Dynamics of disordered harmonic lattices

Daniel N. Payton III

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DYNAMICS OF DISORDERED HARMONIC LATTICES

A Dissertation
Presented to
the Faculty of the Graduate School
University of Missouri at Rolla

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by
Daniel N. Payton, III
May 1966
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CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1. Lattice Dynamics of Perfect Crystals</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2. Isolated Defects</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>3. Disordered Systems</td>
<td>9</td>
</tr>
<tr>
<td>II</td>
<td>Frequency Spectra</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>1. The Method of Negative-Factor-Counting</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>2. Review of Dean's Work</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>3. Calculational Procedures</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>4. Frequency Spectra and Normal Modes</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>5. Comparison with Other Results</td>
<td>113</td>
</tr>
<tr>
<td>III</td>
<td>Special Frequencies</td>
<td>117</td>
</tr>
<tr>
<td>IV</td>
<td>Thermodynamic Properties of Disordered Crystals</td>
<td>127</td>
</tr>
<tr>
<td>V</td>
<td>Energy Transport in Disordered Harmonic Crystals</td>
<td>137</td>
</tr>
<tr>
<td>VI</td>
<td>Summary</td>
<td>145</td>
</tr>
<tr>
<td></td>
<td>Bibliography</td>
<td>149</td>
</tr>
<tr>
<td></td>
<td>Appendix</td>
<td>156</td>
</tr>
<tr>
<td></td>
<td>Vita</td>
<td>162</td>
</tr>
</tbody>
</table>
LIST OF TABLES

Table | Page
---|---
I. Correspondence Between Spectral Lines and Island Structures in the Linear Chain | 81
II. Correspondence Between the Spectral Lines and Localized Structures in the Cubic Lattice | 104
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Enumeration of the Lattice Sites for the Square Lattice</td>
<td>37</td>
</tr>
<tr>
<td>2. Enumeration of the Lattice Sites for the Triangular Lattice</td>
<td>44</td>
</tr>
<tr>
<td>3. Enumeration of Nearest-neighbor Sites in the Simple Cubic Crystal</td>
<td>47</td>
</tr>
<tr>
<td>4. Calculated and Analytic Spectra of a Monatomic Linear Chain</td>
<td>60</td>
</tr>
<tr>
<td>5. Effect of Varying Concentrations on the Frequency Spectrum</td>
<td>61</td>
</tr>
<tr>
<td>6. Effect of Varying Mass Ratios</td>
<td>64</td>
</tr>
<tr>
<td>7. Effect of Varying Lengths of Chains</td>
<td>66</td>
</tr>
<tr>
<td>8. The Effect of Order</td>
<td>69</td>
</tr>
<tr>
<td>9. Frequency Spectrum of Two Monatomic Connected Chains</td>
<td>70</td>
</tr>
<tr>
<td>10. Frequency Spectra of Ternary Chains</td>
<td>71</td>
</tr>
<tr>
<td>11. Effects of Disordered Force Constants in Monatomic Chains</td>
<td>73</td>
</tr>
<tr>
<td>12. Frequency Spectra of Binary Chains with Realistic Force Constants</td>
<td>76</td>
</tr>
<tr>
<td>13. Frequency Spectra of Mixed Diatomic Chains</td>
<td>78</td>
</tr>
<tr>
<td>14. Identification of Frequency Peaks</td>
<td>80</td>
</tr>
<tr>
<td>15. Sample Eigenvectors for a Disordered Chain of 200 Atoms</td>
<td>82</td>
</tr>
<tr>
<td>16. Blocking of Amplitude by Heavy Impurities</td>
<td>84</td>
</tr>
<tr>
<td>17. Frequency Spectra of Chains with Continuous Masses and Force Constants</td>
<td>86</td>
</tr>
<tr>
<td>18. Frequency Spectra of Ordered Diatomic Chains with Continuous Random Force Constants</td>
<td>87</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>19. The Effect of Varying the Concentration in the Square Lattice</td>
<td>89</td>
</tr>
<tr>
<td>20. The Effect of Varying Mass Ratios on the Frequency Spectrum of the Square Lattice</td>
<td>91</td>
</tr>
<tr>
<td>21. The Effect of the Shape of the Square Lattice on the Frequency Spectrum</td>
<td>92</td>
</tr>
<tr>
<td>22. Comparison of Equal and Unequal Force Constants</td>
<td>93</td>
</tr>
<tr>
<td>23. Frequency Spectra of the Triangular Lattice</td>
<td>95</td>
</tr>
<tr>
<td>24. Typical Eigenvectors of the Isotopically Disordered Square Lattice</td>
<td>96</td>
</tr>
<tr>
<td>25. Frequency Spectra of the Simple Cubic Lattice with Varying FA</td>
<td>99</td>
</tr>
<tr>
<td>27. The Effect of Equal and Unequal Force Constants in the Simple Cubic Lattice</td>
<td>102</td>
</tr>
<tr>
<td>28. Identification of Modes in the Simple Cubic Lattice</td>
<td>105</td>
</tr>
<tr>
<td>29. Ordered Diatomic Cubic Lattice Spectrum</td>
<td>106</td>
</tr>
<tr>
<td>30. Mixed Diatomic Cubic Lattice Spectrum</td>
<td>106</td>
</tr>
<tr>
<td>31. Typical Eigenvectors of the Isotopically Disordered Simple Cubic Lattice</td>
<td>107</td>
</tr>
<tr>
<td>32. Resonance Modes in the Simple Cubic Lattice</td>
<td>110</td>
</tr>
<tr>
<td>33. Approximate Body-Centered Cubic Spectrum</td>
<td>111</td>
</tr>
<tr>
<td>34. Approximate Face-Centered Cubic Spectrum</td>
<td>111</td>
</tr>
<tr>
<td>35. Exact Frequency Spectrum of the Body-Centered Cubic Lattice</td>
<td>112</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>36</td>
<td>Frequencies of Isolated Islands in the Linear Chain</td>
</tr>
<tr>
<td>37</td>
<td>Frequencies of Isolated Islands in the Square Lattice</td>
</tr>
<tr>
<td>38</td>
<td>Thermodynamic Properties of the Square Lattice</td>
</tr>
<tr>
<td>39</td>
<td>Comparison of Specific Heats of the Ordered and Disordered Realistic Chains</td>
</tr>
<tr>
<td>40</td>
<td>Comparison of Specific Heats of the Simple Cubic Lattice with Varying Impurity Concentrations</td>
</tr>
<tr>
<td>41</td>
<td>Cooling Curves of the Linear Harmonic Chain</td>
</tr>
</tbody>
</table>
DYNAMICS OF DISORDERED HARMONIC LATTICES

An Abstract of a Dissertation
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Extensive numerical and analytic studies of vibrational spectra, normal modes, thermodynamic properties, and dynamical properties of harmonic systems with varying degrees of substitutional disorder have been made. The effects on observable properties of random mixtures of two or more species of atoms with differing masses and differing couplings to nearest- and next-nearest-neighbors have been investigated. Using the IBM-7030 digital computer, spectra for linear chains of 100,000 atoms have been obtained. Calculations in two and three dimensions have been limited to arrays of approximately 1000 atoms. Varying composition, mass ratio, and order affect the spectra in two and three dimensions in ways analogous to those effected in the linear chain. A physical interpretation of the complex nature of the disordered spectrum is given. The effects of disorder on the dynamics of binary disordered harmonic chains have been studied and have been found to be quite pronounced.
I. INTRODUCTION

1. Lattice Dynamics of Perfect Crystals

The foundations of the field of lattice dynamics were laid more than fifty years ago in the classic paper by Born and von Karman. However, much earlier, in Newton's "Principia," a description of a mechanical lattice model can be found which is the same as is widely used today. In his "Baltimore Lectures" Lord Kelvin described his researches into such advanced subjects as the vibrational properties of diatomic lattices. He had shown that the frequency spectrum was separated into two bands and that waves driven with a frequency not included in the bands are not propagated through the lattice and damp out in a distance which depends on the difference between the driven frequency and the band edges. In these lectures the qualitative description of lattice vibrations was begun. The Born-von Karman paper was to take these ideas and develop them into a theory.

Born and von Karman assumed the atoms were held in their equilibrium positions by harmonic restoring forces and wrote down the differential-difference equations which govern the motion of these atoms. They solved these equations for the simple cubic lattice in the limited sense that they were able to calculate the propagation velocity and dispersion of waves propagating in an arbitrary direction. Only in the considerably simpler linear chain were they able to solve for the spectral distribution of normal modes and, hence, calculate the specific heat as a function of temperature.
In the same year a paper by Debye\textsuperscript{3} appeared in which he proposed his now-famous approximation to the frequency spectrum of a three-dimensional lattice. As is well known, the Debye approximation is simpler and more direct than the Born-von Karman approach; and it was for this reason that the latter was eclipsed for nearly twenty-five years. The Debye approach, however, is less fundamental in that it ignores the atomic structure of the crystal while correlating the thermal and elastic properties; whereas the Born-von Karman method calculates both properties in terms of the elementary interatomic forces. Born appreciated the importance of this basic approach and continued to work with his collaborators developing lattice dynamics to include quantum effects and to deal with non-central forces. In 1954 Born and Huang\textsuperscript{4} published a comprehensive survey of the current methods of lattice dynamics which are refinements of the original approach of nearly fifty years earlier. Born pointed out at the Copenhagen Conference on Lattice Dynamics\textsuperscript{5} that his career as an author of scientific books began and ended with publications on the same subject.

Born and Huang set down certain principles which are necessary to approach the problem in a systematic manner. They can be summarized as follows:

(1) The many-body Schrödinger equation which governs the motion of the nuclei and electrons in the crystal is very complicated. If the adiabatic approximation is made, the problem is more tractable. This is a fundamental assumption of lattice dynamics and its validity is established by the famous paper by Born and Oppenheimer.\textsuperscript{6} The latter paper showed that the deviations from the adiabatic approximation could
be expressed in an expansion in powers of \((m/M)^{1/2}\) where \(m\) and \(M\) are the masses of the electron and the nucleus respectively. The motions of the electrons can be ignored if the adiabatic approximation is valid, and the effect of the electrons can be replaced by a suitable interaction potential between nuclei. This potential can be expanded in powers of the displacements of the nuclei from equilibrium

\[ \Phi = \Phi_0 + \Phi_1 + \Phi_2 + \Phi_3 + \cdots \]

where \(\Phi_r\) is of \(r^{th}\) order in the displacement. There is general agreement that the adiabatic approximation is valid for solidified inert gases, ionic crystals, and covalent crystals; for metals there is some controversy because of the nonlocalizability of the electrons.

(2) The harmonic approximation is made by terminating the expansion of the interaction potential after the term quadratic in the nuclear displacements from equilibrium.

(3) Then, when the equations of motion are written down, one has an eigenvalue equation of the form

\[ \det |A_{ij} - \omega^2 \delta_{ij}| = 0 \]

where \(\omega\) is the circular frequency and \(\delta_{ij}\) is the Kronecker delta. The solutions of this equation give the frequencies of normal modes of vibration of the crystal. The matrix \(A_{ij}\) is called the dynamical matrix and is of order \(sN\) where \(s\) is the number of dimensions and \(N\) is the
number of atoms. Since in a crystal there are sN frequencies, it is convenient to refer to the distribution of frequencies, or frequency spectrum (density of states), rather than the individual frequencies. There are two quantities used quite generally in representing the frequency spectrum. They are the following: $g(w)dw$ which is the fraction of frequencies in the interval $(w,w + dw)$ as $dw \to 0$ and $G(w^2)dw^2$ (which will also be denoted later $D(w^2)dw^2$ for computational reasons) which is the fraction of squared frequencies in the interval $(w^2,w^2 + dw^2)$. These are defined such that

$$g(w)dw = G(w^2)dw^2$$

and

$$\int_0^\infty g(w)dw = 1.$$ 

In the later thirties Blackman\textsuperscript{7} published several papers in which he pointed out the inadequacies of the Debye method. After twenty-five years the Born-von Karman approach was finally to be used. In his papers Blackman made the first use of the root sampling method of lattice-dynamical calculation. Since at that time any numerical method was very laborious, he chose a very simple model and used a coarse mesh for his calculations. Even this rough calculation clearly showed that
the true spectrum was much different from that obtained by the Debye method.

The root sampling method was tedious and only moderately accurate with the computing devices then available. It is not surprising that considerable effort was expended to find a substitute method which was accurate. None of these methods devised was completely satisfactory, and with the advent of high-speed computers numerical results have become quite easy to obtain by the root sampling method.

From the search for a substitute, two noteworthy methods appeared. Montroll\textsuperscript{8} developed a method originated by Thirring\textsuperscript{9} which made use of the even moments $\mu_{2r}$ of the spectrum

$$\mu_{2r} = \int_0^\infty v^{2r} g(v) dv$$

to calculate various observable quantities. This method has been used for many years although its accuracy is severely limited in the calculation of frequency spectra because of its slow convergence. A thorough exposition of the moment method as well as the root sampling method is contained in the review book by Maradudin, Montroll, and Weiss.\textsuperscript{10}

A highly ingenious method was invented by Leighton\textsuperscript{11} in the forties. By modeling successive frequency surfaces in plaster of Paris and weighing the results, he obtained frequency spectra for the face-centered cubic lattice with nearest and next-nearest neighbors. These
results were compared with the experimental results from solid argon (primarily the specific heat).

In 1947 Montroll\textsuperscript{12} indicated that there exist certain singular points in the frequency spectrum of the simple cubic lattice. A similar result was obtained by Bowers and Rosenstock\textsuperscript{13} for the transverse vibrations of a two-dimensional square lattice. In 1952 Smollett\textsuperscript{14} studied the in-plane vibrations of a two-dimensional lattice and found similar singularities. In his paper Smollett put forth topological arguments to explain these singular points. In 1953 Van Hove\textsuperscript{15} generalized Smollett's arguments and calculated the possible types of singularities that $g(\omega)$ might have in two- and three-dimensional lattices.

In more recent years, as previously mentioned, the root sampling method has become quite popular as a calculational tool. The moment method has been used recently as a means of directly calculating thermodynamic quantities without the necessity of first calculating the frequency spectrum. The thermodynamic properties of a lattice are rather insensitive to the specific form of the frequency spectrum; calculations using moments converge much more rapidly for thermodynamic quantities than for frequency spectra.

In the case of metals where there is some doubt about the validity of the adiabatic approximation because of the quasi-free electron behavior, a new method of calculation has been applied. This method, called the shell model, considers the electrons as a mass shell surrounding the nucleus and coupled to the nucleus, other nuclei, and other electron shells by springs. Inherent in this method is a large
number of parameters with which many real systems can be fit. This method was developed by Cochran.\textsuperscript{16}

Some very extensive calculations for metals have been made by Overton.\textsuperscript{17} He has used the root sampling method to calculate an accurate frequency spectrum for copper.

It can be seen that lattice dynamics of perfect crystals has progressed over the past fifty years to a highly polished art. The premise for the solution of such problems is the exact periodicity of the perfect crystal.

Very few substances, however, are pure; and when impurities are added, the essential simplification achieved by the periodicity is destroyed. Indeed, the problem of impurities is an interesting one and is the one which the author wishes to discuss.

2. Isolated Defects

Since crystals are never free of impurities, it is interesting to investigate the observable effects of impurities. The impurity problem materialized as a problem of great interest with the advent of the semiconductor.

The first serious work on the effects of defects on lattice vibrations was done in 1943 by Lifshitz\textsuperscript{18} in the Soviet Union. He invented a Green's function technique for isolated defects which was the framework for the basic method used quite widely today. At the time of publication Lifshitz's early work was published in what was at that time a relatively inaccessible language in a relatively inaccessible
journal. The journal was later translated into English in the Soviet Union.

Independently, in 1955 Montroll and his collaborators\textsuperscript{19} at the University of Maryland undertook a similar project with quite similar results. Montroll also used the Green's function-complex integration technique to calculate the effects of isolated defects on the frequency spectrum and various thermodynamic functions.

It was realized by the early investigators that if defects were present in the crystal a shift in the frequencies of the normal modes would occur. In particular, if the defect was the substitution of an atom which was lighter (heavier) than the host atoms, the eigenfrequencies of the normal modes would be shifted to higher (lower) frequencies by an amount of order $1/N$ where $N$ is the number of atoms in the crystal. In the case of a light atom in a heavier host it could be shown that one eigenfrequency, or normal mode, would be shifted above the maximum frequency of the host lattice by an amount greater than $O(1/N)$. Since this one mode is higher in frequency than the maximum frequency which can be propagated by the host lattice, this upper mode corresponds to a localized mode. These facts and the applicable development are due to Lord Rayleigh.\textsuperscript{20}

The formal solution of the defect problem has been displayed and discussed by Nardelli.\textsuperscript{21} In his review he develops the defect problem from a Green's function approach which is similar to that used by Montroll, et al., and Lifshitz, et al., except that the formulation is more formal and concise.
The defect problem in lattice dynamics received considerable impetus from the analogous problem of electrons in impure solids. The latter problem was often treated as the quantum mechanical problem of an array of potentials with one differing from the rest. Localization of the electron wave packet which is analogous to local modes in lattice vibrations was indicated by Lax. 22

A situation similar to the local mode due to a light defect is the resonant mode. 23 This mode occurs when a heavy impurity is substituted into a relatively lighter host lattice. This mode, however, occurs only in two- and three-dimensional lattices and has only recently been verified experimentally. 24 It is very difficult to observe since it is an in-band resonance. Due to the fact that all eigenvector calculations previously published have been in one dimension only, there have been no calculational verifications of the resonant modes.

3. Disordered Systems

The solution of the isolated defect problem was limited in its usefulness for all but the lowest concentrations of impurities. In fact, in nature the defects or impurities are not really isolated but are distributed randomly throughout the crystal lattice. This poses new problems since the lattice is no longer subject to the strict symmetries of the Bravais net.

Dyson 25 in 1953 was the first to attack the problem of lattice vibrations in disordered systems. He considered a one-dimensional disordered chain and derived an expression for the frequency spectrum.
This expression was given in terms of the solution of a linear, homogeneous integral equation. He presented a solution of this equation in closed form only for a simple but physically unrealistic model of a chain in which the masses and force constants take on any positive value 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 all of the force constants equal (isotopic disorder) the subsidiary integral equation reduces to a functional equation. This functional equation has more recently been rederived somewhat more directly by Dean and Martin. \(^{26}\) Dyson, however, did not attempt to solve the equation he derived and seemed to underestimate the difficulty of a numerical solution. Dyson's technique, moreover, cannot be generalized to higher dimensions.

Dyson's paper provoked much interest in the disorder problem and was followed by many papers alleging to generalize Dyson's technique. However, these were basically different in that Dyson's method was exact while these were in reality perturbation treatments. One of the more complete of these treatments was done by Maradudin, Mazur, Montroll, and Weiss. \(^{27}\)

A true generalization of the basic technique of Dyson was accomplished by Englman \(^{28}\) in a very abstract treatment of the theory of random matrices. This very pretty treatment has the singular restriction, as did Dyson's method, that the integral equations obtained do not appear amenable to numerical solution.

Other than the Dyson solution there is but one special case of a disordered system which can be solved analytically. That is the case
of the isotopically disordered chain in which one of the components is
of infinite mass. This solution was given by Domb, Maradudin, Montroll,
and Weiss\(^{29}\) in 1959. The spectrum obtained is a very special one given
by a series of delta-functions of varying strengths located at the
normal mode frequencies of the finite light atom chains formed by the
barriers imposed by the infinite masses.

These two solutions -- the one by Dyson and infinite mass ratio
solution -- are the only two analytic exact spectra which have been
obtained for the disordered chain. No work has been done analytically
in higher dimensions. Although simplifications of Dyson's technique
for one dimension -- such as the ones by Bellman\(^{30}\) and Dean and
Martin\(^{26}\) -- exist, the equations have not yet been solved.

Three years after Dyson's paper appeared, Schmidt\(^{31}\) obtained a
solution somewhat similar to Dyson's by the application of the method
of transfer matrices. In this method the equations of motion are
written as \(2 \times 2\) matrix equations. Thus

\[
\begin{pmatrix}
u_i \\ u_{i+1}
\end{pmatrix} =
\begin{pmatrix}
0 & 1 \\ -1 & 2 - \frac{m_i \omega^2}{\gamma}
\end{pmatrix}
\begin{pmatrix}
u_{i-1} \\ u_i
\end{pmatrix}
\quad i = 1, 2, \ldots, N, \quad (I.3.1)
\]

is the equation of motion for the \(i^{th}\) atom in the chain where \(u_i\) is the
displacement from equilibrium of the \(i^{th}\) atom, \(m_i\) is the mass of that
atom, \(\gamma\) is the uniform force constant, and \(\omega\) is the frequency. From the
application of this technique Schmidt obtains a functional equation
which must be solved numerically. This again presented a problem, but
recently Agacy has managed to solve Schmidt's equation numerically to obtain a frequency spectrum.

The method of transfer matrices was applied, independently of Schmidt, by Hori and Asahi and Hori. In this work the equations are slightly different in form from those of Schmidt, but the essential point is that the line of reasoning is quite similar and is as follows:

\[ U_{d+1} = T_d U_d \quad i = 1, 2, \ldots, N \quad (I.3.2) \]

where the \( U_d \) are the two component vectors as above and the \( T_d \) are the \( 2 \times 2 \) matrices called the transfer matrices. This set of equations can be condensed into the single relation

\[ U_N = T_{N-1} T_{N-2} \cdots T_1 U_1 , \quad (I.3.3) \]

and after imposing a cyclic boundary condition, one is lead to the following eigenvalue relation:

\[ \text{Trace } H = 2 \quad (I.3.4) \]

where

\[ H = T_{N-1} T_{N-2} \cdots T_1 . \quad (I.3.5) \]

Attempts were made to obtain the spectrum for the disordered chain, but
great care must be taken when averaging over an ensemble, and there seems to be no justification in regarding the equation

\[ \langle \text{Trace } \mathbb{H} \rangle = 2 , \quad (I.3.6) \]

where the brackets represent an arithmetic mean over the chains of the ensemble, as a relation which leads to the correct average frequency distribution. Equation (I.3.6) leads to the result that the frequency spectrum is that of a monatomic lattice with a mass equal to the mean mass. This result is a valid approximation at low frequencies but is completely wrong at higher frequencies. It can be shown that the correct equation should be one including a geometrical mean,

\[ \langle \text{Trace } \mathbb{H} - 2 \rangle_{G} = 0 \quad (I.3.7) \]

where \( G \) indicates a geometrical mean.

Lifshitz and Stepanova\textsuperscript{35} presented a formal method for calculating the frequency spectrum and the Helmholtz free energy of a random lattice. Their approach uses the linear operator theory developed earlier by Lifshitz\textsuperscript{18} and is based on an expansion in powers of the concentration of one type of atoms in a host lattice of another type. This method is applicable to higher dimensions, but the calculations have never been made. Also, the accuracy of the method is limited because of the perturbation technique employed. Langer\textsuperscript{36} more recently has used field theoretical techniques to calculate the frequency spectrum; however, again, the solutions obtained are valid only for low
concentrations of one of the species due to the perturbation expansion. Recently, Lifshitz\textsuperscript{37} has derived the shapes of the spectra of disordered lattices near the band edges.

Another technique which has had much use in the past few years is the moment trace method. This method is discussed thoroughly in the review by Maradudin, Montroll, and Weiss.\textsuperscript{10} A detailed study of the frequency spectrum of the one-dimensional chain was reported by Domb, Maradudin, Montroll, and Weiss.\textsuperscript{29} Domb, et al.,\textsuperscript{38} and Bradley\textsuperscript{39} have calculated the moments for three-dimensional lattices. The moment trace technique fails to provide an accurate picture of the frequency spectra of disordered lattices due to the slowness of convergence of the moments. The calculation of thermodynamic quantities, however, seems to be enhanced by the moment trace technique, since this calculation is relatively insensitive to the fine structure of the frequency spectrum.

The moment trace technique is based on the theorem that

\[ \mu_i = \text{Trace} \left( \lambda^{i} \right) \]  \hspace{1cm} (I.3.8)

where \( \mu_i \) is the \( i^{\text{th}} \) moment of the eigenvalue distribution of the matrix \( \Lambda \). Thus in the physical problem

\[ \mu_{2i} = \int G(w^2) w^{2i} dw^2 \]  \hspace{1cm} (I.3.9)

as we had earlier. Using the methods of Domb, et al.,\textsuperscript{29} to find the
moments, the expression (I.3.9) could then be inverted to find the
temperature distribution. The spectra calculated in this manner were
found to be smooth in character with a few rounded maxima and minima.
In the cases of high mass ratio and low concentrations of light atoms
in a heavier host lattice, distinct impurity bands were found at fre-
cquencies higher than the maximum frequency of the host lattice. They
concluded that the two bands observed were caused by different circum-
cstances. The lower band was attributed to local modes of single light
atoms in the host lattice, and the upper band was attributed to re-
placements of heavy atoms by light atoms in ordered arrangements
(IHIIH • • •) in the chain. The basic idea in the explanation of these
bands is correct to a certain extent. It is, however, true that there
are many more than two bands as will be shown later. The moment trace
method cannot, however, give enough detail about the spectrum to show
its fine structure as has been done recently.

Dean 40 has calculated the spectra of disordered binary systems
using a direct numerical technique based on the properties of Sturm
sequences. The mathematics of the method and the use of the Sturm se-
quence was discussed by Givens 41 in his work on the characteristic
values of symmetric matrices. Dean's method will be discussed in great
detail later, since it is the method used in the present author's calcu-
lations.

The results obtained by Dean and his collaborators have shown that
the spectra of isotopically disordered chains are quite irregular and
show a great deal of fine structure at higher frequencies. It was shown
later 42 that those peaks which occur correspond to the frequencies of
local modes due to light defect islands in the heavy host lattice. Dean included nearest neighbors only in one-dimensional systems, and later, Martin\textsuperscript{43} extended Dean's results to next-nearest-neighbor interactions. In doing this Martin found a general depression of the peaks in the spectrum to lower values of the frequency as the relative strength of the second-nearest-neighbor interaction was increased. The general features of the spectrum remain unchanged. The most interesting point in Dean's method is its ability to be extended to higher dimensions. The basic technique has been extended to two dimensions by Dean and Bacon\textsuperscript{44} and Dean and Martin,\textsuperscript{45} and calculations of the frequency spectrum of the disordered square and honeycomb lattices have been made by Dean and Bacon.\textsuperscript{44} The extension of this same technique to three dimensions including the simple cubic, body-centered cubic, and face-centered cubic has been made by Payton and Visscher.\textsuperscript{46}

In showing that the higher frequency peaks corresponded to the local modes of light defect islands, Dean and Bacon\textsuperscript{47} calculated the eigenvectors for isotopically disordered chains of 50 atoms. A similar study had been carried out somewhat earlier by Rosenstock and McGill\textsuperscript{48} on a chain of 16 atoms using a modification of the transfer matrix method. Both of these calculations showed the existence of localized modes in disordered chains. The author has shown the existence of similar localized modes in two and three dimensions using a direct diagonalization procedure.

Borland\textsuperscript{49} has derived an exact formula for the integrated spectrum (the fraction of frequencies less than $w^2$) of the disordered diatomic chain at a discrete set of points. For the isotopic chain of mass
ratio $\geq 2:1$ he finds

$$M(j^2) = \frac{(1 - \tau^J)}{(1 - \tau^{J+1})} \quad (I.3.10)$$

where $J$ is any positive integer, $w_j^2$ is the squared frequency at a special point

$$w_j^2 = \frac{1}{2} w_L^2 \left(1 + \cos \frac{\pi}{J + 1}\right) \quad (I.3.11)$$

where $w_L$ is the maximum frequency of the lattice, and $\tau$ is the concentration of light atoms. The points defined in the latter equation correspond to minima in the derived spectrum of Dean and also correspond to the so-called "special," or forbidden, frequencies of Matsuda.\textsuperscript{50} The numerical values of the integrated spectrum agree with those values calculated by Dean. Agacy\textsuperscript{32} in his numerical solution of Schmidt's functional equations obtained a derived spectrum which agrees closely with Dean's work and an integrated spectrum which has values in close agreement with those of Borland at his special points. A more thorough discussion of the special frequencies will be given later.
II. FREQUENCY SPECTRA

1. The Method of Negative-Factor-Counting

Since the original paper by Dyson on disordered systems appeared, several different versions and generalizations have been published as has been discussed earlier. Many of these methods can be categorized quite generally into a broad classification which may be described as the method of negative-factor-counting. This general classification includes the varied, but basically similar, approaches of Dyson,\(^{25}\) Dean,\(^{40}\) Bellman,\(^{30}\) Schmidt,\(^{31}\) Englman,\(^{28}\) and des Cloizeaux.\(^{51}\) It is probably most succinct to regard these theories as based upon the connection between the density of the eigenfrequency distribution and the number of negative factors in a product representation of the secular determinant.

There are two approaches that the author would like to discuss. The two are basically the same in principle utilizing the method of negative-factor-counting but demonstrating separately the physical problem and the calculational procedure the author has employed.

First, let us set up the equations of motion for a one-dimensional system, and they will be generalized later to higher dimensions. Consider a chain of \(N\) masses each of which is coupled to its nearest neighbors by elastic springs obeying Hooke's law. The equations of motion are the well known linear finite difference equations

\[
m_i \ddot{x}_i = \gamma_i (x_{i+1} - x_i) + \gamma_{i-1} (x_{i-1} - x_i) \quad (i = 1, 2, \cdots, N) \quad (\text{II.1.1})
\]
where $m_i$ is the mass at the $i^{th}$ position (displaced $x_i$ from its equilibrium position), and $\gamma_i$ is the force constant of the spring joining the $i$ and $(i+1)^{th}$ masses. The time is separable, $x_i = -\omega^2 x_i$, where $\omega$ is the frequency; and the equations (II.1.1) reduce to the form

$$\left(2 - \frac{m_i \omega^2}{\gamma}\right)x_i = x_{i+1} + x_{i-1} \quad \text{(II.1.2)}$$

where we have taken the isotopic case in which the force constants are all equal, $\gamma_i = \gamma = \gamma$. If we write

$$Z_i = \frac{x_{i-1}}{x_i} \quad \text{(II.1.3)}$$

we have

$$Z_{i+1} = \frac{1}{\left(2 - \frac{m_i \omega^2}{\gamma} - Z_i\right)} \quad \text{(II.1.4)}$$

where $Z_i$ is the ratio of the successive displacements $x_{i-1}$ and $x_i$.

We shall now use a theorem attributable to Rosenstock and McGill which relates the number of eigenvalues less than a particular frequency to the number of nodes in the vector generated by successive application of Equation (II.1.2) using that frequency (hence the number of sign changes or negative $Z_i$'s). If we have $N$ particles in our system, we know there will exist $N$ eigenvalues; and we can label these eigenvalues
\( \lambda^{(k)}, k = 1, 2, \cdots, N; \) and we will order them such that \( \lambda^{(t)} \leq \lambda^{(m)} \) if \( t < m \). We then define the normal mode, or eigenvector, as the function of position which is obtained if one plots the displacement amplitude \( x_i \) of the \( i \)th atom in a one-dimensional chain versus \( i \) and then connects adjacent points by straight lines. Rosenstock and McGill showed that the normal mode corresponding to \( \lambda^{(k)} \) has precisely \( k - 1 \) nodes. That is exactly one normal mode with no zeros (except for \( i = 0 \) and \( i = N + 1 \) if we impose fixed boundary conditions), one mode with one zero, one mode with two zeros, \( \cdots \), and one mode with \( n - 1 \) zeros; hence the larger the number of zeros the higher the frequency of the mode. Thus if an eigenfrequency is known, one can find how many eigenfrequencies exist which are less than the known one by counting the nodes of the eigenvector corresponding to the known eigenfrequency.

If we now define the integrated frequency spectrum, \( M(w'^2) \), to be the number of eigenvalues of \( w^2 \) less than \( w'^2 \) per unit mass, it can be seen that \( M(w'^2) \) is just the fraction of negative \( Z \)'s obtained by successive applications of (II.1.4). One knows \( Z_1 = 0 \) (if we have fixed boundaries, \( x_0 = 0 \)), and \( Z_2 \) may be chosen arbitrarily. Doing this, one can generate a set of \( N \) \( Z \)'s and find the value of the integrated spectrum at any point. It is well known\(^5\) that this procedure is accurate and converges for any \( w'^2 \) which is an eigenvalue of the system. This procedure can be employed even at points where \( w'^2 \) is not an eigenvalue, since the sign is preserved even though the sizes of the \( Z \)'s become very large. The divergence of the \( Z \)'s can be renormalized, if desired, as long as the signs are preserved. This is a very simple method of computing the integrated spectrum. By a simple numerical
differentiation the derived spectrum, \( G(w^2) \), can be obtained.

However, a method was employed by the author in his calculations which is somewhat more desirable from the calculational standpoint. This method is due to Dean^40 and is an application of a Sturm sequence technique discussed by Givens^41 earlier. By introducing new variables, \( y_i = \frac{m_i}{k} x_i \), the equations (II.1.1) may be reduced to

\[
\beta_i y_{i-1} + (\alpha_i - w^2) y_i + \beta_{i+1} y_{i+1} = 0
\]  

(II.1.5)

where

\[
\begin{align*}
\alpha_i &= (\gamma_i + \gamma_{i-1})/m_i \\
\beta_i &= -\gamma_{i-1}/(m_{i-1} m_i)^{1/2}
\end{align*}
\]  

(II.1.6)

with the fixed boundary conditions

\[
\beta_1 = \beta_{N+1} = 0 .
\]  

(II.1.7)

This set of equations has solutions only if the determinant of the coefficients (the secular determinant or the determinant of the dynamical matrix) is zero, or

\[
\det (A_{ij} - I_{ij} w^2) = 0
\]  

(II.1.8)
where

\[
\begin{align*}
A_{ii} &= \alpha_i \\
A_{ii+1} &= A_{i+1} = \beta_{i+1} \\
\text{all other } A_{ij} &= 0
\end{align*}
\]

(II.1.9)

and \( I \) is the unit matrix.

It is not necessary to consider the effect of the imposition of the fixed boundary conditions on the frequency spectrum since we are going to consider a chain with \( N \) large. From a theorem by Lederman\(^{53}\) we know the effect of the boundary conditions on any system such as this is of \( O(N'/N) \) where \( N \) is the total number of atoms in the system and \( N' \) is the number of atoms restricted by the boundary conditions. In the linear chain the effect is of \( O(2/N) \) which is negligible in the case of large \( N \). The method which will follow will strictly give only the spectral distribution for the mean over a statistical ensemble of chains. However, it is a well known result of statistical mechanics\(^{54}\) that this is the correct spectrum of any individual chain as \( N \) approaches infinity.

Consider the polynomials of the sequence \( g_0(v) \equiv 1, g_1(v), g_2(v), \ldots, g_N(v) \), where \( v = \omega^2 \) and
An expansion of this determinant about the elements of the last row (or column) yields the relation

\[ g_1(v) = (\alpha_1 - v)g_{i-1}(v) - \beta_i^2 g_{i-2}(v) \quad (i = 2, 3, \ldots, N) \]  

(II.1.11)

The sequence of functions \( g_0(v), g_1(v), g_2(v), \ldots, g_N(v) \) can be seen to satisfy the conditions for which Sturm's theorem is valid. This theorem can be stated as follows:

**Theorem:** If \( a \) and \( b \) are any real numbers such that \( b > a \), then the number of roots of the equation \( g_N(v) = 0 \) which lie in the interval \( a \leq v < b \) is equal to \( \nu(b) - \nu(a) \) where
The number of variations of sign between consecutive members of the sequence $g_0(\xi), g_1(\xi), g_2(\xi), \ldots, g_N(\xi)$.

Ambiguities arising from a possible zero in the sequence can be overcome by assigning arbitrarily the sign of the preceding member of the sequence to it.

Applying this theorem to the spectrum of roots of (II.1.8), or $g_N(v) = 0$, the spectrum of eigenvalues of the dynamical matrix can be obtained. The unnormalized integrated spectrum, $M(v)$, is just $v(v) - v(-\infty)$, or

$$M(v) = v(v) \quad (II.1.12)$$

the total number of sign changes in the sequence.

If we look at the solution of the problem in more detail, we can see how to obtain the results achieved by Dyson. Equation (II.1.11) can be written in the form

$$h_i(v') = (\alpha_i - v') - \beta_i^2/h_{i-1}(v') \quad (i = 2, 3, \ldots, N) \quad (II.1.13)$$

where

$$h_i(v') = g_i(v')/g_{i-1}(v') \quad (II.1.14)$$

and $v'$ is chosen such that $g_{i-1}(v') \neq 0$. This choice poses no restriction in later work, for if $v$ is chosen such that $g_{i-1}(v) = 0$, $v$ can be
incremented by a small amount $\epsilon$, and then the limit as $\epsilon \to 0$ can be taken. This is indeed the calculational procedure.

If the probability distribution function of $h_1(v')$ is $H(h_1)$, then neglecting the influence of the ends of the chain, the a priori probability distribution of any other $h_i(v')$, in particular $h_{i-1}(v')$, is given by $H(h)$. It is at this point that the ensemble average is introduced.

From (II.1.11) and (II.1.14) it can be seen that the $h_{i-1}$ and $(\alpha_i, \beta_i)$ are uncorrelated. On equating the probabilities of both sides of (II.1.13), the following equation is obtained for $H(h)$:

$$H(h) = \sum_i P(\alpha_i, \beta_i) \frac{\beta_i^2}{(\alpha_i - v' - h)^2} H\left(\frac{\beta_i^2}{\alpha_i - v' - h}\right)$$

(II.1.15)

where the $P(\alpha_i, \beta_i)$ denotes the probability of a given value for the pair $(\alpha_i, \beta_i)$ and is dependent on the ordering of the system. The summation extends over all possible pairs of $(\alpha_i, \beta_i)$. For a liquid $P(\alpha, \beta)$ becomes a continuous probability distribution.

Sturm's theorem shows that the fraction of negative terms in the sequence $h_1(v'), h_2(v'), \ldots, h_N(v')$ is equal to the fraction of eigenfrequencies less than $v'$; furthermore, since we take all of the $h_i(v')$ to be described by the same probability function for the case of large $N$, this fraction is just the probability of the $h_1(v')$ being negative, or
\[ M(v') = \int_{-\infty}^{0} H(h) \, dh. \]  

(II.1.16)

The argument for a general value of \( v \) other than \( v' \) can be made quite rigorous and has been done by Dean.\(^4\) The author has followed Dean's exposition of the Sturm sequence method quite closely for it explores the simplicity which is inherent in this technique.

It is interesting to compare (II.1.15) obtained by the Sturm sequence method with the rigorous equation derived by Dyson. With the proper identifications the equations are identical.

Consider the generalization of the method to higher dimensions than the linear chain. In the case of two and three dimensions the dynamical matrix is a tridiagonal block matrix of the following form:

\[
\mathbf{S} = \begin{pmatrix}
A_1 & B_2 & 0 \\
B_2^T & A_2 & B_3 \\
0 & B_{N}^T & A_N
\end{pmatrix}.
\]  

(II.1.17)

The partitioning is the same for rows and columns; \( A_j \) is a square
symmetric matrix of order (say) $t_j$; and $B_j$ is of order $(t_{j-1} \times t_j)$ with $B_j^T$ the transpose of $B_j$. All other elements of $S$ are zero. We wish to find the spectrum of eigenvalues of matrices like $S$. In the two-dimensional case the matrices $A_j$ and $B_j$ are simple matrices; while in three dimensions $A_j$ and $B_j$ are composed of block matrices themselves. This will be described in more detail later.

Dean's technique is based on the negative eigenvalue theorem which is an extension of the Sturm sequence theorem used previously. A short proof of the negative eigenvalue theorem can be found in the paper by Dean and Bacon on page 81. If we use the symbol $\eta()$ operating on a matrix to denote the number of negative eigenvalues of that matrix, the negative eigenvalue theorem states that

$$\eta(S - w^2 I) = \sum_{i=1}^{m} \eta(U_i)$$  \hspace{1cm} (II.1.18)

where

$$U_i = A_i - w^2 I - B_i^T U_{i-1} B_i \quad (i = 2,3,\ldots,m)$$  \hspace{1cm} (II.1.19)

and $I$ is the unit matrix of proper order. For a given value of $w^2$ it can be shown that the number of eigenfrequencies less than $w^2$ is just the fraction of the eigenvalues of the dynamical matrix which are negative. A simplification of this method for calculational procedures can be made and will be given later. A more detailed description of the
negative eigenvalue method for two dimensions can be found in the paper by Dean and Martin\textsuperscript{45} and the review by Hori.\textsuperscript{56}

2. Review of Dean's Work

It is necessary to review the work done by Dean and his colleagues in more detail since these works are quite similar to some of the author's early results which will be discussed later. Using the calculational procedure of the Sturm sequence method, Dean has obtained frequency spectra for binary, isotopically disordered chains. He then extended this to glass-like chains in which the force constants vary according to some probability distribution simulating the random spatial order of a glass. Dean and Bacon\textsuperscript{44} have published the results of some rudimentary calculations of the square lattice and the honeycomb lattice. These calculations were limited in scope because of the size and speed of their computing facilities. In this section we shall look at the results obtained by Dean and his associates a bit closer.

In a series of papers\textsuperscript{40} Dean investigated the effects of various situations arising in isotopically disordered chains. He studied the statistical properties of the chains that he used in his later calculations. He found that, due to the finite length of his chains the exact fraction of light atoms was not predictable. His method of generating the random chains was essentially the same as that used by the author. Each element is given an \textit{a priori} probability of being one of two types of atoms, and a random number is used to determine which will be at that site. This probability can be more than just the
desired concentration of one of the atoms if one wishes to impose long- or short-range order on the system. Dean investigated the effects of the Monte Carlo method of chain generation for chains of lengths varying from 1000 atoms to 32,000 atoms. He calculated the spectra of these chains and the spectra of the same chains with the order of the masses inverted to obtain a "mean" frequency spectrum. This "mean" spectrum was, of course, always for a chain of half light atoms and half heavy atoms. It was clear from Dean's earliest published results that the moment trace technique was wholly inadequate for determining the frequency spectrum, since it could not yield the irregular spectrum he found.

In subsequent papers Dean calculated the spectrum of disordered chains with varying concentrations of light atoms in a heavy host chain. He did this for varying concentrations in chains of 8000 atoms with mass ratios of 2:1 and 3:1. With the sets of figures given in his papers Dean shows how the frequency spectrum changes with the concentration of one type of atom. In the monatomic heavy atom chain the characteristic spectrum of the perfect linear chain is seen to be of the U-shaped form described previously. As light atoms are added randomly, the upper peak of $G(w^2)$ decreases in size, and new peaks appear at frequencies higher than the maximum of the heavy atom chain. As the concentration of light atoms is increased, more peaks appear until the chain is purely light atoms; and the frequency spectrum becomes the U-shaped spectrum of the monatomic light atom chain.

The explanation of these peaks which appear at low concentrations of the light atoms in a heavy atom host lattice was the subject of much
of the discussion in the latter two of this series of Dean's papers. Generally speaking, his interpretation of the peaks as being the frequencies due to modes localized near certain light islands of impurities in the heavy lattice was a correct one. It will be shown later by the present author that the interpretation of these peaks and the subject of special frequencies are intimately related.

Dean's work which has just been described used only the nearest neighbor interactions in the chain. Martin\textsuperscript{43} generalized Dean's work to the case of next-nearest neighbor interactions in the linear chain. In this case the dynamical matrix is of band-diagonal form with the principal diagonal and first two off-diagonals on either side non-zero, and all of the rest of the matrix elements zero. The sequence of determinants for this case can be treated in a manner similar to that of (II.1.11). All of the Sturm sequence techniques apply to this case, and the frequency spectrum is easily calculated. Martin investigates the consequences of changing the strength of the next-nearest-neighbor force constants while keeping the nearest-neighbor constants fixed. In doing this he finds that the inclusion of longer range interactions does not tend to smooth the peaked structure; in fact, the peaks are narrowed and heightened. Also there is a general shift in normal mode frequencies toward lower values of the frequency as the strength of the next-nearest-neighbor interaction is increased. The individual peaks of the frequency spectrum retain their identities through this shift. In the last paragraphs of his paper Martin discusses the possibility of constructing an approximate spectrum by simply knowing the structure of the chain. This is certainly possible in some cases as will be seen later.
After considering isotopically disordered chains, Dean\textsuperscript{57} studied the effects of varying the force constants in the linear chain while fixing the masses in either a simple monatomic chain or a perfect diatomic chain (ABABAB \cdots). This corresponds to the physical situation of spatial disorder as in a glass. The one-dimensional approximation is not realistic but reveals some effects which seem to be consequences of the disorder and not the dimensionality. The case of the monatomic chain with the force constants varying randomly and continuously is analogous to the problem of electrons in a random array of identical potentials. This problem has been treated by Borland.\textsuperscript{58} He found localization of the electron, and by analogy it can be shown that there will be localized modes in the frequency spectrum. This means there will be modes present with frequencies greater than the maximum frequency of the isotopic chain with the mean force constant. This is indeed the case. A similar situation exists for the ordered diatomic chain with force constants varying randomly and continuously. Dean also calculated the eigenvectors of several such systems and found the modes to be localized although not to the extent of the localization of the modes in the isotopically disordered binary chain.

Recently, Dean and Bacon\textsuperscript{44} have extended the calculational procedure outlined by Dean and Martin\textsuperscript{45} to the two-dimensional square and honeycomb lattices. The first of these lattices is easier to calculate in that by using a central-non-central force model the x- and y-motions are separable and degenerate. This cuts the number of variables per atom in half and allows one to calculate a lattice with double the number of atoms in the same machine time. The spectra obtained were
somewhat crude because of the coarse calculational mesh employed; how-
ever comparison with the shape of the analytic solution of the mono-
tomic square lattice\textsuperscript{12} shows that the spectrum is basically correct.
Again the spectrum changes from that of a perfect heavy atom lattice to
that of a perfect light atom lattice as the concentration increases.
This change occurs in a somewhat continuous fashion with high frequency
peaks appearing at low concentrations of the light atoms. The same is
true of the honeycomb lattice to a limited extent. The model chosen by
Dean and Bacon gives singularities at zero frequency and the maximum
frequency for the pure lattice spectrum, and the spectrum appears to
have little relation to the analytic solution of the monatomic honey-
comb lattice. One of the primary causes for this is the coarseness of
the calculational mesh which does not show the exact behavior of the
frequency spectrum near the singularities of the analytically deter-
ned monatomic spectrum. The boundary conditions which are imposed
are responsible for some small fluctuations due to periodicity. The
boundary conditions are the same as those used by the author and will
be discussed in a later section.

Dean\textsuperscript{59} has carried out calculations on linear systems of the
mixed-diatomic type (ABABCABCBABCB ... ) where there exists an ordered
host lattice with impurities of a third type. This lattice has great
promise in three dimensions since the compounds of the NaCl structure\textsuperscript{60}
have an interpenetrating face-centered cubic structure which can be
calculated for nearest-neighbor interactions by using a mixed diatomic
mass distribution on a simple cubic lattice. Dean's work has been in
one dimension, and the spectra have not yet been published. The author
has calculated this type of frequency spectra in the linear chain and in three dimensions. The results of these calculations will be discussed later.

3. Calculational Procedures

The numerical calculations made by the author have been performed at Los Alamos Scientific Laboratory (LASL) on the Laboratory's IBM 7030 digital computer. This computer was until recently the world's fastest computer and possesses a storage capacity of approximately 90,000 words of memory in the fast access core storage. In addition, disc and tape storage was available. The output from the computer was recorded on paper and on microfilm by an SC 4020 plotter. It was through the use of this plotter and the subroutines available at LASL that most of the figures in this thesis which reflect calculational output were plotted. The programs were written by the author in Fortran IV and, generally, were restricted to a running time of less than ten minutes.

In the present section the author will set forth the procedures used in the calculation of the frequency spectra in one, two, and three dimensions while displaying the models used and the approximations made. The remainder of this section will be devoted to the explanation of the various lattices studied by the author in his calculations and the techniques employed.

The equations of motion for a random isotopic chain with nearest-neighbor interactions in the harmonic approximation have been given, (II.1.5) and (II.1.6). It can be seen, as was previously displayed,
that the secular determinant, $|\mathbf{\tilde{G}}| = |A - \nu \mathbf{I}|$ (where $A$ is the dynamical matrix and $\nu = \omega^2$), is of tridiagonal form. Using the procedures outlined for this case earlier, the value of the integrated spectrum can be obtained at a finite mesh of points. This is done by counting the number of sign changes in the generated sequence $\tilde{g}_0, \tilde{g}_1, \tilde{g}_2, \ldots, \tilde{g}_N$ of (II.1.11) for each value of $\nu$ on the mesh. The number of sign changes when normalized gives the fraction of squared frequencies less than the squared frequency of the mesh point. When these values of the integrated spectrum are plotted as ordinates on a graph with the values of the squared frequency at the mesh points as the abscissae, the resulting curve is the integrated frequency spectrum and increases monotonically as a function of $\nu$ from zero to one. The derivative of the integrated frequency spectrum, $M(\nu)$, is the density of states or derived spectrum, $G(\nu)$, or

$$G(\nu) = \frac{dM(\nu)}{d\nu}. \quad (II.3.1)$$

This derivative was taken numerically on the computer, and the density of states was plotted versus the frequency squared.

The mass distributions for the random isotopic chains were generated by a Monte Carlo method employing a local order parameter. The random process was supplied by a random-number-generator routine. In the one-dimensional problem it was not necessary to store the actual chain, and calculations of very long chains were therefore possible. As an example of calculation time, the frequency spectrum for a chain of 100,000 atoms could be calculated at 100 mesh points in slightly more
than ten minutes.

In the process of interpreting the spectra of the linear chains, it became obvious that it was desirable to know the eigenvectors of some of the higher eigenfrequencies in the disordered chain to determine whether these modes were, in reality, localized. Several methods of direct diagonalization of the dynamical matrix were employed with the most general of these being an adaptation of the Givens-Householder technique of Ortega. In this technique a general symmetric matrix is reduced to tridiagonal, or Jacobian, form by a similarity transformation with an orthogonal matrix. In the usual process the orthogonal matrix is obtained as a product of a number of simple orthogonal matrices known as plane rotations. However, Householder and Bauer demonstrated an alternative method of reduction to Jacobi form in which the orthogonal matrix is obtained as a product of simple orthogonal matrices which are not plane rotations. This method of Householder coupled with the Givens method of finding the eigenvalues of tridiagonal matrices has not attracted the attention it probably deserves. It is extremely fast and accurate with the added advantage that it is easy to code.

The one-dimensional eigenvector problem did not require the use of the Householder reduction of the matrix to Jacobi form. Because of this fact long chains could be solved exactly to investigate the normal modes. The typical running time for a chain of 200 atoms was about 0.5 seconds per eigenvector. The eigenvectors were then plotted on microfilm such that the displacement amplitude, $x_i$, of the $i^{th}$ atom was plotted versus $i$, the atom position. The points plotted in this manner
were then connected.

In the square lattice we consider an array as shown in Figure 1. Using the model of Montroll and Potts in which motions in $x$ and $y$ are separated, $\gamma_{ij}$ is the central force constant between the $i$ and $j$th atoms, and $\gamma'_{ij}$ is the non-central force constant between the atoms. Letting $m_i$ be the mass at the $i$th site and $x_i$ be the displacement from equilibrium of the $i$th mass, the equation of motion in the $x$-direction for a non-boundary atom is

$$m_i \ddot{x}_i = \gamma'_{ii+1}(x_{i+1} - x_i) + \gamma'_{ii-1}(x_{i-1} - x_i)$$

$$+ \gamma_{ii+n}(x_{i+n} - x_i) + \gamma_{ii-n}(x_{i-n} - x_i)$$  (II.3.2)

where we have assumed nearest-neighbor interactions only. The numbering scheme is apparent from Figure 1. In the harmonic approximation, the set of equations (II.3.2) for all atoms reduce to the linear algebraic set

$$[M - \omega^2]u = 0.$$  (II.3.3)

The matrix $M$ is the dynamical matrix of the square lattice and has the proper block tridiagonal form.
Figure 1. Enumeration of the Lattice Sites for the Square Lattice.
where $\mathbf{B}_{\mathbf{A}^T}$ is the transpose of $\mathbf{B}_{\mathbf{A}}$ and where the submatrix $\mathbf{A}_{\mathbf{d}}$ is of Jacobian form:

\[
\mathbf{A}_{\mathbf{d}} = \begin{bmatrix}
  a(i-1)n+1 & b(i-1)n+2 & 0 \\
  b(i-1)n+2 & a(i-1)n+2 & b(i-1)n+3 \\
  \vdots & \vdots & \ddots \\
  0 & b_{in} & a_{in}
\end{bmatrix}
\]  

(II.3.5)

and the $\mathbf{B}_{\mathbf{A}}$ are diagonal with an additional element at the lower left corner,
and $\mathbf{u}_1$ is the column vector of the mass normalized displacements. It can easily be shown from (II.3.2) and (II.3.3) that the elements $a_i$, $b_i$, and $c_i$ are simple functions of the atomic masses and force constants,

$$a_i = \left( \gamma_{i-1} + \gamma_{i+1} + \gamma_{i+n} + \gamma_{i-n} \right) / m_i$$

$$b_i = -\gamma_{i-1} / (m_{i-1})^{\frac{1}{2}}$$

$$c_i = -\gamma_{i-n} / (m_{i-n})^{\frac{1}{2}}$$

In the development of these equations a set of boundary conditions has been used which gives the matrix $M$ a form in which the off-diagonal elements are close to the principal diagonal and the matrix is as uniform (with respect to zero and non-zero elements) as possible. This reasoning will become clear when the calculational procedure is established. The boundaries in the $x$-direction are rigid walls and in the
y-direction the atoms are restricted in a pseudo-periodic manner. Thus in the y-direction the atom 2n has a non-central force interaction with the atom 2n + 1. The imposition of this cyclic or toroidal boundary condition has very little influence even in moderately-sized lattices. The author has calculated the case in which both boundaries are rigid and there appears to be no significant different in lattices of approximately 1000 atoms with a minimum dimension of six atoms.

To calculate the frequency spectra of two-dimensional lattices the author has employed a method explored by Dean and Bacon based on elementary determinant theory and the negative eigenvalue theorem. Following the notation used by Dean and Bacon, let

$$\text{L}^{(1)}_{\text{M}} = \lambda_{ij}^{(1)} = M - \omega_{\text{M}}^2$$  \hspace{1cm} (II.3.8)

where $M$ is the dynamical matrix for any lattice of $N$ atoms considered. The $N \times N$ symmetric matrix $\text{L}^{(1)}_{\text{M}}$ can be partitioned as follows:

$$\text{L}^{(1)}_{\text{M}} = \begin{bmatrix}
\bar{X}_1 & Y_1 \\
- \bar{X}^T_1 & Z_1
\end{bmatrix}$$  \hspace{1cm} (II.3.9)

where the submatrix $X_1$ is of order unity and $Z_1$ is of order $N - 1$. In other words $\bar{X}_1 = \lambda_{11}^{(1)}$, and $Y_1$ is a row matrix with $\bar{Y}_1^T$ its transpose. Recalling the use of the symbol $\eta()$ to indicate the number of negative eigenvalues of the argument matrix, the negative eigenvalue theorem states that
With the \((N - 1 \times N - 1)\) matrix \(\mathbf{L}_2^{(2)}\) defined by
\[
\mathbf{L}_2^{(2)} = \mathbf{Z}_1 - \mathbf{X}_1 \mathbf{T}_{11}^{-1} \mathbf{X}_1
\]
\[= Z_1 - X_1^T X_1 / \ell_{11}^{(1)} \]  

Since \(\eta(\mathbf{X}_1)\) is either one or zero, the problem is reduced to finding \(\eta(\mathbf{L}_2^{(2)})\). The matrix \(\mathbf{L}_2^{(2)}\) can be reduced in an analogous manner giving \(\mathbf{X}_2\) and \(\mathbf{L}_3^{(3)}\). Repetition of this process gives the result
\[
\eta(\mathbf{L}_k^{(k)}) = \sum_{i=1}^{N} \eta(\mathbf{X}_i) 
\]

enabling the number of eigenvalues smaller than \(\omega^2\) to be found by counting the number of negative elements in the sequence \(\ell_{11}^{(1)}, \ell_{11}^{(2)}, \ell_{11}^{(3)}, \ldots, \ell_{11}^{(N)}\).

The procedure for spectra calculations is then to compute the sequences of matrices \(\mathbf{L}_1^{(1)}, \mathbf{L}_2^{(2)}, \ldots, \mathbf{L}_N^{(N)}\) and to note the signs of the upper left elements of these matrices. The generating relation for the sequence is just the generalization of (II.3.11),
\[
\mathbf{L}_j^{(j+1)} = \mathbf{Z}_j - \mathbf{X}_j \mathbf{T}_{j1}^{-1} \mathbf{X}_j / \ell_{11}^{(j)} \quad (j = 1, 2, \ldots, N - 1) \quad (\text{II.3.13})
\]
This technique is formally identical to the reduction process of Gaussian elimination -- a technique used for matrix inversion and the solution of sets of linear equations. An error analysis has been made by Wilkinson, and the method of Gaussian elimination is accurate in all cases except where any of the upper left elements \((t^{(j)}_{11})\) are very small. This is never the case in the above application of this reduction process.

Let us now consider the triangular lattice briefly. If we count the atoms in the manner shown in Figure 2, the equation of motion for the \(i^{th}\) atom with central and non-central force constants between nearest neighbors only is

\[
\begin{pmatrix}
\ddot{x}_i \\
\ddot{y}_i
\end{pmatrix}
= m_i \begin{pmatrix}
\gamma_{ii+1} & 0 \\
0 & \gamma'_{ii+1}
\end{pmatrix}
\begin{pmatrix}
x_{i+1} \\
y_{i+1}
\end{pmatrix}
- \begin{pmatrix}
x_i \\
y_i
\end{pmatrix}
+ \begin{pmatrix}
\gamma_{ii-1} & 0 \\
0 & \gamma'_{ii-1}
\end{pmatrix}
\begin{pmatrix}
x_{i-1} \\
y_{i-1}
\end{pmatrix}
- \begin{pmatrix}
x_{i} \\
y_{i}
\end{pmatrix}
+ \frac{1}{4}
\begin{pmatrix}
\gamma_{ii+n} + 3\gamma'_{ii+n} & \sqrt{3}(\gamma_{ii+n} - \gamma'_{ii+n}) \\
\sqrt{3}(\gamma_{ii+n} - \gamma'_{ii+n}) & \gamma_{ii+n} + 3\gamma'_{ii+n}
\end{pmatrix}
\begin{pmatrix}
x_{i+n} \\
y_{i+n}
\end{pmatrix}
- \begin{pmatrix}
x_{i} \\
y_{i}
\end{pmatrix}
\]
These equations can be put into the form (II.3.8),
Figure 2. Enumeration of the Lattice Sites for the Triangular Lattice.
\[(M_T - w^2 I)u = 0 \quad (\text{II.3.15})\]

where \(M_T\) is the dynamical matrix of coefficients for the triangular lattice, and \(u\) is the column vector of the displacements, \[u^\text{T} = (x_1, y_1, x_2, y_2, \ldots, x_{mn}, y_{mn}) \quad (\text{II.3.16})\]

It is obvious that the motions of the triangular lattice are not separable in the \(x\)- and \(y\)-directions except in the case of equal central and non-central force constants, \(\gamma_{ij} = \gamma_{kl} = \gamma = \gamma'_{ij} = \gamma'_{kl} \).

The frequency spectrum can be determined in a manner similar to that explained for the square matrix using the substitution

\[\lambda^{(1)} = M_T - w^2 I \quad (\text{II.3.17})\]

The value of the integrated spectrum is calculated at a finite mesh of points in \(w^2\), and from this mesh the derived spectrum can be obtained. The generation of the mass sequences in two and three dimensions is essentially the same as employed in the linear chain.

To understand the peaks found at the upper end of the derived spectra it was necessary to solve equations like (II.3.3) exactly for the eigenvalues \(w^2\) of \(M_b\) and the eigenvectors, \(u\). This was accomplished by direct diagonalization of the dynamical matrix and calculation of the eigenvectors. The eigenvectors were plotted in stereo pairs as displacements in a suitable grid representing the lattice with which the
problem dealt. Using a stereo viewer the displacements could be observed directly.

It can now be seen how the method of calculating the integrated spectrum in two dimensions is also applicable to the three-dimensional problem provided the proper matrices are employed and the computing facilities are adequate. Let us first consider the simple cubic lattice.

Using a central-non-central harmonic force model for the nearest-neighbor interactions in a simple cubic lattice, the motions in the three dimensions are again degenerate and separable. The equation of motion in the x-direction for a non-boundary atom is

\[ m_i \ddot{x}_i = \gamma'_{ii+1}(x_{i+1} - x_i) + \gamma'_{ii-1}(x_{i-1} - x_i) + \gamma'_{ii+n}(x_{i+n} - x_i) + \gamma'_{ii-n}(x_{i-n} - x_i) + \gamma'_{ii+mn}(x_{i+mn} - x_i) + \gamma'_{ii-mn}(x_{i-mn} - x_i) \quad (II.3.18) \]

where, as usual, \( \gamma_{ij} \) and \( \gamma'_{ij} \) are the central and non-central force constants between the \( i \) and \( j \)th atoms. Similar equations hold for the \( y \)- and \( z \)-motions. The numbering of the atoms is shown in Figure 3.

Again the equations of motion can be reduced to the form

\[ (M_{sc} - \omega^2 \mathbf{I}) \mathbf{u} = 0 \quad (II.3.19) \]
Figure 3. Enumeration of Nearest-Neighbor Sites in the Simple Cubic Crystal.
where the dynamical matrix for the simple cubic lattice, $M_{\text{sc}}$, is a matrix of the following form for a lattice of $n \times m \times \ell$ atoms:

$$
M_{\text{sc}} = \begin{bmatrix}
A_1 & C_2 & D_3 \\
C_2^T & A_2 & C_3 & D_4 & 0 \\
D_3^T & C_3^T & A_3 & C_4 & D_5 \\
& & & & \\
& & & & \\
0 & D_{\ell}^T & C_{\ell}^T & A_{\ell}
\end{bmatrix}
$$

(II.3.20)

where the $n \times n$ matrix $A_1$ is

$$
A_1 = \begin{bmatrix}
a(i-1)n+1 & b(i-1)n+2 \\
b(i-1)n+2 & a(i-1)n+2 & b(i-1)n+3 \\
& & & \\
& & & \\
0 & b_{in} & a_{in}
\end{bmatrix},
$$

(II.3.21)

the $n \times n(m - 1)$ matrix $C_4$ is
and the $n \times n$ matrix $D_d$ is given by the diagonal matrix

$$D_d = \begin{bmatrix}
    d(i-1)n+1 & 0 & 0 & \cdots & 0 \\
    0 & c(i-1)n+2 & 0 & \cdots & 0 \\
    \vdots & \vdots & \ddots & \ddots & \vdots \\
    0 & \cdots & 0 & c_{in} & 0 \cdots 0 \\
    b(i-1)n+1 & \cdots & \cdots & \cdots & d_{nm} \\
\end{bmatrix} \quad (\text{II}.3.22)$$

where the elements of these matrices are given by simple relations of the masses and force constants,

$$\begin{align*}
a_i &= (\gamma_{ii+1} + \gamma_{ii-1} + \gamma_{ii+n} + \gamma_{ii-n} + \gamma_{ii+mn} + \gamma_{ii-mn})/m_i \\
b_i &= -\gamma_{ii-1}/(\sqrt{m_i m_{i-1}}) \\
c_i &= -\gamma_{ii-n}/(\sqrt{m_i m_{i-n}}) \\
d_i &= -\gamma_{ii-mn}/(\sqrt{m_i m_{i-mn}}) \quad (\text{II}.3.24)
\end{align*}$$
In developing this matrix, $M_{bc}$, boundary conditions have been employed in the same manner as in two dimensions with two sides of the lattice fixed and toroidal boundaries in the other two directions.

The extension of the calculations from the square lattice to the simple cubic lattice is in principle a trivial one. The code for the frequency spectrum calculations is essentially the same with minor modifications. Due to this fact the calculation times are comparable in magnitude. In the square lattice the time required to calculate the frequency spectrum is proportional to the square of the width and directly proportional to the length and the number of mesh points calculated. Since the cross-section of the simple cubic lattice plays a role in the dynamical matrix which is analogous to the width in the square lattice, the calculation time for simple cubic lattices is proportional to the square of the number of atoms in the cross-section of the lattice, $(n \times m)^2$, and is directly proportional to the length, $l$, and the number of mesh points calculated. For example, a square lattice of $30 \times 30$ atoms requires ten minutes to calculate 25 mesh points; while a lattice of $40 \times 30$ atoms requires 19 minutes to calculate the same number of mesh points. The same calculation can be done for a lattice of $30 \times 40$ atoms in 13 minutes. The simple cubic lattice requires 14 minutes to calculate 25 mesh points for a lattice of $6 \times 6 \times 25$ atoms. It can be seen that even the simplest of three-dimensional lattices is quite time consuming. In the more complicated two-dimensional case, the triangular lattice, the running time is longer because of the inseparability of the two dimensions. A typical running time would be approximately five minutes for 25 mesh points for a lattice of
10 × 50 atoms. In the more complicated cubic lattices where the equations of motion are not separable, the running time increases drastically. An example of a typical code used in the frequency spectrum calculations is given in Appendix I.

The remaining common cubic lattices are the body-centered cubic and the face-centered cubic. The equations of motion for these lattices are similar with the principal differences being the force constant matrices and the indexing. The author has calculated spectra for both with the simplification of only one degree of freedom per atom. This is, of course, unrealistic in concept but does give the acoustic spectrum quite readily. The calculational procedures are like those of the simple cubic lattice, and the results give some idea of the effect of disorder on the spectrum. These calculations will not be discussed in detail here because of their limited usefulness and their similarity to the simple cubic calculation. Instead the author would like to develop the equations for the body-centered cubic lattice in a manner similar to that done for the simple cubic. In an analogous fashion the face-centered cubic equations can be developed and the spectrum can be found. The extension from body-centered cubic to face-centered cubic is somewhat trivial, and the author will not do it here.

Consider a body-centered cubic lattice of masses connected to nearest and next-nearest neighbors by central and non-central springs and arranged in a parallelepiped array. The array is formed in the dimensions of \( n \) atoms high, \( m \) atoms wide, and \( t \) atoms long. The parallelepiped shape is chosen for simplicity and symmetry of indexing the variables. Assuming the rigid boundaries in one direction and toroidal
boundaries in the other two directions, the equations of motion for non-boundary atoms can be written in terms of the displacements from equilibrium and the central and non-central force constants of the \( n \)th nearest neighbors given by \( \alpha_{ij}^{(n)} \) and \( \beta_{ij}^{(n)} \), respectively. They are the following:

\[
m_i \ddot{x}_i = \sum_{mn} F_{i(i+mn)} (x_{i+mn} - x_i) + \sum_{mn-1} F_{i(i+mn-1)} (x_{i+mn-1} - x_i) \\
+ \sum_{mn-n} F_{i(i+mn-n)} (x_{i+mn-n} - x_i) + \sum_{mn-n-1} F_{i(i+mn-n-1)} (x_{i+mn-n-1} - x_i) \\
+ \sum_{mn+n+1} F_{i(i-mm+n+1)} (x_{i-mm+n+1} - x_i) + \sum_{mn+n} F_{i(i-mm+n)} (x_{i-mm+n} - x_i) \\
+ \sum_{mn+n+1} F_{i(i-mm+n+1)} (x_{i-mm+n+1} - x_i) + \sum_{mn} F_{i(i-mm)} (x_{i-mm} - x_i)
\]

(II.3.25)

\[
+ \sum_{i+2mn-n-1} F_{i(i+2mn-n-1)} (x_{i+2mn-n-1} - x_i) + \sum_{i-2mn+n+1} F_{i(i-2mn+n+1)} (x_{i-2mn+n+1} - x_i) \\
+ \sum_{i+n} F_{i(i+n)} (x_{i+n} - x_i) + \sum_{i-n} F_{i(i-n)} (x_{i-n} - x_i) \\
+ \sum_{i+1} F_{i(i+1)} (x_{i+1} - x_i) + \sum_{i-1} F_{i(i-1)} (x_{i-1} - x_i)
\]

where the matrices for the nearest-neighbor force constants are
and the matrices for the next-nearest-neighbor force constants are

\[
\mathbf{F}_{jk}^{(1)} = \begin{bmatrix}
\alpha_{jk}^{(1)} & \beta_{jk}^{(1)} & \beta_{jk}^{(1)} \\
\beta_{jk}^{(1)} & \alpha_{jk}^{(1)} & \beta_{jk}^{(1)} \\
\beta_{jk}^{(1)} & \beta_{jk}^{(1)} & \alpha_{jk}^{(1)} 
\end{bmatrix}, \quad (II.3.26)
\]

\[
\mathbf{g}_{jk}^{(1)} = \begin{bmatrix}
\alpha_{jk}^{(2)} & 0 & 0 \\
0 & \beta_{jk}^{(2)} & 0 \\
0 & 0 & \beta_{jk}^{(2)} 
\end{bmatrix}, \quad (II.3.27a)
\]

\[
\mathbf{g}_{jk}^{(2)} = \begin{bmatrix}
\beta_{jk}^{(2)} & 0 & 0 \\
0 & \alpha_{jk}^{(2)} & 0 \\
0 & 0 & \beta_{jk}^{(2)} 
\end{bmatrix}, \quad (II.3.27b)
\]
The dynamical matrix now assumes the form of a band matrix of block matrices

\[
\begin{bmatrix}
A_1 & B_1 & \ldots & C_{(mm-n)} & C_{(mm)} & \ldots & D_1 & \ldots & 0 \\
B_{1T} & A_2 & B_2 & C_{(mm-n)} & C_{(mm)} & D_2 & \ldots & \ldots & \ldots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \ddots & \ddots \\
C_{(mm-n)T} & C_{(mm)T} & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\
D_{1T} & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \ddots & \ddots \\
0 & D_{T-2mn+n+1} & C_{(mm)nT} & C_{(mm-n)T} & D_{T-1} & A_{T} \\
\end{bmatrix}
\]

\[
M_{BCC} = \begin{bmatrix}
A_1 & B_1 & \ldots & C_{(mm-n)} & C_{(mm)} & \ldots & D_1 & \ldots & 0 \\
B_{1T} & A_2 & B_2 & C_{(mm-n)} & C_{(mm)} & D_2 & \ldots & \ldots & \ldots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \ddots & \ddots \\
C_{(mm-n)T} & C_{(mm)T} & \ldots & \vdots & \vdots & \vdots & \ddots & \ddots & \ddots \\
D_{1T} & \ldots & \ldots & \ldots & \ldots & \ldots & \ddots & \ddots & \ddots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \ddots & \ddots \\
0 & D_{T-2mn+n+1} & C_{(mm)nT} & C_{(mm-n)T} & D_{T-1} & A_{T} \\
\end{bmatrix}
\]

The displacements from equilibrium are given by the vectors

\[
\mathbf{z}_d^T = (x_1, y_1, z_1).
\]
These matrices are themselves composed of matrices in the following manner:

\[
A_j = \begin{bmatrix}
U^{(j-1)n+1} & V^{(3)}_{(j-1)n+1} \\
V^{(3)}_{(j-1)n+1} & U^{(j-1)n+2} & V^{(3)}_{(j-1)n+2} \\
& & \ddots & \ddots \\
0 & & & V^{(3)}_{j-1n-1} & U_{j-1n}
\end{bmatrix}, \quad (\text{II.3.30})
\]

\[
B_j = \begin{bmatrix}
V^{(2)}_{(j-1)n+1} \\
& \ddots & \ddots \\
V^{(3)}_{j-1n} & \ddots & V^{(2)}_{j-1n}
\end{bmatrix}, \quad (\text{II.3.31})
\]

\[
C_{(k+1)} = \begin{bmatrix}
\tau^{(k)}_{(j-1)n+1} & \tau^{(k+1)}_{(j-1)n+1} \\
\tau^{(k+1)}_{(j-1)n+1} & \ddots & \ddots \\
& & \ddots & \ddots \\
0 & \tau^{(k)}_{j-1n} & \tau^{(k+1)}_{j-1n} & \ddots
\end{bmatrix} \quad (\text{II.3.32})
\]
and

\[
D_{ij} = \begin{bmatrix}
    v^{(1)}_{(i-1)n+1} & 0 \\
    \vdots & \vdots \\
    0 & v^{(1)}_{(i-1)n+2}
\end{bmatrix}. \quad (\text{II.3.33})
\]

The block submatrices are defined as follows:

\[
U_{ij} = \begin{bmatrix}
    a & b & b \\
    b & a & b \\
    b & b & a
\end{bmatrix}. \quad (\text{II.3.34})
\]

with

\[
a = \alpha^{(1)}_{ii+mn} + \alpha^{(1)}_{ii-mn} + \alpha^{(1)}_{ii+mn-1} + \alpha^{(1)}_{ii-mn+1} + \alpha^{(1)}_{ii+mn-n} \\
+ \alpha^{(1)}_{ii-mn+n} + \alpha^{(1)}_{ii-mn+n+1} + \alpha^{(1)}_{ii+mn-n} + \alpha^{(1)}_{ii+2mn+n+1} \\
+ \alpha^{(2)}_{ii+2mn-n-1} + \beta^{(2)}_{ii+n} + \beta^{(2)}_{ii-n} + \beta^{(2)}_{ii+1} + \beta^{(2)}_{ii-1}
\]

\[
b = \beta^{(1)}_{ii+mn} + \beta^{(1)}_{ii-mn} + \beta^{(1)}_{ii+mn-1} + \beta^{(1)}_{ii-mn+1} \\
+ \beta^{(1)}_{ii-mn+n} + \beta^{(1)}_{ii+mn-n} + \beta^{(1)}_{ii+mn+n+1} + \beta^{(1)}_{ii+mn-n-1}
\]. \quad (\text{II.3.35})
and

\[
\mathbf{M}^{(k)} = \begin{bmatrix}
\alpha^{(1)}_{ii+k} & \beta^{(1)}_{ii+k} & \beta^{(1)}_{ii+k} \\
\beta^{(1)}_{ii+k} & \alpha^{(1)}_{ii+k} & \beta^{(1)}_{ii+k} \\
\beta^{(1)}_{ii+k} & \beta^{(1)}_{ii+k} & \alpha^{(1)}_{ii+k}
\end{bmatrix} \cdot (m_1 m_{i+k})^{-\frac{1}{2}}. 
\] (II.3.36)

The V-matrices are given by

\[
\mathbf{V}^{(1)} = -G^{(1)}_{ii+2mn-n-1} \cdot (m_1 m_{i+2mn-n-1})^{-\frac{1}{2}} \\
\mathbf{V}^{(2)} = -G^{(2)}_{ii+n} \cdot (m_1 m_{i+n})^{-\frac{1}{2}} \\
\mathbf{V}^{(3)} = -G^{(3)}_{ii+1} \cdot (m_1 m_{i+1})^{-\frac{1}{2}}
\] 

As can be seen, the matrix \( M_{BCC} \) is symmetric but quite complex in form. It is because of this complexity that the spectrum of eigenvalues is difficult to obtain. The problem is not difficult to code for the computer but is rather tedious. The program has been written and has been run on the computer for the case including second-nearest neighbor interactions for a lattice of 492 atoms. This is a matrix of order 1476 \( \times \) 1476. The running time is quite long. The problem has been done using only nearest-neighbor interactions and was found to be tractable with the present means of computation. It still requires a
considerable amount of time. For a lattice of $6 \times 6 \times 12$ atoms the running time per mesh point on the spectrum is approximately one minute.

The general form of the equations of motion and the dynamical matrix for the face-centered cubic lattice is quite analogous to that of the body-centered cubic.

Again in the three-dimensional calculations the form of the vibrational modes was investigated by direct diagonalization of the dynamical matrices. This could be done for all of the lattices except the body-centered cubic and face-centered cubic with three degrees of freedom per atom. Results were obtained for small blocks of the lattices of $6 \times 6 \times 6$ atoms and were plotted in stereo pairs for ease of viewing.

4. Frequency Spectra and Normal Modes

The author has made extensive calculations of the frequency spectra of various lattices in one, two, and three dimensions. The primary goal of these calculations was to investigate the effects of disorder on the frequency spectra of harmonic crystals. This has been accomplished and will be described in the present section. Most of the results of these calculations presented in the figures of this section will be in the precise form that they were obtained from the computer. The results will be described in the order of the dimensionality of the lattice concerned and, consequently, in the order of the complexity of the problem.
The units used in the calculations were chosen arbitrarily. In the general binary isotopic lattice the choice of the force constant does not determine the units; there remains an arbitrariness in the units of time. For simplicity the values of the light mass and the force constant were chosen to give the maximum frequency of the monatomic light chain a value of 2.0 reciprocal time units. The change of scale to a different system of units is effected by the trivial device of changing the scale of the frequency squared, \( \omega^2 \), provided the mass ratio and force constants are suitable for the system considered. A system of atomic dimensions will have a maximum squared frequency of the order of \( 10^{25} \text{ sec}^{-2} \).

For a comparison of the method of calculation with an analytic solution consider the monatomic linear chain. The analytic solution is the well known U-shaped form \( D(\nu) = \pi^{-1} [4 - (\nu - 2)^2]^{-\frac{1}{2}} \) for values of \( 0 < \nu < 4 \), where \( \nu = \omega^2 \) and \( D(\nu) \) is the derived spectrum or density of states. In Figure 4 the analytic solution is plotted as the upper curve. The lower curve is the calculated frequency spectrum for a monatomic chain of 100,000 atoms. The ordinates of the figures of this section have an arbitrary scale.

Introduction of foreign atoms into the monatomic chain has a profound effect upon the frequency spectrum. In particular, if masses of one third the mass of the atoms in the monatomic chain are inserted randomly, high frequency peaks are formed in the spectrum at frequencies above the maximum frequency of the host lattice. This can be seen in Figure 5. The concentration of light atoms, \( F_A \), is the fraction of the atoms in the chain which are light atoms. The cases considered in
Figure 4. Calculated and Analytic Spectra of a Monatomic Linear Chain.
Figure 5. Effect of Varying Concentrations on the Frequency Spectrum.
Figure 5. Continued.
Figure 5 range from the monatomic heavy atom chain (Figure 5a) to the monatomic light atom chain (Figure 5k). The interval plotted is the mesh size used in the calculations and is 0.04 reciprocal time units squared.

A comparison of the spectra of chains of varying mass ratios \( R \) can be seen in Figure 6. It can be seen that the spectra for mass ratios of 1:1.25 and 1:1.5 are rather smooth compared to those of higher mass ratios. In these spectra the force constant and light mass are fixed and the mass of the host chain is varied. The shift of the continuum of the heavy host to a smaller and smaller portion of the total range of the squared frequency as the mass ratio increases can be seen. Since \( FA = 0.5 \) in all of Figure 6, this shift preserves the area of the continuum portion of the graph. The ordinate scales of the graphs vary.

In Figure 6h the finite approximation to the binary chain with one of the masses infinite is shown. The mass ratio is 1:10,000, and the light atoms are dynamically isolated from each other. Each spike represents a normal mode (or degenerate modes) of an isolated island and is proportional in strength to the number of islands in the chain with that normal mode frequency. In the limit of infinite mass ratio and zero mesh size the spectrum would be a series of delta-functions.

It is worthwhile at this point to consider the effect of the finite length of the chain. In Figure 7 the spectra of chains of varying lengths are displayed. The mass ratio is 1:2, and the concentration is 0.5. The lengths vary from 1000 to 100,000 atoms. It can be seen that the difference is insignificant once the average spacing of
Figure 6. Effect of Varying Mass Ratios
Figure 6. Continued
Figure 7. Effect of Varying Lengths of Chains.
Figure 7. Continued.
levels \((1/N)\) is appreciably smaller than the calculational mesh size. The ragged appearance of the spectra of the shorter chains is caused by the comparability in magnitude of the average spacing of levels and the mesh size. This becomes a serious problem in higher dimensions when one is limited by calculational time to lattices of approximately 1000 atoms.

By imposing an \textit{a priori} short range order on the mass sequence generator, ordered binary lattices could be studied. The requirement of complete short range order \((\text{SI} = 1.0)\) creates the ordered diatomic crystal studied by Maradudin, Mazur, Montroll, and Weiss.\(^{27}\) Figure 8 demonstrates the progression of the spectra as the order is made complete. The degree of short range order is given by \text{SI} and ranges from zero to one for systems ranging from random to completely ordered. By allowing the order parameter to become near \(-1\) an interesting chain can be generated. This chain was a concatenation of two monatomic chains of different masses. The spectrum for this chain is not a surprising one; it is the superposition of two monatomic chain spectra shown in Figure 9.

Using the same calculational procedure and varying the mass distribution yielded many interesting results. A ternary chain could be generated in a manner similar to the binary chain; and the disordered ternary chain spectrum proved to be quite similar to that of the binary chain. Shown in Figure 10 are three spectra for masses in equal portions, with the mass ratios of \(1:2:3\), \(1:2.5:3\), and \(1:1.5:3\). In the case where the intermediate mass is the mean mass, Figure 10a, the spectrum looks somewhat similar to the binary chain with \(FA = 0.4\),
Figure 8. The Effect of Order
Figure 9. Frequency Spectrum of Two Monatomic Connected Chains
Figure 10. Frequency Spectra of Ternary Chains
Figure 5e, except for a broadening of the impurity bands and dissipation of the continuum near \( w^2 = 2.0 \) due to local modes of the intermediate atoms in heavy atom clusters. Making the intermediate mass larger than the mean increases this effect. Decreasing the intermediate mass, however, brings the spectrum closer to that of a binary chain with predominantly light masses (e.g. Figure 10c).

The effect of spatial disorder can be achieved most simply by randomizing the force constants in some suitable way. It is logical to investigate the case analogous to the binary isotopic chain -- the monatomic chain with binary disordered force constants. The physical significance of this system may be somewhat obscure, but it is quite like the physical system of alloys of the beta-brass type -- CuZn and CoFe. The components of these alloys have almost identical masses. Thus our model of differing spring constants might give some indication of the frequency spectrum of such systems.

If the equations of motion of the linear chain are examined, it can be seen that the masses and the force constants assume conjugate roles in the frequency spectrum. Stronger springs in a host chain of relatively weaker springs will have an effect similar to that of lighter atoms in a relatively heavier host chain. In Figure 11 we see a display similar to Figure 5 except that in the present figure we have randomly replaced strong springs with relatively weaker ones with the concentration of weak springs given by \( FC \). The ratio of the weak to strong force constants is 1:3. The spectra shown are for chains of 8000 atoms.
Figure 11. Effects of Disordered Force Constants in Monatomic Chains
(e) FC = 0.5

(f) FC = 0.25

(g) FC = 0.5, SI = 1.0

Figure 11. Continued
Upon the introduction of a correlation between the force constants and the masses, a more physical system can be treated. Consider a binary system of atoms. These atoms will generally be bound with three types of bonds -- those when the two species form bonds with themselves and when they form bonds with each other. Thus a realistic system would be a chain of two types of masses, A and B, with force constants \( \gamma_{AA}, \gamma_{AB}, \) and \( \gamma_{BB} \) representing the nearest neighbor force constants between two A atoms, A and B atoms, and two B atoms respectively. This system has been calculated and the spectra are plotted in Figure 12. In (a) the spectrum is markedly different from the isotopic case (Figure 5f) with the local mode peaks quite pronounced and the continuum quite like the monatomic heavy atom chain. In this case the ratio \( \gamma_{AA} : \gamma_{AB} : \gamma_{BB} \) is 2:1:2. As this ratio is decreased to 4:3:4, the spectrum begins to resemble that of the isotopic case more closely. This can be seen in Figure 12b. In Figure 12c the spectrum for the inverse of (a) is shown. The force constant ratio here is 1:2:1, and quite different results are obtained. The mass ratio in all of these cases is 1:3. The important features of all of these spectra are the irregular peaks occurring at the higher values of the squared frequency.

Another physically interesting problem which can be approached in one dimension is the NaCl-KCl mixture. This is a mixed diatomic lattice which is represented in a one-dimensional representation as an ordered binary chain with one of the masses randomly replaced by a third mass. Thus, the even sites, say, will be occupied by one type of mass, while the odd sites are randomly occupied by one of two other types of masses. The spectra for isotopically disordered, mixed dia-
(a) $\gamma_{AA} = \gamma_{BB} = 2\gamma_{AB}$

(b) $\gamma_{AA} = \gamma_{RB} = \frac{4}{3}\gamma_{AB}$

(c) $\gamma_{AA} = \gamma_{BB} = \frac{3}{2}\gamma_{AB}$

Figure 12. Frequency Spectra of Binary Chains with

Realistic Force Constants.
tomic chains with mass ratios of 1:1.54:1.7, 1:2:3, and 1:5:3 are given in Figure 13. This mass ratio is in the form of \(A:B:C\) for a chain with the structure \(\text{ABCBCABCABCBAB} \ldots\). The ratio used in Figure 13a is the ratio of the masses in the NaCl-KCl mixture. It can be seen that the spectrum again is split into bands but not into the widely separated bands of the ordered diatomic chain. In Figure 13b the spectrum is separated into three bands; while in (c) the heavy mass is intermediate and creates a form of a host lattice with lighter impurities which are effectively isolated islands. This is somewhat reminiscent of the binary case with the infinite mass ratio.

It is quite instructive to look a bit closer at the detailed spectrum of the isotopically disordered binary chain. Consider the spectrum of a chain of 16,000 atoms with equal amounts of light and heavy atoms with the mass ratio 1:3 (Figure 14). The structure at lower values of the squared frequency (elastic limit) is quite similar to the spectrum of the monatomic host chain. However at higher frequencies the structure becomes quite complex with peaks and zero points or forbidden frequencies. If one examines Figure 5 closely, one sees these forbidden frequencies remain forbidden even to high concentrations of light atoms. These points correspond to the special frequencies of Borland \(^49\) and to the "special" or forbidden frequencies of Matsuda.\(^50\) Borland was able to calculate the values of the integrated spectrum at these points; while Matsuda proved that these frequencies are forbidden. There is a definite physical interpretation of these frequencies, and it will be given in a later section.
Figure 13. Frequency Spectra of Mixed Diatomic Chains

(a) Masses 1, 1.54, 1.7

(b) Masses 1, 2, 3

(c) Masses 1, 5, 3
In Figure 14 certain peaks have been identified with arrows and labels. The explanation of these labels is given in Table I. These correspond to frequencies of islands in the chain. When these islands occur sufficiently close that the perturbation of the eigenfrequencies can be seen by our calculational mesh, the frequencies are shifted to higher values as in the case of $D_4$ and G. Of course, one realizes that some modes of isolated islands are degenerate with other configurations. For example the antisymmetric mode of the island of three light atoms, $C_2$, which has displacements of the form $\ldots$ is degenerate with the isolated system of two light atoms separated by a heavy atom ($\ldots$) in its antisymmetric mode.

Examples of the displacements of the atoms in the chain in their normal modes can be seen in Figure 15. The displacements of the $i^{th}$ atom are plotted versus the atom number and these points are then connected sequentially. In Figure 15a-d four of the lower frequency wave-like modes of the chain are shown; while in (e)-(h) some intermediate frequency modes are shown. Even the continuum modes are localized to some degree. The maximum frequency for the monatomic host chain lies between the modes shown in (g) and (h). The strongly localized modes are shown in (i) through (l) of Figure 15. The legend contains a series of ones and threes which indicate the composition of the chain, the mass ratio being 1:3.

If a light chain with a few heavy impurities is considered, an interesting result is found. The heavy atoms act as amplitude blocks in the wave-like modes of the light atom chain. This is shown in Figure 16. The positions of the heavy atoms can readily be found
Figure 14. Identification of Frequency Peaks
The monatomic host lattice is the heavy (H) lattice with islands of light (L) atoms. The lettering of the lines is taken from Figure 14.

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<tr>
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<td>A</td>
<td>-L-</td>
<td>E</td>
<td>-LLLLL-</td>
</tr>
<tr>
<td>B</td>
<td>-LL-</td>
<td>F</td>
<td>-LLLLLLL-</td>
</tr>
<tr>
<td>C</td>
<td>-LLL-</td>
<td>G</td>
<td>-LLLLLLLHHL-</td>
</tr>
<tr>
<td>D</td>
<td>-LLLL-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: The subscript denotes the mode number of the island with 1 indicating the lowest symmetric mode.
Figure 15. Sample Eigenvectors for a Disordered Chain of 200 Atoms.
Figure 15. Continued
Figure 16. Blooming of Amplitude by Heavy Impurities.
without looking at the legend to see the chain composition. The mass ratio is 1:3.

Using the author's code for the spectral calculations, a wide variety of systems can be calculated with ease. By substituting a continuous force constant distribution subject to a given probability, calculations can be made on glass-like chains and chains with continuous mass distributions. In Figure 17 the results of some calculations of chains with continuous mass and force constant distributions are shown. In (a) and (b) of this figure the chains are isotopic with continuous random mass distributions from the ratios of 1:2 to 1:1 and from 1:3 to 1:1 respectively. The probability distribution employed is uniform so that any mass between these limits is equally probable and uncorrelated with its neighbors. The spectra obtained are quite smooth. In (c) of Figure 17 the chain is monatomic with the force constants chosen in a manner similar to that used in choosing the masses above. These spectra are for chains of 8000 atoms, and represent the spectra which would be obtained from an exact solution of the Dyson equations.

Consider further the ordered diatomic chain with a continuous distribution of force constants. Applying a mass ratio of 1:2 and allowing the force constants to be chosen randomly with a continuous distribution, the spectra shown in Figure 18 were calculated. The chains used are 8000 atoms long. In (a) the chain is isotopic while in (b) through (d) the force constants are uniformly distributed in the ranges of $0.75 < \gamma < 1.25$, $0.5 < \gamma < 1.5$, and $0 < \gamma < 2$. This force constant distribution causes a rounding of the spectrum until it assumes the smooth character of the monatomic chain with a continuous,
Figure 17. Frequency Spectra of Chains with Continuous Masses and Force Constants.
Figure 18. Frequency Spectra of Ordered Diatomic Chains

with Continuous Random Force Constants.
random distribution of force constants.

Let us now turn to two-dimensional lattices and consider first the square lattice. We will analyze the results of the author's calculations in a manner similar to that used in one-dimensional chains.

A comparison of the effects on the spectrum of the addition of light atoms into a heavy atom square lattice is shown in Figure 19. The spectra all show the characteristic shape of the continuum of the heavy atom lattice at lower values of the frequency. Since in these spectra the lattices had equal central and non-central force constants, the single logarithmic singularity of the perfect crystal spectrum appears as a finite peak. We see that there exist, once again, peaks at higher values of the frequency. These peaks correspond to the localized modes of light impurities in the heavy atom host lattice. In the transition from the impurity concentration (FA) of 0.25 to 0.5 a marked change in the spectrum occurs. The spectrum becomes relatively smooth without the isolated peaks. As the concentration increases the peak due to single atom local modes decreases because more two- and three-atom islands are formed. This effect is maintained as the light atom island concentration is increased. The individual peaks become smaller and more peaks appear. Finally, at a concentration of approximately 0.5 the probability of a light island of infinite extent being formed in an infinite lattice becomes unity. It is at this point that the spectrum becomes relatively smooth. This concentration is called the critical percolation concentration. The theoretical concentrations of the triangular and square lattices are approximately 0.51 and 0.55 respectively. The very smooth spectrum of (d) is indicative of
Figure 19. The Effect of Varying the Concentration in the Square Lattice

(a) FA = 0.15
(b) FA = 0.25
(c) FA = 0.5
(d) FA = 0.7
the passing near this critical concentration. The size of the lattices in this figure is 30 x 30 atoms.

Figure 20 shows the behavior of the spectrum as the mass ratio is increased from 1:2 to 1:1000. The concentration of light atoms is 0.25, and the lattice size is again 30 x 30 atoms. Due to the rather large concentration of light atoms very large islands of light atoms are formed and the infinite spectrum (1:1000) is somewhat smoother than if the concentration were low enough that small islands were all that were formed. In this figure it can be seen how the individual peaks move as the mass ratio increases.

The question of the effect of the boundaries of the finite lattices upon the spectra is quite interesting. Figure 21 shows the spectra calculated for various shapes of the square lattices with approximately the same number of atoms in each lattice. In (a) the lattice is 8 x 112 atoms, and consequently, 27% of the atoms are surface atoms. In (b) the lattice is 16 x 56 atoms with 16% surface atoms; while in (c) 13% of the atoms are surface atoms in a lattice of 30 x 30 atoms. In all three cases the mass ratio was 1:3, FA was 0.1, and the central-to-non-central-force-constant ratio was 4:1. The difference of appearance is due to the difference of mesh size used in these calculations. It is interesting to note the double peak in the continuum portion of the spectrum caused by the unequal central and non-central force constants. This splitting is shown in Figure 22 for lattices of 30 x 30 atoms with FA = 0.14. In Figure 22a the force constants are equal, and in (b) the ratio is \( \gamma = \frac{5}{3} \gamma' \). The mass ratio in both lattices is 1:3. The splittings in the high frequency peaks
Figure 20. The Effect of Varying Mass Ratios on the Frequency Spectrum of the Square Lattice.
Figure 21. The Effect of the Shape of the Square Lattice on the Frequency Spectrum.
Figure 22. Comparison of Equal and Unequal Force Constants.

(a) $\gamma = \gamma'$

(b) $\gamma = 5/3 \gamma'$
induced by the unequal force constants is evident.

A few spectra for the triangular lattice are given in Figure 23. The lattice is a parallelogram section of $10 \times 50$ atoms. The mass ratio is $1:3$ with $\gamma = \gamma'$. Spectra for values of the concentration of 0.1 and 0.2 are given in (a) and (b) with (c) being the spectrum of the monatomic light lattice. In the triangular lattice as in the previous cases the isolated peaks due to local modes are present.

The eigenvectors of the normal modes of a square lattice are shown in Figure 24. The displacements of the atoms are plotted in the transverse direction for ease of viewing and are the actual displacements in one of the axes lying in the plane of the lattice. The equilibrium positions of the atoms are plotted with an L or H signifying which kind of atom occupies that site. The eigenvectors are in the form of stereo pairs which can be seen in stereo by using a viewer of the type used in aerial photography and cartography. The figure can be divided into three parts. The lower frequency modes are shown in (a) through (c), and the intermediate frequencies are shown in (d) through (f). In the last three the highly localized modes are seen. The pertinent information about the lattices is shown in the figure.

The spectra obtained from the calculations for three-dimensional systems conformed to expectations. The spectrum of a simple cubic lattice of two masses in a disordered arrangement possesses the continuum spectrum of the monatomic heavy atom lattice and the high frequency peaks of the modes localized about the light atoms. Figure 25 shows the variation of the spectrum of a simple cubic lattice of $6 \times 6 \times 25$ atoms when the concentration of the light atoms is changed. The
Figure 23. Frequency Spectra of the Triangular Lattice
Figure 24. Typical Eigenvectors of the Isotopically Disordered Square Lattice.
Figure 24. Continued.
Figure 24. Continued.
Figure 25. Frequency Spectra of the Simple Cubic Lattice with Varying FA.
calculational mesh is rather coarse in this figure and does not show the fine structure at higher frequencies when the light impurity concentration is low. Again the critical percolation concentration plays an important role in determining the smoothness of the frequency spectrum. For three-dimensional crystals the critical concentration is lower than in two dimensions. The critical concentrations for the simple cubic, body-centered cubic, and face-centered cubic are 0.28, 0.22, and 0.18 respectively. Thus localized modes will only exist in concentrations less than these. The mass ratio of the lattices shown in Figure 25 is 1:2, and equal central and non-central force constants were employed. The continuum portion of the spectrum below the heavy atom lattice maximum frequency \( w^2 = 6.0 \) follows the general shape given by Montroll closely with some fluctuations caused by the periodicity of the boundary conditions.

The effect of varying the mass ratio is shown in Figure 26 where the concentration is 0.5, and the size of the lattice is \( 6 \times 6 \times 20 \) atoms. The concentration shown here is greater than the critical concentration, and, consequently, the individual isolated island peaks do not appear sharply separated. The stability of the spectrum of light atoms can be seen as the spectrum of frequencies of vibrations of the heavy atoms in the continuum is shrunk to low frequencies. The central and non-central force constants were equal in these calculations.

The result of unequal central and non-central forces can be seen in Figure 27. In (a) the force constants are equal while in (b) \( \gamma = \gamma' \). The effect on the continuum portion of the spectrum is masked by the coarseness of the calculational mesh. The size of the lattices in
Figure 26. Frequency Spectra of the Simple Cubic Lattice with Varying Mass Ratios.
Figure 27. The Effect of Equal and Unequal Force Constants in the Simple Cubic Lattice.
these spectra is $6 \times 6 \times 20$, and the concentration of light atoms is 10%.

In Figure 28 the spectrum for a lattice of $6 \times 6 \times 25$ atoms with a mass ratio of 1:3 and a concentration of light atoms of 0.25 is shown. The frequencies of various configurations of light islands are designated by letters which are identified in Table II. Again some of the islands are degenerate.

If the masses are ordered as in the perfect diatomic crystal, the spectrum takes on the form shown in Figure 29. This spectrum is for a lattice of $5 \times 5 \times 20$ atoms with a mass ratio of 1:1.1. This low mass ratio is the reason the gap between the acoustic and optical branches is so small. Also occurring in this lattice was one very light impurity atom. It is the local mode due to this single impurity which splits the gap.

As was mentioned earlier, crystals of the NaCl-KCl type are of interest since the interpenetrating face-centered cubic structure can be calculated using a simple cubic basis with the proper mass distribution. The results of a calculation of the frequency spectrum for a crystal of this type with the masses in the same ratio as the NaCl-KCl crystal is shown in Figure 30. The size of the lattice is $5 \times 5 \times 20$ atoms with equal amounts of KCl and NaCl. An interesting feature is the manner in which the gap between the optical and acoustic branches is filled. In this calculation $\gamma = \gamma'$.

The eigenvectors of some normal modes of the isotopically disordered simple cubic crystal are given in Figure 31. These range from the low frequency wave-like modes to the localized modes of high frequencies.
TABLE II

CORRESPONDENCE BETWEEN THE SPECTRAL LINES AND LOCALIZED STRUCTURES IN THE CUBIC LATTICE

The monatomic H-lattice is the base lattice. The lettering of lines refers to Figure 28.

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Figure 28. Identification of Modes in the Simple Cubic Lattice.
Figure 29. Ordered Diatomic Cubic Lattice Spectrum.

Figure 30. Mixed Diatomic Cubic Lattice Spectrum.
Figure 31. Typical Eigenvectors of the Isotopically Disordered Simple Cubic Lattice.
Figure 31. Continued.
The characteristics of the lattice are given in the legend for each stereo pair. The squared frequency (GNU) is given in the units that have been used throughout this discussion. The slight difference between the actual FA and the imposed FA reflects the finiteness of the mass sequence generated. The displacements have been plotted in the z direction and z-planes of the atoms have been connected by lines. The letters L and H indicate the equilibrium positions of the light and heavy atoms.

The introduction of a heavy atom into a light lattice will create a resonant mode in a simple cubic lattice as shown in Figure 32. The heavy atom is at the center of the $5 \times 5 \times 5$ atom lattice.

In Figures 33 and 34 the frequency spectra for the one-degree-of-freedom model of the body-centered cubic and face-centered cubic lattices are shown. Figure 33 shows the spectrum for a body-centered cubic lattice with a mass ratio of 1:3 and an impurity concentration of 0.26. This lattice is $6 \times 6 \times 6$ atoms. This spectrum shows the high frequency peaks due to the light atom islands. Figure 34 shows the spectrum for a face-centered cubic lattice of $6 \times 6 \times 6$ atoms with a mass ratio of 1:3 and a light atom concentration of 0.09. The localized mode peaks are apparent.

Figure 35 shows the exact spectrum of the body-centered cubic lattice with three degrees of freedom and next-nearest-neighbor forces. This calculation is quite time consuming, and, consequently, the mesh must be coarse. The mass ratio is 1:3, and the lattice is made up of $5 \times 5 \times 12$ atoms. The concentration of light atoms is approximately 0.1. It can be seen once again that high frequency peaks occur due to
Figure 32. Resonance Modes in the Simple Cubic Lattice.
Figure 33. Approximate Body-Centered Cubic Spectrum.

Figure 34. Approximate Face-Centered Cubic Spectrum.
Figure 35. Exact Frequency Spectrum of the Body-Centered Cubic Lattice.
the local modes of vibration of light impurity islands.

The results which have been described in this section are representative of the extensive calculations which have been made by the author in his detailed study of the effects of disorder on the vibrations of harmonic lattices.

5. Comparison with Other Results

It is enlightening to compare the author's results with results obtained by others. Since the major calculations of the frequency spectrum have already been discussed in Chapter I, the author will compare the frequency spectra obtained in this work with some experimental results which have been published.

Probably the earliest experimental verification of local mode peaks due to defects was by Mozer, Otnes, and Myers in 1962. Using the technique of inelastic scattering of neutrons, they were able to measure at least qualitatively a defect mode of vibration.

When low energy neutrons are scattered from a perfect crystal the one-phonon part of the differential inelastic scattering cross-section for incoherent scattering is given by

\[
\frac{\text{d} \sigma_{\text{inc}}}{\text{d} k'} = \frac{\hbar}{M k} e^{-2W} \left( \frac{k' - k}{k'} \right)^2 \left[ \frac{1}{\exp \left( \frac{\hbar \omega}{k_B T} \right) - 1} + 1 \right] g(\omega) \quad (\text{II.5.1})
\]

where
and \( M \) is the mass of the scattering atom, \( k_B \) is the Boltzmann constant, \( m \) is the mass of the neutron, \( k \) and \( k' \) are the incident and final wave vectors of the neutron, \( e^{-2W} \) is the Debye-Waller factor, and \( g(w) \) is the phonon distribution function. Equations (II.5.1) and (II.5.2) completely determine the values of \( g(w) \) since all of the other quantities are known in principle or can be determined experimentally. The calculation of the Debye-Waller factor in a disordered lattice is a difficult problem and remains the most difficult step in determining the frequency spectrum from the measured incoherent inelastic one-phonon scattering cross-sections for high concentrations of defects. The scattering experiment is difficult, and at the present time the resolution is somewhat poor. However, there are several experiments which have shown the basic structure of the frequency spectrum of a crystal with defects.

In their work Mozer, et al. used nickel-doped palladium crystals and found that the spectra of various concentrations of nickel in palladium followed a pattern in going from pure nickel to pure palladium similar to that demonstrated in the previous section. Their results show that qualitatively the transition from pure solvent to pure solute in solid solutions is as shown in Figure 5. The resolution of their experiment is not sufficient to determine any fine structure. Another problem they encountered is that palladium is primarily a coherent scatterer thus making the incoherent scattering cross-section difficult to measure.
Within the past year more experimental results have been published which shed light on the frequency spectra of disordered defect systems. One of these by Rubin, Peretti, Verdan, and Kley\textsuperscript{71} measures the defect mode of hydrogen in vanadium. Since vanadium hydride is almost totally an incoherent scatterer and the mass ratio is 51:1, one would expect from the author's results to obtain a pronounced peak due to the localized modes which is well removed from the continuum spectrum of vanadium. Putting our results into the units appropriate for vanadium one would expect the maximum of the vanadium continuum to be 30 mev (using now energy units). From calculations made by the author for body-centered cubic lattices with a mass ratio of 51:1, isotopic force constants, and a light atom concentration of approximately 1%, the peak due to modes localized around light atoms occurs at approximately 140 mev. The spectrum given by Rubin, et al. for hydrogen in vanadium shows a peak at approximately 100 mev. Since the proton in a vanadium lattice occupies a very small volume, it seems possible that it might act very much like a vacancy in causing a softening of the force constants around it.\textsuperscript{19} It would take very little softening of the force constants to reduce this peak calculated for the isotopic lattice to the experimental value found by Rubin, et al.

Another experimental result of interest is the work by Mitra and Brada.\textsuperscript{72} They investigated the infrared absorption in alkali halides containing U-centers. The U-center consists of an $\text{H}^-$ ion occupying the vacated halogen ion site. Infrared absorption due to U-center local modes has been observed also by Schaeffer.\textsuperscript{73} From the structure of the absorption spectrum found by Mitra and Brada it can be seen that the
author's spectra for such systems (Figure 29) is in qualitative agreement with the actual spectra.

The structure of the alkali halide spectra calculated by the author is in agreement qualitatively with spectra calculated by Karo and Hardy. They have calculated the spectra for the perfect alkali halide lattices using the root sampling method.

From these few examples it can be seen that the nature of the frequency spectra calculated by the author is qualitatively substantiated by experiment. Some of the agreements may be somewhat surprising since one would not expect the harmonic model used by the author to describe the spectrum of a metal. However, the agreement with hydrogen in vanadium is very close. When more accurate experiments are performed on the inert-gas solids, we will know more about the validity of the harmonic model as a description of physical systems.
III. SPECIAL FREQUENCIES

After Dean's first machine calculations of the spectra of disordered harmonic chains were reported, it became obvious that the moment trace-method was inadequate for spectrum calculations. Dean showed a posteriori that a number of peaks in the spectrum can be associated with various types of defects in otherwise ordered chains. Until late 1963 no a priori theory had been proposed which explained such irregular behavior as was found in the frequency spectrum. Matsuda attempted such an explanation using an extension of the transfer matrix method.

In his note he shows that the irregularity of the spectra is to be expected since there must be a number of special frequencies at which \( G(w^2) = 0 \) when the mass ratio is sufficiently large. Matsuda proves through a rather complex argument that in an infinite chain of isotopically disordered masses if

\[
\omega(p) = \omega_L \sin \left( \frac{p\pi}{2} \right)
\]

where \( p \) is a rational number and \( 0 < p < 1 \) with \( \omega_L \) the maximum frequency of the monatomic light atom chain, then there exists a finite critical mass ratio such that \( G(\omega(p)^2) = 0 \) for all mass ratios greater than the critical one independent of the concentration and arrangement of the atoms as long as there are islands of light atoms in the chain.

At nearly the same time but independently, Borland was also seeking an a priori reason for the complex spectra of the disordered
chain. Using a method quite similar to a basic method outlined earlier, (II.1.2) to (II.1.4), Borland showed that the integrated spectrum can be calculated analytically at a discrete set of frequencies given by

$$w^2_J = \frac{2}{m} (2 + 2 \cos (\pi/J)),$$  \hspace{1cm} (III.1)

where $J$ is an integer greater than one. With a mass ratio of two in a disordered chain the two transformations corresponding to (II.1.4) at the light atom sites and at the heavy atom sites are seen to be respectively,

$$Z_{i+1} = -\frac{1}{2 \cos \pi/J + Z_n} \quad \text{(light)}$$

$$Z_{i+1} = -\frac{1}{2 + 4 \cos \pi/J + Z_n} \quad \text{(heavy)}$$ \hspace{1cm} (III.2)

Take $J = 2$ as an example. As we have seen earlier $Z_1$ is arbitrary when the boundary conditions are rigid walls. We can for simplicity choose $0 > Z_1 > -1$ for $J = 2$. Borland shows that results are independent of this choice for $Z_1$. As we progress down the chain applying one of the equations (III.2) at each site, we can predict how many of the $Z_i$'s will be negative by the nature of the transformations. The values of $Z_i$ will always fall into two sets because of the monotonic form of $Z_{i+1}$. Let us call these sets $\{X_1\}$ and $\{X_0\}$ where $\{X_0\}$ contains all values of $Z_i$ in the interval $(0, -1)$ and $\{X_1\}$ contains all of the points in the interval $(1, \infty)$. Further let the probability of $Z_i$ being in $\{X_0\}(\{X_1\}$
be \( f_0(f_1) \). We can see that the only way to achieve \( Z_{i+1} \) in \( \{X_i\} \) is to be in \( \{X_0\} \) with \( Z_i \) and have the \( i \)th atom be a light atom. Thus the probabilities of the \( Z_{i+1} \) being in each set can be determined. We have the relations for a concentration \( \tau \)

\[
f_0 + f_1 = 1
\]

\[(III.3)\]

\[
f_1 = \tau f_0,
\]

and consequently,

\[
f_0 = \frac{1}{1 + \tau}.
\]

Now \( f_0 \) is the probability that \( Z_i \) will be negative, and thus by the negative eigenvalue theorem

\[
M\left(\omega_{J=2}^2\right) = f_0
\]

\[(III.5)\]

\[
= \frac{1}{1 + \tau}.
\]

A similar procedure for the \( J \)th squared frequency yields a result for the integrated spectrum of

\[
M\left(\omega_{J}^2\right) = \frac{1 - \tau^J}{1 - \tau^J}.
\]

\[(III.6)\]
The arguments for $J > 2$ are quite similar to the one for $J = 2$. It can easily be seen upon careful examination of equations (III.2) that this derivation is valid for all mass ratios greater than two.

These frequencies at which Borland was able to calculate the integrated spectrum are identical to the special frequencies of Matsuda. By a variation argument it can be shown that these frequencies yield zero points on the derived spectrum in accordance with Matsuda's proof.

Borland compared his values of the integrated spectrum with those computed by Dean\textsuperscript{30} and Agacy\textsuperscript{32}. The variation among the three values compared was never more than 0.2%.

Hori\textsuperscript{75} generalized the work of Matsuda to include all rational values of $p$. Letting $Q(p)$ be the critical value of the mass ratio for the frequency $w(p)$ to become a forbidden frequency, Hori has shown that the minimum of $Q(m/n)$ is given by

$$Q(m/n) = 1 + \cot \left( \frac{\pi}{2n} \right) \cot \left( \frac{m\pi}{2n} \right)$$

(III.7)

where $m$ and $n$ are integers prime to each other and $m < n$. It can be shown that the integrated spectrum, $M(w^2)$, can be obtained at any frequency $w = w(m/n)$ as long as the mass ratio is greater than or equal to $Q(m/n)$. As the mass ratio becomes infinite all frequencies become special frequencies.

In a series of articles Hori and Matsuda\textsuperscript{76} have studied the spectra of disordered systems using the method of phases. The method of phases is an extension of the transfer matrix method and becomes
quite involved in abstract terminology. This method will not be dis-
cussed here. In these papers they use a Saxon-Hutner-type theorem\textsuperscript{77} to
describe the forbidden bands. Their values derived for the special
frequencies agree with those found by others but do not account for all
of the zeros in Dean's spectra. They attribute this to machine errors
in Dean's work. The present author feels this is an invalid escape.

The shape of the spectrum near these special frequencies is of
considerable interest. Using the framework of Borland's technique and
applying a variation in the squared frequency, it can be shown that the
shape at the upper edge of the impurity band below the special frequen-
cy is exponential. The form near the \( j \)th special frequency is
\[
\exp \left[ -\frac{\sigma}{(w - w_j)^2} \right]
\] for values of \( w \) near \( w_j^2 \). The constant \( \sigma \) is de-
pendent upon the concentration and the mass ratio. This is in general
agreement with results found by Lifshitz\textsuperscript{78} in his work on the shape of
the energy spectrum near band edges. Machine calculations have been
made by the author which investigate the shape of the spectrum near
these points. The shape found in these calculations is the same as
predicted and varies with the concentration of light atoms in the chain
in a manner quite similar to that predicted analytically.

Special frequencies have been found to exist \textit{a priori} in only
one-dimensional systems. The primary reason for this limitation of the
work is obvious. All of the \textit{a priori} methods of special frequency
calculations that exist are based on techniques which are valid for
one-dimensional systems only. Extensions of the transfer matrix method
to two-dimensional systems as done by Asahi\textsuperscript{79} are not applicable to
prove anything about the existence of special frequencies in higher
dimensions. Until a more ingenious method of determining the exact frequency spectrum analytically is found, the question of a priori special frequencies in higher dimensions will remain open.

An insight into this question can be obtained on a qualitative level by investigating the physical significance of the special frequencies. In one dimension it is a well known result that the frequency of a mode localized about a light atom, M, in heavier host lattice (mass M') is a monotone decreasing function of M'/M. Thus, as long as M'/M ≥ Q(m/n) the integrated spectrum at \( w = w(m/n) \) is independent of M'/M and can be calculated as if M'/M → ∞ for which the exact treatment is feasible.\(^29\) The whole chain can be treated as a series of finite chains of light atoms of mass M. The normal mode frequencies of a chain of \( J \) atoms enclosed by rigid walls (M' = ∞) are

\[
\nu = \nu(s/J + 1), \quad s = 1, 2, \ldots, J. \tag{III.8}
\]

The number of normal frequencies not less than \( \nu((n - k)/n) \) in this island is given by \([k(J + 1)/n]\) where \([k]\) denotes the largest integer not exceeding k. Thus the integrated frequency spectrum can be written as

\[
\bar{N}(\nu^2) = 1 - M(\nu^2) = \frac{1}{N}[N(J - 1) + N(J) + \cdots + N(2J - 2)] \\
+ 2[N(2J - 1) + N(2J) + \cdots + N(3J - 2)] \\
+ 3[N(3J - 1) + N(3J) + \cdots + N(4J - 2)] \\
+ \cdots \], \tag{III.9}
\]
where $N(J)$ is the number of islands of $J$ atoms in the chain. The probability of finding a chain of $J$ light atoms embedded in the chain of heavy atoms is the probability of finding the sequence

$$-HLLL \cdots LLH-$$

This probability is simply

$$\frac{N(J)}{N} = (1 - \tau)^2 \tau^J \quad (\text{III.10})$$

where $\tau$ is the concentration of light atoms. Putting (III.10) into (III.9) we have

$$M(w_J)^2 = 1 - (1 - \tau)^2 \left\{ \tau^{J-1} + \tau^J + \cdots + \tau^{2J-2} \right. + 2[\tau^{2J-1} + \tau^{2J} + \cdots + \tau^{3J-2}] + 3[\tau^{3J-1} + \tau^{3J} + \cdots + \tau^{4J-2}] + \cdots \right\} \quad (\text{III.11})$$

This series can be summed directly and gives the result

$$M(w_J)^2 = \frac{1 - \tau^{J-1}}{1 - \tau^J} \quad (\text{III.6})$$

which is the Borland result. These special frequencies are seen to be
frequencies which are forbidden as the mass ratio is decreased from infinity to the critical value $Q(m/n)$. In this transition of the mass ratio from infinity to $Q(m/n)$ no frequencies cross the special frequencies.

To illustrate this behavior the frequencies of isolated islands in a one dimensional chain were calculated as a function of the mass ratio by the author. These are shown graphically in Figure 36. One can see that the special frequencies of Borland ($Q = 2$) that are shown on the graph correspond to the interpretation given above. In a similar manner the frequencies of some isolated islands in a square lattice are shown in Figure 37. The frequency gaps in two dimensions are not as apparent as in one dimension, and consequently, the interpretation becomes more difficult. Since a special frequency is such that no normal mode crosses it as the mass ratio is decreased from infinity to the critical ratio, it is apparent that the critical ratio in the square lattice is larger than in the linear chain. The author feels that there is no doubt that a situation similar in form to the linear chain exists in the square lattice and that special frequencies do exist in the spirit of Hori and Fukushima, i.e., there exist frequencies for which $M(w^2)$ can be calculated analytically as long as the mass ratio exceeds some critical value. At present this seems to be the most fruitful approach although the author wishes to pursue his attempts to develop an a priori analytic treatment of special frequencies in higher dimensions at some later date. The extension of this discussion to three dimensions would not uncover anything enlightening and will not be made here.
Figure 36. Frequencies of Isolated Islands in the Linear Chain.
Figure 37. Frequencies of Isolated Islands in the Square Lattice.
IV. THERMODYNAMIC PROPERTIES OF DISORDERED CRYSTALS

The most common application of the frequency spectrum is to the calculation of the thermodynamic properties of a crystal. The total energy of an eigenstate of a harmonic crystal which is specified by the set of quantum numbers \( \{n_j\} \) is

\[
E_{\{n_j\}} = \sum_j (n_j + \frac{1}{2})\omega_j \quad (IV.1)
\]

where the sum runs over the normal mode frequencies, \( \omega_j \), of the harmonic oscillator. From this the partition function of a vibrating harmonic crystal follows immediately,

\[
Z = \sum_j \exp (-\beta E_{\{n_j\}}) = \prod_l \frac{e^{-\beta \omega_l}}{1 - e^{-\beta \omega_l}} \quad (IV.2)
\]

where \( \beta = 1/k_B T \), \( k_B \) is the Boltzmann constant, and \( T \) is the absolute temperature. The principal thermodynamic quantities can be readily calculated from the partition function using the following relations:

\[
F = -k_B T \ln Z
\]

\[
E = F - T \left( \frac{\partial F}{\partial T} \right)_V
\]

(IV.3)
where $F$ is the Helmholtz free energy, $E$ is the internal energy, $C_V$ is the specific heat at constant volume, and $S$ is the entropy. Using (IV.2) and (IV.3) we have

$$F = k_B T \sum_j \ln \left\{ 2 \sinh \frac{\hbar \omega}{2 k_B T} \right\}$$  \hspace{1cm} (IV.4)

which illustrates that in the harmonic crystal the thermodynamic functions are additive functions of the normal mode frequencies. This has the consequence that these functions can all be expressed as integrals over the frequency spectrum:

$$F = r N k_B T \int_0^\infty \ln \left\{ 2 \sinh \frac{\hbar \omega}{2 k_B T} \right\} G(\omega^2) d\omega^2$$

$$E = \frac{1}{2} r N \int_0^\infty \omega \coth \frac{\hbar \omega}{2 k_B T} G(\omega^2) d\omega^2$$  \hspace{1cm} (IV.5)
\[ C_v = rNk_B \int_0^\infty \left( \frac{\hbar \omega}{2k_B T} \right)^2 \text{csch} \frac{\hbar \omega}{2k_B T} \, g(\omega^2) \, d\omega^2 \]  

\[ S = rNk_B \int_0^\infty \left[ \frac{\hbar \omega}{2k_B T} \coth \frac{\hbar \omega}{2k_B T} - \ln \left\{ 2 \sinh \frac{\hbar \omega}{2k_B T} \right\} \right] g(\omega^2) \, d\omega^2 \]  

where \( r \) is the number of degrees of freedom per unit cell and \( N \) is the number of unit cells.

Calculations using the equations (IV.5) are easily done once the frequency spectrum is known. Calculations have been made by the author for crystals of one, two, and three dimensions. Figure 38 shows the curves obtained for the thermodynamic properties of the square lattice. In (a) the specific heat at constant volume is plotted as a function of temperature in arbitrary units. In (b) the Helmholtz free energy is plotted while in (c) and (d) are plotted the internal energy and entropy respectively as a function of temperature. The arbitrary unit of temperature is such that the maximum temperature plotted in Figure 38 is approximately \( \hbar \omega_L / k \) of the light atom lattice.

In the studies of the linear chain it was discovered that in the isotopic chain the specific heats of the disordered and ordered chains with equal parts of each atom had the same values. Since this is not thought to be the physical situation, the more realistic chain whose frequency spectrum is shown in Figure 12 was used. In this chain the force constant depends upon the two atoms it joins. Figure 39 shows
(a) Specific Heat at Constant Volume

Figure 38. Thermodynamic Properties of the Square Lattice.
Figure 38. Continued.
Figure 38. Continued.
Figure 38. Continued.

(a) Entropy
Figure 39. Comparison of Specific Heats of the Ordered and Disordered Realistic Chains.
the specific heats for an ordered chain and a disordered chain with equal parts of light and heavy atoms. The force constants are in the ratio $\gamma_{AA} = \gamma_{BB} = \frac{1}{2} \gamma_{AB}$, and the mass ratio is $M_A = M_B$. The change in the specific heat is noticeable, and as one would expect, the ordered case rises faster.

A comparison of the effects on the specific heat of impurities which are lighter than the host lattice are shown in Figure 40. The lattice is a simple cubic with $6 \times 6 \times 10$ atoms. The three curves shown are for concentrations of the light atoms of 0, 0.54, and 1.0. The units are arbitrary, but consistent.

The results of isotopic lattice calculations made by the author differ markedly from results found by Bradley and Kahn. In their work they report that at some temperatures the specific heats of the ordered and disordered with the same composition of light and heavy atoms differ by as much as 20%. 
Figure 40. Comparison of Specific Heats of the Simple Cubic Lattice with Varying Impurity Concentrations.
V. ENERGY TRANSPORT IN DISORDERED HARMONIC CRYSTALS

The conduction of heat in insulating crystals is obviously carried out by the lattice vibrations. The mechanism by which this is accomplished is not so obvious. Debye\textsuperscript{82} and Peierls\textsuperscript{83} discussed the heat conduction problem and emphasized that the existence of anharmonicities in the interatomic forces is necessary to yield a finite thermal conductivity. They stressed that in the harmonic lattice energy is propagated through the lattice by travelling sound waves which have no interactions with each other. Consequently, these waves travel undiminished through the lattice, and their propagation is not dependent upon an energy gradient. The addition of anharmonicity in the interaction potential causes the waves to decay and interact; hence the independence of the energy transport from the energy gradient is destroyed. However, the mathematical complication lying in the problem of heat conduction as a higher order phenomenon seems to have impeded its development.

Recently the statistical dynamical approach to the problem of energy transport by lattice vibrations has been developed by several authors.\textsuperscript{84} Statistics is introduced only in the initial conditions, and the time evolution of the initial ensemble is completely determined by the equations of motion. Mazur and Montroll\textsuperscript{85} discussed the ergodicity and the existence of Poincaré cycles in systems of coupled harmonic oscillators. In their work they showed the existence and periods of Poincaré cycles in the linear chain, square lattice, and simple cubic lattice. They derive expressions for certain time relaxed
correlation functions between small numbers of variables. The transport coefficients (diffusion constant, electrical conductivity, and thermal conductivity) associated with irreversible processes in an assembly of particles can be expressed as integrals over these correlation functions by expressions which can be derived by the Kubo method. For example the thermal conductivity tensor \( k_{\mu\nu} \) in a three-dimensional lattice is

\[
k_{\mu\nu} = k_B \beta^2 \int_0^\infty \langle J_{\mu}(0)J_{\nu}(t) \rangle dt
\]  

(V.1)

where \( \beta = 1/k_B T \), and \( J(t) \) is the heat current density in the lattice at time \( t \). The brackets indicate an average over a canonical ensemble at time \( t = 0 \). \( J_{\mu}(t) \) can be expressed in terms of the \( \mu^{th} \) component of the momentum; consequently the ensemble average reduces to the momentum correlation function. Since the calculation of the momentum correlation function is very difficult in the disordered lattice, we will discuss other methods of investigating the energy transport in lattices.

Energy flow in the one-dimensional harmonic lattice was re-examined by Hemmer. He has shown that there exists no essential difference in the spreading velocities of dynamical and thermal disturbances in the harmonic lattice. He further demonstrates that no proportionality between energy flow and temperature gradient exists. Thus the harmonic model is incapable of describing the phenomenon of heat conduction in monatomic lattices. Interest in the harmonic model
of energy transport has grown considerably in the application of this model for disordered lattices.

Kashiwamura and Teramoto\textsuperscript{68} used an exact analytic solution of the one-defect problem in the linear chain to investigate its thermal properties. Using a chain of $2N + 1$ masses connected to nearest neighbors by springs with an impurity atom at the center, they calculated the energy flow under given initial conditions analytically. The most interesting of these was the initial condition in which the left half of the chain was given some initial kinetic temperature, $\theta_k$, defined by

$$\theta_k(i, t) = \frac{M_1}{2k_B} \langle v_i(t)^2 \rangle$$

where $\langle v_i(t)^2 \rangle$ is the average squared velocity of the $i^{th}$ particle at time $t$, and $M_1$ is the mass of the $i^{th}$ particle. The right half of the chain is clamped at zero temperature and zero displacement initially. At time $t = 0$ the right half is unclamped. The approach to stationariness was given for the two cases: (I) $Q \geq 0$ and (II) $Q < 0$ where $Q = M'/M - 1$ and $M'$ is the mass of the impurity and $M$ that of the host. In case I the impurity is heavier than the host, and the ratio of the kinetic temperatures of the left region to the right region as $t$ approaches infinity and the chain becomes long is

$$\frac{\theta_k(h)}{\theta_k(c)} = 1 + 2Q$$
where \( h \) and \( c \) denote the hot and cold regions. For case II the ratio is

\[
\frac{\theta_k(h)}{\theta_k(c)} = 1 - 2|Q|.
\]  

(V.4)

Using the equations of motion of the linear chain with nearest neighbor interactions and the initial condition given above, the author has calculated the ratio in (V.3). To simulate the infinite chain the ends of a finite chain were immersed in a temperature bath which to a large extent prevented reflections of waves. The value found by the author for case I where \( Q = 2 \) was approximately \( \theta_k(h)/\theta_k(c) = 4.7 \). The difference being due to the finiteness of the system even with the temperature baths. In case II the temperatures oscillate as predicted by Kashiwamura and Teramoto, and this ratio could not be determined accurately.

In a more general problem Rubin has studied the effects of disorder on the energy flow in a linear harmonic chain. He defines the local microscopic temperature as

\[
T_j(t) = \frac{1}{kM_j} \langle p_j(t)^2 \rangle
\]  

(V.5)

where \( \langle p_j(t)^2 \rangle \) is the thermal ensemble average of the dispersion of the Gaussian distribution of particle \( j \) at time \( t \). In a chain in which the center \( 2L + 1 \) atoms are initially at a temperature \( T_h \) and the remaining atoms outside this region are clamped, Rubin proves that
where \( j \) is in the hot region and \( \mathcal{E}[j \to j, t] \) is just the energy content of the region of \( 2L + 1 \) atoms at time \( t \) for the special initial value problem where all of the displacements are initially zero and all of the momenta are zero except the momentum of the center atom which is

\[
P_{\text{center}} = M_{\text{center}}^\frac{3}{2}.
\]  

(V.7)

Thus the statistical problem has been reduced to a simple dynamical problem. Rubin finds for the monatomic chain that

\[
\frac{T_j(t)}{T_h} \sim \frac{2}{\pi^L_L}
\]

(V.8)

where \( \tau_L \) is the time in units of the time taken by a signal moving with the group velocity of very long waves to travel from the site zero to site \( L \).

Rubin then carries out the same calculation numerically using a disordered chain. He finds that the temperature curves do not drop as rapidly as the monatomic chain, and as the mass ratio of the two masses in the chain increases, the temperature drops less and less. The interpretation of this is simple. As the mass ratio increases the local modes become more localized. The initial condition used by Rubin to find \( \mathcal{E}[j \to j, t] \) can be expanded in normal modes of the disordered crystal,
\[ M_i \frac{d}{dt} x_i = \frac{d}{dt} \sum_{i=0}^{\infty} \delta_{i,0} -N \leq i \leq N \]

\[ = \frac{d}{dt} \sum_{\text{all } w} C_{iw} u_w \]

where the \( u_w \) are the normal mode coordinates. In this expansion of the Kronecker delta the long wavelength modes will play a negligible part because of the extreme locality of the delta function. Consequently, the values of the coefficients, \( C_{iw} \), will be very small except for large \( w \) (in the local mode region), and mostly local modes will be included in the expansion. Thus, when the one atom is excited initially only the local modes are excited. Once a local mode is excited in the harmonic lattice, it cannot decay since no mechanism exists to cause it to decay. Hence, there is very little energy flow out of the hot region.

Figure 41 shows the results of some calculations by the author using Equation (V.6) to show the cooling of the center of a hot region in a cold chain. The examples of the monatomic chain and the disordered chain with mass ratio 3:1 with equal amounts of each mass are similar to results found by Rubin. The other cooling curves demonstrate the effect of changing the concentration of light atoms, changing the mass ratio, and ordering the chain.

It is somewhat interesting to compare the cooling of the monatomic chain to the cooling of a one-dimensional rod with the initial temperature distribution given by
Figure 41. Cooling Curves of the Linear Harmonic Chain.
\[
T(x,0) = \begin{cases} 
0, & x < -L \\
T_h, & -L \leq x \leq L \\
0, & L < x
\end{cases}
\] (V.10)

The solution of this boundary value problem yields an asymptotic solution of the reduced temperature for large values of time

\[
T(0,t)/T_h \sim \frac{L}{\frac{1}{\eta}} \frac{1}{(2Dt)^{3/2}}
\] (V.11)

where \(D\) is proportional to the thermal conductivity. This expression is quite different from (V.8).

The addition of anharmonicities to the interaction potential should not be difficult with a program presently being worked on by the author and his associates at Los Alamos. The results of these calculations could prove quite interesting in investigating the energy transport in real systems.
VI. SUMMARY

In the present work the author has adapted a method developed by Dean based on Sturm's theorem to investigate the frequency spectra of complex disordered one-dimensional lattices. In his work Dean studied the binary isotopically disordered chain and glass-like chains. The author has calculated the frequency spectra for these systems as a check and has extended the method to more complex systems. Some of the more interesting of these are the systems with continuous mass distributions, ternary chains, chains of the mixed diatomic form, and chains with "realistic" bonds. The primary feature of the results is the complexity of structure of the frequency spectrum. It can certainly be said that the moment trace method does not give an accurate frequency spectrum for the disordered lattice. Only in the chains in which the force constants or masses were allowed to vary continuously and randomly did the frequency spectrum appear smooth. In random binary isotopic chains the special frequencies were observed and the behavior of the spectrum near them was investigated. It was found to be of the form predicted by Lifshitz for the band edges. The form of the normal modes of random chains has been investigated, and the complex structure of the frequency spectrum at larger values of $w^2$ is due to modes localized within light atom islands embedded in a heavier host chain.

Using the negative eigenvalue theorem, the spectrum of the square lattice obtained by Dean and Bacon was corroborated. Once again the frequency spectrum obtained for a random binary isotopic square lattice exhibits the smooth continuum of the monatomic heavy atom lattice with
the spectrum becoming a complex series of peaks at higher values of the squared frequency. By calculating the exact normal modes of these disordered lattices the peaks were found to be due to modes localized about impurity islands.

The triangular lattice was calculated using the same technique. The continuum of the host lattice appears at low frequencies with isolated peaks due to local modes of light impurity islands at higher frequencies outside the host lattice band. The equations of motion displayed show that the two directions of motion of the atoms cannot be separated, and consequently, the calculation of the frequency spectrum becomes more tedious.

The extension of the method to cubic lattices has been made by the author with the resulting frequency spectra conforming to expectations. The spectra of the simple cubic, the body-centered cubic, and the face-centered cubic lattices in the random binary isotopic system all contain the host lattice continuum with peaks at frequencies above the continuum. In the simple cubic lattice the normal modes were calculated to investigate the nature of these high frequency peaks. They were found to be due to the modes localized within light atom impurity islands. This peaked structure becomes relatively smooth as the critical percolation concentration is approached.

Comparisons have been made with other calculations and with experimental determinations of the frequency spectra. The qualitative nature of the spectrum of the binary isotopic system has recently been corroborated using inelastic neutron scattering on a system of hydrogen in vanadium.
A discussion of the special frequencies and their physical significance has been given with evidence suggesting the existence of special frequencies in higher-dimensional systems.

The frequency spectra calculated by the author have been employed to calculate the thermodynamic properties of disordered harmonic crystals. A comparison of the ordered and disordered chains with "realistic" force constants shows a change in the specific heat at constant volume as the crystal passes from the disordered to the ordered phase.

Finally, the dynamical properties of disordered harmonic chains have been discussed in the context of energy transport. It was found that in the random binary isotopic chain energy flow cannot occur because of the infinite lifetime of the local modes in the harmonic chain. However, in the one defect problem results were found to be in agreement with earlier analytical results. It was demonstrated that the addition of an anharmonic term in the interaction potential is necessary to study the thermal conductivity of a disordered chain.
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APPENDIX

DIMENSION A(N+1,N+1),P(MN),GM(MI),GM(MI),Y(2*M+1),
1X(2*M+1),Y(N)

FORTRAN IV CODE FOR CALCULATING THE FREQUENCY SPECTRUM
OF A SQUARE LATTICE OF N X M ATOMS AT Ml POINTS
THE DIMENSIONS GIVEN ARE SYMBOLIC AND MUST BE STATED
NUMERICALLY. IN THIS CODE THE FOLLOWING DEFINITIONS APPLY:
A IS THE SUBMATRIX OF THE DYNAMICAL MATRIX WITH WHICH
WE WORK (SEE REFERENCE 44 OF THIS REPORT), P IS THE SEQUENCE
OF MASSES, GM IS THE SEQUENCE OF SQUARED FREQUENCIES AT
THE MESH POINTS, GM IS THE ARRAY OF VALUES OF THE INTEGRATED
SPECTRUM AT THE MESH POINTS, YI IS THE ARRAY CONTAINING
THE VALUES OF THE DERIVED SPECTRUM AT THE MESH POINTS
FOR PLOTTING PURPOSES, X1 IS THE ARRAY OF VALUES OF THE
SQUARED FREQUENCY FOR PLOTTING THE HISTOGRAM, AND Y IS
THE Y-VECTOR OF EQUATION (11.3.13).

1 READ 2,PL,PM,CC,CNC,FA,GNUMA,GNUMI,N,M,MI,JR
2 FORMAT(10.5/4110)

READ THE FOLLOWING INPUT DATA: PL AND PM ARE THE LIGHT
AND HEAVY MASSES RESPECTIVELY, CC AND CNC ARE THE CENTRAL
AND NON-CENTRAL FORCE CONSTANTS, FA IS THE CONCENTRATION
OF LIGHT ATOMS, GNUMA AND GNUMI ARE THE UPPER AND LOWER
VALUES OF THE SQUARED FREQUENCY FOR WHICH THE SPECTRUM
IS TO BE CALCULATED, N IS THE WIDTH OF THE LATTICE, M
IS THE LENGTH OF THE LATTICE, MI IS THE NUMBER OF MESH
POINTS TO BE CALCULATED, AND JR DETERMINES THE STARTING
POSITION IN THE RANDOM SEQUENCE.

READ 1000, SI
1000 FORMAT(1E10,-5)

READ THE SHORT RANGE ORDER PARAMETER, SI.

MN=M*N
FMN=MN
CALL CHAGEN(MN,PL,PM,FA,JR,SI,P)

GENERATE THE MASS SEQUENCE IN A SUBROUTINE.

FM1=M1
DGNU=(GNUMA-GNUMI)/FM1
GNU=GNUMI+DGNU

GNU IS THE SQUARED FREQUENCY.

MW=4.0*(CC+CNC)/PL
C HW IS USED IN PLOTTING THE RESULTS.
C
NP=N+1
C
BEGIN THE CALCULATIONAL MESH LOOP.
C
DO 100 L=1,MI
IF(GMIL-L.LE.1.E-10) GO TO 101
C
IF WE HAVE ACCOUNTED FOR ALL OF THE FREQUENCIES (N=1.0),
C OMIT CALCULATIONS, INITIALIZE THE REMAINING VALUES, AND
C GO TO OUTPUT.
C
DEFINE THE ORIGINAL UPPER LEFT (N+1)x(N+1) BLOCK MATRIX.
C
DO 10 J=1,NP
DO 10 I=1,NP
IF(I-J)11,12,13
11 IF(I-J+1)14,17,15
14 IF(I-J-N)15,16,15
15 A(I,J)=0.0
GO TO 10
16 JM=N-J-1
A(I,J)=-CC/SQRT(P(I)*P(JMN))
GO TO 10
17 A(I,J)=-CC/SQRT(P(I)*P(J-1))
GO TO 10
12 A(I,J)=(2.0*CC+2.0*CNC1/P(I)-GNU
GO TO 10
13 IF(I-J-1)15,18,19
18 A(I,J)=-CC/SQRT(P(I)*P(I-1))
GO TO 10
19 IF(I-J-N)15,20,15
20 IMN=I-N
A(I,J)=-CC/SQRT(P(I)*P(IMN))
10 CONTINUE
MGNU=1

C MGNU IS THE NUMBER OF NEGATIVE EIGENVALUES OF X IN
C EQUATION (II.3.12).
C
IF(A(1,1))21,22,22
21 MGNU=MGNU+1
22 A11=A(1,1)
MMN1=MN-1
C
BEGIN THE GAUSSIAN ELIMINATION OF EQUATION (II.3.12).
C
DO 23 JT=2,MN
DO 70 J=1,N
Y(J)=A(1,J+1)
70 CONTINUE
DO 72 J=1,N
A11=AJ(J+1)-Y(J)*Y(J)/A11
72 CONTINUE
IF(JT=MN+1)75,76,76
75 DO 27 I=1,N
IF(I-I)28,29,28
29 JTPN=JT+N
A(N+1)=CC/SQRT(P(JTPN)*P(JT))
GO TO .27
28 IF(I-N)30,31,30
30 A(N+1,J)=0.0
GO TO .27
31 JTPN=J+1
JPNM1=JTPN-1
A(N+1,J)=CNC/SQRT(P(JTPN)*P(JPNM1))
27 CONTINUE
DO 32 J=1,N
IF(J-1)34,33,34
33 JTPN=J+1
A(N+1,J)=CC/SQRT(P(JTPN)*P(JT))
GO TO 32
34 IF(J-N)35,36,35
35 A(N+1,J)=0.0
GO TO 32
36 JTPN=J+1
JPNM1=JTPN-1
A(N+1,J)=-CNC/SQRT(P(JTPN)*P(JPNM1))
32 CONTINUE
JTPN=J+1
A(N+1,J)=(2.0*CNC+2.0*CC)/P(JTPN)-GN
GO TO 77
76 DO 78 I=1,NI
A(I,N+1)=0.0
78 CONTINUE
DO 79 J=1,N
A(N+1,J)=0.0
79 CONTINUE
77 IF(A(N+1,1))73,74,74
73 CONTINUE
74 ALL=A(I,1)
23 CONTINUE
C
THE GAUSSIAN ELIMINATION PROCEDURE IS COMPLETE AND
C MGNU CONTAINS THE NUMBER OF NEGATIVE ELEMENTS IN THE
C SERIES OF UPPER LEFT MEMBERS OF THE EQUATION (11.3.12).
C
GN(L)=GNU
GN(L)=GNU
GN(L)=GNU/FMN
GNU=GNU+DGNU
GO TO 100
101 GN(L)=1.0
GN(L)=GNU
GNU=GNU+DGNU
100 CONTINUE
C
C CALCULATE THE ACTUAL CONCENTRATION OF LIGHT ATOMS (AFA).
C
LP=0
DO 52 J=1,MN
IF(P(J))51,51,52
51 LP=LP+1
52 CONTINUE
FLP=LP
AFA=FLP/FMN
C
C PLOT THE INTEGRATED FREQUENCY SPECTRUM ON MICROFILM.
C
CALL ADVCU
CALL LINCNT(32)
WRITE(12,40)
40 FORMAT(8H M(GNU))
CALL LINCNT(59)
WRITE(12,41)
41 FORMAT(60X22H FREQUENCY SQUARED=GNU)
CALL LINCNT(2)
WRITE(12,42)
42 FORMAT(60X15H SQUARE LATTICE)
CALL LINCNT(60)
WRITE(12,43) PL,PM,CC,CNC
43 FORMAT(60X15H FREQUENCY SQUARE=GNU)
CALL LINCNT(61)
WRITE(12,44)DGNU, JR, N, M, FA
44 FORMAT(60X15H SQUARE LATTICE OF15, 2X11H LATTICE OF15,
23H BY15, 6H ATOMS3X4H FA=1PE10.3)
CALL LINCNT(62)
WRITE(12,45) AFA
45 FORMAT(60X11H ACTUAL FA=1PE10.3)
CALL DLNLN(MW,10)
CALL SLLIN(10,03)
CALL SHLIN(MW,02)
CALL PLOTCGN,1,GM1,1,42,1)
C
PRINT THE VALUES OF THE INTEGRATED FREQUENCY SPECTRUM.
C
PRINT 47
47 FORMAT(1H1)
PRINT 42
PRINT 43,PL,PM,CC,CNC
PRINT 44,DGNU, JR, N, M, FA
PRINT 61, AFA
PRINT 46
46 FORMAT(44X4H GNU,8X2H,M 6X))
PRINT 45,((GN(L),GM(L)),L=1,M)
45 FORMAT(1P8El2.3)
C
CALCULATE THE DERIVED SPECTRUM IN HISTOGRAM FORM.
C
Y1(1)=GM(1)
Y1(2)=Y1(1)
Y1M=0.0
X1(1)=GNUMI
X1(2)=GN(1)
X1(3)=GN(1)
DO 50 K=2,M
50 K1=2*K
Y1(K1)=GM(K)-GM(K-1)
K1M=K1-1
Y1(K1M)=Y1(K1)
X1(K1M)=GN(K)
KIP=K1M
50 X1(K1P)=GN(K)
M2=2*K1M+1
Y1(M2)=0.0
M3=2*K1M
X1(M2)=X1(M3)
NORMALIZE THE DERIVED SPECTRUM AND FIND THE MAXIMUM VALUE FOR PLOTTING PURPOSES.

DO 1001 I=1,M2
   Y1(I)=Y1(I)/DGNU
   IF(Y1(I).GT.Y1M) Y1M=Y1(I)
1001 CONTINUE

C PLOT THE DERIVED SPECTRUM ON MICROFILM.

CALL ADV(1)
CALL LINCNT(2)
WRITE(12,42)
CALL LINCNT(32)
WRITE(12,60)
60 FORMAT(8H DGNU))
CALL LINCNT(59)
WRITE(12,41)
CALL LINCNT(60)
WRITE(12,43)PL,PM,CC,CNC
CALL LINCNT(61)
WRITE(12,44)DGNU,JK,N,M,FA
CALL LINCNT(62)
WRITE(12,61)AFA
CALL UGA(120,980,50,910,DGNU,GNUMA,Y1M,0.0)
CALL DLNLNMW,10)
CALL SLLIN(10,03)
CALL SLLIN(MW,02)
CALL PLOT(M2,X1,1,Y1,1,42,1)

C PRINT THE VALUES OF THE DERIVED SPECTRUM.

PRINT 42
PRINT 43,PL,PM,CC,CNC
PRINT 61,AFA
PRINT 44,DGNU,JK,N,M,FA
PRINT 63
63 FORMAT(4X 4H GNU,8X 2H,0 6X))
PRINT 62,(X1(K),Y1(K)),K=1,M3)
62 FORMAT(1P8E12.3)

C READ THE INPUT DATA FOR THE NEXT SPECTRUM TO BE CALCULATED.

GO TO 1

END
SUBROUTINE CHAGE(MN, PL, PM, FA, JR, SI, PI)

GENERATOR OF MASS SEQUENCES WITH SHORT RANGE ORDER.

VARIABLES ARE THE SAME AS IN MAIN PROGRAM.

DIMENSION P(MN)

DO 1 JU=1, JR

1 R=RANDOM(T)
P(J)=PL

DO 3 J=2, MN
R=RANDOM(T)
JM=J-1
IF(P(JM)-PM) .LT. 0.1, 81, 82

41 PAA=FA*(1.0-SI)
IF(PAA-R) .LT. 0.1, 81, 82

81 P(J)=PM
GO TO 3

82 P(J)=PL
GO TO 3

42 PBB*(1.0-FA)*(1.0-SI)
IF(PBB-R) .LT. 0.1, 83, 84

83 P(J)=PL
GO TO 3

84 P(J)=PM
GO TO 3

3 CONTINUE
RETURN
END
VITA

The author was born on July 2, 1940, at Lamar, Missouri, was graduated from Lamar High School in 1958, and was graduated from the University of Missouri School of Mines and Metallurgy with the degree of Bachelor of Science in Physics in 1962. He entered the graduate school of the University of Missouri School of Mines and Metallurgy in September, 1962, under the aegis of a National Defense Education Act Fellowship. During the course of his undergraduate training he was awarded a National Merit Scholarship and a National Science Foundation Undergraduate Research Scholarship. The author completed his research under an Associated Midwest Universities Fellowship at the University of California, Los Alamos Scientific Laboratory.

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