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Koss, Robert Stephen

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DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

Robert Stephen Koss, B.S., M.S.

* * * * *

The Ohio State University
1986

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Department of Physics
To My Parents
ACKNOWLEDGMENTS

I would like to take this opportunity to express my sincere appreciation to the people that helped shape my career.

Thanks go to Dr. Richard C. Phillips of the Chemistry Department of Youngstown State University, who, while trying to teach me physical chemistry, aroused my interest in physics. Pursuing my new found interest in the Physics Department of YSU, I had the pleasure of developing friendships with Dr. William Moorhead and Dr. William Cochran. Thank you both for encouraging me to pursue graduate studies in physics and for your continued support and friendship.

Words fail me in trying to acknowledge the help and guidance of Dr. David Stroud, my advisor at OSU. Let me simply say thanks for your patience and understanding as the material for this thesis was being developed.

The National Science Foundation is gratefully acknowledged for providing financial support.

Finally, to my wife Susan, I offer my sincere thanks for your constant faith in me and your willingness to endure with me all of the trials and tribulations of graduate school.
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FIELD OF STUDY

Major Field: Theoretical Condensed Matter Physics
Specialty: Transport Properties of Inhomogeneous Materials

PUBLICATION

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...
CHAPTER I
INTRODUCTION

This work is concerned with some aspects of the theory of inhomogeneous materials. In particular, it is devoted to a specific though broad class of such materials known as random binary granular composites. A random binary granular composite may be defined as a random mixture of two different homogenous materials; the sense of the term "random" will be made clear below. The materials of interest in the present work are usually normal metals, insulators, or superconductors. The term "granular" is meant to imply that the components forming the composite are macroscopic structures (typically on the order of μm), large enough to have distinct properties of their own. When these individual components form a composite, however, the properties of the composite are generally very different from either of the constituents. The properties of the composite will depend not only on the intrinsic properties of the constituents but also on their topological arrangement.

Random binary composites can be produced in a variety of ways. One way is to take known quantities of two different materials and physically mix them so as to produce a random mixture. For example, a normal metal-insulator composite
might be prepared from small particles of copper (a metal) and polypropylene (an insulator). Suppose an electric field is applied to such a composite. The resulting a.c. or d.c. current can be measured and an attempt may be made to calculate the conductivity of the composite. The observed conductivity of the composite will be different from either that of a bulk conductor or a bulk insulator. If the metal-insulator composite contains only a small fraction of metal, then the current at small values of an applied d.c. electric field will be zero; the composite as a whole will thus be insulating. As more and more metal is added a point will finally be approached at which the composite as a whole conducts. This point is known as the percolation threshold \( p_c \); the behavior of the composite near \( p_c \) is an important property that characterizes random granular composites. By definition \( p_c \) is the volume fraction at which one of the constituents of the composite first forms a closed connected path across the sample. This concept is schematically illustrated in Figures 1. A major aim of this thesis is to study the electrical response of random composites in the neighborhood of the percolation threshold.

In a systematic experimental study of composite systems, one would ideally prepare several samples, each with a different fraction of metal, and measure the response of the system in the presence of an applied electric field. In the present work, we will follow the same procedure, except that
Fig. 1 Illustration of a random binary composite. The shaded regions represent the metallic component. $p$ is the volume fraction of metal. (a) corresponds to below the percolation threshold, (b) illustrates the threshold, and (c) corresponds to above the threshold.
instead of carrying out experiments with real materials in a laboratory we will carry out computer experiments on model materials. This procedure has the advantage that, unlike real materials, the experimental conditions are always exactly known and controllable. A disadvantage is that computer models are limited to small sample size which makes the results configuration dependent. Thus many samples must be averaged to obtain good statistics.

Before discussing the organization of this dissertation it will be useful to give a brief history of previous theoretical work on the transport properties of random composites. This work dates back at least one hundred years to the era of Maxwell and Lord Rayleigh. The review by Landauer and references therein contains an account of this early theoretical work on inhomogeneous systems.

The history of current analytic work on random composite systems began in 1904 with a theory for the dielectric function of a composite material proposed by J.C. Maxwell-Garnett. This Maxwell-Garnett theory is equivalent to the well-known Clausius-Mossotti approach treated in most textbooks of electromagnetic theory. This theory does not predict a percolation threshold for a two component system. It is also an unsymmetric theory - that is, different results are obtained depending on which material is considered to be the host material and which is considered to be the inclusion. The theory is thus unsuitable for the study of
random composites in which the constituents are symmetrically distributed. Both deficiencies are overcome by the so-called effective medium approximation, proposed by Bruggeman in 1935. An excellent review of both theoretical and experimental work is given by Kirkpatrick.

Many of the numerical results in this thesis can be well approximated by the effective medium approximation (EMA), which is derived in the Appendix. However, although the EMA does predict a percolation threshold, it also has certain undesirable features. First, it is not a fully controlled approximation, that is to say, when the theory does agree with experiment it is often unclear whether the agreement is due to the excellence of the theory or to a fortuitous choice of parameters such as the geometrical shape of the particles. Most versions of the EMA assume the particles to be ellipsoidal, an assumption which is satisfactory in most instances. But space cannot be filled with ellipsoids. We have therefore extended the theory to generalized, non-ellipsoidal geometries and applied it to cubic geometries in particular. For other particle shapes, while the extended theory remains valid it is more difficult to carry out calculations in practice.

A second major objection to the EMA is that it does not predict the correct behavior of the composite's properties near the percolation threshold. This problem arises because the EMA is a mean field approximation roughly analogous to
the Weiss molecular field theory of magnetism and to the coherent potential approximation used in the study of metal alloys. Most properties near $p_c$ are described by power laws in $(p - p_c)$ with non-integer exponents (where $p$ is the volume fraction of metal). These exponents are discussed in detail later in this thesis.

Besides their fundamental interest, random composite materials are also of practical importance. An example of a composite occurring in nature is a porous rock containing salt water. Since crude oil is sometimes found in this type of material, the study of such composite materials is of particular importance to the petroleum industry. Another example of a composite is solid rocket fuel. This type of material is used in both space exploration and in defense applications.

While most composites of practical interest are three dimensional the present thesis will be concerned entirely with two dimensional systems. These are prepared using such techniques as thermal evaporation (in which a metal is vaporized and deposited on an insulating substrate) or RF sputtering (where an ionized gas displaces atoms from a bulk metal; these atoms are then deposited at random on an insulating substrate).

This thesis is organized as follows. In Chapter II we review the general theory of classical phenomena in random composite media in the long wavelength limit. Applying
Maxwell's equations in this regime, we derive the partial differential equations governing such systems. By solving these equations by the method of finite differences, we show that the equations can be viewed as a realization of Kirchoff's laws. These equations can then be solved by iteration. The iteration procedure brings with it certain technical problems such as requiring large amounts of computer time and memory. Furthermore, convergence is not guaranteed and is in fact impossible below percolation. Hence, studies of composite media below $p_c$ require other numerical techniques.

The shortcomings of the iterative solution of Kirchoff's laws are readily overcome by an elegant technique based on transfer matrices. Following Derrida, et al., we derive this highly efficient and accurate algorithm from basic network equations. Use of the transfer matrix technique permits us to calculate the effective conductivity of an impedance network exactly and with convergence guaranteed. The only limits on the size of the lattice result from computer time constraints. This method has been previously applied to calculate critical exponents (to be discussed below) to a high degree of accuracy.

The last part of Chapter II is devoted to a review and extension of the scaling theory of random composites near the percolation threshold. This theory is motivated by noting the similarity of percolation to a second order phase transition.
As in second order phase transitions, many properties of composites exhibit power law dependencies near the percolation threshold. For example, the conductivity of a composite usually exhibits a power law behavior:

\[ \sigma_e \sim (p - p_c)^t \]  

(1.1)

where \( \sigma_e \) is the effective conductivity, \( p \) is the volume fraction of metal, \( p_c \) is the percolation threshold and \( t \) is a universal critical exponent which is independent of the details of the system and depends solely on the spatial dimension of the system. By making an analogy with a magnetic phase transition, and following Straley, we represent the conductivity as a homogenous function of certain variables and show that finite size scaling theory, adapted from critical phenomena, can be used to understand its properties near the percolation threshold.

In the remaining chapters we apply the formalism of Chapter II to various specific problems. In Chapter III we calculate numerically the electromagnetic response of a model normal metal-insulator composite and of a model normal metal superconductor composite. We demonstrate that the results found by computer simulation on a lattice are similar to those found from the effective medium approximation.

The transfer matrix technique derived in Chapter II is extended to finite frequencies in Chapter IV. The technique
is then used to verify the scaling forms for the effective conductivity taking into account the effects of both finite size and finite frequency.

In Chapter V we make a judicious choice of circuit elements to represent the metallic and insulating bonds in a composite so as to assure the resulting network is equivalent to a composite of Drude metal and dielectric. The AC transfer matrix is then used to obtain the optical spectrum of this network. We also perform the same calculation using the effective medium approximation and compare the results of the two different methods.

Finally in Chapter VI we consider the subject of dielectric breakdown. Here we are interested in the effects of a high electric field on a metal-insulator composite below percolation. We find that the critical electric field for dielectric breakdown decreases as the percolation threshold is approached from below, and increases with increasing frequency. We find an opportunity to use all the numerical techniques developed earlier in this dissertation to study the breakdown problem and obtain the breakdown field as a function of both metal fraction and frequency. The algorithm we employ here makes large demands on a computer. The chapter concludes with some suggestions for further work that could be done easily on a computer capable of parallel processing.
References for Chapter I


4. R. Landauer in Ref. 1, p. 2.


CHAPTER II
GENERAL FORMALISM

Introduction

In this chapter we develop the necessary theory needed to study certain electrical transport properties of random composite systems. We are interested in the response of the system to an applied d.c. electric field (or a long wavelength electromagnetic wave). We shall develop the theory then from the natural starting place of Maxwell's equations of electricity and magnetism.

We first consider the DC problem of calculating the effective conductivity of a random composite in the presence of an electrostatic field. The usual equations of electrostatics can be applied to this system. We shall look at this problem in some depth because we employ the method of finite differences to solve our equations and justify the use of resistor lattices to represent binary composites. With certain assumptions regarding our system in the quasistatic limit, we can also derive the equations necessary to solve the AC problem, that is, the response of the system when exposed to an electromagnetic field. In both the AC and DC problems, the equations we need to solve to calculate the effective transport coefficient will be shown to be
equivalent to Kirchoff's equations of circuit analysis.

In practice, solving Kirchoff's Laws on a computer is a time consuming endeavor. Some of the practical problems with Kirchoff's Laws are resolved with the use of the transfer matrix algorithm. We derive the transfer matrix directly from Ohm's Law but defer a description of the algorithm to a later chapter.

The effective transport coefficients of a random composite are functions of the concentrations and conductivities of the constituents, and also of the size of the system. Viewed as a function of concentration only, these effective transport coefficients obey power laws in \((p - p_c)\) near the percolation threshold. This behavior is analogous to that of the order parameter in an ordinary second order phase transition. By pursuing this analogy and drawing on the success of scaling theory as applied to second order phase transitions, we can postulate scaling forms for the transport coefficients of a random composite.

**Lattice Concepts**

We shall confine our study to two dimensional random binary granular composites. Since the composite consists of two different materials, having two distinct conductivities, we assume that we can assign a local scalar conductivity \(\sigma(\vec{r})\) at each point \(\vec{r}\) in the material. That is, we assume
that the dimensions of the conducting particles are large with respect to the electronic mean free path.

We wish to determine the effective conductivity of the entire composite. The effective conductivity may be studied by considering the response of the system to an applied electric field. For the moment we consider only a DC field. Figure 2 illustrates this idea. We can calculate the local fields and currents by solving the usual equations of electrostatics:

\[ \nabla \times \mathbf{E}(\mathbf{r}) = 0 \quad (2.1a) \]
\[ \nabla \cdot \mathbf{J}(\mathbf{r}) = 0 \quad (2.1b) \]
\[ \mathbf{J}(\mathbf{r}) = \sigma(\mathbf{r}) \mathbf{E}(\mathbf{r}) \quad (2.1c) \]

where \( \mathbf{E}(\mathbf{r}) \) is the electric field and \( \mathbf{J}(\mathbf{r}) \) is the resulting current density arising from the applied field. From equation (2.1a) we see that \( \mathbf{E} \) can be derived from a scaler potential \( V(\mathbf{r}) \):

\[ \mathbf{E}(\mathbf{r}) = -\nabla V(\mathbf{r}) \quad (2.2) \]

Combining equations (2.1b), (2.1c), and (2.2) yields

\[ \nabla \cdot (\sigma(\mathbf{r}) \nabla V(\mathbf{r})) = 0 \quad (2.3) \]
Fig. 2  Diagram of experimental setup to measure the resulting current drawn by a random composite when exposed to an external electric field. The effective conductivity is readily calculated given the current, applied voltage, and dimensions of the system.
We choose to solve this equation using the method of finite differences. To do this we introduce a square grid of points \( \{ r_i \} \), with spacing \( \Delta r \), thus forming a two dimensional lattice. For simplicity we will apply the method of finite differences to equation (2.3) in one dimension. The extension to two and three dimensions is straightforward but lengthy.

Let \( j(x) = \sigma(x) \nabla \nabla(x) \). Then on the one dimensional lattice:

\[
\nabla \cdot j = \frac{\partial j(x)}{\partial x} = \frac{j(x+\Delta x/2) - j(x-\Delta x/2)}{\Delta x} \tag{2.4}
\]

Using the definition of \( j(x) \) yields

\[
\nabla \cdot j = \frac{1}{\Delta x} \left[ \sigma(x+\Delta x/2) \nabla \nabla(x+\Delta x/2) - \sigma(x-\Delta x/2) \nabla \nabla(x-\Delta x/2) \right] \tag{2.5}
\]

But

\[
\nabla \nabla(x) = \frac{\nabla(x+\Delta x/2) - \nabla(x-\Delta x/2)}{\Delta x} \tag{2.6}
\]

so equation (2.3) becomes

\[
\frac{1}{(\Delta x)^2} \left[ \sigma(x+\Delta x/2)[\nabla(x+\Delta x/2) - \nabla(x)] + \sigma(x-\Delta x/2)[\nabla(x-\Delta x/2) - \nabla(x)] \right] = 0 \tag{2.7}
\]

on the one dimensional lattice. We can now extend this to higher dimensions by writing it as
where the sum is over nearest neighbor lattice sites and $g_{ij}$ is defined as $g_{ij} = \sigma [(r_i^+ + r_j^+) / 2] / \Delta x^2$. This is the equation to be used in subsequent chapters to calculate the conductivity of random composites.

Kirkpatrick\textsuperscript{1,2} has observed that eq. (2.8) is just Kirchoff's current law for a network of conductances. It can be used to model many kinds of composites. For a normal metal-insulator binary composite, for example, one chooses $g_{ij}$ to be 0 or 1 at random. These networks of conductances are obviously related to real composites through the above equations and they, like real composites, will also exhibit a percolation threshold.

There has been recent interest\textsuperscript{3,4} in continuum models of random composites. Using the normal metal-insulator example cited above, in order to transform a continuum model into a discrete one, the metallic bonds are assigned a conductance chosen from a singular random distribution between 0 and 1. This may be a more realistic model for real composites but Feng, et al.,\textsuperscript{5} have shown that the conductivity exponent $\tau$ is the same for both network and continuum models, at least in two dimensions.

To study the AC response of composite materials, i.e., the optical properties, we need to specify that the composite is
in the long wavelength limit. This limit is defined by the requirement that wavelengths of interest are much greater than the interparticle spacing. Such a system can then be treated in the quasistatic limit, that is, as if $\mathbf{\nabla} \times \mathbf{E} = 0$.

The above considerations can be made explicit by considering the Maxwell equation:

$$\mathbf{\nabla} \times \mathbf{H}(\mathbf{r}) = \frac{1}{c} \frac{\partial}{\partial t} \mathbf{D}(\mathbf{r}) + \frac{4\pi \mathbf{J}(\mathbf{r})}{c} \quad (2.9)$$

where $\mathbf{H}(\mathbf{r})$ is the magnetic field, $\mathbf{D}(\mathbf{r})$ is the electric displacement, and $c$ is the speed of light in vacuum (in Gaussian units). If we assume that at each point $\mathbf{r}$ in the composite we can assign a dielectric constant $\varepsilon(\mathbf{r})$ and a conductivity $\sigma(\mathbf{r})$, then we also have the relationships

$$\mathbf{D}(\mathbf{r}) = \varepsilon(\mathbf{r}) \mathbf{E}(\mathbf{r})$$

and

$$\mathbf{J}(\mathbf{r}) = \sigma(\mathbf{r}) \mathbf{E}(\mathbf{r}) \quad (2.10)$$

Assuming $e^{-i\omega t}$ time dependence for the incident electromagnetic wave, we can write equation (2.9) more concisely in the form

$$\mathbf{\nabla} \times \mathbf{H}(\mathbf{r}) = -\frac{i\omega}{c} \varepsilon_r(\omega) \mathbf{E}(\mathbf{r}) \quad (2.11)$$
where we have introduced the complex dielectric function

\[ \epsilon_r(\omega) = \epsilon_0(r) + \frac{4\pi i \sigma(r)}{\omega} \]  \hspace{1cm} (2.12)

which includes both real and imaginary response. Taking the divergence of equation (2.11) and recalling that \( \nabla \cdot (\nabla \times \mathbf{E}) = 0 \) yields

\[ \nabla \cdot [\epsilon_r(\omega) \mathbf{E}(r)] = 0 \]  \hspace{1cm} (2.13)

We have stated the validity of \( \nabla \times \mathbf{E} = 0 \) so that the electric field is still derivable as the negative gradient of the scaler potential \( V(r) \). Thus we have

\[ \nabla \cdot [\epsilon_r(\omega) \nabla V(r)] = 0 \]  \hspace{1cm} (2.14)

as our equation to solve for the AC problem. Notice that this is formally identical to equation (2.3) for the DC problem, with \( \sigma \) replaced by \( \epsilon_r \). We again use the finite difference approximation which gives

\[ \sum_j \epsilon_{ij}(\omega) (V_j - V_i) = 0 \]  \hspace{1cm} (2.15)
where $\xi_{ij}(\omega) = \epsilon (r_i + r_j)/2, \omega$. Comparing this to equation (2.8) demonstrates that the same equation must be solved for both ac and dc response. Thus we may write without loss of generality

$$\sum_j g_{ij} (V_j - V_i) = 0$$

and allow the $g_{ij}$'s to be possibly complex functions of frequency. Random composites can be modeled by making a proper choice of the $g_{ij}$'s. In the following chapters, eqs. (2.16) will be solved for the values of the potential at each lattice point. This information allows us to calculate an effective conductivity for the model composite.

We defer the details of the actual algorithms to later chapters. At this point, we briefly outline how these equations are solved in order for the reader to appreciate the value and efficiency of the transfer matrix technique, which we review in the next section.

Equation (2.16) must be solved at each point $i$ on the lattice. For a 100 x 100 square lattice, this procedure leads to 10,000 simultaneous linear equations. If we specify the voltages on the boundaries parallel to the field and employ cyclic boundary conditions perpendicular to the field, we are left with 9,800 unknowns. One way to solve these equations is by iteration. Rewriting equation (2.16) as
\[ v_i^{(n)} = \frac{\sum_j g_{ij} v_j^{(n-1)}}{\sum_j g_{ij}} \]  

we have an implied iteration procedure for the potential, where the superscripts (n) and (n-1) refer to the nth and (n-1)st iterations respectively. Depending on the value of p (which determines the \( g_{ij} \)'s) this procedure can use a tremendous amount of computer time. The closer \( p \) is to \( p_c \), the more iterations are required to achieve convergence. Since our interest is in the neighborhood of \( p_c \), clearly a better method for obtaining the effective conductivity would be desirable.

**The Transfer Matrix Method**

The basic idea of the Transfer Matrix Method\(^6,7\) is to calculate the conductivity of the lattice as it is being constructed. We will see that this method requires less computer time than solving Kirchoff's law and that the conductivity that we ultimately calculate will be the exact conductivity of the lattice. In the iterative solution of Kirchoff's equations, iteration is performed until some convergence criteria is satisfied. Thus the solution is approximate by the nature of the numerical method.
Fig. 3 Construction of horizontal strip used in the transfer matrix method. In (a) the strip is constructed to column $L$ and is characterized by the matrix $A_L$. (b) shows the addition of the $L+1$ column by adding horizontal resistors $h_i$ and vertical resistors $v_i$. The strip is characterized by the matrix $A_{L+1}$. 
Consider Fig. (3a). For a lattice of width $N$ we let the horizontal bonds on the first and $(N+1)$st row have zero resistance, that is, we assume these bonds to be buses. We assume that we have constructed $L$ columns, each of width $N$, and that the lattice that we have so far constructed is described by a $N \times N$ matrix $\mathbf{A}_L$. The currents in the wires are related to the applied voltages through $\mathbf{A}_L$ as

\[
\begin{pmatrix}
I_1 \\
I_2 \\
\vdots \\
I_N
\end{pmatrix}
= \mathbf{A}_L
\begin{pmatrix}
U_1 \\
U_2 \\
\vdots \\
U_N
\end{pmatrix}
\]

or more compactly as

\[
\mathbf{I} = \mathbf{A}_L \mathbf{U}
\]

which defines $\mathbf{A}_L$.

We now wish to see how the matrix $\mathbf{A}_L$ is transformed into $\mathbf{A}_{L+1}$ when we construct the $(L+1)$st column to our lattice, which consists of horizontal and vertical resistors $h_i$ and $v_i$ respectively, as seen in figure (3b). By analogy with equation (2.19), $\mathbf{A}_{L+1}$ is defined as $\mathbf{I}' = \mathbf{A}_{L+1} \mathbf{U}'$.

We first consider the effect of adding only the horizontal resistors. The voltages $U_i$ are related to the voltages $U_i'$. 
through Ohm's Law

\[ U_i = U'_i - h_i I_i \]  \hspace{1cm} (2.20)

or in matrix form

\[ \mathbf{U} = \mathbf{U}' - \mathbf{H} \mathbf{I} \]  \hspace{1cm} (2.21)

where the matrix \( \mathbf{H} \) is defined as \( H_{ij} = h_i \delta_{ij} \) and is diagonal. Now using the definition of \( \mathbf{A}_L \) in equation (2.19), we can rewrite equation (2.21) as

\[ \mathbf{U} = \mathbf{U}' - \mathbf{H} \mathbf{A}_L \mathbf{U} \]

or

\[ \mathbf{U} = ( \mathbf{A}_L + \mathbf{H} \mathbf{A}_L )^{-1} \mathbf{U}' \]  \hspace{1cm} (2.22)

Left multiplying by \( \mathbf{A}_L \) and using equation (2.19) gives the currents in the horizontal resistors of column \((L+1)\) as

\[ \mathbf{I} = \mathbf{A}_L ( \mathbf{A}_L + \mathbf{H} \mathbf{A}_L )^{-1} \mathbf{U}' \]  \hspace{1cm} (2.23)

Since \( \mathbf{I} = \mathbf{I}' \), we have from the definition of \( \mathbf{A}_{L+1} \)

\[ \mathbf{A}_{L+1} = \mathbf{A}_L ( \mathbf{A}_L + \mathbf{H} \mathbf{A}_L )^{-1} \]  \hspace{1cm} (2.24)

as the new matrix describing our system when horizontal resistors are added to the \((L+1)\)st column.
Next we consider the effect of the vertical resistors \( v_i \). The current \( j_i \) in vertical resistor \( v_i \) is:

\[
\begin{align*}
    j_i &= \frac{U'_{i+1} - U'_i}{v_i} \\
    \text{(2.25)}
\end{align*}
\]

We now apply Kirchoff's current law to site \( i \) of column \( (L+1) \)

\[
\begin{align*}
    I'_i &= I_i + j_{i-1} - j_i \\
    \text{(2.26)}
\end{align*}
\]

and using equation (2.25) gives

\[
\begin{align*}
    I'_i &= I_i + \left( \frac{1}{v_{i+1}} + \frac{1}{v_i} \right) U'_i - \frac{1}{v_{i+1}} U'_{i+1} - \frac{1}{v_i} U'_i \\
    \text{(2.27)}
\end{align*}
\]

or in matrix form

\[
\begin{align*}
    \mathbf{I}' &= \mathbf{I} + \mathbf{V} \mathbf{U}' \\
    \text{(2.28)}
\end{align*}
\]

where the matrix \( \mathbf{V} \) is defined as

\[
\begin{align*}
    V_{ij} &= \left( \frac{1}{v_{i+1}} + \frac{1}{v_i} \right) \delta_{ij} - \frac{1}{v_{i+1}} \delta_{j,i+1} - \frac{1}{v_i} \delta_{j,i-1} \\
    \text{(2.29)}
\end{align*}
\]

Using equation (2.23), (2.28) becomes
which gives us \( \overrightarrow{\mathbf{I}}' \) in terms of \( \overrightarrow{U} \). Then by definition of \( \overrightarrow{A}_{L+1} \) we have

\[
\overrightarrow{A}_{L+1} = \overrightarrow{V} + \overrightarrow{A}_L (\overrightarrow{1} + \overrightarrow{H} \overrightarrow{A}_L)^{-1}
\]  

(2.31)

as the matrix describing our system when column \((L+1)\) is added.

We can in principle keep building our lattice to a very great length or until our computer budget runs dry, and there is ample justification in doing so. One of the problems with solving Kirchoff's equations is that we must run a large number of samples and take averages. With the Transfer Matrix we can construct a very long strip of width \(N\), which will automatically take into account the necessary configurational averages.

The goal here is to calculate the conductivity of a random composite. By choosing the \( h_i \)'s and \( v_i \)'s to be \( 0 \) or \( 1 \) at random, we see that we have a model of a metal-insulator composite. Other types of composites can be constructed similarly.

Suppose we want to calculate the conductivity of an \( N \times M \) diluted resistor lattice. We construct \( M \) columns, each of
width N. By following the procedure described above we compute the matrix $A_N$. Next, we add one more column consisting of all infinite resistors, and we set $U_2, U_3, \ldots, U_N = 0$. With this choice, we effectively connect our battery across the sample. $U_1$ equals the applied voltage, i.e., the value of the voltage at the positive terminal of the battery, while $U_N$ will be the negative terminal, i.e., $U_N = 0$. The $(M+1)$st column of infinite resistors prevents all of the current entering our system ($I_1^*$) from going directly to ground. Thus the $(M+1)$st column serves to make $I_2, I_3, \ldots, = 0$.

From equation (2.18) we finally have

$$I_1 = A_{11} U_1$$

(2.32)

where $I_1$ is the current our system draws from the battery $U_1$. We need to take care not to confuse conductivities with conductances: $A_{11}$ is the conductance of the lattice, i.e., the reciprocal of the Ohm's Law resistance. The conductivity is defined as

$$\sigma = j / E$$

(2.33)

where $j$ is the current density resulting from the applied electric field $E$. The current density can be obtained from
the current by dividing by the cross-sectional area of the lattice, which in two dimensions gives

\[ j = \frac{I_1}{M} \]  \hspace{1cm} (2.34)

The electric field is simply \( U_1 \)/N, so the conductivity of our NxM lattice is obtained from

\[ \sigma = \frac{A_{11} U_1 N}{M} \]  \hspace{1cm} (2.35)

Scaling

We have already noted that electrical and optical properties of a composite are very different from those of the constituents of the composite. These differences are particularly conspicuous near the percolation threshold. For a composite consisting of materials described by conductivities \( \sigma_1 \) and \( \sigma_2 \), then for \( \sigma_2 = 0 \) (a normal metal - insulator composite) and near the percolation threshold of material 1, the effective conductivity of the composite \( \sigma_e \) exhibits the power law form

\[ \sigma_e \sim \sigma_1 (p - p_c)^t \] \hspace{1cm} (p > p_c) \hspace{1cm} (2.36)
If $\sigma_1 = 0$ and $\sigma_2 = \text{finite}$ (a normal metal - superconductor composite), then for $p$ approaching $p_c$ from below the threshold, $\sigma_e$ diverges as

$$\sigma_e \sim \sigma_2 (p_c - p)^{-s} \quad (p < p_c) \quad (2.37)$$

Here $p$ is the volume fraction of material 1, $p_c$ is the percolation threshold, and $t$ and $s$ are believed to be universal exponents. The term "universal" implies that the exponents $t$ and $s$ are independent of the details of the system and depend only on the dimensionality of the system. This is in contrast to $p_c$ which is sensitive to the underlying microstructure.

This power law behavior suggests a close analogy between the percolation transition and conventional continuous phase transitions. The analogy further manifests itself in the existence of a characteristic correlation length $\xi$, which describes the formation of a connected cluster and its subsequent growth as the percolation threshold is approached. The correlation length is believed\(^8\) to obey a power law form, diverging as

$$\xi \sim |p_c - p|^{-\nu} \quad (2.38)$$

where $\nu$ is another critical exponent with the same degree of universality as $s$ and $t$. 
By pursuing this analogy between the percolation
transition and other critical phenomena, much progress has
been made in our understanding of the properties of composite
materials. For a composite consisting of two materials with
conductivities \( \sigma_1 \) and \( \sigma_2 \), Straley\(^9\) has proposed that the
two variables characterizing the "phase diagram" are \((p-p_c)\)
and the ratio \( \sigma_2 / \sigma_1 \), which are analogous respectively to
temperature and magnetic field in a magnetic phase
transition. The critical point is \( p - p_c = 0, \sigma_2 / \sigma_1 = 0 \).

By analogy to the magnetization in a magnetic phase
transition we will assume that the effective conductivity of
our composite is a homogenous function of its arguments,
\( p - p_c \) and \( \sigma_2 / \sigma_1 \). Then by the definition of a homogeneous
function, we have

\[
\frac{\sigma_e}{\sigma_1} = \lambda \left( \frac{1}{\Delta p} + \frac{(t+s)}{t} \frac{\sigma_2}{\sigma_1} \right) \quad (\Delta p > 0)
\]

\[
\frac{\sigma_e}{\sigma_2} = \lambda \left( \frac{1}{s\Delta p} + \frac{(t+s)}{s} \frac{\sigma_1}{\sigma_2} \right) \quad (\Delta p < 0)
\]

(2.39)

where \( \Delta p = p - p_c \), \( \lambda \) is an arbitrary scaling parameter, and
\( F_+ \) and \( F_- \) are scaling functions above and below the
percolation threshold respectively.

There is one more variable that will be useful to consider
in a scaling theory, namely the size of the system. For fixed
electric field, the conductivity of a composite is
proportional to the current density. As the linear size of the system $L$ increases, the current density decreases. We thus include the variable $1/L$ in our homogeneous function representation, giving for $\Delta p > 0$

$$\frac{\sigma e}{\sigma_1} = \lambda F_+ \left[ \lambda^{-1/t} \Delta p , \lambda^{-(t+s)/t} \frac{\sigma_2}{\sigma_1} , \lambda^{-\nu/t} \frac{1}{L} \right]$$

(2.40a)

and for $\Delta p < 0$

$$\frac{\sigma e}{\sigma_2} = \lambda F_- \left[ \lambda^{1/s} \Delta p , \lambda^{(t+s)/s} \frac{\sigma_2}{\sigma_1} , \lambda^{\nu/s} \frac{1}{L} \right]$$

(2.40b)

If the assumption of a homogeneous function representation is correct, these scaling forms must reduce to the experimental observations we stated earlier in the appropriate limits. We now investigate what requirements these observations impose on $F_+$ and $F_-$. Consider for the time being an infinite lattice so that $1/L = 0$ in equation (2.40). Now if $\sigma_2 = 0$, we have from equation (2.40a)

$$\frac{\sigma e}{\sigma_1} = \lambda F_+ \left( \lambda^{-1/t} \Delta p , 0 , 0 \right)$$

(2.41)

If we choose $\lambda^{-1/t} \Delta p = 1$, we recover equation (2.36)
On the other hand if \( \sigma_1 = \sigma_2 = \text{finite} \), and we choose \( \lambda^{1/s} \Delta p = 1 \), we recover equation (2.37)

\[
\frac{\sigma_1}{\sigma_2} = (\Delta p)^{-s} F_-(1, 0, 0)
\]  

These results all hold for an infinite sample. When composites are modeled by resistor lattices these lattices are inevitably of finite extent. It is therefore interesting to see what effect the size of the lattice has on our scaling forms.

Let us assume \( \sigma_2 = 0 \). Then for a finite lattice at \( p = p_c \), equation (2.40a) becomes

\[
\frac{\sigma}{\sigma_1} = \lambda F_+ \left[ 0, 0, \lambda^{-\nu/t} \frac{1}{L} \right]
\]  

Choosing \( \lambda^{-\nu/t}/L = 1 \) yields

\[
\frac{\sigma}{\sigma_1} = L^{-t/\nu} F_+(0, 0, 1)
\]  

which states that \( \sigma /\sigma_1 \) varies as \( L^{-t/\nu} \) exactly at \( p = p_c \). This result is the basis of finite size scaling.
whereby the ratio $t/v$ can be determined by plotting $\log(\sigma_e/\sigma_1)$ versus $\log L$. By combining finite size scaling with the transfer matrix method, we have a powerful method of determining the critical exponents very accurately. Some applications of this procedure at finite frequencies are given later in this thesis.

Summary

We have shown that by applying Maxwell's equations to a random composite, and using the finite difference approximation, Kirchoff's current laws are obtained. Thus a random composite may be modeled with a suitable choice of circuit elements placed at random on a lattice.

By making the analogy with ordinary thermodynamic phase transitions, we were able to postulate scaling forms for the effective conductivity of random granular composites.

Whether one chooses to solve Kirchoff's equations or to use the transfer matrix technique depends on the specific problem. If the effective conductivity is sought, particularly in the neighborhood of the percolation threshold, the transfer matrix is unsurpassed in speed and accuracy. However, there are many problems where a knowledge of the potential at each lattice site is desired and this information can only be obtained by solving Kirchoff's equations.
References for Chapter II

10. See reference 8.
CHAPTER III

DC AND AC TRANSPORT PROPERTIES

Introduction

This chapter will be devoted to solving equation (2.16), Kirchoff's law for a random network of conductances, for two problems. The first, a DC problem, is an extension of equation (2.16) to include next nearest neighbor interactions. A physical realization of this model is a random composite made of metallic squares, placed at random on a two-dimensional square lattice of insulating substrate (see figure 4). To prepare such a random composite, photolithographic techniques are used to produce a mask on an insulating substrate. The mask is then exposed to metal either by thermal evaporation or by rf sputtering, as discussed in Chapter I. The resulting composite can conduct via electrical contacts through the corners of the squares. The resulting percolation threshold is lower than that found when only conduction to adjacent squares is allowed. We will obtain a new critical exponent related to the strength of the corner interaction.

The second problem we consider is an AC problem. Garner and Stroud have applied the EMA at finite frequencies to a
Fig. 4  Computer generated random composite consisting of metallic squares (shaded in the figure), on an insulating substrate.
random composite composed of normal metal and superconductor. We use their model for the conductivity of the superconducting component, and find that, when this model is placed on a lattice, the results compare favorably with the EMA predictions.

We begin by describing the general algorithm for solving eq. (2.16). To illustrate the algorithm, we consider a normal metal - insulator composite with nearest-neighbor interactions on a square lattice. Recall equation (2.16):

$$\sum_j g_{ij} (V_j - V_i) = 0$$

(3.1)

where $V_i$ is the potential at site $i$ on the two dimensional lattice and $g_{ij}$ is the conductance of the bond joining site $i$ to its nearest neighbor site $j$. A random normal metal - insulator composite can be modeled by choosing the $g_{ij}$'s to be 0 or 1 at random, $g_{ij} = 1$ representing a metallic bond and $g_{ij} = 0$ an insulator.

To model a random composite, the $g_{ij}$'s must be chosen at random. Before we can do this we must make a distinction between what are known as the "bond problem" and the "site problem". In the bond problem, a fraction of the bonds are removed at random, i.e., assigned conductances $g_{ij} = 0$. In the site problem, lattice sites are removed at random. Removal of a site implies that all bonds connecting that site
to its nearest neighbor sites are assigned $g_{ij} = 0$. The bond and site problems are indeed two distinct problems, with different percolation thresholds but similar power laws describing the conductivities.

As an example, let us consider site percolation on a two dimensional square lattice. The procedure for modeling a normal metal - insulator composite is to construct a two dimensional square lattice and assign a random number $r$ between 0 and 1 to each site of the lattice. If we denote the desired site fraction of metal as $p$, then for $r_i \leq p$, we label site $i$ as "conducting". If nearest neighbor sites $i$ and $j$ are both conducting, we assign $g_{ij} = 1$. Otherwise $g_{ij} = 0$.

Having now specified the arrangement of conductances on the lattice, we need to specify the boundary conditions. For a two dimensional square lattice we have four boundaries to consider. We specify the potential at each site at the top of our lattice to have a potential of unity and each site at the bottom of the lattice to have potential zero. Thus we have set up a potential gradient from top to bottom, this then giving rise to an electric field (see fig. 5). We employ cyclic boundary conditions in the direction perpendicular to the field by connecting pairs of points on opposite sides of the lattice with random conductances.
Fig. 5  Illustration of a resistor network used to numerically simulate a random binary composite. A potential gradient is set up from top to bottom. Cyclic boundary conditions (not shown) are employed in the direction perpendicular to the field.
We now wish to solve equation (3.1) to find the potential at each point of our lattice. To do this, we rewrite equation (3.1) as

\[ V_i = \frac{\sum_j g_{ij} V_j}{\sum_j g_{ij}} \]  

(3.2)

This equation will be solved by iteration, that is to say we will make an intelligent guess of \( V_j \) at each lattice point, insert this into the right-hand side of eq. (3.2), and solve the equation to obtain a new value of \( V_i \) for each lattice site. We then use this new value on the right side of (3.2) and repeat this process until the values obtained on two successive iterations meet some prescribed convergence criterion. A reasonable initial choice for the potentials for our choice of boundary conditions, is to let the initial values of the potentials reflect a constant drop in each row of the lattice, as would be the case if the lattice consisted only of unit conductances.

Rewriting eq. (3.2) to reflect this iteration procedure we obtain:
where the superscripts \( (n) \) and \( (n+1) \) refer to the iteration number. A reasonable convergence criterion is that for every site \( i \), we have

\[
\left| \frac{v_i^{(n+1)} - v_i^{(n)}}{v_i^{(n)}} \right| < \epsilon \quad (3.4)
\]

where \( \epsilon \) is typically on the order of \( 10^{-5} \).

We can increase the speed of this calculation somewhat by rewriting equation (3.3) as

\[
v_i^{(n+1)} = \frac{\sum_j g_{ij} v_j^{(n+1)} + \sum_j g_{ij} v_j^{(n)}}{\sum_j g_{ij}} \quad (3.5)
\]

This equation says that we use the new values of the voltages as they are calculated rather than waiting until the next iteration to use them. We have used eq. (3.5) in the calculations below; no attempt was made to use under-relaxation or over-relaxation throughout this work.
Once we have calculated the potential at each point of the lattice, it is a simple matter to obtain the effective conductivity. One way of doing this is to calculate the power dissipated in each bond of the lattice. The power dissipated in the conductor joining sites \( i \) and \( j \) is

\[
P_{ij} = g_{ij} V_{ij}^2
\]

(3.6)

where \( V_{ij} \) is the potential difference between sites \( i \) and \( j \). The total power dissipated in the lattice is found by summing the power dissipated in each bond over all the bonds in the lattice

\[
P_{\text{tot}} = \sum_{\langle i,j \rangle} P_{ij}
\]

(3.7)

where \( \langle \cdots \rangle \) implies a sum over nearest neighbor lattice sites. We also have the relationship \( P_{\text{tot}} = I V_{\text{app}} \) where \( V_{\text{app}} \) is the applied voltage (which was specified to be unity by our choice of boundary conditions) and \( I \) is the current the sample draws from the voltage source. The effective conductance of the sample is defined as:

\[
\mathcal{g}_{\text{eff}} = I / V_{\text{app}}
\]

(3.8)
Combining the above equations yields

\[ P_{\text{tot}} = g_{\text{eff}} + \sigma_{\text{eff}} \]

where the last equality holds only for a two dimensional square lattice.

Among the problems that can be solved using this technique are the determination of the percolation threshold and the calculation of the exponent \( t \). The former problem can be solved by doing calculations on several samples, each with a different value of \( p \). A graph of \( \sigma_{\text{eff}} \) versus \( p \) will go to zero at the percolation threshold. The latter problem is solved by graphing \( \log \sigma_{\text{eff}} \) versus \( \log A_p \), the slope of the graph being equal to the exponent \( t \).

If we use this procedure for another configuration of conductances, i.e., assign a different set of random numbers to each of the lattice sites, we would obtain different values for the percolation threshold and the conductivity exponent \( t \). This sample-to-sample variation is due to finite size effects which are very important in the vicinity of the percolation threshold. In order to obtain consistent results, one would have to obtain the conductivity for many realizations of each volume fraction and perform an average over all the configurations. But there exists many types of averages, for example arithmetic, geometric, and harmonic...
averages. These all should give the same results for a sufficiently large sample, but once again the finite size of the samples are a problem.

These finite size effects can be understood in the context of the correlation length $\xi$. $\xi$ is defined for an infinite sample and below the threshold it is roughly equal to the size of a conducting cluster. For $\xi$ small compared to the sample size, we should obtain the correct critical behavior. But when $\xi$ is comparable to the size of the sample (as is the case near the threshold) fluctuations occur because a finite fraction of configurations will continue to conduct as we pass through the threshold.

A better approach is to perform the calculations exactly at the percolation threshold and invoke finite size scaling arguments to obtain the correct critical behavior. We explore this approach in the next chapter.

**First Application: Corner Conduction**

Sheng and Kohn\textsuperscript{2} have pointed out that there is a discrepancy between measurements on real composites and the predictions of resistor network calculations, which they attributed to corner conduction. The composite they considered was composed of conducting and insulating squares placed at random on a square lattice. Using a clustered mean-field theory they have shown that there exist two
percolation thresholds in 2d composites, one arising from a continuous path formed by squares having either a common side or a common corner connected, and the other from a path formed by squares having at least one common side.

We wish to modify the usual nearest-neighbor resistor network model to numerically test their predictions on a resistor lattice. To allow for the effects of corner conduction, we extend the sum in equation (3.5) to include next nearest neighbors. We also make a distinction between the $g_{ij}$'s joining nearest neighbor sites and those joining next nearest neighbor sites. We treat site percolation and assign a random number $r$ to each site of the lattice as described earlier. If $i$ and $j$ are either nearest neighbor (nn) or next nearest neighbor (nnn) sites and both $r_i$ and $r_j$ are less than or equal to the site fraction $p$, we label the bonds connecting them as conducting and assign $g_{ij}$ according to the rule:

$$
g_{ij} = 1 \quad \text{if } i \text{ and } j \text{ nn}$$
$$
g_{ij} = g_{diag} \quad \text{if } i \text{ and } j \text{ nnn}$$

(3.10)

where $g_{diag}$ represents the conductance of the next nearest neighbor conducting bonds. For all other cases $g_{ij} = 0$. It is reasonable to assume that $0 < g_{diag} < 1$ since the contact area joining two corners of our conducting squares is less than the contact area joining two adjacent sides.
Figure 6 shows the effective conductivity as a function of metallic volume fraction for several choices of $g_{\text{diag}}$ for a 75 x 75 lattice. For $g_{\text{diag}}$ nonzero we see the lattice as a whole continues to conduct below the percolation threshold established by the lattice with only nearest neighbor interactions. We see no evidence of a double threshold as seen by Sheng and Kohn, but there is a definite shift to lower values of $p$ as the strength of the diagonal bonds is increased. This gives support to their theory that corner-corner interactions are important near the percolation threshold.

Since $g_{\text{eff}}$ depends on the value of $g_{\text{diag}}$, we looked for a power law behavior, i.e., $g_{\text{eff}} \sim g_{\text{diag}}^x$ near the nearest neighbor percolation threshold. Because of large fluctuations near $p_c$, we used a 200 x 200 lattice and averaged over 10 configurations. The calculation was performed at $p = 0.593$, the percolation threshold for nearest-neighbor site percolation. Figure 7 shows that $g_{\text{eff}}$ does indeed exhibit a power law form. We find $x = 0.37^{+0.04}$, a value which does not seem to be related to any other of the usual critical exponents.
Fig. 6 Effective conductivity as a function of site fraction of metal. The effective conductivity is normalized to unity for a full lattice. Results are for a 75 x 75 square lattice.
Fig. 7 Effective conductivity as a function of diagonal conductivity. Results are for 10 realizations of a 200 x 200 square lattice. The calculation was performed at the percolation threshold of a site diluted lattice with no next nearest neighbor interactions.
Second Application: Normal Metal-Superconductor Composites

As an a.c. application of the same formalism, we would next like to develop a model for the response of a normal metal - superconductor (N/S) composite near the percolation threshold. Garner and Stroud\(^1\) have used the effective medium theory (EMA) to show that the effective conductivities of a N/S composite are drastically different than that of a bulk superconductor. In this section we will model such a composite with a random impedance lattice and show that the numerical solution of the network equations agrees favorably with the predictions of the EMA.

Using the BCS\(^3\) theory of superconductivity, Mattis and Bardeen\(^4\) found for the zero temperature frequency dependent conductivity of a superconductor the following expression:

\[
\sigma_S = \sigma_{1S} + i \sigma_{2S} \tag{3.11a}
\]

where

\[
\frac{\sigma_{1S}}{\sigma_n} = \left(1 + \frac{2\Delta}{\hbar\omega}\right) E(k) - \frac{4\Delta}{\hbar\omega} K(k) \quad \hbar\omega > 2\Delta \tag{3.11b}
\]

and

\[
\frac{\sigma_{2S}}{\sigma_n} = \frac{1}{2} \left(1 + \frac{2\Delta}{\hbar\omega}\right) E(k') - \frac{1}{2} \left(1 - \frac{2\Delta}{\hbar\omega}\right) K(k') \tag{3.11c}
\]

where \(\Delta\) is the zero temperature superconducting energy gap.
E(k) and K(k) are complete elliptic integrals of the first and second kind respectively, $\sigma_n$ is the conductivity of the superconductor when in its normal state, and

$$k = \frac{1 + \omega^2}{1 + 2\omega} ; \quad k' = (1 - k^2)^{1/2} \quad (3.12)$$

We choose a convenient set of units where $\hbar/2\Delta = 1$; our expressions become

$$\frac{\sigma_{1s}}{\sigma_n} = \left(1 + \frac{1}{\omega}\right) E(k) - \frac{2}{\omega} K(k) \quad \omega > 1 \quad (3.13a)$$

$$\frac{\sigma_{2s}}{\sigma_n} = \frac{1}{2} \left(1 + \frac{1}{\omega}\right) E(k) - \frac{1}{2} \left(1 - \frac{1}{\omega}\right) K(k) \quad (3.13b)$$

$$k = \frac{|1 - \omega|}{|1 + \omega|} \quad (3.13c)$$

Figure 8 shows a graph of equations (3.13), which represent the optical response of a bulk, type I superconductor. The principle features of the response will be significantly altered by the addition of normal metal to form a binary composite. From the figure we see that in the bulk superconductor, $\sigma_{1s}/\sigma_n$ approaches unity and $\sigma_{2s}/\sigma_n$ approaches zero at high frequencies. In the low frequency regime $\sigma_{2s}/\sigma_n$ diverges as $1/\omega$, representing the inductive response of a perfect conductor. $\sigma_{1s}/\sigma_n$ is exactly zero for $\omega < 1$. 
Fig. 8  Mattis-Bardeen complex conductivity of a superconductor at zero degrees Kelvin. See the text for details. Note the lack of absorption for frequencies less than $2\Delta/\hbar$. 
corresponding to the lack of absorption below the superconducting energy gap. $\sigma_{1s}/\sigma_n$ exhibits a delta function at zero frequency (not shown in figure 8) corresponding to the infinite D.C. conductivity of a superconductor.

In order to develop a lattice model for this system, recall that the conductances in equation (3.1) can include both real and imaginary response. Thus, this S/N composite can be modeled by assigning the $g_{ij}$'s according to the rule:

$$
\sigma_{ij} = \sigma_n/ \quad \text{if } p > r_i \text{ or } r_j
$$

$$
\sigma_{ij} = \sigma_s \quad \text{if } p < r_i \text{ and } r_j
$$

(3.14)

where $\sigma_n/ \sigma_n$ is the conductivity of the normal metal, $r_i$ is the random number assigned to each lattice site (we are again treating the site problem), and $p$ is the volume fraction of superconductor that we desire in our lattice. We apply a voltage of $e^{-i\omega t}$ to the top of our lattice, zero to the bottom, and employ cyclic boundary conditions in the direction perpendicular to the field. Equation (3.1) is again solved by iteration for the now complex potential at each lattice site.
Knowing the potential at each site, we can calculate the current in each bond as

$$ j_{ij} = \sigma_{ij} \Delta V_{ij} \quad (3.15) $$

where $\Delta V_{ij}$ is the magnitude of the complex potential difference between lattice sites $i$ and $j$. Summing the currents over all bonds and dividing by the total number of bonds produces the average current $<J>$. Then $\sigma_{\text{eff}}$ is defined as

$$ \sigma_{\text{eff}} = \frac{<J>}{<E>} \quad (3.16) $$

where $<E>$ is the average electric field and is equal to $1/N$, the reciprocal of the size of the lattice. The effective conductivity is related to the effective complex dielectric function $\varepsilon_{\text{eff}}(\omega)$ by the general relation:

$$ \varepsilon_{\text{eff}}(\omega) = 1 + \frac{4\pi i \sigma_{\text{eff}}(\omega)}{\omega} \quad (3.17) $$

which implies that the optical absorption is determined by the real part of $\sigma_{\text{eff}}(\omega)$.

The real and imaginary parts of $\sigma_{\text{eff}}$ are shown in figures 9 and 10 for the ratio $\sigma_n/\sigma_n = 1$ and for several choices of $p$, the volume fraction of superconductor. For $p = 1$ the
Mattis-Bardeen results are recovered and for $p = 0$ the only absorption arises from the frequency independent conductivity of the normal metal. For fractions between these two extremes, we would expect $\sigma_{\text{eff}}$ to lie between these lines; this is seen for frequencies above the optical absorption gap $\omega = 1$. But we also see an anomalous absorption below the gap that we do not see in a bulk superconductor, but which is predicted by the effective medium theory of Garner and Stroud (GS). For this ratio of $\sigma_n / \sigma_n'$, $\sigma_{\text{eff}}$ has a minimum at a frequency of approximately 1.3.

GS have done calculations at other ratios $\sigma_n / \sigma_n' < 1$. We elected to obtain $\sigma_{\text{eff}}$ for a ratio of 10, which would roughly correspond to a Cu-Pb composite. These results are shown in figures 11 and 12. The general features are preserved but we note that the minimum in the real part of the effective conductivity decreases with decreasing $p$, varying from 1.4 near $p=1$ to 1.0 for $p$ well below the percolation threshold.
Fig. 9 Real part of the effective conductivity plotted as a function of frequency for several values of metallic volume fraction. Calculations were performed for a 75 x 75 square lattice. $\sigma_n/\sigma_n' = 1$. 
Fig. 10  Imaginary part of the effective conductivity as a function of frequency. Details are the same as for Fig. 9.
Fig. 11 Same as Fig. 9 with $\sigma_n/\sigma_n' = 10$. 
Fig. 12 Same as Fig. 10 with $\sigma_n/\sigma_n' = 10$. 
References for Chapter III

Chapter IV

Finite Size - Finite Frequency Scaling Forms

Introduction

We have shown in Chapter II that the conductances appearing in equation (2.16) can be dependent on frequency. It was also demonstrated in the last chapter that using frequency dependent conductances yields results in agreement with analytic theories. It remains to generalize the scaling forms of Chapter II to frequency dependent conductances.

We will develop a model for a normal metal - insulator random composite at finite frequency. At nonzero frequencies, the insulating component has a nonzero conductivity. Such a model is obviously more realistic than the simple resistance lattices of the last chapter, since insulators do indeed conduct at a.c. and our previous resistor lattice models did not reflect this important fact.

We will postulate a frequency dependent - finite size dependent scaling form for the complex conductivity near the percolation threshold and show numerically that it is valid by applying it to a model composite. The numerical calculations are carried out using the transfer matrix technique of Chapter II.
We propose that the conductivities appearing in the scaling forms of Chapter II may be possibly complex frequency dependent functions

\[
\frac{\sigma_e(\omega)}{\sigma_1(\omega)} = \lambda F_+ \left[ \lambda^{-1} \frac{\sigma_2(\omega)}{\sigma_1(\omega)}, \lambda^{-1/\Delta p} \right]
\]  
valid for \( \Delta p > 0 \), and

\[
\frac{\sigma_e(\omega)}{\sigma_2(\omega)} = \lambda F_- \left[ \lambda \frac{(t+s)/s}{\sigma_1(\omega)}, \lambda^{-1/s} \Delta p \right]
\]  
for \( \Delta p < 0 \). Eqs. (4.1) are just analytic continuations to finite frequency of the scaling forms presented in Chapter II and the symbols have the same meaning. Choosing \( \lambda = (\Delta p)^{t} \) in equation (4.1a) and \( \lambda = (\Delta p)^{-s} \) in equation (4.1b) yields scaling forms in terms of a single variable:

\[
\frac{\sigma_e(\omega)}{\sigma_1(\omega)} = (\Delta p)^{t} G_+ \left( \frac{\sigma_2/\sigma_1}{(\Delta p)^{t+s}} \right) \quad \Delta p > 0
\]  

\[
\frac{\sigma_e(\omega)}{\sigma_1(\omega)} = (\Delta p)^{-s} G_- \left( \frac{\sigma_2/\sigma_1}{(\Delta p)^{t+s}} \right) \quad \Delta p < 0
\]  

where \( G_+ = F_+(\Delta p)^{(t+s)}, 1 \)
The scaling expressions (4.2) are appropriate for an infinite sample, i.e., one with linear dimensions $R \gg \xi$, where $\xi$ is the correlation length we mentioned in Chapter II. For $p < p_c$, $\xi$ describes the linear dimensions of a typical cluster. We consider natural generalization of equations (4.2) to a finite size sample:

$$\frac{\sigma_e}{\sigma_1} = |\Delta p|^{-s} G_+ \left[ \frac{\sigma_2/\sigma_1}{|\Delta p|^{t+s}}, \frac{\xi}{R} \right] \quad \Delta p > 0 \quad (4.3a)$$

$$\frac{\sigma_e}{\sigma_2} = |\Delta p|^{t+s} G_+ \left[ \frac{\sigma_2/\sigma_1}{|\Delta p|^{t+s}}, \frac{\xi}{R} \right] \quad \Delta p < 0 \quad (4.3b)$$

where we have dropped the explicit frequency dependence in the $\sigma$'s. Scaling forms equivalent to the above have been proposed by Solla and Ashcroft$^1$ and more recently by Luck$^2$ and Bug et al.$^3$. In the limit $R \to \infty$, equations (4.2) are recovered.

We now transform equation (4.3a) into a form that is more convenient for numerical testing. A similar transformation may be carried out for equation (4.3b). We first write

$$\frac{\sigma_e}{\sigma_1} = |\Delta p|^{t/(t+s)} G_+ (x, y) = \left( \frac{\sigma_2}{\sigma_1} \right)^{t/(t+s)} \left( \frac{1}{x} \right)^{t/(t+s)} G_+ (x, y) \quad (4.4)$$
We now introduce a new function, $H(x, y)$, defined by:

\[
G_+ (x, y) = \left( \frac{1}{x} \right)^{t/(t+s)} H(x, y) \tag{4.5}
\]

Next we replace the variables $x$ and $y$ by the new variables $x$ and $u = x^{v/(t+s)}/y$. In terms of the new variables $x$ and $u$ we have

\[
\frac{\sigma_e}{\sigma_1} = \left( \frac{\sigma_2}{\sigma_1} \right)^{t/(t+s)} H(x, u) \tag{4.6}
\]

Finally, precisely at $p = p_C$, the variable $x$ becomes infinite and we have

\[
\frac{\sigma_e}{\sigma_1} = \left( \frac{\sigma_2}{\sigma_1} \right)^{t/(t+s)} J \left[ R \left( \frac{\sigma_2}{\sigma_1} \right)^{u/(t+s)} \right] \tag{4.7}
\]

where $J(u) = \lim_{x \to \infty} H(x, u)$. This form is readily tested numerically by calculating the complex effective conductivities of samples of different linear dimensions $R$, and showing that they can be represented by the same universal function (4.7). This test provides a reasonably stringent test of the validity of the original finite size, finite frequency relation in equation (4.3a).
Algorithm

In developing the theory of the transfer matrix technique in Chapter II we have essentially described the algorithm. A lattice is constructed column by column and the transfer matrix $A$ is updated as:

$$\overrightarrow{A_{L+1}} = \overrightarrow{A_L} \left( I + H A_L \right)^{-1}$$  \hspace{1cm} (4.8)

While this method will work, it has the disadvantage of having to invert possibly large matrices. In practice, the lattice is constructed a bond at a time and the transfer matrix is updated immediately upon adding a bond. It can be shown that if one adds a horizontal resistor to site $a$ of our lattice, the $(i,j)$ element of the updated transfer matrix is obtained from:

$$A_{L+1}(i,j) = A_L(i,j) - \frac{A_L(i,a) A_L(a,j) R}{1 + A_L(a,a) R}$$  \hspace{1cm} (4.9)

Similarly if one adds a vertical resistor to connect sites $a$ and $b$ of column $L+1$, the updated transfer matrix elements $A_{L+1}'(i,j)$, are given by:

$$A_{L+1}'(i,j) = A_{L+1}(i,j) + \frac{(\delta_a, j - \delta_{b}, j)(\delta_{a}, 1 - \delta_{b}, 1)}{R}$$  \hspace{1cm} (4.10)
From equation (4.10) we see that if we were to add an infinite vertical resistor to the lattice, the transfer matrix remains unchanged. Thus the calculation goes faster near percolation, in contrast to the iterative procedure used for solving Kirchoff's equations.

Recall from Chapter II that the entire derivation of the transfer matrix technique was based on Ohm's Law, $V = I R$. Now Ohm's Law is also valid for reactive circuit elements. Thus, by formally replacing the resistive term $R$ in equations (4.9) and (4.10) by a complex impedance $Z$, we immediately generalize the method to impedance networks, or, in the context of this dissertation, to the a.c. response of composites.

We now apply this method to demonstrate the validity of the scaling forms given earlier in this chapter. We again treat the site problem and assign a random number to each site of an $N \times L$ lattice. Note that the lattice with $N$ sites per column actually has $W = N-1$ vertical bonds. If two nearest neighbor sites have random numbers less than some predetermined value $p$ (the desired site fraction), we label the two sites as conducting and place a metallic bond with real impedance $Z = R$ joining them. Otherwise we join the sites with an insulating bond represented by a capacitor with a purely imaginary impedance $Z = -i/\omega C$ where $C$ is a real capacitance. This random RC network will serve as our model normal metal - insulator composite upon which we will test
our scaling forms.

The lattice is constructed and the transfer matrix is updated with the addition of each bond according to equations (4.9) and (4.10). With a voltage of unit amplitude applied across the lattice, the complex current is given by

\[ I = A(1,1) \text{ as was discussed in Chapter II.} \]

**Results**

In order to verify equation (4.3a) we first assume, in agreement with established theory, that \( \xi \) varies as \((\Delta p)^{-\nu}\) near \( p_c \). We must graph \( (\sigma_0/\sigma_1) |\Delta p|^{-t} \) against the variable \( \sigma_2/\sigma_1 |\Delta p|^{-(t+s)} \) for fixed values of the second variable \( |\Delta p|^{-\nu}/W \). The value of \( p_c \) for site percolation in 2d is known numerically to be 0.592974 and the ratio \( t/\nu = 0.973 \) from numerical studies based on the transfer matrix algorithm and finite size scaling theory5,6. The exponents \( t \) and \( s \) are equal in 2d by an exact duality relation7. Denoting the metallic conductivity as \( \sigma_1 \) and the insulating conductivity as \( \sigma_2 \), we have for the ratio \( \sigma_2 /\sigma_1 = i\omega C \) (where we have taken the value of the resistor to be unity). The results of our calculations are shown in figures 13 and 14 for the real and imaginary parts of the effective conductivity respectively. For \( \Delta p^{-\nu}/W = 4.94 \) we have carried out two calculations at different fractions of the metallic component, but preserving the value of the ratio. We see that
the two curves lie upon each other as required by Eq. (4.3a). An additional calculation was performed at $\Delta p^{-v}/W = 2.63$ and we see that this produces another curve, at least at low frequencies. These results provide evidence that the scaling form (4.3a) is indeed valid, at least for $\Delta p > 0$ and in two dimensions.

We have also carried out simulations precisely at $p = p_c$ in order to verify the scaling form (4.7) and to calculate the scaling function $J(u)$ explicitly. In order to verify equation (4.7) we must graph $(\sigma_2/\sigma_1)^{-t/(t+s)} \sigma_e$ against $W (\sigma_2/\sigma_1)^{v/(t+s)}$ for several sample widths $W$, and adjusted $\omega$ accordingly to keep the variable $W (\sigma_2/\sigma_1)^{v/(t+s)}$ constant. The results are shown in figures 15 and 16 and provide perhaps even stronger evidence that our original scaling forms are valid because we have eliminated the variable $p$ by working precisely at the percolation threshold.

Finally we show the scaling function itself at the percolation threshold. Letting $X = W (\sigma_2/\sigma_1)^{v/(t+s)}$, then

$$J(X) = \left(\frac{\sigma_2}{\sigma_1}\right)^{-t/(t+s)} \sigma_e$$

(4.11)

We show the real and imaginary parts of $J(X)$ plotted against the variable $X$ in figures 17 and 18 respectively. To the best of our knowledge this is the first time a scaling function has been calculated explicitly.
Fig. 13 Verifying the real part of Eq. (4.3a). See text for details. For fixed values of the ratio $(\Delta \rho)^{-\nu}/W$, the curves lie upon one another.
Fig. 14  Same as Fig. 13 for the imaginary part of Eq. (4.3a).
Fig. 15 Verifying the real part of Eq. (4.7). Calculations were performed precisely at the percolation threshold. See text for details.
Fig. 16  Same as Fig. 15 for the imaginary part of Eq. (4.7).
Fig. 17  The real part of the scaling function given in Eq. (4.11).
Fig. 18 The imaginary part of the scaling function given in Eq. (4.11).
References for Chapter IV


Chapter V
Surface Plasmon Modes

Introduction

We have seen in the last chapter that an insulator has a capacitive response to an external a.c. field, or, equivalently, an insulator can be viewed as having a frequency dependent conductivity. Metals also possess a frequency dependent conductivity and our previous models, in which metallic bonds are represented by a simple resistor correspond to frequency independent conductivity. Furthermore, metal-insulator composites are known to possess surface plasmon modes or Mie resonances which analytic theories predict but which our earlier models failed to produce. These modes are an important absorption mechanism in metal-insulator composites and they should be accounted for in a complete theory.

In this chapter we will show that by making a judicious choice of circuit elements to represent metals and insulators, we can obtain the absorption spectrum of a Drude metal - insulator composite. We will also show that these results agree favorably with ema predictions.
Theory

In order for a lattice model of a random composite to show resonance effects, we must include an inductive element in our previous RC networks. Let us represent a metallic bond by a series resistor - inductor, in parallel with a capacitor. An insulating bond will, as in the previous chapter, be represented by a single capacitor. This arrangement is shown in figure 19. The admittance of these circuit elements, which is also equal to the conductance, are defined as the current at frequency $\omega$ divided by the applied voltage at the same frequency. For the circuit elements of Fig. 19, these take the form:

$$g_M = \frac{1 + i\omega RC - \omega^2 LC}{R + i\omega L} \quad (5.1)$$

$$g_I = i\omega C'$$

where $R$ is the resistance of the conducting element, $L$ is the inductance, and $C$ is the capacitance. $C'$ is the capacitance of the insulating element. We now choose $L = C = C' = 1$, and with the definition of a characteristic relaxation time $\tau = 1/RC$, the ratio $g_M/g_I$ takes the form:

$$\frac{g_M}{g_I} = 1 - \frac{1}{\omega(\omega-1/\tau)} \quad (5.2)$$
Fig. 19 Arrangement of circuit elements to produce a model Drude metal - insulator composite. (a) corresponds to a metallic bond and (b) an insulating bond.
In two dimensions, the ratio of the conductances \( g_M / g_I \) is equal to the ratio of conductivities \( \sigma_M / \sigma_I \), and it is this latter ratio we choose to work with.

The connection between this model and a composite of Drude metal and insulator can be seen in the following way. Let us consider a Drude metal with dielectric function given by:

\[
\epsilon_M = 1 - \frac{\omega_p^2}{\omega(\omega - i/\tau)}
\]  

and an insulator with dielectric function \( \epsilon_I = 1 \). The ratio \( \epsilon_M / \epsilon_I \), then takes the form:

\[
\frac{\epsilon_M}{\epsilon_I} = 1 - \frac{\omega_p^2}{\omega(\omega - i/\tau)}
\]  

This ratio is formally identical to the ratio given in equation (5.2) if we take the plasma frequency equal to unity. The optical absorption of the latter system, i.e., the spectrum of frequencies where the system absorbs energy from the applied electromagnetic wave, is given by \( \text{Im } \epsilon_e \) and the absorption of the former is given by \( \text{Re } \sigma_e \), where \( \epsilon_e \) and \( \sigma_e \) are the effective dielectric function and effective conductivity of the entire system respectively. The two are related through the identity:

\[
\text{Re } \sigma_e = \frac{\omega}{4\pi} \text{Im } \epsilon
\]  

(5.5)
Thus by calculating the $\text{Re } \sigma_e$ of the lattice model, we are calculating the absorption spectra of a Drude metal-insulator composite by virtue of equation (5.5). The surface plasmon modes will manifest themselves as resonances in this LRC circuit model of a random metal-insulator composite.

**Results**

We again elect to treat the site problem and carry out numerical simulations using the transfer matrix algorithm. A random number $r$ ($0 < r < 1$) is assigned to each lattice site. If two nearest neighbor sites have random numbers less than the desired site fraction of metal $p$, we label the sites conducting and assign a metallic bond with conductivity $\sigma_M$ given in equation (5.1). Otherwise we connect the sites by an insulating bond with conductivity $\sigma_I$, also given in equation (5.1).

Our results for the real part of the effective conductivity are shown in Figs. 20 - 37. Details of the parameters for each calculation are given in the figure captions. The results may be summarized as follows:

(i) The absorption band (defined as the region where $\text{Re } \sigma_e \neq 0$) can be divided roughly into two parts. One part is the network analog of the surface plasmon resonances described above, and spread typically over a broad range of frequencies in the range ($0 < \omega < 1$). The other is the
"Drude peak", centered at zero frequency, and appearing only above the metallic percolation threshold and corresponding to finite d.c. conductivity.

(ii) The bottom of the absorption band is separated from zero frequency by a gap which appears to go to zero at the percolation threshold, and to increase with $|\Delta p|$ on either side of the threshold. This feature is somewhat blurred by the resistive damping (i.e., finite $1/\tau$), and by the fact that the samples are quite small due to computer time constraints. We believe that in the limit of very little damping and very large sample size that the gap would become even more prominent than it is in our calculations. The results are not accurate enough to ascertain if the gap goes to zero according to some power law in $\Delta p$. Such a power law dependence has been predicted by Stroud\textsuperscript{1} using the effective medium approximation, and also by Bergman and Imry\textsuperscript{2} on more general grounds.

(iii). When $1/\tau$ is small there is a great deal of fine structure; this fine structure can be seen in figures 29 - 37 where the resistive damping has been reduced. We find that this structure in the absorption curves varies greatly from sample to sample. In the limit of very large sample size and very low damping, we speculate that this structure would average out leaving a smooth absorption curve with little if any prominent features. The samples used in these calculations are not large enough to confirm this prediction
however. Much larger samples, and correspondingly more computer time, would be required to confirm this smoothness in the large sample limit.

Comparison to Mean Field Theory

The results discussed above can be put in perspective by comparing them with a simple analytic theory, the effective medium approximation (EMA). The same technique is used in applying the effective medium theory to a random resistor lattice as in applying it to a continuous random composite (which is discussed in the Appendix).

The distribution of potentials in a random resistor lattice may be thought of as arising from the applied potential which decreases by a constant amount for each row of lattice sites, and a local potential due to the effects of the random resistors. As in the continuum composite, we represent the effects of the random resistors by an effective resistor $R_e$, defined so that the potentials inside the lattice is equal to the applied potential. $R_e$ is found by requiring that the extra voltage, produced by replacing $R_e$ by the individual resistors $R_{ij}$, shall on the average vanish.

Watson and Leath\textsuperscript{3} have shown that the extra voltage drop produced when the effective resistance $R_e$ is replaced by $R = R_e + \Delta R$ is:
This result can be immediately generalized to finite frequencies if the resistances $R$ are replaced by complex impedances $Z$.

In the site problem, the metallic sites of the lattice occur with probability $p$. If two nearest neighbor sites are present, then in our model, they are connected by a metallic bond with impedance $Z_M$ (found by taking the reciprocal of the expressions in equation (5.1)). Otherwise the sites are connected by an insulating bond of impedance $Z_I$. Thus the metallic bonds occur with probability $p^2$ and the insulating bonds with probability $(1-p^2) = 2p(1-p) + (1-p)^2$. Inserting this distribution in equation (5.6) yields a quadratic equation for the effective impedance of the random network:

$$
\Delta V_R = \frac{-(\pi-1) \Delta R \ Re I}{2\Delta R + \pi Re} \quad (5.6)
$$

This equation is readily solved for $Z_e$ in terms of $Z_M$, $Z_I$, and $p$. The real part of the resulting effective conductivities are shown in figures 38 - 47. The lattice calculations agree qualitatively with the EMA in that the structure seen in the network model is probably due to finite
size effects and the bottom of the absorption band is separated from d.c. by a gap that goes to zero as the percolation threshold is approached from either side.
Fig. 20  Absorption spectrum of a model Drude metal - insulator composite. Calculations were done on a 10 x 100 lattice using the transfer matrix algorithm. In the figure R = 1 and p (the fraction of metal) = 0.1.
Fig. 21  Same as Fig. 20 with $p = 0.2$. 

\[\text{Re} \sigma(\omega), \text{Arbitrary Units}\]

- $p = 0.2$
- $R = 0.1$
- $10 \times 100$
Fig. 22  Same as Fig. 20 with $p = 0.03$. 

$p = 0.3$ 
$R = 0.1$ 
$10 \times 100$
Fig. 23  Same as Fig. 20 with $p = 0.4$. Note the appearance of the zero frequency delta function indicating that this particular configuration has percolated at d.c.
Fig. 24  Same as Fig. 20 with $p = 0.5$. 

$\text{Re}\sigma(\omega)$, Arbitrary Units

$p = 0.5$
$R = 0.1$
$10 \times 100$
Fig. 25  Same as Fig. 20 with $p = 0.6$. 

$p = 0.6$
$R = 0.1$
$10 \times 100$
Fig. 26 Same as Fig. 20 with $p = 0.7$. 

$p = 0.7$
$R = 0.1$
$10 \times 100$
Fig. 27 Same as Fig. 20 with $p = 0.8$. 

$p = 0.8$

$R = 0.1$

$10 \times 100$
Fig. 28  Same as Fig. 20 with $p = 0.9$
Fig. 29  Same as Fig. 20 with reduced resistive damping. Note the fine structure. Calculations were performed on a 15 x 50 lattice. $R = 0.01$ and the plasma frequency is taken to be unity. $p = 0.1$. 
Fig. 30  Same as Fig. 29 with $p = 0.2$. 
Fig. 31 Same as Fig. 29 with $p = 0.3$. 

$p = 0.3$

$R = 0.01$

$15 \times 50$
Fig. 32 Same as Fig. 29 with $p = 0.4$. Note the appearance of the zero frequency Drude peak indicating this configuration will conduct at d.c.
Fig. 33  Same as Fig. 29 with $p = 0.5$. 

$P = 0.5$

$R = 0.01$

$15 \times 50$
Fig. 34  Same as Fig. 29 with $p = 0.6$. 

$p = 0.6$

$R = 0.01$

$15 \times 50$
Fig. 35  Same as Fig. 29 with $p = 0.7$. 

$p = 0.7$
$R = 0.01$
$15 \times 50$
Fig. 36  Same as Fig. 29 with $p = 0.8$. 

$p = 0.8$
$R = 0.01$
$15 \times 50$
Fig. 37  Same as Fig. 30 with $p = 0.9$. 

$p = 0.9$

$R = 0.01$

$15 \times 50$
Fig. 38 Absorption Spectrum of a Drude metal - insulator composite as predicted by the effective medium approximation. $R = 0.1$ and $p = 0.1$. 
Fig. 39  Same as Fig. 38 with $p = 0.2$. 

$p = 0.2$

$R = 0.1$

EMA
Fig. 40  Same as Fig. 38 with $p = 0.3$. 

$p=0.3$  
$R=0.1$  
EMA
Fig. 41 Same as Fig. 38 with $p = 0.4$. 

$\text{Re} \sigma_e(\omega)$

$p=0.4$

$R=0.1$

EMA

$\omega/\omega_p$
Fig. 42 Same as Fig. 38 with $p = 0.5$. 

$p = 0.5$

$R = 0.1$

EMA
Fig. 43 Same as Fig. 38 with $p = 0.6$. 

$R = 0.1$ 

EMA
Fig. 44 Same as Fig. 38 with $p = 0.7$. 

$p = 0.7$

$R = 0.1$

EMA
Fig. 45 Same as Fig. 38 with $p = 0.8$. 

$p = 0.8$
$R = 0.1$
EMA
Fig. 46  Same as Fig. 38 with $p = 0.9$. 

$R = 0.1$

EMA
Fig. 47  Same as Fig. 38 with $p = 1.0$. 

$\text{Re} \sigma_\theta(\omega)$

$p = 1.0$
$R = 0.1$
EMA
References for Chapter V

Chapter VI
Dielectric Breakdown in Metal-Insulator Composites

Introduction

In a parallel plate capacitor filled with a dielectric and connected to a d.c. voltage source, charges build up on the capacitor plates and energy is stored in the electric field within the dielectric. If the potential difference across the capacitor plates is large enough, the dielectric will breakdown and start to conduct. Microscopically, the high electric field excites electrons out of the valence band of the insulating dielectric and promotes them to the conduction band. The magnitude of the energy gap between the valence band and the conduction band is expected to be proportional to the critical electric field at which breakdown occurs.\textsuperscript{1}

Bowman and Stroud\textsuperscript{2} have considered the effects of high electric fields on a model metal-insulator composite below the percolation threshold of the metal, and calculated the initial breakdown field as a function of metallic volume fraction. They found a power law behavior in the breakdown voltage. However, due to finite size effects, precision was not good enough to extract an exponent. Duxbury et. al.,\textsuperscript{3} have considered the effects of sample size on the
breakdown field. They have found that the breakdown field
does indeed depend on the size of the sample as well as the
initial volume fraction of metal.

In this chapter we will consider the same dielectric
breakdown problem at finite frequencies. The fact that the
conductivity of an insulator increases with increasing
frequency makes this an interesting problem. From a technical
point of view, we find occasion here to use both the transfer
matrix algorithm and Kirchoff's Laws to determine the initial
breakdown voltage as a function of metallic volume fraction
and frequency.

The Model

For this study, we elect to treat the bond problem where
individual bonds are randomly placed on a two dimensional
square lattice. A random number is assigned to each bond of
the lattice; if the random number is less than a
predetermined value \( p \) (the fraction of metal we desire), the
bond is labeled conducting and assigned a conductivity
\( \sigma_{ij} = 1 \), where \( i \) and \( j \) are the lattice sites joined by the
conducting bond. Otherwise an insulating bond with
conductivity \( \sigma_{ij} = i\omega C \) is used where \( C \) is a real capacitance.

We wish to study the breakdown of the insulating
constituent of the composite. Hence, we work at metallic
volume fraction \( p \), less than the metallic percolation
threshold $p_C$; for $p > p_C$, the composite will conduct primarily through the metallic bonds and the dielectric will not break down. The percolation fraction for the bond problem is $p_C = 1/2$ exactly.\textsuperscript{4}

We arbitrarily choose the critical voltage, i.e., the voltage above which the dielectric bonds break down, to be unity. To find the initial breakdown voltage of the lattice, we apply a potential difference of $V = V_0 e^{i\omega t}$ across the lattice. The boundaries perpendicular to the applied field are free.

To determine the initial breakdown voltage we proceed as follows. First, the d.c. transfer matrix algorithm is employed to determine if a given sample is indeed below the percolation threshold. If the particular configuration of resistors forms a connected path across the sample, we stop because the sample will already be conducting at d.c. If the sample indeed lies below the percolation threshold, Kirchoff's Laws are then solved for the values of the complex potentials at each lattice site. The magnitude of the potential differences across each capacitor in the sample is calculated and the capacitor having the largest voltage drop is labeled the "hottest" one. This is the capacitor that will arc first. The magnitude of the applied voltage is increased until the voltage across this capacitor equals the critical value, this then being the breakdown voltage. The breakdown field is obtained by dividing the breakdown voltage by the
size of the lattice.

Whether or not the breakdown cascades is an interesting question. When the first insulating bond breaks, the sample may still be below the percolation threshold. The question is, does the applied voltage have to be increased further to break the next insulating bond or will the insulator continue to break down at the critical voltage needed to break the first bond?

In order to answer this question, Kirchoff's laws would have to be solved again after replacing the first broken bond by a resistor. Unfortunately, when the first capacitor to arc becomes metallic, the potential distribution is severely modified. This means that the entire potential distribution needs to be calculated after the first broken capacitor is replaced by a resistor. To compound the problem, this new resistor brings the network even closer to the percolation threshold where convergence of Kirchoff's laws is very slow. Because of these computer time constraints, the question of cascading has not been addressed in this thesis, but it is nevertheless a very interesting problem and well worth the effort of future investigators.
Figure 48 shows the variation of the breakdown field $E_b$ with concentration of metal for two different frequencies. The data points represent one realization of a 60 x 60 lattice. The scatter in the graph is probably due to a combination of configuration dependence and finite size effects. If an average of many samples were calculated, we expect that this scatter would be greatly reduced and we would have a smooth line. The sample to sample variations then could be used to calculate an average deviation which would give an indication of the accuracy of our results.

The calculations require a large amount of computer time at low frequencies because Kirchoff's equations converge very slowly. Even from this limited data however, we can still see a decrease in the breakdown field at fixed frequency as the metallic percolation threshold is approached from below. This can be qualitatively understood in the static limit by considering the picture shown in figure 49. Close to the percolation threshold, we have large isolated clusters of metal separated by thin channels of insulator. The capacitance of this structure varies as $A/d$, where $A$ is the area or length of the metallic regions and $d$ is the separation. The cluster size is roughly given by the correlation length, which diverges near $p_c$ as $(p_c - p)^{-\nu}$, and the distance between clusters remains constant at one
bond length as the threshold is approached. Thus the effective capacitance becomes very large near $p_c$. As we approach percolation, more and more charge is being stored on the surface of the metallic clusters. Hence it takes a smaller external field to make the charge arc across the insulating gap.

Of perhaps more interest is the variation of the breakdown field with frequency, plotted for two concentrations in Fig. 50. The scatter in the data points once again are the result of using only one configuration. At $\Delta p = 0.1$, the breakdown field appears to become independent of frequency at sufficiently low frequency. At $\Delta p = 0.01$ the same frequency-independence is expected but not until lower frequencies are reached than those studied here. The breakdown fields also approach a constant value at high frequencies, so that the breakdown field is independent of both $\Delta p$ and $\omega$ at high frequencies.

The frequency dependance of the breakdown field can be qualitatively understood within the simple capacitor model given previously. For fixed $\Delta p$, the capacitance of the composite is also fixed. As frequency is lowered, the conductivity of the insulating regions is also lowered and more charges are able to build up on the surface of the metallic clusters. As a result, a lower applied field is required to achieve breakdown.

To be more specific, imagine the model proposed in figure
The 'blobs' represent metallic regions and have resistance $R$ and linear dimension of the order $\xi$. The area between blobs is a capacitor as discussed in our earlier qualitative model. For an applied voltage with amplitude $V_0$, the voltage drop $V$ across a single capacitor, i.e. a blob-blob junction, is:

$$ V = \frac{V_0}{\sqrt{1 + (\omega RC)^2}} \quad (6.1) $$

There are of the order $L/\xi$ such voltage drops, connected in series across the sample. Thus the total voltage drop in the capacitors is:

$$ V_C = \frac{L}{\xi} \frac{V_0}{\sqrt{1 + (\omega RC)^2}} \quad (6.2) $$

If $V_b$ is the critical applied voltage needed to achieve breakdown, then the breakdown condition is $V_0 = V_b$. For convenience, we take the breakdown voltage of the individual capacitors to be unity. The breakdown field is then given by:

$$ E_b = 14 \pi l v \sqrt{1 + (\omega RC)^2} \quad (6.3) $$

The data are not inconsistent with the predictions of this simple model, at least at low frequencies. Hui\textsuperscript{5} has proposed
a model based on the nodes-link-blobs picture where the breakdown field varies as $(\Delta p)\nu$ in the static limit. Our simple model also reduces to this result at zero frequency. At very low frequencies the breakdown field should still be independent of frequencies and we are starting to see this in the upper curve of figure 50. More data is certainly needed to validate these predictions conclusively.

If we write the resistance of the blobs as $R = \xi r$, where $r$ is the resistance of a single link within the blob, and define a critical frequency $\omega_c$ by:

$$\omega_c = \frac{1}{\xi r C} \quad (6.4)$$

then we may write the expression for the breakdown field as:

$$E_b = |\Delta p| \nu \left( 1 + \left( \frac{\omega}{\omega_c} \right)^2 \right)^{\frac{1}{2}} \quad (6.5)$$

This critical frequency roughly corresponds to the frequency at which the breakdown field starts to show frequency dependance. We are starting to see this behavior in the upper curve of Fig. 50 but we were not able to perform calculations at sufficiently low frequencies near the percolation threshold to see this in the lower curve.
Fig. 48 Initial breakdown field as a function of volume fraction of conductor. The lattice is 60 x 60 bonds. Shown are two different frequencies.
Fig. 49  Diagram of a metal - insulator composite just below the percolation threshold. The "M"'s represent the metallic regions. Note the large isolated regions of metal separated by narrow channels of insulator.
Fig. 50 Initial breakdown field as a function of frequency for a 60 x 60 bond lattice. Shown are two different volume fractions of metal. Note that the upper curve is starting to show frequency independence at low frequencies. See text for explanation.
Fig. 51  Model of a metal - insulator composite below the percolation threshold. Sample is of linear dimension L and the metallic 'blobs' are of linear dimension $\xi$. See text for development of a theory.
References for Chapter VI


2. D. Bowman and D. Stroud, private communications.


5. P.M. Hui, private communication.
Appendix

The effective medium approximation (EMA) has been used throughout this dissertation as a simple analytic theory to be compared to the numerical results. We now present a simple derivation of this approximation.

We consider a random binary composite with constituents having conductivities $\sigma_1$ and $\sigma_2$. Further we imagine the composite to be "cellular", the $i^{th}$ cell composed of material with conductivity $\sigma_i$ and occupying volume $v_i$. The term "cellular" implies that every point in the composite is assumed to lie in either one or another of the cells. For convenience we also assume the cells to be spherical; the generalization to other shapes is straightforward.

To compute the effective conductivity of the composite exactly we would need to find the local fields $\vec{E}(\vec{x})$ and currents $\vec{j}(\vec{x})$ at each point $\vec{x}$ in the composite in the presence of an applied field $\vec{E}_0$. The effective conductivity $\sigma_e$ would then be given by $\langle \vec{j}(\vec{x}) \rangle = \sigma_e \langle \vec{E}(\vec{x}) \rangle$, the brackets denoting a volume average. Because $\vec{j}(\vec{x})$ and $\vec{E}(\vec{x})$ are random functions of position, these averages can only be computed approximately.

The effective medium approximation is analogous to the Weise molecular field approximation used in the study of
magnetism and is as follows. We imagine the $i^{th}$ cell, instead of being surrounded by its actual environment, to be embedded in an effective medium of conductivity $\sigma_e$. This idea is illustrated in figure 52. In the presence of an applied electric field $\vec{E}_0$, the total field far from the cell will then be the sum of two parts: (i) the applied field, and (ii) an electric dipole field with dipole moment given by

$$\vec{p}_{dip} = \frac{3}{4\pi} \frac{\sigma_i - \sigma_e}{\sigma_i + 2\sigma_e} \bar{E}_0$$  \hspace{1cm} (A.1)$$

Taking a volume average, we have for the total average electric field:

$$\langle \vec{E}_{tot} \rangle = \vec{E}_0 + \langle \vec{E}_{dip} \rangle$$  \hspace{1cm} (A.2)$$

The self-consistency condition defining the EMA is the requirement $\langle \vec{E}_{dip} \rangle = 0$. From equation (A.1) and the relationship

$$\int \vec{E}_{dip} \, d^3r = -\frac{4\pi}{3} \vec{p}_{dip}$$  \hspace{1cm} (A.3)$$
together with the definition of a volume average, we obtain equation:
where $p$ is the volume fraction of material 1. This is a quadratic equation that can easily be solved for the effective conductivity $\sigma_e$ in terms of $\sigma_1$, $\sigma_2$, and $p$. The physical solution can be determined by requiring that $\sigma_e$ be continuous, or, in the case of complex conductivities, that $\Re \sigma_e > 0$.

At finite frequencies it is sometimes more convenient to work with complex dielectric functions rather than conductivities. Stroud has shown that in the quasistatic limit the conductivities appearing in equation (A.4) can formally be replaced by dielectric functions giving:

$\frac{p}{\sigma_1+2\sigma_e} \sigma_1 - \sigma_e + (1 - p) \frac{\sigma_2 - \sigma_e}{\sigma_2+2\sigma_e} = 0 \quad (A.4)$

At smaller wavelengths where the quasistatic approximation breaks down, Stroud and Pan have derived an EMA based on scattering theory. Using a full multipole expansion for the scattered waves, they found that eddy currents in the metal particles are an important absorption mechanism. Their theory reduces to equation (A.5) in the long wavelength limit.
Fig. 52 Illustration of the effective medium approximation. The composite consists of materials with conductivities $\sigma_i$ and $\sigma_x$. The EMA is defined by imagining the $i^{th}$ cell to be surrounded by an effective medium with conductivity $\sigma_\infty$. 
References for Appendix