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PROPERTIES OF DISORDERED CONTINUOUS AND DISCRETE SOLIDS

By

Branislav R. Djordjević

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ABSTRACT

PROPERTIES OF DISORDERED CONTINUOUS AND DISCRETE SOLIDS

By

Branislav R. Djordjević

In this thesis I have studied both continuous and discrete disordered solids. The focus is on the calculations of the effective conductivity and the corresponding spectral function in random binary composites, and on the computer modeling of amorphous materials. The spectral function is fully determined by the geometry of the two-phase medium. I examine the case of circular inclusions randomly distributed in a conducting sheet. I calculate the effective conductivity to second order in the concentration of inclusions f. The spectral function for this problem is found to be a truncated Lorentzian with weight f and with the width that is proportional to f, and the final result is written in a very simple form. Various two dimensional problems are discussed and it is shown how one can use the conformal mapping technique to calculate the effective conductivity, when the inclusions are polygonal holes. I have also studied the properties of a topologically disordered networks - amorphous solids. I computer generated a very large (4096 atom) model of amorphous diamond using the Wooten-Weaire method. Starting from the perfect diamond crystalline super-cell, I first randomize the structure by introducing topological disorder through random bond switches at a sufficiently high simulation temperature. Subsequently, the simulation temperature is reduced in stages, and the topological and geometrical relaxation takes place using the Keating potential. After a long annealing process, a random network of comparatively low energy is obtained. I calculate the pair distribution function, and all other relevant quantities for the final relaxed structures. I minimize the total strain energy by adjusting the density of the sample. I compare the results for amorphous diamond with the results I obtained for amorphous silicon, and also with the recent experimental measurement of the structure factor for (predominantly tetrahedral) amorphous carbon. Finally, I examine the elastic properties of amorphous networks. The amorphous diamond model is bond-diluted, and a sequence of amorphous structure with different mean coordination $\langle r \rangle$ is obtained. I calculate the bulk modulus as a function of the mean coordination. I compare my results with those that were obtained using the crystalline super-cell as an underlying structure on which the bond dilution is performed. My simulations show that the bulk modulus as a function of the mean coordination obeys the same power low, no matter what the underlying lattice is - amorphous or a crystalline. All results of my research are presented on the comprehensive historical background of the modeling of amorphous networks.

I dedicate this Thesis to my late father Rista Djordjević who suddenly died in July 1995.

I equally dedicate this Thesis to my wife Dragana Vasiljević.

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Chapter 1

Introduction

In the last three decades or so, disordered properties of matter attracted a lot of attention in the condensed-matter physics community. The development of new mathematical and computational tools resulted in the major conceptual turning point in our understanding of the properties of matter. Even though most physical systems that exist in nature are disordered, traditional physics was mainly interested in simple, crystalline, regular or, in general, well ordered systems. This was not only because it was easier to treat such ordered systems with the existing mathematical tools (an enormous work had needed to be done to acquire satisfactory understanding even of such simple systems!), but also because the concept of nature held by most physicists was still that of the older times, when the idea of order, or rational ordering of nature, was the main driving force for physicists to try to discover that hidden order of nature behind the seemingly chaotic appearance of things. Generally accepted aesthetics, the measure of beauty of physical laws which governs the Universe, was the aesthetics of order. Here is one example of this acceptance in words of John Tyndall ¹ in one of his public lectures:

To many here present a block of ice may seem of no more interest and beauty than a block of glass; but in reality it bears the same relation to glass that orchestral harmony does to the cries of the marketplace. The ice is music, the glass is noise; the ice is order, the glass is confusion. In the glass, molecular forces constitute an inextricably entangled skein; in ice they are woven to a symmetric texture...

This attitude has been changed in the last three decades when many difficult problems in disordered systems have become tractable.

In this thesis, I will present some of the new concepts which are used when dealing with both continuous and discrete disordered systems. The emphasis will be on two classes of media: random binary composites, and amorphous materials.

¹J. Tyndall, "Heat = A Mode of Motion." Longmans, Green, London, 1863. The reference is taken from: Wooten and Weaire (1987).

Chapter 2

Continuous Disordered Media

2.1 Introduction

In this chapter I will give a brief account of the research that has been done in calculating the effective values of various physical quantities in disordered continuous media. The system in consideration is a continuous media host which contains inclusions of various shapes, randomly distributed over the sample. The inclusions are of macroscopic size, but small compared to the size of the sample. They can have sharp corners (e.g. polygons in 2d), or they can be of round shape (e.g. elliptical, or circular in 2d, or spherical in 3d). One wants to calculate the effective quantities in different kind of problems: electrical conduction, magnetic permeability, heat conduction, etc. All these problems are mathematically equivalent, and I will speak only about the electrical conductivity calculation in such systems. Instead of the language of conductivity adopted here, one could use the language of dielectric constants. All results are straightforwardly translatable from one language to another.



Figure 2.1: 2d example of a random composite. The system has effective conductivity σ , and contains regions with conductivities σ_0 (white) and σ_1 (black).

2.2 Effective Conductivity

The conductivity of random composites has long been a subject of interest, dating back to the time of Maxwell (1873) and perhaps even further. The number of exact results is limited, but these few exact results have a special importance in testing and evaluating approximate theories and judging the accuracy of computer simulations.

The system in consideration is schematically represented in Figure 2.1. The black inclusions can in principle be of an arbitrary shape, but most of the earlier work had been done for the case of spherical particles immersed in a matrix of uniform conductivity thus creating a statistically homogeneous and isotropic suspension. The problems of electrical conduction, electric permittivity, magnetic permeability and heat conductivity are mathematically equivalent, and knowing the solution of one of those problems, one can get the solution of any other one by appropriately renaming the symbols appearing in it. Maxwell (1873) solved the problem to first order of the concentration f, taking into account only the induced dipole moments of the spherical particles. The effective conductivity of the suspension he found, can be written in the following form

$$\frac{\sigma}{\sigma_0} = 1 + 3\gamma f, \tag{2.1}$$

where f is the concentration of spheres and γ is dimensionless parameter defined as

$$\gamma = \frac{\sigma_1 - \sigma_0}{\sigma_1 + 2\sigma_0}.\tag{2.2}$$

The numerical factors 3 and 2 which respectively appear in Equations (2.1) and (2.2), are actually d and d - 1, where d is the dimension of the system. We shall come back to this when we discuss 2d case in details.

Lord Rayleigh (1892) took into account the contribution of induced octupole moments to the effective conductivity and thus showing that Maxwell's formula is accurate only for small volume fractions.

Peterson and Hermans (1969) calculated the effective dielectric constant of a suspension of parallel cylinders and spheres to the order of f^2 , using the method of reflections to solve the two-sphere problem. Jeffrey (1973) calculated the average heat flux of the random suspension of spheres also to the order of f^2 , using the general method deviced by Batchelor (1972) for the averaging of interactions between spheres to obtain bulk properties of suspensions. To solve the two-sphere problem Jeffrey used twin spherical expansions first formalized by Ross (1968).

2.3 Spectral Functions

The use of the spectral function probably dates back to Foster (1924) for discrete resistor networks. This approach was applied to single cubical inclusions by Fuchs (1975). The general theory for continuous media was further developed by Bergman (1978) and by Milton (1981). It was subsequently put on a more rigorous basis by Golden and Papanicolaou (1983). Extensive numerical evaluations of the spectral function in the low-concentration limit have been performed by Felderhof and coworkers (1982, 1989, 1992). A discussion of the discrete resistor case, especially near percolation, has been given by Straley (1979). Day and Thorpe (1996) further developed the calculation of the spectral function for discrete resistor networks, for arbitrary concentrations.

Despite this activity, spectral functions are not much used in this area, and the subject has become a bit of a backwater. This is unfortunate as this is potentially a very powerful formalism, that could lead to important insights into system behaviour. The attraction is that there is a single real function that characterizes the behavior of the system, for a fixed geometry. Even if the (complex) conductivities of the two components change, by varying the frequency or the temperature, the *same* spectral function describes the response of the composite. Thus the spectral function is determined by the geometry of the two-phase medium, and so it should be possible to find numerical algorithms to calculate it directly and efficiently. This has not yet been possible, although significant progress has been made recently by Day and Thorpe (1996).

It has been shown first by Bergman (1978, 1986) that for any two-phase composite medium, provided Maxwell's equations of electrostatics hold, the effective conductivity (or dielectric constant) can be written as

$$\frac{\sigma}{\sigma_0} = 1 - \int_0^1 \frac{g(u)du}{t-u},$$
(2.3)

where parameter t is defined as

$$t = \frac{\sigma_0}{\sigma_0 - \sigma_1}.\tag{2.4}$$

Equation (2.3) holds in any dimension d, and serves to define the spectral function g(u) as a transform on the conductivity σ , which is the function of the material parameter t.

The spectral function g(u) is a real, positive semidefinite function for 0 < u < 1, and zero outside this range. The spectral function is fully determined by the random geometry of the two-phase medium. Quite generally, for a system which on average is *uniform* the total weight of the spectral function is:

$$\int_{0}^{1} g(u) du = f,$$
 (2.5)

where f is the concentration as before, or in other words, the volume fraction of the phase σ_1 in the host σ_0 .

If in addition the system on average is isotropic, then the first moment of the spectral function is given by:

$$\int_{0}^{1} ug(u)du = \frac{f(1-f)}{d},$$
(2.6)

where d is the dimension.

It is convenient sometimes to define the normalized $moments < u^n > of$ the spectral function by

$$\langle u^n \rangle = \frac{\int_0^1 \langle u^n \rangle g(u) du}{\int_0^1 g(u) du},$$
 (2.7)

so that from (2.6) we have for the first moment

$$\langle u \rangle = \frac{1-f}{d}.$$
 (2.8)

In the case when the inclusions are spheres (3d) or circles (2d), if we approximate the spectral function by a δ function with weight and location such that the sum rules (2.5) and (2.6) are satisfied, then (2.3) leads to the well known Clausius-Mossotti or Maxwell Garnett formula [see the Equation (2.12) in Felder-hof and Jones (1989) for 3d case]. Explicitly, in d dimensions,

$$g_{CM}(u) = f\delta\left(u + \frac{f}{d}(1-f)\right)$$
(2.9)

leads to

$$\frac{\sigma_{CM}}{\sigma_0} = 1 + \frac{\mathrm{d}f}{1 - f - \mathrm{d}t}.$$
(2.10)

Instead of using t, we can define another material parametar γ , which will be later used throughout the rest of the text. Again, in **d** dimensions,

$$\gamma = \frac{\sigma_1 - \sigma_0}{\sigma_1 + (\mathbf{d} - 1)\sigma_0},\tag{2.11}$$

which in 2d reduces to (2.2)

From (2.11) and (2.4) follows

$$dt = \frac{\gamma - 1}{\gamma}.$$
 (2.12)

Substituting (2.12) in (2.10) we have another useful expression for the effective conductivity of the mixture

$$\frac{\sigma}{\sigma_0} = \frac{1 + (\mathbf{d} - 1)f\gamma}{1 - f\gamma}.$$
(2.13)

Assuming that the volume fraction f is small, we can expand (2.13) in Taylor series and get the effective conductivity for spherical (circular) inclusions to the first order in f

$$\frac{\sigma}{\sigma_0} = 1 + \mathrm{d}f\gamma + \cdots. \tag{2.14}$$

I will show later how one can go further in this expansion of the effective conductivity, to the second order in f in the case of *circular inclusions*.

It would be desirable to know the spectral function directly from the given random geometry, and then calculate the effective conductivity from (2.3), but at this stage of the theory, this is not possible. Instead, in order to collect information about spectral functions, one must first calculate the effective conductivity, and then extract the form of the spectral function from that, by taking the imaginary part of the effective conductivity σ/σ_0 . Indeed, if we change the sign in (2.3)

$$\frac{\sigma}{\sigma_0} = 1 + \int_0^1 \frac{g(u)du}{u-t}$$
(2.15)

and recall the well known formula from the theory of analytic functions (see e. g. Mathews and Walker 1970)

$$\int \frac{g(u)du}{u-t-i\epsilon} = \wp \int \frac{g(u)du}{u-t} + i\pi g(u), \qquad (2.16)$$

where φ is the Cauchy principal value, or in the somewhat symbolic but useful form

$$\frac{1}{u-t-i\epsilon} = \wp \frac{1}{u-t} + i\pi \delta(u-t).$$
(2.17)

Substituting (2.17) into (2.3), and separating the real and imaginary parts it follows that imaginary part of the effective conductivity can be written as

$$Im\left(\frac{\sigma}{\sigma_0}\right) = \pi g(u), \qquad (2.18)$$

or solving for spectral function

$$g(u) = \frac{1}{\pi} Im\left(\frac{\sigma}{\sigma_0}\right).$$
 (2.19)

To calculate the spectral function one thus has to know the effective conductivity. The effective conductivity can always be found in principle from the induced dipole moment on the whole sample, that is produced by the induced charge on the boundaries between the regions of σ_0 and σ_1 , shown in Figure 2.1 (Hetherington and Thorpe 1992, Thorpe 1992). We shall see later how one can calculate the induced dipole moment in various cases.

There is another useful form in which we can write Clausius–Mossotti formula, in terms of the mean polarizability of a single inclusion. In d dimension

$$\frac{\sigma - \sigma_0}{\sigma + (d - 1)\sigma_0} = \frac{n\overline{\beta}}{d},$$
(2.20)

where n is the number of the inclusions per unit volume V_0 in d-dimesional space, and $\overline{\beta}$ is the mean polarizability of a single inclusion. Solving (2.20) for σ/σ_0 , and using the following relations

$$\overline{\beta} = \mathrm{d}V_0\gamma \tag{2.21}$$

and

$$f = nV_0, \tag{2.22}$$

and one arrives back at the formula (2.13).

2.4 Two-dimensional Case

Since my work which deals with the continuous random media was done on twodimensional systems, I will now present some characteristics of the 2d systems, as well as derive some formulas valid only in 2d which will be later extensively used. By two-dimensional system we do not mean that the physical space of the problem is two-dimensional, but only that there is no dependence on one Cartesian coordinate, as for example in the case of aligned fibers.

2.4.1 Reciprocity Theorem

The reciprocity theorem states that if the conductivity of the two-phase medium in 2d is $\sigma(\sigma_0, \sigma_1)$, and if the geometry is kept fixed but σ_0 and σ_1 are interchanged, to give a conductivity $\sigma(\sigma_1, \sigma_0)$, then these two conductivities are related by

$$\sigma(\sigma_0, \sigma_1)\sigma'(\sigma_1, \sigma_0) = \sigma_0 \sigma_1. \tag{2.23}$$

We are interested in a special case of (2.23) when one component, say σ_1 is present in small amounts, so that the other one with σ_0 can be considered as a host. In other words, this is to say that the volume (area) fraction of the component σ_1 , f, is small. Then, we can write an expression for the effective conductivity which is, to first order in f, equivalent to (2.23)

$$\frac{\sigma}{\sigma_0} = 1 + \gamma G(\gamma) f + \cdots, \qquad (2.24)$$

where

$$\gamma = \frac{\sigma_1 - \sigma_0}{\sigma_1 + \sigma_0},\tag{2.25}$$

which is the general expression (2.11) with d substituted by 2, and $G(\gamma)$ must be an *even* function of γ . To see that, rewrite (2.24) for the two interchanged geometries, and with the explicit σ dependence on σ_0 and σ_1

$$\sigma(\sigma_0, \sigma_1) = \sigma_0 + \sigma_0 \gamma G(\gamma) f, \qquad (2.26)$$

where σ_1 is present in small quantities, and

$$\sigma(\sigma_1, \sigma_0) = \sigma_1 - \sigma_1 \gamma G(-\gamma) f, \qquad (2.27)$$

where the geometry was inversed, so that σ_0 now is present in small quantities. Multiplying (2.26) by (2.27), we see that, to first order in f, the reciprocity theorem is restored, if the function $G(\gamma)$ is even, so that linear terms in f cancel each other on the right-hand side, leaving the expression $\sigma_0\sigma_1$ as in (2.23).

From the other side, writing the effective conductivity ad hoc in the form (2.24), may seem to be too hard to guess a priori. To get a hint about the correct form of the conductivity in the low concentration limit of one of the components, we shall solve the problem first in the *weak* scattering limit, and then, generalize it. The *weak* scattering limit occurs when the two conductivities σ_1 and σ_0 do not differ much, i.e. when the difference $\sigma_1 - \sigma_0$ is small quantity. Then, using perturbation theory (Landau and Lifshitz 1960) to second order in $\sigma_1 - \sigma_0$, one can solve the problem exactly to obtain (Landau and Lifshitz 1960)

$$\sigma = \overline{\sigma} - \frac{\overline{(\sigma - \overline{\sigma})^2}}{3\overline{\sigma}},\tag{2.28}$$

where the bar represents an average. This formula is valid for 3d case, and it is easy to see that in 2d case which we have here, we have to replace 3 by 2 in (2.28). Explicitly,

$$\overline{\sigma} = (1-f)\sigma_0 + f\sigma_1$$

$$\overline{\sigma^2} = (1-f)\sigma_0^2 + f\sigma_1^2 \qquad (2.29)$$

and (2.28) can be transformed to

$$\sigma = \overline{\sigma} - \frac{\overline{\sigma^2} - \overline{\sigma}}{2\overline{\sigma}}.$$
 (2.30)

Substituting the expressions (2.29) into (2.30) we get

$$\sigma = \sigma_0 + f(\sigma_1 - \sigma_0) - \frac{f(1 - f)(\sigma_1 - \sigma_0)^2}{2[\sigma_0 + f(\sigma_1 - \sigma_0)]}.$$
 (2.31)

Now, we expand the expression (2.31) in terms of small quantity λ defined as

$$\lambda = \frac{\sigma_1 - \sigma_0}{\sigma_0} \tag{2.32}$$

to get

$$\frac{\sigma}{\sigma_0} = 1 + f\lambda - \frac{f\lambda^2}{2} + \frac{f^2\lambda^2}{2} + \frac{f^2\lambda^3}{2}.$$
 (2.33)

Expressing λ through γ as defined in (2.25), and expanding the new expression assuming γ is small quantity, and keeping only terms to first order in f we get

$$\frac{\sigma}{\sigma_0} = 1 + f\gamma[2 - O(\gamma^2) + \cdots] + O(f^2).$$
 (2.34)

Comparing (2.34) to (2.24), we see, first that in the *weak* scattering limit, the function $G(\gamma)$ is generally given as

$$G(\gamma) = 2 + O(\gamma^2), \qquad (2.35)$$

no matter what particular shape inclusions have.

We shall come back to this when we present our results for the case of circular inclusions where we shall include f^2 terms in (2.24) using again the restrictions imposed by the reciprocity theorem.

The quantity γ defined in (2.25), for a given finite conductivity of the host σ_0 is always within the range [-1, +1]. When $\gamma = -1$ we have a hole as inclusion, i.e. $\sigma_1 = 0$. In the other limiting case, when $\gamma = +1$ we have a perfectly conducting inclusion, i.e. $\sigma_1 \to \infty$. Of course, when $\gamma = 0$, that means that there are no inclusions at all.

2.4.2 Effective Conductivity

In 2d it is convenient to change variables in the basic equation for the effective conductivity (2.3). Using the variable γ defined in (2.25) instead the variable tdefined in (2.4), and with $x' \equiv u - \frac{1}{2}$ and $h(x') \equiv g(x' + \frac{1}{2})$, we may rewrite (2.3) as

$$\frac{\sigma}{\sigma_0} = 1 + 2\gamma \int_{-\frac{1}{2}}^{\frac{1}{2}} \frac{h(x')dx'}{1 + 2\gamma x'},$$
(2.36)

where

$$\int_{\frac{1}{2}}^{\frac{1}{2}} h(x')dx' = f,$$
(2.37)

and

$$\int_{\frac{1}{2}}^{\frac{1}{2}} x'h(x')dx' = -\frac{f^2}{2}.$$
(2.38)

The first moment $\langle x' \rangle$, defined generaly in (2.8) is now given by

$$\langle x \rangle = \frac{1-f}{d} - \frac{1}{2} = -\frac{f}{2},$$
 (2.39)

for d = 2.

The spectral function is now a real positive function in the interval $-\frac{1}{2} < x < \frac{1}{2}$, and zero outside this range. The sum rules (2.37) and (2.38) are, of course, special case of (2.5) and (2.6) in 2d.

2.5 Conclusion

In the next chapters I restrict myself on two-dimensional systems, and show how one can calculate the spectral function in various cases, in the low concentration limit. For the case of circular inclusions I will show in details how one can go one step further from the low concentration limit to include pair terms in the induced dipole moment, i.e. f^2 terms in conductivity. I will explain the importance of the conformal mapping techniques for the case of polygonal and star-shaped holes. Finally, I will briefly explain the use of Fredholm equation for the general case of polygonal inclusions, give an example of the discrete resistor network in the low-concentration limit, and the results of the effective medium theory.

Chapter 3

Review of the Results for various two-dimensional systems

3.1 Introduction

The general case of the inclusions of arbitrary γ and of arbitrary shape is, of course, very difficult. Practically the only solvable problems are the circular and elliptical inclusions, and we were able to include the pair terms in the condictivity only for circular inclusions. Even simple shapes of the inclusion like an equilateral triangle make the problem too difficult if γ is arbitrary. Only for the particular values $\gamma = \pm 1$ can one relatively simply solve the problem for polygonal inclusions using conformal mapping techniques. These limiting values of γ correspond to a hole ($\gamma = -1$) or superconducting inclusion ($\gamma = 1$). If γ is arbitrary then one has to solve numerically the Fredholm equation for the induced charge around the polygonal inclusion (Hetherington & Thorpe 1992). Nevertheless, it is very useful to have solution of the problems with the holes of various shapes. This has been extensively studied by Thorpe (1992) who calculated the effective conductivity for

various shapes of inclusions with straight edges. Of course, when we fix the value of γ , as for the holes or superconducting inclusions, our goal is only to calculate the effective conductivity. The calculation of the spectral function, requires a variable γ , which in most cases is an impossible task.

We shall first present an example where the exact solution exists, which is for elliptical inclusions. Then we shall follow the work of Thorpe (1992) in presenting the various results for different shapes of the inclusions when the straight lines make their edges. For that purpose we shall introduce the conformal mapping technique, and in particular, Schwarz-Christoffel transformation which is very useful for the mapping of the regions with straight edges.

3.2 Elliptical Inclusions

A useful example that can be solved exactly is provided by the case of elliptical inclusions. The three-dimensional case of a dielectric ellipsoid in a uniform external electric field is solved in Landau & Lifshitz (1960. p. 44). If a, b and c are the semi-axes of the ellipsoid, and if the external field is along a-axis (i.e. x-axis), then the field inside the ellipsoid is given by (Landau & Lifshitz 1960, p. 44, equation (8.8)):

$$E_x^i = \frac{E_0}{1 + \left(\frac{\epsilon_1}{\epsilon_0} - 1\right) n_x},\tag{3.1}$$

where ϵ_1 and ϵ_0 are dielectric permeabilities of the inclusion and of the host, respectively, and n_x is the *depolarization coefficient* given by (Landau & Lifshitz 1960, p.26, equation (4.25))

$$n_x = \frac{1}{2}abc \int_0^\infty \frac{ds}{(s+a^2)^{3/2}(s+b^2)^{1/2}(s+c^2)^{1/2}},$$
(3.2)

where a, b and c are semi-axes of the ellipsoid. The integral in (3.2) is an elliptic integral.

The 2d limit of the ellipse we get letting $c \longrightarrow \infty$ in (3.2). The depolarization coefficient is then:

$$n_x = \frac{1}{2}ab \int_0^\infty \frac{ds}{(s+a^2)^{3/2}(s+b^2)^{1/2}}.$$
(3.3)

The integral in (3.3) can be solved in terms of elementary functions to give

$$n_x = \frac{b}{a+b},\tag{3.4}$$

where a and b are semi-major and semi-minor axes of the ellipse respectively. If the external field is along the b semi-axis, the depolarization coefficient is

$$n_y = \frac{a}{a+b}.\tag{3.5}$$

Now, we can substitute (3.4) into the expression for the field inside the elliptical inclusion (3.1) to get

$$\mathbf{E}_{x}^{i} = \frac{\mathbf{E}_{0}}{1 + \left(\frac{\epsilon_{1}}{\epsilon_{0}} - 1\right)\frac{b}{a+b}}.$$
(3.6)

We see that the field inside the elliptical (as well as ellipsoidal) inclusion is *uniform*, which makes the exact solution possible in this case.

Imagine now that we have a small concentration of elliptical inclusions, randomly distributed in the host, but all oriented along the external field E_0 . We can now consider the electric field averaged over volumes which are large compared with the scale of the inhomogeneities. The mixture is a homogeneous medium with respect to such an average field, and it can be characterised by an effective dielectric permeability ϵ . If $\overline{\mathbf{E}}$ and $\overline{\mathbf{D}}$ are the field and induction averaged in this way, then, by definition of the effective dielectric permeability ϵ :

$$\overline{\mathbf{D}}_x = \epsilon \overline{\mathbf{E}}_x, \tag{3.7}$$

where we assumed that external field is along the x-axis.

To find ϵ we write:

$$\frac{1}{V}\int (\mathbf{D}_{x} - \epsilon_{0}\mathbf{E}_{x}) \equiv \overline{\mathbf{D}}_{x} - \epsilon_{0}\overline{\mathbf{E}}_{x}.$$
(3.8)

The integrand in (3.8) is zero except within inclusions, where $\mathbf{E}_x = \mathbf{E}_x^i$, and $\mathbf{D}_x = \epsilon_1 \mathbf{E}_x^i$. Taking the *uniform* inside field \mathbf{E}_x^i , outside of the integral, we get

$$f(\epsilon_1 - \epsilon_0) \mathbf{E}_x^i = \overline{\mathbf{D}}_x - \epsilon_0 \overline{\mathbf{E}}_x, \qquad (3.9)$$

where f is the volume fraction of the inclusions $\Delta V/V$.

We have already found the field inside a single elliptical inclusion, \mathbf{E}_x^i , which is placed in an external field \mathbf{E}_0 (3.6). Here, there are many elliptical inclusions randomly dispersed in the host medium, but oriented in the same direction. This mixture gives rise to a mean field which we can consider as being the true external field with respect to each elliptical inclusion in the emulsion. Thus, using (3.6), with the mean field $\overline{\mathbf{E}}_x$ as the external field, and substituting this expression into (3.9), we get the proportionality coefficient between $\overline{\mathbf{D}}_x$ and $\overline{\mathbf{E}}_x$

$$\frac{\epsilon}{\epsilon_0} = 1 + \frac{\epsilon_1 - \epsilon_0}{b\epsilon_1 + a\epsilon_0}(a+b)f, \qquad (3.10)$$

or translated in terms of the conductivites,

$$\frac{\sigma_{||}}{\sigma_0} = 1 + \frac{\sigma_1 - \sigma_0}{b\sigma_1 + a\sigma_0} (a+b)f.$$
(3.11)

Equation (3.11) gives the effective conductivity of the mixture when the external field is parallel to the semi-major axis a of the elliptical inclusions.

If the external field is aligned with the minor semi-axis of the ellipse b, the effective conductivity is given by

$$\frac{\sigma_{\perp}}{\sigma_0} = 1 + \frac{\sigma_1 - \sigma_0}{a\sigma_1 + b\sigma_0} (a+b)f.$$
(3.12)

Formula (3.11) is given in the paper by Hetherington & Thorpe (1992), but with a and b permuted. This becomes obvious if we consider the special case when the inclusion is a hole, i.e. when $\sigma_1 = 0$ ($\gamma = -1$). Then from our formula (3.11) we get

$$\frac{\sigma_{||}}{\sigma_0} = 1 - \frac{a+b}{a}f,\tag{3.13}$$

where f is the area fraction of the ellipses and can be expressed as

$$f = ns, \tag{3.14}$$

where n is the number of ellipses per unit area, each with area $s \equiv \pi ab$. Substituting this into (3.13) and finding the same hole-limit of (3.12) we get the following two expressions

$$\frac{\sigma_{\parallel}}{\sigma_0} = 1 - n\pi b(a+b),$$

$$\frac{\sigma_{\perp}}{\sigma_0} = 1 - n\pi a(a+b),$$
(3.15)

which are correct [see equation (40) in the paper by Thorpe (1992)].

Averaging over the two orientations of the elliptical inclusions, which is equivalent to an isotropic average, we obtain the conductivity in the form (2.24)with

$$G(\gamma) = \frac{2}{1 - \left(\frac{a-b}{a+b}\right)^2 \gamma^2}.$$
(3.16)

Thus, for the elliptical inclusions, the function $G(\gamma)$ is obviously *even*, as it should be.

Thus, for *circular* inclusions, to first order in volume fraction f, we have the *exact* result

$$G(\gamma) = 2. \tag{3.17}$$

This result is correct for all γ in the case of circular inclusion, while (2.35) is correct only in the *weak* scattering limit, but for *any* shape of inclusions.
With the use of (2.36) and (2.24) we can easily calculate the *spectral* function h(x) for this problem (we use the dummy variable x here instead of x'). Thus, for the randomly oriented elliptical inclusions, to the first order in f, the spectral function is

$$h(x) = \frac{f}{2} \left[\delta \left(x - \frac{1}{2} \left(\frac{a-b}{a+b} \right) \right) + \delta \left(x + \frac{1}{2} \left(\frac{a-b}{a+b} \right) \right) \right], \quad (3.18)$$

where a and b are the major and minor semi-axes of the ellipse.

It is easy to check that the result (3.18) is compatible with the first sum rule (2.37) but NOT with the second sum rule (2.38). This is because we did not include *pair terms* representing interactions between elliptical inclusions. The inclusion of the pair terms is not straightforward and the only case when this can be done exactly is the case of circular inclusions, which I will discuss in detail later.

The function $G(\gamma)$ in (3.16) has two simple poles. In the limit of a slit (b = 0), the two poles have equal weight and are at $x = \pm \frac{1}{2}$, which are the outer limits of the allowed spectral region. In the limit when the ellipses become circles (a = b), the two poles come together to form a single pole at the origin with weight f.

In the limit of a *slit*, note that *perpendicular* conductivity (3.15) becomes

$$\frac{\sigma_{\perp}}{\sigma_0} = 1 - n\pi a^2, \tag{3.19}$$

where a is the half length of the slit. We shall get this result again later, using the conformal mapping technique.

Using (2.24) together with (3.16) we can calculate the effective conductivity in the limit of *n* randomly oriented *slits*, each of length 2*a*. The slit limit (stick-like holes) is achieved as before with $\sigma_1 = 0$ and $b \rightarrow 0$. And because $f \equiv n\pi ab$ for ellipses, the effective conductivity becomes

$$\frac{\sigma}{\sigma_0} = 1 - \frac{1}{2}n\pi a^2.$$
(3.20)

3.3 Conformal Mapping Technique

The conformal mapping technique is very powerful for solving many problems in two-dimensions which involve Laplace's equation (Churchill et al. 1974; Nehari 1952; Smythe 1939).

As we shall see it is very convenient to use the conformal mapping technique for the calculation of the effective conductivity when the inclusions are either holes ($\gamma = -1$), or perfectly conducting ($\gamma = 1$). For arbitrary γ , and for inclusions with straight edges, conformal mapping is not useful and one has to solve Fredholm integral equation for the induced charge density around the inclusion. The properties of the conformal mappings

$$w = w(z)$$
, where $z = x + iy$ $w = u + iv$, (3.21)

make them particularly useful for the solution of many problems in electrostatics, magnetostatics, heat flow, hydrodynamics, elasticity, and other fields.

First, the real and imaginary coefficients of every analytic function of a complex variable z are harmonic functions of x and y, i.e. they satisfy Laplace's equation

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} = 0 \qquad \qquad \frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} = 0. \tag{3.22}$$

Second, The Cauchy-Riemann conditions imply

$$\frac{\partial u}{\partial x}\frac{\partial v}{\partial x} + \frac{\partial u}{\partial y}\frac{\partial v}{\partial y} = (\nabla u) \cdot (\nabla v) = 0, \qquad (3.23)$$

which means that the vectors ∇u and ∇v are perpendicular to each other. These vectors are perpendicular to the curves u = constant and v = constant, respectively, so that the curves themselves are mutually perpendicular. Usually, one takes one of the functions, u or v, for the potential function, while the other one is then the stream function. The choice for the potential is arbitrary and depends on the given problem. The function w = u + iv is then a complex potential.

Third, the transformation w = w(z) is conformal, which means that the angle of intersection of two curves in the z-plane stays the same in the w-plane after the mapping. This follows from the analytic property

$$w(z) - w(z_0) \approx w'(z_0)(z - z_0),$$
 (3.24)

when z is close to z_0 . The mapping is not conformal at a singular point of the transformation, that is, a point where the function w(z) or its inverse w(z) is not analytic.

The power of conformal mapping technique is that it is usually possible to find such a transformation which maps a complicated problem in the z-plane, into a very simple problem in w-plane which can be solved by inspection. One looks for a transformation which produces much a simpler boundary configuration in the w-plane.

3.3.1 Example

As a simple, but instructive example we can use conformal mapping to find the electrostatic potential of the charged rectangular conducting boundary as in Figure 3.1.

Let assume such boundary conditions that potential ϕ equals to zero along the axes x = 0 and y = 0. The transformation



Figure 3.1: Application of the conformal mapping $w(z) = z^2$. Inside corner of conducting sheet (a) maps into the upper w half-plane (b).

.

$$w(z) = z^2 \tag{3.25}$$

transforms the inside corner in Figure 3.1(a) into the upper half of the w-plane, in Figure 3.1(b). In other words, the rectangular boundary is transformed into the real u axis in the w-plane. As before, z = x + iy, and w = u + iv. The new problem in the w-plane is now trivial. The electric field in the w-plane is uniform, and it is obvious that the solution for the complex potential Φ in the w-plane is

$$\Phi = -Cw = -Cu - \mathbf{i}Cv = \psi + \mathbf{i}\phi, \qquad (3.26)$$

from which we see that

$$\psi = -Cu \qquad \phi = -Cv, \qquad (3.27)$$

where C is a real constant We choose the imaginary part of the complex potential Φ as the potential function, and the real part is now the stream function which describes the electric field lines. It satisfies transformed boundary conditions that it is zero along the real u-axis, i.e. when v = 0.

Using (3.25) the complex potential becomes

$$\Phi = -Cz^{2},$$

= -C(x² - y² + i2xy). (3.28)

(3.29)

Thus, we now have the solution of our original potential problem in the z-plane

$$\phi = -2Cxy \tag{3.30}$$

with the constant $C = E = \tau/\epsilon_0$, where E is the homogeneous electric field in the w-plane, and τ is the charge density on the surface of the conducting lower half of the w-plane, and ϵ is the dielectric permeability.



Figure 3.2: Schwarz-Christoffel transformation maps polygonal vertices A_k onto points a_k on the real axis in the w-plane.

3.3.2 Schwarz-Christoffel Transformation

The Schwarz-Christofell transformation is very powerful when the region to be mapped has the boundaries which consist entirely of line segments (see Silvermann 1974). The obvious example is a polygon with n vertices. The Schwarz-Christoffel transformation maps the interior or exterior of a polygon in z-plane, onto the upper half of the w-plane, as shown in Figure 3.2.

For our purposes it is enough to start from the general form of the transformation and to understand its applications in different cases. Generally the Schwarz-Christroffel transformation is given by the following integral

$$z = C \int_{C_1}^{w} (w - a_1)^{\frac{\alpha_1}{\pi} - 1} (w - a_2)^{\frac{\alpha_2}{\pi} - 1} \cdots (w - a_n)^{\frac{\alpha_n}{\pi} - 1} dw + C_2,$$
(3.31)

where the real numbers a_n are the images of the polygonal vertices A_n , and α_n



Figure 3.3: Mapping of the half-strip $-\pi/2 < Re(z) < \pi/2$ onto the upper halfplane Im(w) > 0.

are the *internal* angles of the polygon, as shown in Figure 3.2. With no loss of generality we can fix the constant C_1 to zero. Namely, changing C_1 amounts only to changing C_2 . There is a theorem (see Silvermann 1974) which proves that specification of three points a_1 , a_2 , a_3 on the real *u*-axis corresponding to three vertices A_1 , A_2 , A_3 of the polygon automatically determines the remaining points a_4, \dots, a_n and the constants C and C_2 . The actual determination of a_4, \dots, a_n, C, C_2 is the main difficulty when using the Schwarz-Christoffel transformation.

It can be proved that the main formula (3.31) still holds even if one of the real points a_k is infinite, and also if one of the vertices of the polygon A_k is infinite. In those cases, one has simply to include only remaining (finite) points a_k , or vertices A_k . If one of the vertices of the polygon is at infinity, we have the case of an open region bounded by the straight segments in Figure 3.3.

The *internal* angle α_k is defined as the angle which belongs to the region mapped, which is, by convention, always the region to the left as we pass along the polygonal boundary in the given direction. In Figure 3.3 we pass along the rectangular boundary of the half-strip in the anti-clockwise direction, so that the desired mapping region is to the left. We can regard the half-strip as a "degenerate triangle" with a vertex at infinity. In practice we just have to include the two finite vertices A_1 and A_2 into transformation (3.31). We choose points a_1 and a_2 to be -1 and +1 respectively. The internal angles α_1 and α_2 are both equal to $\pi/2$. Substituting these values into (3.31) we get

$$z = C' \int_0^w (w+1)^{-1/2} (w-1)^{-1/2} dw + C_1, \qquad (3.32)$$

or

$$z = C \int_0^w \frac{dw}{\sqrt{1 - w^2}} + C_1 = C \arcsin w + C_1.$$
(3.33)

To determine the constants C and C_1 we note that the real points $-\pi/2$ and $+\pi/2$ in the z-plane, map into the real points -1 and +1 in the w-plane respectively. In other words from (3.33)

$$\begin{array}{rcl}
-\frac{\pi}{2} &=& -C\frac{\pi}{2} + C_1, \\
\frac{\pi}{2} &=& C\frac{\pi}{2} + C_1, \\
\end{array} \tag{3.34}$$

which gives $C = 1, C_1 = 0$. Thus the mapping finally becomes

$$z = \arcsin w, \tag{3.35}$$

with inverse

$$w = \sin z, \tag{3.36}$$

or

$$u + iv = \sin(x + iy),$$

= $\sin(x)\cos(iy) + \cos(x)\sin(iy),$ (3.37)
= $\sin(x)\cosh(y) + \cos(x)\sinh(y).$

Separating the real and imaginary part in the last formula we get

$$u = \sin(x)\cosh(y),$$

$$v = \cos(x)\sinh(y).$$
 (3.38)

Dividing the first equation in (3.38) by $\cosh(y)$, and the second by $\sinh(y)$, squaring and then adding them, we get

$$\frac{u^2}{\cosh^2(y)} + \frac{v^2}{\sinh^2(y)} = 1.$$
(3.39)

Similarly, dividing by sin(x) and cos(x), squaring and substracting, we get

$$\frac{u^2}{\sin^2(x)} - \frac{v^2}{\cos^2(x)} = 1.$$
(3.40)

We see that according to (3.39) the curves in the *w*-plane on which y = constantare confocal ellipses, while looking at (3.40) we see that the curves on which x = constant are confocal hyperbolas in *w*-plane. In this way, if we consider a uniform complex potential Φ in the *z*-plane

$$\Phi = -|\mathbf{E}|z,\tag{3.41}$$

depending on the choice of the potential and stream function in the z-plane, we obtain the solution for either the potential around a *charged conducting strip* of width 2 which is perpendicular to the w-plane, or the potential due to the *slot in* a conducting sheet.

Going back to the Figure 3.1 we can see that the transformation $w(z) = z^2$ is just a special case of Schwarz-Christoffel transformation. Indeed, considering the inside corner in Figure 3.1 as a degenerate polygon, and applying the equation (3.31) with $a_1 = 0$, and $\alpha_1 = \pi/2$, we get

$$z = C \int_0^w \frac{\mathrm{d}w}{\sqrt{w}} + C_1.$$
 (3.42)

Because 0 in the z-plane maps onto 0 in the w-plane, we get $C_1 = 0$. If we choose that 1 in the z-plane maps onto 1 in the w-plane, we get

$$1 = C \int_0^1 \frac{\mathrm{d}w}{\sqrt{w}},$$

$$1 = 2C,$$
(3.43)

from which we have C = 1/2. Substituting constants we found into (3.42), solving the integral, and inverting the equation, we get

$$w = z^2, \tag{3.44}$$

which is the transformation we used before.

3.4 Circular Hole

The example of the *circular* hole is very useful as a starting point in treating general case of a polygonal inclusion. It has been shown (Thorpe 1992) that the effective conductivity of a sheet containing a few randomly distributed holes can be written to the first order in f as

$$\frac{\sigma}{\sigma_0} = 1 - \alpha f + O(f^2). \tag{3.45}$$

In all cases the total induced *charge* around the hole is zero. In the case of circular-hole inclusion the induced charge only has a dipole term, that leads to a



Figure 3.4: A sketch of the flow around the circular hole in the upper half of the z-plane. The upper half of the z-plane outside the circle maps onto the upper half of the w-plane. $z = \pm a$ maps into $w = \pm 1$, and z = ia maps into w = 0.

potential that decays as r^{-1} where r is the distance from the hole. For holes of other shapes there are also an infinite number of higher-order multipole moments, but only the *dipole* moment, i.e. the dominant term in the far field, contributes to the coefficient α in (3.45) (Thorpe 1992).

Thus, our goal is to find the reduction in conductivity caused by the hole, i.e. the coefficient α . Imagine that there is a circular hole present in a conducting sheet, as shown in Figure 3.4. Due to the symmetry of the hole, it is enough to solve for the flow in the upper half of the z-plane.

The conformal mapping between the upper halves of the z- and w-planes (see Figure 3.4) is given by

$$w = \frac{a}{2} \left(\frac{z}{a} + \frac{a}{z} \right), \tag{3.46}$$

where *a* is the radius of the hole. In the *w*-plane the complex potential Φ is given as

$$\Phi = -E_0 w = -E_0 u - \mathbf{i} E_0 v = \phi + \mathbf{i} \psi, \qquad (3.47)$$

where E_0 is the electric field far from the hole. Substituting the conformal mapping (3.46) in (3.47) we get

$$\Phi = -\frac{E_0}{2} z \left(1 + \frac{a^2}{z^2} \right).$$
 (3.48)

The actual potential ϕ is taken here as the real part of Φ , and noting that as before $z = x + iy = r \cos \theta + ir \sin \theta$, the potential ϕ is given as

$$\phi = -\frac{E_0}{2} r \cos \theta \left(1 + \frac{a^2}{r^2} \right),$$

$$\phi = -E'_0 r \cos \theta \left(1 + \frac{a^2}{r^2} \right),$$
(3.49)

where E'_0 is the new scaling factor for the electric field at infinity. Using $E_r = -\partial \phi / \partial r$ we can calculate the radial component of the electric field in the z-plane which is

$$E_r = E'_0 \cos \theta \left(1 - \frac{{u^2}}{r^2} \right). \tag{3.50}$$

There is obviously no normal current flow into the hole, and because of symmetry there is also no normal current flow into the x-axis of the z-plane. These simple Neumann boundary conditions (Churchill *et al.* 1974) make this problem straightforward to solve. We see from (3.50) that

$$E_{r=a} = 0,$$
 (3.51)

as it should be at the circular boundary.

We shall find the effective conductivity of the system by calculating the change in the *Joule heating* upon the introduction of the hole (see Thorpe 1992). Imagine a large concentric circle of radius *R* drawn around the circular hole. First,

i i ٥V wb. ł þ W. 15 ť . if there is no hole in the system the potential at any point on that circle is given by

$$\phi_{\text{no hole}} = -E_0 R \cos \theta, \qquad (3.52)$$

while in the presence of the hole, using (3.49) with r = R, the potential is

$$\phi_{\text{with hole}} = -E'_0 R \cos \theta \left(1 + \frac{a^2}{R^2}\right).$$
 (3.53)

Assuming that far from the hole potential is fixed, no matter whether the hole is present or not, we can equate (3.52) and (3.53) to get

$$E_0 = E'_0(1+f), (3.54)$$

where

$$f = \frac{\pi a^2}{\pi R^2} \tag{3.55}$$

is the area fraction of the hole.

Consider the volume V inside the large circle with radius R, but excluding the volume of the circular inclusion itself. The Joule heating \mathcal{J} within that volume is given by

$$\mathcal{J} = \int_{V} (\mathbf{j} \cdot \mathbf{E}) dV, \qquad (3.56)$$

where **j** is the current density, and **E** is the electric field, integrated over the whole volume. Using the known relations $\mathbf{E} = -\nabla \phi$, $\nabla \cdot \mathbf{j} = 0$, and

$$\nabla(\mathbf{j}\phi) = \phi\nabla\mathbf{j} + \mathbf{j}\nabla\phi, \qquad (3.57)$$

we get for Joule heating

$$\mathcal{J} = -\int_{V} \nabla \cdot (\mathbf{j}\phi) dV. \tag{3.58}$$

Transforming the volume integral into a surface one we finally get

$$\mathcal{J} = -\int_{S} \phi(\mathbf{j} \cdot \mathbf{n}) dS, \qquad (3.59)$$

whe flow the Can wŁ 3. 'n Ba ír W Q where the integration goes over the outer surface only because there is no current flow into the inner surface, and \mathbf{n} is the unit normal on the surface element on the outer surface.

Now, the *change* in the Joule heating upon the introduction of the hole can be written as

$$\delta \mathcal{J} = -\int_{S} \phi(\delta \mathbf{j} \cdot \mathbf{n}) dS.$$
(3.60)

Using $\mathbf{j} = \sigma_0 \mathbf{E}$, and noticing that $\delta \mathbf{j} \cdot \mathbf{n} = \sigma_0 \Delta E_r$, with the help of (3.50) we get

$$\delta \mathbf{j} \cdot \mathbf{n} = -2\sigma E_0' f \cos \theta, \qquad (3.61)$$

where σ_0 is the conductivity of the host. Substituting (3.61) into (3.60), using (3.52) and performing the integration, we get the final expression for the *change* in the Joule heating upon the introduction of the hole

$$\delta \mathcal{J} = -2E_0 E'_0 \sigma_0 \pi a^2. \tag{3.62}$$

Balancing the energies we get

$$\pi R^2 \sigma E_0^2 = \pi R^2 \sigma_0 E_0^2 - 2E_0 E_0' \sigma_0 a^2, \qquad (3.63)$$

from which using (3.54) we get

$$\frac{\sigma}{\sigma_0} = 1 - 2n\pi a^2 = 1 - 2f, \tag{3.64}$$

where n is the number of inclusions per unit area.

The factor a^2 in (3.64) comes from the coefficient in the *dipole term* 1/z of the conformal mapping in (3.48).

Now, if we assume that the conformal mapping is

$$z = C\left[w + \frac{A}{w} + O\left(\frac{1}{w^2}\right)\right],\tag{3.65}$$

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then inverting (3.65)

$$w = \frac{z}{C} \left[1 - \frac{AC^2}{z^2} + OO\left(\frac{1}{z^3}\right) \right], \qquad (3.66)$$

and comparing (3.66) with (3.48), we see that, in general, instead of having a^2 in the expression for conductivity (3.64) we have the product $-AC^2$. Thus the general result for the conductivity is

$$\frac{\sigma}{\sigma_0} = 1 + 2n\pi AC^2 + O(n^2). \tag{3.67}$$

This simple result is possible only because the higher order multipole terms integrate out to zero, and only the dipole term contributes to the conductivity (Thorpe 1992). The formulas (3.65) and (3.67) are very useful for calculating the effective conductivity when polygonal holes are present.

3.5 Slit

We shall apply the Schwarz-Christoffel transformation (3.31 to the slit that lies in the z-plane as shown in Figure 3.5, and use the result (3.67) of the previous section to find the effective conductivity when the current flow is perpendicular to the slit. The slit is of the length 2a and only the upper half of it is shown in Figure 3.5. Due to the symmetry it is enough to solve for the flow in the upper half of the z-plane. The current flow is perpendicular to the axis of the slit.

Applying the Schawrz-Christoffel transformation (3.31) we get

$$z = C \int_{C_1}^{w} (w+1)^{\frac{\pi/2}{\pi}-1} (w)^{\frac{2\pi}{\pi}-1} (w-1)^{\frac{\pi/2}{\pi}-1} dw + C_2,$$

= $C \int_{C_1}^{w} \frac{w}{\sqrt{w^2-1}} dw + C_2,$
= $C \sqrt{w^2-1} + C_2.$ (3.68)



Figure 3.5: Mapping the upper half of the z-plane with a slit onto the upper half of the w-plane.

If the point w = 1 in the w-plane corresponds to the point z = 0 in the z-plane, we see from (3.68) that $C_2 = 0$. From the other side, if the point *ia* in the z-plane maps into w = 0, it follows that C = a, and the mapping becomes

$$z = a\sqrt{w^2 - 1}.$$
 (3.69)

Expanding the mapping (3.68) for large w we get

$$z = C\left[w + \frac{A}{w} + O\left(\frac{1}{w^2}\right)\right].$$
(3.70)

Comparing (3.68) with (3.67), and using C = a, we get for the conductivity

$$\frac{\sigma_{\perp}}{\sigma_0} = 1 - n\pi a^2, \tag{3.71}$$

which is the same result as (3.19) we got before as a limit from the solution for the elliptical inclusion.

3.6 Effective Conductivity for Polygonal Holes

The effective conductivity for the systems with polygonal holes was studied by Thorpe (1992), and in this section we will present the main results of this work. For regular n-gons it is not necessary to do any rotational averaging because the symmetry of regular n-gon is high enough that the conductivity tensor reduces to a constant σ times the unit tensor. In all cases there is a rotation axis of order 3 or higher, which is the necessary condition for isotropy. In the case of anisotropic inclusions like diamond-shaped or rectangular, one has to calculate separately the parallel and the perpendicular effective conductivity, and then to do the rotational averaging. In all cases there is a reflection plane and it is centered on the x-axis, so that it is enough to solve for the flow in the upper half-plane.



Figure 3.6: The region outside the upper half of an equilateral triangle in the zplane maps into the upper half of the w-plane. The three vertices of the triangle, $0, a\sqrt{3}/2 + ia/2, a\sqrt{3}/2$ map into the points 0, 1, and k (k > 1) in the w-plane, respectively.

3.6.1 Equilateral Triangle

The equilateral triangle of side a in the z-plane is positioned as shown in Figure 3.6.

Using the Schwarz-Christofell transformation (3.31) for this triangle, the conformal mapping becomes

$$z = C \int_{C_1}^{w} \frac{(w-1)^{2/3}}{w^{1/6}(w-k)^{1/2}} dw + C_2.$$
(3.72)

Equating the distances between corresponding points in z- and w-planes we can

00 E :e Ś W 0 S tł t(• obtain the relevant constants k and C in (3.72).

$$a = 2C \int_{1}^{k} \frac{(w-1)^{2/3}}{w^{1/6}(k-w)^{1/2}} dw = C \int_{0}^{1} \frac{(1-w)^{2/3}}{w^{1/6}(k-w)^{1/2}} dw.$$
(3.73)

Equation (3.73) is an equation for k. Calculating the integrals on both sides (in terms of Beta and Hypergeometric functions) gives k = 4/3, and the right-hand side of (3.73) gives

$$a = C \frac{8\pi^2}{3\sqrt{3}\Gamma^3\left(\frac{1}{3}\right)},\tag{3.74}$$

where $\Gamma(\frac{1}{3})$ is a gamma function (Abramowitz & Stegun 1970). Expanding the conformal mapping (3.72) for large w we get

$$z = C\left[w + \left(\frac{1}{2}k - \frac{2}{3}\right)\ln w - \frac{\frac{3}{8}k^2 - \frac{1}{3}k - \frac{1}{9}}{w} + O\left(\frac{1}{2}w^2\right) + \text{const.}\right].$$
 (3.75)

Substituting k = 4/3 in (3.75) the term in $\ln w$ vanishes as it should, because the net induced charge around the inclusion is zero. Comparing the expansion (3.75) with the general form of expansion (3.65) gives $A = -\frac{1}{9}$. Using this result together with (3.74) and substituting the obtained expressions for A and C into the general form for conductivity (3.67), we get

$$\frac{\sigma}{\sigma_0} = 1 - \alpha_3 f = 1 - \frac{\sqrt{3}\Gamma^6\left(\frac{1}{3}\right)}{8\pi^3} f = 1 - (2.5811...)f, \qquad (3.76)$$

where the area fraction f is here $f = \frac{1}{4}n\sqrt{3}a^2$ (Thorpe 1992).

3.6.2 Square

The upper half of the square is shown in Figure 3.7. The reflection plane is again positioned along the *x*-axis. The three vertices of the square in the *z*-plane, $-\frac{a}{\sqrt{2}}$, 0 and $\frac{a}{\sqrt{2}}$ map into the points -1, 0 and 1 in the *w*-plane, respectively. Schwarz-Christofell transformation (3.31) gives the following conformal mapping

$$z = C \int_{C_1}^{w} \left(\frac{w^2}{w^2 - 1}\right)^{\frac{1}{4}} dw + C_2.$$
 (3.77)



Figure 3.7: The region outside the upper half of a square in the z-plane maps into the upper half of the w-plane. The three vertices of the square, $-a/\sqrt{2}$, 0, and $a/\sqrt{2}$, map into the points -1, 0, and 1 in the w-plane, respectively.

As before, equating the distances between the corresponding points in zand w-plane we get

$$a = C \int_0^1 \left(\frac{w^2}{1 - w^2}\right)^{\frac{1}{4}} dw, \qquad (3.78)$$

and solving the integral in (3.78) we get the constant C

$$a = C \frac{2\pi^{\frac{3}{2}}}{\Gamma^2\left(\frac{1}{4}\right)}.$$
 (3.79)

Expanding the conformal mapping (3.77) for large w leads to

$$z = C\left[w - \frac{1}{4w} + O\left(\frac{1}{w^2}\right)\right] + \text{const.},\tag{3.80}$$

which gives for the dipole term coefficient $A = -\frac{1}{4}$. Using this and (3.79), and then comparing (3.80) with (3.67) we get (Thorpe 1992)

$$\frac{\sigma}{\sigma_0} = 1 - \alpha_4 f = 1 - \frac{\Gamma^4\left(\frac{1}{4}\right)}{8\pi^2} f = 1 - (2.1844...)f, \qquad (3.81)$$

with $f = na^2$.

Generally, for a regular N-gon, the conductivity can be written as

$$\frac{\sigma}{\sigma_0} = 1 - \alpha_N f + O(f^2), \qquad (3.82)$$

where we want to calculate α_n .

3.6.3 Regular Polygon

In the case of a regular N-gon it is more convenient to use a different mapping than in the previous paragraphs if we want to find the general expression for α_N in (3.82). We use the transformation (Thorpe 1992) which maps the exterior of a regular *n*-gon in the *z*-plane into the exterior of a unit circle in the *w*-plane

] u E W. 3 ця р(Ţ Ľ; Tł θq (à) fur che be (Muskhelishvili 1963). The N vertices of the N-gon map into N points on the unit circle at the N roots of unity $exp(2\pi i k/N)$. The mapping is

$$z = C \int_{C_1}^{w} \left(1 - \frac{1}{w^2} \right)^{\frac{2}{N}} dw + C_2.$$
 (3.83)

Expanding the mapping (3.83) for large w gives

$$z = Cw\left(1 + \frac{2}{N(N-1)w^{N}} + \frac{N-2}{N^{2}(N-1)w^{2N}} + \cdots\right) + \text{const.},\qquad(3.84)$$

where C = 1 if potential is to be the same far from the N-gon and the circle. There is no dipole term in (3.84), so one cannot use (3.67) here. Instead, one should use the mapping (3.83) itself. Equating the distance between the corresponding points (3.83) gives for the side *a* of the N-gon

$$a = \int_0^{\pi} (2\sin\theta)^{\frac{2}{N}} d\theta = 2^{\frac{4}{N}} \frac{\Gamma^2 \left(\frac{1}{2} + \frac{1}{N}\right)}{\Gamma \left(1 + \frac{2}{N}\right)}.$$
 (3.85)

The ratio of the area of the N-gon to the area of the circle is

$$\frac{a^2}{4\pi}\cot\left(\frac{\pi}{N}\right).\tag{3.86}$$

Using the expression for the conductivity for the circle (3.45) and comparing with (3.82) (f = ns) we find that the coefficient α_N is just twice of the inverse of (3.86)

$$\alpha_N = \frac{\tan\left(\frac{\pi}{N}\right)}{2\pi N} \frac{\Gamma^4\left(\frac{1}{N}\right)}{\Gamma^2\left(\frac{2}{N}\right)}.$$
(3.87)

The general result for α_N (3.87), of course, reproduces the previous results for the equilateral triangle (N = 3), and for the square (N = 4), which can be seen by calculating the right-hand side of (3.87) using the relations between the gamma functions with different arguments (Abramowitz & Stegun 1970). It can be also checked that in the limit as $N \to \infty$, the equation (3.87) gives $\alpha_{\infty} = 2$, as it must be for the circle.

Tab J C

shape	n	$lpha_N$
triangle	3	2.5811
square	4	2.1884
pentagon	5	2.0878
hexagon	6	2.0486
septagon	7	2.0298
octagon	8	2.0197
	9	2.0137
	10	2.0099
	11	2.0074
	12	2.0057
:	:	•
circle	∞	2

Table 3.1: Showing the exact results for the coefficient α_N in the conductivity $\sigma/\sigma_0 = 1 - \alpha_N f + O(f^2)$ for various regular polygonal holes from (3.87).

Summary of the results for the effective conductivity in the case of *regular* polygonal *holes* given generally by formula (3.82) with α_N given by (3.87), is shown in the Table 3.1 (Thorpe 1992).

3.6.4 Diamond Shape

As an example of the *anisotropic* holes we shall present here results for the inclusion of diamond shape. In the similar manner, finding the appropriate conformal mapping, one can solve the problem of the rectangular hole (Thorpe 1992).

In the case of a diamond shaped inclusion, one has to treat separately the



Figure 3.8: The region outside the upper half of a diamond in the z-plane maps into the upper half of the w-plane. The three vertices of the diamond, -a, ib, and a, map into the points -1, 0, and 1 in the w-plane, respectively.

two limiting orientations of the diamond. If the longer diagonal of the diamond is 2a, and the shorter 2b, then we first treat the case when the longer diagonal is aligned with x-axis, i.e. when the current flow is parallel to the longer dimension of diamond. When the current flow is perpendicular to the longer dimension, we can get the result by interchanging a and b in the result for parallel orientation. The parallel orientation of diamond is shown in Figure 3.8.

Writing the Schwarz-Christoffel transformation for this case we get the conformal mapping as

$$z = C \int_{C_1}^{w} \left(\frac{w^2}{w^2 - 1}\right)^{\frac{y}{\pi}} dw + C_2, \qquad (3.88)$$

where the angle θ is given by $\tan \theta = b/a$. The only relevant constant C is obtained

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by equating the distances between corresponding points to get

$$\sqrt{a^2 + b^2} = C \int_0^1 \left(\frac{w^2}{1 - w^2}\right)^{\frac{\theta}{\pi}} dw,$$

= $C \frac{\Gamma\left(1 - \frac{1}{\pi}\arctan\left(\frac{a}{b}\right)\right), \Gamma\left(1 - \frac{1}{\pi}\arctan\left(\frac{b}{a}\right)\right)}{\sqrt{\pi}}.$ (3.89)

The dipole term coefficient can be found as before by expanding the mapping (3.88) for large w

$$z = C\left(w - \frac{\theta}{\pi w} + O\left(\frac{1}{w^2}\right) + \text{const.}\right), \qquad (3.90)$$

which gives $A = -\theta/\pi$. Combining these results and using (3.67) leads to the expression for the effective conductivity

$$\frac{\sigma_{\parallel}}{\sigma_0} = 1 - fF_{\parallel},\tag{3.91}$$

where

$$F_{||} = \frac{\pi(a/b + b/a) \arctan(b/a)}{\Gamma^2(1 - (1/\pi) \arctan(a/b))\Gamma^2(1 - (1/\pi) \arctan(b/a))},$$
(3.92)

and the area fraction is f = 2nab where *n* is the number of inclusion per unit area. When the diamond is oriented perpendicular to the *x*-axis, the conductivity σ_{\perp} can be obtained by interchanging *a* and *b* in (3.92).

The results for the case of rectangular inclusions are also obtained by Thorpe (1992). In all cases the results obtained for holes can be also applied to superconducting inclusions using the reciprocity theorem (Keller 1964). The reciprocal problems for all examples in this section have the hole replaced by a superconducting inclusion, and the equipotential lines become the current flow lines. The results for the reciprocal problem are the same, except that the conductivity is replaced by the resistivity and the sample is rotated by $\pi/2$. This rotation matters only for the anisotropic inclusions like diamond, and there one should

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Figure 3.9: The geometry of an (n = 3) star. The shape is determined by the ratio of the radii of the inner circle b to outer circle a (Thorpe 1992).

interchange the subscripts for parallel \parallel and perpendicular \perp in the expressions for conductivity.

3.6.5 Star-shaped Holes

The problem of a N-pointed star-shaped hole was solved by Hetherington & Thorpe (1992). An example of the 3-pointed star is shown in Figure 3.9.

The conformal mapping of the star onto the unit circle, such that Npoints around the outer circle of radius a and N points around the inner circle of radius b, are mapped onto the 2N points uniformly spaced around the unit circle in the w-plane, is

$$z = C \int_{C_1}^{w} \left(\frac{w^N - 1}{w^N}\right)^{1 - 2\theta/\pi} \left(\frac{w^N}{w^N + 1}\right)^{1 - 2\theta/\pi - 2/N} dw + C_2, \qquad (3.93)$$

whe Th , poi T g1; lr 5 V f where

$$\tan \theta = \frac{b \sin(\pi/N)}{a - b \cos(\pi/N)}.$$
(3.94)

The cute angle of the star is 2θ . Equating the distance between corresponding points we get

$$b\sin\left(\frac{\pi}{N}\right) = 2^{2/n} \pi \frac{\Gamma\left(\frac{1}{N} + \theta\pi\right)}{\Gamma\left(\frac{1}{N}\right)\Gamma\left(\frac{\theta}{\pi}\right)}.$$
(3.95)

The area of the star is

$$\frac{Nb^2 \sin(\pi/N) \sin(\pi/N+\theta)}{\sin\theta}$$
(3.96)

and comparing with (3.82) we get

$$\alpha_N = 2\left(\frac{\text{area circle}}{\text{area star}}\right) = \frac{2\sin(\pi/N)\sin\theta}{2^{4/N}N\pi\sin(\pi/N+\theta)}.$$
(3.97)

In terms of the number of inclusions n = f/area star, the conductivity is given by

$$\frac{\sigma}{\sigma_0} = 1 - 2\pi n \left[\frac{a\Gamma(1 - 1/n - \theta/\pi)}{2^{2/n}\Gamma(1 - 1/n)\Gamma(1 - \theta/\pi)} \right]^2.$$
(3.98)

When $\theta = 0$, the star reduces to *n* sticks which are pointing outwards radially from a central point. The conductivity (3.98) reduces to

$$\frac{\sigma}{\sigma_0} = 1 - \frac{2\pi a^2 N}{2^{\frac{4}{n}}}.$$
 (3.99)

When n = 2 the result (3.99) reduces to the already obtained result (3.20) for a dilute collection of randomly oriented sticks, each of length 2a (Hetherington and Thorpe 1992; Thorpe 1992).
3.7 General Case of Inclusions with Sharp Corners

Results for polygonal inclusions presented in previous sections were possible to obtain only for the limiting case when inclusions are either holes ($\gamma = -1$) or perfectly conducting ($\gamma = +1$). In this case only it is possible to use the conformal mapping technique to solve the problem (Thorpe 1992).

In order to get results for a general polygonal inclusion (arbitrary γ), it is necessary to use a numerical method. The induced charge $\rho(s)$ on the boundary of the polygon is given by the Fredholm equation (Hetherington & Thorpe 1992)

$$\rho(s) = 2\gamma \hat{\mathbf{n}}(s) \cdot \mathbf{E}_0 + \frac{\gamma}{2\pi} \oint \hat{\mathbf{n}}(s) \cdot \nabla_r \ln |\mathbf{r}(s) - \mathbf{r}'(s')| \rho(s') ds', \qquad (3.100)$$

where the integration is around the polygonal boundary. The vector $\mathbf{r}(s)$ goes to a point s on the polygonal boundary, which has a unit normal $\hat{\mathbf{n}}(s)$, and s measures the distance around the perimeter to the point r. The external applied field is \mathbf{E}_0 and the logarithmic term is the 2d Coulomb propagator. Equation (3.100) determines the induced charge and hence the dipole moment from which we can find $G(\gamma)$ in the expression for conductivity (2.24). In solving (3.100), great care must be taken at the corners of the polygons where the current density is singular (see Hetherington & Thorpe 1992). It has been found by Hetherington and Thorpe (1992) that the results for regular polygonal inclusions with arbitrary γ can be well fit by the interpolation formula

$$G(\gamma) = \frac{2}{\sqrt{1 - c^2 \gamma^2}},$$
 (3.101)

where the constant

$$c = \sqrt{1 - \frac{4}{\alpha_N^2}} \tag{3.102}$$

is chosen to get the correct result at $\gamma = \pm 1$. The interpolation formula (3.101) was found to be quite accurate for all real $\gamma^2 \leq 1$, which covers the region where both the conductivities σ_0 and σ_1 are real and positive. The form (3.101) is only an interpolation formula and it would be misleading to conclude that there are branch cuts at $\gamma = \pm 1/c$ (which corresponds to $x = \pm c/2 = \pm 0.316$), which are outside the region for which (3.101) is valid. Hetherington and Thorpe attempted to find the spectral function directly by examining the simple poles that occur on the real axis in the complex γ plane when the charge density in (3.100) is discretised. The result for the equilateral triangle is shown in Figure 3.10. It consists of 64 poles on the real x-axis that have been broadened by convolution with a Lorentzian (Figure 3.10 solid curve). It can be seen that the spectral function h(x) is even as expected. When the interpolation formula (3.101) is used to derive the spectral function a similar curve, broadened with a Lorentzian, is obtained (Figure 3.10). The similarity of these two results gives some confidence in the general shape of the spectral function. This shape is very different from the result for the ellipse, and is broad, rather than having one or two delta functions.

If the same procedure was followed for regular polygons, it is reasonable to expect the spectral function to become narrower, with the spectral weight confined to $|x| \leq 1/N$, as the number of sides N increases, and therefore approaching a delta function at the origin in the circle limit $(N \to \infty)$. The spectral function is determined by the spectrum of the operator

$$\hat{\mathbf{n}}(s) \cdot \nabla \ln | \mathbf{r}(s) - \mathbf{r}'(s') |.$$
(3.103)

The only parameter in this operator is the boundary $\mathbf{r}(s)$. A method of going directly from $\mathbf{r}(s)$ to the spectral function would be most attractive. Furthermore, more work is also needed on the nature of the singularities at the edges of the



Figure 3.10: Spectral function for triangular inclusions in the dilute limit. The area under the curves is f but is shown as unity. The solid curve is from the numerical solution of the integral equation (3.100). The dashed lines are speculated spectral limits at $x = \pm 1/3$. The dot-dash curve is the spectral function derived from the interpolation formula (3.101), which has band edges at $\pm c$ where c = 0.316. Both results are broadened with a Lorentzian with a full width of 0.06 at half the maximum height (Thorpe, Djordjević and Hetherington 1994).

spectral function which is unknown at present.

3.8 Random Resistor Network

All our previous discussion has referred to the continuum problem. Random resistor network is an example of a *discrete* random media for which one can apply the general method developed in Chapter 2, to calculate the effective conductivity and the spectral function in the low concentration limit. Basic equations for the effective conductivity and spectral function (2.24)-(2.3) still hold, if the area fraction f is now the fraction of the resistors (conductances) that are present in the network (Foster 1924; Straley 1979). This approach has been criticized by Straley (1979) as not being much of use around percolation, which occurs for larger concentration of conductances f. Recently, Thorpe and coworkers (1994) calculated the spectral function for the random resistor network in the low concentration limit. They also obtained the result for effective medium theory, for the square net and for the whole range of concentration f. Finally, Day and Thorpe (1996) presented a derivation of the spectral function which identifies it as a density of states. They did direct numerical calculations of the spectral function of two dimensional square lattice for the whole range of concentartion f, applying the $Y - \Delta$ transformation as an algorithm to obtain the effective conductivity of the random network. The analytic expressions for the first five moments of the spectral function are also obtained.

The discrete random system in question, say the square lattice, can be created in two different ways, i.e. with two different distribution geometries. In the first geometry each bond is randomly assigned a conductance σ_0 with probability 1 - f, and a conductance σ_1 with the probability f. In this way the random system is created by random bond substitution. In the second geometry, which is referred to as random site substitution, each site is assigned label A with probability 1 - f and label B with probability f. If the two neighboring sites are labelled differently, i.e. if they create bond A - B, then half of that bond, which is adjacent to site A, is assigned a conductance σ_0 , while the other half, which is adjacent to B, is assigned a conductance σ_1 . Thus the bond A - B consists of the two conductances σ_0 and σ_1 connected in series. Thus the conductance of the A - B bond is $\sigma_b = \sigma_0 \sigma_1/(\sigma_0 + \sigma_1)$.

It is convenient in this section to use the spectral function which is confined in the interval [0,1] instead in the symmetric interval [-1/2, +1/2]. The effective conductivity is then given by (2.3) which we shall rewrite here in the more explicit form

$$\frac{\sigma(t,f)}{\sigma_0} = 1 - \int_0^1 \frac{h(x,f)dx}{t-x}.$$
 (3.104)

The spectral function h(x, f) (we show here the explicit dependence of the spectral function on concentration f) can be calculated by

$$h(t,f) = \frac{1}{\pi} \lim_{\epsilon \to 0} Im \left[\frac{\sigma(t + i\epsilon, f)}{\sigma_0} \right], \qquad (3.105)$$

where t and ϵ are real, and the variable t is given as before by (2.4). Thus, to obtain the spectral function one has to calculate the effective conductivity for complex t.

Unlike in the continuum problem, here for a given lattice substitution type, the geometry is completely determined by the fraction of the second phase f, and we have the *exchange relation*

$$\sigma(\sigma_0, \sigma_1, f) = \sigma(\sigma_1, \sigma_0, 1 - f). \tag{3.106}$$

which connects the conductivities of the original problem and the one where the

roles of the host and inclusions are inverted. Similarly, it has been shown (Day and Thorpe 1996) that the corresponding spectral functions are connected by the following relation

$$th(t, f) = (1 - t)h(1 - t, 1 - f) + W(f)t\delta(t),$$
(3.107)

where the weight of the delta function W(f) is

$$W(f) = 1 - \int_0^1 \frac{h(x, 1-f)dx}{1-x}.$$
(3.108)

The identity (3.107) applies generally to any uncorrelated random lattice in any dimension, and also to infinitely interchangeable cellular materials, but it does *not* apply to most continuum problems where the geometry of the host is very different from the geometry of the inclusion.

From the other side, for the *electrically isotropic* lattice the reciprocity relation (Straley 1977) is

$$\sigma(\sigma_0, \sigma_1, L)\sigma(\sigma_1, \sigma_0, D) = \sigma_0 \sigma_1, \qquad (3.109)$$

where L denotes the original lattice and D its dual lattice. The dual lattice is constructed by placing a bond with conductance σ_0 , σ_1 perpendicular to every bond of the lattice L with conductance σ_1 , σ_0 . The 2d square net with random bond substitution (dual lattice is not relevant for the site substitution when there are three types of bonds in the system), is electrically isotropic and self dual and (3.109) becomes

$$\sigma(\sigma_0, \sigma_1)\sigma(\sigma_1, \sigma_0) = \sigma_0 \sigma_1. \tag{3.110}$$

Combining (3.106) and (3.110) it follows

$$\sigma(\sigma_0, \sigma_1, f)\sigma(\sigma_1, \sigma_0, 1 - f) = \sigma_0\sigma_1, \qquad (3.111)$$

or in terms of the variable t

$$\frac{\sigma(t,f)}{\sigma_0}\frac{\sigma(t,1-f)}{\sigma_0} = \frac{t-1}{t}.$$
(3.112)

At percolation when $f = f_c = 1/2$, (3.111) and (3.112) reduce to the following respective equations

$$\sigma(\sigma_0, \sigma_1) = \sqrt{\sigma_0 \sigma_1} \tag{3.113}$$

and

$$\frac{\sigma(t, 1/2)}{\sigma_0} = \sqrt{\frac{t-1}{t}}.$$
 (3.114)

From this one can extract the *exact* result for the spectral function at percolation

$$h(t, 1/2) = \frac{1}{\pi} \sqrt{\frac{1-t}{t}}.$$
(3.115)

3.8.1 Dilute Limit

It has been shown (Thorpe and Tang 1987) that in the low concentration limit, $f \ll 1$, the effective conductivity can be written as

$$\sigma(\sigma_0, \sigma_1, f) = \sigma_0 + f \frac{(\sigma_1 - \sigma_0)}{f_I \left(\frac{\sigma_1}{\sigma_0} - 1\right) + 1},$$
(3.116)

where f_I is determined from the initial slope of the effective conductivity when $\sigma_1 = 0$ and depends on the lattice. For 2d square net *bond* substitution $f_I = \frac{1}{2}$, while for *site* substitution $f_I = 1 - \frac{1}{\pi}$. The equation (3.116) holds for both bond and site substitution, if the site substitution is defined as described above. Note that other definitions of the site substitution are possible (Thorpe and Tang 1987; Thorpe, Djordjević and Hetherington 1994) where the site defect introduces all bonds adjacent to it to have a conductivity σ_1 , if the host bonds have a conductivity ity σ_0 . In this case equation (3.116) holds only for bond substitution, and one has

to write another equation for the site substitution [see equation (6.3) in Thorpe, Djordjević and Hetherington 1994].

Using the t variable equation (3.116) can be rewritten as

$$\frac{\sigma(t,f)}{\sigma_0} = 1 - \frac{f}{t - f_I},$$
(3.117)

from which using (3.105) the spectral function is obtained

$$h(t, f) = f\delta(t - f_I).$$
 (3.118)

In the high concentration limit, $1 - f \ll 1$, we can invert the roles of the host and the inclusions, and write similarly

$$\sigma(\sigma_1, \sigma_0, 1 - f) = \sigma_1 + (1 - f) \frac{(\sigma_0 - \sigma_1)}{f_I \left(\frac{\sigma_0}{\sigma_1} - 1\right) + 1}$$
(3.119)

and the effective conductivity normalized again by σ_0 is given by

$$\frac{\sigma(t,f)}{\sigma_0} = 1 - \frac{f_I(1-f)}{(1-f_I)(1-t-f_I)} - \frac{(f-f_I)}{(1-f_I)t},$$
(3.120)

which gives for the spectral function

$$h(t,f) = \frac{f_I(1-f)}{(1-f_I)}\delta(1-t-f_I) + \frac{(f-f_I)}{(1-f_I)}\delta(t).$$
(3.121)

The equation (3.121) is an example of the general exchange relation between the spectral functions (3.107).

The poles of the normalized effective conductivity correspond to the resonances of the network (Day and Thorpe 1996). This can be physically understood by considering a network of pure capacitors capacitors $\sigma_0 = i\omega C$ and inductors $\sigma_1 = 1/(i\omega L)$. Then $q = \sigma_1/\sigma_0$ is real and negative, and the effective conductivity will diverge at the resonance frequencies of the system. If either σ_0 or σ_1 has any resistive component (a real part), q will have an imaginary component and the system will be damped and the effective conductivity will not diverge. So the singularities are confined to q real and negative. In this case the variable $t = \sigma_0/(\sigma_0 - \sigma_1)$ is real too. Nevertheless, to obtain the spectral function h(t, f) one has to calculate the effective conductivity for *complex t*, by adding a small imaginary part ϵ to it (Day and Thorpe 1996).

3.8.2 Effective Medium Theory

The effective medium theory for the conductivity can be constructed from the results for the dilute limit in the usual way (Briggeman 1935; Day and Thorpe 1996). Substituting the effective conductivity σ instead of σ_0 in (3.116) and summing over the all components in the system, we get the self-consistent effective medium theory equation

$$\sum_{n} \frac{f_n(\sigma_n - \sigma)}{(1 - f_I)\sigma + f_I\sigma_n} = 0, \qquad (3.122)$$

from which, in the case of only two components in the system, σ_0 and σ_1 , we get

$$f\frac{(\sigma_1-\sigma)}{1+f_I\left(\frac{\sigma_1}{\sigma}-1\right)}+(1-f)\frac{(\sigma_0-\sigma)}{1+f_I\left(\frac{\sigma_0}{\sigma}-1\right)}=0.$$
(3.123)

This leads to a quadratic equation for the normalized effective conductivity σ/σ_0 from which one can extract the general form of the spectral function (see Day and Thorpe 1996 for details).

For random *bond* substitution and the square net $f_I = \frac{1}{2}$ the spectral function is given by (Day and Thorpe 1996)

$$h(t,f) = \frac{\sqrt{f(1-f) - (t-\frac{1}{2})^2}}{t\pi} , \text{ for } 0 \le f(1-f) - (s-1/2)^2$$

= 0 , otherwise (3.124)

In the effective medium theory the percolation threshold is $f_c = 1 - f_I$, but for random bond substitution this coincides with the exact percolation threshold, $f_c = \frac{1}{2}$. The equation (3.124) becomes

$$h(t, f_c) = \frac{1}{\pi} \sqrt{\frac{1-t}{t}}$$
(3.125)

which is the same expression as the *exact* result (3.114) obtained before. This suggests that effective medium theory might be a useful guide at higher concentrations for deducing the overall form of the spectral function. An example of the system which obeys formulas (3.113), (3.114) and (3.115), is an infinite chess board with an equal number of black and white squares. We note, that all formulas given here in the dilute limit and in the effective medium theory are equivalent to the corresponding formulas for bond substitution in Thorpe, Djordjević and Hetherington (1994), which can be easily seen if we introduce the variable $\gamma = (\sigma_1 - \sigma_0)/(\sigma_1 + \sigma_0)$ instead the variable $t = \sigma_0/(\sigma_0 - \sigma_1)$, and then express all results in term of the new variable x defined as $x = -\frac{1}{2\gamma}$. Thus, for example, one can rewrite formula (3.124) in the following form

$$h(x, f) = \frac{2\sqrt{f(1-f)-x^2}}{\pi(1+2x)} , \text{ for } x^2 \le f(1-f)$$

= 0 , otherwise. (3.126)

and, at percolation, equation (3.125) can be expressed as

$$h(x,f) = \frac{1}{\pi} \sqrt{\frac{1-2x}{1+2x}}.$$
(3.127)

In Figure 3.11, we plot the spectral function (3.126) for several concentrations f, including the the spectral function at percolation concentration f = 1/2 (3.127) (see Thorpe, Djordjević and Hetherington 1994).

Day and Thorpe (1996) have performed computer simulations for both site and bond substitution on a square lattice, and compared the obtained spectral



Figure 3.11: Spectral function h(x, f) for various concentrations f from the effective medium theory, as given by equations (3.126) and (3.127) (Thorpe, Djordjević and Hetherington 1994).

function with the predictions of effective medium theory. For illustration, we shall give here just results for the *bond* substitution shown in Figure 3.12. For more details about the simulation technique and their analytical calculation of the first five moments of the spectral function, the reader is referred to the work of Day and Thorpe (1996).

3.9 Conclusion

All results presented in this Chapter are valid only in the low concentration limit $f \ll 1$, when the inclusions can be regarded as well separated and thus noninteracting. In other words, the effective conductivity and the spectral function is correctly obtained to the first order in concentration f. The only exception to this is the computer simulation results of Day and Thorpe (1996), and the results of the effective medium theory, which are valid in the entire range of concentration f. We have shown that exact solution exists only in a few cases, namely for elliptical (circular) inclusions. The conformal mapping technique turned out to be a very powerful tool for calculating the effective conductivity for particular type of inclusions (holes or perfectly conducting inclusions) which may have sharp corners. The problem becomes much more difficult for inclusions with arbitrary γ if they contain sharp corners. In this case one has to numerically solve a Fredholm equation for the induced charge density around the perimeter of the inclusion. It appears that the only *direct* numerical calculation of the spectral function [from the general definition (2.19) or (3.105) has been done in computer simulations of Day and Thorpe (1996) on the discrete random square net. This has been possible because of the use of a powerful $Y - \Delta$ transformation technique (Frank and Lobb 1988) which calculates the effective conductivity of a random network



Figure 3.12: The spectral function h(t, f) for a two-dimensional square net with random *bond* disorder at different inclusion concentrations f. The solid lines are data from the simulations. The dashed lines are the effective medium theory given by (3.124). For f > 0.5 the dotted lines are the spectral function at (1 - f) transformed by (3.107) (Day and Thorpe 1996).

very efficiently. Finally, the effective medium theory seems to give very good results for intermediate concentrations around the percolation treshold f_c , and thus proves itself useful for deducing the overall shape of the spectral function.

In the next Chapter we shall present our results for another case when one can go beyond the linear approximation in concentration f to include f^2 terms, or in other words, the pair interaction between the inclusions. So far, this was possible to do only for circular inclusions (Djordjević *et al.* 1996), and for random resistor network (Day and Thorpe 1996).

Chapter 4

Pair Terms for Circular Inclusions

4.1 Introduction

The conductivity (or dielectric behavior) of a binary composite system is conveniently expressed in terms of a spectral function, which is determined by the geometry of the composite. In this Chapter we examine the case of circular inclusions in a conducting sheet and keep terms up to second order in the inclusion concentration f. The two inclusion problem can be solved exactly using multiple images (Djordjević et al. 1996), and we use this solution to construct the spectral function. We show that the spectral function is a truncated Lorentzian, that can be calculated in a simple closed form. Both the weight and the width of the spectral function are linear in f.

Exact results for the properties of composite materials are rare, and so the few that exist are particularly important as aids to our understanding. Although spectral functions are widely used in physics, their use in composite materials has not been widespread. This is mainly because this attractive formalism is difficult to apply to particular composite geometries, because of the numerical difficulty of computing the spectral function. In this paper we examine a non-trivial example of a spectral function that can be calculated exactly. This example involves the calculation of the spectral function of a sheet containing circular inclusions with a different conductivity from that of the host. Using the well-known technique of multiple dipole images, the terms in the effective conductivity up to second order in the concentration of inclusions f can be found. We have been able to express the spectral function in a rapidly convergent series. We show that the spectral function is a truncated Lorentzian with weight f and a width that is proportional to f, and we are able to give the final result in a very simple form.

Here, we will apply the general formalism of Chapter 2 to a two dimensional sheet containing circular inclusions, and obtain the spectral function to second order in the area fraction f of inclusions. In other words, we shall add one more term (f^2) in the effective conductivity (2.24) and then calculate its imaginary part to obtain the spectral function. The layout of this Chapter is as follows. In the next section we restrict the form of the conductivity σ by using the reciprocity theorem (2.23) that is valid in 2d, generalizing the previous result (2.24) from Chapter 2. In section 4.3, we use the method of multiple images to write down the position and strengths of the dipoles in a pair of circular inclusions. In section 4.4, we examine the results in more detail, particularly for the case of perfectly conducting inclusions. In section 4.5, we obtain the effective conductivity by averaging over the dipole moments of the pairs that we have found previously. This solution is then tortured into a form from which the spectral function can be derived in sections 4.6 and 4.7. Finally in the conclusions, we discuss the uses of this kind of approach.

4.2 General Form for the Two-dimensional Conductivity to the Second Order in f.

The problem of circular and polygonal *holes* in two-dimensional conducting sheet was recently investigated (Thorpe 1992) up to the *first* order in the area fraction of inclusions, using the conformal mapping technique. From the other side, the general problem for circular inclusions had been solved earlier up to the *second* order (Peterson & Hermans 1968) using *bipolar coordinates*.

We use the method of electrical images to solve the problem of the effective conductivity in the conducting sheet containing circular inclusions of an arbitrary conductivity. This method is not limited to holes and perfectly conducting inclusions as is the conformal mapping technique.

We first consider one isolated pair of identical circles with radius a separated by a distance R. Considering the two independent cases of parallel and perpendicular external electric field, we construct the infinite set of *dipole*, or *dublet* images (Binns & Lawrenson 1962). Each dipole image is found in a simple continued-fraction-form. We find and solve the appropriate difference equation for successive dipole images to get all dipole moment images, now in closed form, in terms of hyperbolic functions. All further calculations are based on these dipole images. Naturally, the total dipole moment of the two circles is given by the sum of all image-dipole moments in the case of parallel external field, and by the **same** sum, but with *alternating* signs in the case of perpendicular external field.

The reciprocity theorem (Keller 1964; Mendelson 1974) (2.23) for the two

phase medium in 2d, states that following relation must hold (Hetherington & Thorpe 1992) [we are rewriting here the equation (2.23) from Chapter 2].

$$\sigma(\sigma_0, \sigma_1)\sigma'(\sigma_1, \sigma_0) = \sigma_0 \sigma_1, \tag{4.1}$$

where σ_0 and σ_1 are conductivities of two phases, and $\sigma(\sigma_0, \sigma_1)$ and $\sigma'(\sigma_1, \sigma_0)$ are the effective conductivities of the original system and the one with the same geometry but σ_0 and σ_1 interchanged.

We find the generalization of the effective conductivity (2.24) (See Hetherington & Thorpe 1992) to the *second* order in the concentration f of the inclusion phase 1 in the host phase 0. The effective conductivity then must be of the following form

$$\frac{\sigma}{\sigma_0} = 1 + f\gamma G(\gamma) + f^2 H(\gamma) + O(f^3), \qquad (4.2)$$

where

$$\gamma = \frac{\sigma_1 - \sigma_0}{\sigma_1 + \sigma_0},\tag{4.3}$$

and the function $G(\gamma)$ is an *even* function of γ (Hetherington & Thorpe 1992) as follows from the reciprocity theorem (4.1). Similarly, for interchanged phases 0 and 1, $(\gamma \Longrightarrow -\gamma)$ the effective conductivity σ' is given as

$$\frac{\sigma'}{\sigma_1} = 1 - f\gamma G(\gamma) + f^2 H(-\gamma) + O(f^3).$$
(4.4)

Multiplying (4.2) by (4.4) and using the reciprocity theorem (4.1), we get to the second order in concentration f

$$H(\gamma) + H(-\gamma) - \gamma^2 G^2(\gamma) = 0,$$
 (4.5)

from which it is clear that function $H(\gamma)$ must generally be of the form

$$H(\gamma) = \frac{1}{2}\gamma^2 G^2(\gamma) + \gamma L(\gamma), \qquad (4.6)$$

where the function $L(\gamma)$ is an *even* function of γ .

The weak scattering limit (see also Hetherington & Thorpe 1992) gives $L(\gamma) = \gamma F(\gamma)$, where $F(\gamma)$ is an odd function of γ (proportional to γ for small γ), and F(0) is zero. So, finally (4.2) becomes

$$\frac{\sigma}{\sigma_0} = 1 + f\gamma G(\gamma) + \frac{1}{2} f^2 \gamma^2 G^2(\gamma) + f^2 \gamma^2 F(\gamma) + O(f^3), \qquad (4.7)$$

where $G(\gamma)$ and $F(\gamma)$ are an *even* and *odd* function of γ , respectively. The area fraction f can be written as

$$f = n\pi a^2, \tag{4.8}$$

where n is the number of inclusions per unit area, each with area πa^2 . Two usual limits are obtained when the inclusion is a hole ($\gamma = -1$) and when the inclusion is perfectly conducting ($\gamma = 1$). Equation (4.7) is valid generally but for *circular* inclusions $G(\gamma) = 2$ as derived before (3.17) (See Thorpe 1992). So, for *circles* as inclusions (4.7) simplifies to

$$\frac{\sigma}{\sigma_0} = 1 + 2\gamma f + 2\gamma^2 f^2 + \gamma^2 f^2 F(\gamma) + O(f^3), \tag{4.9}$$

and our goal is to calculate the function $F(\gamma)$ which contains the *pair* terms in the effective conductivity.

We relate the function $F(\gamma)$ to the pair contribution to the *polarizability* $\Delta\beta$. This is defined as the mean change in the polarizability of a single inclusion, due to the presence of the other inclusions. To leading order, $\Delta\beta$ can be obtained from the dipole moment of pairs. Indeed we have stressed in previous papers (Thorpe 1992, Hetherington & Thorpe 1992) that the conductivity of a sample is directly related to the dipole moment of *all* the inclusions. Once we have all dipole moment images in the aligned and perpendicular external field, it is

straightforward to find the polarizability change $\Delta\beta$ by averaging the parallel and perpendicular two-circle total dipole moment and integrating over the whole sheet. Then we use relation

$$\gamma^2 f^2 F(\gamma) = n \Delta \beta. \tag{4.10}$$

4.3 Dipole Moments

We shall first consider the case of an *aligned (parallel)* external electric field with respect to the line connecting the centers of the two circles, as shown in Figure 4.1. Circles are *not* charged and have an *arbitrary* conductivity σ_1 . In the external field they become polarized, i.e. there is an induced dipole moment on each circle. So, it is intuitively clear that we have to deal with *dipoles* in constructing the infinite set of images which solves this electrostatical problem.

The images of a dipole can be derived from the combination of the separate images of the pair of charges forming the dipole (see Binns & Lawrenson 1962, pp.48-53). By definition, a two dimensional dipole is a combination of a positive line charge and a negative line charge, an infinitesimal distance apart, so arranged that the product of charge and distance remains finite.

One circle in a uniform external field is completely described by one dipole at the center of the circle. We start from that dipole at the center of one circle which we denote by p_1 , given by

$$p_1 = 2\pi\gamma E_0 a^2. (4.11)$$

Assuming that we started from the circle to the right, and taking in account the presence of the other circle to the left, we find the dipole image p_2 of



Figure 4.1: Orientation of the dipole images for two circles in a parallel applied field E_0 , showing the notation in the text (Djordjević *et al.* 1996).

 p_1 in the circle to the left. Now, we find the next dipole image p_3 of p_2 in the circle to the right. Continuing in that way we construct an infinite set of dipole images. Odd numbered images are all inside the right circle, and all even numbered images are inside of the left circle. But, due to the symmetry between the two circles, there must be another infinite set of images generated by placing the first dipole p_1 at the center of the left circle. The complete solution of the problem consists of two infinite sets of images, redistributed in such a way that each circle now has the same infinite set of images $p_1, p_2, p_3...$, which are given in the simple, continued fraction form

$$p_{2} = \gamma \left(\frac{a}{R}\right)^{2} p_{1},$$

$$p_{3} = \gamma \left(\frac{a}{R - \frac{a^{2}}{R}}\right)^{2} p_{2},$$

$$p_{4} = \gamma \left(\frac{a}{R - \frac{a^{2}}{a^{2}}}\right)^{2} p_{3},$$

$$(4.12)$$

where γ is given by (4.3), *a* is the radius of each circle, *R* is the separation between their centers, and p_1 is given by (4.11). All images of dipole moments have the same direction, along the applied field, as shown in Figure 4.1.

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The case of the *perpendicular* external field is shown in Figure 4.2. Due to the direction of the applied field, all dipole moments are now perpendicular to the horizontal connecting the centers of the two circles. The first dipole image p_2 now has the opposite direction with respect to the initial dipole p_1 . The alternating direction of successive images is the only new thing here, so we can repeat essen-

t,

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tially the same procedure we used for the parallel field case, to get exactly the same infinite set of dipole images whose *magnitudes* are given by (4.11) - (4.12), as before. Alternating orientation of these dipoles are represented symbolically in Figure 4.2.

Positions of the first few images in both circles, measured from their respective centers, as shown in Figures 4.1 and 4.2, are found in the similar continued fraction form.

$$x_{1} = 0,$$

$$x_{2} = \frac{a^{2}}{R},$$

$$(4.13)$$

$$x_{3} = \frac{a^{2}}{R - \frac{a^{2}}{R}},$$

$$x_{4} = \frac{a^{2}}{R - \frac{a^{2}}{R - \frac{a^{2}}{R}}},$$
...

These positions hold for both the parallel and perpendicular case.

Combining (4.11)-(4.13), it is easy to see that the dipole moments satisfy the following *difference* equation

$$\frac{1}{\sqrt{p_{s+1}}} + \frac{1}{\gamma\sqrt{p_{s-1}}} = \frac{R}{a} \frac{1}{\sqrt{\gamma p_s}}.$$
(4.14)

Solution of (4.14) gives all dipole images in terms of hyperbolic functions,

$$p_s = 2\pi E_0 a^2 \gamma^s \left(\frac{\sinh \alpha}{\sinh s\alpha}\right)^2, \qquad (4.15)$$



Figure 4.2: Orientation of the dipole images for two circles in a *perpendicular* applied field E_0 , showing the notation in the text (Djordjević *et al.* 1996).

where α is given by the relation

$$\cosh \alpha = \frac{R}{2a}.\tag{4.16}$$

The equation (4.15) is our main result for dipole moment images, and all further calculations are based on it.

4.4 Perfectly Conducting Inclusions

As an interesting sideline, we look at some properties of a single pair of inclusions. The formulae for this case have a particularly simple form. We calculate the total dipole moment of the two *perfectly conducting* ($\gamma = 1$) circular inclusions in an external field, separated by distance R. It is conceptually obvious that in the *parallel* field, the total dipole moment is given by the sum of all dipole images multiplied by factor 2 (two circles)

$$P_{||} = 2\sum_{s=1}^{\infty} p_s.$$
(4.17)

Using (4.15) we have for perfectly conducting circles

$$P_{\parallel} = 4\pi E_0 a^2 \sum_{s=1}^{\infty} \left(\frac{\sinh \alpha}{\sinh s\alpha} \right)^2, \qquad (4.18)$$

which is the total dipole moment of two circles in the parallel external field.

In a *perpendicular* external field, the only difference is the *alternating* orientation of the consecutive dipole moments, while they still have the same magnitudes as in the parallel field case. So, we can write

$$P_{\perp} = 4\pi E_0 a^2 \sum_{s=1}^{\infty} \left(-1\right)^{s+1} \left(\frac{\sinh \alpha}{\sinh s\alpha}\right)^2.$$

$$(4.19)$$

Using (4.18) and (4.19), we numerically calculate the total dipole moment dependence on the separation R/a of the two circular inclusions, in both cases.

These graphs are shown in Figure 4.3. When the circles touch, (4.18) and (4.19) give *exact* values for the two dipole moments (with $\alpha \longrightarrow 0$).

$$P_{\parallel} = 4\pi E_0 a^2 \sum_{s=1}^{\infty} \frac{1}{s^2} = 4\pi E_0 a^2 \zeta(2) = \frac{2}{3} E_0 a^2 \pi^3, \qquad (4.20)$$

$$P_{\perp} = 4\pi E_0 a^2 \sum_{s=1}^{\infty} \left(-1\right)^{s+1} \frac{1}{s^2} = 2\pi E_0 a^2 \zeta(2) = \frac{1}{3} E_0 a^2 \pi^3, \qquad (4.21)$$

where the sums are expressed in terms of the Riemann zeta function (Gradshteyn & Ryzhik 1965).

In this particular case of *perfectly conducting* circular inclusions, and in *parallel* external field, each consecutive dipole image introduces some *change of* the potential on each circle. The first few contributions in the decreasing potential of the circle O_1 , which correspond to the first few dipole images $p_1, p_2, p_3, ...,$ are

$$V_1 = 0,$$

$$V_{2} = -\frac{1}{2\pi} \frac{p_{1}}{R},$$

$$V_{3} = -\frac{1}{2\pi} \frac{p_{2}}{R - \frac{a^{2}}{R}},$$

$$V_{4} = -\frac{1}{2\pi} \frac{p_{3}}{R - \frac{a^{2}}{R - \frac{a^{2}}{R}}},$$
(4.22)

where p_1, p_2, p_3, \dots are given by (4.11) and (4.12). In general

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$$V_{s} = \frac{x_{s} p_{s-1}}{2\pi a^{2}}.$$
 (4.23)



Figure 4.3: Total dipole moment, P_{\parallel} and P_{\perp} of two perfectly conducting circles in parallel and perpendicular external field. The two diamond symbols when the circles touch at R/a = 2, are from equations (4.20) and (4.21) (Djordjević *et al.* 1996).

In the absence of inclusions, the external electric field E_0 creates a potential difference between the two centers given by

$$\Delta V_E = E_0 R. \tag{4.24}$$

The total potential difference, i.e. voltage ΔV , between the two perfectly conducting circles in the external field is given by

$$\Delta V = \Delta V_E - 2 \sum_{s=2}^{\infty} |V_s|. \qquad (4.25)$$

Combining (4.12), (4.13) and (4.22) the total voltage can be expressed in terms of a sum over hyperbolic functions

$$\Delta V = E_0 a \left(\frac{R}{a} - 2 \sum_{s=2}^{\infty} \frac{(\sinh \alpha)^2}{\sinh s \alpha \sinh (s-1)\alpha} \right).$$
(4.26)

The series in (4.26) is summable to a simple form. To show this rewrite this sum with the help of (4.16) and in terms of the new variable $y = e^{\alpha}$. (4.26) then becomes

$$\Delta V = E_0 a \left[y + \frac{1}{y} - 2 \left(y - \frac{1}{y} \right)^2 \sum_{s=2}^{\infty} \frac{1}{(y^s - y^{-s}) \left(y^{s-1} - y^{-(s-1)} \right)} \right].$$
(4.27)

Rewriting in terms of partial fractions (4.27) becomes

$$\Delta V = E_0 a \left[y + \frac{1}{y} + 2 \left(y - \frac{1}{y} \right) \sum_{s=2}^{\infty} \left(\frac{1}{y^{2s} - 1} - \frac{1}{y^{2s-2} - 1} \right) \right]. \quad (4.28)$$

Writing explicitly the first few terms in the sum it is easy to see that only one term in the second partial fraction survives for s = 2, while all others cancel each other to give

$$\Delta V = E_0 a \left(y - \frac{1}{y} \right) \tag{4.29}$$

and hence,

,

$$\Delta V = E_0 \sqrt{R^2 - 4a^2}. \tag{4.30}$$

This remarkably simple result for the voltage between two perfectly conducting circular inclusions is shown graphically in Figure 4.4. Presumably (4.30) can be derived by a more elementary method, but we have been unsuccessful in doing so.

4.5 Effective Conductivity

As we mentioned in the Introduction, the problem is to find the function $F(\gamma)$ in (4.9). The function $F(\gamma)$ contains the information about the long range Coulomb interaction between all pairs of circles. Obviously, we have to connect the function $F(\gamma)$ with our solution for dipole moment images (4.15). But the dipole moment p is related to *polarizability* by the relation $p = \beta E_0$, where β is the polarizability. So, we first relate $F(\gamma)$ to the pair correction in the polarizability.

Introducing an effective conductivity σ in the observed region containing π circles per unit area, and the *mean* polarizability of a single inclusion $\overline{\beta}$, we find the Clausius-Mossotti type result [see the general equation (2.20)]

$$\frac{\sigma - \sigma_0}{\sigma + \sigma_0} = \frac{n\bar{\beta}}{2} \tag{4.31}$$

which defines $\overline{\beta}$ (see the general equation (2.20)) The mean polarizability $\overline{\beta}$ contains higher order effects, so we solve (4.31) for σ/σ_0 , and expand it to second order in n

$$\frac{\sigma}{\sigma_0} = 1 + n\bar{\beta} + \frac{n^2\bar{\beta}^2}{2} + \dots$$
(4.32)

Separating the single site and the correction due to pairs in $\overline{\beta}$, we put

$$\bar{\beta} = 2\pi a^2 \gamma + \Delta \beta, \tag{4.33}$$



Figure 4.4: Voltage between the two *perfectly conducting* circles in the external field is shown as a solid line. The dashed line would be the voltage in the absence of the conducting circles, (i.e., just host material) (Djordjević *et al.* 1996).

where $\Delta\beta$ is the *change* in the polarizability due to the presence of other inclusions nearby. Therefore we find (4.9) in the form

$$\frac{\sigma}{\sigma_0} = 1 + 2\gamma f + 2\gamma^2 f^2 + n\Delta\beta \tag{4.34}$$

which is consistent with (4.10).

The change to the average dipole moment can be written as

$$\bar{P}' = n \, \int_0^{2\pi} \int_{2a}^\infty (P'_{||} \cos^2 \theta + P'_{\perp} \sin^2 \theta) \, d\theta \, R \, dR, \tag{4.35}$$

where P'_{\parallel} and P'_{\perp} [and hence \bar{P}'_{\parallel} don't contain p_1 [as designated by the primed quantities], but are summed over all the *other* induced dipoles as in (4.18). Terms containing p_1 are already taken in account, in the single site part of polarizability (terms proportional to f in (4.34)).

The series (41) is only conditionally convergent as the leading term invoving p_2 is divergent unless the angular integration is done first. Integration over θ gives factor π , and even dipole images cancel out in the integrand, leaving only odd terms doubled. The elimination of the even terms is necessary in order for $F(\gamma)$ to be an odd function of γ as required by the reciprocity theorem and discussed in section II. It may also be possible to show that the even terms vanish in (41) using methods similar to Felderhof, Ford and Cohen (1982), but this is a lengthy procedure that we have not attempted as we know that the even terms in (41) must integrate to zero using the reciprocity theorem. In three dimensions, the reciprocity theorem cannot be invoked and hence it is necessary to do the analysis surrounding the analogous equation (3.35) in Felderhof, Ford and Cohen (1982).

Recalling the relation between the polarizability and the dipole moment, we can write

$$\Delta\beta = \frac{\bar{P}}{E_0} = \frac{2f}{E_0 a^2} \int_{2a}^{\infty} (p_3 + p_5 + p_7 + \dots) R \, dR. \tag{4.36}$$

The behavior at large R in the integrand in (4.35) is dominated by the n =3 term in the summations in (4.18) and (4.19) which leads to the assymptotic form of the integrand in (4.35) going as R^{-4} , which leads to an absolutely convergent integral in (4.35) and (4.36). With the help of (4.10) the function $F(\gamma)$ is written as

$$F(\gamma) = \frac{2}{\pi E_0 a^4} \int_{2a}^{\infty} \frac{(p_3 + p_5 + p_7 + \ldots)}{\gamma^2} R \, dR. \tag{4.37}$$

Using the hyperbolic function form of dipole images (4.15), we have the following expression

$$F(\gamma) = 16 \int_0^\infty \sum_{s=1}^\infty \gamma^{2s-1} \frac{\sinh^3 \alpha \cosh \alpha}{\sinh^2 (2s+1)\alpha} \, d\alpha. \tag{4.38}$$

Finally, (4.38) can be written in the form

$$F(\gamma) = 16 \left(K_1 \gamma + K_2 \gamma^3 + K_3 \gamma^5 + K_4 \gamma^7 + \ldots \right),$$
(4.39)

where K_s is given by

$$K_{s} = \int_{0}^{\infty} \frac{\sinh^{3} \alpha \, \cosh \alpha}{\sinh^{2} (2s+1)\alpha} \, d\alpha. \tag{4.40}$$

Substituting (4.39) into (4.9) we have found the expression for the effective conductivity to the *second order* in the area fraction of the inclusions, f, for any value of γ between 0 and 1:

$$\frac{\sigma}{\sigma_0} = 1 + 2\gamma f + \left[2\gamma^2 + \left(16K_1\gamma^3 + 16K_2\gamma^5 + 16K_3\gamma^7 + \cdots\right)\right]f^2, \quad (4.41)$$

where K_s are given by (4.40). It is useful to simplify the coefficients K_s . First, we transform the integral (4.40) using the identity

$$\frac{1}{\sinh^2 \left[(2s+1)\alpha \right]} = \sum_{j=1}^{\infty} \frac{4j}{\exp\left[2j\alpha(2s+1) \right]}$$
(4.42)

Table 4.1: Taylor series for circular inclusions of conductivity ratio parameter γ .

Taylor series

Circle	$F(\gamma)$	$= 0.666667 \ \gamma \ + \ 0.05567 \ \gamma^3 \ + \ 0.01317 \ \gamma^5 \ + \ 0.00464 \ \gamma^7 \ + \ 0.00204 \ \gamma^9$
		+ 0.00104 γ^{11} + 0.00058 γ^{13} + 0.00035 γ^{15} + 0.00022 γ^{17} + 0.00015 γ^{19}
		+ 0.00010 γ^{21} + 0.00007 γ^{23} + 0.00005 γ^{25} + 0.00004 γ^{27} + 0.00003 γ^{29}
		+ 0.00002 γ^{31} + 0.00002 γ^{33} + 0.00002 γ^{35} + 0.00001 γ^{37} +

which can be easily checked (Gradshteyn & Ryzhik 1965). Substituting (4.42) into (4.40) we have the following expression for the coefficients K_s

$$K_{s} = 4 \sum_{j=1}^{\infty} j \int \sinh^{3} \alpha \cosh \alpha \exp\left[-2j\alpha(2s+1)\right] d\alpha$$
(4.43)

which was previously found by Peterson and Hermans (1968), using bipolar coordinates.

Substituting $\omega = exp[-2j\alpha(2s+1)]$ in (4.43), carrying out the integration over α , and using 8.362 (1) (Gradshteyn & Ryzhik 1965), we express the result in terms of the digamma (Ψ) function

$$K_{s} = \frac{1}{4(2s+1)^{2}} \left[\Psi\left(\frac{1}{2s+1}\right) + \Psi\left(\frac{-1}{2s+1}\right) - \Psi\left(\frac{2}{2s+1}\right) - \Psi\left(\frac{-2}{2s+1}\right) \right]$$
(4.44)

which was also found by Peterson and Hermans (1968). The tabulated values of the digamma function were used to construct Table 4.1.

In Figure 4.5, we show a plot of $F(\gamma)$, using the Taylor expansion shown in Table 4.1, with enough terms so that convergence was obtained even at $\gamma = 1$. This required about 100 terms to get 4 figure accuracy. We have used an approximate interpolation form to fit the result for $F(\gamma)$.

$$F(\gamma) = \frac{2}{3} \frac{\gamma}{(1 - b\gamma^2)^c}.$$
 (4.45)

The coefficients b and c were chosen to reproduce the result at $\gamma = 1$, and known behaviour of $F(\gamma)$ for small γ .

$$F(\gamma) = \frac{2}{3}\gamma$$
 for small γ , and $F(1) = 0.744989676...$ (4.46)

Here the ... following a number denotes that it is known exactly to that number of digits.

Peterson and Hermans (1968) contains a numerical error. The last two given coefficients in their formula (67) are 0.0194 and 0.00505. That should be corrected to 0.0198... and 0.00697..., respectively.

4.6 Analytic Continuation of the Pair Term

We shall need the both the real and imaginary parts of $F(\gamma)$ for the calculation of the spectral function in the next section. The imaginary part can be obtained by analytic continuation. Starting from (4.38) we rewrite it in slightly different form:

$$F(\gamma) = 16 \int_0^\infty \sinh^3(\alpha) \cosh(\alpha) \sum_{s=1}^\infty \frac{\gamma^{2s-1}}{\sinh^2[(2s+1)\alpha]} d\alpha.$$
(4.47)

The sum in the integrand

$$A(\gamma) \equiv \sum_{s=1}^{\infty} \frac{\gamma^{2s-1}}{[e^{\alpha(2s+1)} - e^{-\alpha(2s+1)}]}$$
(4.48)

can be rearranged and expanded in the series



Figure 4.5: Interpolation formula (smooth curve) for the function $F(\gamma)$ (crosses). The diamond symbol when $\gamma = 1$ is from equation (4.39) (Djordjević *et al.* 1996).
$$A(\gamma) = \sum_{s=1}^{\infty} \gamma^{2s-1} \left[e^{-2\alpha(2s+1)} + 2e^{-4\alpha(2s+1)} + 3e^{-6\alpha(2s+1)} + \cdots \right]. \quad (4.49)$$

Introducing the new index $\nu \equiv s - 1$ we can transform the (4.49) into

$$A(\gamma) = \gamma \sum_{\nu=0}^{\infty} \left[\left(\frac{\gamma}{e^{2\alpha}} \right)^{2\nu} e^{-6\alpha} + 2 \left(\frac{\gamma}{e^{4\alpha}} \right)^{2\nu} e^{-12\alpha} + 3 \left(\frac{\gamma}{e^{6\alpha}} \right)^{2\nu} e^{-18\alpha} + \cdots \right].$$

$$(4.50)$$

The summation over ν is possible for each term in the brackets to give

$$A(\gamma) = \gamma \left[\frac{e^{-6\alpha}}{1 - \left(\frac{\gamma}{e^{2\alpha}}\right)^2} + \frac{2e^{-12\alpha}}{1 - \left(\frac{\gamma}{e^{4\alpha}}\right)^2} + \frac{3e^{-18\alpha}}{1 - \left(\frac{\gamma}{e^{6\alpha}}\right)^2} + \cdots \right]$$
(4.51)

which can be expressed in terms of the variable $x = -1/2\gamma$.

$$A(x) = -\frac{x}{2} \sum_{m=1}^{\infty} \frac{m e^{-6m\alpha}}{(x)^2 - \left(\frac{e^{-2m\alpha}}{2}\right)^2}.$$
 (4.52)

We write the function $F(\gamma)$ in (4.47) in terms of the new variable x

$$F(x) = -32x \int_0^\infty \sinh^3(\alpha) \cosh(\alpha) \left[\sum_{m=1}^\infty \frac{m e^{-6m\alpha}}{x^2 - \left(\frac{e^{-2m\alpha}}{2}\right)^2} \right] d\alpha, \quad (4.53)$$

or

$$F(x) = -2x \sum_{m=1}^{\infty} \int_{0}^{1/2} \frac{(2x')^{2} \left[(2x')^{-1/2m} - (2x')^{1/2m} \right]^{3} \left[(2x')^{-1/2m} + (2x')^{1/2m} \right]}{x^{2} - x'^{2}} dx,'$$

$$(4.54)$$

where we have introduced another new variable $x' = \frac{1}{2}exp(-2m\alpha)$. Finally, transforming this expression into partial fraction form, we get after some manipulations

$$F(x) = \int_{-1/2}^{1/2} \frac{\sum_{m=1}^{\infty} \xi_m(|x'|)}{x - x'} dx', \qquad (4.55)$$

where (writing the dummy variable x' as x)

$$\xi_m(|x|) = 4x^2 \left((2|x|)^{-1/2m} - (2|x|)^{1/2m} \right)^3 \left((2|x|)^{-1/2m} + (2|x|)^{1/2m} \right)$$

$$(4.56)$$

and hence, reading from (4.55) we obtain imaginary part of F(x) as

$$ImF(x) = \sum_{m=1}^{\infty} \xi_m(|x|),$$
 (4.57)

for -1/2 < x < 1/2. This derivation was done by J. Hetherington. Near x = 0 there is a cusp

$$ImF(x) = 1 - 2 |x| + \mathcal{O}(|x|^{\frac{4}{3}})$$
 (4.58)

which is caused by the large number of widely separated pairs of circles. We use ImF(x), given in (4.57), to construct the spectral function in the next section.

4.7 Spectral Representation

It is convenient to employ here the variables used for the spectral function in Chapter 2. Its properties were summarized in equations (2.36) - (2.38), where the effective conductivity is expressed through the spectral function which is symmetric with respect to the origin x = 0, and the first and second moment of the spectral function are given. For simplicity for the rest of this section, we drop the prime on x. We shall rewrite formulas (2.36)-(2.38) here

$$\frac{\sigma}{\sigma_0} = 1 + 2\gamma \int_{-\frac{1}{2}}^{\frac{1}{2}} \frac{h(x)dx}{1 + 2\gamma x},$$

$$\int_{\frac{1}{2}}^{\frac{1}{2}} h(x)dx = f,$$

$$\int_{-\frac{1}{2}}^{\frac{1}{2}} x'h(x')dx' = -\frac{f^2}{2},$$
(4.59)

where f is concentration (volume fraction) of the phase σ_1 in the host of σ_0 .

The first moment $\langle x \rangle$, as we have seen (2.39) is given by

$$\langle x \rangle = -\frac{f}{2}.\tag{4.60}$$

The higher moments of the spectral function h(x) depend on the *detailed* geometry and are not general like the first moment given by (4.60). For example the second moment for the present case is given by

$$\langle x'^2 \rangle = 2K_1 f, \tag{4.61}$$

where $16K_1$ is the leading term in (4.38) and from (4.44) has the numerical value $K_1 = \frac{1}{24}$. Hence we have

$$\langle x'^2 \rangle = \frac{f}{12}.\tag{4.62}$$

The spectral function h(x) is formed by taking the imaginary part of σ/σ_0 given by (4.9) and rearranged so that a self energy is in the denominator. Such rearrangement can be accomplished formally [see for example Felderhof and Jones (1986) and Cichocki and Felderhof (1985)]. We have been content to write the conductivity in the form (4.63), which when expanded is equivalent to (4.34) to second order in the concentration f:

$$\frac{\sigma}{\sigma_0} = \frac{1}{1 - \frac{2\gamma f}{1 + \gamma f \left[1 - \frac{1}{2}F(\gamma)\right]}}.$$
(4.63)

Taking the imaginary part of (4.63) (substituting $\gamma = -1/2x$ as before) we have

$$h(x) = \frac{f}{\pi} \frac{\left[\frac{f}{4}ImF(x)\right]}{\left[x + \frac{f}{2} + \frac{f}{4}ReF(x)\right]^2 + \left[\frac{f}{4}ImF(x)\right]^2},$$
(4.64)

where ReF(x) is the real part of the function F. We obtained it from the known imaginary part in (4.56) and (4.57) using Kramers-Kronig relation. Both ImF(x) and ReF(x) are shown in Figure 4.6. We plot the spectral function given by (4.64), for several concentrations f in Figure 4.7, using the complete expression (4.64). Of course, the form (4.63) is not unique to second order in concentration f. Many other forms can be written down which when expanded will give the conductivity σ correct to order f^2 [see (4.2)].

We note that Felderhof and Jones (1989) also use a continuued fraction in their Eq. (3.11) identical to our (4.64). We prefer the form (4.63) as it leads to a single smooth spectral function as shown in Figure 4.7. The single delta function in the single inclusion limit, is broadened by the *interactions* between the inclusions at higher concentrations, so that the width is proportional to f as shown in Figure 4.7.

Similar behavior is in the spectral function associated with the vibrations of light point defects in solids (Elliott, Krumhansl and Leath 1974). We note that there are no isolated poles in the expression (4.63) and hence no delta functions in the spectral function, as can be seen from Figs. (4.7) and (4.8). This can easily be checked as our spectral functions obeyed the sum rules given in (4.59). We interpret the spectral function in the low concentration limit as being analogous to the broadening of single impurity lines, due to interactions between the pairs of light mass defects in solids (Elliott, Krumhansl and Leath 1974). We note that (Felderhof and Jones 1989) found two isolated delta functions in the spectral function in three dimensions, in addition to a continuous part. These delta functions we believe are unphysical and result from the neglect of higher order multipoles, even at the pair level. Because of the simplifications possible in two dimensions we have been able to sum up *all* the contributions at the pair level, via the infinite set of dipole images. As a result there are no unphysical delta functions in the



Figure 4.6: ImF(x) and ReF(x) for circles, with $x = -1/(2\gamma)$. The real part is obtained from the known imaginary part (4.56) and (4.57), using Kramers-Kronig relation. Note that ImF(x) = 0 for $x^2 > 1/4$ (Djordjević *et al.* 1996).



Figure 4.7: Spectral function for several values of inclusion area fraction, using (4.64), f = 0.01; 0.05; 0.10; 0.20 (Djordjević *et al.* 1996).

spectral function. If we have truncated the expansion (4.39) after the first few terms, we would have obtained a spectral function with many delta functions, that only form a single continuous function as the series (4.39) is summed to infinity.

In the dilute limit the spectral function becomes Lorentzian. For small concentrations f, and for small x, using (4.46) and (4.58), we can make the approximation F(x) = i, i.e. $ReF(x) \approx 0$ and $ImF(x) \approx 1$, and the spectral function becomes

$$h(x) = \frac{f}{\pi} \frac{\frac{f}{4}}{\left(x + \frac{f}{2}\right)^2 + \left(\frac{f}{4}\right)^2}.$$
 (4.65)

In Figure 4.8 we show the spectral function calculated from the full expression (4.64) and the Lorentzian form (4.65), for two small concentrations. It can be seen that the differences between these two forms only become apparent at higher values of the area fraction f, where the pair approximation breaks down.

It is easy to find the real part of σ/σ_0 in the dilute limit:

$$Re\left(\frac{\sigma}{\sigma_{0}}\right) = 1 - \frac{2f(2x+f)}{\left(\frac{f}{2}\right)^{2} + (2x+f)^{2}}.$$
(4.66)

Then, assuming complex x, it is straightforward to show that complex effective conductivity has the following form

$$\frac{\sigma}{\sigma_0} = 1 - \frac{f}{x + \frac{f}{2} + i\frac{f}{4}},\tag{4.67}$$

where x is now an arbitrary point in the complex plane. Formula (4.67) reproduces correct imaginary and real part as given by (4.65) and (4.66), respectively. Of course, the form (4.67) is not correct as the single pole is off the real axis, which is not allowed. Also the Lorentzian extends out to $\pm\infty$, which violates the fact that the spectral function is only non-zero between $\pm \frac{1}{2}$. Nevertheless, the Lorentzian



Figure 4.8: Lorentzian shape of spectral function h(x) from (4.65) compared with the exact result (4.64). The Lorentzian is shown as the dashed line, and the exact result as the solid line, for two concentrations f = 0.05 and f = 0.10 (Djordjević *et al.* 1996).

form, and hence (4.67), form a good approximation for small f and x, as shown in Figure 4.8.

We also define the function

$$M(\gamma) \equiv \frac{\sigma - \sigma_0}{\sigma + \sigma_0}.$$
(4.68)

It can be shown that imaginary part of M(x) is given by

$$ImM(x) = \frac{f}{2} \frac{\frac{f}{4}ImF(x)}{\left[x + \frac{f}{4}ReF(x)\right]^2 + \left[\frac{f}{4}ImF(x)\right]^2}$$
(4.69)

which in the dilute limit becomes

$$ImM(x) = \frac{f}{2} \frac{\frac{f}{4}}{x^2 + \left(\frac{f}{4}\right)^2},$$
(4.70)

which is both Lorentzian and an even function of x.

In Figure 4.9 we contrast plots of the full expression (4.69) and Lorentzian form (4.70) of function ImM(x), for two concentrations. Comparing Figure 4.9 with Figure 4.8 we see that function ImM(x) given by (4.69) keeps its approximate Lorentzian form up to relatively higher concentrations than does the spectral function h(x).

4.8 Conclusions

We have shown that the spectral function for a sheet containing holes can be calculated correct to second order in the area fraction of inclusions f. The result is a truncated Lorentzian that for all practical purposes is a Lorentzian in the range of interest. A knowledge of the spectral function permits the (complex) conductivity, σ , for any (complex) values of σ_0 and σ_1 to be found, by doing a single integral. This is particularly useful if there is a parameter in the composite



Figure 4.9: The function ImM(x) in the dilute limit. The solid curve is the exact result from (4.69), and the dashed curve is the Lorentzian approximate (4.70). Results are shown for two concentrations f = 0.05 and f = 0.10 (Djordjević *et al.* 1996).

that can be varied at fixed geometry. Examples would be the frequency and the temperature.

The calculation in 2d was possible because an exact solution to this problem is available in terms of multiple images. We have managed to do an analytic continuation which has allowed the spectral function to be found which is finite only over a narrow region at low concentration.

Similar spectral functions can also be used in discrete systems made up of resistors (Foster 1924 and Straley 1979). Spectral functions are widely used in physics to study electronic and vibrational excitations. They have proved especially useful in systems containing impurities, where local modes can occur (Elliott, Krumhansl and Leath 1974). The weight in the absorption spectrum goes like the defect concentration f and the width is determined by the interaction between defects and goes also as f. The reason for this close analogy between these two somewhat disparate situations is not entirely clear at the present time.

Chapter 5

Discrete Disordered Media

5.1 Introduction

In the preceding chapters we have studied the properties of the *continuous* disordered media. The only exception to that was the case of the *discrete* random resistor network, which we presented at the end of Chapter 3. We shall now turn our attention to another wide class of *discrete* disordered systems. These are *topologically* disordered networks, or amorphous solids.

5.2 Topological Disorder

A perfect crystal is the structure in which the atoms, or groups of atoms, are arranged in a pattern that repeats itself periodically in the three dimensions to an infinite extension. For instance, crystalline diamond makes a lattice which is produced by periodical repetition of the 8-atom diamond cubic cell in all three spatial direction. A piece of the crystalline diamond structure is shown in Figure 5.1. Amorphous materials do not have the periodicity (long range order)



Figure 5.1: A piece of a crystalline diamond structure. One of the characteristic sixfold rings in a crystalline diamond structure is shown by the highlighted atoms.



Figure 5.2: Schematic sketches of the atomic arrangements in (a) a crystalline solid, (b) an amorphous solid, and (c) a gas. (Taken from: Zallen 1983.)

characteristic of a crystal. Starting from a crystalline structure and slightly displacing every atom in a random manner, the periodicity is certainly destroyed, but the random structure obtained is not yet amorphous. An amorphous structure is *topologically* different from a crystalline one. Thus, to obtain an amorphous structure from crystalline one, it is necessary not only to introduce randomness in the atomic positions, but also to change the topology of the original perfect lattice. We can schematically sketch atomic arrangements in three typical cases: a crystal, an amorphous solid, and a gas, as in Figure 5.2.

In Figure 5.3 we show a piece of the 3d amorphous diamond structure which was obtained in our computer simulations, and which we shall talk about in the next Chapter. The two networks in Figures 5.1 and 5.3 are topologically different: while the crystalline diamond network possess only 6-fold rings of atoms, the amorphous network also has 5-fold, 7-fold, and higher order rings, and consequently the number of 6-fold rings is reduced from its crystalline value.



Figure 5.3: A piece of an amorphous diamond structure (Djordjević et al. 1995).



Figure 5.4: (a) Hypothetical crystalline compound A_2B_3 . (b) Amorphous form of the same compound. (Taken from: Elliott 1984.)

Similarly, binary compounds like SiO_2 , can be found both in the crystalline and in the amorphous state, the later being topologically different from the crystalline SiO_2 . Schematic two-dimensional representations of the crystalline and amorphous structures for a hypothetical A_2B_3 compound are shown in Figure 5.4. In the rest of this dissertation we shall be mainly interested in elemental amorphous structures, even though we shall briefly mention how one can make a computer model of an amorphous binary compound.

5.3 Distribution Functions

The experimental evidence of a fundamental difference between the crystalline and amorphous structures is given by the diffraction patterns obtained when an incident monoenergetic collimated beam of either X-rays, neutrons or electrons, is scattered from the atoms of the structure. In the case of a crystal, a beam of, say, X-rays is elastically scattered from regular Bragg planes, according to the



Figure 5.5: Typical diffraction patterns for a crystal (a), and for an amorphous material (b). (Taken from Elliott 1984.)

Bragg condition for the constructive interference of the outgoing beams

$$2d\sin\theta = n\lambda$$
, (5.1)

where d is the spacing of the two Bragg's planes, 2θ is the scattering angle and λ is the wavelength of the incident X-ray beam. As a consequence, a characteristic diffraction pattern with a series of a sharp spots is obtained [Figure 5.5(a)]. In amorphous materials such sharp structure in the scattering pattern is absent, and all one sees is a concentric sequence of diffuse rings, as shown in Figure 5.5(b). A collection of a large number of small randomly oriented perfect crystals would produce a sequence of concentric sharp rings. Thus, unlike in the case of crystals, the variation of the intensity in the diffraction pattern of amorphous materials cannot be used to determine a well-defined structure. The most one can determine is the distribution in the separation of pairs of atoms, usually expressed in the form of a distribution function.

There are at least four different (related) distribution functions that are

used in the literature, and there is a certain amount of confusion in how different authors name them. We shall introduce here all four of them and explain their mutual relation. Ditribution functions serve as the most common way of describing amorphous structures. They can be calculated from the theoretical models, or deduced from scattering experiments.

We shall start with defining Pair Distribution Function (PDF). If the average number density of the structure is $n_0 = N/V$, where N is the total number of atoms, and V is the volume of the sample, then we can generally write

$$P(r) = \frac{1}{n_0 N} \langle \sum_{i \neq j} \delta[\mathbf{r} - (\mathbf{R}_i - \mathbf{R}_j)] \rangle, \qquad (5.2)$$

where **bold-faced** letters denote vectors, angular brackets represent the ensemble or configuration average, and the vectors \mathbf{R}_i represent the positions of all the atoms in the structure. The sum in (5.2) picks up a delta function whenever any two atoms anywhere in the sample are separated by $\mathbf{R}_i - \mathbf{R}_j$. This step is done for each possible configuration, and a weighted average of the results is taken in the usual thermodynamic way. The result is made dimensionless by dividing by Nn_0 . In the crystalline structure the result will actually depend on direction, and in this case we should write $P(\mathbf{r})$. However, for amorphous structures the result will be isotropic, so that it is enough to write P(r) for the PDF. In any case, the meaning of the function P(r) is the following: if there is an atom at the origin, $P(\mathbf{r})$ describes the probability that there will be an atom at \mathbf{r} , averaged over all atoms being at the origin. For example, if we compute $P(\mathbf{r})$ for a crystal, taking \mathbf{r} in the direction of one of the edges of the unit cell, we find a narrow Gaussian distribution about each lattice site. In the extreme case of the perfect gas, where an atom at the origin has no effect at all on the uniform distribution of other atoms, P(r) = 1. This is shown in Figure 5.6. Typical shape of the PDF for



Figure 5.6: Typical shape of the Pair Distribution Function for a crystal, computed along the one of the edges of the crystalline unit cell. This is the PDF calculated for the crystalline GaAs at 10K (Chung and Thorpe 1996). Gaussian peaks are due to the thermal broadening of delta-functions in (5.2), and are taken in the account by performing thermodynamic average. The horizontal line is PDF for a perfect gas. The distance has been normalized by the nearest-neighbor distance d_0 .

amorphous structures is shown in Figure 5.7.

If we ignore the thermal broadening, we can simply write for the PDF

$$P(\mathbf{r}) = \frac{1}{n_0 N} \sum_{\mathbf{r}_s \neq 0} \delta(\mathbf{r} - \mathbf{r}_s), \qquad (5.3)$$

where the \mathbf{r} , are the lattice translation vectors. If we integrate both sides of (5.3) over the volume of the sample we get

$$n_0 \int P(r) d^3r = \frac{1}{N} \sum_{\mathbf{r}, \neq 0} \int \delta(\mathbf{r} - \mathbf{r}_s) d^3r = N - 1, \qquad (5.4)$$

where the (-1) comes from explicitly excluding the atom at the origin in both (5.3) and (5.2). Thus, $n_0 P(r) d^3 r$ gives the probability of finding an atom at a point $d^3 r$ which is a distance **r** from another particle at the origin.



Figure 5.7: Typical shape of the Pair Distribution Function for an amorphous sample. This is the PDF calculated for the amorphous silicon (Djordjević *et al.* 1995).

Assuming that the sample is isotropic, we can calculate the average number of atoms in a spherical shell centered on a particle at the origin, and dr thick, thus introducing a new distribution function

$$\int_{\text{shell}} n_0 P(r) d^3 r = 4\pi r^2 n_0 P(r) dr = n_0 G(r).$$
 (5.5)

The equation (5.5) defines G(r), which is called the *Radial distribution Function* (RDF)

$$G(r) = 4\pi r^2 P(r). (5.6)$$

We see that, on average, the RDF increases parabolically with the distance r. Typical shapes of the RDF in a crystal, glass and a gas are shown in Figure 5.8.

The Radial Distribution Function is the most used distribution function in the literature on amorphous solids. The appeal of the RDF is that it gives a rather direct physical picture of the spatially averaged structure. However, one has to



Figure 5.8: Typical shapes of the Radial Distribution Functions for (a) a crystalline solid, (b) an amorphous solid, and (c) a gas. These distributions schematically correspond to the atomic arrangements sketched in Figure 5.2.(Taken from Zallen 1983.)

keep in mind that the RDF (and other distribution functions from this section) are only one-dimensional representations of a three-dimensional structure, and thus contain incomplete information about it. Nevertheless, the RDF is a useful tool for investigating the complex structure of amorphous materials.

Integrating the RDF over the distances which include just the first peak of G(r) we get the total number of atoms in the first coordination shell Z

$$\int_{\text{first peak}} G(r) dr = Z. \tag{5.7}$$

The position of the first peak in RDF, r_1 , gives a value for the nearest-neighbor bond length, and the position of the second peak r_2 gives the next-nearestneighbor bond length. It is easy to see that the knowledge of r_1 and r_2 gives a value for the bond angle θ

$$\theta = 2 \arcsin\left(\frac{r_2}{2r_1}\right) \tag{5.8}$$

The width of the first peak is generally caused by thermal vibrations, but in the static limit (ignoring thermal and zero-point effects) for amorphous solids, it is due to the deviations in bond lengths. Similarly, the width of the second peak is caused by the static deviations in the bond angles in amorphous solids. The origin of structural features in the RDF is schematically shown in Figure 5.9.

There are two more distribution functions used in the literature. The first one, C(r), is called *Pair Correlation Function* and is defined through RDF as

$$C(r) = \frac{G(r)}{r} \tag{5.9}$$

and thus goes linearly with r. The Pair Correlation Function (PCF) has two advantages over RDF. First, it permits structural data to be reasonably presented over a greater range of r, because of its linear behavior. Second, more fundamentally, it is in PCF where experimental broadening is symmetric and r independent (Wooten and Weaire 1987; Etherington *et al.* 1982). Thus, PCF represent better way of comparison between the theory and experiment, then RDF. A typical shape of the PCF is shown in Figure 5.10.

The second distribution function, D(r), and the last one we shall introduce here, is called *Reduced Radial Distribution Function* (RRDF) and is defined as

$$D(r) = \frac{G(r)}{r} - 4\pi r n_0.$$
 (5.10)

It called *reduced* because it oscillates about zero since the average density background curve has been subtracted. Because it is a difference curve and is weighted by a factor r, in many cases it displays structural correlations more clearly than the RDF itself (Elliott 1984). A typical shape of an RRDF is shown in Figure 5.11.



Figure 5.9: Schematic illustration of the origin of structural features in RDF for an amorphous solid. Atoms are shown as lying on sharply def d rings, for simplicity. (Wooten and Weaire 1987.)



Figure 5.10: Typical shape of PCF for an amorphous solid. (Wooten and Weaire 1987.)



Figure 5.11: Typical shape of the RRDF for an amorphous solid. (Taken from Elliott 1984.)

5.4 Structure Factor vs. Pair Distribution Function

It is well known that the static Structure Factor (SF), for, say, X-ray scattering in the amorphous sample is given by

$$S(\mathbf{Q}) = \frac{1}{N} \mid \sum_{i=1}^{N} exp(\mathbf{i}\mathbf{Q} \cdot \mathbf{R}_i) \mid^2,$$
(5.11)

where \mathbf{Q} is the momentum transfer vector and \mathbf{R}_i are atomic positions in the structure.

The Structure Factor defined in (5.11) is an important quantity in both experimental measurements and theoretical calculation. In crystals, $S(\mathbf{Q})$ gives the Bragg peaks and is at the foundation of crystallography. In amorphous maints of the intensity in X-ray scattering, terials, from the experimental measur one can usually determine the structure factor $S(\mathbf{Q})$, from which one can find PDF, P(r), and compare it with the predictions of theoretical models. Furthermore, $S(\mathbf{Q})$ is an important quantity for establishing the criteria of randomness in modeling amorphous structures (Wooten and Weaire 1986). Whatever method we use to create a random structure, it is useful to calculate $S(\mathbf{Q})$ for the structure, along one particular direction in \mathbf{Q} -space. As we said, in a crystal, $S(\mathbf{Q})$ is obtained as a set of delta functions located at certain values of \mathbf{Q} , which correspond to the Bragg peaks along the chosen direction in \mathbf{Q} -space. The sample is well randomized if $S(\mathbf{Q})$ becomes smeared over all values of the wave vector Q equally, so that, ideally, there are no remnants of the Bragg peaks in the original crystalline structure, which become small and comparable to values of $S(\mathbf{Q})$ for any other **Q**. We have used this criterion in creating our computer models of amorphous diamond, and amorphous silicon. In Figure 5.12 we show S(Q) for a crystlline, and also for several randomized structures (Wooten and Weaire 1986).

We now want to connect the Structure Factor, (\mathbf{Q}) with the Pair Distribution Function, P(r). For that, we have to calculate the configurational average of $S(\mathbf{Q})$ for the real sample (see Cusack 1987, pp.56-60).

Let us introduce the single-particle density function, $\nu(\mathbf{r})$

$$\nu(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{R}_i).$$
(5.12)

It is obvious that

$$\int \nu(\mathbf{r}) d\mathbf{r} = N. \tag{5.13}$$

Introducing $\nu(\mathbf{r})$ into (5.11) it can be shown that $S(\mathbf{Q})$ can be alternatively written as

$$S(\mathbf{Q}) = \frac{1}{N} \int \nu(\mathbf{r}_1) exp(\mathbf{i}\mathbf{Q} \cdot \mathbf{r}_1) d\mathbf{r}_1 \times \int \nu(\mathbf{r}_2) exp(\mathbf{i}\mathbf{Q} \cdot \mathbf{r}_2) d\mathbf{r}_2.$$
(5.14)

Rewriting (5.14) as

$$S(\mathbf{Q}) = \frac{1}{N} \int \nu(\mathbf{r}_1) \nu(\mathbf{r}_2) exp[\mathbf{i}\mathbf{Q} \cdot (\mathbf{r}_1 - \mathbf{r}_2)] d\mathbf{r}_1 d\mathbf{r}_2, \qquad (5.15)$$

changing the variables so that $\mathbf{r}_2 \rightarrow \mathbf{r}'$, $\mathbf{r}_1 - \mathbf{r}_2 \rightarrow \mathbf{r}$, and after some algebraic manipulation we get

$$S(\mathbf{Q}) = \frac{1}{N} \int F(\mathbf{r}) exp(\mathbf{i}\mathbf{Q} \cdot \mathbf{r}), \qquad (5.16)$$

where, using the properties of delta function, the function $F(\mathbf{r})$ is obtained as

$$F(\mathbf{r}) = \sum_{i,j} \delta[\mathbf{r} - (\mathbf{R}_i - \mathbf{R}_j)].$$
(5.17)

So, to calculate the average $S(\mathbf{Q})$ from (5.16), one has to calculate the average of the function $F(\mathbf{r})$.



Figure 5.12: Values of the S(Q) computed along (111) direction of the 216-atom periodic Si unit cell. (a) The crystalline diamond cubic structure. (b) - (d) More and more randomized structures (Wooten and Weaire 1986).

Going back to the definition of PDF, (5.2), we note that the atom at the origin is excluded in the definition of PDF, while *all* atoms are taken in the sum in (5.17). Then it is obvious that we can write

$$\langle F(\mathbf{r}) \rangle = \langle \sum_{i,j} \delta[\mathbf{r} - (\mathbf{R}_i - \mathbf{R}_j)] \rangle,$$

= $\langle \sum_{i \neq j} \delta[\mathbf{r} - (\mathbf{R}_i - \mathbf{R}_j)] \rangle + N \delta(\mathbf{r}).$ (5.18)

The first term in the second line of (5.18) is just equal to $Nn_0P(\mathbf{r})$, as given by (5.2), so that we can write

$$\langle F(\mathbf{r})\rangle = n_0 N P(\mathbf{r}) + N\delta(\mathbf{r}),$$
 (5.19)

or for the average of the Structure Factor,

$$\langle S(\mathbf{Q})\rangle = \int_{V} [n_0(P(\mathbf{r}) - 1) + n_0 + \delta(\mathbf{r})] exp(\mathbf{i}\mathbf{Q}\cdot\mathbf{r}) d\mathbf{r}$$
(5.20)

which gives, using the properties of the delta function,

$$\langle S(\mathbf{Q})\rangle = 1 + n_0 \int_V [P(\mathbf{r}) - 1] exp(\mathbf{i}\mathbf{Q} \cdot \mathbf{r}) d\mathbf{r} + (2\pi)^3 \delta(\mathbf{Q}).$$
(5.21)

The term $\delta(\mathbf{Q})$ in (5.21) implies strong scattering intensity in the forward direction with $|\mathbf{Q}| = 0 = \theta$ [see Eqn. (5.1)]. This peak would fall in the incident beam and not be observed in pratctice. In any case, this term should be replaced by another term which properly takes in account the shape and the size of the sample in the integration (5.20) (see Guinier 1955), but we can neglect this term anyway because it does not contain information about the structure and is negligible unless Q is very small in which event θ would be too near the incident beam direction for observation.

Transforming (5.21) into spherical coordinates and separating the variables we finally get the connection between the Pair Distribution Function and the averaged Structure Factor, I(Q),

$$I(Q) \equiv \langle S(Q) \rangle = 1 + n_0 \int_0^\infty [P(r) - 1] \frac{\sin Qr}{Qr} 4\pi r^2 dr.$$
(5.22)

We assumed in (5.22) that the system is *isotropic*. Noting that $P(r) \rightarrow 1$ as $r \rightarrow \infty$, we can see from (5.22) that $I(Q) \rightarrow 1$ as $Q \rightarrow \infty$.

Finally, we note that inferring I(Q) from the observed intensity in scattering experiments is not always straightforward. For the detailed analysis of the problems regarding this problem, the reader is referred to Etherington *et al.* (1982).

Chapter 6

Historical Background of Modeling Random Networks

Modeling of amorphous structures can be divided in two large classes. The first one is the Dense Random Packing of hard spheres, (DRP), in all its varieties, and the second is based on the Continuous Random Network, (CRN), concept. The DRP model was very successful in explaining the amorphous structure of some liquids, amorphous metals, ionic solids and molecular organic solids. Atoms in these systems are connected with each other predominantly by non-directional forces, which makes DRP a suitable model for the description of these materials. DRP modeling has been pioneered by Bernal (1959,1964), and subsequently developed by Finney (1970), Bennett (1972) and others. For a review of modeling amorphous metals with DRP models see an excellent and comprehensive article of Cargill (1975). In this Thesis, however, we shall focus our attention only on the Continuous Random Network models which are suitable for describing the structures of most non-metallic materials with predominantly covalent directed bonds, namely, covalent glasses. Covalent glasses posses much higher degree of short-range order than metallic glasses and it is dominated by covalent bonding with definite number of nearest neighbors, bond lengths and bond angles. The prototypical covalent amorphous solids are amorphous silicon, (a - Si), and amorphous germanium, (a - Ge) which belong to the semiconductors of a Group-*IV*. Every atom in these structures has for nearest neighbors, i.e. it is tetrahedrally coordinated.

We note here that the invention of the term *continuous* in connection to random networks is somewhat unfortunate, because random networks are, in fact, paradigmatically *descrete* in their structure. By "continuous" it is meant that one can build an amorphous network continuously, starting from the short-range order unit, to indefinite size without including unsatisfied bonds or breaking the structure. In other words, "continuous" means that there are no identifiable boundaries in the structure, separating regions of distinctly different type of structure.

6.0.1 Hand-built CRN Models

The first attempts to explain the structure of covalent glasses, around 1930, were based on, then very natural, hypothesis that amorphous materials actually consist of very large number of elemental microcrystals, randomly arranged into a very fine polycrystalline structure, which appears as amorphous. All attempts to fit the experimental data with such microcrystallite models failed, and the early idea of a *continuous random network* of Zachariasen (1932) became soon the only viable alternative. It was proposed by Zachariasen that "...the atomic arrangement in glass is characterized by an extended three-dimensional network which lacks symmetry and periodicity." In Figure 6.1 we show the historical schematic diagram of Zachariasen which represent his CRN model of amorphous silica. But



Figure 6.1: Zachariasen's schematic 2d diagram represents his CRN model for amorphous silica. Open circles are two-fold coordinated oxygen atoms, and black dots are Si atoms which are four-fold coordinated in 3d (Zachariasen 1932).

the first models based on the Zachariasen's ideas were built much later. One of those was the one for SiO_4 , done by Bell and Dean (1966,1972). This was a hand-built model and is shown in Figure 6.2. This model was quite successful in explaining the diffraction data. In building the model, Bell and Dean used basic units consisting of a central Si atom and four rigid wires in perfect tetrahedral arrangement. The O atoms were attached by inserting the wires into pre-drilled holes in the O atoms. The model was built to have a mean Si - O - Si bond angle close to 160°, but without any particular bond angle distribution. It maintained full coordination without dangling bonds in its interior. The model consisted of 614 atoms. Atomic coordinates were determined with the help of photographic techniques. From those coordinates the *rms* bond-length deviation was small in agreement with the experiment, while the bond-angle deviation function was computed and was in good agreement with the diffraction data of Mozzi and Warren (1969), as shown in Figure 6.3.

Very soon, amorphous elemental semiconductors were intensively studied. The amorphous Group-IV semiconductors, a - Si and a - Ge, came to be regarded as prototypical covalent amorphous solids. It was not clear in the begining whether tetrahedral bonds in such systems can be randomly connected *ad infinitum* in a disordered manner, or not. It was believed by Phillips (1979,1981), that for instance, amorphous silicon, due to its *overconstrained* structure (a notion that will be explained in detail later), must necessarily have a discontinuous structure, in which regions of continuous random network are limited in size. But it is obvious that, in principle, there is a very close connection between a - Si and amorphous silica. A random network model for one can be easily converted into



Figure 6.2: The hand-built model of Bell and Dean for amorphous silica (Bell and Dean 1966).



Figure 6.3: Comparison of the RDF for SiO_4 derived from the model of Bell and Dean (1972) with the experimental reults of Mozzi and Warren (1969). (Taken from: Zallen 1983.)

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a corresponding model for the other, by adding or substracting the oxygen atoms which link the silicon atoms and introducing a weak bond-bending force at oxygen sites.

The first CRN model for a tetrahedrally bonded amorphous solid was built by Polk (1971) and is shown in Figure 6.4. There were no particular rules used in building Polk's model, except that there were no dangling bonds left within the interior of the structure. Whenever a choice about the bonding of a new atom should be decided, simply an arbitrary, random choice was made, just as in the work of Bell and Dean. The model contained substantial number of five-, sixand seven-membered rings which ensured generation of a non-crystalline structure. There were no dangling bonds in the interior of the structure. Bond-length deviations werere restricted within 1%, and bond-angle deviations were within $\pm 10^{\circ}$ about the tetrahedral angle of 109°. The model consisted of 440 atoms. In Figure 6.5 we show the RDF for Polk model compared to the experimental result of Moss and Graczyk (1969).

The original Polk model was physically extended to 519 atoms and refined by Polk and Boudreaux (1973). The refinement was in reducing the deviation of nearest-neighbor bond lengths from 1% to 0.2% using precise laser-beam measurements of the atomic coordinates and computer techniques. Steinhardt *et al.* (1974) and Duffy *et al.* (1974) used 519 model of Polk and Boudreaux (1973) and refined it further. This refinement consisted of introducing the Keating (1966) potential in the structure and relaxing the system toward the minimum of the elastic energy in terms of the bond lengths and bond angles.

The method of relaxation adopted by Steinhardt et al. (1974), which we also used in creating our models of amorphous diamond, is to move each atom


Figure 6.4: Polk's original hand-built model for amorphous silicon (Polk 1971).



Figure 6.5: Comparison of RDF for Polk model of amorphous silicon (1971) with the RDF deduced from the experimental measurements of Moss and Graczyk (1969). (Taken from: Zallen 1983.)

separately and sequentially, while keeping the coordinates of the other atoms fixed, until there is no force on it. This process is iteratively repeated until the convergency is achieved. In this way Steinhardt et al. found new, relaxed coordinates of 519-atom model of Polk and Boudreaux. On the other hand, they also built a new 201-atom model starting from a 21-atom cluster with new atoms serially added. Whenever a small group of atoms was added to the growing cluster their positions were relaxed by computer to minimize the forces on them. Thus, the connectivity of this network is determined by the relaxation procedure. They did not find any significant structural difference between the two models. Duffy et al. (1974) used the same 519-atom model of Polk and Boudreaux but adopted different relaxation procedure. Each atom was simultaneously moved in the direction of force on it, a distance proportional to that force. After each move the forces are recalculated, the atoms moved again, and the process iterated until the forces and displacements become small. In this way they obtained results which were pretty much the same as those of Steinhardt et al.. In Figure 6.6 we show the RDF obtained from the relaxed 519-atom model of Steinhardt et al. (1974), compared with the experimentally derived RDF.

Provoked by the controversy involving the presence of five-membered rings in amorphous III - V compounds like GaAs, which would, of course imply the occurence of energetically unfavorable, "wrong" bonds between like atoms, and to check if different ring statistics would produce different RDFs, Connell and Temkin (1974) built a model of a - Ge with no odd-membered rings. The model consisted of 238 plastic and metal tetrahedra. This model did not produce any improvement of the agreement with experiment. Our own calculations of RDF for a - Si and a - C show that RDF is very similar for different ring statistics



Figure 6.6: Comparison of the RDF of a relaxed CRN model of a - Ge by Steinhardt *et al.* (1974) with the experimentally derived curve. (Taken from: Zallen 1983.)

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(Djordjević et al. 1995).

It is interesting to mention that there was an early effort to build a model for amorphous diamond. This was hand-built model of Kakinoki *et al.* (1960) which consisted of about 100 atoms. To construct an "amorphous" structure, the authors used two basic units, the first with tetrahedral symmetry of diamond lattice, and the second with the trigonal symmetry of graphite. The C - Cbond lengths were different in those two units, and equal to those in crystalline diamond and graphite, respectively. To reproduce electron diffraction data the individual regions in the structure dominated by either diamond-like or graphitelike structure, were supposed not to be of larger size than a few Angstroms. To our knowledge no detailed analysis of this model have been done, but we could argue that this model is conceptually wrong for describing an amorphous solid.

All these early hand-built models suffered from the their finite sizes, or in other words, from the lack of periodic boundary conditions. In these relatively small models, a large fraction of the atoms were necessarily located close to the surface. This complicates the analysis of the bulk properties, and calculation of the RDF. The first hand-built model which had the periodic boundary conditions implemented was made by Henderson (1974). The model consisted of 61 atoms.

6.0.2 Computer-built CRN Models

Maybe the very first computer modeling of this kind was done by Kaplow *et al.* (1968). They tried to simulate the structure of amorphous selenium and to compare it to the experimental results. The method Kaplow *et al.* adopted in creating computer model is a good example of a misconception that one can make an amorphous structure just by randomizing the atomic coordinates in a

crystalline structure. This is exactly what the authors did in this early work. They computer-generated coordinates of crystalline arrangement of about of 100 atoms, and then used Monte Carlo procedure to randomize these coordinates. Only those which improved RDF were accepted. After about 10⁵ moves a "reasonable" agreement with experiment was achieved. The problem with this procedure, as we have already mentioned before, is that obtained structure is topologically identical to the crystalline one, and thus can not be expected to give good description of the amorphous selenium.

Henderson *et al.* experimented with computer algorithms for creating structures with periodic boundary conditions, but they did not succeed in getting good agreement with experiment. Nevertheless, the approach of Henderson, with generating periodic structures and with using a simple computer algorithm, inspired later work on computer modeling. In contrast to this approach, Shevchik (1973) and Polk and Boudreaux (1973) tried to imitate in their algorithm the hand-building process and that proved to be very cumbersome procedure.

As we have already stressed, a truly amorphous structure created by a successful randomization of the crystalline atomic positions, must be topologically different from the structure of its crystalline parent, and it must have perfect connectivity. One obvious technique to ensure these two requirements, for instance in creating amorphous silicon, is to start from the diamond cubic structure, remove one atom at random, and rejoin the four dangling bonds in pairs. In this way the number of atoms in the structure clearly decreases, but the topology is changed due to the fact that six-membered rings of the crystalline structure are destroyed, while five-, and seven-membered rings are introduced. Four-fold connectivity of the network is preserved. This method was used by Alben *et al.* (1975) who used 64-atoms crystalline supercell as a starting point, and ended up with a 58-atoms model of amorphous silicon. In an unpublished work of Wooten and Weaire (see Wooten and Weaire 1987) similar studies were done on models that contained 700 - 1000 atoms. Results were less then impressive. Calculated RDFs are in poor agreement with experiment. The structures obtained in this way have large bond-angle distortions, and it was concluded that they are not satisfactory as models of amorphous silicon.

The other technique which illustrates the topological connection between the structure of vitreous silica and amorphous silicon, was employed by Evans *et al.* (1974, 1975). They used a decoration transformation (see Wright *et al.* 1980) of the vitreous silica random network model of Evans and King (1966) which involved removing the oxygen atoms, rejoining the two dangling bonds and adjusting the new network to have the meand bond length appropriate for amorphous silicon. The model achieved relatively good agreement with experiment in the first two peaks, but the model pair correlation function exhibits too much structure at higher separations.

The first approach to computer generation of periodic random networks was extensively developed by Guttman (1974, 1976). His aim was to construct an ideal random network with four-fold coordination which would describe the structure of amorphous germanium. Guttman does not use a single computer algorithm, but otherwise his approach is quite similar to the Wooten and Weaire method (1987) which we used in our modeling of amorphous diamond. Guttman starts from the crystalline super-cell which contains many unit cells of the crystal; periodic boundary conditions are applied. There are no bonds in the model initially. Bonds are introduced in the stochastic way: four neighbors are selected

at random from the given set of atoms which is assigned to each atom in the lattice. Thus four bonds are constructed at a time, and the process is repeated until, hopefully, the desired network is created. Guttman noticed that the probability of constructing a fully four-fold coordinated network in this way was decreasing with the size of the model. The size of the model varied from 64 atoms to 512 atoms. The structure was relaxed using a simple Hooke's-law bond-stretching, and bond-bending term. Guttman also varied the super-cell size to find the optimal density which minimizes the total strain energy. He found that the optimal model density was 15% greater than the observed crystalline density, while the density of a - Ge experimentally was found to be within the few percent of the crystalline density. Furthermore, a large compressive stress was introduced by random bonding assignments, and the rms angular deviation from the perfect tetrahedral angle ($\theta_0 = 109.47$) was found to be about 17°; much greater than the experimental value of abut 10° (see Etherington et al. 1982). Guttman then used a specific topological rearrangement to generate random network. In Figure 6.7 we show two examples of Guttman's bond rearrangements, or bond switches. The switch is accepted if it lowers the energy of the network, and rejected if it does not. In this way RDF was slightly improved, but the models still did not agree very well with experiments, because all Guttman's models contained many dangling dangling bonds.

6.1 Wooten–Weaire Method

Before we present the Wooten-Weaire method which we adopted in our computer modeling studies of amorphous diamond, we shall make a small digression here to describe the characteristics of the different sizes of models made for tetrahedrally



Figure 6.7: Two examples of bond switches used by Guttman (1976). Sixmembered rings of the crystalline lattice are shown, and four atoms are selected. A path 1-2-3-4 is defined and bonds 1-2 and 3-4 are exchanged with non-bonds 2-3 and 4-1 respectively.

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Figure 6.8: Crystalline diamond cubic cell.

bonded amorphous semiconductors which in the crystalline phase have diamond lattice structure. In figure 6.8 we show the unit cubic cell of the crystalline diamond. A super-cell of the crystalline diamond can be created by adding additional unit cells along the three coordinate axis. Thus, if there are 2 unit cells per axis, that creates a super-cell of 8 unit cells, each containing 8 atoms, which gives 64-atom model. Similarly, if there are 3 unit cells along each axes, that gives $3 \times 3 \times 3 \times 8 = 216$ -atom model. In this way, models consisting of 64, 216, 512, $1000, \ldots, 4096$ appear in the literature. Thus it is easy to tabulate the linear sizes of the various super-cells. For instance, in Table 6.1 we show the list of linear sizes, L, of the super-cell cube for Si and C, given in Angstroms. The numbers Table 6.1: Linear super-cell sizes, (L), in Angstroms, for Si and C used in modeling of a - Si and a - C (Djordjević *et al.* 1995). N is the number of atoms in the model.

N	L _{Si}	L_C		
216	16.2813	10.7004		
512	21.7084	14.2672		
1000	27.1354	17.8340		
4096	43.4167	28.5344		

in Table 6.1 are used to calculate the number density N/L^3 of the model before one allows the size of the super-cell to vary until the total strain energy is at minimum.

6.1.1 Keating Potential

In the Wooten and Weaire model of a - Si and a - Ge, the Keating potential is adopted to describe the interaction between the atoms. Keating potential was introduced eariler to fit the elastic and vibrational properties of Group-IV elements (Keating 1966). It represents a semiempirical description of bond-stretching and bond-bending forces and involve only few parameters. It consists of two terms, the first being the bond-stretching one, and the second the bond-bending.

$$V = \frac{3}{16} \frac{\alpha}{r_0^2} \sum_{l,i} \left(\mathbf{r}_{li} \cdot \mathbf{r}_{li} - r_0^2 \right)^2 + \frac{3}{8} \frac{\beta}{r_0^2} \sum_{l \{i,i'\}} \left(\mathbf{r}_{li} \cdot \mathbf{r}_{li'} + \frac{1}{3} r_0^2 \right)^2, \tag{6.1}$$

where α and β are bond-stretching and bond-bending force constants, respectively, and d is the strain-free equilibrium bond length in the diamond structure. For Si its value is d = 2.35Å, and for Ge d = 2.46Å. Note, however, that the second term in (6.1) depends not only on the angle between the bonds, but also on the bond lengths, and thus contains cross terms. The first sum in (6.1) is on all atoms l and their four neighbors i. The second sum is on all atoms and pairs of distinct neighbors and thus represents three-body part of the potential.

Central bond-streching forces are not enough to stabilize the structure, because the number of constraints imposed by maintaining fixed bond lengths is smaller than the number of degrees of freedom. This will be explained in more detail in Chapter 8, where we shall discuss the elastic properties of diluted amorphous diamond. At the moment it is enough to stress the importance of the bond-bending forces for creating a stable network. Bond-bending three-body force could be, in principle, simulated by introducing an extra fictitious bond for each 5 independent angular constraints. This is a sometimes useful strategy for investigating rigidity problems in networks, but for simulating the amorphous structures it is more realistic to use angular term in Keating potential. In practice, bond-stretching forces are much larger than bond-bending forces. Wooten and Weaire followed Martin (1970) by taking $\beta/\alpha = 0.285$ in building their model of a - Si and a - Ge. Due to the dominance of the α term, when the model is relaxed to minimize energy, all bonds relax to within a few percent to their ideal unstretched length, but because this is not enough to stabilize the structure, the β term defines the stable structure which minimizes the bond-bending energy. Thus, the total energy is roughly proportional to β , and relaxed structure is independent of β/α (Wooten and Weaire 1985; 1987). The Keating potential is schematically show in Figure 6.9.



Figure 6.9: The Keating potential bond-stretching (α) , and bond-bending (β) terms. (Taken from: Wooten and Weaire 1987.)

6.1.2 Wooten-Weaire Bond Switch

Wooten et al. (1985) created a new model of amorphous silicon and germanium which significantly improved the agreement with experiment. It consisted of 216 atoms. A new be 4-s itch was invented which does not produce large bond-length and bond-angle dostortions, and is simple and the only one used in the two-stage process which creates the model. This new bond switch is shown in Figure 6.10. The bond switch presented in Figure 6.10 is characterized by switching two second-neighbor bonds that are parallel to each other in the perfect diamond structure. This is a local rearrangement of bonds that creates minimal strain into originally strain-free perfect diamond structure, which was not the case for Guttman's switch (Figure 6.7). Atoms are numbered, their coordinates are listed, and neighbor-table is created. Bonds 1-2 and 5-6 in Figure 6.10 are parallel, and can be a candidates for switch. The switch consists of breaking those two





Figure 6.10: Wooten-Weaire bond switch. (a) Configuration of bonds in the diamond cubic structure. (b) Relaxed configuration after switching two bonds.

bonds, and creating two other bonds, 1-5 and 2-6. The switch is not acceptable if new bonds are longer than 1.7 times the unstretched nearest-neighbor bond, which is the length slightly larger than the second-neighbor distance, as it should be if a successful bond switch is to be made in the original crystalline structure.

One can define a ring as any closed non-returning path of bonds. The number of n-membered rings defined in this way increases with n. An *irreducible ring* is defined as one that has no shortcuts across it. That is, given any two atoms (vertices) on the ring, there is no shorter path between the two atoms (as measured by the number of bonds along the path) than a path on the ring itself. One advantage of such rings for topological purposes is that the number of n-membered rings goes to zero for large n, but no topologically important rings are omitted, and the complete table of ring statistics remains finite (Wooten and Weaire 1996).

The perfect diamond structure has only 6- membered irreducible rings. The introduction of a bond switch changes the ring statistics by destroying evenmembered rings and creating odd-membered rings, 5-, 7-, 9-, etc. membered rings. This process is schematically shown in 2d case in Figure 6.11.

When the structure is already randomized, bonds that are switched are chosen to be approximately parallel by ensuring that they do not belong to the same 5-, 6-, or 7-membered ring.

6.1.3 Initial Randomization of the Crystalline Lattice

Taking the crystalline super-cell of 216 atoms, the initial randomization is achieved by introducing a large number of bond switches in a random manner, at the temperature just above the melting point. Note that the *temperature* used in the



Figure 6.11: 2d schematic representation of a Wooten-Weaire topological bond switch. There are *four* 6-membered rings initially (diamond structure), and after a bond switch is made *two* 5-, and *two* 7-membered rings are created.

present context is the effective *simulation* temperature and it does not correspond to a real temperature. It is meaningful only within the simulated annealing environment which will be described in the next Section. Similarly, in the context of the simulated annealing, the melting point is defined as that temperature for which the mean square displacement of the atoms from their positions in the diamond structure increases linearly with time and the structure factor I(k), introduced in Chapter 5. approaches a value of order 1/N. This differs from the true melting behavior of a - Si and a - Ge in that tetrahedral bonding is preserved. For a - Si and $\beta/\alpha = 0.285$ the melting point is kT = 1.0eV (Wooten and Weaire 1987). The temperature appears here through the inclusion of Boltzmann factor, exp(-E/kT), which describes the probability of the acceptance of a given bond switch. The inclusion of a Boltzmann factor in the initial randomization process is inspired by its use in the second stage of the model building which will be described in the next Subsection. The melted structure has large bondangle deviations, and the subsequent process of annealing is supposed to decrease those deviations to their experimentally observed values. That means that the melted structure has a large amount of strain which is partially released in the annealing process. Bond-length deviations are not so big in the melted structure because local cluster of atoms around every new bond switch is relaxed under Keating potential. We stress again that the initial randomized structure is not really melted; it still has tetrahedral bonding and it is still solid. We use the term *melting* conditionally, only within the simulated annealing environment.

One bond switch introduced into the crystalline diamond super-cell affects the topology of the structure by destroing 12 six-membered rings, and simultaneously creating 4 five-membered, and 16 seven-membered rings. During the process of initial randomization, RDF becomes gradually featureless, reflecting, from the very beginning, the amorphous nature of the created structure. In Figure 6.12, Pair Correlation function is shown for various stages of the initial randomization (Wooten and Weaire 1987). The initial randomization must be accomplished at the temperature which is high enough to prevent the returning to the crystalline phase after the subsequent annealing process.

6.1.4 Annealing: Geometrical and Topological Relaxation

Geometrical relaxation can be achieved in different ways. The conjugant gradient method is an obvious choice, but for these tetrahedrally bonded structures the simplest relaxation method, used first by Steinhardt *et al.* (1974), is sufficient. In this method, as we have already briefly mentioned, after a bond switch is made, the force (vector) on each atom involved is calculated, and also the force gradient (tensor), and each atom is sequentially moved toward its equilibrium position while other atoms are kept fixed. The vector displacement, $\Delta \mathbf{r}$, of each atom is found from a Taylor series expansion for the force about the minimum energy atomic position

$$\nabla V_{\mathbf{r}} = -(\nabla^2 V_{\mathbf{r}}) \Delta \mathbf{r} \tag{6.2}$$

which requires a matrix inversion of the gradient tensor. This process is repeated many times until the convergence to equilibrium is achieved.

After the initial randomization produced a disordered, but highly strained model, it is necessary to continue with creating new bond switches searching for those which will lower the strain energy. Of course, the lowest energy possible is zero, i.e. that of crystal. So one has to be careful to avoid returning to the crystalline state during the process of annealing. Wooten and Weaire (1987) showed



Figure 6.12: Pair Correlation Function for different amounts of randomization. (a) The ideal crystalline diamond structure. (b)-(f), PCF for different concentrations of bond switches per atom, c = 0.06, 0.12, 0.18, 0.24, and 0.30, respectively. (Taken from: Wooten and Weaire 1987.)

that the system indeed returns to the original crystalline diamond structure if in the initial process of randomization the number of introduced bond switches was not large enough. They found that if the number of bond switches per atom that randomizes the lattice in the beginning is c > 0.6, annealing does not return the system back to the crystalline structure, and the energy of the final relaxed structure is comparatively low. Here c is the number of bond switches per atom. For $c \approx 0.3$ the system did return to the crystalline state. So, to make sure that the long process of annealing will lead to an acceptable final amorphous structure, one has to deal with two initial parameters: the melting temperature, and the number of bond switches that is introduced in the crystalline structure at the beginning. If the initial temperature is too high the subsequent annealing is not able to bring the system down to an acceptably low energy, and the obtained model has too much strain in it. In other words, with too high initial temperature the system is trapped in one of the numerous metastable states of relatively high energy. From the other side, the number of bond switches has also to be chosen optimally: if there are too many of them in the beginning, than again, the system will not be able to release a sufficient amount of energy during the annealing process, and the RDF of the final structure will show that the system has too large bond-length and bond-angle distortions. Wooten and Weaire found that for creating a - Simodel the optimal melting temperature for the initial process of randomization has to be kT = 1eV. As we explained in the previous Section, this 10,000K high temperature is meaningful only within the simulated annealing environment.

The annealing process itself is based on Metropolis Monte Carlo algorithm (1953) already applied in the literature to general problems of optimization by simulated annealing (Kirkpatrick *et al.* 1983; Vanderbilt and Louie 1984). The

Metropolis algorithm is generally used as an efficient simulation of a collection of atoms in equilibrium at a given temperature. In the process of creating a model of an amorphous structure, the introduction of topological rearrangements (bond switches) change the total strain energy of the lattice at given temperature. If that change, $\Delta E = E_{ini} - E$, (where E is the strain energy after a bond switch is introduced) is negative, i.e. if the introduction of a bond switch lowers the total energy, this bond switch is accepted. On the other hand, if the ΔE is positive (increases the total energy), that bond switch is still accepted, but with the probability $P(\Delta E) = exp(-\Delta E/kT)$. In practice, a random number uniformly distributed in the interval (0, 1) is chosen each time when a bond switch is introduced, and ΔE is calculated. If the picked random number is less than $P(\Delta E)$ than the new configuration of atoms is accepted. If the random number is greater than $P(\Delta E)$ the new configuration of atoms is rejected and the original one (before the bond switch was introduced) is used to start the next step. Of course, the next step always consists of introducing the new bond switch, i.e., in repeating the described basic step. When this is done many times, the procedure simulates the behaviour of the system at given temperature T, as it reaches the thermal equilibrium. The choice of $P(\Delta E)$ in the exponential form has the consequence that the system evolves into a Boltzmann distribution. It should be noted here, that the temperature T in the Metropolis algorithm is simply a control parameter, not the real temperature of the system. In making a model of an amorphous structure one essentially deals with the static structures where all dynamics the non-zero physical temperatures introduce in the system are neglected. The only place when the finite temperature effects come into a consideration is the broadening of the calculated raw RDF by convoluting it with Gaussian to simulate the

existing thermal broadening of the measured RDF in experiments (Etherington $et \ al.$ 1982). In all other instances when we speak about temperature, we mean by it just a parameter in the probability function in Metropolis algorithm.

The introduction of the Boltzmann factor is essential in the process of annealing because it is able to lift the structure out of a metastable state of higher energy, thus enabling it to find another path in the configurational space toward the lower-energy states. Without it the system would not be permitted to ever increase its energy, and thus it would be easily trapped in a metastable state with no way out. It has been noted (Wooten and Weaire 1987) that allowing the presence of the 4-membered rings in the annealing process facilitated the convergence toward the energy minimum, and helped to avoid trapping into highenergy metastable states.

Thus, after the structure has been initially randomized by the introduction of large number of bond switches, the temperature is then reduced in small steps, and at each temperature the system is kept long enough by introducing new bond switches and using Metropolis algorithm until the system is in the equilibrium. As we already mentioned this is followed by the Keating relaxation of the local regions affected by a bond switch. A sequence of the temperatures is chosen, and at the end, when the temperature is zero, one hopes to obtain the structure with all characteristics of amorphous materials. Wooten and Weaire (1985; 1987) obtained in this way good model for a - Si and a - Ge. Their final 216-atom structure had the rms bond-angle deviation about 12.6°, which is a significant reduction from about 22° which the initial randomized structure had. Consequently, the energy of their amorphous models was comparatively low. We shall see in the next Chapter that our 4096-atom model of a - Si exhibits even lower rms bondangle deviation $(10.5^{\circ} - 11^{\circ})$ which corresponds to the lower strain energy per atom than in Wooten and Weaire models. Nevertheless, some physicists object that there is still too much strain present in the amorphous structures obtained by using Wooten-Weaire method, and that a modification of it is needed if one wants to produce more realistic, less strained amorphous structures (Mousseau 1996 (a)).

In Figure 6.13 we show the Pair Correlation Function as it evolves in the annealing process (Wooten and Weaire 1987). The Wooten and Weaire model of a - Ge and a - Si (1985) has a slight remnant of the original crystal visible in the structure factor, but nevertheless, there was no serious discrepancy with experiment (Wooten and Weaire 1987). The slight memory of the diamond cubic structure that remained in the amorphous structure is the consequence of the insufficient initial randomization and not from the annealing process. It should be noted here that the only essential difference between the a - Si and a - Ge is a simple scaling in proportion to the bond lengths (d = 2.35Åfor Si, and d = 2.46Åfor Ge). Otherwise, the experimental data are practically identical for a - Si and a - Ge. In Figure 6.14 we show the pair correlation function obtained in Wooten and Weaire model for a - Ge compared with experiment. The discrepancy in PCF at high r are related to the presence of inhomogeneities in the real sample which are not taken in account in fully tetrahedrally connected models, which always have slightly higher density than samples produced experimentally.

6.2 Further Developments

Wooten and Weaire (1989) used their method to generate a model of the interface between the crystalline and amorphous silicon. Their model consisted of 512 Si



Figure 6.13: The pair correlation function at three points in the annealing process (Wooten and Weaire 1987). The rms bond-angle deviations, from top to bottom, are 15.6°, 13.2°, and 12.6°, respectively.



Figure 6.14: Comparison of PCF for a - Ge. Thin line is the Wooten and Weaire model (1985), and thick line is experimental.

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Figure 6.15: A computer-generated picture of the crystalline/amorphous silicon interface model (Wooten and Weaire 1989).

atoms and was partitioned into two regions. One region of 192 atoms bounded by (100) interfaces was held at zero temperature. The remaining region of 320 atoms was randomized at kT = 1eV and then annealed. In Figure 6.15 we show the generated interface model. The structure factor drops to a value characteristic of the bulk amorphous region over a distance of about 3Å. The rms bond-angle deviation in the amorphous region is 12°. After the annealing process was done, the whole structure is relaxed under the Keating potential. Atoms in the first crystalline layer had the rms displacement of about 0.21Å. It was noted that if the cell was held at half the melting point for a time much longer than the time required to make good interface model, the amorphous region crystalizes. Another application of the Wooten-Weaire method was done by Mousseau and Lewis (1990) in their computer simulations of amorphous silicon hydrides. The starting point is a model of amorphous silicon obtained by Wooten-Weaire method. Instead of the Keating potential the authors use Stillinger-Weber potential (Stillinger and Weber 1985) to describe the interaction between atoms. They introduce pairs of H atoms in the a - Si structure in such a way that the the fourfold coordination is preserved. The nearest-neighbor Si atoms were allowed to have to each bond to either one, or two H atoms. After each introduction of hydrogen pairs, the structure is Monte Carlo relaxed using a finite number of Wooten-Weaire bond switches, and relaxed using the Stillinger-Weber potential. The process is repeated until the desired concentration of H atoms is achieved. Mousseau and Lewis calculate Si - Si, Si - H, and H - H partial pair distribution functions, as well as corresponding static factors, and find that the agreement between the model and experiment improves with H concentration.

As we have seen, the Wooten-Weaire annealing method for generating amorphous networks does not have a firm prescription of how one can obtain a good model at the end of a long simulation process. The initial randomizing (melting) temperature, the number of the bond switches introduced during initial randomization, the time system is to be held at a given temperature, the sequence of temperatures, these are some of the parameters one has to play with during the creation of a model. This requires certain amount of intuition and experience that one has to develop to create a successful model. The authors colloquially call this method *shake and bake* (Wooten and Weaire 1987). There have been attempts to improve the efficiency of Wooten-Weaire method by designing an optimal temperature schedule for the annealing, as well as to increase speed of the whole process (O'Mard 1993) by allowing only 5-,6-, or 7-membered rings in the structure. The annealing algorithm was performed on parallel computer system. The optimal temperature schedule was found to be an inverse logarithmic function (O'Mard 1993). The author reports that the parallel algorithm was run using ten processors, and the 512-atom model took 140 hours of *real time*. The author argues that his parallel algorithm with the temperature schedule and the ring-type restriction, works better than the original Wooten-Weaire method. Indeed, O'Mard obtained rms bond-angle deviation of 11.65° in his model, which is lower than 12.34° – the value he obtained using the original Wooten-Weaire method.

Our objection to the claims that O'Mard's algorithm is qualitatively better than the original Wooten–Weaire method is based on our own results obtained in modeling amorphous silicon and amorphous diamond. We have used the original Wooten-Weaire method in constructing 216-, 512-, and 4096-model of a - Si. In the next Chapter it is shown that our 512 model of a - Si has even smaller rms bond-angle deviation than O'Mard's model. If 4-membered rings are excluded our model has rms bond-angle deviation of 11.06°, and with 4-membered rings allowed we got even smaller value of 10.54°. Furthermore, the real time that was needed to create our 512 models was certainly less that 140 hours reported in O'Mard's simulations, although due to the shake and bake nature of Wooten-Weaire method we do not have a precise number for the elapsed time in creation of our models which were all produced on ALPHA-DEC workstation. So, it seems that the small numerical improvement O'Mard achieved in his simulations can not be attributed exclusively to the temperature schedule used, and to the restriction of ring types. It still remains to be determined if the 'improvements' in the O'Mard algorithm really improve the Wooten-Weaire algorithm.

6.3 Conclusions

Early attempts to build a model of an amorphous structure by hand, even though clumsy, laid the path for the implementation of computer algorithms which led to the creation of very successful models. The idea of a microcrystallite nature of amorphous materials was abandoned in favor of continuous random network concept. Periodic boundary conditions were included, and increasing awareness of the importance of topology in amorphous materials led to the invention of the Wooten-Weaire topological bond switch, which, implemented into a Metropolis simulated annealing algorithm, proved to be a powerful way to create a topologically realistic amorphous structure using a computer. Designed originally for tetrahedrally bonded amorphous elemental compounds, the Wooten-Weaire method is adaptable to treat other systems as well, like vitreous silica, or amorphous mixture of diamond and graphite-like carbon atoms. The continuous random network model which well describes covalent glasses should be understood as an idealisation of real amorphous structures, in the same sense as a perfect crystal is an idealisation of real crystals one can find in nature. CRN models can serve as reference ideal amorphous structures to describe more realistic amorphous structures which usually contain voids and various kind of defects.

Chapter 7

Modeling Amorphous Diamond

7.1 Introduction

As we have seen in Chapter 6, a great deal of work has been done on modelling amorphous silicon and germanium. The structure is well understood and widely accepted as being a continuous random tetrahedral network (Polk 1971, Steinhardt et al. 1974). In the early seventies it was still not completely clear if continuous random networks could be continued outwards indefinitely without introducing dangling bonds in the structure, or large vacancies. Subsequently, it was understood that this was possible by allowing slight variations in bond lengths and bond angles which accommodate all the connectivity strains. Ziman, however, wrote in 1979, that "carbon bonds would not allow these strains so ideal 'glassy diamond' does not seem to exist" (Ziman 1979). In this Chapter we shall show the opposite, presenting a good CRN model of amorphous tetrahedrally bonded carbon. There has been growing interest recently in tetrahedral amorphous diamond (Drabold et al. 1994), largely because McKenzie and coworkers (McKenzie et al. 1991), and others (Lossy et al. 1992, Gaskell et al. 1992) have successfully grown an *amorphous* form of carbon, which is predominantly (85%-90%) fourfold coordinated.

In this Chapter we present our computer-generated continuous network model of tetrahedrally bonded amorphous diamond (Djordjević *et al.* 1995), constructed by a method introduced by Wooten, Weaire and Winer (Wooten *et al.* 19885, Wooten and Weaire 1987) as described in the previous Chapter. We hope this large model will serve as a useful reference point for discussions of the observed structures of various forms of amorphous carbon, which in reality (to date) always contain varying amounts of graphitic bonding. Our periodic supercell cell consists of 4096 = 8×8^3 atoms. For the sake of comparison, we have constructed similar models for amorphous silicon. Furthermore, we make two different structures for both cases; one where four-membered rings are allowed, and the other where four-membered rings are forbidden.

The layout of this Chapter is as follows. First, we shall give a short overview of relevant properties of amorphous diamond. We than present and compare results for all four models, and with the experimental measurements. Discussion and conclusions follow.

7.2 Wooten-Weaire Method

The method is described in detail in the previous Chapter and we give here just a brief summary in which we refer to our amorphous diamond model (Djordjević *et al.* 1995). The starting structure is a perfect diamond crystal. Periodic boundary conditions are imposed so that the structure is fully tetrahedrally coordinated, i.e., there are no dangling bonds anywhere. The bond-bending and bond-stretching forces are described by a Keating potential (Martin 1970, Keating 1966) as given

;	Silicon Carbon		
α (dyn/cm)	0.485×10^{3}	1.293×10^{3}	
eta/lpha	0.278	0.655	
r ₀ (Å)	2.35	1.535	
L (Å)	43.42	28.53	

Table 7.1: The values of the parameters used in the models of C and Si (Djord-jević *et al.* 1995). These were obtained from measurements of phonon dispersion relations and elastic constants in crystalline materials (Martin 1970).

by the Equation (6.1) and rewritten here

$$V = \frac{3}{16} \frac{\alpha}{r_0^2} \sum_{l,i} \left(\mathbf{r}_{li} \cdot \mathbf{r}_{li} - r_0^2 \right)^2 + \frac{3}{8} \frac{\beta}{r_0^2} \sum_{l\{i,i'\}} \left(\mathbf{r}_{li} \cdot \mathbf{r}_{li'} + \frac{1}{3} r_0^2 \right)^2$$
(7.1)

where α and β are diamond bond-stretching and bond-bending force constants respectively, and r_0 is the *strain-free* equilibrium bond length in the diamond structure. There are 4096 atoms placed in a box of size L. The numerical values of all the parameters used in our work are given in Table 7.1 (see Martin 1970).

The first step after generating the initial crystal structure is to randomize the network sufficiently, so that subsequent annealing will not lead the system back to the crystalline state. The randomization process is realized by the introduction of many bond rearrangements (bond switches) (Wooten and Weaire 1987) at a temperature just above the melting point for the model. The melted structure had $\Delta \theta \approx 22^{\circ}$ for the rms bond angle deviation. A useful criterion as to whether the system is melted or not, is the structure factor $I(\mathbf{k})$ associated with the (111) direction for the diamond cubic structure. (We use here \mathbf{k} to denote wave vector, instead of \mathbf{Q} which was used in Chapter 5.) If this quantity is of roughly comparable intensity for all k values, then the structure is well randomized (Wooten and Weaire 1987), and all memory of the original crystalline structure is gone. The bond rearrangements maintain four-fold coordination at each atom thus introducing large strains in the structure.

In the second stage of the procedure, the temperature is reduced in small steps, and at each new temperature thermal equilibrium is established. The system is relaxed *geometrically* (the release of the strain energy allowing the stretching and bending of bonds, according to Keating potential (Keating 1966)), and *topologically* (creating more bond switches in the system). As a consequence, the total strain energy, rms bond-angle deviation and rms bond-length deviation are decreased until an optimized amorphous structure is created as the temperature approaches zero. A piece of the obtained structure is shown in Figure 7.1.

The presence of four-membered rings in the structure makes a successful annealing process easier, while the absence of four-membered rings increases the probability that the system will be trapped in an unsatisfactory metastable state. When four-membered rings are allowed, the final structure contains only a tiny fraction of four-membered rings, even though there was a large number of such rings at the beginning of the process (in the melted structure after the first randomization).

7.3 Discussion of Amorphous Carbon

Since McKenzie and coworkers (McKenzie *et al.* 1991) have obtained 85% - 90% four-fold coordinated amorphous carbon by plasma-arc deposition, there has been an increasing interest in amorphous diamond-like carbon. These diamond-like carbon films are found to be hard, optically transparent, and chemically inert, which makes them potentially important for applications in coating technology



Figure 7.1: A piece of computer-generated tetrahedral amorphous diamond structure (Djordjević $et\ al.$ 1995).

and also for use as wide band gap semiconductors. It is known that amorphous silicon and amorphous germanium exhibit a striking similarity in the shape of their radial distribution functions (see Etherington *et al.* 1982 and Wooten *et al.* 1985). In both of these materials the bond streching forces are dominant compared to the weaker bond-bending forces. Amorphous carbon is different with respect to both a-Si and a-Ge because of very strong chemical bonding, and because the bond-bending forces are much larger relative to the bond-streching forces. The ratio of bond-bending to bond-stretching forces β/α is 2.4 times larger for carbon than for silicon (see Table 7.1). One might have expected a different amorphous structure for carbon (i.e. different ring statistics etc.) compared with silicon and germanium, because of the greater bond stiffness of carbon. This was the initial motivation for this work, but our results show that the Pair Distribution Function (PDF) of tetrahedral amorphous diamond is remarkably similar to the PDF's of amorphous silicon and amorphous germanium.

7.4 **Results and Comparisons**

We constructed four different models: two for amorphous carbon, and two for amorphous silicon. We were interested in the ring statistics, and whether the presence of the four-membered rings makes any significant difference in the final structure. So, one amorphous carbon (silicon) model was constructed with four-membered rings present and the other without four membered rings. We calculated the total strain energy, rms-bond length, rms bond-length deviation, rms angle deviation, and the mean angle between the bonds. Also, we calculated the number of 4-,5-,6-, and 8-membered irreducible rings present. The definition of a irreducible ring is given in Chapter 6, together with the discussion of their

Table 7.2: The structural parameters for the models discussed in this Chapter (Djordjević *et al.* 1995), at two densities - the crysalline density $(\rho/\rho_0 = 1.000)$ and the optimal density. The number of irreducible rings per site n_r is independent of the density as the topology is not changed when the density is varied, and it drops to zero for large r.

	Si(4)		Si		C(4)		С	
$ ho/ ho_0$	1.000	1.025	1.000	1.033	1.000	1.050	1.000	1.054
$< r > /r_0$	0.996	0.988	0.997	0.987	0.996	0.980	0.997	0.980
$< heta>^{\circ}$	109.24	109.23	109.25	109.23	109.31	109.30	109.31	109.30
$\Delta r/r_0(\%)$	2.52	2.46	2.65	2.57	4.39	4.31	4.40	4.31
$\Delta heta^{\circ}$	10.51	10.54	11.02	11.06	9.29	9.31	9.06	9.08
E(eV)/atom	0.336	0.334	0.367	0.362	0.757	0.741	0.731	0.715
n_4	0.015		0		0.009		0	
n_5	0.491		0.523		0.472		0.457	
n_6	0.698		0.676		0.760		0.800	
n_7	0.484		0.462		0.472		0.498	
n_8	0.156		0.164		0.156		0.143	

importance for topological purposes All results are presented in Table 7.2.

We tested the influence of the sample density on the strain energy, and found that the crystalline density is *not* the optimal one for the amorphous structure. In all cases, a slightly larger density gave a smaller strain energy when using the Keating potential. The Stillinger-Weber potential (Stillinger and Weber 1985) goes in the opposite direction for silicon: slightly smaller density gave the smallest strain energy (Wooten and Weaire 1987). The small density differences should therefore not be taken seriously, although it is proper to optimise the density to
give the smallest strain energy within a given model. The optimal density was determined by fitting a parabola to a plot of strain energy as a function of density, and finding the minimum, given in Table 7.2.

From the coordinates of the final amorphous structure obtained for the optimal density, we calculated the PDF, which is given as:

$$P(r) = \frac{G(r)}{4\pi r^2 \rho_0}$$
(7.2)

where G(r) is the radial distribution function defined in Chapter 5, and ρ_0 is the number density of the system:

$$\rho_0 = \frac{N}{L^3} \tag{7.3}$$

where N = 4096, and L is the *actual* size of the supercell (either the original supercell size as given in Table 7.1, or the optimized one). For comparison, we rescale the PDF of silicon to that of carbon, with the distance scaled by r_0 , the nearest neighbor distance in the crystalline form. The four PDF's are shown in Figure 7.2.

Using a Fourier transformation, the structure factor can be written (see equation (5.22) as

$$I(k) = 1 + \frac{4\pi\rho_0}{k} \int_0^\infty r[P(r) - 1]\sin(kr)dr$$
(7.4)

where r_0 is the strain free nearest neighbor distance for the crystalline structure as given in Table 7.1. We calculate the structure factor for the four models which are shown in Figure 7.3. Because there is no contribution to the integral (5) when P(r) approaches unity, it can be seen from Figure 7.2 that this integral should (and does) converge well, with only a few *termination* ripples at small k.



Figure 7.2: Pair distribution functions P(r) for amorphous carbon and amorphous silicon models, with, and without four-fold rings (Djordjević *et al.* 1995). All models are at the optimized density.



Figure 7.3: Structure Factors I(k) caculated from the corresponding pair distribution functions shown in Figure 7.2 (Djordjević *et al.* 1995).

7.5 Discussion

The most striking feature of the results in Table 7.2 is that there are no major differences between amorphous carbon and amorphous silicon. We considered two densities, the crystalline density, and the density which minimizes the total strain energy. The rms bond lengths, $\langle r \rangle /r_0$, of carbon and silicon are about the same, and slightly *smaller* than in the crystalline diamond structure. The rms bond-length deviation, $\Delta r/r_o$, is *larger* for carbon by 44%. This is the one of the most significant differences between carbon and silicon. The rms bond-angle deviation, $\Delta \theta^o$, is *smaller* for carbon by 18%, as would be expected because of the larger angular force reflected through the larger value of β/α . Ring statistics are also very similar, except that there are more six-membered irreducible rings (Wooten and Weaire 1987) in carbon, and fewer five-membered rings than in silicon.

The optimal density results given in the second sub-columns in Table 7.2, show the following features. The energy is minimized, in all cases, at a slightly *higher* density than the crystalline one. The rms bond length, the mean bond angle, and the rms bond-length, are slightly *decreased*, while the rms bond-angle deviation is slightly *increased*.

Looking at Figure 7.2, one can see a surprisingly good matching between the PDF's of carbon and silicon. Their general shape is the same. The first peak is shifted towards to a value slightly smaller than unity; the crystalline value. This is true even at the crystalline density, and corresponds to the rms relative bond-length, which is smaller than one in the crystalline state, i.e. the mean bond length in the amorphous structure is slightly smaller than in the crystal (1.544Å). The carbon first peak is broader than the silicon first peak, which is correlated with the larger rms bond-length deviation in carbon. This represents a different aportioning of the strain energy between bond length strain and bond angle strain in carbon and silicon. The ratio of the strain energy associated with the bond angle (second term in the Keating potential) and the bond length (first term in the Keating potential) for carbon is found to be 1.57, while for silicon it is 2.73. This means that relatively *less* energy is stored as bond bending strain in carbon, when compared with silicon. Nevertheless the overall features of PDF's are essentially unchanged between carbon and silicon.

Figure 7.3 shows again great similarity in the structure factor for carbon and silicon. Furthermore, it fits relatively well the measured structure factor for amorphous, diamond-like carbon, as shown in Figure 7.4 (see Gilkes *et al.* 1995, Figure 1). It should be remembered that these experiments are on samples containing 10% - 15% graphitic bonding so that a detailed comparison between our model and experiment is not appropriate at this time. Graphitic regions can be incorporated into computer generated models using molecular dynamics and other techniques (Wang and Ho 1993). However these models are much smaller than ours [the model in (Wang and Ho 1993) contains 216 atoms] so that a detailed comparison of these models with experimental structure factors is also premature. It must also be realised that carbon films (Gilkes *et al.* 1995) contain some hydrogen which will have some effect on the PDF and structure factor.

Our very large (4096 atom) and realistic structural model of amorphous diamond is potentially very appealing for addressing some of the other important issues of the physics of amorphous solids. One of those is the nature of the band tails in the electronic density of states in amorphous materials (Mott and Davis 1979). Recently, Dong and Drabold (1996) used our structural model of



Figure 7.4: A comparison of the structure factor from our computer-generated model of amorphous tetrahedral diamond with four-fold rings (dashed line) (Djord-jević et al. 1995), and the structure factor measured by Gilkes et al. (1995) (solid line), on samples containing 10% - 15% grahitic regions.

amorphous diamond to study the nature of the electronic localization in three dimensions in the presence of topological disorder. The crystalline diamond cell has a defect-free gap between the valence and the conduction bands, with sharp band egde. Dong and Drabold (1996) found that our amorphous diamond model has extended band tailing at both valence and conduction bands, as well as few defect states in the middle of the band gap. The defect states which are highly localized, are caused by the atoms with the few largest bond angle distortions. The band tail states change from highly localized states that surround some defect cores, to less localized states that are within larger clusters, finally to the extended states that are distributed throughout the cell, when the energy moves from midgap into the valence states. The authors present a very simple picture that suggest that any mechanism causing approximately Gaussian bond angle disorder must lead to the *exponential* tails (Dong and Drabold 1996).

7.6 Conclusion

Although carbon has much stiffer bond-bending forces than silicon (i.e. a much larger value of β/α , the ratio of bond-bending to bond-stretching force constants in the Keating model), this doesn't influence the pair distribution function significantly (Djordjević *et al.* 1995). The bond-angle deviations are slightly smaller in amorphous tetrahedral diamond compared with amorphous silicon and amorphous germanium, but they cannot be *too* small, as the atoms are constrained to be in a fully tetrahedrally coordinated random network. Indeed our experience in constructing random networks leads us to postulate that a rms bond-angle deviation of at least 7° is required if the network is not to contain crystalline regions and so be a two phase mixture. Our very large and realistic structural model

of amorphous diamond also provides a good tool for studying other important issues of the physics of amorphous materials, for instance, the nature of electronic localization in three dimensions in the presence of topological disorder.

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Chapter 8

Elastic Properties of Random Networks

8.1 Introduction

As we have seen in Chapters 6 and 7, continuous random network (CRN) models, first introduced by Zachariasen (1932), are very successful in describing networks of covalent glasses. Covalent glasses consist of atoms that make from two to four covalent bonds, generally with specified bond lengths and bond angles. A network glass can be regarded as a mechanical structure and one can analyse its mechanical and elastic properties in terms of the network stability. This approach dates back to Maxwell's work in the mid-nineteenth century (Maxwell 1864). It has been applied to glasses by Phillips (1979, 1980, 1981).

8.2 Rigid and Floppy Networks

Maxwell discussed the stability of a hinged connected frameworks in terms of the relation between the number of constraints and the number of degrees of freedom. If the simple network consists of N_b bars connected at N hinged joints in 2d, the number of constraints N_c is equal to the number of bars N_b . The number of internal degrees of freedom is 2N-3, where 2 rigid rotations and 1 rigid translation are subtracted as being not internal degrees of freedom. Maxwell concluded that the stability of 2d network is described by the following inequalities

$$N_b > 2N - 3,$$
 stable,
 $N_b < 2N - 3,$ unstable. (8.1)

In 3d stability condition (8.1) becomes

$$N_b > 3N - 6,$$
 stable,
 $N_b < 3N - 6,$ unstable. (8.2)

These two conditions describe so called *overconstrained* (*rigid*), and *undercon*strained (floppy) networks respectively. For large networks, one can neglect the rigid translations and rotations, and in 3d, the conditions which separates rigid from floppy networks become

$$N_b > 3N$$
, rigid,
 $N_b < 3N$, floppy. (8.3)

The number of constraints is equal to the number of bars only approximately, and Maxwell's condition of stability (8.2) should be understood, in the spirit of mean field theory, as an average global condition - which is, however, very good one (Thorpe 1983, 1985). Another way to look at Maxwell's result is to replace rigid bars by Hooke springs and to calculate the vibrational frequencies of the network. This is the standard problem in classical mechanics. The eigenfrequencies are calculated by diagonalising the dynamical matrix. If the network is floppy, there will be certain number F of eigenfrequencies that are zero. These modes are called *floppy modes* (Thorpe 1995). The number of floppy modes F is given in 3d by

$$F = 3N - N_c, \tag{8.4}$$

where 3N is the number of degrees of freedom, and N_c is the number of linearly independent constraints. Recalling equation (8.3) we can conclude that

if
$$F > 0$$
, network is floppy. (8.5)

If the network is overconstrained, i.e. if constraints become more and more dependent, equation (8.4) would give *negative* F - the quantity which is by definition non-negative. In practice, good results can be obtained assuming that

$$F = \max[3N - N_c, 0]. \tag{8.6}$$

In covalent network glass, (represented by a CRN model), the interatomic forces are well described by a Keating type of potential (7.1), which contains bondstretching part (proportional to α force constant), and bond-bending part (β force constant). Thus, constraints imposed on the network are those associated with the fixed bond lengths, and fixed bond angles. There is one α -force constraint per bond and 2r - 3 independent β -force angular constraints around an atom with $r \geq 2$ bonds. If there are n_r atoms in the network with r bonds (r = 2, 3, 4), then the total number of constraints is given by

$$N_c = \sum_{r=2}^{4} n_r \left[\frac{r}{2} + (2r - 3) \right].$$
(8.7)

Noting that

$$N = \sum_{r=2}^{4} n_r,$$
 (8.8)

the mean coordination of the network is defined as

$$\langle r \rangle = \frac{\sum_{r=2}^{4} r n_r}{\sum_{r=2}^{4} n_r}.$$
 (8.9)

The fraction $f \equiv F/(3N)$ is given by

$$f = \left[3\sum_{r=2}^{4} n_r - \sum_{r=2}^{4} n_r \left[\frac{r}{2} + (2r-3)\right]\right] / (3N)$$
(8.10)

which can be rewritten in terms of mean coordination $\langle r \rangle$ (8.9) as

$$f = 2 - \frac{5}{6} \langle r \rangle. \tag{8.11}$$

Thus, from (8.11), the number of floppy modes f is zero, at the mean coordination $\langle r \rangle = 2.4$. The Maxwell conditions of stability (8.3) can be thus reformulated as

if $\langle r \rangle > 2.4$ network is rigid,if $\langle r \rangle < 2.4$ network is floppy.(8.12)

This concept that network glasses can be divided into two different types was first introduced by Phillips (1979,1981). It was further discussed by Döhler *et al.* (1983) and subsequently made more rigorous by Thorpe (1983). For the covalent glasses which do not have dangling bonds (r = 1), the mean coordination is in the range from 2 to 4. When $\langle r \rangle = 2$, f = 1/3, which means that one third of all the eigen-modes are floppy. This corresponds to the floppy network which consists of long polymeric chains. As new bonds, i.e. cross links are added, f drops toward zero when the network becomes rigid. In the region $2 < \langle r \rangle < 2.4$, there are rigid and floppy regions in the structure, but rigid regions do not percolate. For $\langle r \rangle >$ 2.4 the network becomes amorphous solid in which rigid regions percolate. This result can be corrected for dangling bonds (Thorpe 1995). Thus, at the critical mean coordination, a rigidity phase transition occurs. An extensive research has been recently done by Thorpe *at al.* (1996), Jacobs and Thorpe (1995, 1996) and Jacobs and Hendrickson (1996), to determine the universality class of this rigidity percolation phase transition by calculating the critical exponents.

8.3 Elastic Constants of Random Networks

The ideas from preceeding section have been tested numerically by He and Thorpe (1985). They calculated both the number of floppy modes f, and three elastic moduli, C_{11}, C_{44} and bulk modulus B, for random networks with varying mean coordination. These physical quantities couple most directly to the rigidity phase transition.

To build large number of random network He and Thorpe used bonddilution of the crystalline diamond lattice. They start from 512-atoms crystalline diamond supercell that has $\langle r \rangle = 4$. The atoms interact via the Keating potential (7.1) with $\beta/\alpha = 0.2$. Then, bonds are removed in random manner, maintaining the structure with periodic boundary conditions. When a bond is removed all the α and β terms associated with it are removed from the Keating potential. No dangling bonds were permitted, so an arbitrary atom can have 2, 3 or 4 bonds. After certain number of bonds is removed, the structure is relaxed using the Keating potential. The initial crystalline structure, which serves here as a kind of a reservoir of bonds, is a stress-free network. After some bonds are removed, a small stress is introduced, but subsequent relaxation releases this stress and the system is again at zero strain energy. In this way a sequence of random networks was obtained in the whole range of allowed mean coordination. For each of those mean coordinations there were three samples with different statistics, generated by using three different random number generators. Also, one of these three samples had an enhanced number of 2-fold coordinated atoms at the expense of 3-fold sites. This served to test the general prediction that the properties of the network depend mainly on $\langle r \rangle$ and not on other parameters. All results were averaged over these three statistical configurations.

The computed f drops linearly as predicted by the mean field theory (8.11) but it has a small tail around the mean field transition point. Elastic constants C_{11} and C_{44} (averaged over the x, y and z directions), and the bulk modulus $B = \frac{1}{3}(C_{11} + 2C_{12})$, are computed with use of standard techniques (Feng *et al.* 1985; Feng and Sen 1984). The 512-atom supercell is redefined by an external strain ϵ and the elastic modulus C is obtained from the elastic energy $\frac{1}{2}C\epsilon^2$ after the network has been fully relaxed. The result is shown in Figure 8.1. He and Thorpe made a least-squares fit to the computed data and found that, within the range $2.4 < \langle r \rangle < 3.2$ all three elastic constants are very well approximated by the power low of the form (see Figure 8.1)

$$C = \text{const.}(\langle r \rangle - 2.4)^{1.5}.$$
 (8.13)

The equation (8.13) does not fit the data well at larger values of $\langle r \rangle$. In earlier studies, when the simple central-force models were used, elastic constants were linear in $\langle r \rangle$ in the whole range, with the exception of a small tail near critical region (Feng *et al.* 1985).

Recently, Franzblau and Tersoff (1992) performed computer simulations similar to those of He and Thorpe (1985) to calculate the elastic constants of random networks. They employed a direct algebraic approach in calculating elastic constants (Franzblau and Tersoff 1992). Their model has 216 atoms, but all results



Figure 8.1: Elastic moduli averaged over three different samples as a function of the mean coordination $\langle r \rangle$ for $\beta/\alpha = 0.2$. Solid lines are power low fit curves. (He and Thorpe 1985).

are obtained in the wide range of the force-constants ratio $\Gamma_c \equiv \beta/\alpha$ over 4 orders of magnitude. The authors also use the same method of bond-depletion like He and Thorpe (1985), and the underlying structure is again crystalline diamond lattice. The main graphical results are given for $\Gamma_c = 0.655$ which is the value for diamond lattice. This is significantly larger value than one used in work of He and Thorpe which is $\Gamma_c = 0.2$. Franzblau and Tersof found that for this particular, diamond value of Γ_c , all three elastic constants they computed $(C_{11}, C_{44}$ and shear constant $C_s \equiv (C_{11} - C_{12})/2$) follow very well the following power low in the whole range of $\langle r \rangle$

$$C = \text{const.}(\langle r \rangle - 2.394)^{1.40}.$$
 (8.14)

The elastic constant C_{44} behaves very accurately according to power low in the whole range of parameter Γ_c

$$10\Gamma_c < \Gamma < \Gamma_c/1000. \tag{8.15}$$

The exponent in the power low (8.14) vary from 1.35 to 1.89 within the range of Γ_c .

The other elastic constants exhibit more complex behavior. For either very small or very large Γ_c , C_{11} deviates considerably from the power low. Also, C_s deviates for large Γ_c , but it obeys the power low closely for small Γ_c .

Note that results of Franzblau and Tersoff (1992) are partially consistent with earlier results of He and Thorpe (1985) which were done for small value of $\Gamma_c = 0.2$. According to Franzblau and Tersoff, C_{11} deviates significantly from the power low for small Γ_c , and so it is not surprising that He and Thorpe (1985) were not able to fit C_{11} and B constants in the whole range of $\langle r \rangle$ with the power low. But, it remains unclear why it was not possible to fit the elastic constant C_{44} with the power low in simulations of He and Thorpe (1985), when according to Franzblau and Tersoff (1992) that was possible in their simulations within the wide range of Γ_c .

8.4 Bond–dilution of Amorphous Diamond Network

All existing computer simulations of elastic properties of random networks are performed by using a crystalline lattice as the underlying structure. In other words, the crystalline lattice is transformed into a random network by removing certain number of bonds at random, and subsequently relaxing the diluted structure. As we have stressed in Chapter 6, one has to be very careful in creating models of amorphous materials to avoid any crystalline memory in the final random network. Thus, one can be suspicious about the true amorphousness of the random network obtained by the random removal of bonds from an ideal crystalline structure. Conceptually, it is more appropriate to start from an amorphous fully connected network, and then perform bond-dilution on it, thus creating a sequence of random networks with different mean coordinations. We use our 512-atoms CRN model of *amorphous* diamond as this more realistic underlying structure. Repeating the basic guidelines presented in the work of He and Thorpe (1985), we calculate the bulk modulus $B \equiv (C_{11} + 2C_{12})/3$ as a function of the mean coordination $\langle r \rangle$ (Djordjević and Thorpe 1996).

Our amorphous diamond network is fully 4-fold coordinated and has a large stress stored in bond-stretching and bond-bending parts of Keating potential (7.1). This is the main difference with respect to earlier work where the starting structure was a stress-free crystalline lattice. In the present case, removal of certain number of bonds releases significant amount of elastic energy, and after subsequent relaxation the structure still has a significant amount of stress. Thus, while the strain energy is always zero when the crystalline lattice is diluted, here the strain energy drops from the value it has in our amorphous diamond model, to zero near the transition point $\langle r \rangle = 2.4$. In fact, we do not expect that the strain energy in particular, must become exactly zero at the mean field critical mean coordination, because at the critical point there are still many isolated rigid regions which do not percolate, but contain a certain amount of strain energy. It is a different question how those isolated rigid regions effect the behavior of the bulk modulus *B*. Being isolated, it may happen that they do not make any impact on the macroscopic stiffness of the structure which is described by the bulk modulus. However, to our knowledge, this question remains inconclusive at this stage of understanding of rigidity percolation phase transition.

We designed programs that remove bonds from the amorphous diamond network in several different ways. The obvious one does not impose any restriction except that it does not allow creation of dangling bonds, thus fixing the possible atomic coordination to 2, 3, or 4. As a consequence, when a large number of bonds is removed, i.e. when $\langle r \rangle \rightarrow 2$, there are many long linear polymeric chains in the structure. Of course, if one wants to decrease the mean coordination to 2, linear chains must form. But if we are mainly interested in the region $2.3 < \langle r \rangle < 4.0$, than we can construct various random networks with the same $\langle r \rangle$. Thus, at $\langle r \rangle = 2.59$ we have made *four* different structures. The first is already mentioned – it has long linear polymeric chains. The second has only short linear chains that contain not more than *three* 2-fold coordinated atoms. The third one has only *two*-atom linear chains, and in the fourth one all 2-fold coordinated atoms are isolated from each other. It was possible to construct random networks with different type of chains even for lower values of $\langle r \rangle$, but we did not explore this in more details. For our calculation of bulk modulus we used the first, nonrestrictive style of bond removal, so the polymeric chains are present in all our random structures at low $\langle r \rangle$.

The initial structure is fully connected amorphous diamond network with the mean coordination $\langle r \rangle = 4.0$. To avoid any possible correaltions between our random networks in a sequence of different $\langle r \rangle$, we adopted the following strategy. First, we remove small number of bonds, say 20, relax the lattice using the Keating potential, and calculate the mean coordination $\langle r \rangle$, and the total strain energy E. We repeat that process 10 times using different random number generators, and so produce 10 samples for a given $\langle r \rangle$, over which we perform the average. To further decrease the mean coordination, we do not continue from the structure that has been previously obtained, but rather we go back to our fully connected amorphous diamond network, and remove now 40 bonds, relax the diluted system an calculate new, smaller, value of $\langle r \rangle$ on 10 different samples. In the next step, we go back to the initial structure and remove 20 more bonds (i.e. 60 bonds), etc.... Each time we increase the number of bonds we remove, the greater stress is released from the initial amorphous diamond structure and the total elastic energy drops down.

8.5 Strain Energy and Bulk Modulus

It has been already reported (He and Thorpe 1985) that the relaxation process becomes very difficult for approximately $\langle r \rangle < 2.6$, even when the crystalline stress-free lattice is used for bond-dilution. In that range of mean coordinations, He and Thorpe used an extrapolation technique to obtain the behaviour at longer times (i.e. larger number of steps in the relaxation procedure) than could be probed. In our calculation it is even more difficult to perform the relaxation at small values of $\langle r \rangle$, but we did not need to use any extrapolation techniques for mean coordination as low as 2.20, which was small enough for our purposes. In Figure 8.2 we show the total strain energy as a function of the mean coordination $\langle r \rangle$. For large mean coordinations the relaxation is very fast, and only 500 relaxation steps are needed. For small mean coordinations the number of relaxation steps has been considerably increased to achieve the convergency. The required convergency has been kept constant, and the number of relaxation steps was variable so that, at small mean coordinations, it increased to 50,000 and more.

The bulk modulus B has been calculated in a standard way by redefining the size of the supercell uniformly along all three coordinate axes. For each mean coordination, and for each of the ten configurations, we have included the supercell size as a variable in the relaxation subroutine. In this way the structure is relaxed not only with respect to the α - and β -forces in the Keating potential, but simultaneously also with respect to the size of the supercell. In this way we obtained the reference point for bulk modulus calculations. Starting from that optimal supercell size, we redefined the supercell four times – two times increasing the supercell size sequentially, and two times decreasing the supercell size sequentially with respect to the original optimal size which minimizes the total elastic energy. By sequentially, we mean that we take coordinates of the atoms when the supercell is of optimal size, and apply a small uniform strain which slightly compresses the lattice. Then we relax the structure with Keating potential, calculate the new coordinates of all atoms, and apply the same strain again, using



Figure 8.2: Dots represent the total strain energy averaged over 10 different configurations, as a function of the mean coordination $\langle r \rangle$. The solid line is the best fit power-law curve. The energy is given in eV per atom (Djordjević and Thorpe 1996).

the updated coordinates from the previous configuration. In this way we obtain the values of the total strain energy at *five* different supercell sizes. These points should, in principle, form a parabola, which, of course, is the reflection of the harmonic nature of the Keating potential. The bulk modulus B is, up to the constant prefactor, equal to the curvature of that parabola. The problem that arises when diluting our amorphous underlying structure is common for all amorphous materials - one can spontaneously and unpredictably jump from one to another *metastable* state with different energy. If that happens in the program, one has to reject that situation, and to repeat the search for parabolic energy dependance again. This occurs very often and makes the computation painfully slow, if one does not first find the minimum energy with respect to the supercell size (Mousseau 1996 (b)). This is why we implemented simultaneous minimization of energy with respect to the supercell size. When that minimum is used to redefine the supercell, it is very rare that system jumps from one to another metastable state. In Figure 8.3 we show a typical jump in energy which occurs in amorphous networks. With careful examination we were able to reconstruct the 'missing' parts of the two parabolas, thus obtaining two different minima which correspond to two metastable states of the system, as shown in Figure 8.4.

We have investigated the nature of the two states that appear in our bonddepleted amorphous structure in more details. It became clear that the value of the energy minimum does not depend only on the supercell size, but also on the particular history of changes that were imposed upon the system. We were able to identify the atoms whose motion is responsible for the existence of these two energy states. Comparing the atomic coordinates of the structure in these states we made a picture which shows 512 atoms in one of the states while black bars



Figure 8.3: The system is systematically redefined by increasing the size of the supercell (arrows). The energy values all follow a parabolic curve, until a jump to a lower energy state occurs, and the second parabolic curve is created. Energy is in eV per atom, and mean coordination is $\langle r \rangle = 2.59$ (Djordjević and Thorpe 1996).



Figure 8.4: The picture shows two different energy minima which are characteristic for amorphous materials. Energy is in eV per atom, and mean coordination $\langle r \rangle = 2.59$ (Djordjević and Thorpe 1996).

that are drown represent the displacement of the given atom to another position which it has when the structure is in other energy state. Thus relatively small fraction of atoms is involved in repositioning which gives rise to the existence of a second state. This is shown in Figure 8.5.

Using the neighbor list for the structure we idendified the connectivity of the atoms involved in that motion. It turned out that all atoms there moved the most belong to the linear polymeric chains, as shown in Figure 8.6.

We spent some time on searching for two states of particularly small difference in energy, hoping to find so called *tunneling modes* that exist in amorphous systems. A common characteristic of all amorphous materials is a quasilinear term in the specific heat at low temperatures. This has been successfully interpreted phenomenologically in terms of a tunneling model, in which atoms, or groups of atoms, tunnel between the two lowest-energy states in a double potential well (Phillips 1972; Anderson et al. 1972; Phillips 1985). The tunneling is a very subtle process which involves energy differences of about $10^{-4}eV$ (Cusack 1987). Detailed microscopic models for the tunneling process is still missing. Amorphous elemental compounds like a - Si, a - Ge, or a - C, are of particular interest because of their relatively simple structure. Although it once seemed that the rigidity of the fully coordinated tetrahedral networks would prevent the possibility for tunneling states to exist, the experimental evidence is quite strong that tunneling states exist in these materials (Duquesne and Bellessa 1983). There were attempts to create a tunneling model which would explain the anomalous properties of vitreous silica (Vukcevich 1972), and an early computer simulation of tunneling states in random network glasses for a - Si and a - Ge (Smith 1979). In spite of all these attempts a satisfactory microscopic model for the tunneling



Figure 8.5: The picture shows 512 atoms in their positions which correspond to one of the states described by parabolas in Figure 8.4. The black bars represent the displacements of some atoms which give rise to the existence of the second state. Mean coordination is $\langle r \rangle = 2.59$ (Djordjević and Thorpe 1996).



Figure 8.6: The picture shows polymeric chains of atoms that are involved in the motion which gives rise to the existence of two states for the structure with $\langle r \rangle = 2.59$ (Djordjević and Thorpe 1996).

modes still does not exist. We were not successful in our search for tunneling states in our random networks. From Figure 8.3 one can see that the typical total energy difference between the two states we have in our structures, is about $512 \times 0.0002 = 0.1 eV$ which is three orders of magnitude larger energy than one typically involved in the tunneling modes. Nevertheless, detailed analysis of the energy minima in our random networks helped us to develop a program which easily finds the regions of parabolic energy dependence on the applied strain, which was crucial for extracting the value of the bulk modulus B.

In Figure 8.7 we show our computed bulk modulus B as a function of the mean coordination $\langle r \rangle$. It is clear from Figure 8.7 that the underlying initial structure from which a random network is obtained by bond dilution, does not make significant difference in the behavior of the bulk modulus. Our amorphous starting network, upon the bond-depletion produced the bulk modulus which almost exactly follows the power law of Franzblau and Tersoff (1992). The small discrepancy for the middle range of mean coordinations could be the consequence of the bad statistics we had in our calculation having only 10 samples for averaging. The other possibility is the fact that Franzblau and Tersoff (1992) do not give the explicit value of the force constants ratio Γ_c apart from stating that this is the diamond value. We have used $\Gamma_c = 0.655$ which is the value we had in our anorphous diamond model.

An interesting result from our simulations is the behavior of the optimal supercell size L_{min} , i.e. that one which minimizes the total strain energy at given $\langle r \rangle$. In Figure 8.8 we show that as more and more bonds are removed from the initial amorphous diamond structure, the optimal supercell size first slightly increases until about $\langle r \rangle = 2.7$. Further reduction of the mean coordination is



Figure 8.7: Dots represent our result for the bulk modulus B as a function of the mean coordination $\langle r \rangle$, for bond-depleted *amorphous* diamond lattice (Djordjević and Thorpe 1996). Each dot is obtained from the curvature of a parabola like one of those in Figure 8.4, and averaged over 10 configurations. The solid line represent the bulk modulus obtained by bond-depletion of the *crystalline* diamod lattice (Franzblau and Tersoff 1992). $\Gamma_c = 0.655$.

followed by a sudden decrease of the optimal supercell size.

We interpret this behavior as a collapse of the network due to the presence of the long linear polymeric chains. The two-fold coordinated atoms in these chains can come arbitrarily close to each other, because of the lack of an exclusion volume that initially existed due to the tetrahedral coordination of the amorphous network. To test this hypothesis we calculated the pair distribution function for four different mean coordinations, $\langle r \rangle = 2.44, 2.75, 3.06, 3.38$ (Figure 8.9). At small $\langle r \rangle = 2.44$ there are many peaks close to the origin, before the first and second peak that correspond to the nearest-neighbor, and the next nearestneighbor distance in the fully connected amorphous diamond, respectively. These additional peaks that occur at very small distances, are the consequence of the collapse of the network when the two-fold coordinated atoms in linear chains come very close together. This looks like a phase transition which occurs much before the rigidity percolation phase transition occurs at about $\langle r \rangle = 2.4$. If we artificially introduced an exclusion volume around each atom in the network, the collapse would not occur. Collapse is triggered by the large stress that is present in the initial amorphous diamond network. As we said, at small $\langle r \rangle$, large number of bonds were first randomly removed from the fully connected amorphous diamond network. Because of that, the stress in the network suddenly drops and the atoms are free to move toward the equilibrium positions which occurs in the process of relaxation. Because the exclusion volume of an atom is much smaller for small mean coordination, those atoms that belong to linear chains can approach each other very closely. In earlier work of He and Thorpe (1985) and of Franzblau and Tersoff (1992), where the underlying structure for bond removal was a stress-free crystalline diamond lattice, such a triggering mechanism was absent because the



Figure 8.8: The optimal supercell size which minimizes the total energy, L_{min} , as a function of the mean coordination $\langle r \rangle$. The length is given in Å(Djordjević and Thorpe 1996).



Figure 8.9: Pair distribution function calculated for $\langle r \rangle = 2.44(a), 2.75(b), 3.06(c), 3.38(d)$ (Djordjević and Thorpe 1996).

random network has zero strain energy for all mean coordinations.

The slight increase of the L_{min} in the region from 2.7 $\langle r \rangle \langle 4.0$ could be explained by the fact that the mean angle in our amorphous diamond model is, (as it is usual in amorphous networks), slightly *smaller* than the tetrahedral angle in the crystalline diamond structure which is $\theta_0 = 109.47^{\circ}$. Our amorphous diamond network has the mean bond angle $\langle \theta \rangle = 109.31^{\circ}$. Thus, in the beginning of the bond removal, the remaining bonds tend to relax toward the tetrahedral angle which means the slight expansion of the supercell.

8.6 Conclusion

Earlier calculations of the elastic properties of amorphous networks were done assuming that the bond dilution af a *crystalline* lattice and the subsequent relaxation, gives an acceptable sequence of amorphous networks, which is suitable for the calculation of the elastic properties. In our simulations, we have used a true *amorphous* structure for bond dilution, and calculated the bulk modulus as a function of the mean coordination. Our results show that in both cases the bulk modulus obeys practically the same power law, which suggests that for the elastic properties, the initial structure (before the bond dilution takes place) is not of a great importance. We have described the difficulties one encounters in dealing with a true amorphous structure which contains large strain, which are connected with different energy minima, i.e. different metastable states, that exist in amorphous materials. Finally, we showed that for small mean coordinations a collapse of the lattice cell occurs, due to the presence of many two-fold coordinated atoms, which significantly reduces the exclusion volume of an average atom, while the large strain in the structure triggers the collapse after a large fraction 187

of bonds is removed.

Chapter 9

Conclusion

In this thesis I have studied disordered properties of both continuous and discrete random media. I focused on the two-phase composites in two dimensions, random resistor networks, and on computer modeling of topologically disordered networks – amorphous solids. Results for the effective conductivity and the spectral function calculations, presented in Chapters 2, 3 and 4, are valid only in the low concentration limit $f \ll 1$, when the inclusions can be regarded as well separated and thus non-interacting. In other words, the effective conductivity and the spectral function is correctly obtained to the first order in concentration f. The only exception to this is the computer simulation results of Day and Thorpe (1996), the results of the effective medium theory, which are valid in the entire range of concentration f, and the results I obtained for the case of circular inclusions (Djordjević et al. 1996). I have shown that exact solution exists only in a few cases, namely for elliptical (circular) inclusions. The conformal mapping technique turned out to be a very powerful tool for calculating the effective conductivity for particular type of inclusions (holes or perfectly conducting inclusions) which may have sharp corenrs. The problem becomes much more difficult for inclusions with arbitrary γ if they contain sharp corners. In this case one has to solve numerically Fredholm equation for the induced charge density around the perimeter of the inclusion. It appears that the only *direct* numerical calculation of the spectral function (from the general definition (2.19) or (3.105)) has been done in computer simulations of Day and Thorpe (1996) on the discrete random square net. This has been possible because of the use of a powerful $Y - \Delta$ transformation technique (Frank and Lobb 1988) which calculates the effective conductivity of a random network very efficiently. Finally, the effective medium theory seems to give very good results for intermediate concentrations around the percolation threshold f_c , and thus proves itself useful for deducing the overall shape of the spectral function.

I have shown that the spectral function for a sheet containing holes can be calculated correct to second order in the area fraction of inclusions f. The result is a truncated Lorentzian that for all practical purposes is a Lorentzian in the range of interest. A knowledge of the spectral function permits the (complex) conductivity, σ , for any (complex) values of σ_0 and σ_1 to be found, by doing a single integral. This is particularly useful if there is a parameter in the composite that can be varied at fixed geometry. Examples would be the frequency and the temperature. The calculation in 2d was possible because an exact solution to this problem is available in terms of multiple images. An analytic continuation has been successfully done, which has allowed the spectral function to be found which is finite only over a narrow region at low concentration. Similar spectral functions can also be used in discrete systems made up of resistors (Foster 1924 and Straley 1979). Spectral functions are widely used in physics to study electronic and vibrational excitations. They have proved especially useful in systems containing
impurities, where local modes can occur (Elliott, Krumhansl and Leath 1974). The weight in the absorption spectrum goes like the defect concentration f and the width is determined by the interaction between defects and goes also as f. The reason for this close analogy between these two somewhat disparate situations is not entirely clear.

Chapters 5, 6, and 7, deal with the discrete random media, namely amorphous solids. I have studied computer modeling of amorphous tetrahedral semiconductors, particularly of amorphous diamond. Early attempts to build a model of an amorphous structure by hand, even though clumsy, laid the path for the implementation of computer algorithms which led to the creation of very successful models. The idea of a microcrystallite nature of amorphous structure was abandoned in favor of continuous random network concept. Periodic boundary conditions were included, and increasing awareness of the importance of topology in amoprhous materials led to the invention of the Wooten-Weaire topological bond switch, which, implemented into a Metropolis simulated annealing algorithm, proved to be a powerful way to create a topologically realistic amorphous structures on computer. Designed originally for tetrahedrally bonded amorphous elemental compounds, the Wooten-Weaire method is easily adaptable to treat other systems as well, like vitreous silica, or amorphous mixture of diamond and graphite-like carbon atoms. The continuous random network model which well describes covalent glasses should be understood as an idealisation of real amorphous structures, in the same sense as a perfect crystal is an idealisation of real crystals one can find in nature. CRN models can serve as a reference ideal amorphous structures to describe more realistic amorphous structures which usually contain voids and various kind of defects.

I have computer generated a very large (4096 atom) model of amorphous diamond (Djordjević et al. 1995), and calculated all relevant quantities that describe the obtained amorphous structure. My results show that although carbon has much stiffer bond-bending forces than silicon (i.e. a much larger value of β/α , the ratio of bond-bending to bond-stretching force constants in the Keating model), this doesn't influence the pair distribution function significantly (Djordjević et al. 1995). The bond-angle deviations are slightly smaller in amorphous tetrahedral diamond compared with amorphous silicon and amorphous germanium, but they cannot be too small, as the atoms are constrained to be in a fully tetrahedrally coordinated random network. Indeed our experience in constructing random networks leads us to postulate that a rms bond-angle deviation of at least 7° is required if the network is not to contain crystalline regions and so be a two phase mixture. Our very large and realistic structural model of amorphous diamond also provides a good tool for studying other important issues of the physics of amorphous materials, for instance, the nature of electronic localization in three dimensions in the presence of topological disorder (Dong and Drabold 1996).

Finally, in Chapter 8, I have studied the elastic properties of amorphous networks, using my large model of amorphous diamond as a starting structure. Earlier calculations of the elastic properties of amorphous networks were done assuming that the bond dilution af a *crystalline* lattice and the subsequent relaxation, gives an acceptable sequence of amorphous networks, which is suitable for the calculation of the elastic properties (He and Thorpe 1985; Franzblau and Tersoff 1992). In my simulations, I have used a true *amorphous* structure for bond dilution, and I have calculated the bulk modulus as a function of the mean coordination. My results show that in both cases the bulk modulus obeys practically the same power low, which suggests that for the elastic properties, the initial structure (before the bond dilution takes place) is not of a great importance. I have described the difficulties one encounters in dealing with a true amorphous structure which contains large strain, which are connected with different energy minima, i.e. different metastable states, that exist in amorphous materials. Finally, I showed that for small mean coordinations a collapse of the lattice cell occurs, due to the presence of many two-fold coordinated atoms, which significantly reduces the exclusion volume around an average atom, while the large strain in the structure triggers the collapse after a large fraction of bonds is removed.

I believe that this thesis could be a valuable comprehensive resource for anybody interested in the current state and the historical background of these particular fields of research. At the same time, I hope that the contribution I made, especially in computer modeling of amorphous networks, will be useful for the researchers who are interested in having large and realistic models of an amorphous solid for calculations of electronic and other properties of these materials. I also hope that my computer models will inspire more work on computer modeling of amorphous materials itself, because I have no doubts that the era of computer modeling is still at its beginnings.

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