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Spectral Density Functions for Disordered Systems

Dennis Gene Hall

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NOTES
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A dissertation presented to the Graduate Council of The University of Tennessee in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

This work describes a Monte Carlo calculation of the spectral density function $A(k,E)$ for a one-dimensional model of an amorphous solid. The model contains an adjustable short-range order parameter and $A(k,E)$ is obtained for several values of that parameter. The Hamiltonians considered are: (1) the Hamiltonian describing an electron moving in a potential consisting of randomly placed delta functions, (2) the Hamiltonian describing a system of coupled harmonic oscillators, and (3) a tight-binding Hamiltonian describing in a simplified way either electrons or spin-waves.

A major aim of the present work was to apply the insight gained from this numerical calculation to interpret the qualitative features of recent neutron scattering data on amorphous systems. In the absence of a reliable theory of elementary excitations in structurally disordered systems, model calculations become extremely important in pointing out the properties to be expected of such systems. The spectral density $A(k,E)$ is a particularly important quantity in this regard since $A(k,E)$ gives the single-particle contribution to the dynamic form factor of neutron scattering theory.

As another application of the model calculation, the spectral density is obtained in the quasicrystalline approximation (QCA) for the problem of an electron in a one-dimensional liquid metal. The QCA and exact spectral densities are compared and it is shown that the QCA fails in the strong scattering regime.

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CHAPTER I

INTRODUCTION

Throughout the history of Solid State Physics, the ordered crystal has played the central role in both theoretical and experimental investigations. There is, however, a growing interest in systems such as liquid metals and amorphous solids for which disorder is a fundamental concept. Disorder can be categorized as substitutional, structural, or a combination of the two. Substitutional disorder is characteristic of the binary alloy $A_x B_{1-x}$ in which A-atoms and B-atoms are randomly distributed on the sites of a periodic lattice. Even in a perfectly random system there will be clusters of A-atoms, clusters of B-atoms, and so on, but these tendencies can be accentuated if short-range order exists. Structural disorder is typical of an amorphous solid or a liquid metal in which the atomic sites are randomly distributed. Local correlations of the atomic positions must be present at least to the extent necessary to prevent overlap of the atomic sites.

In attempting to predict the properties of the electronic excitations in disordered systems, the inherent lack of symmetry presents a formidable theoretical problem. A suitable approximation which adequately describes the electronic properties of substitutional binary alloys in the

absence of short-range order, the coherent potential approximation, was found in 1967. No approximation has yet proven successful in describing the properties of systems with structural disorder where the inclusion of the effects of short-range order is essential.

The present work describes a numerical investigation of the properties of elementary excitations in a one-dimensional model of a structurally disordered system. The spectral density function $A(k,E)$, related to the imaginary part of the single-particle Green's function, has been calculated for several Hamiltonians. $A(k,E)$ describes the probability of finding a single-particle excitation with energy E and wavenumber k . This k -dependence makes the spectral density particularly sensitive to the effects of structural disorder. In the absence of a reliable theory for excitations in such systems as amorphous solids and liquid metals, numerical investigations become the only means available for interpreting experimental results. It is the principal aim of this work to apply the insight gained from the model calculations to recent neutron inelastic scattering measurements of the magnetic excitations in an amorphous ferromagnet. The calculations in Chapter III lead to a reasonable conclusion regarding these magnetic excitations as well as a prediction of the properties of vibrational excitations in an amorphous solid. The second aim of this

work is a comparison of the exact results with $A(k,E)$ obtained in the quasicrystalline approximation (QCA). This comparison points out the failure of the approximation in the strong-scattering regime and is described in Chapter 1.

This chapter will describe the efforts in the theory of electronic excitation in disordered systems. Part A will be devoted to a discussion of the coherent-potential approximation for binary alloys. Part B will demonstrate how structural disorder is incorporated into theories of electronic excitations in liquid metals. Part C will consider numerical investigations.

A. Substitutional Disorder: The Binary Alloy

Modern theories of the electronic properties of disordered systems are generally formulated in terms of Green's functions. The Green's function $G^{\pm}(\vec{r}, \vec{r}'; E)$ is a solution of the equation

$$(E - H \mp i\eta) G^{\pm}(\vec{r}, \vec{r}'; E) = \delta(\vec{r} - \vec{r}'), \quad \text{I.A.1}$$

where H is the Hamiltonian:

$$H = -\frac{\hbar^2}{2m} \nabla^2 + \sum_{n=1}^N V_n(\vec{r} - \vec{R}_n), \quad \text{I.A.2}$$

with V_n the potential for the ion at site n and η is a

positive infinitesimal. Upon introducing the exact eigenstates $\psi_n(\vec{r})$ of the Hamiltonian with eigenvalues E_n , $G^\pm(\vec{r}, \vec{r}'; E)$ can be written

$$G^\pm(\vec{r}, \vec{r}'; E) = \sum_n \frac{\psi_n(\vec{r}) \psi_n^*(\vec{r}')}{E - E_n \mp i\eta}. \quad \text{I.A.3}$$

It is more convenient to work with the propagator, or resolvent,

$$G(z) = (z - H)^{-1}, \quad \text{I.A.4}$$

defined such that

$$G^\pm(\vec{r}, \vec{r}'; E) = \langle \vec{r} | G(z) | \vec{r}' \rangle, \quad \text{I.A.5}$$

with $z = E \mp i\eta$. Both the Green's function and the resolvent defined above contain explicit dependence upon the arrangement of atoms in a particular system. The quantity of interest is the configuration averaged Green's function, or the configuration averaged resolvent, denoted by $\langle G^\pm(\vec{r}, \vec{r}'; E) \rangle$, or $\langle G(z) \rangle$, where $\langle \dots \rangle$ denotes an average over all configurations in the statistical ensemble.

A history of the developments in the theory of the electronic properties of binary alloys has been given by Faulkner (1) and will not be repeated here. The most successful approximation used in the alloy problem has been

the coherent potential approximation (CPA) of Soven (2). The CPA has been discussed by Velicky, Kirkpatrick, and Ehrenreich (3) and has been successfully applied to real systems by Stocks, Williams, and Faulkner (4, 5, 6). In attempting to calculate $\langle G(z) \rangle$ it is assumed that there exists an effective Hamiltonian H_{eff} such that

$$\langle G(z) \rangle = (z - H_{\text{eff}})^{-1}, \quad \text{I.A.6}$$

with H_{eff} an unknown quantity. Let K be some starting approximation to H_{eff} . The propagator associated with K is then

$$R(z) = (z - K)^{-1}. \quad \text{I.A.7}$$

Using the operator identity

$$(A - B)^{-1} = A^{-1} + A^{-1}B(A - B)^{-1}, \quad \text{I.A.8}$$

with $A = z - K$ and $B = H_{\text{eff}} - K$ gives

$$\langle G(z) \rangle = R(z) + R(z) (H_{\text{eff}} - K) \langle G(z) \rangle. \quad \text{I.A.9}$$

Similarly, Eq. I.A.8 with $A = z - K$ and $B = H - K$ gives

$$G(z) = R(z) + R(z) (H - K)G(z). \quad \text{I.A.10}$$

Defining the T-matrix for the system such that

$$T(K)R(z) = (H - K)G(z), \quad \text{I.A.11}$$

one can write

$$G(z) = R(z) + R(z)T(K)R(z), \quad \text{I.A.12}$$

with $T(K)$ satisfying the equation

$$T(K) = (H - K) + (H - K)R(z)T(K). \quad \text{I.A.13}$$

Eq. I.A.12 can be used to establish a relationship between $\langle G(z) \rangle$ and $\langle T(K) \rangle$

$$\langle G(z) \rangle = R(z) + R(z) \langle T(K) \rangle R(z). \quad \text{I.A.14}$$

Combining Eqs. I.A.6, I.A.7, and I.A.14 gives

$$H_{\text{eff}} = K + \langle T(K) \rangle \{1 + R(z) \langle T(K) \rangle\}^{-1}. \quad \text{I.A.15}$$

This equation demonstrates that the self-consistent solution $H_{\text{eff}} = K$ would be obtained if K were defined such that

$$\langle T(K) \rangle = 0. \quad \text{I.A.16}$$

No approximations have been made up to this point. However, Eq. I.A.16 is not particularly helpful as the T -matrix for the complete system is not known.

In an effort to relate the condition expressed in Eq. I.A.16 to single-site operators, let us make the assumption that $(H - K)$ can be written as a sum of the site quantities $V_n(\vec{r} - \vec{R}_n) = V_n$. That is, assume

$$H - K = \sum_n V_n. \quad \text{I.A.17}$$

Combining this assumption with Eq. I.A.11 gives the equation

$$\sum_n V_n G(z) = T(K) R(z), \quad \text{I.A.18}$$

or, with Eq. I.A.12,

$$T(K) = \sum_n V_n \{1 + R(z) T(K)\}. \quad \text{I.A.19}$$

Introducing the quantities $Q_n(K)$ and $t_n(K)$ such that

$$T(K) = \sum_n Q_n(K), \quad \text{I.A.20}$$

and

$$t_n(K) = \{1 + V_n R(z)\}^{-1} V_n, \quad \text{I.A.21}$$

the single-scattering matrix for the potential V_n (note that t_n obeys the relation $t_n = V_n + V_n R(z) t_n$, a result which will be used later) an expression can be developed relating $T(K)$ to contributions from single-sites. Setting

$$\begin{aligned} Q_n(K) &= V_n \{1 + R(z) T(K)\} \\ &= V_n \{1 + R(z) Q_n(K) + R(z) \sum_{m \neq n} Q_m(K)\}, \end{aligned} \quad \text{I.A.22}$$

and rearranging terms yields

$$T(K) = \sum_n t_n(K) \{1 + R(z) \sum_{m \neq n} Q_m(K)\}. \quad \text{I.A.23}$$

Iteration of the above equation results in the series

$$T(K) = \sum_n t_n(K) + \sum_n t_n(K) R(z) \sum_{m \neq n} t_m(K) \\ + \sum_n t_n(K) R(z) \sum_{m \neq n} t_m(K) R(z) \sum_{l \neq m} t_l(K) + \dots$$

I.A.24

as first given by Edwards (7).

At this point, the approximation is made that the average of the product in Eq. I.A.23 may be replaced by the product of the averages,

$$T(K) = \sum_n \langle t_n(K) \rangle \{1 + R(z) \sum_{m \neq n} \langle Q_m(K) \rangle\}. \quad \text{I.A.25}$$

The terms neglected in writing Eq. I.A.25 are

$$\langle t_n(K) R(z) \sum_{m \neq n} \{Q_m(K) - \langle Q_m(K) \rangle\} \rangle, \quad \text{I.A.26}$$

and include the statistical correlations between site n and all other sites. In Eq. I.A.25, the wave incident on site n contains no information about the actual configuration surrounding site n . By noting that $T - Q_n = \sum_{m \neq n} Q_m$, Eq. I.A.25 becomes

$$\langle T(K) \rangle = \sum_n \{1 + \langle t_n(K) \rangle R(z)\}^{-1} \langle t_n(K) \rangle \{1 + R(z) \langle T(K) \rangle\},$$

I.A.27

and inserting this into Eq. I.A.15 gives the result

$$H_{\text{eff}} = K + \sum_n \langle t_n(K) \rangle \{1 + R(z) \langle t_n(K) \rangle\}^{-1}. \quad \text{I.A.28}$$

Within the approximation that correlations between scatterers can be neglected, the self-consistent solution $H_{\text{eff}} = K$ is obtained by determining K from the equation

$$\langle t_n(K) \rangle = 0. \quad \text{I.A.29}$$

For a binary alloy, the site n is occupied by an A-atom or a B-atom and the condition expressed in Eq. I.A.29 becomes

$$c_A t_A(K) + c_B t_B(K) = 0, \quad \text{I.A.30}$$

where c_A and c_B are the (known) concentrations of A-atoms and B-atoms, respectively. After solving for K , which may not be a simple task, $R(z)$ can be formed and is now equal to $\langle G(z) \rangle$. From $\langle G(z) \rangle$, the density of states $\langle \rho(E) \rangle$ and related quantities are obtained. For example,

$$\langle \rho(E) \rangle = - \frac{1}{\pi} \text{ImTr} \langle G(z) \rangle, \quad \text{I.A.31}$$

where the abbreviation Tr indicates the trace of a matrix.

The CPA is a single-site approximation. The physical content of the approximation lies in the replacement of the actual disordered system by an effective medium. The medium is characterized by a coherent potential which does not depend upon the atomic sites or what occupies those sites,

but does depend upon the energy. The medium is determined from the condition that if that part of the coherent potential associated with the site n is removed and replaced by an actual constituent of the system (an A-atom or a B-atom) there should be no additional scattering introduced on the average. The CPA is a self-consistent approximation in the sense that the resolvent describing propagation of a wave in the effective medium is the actual $\langle G(z) \rangle$ which itself depends upon the medium in question.

Efforts have been made by several authors to go beyond the single-site approximation to describe scattering by pairs and higher configurations. A recent numerical investigation by Nickel and Butler (8) has demonstrated the existence of nonanalyticities in $\langle G(z) \rangle$ calculated from various multi-site schemes. They suggest that nonanalyticity may be a general feature of higher-order self-consistent approximations and such approximations should be treated with caution until their analytic properties are fully appreciated.

B. Structural Disorder

The problem of describing the properties of electronic excitations in structurally disordered solids and liquid metals is considerably different from the alloy problem described above. It is necessary to include at some stage

of the calculation an appropriate description of the statistical correlations of the scattering centers. The paragraphs which follow provide a synopsis of several theoretical attempts at incorporating short-range order into a theory of the electronic properties of a liquid metal.

The Hamiltonian under consideration is of the same form as that given in Eq. I.A.2 and for convenience let

$$H_0 = \frac{\hbar^2}{2m} \nabla^2. \quad \text{Defining } G(z) = (z - H)^{-1} \text{ and } G_0(z) = (z - H_0)^{-1}$$

one can write the average propagator $\langle G(z) \rangle$ in terms of an average T-matrix

$$\langle G(z) \rangle = G_0(z) + G_0(z) \langle T \rangle G_0(z), \quad \text{I.B.1}$$

as in Eq. I.A.14. The notation $\langle T \rangle$ means

$$\langle T \rangle = \int T(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N) P(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N) d^3R_1 d^3R_2 \dots d^3R_N, \quad \text{I.B.2}$$

where $P(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N) d^3R_1 d^3R_2 \dots d^3R_N$ gives the probability that N ions will be centered at $\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N$ within $d^3R_1 d^3R_2 \dots d^3R_N$. In Eq. I.B.2, the dependence of the T-matrix upon the ion positions has been made explicit. As in Eq. I.A.20, the T-matrix is written as a sum of single-site contributions $T = \sum_{\alpha} Q_{\alpha}$. Eq. I.B.2 becomes

$$\langle T \rangle = \sum_{\alpha} \int Q_{\alpha}(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N) P(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N) \prod_{j=1}^N d^3R_j. \quad \text{I.B.3}$$

The conditional probability $P(\vec{R}_\alpha | \vec{R}_1, \dots, \vec{R}_{\alpha-1}, \vec{R}_{\alpha+1}, \dots, \vec{R}_N)$ gives the probability of finding the remaining $N-1$ scatterers if the one at $\vec{R}_\alpha$ is held fixed, and is given by

$$P(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N) = P(\vec{R}_\alpha) P(\vec{R}_\alpha | \vec{R}_1, \dots, \vec{R}_{\alpha-1}, \vec{R}_{\alpha+1}, \dots, \vec{R}_N), \quad \text{I.B.4}$$

where

$$P(\vec{R}_\alpha) = \int P(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N) \prod_{j \neq \alpha} d^3 R_j. \quad \text{I.B.5}$$

Defining $\langle Q_\alpha \rangle_\alpha$ to be the conditional average of Q_α

$$\langle Q_\alpha \rangle_\alpha = \int Q_\alpha(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N) P(\vec{R}_\alpha | \vec{R}_1, \dots, \vec{R}_{\alpha-1}, \vec{R}_{\alpha+1}, \dots, \vec{R}_N) \prod_{j \neq \alpha} d^3 R_j, \quad \text{I.B.6}$$

Eq. I.B.3 can be written

$$\langle T \rangle = \sum_\alpha \int \langle Q_\alpha \rangle_\alpha P(\vec{R}_\alpha) d^3 R_\alpha. \quad \text{I.B.7}$$

Since each site in the system is equivalent, the sum over α contributes a factor of N . The probability of finding a single ion is the same for all $\vec{R}_\alpha$ and Eq. I.B.7 reduces to

$$\langle T \rangle = NP(\vec{R}) \int \langle Q_\alpha \rangle_\alpha d^3 R_\alpha = n \int \langle Q_\alpha \rangle_\alpha d^3 R_\alpha, \quad \text{I.B.8}$$

with n the mean density.

To calculate $\langle T \rangle$, one needs a means of evaluating the restricted average $\langle Q_\alpha \rangle_\alpha$. Recalling Eq. I.A 23, Eq. I.B.6 can be cast in the form

$$\langle Q_\alpha \rangle_\alpha = t_\alpha + t_\alpha G_0(z) \int \{ \sum_{\beta \neq \alpha} Q_\beta \} P(\vec{R}_\alpha | \vec{R}_1, \dots, \vec{R}_\alpha - 1, \dots, \vec{R}_\alpha + 1, \dots, \vec{R}_N) \prod_{j \neq \alpha} d^3 R_j. \quad \text{I.B.9}$$

By making use of the conditional probabilities, one can reduce Eq. I.B.9 to an integral of $\langle Q_\alpha \rangle_{\beta\alpha}$, the average of Q_α over all but two coordinates $\vec{R}_\alpha$ and $\vec{R}_\beta$. The conditional probability density with $\vec{R}_\alpha$ and $\vec{R}_\beta$ held fixed is related to that for site α held fixed by

$$\begin{aligned} P(\vec{R}_\alpha) P(\vec{R}_\alpha | \vec{R}_1, \dots, \vec{R}_\alpha - 1, \vec{R}_\alpha + 1, \dots, \vec{R}_N) \\ = P(\vec{R}_\alpha, \vec{R}_\beta) P(\vec{R}_1, \dots, \vec{R}_\alpha - 1, \vec{R}_\alpha + 1, \dots, \vec{R}_\beta - 1, \vec{R}_\beta + 1, \dots, \vec{R}_N). \end{aligned} \quad \text{I.B.10}$$

Combining Eqs. I.B.9 and I.B.10 one obtains

$$\langle Q_\alpha \rangle_\alpha = t_\alpha + t_\alpha G_0(z) (N-1) \int Q_{\beta\alpha} \{ P(\vec{R}_\alpha, \vec{R}_\beta) / P(\vec{R}_\alpha) \} d^3 R_\beta \quad \text{I.B.11}$$

The quantity $(N-1) P(\vec{R}_\alpha, \vec{R}_\beta) / P(\vec{R}_\alpha)$ can be expressed as $ng(\vec{R}_\alpha - \vec{R}_\beta)$ where $g(\vec{R}_\alpha - \vec{R}_\beta)$ is the radial distribution function and gives the probability of finding an atomic site at $\vec{R}_\beta$ if one is known to be at $\vec{R}_\alpha$. Eq. I.B.11 becomes

$$\langle Q_\alpha \rangle_\alpha = t_\alpha + t_\alpha G_0(z) n \int \langle Q_\beta \rangle_{\beta\alpha} g(\vec{R}_\alpha - \vec{R}_\beta) d^3 R_\beta. \quad \text{I.B.12}$$

Continuing along this line generates a similar relation between $\langle Q_\beta \rangle_{\beta\alpha}$ and $\langle Q_\gamma \rangle_{\gamma\beta\alpha}$ and so on. Approximations enter by introducing a procedure for decoupling averages from higher order averages.

The earliest, and simplest, decoupling scheme was proposed by Lax, 1951 (9) and is known as the quasicrystalline approximation (QCA). In Lax's description, $\langle Q_\beta \rangle_{\beta\alpha}$ is replaced by $\langle Q_\beta \rangle_\beta$ and Eq. I.B.12 reduces to

$$\langle Q_\alpha \rangle_\alpha = t_\alpha + t_\alpha G_0(z) n \int \langle Q_\beta \rangle_\beta g(\vec{R}_\alpha - \vec{R}_\beta) d^3 R_\beta, \quad \text{I.B.13}$$

which corresponds to truncating the hierarchy of equations of the type Eq. I.B.12 at first order. By iterating Eq. I.B.13 the series

$$\begin{aligned} \langle Q_\alpha \rangle_\alpha &= t_\alpha + t_\alpha G_0(z) n \int g(\vec{R}_\alpha - \vec{R}_\beta) t_\beta d^3 R_\beta \\ &+ t_\alpha G_0(z) n \int g(\vec{R}_\alpha - \vec{R}_\beta) t_\beta G_0(z) n \int g(\vec{R}_\beta - \vec{R}_\gamma) t_\gamma d^3 R_\gamma d^3 R_\beta + \dots \end{aligned} \quad \text{I.B.14}$$

results. For certain potentials, this series can be summed in closed form in a momentum representation. Eq. I.B.14 can be inserted in Eq. I.B.8 to obtain $\langle T \rangle$ which in turn determines $\langle G(z) \rangle$ according to Eq. I.B.1.

An alternative procedure for decoupling Eq. I.B.12 was suggested by Schwartz and Ehrenreich, 1971 (10). They introduce the self-energy $\Sigma(z)$ defined such that

$$\langle G(z) \rangle = (z - H_0 - \Sigma(z))^{-1}, \quad \text{I.B.15}$$

and the local self-energy for the α^{th} site σ_α

$$\sigma_\alpha = \langle Q_\alpha \rangle_\alpha G_0 G^{-1}. \quad \text{I.B.16}$$

$\Sigma(z)$ is obtained from σ_α according to

$$\Sigma(z) = n \int \sigma_\alpha d^3 R_\alpha. \quad \text{I.B.17}$$

Their decoupling approximation can be shown to be

$$\langle Q_\beta \rangle_{\beta\alpha} G_0(z) = \langle Q_\beta \rangle_\beta G_0(z) \langle G(z) \rangle^{-1} \langle G(z) \rangle_\alpha, \quad \text{I.B.18}$$

where

$$\langle G(z) \rangle_\alpha = \int G(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N; z) P(\vec{R}_\alpha | \vec{R}_1, \vec{R}_2, \dots, \vec{R}_N) \prod_{j \neq \alpha} d^3 R_j, \quad \text{I.B.19}$$

and obeys the relation

$$\langle G(z) \rangle_\alpha = \langle G(z) \rangle + \langle G(z) \rangle \bar{t}_\alpha \langle G(z) \rangle. \quad \text{I.B.20}$$

The operator $\bar{t}_\alpha$ is a rather complicated operator, however upon defining the quantity

$$\tilde{\sigma}_\alpha = - n \int [g(\vec{R}_\alpha - \vec{R}_\beta) - 1] \sigma_\beta d^3 R_\beta, \quad \text{I.B.21}$$

a pair of self-consistent equations are developed for $\tilde{t}_\alpha$ and σ_α in terms of $\langle G(z) \rangle$ and V_α , the potential on site α ,

$$\sigma_\alpha = V_\alpha + V_\alpha \langle G(z) \rangle \tilde{t}_\alpha, \quad \text{I.B.22}$$

and

$$\tilde{t}_\alpha = (V_\alpha - \tilde{\sigma}_\alpha) + (V_\alpha - \tilde{\sigma}_\alpha) \langle G(z) \rangle \tilde{t}_\alpha. \quad \text{I.B.23}$$

Eqs. I.B.22 and I.B.23 are the principal equations of what Schwartz and Ehrenreich call the self-consistent approximation (SCA). This method is self-consistent in the sense that σ_α and $\tilde{t}_\alpha$ are determined in terms of the configuration averaged propagator $\langle G(z) \rangle$ which itself depends upon σ_α through $\Sigma(z)$. Schwartz and Ehrenreich have shown that the decoupling procedure used to obtain the SCA leads to the CPA when applied to a substitutional binary alloy.

Attempts have been made to develop a direct extension of the CPA to the liquid metal problem. Faulkner, 1970 (11) has constructed the CPA for a liquid metal in the absence of short-range order and found it to be equivalent to results obtained by Klauder (12) using a perturbation theoretic treatment. Gyorffy, 1970 (13) has generalized the CPA for liquids to include short-range order, developing a

self-consistent treatment which predated the Schwartz-Ehrenreich scheme mentioned above. Gyorffy's treatment was later refined and extended by Korringa and Mills, 1972 (14). The treatment of Korringa and Mills is described below.

Again, the Hamiltonian of interest is $H = H_0 + \sum_i V_i$ with $G(z) = (z - H)^{-1}$ and

$$\langle G(z) \rangle = [z - H_0 - W(z)]^{-1}, \quad \text{I.B.24}$$

where $W(z)$ is the coherent potential to be determined. By defining H_1 and T such that

$$H_1 = \sum_i V_i - W(z), \quad \text{I.B.25}$$

and

$$T \langle G(z) \rangle = H_1 G(z), \quad \text{I.B.26}$$

one can write

$$G(z) = \langle G(z) \rangle + \langle G(z) \rangle T \langle G(z) \rangle. \quad \text{I.B.27}$$

Averaging both sides of Eq. I.B.27 requires

$$\langle T \rangle = 0. \quad \text{I.B.28}$$

Korringa and Mills introduce the operators $\hat{T}$ and $-q$ as the local and nonlocal contributions, respectively, to T

$$T = \hat{T} - q. \quad \text{I.B.29}$$

A bit of algebra reveals that

$$q = W(z) + W(z) \langle G(z) \rangle T, \quad \text{I.B.30}$$

from which it follows that

$$\langle q \rangle = \langle \hat{T} \rangle = W(z). \quad \text{I.B.31}$$

Writing $\hat{T} = \sum_i Q_i$ with the defining relation

$$Q_i = v_i + v_i \langle G(z) \rangle T, \quad \text{I.B.32}$$

one can demonstrate that

$$Q_i = t_i + t_i \langle G(z) \rangle \left(\sum_{j \neq i} Q_j - q \right). \quad \text{I.B.33}$$

Multiplying Eq. I.B.33 by $\delta(\vec{R} - \vec{R}_i)$, averaging, summing over i , and defining the mean density $\rho(\vec{R})$ and the mean local operator $Q(\vec{R})$.

$$\rho(\vec{R}) Q(\vec{R}) = \sum_i \delta(\vec{R} - \vec{R}_i) Q_i, \quad \text{I.B.34}$$

one obtains

$$\begin{aligned} \rho(\vec{R}) Q(\vec{R}) &= \rho(\vec{R}) t(\vec{R}) + t(\vec{R}) \langle G(z) \rangle \int d^3 R' \sum_i \sum_{j \neq i} \\ &\quad \langle \delta(\vec{R} - \vec{R}_i) \delta(\vec{R}' - \vec{R}_j) Q_j \rangle \\ &= t(\vec{R}) \langle G(z) \rangle \sum_i \delta(\vec{R} - \vec{R}_i) q. \end{aligned} \quad \text{I.B.35}$$

where $g(\vec{R} - \vec{R}') = g(\vec{R}, \vec{R}')$ is the radial distribution function defined earlier in this section. Substitution of Eqs. I.B.37 and I.B.38 into Eq. I.B.35 and defining $\bar{g}(\vec{R} - \vec{R}') = g(\vec{R} - \vec{R}') - \rho(\vec{R}')$ (following Korringa and Mills) one finds

$$Q(\vec{R}) = t(\vec{R}) + t(\vec{R}) \langle G(z) \rangle \int d^3\vec{R}' \bar{g}(\vec{R} - \vec{R}') Q(\vec{R}'). \quad \text{I.B.39}$$

Along with the definition of $t(\vec{R})$

$$\rho(\vec{R}) t(\vec{R}) = \sum_i \langle \delta(\vec{R} - \vec{R}_i) t_i \rangle. \quad \text{I.B.40}$$

Eqs. I.B.24, I.B.36, and I.B.39 constitute a self-consistent scheme for obtaining $\langle G(z) \rangle$.

Of the above three schemes for computing the electronic properties of liquid metals, only the non-self-consistent QCA is easily applied to even simple model systems. Other approximations have been suggested to treat the liquid metal problem, but they are more complicated than those mentioned above. Notable among these are the effective-medium approximation of Roth, 1974 (15) and the approximation of Ishida and Yonezawa, 1973 (16).

C. Numerical Investigations

Along with attempts to develop suitable approximate descriptions of the properties of excitations in disordered systems, considerable effort has gone into numerical

calculations on model systems. These model calculations are useful for evaluating suggested approximations and for pointing out features related to the effects of disorder. A review of the numerical work on vibrational systems has been given by Dean (17).

In a recent study of the electronic states in a one-dimensional liquid metal, Peterson, Schwartz, and Butler (PSB) (18) reported a comparison of the exact integrated density of states $n(E)$ to calculations of $n(E)$ from three approximate theories. The approximations considered in that work were the self-consistent theories of Schwartz and Ehrenreich (10) and Gyorffy (13) (as extended by Korringa and Mills (14)), and the non-self-consistent quasicrystalline approximation of Lax (9). The basic elements of these theories were discussed in the preceding section. Somewhat surprisingly, $n(E)$ obtained from the QCA and $n(E)$ obtained from the self-consistent theories all gave about the same level of agreement with the exact results. Each theoretical description gives very good agreement with the exact results in the weak-scattering regime, but none of them provides an adequate description in the strong-scattering regime.

Numerical investigations of model systems have generally been directed toward calculating either the density of states or the integrated density of states. There have been relatively few calculations of momentum dependent quantities such as the spectral density $A(\vec{k}, E)$ defined as

$$A(\vec{k}, E) = - \frac{1}{\pi} \text{Im } G(\vec{k}, E), \quad \text{I.C.1}$$

where $G(\vec{k}, E)$ is the Fourier transform of the one-particle Green's function. Recently a numerical calculation of the spectral density function for electronic excitations in a binary alloy has been presented by Alben, Blume, Krakauer, and Schwartz (19). Comparing their results with the CPA results for the same system showed the CPA in excellent agreement. The same technique has been applied by Alben and Thorpe (20) to a calculation of the spin-wave spectrum in a random antiferromagnet.

The earliest calculation of $A(\vec{k}, E)$ for an exactly solvable model was reported by Halperin (21) in 1965. Halperin developed a formalism for calculating the spectral density for a particle moving in a one-dimensional "white-Gaussian-noise" potential. The white-Gaussian-noise potential is so termed because the Fourier components of the potential have a Gaussian distribution and no correlations exist between Fourier components at different frequencies. No short-range order is included in such a model.

The chapters which follow describe an adaptation of Halperin's formalism to Monte Carlo calculations of the spectral density $A(k, E)$ for elementary excitations in amorphous systems with short-range order. Several Hamiltonians have been studied and the results of the calculation have

been compared to the spectral density obtained in the quasicrystalline approximation. The qualitative features of recent neutron scattering measurements are interpreted based on these calculations.

CHAPTER II

THE SPECTRAL DENSITY FOR AN ELECTRON IN A ONE-DIMENSIONAL LIQUID METAL

This chapter describes a Monte Carlo calculation of the spectral density function $A(k,E)$ for an electron moving in a one-dimensional model of a liquid metal. This study is complementary to the calculation of the exact integrated density of states by Peterson, Schwartz, and Butler (PSB) (18) mentioned in the previous chapter. The exact $A(k,E)$ will be compared to that calculated within the quasicrystalline approximation (QCA) of Lax (9). Part A describes the one-dimensional model, Part B gives the procedure for calculating $A(k,E)$, Part C discusses the convergence of the spectral density, and Part D outlines the properties to be expected of the spectral density for a disordered system and compares the QCA and exact numerical results.

A. The Model System

The statistical model chosen for this study is the so-called hard rod model of the classical one-dimensional fluid (22). This model has been used by PSB (18). The model can be pictured as the one-dimensional equivalent of the hard-sphere model often used in three-dimensional treatments of liquids and gases. N identical line segments

of length a are distributed on a line of length Nl subject to the condition that they do not overlap. The atomic positions are taken to be at the centers of these segments. The minimum separation between nearest-neighbors is the length a and the average separation is the length l . The hard-rod distribution is illustrated in Figure 1. The parameter $\alpha = a/l$ is a measure of the amount of disorder in the system with $\alpha = 1$ indicating perfect order, $\alpha = 0$ indicating complete disorder (Poisson distribution), and suitable choices of α indicating intermediate levels of disorder. Quantitatively, the probability of finding a nearest-neighbor at a distance d from a given atom is

$$p(d) = \frac{\theta(d - a)}{l - a} \exp \left\{ - \frac{d - a}{l - a} \right\} \quad \text{II.A.1}$$

where $\theta(x)$ is zero for $x < a$ and one for $x > a$.

The interaction between an electron and the system of N atoms is described by the potential

$$V(x) = - \Delta \sum_{j=1}^N \delta(x - x_j), \quad \text{II.A.2}$$

where x_j is the position of the j^{th} atom and Δ is the strength of the delta function potentials. The quantities $d_j = x_j - x_{j-1}$ are random quantities obtained from a random number generating subroutine consistent with Eq. II.A.1.

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Figure 1. Schematic representation of the hard-rod liquid.

Let R_j be a random variable distributed uniformly on the interval $(0,1)$. The random variable d_j with probability density $p(d_j)$ is obtained from the equation

$$R_j = \int_a^{d_j} p(y) dy. \quad \text{II.A.3}$$

For the hard-rod distribution, this becomes

$$d_j = a + l(\alpha - 1) \ln(1 - R_j), \quad \text{II.A.4}$$

and can be used to construct the one-dimensional model described above.

B. Calculation of the Spectral Density

The spectral density $A(k, E)$ was defined in Eq. I.C.1. It is related to the density of states by

$$\rho(E) = \frac{1}{2\pi} \int A(k, E) dk, \quad \text{II.B.1}$$

in one dimension. $A(k, E)$ can be written in terms of the one-electron wavefunctions $\psi_j(x)$

$$A(k, E) = \lim_{L \rightarrow \infty} \frac{1}{L} \left\langle \sum_j \left| \int_0^L e^{ikx} \psi_j(x) dx \right|^2 \delta(E - E_j) \right\rangle, \quad \text{II.B.2}$$

where the wavefunctions are solutions of the Schrodinger equation

$$\left\{ -\frac{d^2}{dx^2} + V(x) \right\} \psi_j(x) = E_j \psi_j(x), \quad \text{II.B.3}$$

with $V(x)$ given in Eq. II.A.2. Halperin (21) has reduced the calculation of $A(k, E)$ to a simpler form than Eq. II.B.2.

This procedure is described below.

Let us define for each potential configuration in the statistical ensemble a function $\phi(x; E)$ to be the unique solution of Eq. II.B.3 for energy E subject to the boundary conditions

$$\left. \frac{\partial \phi(x; E)}{\partial x} \right|_{x=0} = z_0 \phi(0; E), \quad \text{II.B.4}$$

and

$$\left. \frac{\partial \phi(x; E)}{\partial x} \right|_{x=L} = z_L \phi(L; E), \quad \text{II.B.5}$$

where z_0 and z_L are arbitrary constants. Halperin defines the functions

$$z(x; E) = \frac{\partial \phi(x; E)}{\partial x} / \phi(x; E), \quad \text{II.B.6}$$

and

$$U_1(x; E) = \left\{ \int_0^x e^{ikx'} \phi(x'; E) dx' \right\} / e^{ikx} \phi(x; E), \quad \text{II.B.7}$$

in terms of which $A(k, E)$ is to be written, and the two auxiliary functions

$$U_2(x; E) = \left\{ \int_0^x \phi^2(x'; E) dx' \right\} / \phi^2(x; E), \quad \text{II.B.8}$$

and

$$U_3(x; E) = \frac{\partial z(x; E)}{\partial x}. \quad \text{II.B.9}$$

The last two functions are solutions of the equations

$$\frac{\partial U_2(x; E)}{\partial x} = 1 - 2z(x; E)U_2(x; E), \quad \text{II.B.10}$$

and

$$\frac{\partial U_3(x; E)}{\partial x} = -1 - 2z(x; E)U_3(x; E). \quad \text{II.B.11}$$

From these it can be shown that

$$U_3(x; E) = -U_2(x; E), \quad \text{II.B.12}$$

for all x and since $U_2(x; E)$ is positive, $U_3(x; E)$ must be a negative quantity. Using the scaling properties of the delta-functions, it is easily demonstrated that

$$\sum_i \delta(E - E_i) = \left| \frac{\partial z(L; E)}{\partial E} \right| \delta\{z_L - z(L; E)\}. \quad \text{II.B.13}$$

Upon making the appropriate substitutions in Eq. II.B.2 one obtains

$$A^L(k, E) = \frac{1}{L} \langle |U_1(L; E)|^2 / U_2(L; E) \rangle_i \delta(E - E_i), \quad \text{II.B.14}$$

$$A^L(k, E) = \frac{1}{L} \langle |U_1(L; E)|^2 / U_2(L; E) \rangle \{U_3(L; E) \delta\{z_L - z(L; E)\}\}, \quad \text{II.B.15}$$

$$A^L(k, E) = \frac{1}{L} \langle |U_1(L; E)|^2 \delta\{z_L - z(L; E)\} \rangle. \quad \text{II.B.16}$$

If the function $\phi(x; E)$ can be constructed, Eq. II.B.16 provides a means of calculating $A(k, E)$.

Suppressing momentarily the arguments of U_1 and z , the average in Eq. II.B.16 can be written as

$$A^L(k, E) = \frac{1}{L} \iint |U_1|^2 \delta(z_L - z) P(U_1, z) dU_1 dz, \quad \text{II.B.17}$$

where $P(U_1, z)$ is the joint probability density for the random variables z and U_1 . Performing the z -integral gives

$$A^L(k, E) = \frac{1}{L} \int |U_1|^2 P(U_1, z_L) dU_1. \quad \text{II.B.18}$$

As L becomes large, $A^L(k, E) \rightarrow A(k, E)$ and must be independent of the arbitrary constant z_L . The probability density $P(U_1, z_L)$ must approach $P(U_1)$, a quantity independent of z_L as $L \rightarrow \infty$. The spectral density, then, is given by

$$A(k, E) = \lim_{L \rightarrow \infty} \frac{1}{L} \langle |U_1(L; E)|^2 \rangle. \quad \text{II.B.19}$$

The determination of $A(k, E)$ in Eq. II.B.19 can be further simplified by taking advantage of the properties of the delta function potentials indicated in Eq. II.A.2. Let $A(x)$ be defined such that

$$A(x) = \{ ik \phi(x; E) e^{ikx} - e^{ikx} \phi'(x; E) \} \quad \text{II.B.20}$$

with $\phi(x; E)$ the solution of the Schrodinger equation as given in Eq. II.B.3. Differentiating $A(x)$ and substituting for the second derivative $\phi''(x; E)$ from the Schrodinger equation yields

$$\frac{d}{dx} A(x) = e^{ikx} \phi(x; E) (E - k^2) - e^{ikx} V(x) \phi(x; E). \quad \text{II.B.21}$$

Integrating both sides and rearranging terms provides the form

$$\int_0^L e^{ikx} \phi(x; E) dx = \frac{1}{(E - k^2)} \left[\int_0^L e^{ikx} V(x) \phi(x; E) dx + A(x) \right]_0^L \quad \text{II.B.22}$$

Dividing both sides by $e^{ikL} \phi(L; E)$ and recalling the definition of $U_1(x; E)$ one obtains

$$U_1(L;E) = \frac{1}{(E - k^2)} \left[\frac{\int_0^L e^{ikx} V(x) \phi(x;E) dx}{e^{ikL} \phi(L;E)} + \frac{A(x)}{e^{ikL} \phi(L;E)} \Big|_0^L \right].$$

II.B.23

Inserting the definition of $V(x)$ for this model in the above equation and performing the integration leads to the result

$$U_1(L;E) = \frac{1}{(E - k^2)} \left[\frac{-\Delta \sum_{j=1}^N \exp\{ikx_j\} \phi(x_j;E)}{\exp\{ikL\} \phi(L;E)} + \frac{A(x)}{e^{ikL} \phi(L;E)} \Big|_0^L \right]$$

II.B.24

The second term in the above equation can be written explicitly as

$$\begin{aligned} & \frac{A(x)}{\exp\{ikL\} \phi(L;E)} \Big|_0^L \\ &= ik - z(L;E) - e^{-ikL} \left\{ ik \frac{\phi(0;E)}{\phi(L;E)} - \frac{\phi'(0;E)}{\phi(L;E)} \right\}. \end{aligned} \quad \text{II.B.25}$$

The amplitude of the wavefunction $\phi(x;E)$ grows exponentially with increasing x and the term in curly brackets in Eq. II.B.25 becomes negligible in a numerical calculation (23, 24). The final expression for $U_1(L;E)$ is

$$U_1(L;E) = \frac{1}{(E - k^2)} \left[\frac{-\Delta \sum_{j=1}^N \exp(ikx_j) \phi(x_j;E)}{\exp(ikL) \phi(L;E)} + ik - z(L;E) \right] \quad \text{II.B.26}$$

Substituting this in Eq. II.B.19 provides an expression for evaluating the spectral density in terms of the values of the wavefunctions at the sites x_j .

The wavefunctions $\phi(x_j;E)$ can be constructed by a transfer matrix method. The interval $x = 0$ to $x = L$ is divided into N cells. The i^{th} cell is that region of the x -axis bounded by the delta functions at x_{i-1} on the left and x_i on the right. In the i^{th} cell, the wavefunctions have the form

$$\phi_i(x;E) = A_i e^{i\gamma x} + B_i e^{-i\gamma x}, \quad \text{II.B.27}$$

(real wavefunctions could also be used) where $E = \gamma^2$. The continuity conditions on $\phi_i(x;E)$ are (25)

$$\phi_{i+1}(x_i;E) = \phi_i(x_i;E), \quad \text{II.B.28}$$

and

$$\phi'_{i+1}(x_i;E) - \phi'_i(x_i;E) = -\Delta \phi_i(x_i;E). \quad \text{II.B.29}$$

A transfer matrix M can be defined which carries the values of $\phi'_i(x_{i-1};E)$ and $\phi_i(x_{i-1};E)$ into the values $\phi'_i(x_i;E)$ and $\phi_i(x_i;E)$,

$$\begin{bmatrix} \phi'_i(x_i;E) \\ \phi_i(x_i;E) \end{bmatrix} = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} \begin{bmatrix} \phi'_i(x_{i-1};E) \\ \phi_i(x_{i-1};E) \end{bmatrix}. \quad \text{II.B.30}$$

Application of the matching conditions defined above to the wavefunction in Eq. II.B.27 yields the matrix

$$M = \begin{bmatrix} \cos(\gamma d_i) & -\gamma \sin(\gamma d_i) \\ \frac{1}{\gamma} \sin(\gamma d_i) & \cos(\gamma d_i) \end{bmatrix}. \quad \text{II.B.31}$$

The two equations contained in the matrix equation can be written explicitly as

$$\phi'_i(x_i;E) = \cos(\gamma d_i) \phi'_i(x_{i-1};E) - \gamma \sin(\gamma d_i) \phi_i(x_{i-1};E) \quad \text{II.B.32}$$

and

$$\phi_i(x_i;E) = \frac{1}{\gamma} \sin(\gamma d_i) \phi'_i(x_{i-1};E) + \cos(\gamma d_i) \phi_i(x_{i-1};E). \quad \text{II.B.33}$$

Dividing Eq. II.B.33 by Eq. II.B.32 and applying the matching conditions on the wavefunction and its derivative yields

$$z_{i+1}(x_i; E) = \frac{z_i(x_{i-1}; E) - \gamma \tan(\gamma d_i)}{\frac{1}{\gamma} \tan(\gamma d_i) z_i(x_{i-1}; E) + 1} - \Delta \quad \text{II.B.34}$$

an expression which can be used to generate a sequence of values of the logarithmic derivatives $z_{i+1}(x_i; E) = \phi'_{i+1}(x_i; E)/\phi_{i+1}(x_i; E)$ in terms of the energy, the strength of the potential, and the random variable d_i . Eq. II.B.33 can be recast in the form

$$\phi_i(x_i; E) = \phi_{i-1}(x_{i-1}; E) \left[\frac{1}{\gamma} \sin(\gamma d_i) z_i(x_{i-1}) + \cos(\gamma d_i) \right], \quad \text{II.B.35}$$

and can be used to provide the wavefunctions needed to evaluate $A(k, E)$ numerically.

C. Convergence of $A(k, E)$

Eq. II.B.19 shows that the configuration averaged spectral density $A(k, E)$ is the mean value of the random variable $f_L(k, E) = \frac{1}{L} |U_1(L; E)|^2$. It remains to be shown how one calculates that average value. The configuration averaged integrated density of states $n(E)$ is related to the average number of nodes per unit length of $\phi(x; E)$ (26). The number of nodes per unit length of $\phi(x; E)$ for a one-dimensional system converges on its average value with zero variance as the length of the system increases. The number

of nodes per unit length is, then, an ergodic quantity (in the statistical sense) and $n(E)$ can be determined by a node-counting technique on a single long chain of atoms. The remainder of this section will be devoted to an analysis of the convergence properties of the random variable $f_L(k, E)$. It will be demonstrated that $f_L(k, E)$ is not ergodic (27) (in the statistical sense) and that the mean of the distribution of $f_L(k, E)$ cannot be calculated by calculating $f_L(k, E)$ for a single long chain of atoms.

The ratio $g(x; E) = \phi(x; E)/\phi(L; E)$ is a random process for $x \geq 0$ and is assumed for simplicity to be real. Let us define the random function of k and E

$$f_L(k, E) = \frac{1}{L} \left| \int_0^L e^{ikx} g(x; E) dx \right|^2, \quad \text{II.C.1}$$

for a system of length L . The spectral density is given by

$$A(k, E) = \lim_{L \rightarrow \infty} \langle f_L(k, E) \rangle. \quad \text{II.C.2}$$

Eq. II.C.2 can be put in the form

$$A(k, E) = \lim_{L \rightarrow \infty} \frac{1}{L} \int_0^L \int_0^L e^{ik(x-y)} \langle g(x; E) g(y; E) \rangle dx dy. \quad \text{II.C.3}$$

The quantity in averaging brackets is the correlation function of the random process $g(x;E)$. It is assumed that this correlation function depends on the difference $x - y$.

$$R(x - y) = \langle g(x;E)g(y;E) \rangle, \quad \text{II.C.4}$$

and the spectral density becomes

$$A(k,E) = \lim_{L \rightarrow \infty} \frac{1}{L} \int_0^L \int_0^L e^{ik(x-y)} R(x - y) dx dy. \quad \text{II.C.5}$$

This demonstrates that the configuration averaged spectral density $A(k,E)$ is given by the Fourier transform of the correlation function $R(x - y)$. Algebraic manipulation of Eq. II.C.5 (see Appendix A) noting that $R(x - y) = R(y - x)$ yields

$$A(k,E) = \lim_{L \rightarrow \infty} \frac{L}{2} \int_0^L \left(1 - \frac{u}{L}\right) \cos(ku) R(u) du, \quad \text{II.C.6}$$

which is readily reduced to give

$$A(k,E) = \int_0^\infty \cos(ku) R(u) du \quad \text{II.C.7}$$

Eq. II.C.7 is a convenient expression for the spectral density for the discussion which follows.

The random variable $f_L(k,E)$ has the average value $A(k,E)$ in the limit $L \rightarrow \infty$. To be a consistent estimator of the

spectral density, $f_L(k, E)$ must, for each k and E , approach $A(k, E)$ with zero variance as L increases to infinity. That this is not the case in general can be demonstrated by a simple example. Let $g(x; E)$ be a normal process with mean zero. The objective is to calculate the variance σ^2 of $f_L(k, E)$ as $L \rightarrow \infty$. The variance is defined by the relation

$$\sigma^2 = \langle \{f_L(k, E) - \langle f_L(k, E) \rangle\}^2 \rangle, \quad \text{II.C.8}$$

or

$$\sigma^2 = \langle \{f_L(k, E)\}^2 \rangle - \langle f_L(k, E) \rangle^2. \quad \text{II.C.9}$$

The first of the two quantities on the right-hand side of Eq. II.C.9 is given by

$$\begin{aligned} \langle \{f_L(k, E)\}^2 \rangle = \\ \frac{1}{L^2} \int_0^L \int_0^L \int_0^L \int_0^L e^{ik(w-x+y-z)} \langle g(w; E) g(x; E) g(y; E) g(z; E) \rangle dw dx dy dz. \end{aligned} \quad \text{II.C.10}$$

A tedious but straightforward calculation utilizing the properties of normally distributed random variables provides the result (see Appendix B)

$$\lim_{L \rightarrow \infty} \langle \{f_L(k, E)\}^2 \rangle = 2 \lim_{L \rightarrow \infty} \langle f_L(k, E) \rangle^2, \quad \text{II.C.11}$$

from which it follows that

$$\sigma^2 = \lim_{L \rightarrow \infty} \langle f_L(k, E) \rangle^2 = A^2(k, E). \quad \text{II.C.12}$$

This example shows that $f_L(k, E)$ in the limit $L \rightarrow \infty$ is not a self-averaging quantity, but is a random variable with unknown distribution and average value $A(k, E)$. For the simple statistics chosen for this example, the proof can be carried one step further to show that $f_L(k, E)$ for large L is exponentially distributed with mean value $A(k, E)$ (28). In general, the distribution function cannot be found and $A(k, E)$ can only be obtained by calculating $f_L(k, E)$ for several long chains. This amounts to generating several values of $f_L(k, E)$ consistent with the unknown distribution function and averaging the results to obtain $A(k, E)$.

The above discussion should not be interpreted to mean that for a given system of length L ($L \rightarrow \infty$) the spectral density has no meaning. $f_L(k, E)$ is not the spectral density for a particular system, it is a random variable whose mean value is the spectral density. In fact, there does exist a means of obtaining $A(k, E)$ by constructing only a single long chain of atoms (27). Consider a single system of length L with L large. This system can be broken up into n segments of length L_0 . Let us define the quantities

$$\hat{f}_L(k, E) = \frac{1}{L} \left| \int_{(j-1)L_0}^{jL_0} e^{ikx} g(x; E) dx \right|^2, \quad \text{II.C.13}$$

and

$$\hat{A}(k, E) = \frac{1}{n} \sum_{j=1}^N \hat{f}_j(k, E). \quad \text{II.C.14}$$

Performing an analysis of $\hat{A}(k, E)$ similar to that described above gives the mean value $M\{\dots\}$ and variance $V\{\dots\}$ to be

$$\lim_{L_0 \rightarrow \infty} M\{\hat{A}(k, E)\} = A(k, E), \quad \text{II.C.15}$$

and

$$\lim_{\substack{n \rightarrow \infty \\ L_0 \rightarrow \infty}} V\{\hat{A}(k, E)\} = 0. \quad \text{II.C.16}$$

The quantity $\hat{A}(k, E)$ is, then, a consistent estimator of $A(k, E)$ for large n and L_0 and requires that one construct only a single chain of atoms. This method of finding $A(k, E)$ has practical disadvantages, however. As mentioned in Part B of this chapter, the wavefunction $\phi(x; E)$ grows exponentially with x and the limit of large n with large L_0 could not be achieved. Therefore, in this work, $A(k, E)$ is determined by calculating $f_L(k, E)$ for several chains and averaging the results.

D. Comparison of the QCA and Exact Results

The general features to be expected of $A(k, E)$ for a disordered system can be understood by considering the properties of the correlation function $R(u)$. In general, the spectral density is related to the correlation function by (see Eq. II.B.7)

$$A(k, E) = \int_{-\infty}^{\infty} e^{-iku} R(u) du, \quad \text{II.D.1}$$

where $R(u)$ depends upon E . Borland (23) has shown that the eigenfunctions for a one-dimensional disordered system are exponentially localized. Let us assume that the wavefunction is exponentially localized at the origin with an oscillatory component described by a single cosine factor. The correlation function then has the form

$$R(u) = \langle g^2(0; E) \rangle e^{-\rho u} \cos(\beta u), \quad \text{II.D.2}$$

or

$$R(u) = \sigma_g^2 e^{-\rho u} \cos(\beta u). \quad \text{II.D.3}$$

The spectral density is obtained by performing the integration in Eq. II.D.1.

$$A(k, E) = \sigma_g^2 \left[\frac{\rho}{(k - \beta)^2 + \rho^2} + \frac{\rho}{(k + \beta)^2 + \rho^2} \right]. \quad \text{II.D.4}$$

In a perfectly ordered system, the electronic states are extended and $\rho = 0$. Taking the limit $\rho \rightarrow 0$ in Eq. II.D.4 and using the identity

$$\delta(x - x_0) = \frac{1}{\pi} \lim_{\eta \rightarrow 0} \frac{\eta}{(x - x_0)^2 + \eta^2}, \quad \text{I.D.5}$$

gives the ordered-system spectral density

$$A(k, E) = \pi \sigma_g^2 [\delta(k - \beta) + \delta(k + \beta)], \quad \text{II.D.6}$$

as a pair of delta functions. For a disordered system, the delta functions become broadened into Lorentzian lineshapes. If ρ is very large, corresponding to a highly localized state, the spectral density will be very broad and flat and may wash out entirely. The parameters σ_g , ρ , and β depend upon the energy and the potential, and would be difficult to calculate for even a simple model. Nevertheless, the example cited above leads one to expect broadening of the peaks in $A(k, E)$ to be a general feature for disordered systems.

The formal details of the quasicrystalline approximation (QCA) were given in Chapter I. The QCA has been applied to the model of Chapter II, Part A, by PSB (18). In what follows, the basic equations of the QCA are presented and the reader is referred to reference 18 for further details. Within the QCA, the spectral density is obtained according to Eq. I.C.1 from the Green's function

$$G(k, E) = [E - k^2 - \Sigma(k, E)]^{-1}, \quad \text{II.D.7}$$

where $\Sigma(k, E)$ is the self-energy. The numerical ingredients for determining $\Sigma(k, E)$ are $g^-(k)$, the Fourier transform of the two-particle distribution function (obtained from the hard-rod distribution function, see PSB)

$$g^-(k) = \frac{e^{ika}}{1 - e^{ika} - ikl(1 - \alpha)}, \quad \text{II.D.8}$$

and the atomic scattering operator $\tau^{(0)}(E)$ given by

$$\tau^{(0)}(E) = - \frac{2\Delta\gamma}{2\gamma - i\Delta}, \quad \text{II.D.9}$$

where $\gamma = \sqrt{E}$. In terms of the above,

$$\Sigma(k, E) = \frac{\tau^{(0)}(E)}{l} [1 - \tau^{(0)}(E) G_0''(k, E)]^{-1}, \quad \text{II.D.10}$$

where

$$G_0''(k, E) = \frac{-i}{2\gamma} [g^-(\gamma + k) + g^-(\gamma - k)] - [l(E - k^2)]^{-1}. \quad \text{II.D.11}$$

To compare the QCA and the numerical results, the energy scale is chosen such that the energy of the bound state of an isolated delta function is minus one, i.e., $E = -(\frac{\Delta}{2})^2 = -1$. In each of the comparisons to be presented, the spectral

density is obtained by an average over one-hundred chains. The number of atoms in each chain was either 500 or 1000 depending upon the level of disorder involved. It is an unfortunate consequence of the numerical method that the chain length which can be used is limited by the exponential growth in amplitude of $\psi(x;E)$ with increasing x . This feature places an effective limit on the level of disorder available to investigation.

As mentioned in Chapter I, the integrated density of states $n(E)$ obtained from the QCA gave very good agreement with exact results for positive energies. In Figure 2 is shown a comparison of the QCA and exact spectral densities for $E = .50$ and two values of α . The small arrows indicate the positions of the delta functions for an ordered system ($\alpha = 1$) with lattice spacing $l = 10$. The positions are determined from the Kronig-Penney relation

$$\cos(kl) = \cos(\gamma l) - \frac{\Delta}{2} \frac{\sin(\gamma l)}{\gamma}, \quad \text{II.D.12}$$

where $\Delta = 2.0$. For the disordered system, Figure 2 shows a broadening in response to decreasing α and a diminishing (at $\alpha = .91$) and vanishing (at $\alpha = .50$) strength of the first two peaks in $A(k,E)$. The QCA appears to give a very reasonable description of this behavior, although there are slight differences when compared to the numerical results,

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Figure 2. Comparison of QCA (smooth curve) and exact (histogram) spectral densities $A(k, E)$ for $\alpha = .50$ (foreground) and $\alpha = .91$ (background) and energy $E = .50$. Arrows indicate positions of ordered-system δ -functions.

particularly near $k = .60$ for $\alpha = .91$. At higher energies, the agreement is even better as shown in Figure 3 for $\alpha = .91$ and $E = 5.0$.

Turning now to the negative energy behavior, the results of the numerical calculations are shown in Figure 4 for $E = -1.0$ and $\alpha = .91$. One finds broadened peaks in $A(k,E)$ near the k -values determined from Eq. II.D.12. It can be shown (see Appendix C) that within the framework of the QCA the self-energy is a real quantity for all energies independent of α and consequently $A(k,E)$ for constant E is a series of delta functions. As observed from Figure 4, $A(k,E)$ is noticeably broadened indicating the failure of the QCA to provide an adequate description at negative energies. The QCA does predict the positions of the peaks shown in Figure 4 and is therefore not without merit. Unfortunately, we cannot test the QCA at smaller values of α for the reasons mentioned earlier.

In summary, this study indicates that the QCA does in fact predict the essential features of the positive energy behavior of the spectral density as well as the integrated density of states. At negative energies, as far as this study can determine, the QCA is able to predict the positions of the peaks in $A(k,E)$, but allows no broadening in response to structural disorder. Continued work is needed to remedy the problems of the QCA at negative energies, but the QCA remains a rather good first approximation.

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Figure 3. Comparison of QCA (smooth curve) and exact (histogram) spectral densities $A(k,E)$ for $\alpha = .91$ and energy $E = 5.0$. Arrows indicate positions of ordered system δ -functions.

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Figure 4. Exact spectral density $A(k, E)$ for $\alpha = .91$ and $E = -1.0$. Arrows indicate positions of ordered-system δ -functions.

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CHAPTER III

TIGHT-BINDING SYSTEMS: THE EFFECTS OF SHORT-RANGE ORDER

This chapter presents a study of the effects of short-range order upon the spectral density function for excitations described by a tight-binding form of Hamiltonian. The scheme developed in Chapter II is applied to the harmonic oscillator Hamiltonian appropriate to lattice vibrations and a tight-binding Hamiltonian describing in a simplified way either electrons or spin waves. Both are studied for nearest-neighbor interactions. Part A describes the details of the calculation for the above Hamiltonians, Part B presents the results of the calculations, and Part C discusses the application of those results to some recent neutron scattering measurements on an amorphous system.

A. The Spectral Density

The one-dimensional model used in this chapter is the hard-rod model described in Chapter II. The first Hamiltonian to be considered is the harmonic oscillator Hamiltonian

$$H = \sum_{n=1}^N \frac{p_n^2}{2m} + \frac{1}{2} \sum_{n=1}^N \beta_{n+1} (u_{n+1} - u_n)^2, \quad \text{III.A.1}$$

where p_n and u_n are the momentum and displacement operators for the atom of mass m (hereafter set to unity) on site n , and β_{n+1} is the spring constant which couples sites $n + 1$ and n . The second is a tight-binding Hamiltonian

$$H\psi(n) = K_n\psi(n) + M_n\psi(n-1) + M_{n+1}\psi(n+1). \quad \text{III.A.2}$$

$\psi(n)$ gives the probability amplitude for finding an excitation at site n , and K_n and M_n are the diagonal and off-diagonal matrix elements, respectively. The calculation of the spectral density for the two Hamiltonians are very similar. Details of the calculation will be given only for the tight-binding Hamiltonian, Eq. III.A.2, to be followed by a discussion of the differences that occur for the harmonic oscillator (phonon) system.

The off-diagonal matrix elements M_{n+1} were modeled by an exponential function of the distance $d_{n+1} (= x_{n+1} - x_n)$ between sites $n + 1$ and n ,

$$M_{n+1} = M_0 \exp\{1 - d_{n+1}/\ell\}. \quad \text{III.A.3}$$

The diagonal matrix elements were set to unity for all n and the parameter M_0 was set equal to $-1/2$. For an ordered system ($\alpha = 1$) these choices lead to a dispersion relation given by

$$E(Q) = 2 \sin^2(Q/2), \quad \text{III.A.4}$$

in units where the average spacing l has been set equal to unity. For the duration of this chapter, the variable Q is used to designate wavevector in order to adopt a notation which will be compatible with that of the experimental results to be discussed in Part C of this chapter.

The spectral density $A(Q,E)$ is defined as

$$A(Q,E) = \lim_{N \rightarrow \infty} \frac{1}{N} \left\langle \sum_{j=1}^N \exp(-iQx_n) \psi_j(x_n) \right|^2 \delta(E - E_j) \rangle,$$

III.A.5

where ψ_j is the j^{th} eigenfunction with energy eigenvalue E_j . As in Chapter II, the calculation of $A(Q,E)$ proceeds from Halperin's (21) reduction of Eq. III.A.5. Actually it will be seen that the treatment presented here is slightly different from Halperin's. Let us define the function

$$y(x_n; E) = M_n \frac{\phi(x_{n-1}; E)}{\phi(x_n; E)}, \quad \text{III.A.6}$$

where $\phi(x_n; E)$ is defined to be the unique solution for energy E of the difference equation

$$M_n \phi(x_{n-1}; E) + M_{n+1} \phi(x_{n+1}; E) + (K_n - E) \phi(x_n; E) = 0,$$

III.A.7

subject to the conditions

$$y(x_1; E) = y_0, \quad \text{III.A.8}$$

and

$$y(x_{N+1}; E) = y_N, \quad \text{III.A.9}$$

where y_0 and y_N are arbitrary constants. Paralleling the treatment of Chapter II, let us define the three functions

$$U_1(x_n; E) = \sum_{n'=1}^{n-1} \exp(-iQx_{n'}) \phi(x_{n'}, E) / \exp(-iQx_n) \phi(x_n; E), \quad \text{III.A.10}$$

$$U_2(x_n; E) = \sum_{n'=1}^{n-1} \phi^2(x_{n'}, E) / \phi^2(x_n; E), \quad \text{III.A.11}$$

and

$$U_3(x_n; E) = \frac{\partial}{\partial E} y(x_n; E). \quad \text{III.A.12}$$

In terms of these functions, the spectral density can be written as

$$A(Q, E) = \lim_{N \rightarrow \infty} \frac{1}{N} \left\langle \frac{|U_1(x_{N+1}; E)|^2}{U_2(x_{N+1}; E)} |U_3(x_{N+1}; E)| \delta(y_N - y(x_{N+1}; E)) \right\rangle. \quad \text{III.A.13}$$

It is straightforward to demonstrate that $U_2(x; E)$ and $U_3(x; E)$ satisfy the equations

$$U_2(x_{n+1}; E) = \frac{y^2(x_{n+1}; E)}{M_{n+1}^2} [U_2(x_n; E) + 1], \quad \text{III.A.14}$$

and

$$U_3(x_{n+1}; E) = \frac{y^2(x_{n+1}; E)}{M_{n+1}^2} [U_3(x_n; E) - 1], \quad \text{III.A.15}$$

from which it follows that

$$U_3(x_n; E) = - U_2(x_n; E). \quad \text{III.A.16}$$

Since $U_2(x; E)$ is a positive quantity, $U_3(x; E)$ must be negative. Eq. III.A.13 reduces to

$$A(Q, E) = \lim_{N \rightarrow \infty} \frac{1}{N} \langle |U_1(x_{N+1}; E)|^2 \delta\{y_N - y(x_{N+1}; E)\} \rangle. \quad \text{III.A.17}$$

As in Chapter II, this expression is further reduced by dispensing with the delta function for a long system to obtain

$$A(Q, E) = \lim_{N \rightarrow \infty} \frac{1}{N} \langle |U_1(x_{N+1}; E)|^2 \rangle. \quad \text{III.A.18}$$

Along with Eq. III.A.3 and Eq. III.A.4, Eq. III.A.7 is used to generate a sequence of wavefunctions $\phi(x_n; E)$. These are substituted, in turn, into Eq. III.A.18 to obtain $A(Q, E)$.

The calculation proceeds in the same way for the phonon Hamiltonian with two exceptions. First, the spectral density is customarily written in terms of the frequency ω and becomes

$$A(Q, \omega) = \lim_{N \rightarrow \infty} \frac{2\omega}{N} \langle |U_1(x_{N+1}; \omega)|^2 \rangle. \quad \text{III.A.19}$$

Secondly, the functions $Q(x_n; \omega)$ are solutions of the equation of motion

$$\beta_{n+1} \phi(x_{n+1}; \omega) + \beta_{n-1} \phi(x_{n-1}; \omega) - (2\beta_n - \omega^2) \phi(x_n; \omega) = 0. \quad \text{III.A.20}$$

The spring constants were modeled by an exponential function

$$\beta_{n+1} = \beta_0 \exp\{1 - d_{n+1}/l\}, \quad \text{III.A.21}$$

similar to the matrix elements for the tight-binding system. The constant β_0 was set equal to unity. This choice leads to the ordered-system dispersion relation

$$\omega(Q) = 2|\sin(Q/2)|. \quad \text{III.A.22}$$

The convergence properties of the spectral density were thoroughly discussed in Chapter II and the arguments will not be repeated here. In the results to be shown, $f_N(Q, E)$ was calculated for each of one-hundred chains and the results

averaged to given $A(Q,E)$. The number of atoms in a single chain was in all cases $N = 500$.

B. Results of the Calculation

For an ordered system, the spectral density for constant energy consists of a series of delta functions located at the values $Q = Q(\omega)$ satisfying the appropriate dispersion relation. As discussed in Chapter II, these delta functions broaden as the system disorders. In Figure 5 is shown the phonon spectral density $A(Q,\omega)$ for $\alpha = .75$ and $\omega = .50$. The positions of the ordered-system delta functions are obtained from Eq. III.A.22 and are indicated by arrows in the figure. Long wavelength excitations are rather insensitive to short-range (local) disorder as evidenced by the sharpness of the peak in $A(Q,\omega)$ near $Q = 0$. In what would be the second zone for an ordered system, $A(Q,\omega)$ is no longer distinguishable as two separate peaks and appears as a single broad structure, shifted toward higher Q from the ordered-system positions. Clearly, the effects of reducing α from unity are most pronounced in the "second-zone." For the remainder of the results to be presented in this chapter, the peak in the spectral density in the "first zone" will be omitted. The tight-binding results will be discussed first, followed by those for the phonon system.

Figure 5. Spectral density $A(Q, \omega)$ as a function of Q for $\omega = .50$ and $\alpha = .75$ for the vibrational system. Arrows indicate positions of ordered-system δ -functions.

Plotted in Figure 6 are the tight-binding system spectral densities for $\alpha = .85$ and four (fixed) energies. The features to be noted in Figure 6 are: (1) that the peaks in $A(Q,E)$ are broadened from the delta functions obtained for an ordered system, (2) that the peaks in $A(Q,E)$ are located near the ordered system peaks (indicated by arrows), and (3) that the strength of the peaks is smallest for low energy. The dominant effect of short-range order is to produce a broadened and slightly shifted version of the ordered-system dispersion. Upon decreasing α to .75 the spectral density takes on the features shown in Figure 7. $A(Q,E)$ is plotted for the same four energies as in Figure 6, however, the scale has been reduced by a factor of two relative to Figure 6. The peaks in $A(Q,E)$ for $\alpha = .75$ are quite broad and are shifted markedly toward higher Q . The weighting is such that the mid-band energy $E = 1.0$ becomes the strongest feature in the "second zone." The gradual broadening and shifting of the features in $A(Q,E)$ with decreasing α is illustrated in Figure 8, where the spectral density is plotted as a function of Q for $E = .50$ and three values of α . At $\alpha = .50$, nothing remains of the ordered system behavior.

The phonon spectral density $A(Q,\omega)$ is shown in Figure 9 for four values of ω and $\alpha = .85$. Again, the arrows indicate the positions of the ordered-system delta functions

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Figure 6. Spectral density $A(Q, E)$ as a function of Q for $\alpha = .85$ and four values of E for the tight-binding system. Arrows indicate ordered-system δ -functions.

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Figure 7, Spectral density $A(Q, E)$ as a function of Q for $\alpha = .75$ and four values of E for the tight-binding system. Arrows indicate positions of ordered-system δ -functions.

Figure 8. Spectral density $A(Q, E)$ as a function of Q for $E = .50$ and three values of α for the tight-binding system. Arrows indicate positions of ordered-system δ functions.

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Figure 9. Spectral density $A(Q, \omega)$ as a function of Q for $\alpha = .85$ and four values of ω for the vibrational system. Arrows indicate positions of ordered-system δ -functions.

as determined from Eq. III.A.22. As with the tight-binding results, the peaks in $A(Q, \omega)$ are shifted toward Q and are broadened. The weighting at low energy is quite different from that of the tight-binding system. The strong-weighting can be understood for noting that, for an ordered system (29)

$$A(Q, \omega) = \frac{1}{2\omega} [\delta\{\omega - \omega(Q)\} - \delta\{\omega + \omega(Q)\}]. \quad \text{III.B.1}$$

For $\alpha = .85$, the model system is not far from the ordered-system limit $\alpha = 1$. Unless the states move drastically in $\omega - Q$ space when α is decreased slightly from unity, the presence of the factor of ω^{-1} in Eq. III.B.1 requires that the strongest weighting occur for $\omega \rightarrow 0$. Plotted in Figure 10 are the phonon spectral densities for the same four values of fixed ω with $\alpha = .75$. The scale of Figure 10 has been reduced by a factor of ten relative to that of Figure 9. Broadening and shifting of the peaks in $A(Q, \omega)$ have continued with $A(Q, \omega)$ for $\omega \leq .50$ no longer distinguishable as two distinct peaks. In addition, $A(Q, \omega)$ for $\omega = .10$ is no longer more strongly weighted than that for $\omega = .50$. Figures 11 and 12 point out more clearly the broadening and shifting of $A(Q, \omega)$ with decreasing α for $\omega = .10$ and $\omega = .50$, respectively. In both cases, all vestiges of the ordered-system peaks in the spectral density have vanished for $\alpha = .50$.

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Figure 10. Spectral density $A(Q, \omega)$ as a function of Q for $\alpha = .75$ and four values of ω for the vibrational system. Arrows indicate positions of ordered-system δ -functions.

Figure 11. Spectral density $A(Q, \omega)$ as a function of Q for $\omega = .10$ and three values of α for the vibrational system. Arrows indicate positions of ordered-system δ -functions.

Figure 12. Spectral density $A(Q, \omega)$ as a function of Q for $\omega = .50$ and three values of α for the vibrational system. Arrows indicate positions of ordered-system δ -functions.

C. Relation to Experiment

The results of Part B of this chapter can be used to gain insight into the general features of excitations in three-dimensional systems. The structure in the spectral density does not contain any systematic distortion due to the one-dimensionality of the system, such as the logarithmic singularities in the density of states. For the phonon system discussed earlier in this chapter with $\alpha = 1$ (perfect order), the Green's function in one dimension takes the form

$$G(Q, \omega) = \frac{1}{\omega^2 - \omega^2(Q) + i\eta} . \quad \text{III.C.1}$$

In three dimensions, the Green's function becomes

$$G^{\alpha\beta}(\vec{Q}, \omega) = \sum_{\mu=1}^3 \left\{ \frac{\epsilon^{\alpha}(\mu, \vec{Q}) \epsilon^{\beta}(\mu, \vec{Q})}{\omega^2 - \omega_{\mu}^2(\vec{Q}) + i\eta} \right\}, \quad \text{III.C.2}$$

where μ is a polarization index and $\epsilon^{\alpha}(\mu, \vec{Q})$ is a normalized eigenvector used to diagonalize the force constant matrix $D_{\vec{Q}}^{\alpha\beta}$ according to

$$\sum_{\beta} D_{\vec{Q}}^{\alpha\beta} \epsilon^{\beta}(\mu, \vec{Q}) = D_{\vec{Q}}^{\mu} \epsilon^{\alpha}(\mu, \vec{Q}). \quad \text{III C.3}$$

The quantity $\omega_{\mu}^2(\vec{Q})$ is related to $D_{\vec{Q}}^{\mu}$ by

$$\omega_u^2(\vec{Q}) = \omega_0^2 + D_Q^k, \quad \text{III.C.4}$$

with ω_0 a "bare" Einstein phonon frequency. The Green's functions in one and three dimensions have essentially the same form with the single difference that the latter contains a sum over polarizations. The spectral densities obtained from both Green's functions can be put in a form similar to Eq. III B.1 containing delta functions with a weighting factor of ω^{-1} . The spectral density demonstrates the changes in the one-particle states of the model system in response to structural disorder and the general features can be expected to carry over into three dimensions.

Figure 13 shows some recent neutron scattering measurements on the amorphous ferromagnet Co_4P published by Mook, Wakabayashi, and Pan (30). Shown in Figure 13 are plots for six energies of the neutron inelastic scattering intensity as a function of Q . Above some energy E_1 , one observes a small peak centered between two larger ones. With decreasing energy the pattern becomes double-peaked and at some energy E_0 , finally becomes single-peaked. Below E_0 there exists a small broad structure independent of energy and located near the first peak in the liquid structure factor $S(Q)$ (near $Q = 3.13\text{\AA}^{-1}$). In analyzing this data, Mook et al. suggested that if one were to neglect the small central peak at energies above E_1 and the small structures below E_0 ,

Figure 13. Neutron scattering intensity as a function of Q for several energies (Energy increases vertically) from Mook et al. (30).

the peak positions of the remaining features can be plotted as shown in Figure 14. This dispersion relation is reminiscent of (30) that observed for rotons (31), suggesting that a new magnetic excitation has been found.

In using the results presented earlier in this chapter to analyze this data, it is useful to establish the role of the spectral density in neutron inelastic scattering. The differential cross-section for scattering from lattice vibrations (phonons) is given by

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{Q_2}{2\pi Q_1} S(\vec{Q}, \omega), \quad \text{III.C.5}$$

where $\vec{Q}_1$ and $\vec{Q}_2$ are the initial and final momenta of the incident neutron, $d\Omega$ is an infinitesimal volume element, and $S(\vec{Q}, \omega)$ is the dynamic form factor. $S(\vec{Q}, \omega)$ can be written as

$$S(\vec{Q}, \omega) = \sum_n \left| \langle n | \sum_j e^{i\vec{Q} \cdot \vec{r}_j} | 0 \rangle \right|^2 \delta(\omega - \omega_{n0}), \quad \text{III.C.6}$$

where $|n\rangle$ is an excited state of the system and $|0\rangle$ is the exact ground state. ω_{n0} is the difference in energy between the ground state and the excited state

$$\omega_{n0} = E_n - E_0. \quad \text{III.C.7}$$

Expanding $S(Q, \omega)$ and neglecting those terms describing multiple excitations gives

Figure 14. Suggested analysis of data in Figure 13; from Mook et al. (30).

$$S(Q, \omega) = N e^{-2W(Q)} [I(Q) \delta(\omega) + Q^2 \lambda(Q, \omega)], \quad \text{III.C.8}$$

where $I(Q)$ gives the strength of the elastic scattering contribution to $S(Q, \omega)$ and $2W(Q)$ is the Debye-Waller factor. It is clear from Eq. III.C.8 that the spectral density $\lambda(Q, \omega)$ gives the inelastic scattering contribution to $S(Q, \omega)$ from single-particle excitations. For a one-dimensional system, one cannot actually calculate $S(Q, \omega)$ or the liquid structure factor $S(Q)$ defined as

$$S(Q) = \frac{1}{N} \int S(Q, \omega) d\omega. \quad \text{III.C.9}$$

The Debye-Waller factor $2W(Q)$ diverges in one-dimension resulting in $S(Q, \omega) = 0$ for all Q and ω . However, this is of no great importance in this work because it is unphysical to scatter from a hypothetical one-dimensional chain. To the extent to which the one-dimensional system used here can be taken as a model for the effects of short-range order in a solid, the spectral densities in Figure 5, page 55, Figure 6, page 57, Figure 7, page 58, Figure 8, page 59, Figure 9, page 60, Figure 10, page 62, Figure 11, page 63 and Figure 12, page 64, can be used to interpret the qualitative features of neutron scattering measurements.

By comparing Figures 6, 7, 9, and 10 respectively, it emerges as a common feature that the low energy states in a

tight-binding system do not vanish with the introduction of structural disorder. A comparison of Figures 6, page 57 and 13, page 67, makes it appear quite likely that the structure below E_0 in Figure 13 is real. The calculations indicate that the observations are better explained as a manifestation of the effects of structural disorder upon the ordinary spin waves of the system than as a new type of elementary excitation.

The present calculation also permits a prediction as yet untested by experiment. The results for the vibrational system differ from those of the tight-binding system principally in the weighting of the low energy states. Figures 9 and 10, pages 60 and 62, suggest that if an experiment similar to that of Mook et al., were performed on a phonon system, a single peak in the second zone would be found for each energy below a "minimum" energy E_0 , and this peak would be larger than the one that appears in the spin-wave case.

CHAPTER IV

SUMMARY

The preceding chapters have described a numerical investigation of the effects of short-range order on the spectral density function for a one-dimensional model of an amorphous solid. In Chapter II, the calculation was described in detail and applied to a model of an electron in a potential consisting of randomly placed delta functions. The spectral density $A(k,E)$ was found to be given by the mean of the random variable $f_L(k,E)$ in the limit $L \rightarrow \infty$. The convergence properties of $f_L(k,E)$ were examined and found to possess the interesting feature that as $L \rightarrow \infty$, $f_L(k,E)$ is not self-averaging (ergodic). That is, $f_L(k,E)$ does not approach its mean value with zero variance as L becomes large. It was shown that an alternative procedure exists for calculating $A(k,E)$ for a single long chain of atoms, but that method leads to numerical difficulties. The actual determinations of $A(k,E)$ was made by calculating $f_L(k,E)$ for several moderately long chains and averaging the results.

The model calculation in Chapter II was compared with $A(k,E)$ obtained in the quasicrystalline approximation (QCA). The QCA agreed very well with the essentially exact results in the positive energy (weak-scattering) regime, but proved inadequate in the negative energy (strong-scattering) regime.

These conclusions are consistent with earlier results for the integrated density of states.

In Chapter III, the spectral densities associated with a tight-binding Hamiltonian and a phonon Hamiltonian were studied. For both the tight-binding and phonon systems, the dominant effect of short-range order in a structurally disordered model is to produce a broadened and slightly shifted (in Q) version of the ordered-system spectral density. The most striking difference between the spectral densities for the two systems is the weighting given to low energy states. The model calculations of Chapter III were used to analyze the qualitative features of recent neutron inelastic scattering measurements on an amorphous ferromagnetic system. Based on the calculations, the experimental data support the conclusion that the observed excitations were ordinary spin waves, with properties suitably altered by the structural disorder of the system.

The treatments presented in this work by no means exhaust the possible applications of the numerical method. A natural extension of the work in Chapter II would be a calculation of $A(k, E)$ for a model binary alloy and a comparison with the spectral density obtained from the coherent potential approximation (CPA). The methods of Chapter III could be applied to an investigation of the vibrational properties of a binary alloy.

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APPENDICES

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APPENDIX A

DERIVATION OF EQ. II.C.6

Consider the integral

$$I = \int_0^L \int_0^L f(x - y) dx dy. \quad A.1$$

Insert a delta function integration

$$I = \int_0^L \int_0^L \int_{-L}^L \delta\{u - (x - y)\} f(u) du dx dy. \quad A.2$$

Rearranging orders of integration and splitting the integration over u into positive and negative contributions yields

$$\begin{aligned} I = & \int_{-L}^0 f(u) \int_0^L \int_0^L [\delta\{y - (x - u)\} dy] dx du \\ & + \int_0^L f(u) \int_0^L \int_0^L [\delta\{y - (x - u)\} dy] dx du. \end{aligned} \quad A.3$$

Substituting $u = -u'$ in the first integral gives

$$\begin{aligned} I = & \int_0^L f(-u) \int_0^L \int_0^L [\delta\{y - (x + u)\} dy] dx du \\ & + \int_0^L f(u) \int_0^L \int_0^L [\delta\{y - (x - u)\} dy] dx du, \end{aligned} \quad A.4$$

where u is always positive. The first integral in Eq. A.4 is nonzero only if $0 \leq x \leq (L - u)$. The second integral is nonzero only if $u \leq x \leq L$. Eq. A.4 becomes

$$I = \int_0^L f(-u) \int_0^{L-u} [\int_0^L \delta\{y - (x + u)\} dy] dx du \\ + \int_0^L f(u) \int_u^L [\int_0^L \delta\{y - (x - u)\} dy] dx du. \quad A.5$$

Performing the integration indicated results in

$$I = \int_0^L (L - u) \{f(u) + f(-u)\} du. \quad A.6$$

Application of Eq. A.6 to Eq. II.C.5 with $f(x - y) = e^{ik(x-y)}$ $R(x - y)$ leads directly to Eq. II.C.6.

APPENDIX B

DERIVATION OF EQ. II.C.11

The reduction of Eq. II.C.10 begins by noting that for normally distributed random variables with zero mean,

$$\begin{aligned} \langle g(w;E)g(x;E)g(y;E)g(z;E) \rangle &= \langle g(w;E)g(x;E) \rangle \langle g(y;E)g(z;E) \rangle \\ &+ \langle g(w;E)g(y;E) \rangle \langle g(x;E)g(z;E) \rangle \\ &+ \langle g(w;E)g(z;E) \rangle \langle g(x;E)g(y;E) \rangle. \end{aligned} \quad \text{B.1}$$

This property of normally distributed random variables can be found in standard texts on probability (see, for example, reference 32). Substituting Eq. B.1 into Eq. II.C.10 gives

$$\begin{aligned} \langle \{f_L(k,E)\}^2 \rangle &= \left[\frac{1}{L} \int_0^L \int_0^L e^{ik(w-x)} \langle g(w;E)g(x;E) \rangle dw dx \right] \\ &\quad \left[\frac{1}{L} \int_0^L \int_0^L e^{ik(y-z)} \langle g(y;E)g(z;E) \rangle dy dz \right] \\ &+ \frac{1}{L^2} \left[\int_0^L \int_0^L e^{ik(w-z)} \langle g(w;E)g(z;E) \rangle dw dz \right] \\ &\quad \left[\int_0^L \int_0^L e^{ik(y-x)} \langle g(y;E)g(x;E) \rangle dy dx \right] \\ &+ \frac{1}{L^2} \left[\int_0^L \int_0^L e^{ik(w+y)} \langle g(w;E)g(y;E) \rangle dw dy \right] \end{aligned}$$

$$\left[\int_0^L \int_0^L e^{-ik(x+z)} \langle g(x;E) g(z;E) \rangle dx dz \right]. \quad B.2$$

The first two terms are easily identified as $\langle f_L(k,E) \rangle^2$ and Eq. B.3 simplifies to

$$\begin{aligned} \langle \{f_L(k,E)\}^2 \rangle &= 2 \langle f_L(k,E) \rangle^2 \\ &+ \frac{1}{L^2} \left[\int_0^L \int_0^L e^{ik(w+y)} \langle g(w;E) g(y;E) \rangle dw dy \right] \\ &\left[\int_0^L \int_0^L e^{-ik(x+z)} \langle g(x;E) g(z;E) \rangle dx dz \right]. \quad B.3 \end{aligned}$$

It will now be demonstrated that in the limit $L \rightarrow \infty$, the first of the two integrals in the second term of the above equation vanishes.

Let $R(w - y) = \langle g(w;E) g(y;E) \rangle$ and let us define

$$J = \frac{1}{L} \int_0^L \int_0^L e^{ik(w+y)} R(w - y) dw dy. \quad B.4$$

As in Appendix A, introducing a delta function integration puts J in the form

$$J = \frac{1}{L} \int_{-L}^L \int_0^L \int_0^L e^{ik(u+2y)} R(u) \delta\{u - (w - y)\} dw dy du. \quad B.5$$

Performing exactly the same separation of the integral as that of Appendix A and invoking $R(u) = R(-u)$ gives

$$J = 2 \int_0^L R(u) e^{ikL} \left[\frac{\sin(k(L-u))}{kL} \right] du. \quad \text{B.6}$$

Taking the limit of J as $L \rightarrow \infty$ gives zero.

APPENDIX C

THE QCA SELF-ENERGY

It will be shown here that the self-energy $\Sigma(k, E)$ is, for negative energies, a real quantity for the model described in Chapter II. Let us define $K = |E|^{1/2}$. For negative energy the scattering operator, is real and given by

$$\tau^{(0)}(E) = - \frac{2\Delta K}{2K - \Delta} . \quad C.1$$

It remains to be shown that the quantity $G_0''(k, E)$ defined in Eq. II.D.11 is real. Replacing γ by iK in Eq. II.D.11 shows that $g^-(\gamma + k) + g^-(\gamma - k) = g^-(iK + k) + g^-(iK - k)$ is the quantity of interest,

$$\begin{aligned} g^-(\gamma + k) + g^-(\gamma - k) &= \frac{e^{ika} e^{-Ka}}{1 - e^{ika} e^{-Ka} - i(iK + k)\ell(1 - \alpha)} \\ &+ \frac{e^{-ika} e^{-Ka}}{1 - e^{-ika} e^{-Ka} - i(iK - k)\ell(1 - \alpha)} . \end{aligned} \quad C.2$$

Changing the denominators slightly gives

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$$\begin{aligned}
g^-(\gamma + k) + g^-(\gamma - k) = & \frac{e^{ika} e^{-Ka}}{1 - e^{ika} e^{-Ka} + (K - ik)l(1 - \alpha)} \\
& + \frac{e^{-ika} e^{-Ka}}{1 - e^{-ika} e^{-Ka} + (K + ik)l(1 - \alpha)} .
\end{aligned}$$

C.3

This shows that the quantity $g^-(\gamma + k) + g^-(\gamma - k)$ is the sum of a complex quantity and its complex conjugate and hence is real. Therefore, all quantities in Eq. II.D.10 are real and so the self-energy is real.