects separated by a distance r (greater than several lattice spacings) is

$$\Omega = \begin{cases} A e^{-\alpha r} & \text{in one dimension} \\ (A/r) e^{-\alpha r} & \text{in three dimensions.} \end{cases} \quad (\text{IV.3})$$

The constants A and α depend on the nature of the defects. Hence the fraction of defect pair frequencies split by amounts $< \Omega$ are

$$1-D: \quad N(\Omega) = \begin{cases} (\Omega/A)^{2\rho/\alpha} & \Omega < A \\ 1 & \Omega > A \end{cases} \quad (\text{IV.4})$$

$$3-D: \quad N(\Omega) = \exp \left\{ -\frac{4\pi}{3} \rho [r(\Omega)]^3 \right\}$$

where $r(\Omega)$ is obtained by solving (IV.3) for r . We have plotted $N(\Omega)$ in Fig. 8 for the particular choice $A = \alpha = 1$, $\rho = 0.2$.

The line width of a defect level due to concentration

³¹ Prigogine, Bingen, and Jeener, *Physica* **20**, 383, 516 (1954).

³² A. A. Maradudin and G. H. Weiss (to be published).

³³ I. M. Lifshitz and G. I. Stepanova, *Soviet Phys. JETP* **3**, 656 (1956).

³⁴ H. Schmidt, *Phys. Rev.* **105**, 425 (1957).

³⁵ S. Chandrasekhar, *Revs. Modern Phys.* **15**, 1 (1943).

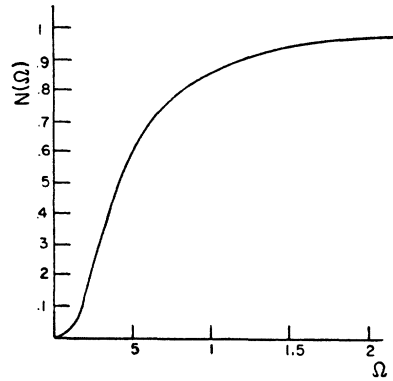


FIG. 8. $N(\Omega)$ is the fraction of defect pair frequencies split by amounts $< \Omega$.

splitting is

$$\bar{\Omega} = - \int_0^{\infty} \Omega \frac{dN(\Omega)}{d\Omega} d\Omega = \int_0^{\infty} \Omega(r) W(r) dr$$

$$= \begin{cases} 2\rho A / (\alpha + 2\rho); & 1-D \\ 4\pi A \rho \int_0^{\infty} r \exp\left\{-\alpha r - \frac{4\pi}{3}\rho r^3\right\} dr. & 3-D \end{cases}$$

As $\rho \rightarrow 0$ in the 3D case

$$\bar{\Omega} \sim 4\pi A (\rho/\alpha^2).$$

When defects are present in a lattice in large numbers their influence on thermodynamic quantities can usually be expressed as a power series in the defect concentration. The systematic development of the coefficients for such series has been described elsewhere.²⁶ We now adapt such expansions to expansions in powers of one minus the long-range order parameter for slightly disordered lattices.

In the usual treatments of the order-disorder transition whether by the various approximate methods of Bragg and Williams, Bethe, Kirkwood, and others, or on the basis of the Ising model, it is assumed that the interaction between the vibrational and configurational contributions to the partition function for the lattice is negligible so that the partition function Z can be expressed as

$$Z = Z_{\text{vib}} Z_{\text{config}}$$

where the first factor is independent of the degree of order in the lattice. However, as we will see below, disorder in a lattice can conveniently be expressed in terms of the interchange of positions of different pairs of unlike atoms. Thus the disordering process can be regarded as equivalent to the introduction of substitutional defects at various lattice sites.

We assume that a long-range order parameter is given and estimate averages over all configurations consistent with that order parameter. We do not discuss the more difficult problem in which the configurational interaction constants vary with instantaneous lattice spacings during vibration.

We again consider the three-dimensional simple cubic lattice with nearest neighbor central and non-central force interactions between the particles. There are $2N$ particles in the lattice of which N are of mass M_1 and N are of mass M_2 . We can regard it as being made up of two interpenetrating sublattices one of which we call the α sublattice and the other we call the β sublattice. In the ordered state the α sublattice is occupied by particles of mass M_1 only while the β sublattice is occupied by particles of mass M_2 only. Furthermore the six nearest neighbor sites to an α site are all β sites and vice versa. Following Bragg and Williams³⁶ we now introduce a long-range order parameter R which is defined by

$$R = 2r_\alpha - 1 = 2r_\beta - 1, \quad (\text{IV.5})$$

where r_α and r_β are the fractions of α atoms on β sites and β atoms on α sites, respectively. When $r_\alpha = r_\beta = 1$, $R = 1$, and this corresponds to a state of perfect order. When $r_\alpha = r_\beta = 0$, $R = -1$, and this also corresponds to a state of perfect order since here every α atom is on a β site and vice versa. Thus the long-range order parameter R is symmetric about $r_\alpha = r_\beta = \frac{1}{2}$ for which $R = 0$, and this corresponds to a state of complete disorder. We will accordingly consider only those values of R which satisfy

$$0 \leq R \leq 1.$$

We consider now how the degree of order decreases in the lattice. The first degree of disorder corresponds to the interchange of the positions of any two unlike particles in the lattice. In this case $r_\alpha = r_\beta = 1 - 1/N$ so that

$$R_1 = [(2N - 2)/N] - 1 = 1 - (2/N).$$

The next degree of disorder corresponds to a second pair of unlike particles interchanging their positions and for this case $r_\alpha = r_\beta = (N - 2)/N$ so that

$$R_2 = [(2N - 4)/N] - 1 = 1 - 4/N.$$

In general the n th degree of disorder corresponds to the interchange of the positions of n different pairs of unlike particles, and here

$$R_n = (N - 2n)/N = 1 - (2n/N). \quad (\text{IV.6})$$

We can now apply these results to the expansion of an arbitrary additive function of the normal mode frequencies of a disordered lattice in powers of the parameter $(1 - R)$ for $R \geq 0$. Let us assume that n different pairs of unlike particles have interchanged their positions. Let us denote the functions of interest by $S(\mathbf{r}_{12}^{(1)}, \mathbf{r}_{12}^{(2)}, \dots, \mathbf{r}_{12}^{(n-1)}, \mathbf{r}_{12}^{(n)})$ where $\mathbf{r}_{12}^{(j)} = \mathbf{r}_1^{(j)} - \mathbf{r}_2^{(j)}$ is the vector joining the positions of the j th interchanging pair. Now it is clear that any given degree of disorder in the lattice can be realized in many different ways. For example the first degree of disorder

³⁶ W. L. Bragg and E. J. Williams, Proc. Roy. Soc. (London) **A145**, 699 (1934).

can be realized in N^2 distinct ways corresponding to the interchange of any one of the N particles on the α sublattice with any one of the N particles on the β sublattice. In order that our results be applicable to a real crystal lattice we must therefore average $S(\mathbf{r}_{12}^{(1)}, \dots, \mathbf{r}_{12}^{(n)})$ over all distinct configurations of the n interchanged pairs. Since this latter function depends only on the number of interchanged pairs we may denote it by $S(n)$. The averaging process may include any correlations between interchanged pairs. However, the results given below are completely general; the passage from the $S(\mathbf{r}_{12}^{(1)}, \dots, \mathbf{r}_{12}^{(n)})$ to the $S(n)$ includes all such information and may be handled in an analogous fashion to that given in reference 26 for a similar problem.

By a well-known formula from the calculus of finite differences $S(n)$ can be expressed in the form

$$S(n) = \sum_{j=0}^n \binom{n}{j} \Delta^j S(0) = S(0) + n[S(1) - S(0)] + \frac{n(n-1)}{2!} [S(2) - 2S(1) + S(0)] + \dots \quad (\text{IV.7})$$

where

$$\Delta S(0) = S(1) - S(0) \quad (\text{IV.8a})$$

and

$$\Delta^{k+1} S(0) = \Delta(\Delta^k S(0)). \quad (\text{IV.8b})$$

We can now introduce the long-range order parameter into the expansion given by Eq. (IV.7) since by Eq. (IV.6)

$$n = \frac{N}{2}(1 - R_n) \quad \text{if } R_n > 0. \quad (\text{IV.9})$$

In the following we will omit the subscript n in Eq. (IV.9) and will express our results in terms of R . If as $N \rightarrow \infty$

$$S(0) = S_0$$

$$\Delta S(0) = S(1) - S(0) = \frac{S_1}{2N} \quad (\text{IV.10})$$

$$\Delta^2 S(0) = S(2) - 2S(1) + S(0) = \frac{S_2}{4N^2} \text{ etc.,}$$

and $n \rightarrow \infty$ while $N \rightarrow \infty$ in such a manner that $(n/N) = \frac{1}{2}(1 - R)$, Eq. (IV.7) becomes

$$S(R) = S_0 + \frac{S_1}{4}(1 - R) + \frac{S_2}{32}(1 - R)^2 + \frac{S_3}{384}(1 - R)^3 + \dots \quad (\text{IV.11})$$

A similar expansion exists about the point $R = -1$. Through the use of known series which give expan-

sions of a function about two points we find that for $-1 < R < 1$

$$S(R) = S_0 + \frac{S_1}{8}(1 - R^2) + \frac{1}{32}(S_1 + \frac{1}{4}S_2)(1 - R^2)^2 + \dots \quad (\text{IV.12})$$

Since S has been specified to be an additive function of the normal mode frequencies of the lattice we can obtain convenient expressions for the S_j 's by employing Eq. (III.4). Then since we can express $S(\mathbf{r}_{12}^{(1)}, \mathbf{r}_{12}^{(2)}, \dots, \mathbf{r}_{12}^{(n)}) - S(0)$ as

$$S(n) - S(0) = \frac{1}{2\pi i} \int_0^1 f(z) d \ln |\Delta_n(z)| \quad (\text{IV.13})$$

where the right-hand side depends explicitly on the coordinates of n distinct pairs of interchanged particles, we obtain the following expression for $\Delta^n S(0)$:

$$\Delta^n S(0) = \left\langle \frac{1}{2\pi i} \int_c f(z) \times \frac{\prod_{j=k, k-2, \dots, \neq 0} |\Delta_j(z)|^{\binom{k}{j}}}{\prod_{j=k-1, k-3, \dots, \neq 0} |\Delta_j(z)|^{\binom{k}{j}}} d \ln \right\rangle \quad (\text{IV.14})$$

where $\langle \rangle$ denotes an average over all the distinct configurations that the n interchanged pairs of particles can assume. The first two $\Delta^n S(0)$ are

$$\Delta S(0) = \left\langle \frac{1}{2\pi i} \int_c f(z) d \ln |\Delta_1(z)| \right\rangle \quad (\text{IV.15a})$$

$$\Delta^2 S(0) = \left\langle \frac{1}{2\pi i} \int_c f(z) d \ln \frac{|\Delta_2(z)|}{|\Delta_1(z)|^2} \right\rangle. \quad (\text{IV.15b})$$

Equations (IV.10), (IV.11), and (IV.14) constitute a formal solution to our problem.

Several specific calculations have been made for the zero-point energy for a one-dimensional chain. If we assume that the chain has $2N$ particles, then a detailed evaluation of the integrals involved yields as the zero point energy per particle

$$\frac{E_0(R)}{2N} = \frac{\hbar\omega_L}{\pi} [0.9995 - 0.000109(1 - R^2) + 0\{(1 - R^2)^2\}] \quad M_1 = 1.2M_2 \quad (\text{IV.16})$$

$$\frac{E_0(R)}{2N} = \frac{\hbar\omega_L}{\pi} [0.9892 - 0.00151(1 - R^2) + 0\{(1 - R^2)^2\}] \quad M_1 = 2M_2$$

where the values of the zero point energy for the ordered lattices have been calculated from the expression given in reference 27. ω_L is the maximum normal mode frequency of the unperturbed lattice. We thus see that the zero-point energy of the chain is lowered by disordering, in agreement with other results of Prigogine, Bingen, and Jeener,³¹ and Maradudin and Weiss.³²

This same approach has been exploited²⁶ to yield the low concentration expansion of additive functions of the normal mode frequencies. If we denote by c the concentration of A atoms in a lattice of B atoms, and we express the mass of the foreign A atoms by $M(1-\epsilon)$ where M is the mass of the B atoms, then we may express $S = \sum f(\omega_j)$ in the form

$$S = \sum_{n=0}^{\infty} a_n(\epsilon)c^n. \quad (\text{IV.17})$$

The method of this section has been used in finding the following expression for the average zero-point energy per particle of a linear chain

$$\begin{aligned} \frac{E_0(c)}{N} = \frac{\hbar\omega_L}{\pi} & \left\{ 1 + \left[\frac{1}{2}(1-\epsilon^2)^{-\frac{1}{2}} \cos(-\epsilon) - \frac{\pi}{4} \right] c \right. \\ & - \left[\epsilon^2 \left(\frac{\pi-3}{8} \right) + \epsilon^3 \left(\frac{16-5\pi}{16} \right) \right. \\ & \left. \left. + \epsilon^4 \left(\frac{63\pi-200+3\sqrt{2} \tanh^{-1}2^{-\frac{1}{2}}}{96} \right) \right. \right. \\ & \left. \left. + 0(\epsilon^5) \right] c^2 + 0(c^3) \right\}. \quad (\text{IV.18}) \end{aligned}$$

In spite of the ingenuity shown by the authors listed at the beginning of this section, very few results have been actually calculated by their methods. Only Prigogine, Bingen, and Jeener³¹ have attempted any discussion based on a detailed evaluation of their formulae. Maradudin and Weiss³² derived a formal solution for the evaluation of additive functions of the normal mode frequencies [of the form given in Eq. (III.1)] that can be adapted to a numerical calculation, at least of the first few terms of the relevant expansions. Their method has the advantage that it is independent of dimension, and that the convergence properties of the resulting series can be discussed (it appears that at least in some cases, the perturbation series of reference 31 do not converge). We give a brief outline of the method.

We may start with an expression for $S = \sum_j f(\omega_j)$ as a contour integral as in Eq. (III.2). Since the secular determinant can be factored:

$$|M(\omega)| = |M_0(\omega)| |\Delta(\omega)| \quad (\text{IV.19})$$

where $M_0(\omega)$ and $\Delta(\omega)$ have been defined in previous

paragraphs we may write

$$\begin{aligned} S = S_0 + \Delta S = \frac{1}{2\pi i} \int_c f(z) d \ln |M_0(z)| \\ + \frac{1}{2\pi i} \int_c f(z) d \ln |\Delta(z)|. \quad (\text{IV.20}) \end{aligned}$$

Presumably one knows the value of S_0 so that all we need to find is the value of ΔS . To do this we write $|\Delta(\omega)|$ in the form

$$|\Delta(\omega)| = \prod_j (1 + \lambda_j) \quad (\text{IV.21})$$

where the λ_j are the eigenvalues of $M_0^{-1}(\omega)\delta M(\omega)$. Hence, if each λ_j satisfies the condition $|\lambda_j| \leq 1$ we may write

$$\begin{aligned} \ln |\Delta(\omega)| &= \sum_j \ln(1 + \lambda_j) \\ &= \sum_j \lambda_j - \frac{1}{2} \sum_j \lambda_j^2 + \frac{1}{3} \sum_j \lambda_j^3 - \dots \end{aligned} \quad (\text{IV.22})$$

Denoting the matrix $M_0^{-1}(\omega)\delta M(\omega)$ by $D(\omega)$ we finally find

$$\ln |\Delta(\omega)| = \sum_{n=1}^{\infty} (-1)^n \frac{\text{Tr}(D^n)}{n}. \quad (\text{IV.23})$$

Henceforth we shall confine ourselves to the simple case in which we have two types of atoms, A atoms and B atoms, the A 's having mass M_1 and the B 's having mass M_2 . We assume that an A atom occupies a lattice site with probability p and a B atom occupies a lattice site with probability $1-p$. All of the spring constants are assumed to be equal. The method is of greater generality, and other more complicated situations can be treated using it.

We may write the mass at lattice site $\mathbf{m} = (m_1, m_2, m_3)$ as

$$M(\mathbf{m}) = \bar{M} + \sigma_{\mathbf{m}} \Delta M, \quad (\text{IV.24})$$

where $\sigma_{\mathbf{m}}$ is a random variable with the property

$$\sigma_{\mathbf{m}} = \begin{cases} \frac{M_1 - \bar{M}}{\Delta M} & \text{with probability } p \\ \frac{M_2 - \bar{M}}{\Delta M} & \text{with probability } 1-p. \end{cases} \quad (\text{IV.25})$$

The choice of \bar{M} and ΔM is arbitrary and can be chosen in several ways all of which are consistent with the conditions $|\lambda_j| \leq 1$. Now we may choose the matrix $M_0(\omega)$ to be the secular matrix corresponding to a lattice consisting only of atoms of mass \bar{M} . The elements of $M_0(\omega)$ and $M_0^{-1}(\omega)$ are known through the work of Montroll and Potts.¹⁹ In particular, the expression for

the $a_{\mathbf{m}, \mathbf{m}'^{(-1)}}$, the elements of $M_0^{-1}(\omega)$, are

$$a_{\mathbf{m}, \mathbf{m}'^{(-1)}} = N^{-n} \sum_{\mathbf{s}} [\lambda_0(\mathbf{s})]^{-1} \times \exp[2\pi i \mathbf{s} \cdot (\mathbf{m} - \mathbf{m}')/N], \quad (\text{IV.26a})$$

where n is the dimensionality of the lattice and

$$\lambda_0(\mathbf{s}) = \bar{M}\omega^2 - 2 \sum_{j=1}^n \gamma_j \left(1 - \cos \frac{2\pi s_j}{N} \right). \quad (\text{IV.26b})$$

When the ΔM and \bar{M} are chosen so that $|\lambda_j| < 1$ (it can be shown³² that this is always possible) then we may write

$$\text{Tr}(D^k) = (\Delta M \omega^2)^k \sum_{\mathbf{m}_1} \cdots \sum_{\mathbf{m}_k} a_{\mathbf{m}_1 \mathbf{m}_2^{(-1)}} \cdots a_{\mathbf{m}_{k-1} \mathbf{m}_k^{(-1)}} \sigma_{\mathbf{m}_1} \cdots \sigma_{\mathbf{m}_k}. \quad (\text{IV.27})$$

This expression together with Eqs. (IV.20), (IV.23), (IV.24), and (IV.26) is a formal expression for S .

When there is disorder in the lattice we are interested in $\langle \Delta S \rangle$ the value of ΔS averaged over all possible configurations. If ΔM is so small that $(\Delta M)^2$, $(\Delta M)^3$, \cdots can be neglected in comparison then we may write for ΔS

$$\Delta S \sim \frac{\Delta M}{2\pi i} \sum_{\mathbf{m}} \sigma_{\mathbf{m}} \int_c g(z) d\{z^2 a_{\mathbf{m} \mathbf{m}^{(-1)}}(z)\}. \quad (\text{IV.28})$$

The element $a_{\mathbf{m} \mathbf{m}^{(-1)}}$ is independent of \mathbf{m} . The randomness of ΔS is now described by the term $\sum_{\mathbf{m}} \sigma_{\mathbf{m}}$. If N is large $\sum_{\mathbf{m}} \sigma_{\mathbf{m}}$ has a Gaussian distribution with a mean equal to

$$\langle \sum_{\mathbf{m}} \sigma_{\mathbf{m}} \rangle = \frac{N^n}{\Delta M} [pM_1 + (1-p)M_2 - \bar{M}] \quad (\text{IV.29a})$$

and variance

$$\langle \sum_{\mathbf{m}} \sigma_{\mathbf{m}}^2 \rangle = \frac{N^{2n}}{(\Delta M)^2} [p(1-p)(M_1 - M_2)^2]. \quad (\text{IV.29b})$$

In general it is not possible to neglect higher powers of ΔM so that we will essentially find a perturbation expansion in powers of ΔM , using Eq. (IV.23). Let us denote $\langle \sigma^i \rangle$ by β_j . Then, in averaging terms in the expression, Eq. (IV.27), for $\text{Tr}(D^k)$ we must partition each summation since, for example, $\beta_2 \neq \beta_1^2$. Thus different types of terms arise from the double sum as follows

$$\begin{aligned} & \sum_{\mathbf{m}_1} \sum_{\mathbf{m}_2} a_{\mathbf{m}_1 \mathbf{m}_2^{(-1)}} a_{\mathbf{m}_2 \mathbf{m}_1^{(-1)}} \langle \sigma_{\mathbf{m}_1} \sigma_{\mathbf{m}_2} \rangle \\ &= \beta_2 \sum_{\mathbf{m}} \{a_{\mathbf{m} \mathbf{m}^{(-1)}}\}^2 \\ &+ \beta_1^2 \sum_{\mathbf{m}_1} \sum'_{\mathbf{m}_2} a_{\mathbf{m}_1 \mathbf{m}_2^{(-1)}} a_{\mathbf{m}_2 \mathbf{m}_1^{(-1)}}, \quad (\text{IV.30}) \end{aligned}$$

where the prime excludes the values $\mathbf{m}_1 = \mathbf{m}_2$ in the summation. We get a similar separation of terms into "irreducible" sums from higher terms, and a discussion of these sums can be given very similar to the discussion of cluster integrals in the theory of imperfect gases. An expansion of

$$N^{-n} d \langle \ln |\Delta(\omega)| \rangle$$

up to terms of order $(\Delta M)^2$ is

$$\begin{aligned} & N^{-n} d \langle \ln |\Delta(\omega)| \rangle \\ &= \frac{2\beta_1}{\omega} [a_1(\omega) - \mu^{-1} a_2(\omega)] d\omega \\ &+ 2(\beta_1^2 - \beta_2) \frac{a_1(\omega)}{\omega} [a_1(\omega) - \mu^{-1} a_2(\omega)] d\omega \\ &- 2 \frac{\beta_1^2}{\omega} [a_2(\omega) - \mu^{-1} a_3(\omega)] d\omega + \cdots, \quad (\text{IV.31}) \end{aligned}$$

where $\mu = \Delta M / \bar{M}$ and the $a_k(\omega)$ are irreducible sums given by

$$\begin{aligned} a_k(\omega) &= \frac{(\Delta M \omega^2)^k}{N^n} \sum_{\mathbf{m}_1} \cdots \sum_{\mathbf{m}_k} a_{\mathbf{m}_1 \mathbf{m}_2^{(-1)}} \cdots a_{\mathbf{m}_{k-1} \mathbf{m}_k^{(-1)}} \\ &= \frac{(\Delta M \omega^2)^k}{N^n} \sum_{\mathbf{s}} [\lambda_0(\mathbf{s})]^{-k}. \end{aligned} \quad (\text{IV.32})$$

Different types of irreducible sums appear in higher order terms of the expansion begun in Eq. (IV.31). A detailed discussion of these points is found in reference 32.

The most convenient contour to use for evaluating the integrals of Eq. (IV.20) is a semicircle with the diameter on imaginary axis, and the circular part in the right half-plane. A general expression for $a_k(i\omega)$ with ω real, can be given in terms of generalized hypergeometric functions.

Several calculations for particular functions $f(\omega)$ have been made. The simplest example is $f(\omega) = \frac{1}{2} \hbar \omega$, the zero-point energy. In one dimension the average value of the zero point energy is given by

$$\begin{aligned} & \frac{E_0 + \langle \Delta E_0 \rangle}{N} \\ &= \frac{\hbar \omega_L}{\pi} [1 - 0.5\beta_1 \mu + (0.3927\beta_2 - 0.0177\beta_1^2) \mu^2 \\ &+ (0.6073\beta_1 \beta_2 - 0.3333\beta_3 - 0.5862\beta_1^3) \mu^3 \\ &+ (0.2946\beta_4 + 0.0933\beta_2^2 + 1.6667\beta_1 \beta_3 \\ &+ 1.7687\beta_1^4 - 3.7358\beta_1^2 \beta_2) \mu^4 + 0(\mu^5)], \quad (\text{IV.33}) \end{aligned}$$

whose ω_L is the maximum frequency of the lattice

with masses \bar{M} . For the special choice of parameters

$$\bar{M} = pM_1 + (1-p)M_2 \quad \Delta M = M_1 - M_2. \quad (\text{IV.34})$$

Equation (IV.33) simplifies to

$$\begin{aligned} \frac{E_0 + \langle \Delta E_0 \rangle}{N} = & \frac{\hbar\omega_L}{\pi} \{ 1 + 0.3927p(1-p)\mu^2 \\ & + [0.2945p(1-p)(1-6p+6p^2) \\ & + 0.9769p^2(1-p)^2]\mu^4 + 0(\mu^6) \} \quad (\text{IV.35}) \end{aligned}$$

since all of the odd moments are zero. This corresponds to the choice of made by Prigogine, Bingen, and Jeener. However, it appears that the parameters of Eq. (IV.34) do not always insure the convergence of Eq. (IV.35). The two-dimensional calculation is carried out to terms of order μ^2 in reference 32. The μ^2 correction to the specific heat for the linear chain, using the definitions of Eq. (IV.34) is

$$\langle \Delta C_v \rangle = \frac{p(1-p)k\omega_L\beta^2}{2} \left\{ \frac{\omega_L}{\sinh^2\beta\omega_L} - \frac{\beta\omega_L^2 \cosh\beta\omega_L}{\sinh^3\beta\omega_L} \right\} \mu^2 \quad \beta = \frac{1}{kT}, \quad (\text{IV.36})$$

and the μ^2 correction to the Helmholtz free energy is

$$\langle \Delta F \rangle = \left\{ \frac{\hbar\omega_L p(1-p)}{8} \operatorname{ctnh} \left(\frac{\hbar\omega_L}{2kT} \right) \right\} \mu^2. \quad (\text{IV.37})$$

When we use the foregoing technique to find the frequency distribution we find that the calculation yields a series in delta functions and derivatives of delta functions. While this series does not describe the frequency distribution it can be shown that if one integrates functions using the partial sums of this series the result will be correct. This is how $\langle \Delta C_v \rangle$ and $\langle \Delta F \rangle$ were calculated.

In preparation for a discussion of the frequency spectrum of a disordered lattice of a mixture of two isotopes we suggest that the largest frequency can be expected to be that of a monatomic lattice composed of the light isotope. Suppose our mixture has equal numbers of both species and let the number of particles N^3 approach infinity. Now divide the system into many cells in such a way that a large number of particles remain in each cell (and such that this number approaches infinity as $N \rightarrow \infty$). If the surface force constants of each cell are set equal to zero we find (following Ledermann³⁷) that a very small number of frequencies (compared with N^3) are changed by the process. As $N \rightarrow \infty$ we are certain to find at least one isolated cell with all light atoms. Such a cell will yield a frequency equal to that of a lattice of pure

light component. By Rayleigh's theorem no frequency can be higher than this in any other cell. It is conjectured that in a three-dimensional lattice this high-frequency point is approached by a tail in the frequency spectrum. However, in the one-dimensional case the spectrum may have an infinite tangent at this point.

We now find approximate expressions for the frequency spectrum of a completely disordered diatomic linear chain by the moment-trace method.³⁸ We again assume that force constants remain unchanged in the disordering process.

The squares of the normal mode frequencies of a lattice are the characteristic roots of a matrix called the "dynamical matrix" which we denote by D^2 . If we denote the j th characteristic root of D^2 by $\lambda_j = \omega_j^2$ we see that for every λ_j there exist two frequencies $-\omega_j$ and $+\omega_j$, the positive one of which is to be used in obtaining the vibrational properties of the lattice. The frequency distribution function $g(\omega)$ is defined such that $Ng(\omega)d\omega$ is the number of normal mode frequencies in the range ω to $\omega+d\omega$ where N is the total number of degrees of freedom of the lattice. It is clear that $g(\omega) = g(-\omega)$. We have just shown that the frequency spectrum of a disordered isotope lattice is nonvanishing over only a finite range of frequencies, i.e., there exists a maximum frequency ω_L which for the isotopic lattices considered is equal to the maximum frequency of the monatomic lattice composed exclusively of the light masses.

With these results we see that the odd moments of the frequency distribution function, μ_{2k+1} vanish, while the even moments are nonvanishing and are given by

$$\begin{aligned} \mu_{2k} &= \int_{-\omega_L}^{\omega_L} \omega^{2k} g(\omega) d\omega / \int_{-\omega_L}^{\omega_L} g(\omega) d\omega \\ &= \int_0^{\omega_L} \omega^{2k} g(\omega) d\omega \quad (\text{IV.38}) \end{aligned}$$

since

$$\int_0^{\omega_L} g(\omega) d\omega = 1.$$

If we use the theorem of matrix algebra which states that the sum of the k th powers of the characteristic roots of a matrix equals the trace of the k th power of the matrix we find in our case that

$$\operatorname{Tr} D^2_k = \sum_j \lambda_j^k = \sum_j \omega_j^{2k}.$$

Since the order of the dynamical matrix is N , the average value of the $2k$ th power of the normal mode

³⁷ W. Ledermann, Proc. Roy. Soc. (London) **A182**, 362 (1944).

³⁸ E. W. Montroll, J. Chem. Phys. **10**, 218 (1942); **11**, 481 (1943).

frequencies is

$$\frac{1}{N} \sum_i \omega_j^{2k} = \frac{1}{N} \text{Tr } D^{2k}$$

which by definition is the $2k$ th moment of the frequency distribution function

$$\mu_{2k} = \int_0^{\omega_L} \omega^{2k} g(\omega) d\omega = \frac{1}{N} \text{Tr } D^{2k}. \quad (\text{IV.39})$$

Knowing the matrix D^2 we can in principle calculate all the moments of the frequency distribution function, and it only remains to reconstruct the distribution function from a knowledge of its moments.

Following a well-known technique we expand $g(\omega)$ in terms of Legendre polynomials

$$g(\omega) = \sum_{n=0}^{\infty} a_n P_n \left(\frac{\omega}{\omega_L} \right) \quad (\text{IV.40})$$

where the coefficients a_n are given by

$$a_n = \frac{2n+1}{2} \int_{-1}^1 g(x\omega_L) P_n(x) dx. \quad (\text{IV.41})$$

Since $P_n(x)$ has the parity of n , and $g(\omega)$ is an even function of ω , we see from Eq. (IV.41) that the odd coefficients a_{2n+1} vanish. Furthermore, recalling Eq. (IV.39) we see that a_{2n} is given as a linear combination of the moments $\mu_0, \mu_1, \dots, \mu_{2n}$, whose coefficients depend on the coefficients of x^{2n} in the expression for $P_{2n}(x)$. The final result is that

$$\omega_L a_{2k} = (4k+1) P_{2k}(x) |_{x^2 = u_k} \quad (\text{IV.42})$$

where we have introduced the dimensionless moments $u_{2k} = \mu_{2k}/\omega_L^{2k}$. Explicit expressions for the first few coefficients are

$$\begin{aligned} \omega_L a_0 &= 1 \\ \omega_L a_2 &= (5/2)(3u_2 - u_0) \\ \omega_L a_4 &= (9/8)(35u_4 - 30u_2 + 2u_0) \\ \omega_L a_6 &= (13/16)(231u_6 - 315u_4 + 105u_2 - 5u_0) \\ \omega_L a_8 &= (17/128)(6435u_8 - 12012u_6 + 6930u_4 \\ &\quad - 1260u_2 + 35u_0). \end{aligned} \quad (\text{IV.43})$$

If the frequency distribution function is a reasonably smooth function of ω , i.e., it has no singularities, then an expansion in a finite number of Legendre polynomials can be expected to give a qualitatively good description of the distribution function. It is well known that⁶ the frequency spectra for monatomic one- and two-dimensional lattices contain sharp infinities, and Mazur²⁰ has recently shown that the frequency spectrum

of an alternating diatomic lattice with only nearest neighbor interactions contains infinities in the three-dimensional case as well. However, even in these cases, calculations of the frequency spectra which have been carried out using from ten to fourteen moments^{38,39} have reproduced all of the qualitative features of the spectrum such as the occurrence of the requisite number of peaks, and even some of the quantitative features such as the locations of the peaks, which have subsequently been verified by more accurate calculations. It has been conjectured that these infinities which occur in the ordered lattices would tend to be "washed out" in the randomly disordered lattices since in this case averaging the spectrum over all configurations of the lattice would destroy any tendency for large numbers of frequencies to be localized in a small frequency range. If this is the case, then the moment-trace method will yield a good picture of the frequency spectrum, the accuracy improving as higher moments are calculated.

We outline briefly the method of evaluating the moments for the disordered linear chain. Calculations for two- and three-dimensional lattices are being carried out in the same way.

Consider a linear chain composed of two kinds of particles, one kind having a mass M_1 , and the second kind having a mass M_2 . The probability that a given lattice site is occupied by a particle of mass M_1 is p , and the probability for occupation by a particle of mass M_2 is $1-p$. It is further assumed that the force constant γ of the "springs" which link nearest neighbor masses is the same for all springs ("isotope case").

The elements $(D^2)_{ij}$ of the dynamical matrix are (assuming the cyclic boundary condition)

$$\begin{aligned} (D^2)_{ij} &= \frac{2\gamma}{M_i} \delta_{ij} - \frac{\gamma}{(M_i M_{i-1})^{1/2}} \delta_{i-1,j} \\ &\quad - \frac{\gamma}{(M_i M_{i+1})^{1/2}} \delta_{i+1,j} \end{aligned} \quad (\text{IV.44})$$

where $i, j = 1, 2, \dots, N$. With the aid of this expression $\text{Tr } D^{2k}$ was evaluated for $k=0, 1, 2, \dots, 7$, and was then averaged over all configurations of the masses. As an example we calculate $\langle \mu_2 \rangle$ and $\langle \mu_4 \rangle$ (of course $\langle \mu_0 \rangle = 1$). From Eq. (IV.44) we have that

$$\begin{aligned} \langle \mu_2 \rangle &= \frac{1}{N} \langle \text{Tr } D^2 \rangle = \frac{1}{N} \left\langle \sum_i \frac{2\gamma}{M_i} \right\rangle = 2\gamma \left\langle \frac{1}{M_j} \right\rangle \\ &= 2\gamma \left(\frac{p}{M_1} + \frac{1-p}{M_2} \right) \end{aligned} \quad (\text{IV.45})$$

³⁹ E. W. Montroll and D. C. Peaslee, J. Chem. Phys. 12, 98 (1944).

TABLE I. Moments of the frequency distribution function for a disordered linear chain ($M_1=2M_2$; $p=\frac{1}{2}$).

$\langle\mu_0\rangle=1$	$\langle\mu_8\rangle=(487/4096)=0.118896$
$\langle\mu_2\rangle=(3/8)=0.375$	$\langle\mu_{10}\rangle=(3063/32768)=0.093475$
$\langle\mu_4\rangle=(29/128)=0.2265625$	$\langle\mu_{12}\rangle=0.075788$
$\langle\mu_6\rangle=(81/512)=0.158203$	$\langle\mu_{14}\rangle=0.062854$

TABLE II. Coefficients in the Legendre polynomial expansion of the frequency distribution function for a disordered linear chain.

$\omega_L a_0=1$	$\omega_L a_8=-0.353140$
$\omega_L a_2=0.3125$	$\omega_L a_{10}=-0.322029$
$\omega_L a_4=-0.360352$	$\omega_L a_{12}=-0.01314$
$\omega_L a_6=-0.363403$	$\omega_L a_{14}=0.071460$

and

$$\begin{aligned}
 \langle\mu_4\rangle &= \frac{1}{N} \langle \text{Tr} D^4 \rangle \\
 &= \frac{1}{N} \left\langle \sum_i \left[\frac{4\gamma^2}{M_i^2} + \frac{\gamma^2}{M_{i-1}M_i} + \frac{\gamma^2}{M_iM_{i+1}} \right] \right\rangle \\
 &= 4\gamma^2 \left\langle \frac{1}{M_i^2} \right\rangle + 2\gamma^2 \left\langle \frac{1}{M_iM_{i+1}} \right\rangle \\
 &= 2\gamma^2 \left\{ \frac{2p(1+p)}{M_1^2} + \frac{2p(1-p)}{M_1M_2} \right. \\
 &\quad \left. + \frac{2(1-p) + (1-p)^2}{M_2^2} \right\}. \quad (\text{IV.46})
 \end{aligned}$$

The expressions for the higher moments rapidly become more cumbersome and will not be given here. Numerical calculations were carried out for this model for the particular choice $M_1=2M_2$, $p=\frac{1}{2}$. The numerical values for the first fourteen moments in this case are given in Table I, and the first nine coefficients in the Legendre function expansion of the frequency distribution function are given in Table II. The frequency spectrum obtained from the first fourteen moments is shown in Fig. 9. For comparison the corresponding spectrum calculated to the same

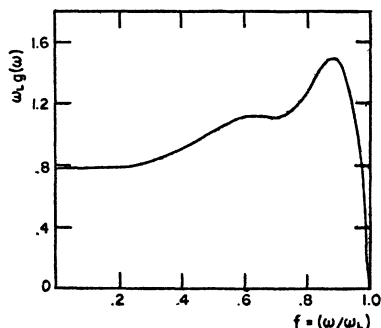


FIG. 9. The frequency spectrum of a one-dimensional disordered lattice constructed from its first fourteen moments. $M_1=2M_2$, and $p=\frac{1}{2}$.

approximation for the ordered (alternating) diatomic linear chain is plotted in Fig. 10.

It is known that

$$\omega_L^2 = \lim_{n \rightarrow \infty} (\mu_{2n+2}/\mu_{2n}). \quad (\text{IV.47})$$

The values of this ratio for $n=0$ to $n=6$ are 0.37, 0.60, 0.70, 0.75, 0.79, 0.81, 0.82, which seem to be approaching the limit 1 as would be the case if our remarks on the nature of the highest frequency are correct.

The more general case in which the force constant of the "spring" joining two masses depends on the nature of the two masses has been studied by Oguchi and Takagi,⁴⁰ who calculated the first eight moments for a disordered binary chain and constructed the frequency spectrum in the manner described above.

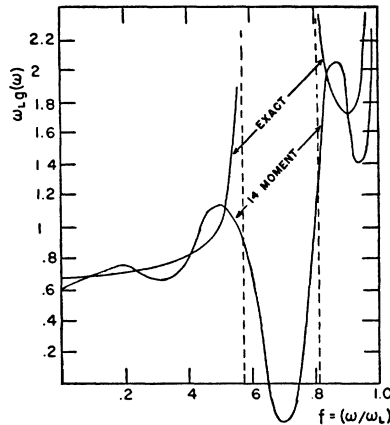


FIG. 10. The frequency spectrum of a one-dimensional ordered diatomic lattice with

$$M_1=2M_2.$$

The fourteen-moment curve is calculated on the same basis as that of the disordered lattice spectrum of Fig. 9.

They were able to study the variation in the frequency spectrum with changes in the short-range order parameter. In an earlier paper Oguchi and Hiroike⁴¹ studied the effects of disorder on the vibrational contribution to the specific heat of two-dimensional binary lattices using the moment-trace method, and the three-dimensional case has been studied by Shibuya, Fukuda, and Fukuroi.⁴² A discussion of these papers and references to other Japanese work on similar problems is given in the review article by Muto and Takagi.⁴³

Plots of the heat capacity of binary substitutional alloys as a function of temperature generally have a λ point at the critical temperature, associated with the disappearance of long-range order. It is usually assumed for simplicity that the heat capacity contributions of

⁴⁰ Y. Takagi and T. Oguchi, *Busseiron Kenkyu* 34, 44 (1951).

⁴¹ T. Oguchi and K. Hiroike, *Busseiron Kenkyu* 33, 37 (1950).

⁴² Shibuya, Fukuda, and Fukuroi, *Busseiron Kenkyu* 37, 160 (1951); 41, 17 (1951).

⁴³ T. Muto and Y. Takagi in *Solid State Physics*, edited by F. Seitz and D. Turnbull, (Academic Press, Inc., New York, 1955), Vol. 1, p. 193.

lattice vibrations and configurational interactions are independent and that the observed heat capacity is merely the sum of these two independent contributions.

An improvement of this approximation can be made by observing the frequency spectrum to be a function of the degree of order of the alloy. A family of vibrational heat capacity curves can be constructed for various degrees of order (see Fig. 11). We have supposed the Debye- Θ to be increased by disordering. Then the vibrational heat capacity is to be selected from lower and lower curves as the degree of disorder (and temperature) increase. A sharp drop to the lowest (completely disordered) curve occurs at T_c . The thick line curve in Fig. 11 shows schematically how the vibrational contribution to the heat capacity varies with temperature in materials which do not undergo a structural change.

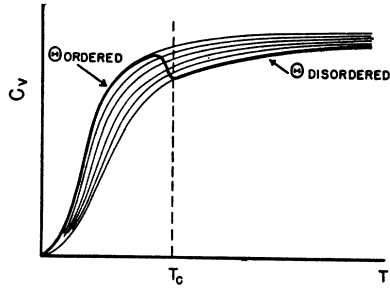


FIG. 11. A sketch of the heat-capacity curves for disordered lattices for various degrees of disorder. The thick line curve shows schematically how the vibrational contribution to the heat capacity varies with temperature. T_c is the Curie temperature for disorder.

The sharpness of the λ point is the result of the configurational contribution to the heat capacity.

APPENDIX A. EFFECT OF CHANGES OF DYNAMICAL PARAMETERS AND THE INTRODUCTION OF CONSTRAINTS ON VIBRATIONAL FREQUENCIES¹⁰

We express the kinetic and potential energies of a system of coupled oscillators as

$$T = \frac{1}{2} \sum_{j=1}^m M_j \dot{Q}_j^2 \quad \text{and} \quad V = \frac{1}{2} \sum_{j=1}^m c_j Q_j^2$$

in terms of the normal coordinates $\{Q_j\}$. The squares of normal mode frequencies ω_j^2 are

$$\omega_j^2 = c_j / M_j.$$

Now suppose the system to be altered so that terms

$$\delta T = \frac{1}{2} \alpha (f_1 \dot{Q}_1 + f_2 \dot{Q}_2 + \cdots + f_m \dot{Q}_m)^2 \quad (\text{A.1a})$$

and

$$\delta V = \frac{1}{2} \gamma (f_1 Q_1 + f_2 Q_2 + \cdots + f_m Q_m)^2 \quad (\text{A.1b})$$

are added, respectively, to T and V . If we set $\gamma = 0$ and $\alpha = M_j' - M_j$, the alteration in the kinetic energy is the result of a change in the mass of the j th oscillator from M_j to M_j' . On the other hand, the alteration of a single spring constant might lead to $\alpha = 0$ and $\gamma \neq 0$. The setting of $\alpha = 0$ and $\gamma = \infty$ corresponds to a con-

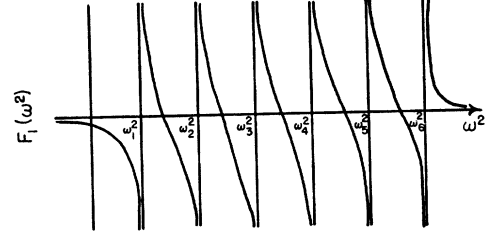


FIG. 12.

straint of the system such that

$$f_1 Q_1 + f_2 Q_2 + \cdots + f_m Q_m = 0,$$

for any other value of $\sum_j f_j Q_j$ would cause the total potential energy to become infinite thus making the corresponding configuration impossible. The fixing of the center of mass of a lattice with one degree of freedom per lattice point can be introduced into its dynamics through the proper choice of the f_j 's. Three such conditions are required for a lattice with three degrees of freedom per lattice point.

The equations of motion of our altered system yield, after letting $Q_j = u_j e^{i\omega t}$

$$(-M_1 \omega^2 + c_1) u_1 + f_1 (\gamma - \alpha \omega^2) (f_1 u_1 + f_2 u_2 + \cdots) = 0,$$

$$(-M_2 \omega^2 + c_2) u_2 + f_2 (\gamma - \alpha \omega^2) (f_1 u_1 + f_2 u_2 + \cdots) = 0, \quad \text{etc.}$$

The characteristic equation for the determination of normal mode frequencies is obtained by multiplying the first equation by $f_1 / (c_1 - M_1 \omega^2)$ the second by $f_2 / (c_2 - M_2 \omega^2)$, etc., and adding the resulting equations to obtain

$$F(\omega^2) = \sum_{j=1}^m \frac{f_j^2}{M_j \omega^2 - c_j} + \frac{1}{\alpha \omega^2 - \gamma} = 0. \quad (\text{A.2})$$

The numerator of this function is a polynomial of degree m in ω^2 and $F(\omega^2)$ has m roots. Let ϵ be a small positive number. Then

$$F(\omega_j^2 - \epsilon) \rightarrow -\infty \quad \text{as} \quad \epsilon \rightarrow 0$$

$$F(\omega_j^2 + \epsilon) \rightarrow +\infty \quad \text{as} \quad \epsilon \rightarrow 0.$$

Hence, if $\omega_0^2 = \gamma / \alpha$ and $\omega_1^2 < \omega_2^2 < \cdots < \omega_j^2 < \omega_0^2 < \omega_{j+1}^2 < \cdots < \omega_m^2$, $F(\omega^2)$ suffers a change in sign in each interval

$$(\omega_2^2, \omega_1^2), \quad (\omega_3^2, \omega_2^2), \quad \cdots, \quad (\omega_0^2, \omega_j^2), \\ (\omega_{j+1}^2, \omega_0^2), \quad \cdots, \quad (\omega_m^2, \omega_{m-1}^2).$$

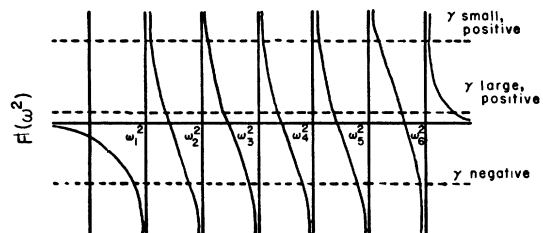


FIG. 13.

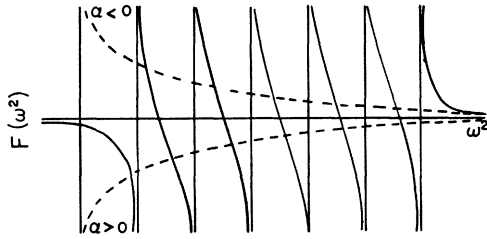


FIG. 14.

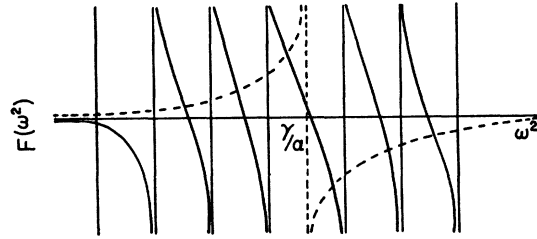


FIG. 15.

Therefore, the square of a normal mode frequency lies in each of these intervals (Rayleigh¹⁰). The alteration characterized by (A.1) causes each of the unperturbed original ω_j^2 to be moved in the direction of ω_0^2 . Each new frequency falls between a pair of those of the unperturbed system except that two fall between ω_j^2 and ω_{j+1}^2 .

We now discuss several special cases of interest in lattice vibration problems. Generally the changes in masses and force constants with which we will be concerned do not cause the lattice to be unstable to small oscillations. That is, we assume that ω^2 is never negative. If we rewrite (A.2) as

$$F(\omega^2) = F_1(\omega^2) - F_2(\omega^2)$$

with

$$F_1(\omega^2) = \sum_{j=1}^m \frac{f_j^2}{M_j \omega^2 - c_j} \quad \text{and} \quad F_2(\omega^2) = \frac{-1}{\alpha \omega^2 - \gamma},$$

the determination of the zeros of $F(\omega^2)$ is achieved by observing the intersection of $F_1(\omega^2)$ and $F_2(\omega^2)$ when both functions are plotted together. $F_1(\omega^2)$ has been plotted schematically in Fig. 12 for $m=6$. If we

set (a) $\alpha=0$ and $\gamma>0$, then $F_2(\omega^2)$ is a straight line represented by a dotted line in Fig. 13. As $\gamma \rightarrow \infty$ this line approaches the horizontal axis in the figure. All frequencies are raised when $\alpha=0$ and $\gamma>0$ as can be seen by the location of the intersection of the dotted lines with the $F_1(\omega^2)$ curves. Notice that only one frequency escapes from the original frequency range (ω_m^2, ω_1^2). As $\gamma \rightarrow \infty$, this frequency also becomes infinite; (b) if $\alpha=0$ and $\gamma<0$ then all frequencies are reduced; (c) if $\gamma=0$ then $F_2(\omega^2) = 1/\alpha\omega^2$ is schematically represented in Fig. 14 by the dotted curve in the fourth quadrant when $\alpha>0$ and by that in the first quadrant when $\alpha<0$. Hence all frequencies are reduced when $\alpha>0$ while all are increased when $\alpha<0$; (d) if both $\gamma>0, \alpha>0$, $F_2(\omega^2)$ is positive for small ω^2 and negative for large ω^2 with a singularity at γ/α . This is plotted schematically in Fig. 15 where we notice that all frequencies squared ω_j^2 , are shifted towards the critical value γ/α .

In cases (a) and (c) we note that one frequency has been removed from the dense collection of normal mode frequencies.