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TOPICS IN THE PHYSICS OF DISORDERED MEDIA

DISSERTATION

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

By

Xifeng Zhang, B.S., M.S.

1995

Dissertation Committee:
David G. Stroud
Charles A. Ebner
C. David. Andereck

Approved by
David G. Stroud
Adviser
Department of Physics
To my parents and my wife
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VITA

February 25, 1962 .................................................. Born in Jining, P. R. China

1979-83 .................................................. Peking University
    B.S. in Physics

1983-86 .................................................. Peking University
    M.S. in Physics

1986-89 .................................................. Research Associate, Department of
    Physics, Peking University, Beijing, PRC

1989-92 .................................................. Teaching Associate, Department
    of Physics, The Ohio State University, Columbus, Ohio, USA

1992-Present .................................................. Research Associate, Department
    of Physics, The Ohio State University, Columbus, Ohio, USA

Publications

Research Publications


**Fields of Study**

Major Field: Physics.

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CHAPTER I

Introduction

This dissertation is composed of two independent parts: numerical studies of the electrical and optical properties of binary composites; and molecular dynamical simulation of diffusion properties of liquids.

We will present the numerical simulation of electrical and optical properties of binary composites in the first part, which includes Chapter II, III, and IV. A binary composite, by definition, is a mixture of two components. In contrast to an alloy, however, the two components are not combined at an atomic level. Instead, each component typically exits in the form of grains, which are much larger than atomic size, but much smaller than the sample size. The grains can have simple regular shapes, such as spheres, or they can have a variable random shapes.

The behavior of a single grain can be characterized by the macroscopic physical parameters of the component in bulk form. On the other hand, the composite itself is microscopically inhomogeneous. If the scale we are interested in a problem is much larger than the typical grain size in a composite, effective physical quantities can be used to describe the behavior of the composite. Generally, the physical properties of a composite depend on the physical properties of its components. For example,
In the case of the optical properties of composite materials, the wavelength of the electromagnetic radiation is one characteristic scale. In the low frequency limit, where the wavelength may be much larger than the typical grain size (usually $10^2 - 10^3 \text{Å}$ in a metal insulator composite), the composite can be described in terms of effective properties, such as effective conductivity, effective dielectric constant, and effective nonlinear susceptibility. In the following three chapters, we will numerically calculate these electrical and optical parameters using several methods, principally a numerical technique known as the transfer-matrix algorithm.

In the following chapter, Chapter II, we will review the transfer-matrix method, and describe how to use it to calculate the electrical and optical properties of composite materials. We will describe the algorithm of the numerical method in greater detail than available in other references. Its implementation on computers of different architectures, including scalar, distributed and massively parallel computers, will also be presented. Although our computations were mainly carried out in scalar machines, the implementation schemes on parallel systems discussed in this chapter may be useful for further calculations. Such calculations may involve larger systems, which requires more computing power in order to reduce finite-size effects. While the implementation schemes for massively parallel computers are discussed for Cray T3D and Intel Paragon XP/S in particular, they can be used on other parallel systems without much modification. The second part of Chapter II, in which the parallel computing scheme is discussed, is written based on a term paper of a computer science course that the author took at OSU.
In Chapter III, the transfer-matrix method is used to simulate the linear electrical and optical properties of bulk 3D composites, as well as thin composite films of different thicknesses. Since composite materials often exist in the form of thin film, such as coatings on substrates, the study of electric and optical properties of such thin film is of potential practical value. Such thin films can be used, for example, to control the optical properties of radar-absorbing materials. The study of thin films is also significant for basic physical questions such as the effects of dimensionality on the percolation threshold and the resulted critical exponents.

The main result of our study is that the crossover of the composite thin films from 2D to 3D behavior occurs quite quickly as the film thickness increases. This crossover strongly affects such linear electrical and optical properties as the percolation threshold and the surface-plasmon resonance frequency. We also compared to the predictions of a new effective medium theory, and to a scaling theory of Neimark. Whenever comparison is possible, the numerical results agree well with the predictions of both theories.

In Chapter IV, the last chapter of the Part I, we extend this work to the study of nonlinear electrical and optical properties. In particular, we calculate the third order Kerr nonlinear susceptibility of a variety of composite geometries, including random composites and composites containing embedded fractals. In many cases, we find that the nonlinear susceptibility can be enhanced hugely. For example, we find the source of this enhancement is fluctuation in the local electric field. Significant enhancement in the effective nonlinear susceptibility of composites with embedded fractals of proper
size, composites near the percolation threshold, and dielectric-metal composites low concentration of the metallic component (this last can give huge enhancement for the frequencies around the surface-plasmon frequency).

In the Part II of this dissertation, we will present some numerical results relating to the molecular dynamical simulation of liquids, especially the calculation of diffusion constants. In Chapter V, we describe our molecular-dynamical method and some test simulations for Lennard-Jones liquids. In this chapter, we calculated the diffusion constants of pure Lennard-Jones liquid at various temperatures, as well as the diffusion constants of various impurities in Lennard-Jones fluid. The impurities interact with the host atoms via Lennard-Jones potentials with different parameters than those of the host Lennard-Jones potential. Our simulation results illustrate the effects of temperature and different impurity-host potentials on the value of diffusion constants. From the temperature dependence in the pure Lennard-Jones case, we extract an effective activation energy, which is in good agreement with available experimental results. For systems containing impurities, we find that impurity size, not its strength, is the most important factor affecting the diffusion constant.

Our final goal in studying the diffusion constants of liquids is to find a way to calculate the diffusion constant of liquid semiconductors. Since directional forces play an important role in liquid semiconductors, finding a proper interatomic potential to represent this directional interaction is a challenge prerequisite to a molecular dynamical study. Although we have not yet achieved this goal, we have tested various proposed model, including the well-known Stillinger-Weber potential and a bond
charge model. Our study of this topic is presented in Chapter VI.
Part 1

Electrical and Optical Properties of Binary Composites
CHAPTER II

Computer Simulation of Impedance Network With Transfer-Matrix Method

2.1 Introduction

The physical properties of a composite material are often studied numerically. In order to use certain numerical methods, it is often useful to discretize the composite over a simple network. The physical properties of the composite material are characterized by effective parameters, which can be calculated on this discreted network more easily than in a continuum. [The fundamental physical justification for network discretization in composites will be discussed in Chapter III.]

A wide variety of numerical techniques have been used to calculate the effective conductivity of impedance networks. One early approach uses the so-called relaxation method [1], which permits solution of the network the Kirchhoff equations directly. The main drawback of this method is its slow convergence near the percolation threshold, a phenomenon known as "critical slowing-down". In two dimensions, a propagative algorithm, based on repeat use of the so-called star-triangle (also called $\Delta-Y$) transformation, can be used to calculate the conductance of a finite network ex-
actly [2, 3]. While the Δ-Y method does not have the critical slowing-down problem of the relaxation technique, it has so far been used only for two-dimensional lattices and the extension to higher dimensional network, if possible at all, is quite difficult.

The transfer-matrix method, pioneered by Derrida and Vannimenus [4] in the middle 1980's, avoids the drawbacks of both the relaxation and the star-triangle methods. It is also one of the most accurate numerical methods available for calculating the conductivity of random networks. This method deals with a sample which is infinite in the longitudinal direction and finite in the other directions. To calculate the conductivity of a d-dimensional network in this approach, the network is built up gradually by successively adding one (d-1)-dimensional layer at a time in the longitudinal direction. The conductivity of the network at a given stage is determined by the transfer matrix derived for network at the previous stage, and the configuration of the newly-added layer. In the realistic calculations, the number of layers, i.e., the length in the longitudinal direction, is finite, but much larger than the dimensions in the transverse directions.

The transfer matrix has been used very successfully in determining the exponents $s$ and $t$, which are related to the percolation transition in composite materials. The most accurate numerical values for the exponents are due to this method. Indeed, the accuracy of the transfer-matrix approach is really limited only by the computing power not by intrinsic limitations of the method. A special-purpose computer called PERCOLA, has been built in Europe based on the transfer-matrix algorithm, and used to calculate several percolation exponents.
Massively parallel processors (MPP), such as Cray T3D and Intel Paragon, can also give sufficient computing power for most calculations based on this algorithm. The programming paradigm on MPP machines is different from the ordinary scalar computers. For example, a synchronization mechanism has to be used to coordinate the processors, and the data need to be distributed among the local memories so as to minimize network communication.

In this chapter, we will introduce the transfer-matrix algorithm and also discuss some implementation issues for different computers. In the case of distributed computing systems, we give an implementation schemes. In the following two chapters, we use the transfer matrix method to study the linear and nonlinear electrical and optical properties of various binary composite materials. The computations in these chapters were performed mainly on scalar computers, such as DEC Alpha workstations.

This chapter is organized as follows: In the next section, the transfer-matrix algorithm is discussed. In Section 2.3, we give basic implementation methods for matrix inversion and for storing matrices which are required in calculating the electric field distribution. These are the basic implementation issues for scalar computers. For distributed parallel computers, there are additional implementation issues which need to be addressed. These include processor synchronization and data distribution among processors, both of which will be discussed in Section 2.4. The performances of the transfer-matrix algorithm, as implemented on different systems, will be estimated whenever possible. Finally, Section 2.5 gives a brief concluding discussion.
2.2 Transfer-Matrix Algorithm

The transfer-matrix algorithm is most easily explained using a 2D square network. Simple extensions can give the algorithm for higher-dimensional simple cubic networks. Figure 2.1(a) shows an $N \times L$ network with $N = 4$, $L$ being the length in the longitudinal direction. A fixed voltage maintained by a battery is applied to each site on the right most layer (the $L^{th}$ layer of the network). Obviously, current flows from each battery to its attached site. The magnitude of this current depends on the configuration of the whole network, the voltage applied by the battery to the site, and the voltages applied to all the other sites in the layer. The I-V relations for all the sites on $L^{th}$ layer can be expressed by

\[
\begin{pmatrix}
I_1 \\
I_2 \\
\vdots \\
I_N
\end{pmatrix}
= A_L
\begin{pmatrix}
U_1 \\
U_2 \\
\vdots \\
U_N
\end{pmatrix}.
\tag{2.1}
\]

Here $I_i$ ($i=1,2,...,N$) is the current flowing into site $i$ from the battery of voltage $U_i$, while $A_L$ is defined as the admittance matrix of the $N \times L$ network. If we add another layer (the $(L + 1)^{th}$ layer), the network becomes a $N \times (L + 1)$ strip, as shown in Figure 2.1(b). We can write another I-V relation similar to Eq. (2.1) with a new admittance matrix $A_{L+1}$, to determine the currents in the new layer.

\[
\begin{pmatrix}
I'_1 \\
I'_2 \\
\vdots \\
I'_N
\end{pmatrix}
= A_{L+1}
\begin{pmatrix}
U'_1 \\
U'_2 \\
\vdots \\
U'_N
\end{pmatrix}.
\tag{2.2}
\]
From Ohm's law, one can show [4] that \( A_L \) and \( A_{L+1} \) satisfy a recursive relation,

\[
A_{L+1} = V + A_L(I + HA_L)^{-1}.
\]

Here \( I \) is an identity matrix, and \( V \) is a tridiagonal matrix which represents the change in the admittance matrix caused by the vertical bonds on \((L + 1)^{th}\) layer. \( V \) is given by

\[
V_{ij} = \frac{1}{v_i} + \frac{1}{v_{i-1}} \delta_{ij} - \frac{1}{v_i} \delta_{j,i+1} - \frac{1}{v_{i-1}} \delta_{j,i-1}.
\]

where \( v_i \) is the resistance of the vertical bond which connects site \( i \) and site \((i + 1)\) in the \((L + 1)^{th}\) layer. Matrix \( H \) is diagonal and determined by resistances, \( h_i \), of the horizontal bonds connecting \( L^{th} \) and \((L + 1)^{th}\) layers,

\[
H_{ij} = h_i \delta_{ij}.
\]

Using Eq. (2.3), we can calculate the admittance matrix of a \( N \times L \) network recursively, starting from \( A_0 = 0 \) and ending at the \( L^{th} \) layer. The only information needed is the configuration of the \( N \times L \) network. The effective conductivity per unit length of the network is given by the first element of the final admittance matrix:

\[
\Sigma_N = \lim_{L \to \infty} A_L(1, 1)/L.
\]

where we actually average the total conductance of the whole network over \( L \) layers.

Now we can calculate the conductivity of a \( N \times L \) network. First, we calculate the admittance matrices by repeatedly using Eq. (2.3) until we reach the right-most layer. Then we use Eq. (2.6) to calculate the effective conductivity.

Sometimes we need to know the voltage distribution, in order to calculate certain physical properties of the system, such as, the third-order nonlinear conductivity.
Figure 2.1: Schematic illustrating the transfer-matrix method
To accomplish this, Bergman and Duering [6] proposed an extended transfer-matrix method which can be used to calculate the voltage distribution. To do so, we have to calculate the admittance matrices starting from the right side of a given network (we call these right matrices), in addition to the left matrices, which were calculated starting from left to right as in Figure 2.1. For each layer, two admittance matrices are thus calculated. We denote these as \((A^L_i)\) for the left-hand matrix and \((A^R_i)\) for the right one. Both are calculated by using Eqs.\((2.3)\)-(\(2.6\)).

The voltage distribution on \(L^{th}\) layer is obtained by solving the set of linear equations,

\[
\sum_{i=2}^{N} (A^L_{ki} + A^R_{ki})U_i = -A^L_{k1} - A^R_{k1} ; \quad k = 2, 3, \ldots, N.
\] (2.7)

where \(U_i\) is the voltage on site \(i\) on a given layer. From Eq. \((2.7)\), once the corresponding admittance matrices \(A^L\) and \(A^R\) are obtained, the voltages on each site in the layer can be easily calculated by simply solving a set of linear equations.

A problem which emerges in solving for the voltage distribution is how to store the \(2L \times (N \times N)\) matrices needed for a \(N \times L\) network. We will deal with this problem in the next section.

### 2.3 Basic Implementation Issues

In this section, we discuss only some generalities regarding implementation techniques, which will be applicable to both ordinary scalar computers and to MPP's.
Figure 2.2: A sketch illustrating how the horizontal bonds in a layer transform into an equivalent $N \times N$ network segment; here $N = 4$. The resistors labeled "null" and the wire have zero resistance; and the infinity resistors have infinite resistance. A random resistor has the resistance of a randomly generated bond, which usually has finite resistance.
2.3.1 Matrix Inversion.

There is a more efficient way to implement the matrix inversion in Eq. (2.3) than the implementation by direct matrix inversion. For a typical network, especially a network used to model a random composite, in order to reduce the numerical fluctuation, it is usually necessary to consider a network of length $L$ more than a thousand. If we simply use Eq. (2.3) directly, we need to invert the matrix $(I + HA_L)$ a total of $L$ times. This is a very expensive computation for the non-sparse matrices which appear in the transfer-matrix method. There is a way to avoid this expensive direct matrix inversion. Normally, a layer can be replaced by an equivalent $N \times N$ network segment, as shown in Figure 2.2. In the segment, each layer has only one horizontal and no vertical random resistors, except for the right-most layer. Matrix $V$ in Eq. (2.3) is zero for these layers, and matrix $H$ has at most one non-zero element, namely

$$H_{ij} = h_i \delta_{il} \delta_{lj}. \quad (2.8)$$

Since the first horizontal bond has zero resistance, $l = 2, 3, \ldots, N$, where $l$ is the integer number which labels site connected only by the horizontal random bond in a layer. In the right-most layer, no matrix inversion is needed, since there it contains no non-zero horizontal resistors [See Eq. (2.3)]. Matrix $V$ can be calculated easily from the vertical bonds by using Eq. (2.4).

As an example, let us look at the first layer ($l = 2$) of the equivalent network.
segment in Figure 2.2. The matrix to be inverted is given by

\[
(1 + HA) = \begin{pmatrix}
1 & 0 & 0 & 0 \\
\frac{h_iA_{21}}{1 + h_iA_{12}} & 1 + h_iA_{22} & h_iA_{23} & h_iA_{24} \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
\end{pmatrix}
\]  \quad (2.9)

Here A is the admittance matrix obtained after adding the previous layer. This matrix is similar to a 3-dimensional spatial translation matrix. In fact, the only difference between two is a factor of \(1 + h_2A_{22}\) in the diagonal. By analogy with the inverse of the translation matrix, it is easy to obtain the inverse of the matrix \(1 + HA\). This inverse is,

\[
(1 + HA)^{-1} = \begin{pmatrix}
1 & 0 & 0 & 0 \\
\frac{-h_iA_{21}}{1 + h_iA_{12}} & \frac{1}{1 + h_iA_{12}} & \frac{-h_iA_{22}}{1 + h_iA_{12}} & \frac{-h_iA_{23}}{1 + h_iA_{12}} \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
\end{pmatrix}
\]  \quad (2.10)

There are at most two non-zero elements in each column of the above matrix. Multiplying this matrix by the matrix A, we obtain the second term at the right of Eq. (2.3) as

\[
[A(1 + HA)^{-1}]_{ij} = \begin{cases} 
A_{ij} - \frac{A_{il}h_i}{1 + h_iA_{ll}} & j \neq l \\
\frac{A_{ij}}{1 + h_jA_{jj}} & j = l
\end{cases}
\]  \quad (2.11)

Thus, by using multiple step translations, we have avoided the direct inversion of a matrix when calculating the change in admittance matrix when a new layer is added. We call this technique the multi-step translation method. The contribution from the vertical bonds is easily included by adding the matrix V as given by Eq. (2.4). The calculation of V is clearly both straightforward and inexpensive in computing time.

Let us compare the time requirements for adding \(N\) horizontal bonds using multi-step translation and direct matrix inversion. To add a horizontal bond, we have to compute \(O(N^2)\) elements using Eq. (2.11). While \(O(N^3)\) operations are needed to
add all the horizontal bonds to a given layer. Thus the time scales in the same way as direct matrix inversion. However, in multi-step translation, Eq. 2.11 permits us to use only only a few operations in the inner-most loop. Matrix inversion, on the other hand, usually needs many more operations in the inner-most loop. Based on our experience, we believe that multi-step translation is at least a order of magnitude faster than direct matrix inversion. Another benefit of multi-step translation is its easy parallelization on supercomputers, which should produce an even greater performance improvement.

2.3.2 Matrix Storage

To calculate the voltage distribution using Eq. (2.7), we need both the left and the right admittance matrices in each layer. Once the left matrices are calculated, they must be somewhere before the right matrices are calculated. Many matrices must be retrieved to build up the linear equations needed for solving the voltage distribution. If we simply calculate the left matrices for all the layers and store them before calculating the right matrices, a huge amount of storage space for the matrices would be required. For example, in a $20 \times 20 \times 2K$ network, we would need to store $2000 \times 400 \times 400$ left matrices. Each matrix needs more than two Mbytes of storage in double precision floating point; and the total required storage would be more than 4 Gbytes. Matrix symmetry would only reduce this by half.

Bergman et al. [6] proposed a solution to this problem, which reduces the required storage but increases the computing time roughly by a factor of two. In their approach, the whole network of length $L$ is divided into $M$ blocks, each of length $L/M$
layers. The voltage distribution in the network is calculated by the following steps:

1. The admittance matrices are calculated for each layer in the network from left to right. Instead of saving each matrix for every calculated layer, only one is saved for each block, namely the admittance matrix of the leftmost layer in the block. The total number of saved matrices is $M$.

2. The right admittance matrices are calculated from right to left. For each block, we start from the right-most and stop at the left-most layer. All the $L/M$ calculated right admittance matrices in the block are stored in temporary space.

3. The left admittance matrices for the same block as mentioned in step (2) are recalculated from left to right. To do so, the left admittance matrix for the left-most layer for the block, which is saved in step (1), is read in, and then used as the initial matrix for calculating the left matrices for the other layers in the block. When a left matrix is recalculated, it is combined with the right matrix saved in step (2) for the same layer. The voltage distribution in the layer can be obtained by solving the linear equations built from Eq. (2.7). Once the calculation of the block is finished, the right matrices are no longer needed, except for that of the left-most layer. Thus, the storage space can be released for calculation of the next block. The saved right matrix is that of the left-most layer in the block. It is to be used as the initial matrix for calculating the right matrices of the next block.

4. Steps (1) to (3) are repeated $M$ times, until the voltage distribution of the entire
network is obtained.

In this scheme, only $M + \frac{L}{M} + 1$ matrices need to be stored. If we let $M = L/M$, i.e. $M = \sqrt{L}$, we minimize the number of stored matrices for a given network length. For a 3D $20 \times 20 \times 2000$ network, we now need about 100 Mbytes storage space. In practice, the choice of numbers is made in the opposite way, i.e., determining the maximum number of matrices that can be stored for the given storage resource. The square root of one-half of this maximum number is the maximum calculable network length for the given storage resource. Obviously, therefore, $L$ is determined by the matrix size and the available storage in the system.

This scheme requires $3L$-layer iterations as compared to the $2L$-layer iterations in the first scheme, This is an acceptable compromise considering the positive feature that the calculation can be carried out on small computer systems, such as workstations or even PC's.

2.3.3 Running Time and Memory Usage

The discussion in Section 2.3.1 showed that the running time scales as $N^3L$, where $N$ is the number of bonds in a layer and $L$ is the length of the strip impedance network. The memory usage is only proportional to $N^2$, the number of the matrix elements, and is independent of $L$.

The calculation of voltage distribution consists of two parts: admittance matrix calculation using Eq. (2.3); and the calculation of the voltage distribution using Eq. (2.7). Solving the linear equations for the voltage distribution takes about the
same time as adding one layer in the admittance matrix calculation, for systems of
given left and right admittance matrices. Since methods for solving the linear equa-
tions are well known and supported by libraries in many systems, we will not describe
it here. Suffice it to say that the running time for running such a system scales the
same way as the admittance matrix calculation. The calculation of the matrix $V$ in
Eq. (2.3) is easy and its running time scales as $N$, because $V$ is a sparse matrix. In
the admittance matrix calculation, 98% of the computing time is spent on the second
and less than 1% on the first term of Eq. (2.3). As the matrix size increases, the
second term will take a still larger fraction of the running time. From Amodal's Law,
more optimization effort should be focused on this term.

To summarize, the memory usage for the transfer matrix algorithm scales as $N^2$,
which is not a problem for most systems, but the running time scales as $N^3 L$ for both
admittance matrix and the voltage distribution calculations. As an example, let us
look at a 3D $L_x \times L_y \times L$ network. The number of sites on a layer is $L_x L_y$. The
running time scales as $(L_x L_y)^3 L$, which increases dramatically as the number of sites
in a layer increases. This rapid increase in matrix size, as well as the computing cost,
limit the transverse dimension of the samples which can be calculated on workstation
to less than $20 \times 20$. 
2.4 Implementation Issues on Parallel Computing Systems

2.4.1 Introduction

In the last section, we discussed the implementation of the transfer-matrix algorithm. For scalar architectures, such as RISC workstations, the given implementation schemes can be directly used. The same implementation techniques should also be applicable to vector machines, such as Cray Y-MP. We expect good performance on this kind of machines, since matrix manipulations, which consume most of the computing time, are easy vectorizable. In the next part of this section, we will focus on the specific implementation issues for distributed systems. The implementation issues discussed in last section are still relevant to for these systems. We will give implementation schemes on two kind of distributed systems: heterogeneous distributed and massively parallel processor (MPP) systems. For MPP systems, while the given implementation scheme is given based on Cray T3D and Intel Paragon architectures, the same basic idea is useful for other MPP systems, such as CM-5. For a better understanding the performance analysis, we will discuss the basic architectural features of each system before giving the implementation scheme.

2.4.2 Heterogeneous distributed computers.

A heterogeneous distributed system[13] is a group of autonomous computers (nodes) which are loosely connected by a network. Several software packages can provide us
the platforms of parallel programming. One of the most popular one is called PVM, or "Parallel Virtual Machines". PVM provides all the basic synchronization and communication primitives by way of message passing. Message passing is usually slow, and its communication overhead for fine-grain parallelism is quite expensive. Because of this, we will not discuss implementation of fine-grain parallelism such as matrix partition in admittance matrix calculation. It is possible to improve the performance using some coarse-grain parallelism in the voltage distribution calculation, which takes a lot more computing time than that of the admittance matrix calculation. The following master-slave scheme could speed it up to such an extent that it would take the same running time as calculating the admittance matrices.

We divide the network into blocks as in Section 2.3.2. The parallel transfer matrix algorithm under PVM could be implemented in the following scheme:

1. A node, called the master, starts the left admittance matrix calculation on the network. Before starting, the master first initiates the right admittance calculation on another node, called the chief. Both the master and the chief save the admittance matrices of the first layer in a block. The saved matrices can be accessed by all the nodes in the system.

2. In the previous step the master and his chief work on the network from opposite direction. They will meet somewhere around the middle, assuming they work at the same speed. When they meet, each initiates a slave node to work on the voltage distribution calculation. Each slave takes care of one block. So the blocks to the left side of the meeting point are assigned by the chief and the
blocks on the right side by the master.

3. Next, both the master and the chief continue their calculation of admittance matrices. Whenever a new block is started, they assign the block to a new slave. The slave takes the block as well as the two admittance matrices for the left- and right-most layers of the block. From these two matrices, the slave can calculate all the left and right matrices in the block. It can then combine them to solve the voltage distribution in the block layers as described in last section.

4. The master and chief need to do some book-keeping to keep track of the idle slave pool. Whenever a slave finishes its work, it informs both the master and the chief. They put him back to the idle slave pool for later use.

Considerable acceleration could be achieved in principle with this scheme. Since a single block is much smaller than the whole network, it can be solved quickly. The total running time should approximately equal the time for a one-way calculation of the admittance matrices by the master or chief, whichever is longer. If the master, the chief, and the slaves have the same computing power, the speed up is about a factor of five. 80% of the time is spent on the work done in parallel by the slaves. If the master and his chief has more computing power the running time will be even shorter. One possible combinations is to use two Cray Y-MP processors as the chief and the master, and ordinary workstations as the slaves. The computation time will be determined by the speed of the admittance matrix calculation on the Crays provided that there are enough number of inexpensive processors to use as slaves.
Although this arrangement does not deliver very much speedup, it is a way improve the running speed with easy accessible resources.

The so called *Embarrassed Parallelism* could also be used if many different samples need to be calculated. In this approach, we simply write a program or a unix shell script and use it to distribute each sample to a host. Each host is simply a serial computer, which does all the computation from the admittance matrix to the voltage distribution. The optimum speed-up achievable by this scheme depends on the permissible number of hosts. (Unfortunately, in the Department of Physics, current policy only allows two hosts to be simultaneously used by one user). The main disadvantage of the scheme is the long waiting time. Another problem of the scheme is that such resources as memory or disk space are very limited in a single host. A large-scale problem can therefore not be solved in this way.

### 2.4.3 Massively Parallel Processors (MPP)

Before discussing implementation of the transfer-matrix method on MPP systems, we must first be familiar with the structure of a typical MPP system, such as Intel Paragon and Cray T3D. MPP usually has memory distributed among multiple processing nodes. [9]. Each processing node has an independent processor, which has its own memory, capable of operating on its own data. The nodes are interconnected via a high-speed communication network of a certain topology, for example, a 2D mesh in the Intel Paragon, and a 3D torus in the Cray T3D. The communication network can pass a message from one node to any other within a few microseconds. In some
MPP, such as the Intel Paragon, besides the application processor, each node also has a routing processor to handle message traffic. The separate message processor frees the computing processor from the communication services.

The computation power of a MPP is supported by each individual processor. For example, the Cray T3D uses DEC-Alpha processors, each of which can give more than 100 MFLOPs peak performance. Global memory is distributed among the processing nodes, each of which can have as many as 100 Mbytes. For a system with 256 processing nodes, the global memory can reach 25 Gbytes.

MPP systems use a very high speed communication network to connect its processors. Each processor is connected to its neighbors via bidirectional links of up to several hundred Mbytes/sec bandwidth. Furthermore, some frequently used communication primitives, like barrier and message broadcasting, are often implemented with hardware. This fast communication ability allows fine-grained parallelism to be explored. Fine grained parallelism, which usually requires intensive remote data access, could reduce the throughput if the network cannot match the data demanded by the application processors. Balancing the utilizations of communication and computation resource is important in determining the optimized grain size.

Multiple instruction multiple data (MIMD) programming paradigms are supported by MPP's. To implement the transfer-matrix method, we will use a special case of the MIMD, the single program multiple data (SPMD) implementation, in which all the processors will execute the identical program but on different data. For data access, they can use either shared global memory addressing or message
passing. Our implementation scheme will be given based on explicit massage passing programming model.

As in the last section, we will describe the implementation calculations of admittance matrix and voltage distribution separately. The basic data type is an $N \times N$ matrix to store the current admittance matrix. The bond type on each site in the current layer is stored in another array of $N \times D$ for a $D$-dimensional system. The configuration of a layer can be generated either deterministically or randomly. From the information of the horizontal bonds on the layer and the admittance matrix of the previous network, the second term on the right side of Eq. (2.3) can be calculated, as described in Section 2.3.1. The first term depends only on the vertical bonds on the layer, and can be calculated by simply using Eq. (2.4).

For the MPP systems, we can implement fine-grain parallelism. The matrix is partitioned into blocks. Each block is stored in an application processor. For the admittance matrix calculation, the following parallelization scheme can be used for a $P$-processor system.

1. The rows of an $N \times N$ matrix $A$ are partitioned into $P$ blocks. Each block has $N/P$ rows. Processor $k$ takes care of the block with index ranging $(k - 1) \times N/P \rightarrow k \times N/P - 1$, where $k = 1, 2, \ldots$, and $P$ is the processor number. The block is stored in the local memory of processor $k$ which can access the block without network communication. The block can also be accessed by other processors through the network via explicit or implicit message passing. Also, matrix $V$ in Eq. (2.3) is partitioned, and each block stored in a processor, as
for matrix \( A \).

2. The \( N \) sites in a layer are labeled from 0 to \( N - 1 \), and are partitioned in the same way as the matrix, since each row of the \( N \times N \) matrix corresponds to one site in a layer of \( N \) sites. Each processor generates the bonds for its \( N/P \) sites and sends information about the vertical bonds on the boundary of the block only to its neighboring processors, they need this information to calculate their own blocks of matrix \( V \). Then, each processor waits for messages carrying the vertical bond information from its neighboring processors.

3. Every processor runs a loop \( 0 \rightarrow (N - 1) \). If the loop index is within \( (k - 1) \times N/P \rightarrow k \times N/P - 1 \), i.e., within the row indices of the block the processor locally owns, it generates a vector according to the second row given in Eq. (2.10). To do this, it needs the horizontal bond of the site labeled with the same index and the previous admittance matrix. Then, it packs and broadcasts the vector to other \( P - 1 \) processors. The message is marked with the loop index. Otherwise, if the loop index is not in its block, it waits for a vector from another processor. The message is identified either with the loop index or the processor ID.

4. After a vector message is received, each processor checks the message ID and updates the matrix elements in its block according to Eq. (2.11). After update its block either from the vector created by itself or received from another processor, Every processor is synchronized by a barrier and increment the loop index by one after passing the barrier. If the \( 0 \rightarrow (N - 1) \) loop is not finished,
go to step (3). Otherwise, go to next step.

5. Each processor calculates the elements of Matrix $V$ for the block it locally owns from the bond information it owns and received in step (2). Then adds matrices $V$ and $A$ obtained from step (4). The results are the admittance matrix of the new network. It can be stored for the voltage calculation later on.

6. To add $L$ layers, repeat above steps $L$ times.

Let us examine the performance of the above algorithm. We start by estimating the communication cost. Considering a two-dimensional sample, to add a layer, each processor sends out one message to a neighbors in the vertical direction, broadcasts $N/P$ messages. The message sending to or receiving from a neighbor is very short and will add very little network traffic. Each broadcasted message contains a size $N$ floating-point vector. Total number of $N$ messages are broadcasted. The broadcasted messages dominate the network traffic. Obviously, a barrier mechanism is needed for each iteration of the loop to synchronize the processors. The iteration level synchronization problem is inherited from the recursive relation of the admittance matrices between the current and previous networks. On Cray T3D, barrier is implemented with hardware. It will take less time than the message broadcasting. For Intel Paragon, synchronized message passing, provided in NX library, includes barrier mechanism [17]. Calling barrier function will add $N$ additional broadcasts to finish a layer. The cost of synchronized message passing depends on the traffic condition.
The time that a processor spends on updating its block is totally parallelized if the network traffic overhead is minimal compared to this time, the speed up would be close to \( p \). Even if the network communication takes the same amount of time, we still have \( \frac{p}{2} \) speed up.

The voltage distribution is relatively simple to calculate. We can use the similar scheme as for the heterogeneous distributed computers. Another way is to distribute the matrices in the memory of the processors. After all the matrices are calculated, the processors exchange the matrices. Each one gets the left and right matrices of the layers assigned to it and simply solve the linear equation to get the voltage distribution over the layers. This arrangement will need huge data transfer over the network, which can be done quite efficiently by the block transfer engines which implemented in MPP computers. Because the matrices stored among the local memories of the processors, no file I/O is involved in this scheme. This will speed up the computing also.

2.4.4 Expected Performance on the MPP systems

Let now do a little more quantitative analysis on performance improvement of above algorithms on two MPP systems: Intel Paragon XP/S and Cray T3D. Suppose the block size for each processor is just one row, this is the maximum parallelism we can get with above schemes. For Intel Paragon system, to add a single layer, we need \( N \) synchronized broadcastings. Other message passing can be neglected. Since the broadcast in Intel Paragon is implemented with uni-cast, \( T_1 = \log_2 N \times \tau \) is the broadcast latency, where \( \tau \) is the uni-cast latency. Each broadcasted message have
16 \times N \text{ bytes of data for a complex matrix in addition to the routing information. It}
\text{takes about } T_2 = 16N/200 \text{ microseconds to inject the message into the network if the}
\text{bandwidth of network links is 200 Mbytes per second. If } \tau = 20 \mu s, \text{ for the problem}
\text{as large as } N = 1024, \text{ the first term is still dominate. We can use the first term to}
\text{estimate the network overhead for most of the problems. For example, if } N = 256, \nonumber
\nonumber T_1 = 160 \text{ and } T_2 \approx 20. \nonumber
\nonumber
\text{Since the Cray T3D has much smaller latency (few } \mu s) \text{ and message broadcasting}
\text{is implemented with hardware. The } T_2 \text{ is important also for most of the problem}
\text{sizes. Assume } \tau = 5 \mu s, \text{ for the same example, now } T_1 = 40 \text{ and } T_2 \approx 15 \text{ for 300}
\text{Mbytes per second bandwidth.} \nonumber
\nonumber
\text{The computation done by a processor for adding a horizontal bond includes building}
\text{a vector and update the block it locally owns. Building the vector using Eq. (2.10)}
\text{needs approximately the order of } 10 \times N \text{ floating-point instructions and similar number}
\text{of integer instructions. Approximately, same amount of time is needed for updating the}
\text{matrix block. In Intel Paragon, the i860 microprocessor has about 20M}
\text{instructions per second average performance for floating and, maybe a couple of times}
\text{faster for integer numbers. Around } 200 \mu s \text{ is needed for the processor assuming the}
\text{ } N = 256. \text{ For Cray T3D, since the DEC Alpha processors are several times faster}
\text{than Intel i860, less than } 100 \mu s \text{ is needed.} \nonumber
\nonumber
\text{A reasonable estimation for a single bond would be about 0.4 ms for Intel Paragon}
\text{and 0.1 ms for Cray T3D. Adding a layer of 256 sites takes approximately 0.1 s for}
\text{Intel Paragon and 0.025 s for Cray T3D. For a } 256 \times 2000 \text{ sample, we can calculate}
the effective conductivity in few minutes. The estimation could be over optimistic considering the fact that the performance of the microprocessors could be much worse than the numbers we used for normal code. A more conservative estimation should consider the other overhead in data transfer over the network such as the processor idle waiting for data, the floating point operation speed for the transfer matrix code, and the limitation on the maximum message size. The vector to be broadcasted may have to be cut into pieces and packed in many messages because of the limit. All these factors will reduce the performance significantly. A more conservative estimation should be much less, maybe about one tenth or one twentieth of above ideal performance, i.e., 1.0 to 2.0 s for Intel Paragon and 0.25 to 0.5 s for Cray T3D. Actually, on DEC Alpha workstation, our program runs at the speed of about 25 s per layer. This means the speed up is 50 to 100, which is still very good for most parallel programs on a 256-node Cray T3D. We cannot give number for the speed up of Intel Paragon MPP since we do not have a i860 based workstation to compare with.

In conclusion, MPP systems can provide us more computing power than other systems. Significant speed up can be achieved if parallel transfer matrix algorithm is implemented in these systems.

### 2.5 Conclusion

In this chapter, we discussed the transfer matrix method and its implementation on different computing systems. We have implemented the transfer-matrix algorithm
in scalar computers. The program was used to calculate the results in Chapter III and IV. The calculations were carried out mostly in DEC Alpha workstations. The performance of the program is quite satisfactory.

Due to the difficulty of accessing MPP systems and the limited resources for PVM platform, we have not implement the parallel algorithms yet. From our estimation of the expected performances, we can see parallel systems, especially MPP machines, can give us significant performance improvement in term of running speed as well as the problem size that we can handle. One possible future work on transfer matrix method can be implementation of the parallel algorithm on Cray T3D machine, which becomes more available to the computational scientists. While more detailed implementation problems will come out, the scheme we discussed above will provide us a frame, and in this sense, it is meaningful for future work.

To conclude this chapter, we will give a list of the pros and cons of transfer matrix method. The transfer matrix method has various advantages over other numerical algorithm for impedance network simulations.

1. Can be extended to higher dimensional networks and the algorithms are almost identical to the one in 2D that we have discussed.

2. Can be used for networks with the bonds of complex conductivity.

3. For a given network configuration, the calculated effective conductivity is the exact conductivity of the network for the boundary condition.

4. The computing time does not depend on the specific properties of a network
configuration. No critical slow down near the percolation threshold.

5. For a random network, the average over randomness is carried out automatically by iterating over large number of layers.

6. Required memory space is fixed.

7. Most of the operations involve matrix manipulations, which can be vectorized or parallelized easily.

From this list, we can see that TM method is a very general method. The only limitation of its usage is its rapid time consuming increase as the system increases.
CHAPTER II REFERENCES


CHAPTER III

Numerical Simulations of Linear Electrical and Optical Properties of Composite Materials

3.1 Introduction

In this chapter, we consider the linear optical properties of composite materials, leaving the nonlinear properties to the next chapter. By linear, we mean that the properties we are interested in, such as the conductivity and dielectric constant of our systems, are independent of the intensity of the external field. Linear electrical and optical properties of composites are of wide importance in science and engineering. For example, engineers in oil industry need to know the linear dielectric response of sedimentary rocks in the oil exploration. The sedimentary rock, whose pore space is filled with electrically conducting fluids, such as brine, can be treated as a conductor-insulator composite [1, 2, 3]. Geophysicists may want to know the emission, absorption, and reflection of electromagnetic radiation by snow on the Earth's surface in order to interpret the remote sensing data collected from satellites [4, 5]. These radiative properties are closely related to the linear electromagnetic properties. Again, the snow can be modeled as a composite of ice and air.
Modern research on composite materials started at the beginning of this century. In 1904, Maxwell Garnett [6] first proposed a model now known as the Maxwell-Garnett approximation to describe the optical response of stained glasses. In 1935, Bruggeman [8] introduced the so-called effective medium theory and used it to study the optical properties of composites. Since then, huge numbers of analytical calculations and computer simulations have been carried out on different composite systems [9].

Dielectric response is always one of the most important of composite behaviors. One of the pivotal early experiments on metal-dielectric composites was carried out by a group in the early 1980's at Ohio State University. This group [10] systematically measured the conductivity of Ag-KCl composites as a function of frequency. They gave clear experimental evidence supporting theoretical predictions that the conductivity of the metal-dielectric composites is highly frequency dependent and has features not present in either of the two components. For example, at low Ag concentration, the real part of the conductivity has a sharp peak around the so-called surface-plasmon resonance frequency, and, at a lower frequency (where the real part of conductivity is small), a gap with little absorption. As the metal concentration increases beyond the percolation threshold [11, 12], a Drude peak appears around zero frequency and the gap is found to close up. It reopens again away from percolation threshold.

As noted above, the electromagnetic properties of a composite differ strikingly from those of the constituents [13, 14, 15]. This difference is thought to arise largely
from local fluctuations in the electric field, which are produced by the spatially varying
dielectric function of a composite material. For example, consider a dilute composite
of spherical metal particles embedded in an insulating host, such as the Ag-KCl
composite used in above experiment. In this case, the electric field $E_{in}$ within the
particles is given approximately by $E_{in} = E_0 \frac{3\varepsilon_B}{\varepsilon_A + 2\varepsilon_B}$, where $E_0$ is the external field
far from the particle, and $\varepsilon_B$ and $\varepsilon_A$ are the dielectric functions of the host and the
metal inclusions. At a frequency such that $\text{Re} (\varepsilon_A + 2\varepsilon_B) \approx 0$, $E_{in}$ is very large, even
if the applied field is weak. The composite will absorb strongly at such a frequency.
This resonant absorption arises from the *surface plasmon resonance*. Such resonances
can cause granular metals to absorb strongly in the visible, provided the particles are
small compared to the wavelength of incident radiation. This behavior occurs even
though bulk metals are typically highly reflective at such frequencies. Absorptions of
this kind have been known for centuries, and, indeed, are thought to be responsible
for the beautiful colors of some medieval stained glass windows. A nice review was
given by R. W. Cohen *et al.* in early 1970's. [16].

The optical response of composites depend strongly on the *dimensionality* of the
composite. For example, the surface plasmon resonance frequency is determined by
the *shape* of the particle inclusion in the composite. Thus, if the composite is thin
compared to a typical particle dimension, the shapes of the absorbing particles, and
hence, the resonant frequencies, will be drastically altered. Such dimensionality effects
are of more than academic interest. Composite materials are often prepared in the
form of thin films, which are deposited on various substrates in order to influence
their optical properties. The films may be either thick or thin in comparison to typical particle dimensions. They may then be viewed as either three-dimensional or two-dimensional (3D or 2D). Both limits may occur in practice, as may intermediate cases.

In this chapter, we use a simple network model to study the linear response of metal-dielectric composite systems in two forms: bulk and thin film. The simulations are always carried out in the so-called quasi-static regime in which the electric field is assumed to be expressible as the gradient of a scalar potential. We will treat the models numerically, both at zero and finite frequencies. For the bulk composite, we will study the a.c. properties. The emphasis will be on the surface-plasmon resonance and the effects of percolation on the complex frequency dependent conductivity. Our numerical results show all the features observed in the experiment of Cummings et al. As far as we know, this is the first 3D a.c. numerical simulation using the transfer-matrix method.

For the thin film, we will consider the change in both the d.c. and a.c. behavior as the composite changes from two to three dimensions. Our simulation shows all the features found in bulk composites, and also shows that these features are highly dimensionality dependent. Our main result for the dimensionality dependence is that the three dimensional limit is approached very rapidly - the film behaves quite three-dimensionally even if it is as thin as three or four typical particle diameters. We also find that, in the thin-film regime where this 3D limit is not achieved, the film behaves anisotropically, exhibiting a different effective dielectric response for electric fields
polarized parallel and perpendicular to the film. To account for the crossover from 3D to 2D, we suggest a very simple thickness-modified effective-medium approximation, which accounts qualitatively for most of our results at both zero and finite frequencies.

In next section, we will discuss the quasi-static approximation and the effective medium theory, as well as the results given by the effective medium theory. In Section 3.3, we will present the model and numerical results for 3D impedance network calculations, and compare the results with effective medium approximation results. Section 3.4 is devoted to numerical results for composite thin film, and the comparison of these to the simple effective-medium approximation. A concluding discussion follows in Section 3.5.

3.2 Basic Approximation and Effective Medium Theory

3.2.1 Basic Approximation

We are interested in the electric and optical properties at the low frequency limit, \( \lambda \gg a \), where \( a \) is the typical grain size of each component. In this regime, the composite behaves homogeneously. The electrical properties are characterized by an effective dielectric function, \( \epsilon_e \), which is generally complex and frequency dependent. To an approximation which is good in the limit of long wavelength, \( \epsilon_e \) can be calculated within the so-called quasis-static approximation, under which relevant Maxwell equations for the electric field take the form:
\[ \nabla \times \mathbf{E} = 0 \quad (3.1) \]

and

\[ \nabla \cdot (\epsilon(x)\mathbf{E}(x)) = 0. \quad (3.2) \]

Here \( \mathbf{E}(x) \) and \( \epsilon(x) \) denotes the position-dependent electric field and dielectric functions, respectively. For a binary composite, \( \epsilon(x) \) has the value of either the dielectric constant \( \epsilon_A \) of component A or \( \epsilon_B \) of component B, depending on which region (A or B) contains the point \( x \).

Using Eq. (3.1), we can introduce a scalar potential function \( \Phi(x) \), and \( \mathbf{E}(x) \) can be expressed as the gradient of \( \Phi(x) \):

\[ \mathbf{E}(x) = -\nabla \Phi(x). \quad (3.3) \]

Substituting this relation into Eq. (3.2), we have,

\[ \nabla \cdot (\epsilon \nabla \Phi) = 0. \quad (3.4) \]

This differential equation can be solved to any desired accurate using finite difference approximation on a mesh. For most problems [17, 18], a simple d-dimensional cubic mesh can be used for the finite expansion. As Kirkpatrick has pointed out [19], this simple mesh is both necessary and sufficient for the problem we are interested in. It is not necessary to use other more complicated meshes for the expansion.

After discretizing Eq. (3.4) on the mesh, one obtains a set of difference equations, which are formally identical to the Kirchhoff’s equations for a complex impedance.
network. We can use this d-dimensional simple cubic impedance network to numerically simulate the dielectric properties of a composite material. In the following part of this dissertation, unless otherwise specified, the networks used in our calculations are always assumed to be simple d-dimensional (dD) cubic. Also, unless otherwise specified, the composites are taken as two-component.

3.2.2 Effective Medium Theory

Before moving to the numerical method, let us first review an analytical approach the effective medium approximation (EMA), for calculating the effective conductivity of an impedance network. The EMA was first introduced by Bruggeman [8] in 1935. Long before Bruggeman's work, Maxwell-Garnett [6] provided a formula to explain the colors of stained glasses. Stained glasses typically contain metal spheres small compared to the wavelength of light and embedded in a dielectric. The Maxwell Garnett approximation assumes that the metal sphere suspended in the glass are surrounded by insulating dielectric material, and makes a local field correction due to the polarization of the metal spheres. From its assumptions, it is not surprising that Maxwell-Garnett's theory usually works best for composites in which the concentration of one component is low. The EMA, on the other hand, is a better self-consistent mean-field theory; it is closely related to the coherent-potential approximation, for example, in the theory of electronic states in disordered alloys (the coherent potential approximation) [7]. In fact, it is an old approach to study the transport properties of inhomogeneous media [20].
There are several versions of the EMA, some for continuum media and some for lattices. One formulation is given by Kirkpatrick [19], who considered a simple d-dimensional cubic impedance network. Suppose there is a binary composite of component A and B with bulk conductivity of $\sigma_A$ and $\sigma_B$ respectively. Then the effective conductivity is given by the following self-consistent relation:

$$p_A \frac{\sigma_d - \sigma_e}{\sigma_d + (d-1)\sigma_e} + p_B \frac{\sigma_m - \sigma_e}{\sigma_m + (d-1)\sigma_e} = 0$$ (3.5)

where $p_A$ is the concentration of component A, in terms of volume occupied in the composite and $p_B = 1 - p_A$ is the concentration of B. Generally $\sigma_A$ and $\sigma_B$ are complex numbers, representing bond conductances, which are assumed given for each component of the composite. Eq. (3.5) tells us that $\sigma_e$ depends not only on the concentration $p_A$ but also on the dimensionality ($d = z/2$) of the impedance network, where $z$ denotes the coordination number of a d-dimensional simple cubic network.

From Eq. (3.5), we can calculate $\sigma_e$, for given dimension and concentration, by solving this second-degree algebraic equation with the result

$$\sigma_e = \frac{(dp_A - 1)\sigma_A + (dp_B - 1)\sigma_B \pm \Delta^{1/2}}{2(d - 1)}$$ (3.6)

where $\Delta = (dp_A - 1)^2 \sigma_A^2 + (dp_B - 1)^2 \sigma_B^2 + 2(d - 1 + p_Ap_Bd^2)\sigma_A\sigma_B$. Since we are only interested in binary composite, we can drop the subscript on $p_A$ and replace $p_B$ by $(1 - p)$ without any confusion. The positive sign in Eq. (3.6) corresponds to the physical solution, since all the composites involved in our study are dissipative and must have positive $Re(\sigma_e)$ (this assumes a particular choice of branch cut if $\sigma$ is complex).
To obtain the predictions of the EMA for the percolation threshold, we need to examine $\sigma_e$ in the two extreme cases: conductor-insulator and perfect conductor-conductor composites. For the conductor-insulator mixture, $\sigma_A$ is finite and $\sigma_B = 0$. Setting $\sigma_B = 0$ in Eq. (3.6), we have

$$\sigma_e = \begin{cases} \sigma_A \frac{p - p_c}{1 - p_c} , & \text{if } p > p_c \\ 0 , & \text{otherwise} \end{cases}$$

(3.7)

where $p_c = 1/d$ is the bond percolation threshold of the simple d-dimensional cubic network. By bond percolation, we mean that the network is constructed by bonds with different conductivity. Another way to construct a network uses the different conductivity sites. The conductivity between two neighboring sites depends on the conducting properties of both sites. We can see that a site percolation network can be easily mapped into a bond percolation network.

In the case of perfect conductor-conductor composite, we have $\sigma_A = \infty$ and $\sigma_B = \text{finite}$. Then $\sigma_e$ in Eq. (3.6) becomes

$$\sigma_e = \begin{cases} \sigma_B \frac{p - p_c}{p_c - p} , & \text{if } p < p_c \\ \infty , & \text{otherwise} \end{cases}$$

(3.8)

By comparing the above two equations with the following critical behavior assumed to be valid for $\sigma_e$ at the percolation threshold,

$$\sigma_e \propto \begin{cases} \sigma_A (p - p_c)^{s} , & p < p_c \\ \sigma_B (p - p_c)^{-t} , & p > p_c \end{cases}$$

(3.9)

we can obtain the universal exponents $s$ and $t$ in the effective medium approximation, which are

$$s = t = 1$$

(3.10)
Both are dimensionality independent and have the same value. They do not agree with results from numerous numerical simulations [21, 22, 24, 25, 26, 27]. (\(s = t = 1.30\) for \(d = 2\) and \(s = 2.0, t = 0.76\) for \(d = 3\)). Let us go back to the percolation threshold obtained from Eqs. (3.7) and (3.8):

\[ p_c = 1/d = 2/z. \]  

(3.11)

Previously, Eq. (3.11) predicts that \(p_c\) only depends on the dimensionality. If \(d = 2\), then \(p_c = 0.5\), which is the correct percolation threshold for 2D systems [11, 12]. However, the value \(p_c = 1/3\) for 3D is greater than the widely accepted bond percolation threshold 0.25 obtained from numerical simulations [11, 12].

It is not difficult to see that Eq. (3.6) gives the correct effective conductivity at the limiting values of \(p = 0\) and 1. Actually, from our numerical calculations (see below), the effective medium approximation is also quite successful in the regimes far away from the percolation threshold and only fails, like all other mean-field theories, near the critical point – the percolation threshold. Further discussion regarding this problem will be given in later sections.

As an example, let us apply the EMA to a Drude-metal dielectric composite. We use \(\varepsilon_B = 1\) as the dielectric constant of the dielectric component. The dielectric function for the Drude metal is given as follows:

\[ \varepsilon_A = 1 - \frac{\omega_p}{\omega(\omega + i/\tau)}. \]  

(3.12)

Here \(\omega_p\) is the plasma frequency and \(\tau\) is a characteristic relaxation time. To calculate the effective dielectric function with EMA, it is more convenient to use the dielectric
EMA formula than Eq. (3.6) for conductivity. From the discussion in Subsection 3.2.1, we know that there is a one to one mapping from conductivity form to dielectric form and vice versa. Here we should use the dielectric form because we are interested in the dielectric properties. We have $\nabla \cdot D$ rather than $\nabla \cdot hfJ$, where $D = \epsilon E$ and $J = \sigma E$. We can see that the dielectric EMA formula can be obtained by simply replacing the conductivity $\sigma$ by dielectric function $\epsilon$ in Eq. (3.6).

$$\epsilon_e = \frac{(dp-1)\epsilon_A + (d(1-p)-1)\epsilon_B \pm \Delta^{1/2}}{2(d-1)} \tag{3.13}$$

At a low concentration of the Drude-metal component, Eq. (3.13) gives, when expanded to first order in $p$,

$$\epsilon_e = 1 + dp \frac{\epsilon_A - 1}{\epsilon_A + (d - 1)} + O(p^2) \tag{3.14}$$

which agrees with the Maxwell-Garnett approximation in the limit of $p \ll 1$. This equation shows that, at a frequency such that $[\epsilon_A + (d - 1)] \approx 0$, $\epsilon_e$ becomes very large. There is a strong absorption peak at this frequency due to a sharp increase of $\text{Im}(\epsilon_e)$. This peak corresponds to the surface-plasmon resonance; the corresponding frequency is called the surface-plasmon resonance frequency. For a Drude metal with dielectric function as given in Eq. (3.12), assuming $\omega_p \tau \rightarrow \infty$, the surface-plasmon resonance frequency is

$$\omega_{spr} = \omega_p / \sqrt{d} = \begin{cases} 0.58 \omega_p & 3D \\ 0.71 \omega_p & 2D \end{cases} \tag{3.15}$$

For a typical metal, $\omega_p \sim 10^{15} \text{ sec}^{-1}$, $\omega_{spr}$ is in the visible range, and the absorption at this frequency creates the beautiful colors seen in the stained glasses.
3.3 3D Metal-Dielectric Composite

3.3.1 Network Model

In this section, we will present our numerical simulations of the linear a.c. properties of 3D metal-dielectric composites. As discussed in Section 3.2.1, we can use a simple cubic random impedance network in our simulations. The network has size of $L_x \times L_y \times L_z$, where $L_x$, $L_y$, and $L_z$ are the dimensions in the $x$, $y$, and $z$ directions. We connect the planes of $y = 0$ and $y = L_y$ to two perfectly conducting slabs, which are used as electrodes for externally imposed electric field. Across the two electrodes, a voltage of unit strength is applied. Thus, the boundary conditions in the $y$ direction are fixed at constant voltage. In the $x$ direction, periodic boundary conditions are enforced by connecting each site on the plane $x = 0$ to the corresponding one on the plane $x = L_x$. As described in Chapter II, the transfer-matrix iterations are performed along the $z$ direction. We use $L_z \gg L_x, L_y$, thereby effectively averaging over $L_z/L_x$ samples of size $L_x \times L_z \times L_y$ and greatly reducing numerical fluctuation due to randomness. A bond, either metal or dielectric is placed, with probability $p$ or $1 - p$, on each connection between two nearest neighbor vertices. The occupancies of different bonds are assumed uncorrelated. Figure 3.1 shows the geometry of one layer in the $xy$ plane. The difference between this model and the one used by Derrida and Vannimenus [28, 24] is that our bond are frequency-dependent in the network and complex in order to study the a.c. dielectric properties.

The dielectric component is represented by pure capacitor bonds with capacitance
Figure 3.1: Schematic of calculational geometry. We show a cross-section of an $L_x \times L_y \times L_z$ sample, with $L_x = 5$, $L_y = 8$. The field is applied in the $y$ direction, while periodic boundary conditions are imposed in the $x$ direction.
$C$ and impedance

$$Z_i = -i/(\omega C).$$  \hfill (3.16)

For the metal component, we use a more complicated $RLC$ impedance in order to represent a Drude metal component. In the circuit, an inductor $L$ and a resistor $R$ are in series and the whole $RL$ part is in parallel with a capacitor $C''$. The resistance damps the $LC$ resonance, providing a mechanism of possible optical absorption. By making this choice, we can reproduce the a.c. response of a Drude metal, whose dielectric function is given in Eq. (3.12). In fact

$$Z_i/Z_m = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau)}$$  \hfill (3.17)

where $\omega_p^2 = LC$ and $\tau = L/R$. The dielectric function of the bond is related to the impedance by

$$\varepsilon_m = (i\omega Z_m)^{-1}$$  \hfill (3.18)

In order to make contact with previous numerical results by other workers, we use $\tau = L/R = 10$, rather than the value of 100, which is typical of good metals. We choose units such that $L = C = C'' = 1$. We then calculate the effective admittances for different $p$ and $\omega$.

### 3.3.2 Results

The typical sample size in our calculations is $10 \times 10 \times 5000$. In some samples, we have considered networks as large as $10 \times 10 \times 10000$. We also tried samples of other sizes and found that the samples with $L_z = 5000$ or larger gave good enough averages,
the numerical fluctuation is less than a few percent, while samples with $L_z = 1000$
had obvious statistical fluctuations and were not used.

Figure 3.2 shows $\text{Re} \sigma(\omega)$ for several metal concentrations in arbitrary units. The
resulting spectra are qualitatively similar to the previous numerical results on 2D
impedance networks [29, 30, 31] and give all the features (except for the interband
transitions) observed in Ag-KCl composites [10].

For the samples with very low metal concentration ($p << p_c$), there is signifi­
cant absorption at non-zero frequency around the EMA surface-plasmon resonance
frequency, $\omega_{spr} = 0.58\omega_p$. Below this frequency, there is a gap with little optical
absorption except for a small tail due to finite $\tau$ broadening. As the concentration in­
creases, the absorption peak shifts to the lower frequency. Finally when $p \geq p_c \approx 0.25$,
the gap is closed up and the samples at zero frequency behave like metals, in that
they have a finite Drude peak. The gap is expected to open up again at large $p$, as
predicted by the EMA [32]. Although the reopening of the gap is not obvious in our
numerical results, because of masking by the finite relaxation time, the spectra for
sample of $p = 0.90$ does show signs that a gap is developing [see Figure 3.3]. Also,
at these large concentration, a new surface-plasmon resonance absorption peak due
to the voids is built up around the frequency of $0.8\omega_p$. This is the same frequency as
predicted by the EMA [32].

Figures 3.2 and 3.3 also show the EMA predictions. Other than near the perco­
lation threshold at low frequency, the agreement between our numerical results and
EMA predictions is quite good. The most obvious discrepancy is the difference in
Figure 3.2: Re $g_r(\omega)$ versus $\omega$ for a $(d = 3) 10 \times 10 \times 5000$ network of dielectric and Drude metal bonds, plotted at several metal concentrations $p$. Full lines denote the self-consistent effective-medium approximation. Note: for clarity, curves of $p = 0.01$ are magnified vertically by 5 times and the other curves are displaced vertically by (from top to bottom) 0.5, 0.4, 0.3, 0.2, and 0.1. Arbitrary units are used for the vertical axis.
Figure 3.3: same as Figure 3.2, but for $p = 0.5$ and 0.9. At the latter concentration, we can see that a gap develops and an absorption peak is built up at $\omega \approx 0.8\omega_p$, which corresponds to the void related absorption.
As we stated in Section 3.2.2, the percolation threshold is $1/3$ in the EMA for 3D composites. Although we did not specifically calculated $p_c$ from our numerical results, the curves for $p = 0.2, 0.25$ and $0.30$ do show that the Drude peak appears at zero frequency (a sign that a percolation path is formed by the metal component) for $p$ greater than about $0.25$. This is consistent with the value $p_c = 0.2492$ predicted by large scale numerical calculations [29].

Another discrepancy is the weak shoulder which occurs near $\omega = 0.4\omega_p$ in the numerical results but not in the EMA. Presumably this shoulder, whose frequency is independent of concentration, arises from some kind of finite-size effect (in the $xy$ plane) arising from a localized resonance of a certain circuit configuration in the $xy$ plane. We draw this conclusion because when we increase the dimension $L_x$ and $L_y$ of the impedance network, the strength of the peak at $0.4\omega_p$ decreases. This is confirmed in Figure 3.4, which shows $\text{Re}\sigma_r(\omega)$ for two samples with different $L_x$ ($= L_y$). The peak around $0.40\omega$ disappears for the larger sample, while for the smaller sample, we see that $\text{Re}\sigma(\omega)$ has two peaks, one near $0.58\omega_p$ and one near this same shoulder at $\omega = 0.4\omega_p$.

Let us conclude this section by comparing the numerical method we used and the methods used for 2D surface-plasmon resonance calculations by Koss and Zeng [29, 30]. Because of the modification to the transfer-matrix algorithm we discussed in Chapter 2, our program is much faster than the one used by Koss et al. [29]. It enables us to work on much larger samples and greatly reduces the numerical fluctuations. The calculations by Zeng et al. [30], using the so-called Y-Δ method,
Figure 3.4: $\text{Re} \sigma(\omega)$ versus $\omega$ for two samples which are same except the dimensions in $xy$ directions. Both samples have 1% of Drude metal bonds and the network size of $L_x \times L_y (= L_x) \times 10000$. The peak at $\omega = 0.4\omega_p$ almost disappears for the larger size ($L_x = 15$) sample. For clarity, the curve of $L_x = 15$ is shifted up 0.02 (arbitrary units).
also give results with small numerical fluctuation, but the method is difficult to extend to 3D impedance networks. However, transfer-matrix method, like other numerical methods, still suffers the drawback of being time consuming, especially for large $L_x \times L_y$. As an example, a $10 \times 10 \times 10000$ sample requires $\sim 100$ minutes on a DEC Alpha workstation with a clock speed of around 150 MHz.

### 3.4 Thin Film Composites

Now we turn to the presentation of our results for the thin film composite. We will give the effective conductivities as a function of concentration of one component in both d.c. and a.c. cases. The effective conductivity as a function of frequency in the d.c. case are also presented. Since thin film can be anisotropic, we also studied the effective conductivities for the cases of electric field is parallel and perpendicular to the thin film plane.

#### 3.4.1 Models

In both our d.c. and a.c. calculations, we use a random network of impedances which is slightly changed from the model we used for 3D composite in Section 3.3. Just as the 3D case, the network is a simple cubic mesh on a $L_x \times L_y \times L_z$ lattice with $L_z \gg L_x, L_y$, and planes $y = 0$ and $y = L_y$ held at potentials 0 and V. But now, in the $x$ direction, instead of periodic boundary conditions as in the 3D model, we use free boundary conditions to simulate the thin film geometry. (By "free" we
mean that the nodes at \( x = 0 \) and \( x = L_x \) are connected only to other bonds at the same \( x \) value and to internal nodes.) The bonds are of two types, labelled \( m \) and \( i \), having different complex impedances, with probabilities \( p \) and \( 1 - p \); the occupancies of different bonds are assumed uncorrelated ("bond randomness") as in the model for the 3D composite. Note that the electric field is always applied in the \( y \) direction. Thus, if the electric field is applied in the plane of the film, then \( L_x \) is the film thickness.

To study the thickness effects, we vary \( L_x \) to get samples of different thickness. We keep \( L_y \) fixed at a value which is large enough so that the size effect due to finite \( L_y \) is small. In the case of electric field perpendicular to the plane, \( L_y \) is the film thickness. In this case, we fix \( L_x \) at a large enough value, and change the sample thickness by varying \( L_y \). This convention is adopted so that the electric field is always applied in the \( y \) direction.

For our a.c. calculations, we use the same dielectric and metallic bonds as in Section 3.3. i.e., \( Z_i = -i/(\omega C) \) and \( Z_m = (R + i\omega L)/(1 + i\omega RC' - \omega^2 LC') \). Again, we make this choice because metallic bond reproduces the a.c. response of a Drude metal. To allow comparison with our 3D calculations, we generally assume the same parameters as used in Section 3.3: \( C' = C = L = 1 \) and \( \tau \equiv L/R = 10 \).

We have also carried out a similar series of calculations at zero frequency. In this case, the network is most conveniently described by conductances rather than admittances. The conducting and insulating bonds are assumed to have conductances \( g_m \) and \( g_i \), with \( g_m \gg g_i \). We denote this model as the d.c. Model, to distinguish it
from the above a.c. model.

One feature stands out regarding the electromagnetic response of thin films. In the random isotropic composite in three dimensions calculated in Section 3.3, the effective complex dielectric function is a scalar function, i.e., the dielectric tensor is a multiple of the unit tensor, or equivalently, the dielectric response is independent of the direction of the applied electric field. By contrast, a thin film is generally anisotropic: the dielectric tensor has different components parallel and perpendicular to the film, even if the components of the film are themselves isotropic. This effect is included in our model. Since our field is applied in the $y$ direction, we can probe the components of the dielectric response for electric fields applied in the plane or perpendicular to the plane of the film, by choosing $L_x < L_y$ or $L_x > L_y$. In these cases, the two-dimensional (2D) limit (where the film is only one grain thick) is modeled by choosing $L_x = 1$ and $L_y = 1$ respectively.

3.4.2 Results for Electric Field in the Plane of the Film

We have considered samples of dimension $L_x \times L_y \times L_z$, with $L_y = 20$ and $L_z = 10000$ for all cases such that the electric field is in the plane of the film. By this choice, we are effectively averaging over $10000/L_x$ samples of $L_x \times L_x \times 20$ in each case. In order to interpolate between the 2D and 3D limits, we consider several choices for $L_x$.

We begin with our results at zero frequency. Figure 3.5 shows the effective "in-plane" conductivity $\sigma_e$ of a metal-insulator composite for $L_y = 20$, with $L_x$ (the film thickness in this case) chosen as $L_x = 1, 2, 4,$ and $6$. Clearly, the thinnest
sample is strictly two-dimensional, while the thicker samples interpolate between two and three dimensions, approaching three dimensions in the thickest sample. In all cases, the "metal" bonds, denoted $g_A$, have a conductance of 1000, while the "insulating" bonds have conductance $g_B = 1$. In the 2D limit ($L_x = 1$), there is a clear percolation threshold in $g_e$ near $p_m = 0.5$: for $p_A < 0.5$, the zero-frequency conductance approaches a number of order unity, while for $p_A > 0.5$, $g_e$ increases roughly linearly with $p$. As the sample thickness grows, the percolation threshold diminishes, approaching the well-known 3D limit of about 0.25 at thicknesses as small as $L_x = 6$. A simple effective-medium theory for this decrease is given in the next subsection; its predictions are also shown in Figure 3.5.

We turn now to our a.c. results. In Figure 3.6, we plot $Re \sigma_e(\omega)$ at a fixed frequency $\omega = 0.1 \omega_p$ as a function of concentration for thicknesses $L_x = 1, 2, 4, \text{ and } 6$, comparing the results with the thickness-dependent effective-medium approximation described in the next subsection. Here, $Re\sigma_e(\omega)$ is related to the effective dielectric function $\epsilon_e(\omega)$ by

$$Re\sigma_e(\omega) = Im[\omega\epsilon_e(\omega)]/(4\pi), \quad (3.19)$$

and we are again probing the response to an in-plane electric field. Both percolation and the thickness effects are quite apparent. At very low frequencies, the effective percolation threshold $p_c(L_x)$ moves steadily to lower concentrations as the thickness increases. Note also a bump in the plot of $\sigma_e(\omega, p_A)$ versus $p_A$ at frequencies $\omega = 0.1\omega_p$ near the percolation threshold. This bump is a residue of the surface plasmon band which is discussed further below. The bottom edge of this band approaches zero
Figure 3.5: Zero-frequency effective conductance, $\Re \sigma_e$, for an $L_x \times L_y \times L_z$ disordered simple cubic lattice of impedances, with $L_y = 20$, $L_z = 10000$, and $L_x = 1, 2, 4,$ and 6. The high-conductivity and low conductivity bonds have conductance $g_A = 1000$ and $g_B = 1$. The fraction of high-conductivity bonds is $p_A$. The symbols denote the numerical calculations, while the full and broken curves denote the corresponding EMA results. The symbol $d$, in this and subsequent Figures, denotes the “effective dimensionality” $z/2$ entering into the EMA equation (6). Results for $L_x = 1, 2, 4$ and 6 are vertically offset by 0, 50, 100, and 150 units respectively.
frequency near the percolation threshold but moves away from that frequency when the concentration of metal starts to deviate from $p_c(L_x)$, the percolation threshold at the appropriate thickness.

In Figures 3.7-3.10, we plot the in-plane $\text{Re} \sigma_\perp(\omega, p_A)$, as a function of $\omega/\omega_p$ for several concentrations and thicknesses $L_x = 1, 2, 4$ and $6$. These curves all show two general features. First, at every concentration, we see a broad surface-plasmon band, the analog of the small particle resonances mentioned in the Section 3.1. Above the percolation threshold $p_c(L_x)$, there is also a Drude peak centered at zero frequency. The surface plasmon band is relatively narrow at small concentrations of metal, broadens as the metal concentration is increased, and reaches zero frequency as the metal concentration reaches the thickness-dependent percolation threshold $p_c(L_x)$. At higher concentrations, it narrows again (it would approach zero width as $p_A \to 1$). Near $p_A = 1$, the Drude peak should really be considered as a band of void resonances - that is, local modes in the metal region surrounding the dielectric inclusions. We have discussed the same property for 3D composite in Section 3.3. The Drude peak appears only above the percolation threshold, where the composite has metallic behavior at zero frequency. The integrated intensity of this Drude band should increase proportionally to the zero-frequency conductivity of the composite at the same thickness and concentration. The dimensional crossover is most apparent in Figure 3.9. The films in this figure lie below $p_c(L_x)$ at small thickness $L_x$ but above it at larger $L_x$. The Drude peak therefore appears only at the larger thicknesses.

At any concentration, the center of gravity of the surface plasmon spectrum shifts
Figure 3.6: Real part of the effective conductance, $\text{Re } \sigma_e(\omega)$, for an $L_x \times L_y \times L_z$ disordered simple cubic lattice of impedances, with $L_y = 20$, $L_z = 10000$, and $L_x = 1, 2, 4$ and $6$, and $\omega/\omega_p = 0.1$. Symbols denote the numerical calculations, while the full and broken curves indicate the corresponding effective-medium approximations. Results for $L_x = 1, 2, 4$ and $6$ are vertically offset by $0.0, 0.3, 0.6$ and $0.9$ units respectively.
Figure 3.7: Real part of the effective conductance, \( \text{Re} \sigma_\epsilon(\omega) \), for an \( L_x \times L_y \times L_z \) disordered simple cubic lattice of impedances, with \( L_y = 20 \), \( L_z = 10000 \), and \( L_x = 1, 2, 4, \) and 6. All calculations are carried out at \( p_A = 0.1 \) (\( A = \) metallic component.) Symbols denote numerical results; full curves, EMA results for the dimensionality indicated.
Figure 3.8: Same as Figure 3.7, but for $p_A = 0.3$. 
Figure 3.9: Same as Figure 3.7, but for $p_A = 0.4$. 
Figure 3.10: Same as Figure 3.7, but for metal concentration 0.7.
towards lower frequencies with increasing sample thickness. This is easily understood. In a three dimensional sample, the surface plasmon resonance occurs at a frequency \( \omega_p/\sqrt{3} \), which is the resonance frequency of a small metal sphere embedded in a dielectric host. By contrast, in a 2D sample, the resonance frequency occurs at a higher frequency, \( \omega_p/\sqrt{2} \), which represents the resonance of a metal cylinder in a dielectric host. A sample of intermediate thickness should interpolate between these two limits, as indeed we find.

### 3.4.3 Effective-Medium Approximation

Our numerical results agree quite well with a simple effective-medium approximation (EMA) which interpolates between 2D and 3D. The original version derived by Kirkpatrick [19] for a d-dimensional sample is given in Eq. (3.5). Replacing \( d \) with \( \frac{z}{2} \), where \( z \) is the coordination number in this equation, we obtain,

\[
p_A \frac{\sigma_A - \sigma_e}{\sigma_A + (\frac{z}{2} - 1)\sigma_e} + (1 - p_A) \frac{\sigma_B - \sigma_e}{\sigma_B + (\frac{z}{2} - 1)\sigma_e} = 0. \tag{3.20}
\]

For a simple cubic lattice in three dimensions (\( d = 3 \)), \( z = 6 \), while \( z = 4 \) for a square lattice in \( d = 2 \).

We generalize this formula to thin films simply by taking \( z \) as the average number of nearest neighbors per site-coordination number in the thin film. For the samples considered here, the surface sites on plane \( x = 0 \) and \( x = L_x \) have five nearest neighbors, while those in the interior have six. For thickness \( L_x = 1 \), we have \( z = 4 \).
All these cases can be summarized into one simple formula:

\[ z = [4 + 6(L_x - 1)]/L_x. \] (3.21)

Alternatively, we can interpret (3.21) as stating that the film has an "effective dimensionality" \( d = z/2 = [4 + 6(L_x - 1)]/(2L_x) \).

In Figures 3.5-3.10, we plot our thin-film effective medium approximation as a series of solid curves. In all cases, we use Eq. (3.20), with Eq. (3.21) used for the effective nearest-neighbor number \( z \). The "effective dimensionality" \( d = z/2 \) is also shown. Evidently, there is reasonable agreement between the predictions of this interpolation scheme and our numerical results in all cases, both at zero frequency and at finite frequencies.

Figure 3.11 shows the calculated percolation threshold \( p_c(L_x) \), as predicted by the EMA. This is given by the simple analytical result (see Eq. (3.11)),

\[ p_c(L_x) = \frac{2}{z(L_x)} = \frac{L_x}{3(L_x - 2) + 5}, \] (3.22)

where \( L_x = 1 \) and \( L_x = \infty \) are the 2D and 3D limits. Figure 3.11 also shows a comparison of this equation to a scaling theory of Neimark [33]. The Neimark theory is characterized by an exponent \( \nu_3 \) which describes the divergence of the three-dimensional percolation correlation length \( \xi_{3D} \) near the 3D percolation threshold, as well as by the values of 2D and 3D percolation thresholds, \( p_{c;2D} \) and \( p_{c;3D} \):

\[ p_c(L_x) = p_{c;3D} + (p_{c;2D} - p_{c;3D})L_x^{-1/\nu_3} \] (3.23)

Treating \( \nu_3 \) as an adjustable parameter in this equation, we obtain very good fits to the theory using the EMA values \( p_{c;2D} = 1/2, p_{c;3D} = 1/3 \), and \( \nu_3 \) equal to either
Figure 3.11: Percolation threshold $p_c(L_x)$ plotted as a function of film thickness $L_x$. Solid curve: effective-medium prediction [Eqs. (3.21) and (3.22)]. Dashed curves: prediction of the scaling theory of Neimark, assuming correlation length exponent $\nu_3 = 0.85$ and 0.90, and 3D and 2D percolation thresholds as indicated.
0.85 or 0.90. Both are reasonably close to the accepted value $\nu_3 = 0.85 - 0.9$ [14]. In particular, both the Neimark theory and the EMA predict that the 3D limit is reached very rapidly: already by a thickness of only three layers, the optical properties of the film approach that of a 3D composite.

Since the Neimark scaling theory is relevant only close to a percolation threshold, it does not make much sense to use it to analyze the data of Figures 3.7-3.10 which extend over all concentration. As to the region close to the percolation threshold, the Neimark's theory does have better agreement with our numerical results than the effective medium approximation.

### 3.4.4 Results for Electric Field Perpendicular to the Plane of the Film

We have carried out a somewhat less extensive series of calculations for an electric field perpendicular to the film plane. These boundary conditions are realized by choosing $L_x > L_y$. Figure 3.11 shows a series of representative d. c. calculations for $p_A = 0.2$. The full and dotted lines show two fits to a theory of Neimark in which we also require the fit to produce value of $\sigma_e(L_y = 1)$ (known exactly since all the bonds are then in parallel). According to the Neimark theory, $\sigma_e$ in the direction perpendicular to the film should follow the law

$$\sigma_e \sim \sigma_m L_y^{-t_3/\nu_3},$$

where $\sigma_m$ is the conductivity of the metal, and $t_3$ is the exponent describing the vanishing of the conductivity in a three-dimensional metal-insulator composite near
Figure 3.12: Effective conductivity $\sigma_e$ of a film of thickness $L_y$, assuming Model II and a metal concentration of 0.2 and an electric field applied perpendicular to the film. Open circles: calculations. The full line and dotted line are obtained by fitting of Eq. (3.23) with $t_3 = 1.60$ and $\nu_3 = 0.85, 0.90$. 
percolation. The two fits correspond to $t_3 = 1.60$, with $u_3 = 0.85$ and $u_3 = 0.90$. The fit is excellent for either choice.

The behavior shown in Figure 3.12 is easily understood. For a thickness $L_y = 1$, all the metal and insulating bonds are in parallel, so that the the sample percolates for any choice of metal concentration. At higher thicknesses, the sample eventually falls below the 3D percolation threshold of 0.25. Thus, increasing the sample thickness is equivalent to crossing the percolation threshold, as is seen in Figure 3.12.

Similar behavior can be seen in the a.c. film response in this geometry, as shown in Figure 3.13 Here we once again use the a.c. model to describe both metal and insulating bonds. The different thicknesses are displaced vertically for clarity. In all cases, the concentration of metal bonds is 0.2. The thinnest sample shown lies above the percolation threshold, and each has a Drude peak, which disappears in the thicker samples. In the thinnest sample ($L_y = 1$; not shown), there is no surface plasmon peak, since metal and dielectric are simply in parallel.

The position of the surface plasmon peak is the result of two competing effects. The first is the "thickness" effect, which tends to cause a "red shift" as the sample gets thicker (analogous to the shift from $\omega_p/\sqrt{2}$ to $\omega_p/\sqrt{3}$ which describes single inclusions in 2D or 3D). There is also a "blue shift" which occurs as the sample moves further from the percolation threshold (on either side of the threshold). This shift, at fixed concentration, also depends on thickness. Presumably as a result of a balance between these two effects, there is no consistent shift in the surface plasmon peak with thickness in the samples shown.
Figure 3.13: Real part of the effective conductivity, $\text{Re}\sigma_e(\omega)$, for films of several thicknesses $L_y$, assuming a composite of Drude metal and insulator (a.c. model) with $\omega_p\tau = 10$, $p_A = 0.2$, and electric field perpendicular to the film. The symbols denote numerical results, while the full lines simply connect the calculated points. At $L_y = 1$ (not shown) $\text{Re}\sigma_e$ exhibits a Drude peak but no surface plasmon peak. Curves are displaced vertically for clarity by (from top to bottom) 1.4, 1.1, 0.8, 0.5, 0.2, and -0.1 units.
3.5 Discussion and Future Work

We have calculated both the d.c. and a.c. transport properties of metal-dielectric composite in the form of bulk and thin film. All the calculations are carried out within the quasi-static approximation, using appropriate impedance elements to represent both the metallic and insulating components of the film, and solving the resulting random network using a generalized transfer matrix algorithm. For the 3D composite, our results are consistent with the mean-field theory except for a weak shoulder at $\omega = 0.4\omega_p$ and near the percolation threshold at low frequency. We think the weak peak is associated with some sort of local resonance introduced by the choice of the impedances. Near the percolation threshold, the mean-field theory (EMA) fails because critical phenomena are involved in this regime. Scaling theory has been used to study the critical properties at the percolation.

For the thin film composite, we see a clear cross-over from two-dimensional to three-dimensional behavior in the electrical and optical properties of the film. The cross-over is very rapidly as the film thickness increases. For an in-plane electric field, the percolation threshold decreases with increasing film thickness. In addition, for electric fields both parallel and perpendicular to the plane of the film, the Drude peaks disappear as the percolation threshold is crossed and film becomes insulating in the d.c. limit. For a perpendicular electric field, at certain concentrations, a metal-insulator transition is observed as a function of film thickness. Characteristic frequency shifts in the surface plasmon resonance bands are also observed. For fields
parallel to the film, the results are in good agreement with a simple effective-medium approximation. For fields in both direction, we find good agreement with a scaling theory of Neimark [33]. Finally, the film shows a characteristic transition from isotropy to anisotropy as the film becomes more and more two-dimensional. The cross-over from two to three-dimensional behavior occurs when the film is only a few (of order three) grains thick.

The results we obtain here may be quite useful in treating the optical, far-infrared, and microwave response of real composite materials. For example, they may have important implications for the behavior of suspensions of spheres embedded in a host and coated with a random composite film. Very often, such coatings are only a few grains thick; clearly, the behavior of such coatings will be sensitive to whether they can be treated as two-dimensional or three-dimensional. Another application of our results is in the design of composite films for electromagnetic wave absorption at selected frequencies. We can control the absorption frequencies by varying the film thickness. Our results would also apply, of course, to conventional composite films on flat surfaces. Finally, they might be applicable, in suitable geometries, to rough surfaces, which could be considered as thin composite films of substrate and air.

Future study can be usefully carried out in two directions. One direction would be to study the scaling behavior associated with the cross-over in greater details, for example, to study how the critical exponents change with thickness in the course of the two-dimensional to three-dimensional cross-over. We know that the 2D exponents are different from those of 3D. We expect the exponents change from 2D to 3D in the
cross-over. Another problem that can be studied is to confirm the scaling relations at finite frequency for a thin film, for example, the one recently proposed by R. L. Moore et al. [34]. The data collapse technique could be used in this study.
CHAPTER III REFERENCES


CHAPTER IV

Numerical Studies of the Nonlinear Properties of Composites

4.1 Introduction

As we have seen in Chapter III, the electrical and optical properties of composite media can differ dramatically from those of their constituents [1, 2]. In a simple picture, these differences arise from local electric field fluctuations. The constitutive properties (i.e., the conductivity or the dielectric function) vary widely within the composite. This leads to similar variations in the local electric fields and currents, and hence, to large enhancements or decreases in averaged quantities, relative to their values in homogeneous media.

In a homogeneous material, third order is the leading nonlinear effect. Nonlinearities in composites have attracted considerable recent attention, both at zero frequency [3]-[13] and at finite frequencies [14]-[20]. In this chapter, we are concerned with the Kerr cubic nonlinear properties of various binary composites. In materials with only the Kerr cubic nonlinearity which depends the magnitude of the electric field, the
electric displacement $\mathbf{D}$ and electric field $\mathbf{E}$ are related by

$$
\mathbf{D} = \varepsilon \mathbf{E} + \chi |\mathbf{E}|^2 \mathbf{E}
$$

(4.1)

where $\varepsilon$ and $\chi$ are the (position-dependent) dielectric function and cubic nonlinear susceptibility. As has been discussed elsewhere [9], the effective composite susceptibility $\chi_r$ can be enormously enhanced, relative to its value in a homogeneous medium. As in linear media, this enhancement arises from local field fluctuations, which play an even larger role in nonlinear than in linear response functions [12, 21].

This local field fluctuation-induced nonlinear enhancement in composites has been observed in numerous experiments. In 1983, Jain and Lind [15] measured optical phase conjugation [22] using degenerate four wave mixing configuration (DFWM) in semiconductor-doped glasses. They found strong nonlinear enhancement to the doped semiconductor microcrystals. Later, Ricard et al. [16] measured the same nonlinear effect on small metal (gold and silver) particles suspended in dielectric host such as water or glass. They were able to measure the cubic nonlinear susceptibility of the metal particles and found that it is at least two orders of magnitude larger than the cubic nonlinear susceptibility of the same metals in bulk form. The enhancement is also frequency dependent and the maximum enhancement is at the surface-plasmon resonance frequency. This is consistent with the linear response theory discussed in last chapter, which showed that the electric field inside the metal particles is very large near the surface plasmon resonance. In another recent experiment, Fischer et al. [23] achieved substantial enhancement of cubic nonlinear susceptibility on a composite of two dielectrics. Their sample gives a nonlinear susceptibility, which is
increased by 135% over that of the constituent nonlinear materials. Theoretically, an enhancement of more than a factor of 10 is very possible if the contrast in the linear dielectric properties of the two components are large enough. A composite containing fractal inclusions is another good candidate in which to find an enhanced nonlinear susceptibility. [24]

Large nonlinear response is of both fundamental and practical interest. Like the linear response functions, the nonlinear ones diverge near a percolation threshold. The analytic form of this divergence is of interest as a critical phenomenon. From a practical viewpoint, materials with large $\chi_3$'s are useful as optical elements. One possible application is a fast intensity-dependent optical filters[14], whose absorption coefficient increases as the intensity of light increases. Another important application of nonlinear optical devices may be in optical computers, which use nonlinear related bistable properties. [25].

In this chapter, we consider a variety of ways to enhance the $\chi_3$'s of composite media. In many calculations, we model these composites as random impedance or resistance networks as in Chapter III for linear optical properties. While obviously idealized as descriptions of real materials, these models can be accurately treated numerically. Using recently developed approaches, not only the effective impedances of the networks [26], but also the distribution of electric fields or displacements [27, 28], can be calculated. The fourth moments of these distributions are related, by an exact theorem [9], to the effective cubic nonlinear susceptibility, $\chi_e$, of the networks.

We also compare our numerical results to simple approximations. For random
composites at zero frequency, a nonlinear effective medium approximation [10] qualitatively describes our results. When one of the components is distributed in a non-random fashion, e. g., fractally, the numerical results appear consistent with a new differential effective-medium approximation [20] which is an extension of a previous linear approach [21]. This approach correctly predicts a large enhancement of \( \chi_e \) when linear fractals are embedded in a nonlinear host. Our numerical results for random networks at finite frequencies may be consistent with a somewhat generalized effective-medium approximation. More important, \( \chi_e \) for such networks exhibits a great deal of frequency-dependent structure which is nearly undetectable in the underlying linear response.

Since the models we used for different composites are similar to the ones used in Chapter III, we will not repeat them in this chapter, but will give brief summary whenever necessary.

This chapter is basically organized according to the types of the composites we study. Before presenting our numerical simulations, we first review the formal basis of our calculations, and our method in Section II. The simulation results are given in the following three sections: Section III gives numerical results for random composites at zero frequency, and compares these with a nonlinear effective-medium approximation. Numerical results for fractal clusters in two dimensions (\( d = 2 \)) are presented in Section IV, and compared to the predictions of a nonlinear differential effective medium approximation. Random media at finite frequencies are treated in Section V. Finally a discussion of our results and suggestions for future work is given in Section VI.
4.2 Formalism and Method

The basis of our method is an exact result proved by several authors [9, 31], which connects \( \chi_e \) to the fourth moment of the electric field in the linear limit. We describe this result first at zero frequencies. Consider a composite in which the local current density \( J(x) \) and electric field \( E(x) \) are related by

\[
J(x) = \sigma(x)E(x) + \chi(x)|E(x)|^2E(x),
\]

(4.2)

where \( \sigma(x) \) and \( \chi(x) \) are the local conductivities and cubic nonlinear susceptibilities. Then the theorem [9, 31] states that the effective nonlinear susceptibility \( \chi_e \) is given by

\[
\chi_e = \frac{\sum_i p_i \chi_i < (E \cdot E)^2 >_{i,\text{lin}}}{E_0^4},
\]

(4.3)

where \( < ... >_{i,\text{lin}} \) denotes a volume average over the volume of the \( i^{th} \) component in linear limit (i.e. when \( \chi_i = 0 \)), \( p_i \) is the volume fraction of component \( i \), in the and \( E_0 \) is the space-averaged field within the composite. This theorem is very useful, because it connects the composite nonlinear response to the nonlinear response functions of the constituents, and an average over the linear properties of the composite.

To separate these dependences more explicitly we introduce enhancement factors

\[
e_i = \frac{< (E \cdot E)^2 >_{i,\text{lin}}}{E_0^4}
\]

(4.4)

in terms of which

\[
\chi_e = \sum_i p_i \chi_i e_i.
\]

(4.5)
Evidently, $e_i$ is the fractional increase of the fourth moment of the electric field in the $i^{th}$ component relative to its applied value. It represents the factor by which the nonlinear susceptibility of the $i^{th}$ component is enhanced, per unit volume, in the composite.

A useful approximation for average in Eq. 4.3 is to make the approximate factorization [10, 18].

$$<(E \cdot E)^2>_{i,lin} \approx <(E \cdot E) >_{i,lin}^2.$$  

(4.6)

This factorization is sometimes termed the "nonlinear effective medium approximation" because it approximates the spatially fluctuating electric field within one component by a single value. We expect it to be most accurate when fluctuations in the electric field within one component are not too large. Since $<(E \cdot E) >_{i,lin}$ is given exactly by [12]

$$<E^2>_{i} = \left( \frac{\partial \sigma_i}{\partial \sigma_e} \right) \equiv F_i,$$  

(4.7)

where $\sigma_e$ and $\sigma_i$ are respectively the effective conductivity of the composite and of the $i^{th}$ component, it follows that $\chi_i$ can be written approximately as

$$\chi_e = \sum_i \chi_i F_i^2/p_i.$$  

(4.8)

or equivalently $e_i = F_i^2/p_i$.

The EMA is completed by calculating $\sigma_e$ (or equivalently $F_i$) from some approximation. One possible approximation for $\sigma_e$ is, of course, the linear effective-medium approximation, which in $d$ dimensions is given by

$$\sum_i p_i \frac{\sigma_i - \sigma_e}{\sigma_i + (d-1)\sigma_e} = 0.$$  

(4.9)
However, one may still make the decoupling approximation (4.6) in conjunction with some other approximation for $\sigma_e$ [10]. Indeed, we find in the calculations below that the nonlinear EMA works reasonably well at finite frequencies only if the exact form for $\sigma_e$ (or, at finite frequencies, $\epsilon_e$) is used in Eq. (8).

Eq. (3) is readily generalized to finite frequencies, provided one makes the "quasistatic approximation," where $E$ is expressed as the negative gradient of an electrostatic potential. This is usually reasonable for inhomogeneities much smaller than the wavelength of light in the medium. In the quasistatic limit, the composite is conveniently described in terms of a displacement field $D$, whose imaginary part is related to the usual transport current density,

$$D(x) = \epsilon(x)E(x) + \chi(x)|E(x)|^2E(x). \quad (4.10)$$

and $\chi_e$ is given by expressions similar to (4.3) and (4.5):

$$\chi_e = \frac{\sum_i \chi_i <(E \cdot E^*) (E \cdot E)>_{i,lin}}{E_0^4} \equiv \sum_i p_i \epsilon_i \chi_i. \quad (4.11)$$

Here $E(x)$ now denotes a complex quantity, such that the physical electric field at position $x$ at time $t$ is $\text{Re}[E(x) \exp(-i\omega t)]$. All quantities in Eqs. (4.10) and (4.11) are frequency dependent, and the averages $<...>_{i,lin}$ are still to be carried out in the related linear material.

The decoupling approximation (6) can also be generalized to finite frequencies, with the result

$$\chi_e = \sum_i \chi_i F_i |F_i|/p_i \quad (4.12)$$
where now

\[ F_i = \frac{\partial \epsilon}{\partial \epsilon_i}, \quad (4.13) \]

and \( \epsilon \) and \( \epsilon_i \) are the complex, frequency-dependent dielectric functions of the effective medium and of the \( i^{th} \) component. If one chooses to calculate \( \epsilon \) in the linear EMA, then \( \epsilon \) satisfies

\[ \sum_i p_i \frac{\epsilon_i - \epsilon}{\epsilon_i + (d - 1)\epsilon} = 0. \quad (4.14) \]

In most of our calculations, we will apply Eqs. (4.3) or (4.11) to a binary composite modeled as a cubic mesh of impedances in two or three dimensions (\( d = 2 \) or 3). The impedances are of two types, generally denoted A or B, and are distributed according to various random algorithms as described below. The effective linear conductances or admittances of the networks are calculated using the transfer matrix algorithm [26]. The distribution of electric fields is obtained using a generalization of this algorithm due to Duering et al. [27, 28]. These distributions are needed to calculated the fourth moments from which \( \chi \) is calculated at either zero or finite frequencies. The networks are assumed to be \( L_x \times L_z \) or \( L_x \times L_x \times L_z \) in two or three dimensions (with \( L_z \gg L_x \) and all the L's integer). With this choice of sample, we effectively average over \((L_z/L_x)\) realizations of cubic samples of size \( L_x^d \). The boundaries at \( x = 0 \) and \( x = L_x \) are held at potentials 0 and V respectively. In three dimensions, we impose periodic boundary conditions in the \( y \) direction (this issue does not arise in two dimensions). Further details of the numerical method are given in [28]. Chapter 2 gives more details on the algorithm and implementation.
4.3 Random Binary Composites in 3D: Zero Frequency

We begin by considering a $d=3$ network having two types of bonds, A and B, with conductances $g_A$ and $g_B$ ($g_A > g_B$), present in proportions $p_A$ and $p_B = 1 - p_A$, and distributed at random in the composite. Our calculation is carried out for $L_x = L_y = 10, L_z = 2500$, equivalent to averaging over 250 samples of size $10^3$. Figures 4.1 and 4.2 show the relative enhancements $e_A$ and $e_B$, plotted as functions of $p_A$ for $g_A = 10^4$ and $g_B = 1$ from the numerical results and the corresponding nonlinear effective medium predictions. Clearly, $e_B$ of the numerical results has sharp maxima near the percolation threshold ($p_A = 0.2492$) where the A bonds would first form an infinite connected cluster in an infinite sample. The enhancement is about a factor of 100. $e_A$ also exhibits a sharp increase near $p_A = 0.25$, but has no peak. We also did the same calculations for another composite having components with less contrast: $g_A = 10^3$ and $g_B = 1$. We got the same results except that $e_B$ has a smaller peak around the percolation threshold.

The large values of $e_B$ near percolation can presumably be understood in terms of large current distortions (and consequent field enhancements) near the tips of the large clusters that form near percolation. The greater enhancement for the larger ratio $g_A/g_B$ can also be understood in this way: the larger this ratio, the more radically the fields are distorted, leading to larger field enhancements.

We now compare these results with the predictions of the nonlinear effective-medium approximation, assuming both the decoupling approximation [Eq. (4.6)] and the linear EMA [Eq. (4.9)]. Evidently the EMA predicts, at least qualitatively, the
Figure 4.1: Nonlinear conductivity $\chi_e$ in a three-dimensional ($d = 3$) random binary composite of two conductors at zero frequency, as calculated numerically and using effective medium approximation, assuming component B is linear and component A is nonlinear. The samples have A and B bonds of conductivities $g_A = 10000$ and $g_B = 1$ respectively. The quantities plotted are $\chi_{eA} = p_A e_A$ where $e_A \equiv < E^4 >_A / E_0^4$ and $p_A$ is the concentration of bonds of type A. $< E^4 >_A$ represents the average of the fourth power of the electric field in a bond of type A; $E_0$ is the applied electric field. The effective medium approximation is given by the full curve, which has a maximum at $p_A = 1/3$. The dashed curve simply connects the points from numerical calculations.
Figure 4.2: Same as in Figure 4.1 except the component B is nonlinear and component A is linear.
sharp increase in $e_B$ near the percolation threshold. Similar results using a slightly
different method, and comparable agreement with the EMA, have been obtained by

We now try to interpret the critical behavior near $p_c^4$ in the light of previous work
on network properties near the percolation threshold. In the limit $g_A/g_B \to \infty$, it is
expected [9, 13] that

$$
e_A \propto |p - p_c^A|^{-\kappa + 2t};$$  \hspace{1cm} (4.15)
$$
e_B \propto |p - p_c^A|^{-\kappa' - 2s}. \hspace{1cm} (4.16)$$

Here $t$ and $s$ are the usual percolation critical exponents, defined by

$$
\sigma_e \propto \sigma_A(p_A - p_c)^t \quad (p > p_c);$$  \hspace{1cm} (4.17)
$$
\sigma_e \propto \sigma_B(p_c - p_A)^{-s} \quad (p < p_c). \hspace{1cm} (4.18)$$

while $\kappa$ and $\kappa'$ describe the critical behavior of random resistance fluctuations near
$p_c^A$. Using estimates based on a nodes-links-blobs model of the infinite cluster near
$p_c$, Wright et al [13] have proposed the bounds $1.53 \leq \kappa \leq 1.60$, $0.38 \leq \kappa' \leq 1.02$.
Combined with the currently accepted estimates $t \approx 2.0$ and $s \approx 0.77$ for lattice
percolation in $d = 3$, these imply

$$
e_A \approx (p - p_c)^{2.4 \pm 0.1} \quad (p > p_c);$$  \hspace{1cm} (4.19)
$$
e_B \approx (p_c - p)^{-2.2 \pm 0.4} \quad (p < p_c), \hspace{1cm} (4.20)$$

where the quoted uncertainties are simply guesses based on the bounds for $\kappa$ and $\kappa'$
and the postulated very small error bars on $s$ and $t$. 
Eq. (4.20) implies a strong divergence in $\varepsilon_B$ in $d = 3$, consistent with both our simulations and the EMA.

It seems somewhat surprising that $\varepsilon_B$ as calculated from the EMA is actually larger than that obtained numerically. We speculate that this is an artifact of the finite $L_y$. In the limit of very large $g_A/g_B$, Eq. (4.16) implies that $\varepsilon_B \propto \xi_p^{(\kappa' + 2s)/\nu}$, where $\xi_p$ is the percolation correlation length which diverges on either side of $p_c^A$ according to the power law $\xi_p \propto |p - p_c|^{-\nu}$. Since $\xi_p$ is bounded by the finite transverse dimension $L_y$, the numerically calculated $\varepsilon_B$ cannot exceed an upper bound proportional to $L_y^{(\kappa' + 2s)/\nu}$. In our system, where $L_x$ is only 10, this limits the growth of $\varepsilon_B$. To support our explanation, we carried out a few simulations for larger samples near the percolation threshold. They do give much larger enhancements, though it is still not enough to be comparable to the EMA result. The results are listed in Table 1. This table clearly shows that the $\chi_\ast$ increases very quickly as the sample size increases.

### 4.4 Fractal Distributions in Two Dimensions

A fractal bond structure is a self-similar cluster of bonds, which can be characterized by a relation $M = L^{d_f}$, where $L$ is the fractal size, $M$ is its total mass, and $d_f$ is the dimension of the fractal. Since a fractal bond distribution can greatly influence the linear response of composites [33], it is plausible that fractals will have similar influence on the nonlinear response. We now consider this question, restricting ourselves to $d = 2$, in which relatively large fractals can be considered.

As in $d = 3$, we assume two types of bonds, with conductivities $g_A$ and $g_B$ ($g_A >$
Table 1: Nonlinear conductivities of samples with different sizes. All the samples have the same concentration, $p = 0.25$, of the better conducting component. Column 1 gives the sample dimensions in the $x$ and $y$ directions. Column 2 gives the nonlinear conductivity assuming that only component A is nonlinear and has unit nonlinear conductivity, while column 3 gives the nonlinear conductivity if only component B is nonlinear and has unit nonlinear conductivity. The same length in $z$ direction, $L_z = 2500$, is assumed for all samples.

<table>
<thead>
<tr>
<th>$L_x (L_y)$</th>
<th>$\chi e_A$</th>
<th>$\chi e_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.0433</td>
<td>61.82</td>
</tr>
<tr>
<td>6</td>
<td>0.0452</td>
<td>97.16</td>
</tr>
<tr>
<td>7</td>
<td>0.0315</td>
<td>141.55</td>
</tr>
<tr>
<td>8</td>
<td>0.0294</td>
<td>177.70</td>
</tr>
<tr>
<td>9</td>
<td>0.0274</td>
<td>225.33</td>
</tr>
<tr>
<td>10</td>
<td>0.0202</td>
<td>292.75</td>
</tr>
</tbody>
</table>

$g_B$, present in concentrations $p_A$ and $1 - p_A$. The A bonds are arranged in an ordered "cross" fractal of stage $k$, and embedded in a matrix of B bonds [33]. The fractal is initiated by embedding a cross of four A bonds in a B matrix. A stage-$k$ cross fractal is constructed by adding four stage-$(k-1)$ fractals to the sides of a central stage-$(k-1)$ fractal (cf. Figure. 2 of [33]). Thus, a stage $k$ cluster contains $4 \times 5^{k-1}$ bonds, spans a linear dimension $2 \times 3^{k-1}$, and has fractal dimension $d_f = \ln 5 / \ln 3$. Figure 4.3 is a schematic drawing of the cross fractals at the first several stages.

Table 2 gives our results for ordered fractals in various-sized lattices, assuming $g_A = 10^4$, $g_B = 1$. For ease of comparison, the network in each case has a linear dimension four bonds larger than the enclosed fractal. Evidently, $e_B \gg 1$, while $e_A$ shows no enhancement. Furthermore, $e_B$ increases strikingly with increasing $k$. 

90
Figure 4.3: Skematic drawing of the cross fractals at the first 4 stages.
Table 2: Enhancement of nonlinear susceptibility in two-dimensional square networks containing cross fractals (fractal dimension \( \ln 5/\ln 3 \)) at various stages. The linear dimension of a cross fractal at stage \( k \) is \( 2 \times 3^k \), and it contains \( 4 \times 5^k \) bonds. In order, the columns denote the fractal stage, the linear dimension of the fractal, the linear dimension of the network, the fraction of type-A bonds, and the enhancement of the average value of \( E^4 \) on an A bond and on a B bond (normalized to the applied electric field). The last row corresponds to a random distribution of A bonds. In all these networks, \( g_A = 10^4, g_B = 1 \).

<table>
<thead>
<tr>
<th>Stage</th>
<th>Size</th>
<th>NW Size</th>
<th>( p_A )</th>
<th>( e_A )</th>
<th>( e_B )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>18</td>
<td>22</td>
<td>0.103</td>
<td>0.105</td>
<td>22.686</td>
</tr>
<tr>
<td>4</td>
<td>54</td>
<td>58</td>
<td>0.0743</td>
<td>0.093</td>
<td>178.83</td>
</tr>
<tr>
<td>5</td>
<td>162</td>
<td>166</td>
<td>0.0454</td>
<td>0.064</td>
<td>1383.1</td>
</tr>
<tr>
<td>random</td>
<td>N/A</td>
<td>166</td>
<td>0.100</td>
<td>0.175</td>
<td>1.6447</td>
</tr>
</tbody>
</table>

We have also calculated \( e_A \) and \( e_B \) in fractal networks for which the (fractally arranged) type-B bonds have the larger conductance \( (g_A = 10^{-4}, g_B = 1.0) \). The results [Table 3] show that this type of network produces a smaller enhancement than the reverse situation, but that the nonlinear enhancement is still substantial.

For comparison, we also list \( e_A \) and \( e_B \) in random two-dimensional networks in which \( g_A \) and \( g_B \) have the same values as in the fractal networks. For analogous concentrations of A and B bonds, \( e_B \) is orders of magnitude smaller than in the fractal networks.

Our fractal results are generally consistent with expectations based on calculations for random composites. As described in the previous Section, such systems have a divergent nonlinear response near the percolation threshold. According to some
Table 3: Same as Table 2, but $g_A = 10000$, $g_B = 1$.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Size</th>
<th>NW Size</th>
<th>$p_A$</th>
<th>$\epsilon_A$</th>
<th>$\epsilon_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>18</td>
<td>22</td>
<td>0.103</td>
<td>0.343</td>
<td>1.229</td>
</tr>
<tr>
<td>4</td>
<td>54</td>
<td>58</td>
<td>0.0743</td>
<td>0.814</td>
<td>4.787</td>
</tr>
<tr>
<td>5</td>
<td>162</td>
<td>166</td>
<td>0.0454</td>
<td>5.856</td>
<td>138.0</td>
</tr>
</tbody>
</table>

Table 4: Same as Table 2, but always for a stage-4 cross fractal and networks of various linear dimension.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Size</th>
<th>NW Size</th>
<th>$p_A$</th>
<th>$(\epsilon_A - 1)/p_A$</th>
<th>$(\epsilon_B - 1)/p_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>54</td>
<td>58</td>
<td>0.0743</td>
<td>-12.2</td>
<td>2393.</td>
</tr>
<tr>
<td>4</td>
<td>54</td>
<td>64</td>
<td>0.061</td>
<td>-15.4</td>
<td>363.</td>
</tr>
<tr>
<td>4</td>
<td>54</td>
<td>100</td>
<td>0.025</td>
<td>-69.6</td>
<td>70.2</td>
</tr>
</tbody>
</table>

models, a composite close to the percolation may have a fractal-like structure, with a correlation length $\xi_p$ which grows as percolation is approached. In this sense, a larger fractal is like a system closer to percolation. It should therefore have a larger $\chi_e$ than a smaller fractal, as we observe. Furthermore, just as in the random case, the enhancement is larger when the "non-critical" component, i.e., the material outside the fractal, has the lower conductivity.

Our results for a given stage of fractal depend sensitively on the size of the embedding network. To illustrate this, we have calculated the nonlinear response of three samples generated from the same fractal but with different network sizes, always assuming $g_A = 10^4$, $g_B = 1$ [cf. Table 4]. Evidently, $\epsilon_B$ falls off dramatically.
with increasing network size. To explain this, we show in Figures 4.4 and 4.5 the electrostatic potential for a stage-4 fractal embedded in a $58 \times 58$ network, and a $100 \times 100$ network. Obviously, the electric field enhancement near the fractal tip is enormous when the fractal nearly spans the sample, while for the larger networks there is a smaller (but still very substantial) field enhancement. This is the cause of the large $e_i$'s in these networks. By contrast, the field is nearly uniform, not only within the highly-conducting fractal itself, but also in the nearly-enclosed bays outside the fractal. Because of this screening effect, large fractions of the entire network are nearly an equi-potential. This effect is, of course, absent in a uniformly random two-dimensional network.

When the fractal forms only a very small volume fraction of the network, the most appropriate measure of nonlinear enhancement is $(e_A - 1)/p_A$ or $(e_B - 1)/p_A$, that is, the enhancement per unit volume of fractal material. This quantity is tabulated in the last column of Table 4. As the network becomes very large, this quantity should, in principle, saturate at some fixed value $E_k \gg 1$, which increases rapidly with $k$ (although we have not examined fractals and networks large enough to see this saturation). In short, fractal inclusions efficiently increase the nonlinear susceptibilities of their host media, and, for a given $d_f$, become more efficient as they become larger.

In an attempt to understand our numerical results, we compare them to a quasi-analytical approximation for $\chi_\varepsilon$ in $d = 2$ and $d = 3$. The approximation is based on a fractal cluster of A particles (cluster dimension $R$, fractal dimension $d_f$) embedded in a B host. As discussed in the paper by Hui and Stroud [20], the approximation
Figure 4.4: Electrostatic potential $V(x,z)$ (arbitrary units) for a stage-4 cross fractal (size = 54 bonds) embedded in a $58 \times 58$ square network with periodic transverse boundary conditions, and subjected to a uniform applied field in the $x$ direction.
Figure 4.5: Same as Figure 4.4, but for a stage-4 fractal in a $100 \times 100$ network.
Figure 4.6: Specific nonlinear enhancement \((e_B - 1)/p_A\) [Eq. (4.11)] for a two-dimensional good conductor fractal of conductivity \(\sigma_A = 10^4\) embedded in a conductor host of conductivity \(\sigma_B = 1\). The calculation is carried out using the differential effective-medium approximation [Eqs. (A.6) and (A.7)] in the high-dilution limit. \((e_B - 1)/p_A\) measures the effective nonlinear enhancement if the host is nonlinear and the inclusion is distributed fractally. The horizontal axis represents the "cluster concentration" \(p_{\text{clus}} \equiv (R/a)^{d_f-d}\), where \(R\) is the cluster radius measured in units of the smallest particle dimension \(a\); \(d\) is the dimensionality; and \(d_f\) is the fractal dimension of the cluster. Inset: specific conductivity enhancement \((\sigma_e - \sigma_B)/(p_A\sigma_B)\) for the same composite, as calculated in the linear differential effective-medium approximation [21]. \(\sigma_e\) is the effective linear conductivity of the composite medium containing a dilute suspension of fractals in a host of conductivity constant \(\sigma_B\); \(p_A\) is the total concentration of fractal material in the composite.
Figure 4.7: Same as Figure 4.6, but assuming $d = 3$. 

Specific Enhancement Factor

$\sigma_A = 10^4$, $\sigma_B = 1$

$\log_{10}(\sigma_A - \sigma_B)/(P_Ae)$
proceeds in two stages. [See Appendix A] First, the cluster conductivity and nonlinear susceptibility are calculated in a differential effective-medium scheme. Then the composite susceptibility itself is calculated in the limit of a dilute suspension of clusters.

Figures 4.6 and 4.7 show \((\epsilon_B - 1)/p_A\) in \(d = 2\) and \(d = 3\) for a fractal of conductivity \(\sigma_A\) embedded in a host of conductivity \(\sigma_B\), as calculated using this approximation. \(p_A\) represents the composite volume fraction which is made up of material with conductivity \(\sigma_A\). The horizontal axis denotes the "cluster concentration" \(p_{\text{clus}} \equiv (R/a)^{d_f - d}\), where \(R\) is the cluster radius measured in units of the smallest particle dimension \(a\), and \(d_f\) is the fractal dimension of the cluster. The inset shows the "specific conductivity enhancement" \((\sigma_e - \sigma_B)/(p_A\sigma_B)\) for the same composite, as calculated in the linear differential-effective-medium approximation [21].

Up to a certain maximum of cluster size, \((\epsilon_B - 1)/p_A\) increases greatly. For very large cluster sizes, the specific enhancement begins to decrease and eventually may even become negative, while the enhancement of the linear conductivity departs from a power law in \(p_m\). As shown by Hui and Stroud [21], such a power law is expected in the limit \(\sigma_A/\sigma_B \rightarrow \infty\). Deviations from the power law occur when the effective conductivity of the cluster is no longer orders of magnitude larger than that of the host.

The central result of our fractal simulations - that the nonlinear susceptibility of the composite is greatly enhanced by fractal clusters of impurities - is qualitatively consistent with our differential effective-medium approximation. Our numerical clus-
ter sizes are too small, however, to see the predicted saturation in the enhancement.

4.5 Random Media in Three Dimensions: Nonzero Frequencies

We turn next to calculations for random media in three dimensions at finite frequencies. We use the same impedance networks as in the linear optical properties simulations in Chapter III. We describe the insulating bond by a purely capacitive impedance $Z_i$, 

$$Z_i = \frac{1}{i\omega C_i}, \quad (4.21)$$

and the metallic bond by an $RLC$ circuit, which impedance is,

$$Z_m = \frac{(R + i\omega L)}{(1 + i\omega RC' - \omega^2 LC')} \quad (4.22)$$

In order to compare with the linear calculations, we use the same parameters: $C' = C = L = 1$ and $\tau \equiv L/R = 10$. As has been discussed previously in Chapter III and an article by the Zhang and Stroud [34, 35], the metallic bond is designed to have the impedance of a Drude metal; the LC resonances correspond to the plasmon peaks of such a metal.

Figures 4.8-4.11 show the effective nonlinear susceptibility $\chi_{ei}$ at various frequencies for metal volume concentrations of 1%, 25% (very close to $p_c$ for metallic bonds), 75% (close to $p_c$ of dielectric bonds), and 99%. Here the subscript $i = m$ or $i$, which correspond to only the metal or the insulator as nonlinear component and the other component is linear. In all cases, we have carried out our calculations for $L_x = L_y =$
10. \( L_z = 2500 \).

We have also calculated \( \varepsilon_m(\omega) \) and \( \varepsilon_i(\omega) \) for the same model within the EMA. In carrying out the EMA calculations, we use both the decoupling approximation, Eq. (4.12), and the linear EMA, Eq. (4.14). The corresponding results for different metal concentrations are also given in the figures.

Evidently, in the numerical results for all cases, there is a large enhancement of the nonlinear susceptibility at appropriate frequencies. For \( p_{\text{metal}} = 1\% \), see Figure 4.8(a), \( \text{Re}\chi_{em} \) has two peaks, located at frequencies of \( 0.5\omega_p \) and \( 0.62\omega_p \) separately. We believe the larger peak corresponds to the surface-plasmon resonance enhancement predicted by the effective medium approximation in Section 4.2. The weak peak at \( 0.5\omega_p \), while not predicted by the EMA, is not surprising. It corresponds to the weak resonance we mentioned in the linear effective conductivity of metal-dielectric composite in Chapter III. We attribute this resonance to some local resonance formed in the network [36]. We believe this local resonance is caused by the finite size in the \( x \) and \( y \) directions. As for the dielectric component, the enhancement is relatively small even around the surface-plasmon resonance frequency. [see Figure 4.8(b)]

Similar results are obtained for the complementary composite, i.e., 99% of metal and 1% of insulator component. The peak at \( 0.78\omega_p \) corresponds to the resonance of the metal voids and the weak peak at higher frequency corresponds the another resonance due to the similar local cluster as in the 1% metal concentration sample. The strong electric fields in the metal voids enhance the nonlinear susceptibility of the insulator component up to 3.5 times as much as that of the bulk material, which
is 350 times enhancement to the 1% insulator component of the composite.

For the samples with 25% and 75% metal concentrations, we are more interested in the enhancement due to the percolation effect. The percolations of the critical component, which is the metal at low frequency and insulator at higher frequency, do enhance the nonlinear susceptibility of the other component. For 25% metal concentration, Figure 4.9(b) shows an enhancement by two orders of magnitude over the nonlinear bulk insulator material at frequency close to zero. This result is consistent with the numerical results of zero frequency impedance network discussed in Section 4.3.

For the 75% sample, a several-fold enhancement over the nonlinear bulk metal material is obtained around \( \omega = \omega_p \). The relatively weak enhancement, compare to the non-critical component in the 25% sample, is due to the smaller impedance ratio \( |z_m/z_i| \) at a frequency \( \omega = \omega_p \).

Now let us compare the numerical results with the nonlinear EMA predictions in Figure 4.8-4.11. The nonlinear EMA misses some of the frequency-dependent structure seen in the numerical \( \chi_{em} \) and \( \chi_{ei} \) at the frequency around surface-plasmon resonance. The EMA does reproduce the peak in \( \chi_{em} \) near \( \omega = 0.60\omega_p \) in Figure 4.8 at 1% metal concentration and also the peak in \( \chi_{em} \) near \( \omega = 0.80\omega_p \) in Figure 4.11 at 99% metal. For these two samples, the decoupling approximation and linear EMA are supposed to work well. The EMA also predicts the enhancement at the percolation regimes for the other two samples. Except in Figure 4.9(a) at low frequency, where the metal component is critical, and near the percolation threshold, the EMA predicts a
smaller enhancement than our numerical results. Obviously, the finite size effect does not play a important role other than near the percolation threshold in our numerical simulation.

The EMA results do agree, at least qualitatively, with our numerical results at lower and higher frequencies, i.e., away from the surface-plasmon resonance. At metal concentration of 25%, the EMA agrees with the numerical results very well at low frequency, where the enhancement for the dielectric composite is huge. This agreement is consistent with our zero frequency results shown in Figure 4.1 and 4.2.

We believe that the discrepancy seen in Figure 4.10 comes from the decoupling approximation (4.12). The assumption that the fields in the grains of each component are uniform can be true only when one of the composite has very small concentration, such as the cases of 1% and 99% metal component. Another source of the discrepancy could be from an inaccurate evaluation of the derivative $F_i$ [Eq. (4.13)]. $\chi_\varepsilon$ is far more sensitive to details of the composite microstructure than is $\varepsilon_\varepsilon$ itself, as already noted by [12]. Hence, even if $\varepsilon_\varepsilon$ is accurately given by the EMA, the products $F_i |F_i|$ may not be.

It is well known that the electric field fluctuation in the composite is the mechanism of enhancement. The field fluctuation can be measured by the inverse participation ratio (IPR), which is defined as

$$IPR = \frac{\langle |E|^4 \rangle}{\langle |E|^2 \rangle^2} = \frac{N \sum_{i=1}^{N} |E_i|^4}{(\sum_{i=1}^{N} |E_i|^2)^2}$$

(4.23)

Here $N$ is the number of bonds in the sample. From this definition, we can see that the IPR measures the electric field fluctuation. If the electric field is uniform in
Figure 4.8: Effective nonlinear susceptibility, plotted as a function of frequency, for metal concentration $p_m = 1\%$, as calculated numerically for a $10 \times 10 \times 2500$ network. The dashed lines just connect the numerical data points, and the full lines give the EMA predictions. (a) the effective nonlinear susceptibility if only metal component is nonlinear. (b) same as (a) but only dielectric component nonlinear.
Figure 4.9: Same as Figure 4.8 except 25% metal component.
Figure 4.10: Same as Figure 4.8 except 75% metal component.
Figure 4.11: Same as Figure 4.8 except 99% metal component.
Figure 4.12: The nonlinear enhancement and the Inverse Participation Ratio. IPR is given by the dot-dash curve. The other curves are the same as in Figure 4.8(a) of $p_A = 1\%$. 
Figure 4.13: The enhancement at $\omega/\omega_p = 0.62$ for different metal concentrations. The maximum nonlinear susceptibility is about 15 times as that of the metal material at $p_A = 5\%$, which corresponds to a 1500-fold enhancement over that of the metal component in the composite.
the sample, one third of the bonds, which are along the y-direction, have the same electric field of unity (under proper normalization), and IPR is 3.0 calculated from above definition. The extreme of field fluctuation, though non-physical, would be all the field localized on a single bond with strength of \( \frac{N}{3} \), the definition gives IPR = \( N \).

To see the relation between the electric field fluctuation and the nonlinear enhancement, we have also calculated the IPR for the samples at different frequency. Figure 4.11 shows the IPR for the case of 1% metal concentration. The greater IPR value at the frequencies of \( \omega = 0.50 \) and \( 0.62\omega_p \) means that the electric fields have stronger fluctuation at these frequencies. We believe that the strong electric field fluctuation is caused by the surface-plasmon resonance in metal particles, where the electric field is much stronger than in the host outside.

To find out the possible maximum enhancement, we calculated \( \chi_{em} \) for different metal concentration at \( \omega = 0.62\omega_p \) numerically, and at \( \omega = 0.58\omega_p \) within the EMA. The results are shown in Figure 4.12. While the EMA gives a maximum \( \chi_{em} \) of around 1.5 at metal concentration of less than one percent, the numerical results shows an enhancement by as much as a factor of 15 could be achieved at the metal concentration of about five percent. For typical metals with \( \tau \approx 100 \), the enhancement will be even larger. We have not carry out the numerical calculation in this case, but even the EMA predicts a maximum \( \chi_{em} \) enhancement of more than than 100 for this case.

To summarize this section, we have shown numerically that \( \chi_e \) for a random metal-insulator composite can be greatly enhanced over that of its constituents. The
enhancement is very sensitive to frequency and to composite microstructure. Surface-plasmon resonance or percolation of the critical component will distort the electric field distribution greatly and therefore effectively enhance the nonlinear susceptibility. We found numerically that the greatest specific enhancement is provided by the samples with very low metal concentration. These samples also have low linear absorption and allow electromagnetic waves to penetrate deeper inside than those with higher metal concentrations. A simple effective-medium approximation qualitatively agree with our numerical results and can be used to estimate the enhancement, especially for composites with low concentrations of one component or with the critical component near the percolation threshold. The discrepancy between the numerical and the EMA results is probably caused by the limitation of the decoupling approximation and by the local resonances related to the finite size of the impedance network in our numerical model itself.

4.6 Discussion

We have calculated the cubic nonlinear susceptibility of a variety of composite media, modeled as impedance networks in \( d = 2 \) and \( d = 3 \). At zero frequency, we find large enhancements of the susceptibility in random composites, at concentrations near a percolation threshold. We also obtain very large enhancements when one of the components is present in the form of fractal clusters. Both results are in qualitative agreement with predictions based on a simple effective-medium approach.

For random binary composites at finite frequencies, we also find huge and highly
frequency-dependent enhancements of the nonlinear susceptibility. The relevant frequen-
cies are generally close to the surface-plasmon resonances of the composite or the
percolation threshold of the critical component, where the electric field is locally much
enhanced. In such composites, even though the linear response can be calculated in
an effective-medium approximation, the nonlinear response is in general much more
difficult to predict in this fashion. This is not only due to an intrinsic failure of the
effective-medium approach itself, for example, the decoupling approximation around
the surface plasmon resonance, but also because of the great sensitivity of the relevant
derivative $F_i = \partial \epsilon_e / \partial \epsilon_i$ to small changes in the local microstructure of the composite.

On the basis of these calculations, we conclude that binary composites have many
ways to produce enormous enhancements in the nonlinear susceptibility. Even at large
concentrations, the enhancement is highly frequency-dependent, and highly sensitive
to composite microstructure. It should therefore be possible to "tune" this enhance-
ment to occur at a desired range of frequencies, and hence to produce filters with a
range of potential applications.

As to possible future work, one can use the transfer-matrix method to calculate
other nonlinear susceptibilities, for example, the second harmonic susceptibility, using
the formalism derived by Levy et al. [38]. To continue our third order nonlinear
susceptibility calculation, we could calculate larger sized sample to see the effects
of finite network size on the calculated values of the nonlinear susceptibility. Un-
fortunately, our currently accessible computing power does not allow us to calculate
much larger samples than we have already considered. Some parallel computers, such
as Cray T3D, can certainly provide us the computing power to calculate samples of double size of those we have done. Chapter II gives the schemes of implementing transfer-matrix method on MPP computers.
CHAPTER IV REFERENCES


[38] O. Levy, D. J. Bergman and D. G. Stroud, preprint.
Part 2

Diffusion Properties of Liquids
5.1 Introduction

Molecular dynamical (MD) simulation is an often-used method to study the thermodynamic, the static and dynamical properties of liquids. It allows one to calculate the atomic configuration of the particles in the liquid as a function of time, given the interatomic forces. From the particle configurations at different instants, any desired properties can be computed which depends on their displacements. For example, the diffusion constant of the liquid can be obtained from the displacements by using Einstein relation.

To do MD simulations, we need to know the interatomic forces between the particles in the liquid. Finding the right interatomic interaction forces for liquid molecules is usually a challenge. This is especially true for complex liquids such as liquid semiconductors which don't have simple interatomic interactions as simple liquid metals do. After the interaction is known, the force calculation remains an important issue to consider, because it is usually the most time consuming part of MD simulation.
To calculate the total force acting on an atom, each of the other atoms within the interaction range has to be retrieved. The time required for retrieval and the ensuing force calculation is proportional to the number of atoms inside the cutoff range if only pair interactions are considered. For many-particle interactions, the computing time increases exponentially with the number of particles involved in the interaction. For many computers, the time demanding to include many-body interactions can impose a limitation on the size of the problem that can be handled. Therefore, in order to perform MD simulations on a liquid, given limited computing power, it is very convenient to use a pair potential, if possible, to mimic the interactions between the particles. A particularly widely used pair potential is the Lennard-Jones (LJ) interaction. For any two particles, separated by a distance of $r$ in space, the LJ interaction potential a polynomial in $r$:

$$V(r) = 4\epsilon\left[\left(\frac{r}{\sigma}\right)^{-12} - \left(\frac{r}{\sigma}\right)^{-6}\right]$$ \hspace{1cm} (5.1)

Figure 5.1 gives a picture of this interaction.

The LJ force is simply the derivative of $V(r)$.

$$f(r) = 24\epsilon\left(\frac{\sigma}{r^2}\right)[2\left(\frac{r}{\sigma}\right)^{-12} - \left(\frac{r}{\sigma}\right)^{-6}]$$ \hspace{1cm} (5.2)

Here $\sigma$ and $\epsilon$ are two parameters which characterize the interaction range and strength respectively. One advantage of using Lennard-Jones force is that it only involves very basic addition and product arithmetics, which can be calculated very fast on computers.
Figure 5.1: Lennard-Jones pair potential.
To many liquids, especially the liquids of closed shell elements and organic molecular, Lennard-Jones potential is a good approximation. Using this potential, studies on polymer chains [1] and fluid dynamics at the molecular level [2, 3], are carried out by many workers.

Many properties of Lennard-Jones liquids, including their phase diagrams, structure factors and thermodynamical parameters, have been thoroughly studied with Monte Carlo and MD simulations. [4]-[9]. The purpose of our simulations is to obtain general information about diffusion constants in liquids. We are especially interested in the dependence of diffusion constant on temperature and in the diffusion constants of impurities with different interaction potentials. Although the real liquids, such as liquid semiconductors may behave differently from Lennard-Jones liquids, it is useful to begin with this model calculations as a basis for better understanding of diffusion in real liquids.

The remainder of this chapter is organized as follows. We will review the standard MD simulation method in Section 5.2 and our modification to it. This section includes discussion of Verlet's algorithm, and the implementation of force calculation using linked cells with dynamical linked lists. We also will discuss how to calculate the diffusion constant from simulation data by using a data structure named diffusion meter.

In Section 5.3, we present our results for the variation of diffusion constant with temperature and impurity type. Our conclusions are given in Section 5.4.
5.2 Molecular Dynamical Method

The quantum effects, although may be important for light atoms, are negligible for the dynamical properties we are interested in. Newtonian classical mechanics can be used to describe the motion of particles in the liquid. Consider a system of \( N \) particles interacting with each other with known forces. Newton's second law gives the equations of motion,

\[
\dot{r}_i = v_i, \quad (5.3)
\]

\[
\dot{v}_i = \frac{f_i}{m_i}. \quad (5.4)
\]

Here \( r_i \) is the position, \( v_i \) is the velocity, \( m_i \) is the mass of particle \( i \), and \( f_i \) is the total force acting on particle \( i \) due to the remaining \( N - 1 \) particles. To numerically solve these equations, we can use finite difference methods. The positions and velocities of each particles in the system can be obtained by time integral over a sequence of very short time steps. Several algorithms [10] have been proposed to integrate the above equations of motion. Among them, Verlet's algorithm is probably the most widely used. We use a modified Verlet's algorithm in our simulation program.

5.2.1 Verlet's Algorithm

The original form of Verlet's algorithm [5] has been modified by many workers [10] to reduce the numerical error. We use the so called velocity form [11]. With this algorithm, if we know the positions, velocities and accelerations of each of the \( N \) particles at time \( t \), we can calculate the new positions, velocities and accelerations at
time \( t + \delta t \) in the following sequence:

1. Calculate the positions, \( r(t + \delta t) \), using

\[
r(t + \delta t) = r(t) + \delta t v(t) + \frac{1}{2} \delta t^2 a(t).
\]  

(5.5)

2. Calculate the mid-step velocity, \( v(t + \frac{1}{2}\delta t) \), by relation

\[
v(t + \frac{1}{2}\delta t) = v(t) + \frac{1}{2} \delta t a(t)
\]  

(5.6)

3. Calculate the acceleration, \( a(t + \delta t) \), from the forces acted on the particles. The forces are calculated under the new particle positions obtained in the first step.

4. Calculate the new velocity, \( v(t + \delta t) \), with the new acceleration from step 3.

\[
v(t + \delta t) = v(t + \frac{1}{2}\delta t) + \frac{1}{2} \delta t a(t + \delta t)]
\]  

(5.7)

After finishing step 4, we have the new particle positions, velocities and accelerations. Evidently the order of steps 2 and 3 can be exchanged. By repeating these four steps, we can get the mechanical quantities of the particles at any given time. In the above equations, we have neglected terms of order \((\delta t^4)\) and higher in the calculation of the positions and terms of order \((\delta t^2)\) and higher for the velocities. To make the approximation more accurate, a very small \( \delta t \) can be used. Within a time step \( \delta t \), a particle moves only a very small distances compared to the typical atomic separation.

This algorithm requires storage for \( 3N \) vectors in the memory. For the three-dimensional systems, \( 9N \) double-precision floating point numbers are needed. A system of 1000 particles thus needs less than 1 MByte storage. If \( N \) is less than
10000, the memory usage does not impose any problem for most computers. The force calculation, on the other hand, are more computing demanding. For example, if \( N = 10000 \), an order of a second CPU time is used on force calculation per time step. Usually it accounts for more than 95% of the total computing time.

5.2.2 Force Calculation

The simplest way to calculate the force acting on a particle is to add the forces from each of the other particles in the system. To calculate the forces acting on all the particles, the required computing time is proportional to \( N^2 \) for pair potentials and to a higher power in \( N \) for many-particle interactions. For most interatomic potentials, such as Lennard-Jones potentials, if the separation of two particles is beyond certain range, the effect of their interaction is very small on the MD results. In the case of Lennard-Jones potentials, this range is as short as 2-3\( \sigma \). For the particles beyond this range, the interactions can be simply approximated to zero. This approximation virtually has no effect on calculated physical quantities. We only need to calculate the forces between particles within 2-3\( \sigma \) cut-off range. The cut-off is denoted as \( r_0 \).

The force calculation is conveniently done using a cell structure. We divide the system space into cubic cells of size \( r_0 \). The particles are sorted according to their positions into cells. When we calculate the force on a particular particle, we only check the separations of this particle from other particles in the same cell and in adjacent cells. The particles in more remote cells are separated by distances longer than cut-off range, \( r_0 \), and their interactions with the given particle can be neglected.
To implement the cell structure with dynamical linked lists, we define a data structure called a "node". The node contains a node pointer to form the linked list with other nodes, and also contains all the information needed to describe the particle, such as position, velocity, and acceleration. For each cell, we also define a node pointer as the head of its linked list. The nodes of the particles in each cell are linked together with their node pointers to form a dynamic link list which is headed by the node pointer of the cell. The data of a particle can be easily retrieved starting from the head pointer of its linked list. To calculate the force acting on a particle due to the other particles in the same cell, we can start from the head of the cell pointer, following the links to get the positions of the other particles, and then calculate the forces produced by these particles from knowledge of their separations with the given particle. Under this scheme, the force computation time is proportional to the number of particles $N$ if $N$ is large enough. This is much better than $N^2$ time which would be required in the simplest method. Another advantage that this method is the good data locality. Good data locality gives faster data access and therefore can speed up data processing in CPU.

Since the particles can move from one cell into the neighboring cells, we need to update the linked list frequently. This updating is quite fast compared to the force calculation. We do the updating for every time step before starting the force calculation.

Since we can only deal with limited system size, we use periodic boundary conditions. All the particles are confined in a cubic box. If a particle moves out of the
cubic box by crossing one side, it enters into the the box from the opposite side. To calculate the diffusion constant, we need to know the net displacement of each particle, the net discontinuous change in displacement at the boundary for each particle is stored as a integer-valued vector variable. The net continuous displacement can be recovered from the number of net boundary crossings in the variable. By net boundary crossing, we mean the summation of $+1$'s and $-1$'s corresponding to the crossing two opposite directions.

5.2.3 Program Testing and Performance

Total system energy conservation is one of most frequently-used criteria for testing if a MD program is working correctly. We carried out such a test, finding that the energy is conserved to within a fluctuation of less than one percent for $\delta t < 0.01$ in reduced units. The reduced units is defined by setting $\epsilon$, $\sigma$ and atomic mass to unity. This fluctuation is quite reasonable. As a further test, we also compared our Lennard-Jones liquid simulations with previous MD results. We found good agreements in melting pair distribution function and also melting temperature.

The total momentum of the whole system is another conserved constant. We initialize the velocities of the particles in such a way that the total momentum is zero. After a run of many number of steps, we find it remains zero. Obviously, keeping the total momentum to be zero is necessary in the calculation of diffusion constant.

The performance of our program is fast enough to simulate a system of 4000 atoms
with Lennard-Jones interactions. On the DEC Alpha workstations, it does several time steps per second for the system.

### 5.2.4 Diffusion Constant Meter

To calculate the diffusion constants, we use the Einstein relation. This relation states that the average squared displacement of a particle is proportional to the time.

\[
D = \lim_{t \to \infty} \frac{\langle r^2 \rangle}{6t}
\]

(5.8)

Since \(D\) is a constant for a given sample, a plot of \(\langle r^2 \rangle \sim t\) should approach a straight line of slope \(6D\) for large enough \(t\). We can obtain \(D\) by calculating the slope of the asymptotic long-time part of the curve.

In our C++ program, we used a class to accomplish the diffusion constant calculation. In C++ language, a class is an object that has its own data structure and the operations on the data. The class uses the configuration snap shots of the system during the simulation as the inputs. Each instance of the class is called a diffusion meter, which store the particle configuration at the time when the diffusion meter is initialized. It then calculate \(\langle r^2 \rangle\) whenever we want by calling one of the operation of the class. The operation takes the current configuration and initial configuration it saved and calculate the displacement of each particles from the difference of the two configurations. The average of the squared displacement, \(\langle r^2 \rangle\), then can be calculated. Each diffusion meter generates a data set for a \(\langle r^2 \rangle \sim t\) plot. To reduce the fluctuation of diffusion constant, multiple diffusion meters are used and their data
are averaged to give the final data set for the plot.

5.2.5 Simulation Process

To study the temperature dependence, we start our simulation from a temperature below the melting point and then gradually increase the temperature up to twice as high as the melting temperature. We assigned the atoms to a FCC lattice as the initial configuration for the lowest temperature. Half of the atoms in the system have initial velocities with uniform distribution components whose values are bounded by some maximum. The other half of the atoms in the system are assigned initial velocities chosen to maintain the total momentum of the system at zero. For other temperatures, we use the final configurations of the simulation for the previous lower temperature as the initial configuration for the current temperature.

Whenever we start the simulations at a new temperature, we first warm up the system by scaling the velocities of all the atoms in the system to the kinetic energy corresponding to the given temperature. The scaling is performed once for every 10 time steps. Total of 5000 time steps are used to scale the system into the given temperature. This number of time steps is enough to make the system reach equilibrium state.

After the system is equilibrated, we start to collect the data for diffusion constant calculations. Several sets of data are collected for each simulation run. Each data set is collected by a diffusion meter which starts at a different original time after a designated delay from the previously one. The final data set used for diffusion
constant calculation is obtained by averaging the data sets. The averaged data set has less numerical fluctuation than any given data set collected by a single diffusion meter. This averaging is especially necessary to calculate the diffusion constant of impurities because the number of impurities is usually very small.

To calculate the self-diffusion constant of impurities having a different potential from the host atoms, we consider a liquid alloy. To reduce the effects of interactions between the impurities, we have to keep the impurity concentration very low. On the other hand, the number of impurities must be large enough in order to get adequate statistics for calculating diffusion constant accurately. We try to resolve this dilemma by using as large a number of host atoms as possible and also by averaging as many data sets as possible from different diffusion meters.

For samples with impurities, three kinds of interactions have to be considered: host-host, host-impurity, and impurity-impurity. We model all interactions using two Lennard-Jones potentials with different parameters: we assume one set of $\epsilon$ and $\sigma$ for the host-host interaction, and another for both the host-impurity and impurity-impurity interactions. Since impurity-impurity interaction rarely plays a role in the low impurity regime, this choice should lead to few complications. Our simulation procedure is similar to the one used in most dynamical simulations at finite temperatures. That is, we first let the system relax to equilibrium for a given temperature, then start the data collection. Two final data sets are needed, one to calculate the diffusion constant of the host atoms, and the other for the impurity self-diffusion coefficient. We denote the diffusion coefficient of host and impurity with $D_{\text{imp}}$ and
respectively.

5.3 Results

All of our simulations are carried out in a system of 4000 atoms. For the temperature dependent simulations, all the 4000 atoms are identical. To calculate the diffusion constant of impurities of Lennard-Jones atoms, we use 100 impurities and 3900 host atoms. The duration of each time step, \( \tau \), is 0.002 reduced time unit. For each simulation, we keep the system at the constant temperature by scaling the atomic velocities to the constant kinetic energy of \( E_k = \frac{3}{2} k_B T \), where \( k_B \) is the Boltzman constant and \( T \) is the given temperature. We first let the system evolve 5000 time steps to attain equilibrium. Atomic velocities are scaled to give the specified temperature once every 10 time steps. After equilibration, we start the first diffusion constant meter. The diffusion-constant meter saves the current snap-shot of the atomic positions as the original ones. In the subsequent time steps, the diffusion meter calculates \( \langle r^2 \rangle \), averaged over all the atoms of each component once for every 200 times steps. This process lasts \( 10^4 \) time steps, so that 50 data pairs of \( \langle r^2 \rangle \) and \( t \) are recorded. We use 10 diffusion meters to calculate the diffusion constants of each component in order to reduce the numerical fluctuation. 92 time steps after start of a given diffusion meter, a new meter is initiated. By choosing a delay of 92 time-steps between two successive meters, we can insure that each meter samples at times never sampled by previous meters. Thus, this procedure uses more configurations than a single meter for better statistics.
We define reduced units by choosing $\epsilon$, $\sigma$ and $m$ in Equ. (5.1) as our units of energy, length, and mass. All other units (e.g. of time, diffusion constant, and velocity) are determined from the values of these three parameters. For Ar, $\epsilon/k_B \approx 120$ K, $\sigma = 0.34$ nm [10], and $m = 6.64 \times 10^{-27}$ kg. The deduced units of time $\tau = (m\sigma^2/\epsilon)^{1/2} = 2.152 \times 10^{-12}$ s, and of diffusion constant $D = \sigma^2/\tau = 5.06 \times 10^{-4}$ cm$^2$/s.

The following results are given in reduced units except when explicitly pointed out. The above numbers can be used to get the physical quantities in the more usual (e.g. cgs) units in the case of liquid Ar.

### 5.3.1 Temperature Dependence

We calculated the diffusion constant at a wide range of temperature above the melting points. In our simulations, we keep the atoms in a constant volume for all the temperatures. The corresponding density is chosen as 0.83, close to the density at the triple point ($T = 0.68$ reduced units) of a Lennard-Jones liquid [7]. Figure 5.2 shows the plots of $<r^2> \sim t$ at different temperatures. From the slopes of the best fitting lines to the curves in Figure 5.2, we can calculate the diffusion constants at the temperatures. Figure (5.3) gives the logarithm of the diffusion constant versus inverse temperature, $1/T$. At the triple point, where the temperature is around 0.7, our calculated diffusion constant is very close to experimentally measured result for Ar ($1.6 \times 10^{-5}$ cm$^2$/s [13]). We also compared the radial distribution function, $g(r)$, with what Verlet obtained from his MD simulations and found good agreement. This confirms, on the other hand, that our simulation program is working well.
Figure 5.2: Plots of $< r^2 >$ versus $t$ at different temperatures. All the simulations are carried out on a system of 4000 stoms and at a constant volume with $\rho \approx 0.83$ reduced units.
Figure 5.3: The temperature dependence of diffusion constants obtained from Figure 5.2.
It seems that our simulation gives too low melting temperature (see Figure 5.2), which is as low as 0.6 reduced unit compare to the 0.68 of widely accepted value for Lennard-Jonse liquid. This is caused by the potential and force shifts, which is used to smooth the potential and force at the cut-off distance. These shifts reduce the depth of the Lennard-Jonse potential by approximately 14%, which can explain the difference in melting temperature considering the potential depth is not unity instead of 0.86.

It is difficult to compare our calculated diffusion constants directly with the experimental measurement given by Naghizadeh and Rice [12] on liquid Ar, since the diffusion constants are measured at constant pressure. Considering the weak dependence of measured diffusion constant on pressure, our results agree, at least qualitatively, with the experiment results.

Figure 5.3 shows that $D(T)$ fits with an activation form. The activation energy can be obtained from the slope of the straight line which best fits the calculated points. The resulting activation energy about 1.20$\varepsilon$, very close to the value, 1.04$\varepsilon$, extracted from experiment data of Naghizadeh and Rice.

5.3.2 Dependence on Depth of Impurity Potential

In the Lennard-Jones potential, $\varepsilon$ is the parameter which characterizes the potential strength. We expect that the strength of the impurity potential will affect the diffusion constant of the impurities and possibly also that of the host atoms. To know what effects the potential strength may have on the diffusion constant, we simulated
impurity systems of different impurity potential strength $\epsilon$. Just as in our calculations for the temperature dependence, the density is kept constant, at about 0.83 atoms per reduced volume. Figure 5.4 shows our calculated results for the samples held at temperature of $1.0t/k_B$. Figure 5.4(a) shows the diffusion constants of the host atoms at different impurity $\epsilon$ values. Considering the numerical fluctuation in our simulation, these diffusion coefficients do not show any change as $\epsilon$ varies. This can be explained by Cohen-Turnbull free-volume theory [14, 15]. In this theory, the diffusion constant depends on the free-volume, which in turn depends on the density fluctuation and the interaction range between the atoms in the liquids. The change of $\epsilon$ does not greatly change the free-volume in the liquid because the impurity concentration is very low. Also the change of $\epsilon$ has little affect on the free-volume due to the sharp increase of the repulsive force.

Figure 5.4(b) shows the impurity diffusion constants as a function of $\epsilon_{\text{imp}}$. The general feature is that the diffusion constant increases as the potential strength decreases. Compare to that of the host, the impurity diffusion constant is more dependent on $\epsilon_{\text{imp}}$, but still the effect is not large. As $\epsilon_{\text{imp}}$ changes from 0.5 to 1.5, the diffusion constant changes by about 50%. It is easy to understand that a smaller interaction strength will result in a larger impurity diffusion constant, because the impurity moves more easily than the host atoms under a weaker potential. In the extreme case of $\epsilon = 0$, the impurity will move freely, having very large diffusion constant.
Figure 5.4: Diffusion constants obtained from our MD simulations for different impurity potential strength. The system contains 100 impurity and 3900 host atoms. All the simulations are carried out at a constant volume with number density $\rho \approx 0.83$ and constant temperature of $1.0 \epsilon/k_B$. (a)-host and (b)-impurity.
5.3.3 Dependence on the Size of Impurity

To calculate dependence of the host and impurity diffusion constants on $\sigma_{imp}$, we carried out simulations for samples in the same means as in last section except that now the parameter $\sigma_{imp}$ is changed while $\epsilon$ is kept equal to that of the host. For the samples with $\sigma_{imp}/\sigma_{host} > 1$, we increase the potential cut-off radius and the linked-list cell size in an appropriate manner.

Figure 5.5 shows our results. On the left, Figure 5.5(a) shows the host diffusion constant stays unchanged until $\sigma_{imp}/\sigma_{host}$ becomes larger than unity, where the diffusion constant starts to decreases. By a $\sigma$ value of 1.5, it has decreased by about 50%. This is a significant change considering the very low impurity concentration in the liquid. While the free-volume theory can help us understand the decrease of the diffusion constant when $\sigma > 1.0$, it is hard to explain why the diffusion constant does not change when $\sigma < 1.0$. From experiment, we know that increasing pressure decreases the diffusion constant [12]. The larger impurity size could increase the system pressure significantly, whereas the smaller impurity size could not change the pressure in a liquid which is already under low pressure.

From Figure 5.5(b), we can see that the impurity diffusion constant increases very quickly as $\sigma$ decreases. There is a change by a factor of about 30 from $\sigma_{imp}/\sigma_{host} = 1.5$ to 0.5. The free-volume theory can explain why diffusion constant changes so quickly. When $\sigma$ decreases, the interaction range of impurity decreases proportionally. The smaller the impurity size, the less free-volume is required to migrate to other location and the higher diffusion constant it has.
Figure 5.5: Same as Figure 5.4, except $\epsilon$ is kept at $1.0\epsilon/k_B$ and $\sigma$ is changed from 0.5-1.5 $\sigma_{host}$. (a)-host and (b)-impurity.
5.3.4 Impurity Mass Dependence

We also carried out some simulations for samples containing impurities of different masses but the same interaction potential as the host atoms. We did not find any isotopic effect, within the errors caused by numerical fluctuation in a mass range of 0.5-2.0\(m_{host}\) of our exploration. An impurity mass smaller than this will cause problems in the simulation because the the impurities move very fast at any given temperature, and a very small time step has to be used. We do find obviously isotopic effect for the impurity with mass \(m_{imp} = 10m_{host}\).

5.4 Discussion

In this chapter, we presented the results of numerical experiment on the diffusion constant of a Lennard-Jones liquid. From the temperature dependence, we estimated the activation energy of atomic diffusion. Our result is close to the experimental measurement. For the sample with impurities of different interactions, we calculated the change of potential parameters \(\epsilon\) and \(\sigma\) on the diffusion constants of both host and impurity. Our results shows the impurity size is the dominant effect in affecting the diffusion constants. At the size of half of the host atoms, the impurity diffusion constant is 30 times as large as one in the case that impurity size is 50% larger than the host atoms. Our simulations did not show isotopical effect on the impurity diffusion constant in a range of 0.5-2.0\(m_{host}\). This is due to the numerical fluctuation in our
simulations. The simulation on a sample with \( m_{imp} = 10m_{host} \) does show obvious isotopic effect. The impurity self-diffusion coefficient is smaller than that of the host atoms.

From this study, we can see that the diffusion constant is very sensitive to the interaction range between the atoms in liquid. When we choose a potential to simulate the dynamical properties, we need to be very careful about the parameters which affect the interaction range.
CHAPTER V REFERENCES

CHAPTER VI

Molecular Dynamical Simulation of Diffusion Constants of Liquid Semiconductors

6.1 Introduction

Most semiconductors have elevated melting temperature. This makes the direct measurement of diffusion constant very difficult in the liquid state. Because of this difficulty, not many experimental data for the diffusion coefficient in the liquid state are available. Some workers have tried to use numerical methods, such as molecular dynamic simulation, to quantitatively study the diffusion properties in order to make up for this lack. Unfortunately, there are no reliable interatomic potentials, especially for the study of liquid semiconductors, because the interaction over a wide range of separation is needed. The search for a suitable interatomic potential in a variety of liquids has been one of the biggest challenges in the study of liquids [1].

The study of liquid semiconductors is even more challenging. Unlike simple liquid metals, directional forces play an important role in liquid semiconductors both in the open diamond crystal and in the liquid state. We cannot simply mimic the force simply by using a two-body interaction, since the diamond structure is unstable in the
presence of a purely two-body interaction. Many-body interactions can be included to give the correct force. First-principle methods have been widely used on liquid Si [2, 3] and liquid metals [4], ever since Car and Parrinello proposed the method [5] named after them. Recently, using a similar first-principle method as that of Car-Parrinello, Hafner et al. [6] studied liquid Ge and obtained quite successful results for a variety of properties. While these methods deal the interatomic interactions with the first principle calculation and therefore avoid the difficulty of finding the proper potentials for the directional forces, their demands on computing power severely limits the number of atoms that can be handled. Empirical potentials, such as Tersoff [7]-[10], the modified embedded atom method (MEAM) [11]-[14], and the Stillinger-Weber [15, 16] forms have all been used as input for molecular dynamic simulations of the semiconductors in the solid state. These empirical potentials all use a three-body potential to mimic the effects of the directional force. Among the three potentials, only the Stillinger-Weber potential has been used with some success to liquid Si [17]. Recent published MD simulation studies on Ge shows that Stillinger-Weber potentials are quite successful when used in the solid state [18, 19]. To date, however, there is no indication that such potentials can describe the interactions in liquid Ge.

Wang et al. have calculated the diffusion constant of liquid Ge using the Stillinger-Weber potential and the same parameters as Stillinger and Weber used for Si, except that the energy parameter is scaled down. Using these parameters, they found that crystal Ge melts at a much higher temperature (1450K) than the experimentally measured one. The diffusion constant they calculated at 1575K is about 3.5 ×
which is substantially below the value of around $10 \times 10^{-5} \text{cm}^2/\text{sec}$ estimated from the experimental viscosity. The activation energy they obtained is also too large (0.45 ev/at) compared to the 0.12 ev/at suggested by experiment [22].

Before we can find another potential for Ge in liquid, we first convinced ourselves that Stillinger-Weber potentials are probably the best available empirical potentials to work with. In order to improve on the results of Wang et al., we carried out MD simulation using their program. We determine the melting temperature, which is experimentally a better determined quantity than is the diffusion constant, and which is very sensitive to a three-body interaction parameter, $\lambda$. In next section, we will present our calculations on liquid Ge using a different $\lambda$ value. Instead of using the same parameters as for liquid Si, we determine the parameter $\lambda$, so as to fit the melting temperature of diamond-structure Ge.

The advantage of using empirical potentials over the \textit{ab initio} calculation is that they are less computationally demanding and hence allow larger-scale studies. Nevertheless, the three-body force calculation, as we pointed out in last chapter, is still very computationally expensive compared to the pair force calculation. Ferrante and Tosi [20] have used the bond charge model proposed by Phillips [21] as a basis for a Monte Carlo simulation of liquid Ge. Their results gives quite good agreement between the calculated structure factor and experiment. The idea of the bond charge model is that instead of dealing with the directional force related to covalent bonds between two neighboring atoms, one treats the bond charge themselves as dynamical degrees of freedom in additional to the ions. The bond charges are very localized between the
ions with certain directionality in the solid state, they remain very directional, but are free to move around in the liquid state like free electrons in simple liquid metals. The semiconductor to metal state transition at the melting for semiconductors, such as Si and Ge, can be qualitatively understood within this model.

The bond charge model is especially plausible for liquid semiconductors, because they differ substantially in microstructure from liquid metal. As deduced from structure factor measurements, the coordination number an ion in a liquid semiconductors typically is around 7. This is much smaller than the coordination number of 12 for the close packed simple liquid metals, yet larger than the value of 4 in the diamond structure. Thus the bonds apparently remain quite directional in the liquid state. Considering all these points, Ferrante and Tosi use localized potentials to trap the bonds around ions and use hard-sphere bond-bond potentials to keep the two bonds away from each other. This potential plays the role of the directional force. By changing a parameter which characterizes the localized potential, they were able to find a choice such that the bonds could move away from a ion but still have strong tendency to stay near a given ion. The most important feature of this model is that only three pair potentials are used: between two ions, between two bond charges, and, between an ion and a bond charge. This procedure would get rid of the tedious three-body potentials, if it succeeded.

In Section 6.3, we will try to use a similar bond charge model for MD simulations on the liquid semiconductors. By only with pair potentials, we can simulate much larger systems than either the \textit{ab initio} and empirical potential methods. While we
have not yet had great success with this attempt, the perspective of this model is still very encouraging. We will discuss possible future studies of this model at the end of this section. Finally, in Section 6.4, we give some discussions of our results.

6.2 Simulation of Liquid Ge With Stillinger-Weber Potentials

6.2.1 Interatomic Potentials and Simulation Method

With the Stillinger-Weber two-body and three-body interatomic interactions, the model Hamiltonian of liquid Ge takes the form

$$H = K + \sum_{<i<j>} V_2(R_i - R_j) + \sum_{<i<j<k>} V_3(R_i, R_j, R_k),$$

where $K$ is the kinetic energy; $V_2$ is the two-body potential; and $V_3$ is the three-body potential. $V_2$ and $V_3$ take the form proposed by Stillinger and Weber [15]:

$$V_2 = \epsilon f_{sw}^{(2)}(r_{ij}/\sigma)$$

$$V_3 = \epsilon f_{sw}^{(3)}(r_{ij}/\sigma, r_{jk}/\sigma, r_{ki}/\sigma)$$

$$f_{sw}^{(2)}(r) = A(Br^{-4} - 1)\exp[(r - a)^{-1}], r < a$$

$$f_{sw}^{(2)}(r) = 0, r \geq a$$

$$f_{sw}^{(3)}(r_{ij}, r_{jk}, r_{ki}) = h(r_{ij}, r_{ik}, \theta_i) + h(r_{ji}, r_{jk}, \theta_j) + h(r_{ki}, r_{kj}, \theta_k)$$

$$h(r, s, \theta) = \lambda \exp[\nu(r - a)^{-1} + \nu(s - a)^{-1}](\cos \theta + 1/3)^2,$$

$$if \ r < a \ and \ s < a$$

$$= 0, otherwise.$$
We use the same parameters for Ge as Wang et al. used in their MD simulations, except for $\lambda$, which is determined by fitting to the experimental melting temperature of Ge. The melting temperature of Ge is about 1200K [23]. We found that the MD simulation predicts the melting temperature very close to the measured if $\lambda = 17$ is used.

We carried out MD simulations for samples with 256 Ge atoms. The Ge atoms are initially arranged in diamond structure. Since Ge in liquid state has higher density than in the crystal state, the system is compressed in the solid state to the same density as of the liquid state. The temperature is increased gradually and the volume of the sample is kept at a constant. We studied a temperature range from somewhat below the melting temperature, $T_M$, to around 1.5$T_M$. We used 50000 time steps for each simulation. The duration of a time step is about 0.003 reduced units ($1.363 \times 10^{-13}sec$), which is defined by choosing $\epsilon$, $\sigma$, and mass of Ge atom as the units and energy, distance and mass and all the other units are deduced from them. The system first evolve 5000 time steps to reach equilibrium. The remaining 45000 time steps are used to sample data for the diffusion constant and the distribution function. A similar method as in the last chapter is used to reduce the effects of numerical fluctuation on the data for the diffusion constant. The final data set is an average over a large number of data sets. The time span for sampling the diffusion constant is as high as 12 reduced time units. The average displacement of a atom in this period is more than 2 Å.
6.2.2 Determination of $\lambda$

We calculated the diffusion constant for different $\lambda$ parameters in the Stillinger and Weber three-body potentials. We found that the value of $\lambda$ has a great influence on the diffusion constant as well as on the melting temperature. Rather than using 21, the value of Wang et al. have used for Ge, we can determine $\lambda$ from the well-known experimental melting temperature of Ge given above. We found that $\lambda = 17$ gives the melting temperature very close to the measured (within 50K). To determine the melting temperature, we used both radial distribution function and diffusion constant to check if the system is in liquid state. Both are very sensitive to the temperature change at the melting temperature. If using $\lambda = 17$ as parameter for the three-body potential, the system stays in solid diamond crystal below 1150K and melts above 1170K. We can also determine the melting point from the change of total energy as a function of temperature. The total energy has discontinuity at the melting temperature because the melting is a first order phase transition. The total energy and temperature relation obtained from our simulation is given in Figure 6.1. It does show there is a discontinuity in total energy at about 1200K but it is dropped down instead jump up as in ordinary melting phase transitions. It is probably due to the fact that the system is under high pressure before melting. We expect the total energy of the solid phase will drop down if we decrease its density to the one at atmospheric pressure. We are going to do this simulation soon.
Figure 6.1: Total energy per atom versus temperature. The system is kept at a constant density corresponding to the liquid Ge at atmospheric pressure for all the temperatures and $\lambda = 17$. The vertical axis gives the total energy per atom and the horizontal axis gives the temperature in reduced units. The experimental melting temperature is about 1215K.
Figure 6.2: Curves of mean square displacement versus time at different temperatures.
6.2.3 Temperature Dependence

As we described above, the diffusion constant is calculated from the slope of mean square displacement versus time curve. We calculated the curves at various temperature and plot them in Figure 6.2. The diffusion constants at the temperatures are calculated by fitting the curves to straight lines. Table 5 gives the diffusion constants at different temperatures. Although the diffusion constant is small at low temperatures, it is much larger for a given temperature than the simulation results obtained using λ = 21. The diffusion constants at different temperature are listed in Table 5.

We can estimate the activation energy from the slope of the curve of log D versus 1/T, Figure 6.3. While the first two points at low temperature are far off this line, we can draw a reasonably straight line for the other three points at higher temperature. The estimated activation energy from this straight line is about 0.28 ev/at, which is better than the estimate of 0.45 ev/at obtained by Wang et al., but still much higher than the estimate from experiment.

6.2.4 Radial Distribution Functions

The radial distribution functions at all the temperature show similarity with the experimental results by Gabathuler and Steeb [24], but the structure factors, obtained by Fourier transforming of the radial distribution functions, don’t show the experimentally observed shoulders on the right side of the first peak. Figure 6.4 gives the radial distribution functions.
Table 5: Diffusion constants of liquid Ge at different temperatures, as calculated using the Stillinger-Weber potential with $\lambda = 17$ and a sample of size 216 atoms.

<table>
<thead>
<tr>
<th>Temperature ($\times 22500$ K)</th>
<th>$D \times 10^{-5}$ cm$^2$/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0520</td>
<td>1.91</td>
</tr>
<tr>
<td>0.0540</td>
<td>2.79</td>
</tr>
<tr>
<td>0.0600</td>
<td>3.94</td>
</tr>
<tr>
<td>0.0650</td>
<td>4.85</td>
</tr>
<tr>
<td>0.0700</td>
<td>5.58</td>
</tr>
</tbody>
</table>
Figure 6.3: Diffusion constant of Ge at different temperatures. The results are from the same simulations as for Figure 6.1.
6.3 MD of Bond Charge Model

6.3.1 Model

As we have discussed in the section of introduction, the interatomic force in semiconductors has very strong orientation because of the covalent bonds. Simply using pair potentials cannot include this directional interaction. A bond model was proposed by Phillips and used by Ferrante and Tosi in the Monte Carlo simulation. Figure 6.5 is a sketch of the arrangement of ions and bonds for diamond structure in the model. The bonds are treated as classical dynamical degrees of freedom in addition to the ions. So we have an effectively two-component system, with N ions and 2N bonds, where N is the number of atoms. The pair interaction between two ions is denoted by $f_1(r)$, between two bonds by $f_2(r)$, and, between a bond and an ion by $f_3(r)$, where $r$ is the separation between the pair. In order to do the MD simulation, we need to determine the forms of these three potentials. Once proper pair potentials are found, MD simulation can be performed by using our program described in Chapter V.

6.3.2 Potentials

As a first try, we determine the pair potentials based on the Stillinger-Weber potentials by requiring the following conditions.

1. The ground state is a diamond-structure crystal;
Figure 6.4: Radial Distribution functions at different temperatures. The results are from the same simulations as for Figure 6.1.
Figure 6.5: A sketch of the ions and bond charges in a diamond structure
2. The model should reproduce the predictions of Stillinger and Weber potentials for liquid Si;

3. The model should give the correct melting temperature.

Algebraically, the first two conditions lead to the following two equations:

\[ f_1(r) + 2f_2(r/2) = f_{sw}^{(2)}(r), \]  
\[ \frac{d}{dr}(f_1(r) + 2f_2(r/2)) |_{r=R} = 0. \]  

Here \( R_0 \) is the separation of two ions in the diamond structure and \( f_{sw}^{(2)}(r) \) is the Stillinger-Weber pair potential as given in last section, in which \( a \) is the potential cut-off distance, \( A \) and \( B \) are constants.

\( f_3(r) \) is required to satisfy equations,

\[ f_3(r = 0) = f_{sw}^{(3)}(\theta = 0), \]  
\[ \frac{d}{dr}f_3(r) |_{r=\sqrt{3}R} = 0. \]

\( f_{sw}^{(3)}(r) \) is the SW three-body potential, it is also given in last section. \( R \) is the distance between two neighboring ions in the diamond structure, which is a constant.

From our discussion in last section, we can see, if possible, the third condition can be satisfied by change the value of \( \lambda \) in \( f_{sw}^{(3)} \). To satisfy all the above equations, the three pair potentials can have forms:

\[ f_1(r) = \frac{A}{1 + 2\alpha} \left( Br^{-4} - 1.0 \right) exp \left( \frac{1}{r-a} \right), \]  
\[ f_2(r) = \frac{\alpha A}{1 + 2\alpha} \left( \frac{B}{16} r^{-4} - 1.0 \right) exp \left( \frac{1}{2r-a} \right), \]
\[ f_3(r) = A_3 \left[ \frac{4}{3} - 2 \left( \frac{r}{R} \right)^2 \right] \exp \left( \frac{2.4}{\sqrt{2} r - a} \right). \] (6.15)

In these equations, \( \alpha \) is a parameter which reflects the relative strength of \( f_1(r) \) and \( f_2(r) \). \( A_3 \) is determined by Equs. (6.11) and (6.12) within a constant factor, which can be adjusted to give the correct melting temperature. The mass of the ions, \( M \), is defined as unity in the reduced units and the mass of a bond, \( m \), is an adjustable parameter.

We have carried out some preliminary MD simulations using these potentials. The parameters we used in the simulations are \( \alpha = 1.0 \) and \( m = 0.1 \). We adjust the value of \( \alpha \) to obtain best results. The main conclusion about the potentials is that they can stabilize the diamond structure at zero temperature. At higher temperature, the crystal melts but the expected jump in the total potential energy associated with the melting was not detected. The problem is possibly caused by the fact that our potential between two bonds has a too soft core and the effects of the directional force are not well represented by it.

More improvement to the potentials are needed in order to produce the sharp energy change associated with the first-order melting transition. A possible direction of further study is to use the same potentials employed by Ferrante and Tosi in their Monte Carlo simulation study in our MD simulations. Because one of the Ferrante-Tosi potentials has a very localized attracting part, it cannot be used directly in MD simulation. Specifically, the force cannot be calculated by the derivative of potentials or else the derivative of a localized potential will result a force which change too rapidly at some points in space to efficiently use the MD method. The constrained
MD method could be used to solve this problem.

6.4 Conclusion

In conclusion, we have used molecular dynamical method for different models to study the liquid semiconductors. Using empirical Stillinger-Weber potential, we find the strength of three-body interaction has strong influence on the melting temperature. A new parameter determined from fitting to the experimental melting temperature is used in our simulations. Some improvement has been obtained relative to previous studies. We also presented a bond charge model and a way we have used in the search of the proper potentials. Hope our work will inspire further effort in searching for a proper potential.

Finding proper potentials to include the effect of directional force is the most important and also the most difficulty part of our simulations. The Stillinger-Weber potentials, though working fairly well for liquid Si, is still far from satisfactory for liquid Ge. The bond charge model provide us a possible solution by allowing us to use pair potentials only in molecular dynamically simulating the liquid semiconductors. Further studies need to be done to determine the optimum potentials. So far, in the case of problems that require only a small number of atoms to simulate, first-principle MD methods may provide the best results.
Chapter VI References


Appendix A

Nonlinear Differential Effective-Medium Approximation.

In this Appendix, we describe a simple, quasi-analytical model for the nonlinear response of fractal clusters in $d = 2$ and $d = 3$, generalizing a similar scheme developed for linear response by Hui and Stroud[21].

As a preliminary, consider a composite containing a small volume concentration $p_B$ of inclusions of type B embedded in a host of type A. The inclusions are assumed to be $d$-dimensional hyperspheres (i.e., circles or spheres in $d = 2$ or 3). The $i^{th}$ component ($i = A$ or $B$) is assigned conductivity $\sigma_i$, nonlinear susceptibility $\chi_i$. The effective conductivity $\sigma_e$ of the composite can be calculated exactly, to first order in $p_B$, from the Maxwell-Garnett approximation,

$$\sigma_e = \sigma_A (1 + dp_B t_B), \quad (A.1)$$

where

$$t_B = \frac{\sigma_B - \sigma_A}{\sigma_B + (d - 1)\sigma_A}. \quad (A.2)$$

The analogous result for the nonlinear susceptibility $\chi_e$ was first obtained by Bergman for the case required here, in which both host and inclusion have a finite susceptibility.
It takes the form
\[ \chi_e = \chi_A + p_B(\chi_A \lambda_A + \chi_B \lambda_B), \] (A.3)
where
\[ \lambda_A = \left(-1 + 4t_B + \frac{2(d-1)(d+6)}{d+2}t_B^2 + \frac{4(d-1)(d-2)}{d+2}t_B^3 + \frac{d-1}{3(d+2)}t_B^4 \right) \] (A.4)
and
\[ \lambda_B = \left(\frac{d \sigma_A}{\sigma_B + (d-1)\sigma_A}\right)^4. \] (A.5)

This result is a generalization of one previously obtained by several authors[9] for the case where only the inclusion is nonlinear.

We will use this result to obtain an approximate expression for the nonlinear susceptibility of a cluster. The cluster is constructed by starting with a pure A hypersphere. The concentration of B is incrementally increased by adding B material in the form of hyperspheres. Let the cluster at radius \( R \) have an effective conductivity \( \sigma(R) \), effective susceptibility \( \chi(R) \). Now increase the radius by \( \delta R \), and the volume fraction of type B material by \( \delta p_B \). Then from Eqs. (A.3)-(A.5), we immediately obtain
\[ d\sigma = \delta p_B[\sigma t_B d], \] (A.6)
and
\[ d\chi = \delta p_B[\lambda_A \chi + \lambda_B \chi_B], \] (A.7)
where \( t_B, \lambda_A, \text{ and } \lambda_B \) are given by Eqs. (A.2), (A.4), and (A.5), but with \( \sigma_A \) and \( \chi_A \) replaced by \( \sigma \) and \( \chi \).
Eqs. (A.6) and (A.7) represent ordinary differential equations for the cluster conductivity $\sigma$ and nonlinear susceptibility $\chi$ as functions of $p_B$. They are readily solved numerically in $d = 2$ or $d = 3$. The resulting functions $\sigma(p_B)$ and $\chi(p_B)$ represent effective cluster conductivities and susceptibilities for a cluster of concentration $p_B$. Note that this approach does not necessarily assume that the cluster is a fractal. If, however, the cluster is actually a fractal of fractal dimension $d_f$, then one can relate $p_B$ to the cluster radius $R$ using

$$p_B = 1 - \left( \frac{R}{a} \right)^{(d_f-d)},$$

(A.8)

where we are assuming that component A, present in concentration $1-p_B$, is distributed fractally, and that $a$ is the linear dimension of the smallest A particle.

Once the cluster parameters $\sigma$ and $\chi$ have been calculated, it remains to calculate $\sigma_c$ and $\chi_c$ for the composite itself. In the dilute limit (volume concentration of clusters much less than unity), these may be obtained simply by another application of Eqs. (A.1)-(A.5).
List of References


[31] E. Duering, M. Murat, A. Aharony, and D. J. Bergman, manuscript in preparation.


[67] For many recent papers and references, see, for example, Proceedings of the Third International Conference on the Electrical and Optical Properties of Inhomogeneous Media, W. L. Mochán and R. G. Barrera, editors, volume 207, (Elsevier, Amsterdam, 1994).


[69] T3D Seminar Notes, by Ohio Supercomputer Center.

[70] Paragon XP/S Product View, Intel Corp.


[77] D. M. Pase, Tom MacDonald, Andrew Meltzer, MPP Fortran Programming Model, Cray Research, Inc.


[84] D. Ricard, P. Roussignol, and C. Flytzanis, Optics Letters 10, 511 (1985);


