

**THE CONDUCTIVITY, DIELECTRIC CONSTANT, $1/f$
NOISE AND MAGNETIC PROPERTIES IN
PERCOLATING THREE-DIMENSIONAL CELLULAR
COMPOSITES**

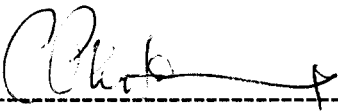
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A thesis submitted to the Faculty of Science, University of the
Witwatersrand, for the Degree of Doctor of Philosophy.

Johannesburg, October 2000

DECLARATION

I DECLARE THAT THIS THESIS IS MY OWN, UNAIDED WORK. IT IS BEING SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE UNIVERSITY OF THE WITWATERSRAND, JOHANNESBURG. THIS THESIS HAS NOT BEEN SUBMITTED BEFORE FOR ANY DEGREE OR EXAMINATION IN ANY OTHER UNIVERSITY



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2ND DAY OF NOVEMBER 2000

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ABSTRACT

Percolation phenomena are studied in a series of composites, each with a cellular structure (small conductor particles embedded on the surfaces of large insulator particles). The DC and AC conductivities, 1/f noise and magnetic properties (in some series) are measured in the systems consisting of Graphite, Graphite-Boron Nitride, Carbon Black, Niobium Carbide, Nickel and Magnetite (Fe_3O_4) as the conducting components with Talc-wax (Talc powder coated with 4% wax by volume) being the common insulating component. Compressed discs of 26mm diameter and about 3mm thickness (with various conductor volume fractions covering both the insulating and conducting region) were made from the respective powders at a pressure of 380MPa and all measurements were taken in the axial (pressure) direction.

The conductivity (σ_m) and dielectric constant (ϵ_m) of percolation systems obey the equations: $\sigma_m = \sigma_c(\phi - \phi_c)^t$ for $\phi > \phi_c$; $\sigma_m = \sigma_i(\phi_c - \phi)^{-s}$ and $\epsilon_m = \epsilon_i(\phi_c - \phi)^{-s'}$ for $\phi < \phi_c$; outside of the crossover region given by $\phi_c \pm (\delta_{dc} \cong (\sigma_i/\sigma_c)^{1/(t+s)})$. Here ϕ_c is the critical volume fraction of the conductor (with conductivity $\sigma = \sigma_c$) and σ_i is the conductivity of the insulator, t and s are the conductivity exponents in the conducting and insulating regions respectively and s' is the dielectric exponent. The values of s and t are obtained by fitting the DC conductivity results to the combined Percolation or the two exponent phenomenological equations. Both universal and non-universal values of the s and t exponents were obtained. The dielectric exponent s' , obtained from the low frequency AC measurements, is found to be frequency-dependent. The real part of the dielectric constant of the systems, has been studied as a function of the volume fraction (ϕ) of the conducting component. In systems where it is measurable beyond the DC percolation threshold, the dielectric constant has a peak at $\phi > \phi_c$, which differs from key predictions of the original Percolation Theory. This behaviour of the dielectric constant can be qualitatively modeled by the phenomenological two exponent equation given in Chapter two of this thesis. Even better fits to the data are

obtained when the same equation is used in conjunction with ideas from Balberg's extensions to the Random Void model (Balberg 1998a and 1998b).

At high frequency and closer to the percolation threshold, the AC conductivity and dielectric constant follow the power laws: $\sigma_m(\phi, \omega) \sim \omega^x$ and $\epsilon_m(\phi, \omega) \sim \omega^{-y}$ respectively. In some of the systems studied, the x and y exponents do not sum up to unity as expected from the relation $x + y = 1$. Furthermore, the exponent q obtained from $\omega_c \propto \sigma_m(\phi, 0)^q$ in all but the Graphite-containing systems is greater than 1, which agrees with the inter-cluster model prediction ($q = (s + t)/t$). The Niobium Carbide system is the first to give an experimental q exponent greater than the value calculated from the measured DC s and t exponents.

1/f or flicker noise (S_v) on the conducting side ($\phi > \phi_c$) of some of the systems has been measured, which gives the exponents k and w from the well-established relationships $S_v/V^2 = D(\phi - \phi_c)^{-k}$ and $S_v/V^2 = KR^w$. V is the DC voltage across the sample with resistance R while D and K are constants. A change in the value of the exponent k and w has been observed with k taking the values $k_1 \sim 0.92 - 5.30$ close to ϕ_c and $k_2 \sim 2.55 - 3.65$ further into the conducting region. Values of w_1 range from $0.36 - 1.1$ and $w_2 \sim 1.2 - 1.4$. These values of w are generally well within the limits of the noise exponents proposed by Balberg (1998a and 1998b) for the Random Void model. The t exponents calculated from k_2 and w_2 (using $t = k/w$) are self-consistent with the t values from DC conductivity measurements. Magnetic measurements in two of the systems (Fe_3O_4 and Nickel) show unexpected behaviour of the coercive field and remnant magnetisation plotted as a function of magnetic volume fraction. Fitting the permeability results to the two exponent phenomenological equation gives t values much smaller than the corresponding DC conductivity exponents.

A substantial amount of data was obtained and analysed as part of this thesis. Experimental results, mostly in the form of exponents obtained from the various scaling laws of Percolation Theory, are presented in tabular form throughout the relevant chapters. The results have been tested against various models and compared

with previous studies. While there is some agreement with previous work, there are some serious discrepancies between the present work and some aspects of the standard or original Percolation Theory, for example the dielectric constant behaviour with conductor volume fraction close to but above ϕ_c . New results have also emerged from the present work. This includes the change in the noise exponent k with $(\phi - \phi_c)$, the variation of the dielectric exponent s' with frequency and some DC scaling results from the Fe_3O_4 system. The present work has dealt with some intriguing aspects of Percolation Theory in real continuum composites and hopefully opened avenues for further theoretical and experimental research.

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CHAPTER ONE

INTRODUCTION: GENERAL

Percolation Theory describes both macroscopically and microscopically disordered systems. Broadbent and Hammersley (1957) introduced Percolation Theory in the form of lattice models, for the flow of fluid through a static random medium. From the lattice models, they observed that no fluid would flow if the number of active bonds or fluid-carrying channels were less than some nonzero value - the percolation threshold (Kirkpatrick 1973). The interest in Percolation Theory increased considerably after it had been suggested that percolation effects may play a role in the conductor-semiconductor transitions seen in some disordered solid state systems (Shante and Kirkpatrick 1971). Since then, many electrical conductivity measurements done on disordered systems have been described and analysed in terms of Percolation Theories.

Extensive use of Percolation Theory and the concept of scaling to model the electrical transport properties of binary composite materials, which consist of mixtures of conductors and insulators, started in the 1970's. Defining ϕ as the volume fraction of the conducting component in a continuum system, Percolation Theory predicts the existence of a critical value of ϕ (denoted by ϕ_c), called the critical volume fraction or percolation threshold, at which a continuous conducting path or infinite cluster first forms within the insulating matrix. At this point the composite goes through a metal-insulator transition (MIT), similar to a second order phase transition. In the vicinity of the percolation threshold, many properties (X) of the composite obey a power law given by:

$$X \propto |\phi - \phi_c|^\alpha \quad (1.1)$$

Here, α is a critical exponent characterising the behaviour of X as ϕ_c is approached from below or above the threshold. The exponent α can be positive or negative depending on what physical quantity is under study in the system. Values of α from computer simulations were found to depend only on the dimensionality of the system (Stauffer and Aharony, 1994 and references therein) and were said to be universal. However, more recent theoretical (for example Kogut and Straley 1979, Halperin *et al.* 1985, Feng *et al.* 1987, Balberg 1987b, Balberg 1998a, 1998b and references therein) and experimental results (Carmona *et al.* 1984, Song *et al.* 1986, Balberg 1987a, Heaney 1995, Wu and McLachlan 1997 and some references therein, Rubin *et al.* 1999, Chitame and McLachlan 2000) in three-dimensional (3D) continuum composites show that α can differ from system to system. Experiments have reported α values ranging from 1.5 – 6.4 in DC conductivity measurements above ϕ_c . Studies have also been done on the transport properties of continuum 2D systems, mostly thin films (see for instance the review articles by Abeles *et al.* 1975, Deutscher *et al.* 1983 and Smilauer 1991).

The power law given by (1.1) is expected to hold only close to the percolation threshold for the investigated physical property of the system, when the properties of the two components are drastically different. Where this is not the case, a variety of effective media theories (see for example Landauer 1979, McLachlan *et al.* 1990, McLachlan 1996) can be employed to model the transport properties of the composites. The one exponent (McLachlan 1987, McLachlan *et al.* 1990) and two exponent (Wu and McLachlan 1997 and 1998, McLachlan *et al.* 1998, Heiss *et al.* 2000) phenomenological equations have recently been used to successfully model the electrical transport properties of composite materials.

A typical value of the critical volume fraction/percolation threshold (ϕ_c) for 3D continuum composites is 0.16, obtained initially when contacting conducting hard spheres are placed at random on a regular lattice (Scher and Zallen 1970, Zallen 1983). A ϕ_c of 0.16 is also obtained when conducting hard spheres are randomly

packed together with equally or near equally sized insulating glass spheres (Fitzpatrick *et al.* 1974). Experiments, which have reported values of ϕ_c close to 0.16, include those of Heaney (1995) and Wu and McLachlan (1997). A number of experiments have shown that the particle size distribution, shape and their orientation can influence the percolation threshold (Kusy 1977, Carmona *et al.* 1984, Balberg *et al.* 1984, Balberg 1987a, Carmona and Mouney 1992, Dovzhenko and Zhirkov 1995). Values of ϕ_c lower than 0.16 have been observed to arise from systems in which the conductor particles have elongated ('less spherical') geometry. This observation has been explained satisfactorily by means of the 'Excluded Volume' concept (Balberg *et al.* 1984, Balberg 1987a, Carmona *et al.* 1984). Composite systems in which the conductor particles are much smaller than the insulator particles also give very low values of ϕ_c (Malliaris and Turner 1971, Kusy 1977, Chitame and McLachlan 2000). Another model giving rise to low percolation thresholds is the grain growth model (McLachlan 1996). The formation of particle aggregates (Adriaanse *et al.* 1997, Brom *et al.* 1998, Connor *et al.* 1998) also gives low ϕ_c values. Percolation thresholds greater than 0.16 have also been observed (Etyan *et al.* 1993, McLachlan *et al.* 1993). In these systems, the conductor particles are usually partially covered by an oxide, amorphous or polymer layer, which lowers the probability of a bond or an electric contact between nearest-neighbour conducting particles.

Experimental studies on 3D continuum percolation systems have concentrated mostly on their electrical transport properties. These include DC and AC electrical conductivity, dielectric constant, 1/f noise, Hall constant, magnetoconductivity and thermoelectric power. Of these properties, the electrical conductivity and dielectric constant are the most extensively studied. Some of the recent important references on DC conductivity include the experimental works of Balberg (1987a) on Carbon Black-polymer composites, Pierre *et al.* (1990b) on Copper particle-polymer composites, Heaney (1995) on Carbon Black-polymer composites, Wu (1997) and Wu and McLachlan (1997) on Graphite-Boron Nitride systems and some of the references in all these articles. Some important reviews include the articles by Clerc *et al.* (1990),

Bergman and Stroud (1992), Nan (1993), which have also dealt with the AC properties of the composites. Recent experiments on AC conductivity include those by Wu and McLachlan (1998) on Graphite-Boron Nitride systems, Connor *et al.* (1998) on Carbon Black-polyethylene terephthalate composites and McLachlan and Heaney (1999) on Carbon Black-polyethylene samples. Other experiments are also reported in McLachlan *et al.* (1998) and Brom *et al.* (1998). The dielectric constant has been specifically studied in the works of Grannan *et al.* (1981) on a Ag-KCl composite, van Dijk (1985) on water-in-oil microemulsion, Benguigui (1985) on a mixture of glass and iron balls, van Dijk *et al.* (1986) on Aerosol OT/water-isooctane microemulsions and more recently on the Fe_3O_4 -Talc-wax system by Heiss *et al.* (2000). Some percolation systems in which $1/f$ noise has been studied include Carbon-wax mixtures (Chen and Chou 1985), thin gold films (Williams and Burdett 1969, Koch *et al.* 1985), Al_2O_3 -Pt cermets (Mantese and Webb 1985, Mantese *et al.* 1986), thin Al, In and Cr foils (Garfunkel and Weissman 1985), Ag/Pt-TFE mixtures (Rudman *et al.* 1986), Ag films (Octavio *et al.* 1987), Copper particle-polymer composites (Pierre *et al.* 1990b), Graphite-Boron Nitride composites (Wu 1997, Wu and McLachlan 1997) and polymer thick film resistors (Dziedzic and Kolek 1998).

Experimental results obtained in the above-mentioned continuum systems have verified many aspects of Percolation Theory, besides providing a significant amount of data to test other theoretical models. Despite all this effort, discrepancies between theoretical and experimental percolation parameters still abound and so more experiments are needed to further advance the development of theoretical models, especially regarding the non-universality of percolation exponents and the behaviour of the real dielectric constant close to but above the DC percolation threshold. The most glaring problem with previous studies on percolation systems is that very few (usually only one or two at the most) of the physical percolation properties were measured in a single system, which makes it difficult to compare and correlate the exponents from different experiments. In his thesis, Wu (1997) tried to address this problem by measuring as many of the properties as was possible in some continuum

mixtures, with very sharp metal-insulator transitions (MITs) made from various concentrations of Graphite and its mechanical but not electrical isomorph, Boron Nitride. Results from this extensive study of three Graphite-Boron Nitride systems (Wu and McLachlan 1997 and 1998) have shed light on some intriguing aspects of Percolation Theory as well as opening avenues for further theoretical and experimental investigation.

The main objective of the study presented in this thesis is to observe a number of percolation phenomena not only in one, but a number of systems, in which the conducting components have the same macroscopic distribution, i.e. small conductor particles embedded on the surface of larger spherical particles, which are the common insulating matrix in this study. The size of the conductor particles is such that they form three-dimensional cellular structures (similar to soap bubbles with the conductor particles being the ‘soap’ solution). The experiments were designed to give a particular macroscopic microstructure, in which ϕ_c is in principle calculable, so that the effect of the different range of conductance (resulting from the different conducting powders) in the same macroscopic distribution can be investigated. To the best of the author’s knowledge, no systematic study of this cellular microstructure has been done previously. Where possible, the measured percolation thresholds and critical exponents are tested against theoretical models and are also compared with previous experiments. The set of exponents, obtained in this thesis from systems with the same basic structure or macroscopic distribution, could pave the way towards providing a better understanding of Percolation Theory and in particular, the universality or non-universality of the percolation exponents.

The non-universality of the exponents was first investigated in continuum percolation systems using two models; the Random Void and Inverse Random Void (Halperin *et al.* 1985, Tremblay *et al.* 1986, Lee *et al.* 1986 and Feng *et al.* 1987), also called the Swiss Cheese and Inverse Swiss Cheese models respectively. The results of this investigation indicated that the Inverse Random Void (IRV) structure gives a

universal t exponent while Random Void (RV)-like structures can give a non-universal t exponent, as experimentally verified by Lee *et al.* (1986). Extreme values of the t exponents ($t > 3.0$) were also experimentally measured (Ezquerro *et al.* 1990, Wu 1997, Wu and McLachlan 1997, Rubin *et al.* 1999, Chitame and McLachlan 2000) which could not be accounted for by these models. In two recent articles, Balberg (1998a, 1998b) has given new theoretical expressions for high t values and some new limits for noise exponents by modifying the original Random Void (RV) and Inverted Random Void (IRV) models (Halperin *et al.* 1985, Tremblay *et al.* 1986 and Feng *et al.* 1987) which can accommodate the extreme values observed in the exponents. However, more experimental results are required to test these ideas. In particular, systems in which the conductivity exponent and the resistance noise exponent are both non-universal would provide a more stringent test of the theory (Balberg, 1998a).

In order to carry out the experimental investigations, different volume fractions of the various conducting powders: Graphite (G), Graphite-Boron Nitride (GBN), Carbon Black (CB), Nickel (Ni), Magnetite (Fe_3O_4) and Niobium Carbide (NbC), each mixed with Talc powder coated with 4% by volume of wax (hereafter referred to as Talc-wax) and compressed into pellets, were used as samples in this study. The ratio of the conductivity of each of the conducting powders to that of the insulator (σ_c/σ_i) is at least 10^9 , which allows the percolation threshold to be estimated with reasonable accuracy. Graphite and Boron Nitride have the same density and crystal structure, Nickel and Magnetite (Fe_3O_4) are magnetic and Niobium Carbide is a superconductor. The different properties of these powders provided systems on which various aspects of Percolation Theory could be investigated.

Percolation phenomena studied in the systems include room temperature DC conductivity, AC conductivity and dielectric constant, $1/f$ noise and magnetic properties (in two of the systems). Resistivity measurements between 4K and 300K

have been done on some selected samples of some of the systems. The next paragraph gives a brief layout of the work presented in the rest of the thesis.

Chapter two presents and discusses the various theoretical expressions and percolation equations used to analyse the results obtained from measurements on the percolation systems studied in this thesis. The presentation starts from the very basic concepts of Percolation Theory and goes on to the more recent theoretical models, which describe the percolative behaviour of the systems. Chapter three describes the sample preparation methods and the various experimental techniques used in this study. In Chapter four some of the experimental results of the DC electrical conductivity and low frequency dielectric constant are shown graphically and the relevant DC parameters (ϕ_c , s and t), obtained from fitting to the two exponent phenomenological equation, are tabulated for all systems. DC scaling results from the Fe_3O_4 system are also presented in this Chapter. The real dielectric constant results, showing unusual behaviour just above ϕ_c and are fitted with some new expressions, are also presented here. Chapter five gives some AC conductivity results (in graphical form) and tables of all the various parameters (mainly power-law exponents) associated with the AC conductivity. Some AC scaling results are also presented in graphical form. Chapter six presents the experimental $1/f$ -noise results obtained from the four systems in which the noise was measurable. The $1/f$ -noise results are analysed as a function of conductor concentration and DC resistance. Chapter seven gives the results of magnetic measurements done on the two systems consisting of Magnetite (Fe_3O_4) and Nickel. The magnetic measurements were done mainly to check for any possible correlation between the magnetic properties and DC electrical conductivity. In all cases, a number of graphs and extensive tables have been used to show the experimental results, which are also compared (where possible) with previously obtained results.

Chapter eight summarises and discusses the main results obtained in the thesis and suggests further measurements that can be done on these and other continuum

systems. Particular emphasis is placed on some unresolved aspects of Percolation Theory such as accurately predicting or accounting for the non-universality of the percolation exponents, the variation of the dielectric constant with volume fraction of the conductor (ϕ) just above ϕ_c , and some aspects of the behaviour of the AC conductivity at high frequency. In the appendix, percolation exponents obtained from various power laws used to analyse the results in this study are plotted against the DC conductivity exponents s and t , and the percolation threshold (ϕ_c) to look for possible correlations.

CHAPTER TWO

THEORY

2.0 Introduction

The electrical and other transport properties of composite materials, consisting of conductor and insulator particles, have received considerable interest from theoreticians and experimentalists alike because of their practical and theoretical importance. A lot of the effort has been directed towards trying to explain how the volume fraction of the components and the microstructure of the composite affect the electrical behaviour. This has led to a number of Percolation and Effective Media models (see for instance the review articles by Landauer 1978, Clerc *et al.* 1990, McLachlan 1990 and 1996, Bergman and Stroud 1992, Nan 1993, Flux 1993 and references therein) being proposed to describe the electrical properties of composites.

This chapter discusses Percolation Theory, as applied to the transport properties of two-phase materials. In simple metal-insulator composites, a microstructure will evolve with the volume fraction (ϕ) of the metallic or conducting component. At some value of ϕ , called the percolation threshold or critical volume fraction (ϕ_c), the composite goes through a percolation transition (Metal-Insulator Transition-MIT), where the previously isolated metallic/conductor clusters coalesce to form a continuous or “infinite” conducting cluster, spanning the entire composite system. Percolation Theory (Clerc *et al.* 1990, Bergman and Stroud 1992, Nan 1993, Wu and McLachlan 1997 and 1998) best describes the electrical properties of composites.

In this work, the critical volume fraction or percolation threshold is discussed mainly in terms of the Kusy (1977) model for small conductor particles coating the surface of large insulator particles. Other models like the grain growth model of McLachlan (1990) and the excluded volume concept (Balberg *et al.* 1984, Carmona *et al.* 1984, Balberg 1987b) are also considered.

The Percolation Equations, used to fit the experimental DC electrical conductivity data on either side of the percolation threshold, allow one to obtain the percolation parameters (s , σ_i , ϕ_c , t and σ_c), which are given in section 2.1.2. A two exponent phenomenological conductivity model equation, which has been used to fit experimental data from the Graphite-Boron Nitride composites (Wu and McLachlan, 1997) is also used to fit the experimental results in this study. The advantage of this equation is that it is analytic, continuous, reduces to the original percolation equations in the regions where they are valid and is found to interpolate between the DC percolation equations above and below ϕ_c . Scaling in the DC regime is dealt with in section 2.1.3. Section 2.1.4 examines the DC percolation exponents, s and t , and some of the models that have been formulated to explain their non-universal values in binary composite systems. In section 2.2, the use of the two exponent phenomenological equation, to model the behaviour of the low frequency real dielectric constant (at a fixed frequency) as a function of conductor volume fraction (McLachlan *et al.* 1998, Heiss *et al.* 2000) is outlined. Above ϕ_c , the behaviour of the dielectric constant is contradictory to the predictions of the original percolation expressions given in section 2.1.2.

The $1/f$ or flicker noise (expressed in terms of voltage fluctuations) and the associated power laws governing its behaviour are given in section 2.3. Formulae previously used for studying $1/f$ noise in percolation systems, and to analyse the results in this work, include Rammal *et al.*'s expressions (1985), which give the noise as a function of conductor concentration and an exponent k . Another power law expression with an exponent w , has the DC resistance as the dependent variable. Both expressions are only valid above the percolation threshold. Note that ideally $w = k/t$. Noise

expressions based on random resistor networks can also be used to model the noise in percolation systems but will not be used in this thesis.

The AC or complex percolation equations (section 2.4), which are derived from a scaling ansatz (Webman *et al.* 1975, Efros and Schlovskii 1976, Straley 1976, 1977, Bergman and Imry 1977, Stroud and Bergman 1982, Bergman and Stroud 1985), and reviewed by Clerc and his collaborators (1990), Bergman and Stroud (1992) and Nan (1993), are given. In practice, these equations only give the power law behaviour of the conductivity or dielectric constant in specific ranges of ϕ . The scaling relationship for AC conductivity and dielectric constant is stated in terms of the exponents x and y needed to interpret the AC measurements at high frequencies. These exponents are also given by the inter-cluster polarisation model expressions, where they are functions of the DC exponents s and t . The expressions based on a two exponent phenomenological equation, recently used to scale the Graphite-Boron Nitride conductivity results (McLachlan *et al.* 1998, Wu and McLachlan 1998), are then given. Magnetic properties of percolation systems are discussed in section 2.5.

2.1 The DC Electrical Properties of Binary Continuum Composites

2.1.1 The Percolation Threshold

Disordered two-phase systems, with insulating and conducting components, usually show a conductor-insulator or metal-insulator (MIT) transition (similar to a second order phase transition) at some specific value of the conductor fraction (ϕ_c), which depends on the microstructures of the system and the morphology of the components. The factors determining ϕ_c are now reasonably understood (Kusy 1977, Carmona *et*

al. 1984, Balberg 1987a and 1987b, McLachlan 1990 and 1996, Nan 1993). Values of ϕ_c observed experimentally lie in the range 0.01 to 0.60. A ϕ_c value of 0.16, previously regarded as the typical value for the critical conductor concentration in 3D composites, is obtained whenever contacting conducting hard spheres are placed at random on a regular lattice or conducting hard spheres are randomly packed using equally or near equally sized insulating and conducting spheres (e.g. metal ball bearings randomly packed with glass balls, Fitzpatrick *et al.* 1974). Recently, $\phi_c = 0.16$ has been taken to mark the boundary between systems where the insulator tends to coat the conductor (generally leading to ϕ_c 's > 0.16) and ones where the conductor tends to coat or surround the insulating component to give $\phi_c < 0.16$. Values of ϕ_c close to 0.16 have been observed experimentally in some continuum systems, usually where the conductor and insulator particles are nearly equal in size (e.g. Wu and McLachlan 1997). Models which lead to the lower values of the percolation threshold include the Kusy (1977) model (based on a model proposed by Malliaris and Turner (1971)), the excluded volume concept (Balberg *et al.* 1984, Balberg 1987b) and the grain growth model (McLachlan 1990).

It has been observed that systems in which the conductor particles are small relative to the insulator give percolation thresholds lower than 0.16. Malliaris and Turner (1971) calculated ϕ_c for R_i/R_c (where R_i and R_c are the insulator and conductor radius respectively) on the premise that each insulating particle was covered by a continuous monolayer coating of the conducting particles at ϕ_c . However, the ϕ_c values obtained using this assumption tended to be higher than those observed in experiments.

Kusy (1977) modified the Malliaris and Turner model by noting that the conducting particles did not have to cover the insulating particles completely to form a conduction path. Instead only a two-dimensional percolating network had to form on the insulating particles at a ϕ_c , which is about half of that needed for a complete coating of the insulating grains. In addition, Kusy noted that the conducting particles not only lie on the surface of the insulating grains but are also trapped in the

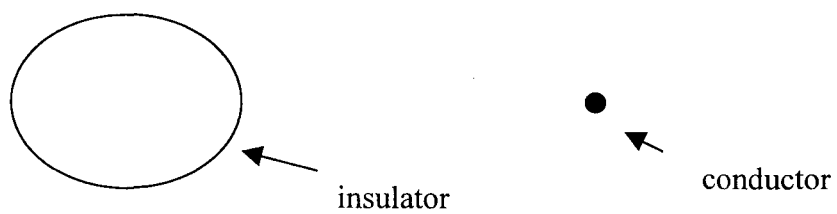
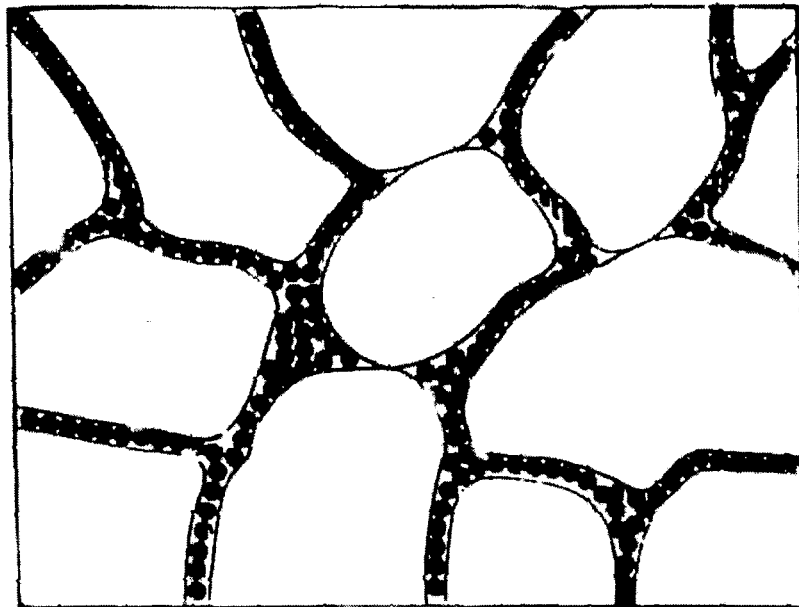


Figure 2.1: Shows the cellular microstructure. The small conductor particles are embedded on the surface of the larger insulator particles. The conducting material trapped in the pores increases the observed value of ϕ_c .

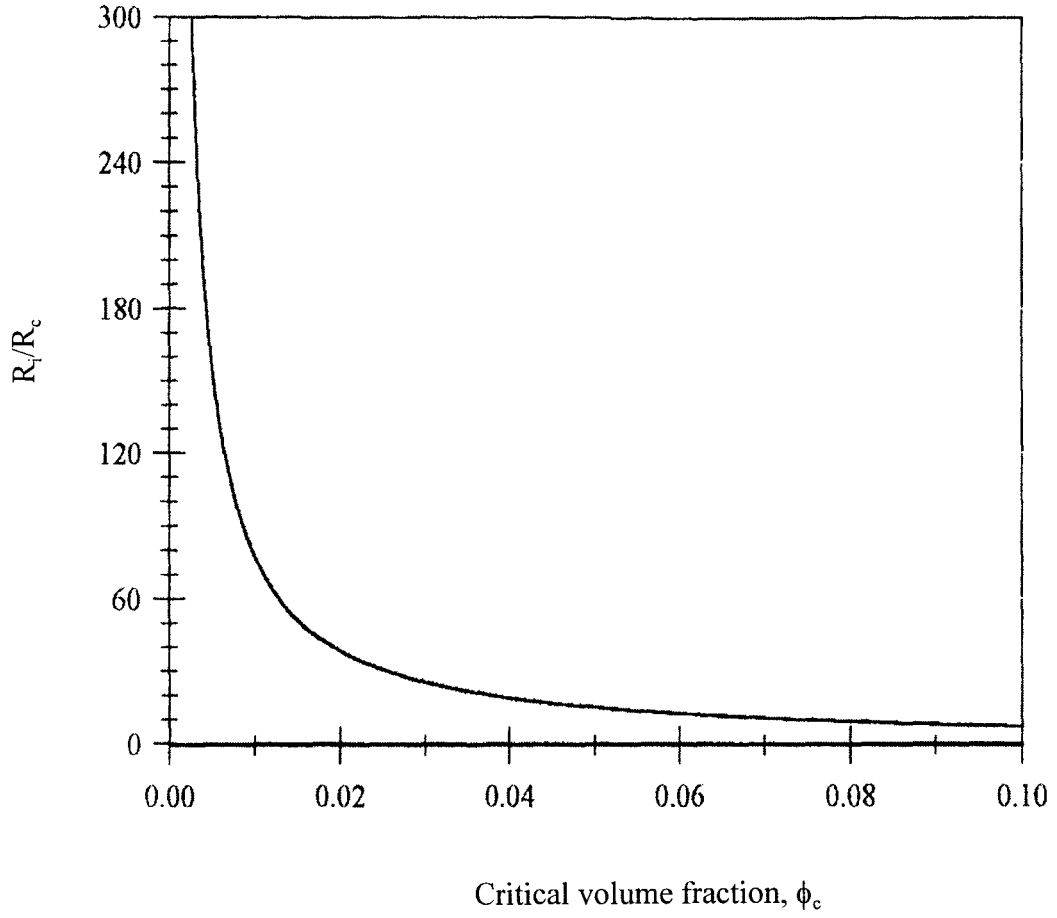


Figure 2.2: Dependence of ϕ_c on the insulator to conductor radius according to the Kusy model ($\phi_c = 1/(1 + KB)$, where $B = R_i/R_c$ and $K = 1.27$).

interstitial sites or pores (Fig. 2.1), which increases the observed value of ϕ_c . Figure 2.2 shows how ϕ_c varies as R_i/R_c increases in accordance with the Kusy model. The practical minimum for the ratio R_i/R_c is 30, which gives a ϕ_c of about 0.03 (after allowance has been made for some of the conducting particles being trapped in the pores). Note that the Kusy model does not apply for $R_i \approx R_c$ as the assumption that the insulating particles are uniformly covered by the conducting particles cannot apply in such a situation.

Conducting particles with an elongated geometry also lead to lower values of ϕ_c . This observation is explained satisfactorily by the excluded volume concept (Balberg *et al.* 1984, Balberg 1987b, Carmona *et al.* 1984). This concept is based on the observation that elongated particles form a percolating network at lower volume fractions than those with spherical shapes. The excluded volume of an object is defined as the volume around the object into which the centre of a similar object is not allowed to enter if overlap between the two objects is to be avoided. Spheres have an excluded volume equal to their true volume but rods and discs have an excluded volume larger than their true volume. In order to experimentally investigate the excluded volume concept, Carmona *et al.* (1984) studied the difference in the ϕ_c obtained for a carbon powder and for randomly oriented carbon fibers, with various length-to-cross-section ratios, bonded in epoxies and silicon elastomers. Their study showed that the excluded volume concept could be used to explain the critical volume fractions obtained with particles of such extreme geometries.

The grain growth model of McLachlan (1990) also leads to lower ϕ_c values. The model starts with the nucleation of a random array of small insulating spheres, which grow to form a random-close-packed lattice with point contacts on the surfaces. As the spheres continue to grow, flat interfacial contacts develop, which push the two-phase material into the interstices. As the areas of interfacial contacts continue to grow, an ever-decreasing volume of interstices consisting of pores and throats is created. When the volume fraction of the insulating spheres is about 0.97, the throats

and pores no longer form a continuous percolation path. Therefore this model gives a ϕ_c of approximately 0.03. However, lower values of ϕ_c (even less than 0.03) have been observed in Carbon Black-polymer composites in which tunneling between aggregates of the carbon black particles play a dominant role, implying that actual physical contact between the conductor particles (in such systems) may not be required to form an infinite conducting network at the percolation threshold. Studies in which extremely low ϕ_c values have been obtained experimentally include the work of Nandi *et al.* (1996), Adriaanse *et al.* (1998) and Ezquerro *et al.* (1998). The structure of Carbon Black particles has also been observed to influence ϕ_c in Carbon Black-polymer composites (Balberg 1987a, Rubin *et al.* 1999 and references therein). The high structure or less spherical Carbon Black particles give lower values of ϕ_c , while the close to spherical or low structure Carbon Black particles tend to give values of ϕ_c higher than 0.16 (Rubin *et al.* 1999).

Values of ϕ_c higher than 0.16 are usually observed in composites where the conductor particles are partially covered by an oxide, amorphous or polymer layer, which lowers the probability of a bond or an electric contact between nearest-neighbour conducting particles. The data obtained in the granular Aluminium-Germanium composite system is an example of a system in which a high ϕ_c ($\phi_c \cong 0.60$) has been observed (McLachlan *et al.* 1993, Etyan *et al.* 1993).

Although a number of models dealing with the critical volume fraction have been considered above, only the Kusy model will be applied in this work, where the small conducting particles attach themselves on the surfaces of the larger and regular spherical Talc-wax particles. However, as they are not completely embedding in the wax, the conducting particles can still make contact as required by the Kusy model. Note also that the Kusy model assumes mono-sized conducting particles, while the conducting powders used in this work show a distribution of the particle sizes (see for instance Fig. 3.2a).

2.1.2 The DC Percolation Equations

When the ratio of the conductivities of the two components of a binary disordered conductor-insulator medium is very small ($\sigma_i/\sigma_c \ll 1$), the conductivity (σ_m) and dielectric constant (ϵ_m) of conductor-insulator composites, which exhibit percolation thresholds, are usually best described by the following normalised percolation equations:

$$\sigma_m = \sigma_c [(\phi - \phi_c)/(1 - \phi_c)]^t \quad ; \quad \phi > \phi_c \quad (2.1a)$$

$$\sigma_m = \sigma_i [(\phi_c - \phi)/\phi_c]^{-s} \quad ; \quad \phi < \phi_c \quad (2.1b)$$

$$\epsilon_m = \epsilon_i [(\phi_c - \phi)/\phi_c]^{-s'} \quad ; \quad \phi < \phi_c \quad (2.1c)$$

Here, σ_m and ϵ_m are the conductivity and dielectric constant of the composite, σ_c the conductivity of the conducting component with volume fraction ϕ , σ_i and ϵ_i are the conductivity and dielectric constant of the insulator and s , t are the dielectric and conductivity exponents respectively. When fitting DC conductivity data in this thesis using the above equations, σ_c , σ_i , t , s and a common ϕ_c , are used as parameters. Note that an additional exponent (s'), obtained from low frequency dielectric (ϵ_m) data and found to be different from the DC conductivity exponent s (as will be shown later through the experimental results in this thesis), has replaced s in eqn. (2.1c).

The region in the immediate neighbourhood of ϕ_c ($\phi \cong \phi_c$) is called the crossover region ($\phi_c \pm \delta_{dc}$) where δ_{dc} is given by:

$$\delta_{dc} = (\sigma_i/\sigma_c)^{1/(t+s)}. \quad (2.2a)$$

In this region, equations (2.1) no longer describe the conductivity of the composite (σ_m) very near ϕ_c (Clerc *et al.* 1990, Bergman and Stroud 1992, Nan 1993). The conductivity (σ_m) in this region obeys the following power law:

$$\sigma_m \propto \sigma_i^{1/(s+t)} \sigma_c^{s/(s+t)}. \quad (2.2b)$$

The difficulty involved in making samples that fall within this region means that the crossover region is not very well characterised in DC conductivity experiments.

A generalised effective media equation, with two microstructure parameters ϕ_c and t , was originally derived as an interpolation between the Bruggeman symmetric and asymmetric effective media theories (McLachlan 1987) and shown to fit a large amount of experimental data (McLachlan *et al.* 1990). The modified (two-exponent, three-microstructure parameter) version of the above phenomenological conductivity equation (Wu and McLachlan 1997, McLachlan *et al.* 1998), which is also continuous and analytical, was successfully used to fit the large amount of experimental data obtained from the Graphite-Boron Nitride composite systems (Wu 1997, Wu and McLachlan 1997) and also the experimental data presented in this thesis. The equation is:

$$(1 - \phi)(\sigma_i^{1/s} - \sigma_m^{1/s})/(\sigma_i^{1/s} + A\sigma_m^{1/s}) + \phi(\sigma_c^{1/t} - \sigma_m^{1/t})/(\sigma_c^{1/t} + A\sigma_m^{1/t}) = 0, \quad (2.3)$$

$$\text{with } A = (1 - \phi_a)/\phi_a.$$

This phenomenological equation reduces to the Bruggeman symmetric equation when $s = t = 1$, and has the mathematical form of the Bruggeman asymmetric equation when

$\phi = 0$ or 1 and $\sigma_i \rightarrow 0$ or $\sigma_c \rightarrow \infty$. It also reduces to the percolation equations (2.1) when $\sigma_i = 0$ or $\sigma_c \rightarrow \infty$ and $0 < \phi_c < 1$. Provided the ratio σ_i/σ_c is very small, identical results are obtained from fits of experimental data to (2.1) and (2.3). Note that for a good theoretical analysis, there should be sufficient data on either side of ϕ_c . Furthermore if there is data in the region $\phi_c \pm \delta_{dc}$, it should be excluded from fits to (2.1).

2.1.3 DC Scaling in a Percolating System

Scaling, as applied to percolation systems, requires that the conductivity σ_m of the composite (in the region around the percolation threshold ϕ_c), assumes the form (Clerc *et al.* 1990, Bergman and Stroud 1992, Nan 1993):

$$\sigma_m \approx \sigma_c |\phi - \phi_c|^t F_{\pm}((\sigma_i/\sigma_c) |\phi - \phi_c|^{-s-t}). \quad (2.4)$$

F_+ is the scaling function for $\phi > \phi_c$ while F_- is the scaling function for $\phi < \phi_c$ and the other symbols have their usual meaning. The scaling requirement for F_+ and F_- is that for $\sigma_i/\sigma_c \ll 1$, two or more theoretical curves, with different values of σ_i/σ_c , should be superimposing functions of x' for all percolation systems, with $x' = ((\sigma_i/\sigma_c) |\phi - \phi_c|^{-s-t})$. For $x' < 1$, F_+ and F_- should give the relevant percolation laws, above and below ϕ_c respectively. In addition, F_+ and F_- coalesce into a single function given by $Kx'^{1/(s+t)}$ for $x' > 1$. The region on either side of ϕ_c for which $x' \geq 1$ is called the crossover region and is given by (cf eqn. (2.2a)):

$$|\phi - \phi_c| \leq (\sigma_i/\sigma_c)^{1/(s+t)}. \quad (2.5)$$

As indicated in section 2.1.2, the percolation equations (2.1) no longer apply in the crossover region where $F_+(x')$ and $F_-(x') \propto x'^{t/(s+t)}$, which leads to (2.2b).

The two exponent phenomenological equation (eqn. (2.3)) for σ_m has been shown to give valid scaling functions for all values of x' (McLachlan 1998). The relevant functions are:

$$F_+(x'_+) = (\sigma_m(\sigma_c, \sigma_i, s, t, \phi_c, \phi) / \sigma_c) ((1 - \phi_c) / (\phi - \phi_c))^t,$$

and

$$F_-(x'_-) = (\sigma_m(\sigma_c, \sigma_i, s, t, \phi_c, \phi) / \sigma_c) (\phi_c / (\phi_c - \phi))^t, \quad (2.6)$$

with $x'_+ = (\sigma_i / \sigma_c) ((1 - \phi_c) / (\phi - \phi_c))^{s+t}$ and $x'_- = (\sigma_i / \sigma_c) (\phi_c / (\phi_c - \phi))^{s+t}$.

In section 4.1.5, these functions will be used to scale data for the Fe_3O_4 system at various temperatures.

2.1.4 The Percolation Exponents

The s and t exponents found in the percolation (eqns. (2.1) and (2.2)) and the two exponent phenomenological equation (eqn. (2.3)) are parameters which are central to Percolation Theory and can presumably be used to characterise different percolation systems. Initially (based on computer simulations on lattices and studies on some real continuum media) it was believed that s and t depended only on the dimension of the

system (Kogut and Straley 1979, Ben-Mizrahi and Bergman 1981, Straley 1982a, 1982b, Bergman and Stroud 1992, Nan 1993 and references therein). In addition, if the local microstructure is isotropic and contains only short-range correlations, the exponents would be independent of the microstructure. In three dimensions, the most widely accepted as universal values of s and t are 0.87 and 2.0 respectively (Bergman and Stroud 1992, Nan 1993, Stauffer and Aharony 1994). All computer simulations and some continuum systems were found to belong to this universal class, but t was found to be 3 or larger in some continuum systems (Halperin *et al.* 1985, Feng *et al.* 1987, Lee *et al.* 1986, Carmona *et al.* 1987, Dupreez and McLachlan 1988, Nan 1993, Heaney 1995, Wu 1997, Wu and McLachlan 1997, Rubin *et al.* 1999, Chitame and McLachlan 2000). It is now widely accepted that many continuum systems show non-universal behaviour.

In explaining the non-universality observed in some continuum systems, Kogut and Straley (1979) noted that if the low conductance bonds (g) in a percolating resistor network had a distribution $h(g) \cong g^{-\alpha}$, with $0 < \alpha < 1$, then the conductivity exponent would be given by:

$$t = t_{un} + \alpha / (1 - \alpha) ; \quad t_{un} = \text{accepted universal value of } t. \quad (2.7)$$

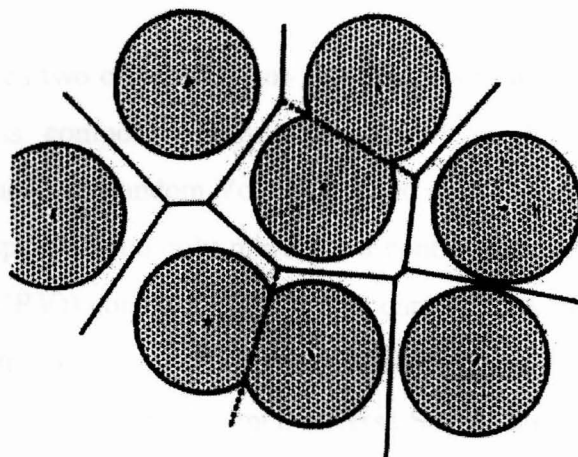
For $\alpha < 0$, $t \cong t_{un}$. In a superconductor-normal resistor network ($\sigma_c \rightarrow \infty$) with a distribution of the normal conductances (now in the σ_i component), with high g values, being characterised by $h(g) \cong g^{-\beta}$; the exponent s is given by (Kogut and Straley 1979):

$$s = s_{un} + (2 - \beta)/(\beta - 1); \quad \text{for } 1 < \beta < 2. \quad (2.8)$$

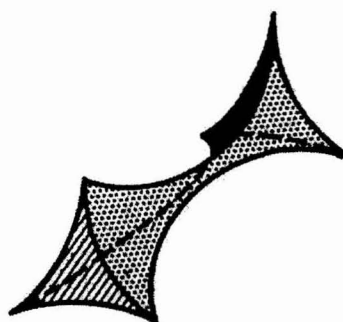
When $\beta > 2$, $s \cong s_{un}$. An apparent limitation of this model is that it does not allow s or t to be lower than s_{un} and t_{un} , yet s and t exponents lower than these two values have been observed in some continuum systems (Błaszkiwicz *et al.* 1991, Chitame and McLachlan 2000).

The Swiss cheese or Random Void model (Halperin *et al.* 1985, Feng *et al.* 1987) was the first realistic model continuum system, which gave a distribution $g^{-\alpha}$, which lead to a non-universal value of t in continuum systems. The model consists of equally sized spherical holes or voids placed at random in a uniform transport medium, where the spherical voids are allowed to overlap with one another. Close to the percolation threshold, the transport properties of a Swiss Cheese model system are determined by the many narrow necks, which are left behind by the removal of the interpenetrating holes/voids. The narrow conducting necks (Fig. 2.3), which join the larger regions of the conducting material, dominate the resistive behaviour and allow the model to be mapped onto a random resistor network, where the necks play the role of occupied bonds. While the occupied bonds in a discrete network model are all identical, the necks in the Swiss Cheese/Random Void model have a wide distribution of widths δ and it is found that the conductance of the necks has a power law dependence on δ , leading to a distribution of the transport strengths of the necks, which give rise to nonuniversal exponents (Halperin *et al.* 1985, Feng *et al.* 1987).

Computer simulations show that random percolation networks with a wide distribution of transport strengths have s or t transport percolation exponents significantly different from that of the discrete network model (Kogut and Straley 1979, Ben-Mizrahi and Bergman 1981, Straley 1982a, 1982b). Therefore, continuum percolation systems, with such a wide distribution of transport strengths, may have critical exponents different from those of discrete random networks. The Random Void model, as outlined above, is also expected to describe the water flow in or electrical conductivity of sedimentary rocks (Keller 1982, Balberg 1986, Halperin



(a)



(b)

Figure 2.3: The Swiss Cheese or Random Void model (a) The solid lines represent occupied or conducting bonds, while the dotted lines represent missing (insulating) bonds. The circles represent the voids. (b) A typical neck configuration of conducting material trapped by the voids [After Halperin, Feng and Sen 1985].

et al. 1985) or composites in which small conducting particles are dispersed among much larger insulating particles (Pike 1978) and this work.

Lee *et al.* (1986), designed two complementary experiments to test the Swiss Cheese model. An Indium-glass composite (insulating spheres randomly placed in a continuous conducting medium-Random Void (RV)) and a Silver-coated-glass/Teflon composite (conducting spheres randomly placed in a continuous insulating medium-Inverted Random Void (IRV)) constituted the model continuum systems. This set of experiments confirmed that the t exponent is not universal in a 3D-continuum RV system but t was found to be universal in their Inverse Swiss Cheese or IRV system (Lee *et al.* 1986), as it should.

Balberg (1987b) proposed a model similar to the inverted Swiss cheese but where the inter-particle (cluster) conduction mechanism is tunneling, which gives:

$$t = t_{\text{un}} + (a/l)(1 - l/a),$$

where a is the average closest approach distance between the particles (which can belong to different clusters) and l is the tunneling distance coefficient. The equation predicts a high t for a high a/l . Note that any real system with a high a/l (high t system) would be very resistive as the particles would be further apart than a system with a low a/l .

Another model predicting $t > 2$ is the links-nodes-blobs (LNB) model of Stanley (1977) and Coniglio (1982), that provides a realistic picture of the backbone on a lattice and in continuum systems. The backbone is defined as the set of bonds that carry current in the conductor-insulator model, which is obtained by removing from the infinite cluster all the dead or dangling ends (refer to Fig. 2.4 and 2.5). A node is

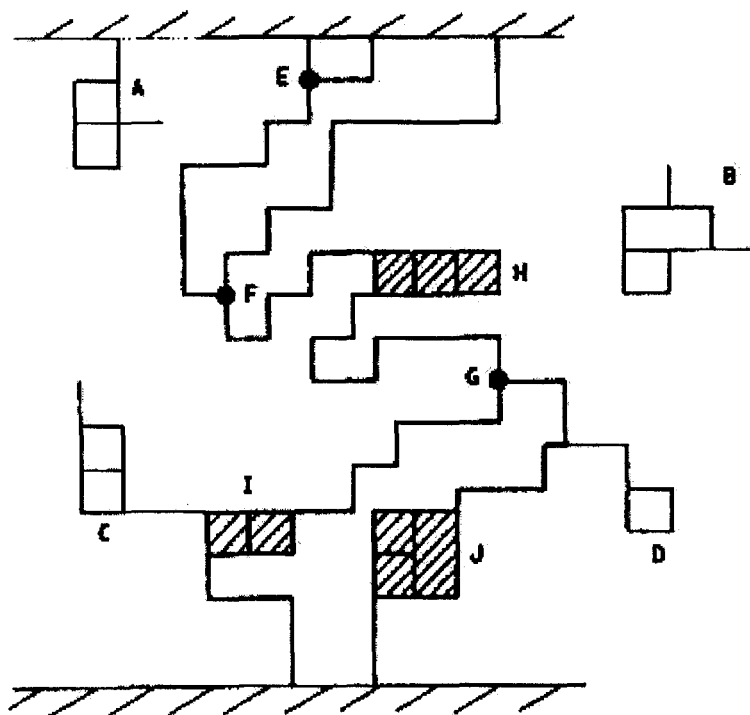


Figure 2.4: A 2D structure of the backbone with the dangling clusters and dead ends. A, B are finite isolated clusters while C, D are dangling (dead end) clusters. E, F and G are **nodes** and the hatched regions H, I and J are **blobs**. A **link** consists of all the backbone bonds between two adjacent nodes (After Bergman and Stroud 1992).

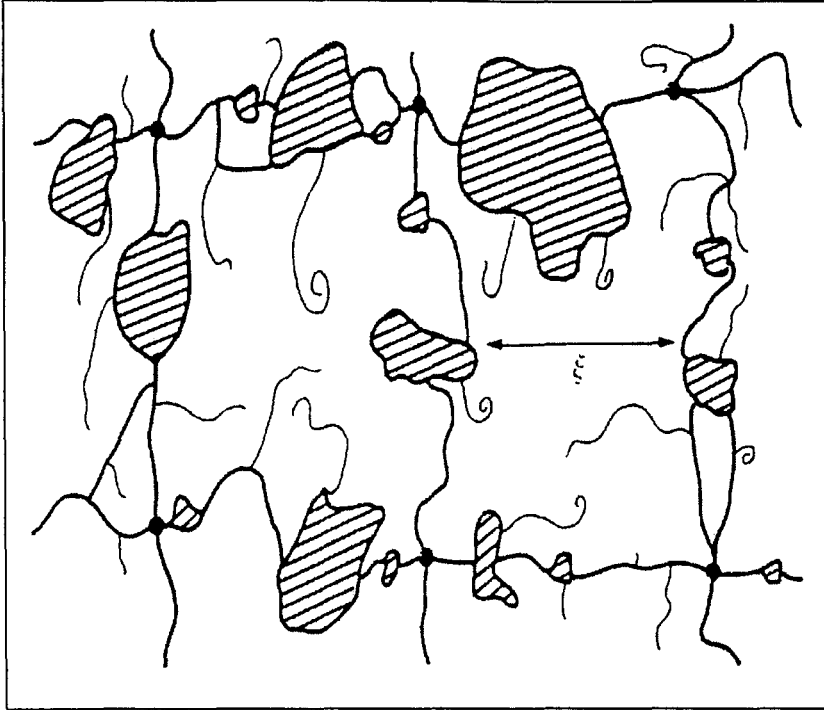


Figure 2.5: Shows the structure of the percolating backbone with the links, nodes, blobs (hatched regions) and 'dead' ends clearly visible (After Stauffer 1985).

any site on the backbone that is connected to the boundaries by at least three independent paths formed of links and blobs (Fig. 2.4). The inter-node spacing, above ϕ_c , is the correlation length ξ , with $\xi \propto (p - p_c)^{-\nu}$ in a lattice, which is equivalent to $(\phi - \phi_c)^{-\nu}$ in a continuum system (Note the divergence of ξ close to ϕ_c). A link consists of single or cutting bonds, which when cut, will interrupt the current flow, while blobs are multiply connected paths on the backbone where each path carries a fraction of the backbone current. Large blobs make a negligible contribution to the measured resistance of the system. This links-nodes-blobs model gives:

$$t = \delta + (d - 2)\nu.$$

Here, d is the dimensionality of the system and as indicated earlier, the exponent ν characterises the divergence of the correlation length (ξ) close to the percolation threshold as follows:

$$\xi \propto |p - p_c|^{-\nu}, \text{ in a lattice system}$$

and

$$\xi \propto |\phi - \phi_c|^{-\nu}, \text{ in a continuum system.}$$

Simulations for a random resistor model show $\delta = 1.12$ in 3D which gives $t = 2.00$ when ν is taken to be 0.88 (Coniglio 1982). A higher t would require that $\delta > 1.12$, which would imply a larger fraction of blobs on the backbone than given by the RV model. Fisch and Harris (1978) give the range $\nu < \delta < \nu/\nu_s$, where ν_s ($= 0.588$) is the correlation length exponent for self-avoiding walks. This gives an upper limit of δ as

1.50 ($\equiv v/v_s = 0.88/0.588$) and gives a t value of 2.38. The upper limit of $t = 2.38$ shows that, in its current form, the links-nodes and blobs model cannot account for t values higher than 2.38.

Balberg (1998a and 1998b) proposed models for new limits for the continuum percolation exponents which can explain still higher values of t . He showed that many of the experimental results reported so far can be accommodated within the framework of the original HFS (Halperin, Feng and Sen 1985, Feng, Halperin and Sen 1987) and TFB (Tremblay, Feng and Breton 1986) theories if one of their original assumptions is removed. The removal of this assumption, according to the new Balberg models, is justified in real systems, as the acting forces may yield a different $h(\epsilon)$ distribution, for small ϵ , than that of the HFS and TFB one. The HFS and TFB theories assumed that the distribution function $h(\epsilon)$ of the geometric proximity parameter ϵ was uniform as $\epsilon \rightarrow 0$, i.e. there is some ϵ_0 such that for $\epsilon < \epsilon_0$, the distribution can be approximated by $h(\epsilon) = h_0$ where h_0 is a constant. Balberg assumes in general that $h(\epsilon) \propto \epsilon^{-\omega'}$, for $\epsilon_{\min} < \epsilon < \epsilon_0$ ($\epsilon_{\min}$ is defined below). For $\omega' = 0$, the HFS and TFB assumption is recovered. For $\omega' > 0$, a distribution is obtained which emphasises the smaller ϵ values as $\epsilon \rightarrow 0$. The $h(\epsilon > \epsilon_{\min})$ distribution is convergent and normalisable for $\omega' < 1$. On the other hand if $\omega' < 0$, a neck distribution which emphasises the larger ϵ values as $\epsilon \rightarrow 0$ becomes dominant. The derivations given below are not complete and the reader is referred to Balberg (1998b), for more detail.

In the Balberg models (1998a and 1998b), the resistance r of each resistor for $\epsilon_{\min} < \epsilon < \epsilon_0$ depends on the geometry of the resistor as $r \propto \epsilon^{-u}$, where u is an exponent related to the dimensionality (d) of the system and which is also model dependent. Furthermore, the average resistance of a resistor in a link with L_l singly connected (bonds) resistors is given by:

$$\langle r \rangle_{L_l} \propto \int_{\epsilon_{\min}}^{\epsilon_0} \epsilon^{-(u + \omega')} d\epsilon ; \quad \epsilon_{\min} < \epsilon < \epsilon_0 \quad (2.9)$$

where $\varepsilon_{\min}$ is the typical smallest ε in the link such that $\varepsilon_{\min} \propto L_1^{-1}$ when $\omega' = 0$ and $\varepsilon_{\min} \propto L_1^{-1/(1-\omega')}$ when $\omega' \neq 0$. When $u + \omega' < 1$, the integral (2.9) converges as $\varepsilon \rightarrow 0$ and $\langle r \rangle_{L_1}$ is a constant. Thus $\langle r \rangle_{L_1}$ has a finite value, which is independent of the proximity to the percolation threshold. Therefore the macroscopic resistance (R) (where $R \propto (p - p_c)^{-t}$) of a system made of resistors with a constant $\langle r \rangle$, has a universal critical behaviour, with $t = t_{\text{un}}$. For $u + \omega' > 1$, $\langle r \rangle$ diverges at $\varepsilon = 0$ and the result of (2.9) must take into account the finite nature of L_1 , upon which the value of $\varepsilon_{\min}$ depends. The integral (2.9) then gives $\langle r \rangle_{L_1} \propto \varepsilon_{\min}^{-(u + \omega' - 1)} \propto L_1^{(u + \omega' - 1)/(1 - \omega')}$. In addition, $L_1 \propto (p - p_c)^{-1}$, from which it follows that $\langle r \rangle_{L_1} \propto (p - p_c)^{-(u + \omega' - 1)/(1 - \omega')}$. In this case, the non-universal exponent (Balberg 1998a and 1998b) determines the critical behaviour of the macroscopic resistance. This exponent is given by:

$$t = t_{\text{un}} + (u + \omega' - 1)/(1 - \omega'). \quad (2.10)$$

which reduces to the TFB expression for t when $\omega' = 0$. For the random void model (Tremblay *et al.* 1986), $u = d - 3/2$ while for the inverted random void system, $u = d/2 - 1$, with d denoting the dimensionality of the system. Non-universal behaviour of resistance requires that $u + \omega' > 1$ and, since $-\infty < \omega' < 1$, it can be seen from (2.10) that $t_{\text{un}} < t < \infty$ for all the cases except the $d = 2$ inverted random void model, where it is impossible to have $u + \omega' > 1$ and $t = t_{\text{un}}$ (Balberg 1998a and 1998b). These results are applicable for the extreme $t > 2.5$ values obtained in composites for which the 3D RV model should be a good description (Pike 1978, Lee *et al.* 1986). The IRV model, which predicts that $t = t_{\text{un}}$ is not applicable to the cellular systems studied in this thesis, since the insulator particles are much larger than the conductor particles.

Heaney (1995) obtained a value of $t = 3$ for a Carbon Black-polymer composite. He associated this value with mean field behaviour, as the carbon black aggregates are known to bind together to form extended, ramified agglomerates, which have the

possibility of interacting with many neighbours. These long-range interactions may cause a narrowing of the critical regime and give rise to mean field characteristics, as is the case in thermodynamic systems. Heaney suggests that the non-universal width of the scaling regime causes some continuum systems to exhibit universal transport behaviour while others exhibit mean field behaviour over the same range of concentration. The mean field regime leads to $t \approx 3$.

Several experimental values of s and one t exponent less than the universally accepted values, for which no theory is available as yet, have been reported in some of the Conductor-Talc-wax systems (Chiteme and McLachlan 2000) and will be discussed later in this thesis.

2.2 The Low Frequency Dielectric Constant Anomaly

The two-exponent phenomenological equation (eqn. (2.3)) given in section 2.1.2 can also be used to analyse dielectric data (McLachlan *et al.* 1998) by inserting complex conductivities (dielectric constants) in the equation. It has been shown experimentally (McLachlan *et al.* 1998 and results presented in this work) that the real dielectric constant, when plotted as a function of ϕ for a fixed frequency ω , does not peak at ϕ_c as predicted in Clerc *et al.* (1990), Bergman and Stroud (1992) and Nan (1993), but continues to increase beyond ϕ_c , eventually reaching a peak at a value of ϕ greater than ϕ_c . The resultant plot has a hump-like appearance and the position of the peak depends on ω , s , t and ϕ_c , ϵ_{ir} and σ_c (where ϵ_{ir} is the real relative dielectric constant of the insulating component). This behaviour of the real dielectric constant has been modeled by equation (2.3) in a not very satisfactory way in a previous publication (McLachlan *et al.* 1998).

Further theoretical investigation of the real dielectric constant behaviour above ϕ_c has been done recently (Heiss *et al.* 2000). It has previously been shown, using (2.3), that at $\phi = \phi_c$, the conductivity of the composite can be written:

$$\sigma_{mc} = \sigma_c / A^{(st)/(s+t)} (\sigma_i / \sigma_c)^{t/(s+t)}, \quad (2.11)$$

up to higher order terms in σ_i / σ_c . In the crossover region, where ϕ lies between $\phi_c - (\sigma_i / \sigma_c)^{1/(s+t)}$ and $\phi_c + (\sigma_i / \sigma_c)^{1/(s+t)}$, the conductivity takes the form (2.2b):

$$\sigma_m \propto \sigma_i^{t/(s+t)} \sigma_c^{s/(s+t)}. \quad (2.12)$$

Using the approximation $\sigma_c = \sigma_{cr}$ and $\sigma_i = -i\omega\epsilon_0\epsilon_r$, the crossover region is found to range between $\phi_c - (\omega\epsilon_0\epsilon_r/\sigma_c)$ and $\phi_c + (\omega\epsilon_0\epsilon_r/\sigma_c)$, which shows that a sample close to ϕ_c will enter the crossover region for a high enough frequency ω . Using the ansatz $\sigma_m^{1/t}(\phi) = \sigma_{mc}^{1/t} + \partial$ in equation (2.3) gives an expression for ∂ , which is:

$$\partial = [\sigma_{mc}^{1/t} \sigma_i^{1/s} (A-1) + \Delta\phi \sigma_c^{1/t} \sigma_{mc}^{1/s}] / [A(t/s+1) \sigma_{mc}^{1/s} - t/s \Delta\phi \sigma_c^{1/t} \sigma_m^{1/s-1/t} - (A-1) \sigma_i^{1/s}]. \quad (2.13)$$

Note that this expression for ∂ does not vanish at ϕ_c because of the additional low order terms, which were previously omitted in (2.11). After replacing σ_{mc} by the right hand side of (2.11) and some rigorous calculation to find the maximum for ∂ , the ϕ value corresponding to the dielectric peak (ϕ_{max}) is then found to be:

$$\phi_{\max} = \phi_c + [(s+t)/2t] [(1-\phi_c)(1-2\phi_c)/\phi_c] A^{-2s/(s+t)} (\sigma_i/\sigma_c)^{2/(s+t)} + \hat{O}((\sigma_i/\sigma_c)^{3/(s+t)}). \quad (2.14)$$

Equation (2.14) shows that the deviation of $\phi_{\max}$ from ϕ_c only starts with the second order term in $(\sigma_i/\sigma_c)^{1/(s+t)}$. Recall that the term $((\sigma_i/\sigma_c)^{1/(s+t)})$ determines the width of the crossover region (eqn. (2.2a)) and note that for a given s , t and ϕ_c , $\phi_{\max}$ depends only on the ratio $(\sigma_i/\sigma_c \equiv \omega \epsilon_0 \epsilon_r / \sigma_c)$. The larger the ratio (σ_i/σ_c) , the further $\phi_{\max}$ is from ϕ_c . On the other hand, the position of $\phi_{\max}$ moves towards ϕ_c for $\sigma_i/\sigma_c \rightarrow 0$, as is to be expected from (2.14).

As noted earlier in this section, equation (2.3) only qualitatively models the dielectric behaviour. In order to better fit the experimental dielectric data, an effective dependence of σ_c on conductor concentration (ϕ) was proposed (Heiss *et al.* 2000), based on the Balberg model (Balberg 1998a and 1998b) for non-universal values of t (see section 2.1.4). The Balberg model assumes that the resistance distribution function $h(\epsilon)$ has the form $\epsilon^{-\omega'}$ as $\epsilon \rightarrow 0$, with $-\infty < \omega' < 1$. For $\omega' > 0$, the model shows that the average resistance in the network can diverge when $\phi \rightarrow \phi_c$, which leads to t values larger than those predicted by the original ($\omega' = 0$) Random Void model. The increase in t beyond its universal value (t_{un}) is included in $t = t_{\text{un}} + t_{\text{nun}} + r$, where t_{nun} is the contribution to the nonuniversal value of t and r is an exponent characterising the extra contribution due to the characteristic resistance of the network diverging at $\phi \rightarrow \phi_c$. To account for the increase in the characteristic resistance close to ϕ_c , σ_c is replaced with σ_{ceff} :

$$\sigma_{\text{ceff}} = \sigma_{00} + \sigma_{c0} [(\phi - \phi_c)/(1 - \phi_c)]^r, \text{ for } \phi > \phi_c \text{ and } r > 0. \quad (2.15)$$

The symbol σ_{00} denotes the nonzero value of σ_c at ϕ_c , so that the effective conductivity (σ_{ceff}) does not vanish at ϕ_c . For $\phi < \phi_c$, it was assumed that $\sigma_{\text{ceff}} = \sigma_{00}$ (Heiss *et al.*

2000). The modification caused by eqn. (2.15) is virtually indiscernible in the first order terms of the solution for σ_m using eqns. (2.1) or (2.3). The dielectric constant, which is given by the second order term just beyond ϕ_c , can be fitted more satisfactorily using eqns. (2.3) and (2.15) than eqn. (2.3) only, as will be shown by the results in section 4.1.4.

2.3 1/f or Flicker Noise in Percolation Systems

When a constant “noise free” current is passed through a resistor, a noise spectrum of the form:

$$S_v(f) = \alpha V^m / (N f^\gamma) \quad (2.16)$$

is observed. Equation (2.16) is Hooge’s generalised empirical formula (Hooge 1969) and gives the noise power spectrum $S_v(f)$ for voltage fluctuations. In eqn. (2.16), V is the average DC voltage across the sample, N is the total number of charge carriers in the sample and α is a dimensionless number. The parameter α is of the order $10^{-5} \rightarrow 10^{-1}$ in small volume metallic samples and as high as $10^3 \rightarrow 10^7$ in granular high- T_c materials. The exponent γ is of the order of unity and as a result, this class of noise is commonly referred to as 1/f noise. If the voltage exponent $m = 2$, then the noise is produced entirely by equilibrium resistance fluctuations and the current acts only as a probe (Bruschi *et al.* 1994, Nandi *et al.* 1996). If the exponent $m \neq 2$, then the noise is believed to be a driven phenomenon (Nandi *et al.* 1996), which can imply the coexistence of other mechanisms.

The physical origin of 1/f noise is still an open question despite the intensive investigations (both theoretical and experimental) that have been carried out on the

phenomenon (see for instance review articles by Hooge *et al.* 1981, Dutta and Horn 1981, Weissman 1988, Tremblay *et al.* 1989, Balberg 1998b and references therein, Stephany 1998). In most approaches, the noise has been modeled in terms of random resistor networks, where each bond is characterised by a resistance r_α , which fluctuates in time with a variance $\langle \delta r_\alpha \rangle$. The relative resistance noise (S_R) is given by $S_R = \langle \delta R^2 \rangle / R^2$, where R is the macroscopic resistance (Yagil *et al.* 1993). The fluctuations in the macroscopic resistance (δR) are related to the local fluctuations (δr_α) by;

$$I^2 \delta R = \sum_i i_\alpha^2 \delta r_\alpha.$$

When the local fluctuations are uncorrelated, $\langle \delta r_\alpha \delta r_\beta \rangle = \delta r_{\alpha,\beta} \langle \delta r_\alpha^2 \rangle$ which gives the expression:

$$S_R = \sum_i i_\alpha^4 \langle \delta r_\alpha^2 \rangle / (\sum_i i_\alpha^2 r_\alpha)^2.$$

If all the resistors have the same average resistance $\langle r \rangle$ and the same mean square fluctuation $\langle \delta r^2 \rangle$, the relative noise then becomes:

$$S_R = \langle \delta r^2 \rangle \sum_i i_\alpha^4 / r^2 (\sum_i i_\alpha^2)^2, \quad (2.17)$$

which shows that 1/f noise measures the fourth moment of the current distribution (Yagil *et al.* 1993).

1/f noise has been used to study percolation systems as a possible means of probing the microstructural inhomogeneities of the composites, especially close to the percolation threshold. Bergman (1989) realised that the microgeometry of the composite plays a much more important role in the determination of 1/f noise than previously thought. This is because in real continuum systems, the bond resistances usually obey a power law distribution and the noise enhancement is produced mainly by the small narrow regions of conducting material or links in the links, nodes and blobs (LNB) model, where the electric field or resistance is abnormally large. It is this sensitivity to local rather than the global features of the microgeometry, which makes 1/f noise a possible method of characterising percolative microstructures. Wright *et al.* (1986) explained the divergence of 1/f noise on approaching the percolation threshold in terms of the decrease in the number of percolation paths or backbones. When the conductor volume fraction in the sample is well above the percolation threshold, current flows through a large number of inter-linked backbones, so that the independent fluctuations in different paths tend to average out and decrease the fluctuation in the total resistance. However, as the conductor fraction approaches the percolation threshold (from the conducting side), the tenuous connectivity of the conducting backbone restricts current flow to a small number of tortuous paths or backbones, which minimises cancellations of independent fluctuations, resulting in an increase of the noise amplitude. Previous measurements (notably Chen and Chou 1985, Garfunkel and Weissman 1985, Mantese and Webb 1985, Mantese *et al.* 1986, Rudman *et al.* 1986, Octavio *et al.* 1987, Song *et al.* 1986, Pierre *et al.* 1990b, Bergman *et al.* 1993, Bruschi *et al.* 1994, Nandi *et al.* 1996, Wu and McLachlan 1997, Dziedzic and Kolek 1998) on percolation systems have been done on both 2D and 3D systems, as a function of the DC resistance of the sample and volume (area) fraction of the conducting component.

In 1986, Rammal, Tannous, Breton and Tremblay introduced a new scaling exponent, k , to describe the divergence of the normalised power spectrum $S_v(f)/V^2$ (expressed

here in terms of voltage fluctuations), close to but on the conducting side of the percolation threshold, through the power law:

$$S_v(f)/V^2 \propto (\phi - \phi_c)^{-k}. \quad (2.18)$$

Using (2.18) and the well known divergence of DC resistance with critical exponent t (eqn. (2.1)) yields:

$$S_v(f)/V^2 \propto R^w, \quad (2.19)$$

which gives a unique prediction for the normalised $1/f$ noise spectrum as a function of the DC resistance where, according to Rammal *et al.* (1985), the exponent w should equal k/t . A plot of S_v/V^2 against R is usually given as it eliminates the statistical fluctuations in σ_m observed when the latter is plotted against $(\phi - \phi_c)$. Note also that for samples close to ϕ_c , the small errors in ϕ are amplified in the $(\phi - \phi_c)$ term. Theoretical predictions (Tremblay *et al.* 1986) give $w = 0.78$ in a 3D random resistor lattice.

In the 3D RV and IRV models, Tremblay *et al.* (1986) calculated w to be 2.15 and 2.40 respectively. Using the predicted t values for the 3D RV and IRV models, the values of w ($\equiv k/t$) are 0.63 ($1.56/2.5 \equiv k_{un}/t_{RV}$) and 0.78 ($1.56/2.0 \equiv k_{un}/t_{un/IRV}$) respectively. The exponent k_{un} is the universal value of the noise exponent k , taken to be 1.56 (Tremblay *et al.* 1986). The exponents, t and w have both been determined experimentally in a number of systems (see for instance Rudman *et al.* 1986, Pierre *et al.* 1990b, Nandi *et al.* 1996, Wu and McLachlan 1997, Rubin *et al.* 1999, Chiteme and McLachlan 2000). However, in most of these experiments, the values of w

obtained are either lower or larger than those predicted by Tremblay *et al.* (1986) in the original RV and IRV models.

Causes suggested for the deviations of experimental results from the current theories include different microscopic noise mechanisms, additional tunneling, noisy hopping conduction, noisy insulators, heating and nonlinear effects and non-uniformity of the samples (Nandi *et al.* 1996). The current literature clearly indicates that the available theories are not able to explain all the experimental results.

Balberg (1998a and 1998b) gave new limits to the noise exponents k and w in an attempt to explain the discrepancies observed in earlier experimental results. A summary of Balberg's arguments on non-universal noise exponents follows. A volume element V is related to ϵ (the proximity parameter, section 2.1) by $V \propto \epsilon^v$. Similar to u , the exponent v is related to the dimensionality of the system and is also model dependant. This approximation leads to $\langle \delta r^2 \rangle \propto \epsilon^{-(2u+v)}$, since $\langle \delta r^2 \rangle / \langle r \rangle^2 \propto 1/V$ and $\langle r \rangle \propto \epsilon^{-u}$. Note also that $\langle \delta r^2 \rangle / \langle r \rangle^2 \propto 1/V$ is derived from the argument that in a random process, the squared variance ($\langle \delta r^2 \rangle$) divided by the average squared $\langle r \rangle^2$, is inversely proportional to the number of elements in the system. The square of the resistance fluctuations in the entire link, $\langle \delta R^2 \rangle_{L1}$, is given by the sum of the powers dissipated by the fluctuations in the individual resistors, i.e. $\langle \delta R^2 \rangle_{L1} \propto L_1 \langle \delta r^2 \rangle_{L1}$. With $h(\epsilon) = h_0 \epsilon^{-\omega'}$, $\langle \delta r^2 \rangle_{L1}$ is now given by:

$$\langle \delta r^2 \rangle_{L1} \propto \int_{\delta} \epsilon^{-(2u+v+\omega')} d\epsilon \quad \delta < \epsilon \leq \epsilon_0, \quad (2.20)$$

where δ is the typical proximity parameter (ϵ) value (or neck diameter) of the single resistor, R_{ξ} , which has the average resistance of a set of links. In the LNB model, δ is given by $R_{\xi} \propto \delta^{-u} \propto L_1$. If R_{ξ} has a universal behaviour ($\langle r \rangle_{L1}$ independent of L_1), then $\delta \propto L_1^{-1/u}$. Combining this with $\langle \delta r^2 \rangle_{L1} \propto \delta^{-(2u+v+\omega'-1)}$ (from (2.20)) leads to:

$$\langle \delta r^2 \rangle_{L1} \propto L_1^{(2u + v + \omega' - 1)/u} \quad (2.21)$$

For this case ($\langle r \rangle_{L1}$ independent of L_1), the relative resistance noise, $S_R = \langle \delta r^2 \rangle_{L1} / \langle r \rangle_{L1}^2$, will deviate from the universal exponent ($k = k_{un}$) only by the exponent in (2.21). Recalling that $L_1 \propto (p - p_c)^{-1}$, the relative resistance exponent is given by:

$$k = k_{un} + (2u + v + \omega' - 1)/u. \quad (2.22)$$

provided $u + \omega' < 1$ (eqn. (2.9)) but $2u + v + \omega' > 1$. Here k_{un} is the universal value of the exponent k . Note that if $2u + v + \omega' < 1$, then (2.20) converges as $\varepsilon \rightarrow \infty$ and $k = k_{un}$.

For the case where the resistance (R_ξ) has a non-universal behaviour ($u + \omega' > 1$), which can be written as $R_\xi \propto L_1 L_1^{(u + \omega' - 1)/(1 - \omega')}$ (section 2.1.4) and using $R_\xi \propto \delta^{-u}$, the corresponding δ value will be given by $\delta \propto L_1^{-1/(1 - \omega')}$. Provided $u + \omega' > 1$, $u, v > 0$ and $2u + v + \omega' > 1$, then the integral (2.20) gives $\langle \delta r^2 \rangle_{L1} \propto \delta^{-(2u + v + \omega' - 1)}$, which when combined with $\delta \propto L_1^{-1/(1 - \omega')}$, yields:

$$\langle \delta r^2 \rangle_{L1} \propto L_1^{(2u + v + \omega' - 1)/(1 - \omega')} \quad (2.23)$$

Since the resistance has the non-universal part of $\langle r \rangle_{L1} \propto L_1^{(u + \omega' - 1)/(1 - \omega')}$, this and (2.23) leads to $S_R \propto L_1^{(v - \omega' + 1)/(1 - \omega')} \propto (p - p_c)^{-(v - \omega' + 1)/(1 - \omega')}$ (from $S_R = \langle \delta r^2 \rangle / \langle r \rangle^2$ and $L_1 \propto (p - p_c)^{-1}$), which in turn gives the non-universal noise exponent k as:

$$k = k_{un} + (v + 1 - \omega')/(1 - \omega'). \quad (2.24)$$

The equations (2.22) and (2.24) give the Tremblay, Feng and Breton (TFB 1986) results for $\omega' \rightarrow 0$.

To check the specific numerical predictions for the real two or three-dimensional RV and IRV models one recalls that $u = d - 3/2$ and $v = d - 1/2$ for the RV and $u = d/2 - 1$ and $v = d/2$ for the IRV models. For universal behaviour of the resistance (R_ξ), $u + \omega' < 1$. For the $d = 2$ RV model, a universal behaviour occurs when $\omega' < 1/2$ and (2.24) yields $k = k_{un} + (3/2 + \omega')/(1/2)$ so that $k/t = k/t_{un} \leq 4.7$. For the IRV model or $\omega' = 0$, $\langle \delta R^2 \rangle_{L,1}$ converges and $k/t = k_{un}/t_{un}$. When $1 > \omega' > 0$, (2.24) yields $k = k_{un} + \omega'/u$. In the case where $u \rightarrow 0$, the value of k diverges and any value between $k_{un}/t_{un} = 0.86$ and $k/t \rightarrow \infty$ is possible; which could account for the extreme experimental results like $k/t > 5$ observed in 2D sandblasted films (Garfunkel and Weissman 1985). The $d = 3$ RV model gives ($t_{un} = 2$ and $k_{un} = 1.56$) $0.78 = k_{un}/t_{un} \leq k/t \leq 2.1$, while $0.78 = k_{un}/t_{un} \leq k/t \leq 2.78$ for the IRV model.

It can be seen from the above paragraph that for all the models (except for $d = 2$ IRV) and for $\omega' > 1/2$, a non-universal behaviour of the resistance will give:

$$k/t = [k_{un} + (v + 1 - \omega')/(1 - \omega')]/[t_{un} + (u + \omega' - 1)/(1 - \omega')] \quad (2.25)$$

The largest k and t exponents are obtained when $\omega' \rightarrow 0$ and the smallest k/t ratio is k_{un}/t_{un} . The validity of the above theoretical prediction of the noise exponent w or k/t

(eqn. (2.25)) has not been fully tested against experimental values obtained from real continuum systems. This is done in Chapter six using results from the present work.

2.4 The AC Conductivity Equations and Scaling

The real AC conductivity of a composite exhibits dispersion, especially for samples near the percolation threshold ϕ_c . The AC conductivity $\sigma_m(\phi, \omega)$ and dielectric constant $\epsilon_m(\phi, \omega)$ for composite percolation systems have been modelled (see for example Clerc *et al.* 1990, Bergman and Stroud 1992, Nan 1993) by means of a scaling ansatz for the complex AC conductivity: $\sigma_m(\phi, \omega) = \sigma_{mr}(\phi, \omega) - i\omega\epsilon_0\epsilon_{mr}(\phi, \omega)$. At zero frequency (the static or DC case), experimental results show that the macroscopic conductivity (σ_m) of the composite is a homogeneous function of the volume fraction of the conducting component (ϕ), the conductivity σ_c (for the conductor) and σ_i (for the insulator):

$$\sigma_m(\phi, \sigma_c, \sigma_i) = \sigma_c f(\phi, h) ; h = \sigma_i/\sigma_c.$$

The function $f(\phi, h)$ is singular at the percolation threshold ($\phi = \phi_c$ and $h = 0$) where the conductivity goes through a percolation transition. Close to this point, where $\Delta\phi = \phi - \phi_c$ and h are small, the conductivity assumes a scaling form (Clerc *et al.* 1990):

$$\sigma_m \approx \sigma_c |\phi - \phi_c|^t F_{\pm}(h |\Delta\phi|^{-s-t}). \quad (2.26)$$

Here F_+ and F_- are the scaling functions above and below the percolation threshold respectively (Webman *et al.* 1975, Efros and Schlovskii 1976, Straley 1976, 1977b,

Bergman and Imry 1977, Stroud and Bergman 1982). The crossover from an insulating to an essentially conducting behaviour occurs in a small region ($\delta\phi$) around ϕ_c given by;

$$(\delta\phi) \sim |\sigma_i/\sigma_c|^{1/(s+t)}. \quad (2.27)$$

At frequencies lower than the plasmon and scattering frequencies (i.e. $< 10^{13}\text{Hz}$) and close to ϕ_c , the scaling relation (2.26) becomes (Clerc *et al.* 1990);

$$\sigma_m(\phi, \omega) \approx \sigma_c |\phi - \phi_c|^t F_{\pm}(i\omega/\omega_0 |\Delta\phi|^{-s-t}), \quad (2.28)$$

in the approximation $\omega_0 = \sigma_c/\epsilon_0\epsilon_r$, where σ_c is the DC conductivity of the conductor and the dielectric (insulator) has zero loss.

The frequency-dependent complex dielectric constant $\epsilon_m(\phi, \omega)$ is defined from $\sigma_m(\phi, \omega)$ by:

$$\epsilon_m(\phi, \omega) = \sigma_m(\phi, \omega)/i\omega, \quad (2.29)$$

Another quantity associated with AC conductivity, the loss angle (δ) is defined as:

$$\tan \delta = \sigma_{mr}/\sigma_{mi} = \epsilon_{mi}/\epsilon_{mr} \quad (2.30)$$

The subscripts “mr” and “mi” denote the real and imaginary quantities respectively. Note that at and near the percolation threshold ϕ_c , the frequency dependent conductivity $\sigma_m(\phi, \omega)$ can be written in the form (Clerc *et al.* 1990):

$$\sigma_m(\phi_c, \omega) \approx K \sigma_c (i\omega/\omega_0)^x; \quad \text{where } K \text{ is a constant and } x \text{ is an exponent.} \quad (2.31)$$

From (2.30) and (2.31), the loss angle assumes a value at ϕ_c (δ_c) given by:

$$\delta_c = \pi/2(1 - x). \quad (2.32)$$

Scaling functions (F_- and F_+) for σ_m , are defined in Clerc *et al.* (1990), Bergman and Stroud (1992) and Nan (1993). These definitions are:

$$\begin{aligned} \sigma_m &= \sigma_c [(\phi_c - \phi)^t] F_-(x_-'), & \phi < \phi_c \\ \text{and} & & (2.33) \end{aligned}$$

$$\sigma_m = \sigma_c [(\phi - \phi_c)^t] F_+(x_+'), \quad \phi > \phi_c,$$

where the scaling functions $F_{\pm}(x_{\pm}')$ depend on the parameters used in (2.1) and (2.3).

$$x_-' = (\sigma_i/\sigma_c)[(\phi_c - \phi)^{s+t}] \text{ or } -i(\omega/\omega_c), \quad \phi < \phi_c$$

with

$$\omega_{c-} = (\sigma_c/\epsilon_0\epsilon_i)[(\phi_c - \phi)^{s+t}], \quad (2.34)$$

and

$$x_+' = (\sigma_i/\sigma_c)[(\phi - \phi_c)^{s+t}] \text{ or } -i(\omega/\omega_{c+}), \quad \phi > \phi_c$$

with

$$\omega_{c+} = (\sigma_c/\epsilon_0\epsilon_i)[(\phi - \phi_c)^{s+t}] \quad [\text{Note } \omega_{c+} \propto \sigma_m(\phi, 0)^{(s+t)/t} \equiv \sigma_m(\phi, 0)^q]. \quad (2.35)$$

Recall that in all the above equations for ω_c , the imaginary parts of the complex quantities σ_c^* and ϵ_r^* have been assumed to be negligible so that $\sigma_c^* = \sigma_c$ and $\epsilon_r^* = \epsilon_r$ and $\sigma_i = -i\omega\epsilon_0\epsilon_r$.

At high frequency and closer to the percolation threshold (ω/ω_c or $x_{\pm}' > 1$), the above equations lead to the following scaling relations:

$$\begin{aligned} \sigma_{mr}(\phi, \omega) &\propto F_{\pm}(i\omega/\omega_c) \propto (i\omega/\omega_c)^x, \\ \epsilon_{mr}(\phi, \omega) &\propto (i\omega/\omega_c)^y, \end{aligned} \quad (2.36)$$

which are sometimes written as:

$$\sigma_m \sim \omega^x \quad \text{and} \quad \epsilon_m \sim \omega^{-y}. \quad (2.37)$$

The exponents x and y are more general than $x = t/(s + t)$ and $y = s/(s + t)$ respectively (cf. eqn. (2.39)), which follow directly from the RC model.

Assuming the complex conductivity is an analytic function of $i\omega$, the exponents x and y should satisfy (Bergman and Imry 1977, Song *et al.* 1986, Hundley and Zettl 1988, Yoon and Lee 1990, Smilauer 1991);

$$x + y = 1. \quad (2.38)$$

There are currently two theories used to explain the AC behaviour of percolation systems: the **intercluster polarisation (R-C model)** and the **non-interacting cluster approximation (Anomalous Diffusion-AD)** models. The inter-cluster polarisation model assumes that the neighbouring conducting clusters are linked together with an interaction capacitance. In the R-C model (Bergman and Imry 1977), the scaling exponents x and y are given by:

$$x = t/(s + t) \quad \text{and} \quad y = s/(s + t), \quad (2.39)$$

where t and s are the conductivity and dielectric exponents respectively. Note that the two exponent phenomenological equation (eqn. (2.3)) also gives (2.39) for the frequency exponents in the appropriate limits. Substituting the above expression for x in (2.32), the loss angle at ϕ_c (δ_c) becomes;

$$\delta_c = \pi/2(s/(s + t)). \quad (2.40)$$

For the universal values of s and t , this expression can be taken to give the universal loss angle δ_{cun} .

In the **non-interacting cluster approximation (AD)**, anomalous diffusion is assumed to occur within a percolation cluster because of the fractal nature of a near infinite or infinite percolation network. The theory of anomalous diffusion on fractal percolation clusters was formulated by Gefen, Aharony and Alexander (1983) for the length scale $a_0 \ll L_s \ll \xi$ (where a_0 is the atomic dimension and ξ is the correlation length defined previously (refer to Fig. 2.5)). Using the Einstein relation for diffusion (Ashcroft and Mermin 1976), Gefen and his colleagues obtained the usual percolation expressions for the conductivity and dielectric constant with the following exponents:

$$x = t/v(2 + \theta) \quad \text{and} \quad y = (2v - \beta)/v(2 + \theta); \quad \text{for } \omega \gg \omega_\xi \propto \xi^{-(2 + \theta)}, \quad (2.41)$$

where v is the correlation length exponent, β is the critical exponent that describes the probability that an arbitrary point belongs to the largest cluster of the system and the parameter $\theta = (t - \beta)/v$ is a critical exponent describing the diffusion process for a short time (c.f. the time taken by an electron to move across a single ‘typical’ cluster). At present, there is no theory that unifies the inter-cluster polarisation (IP/R-C) and anomalous diffusion (AD) models.

The x and y exponents given in eqns. (2.39) and (2.41) are equivalent only if $s + t = v(2 + \theta)$ and $s = 2v - \beta$. In 2D, $s = t$, which would give $x = y = 0.32$ and therefore $x + y \neq 1$. In 3D, the calculated values of x and y in the inter-cluster polarisation model

are 0.70 and 0.30 respectively while the anomalous diffusion model gives $x = 0.58$ and $y = 0.42$, when the universal values of s (0.87) and t (2.00) are used in the relevant expressions. Hence measurements of the exponents in real continuum systems should indicate which model for scaling is more appropriate in analysing the AC properties of percolation systems. However, values close to the anomalous diffusion prediction have never been clearly observed in experiments, including the ones given in this thesis.

New percolation scaling expressions have recently been formulated (Wu and McLachlan 1998), which allow one to generate **continuous and analytical** curves on which the experimental data could be scaled. These are:

$$F_+(x'_+ \equiv \omega/\omega_{c+}) = \sigma_{GM}/\sigma_c((\phi - \phi_c)/(1 - \phi_c))^t. \quad (2.42a)$$

$$F_-(x'_- \equiv \omega/\omega_{c-}) = \sigma_{GM}/\sigma_c((\phi_c - \phi)/\phi_c)^t. \quad (2.42b)$$

The quantity σ_{GM} is obtained from the equation (Wu and McLachlan 1997 and 1998):

$$(1 - \phi)(\sigma_i^{1/s} - \sigma_{GM}^{1/t})/(\sigma_i^{1/s} + A\sigma_{GM}^{1/s}) + \phi(\sigma_c^{1/t} - \sigma_{GM}^{1/t})/(\sigma_c^{1/t} + A\sigma_{GM}^{1/t}) = 0, \quad (2.43)$$

The eqn. (2.43) is equivalent to (2.3) but with σ_m , σ_c and σ_i complex. Using $\sigma_i = \omega\epsilon_0\epsilon_r$ in $x'_+ = \sigma_i/\sigma_c((1 - \phi_c)/(\phi - \phi_c))^{s+t} \equiv \omega/\omega_{c+}$ and $x'_- = \sigma_i/\sigma_c((\phi_c - \phi)/\phi_c)^{s+t} \equiv \omega/\omega_{c-}$ in eqns. (2.42) gives;

$$\omega/\omega_{c+} = (\omega\epsilon_0\epsilon_r/\sigma_c)((1 - \phi_c)/(\phi - \phi_c))^{s+t} \text{ and } \omega/\omega_{c-} = \omega\epsilon_0\epsilon_r/\sigma_c(\phi_c/(\phi_c - \phi))^{s+t}. \quad (2.44)$$

Note that as ω is varied the $F^*_+(x'_+ = \omega/\omega_{c+})$ and $F^*_-(x'_- = \omega/\omega_{c-})$ curves with different σ_i/σ_c , ω/ω_{c+} and ω/ω_{c-} values superimpose for the same t and s values, provided there are compensatory changes in ϕ or ϕ_c to give the same x'_+ , x'_- , ω/ω_{c+} or ω/ω_{c-} values. The limiting slopes of the first order terms of F_+ and F_- against x'_+ , x'_- , ω/ω_{c+} and ω/ω_{c-} are as follows (Wu and McLachlan 1998 and references therein):

$$F_+(x'_+) [\text{and } F^*_+(-i\omega/\omega_{c+})] = 1; \quad \text{for } x'_+ \text{ or } \omega/\omega_{c+} < 1, \quad (2.45a)$$

$$F_-(x'_-) [\text{and } F^*_-(-i\omega/\omega_{c-})] = x'_-(\omega/\omega_{c-}); \quad \text{for } x'_- \text{ and } \omega/\omega_{c-} < 1, \quad (2.45b)$$

$$F_+(x'_+) [\text{and } F^*_+(-i\omega/\omega_{c+})] \propto x'^{t/(s+t)}_+(\omega/\omega_{c+})^{t/(s+t)}; \quad \text{for } x'_+ \text{ and } \omega/\omega_{c+} > 1, \quad (2.45c)$$

$$F_-(x'_-) [\text{and } F^*_-(-i\omega/\omega_{c-})] \propto x'^{t/(s+t)}_-(\omega/\omega_{c-})^{t/(s+t)}; \quad \text{for } x'_- \text{ and } \omega/\omega_{c-} > 1. \quad (2.45d)$$

The above expressions will be tested against the experimental results obtained from the cellular systems in Chapter five.

2.5 Magnetic Properties of Percolation Systems

Previous studies done on magnetic composite materials made from small magnetic particles embedded in a non-magnetic matrix (Gittleman *et al.* 1972, McLachlan and White 1987, Xiao and Chien 1987, Liou and Chien 1988, Gavin and Chien 1990, Fiske *et al.* 1997), show that these composite materials possess some useful properties not found in cast and sintered magnets despite the latter's higher permeability values. For instance, in a composite of a magnetic powder and a polymer, the polymeric matrix forms a coating on the magnetic particles which acts as an insulator to suppress

eddy current losses (Wohlfarth E. P. 1986). Non-percolating polymer based magnets can also be manufactured into complex shapes and sizes with relative ease, usually employing the conventional polymer processing techniques.

Particle-particle interactions have been observed to enhance the electrical and magnetic properties of composites (Fiske *et al.* 1997). At low volume concentration, the filler (magnetic particles) can be modeled as isolated non-interacting spheres and the effective permeability (μ_m) of the composite shows a linear dependence on volume fraction, ϕ (Fiske *et al.* 1997):

$$\mu_m = \mu_0(1 + 3\phi), \quad (2.46)$$

which is a well-known limit of effective media equations (Landauer 1978, McLachlan *et al.* 1990). However, unlike the electrical conductivity, the large ratio of μ_l/μ_h encountered in these studies makes it impossible for one to clearly observe percolation effects in the magnetic properties.

A study of the magnetic behaviour, in systems which have a percolation threshold, as a function of the magnetic volume fraction show dramatic changes of the properties close to the percolation threshold (Xiao and Chien 1987). McLachlan and White (1987) used the one exponent phenomenological general effective media equation (McLachlan 1987) to analyse the permeability of binary magnetic mixtures. The equation, written in terms of magnetic permeability, is:

$$\{(1-\phi)(\mu_l^{1/t} - \mu_m^{1/t})/[\mu_l^{1/t} + [(1-\phi_c)/\phi_c]\mu_m^{1/t}]\} + \{\phi(\mu_h^{1/t} - \mu_m^{1/t})/[\mu_h^{1/t} + [(1-\phi_c)/\phi_c]\mu_m^{1/t}]\} = 0. \quad (2.47)$$

The parameters μ_l , μ_h and μ_m are the permeabilities of the non-magnetic or low permeability component, the high permeability component and the composite medium respectively. Note that eqn. (2.47) depicts a situation where $s = t$. This equation may not be suitable for analysing the results obtained in this thesis as $s \neq t$ (from DC conductivity measurements) in all systems. Therefore, the two-exponent phenomenological equation, (eqn. (2.3)) will be used to fit the magnetic data obtained in this study in chapter seven.

An examination of previous studies has revealed the necessity to investigate both DC electrical conductivity and magnetic properties in the same system so that the two can be correlated. This is because in some cases (Xiao and Chien 1987, Liou and Chien 1988) the percolation threshold referred to was never obtained directly from DC electrical conductivity measurements on their samples. It is clear from these experiments that, without DC conductivity data, no unambiguous ϕ_c can be identified. Since in theory, the DC conductivity shows a sharp percolation transition at ϕ_c for small σ_l/σ_c , it would be interesting to see what effect (if any) this transition would have on the magnetic properties of the magnetic systems studied in this thesis.

CHAPTER THREE

SAMPLE PREPARATION AND EXPERIMENTAL METHODS

3.0 Introduction

The samples studied in this thesis were made as follows. Small conducting powder particles were mixed with large insulator particles of Talc-wax and compacted under pressure to form the pellets. Some of the conductor particles were reduced in size (prior to mixing with the insulator particles) by grinding in a planetary mill so that their mean size was further reduced relative to that of the insulator. The particle sizes and shapes were characterised by means of a Malvern particle size analyser and electron microscopy respectively.

The electrical properties (DC and AC) of the pellet samples were studied as a function of the volume fraction of the conducting component (ϕ) in order to investigate the percolative behaviour of the samples. DC conductivity measurements were done on a Keithley 617 electrometer (for high resistance samples) and an LR 400 resistance bridge (for the low resistance samples). Low frequency (10^{-2}Hz to 10^7Hz) AC measurements were done on a Broadband Dielectric Spectrometer incorporating a Solartron SI1260 and a Novocontrol broadband dielectric converter. This combination enabled the measurement of a higher series resistance and lower loss angles than the instruments used in most previous experiments. High frequency (10^6Hz to 10^9Hz) measurements were done on a Hewlett Parkard HP4291 Impedance analyser after the

previously measured pellets had been cut in order to fit into the Novocontrol sample holder attached to the HP instrument. For 1/f noise measurements, a Hewlett Parkard HP3562a spectrum analyser was used together with the setup shown in Fig. 3.4. All these measurements were done at room temperature (22°C) in a relatively dry atmosphere.

In a system containing Fe_3O_4 as the conducting component, the conductivity was also studied as a function of temperature (from room temperature to 120°C) in order to further investigate both DC and AC scaling. Magnetic measurements were done on the Fe_3O_4 and Nickel systems in order to study the change (if any) of the magnetic properties on moving from the insulating to the conducting region. Results of these and other experiments described in this chapter are given in Chapters 4-7.

3.1 Sample preparation

Several conducting powders [Graphite (G: Lonza, KS75), Carbon Black (CB: Raven 430 ultra powder, Columbian Chemicals Co.), Niobium Carbide (NbC: 51101, 99+%, Johnson Matthey, GMBH Alfa products 1-3 μm), Magnetite (Fe_3O_4 : 97%-325 mesh, Johnson Matthey GmBH Alfa) and Nickel (Ni: CERAC, 99.9% pure, $\sim 5\mu\text{m}$ average)] were each mixed with Talc powder (with a diameter of 200-300 μm) coated with 4% wax by volume. The Talc powder was used as a common insulating matrix. Note that the particle sizes quoted here, for some of the conducting powders, are those specified by the manufacturers. The conductor particles were deliberately chosen to be much smaller than the Talc-wax particles so that they (the conducting particles) formed the surfaces of bubbles surrounding the insulating particles (voids) or a three-dimensional ‘cellular’ structure (Fig. 2.1). As a result, the conducting particles had the same macroscopic distribution in all the systems. The powders were mixed in a way that ensured even distribution of the conductor particles onto the surface of the insulator.

3.1.1 Characterisation of the powders

The powders (with the exception of the Talc-wax, Nickel and Niobium Carbide) were initially ground in a planetary mill (with agate balls) down to a mean size between $9\mu\text{m}$ and $35\mu\text{m}$. In order to characterise the powders by electron microscopy, aluminium stubs of about 30mm diameter and 5mm thick were used as holders for the powders to be examined. A layer of aquadag (colloidal graphite in water) was applied on one face of the stub. When the aquadag was nearly dry, the relevant powder was lightly sprinkled on the stub. The excess powder particles (those not stuck to the aquadag) were shaken off. The low conductivity Talc-wax powder on the stubs was carbon-coated to prevent charge accumulation on the particles before being examined using a JSM 840 scanning electron microscope. Images were obtained at various magnifications in order to estimate the size and shape of the particles. It was not possible to do accurate size measurements using the electron microscope because of the wide distribution of the particle sizes. In some cases, the particles also tended to form aggregates, which could not be easily separated into the individual particles. The principle use of the electron microscopy results was not to size but to observe the particle shapes as the latter play a crucial role in the determination of the percolation threshold. None of the conducting particles are spherical as required by the Kusy model (Kusy 1977) (see examples in Figs. 3.1, which show the scanned images of the electron micrographs).

A Malvern size analyser was used to measure the particle sizes of the powders. The instrument employs a light-scattering method to measure the powder particle sizes using light from a Helium-neon laser ($\lambda \sim 0.63\mu\text{m}$). The powder to be tested was initially made into a paste by mixing with water. Part of the paste was then added slowly to water to form a suspension. The suspended particles (with an obscuration of ~ 0.2) were pumped through a transparent tube at right angles to the laser light so that the powder particles would scatter the light at different angles (depending on their size) as they passed through the tube.

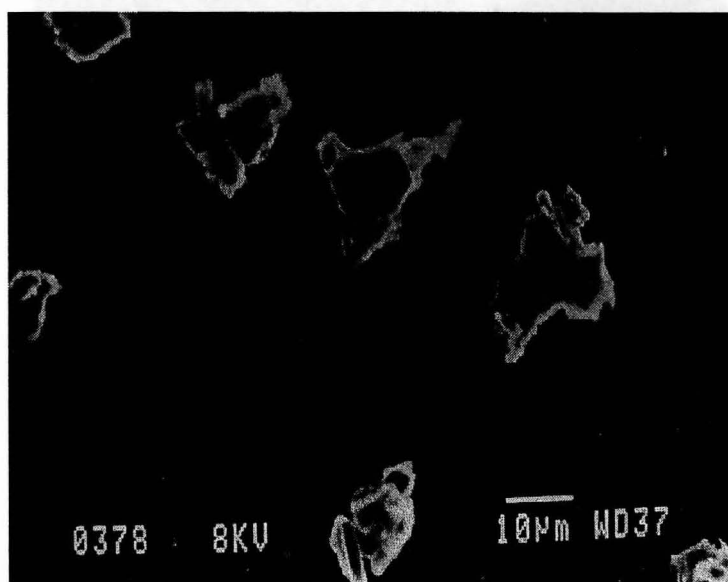


Figure 3.1a: Digital scan of the electron micrograph for the ground Graphite powder showing the irregular shape of the particles.

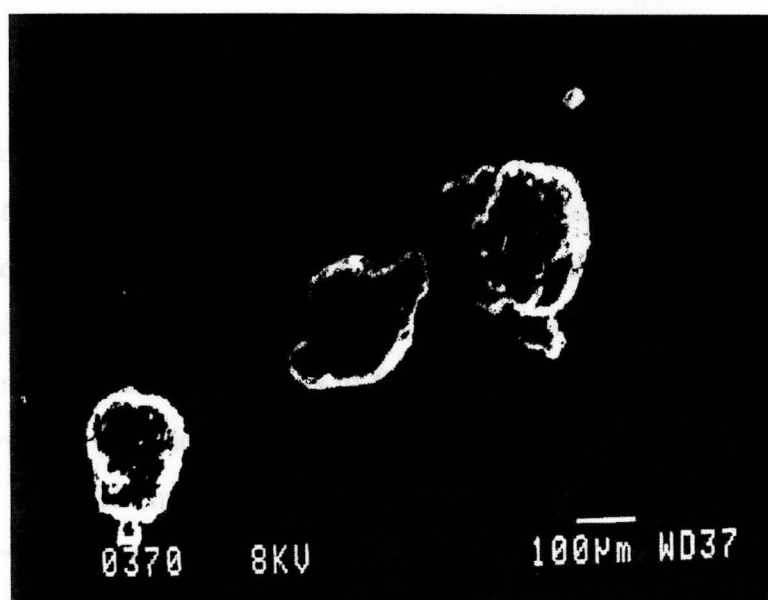
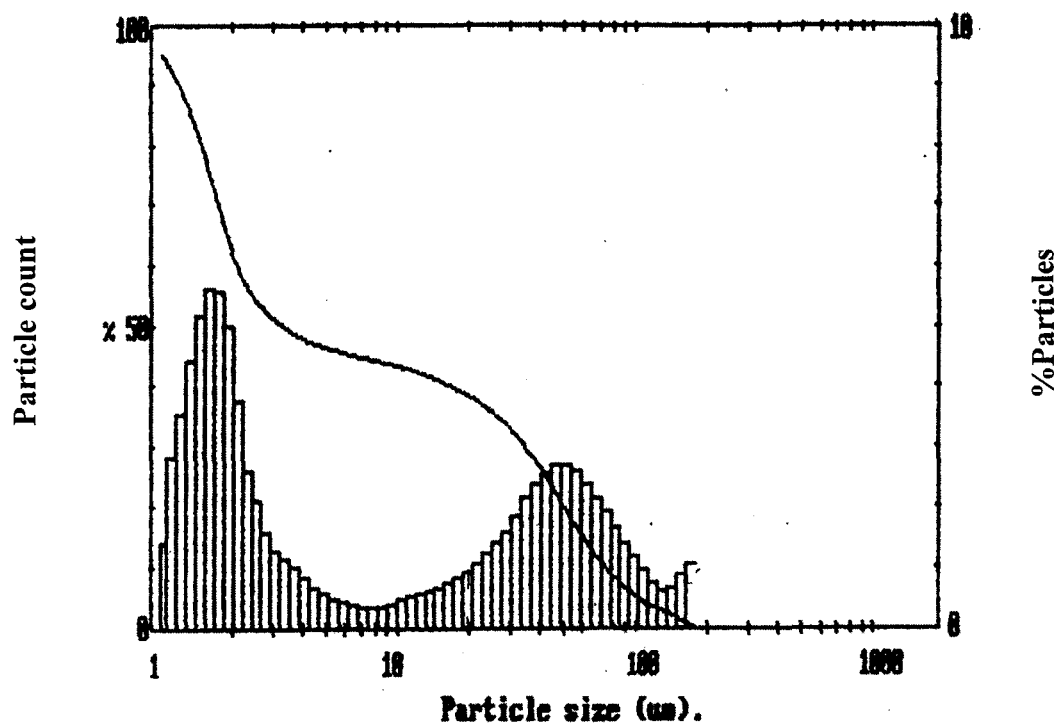


Figure 3.1b: Digital scan of the electron micrograph for the raw Carbon Black powder showing the shape of the particles.

The Malvern size analyser is also equipped with a variable-speed ultrasonic transducer designed to break lumps or aggregates of particles in the paste. However, it is not certain whether the ultrasonic transducer was successful in breaking the aggregates as some of the powders still showed a bimodal distribution. The instrument is also interfaced to a computer for easy operation and to speed up the measurement process. Only a few input parameters are required from the operator at the beginning of each measurement.

The particle size profile was obtained as a visual display on the computer screen as well as a printout. Examples of the later are shown in Figs. 3.2. A point of concern is the fact that some of the powders show a bimodal distribution, implying the existence of extreme sizes of the particles or stable clusters which would lead to further deviation from one of the assumptions of the Kusy model (i.e. mono-sized particles). Table 3.1 shows the particle sizes of all the systems as determined from the Malvern size analyser. In the EM method, the mean diameter was worked out as an average of 10-50 particles appearing on a printed photographic card. In some of the powders tested, the results from Electron Microscopy agree well with those obtained from the Malvern analyser (see Table 3.1). Note that the Malvern output gives two values of the particle size: the **mean** diameter and the **sauter** diameter. In order to avoid repetition, the difference between these two quantities is only emphasised in section 4.1.1, where they give different critical volume fractions when applied to the Kusy model.

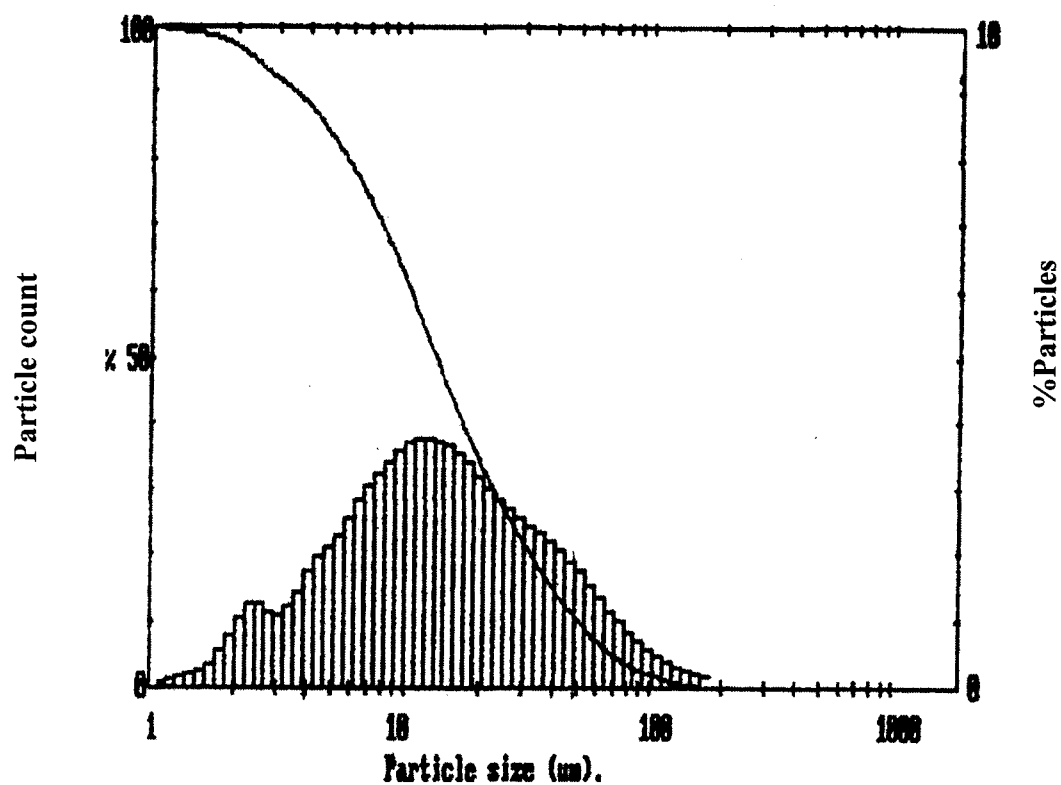


Sauter mean diameter = $25.97\mu\text{m}$, Mean diameter = $3.37\mu\text{m}$

Figure 3.2a: Particle size profile for the NbC powder as obtained from the Malvern size analyser. Note the bimodal distribution of the particle sizes.

Note: Particle count = number of particles counted, as represented by the solid line in the figure.

%Particles = percentage number of particles in each class or histogram.



Sauter mean diameter = $21.79\mu\text{m}$, Mean diameter = $13.31\mu\text{m}$

Figure 3.2b: Particle size profile for the 50% Graphite-50% Boron Nitride powder mixture.

Note: **Particle count** = number of particles counted, as represented by the solid line in the figure.

%Particles = percentage number of particles in each class or histogram.

Table 3.1: The measured particle sizes for the powders.

System	Mean particle size (μm): Malvern Analyser	Sauter diameter (μm): Malvern Analyser
Talc-wax*		
Ground Carbon Black**	7.92	12.84
Raw Carbon Black**	10.89	19.13
Ground Graphite	33.99	40.93
Graphite-B. Nitride	9.71	13.10
Nickel	15.76	28.80
Magnetite (Fe_3O_4)	10.00	12.34
Niobium Carbide**	3.37	25.97

*The Talc-wax particles were too big to be measured with the Malvern particle size analyser as the result obtained from such measurement was unreasonably small in comparison with the EM result (280-330 μm).

** Powders showing a bimodal distribution of particle size. Of these, the NbC gives the most pronounced bimodal profile as shown in Fig. 3.2a.

3.1.2 Preparation of the pellet samples

Samples were prepared by first mixing the conducting and insulating powders in the appropriate proportions. The pre-weighed components were hand-mixed in a glass bowl from which they were transferred to either an agate container or a tumbling bottle. The agate balls usually used for grinding powders in planetary mixing were removed in order to preserve the spherical shape of the soft insulator particles and to allow the small conductor particles to embed on their surface (without too much penetration) during the mixing process, which lasted about 20 minutes. Planetary mixing was used for soft conducting powders, that is, Carbon Black, Graphite and Graphite-Boron Nitride. The harder and/or heavier powders (Niobium Carbide, Nickel and Fe_3O_4) were mixed by tumbling, a more gentle mixing method compared to the planetary mixing. Tumbling involved putting the hand-mixed powders (conductor and insulator) in a bottle (with rods running parallel to its axis) which was in turn put in a slowly rotating drum in which the mixture was tumbled for 20 minutes. About 4 grams of each mixture was gently poured into a die and compressed into a pellet (at a pressure of 380MPa for one-and-half hours) of 26mm diameter and about 3mm thickness. By measuring the actual mass and volume of the pellets, the samples were corrected for porosity through the measured apparent density of the pellets and the calculated or fully compacted density, in order to determine the actual volume fraction (ϕ) of the conducting component in each sample. Electrodes were painted on the flat faces of the pellet using Silver paste. After the paste was dry, a DC measurement was done in order to decide on the next sample to make, which together with the previously measured ones, would give a reasonable sigmoid (log DC conductivity versus conductor volume fraction) curve. Near the percolation threshold, the conductor fraction was added in 0.2% volume increments so as to resolve more closely the details of the divergence of the properties under study near ϕ_c . The procedure was repeated to obtain sufficient samples, in the insulating as well as the conducting region, for all the systems, in order to determine the parameters s , ϕ_c and t , obtained by fitting the DC conductivity results to eqn. (2.3).

3.2 Experimental Methods

3.2.1 DC Conductivity measurements

Two terminal conductivity measurements for samples with resistance over $10^5 \Omega$ were made at room temperature (22°C) using a Keithley 617 electrometer in the V/I mode. In this mode, a known voltage is applied to the sample and the current through the sample is determined using the ammeter inside the Keithley electrometer. A microprocessor inside the Keithley then uses the measured current and known voltage to calculate the resistance. The sample resistances measured using this setup were in the range 10^5 to $10^{14} \Omega$. For the more insulating samples, a source voltage of 100 V was used. This was reduced to 50 V for the less resistive samples. All measurements were done with the sample placed in a shielded Faraday box to reduce external noise. The reading of each sample was recorded after 5 minutes to allow for the digital readout to stabilise. Samples on the conducting side (10^{-3} to $10^5 \Omega$) were measured using an LR400 self-balancing bridge, which was pre-calibrated using standard resistors in the appropriate ranges (0.01Ω to $100 \text{ k}\Omega$). These measurements were done in a pseudo-4-probe configuration (Fig. 3.3) with the silver paint forming the capacitor plates on the flat sides of the pellet. In the high resistance Keithley measurements, the voltage and current leads on the same face were joined to form the two-terminal (two-probe) configuration.

The measured DC resistances were divided by the appropriate geometric factors to obtain the respective DC conductivities, which were then plotted as log conductivity versus the conducting powder volume fraction (ϕ), after the latter had been corrected for porosity. These results were fitted to both the combined Percolation equations (eqns. (2.1a) and (2.1b)) or the two exponent phenomenological equation (eqn. (2.3)) to obtain the values of s , ϕ_c , t , σ_i and σ_c . The uncertainty in these parameters were given by the statistics report in the Scientist fitting program.

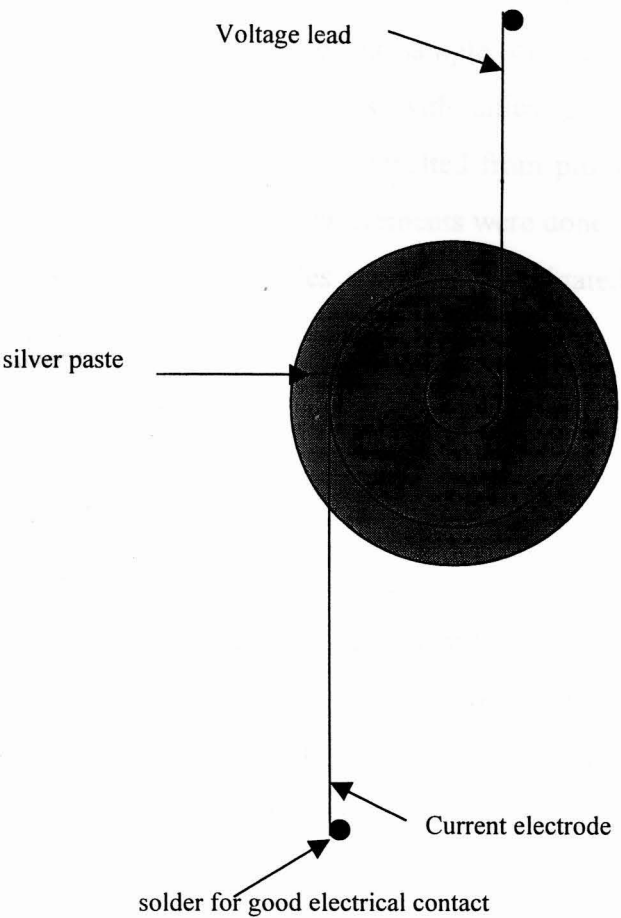


Figure 3.3: The pseudo-four-probe configuration (shown only for one face of the sample).

The first measurements of DC resistance were done within 24hrs of making the sample. No significant change in the resistance was observed at monthly intervals but all the reported results are from measurements taken at least two months after the first measurements. The two-month monitoring period was necessary in order to ensure that there were no changes in the properties of the samples due to ageing. During this period, the samples were kept in dessicators with silica gel to guard against contamination by moisture, which would have resulted from prolonged exposure to the atmosphere. Care was taken to ensure measurements were done on a relatively dry day. The electrical behaviour of the samples was also investigated as a function of frequency as described below.

3.2.2 AC measurements

Metal-insulator composites show a frequency dependent behaviour different from that characterising their components. A study of their AC conductivity determines some critical exponents (x , y), which may be related to those (s , t) determined from DC conductivity measurements. Such studies are essential in testing the various predictions of the scaling laws and other theoretical models. In order to make better measurements on the systems studied in this thesis, a wide frequency range was used than previously done in such experiments. Two separate instruments were used, one for the low frequency (10^{-2} Hz to 10^7 Hz) and the other for the high frequency (10^6 Hz to 10^9 Hz) regime. Note that there is no single instrument capable of doing the measurements equally well over this entire frequency range.

3.2.2.1 Low frequency measurements

These measurements were done on a Novocontrol Broadband Dielectric Spectrometer incorporating a Solartron SI1260 Impedance Analyser and a Broadband Converter.

The whole system was interfaced to a computer running a measurement package called Windetta v.2.4. The combination of the Broadband Spectrometer and the Solartron SI1260 allowed the measurement of lower loss components (in the dielectric or insulating phase, equivalent to $10^{14}\Omega$ at 10^{-2}Hz and $10^8\Omega$ at 10^5Hz in parallel with an ideal capacitor) and has a better resolution of loss or phase angles ($\tan \delta \sim 10^{-4}$ to 10^4) than the instruments used in previous experiments. Samples were all measured in a two-probe configuration (section 3.2.1) because the Broadband converter is a two-terminal instrument. A typical excitation voltage used was 1V. Each sample was measured using frequencies ranging from 10^{-2}Hz to 10^7Hz with 6 points per decade (found to be suitable for the measurements). One of the most outstanding features of the Windetta computer program (used to obtain and process the data) is its ability to display the results of a single measurement in various forms. Examples are the real or imaginary conductivity, impedance, permittivity etc., all as a function of frequency, thus allowing the experimenter to choose the best way of presenting the data (for instance, real conductivity as a function of frequency as most often appears in the literature). Results from the Novocontrol Broadband system were found to be satisfactory only up to frequencies between 10^6 and 10^7 Hz (depending on the volume fraction of the sample), above which the inductance of the leads started affecting the measurement. Further investigation at higher frequency required a different instrument, which is described below.

3.2.2.2 High frequency measurements

The 26mm diameter samples were each cut (using a cylindrical cutter) into three 10mm diameter samples so that they could fit onto the Novocontrol sample holder, attached to the high impedance test head of the HP4291 high frequency instrument. The samples were also sanded flat to a thickness of about 2mm and a layer of silver paint applied on either face of the sample so it could lie between the top and bottom plates of the sample holder without leaving air gaps. In this system, the sample,

mounted between two gold-coated plates, forms a capacitive termination of a rigid 50- Ω coaxial cable.

Before each set of measurements, the instrument was calibrated. The calibration of the HP4291 was done via a three-point (open, short and 50- Ω) calibration technique in order to remove any phase offset due to electrical line length and to achieve the highest possible accuracy. The Novocontrol sample holder also required calibration in the short and open configurations using the previously obtained calibration data of the instrument, after which the sample to be measured could be introduced. The HP4291 measures the reflection coefficient (Γ) of the electromagnetic wave reflected from the sample after transmission down the coaxial cable. The normalised impedance (Z) of the sample is related to Γ through the relation:

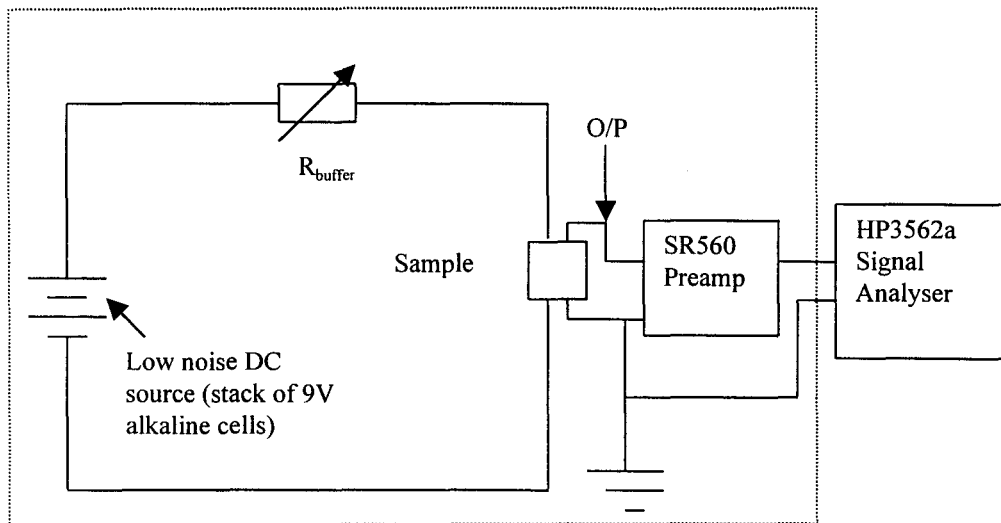
$$Z = (1+\Gamma)/(1-\Gamma)$$

The AC conductivity or permittivity was obtained from the impedance Z by using the appropriate geometric factor of each sample. Measurements were made on samples below ϕ_c , in the transition region as well as on samples just above ϕ_c , in the frequency range 10^6 Hz to 1.8×10^9 Hz at 13 points per decade. The data-collection process was made through the use of a computer package called Windetta v.3.4, which also allows the results to be plotted on the same graph as the low frequency data. In some cases, the high frequency results had to be scaled vertically onto the low frequency data (to give a continuous plot/curve) within the range 10^6 Hz- 10^7 Hz, since the frequency ranges used by the low and high frequency instruments overlapped in this range. The combined plots were used to determine the exponents x , y and q (refer to section 2.4 and Chapter five). Further probing of the systems was done independently by $1/f$ noise measurement, which, in principle, is a more structure-sensitive method.

3.2.3 1/f noise measurements

The setup used for the measurement of 1/f noise in this work is as shown in Fig. 3.4. The low noise voltage source consisted of DC 9V alkaline dry cells connected in series, to give voltage values in steps of 9V up to a maximum of 120V. A wire-wound (low noise) buffer resistor (of at least ten times the sample resistance) was put in series with the sample in order to determine and limit the current through the sample. The output voltage signal was detected by a low noise Stanford preamplifier (SR560) with input impedance of 100M Ω , and whose gain could be adjusted from 10 to 10⁴. For these measurements, the low pass filter was set at 3kHz while the high pass filter was at 0.3Hz. The preamplifier output was then fed to an HP3562a dynamic signal analyser, which measured the noise voltage and displayed the noise power spectrum as a function of frequency (1.2Hz-1001.2Hz). The measurement circuit (except the signal analyser) was placed in a closed steel box with only a tight fitting hole for the output cable to the HP3562a. This reduced the external noise to an insignificant level. The background noise was recorded at zero bias or current from the source. A background noise three orders of magnitude less than the measured sample noise was considered negligible, otherwise the background noise was subtracted from the sample noise. All measurements were done on the conducting side of the percolation threshold ($\phi > \phi_c$) where the sample resistance was within the measurable range ($\sim 10\Omega - 10^6\Omega$) of the equipment. The input impedance of the SR560 preamplifier (100M Ω) limited the highest sample resistance measurable. The uncut disc (diameter 26mm) or pellet samples were used for these measurements in a pseudo-4 probe configuration.

The noise spectrum of each sample was measured as a function of current through the sample. Care was taken to ensure that the spectrum recorded was indeed 1/f noise by noting that the slope γ (as observed on the log-log noise versus frequency on-screen display) was of the order of unity. Each plotted display was the mean of 100 averages. The maximum current through the sample, which was limited in order to avoid



O/P – output, Preamp - preamplifier

Figure 3.4: Showing the Schematic Set-up used for 1/f Noise Measurement.

heating effects, determined the maximum voltage for each sample. In practice, the maximum current (I) through a sample was determined from $I^2R \leq 10\text{mW}$, where R is the sample resistance. By measuring the DC voltage (with a digital multimeter) across the buffer resistance (whose value was known), the actual current flowing through the sample was calculated using Ohm's law. The current and known resistance of the sample were used to calculate the voltage (V) across the sample, which was in turn used to normalise the noise (S_v) to S_v/V^2 . A log-log plot of S_v/V^2 against both $(\phi - \phi_c)$ and sample resistance (R) was done for each of the systems studied to determine the exponents k and w respectively from the slope. Results are shown in Chapter six.

3.2.4 The Magnetite (Fe_3O_4)/Talc-wax system: DC and AC Scaling

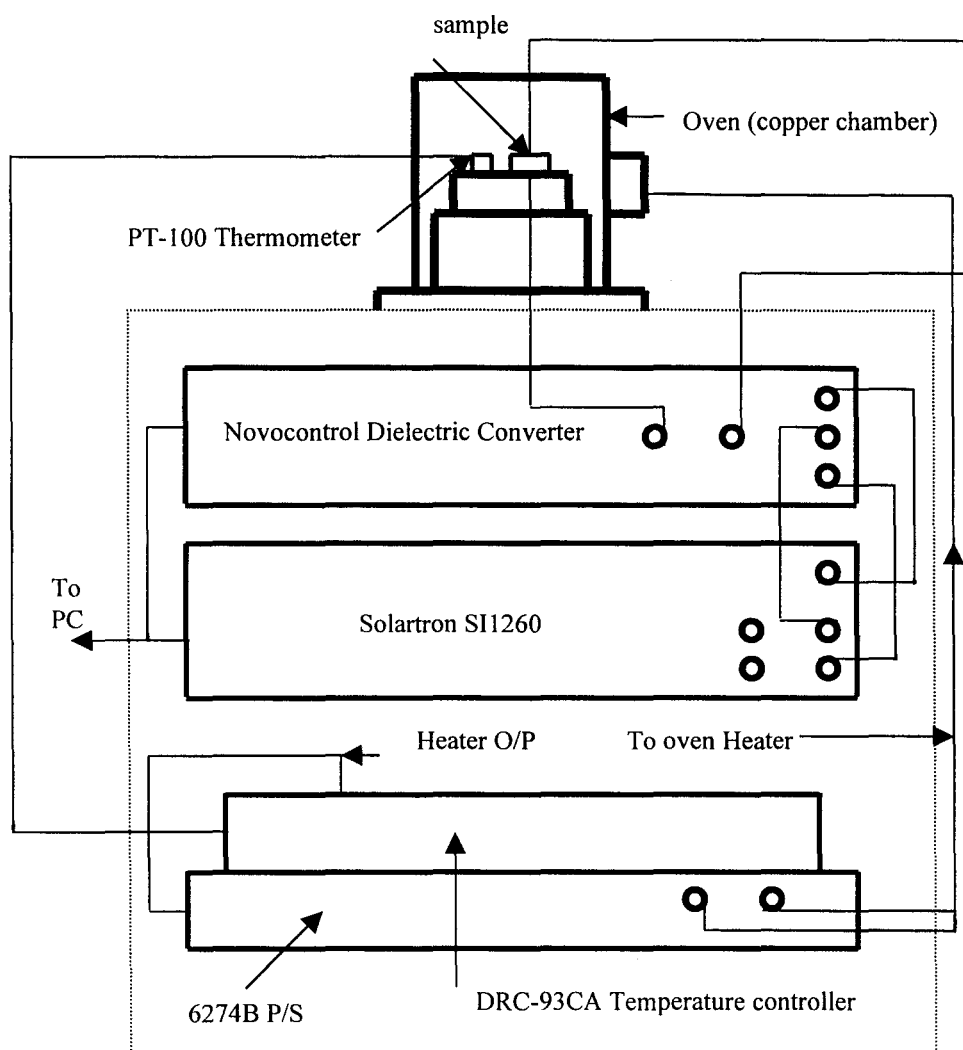
The different properties of the conducting powders used in this thesis produced composites in which some further aspects of Percolation Theory could be tested in the individual systems. One such example is the Magnetite (Fe_3O_4) system in which the scaling of the DC conductivity was investigated as a function of temperature.

The Magnetite (Fe_3O_4) system had some special properties. For instance, of all the conducting powders used in this thesis, Magnetite (Fe_3O_4 , a doped semi-conducting ferromagnetic powder), had the lowest DC conductivity at room temperature ($\sim 2.6303 \times 10^{-3} (\Omega\text{cm})^{-1}$ obtained experimentally), which could be increased by increasing the temperature. According to scaling theory (section 2.1.3), the conductivity results at different temperatures can be superimposed on a single curve using the appropriate scaling functions as given in section 2.1.3. The scaled results at different temperatures for the Fe_3O_4 system are shown in Chapter four. In addition, the low conductivity of Fe_3O_4 at room temperature meant the real part of the dielectric constant (ϵ_{mr}) of the resulting composite could be measured over a wider $(\phi - \phi_c)$ than

the other (higher conductivity) systems, as confirmed by the results shown in section 4.1.4. Attempts to measure the dielectric constant above ϕ_c , in the higher conductivity systems (for instance Graphite and Nickel systems) failed because of limitations in the instrumentation. The Fe_3O_4 powder was also magnetic such that the magnetic properties could be studied as a function of volume fraction of Fe_3O_4 in the same samples used for conductivity measurements.

3.2.4.1 AC and DC measurements as a function of temperature in the Fe_3O_4 system

AC and DC measurements were done on the samples (which had been annealed at 140°C overnight) from room temperature (25°C) to 120°C . A schematic layout of the apparatus used in the measurements is shown in Fig. 3.5. The HP6274B power supply provided power to a 120W heater attached to the wall of the copper chamber (oven). The oven temperature was regulated by the Lakeshore DRC-93CA temperature controller and a PT-100 Platinum resistance thermometer with air as a heat exchange medium. The offset of the Lakeshore controlled the output of the HP6274B power supply. The temperature sensor was placed on the sample stage (a teflon plate strategically located in the middle of the copper chamber) so that it could monitor the sample temperature with reasonable accuracy. Two samples were placed on the teflon stage and measured both on the Keithley 617 electrometer (DC resistance) and Broadband dielectric spectrometer (for AC measurements). All measurements were done at five set temperatures (25, 60, 80, 100 and 120°C) with at least 45 minutes stabilisation time being allowed at each temperature point. The results obtained were tested for DC and AC scaling as well as plotting them so as to obtain the low frequency dielectric exponent s' .



O/P- output, P/S-power supply, PC-personal computer

Figure 3.5: The Schematic setup used to study the temperature-dependence of conductivity and dielectric constant in the Magnetite (Fe_3O_4) system.

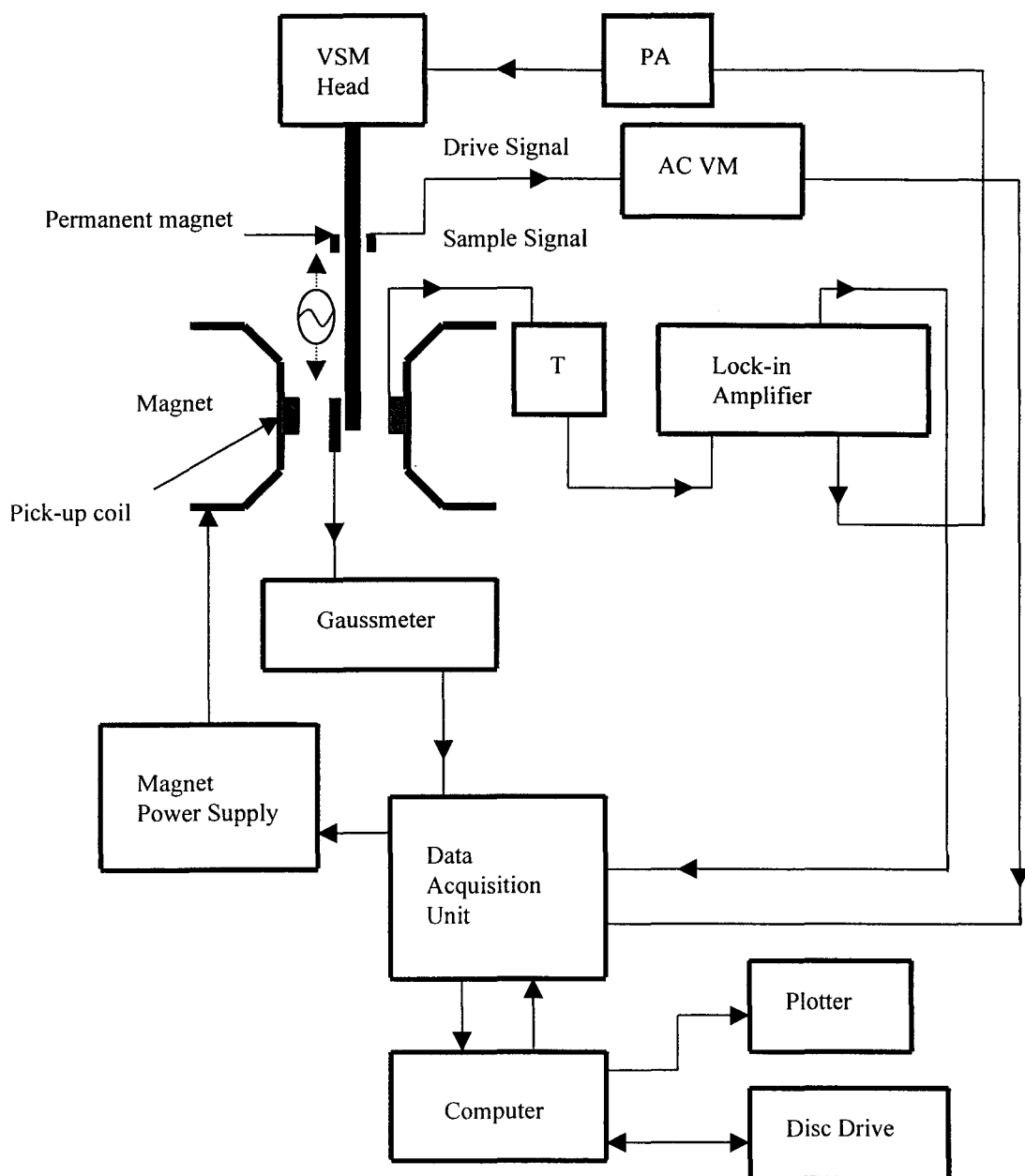
3.2.5 Magnetic measurements

Since the Fe_3O_4 system was also magnetic, its magnetic properties were studied as a function of volume fraction of the magnetic component. These measurements were done at room temperature using existing and some equipment especially made in our laboratory. The magnetic measurements were done in order to investigate the possibility of a correlation between the electrical and magnetic percolation properties of the system. Both DC and low frequency AC measurements were done on the Magnetite (Fe_3O_4) system and the other magnetic system: Nickel-Talc-wax.

3.2.5.1 DC Magnetometer measurements

The DC magnetic measurements were done on a vibrating sample magnetometer (refer to Fig. 3.6 for the block diagram) with the field perpendicular to the flat faces of the discs (axial direction). Measurements were carried out on the samples after they had been stripped of the silver paint electrodes (necessary for the DC and low frequency electrical measurements previously made) by means of amyl acetate solvent. It was verified that the amyl acetate did not affect any other component of the sample except the silver paste. During the measurement, the sample was vibrated in the transverse direction as the field was increased slowly from zero to a maximum value of 6000 gauss. At this point adjustments were made to the sensitivity of the lock-in amplifier, in order to optimise the size of the trace of the hysteresis loop, appearing on the screen due to a particular sample.

Before each set of measurements, the system was calibrated against a standard sample (the most concentrated Nickel sample ($\phi = 0.15$) in this work), from which the calibration constant of the vibrating sample magnetometer was obtained, after which the sample to be measured was introduced. Therefore all measurements were then



VM - voltmeter, VSM - vibrating sample magnetometer, Osc. O/P-Oscillator output,
 ■ - Pickup coils , T-low-noise transformer, PA- power amplifier

Figure 3.6: Block Diagram of the Vibrating Sample Magnetometer.

done relative to the Nickel standard sample. The samples previously used in the DC percolation experiments were measured in order to investigate if a relationship existed between the electrical behaviour and the magnetic properties (especially in the crossover region). The quantities obtained from the hysteresis loop of each sample included the coercive field (H_c) and the remnant magnetisation (M_r). These magnetic properties were plotted as a function of the volume fraction of the magnetic component and the results are given in Chapter seven.

3.2.5.2 AC Susceptibility measurements

The apparatus (hereafter referred to as the susceptometer) used for the measurement of the AC susceptibility is shown in the diagram (Fig. 3.7). The primary coil consisted of two large coils, each of 500 turns arranged in a Helmholtz configuration on the wooden stand. In the region between these coils is a small open pipe of fractionally larger internal diameter than the samples, through which the sample under test passes. Two pickup coils (each of 108 turns) were wound on the outside of the pipe in an anti-Helmholtz configuration in order to detect the sample signal using an SR5208 lock-in amplifier.

Current was supplied to the Helmholtz coils from the internal oscillator of an SR5206 lock-in amplifier through a power amplifier at a frequency of 32.10 Hz to produce a root mean square (rms) field of about one gauss. The amplitude and phase of the current was measured across the 10Ω resistor. This signal was also fed to the reference inputs of the other two lock-in amplifiers. The amplitude of the current was kept constant (to within 1%) by means of a potentiometer on the power amplifier. The phase angle of the SR5208 was always adjusted to be the same as that of the SR530.

The magnetic sample was moved slowly through the pipe using a motor with a speed of 1 revolution per minute. A signal proportional to the magnetic moment of the

sample, was produced in the pick-up coils and was recorded on the Y-axis of two Y-T recorders (one for the real and the other for the imaginary component of the signal) connected to the output lock-in amplifier. The sample signal was in the form of a sine wave and the peak-to-peak amplitude (in mV) on the recorder was taken to be proportional to the magnetic moment of the sample.

To calibrate the susceptometer, a sample of known susceptibility was required. However, as standard samples with the appropriate geometry were difficult to find, the standards were made as follows. The raw or 'pure' Magnetite and Nickel powders were packed into non-magnetic containers, whose dimensions were close to those of the samples used in the measurement, in order that corrections for the demagnetisation constant of the samples were not necessary. To determine μ (χ) small thin pipes (with diameters ten times less than their length) made of paper and 100 turns of copper wire wound in the middle of the pipes, were used to obtain the permeability of the Nickel and Magnetite powders (previously used in making the pellets of the composite systems). The inductance of the pipes was measured (when empty (L_e) and when filled (L_f) with the powders). An AC bridge operated at the same frequency used in the susceptometer (32.10 Hz) was used for the inductance measurement. The permeability of each powder was then calculated from $\mu = L_f/L_e$ at 25% packing factor (arrived at by natural packing of the powders in paper tubes and measuring the apparent density, as opposed to bulk packing $\sim 60\%$). As pointed out earlier, powders with the same packing fraction (25%) were put in paper cups in the form of 26mm diameter and 3mm thick (the same geometry as the samples). The respective peak-to-peak signals were determined on the susceptometer. Using the appropriate equations and the permeability/susceptibility previously measured, this signal was used to find the calibration constant of the system of coils, which was in turn used as a standard for the measurements of the actual samples. The permeability (μ_{mr}) and susceptibility (χ_{mr}) of the samples were determined and these were plotted against the volume fraction of the respective magnetic components. The results are given in Chapter seven.

CHAPTER FOUR

THE DC ELECTRICAL CONDUCTIVITY AND THE LOW FREQUENCY DIELECTRIC CONSTANT

4.0 Introduction

The electrical conductivity and the dielectric constant are the most extensively measured properties of percolation systems. The electrical conductivity and dielectric constant of conductor-insulator composites generally obey the power laws given in section 2.1.2. The DC electrical conductivity of a conductor-insulator composite also goes through a transition from insulating to the conducting region via a crossover region in which the conductivity changes by several orders of magnitude for very small changes in conductor volume fraction. The width of the crossover region depends on the ratio σ_i/σ_c (where σ_c and σ_i are the conductivity of the conducting and insulating components respectively). A small σ_i/σ_c ratio ($<10^{-12}$) results in a very narrow crossover region, which may never be observed experimentally. This chapter gives the DC electrical properties of composites in which the ratio of the conductivities of the components varies from 4.35×10^{-18} to 3.3×10^{-13} at room temperature. The crossover regions for all the systems (except the Fe_3O_4 system and to some extent the NbC system) are too small for samples to be made or found in this region. The relatively large σ_i/σ_c ratio in the Fe_3O_4 system lead to clearly observable but unexpected results for the dielectric constant (ϵ_{mr}) versus volume fraction (ϕ), which will be presented later in this chapter.

The DC conductivity of the composites ($\sigma_m(\phi, 0)$) is fitted using either the combined percolation or the two exponent phenomenological equations (given in chapter two). The fits are equally good and usually give well defined values of ϕ_c , t and s , together with an estimate of the conductivity of the conducting component, σ_c (see Table 4.1). The conductivity of the insulator (σ_i) can usually be measured directly from the $\phi = 0.00$ sample. The critical volume fraction (ϕ_c) values are discussed mainly in terms of the Kusy model (1977). The results for s and t obtained are tested against the predictions of the Random Void or Swiss Cheese model (including the new limits given by Balberg (1998a and 1998b)) and are also compared to previous experimental results. Differences observed between the DC exponent s and s' (the later obtained from low frequency dielectric measurements) confirm that the two exponents are not the same. The variation of the real dielectric constant with volume fraction of the conducting component has been examined. The results of such measurements are found to be in disagreement with original Percolation Theory, which predicts a peak in the dielectric constant at ϕ_c . The two-exponent, three-structure parameter phenomenological equation (eqn. (2.3)) has been shown to qualitatively fit the dielectric constant behaviour as a function of ϕ (McLachlan *et al.* 1998). Even better fits are obtained (Heiss *et al.* 2000) when the equation is used in conjunction with ideas from the new Balberg model for non-universal percolation exponents (Balberg 1998a and 1998b). In one system, with Fe_3O_4 as the conducting component, the DC conductivity has been shown to fit on a scaling curve when the conductivity ratio (σ_i/σ_c) is varied by changing the temperature. The exponent t in the Fe_3O_4 system has been observed to decrease slightly with the ratio σ_i/σ_c , in agreement with previous studies (Lin 1991). As the changes in t with temperature were not very large, the conductivity results for the Fe_3O_4 system, at different temperatures, could still be scaled onto nearly the same theoretical curves. The results are also found to scale even in the region (the curved region in Fig. 4.11) where the original Percolation Theory makes no predictions, indicating the powerful scaling properties incorporated in the two exponent phenomenological equation.

4.1 DC Conductivity Results

The DC conductivity ($\sigma_m(\phi,0)$) behaviour of percolation systems is best illustrated by a plot of the log of conductivity against the volume fraction of the conducting component, to give the typical open-S-curve (called the ‘sigmoid’ curve by some authors). Figures 4.1 - 4.3 show plots for the Graphite, Niobium Carbide and raw Carbon Black systems respectively. Similar plots were done for the other systems and fits to the two exponent phenomenological equation gave the parameters ϕ_c , t and s , shown in Table 4.1 for all the seven cellular systems that were studied. Results obtained through fitting the DC conductivity results to the combined percolation equations agree with the results given in Table 4.1 to well within the experimental error. Also shown in Table 4.1 is the exponent s from dielectric measurements (denoted as s' throughout the thesis) at 1000Hz. Note that the results at 1000Hz are given, as this is the typical frequency used in previous dielectric measurements in the literature. Fitting the results to either the combined percolation or two exponent phenomenological equations gave nearly the same parameters because the ratio of conductivity of the components is high and there are few (if any) data points in the crossover region. Measurements of the DC resistance of the samples were repeated over a period of at least six months and no changes in conductivity or the parameters (ϕ_c , t and s) were observed.

Some parameters obtained from the fitted results of the conductivity show a common trend for all the systems. The extrapolated conductivity (σ_{cf}) of the conducting components obtained from the fit is always found to be lower than the corresponding bulk conductivity (obtained from various sources in the literature) for the particular conducting component. This suggests that inter-particle contacts play a prominent role in determining the conducting/resistive properties of the composites, even at the highest volume fractions (≈ 0.25) of the conducting components, used in this work. If it were not for the inter-particle contact resistance, one would expect that the extrapolated conductivity (σ_{cf}) would be close to the bulk conductivity (σ_{cb}). It should be noted that the Carbon Black used in the present study is the same as that used by

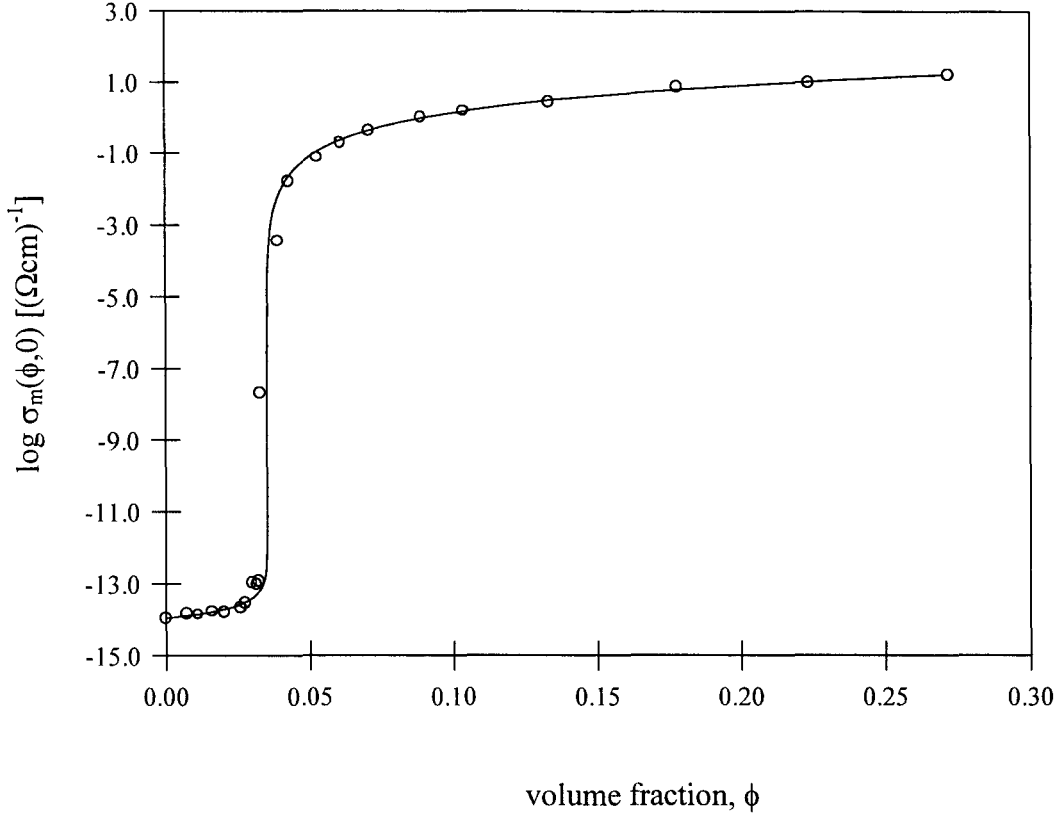


Figure 4.1: Plot of the log of DC conductivity ($\sigma_m(\phi, 0)$) results versus the volume fraction (ϕ) of Graphite for the Graphite system. The solid line is a fit to eqn. (2.3) and the fitting parameters are; $\phi_c = 0.035 \pm 0.002$, $t = 1.93 \pm 0.06$, $s = 0.66 \pm 0.15$, $\sigma_c = 251(\Omega\text{cm})^{-1}$ and $\sigma_i = 1.096 \times 10^{-14} (\Omega\text{cm})^{-1}$.

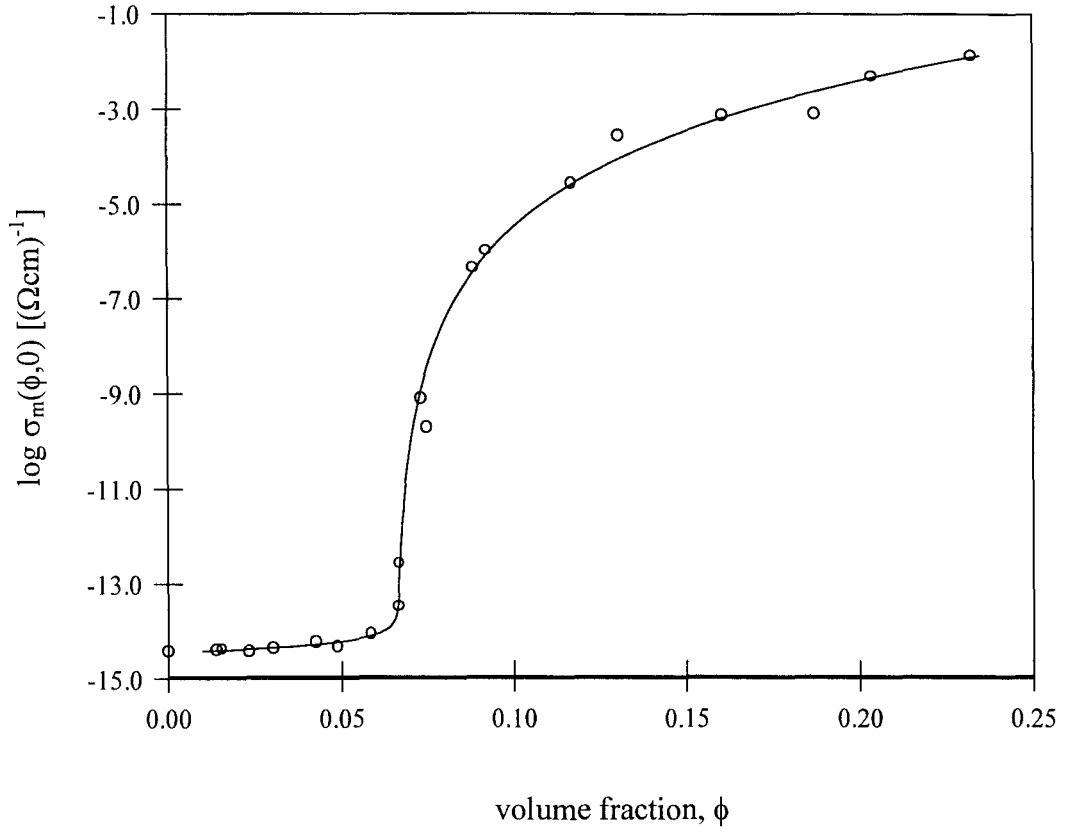


Figure 4.2: Plot of log DC conductivity ($\sigma_m(\phi,0)$) as a function of the volume fraction (ϕ) of Niobium Carbide for the Niobium Carbide system. The solid line is a fit to eqn. (2.3) and the fitting parameters are; $\phi_c = 0.065 \pm 0.006$, $t = 5.25 \pm 0.67$, $s = 0.37 \pm 0.14$, $\sigma_c = 107.2(\Omega\text{cm})^{-1}$ and $\sigma_i = 3.5481 \times 10^{-15} (\Omega\text{cm})^{-1}$.

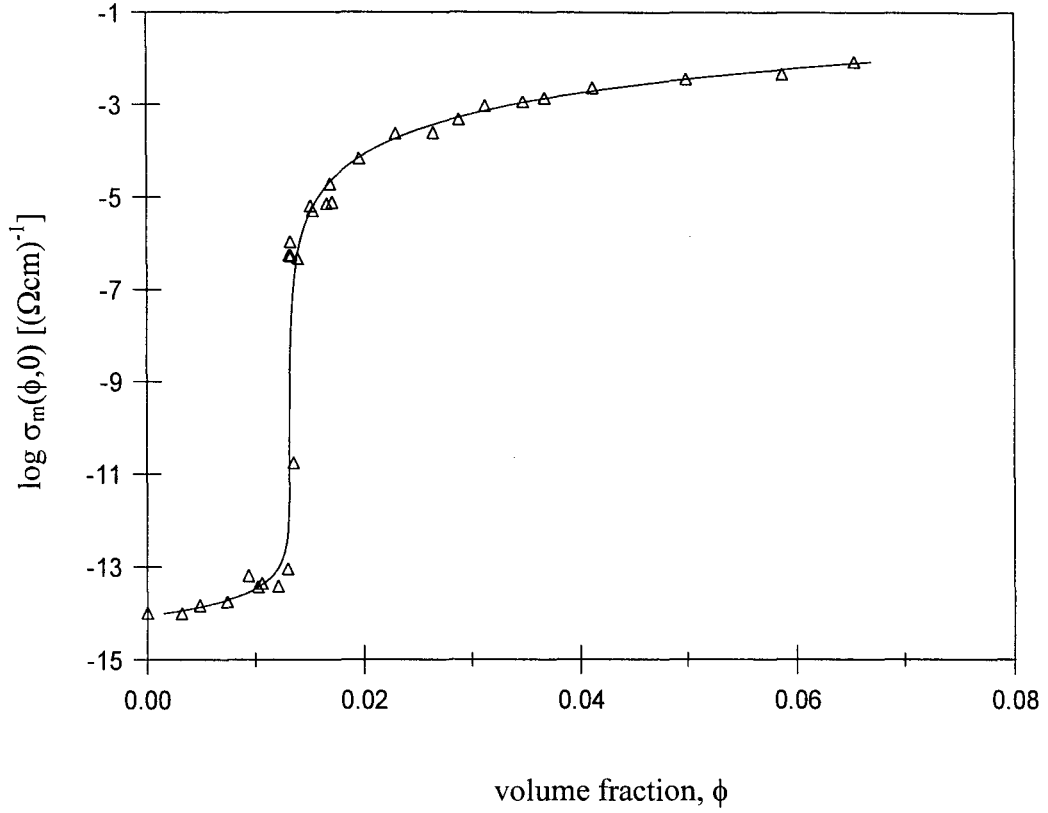


Figure 4.3: Plot of log DC conductivity ($\sigma_m(\phi,0)$) results as a function of the volume fraction (ϕ) of Carbon Black for the raw Carbon black system. The solid line is a fit to eqn. (2.3) and parameters obtained from the fit are; $\phi_c = 0.0131 \pm 0.0006$, $t = 2.26 \pm 0.11$, $s = 0.90 \pm 0.20$, $\sigma_c = 6.166 (\Omega\text{cm})^{-1}$ and $\sigma_i = 9.1201 \times 10^{-15} (\Omega\text{cm})^{-1}$.

Table 4.1: DC Percolation Parameters

Composite System	ϕ_c	t	s	s' (1kHz)
Ground Carbon Black	0.0122 ± 0.0007	2.06 ± 0.10	1.06 ± 0.26	0.36 ± 0.04
Raw Carbon Black	0.0131 ± 0.0006	2.26 ± 0.11	0.90 ± 0.20	0.43 ± 0.03
Ground Graphite	0.035 ± 0.002	1.93 ± 0.06	0.66 ± 0.15	0.50 ± 0.02
Graphite-BN(15%)	0.033 ± 0.001	2.51 ± 0.12	1.28 ± 0.19	0.55 ± 0.04
Nickel	0.025 ± 0.003	1.52 ± 0.15	1.11 ± 0.60	0.38 ± 0.02
Magnetite	0.025 ± 0.003	4.12 ± 0.23	0.45 ± 0.31	0.10 ± 0.01
Niobium Carbide	0.065 ± 0.006	5.25 ± 0.67	0.37 ± 0.14	0.21 ± 0.01
*Graphite-BN coating	0.227 ± 0.009	2.67 ± 0.15	1.25 ± 0.20	

Composite System	$\sigma_{cb}(\Omega\text{cm})^{-1}$	$\sigma_{cf}(\Omega\text{cm})^{-1}$	σ_{cf}/σ_{cb}
Ground Carbon Black	1.00×10^2	3.80×10^0	3.80×10^{-2}
Raw Carbon Black	1.00×10^2	6.17×10^0	6.20×10^{-2}
Ground Graphite	$*(9.0 \pm 0.9) \times 10^1$	2.51×10^2	2.79×10^0
Graphite-BN(15%)	$*(9.0 \pm 0.9) \times 10^1$	9.12×10^2	1.01×10^1
Nickel	1.39×10^5	1.41×10^2	1.01×10^{-3}
Magnetite	4.00×10^{-3}	2.63×10^{-3}	6.58×10^{-1}
Niobium Carbide	3.33×10^4	1.07×10^2	3.21×10^{-3}
**Graphite-BN coating	$*(9.0 \pm 0.9) \times 10^1$	4.40×10^1	4.90×10^{-1}

Note σ_{cb} and σ_{cf} are defined in the text

*The value of σ_{cb} quoted for the Graphite powder was obtained from an article by Dupreez and McLachlan (1988). The value was extrapolated from their data using a single exponent GEM equation (McLachlan 1987). Dupreez and McLachlan also obtained $(1.13 \pm 0.11) \times 10^3(\Omega\text{cm})^{-1}$ in the transverse direction for the same Graphite powder.

**The Graphite-Boron Nitride coating, found to be an independent percolation system, is discussed later in section 4.1.2

Heaney (1995) in his study of Carbon Black-polymer composites. From fittings of his experimental data, Heaney obtained a σ_c for Carbon Black of $66.7 (\Omega\text{cm})^{-1}$, which is closer to the bulk value of $100 (\Omega\text{cm})^{-1}$ quoted in his paper. Note that Heaney's fitted value is an order of magnitude higher than the values obtained in the present study (Table 4.1). Heaney's value can be considered to be a better estimate because he used higher volume fractions of the Carbon Black. Note also the difference in the fitted values of σ_c for the ground and raw Carbon Black systems, which seems to imply that the inter-particle contacts may also be dependent on the shape or angularity of the particles. It is assumed that grinding may have lessened the sharpness of the edges or angularity of the Carbon Black particles in the ground Carbon Black system. Note that the s and t exponents for the two Carbon Black systems are also different. The low t Nickel system and the high t systems with Niobium Carbide show the largest discrepancies between the extrapolated conductivity and the bulk value (i.e. $\sigma_{cf} \ll \sigma_{cb}$). Note that for the Nickel system, there may be an oxide layer on the surfaces of the Nickel particles, which reduces the conductivity.

The discrepancy between the extrapolated σ_c and the bulk value of the conducting component is further illustrated by the difference in the extrapolated σ_c values in three Graphite-containing systems. In the compacted Graphite-Boron Nitride system, Wu (Wu 1997, Wu and McLachlan 1997) found σ_{cf} to be $77.62(\Omega\text{cm})^{-1}$ which is lower than $912.01(\Omega\text{cm})^{-1}$ for the three-component (Graphite, Boron Nitride and Talc-wax) and $251.00(\Omega\text{cm})^{-1}$ for the Graphite-Talc-wax systems studied in this thesis. Unfortunately, there is no σ_{cf} value available for the Graphite-Boron Nitride powder systems studied by Wu for comparison to be made with the compacted system. In addition the Graphite-Boron Nitride coating, which can be taken as an independent percolation system, extrapolates to a mere $44.3(\Omega\text{cm})^{-1}$. The difference observed in the extrapolated σ_c from these systems seems to indicate that the insulating matrix (which affects the distribution of the conducting bonds within the composite) also affects the extrapolated value of σ_c or σ_{cf} . Furthermore, the lower volume fractions of Graphite used in the three-component system might also have contributed to the

discrepancy, considering that the measurements of σ_m should be done to $\phi = 1$ or 100% packing in order to get a reliable value of σ_c .

4.1.1 The Critical Volume Fraction

The values of the percolation threshold or critical volume fraction, ϕ_c obtained for all the systems studied are well under 10% as shown in table 4.1. The two Carbon Black systems are essentially similar as they show a small difference in the ϕ_c values, which overlap within the error bars. The small difference however, can be interpreted as due to the decrease in the Carbon Black mean particle size in the ground system due to grinding in a planetary mill. The ϕ_c of the ground system is found to be smaller than that obtained in the raw Carbon Black system, which agrees with the Kusy model (see Fig. 4.4 below). The Graphite and Graphite mixed with Boron Nitride (15%) systems also show the same critical volume fraction (within the error limits), which is quite interesting as the latter is essentially a three-component system. Particle size analysis of the systems done on the Malvern analyser (Table 3.1) show the mean diameter of the particles of the Graphite and Graphite-Boron Nitride powders differ by a factor of two. The Fe_3O_4 and Nickel systems have the same ϕ_c , perhaps because the mean particle sizes are fairly close. Surprisingly, the NbC system gives the largest value of ϕ_c , despite the NbC powder having the smallest mean particle size.

Recall that the various mechanisms influencing the critical volume fraction (ϕ_c) are now reasonably understood (see for example McLachlan 1990 and 1996, McLachlan *et al.* 1993, Wu and McLachlan 1997, Wu 1997 and references therein). These include the relative sizes (Malliaris and Turner 1971, Kusy 1977) and shape of the component particles (Balberg 1984, Carmona *et al.* 1984, Dupreez and McLachlan 1988, Celzard *et al.* 1996). While all these mechanisms may contribute to ϕ_c in composite systems studied in this thesis, it appears that the relative size of the two components has the largest effect on the percolation threshold. This difference in the size of the particles

leads to low ϕ_c 's according to the Kusy model (1977). The small conductor particles are embedded on the surface of the large insulating Talc-wax particles (which can be regarded as voids similar to those in the Random Void model, where uniformly sized spherical holes are placed at random in a uniform transport medium: refer to section 2.1.4 in this thesis).

Figure 4.4 shows the predicted and experimental ϕ_c values superimposed on the Kusy theoretical curve. The predicted values were obtained from the measured values of the mean size of the particles for each powder using the Malvern results. However there are two ways of describing mean particle sizes obtained from the particle size analysis; the **mean** diameter and the **sauter** diameter. The sauter diameter is obtained by considering the surface area covered by the particle while the mean diameter is calculated from the equivalent spherical volume of the particle. The theoretical points shown in Fig. 4.4 were obtained by finding the ratio of insulator (taken to be $300\mu\text{m}$) to conductor diameter for each system, leading to two 'theoretical' points (one corresponding to the sauter and the other to the mean diameter value) on the Kusy curve. The expected critical volume fraction corresponding to these points can therefore be read on the ϕ_c axis of Fig. 4.4. These results, together with the experimental value, are tabulated as shown in Table 4.2. The Fe_3O_4 system shows good agreement for all the three values of ϕ_c . In general, the mean and sauter diameter ϕ_c values are always greater than the experimentally determined critical volume fraction. The only exception is the Niobium Carbide system, where the mean diameter value is much lower than the experimental ϕ_c . The Niobium Carbide is the only system (besides the Fe_3O_4 system) in which the sauter ϕ_c value is very close to the experimental ϕ_c . The ϕ_c results of Table 4.2 illustrate how the difference in the actual shape and size distribution of the conductor particles give rise to the critical volume fraction of the systems, which differ from those predicted on the basis of spherical and mono-sized particles in the Kusy model. Note that particles used in this study which are approximately spherical show fairly close mean and sauter diameter values. A Kusy value for R_i/R_c (for each system) can be obtained by drawing a line from the

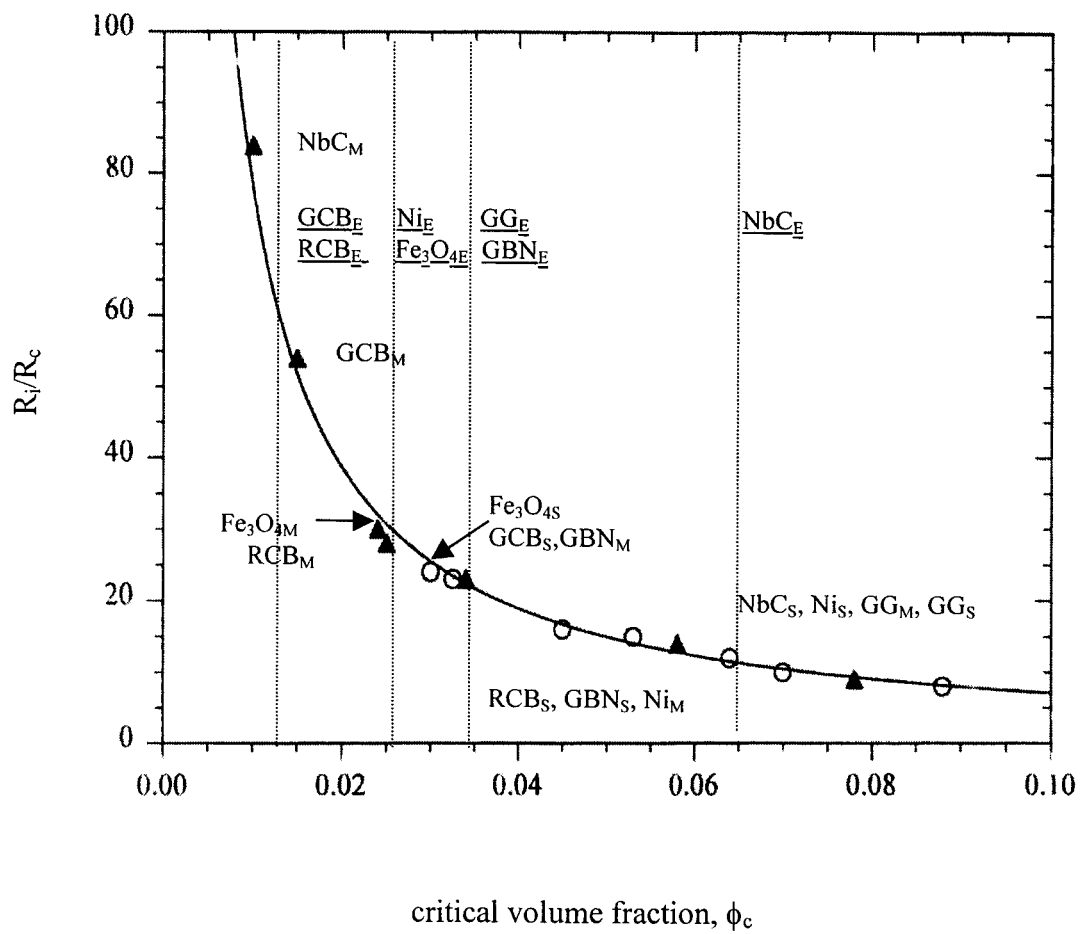


Figure 4.4: The Kusy simulation curve with the experimental results superimposed on it.

- Kusy theoretical curve ———
- Experimental (E) values (.....)
- Sauter mean diameter (S) value (O)
- Mean diameter (M) value ($\blacktriangle$)

Table 4.2: Critical volume fractions for the systems

Composite System	ϕ_{cE}	ϕ_{cM}	ϕ_{cS}
Ground Carbon Black	0.0122 ± 0.0007	0.015 ± 0.005	0.0325 ± 0.0005
Raw Carbon Black	0.0131 ± 0.0006	0.025 ± 0.005	0.0450 ± 0.0005
Ground Graphite	0.035 ± 0.002	0.078 ± 0.005	0.088 ± 0.005
Graphite-BN(15%)	0.033 ± 0.001	0.034 ± 0.005	0.053 ± 0.005
Nickel	0.025 ± 0.003	0.058 ± 0.005	0.070 ± 0.005
Magnetite	0.025 ± 0.003	0.024 ± 0.005	0.030 ± 0.005
Niobium Carbide	0.065 ± 0.006	0.010 ± 0.005	0.064 ± 0.005

ϕ_{cE} – experimental critical volume fraction

ϕ_{cM} – critical volume fraction corresponding to mean diameter

ϕ_{cS} – critical volume fraction corresponding to sauter diameter

Note: The systems all have $\phi_{cS} > \phi_{cM}$ as $R_i/R_{cM} > R_i/R_{cS}$.

point of intersection of the corresponding experimental line (dotted lines in Fig. 4.4) and the Kusy curve, to the R_i/R_c axis.

Although ϕ_c in the cellular systems is dependent on the relative size of the conductor particles to that of the insulator, a closer examination of the systems (taking the particle sizes into account), shows that there may be other factors involved in determining ϕ_c for a particular system. Take for instance the Niobium Carbide and the Graphite systems. From their mean particle sizes ($\sim 3\mu\text{m}$ for NbC and $\sim 30\mu\text{m}$ for Graphite), the Niobium Carbide should have a lower critical volume fraction than the Graphite system (according to the Kusy model) but the reverse is actually true. In fact, the Niobium Carbide-Talc-wax composite has the highest ϕ_c value of all the systems. It is suggested that the heavy, hard and angular NbC particles are knocked into the surfaces of the soft Talc-wax particles during sample preparation in a way that is likely to reduce the probability of contact among the conductor particles on the Talc-wax surface, leading to a high ϕ_c value. The irregular geometry ('high structure') of the Graphite particles, which are in the form of flakes (Fig. 3.1a), might also favour a low percolation threshold according to Balberg (1987a) as discussed in the next paragraph. The relatively light Graphite flakes are likely to coat the Talc-wax particles without penetrating their surfaces to allow for more efficient inter-particle contacts than the Niobium Carbide. As noted earlier, the Nickel and Fe_3O_4 systems have the same value of ϕ_c , but the reason for such a result is not immediately obvious.

The extremely low percolation thresholds of the ground and raw Carbon Black systems also agree well with previous studies of Carbon Black particles embedded in polymers (Brosseau *et al.* 1997, Adriaanse *et al.* 1997, Brom *et al.* 1998 and Connor *et al.* 1998). Connor and his collaborators (1998) studied the conductivity of a composite made of highly structured Carbon Black in an amorphous polymer (polyethylene terephthalate-PET) and obtained $\phi_c = 0.011$, which is in fair agreement with the critical volume fractions obtained for the Carbon Black systems in this work. The low value of ϕ_c observed in Carbon Black systems have been attributed to the formation of aggregates by the Carbon Black particles as noted by Balberg (1987a),

Heaney (1995) and Connor and his co-workers (1998). Balberg (1987a) also observed that there is a correlation between the structure of the Carbon Black particles and values of ϕ_c in Carbon Black-polymer composites. The non-spherical or high structure Carbon Black particles give lower values of ϕ_c than the low structure or close to spherical Carbon Black particles. The high structure particles have more connection points and therefore form a conducting network at a lower ϕ_c than the low structure particles. This observation is supported by the experimental results of Connor *et al.* (1998) and Rubin *et al.* (1999).

A number of previous experiments (Pike 1978, Kusy 1997 and references therein) support the dependence of ϕ_c on the relative size of the constituent particles of the composite. Studies done on RuO₂ – glass composites show ϕ_c values in the range 0.02 – 0.04 (Kusy 1997) depending on the relative sizes of the RuO₂ and glass particles. It was noted that increasing the ratio of the glass to RuO₂ radius reduced the critical volume fraction appreciably. In systems where the conductor and insulator particles are nearly equal in size, a critical volume fraction close to the random distribution value of 0.16 has been observed. A good example is the compacted Graphite-Boron Nitride system of Wu and McLachlan (1997), where $\phi_c \cong 0.150 \pm 0.001$.

4.1.2 The Percolation Exponents

The s and t exponents given in Table 4.1 were obtained from fitting the DC conductivity results to the two exponent phenomenological equation (eqn. (2.3)). As previously noted, fitting the same conductivity results to the combined percolation equations gave similar results well within the experimental uncertainty. These exponents show quite a range of values falling within, below and above the universally accepted values of s and t , taken as 0.87 and 2.00 respectively for 3D percolation systems (Bergman and Stroud 1992, Nan 1993, Stauffer and Aharony 1994).

Four classes of the exponent t can be identified from the results of Table 4.1. The first category consists of the Nickel system with a t exponent well below the universal value. Unfortunately, there is no explanation or model to account for such a low t value. The only data the author is aware of in the literature, with a t exponent close to the Nickel system, is that of Blaszkiewicz *et al.* (1991). Blaszkiewicz and his co-workers used the single exponent ($s = t$) general effective media equation (McLachlan 1987, McLachlan *et al.* 1990) to obtain $t \sim 1.5 - 1.7$ in a Fe_3O_4 -epoxy system.

The second class of t exponents include the Graphite and Carbon Black systems, which give t values very close to the universal value of 2.00. Kogut and Straley (1979) noted that in systems with a narrow range of conductance, a universal t exponent would be observed. It is not clear at this stage what gives rise to the narrow conductance range, which leads to a universal t exponent in the Graphite and Carbon Black systems studied in this thesis. Lee *et al.* (1986) showed experimentally that universality can be obtained in an inverted Random Void (IRV) or inverted Swiss Cheese system, where large conducting spheres are randomly placed in a uniform conducting medium to give a narrow range of conductance distribution. In Lee *et al.*'s IRV model experimental system, Teflon powder of $1\mu\text{m}$ mean diameter was used as the insulator while the conductor was Ag-coated glass spheres with a $10\mu\text{m}$ mean diameter. No overlapping of the spheres was possible as the contacts between them were made without any deformation. The resulting composite had a ϕ_c of 0.170 ± 0.002 and $t = 2.0 \pm 0.2$. The latter is in excellent agreement with the universal t -value. Cellular systems studied in this work in some way resembles the Swiss Cheese or Random Void (RV) model (Halperin *et al.* 1985, Lee *et al.* 1986, Feng *et al.* 1987), in which large and uniform spherical insulating holes or voids are randomly distributed in a uniform conducting medium. A major difference is that in the cellular systems, the small conductor particles, coating the "voids" or large Talc-wax particles, give rise to a complex structure of different links, nodes and blobs, leading to a wide range of conductance distributions. It therefore follows that the close to universal t exponents observed in the three systems with Carbon Black and Graphite powders is

due to a small range of inter-granular (cluster) resistance values, which may be a result of ‘good’ contacts between the conductor particles.

Dupreez and McLachlan (1988) obtained various values of the t exponent in the axial and transverse directions in powder compression experiments involving different forms of Graphite. In these experiments, values of t ranged from 1.5-2.9. These results were in general attributed to anisotropic conductivity and the different shapes of the conductor particles. The t exponents measured in the Nickel, Graphite and Carbon Black systems studied in this thesis lie within the range of t values obtained by Dupreez and McLachlan. In particular, values of the exponent t close to the universal value were obtained in systems consisting of natural flaky Graphite ($t_{ax} = 1.94 \pm 0.05$) and synthetic Graphite powder ($t_{trans} = 2.1 \pm 0.2$). The natural flaky Graphite used by Dupreez and McLachlan (1988) is the same as that used in the present study, therefore it is interesting to note the similarity in the values of t , namely $t_{ax} = 1.94 \pm 0.05$ (Dupreez and McLachlan 1988) and $t_{ax} = 1.93 \pm 0.06$ (Chiteme and McLachlan 2000). This could highlight the role played by the Graphite-Graphite contacts in determining the t exponent.

In other studies, Chen and Chou (1985) obtained $t = 2.3 \pm 0.4$ in a Carbon-wax mixture while Chen and Johnson (1991) reported a value of $t = 2.2 \pm 0.1$ in nodular Nickel in polypropylene. Other instances of t values in the narrow range of 2.0 – 2.3, obtained in related studies involving Carbon Black, are given by Connor *et al.* (1998 and references cited therein). Balberg (1987a) argues that there is a correlation between the structure of the conducting particles, the critical volume fraction (ϕ_c) and the DC conductivity exponent t . Experiments done using Carbon Black of different structure support this argument. According to Balberg, the more irregular the shape of the particles (sometimes called aggregates), the higher the structure. The more “spherical” particles therefore have a lower structure. Balberg (1987a) obtained $t = 2.0$ (with $\phi_c = 0.092$) using a high structure Ketjen Carbon Black, and a higher $t = 2.8 \pm 0.2$ ($\phi_c = 0.104 \pm 0.001$) using Cabot Black (with lower structure particles) in a common polymer matrix. In addition, Rubin *et al.* (1999) used a low-structure Carbon

Black in a polymeric matrix to obtain $t = 6.4 \pm 0.7$ and high ϕ_c of 0.39 ± 0.02 . Based on the above experiments, it may be concluded that the higher the structure of the Carbon Black, the lower the percolation threshold and the closer t is to t_{un} . Conversely, the low structure Carbon Blacks would give a higher ϕ_c and values of t higher than t_{un} (Balberg 1987a, Rubin *et al.* 1999). In a high-structure Carbon Black–polyethylene-terephthalate (PET) composite studied by Connor *et al.* (1998), a t value of 2.17 and a ϕ_c of 0.011 were obtained, these values being very close to those measured in the current two Carbon Black systems ($t = 2.06 \pm 0.10$ and $\phi_c = 0.0122 \pm 0.0007$, $t = 2.26 \pm 0.11$ and $\phi_c = 0.0131 \pm 0.006$ respectively). Hence the Carbon Black systems studied in this thesis appear to obey the powder structure related ϕ_c – t correlation suggested by Balberg and Rubin *et al.*. Unfortunately, there are very few systems in the literature that support Balberg’s ideas on structure– ϕ_c – t correlation. The Carbon Black powder used in the present study, while not exactly spherical, is only lightly irregular and therefore probably does have a high structure (Fig. 3.1b). The difference in structure between the raw and ground Carbon Black systems cannot be observed on the electron micrographs but seems to manifest itself through the ϕ_c and t exponents, which are close to those measured in systems with high structure Carbon Black (e.g. Connor *et al.* 1998).

The third class of exponent t only consists of the Graphite-Boron Nitride-Talc-wax (also referred to as the three-component system) with $t \sim 2.5$. In this system, the combined volume fraction of the Graphite and Boron Nitride was kept fixed at 0.15, leading to a different mode of distribution of the Graphite particles (or a wider conductance distribution). The t exponent observed in the three-component system agrees well with the predictions of the original Random Void model (Halperin *et al.* 1985, Feng *et al.* 1987) or the $\omega' = 0$ case in the new Balberg model (section 2.1.4). Note that the ω' values calculated from the experimental t values using the Balberg formula (eqn. (2.10)), as shown in Table 6.6, are generally very small, especially for the Graphite-Boron Nitride system. This appears to indicate that the random void model may be used to explain the t exponent in the three-component percolation system. However, this is complicated by the fact that the ‘necks’ in the three-

component system are made up of an independent percolation system consisting of Graphite and Boron Nitride powders, making them far more complex than the ‘simple necks’ of the random void system.

Heaney (1995) measured $t = 2.9 \pm 0.1$ in a Carbon Black-polymer composite, a result which he attributed to mean field theory (which gives $t = 3$). Heaney argues that the $t \neq 2$ observed in some conductor-insulator systems occurs because the scaling regime width is narrow and only the mean field regime is probed.

As previously noted (section 2.1.4), the random void system gives a range of narrow necks (refer to Fig. 2.3) joining the larger regions of conducting material. The necks have different lengths and widths, which lead to a large range of intergranular conductances making up the conducting backbone (see Fig. 2.5). Such a system will have a wide distribution of conductance as a result of the different neck geometry. Halperin *et al.* (1985) showed that continuum systems with such a distribution of conductance might give non-universal values ($t > 2.00$) of the percolation exponents. The random void model was investigated experimentally by Lee *et al.* (1986) in a system consisting of Indium-glass composite (insulating spheres randomly placed in a uniform transport medium-RV). The insulating, $30\mu\text{m}$ diameter glass spheres were mixed with $20\mu\text{m}$ (mean diameter) conducting indium particles. The soft indium particles flowed to fill the gaps between the glass particles to create a range of size of conducting necks leading to a wide distribution of conductance. In this system, a pressure-dependent ϕ_c was observed to be in the range $0.04 - 0.10$, with the t exponent remaining unchanged at 3.1. This experiment helped to confirm that t was not necessarily universal in 3D continuum percolation systems. As indicated earlier, their inverted random void system gave a universal t value.

Values close to the t exponent measured in the three-component system were also reported in compacted disc samples of the Graphite-Boron Nitride system studied by Wu and McLachlan (1997). Values of 2.63 ± 0.07 and 2.68 ± 0.13 were measured for t in the axial (pressure direction) and transverse directions respectively. It is important

to note at this point that the three-component system of Graphite, Boron Nitride and Talc-wax studied in this thesis gave $t = 2.51 \pm 0.12$ in the axial (pressure) direction. The t exponents measured in the three-component system and that of Wu and McLachlan overlap within their error bars. The similarity in the t exponents of the systems suggests that the conductivity exponent must be determined mainly by the Graphite-Graphite contacts. Note also that the critical volume fraction (ϕ_c) for the three-component system is 0.033 ± 0.001 while Wu's compacted Graphite Boron Nitride system gave $\phi_c = 0.150 \pm 0.001$ (Wu 1997, Wu and McLachlan 1997). Fizazi *et al.* (1990) also measured and reported a conductivity exponent $t = 2.6$ in a UHWPE (Ultra High Molecular Weight Polyethylene) gel decorated with a conducting polymer (poly-3-octylthiophene).

The last category of t exponents was observed in the Magnetite (Fe_3O_4) and Niobium Carbide systems (all prepared by the more gentle "waterfall" mixing method because of their hardness). The systems show extreme values of the exponent t , much higher than the random void model's predictions. These high t values of the Niobium Carbide and Magnetite systems are also associated with some of the smallest s values ever reported for three-dimensional systems. The new Balberg models (1998a and 1998b) can accommodate the extreme values of the t exponents.

Recall that Balberg (1998a and 1998b) modified the Random Void model by introducing a parameter ω' ($-\infty < \omega' < 1$) in the resistance distribution function (section 2.1.4) to obtain the expression: $t = t_{\text{un}} + (u + \omega' - 1)/(1 - \omega')$, for a non-universal t exponent. The parameter u is related to the dimensionality (d) of the system and is such that $u = d - 3/2$ for the random void (Swiss Cheese) model. Different combinations of ω' and u will give various values of the exponent t . For $\omega' = 0$, the expression gives the original Halperin, Feng and Sen (1985) and Tremblay, Feng and Breton (1986) models. The various t values observed in the systems suggest that there are different values of ω' for very specific cases arising from the different inter-particle conductance ranges that occur within the various systems. The values of ω' may explain the extreme t values obtained in some of the systems. In principle,

noise results can also give ω' values (eqn. (2.24)). Unfortunately in this study, there are no noise results for the extreme t systems.

Extreme values of t have also been reported in previous experiments. Wu (1997) and Wu and McLachlan (1997) reported values of t between 4.80 (axial) and 6.10 (transverse) in Graphite-Boron Nitride powder composites. Wu and McLachlan attributed the abnormally large t values of the powders to the presence of a large number of cavities and micro-voids giving rise to a large range of inter-grain conductance of the Swiss Cheese model as the powder mixtures tended to coat the air cavities. In compacted disc samples of the same composite, values of 2.63 ± 0.07 and 2.68 ± 0.13 were measured for t in the axial and transverse directions respectively. The high pressure used in the compaction process must have removed/reduced the air cavities and improved the inter-particle contacts, leading to the lower values of t . Other studies to have reported extreme values of t include those on Graphite-polyethylene (Ezquerro *et al.* 1990, $t = 6.27$) and Carbon Black-polymer composites (Rubin *et al.* 1999, $t = 6.4 \pm 0.7$). Rubin and his co-authors (1999) attributed the high t exponent to the low structure (nearly “spherical” geometry) of the Carbon Black used in their study and the tunneling percolation model.

In addition to the results obtained from the three-component system, DC parameters ϕ_c , t and s were obtained by treating the Graphite-Boron Nitride coating as a bulk and independent system (i.e. ignoring the Talc-wax volume fraction). Figure 4.5 shows a plot of $\log \sigma_m(\phi, 0)$ for the three-component system versus the volume fraction of Graphite in the Graphite-Boron Nitride coating. Fitting the results to eqn. (2.3) gave the parameters $\phi_c = 0.227 \pm 0.009$, $t = 2.67 \pm 0.15$ and $s = 1.25 \pm 0.20$, very close to $t = 2.51 \pm 0.12$ and $s = 1.28 \pm 0.19$ measured in the ‘parent’ (three-component) system. These values of t and s are also consistent with those obtained by Wu and McLachlan (1997) in the Graphite-Boron Nitride disc samples. Log-log plots of $\sigma_m(\phi, 0)$ versus $(\phi - \phi_c)$ and $(\phi_c - \phi)$ of Graphite-Boron Nitride coating gave the exponents $t = 2.84 \pm 0.14$ and $s = 1.00 \pm 0.10$ respectively. Similar plots on Wu and McLachlan’s compacted Graphite-Boron Nitride system gave $t = 2.74$ and $s = 1.05 \pm 0.10$. These

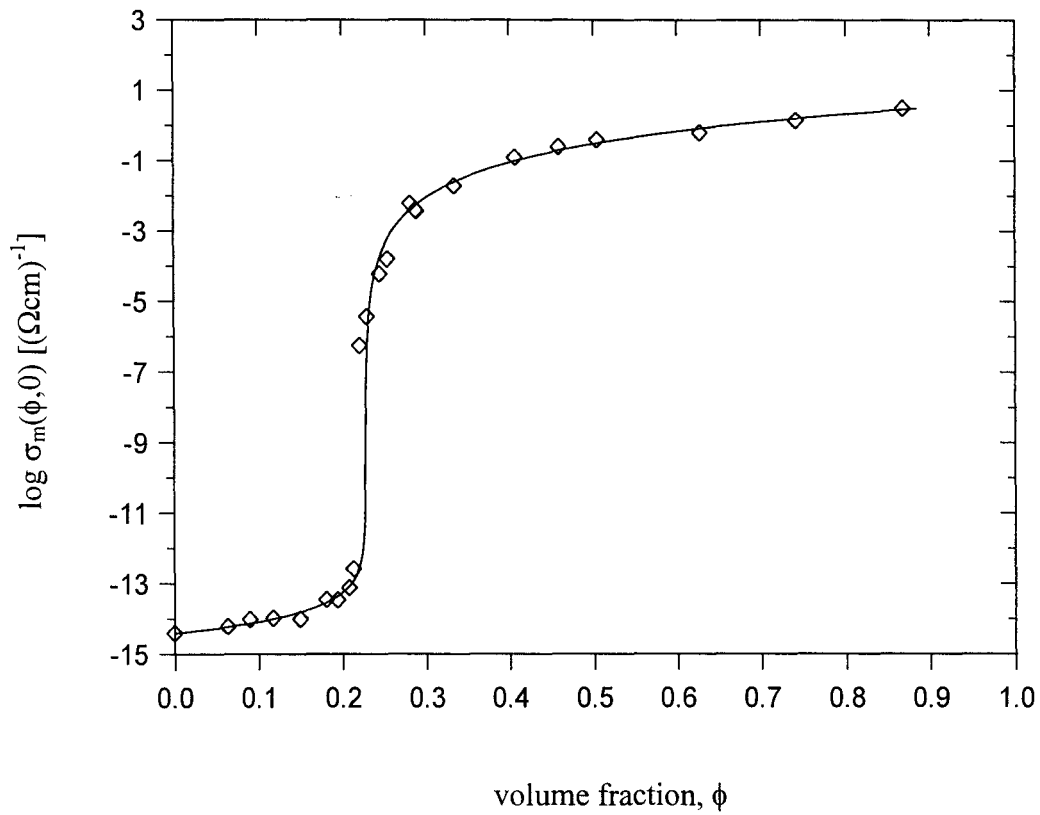


Figure 4.5. Plot of the log of DC conductivity ($\sigma_m(\phi, 0)$) results versus the volume fraction (ϕ) of Graphite for the Graphite-Boron Nitride coating in the Graphite-Boron Nitride system. The solid line is a fit to eqn. (2.3) and the fitting parameters are; $\phi_c = 0.227 \pm 0.009$, $t = 2.67 \pm 0.15$, $s = 1.25 \pm 0.20$, $\sigma_c = 44.3 (\Omega\text{cm})^{-1}$ and $\sigma_i = 3.89 \times 10^{-15} (\Omega\text{cm})^{-1}$.

results show that the Graphite-Boron Nitride coating can be regarded as an independent percolation system. The difference in the values of ϕ_c may be partially attributed to the difference in pressure used in the present study (380MPa) and that used by Wu and McLachlan (200MPa) but more probably because the pressure was applied to the Graphite-Boron Nitride through Talc-wax particles. Lee *et al.* (1986) also observed the dependence of ϕ_c on pressure in a composite system of Indium and Glass. Lee and his co-workers observed that the exponent t was not affected by the change in the pressure used to produce different samples in the same system.

Besides the Random Void model, other models have been put forward to try and explain the high exponents obtained in some continuum percolation systems: Tunneling conduction, which occurs when a thin oxide or polymer layer separates conducting grains, has also been singled out as a probable cause for high t values (Balberg 1987a, Carmona 1987). In the cellular systems, tunneling conduction through an oxide (or polymer barrier) can be ruled out, as the conducting powders were deliberately chosen not to have an oxide layer. In his tunneling model, Balberg (1987a and 1987b) showed that in regular Carbon Black-polymer systems, the particles' morphology influences the distribution of distances separating particle aggregates. Regular and spherical Carbon Black particles give a broad distribution of intergranular distances. As tunneling conduction (not relevant in the cellular systems) is very sensitive to the distances between aggregates, values of the exponent t in such systems can be very high (Balberg 1987a, Pierre *et al.* 1990a, Balberg 1998b and references therein). On the other hand, irregularly shaped Carbon Black particles give a narrow distribution of inter-granular distances, which leads to lower values of t , between 1.6 and 2.1 in 3D (Pierre *et al.* 1990a, Connor *et al.* 1998 and references cited therein).

A considerable amount of the already referenced experimental and theoretical work has mainly focused on the DC conductivity exponent t , but very little has been done on the DC exponent s . In fact, in very few of the previous DC conductivity experiments on percolation systems were measurements done on either side of ϕ_c .

Results done only on the conducting side and just below ϕ_c , are not sufficient to determine a reasonable s -value. The results presented here were taken over a wide range of ϕ values, below and above ϕ_c , which enabled the simultaneous determination of the exponents t and s as well as ϕ_c , σ_c and σ_i . Values of s given in Table 4.1 range from 0.37 to 1.28, with the upper limit given by the three-component system of Graphite, Boron Nitride and Talc-wax. The Niobium Carbide and Fe_3O_4 systems give very small s values, in agreement with those obtained by Wu and McLachlan (1997) on their high t powder systems. Values in the range 0.65 – 1.00, reasonably close to $s_{\text{un}} = 0.87$, are obtained in the plain Graphite and the two Carbon Black systems, whose t values are also reasonably close to the universal value ($t_{\text{un}} = 2.00$).

To the best of the author's knowledge, no previous experiments have reported measurements of the exponent s from DC conductivity measurements other than the work of Wu (1997) and Wu and McLachlan (1997), carried out on three Graphite-Boron Nitride systems. They obtained a value of 1.01 ± 0.05 in Graphite-Boron Nitride disc samples and extremely low values in 50%Graphite-50%Boron Nitride (0.42 ± 0.01) and 55% Graphite-45% Boron Nitride (0.47 ± 0.01) powder systems. All these values were obtained from measurements done in the axial (pressure) direction.

4.1.3 The Dielectric Constant Exponent s' : Variation with Frequency

The exponent s' was obtained from AC dielectric measurements made at various frequencies on the cellular systems. In this study, the measurements were done in the frequency range of 10^{-2}Hz to 10^6Hz . The s' values were obtained as the slopes in the linear fits to the graph of $\log ((\epsilon_{\text{mr}}(\phi))/(\epsilon_{\text{mr}}(\phi = 0)))$ (where ϵ_{mr} is the real part of the dielectric constant) against $\log (\phi_c - \phi)$ as shown in Fig. 4.6 for the Nickel system. The data used to obtain s' were only those points below ϕ_c , where ϕ_c was obtained from DC conductivity measurements (Table 4.1). Dielectric data for all the samples had to be normalised by the dielectric constant of the $\phi = 0.00$ sample ($\epsilon_{\text{mr}}(\phi = 0)$) after

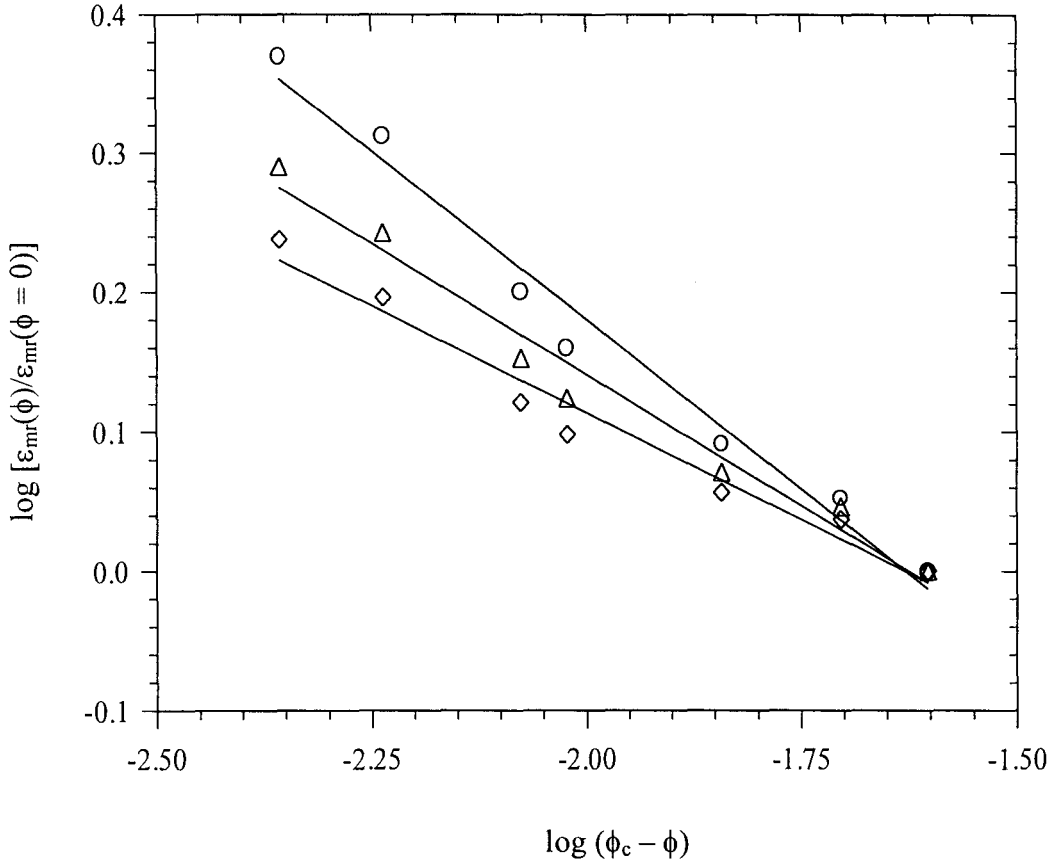


Figure 4.6: Log-log plot of ϵ_{mr} versus $(\phi_c - \phi)$ for the Nickel system at 1Hz (O), 1kHz (Δ) and 1MHz ($\diamond$). The solid lines are the best linear fit to the data which gives the exponent s' at the various frequencies; $s' = 0.48 \pm 0.02$ (1Hz), $s' = 0.38 \pm 0.02$ (1kHz) and $s' = 0.31 \pm 0.02$ (1MHz).

Table 4.3: Experimental values of the Dielectric Exponents

Composite System	s	s' (0.01Hz)	s' (1Hz)
Ground Carbon Black	1.06 ± 0.26	0.71 ± 0.04	0.49 ± 0.04
Raw Carbon Black	0.90 ± 0.20	0.65 ± 0.08	0.47 ± 0.02
Ground Graphite	0.66 ± 0.15	0.79 ± 0.05	0.62 ± 0.03
Graphite-BN(15%)	1.28 ± 0.19	0.70 ± 0.05	0.62 ± 0.05
Nickel	1.11 ± 0.60	0.69 ± 0.02	0.48 ± 0.02
Magnetite	0.45 ± 0.31	0.14 ± 0.01	0.13 ± 0.01
Niobium Carbide	0.37 ± 0.14	0.46 ± 0.03	0.28 ± 0.01

Composite System	s' (100Hz)	s' (1kHz)	s' (1MHz)	s' vs log f slope
Ground Carbon Black	0.39 ± 0.04	0.36 ± 0.04	0.23 ± 0.03	0.06 ± 0.02
Raw Carbon Black	0.44 ± 0.02	0.43 ± 0.03	0.33 ± 0.02	0.03 ± 0.03
Ground Graphite	0.54 ± 0.02	0.50 ± 0.02	0.42 ± 0.01	0.03 ± 0.02
Graphite-BN(15%)	0.57 ± 0.04	0.55 ± 0.04	0.46 ± 0.04	0.02 ± 0.01
Nickel	0.40 ± 0.02	0.38 ± 0.02	0.31 ± 0.02	0.04 ± 0.03
Magnetite	0.11 ± 0.01	0.10 ± 0.01	0.07 ± 0.01	0.04 ± 0.03
Niobium Carbide	0.23 ± 0.01	0.21 ± 0.01	0.18 ± 0.01	0.05 ± 0.06

Note: f in the last column denotes frequency

realising that the latter was highly dispersive. Therefore after this normalisation, the plots at various frequencies all have the value 1 at $\phi = 0$. Results for all the systems are shown in Table 4.3, where it can be clearly seen that s' is frequency-dependent, increasing towards its DC or zero frequency value as the frequency is lowered. Note the large error in s compared to that in s' . Note also that from the original Percolation Theory (see for instance Clerc *et al.* 1990, Bergman and Stroud 1992, Nan 1993), one would expect that the slope at different frequencies in Fig. 4.6 would be the same, but the results presented here show different slopes and hence different s' values. The results shown in Table 4.3 indicate that the DC exponent s is generally larger than the s' value. Note that the values of s' measured at 0.01Hz for ground Graphite and Niobium Carbide systems are slightly greater than the corresponding DC (s) values, but the results still overlap within their error limits.

Plots of s' versus frequency done for the various systems show slightly different slopes (Table 4.3). The maximum slope is obtained from the ground Carbon Black system and the Graphite-Boron Nitride-Talc-wax system gives the least slope. It should also be noted, that the systems with high t exponents (Magnetite (Fe_3O_4) and Niobium Carbide) have extremely small s and s' values. Note the different s' values means that ϵ_{mr} is dispersive below and above ϕ_c , which is not predicted by the original Percolation Theory.

Scaling theory for percolation systems as given by various authors (Webman *et al.* 1975, Efros and Shklovskii 1976, Straley 1977, Bergman and Imry 1977, Stroud and Bergman 1982), and reviewed by Clerc *et al.* (1990) and Bergman and Stroud (1992), Nan (1993), implies that $s = s'$. However, the present results confirm the previous results of Wu and McLachlan (1997) that s obtained from DC measurements and s' (obtained from dielectric measurements) are not the same. Wu and McLachlan measured s (from DC conductivity measurements) and s' (at 100Hz and 1kHz) in three Graphite-Boron Nitride systems described earlier in section 4.1.2. They obtained $s = 1.01 \pm 0.05$ and $s' = 0.53 \pm 0.07$ in the disc samples, $s = 0.42 \pm 0.01$ and $s' = 0.60 \pm 0.01$ in the 50% Graphite and $s = 0.47 \pm 0.01$ and $s' = 0.72 \pm 0.01$ in the 55%Graphite

powder system. The s' values quoted here were measured at 1kHz. Similar to the results obtained in the cellular systems, the low frequency dielectric exponent s' in the compacted Graphite-Boron Nitride system is lower than the DC value. However, the two loosely packed powder systems are the only measured systems to have s' values greater than s , a result that may be attributed to the very different microstructure of the loosely packed powders and compressed disc samples.

Other experiments that have actually measured the exponent s' have implied that it was the same as the DC exponent s (Grannan *et al.* 1981, Chen and Johnson 1991). Grannan *et al.* (1981), obtained a value of $s' = 0.73 \pm 0.07$ in a Silver-Potassium Chloride composite from dielectric measurements at 1kHz. Chen and Johnson (1991), in an experiment involving filamentary and nodular Nickel in a polypropylene matrix, obtained $s' = 0.55 \pm 0.10$ and $s' = 0.62 \pm 0.10$ respectively, suggesting that the shape of the powder may also be important in the determination of the exponent s' .

4.1.4 Variation of the Low Frequency Dielectric Constant with Volume Fraction

Figures 4.7-4.9 show the real part of the dielectric constant at three different frequencies plotted against the volume fraction (ϕ) of the conducting component for the raw Carbon Black, Niobium Carbide and Fe_3O_4 systems respectively. The original Percolation Theory (see for example Clerc *et al.* 1990, Bergman and Stroud 1992, Nan 1993) predicts that the real dielectric constant of the composite, ϵ_{mr} should show a peak at the percolation threshold, ϕ_c (see section 2.2). However, these experimental results and those previously reported (McLachlan *et al.* 1998 and references therein, Heiss *et al.* 2000), show that ϵ_{mr} continues to increase beyond ϕ_c (obtained from DC measurements) and shows a peak for $\phi > \phi_c$. The position and amplitude of this peak is found to be frequency dependent or more specifically $\epsilon_0\epsilon_r\omega/\sigma_c$ dependent (see for example Figs. 4.7, 4.8 and 4.9). The position of the peak moves further out from ϕ_c

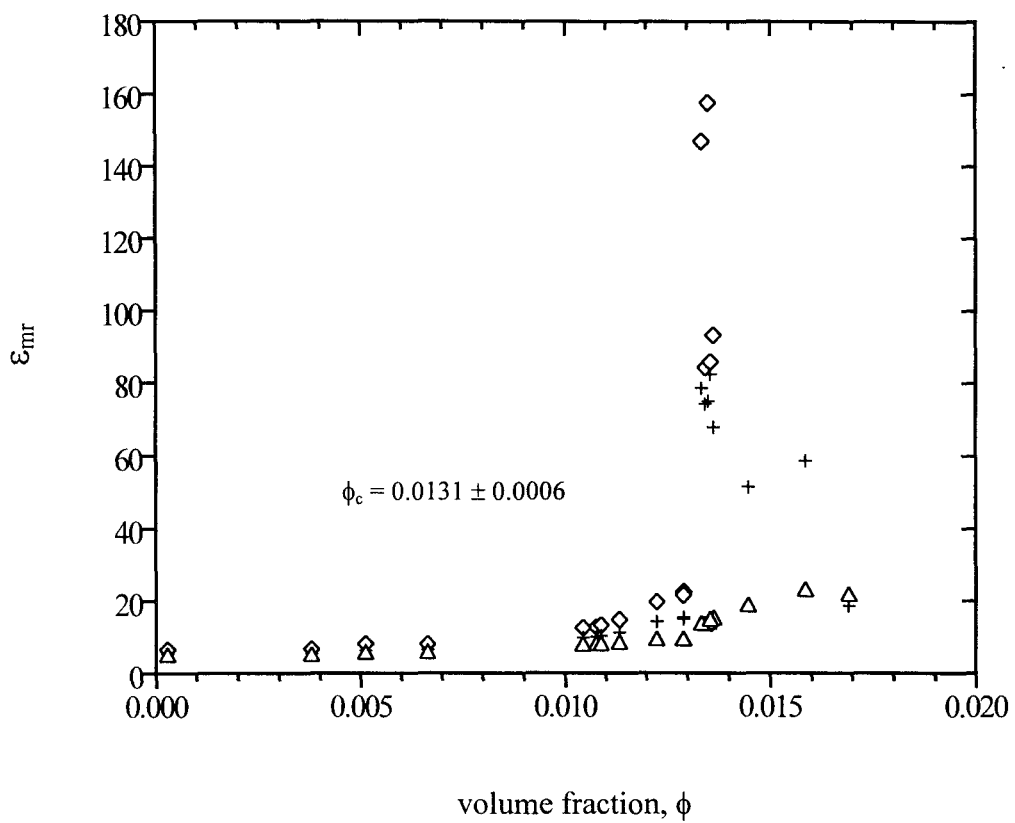


Figure 4.7: The real dielectric constant plotted against volume fraction for the raw Carbon Black system. 10 Hz ($\diamond$), 1kHz (+), 1MHz (Δ).

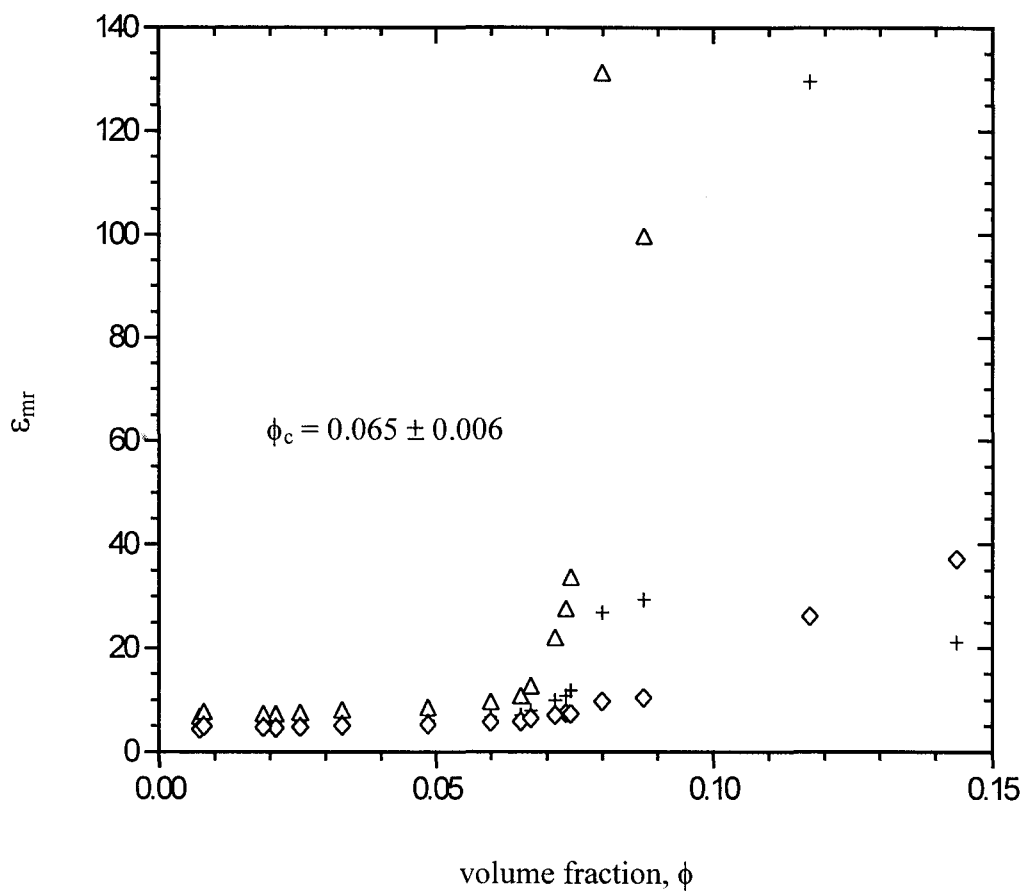


Figure 4.8: The real dielectric constant (ϵ_{mr}) plotted against volume fraction for the Niobium Carbide system at 10 Hz (Δ), 1kHz ($+$) and 1MHz ($\diamond$).

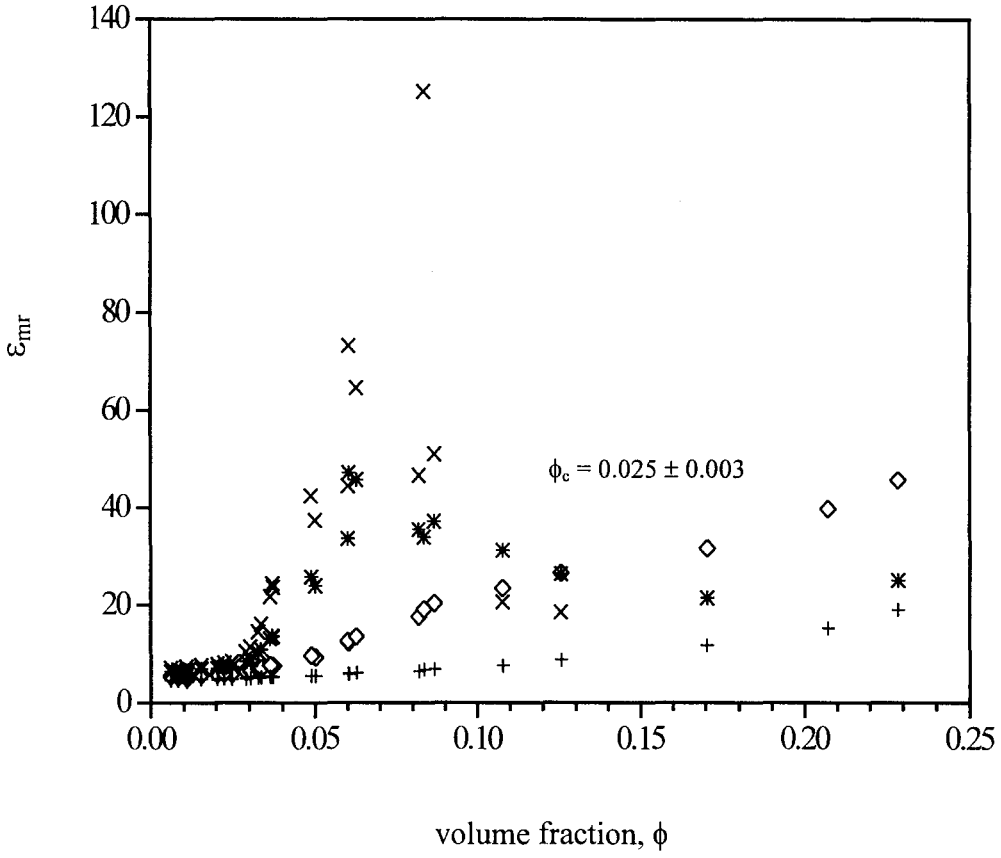


Figure 4.9: Variation of real dielectric constant (ϵ_{mr}) with volume fraction (ϕ) of Magnetite (Fe_3O_4) in a Magnetite-Talc-wax composite at various frequencies; 1Hz ($\times$), 10Hz ($*$), 1000Hz ($\diamond$) and 1MHz ($+$).

with increasing frequency, while the height/amplitude of the peak increases with decreasing frequency. It is now becoming clear that many previous experiments failed to recognise this behaviour because of limitations in the instrumentation (which could not measure very low or high loss angles) and the high conductivity of the conducting components used. In the absence of DC conductivity measurements, some authors could have taken ϕ_c to be the conductor volume fraction corresponding to the dielectric constant peak or their maximum ϵ_{mr} value (Grannan *et al.* 1981, Benguingui 1985). From what is shown in Figs. 4.7 – 4.9, ϕ_c identified in this way can be in excess of the true DC value. The present results were obtained using a Novocontrol Broad Band Dielectric Spectrometer. The accurate measurement of $\tan \delta$ values, from 10^{-3} to 10^3 , enabled the measurements to be made closer to ϕ_c than previously done in such experiments. Note that both the phase and loss angles go through a rapid transition from positive to negative near ϕ_c as the composite moves from the dielectric region to the conducting region and the validity of the measurements is determined by the ability of the measuring equipment to track such changes. Based on the $\tan \delta$ values, the points beyond $\phi = 0.15$ shown in Fig. 4.9 are valid measurements. However, it is not clear why ϵ_{mr} starts to increase again at higher ϕ values for the Fe_3O_4 system. This could well be an instrumental artifact.

Measurements of the dielectric constant in percolation systems discussed in this thesis all show the beginning of a rapid change of ϵ_{mr} near ϕ_c . However, for the high conductivity samples, the instrumentation makes it impossible to do measurements beyond the percolation threshold. Therefore it could not be established whether ϵ_{mr} continues to increase at higher volume fractions of the conductor in the highly conducting systems. Systems for which the ϵ_{mr} results could not be measured beyond ϕ_c in the present work include the two Graphite and Nickel systems. Although the NbC powder is highly conducting, the hard and angular shape of the particles lead to point contacts which causes the NbC-Talc-wax composite to have a lower conductivity, so that ϵ_{mr} could be measured beyond ϕ_c . Note that in low temperature (between 4K and 300K) resistivity measurements, none of the NbC-Talc-wax samples

above the percolation threshold were super-conducting (contrary to expectations). It is unclear what might have led to loss of superconductivity in these samples as the same Niobium Carbide powder in a Potassium Chloride matrix was shown to be super-conducting above ϕ_c , with a $T_c \sim 9K$.

The behaviour of the dielectric constant of the composites (ϵ_{mr}) as a function of volume fraction at a fixed frequency were modeled qualitatively using eqn. (2.3) (McLachlan *et al.* 1998). In a recent article (Heiss *et al.* 2000), a new model, based on eqns. (2.3), (2.11) and (2.14) has been formulated (section 2.2), which better describes the increase of ϵ_{mr} with volume fraction (ϕ) close to and beyond the DC percolation threshold ϕ_c (Fig. 4.10). The new model incorporates (into eqn. (2.3)) ideas proposed by Balberg (1998a and 1998b) on the universality/non-universality of percolation exponents discussed in sections 2.1.4 and 2.3. The resultant theoretical expressions (eqns. (2.11) and (2.14)), when substituted into eqn. (2.3), enable the position and amplitude of the dielectric constant peak to be modeled reasonably well. It is clear from the given experimental data that the position of the peak is dependent on the conductivity ratio $\omega\epsilon_0\epsilon_r/\sigma_c$. The larger the ratio, the further the dielectric constant peak is pushed away from ϕ_c . This behaviour is well illustrated by data from the Fe_3O_4 system, in which the dielectric peak, at the higher frequencies, is observed at volume fractions more than double the DC percolation threshold. It has also been realised (Heiss *et al.* 2000) that systems exist, which can be modeled by eqn. (2.3) alone without incorporating eqns. (2.11) and (2.14). Examples include the water-oil and Aerosol OT/water-isooctane micro-emulsions studied by van Dijk (1985) and van Dijk *et al.* (1986) respectively. This data is given in Fig. 1 of Heiss *et al.* (2000).

The dielectric constant behaviour of the Fe_3O_4 and similar systems could also be qualitatively explained in terms of the high t exponent of the composite as proposed by McLachlan *et al.* (1998). The conductivity of a percolating system with a high t exponent increases more slowly (above ϕ_c) with ϕ than a system with a smaller t exponent. This means that a larger fraction of the conducting component is not on the

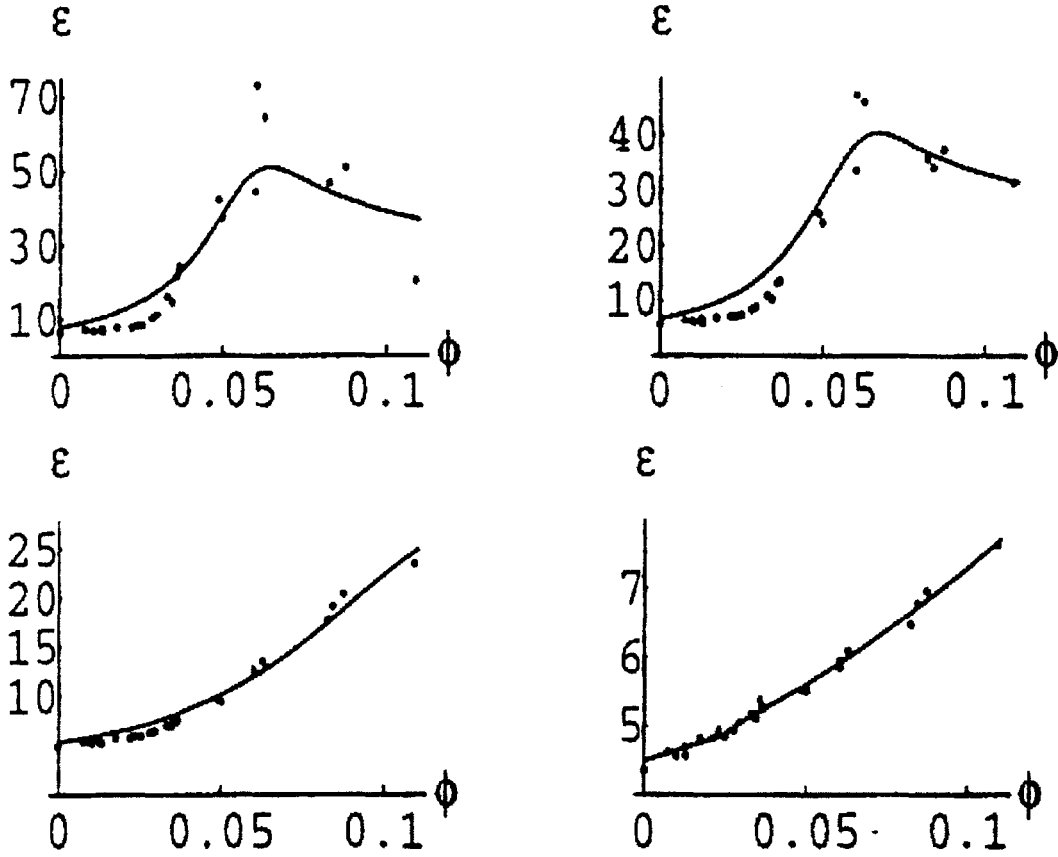


Figure 4.10: The experimental data (ϵ) at 1Hz, 10Hz, 1kHz and 1MHz (top left to right and bottom left to right) plotted as a function of volume fraction (ϕ) of Magnetite (Fe_3O_4) in an (Fe_3O_4)-Talc-wax composite. The theoretical fits (solid lines, from Heiss *et al.* (2000)) are from eqns. (2.3), (2.11) and (2.14). The parameters used are $\sigma_{00} = \sigma_c/10$, $\sigma_c = \sigma_{c0} = 2.63 \times 10^{-1}(\Omega\text{m})^{-1}$. Best fit parameters for (t-r, r, s) = (4.7, 0.5, 0.97), (4.3, 0.7, 0.98), (4.4, 0.6, 1.0) and (5.6, 0.4, 1.6) from top left to right, and bottom left to right. $\phi_c = 0.025 \pm 0.003$ (from DC conductivity measurements).

backbone of a system with a high t than one with a low t . This ‘off the backbone’ conducting material creates nearly conducting links between different sections of the backbone, which are broken by the insulating component, giving rise to ‘internal’ capacitances. These inner ‘dead end’ capacitances continue to affect the dielectric constant above ϕ_c (McLachlan *et al.* 1998), and cause the increase in ϵ_{mr} until they are effectively shorted out by the more conductive backbone, created by further addition of the conducting component, leading to a drop in ϵ_{mr} .

4.1.5 Temperature Dependence and DC Scaling in the Fe_3O_4 system

The objective of the results presented in this section is to study DC conductivity scaling in a Fe_3O_4 -Talc-wax composite by changing the conductivity ratio (σ_i/σ_c) of the components. This is the first time that DC scaling for different σ_i/σ_c values has been done on a real composite system. It was intended that the ratio (σ_i/σ_c) would decrease due to the increase of the DC conductivity (σ_c) of the Magnetite (Fe_3O_4) with temperature. In an experiment designed to characterise the temperature dependence of the conductivity of Fe_3O_4 , the conductivity of a pellet made from the powder was observed to increase by nearly three orders of magnitude when the temperature was increased from 293K (20°C) to 413K (140°C). However, in the Fe_3O_4 -Talc-wax system, it was observed that σ_i increased more rapidly with temperature than the conductivity (σ_c) of the Fe_3O_4 , resulting in a net increase (rather than a decrease) in σ_i/σ_c with temperature, as shown in Table 4.4.

The values of s , t , σ_i and σ_c , shown in Table 4.4, were obtained from fitting the DC conductivity data (at different temperatures) to equation (2.3). ϕ_c was found to be essentially constant. Due to the conflicting changes in σ_i and σ_c , the ratio (σ_i/σ_c) changed by only two orders of magnitude in the temperature range 298K (25°C) to 393K (120°C). However, the change in σ_i/σ_c was still sufficient to move the points on

Table 4.4: Variation of the exponent t with temperature in the Fe₃O₄ system

The fitted ϕ_c was always between 0.025 ± 0.003 and 0.025 ± 0.004 .

Temp. (K)	$\sigma_c (\Omega\text{cm})^{-1}$	$\sigma_i (\Omega\text{cm})^{-1}$	σ_i/σ_c	s	t
298	3.2188×10^{-3}	3.4722×10^{-17}	1.0787×10^{-14}	1.01 ± 0.88	4.24 ± 0.28
333	4.9386×10^{-3}	5.4576×10^{-15}	1.1051×10^{-12}	0.86 ± 0.62	3.91 ± 0.22
353	7.9980×10^{-3}	1.7112×10^{-14}	2.1395×10^{-12}	1.15 ± 2.21	3.90 ± 0.25
373	1.0150×10^{-2}	1.6151×10^{-13}	1.5912×10^{-11}	0.80 ± 1.27	3.76 ± 0.21
393	1.4190×10^{-2}	1.1046×10^{-12}	7.7845×10^{-11}	0.80 ± 1.05	3.71 ± 0.21

a scaling curve (Fig. 4.11), obtained using the scaling relation (2.6) of section 2.1.3. The experimental results (at various temperatures) closest to and again above the percolation threshold were fitted to eqn. (2.3) and yielded new values of t but not ϕ_c as shown in Table 4.4. The values of σ_i and σ_c were obtained as the best fit parameters. Note that values of σ_i close to $\phi = 0.00$ could not be accurately measured in these annealed samples, which made it impossible to obtain reliable values of the exponent s below ϕ_c . However, the values of the s exponent used to obtain the theoretical curves are given in Table 4.4.

Small variations in the exponent t were also observed at each temperature. These variations gave rise to slightly different theoretical curves (the solid lines in Fig. 4.11) onto which the experimental results were scaled. Note that without this small change in t , exactly the same theoretical curve would have been calculated at all temperatures. The theoretical curves below ϕ_c are shown merely for the reader's benefit, as the data was not good enough for scaling to be done in this region. The successful scaling of the experimental points shown on the graph can be seen through their movement along the curve as the temperature increases from room temperature (298K) to 393K and the fact that the experimental points at different temperatures all lie on nearly the same curve. It is also interesting to observe that points in the region $\log [(\sigma_i/\sigma_c)(1 - \phi_c)^{t+s}/(\phi - \phi_c)^{t+s}] \geq 1$ slide smoothly along the curve. The original Percolation Theory does not give an expression to model this region.

The results shown in Table 4.4 show that the exponent t decreases slightly with temperature and the σ_i/σ_c ratio in the Magnetite (Fe_3O_4)-Talc-wax composite. The change in the exponent t observed in the (Fe_3O_4)-Talc-wax system is in qualitative agreement with Lin's observation (1991) in a $\text{PrBa}_2\text{Cu}_3\text{O}_7$ -Ag percolation system. In his system, Lin observed that the exponent t varied from 1.48 to 1.91 as the conductivity ratio changed from 3.125×10^{-5} at 300 K to 4.545×10^{-12} at 30 K. In an effort to explain the values of t below t_{un} , Lin (1991) proposed that the smaller than universal values of the exponent t observed in composite materials may be a result of

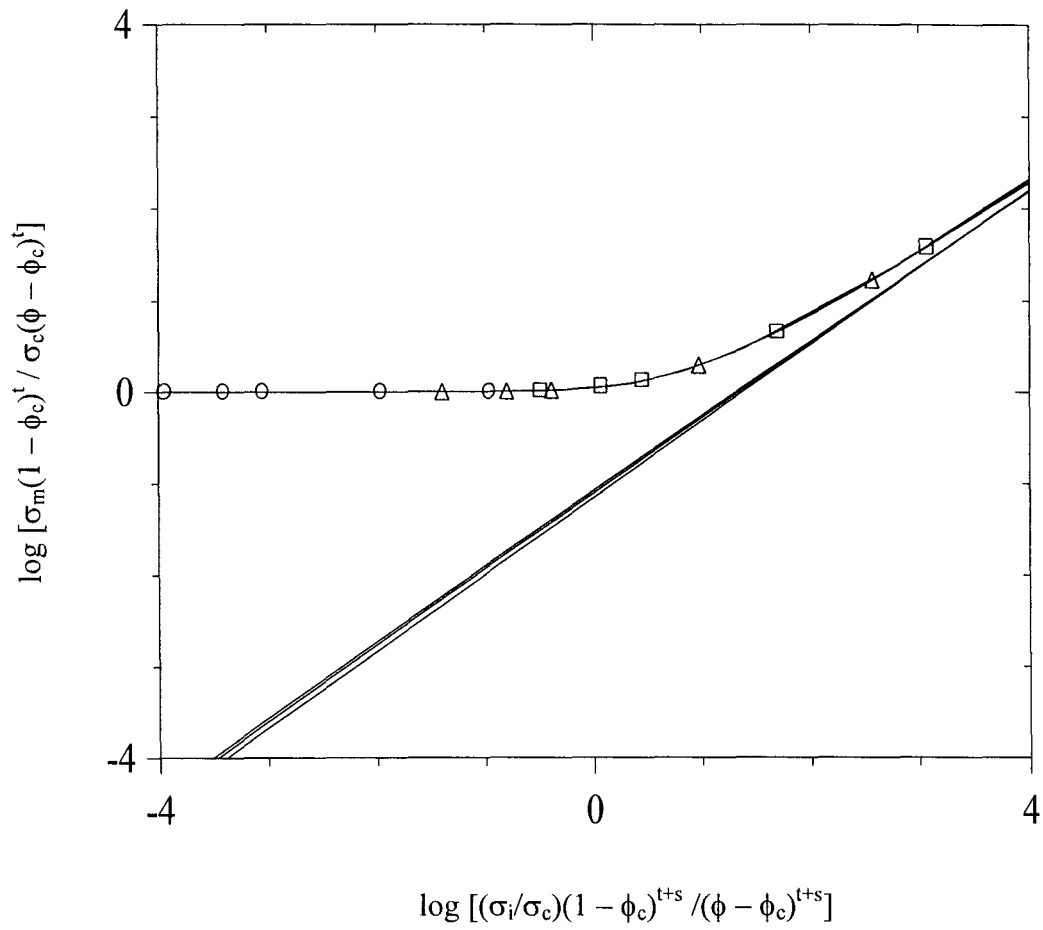


Figure 4.11: DC scaling in a Magnetite (Fe₃O₄)-Talc-wax composite system for samples close to but above ϕ_c at three temperatures; 25°C (O), 80°C (Δ), 120°C (□).

the finite ratio of σ_i/σ_c . Lin's argument does not seem to apply to the present Fe_3O_4 system results. However, his results and those obtained in the Magnetite (Fe_3O_4) system show that, in some systems, increasing the ratio σ_i/σ_c can lower the t exponent.

4.1.6 Variation of the Dielectric Constant with Temperature

In addition to the results already presented on the Fe_3O_4 system in section 4.1.5, the low frequency dielectric constant of the composite (ϵ_{mr}) was found to increase with temperature due to the decrease in $\omega\epsilon_0\epsilon_{ir}/\sigma_c$. The change in ϵ_{ii} (the imaginary component of the insulator dielectric constant) had a negligible effect on the results. Figure 4.12 shows results of the real part of the dielectric constant measured at 1Hz plotted as a function of the volume fraction of Fe_3O_4 at different temperatures. The peak in the dielectric constant shows a big enhancement (from 100 at room temperature up to 400 at 393K) beyond ϕ_c , with the peak occurring at a volume fraction of Fe_3O_4 more than twice the ϕ_c obtained from DC electrical conductivity measurements. Theoretical expressions given in section 2.2 and the article by Heiss *et al.* (2000) can be used to model this behaviour of the dielectric constant beyond ϕ_c . The fitted results are shown in Fig. 4.13. As noted earlier, eqn. (2.3) predicts that the position of the dielectric constant peak is only dependent on $\omega\epsilon_0\epsilon_{ir}/\sigma_c$, which is born out by the experimental results. From Figs. 4.12 and 4.13, it can be observed that a decrease in frequency (which is equivalent to decreasing σ_i) has the same overall effect as an increase in σ_c . The latter can be obtained by an increase in temperature as shown in Figs. 4.12 and 4.13.

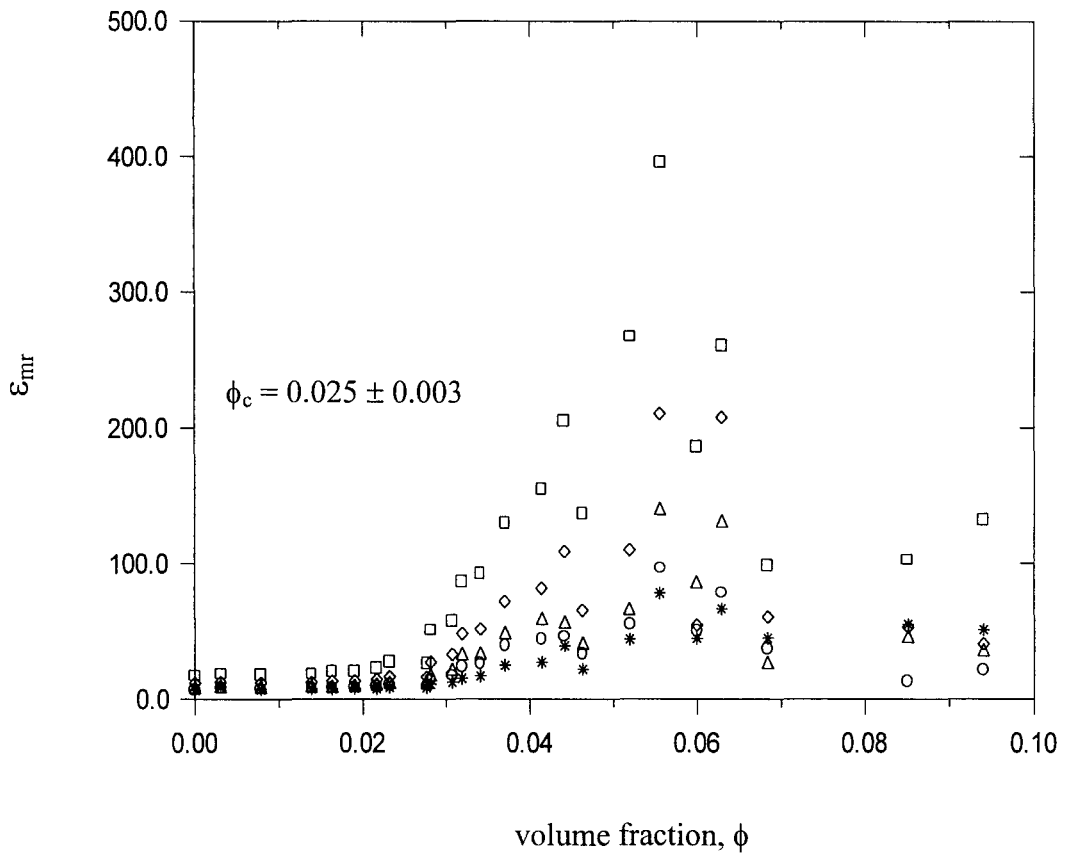


Figure 4.12: The real dielectric constant (ϵ_{mr}) measured at 1Hz plotted against the volume fraction of Fe_3O_4 at various temperatures; 25°C (*), 60°C (o), 80°C (Δ), 100°C ($\diamond$) and 120°C ($\square$) for the (Fe_3O_4)-Talc-wax system.

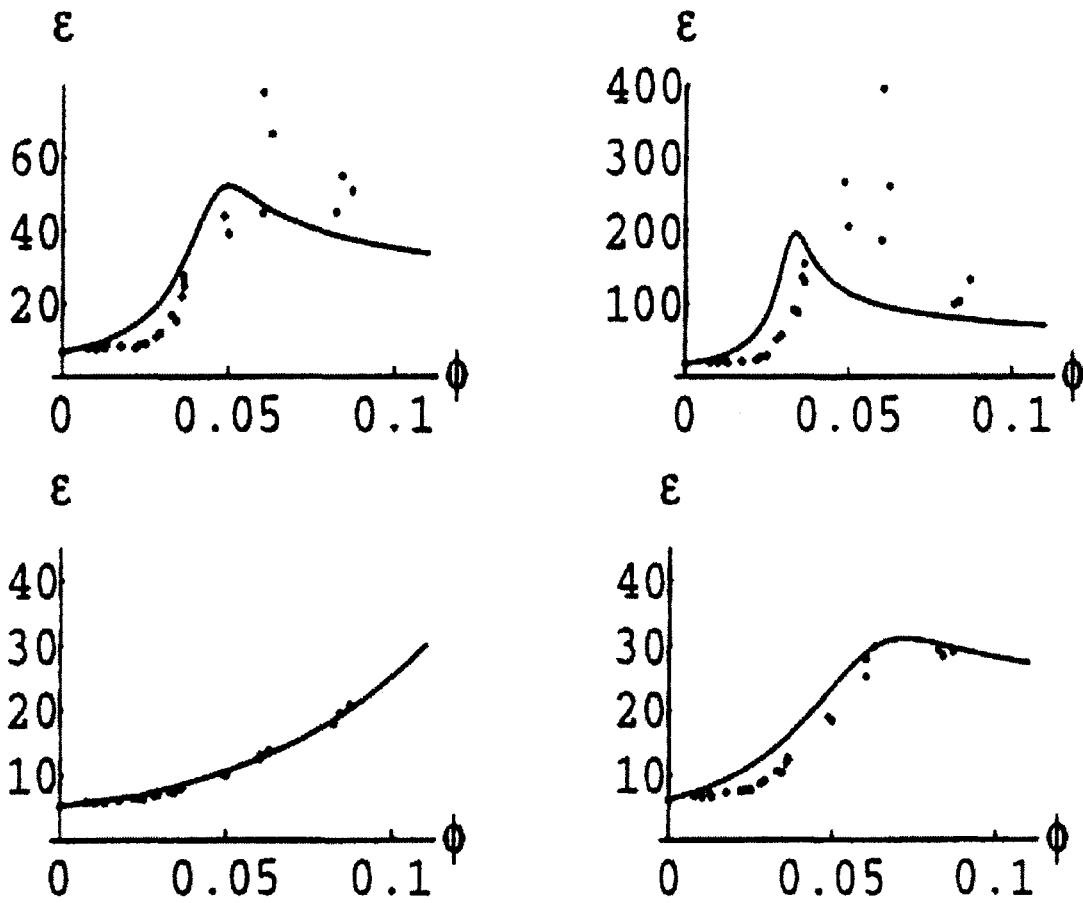


Figure 4.13: Fits of experimental data at 1Hz for $T = 25^{\circ}\text{C}$ (top left) and $T = 120^{\circ}\text{C}$ (top right). The bottom row displays corresponding results for 1kHz. The data is for the (Fe_3O_4) -Talc-wax system. The parameters used are; $\sigma_{c0} = \sigma_c = 3.22 \times 10^{-1}(\Omega\text{m})^{-1}$ at 25°C and $\sigma_{c0} = \sigma_c = 1.42 \times 10^{-1}(\Omega\text{m})^{-1}$ at 120°C . Best-fit parameters (from Heiss *et al.* (2000)) for $(t-r, r, s) = (4.65, 0.5, 1.0), (3.4, 0.6, 1.0), (4.4, 0.6, 1.0)$ and $(3.5, 0.9, 1.0)$ from top left to right, and bottom left to right, again with $\sigma_{00} = \sigma_c/10$ (eqn. (2.15)). $\phi_c = 0.025 \pm 0.003$ (from DC conductivity measurements).

4.3 Summary

The original Percolation Theory is not adequate in explaining the results observed in the composite systems studied in this thesis. Most of the results can be far better modeled by the phenomenological two exponent equation (eqn. (2.3)). For the dielectric results near and beyond ϕ_c , agreement with the data is only achieved by incorporating extensions to the random void model (Balberg 1998a and 1998b) for universality/non-universality of percolation exponents.

The ϕ_c values show reasonably good agreement with the Kusy (1977) model. It is inferred from the theory given by Kogut and Straley (1979) that the various exponents result from the range of conductance that form between the conducting particles. The soft particles appear to form ‘good’ or ‘welded’ joints, which lead to a narrow conductance distribution to give $t \sim t_{un}$. On the other hand, as discussed below, the ‘bad’ or point contacts among the hard and angular conductor particles result in wide conductance distribution and give t much higher than t_{un} . Such an observation is supported by the range of s and t values obtained from the systems with the same macroscopic cellular structure (Table 4.1). A particularly low value of the exponent t was observed in the Nickel system, which cannot be explained by current theoretical models. Close to universal values of the s and t exponents were observed in the Graphite and Carbon Black systems while the three component system of Graphite-Boron Nitride-Talc-wax, gave s and t exponents higher than the universal values. The t exponent in the three-component system agrees well with the predictions of the Random Void/Swiss Cheese model of Halperin *et al.* (1985) and Feng *et al.* (1987) as well as the experimental results obtained by Wu (1997) and Wu and McLachlan (1997) on the compacted Graphite-Boron Nitride system. Wu’s results are also in reasonable agreement with those obtained in the Graphite-Boron Nitride coating, when the coating is taken to be an independent percolation system. Extreme values of the t exponent were observed in the Magnetite (Fe_3O_4) and Niobium Carbide systems, where particularly small values of the s exponent were also measured. The only

model, which is consistent with the t exponents in these two systems, is the new model for non-universal exponents given by Balberg (1998a and 1998b).

The variation of the real dielectric constant with conductor volume fraction ϕ in the systems studied agrees to some extent with Percolation Theory below ϕ_c but the behaviour above ϕ_c exposes the shortcomings of the original Percolation Theory in that the latter (refer to eqn. (2.1c)) does not predict a peak in the dielectric constant beyond ϕ_c but rather a discontinuity or for finite samples a peak at ϕ_c . Note also that eqn. (2.1c) does not incorporate any frequency dependence of the dielectric constant but the experimental results in this thesis show dispersion below ϕ_c and even more complex behaviour above ϕ_c . The results obtained in this study, show clearly that the peak of the dielectric constant occurs beyond ϕ_c in the Fe_3O_4 system, which is also inferred for the other systems measured. The dielectric peak is frequency dependent, shifting to higher volume fractions at high frequencies. The relatively large σ_i/σ_c ratio in the Fe_3O_4 system causes the dielectric peak to be located well beyond ϕ_c as predicted by eqns. (2.3) and (2.14). In accordance with eqn. (2.3), a small conductivity ratio causes the dielectric constant peak to occur closer to ϕ_c , approaching the original percolation limit for $\sigma_i/\sigma_c = 0$. The frequency dependence of s' (the first thorough study of which was presented in this chapter) is also something that warrants further investigation, especially theoretical. The present results and those of Wu and McLachlan (1997) clearly show that the low frequency dielectric exponent s' is not the same as the DC value (s). However, it would appear that systems exist where s' does not vary much with frequency so that s' and s become nearly equal. The Graphite-Talc-wax composite studied in this work appears to belong to such a class of systems.

The DC measurements done on the Fe_3O_4 system at various temperatures ($\equiv$ different σ_i/σ_c ratios), exhibit DC scaling. The results also show that the t -exponent decreases slightly as the conductivity ratio (σ_i/σ_c) of the composite constituents increases as previously observed by Lin (1991). The low frequency real dielectric constant in the

same system (plotted as a function of ϕ at fixed frequency for different temperatures)
near ϕ_c increases appreciably with temperature due to the increase in σ_c .

CHAPTER FIVE

THE AC CONDUCTIVITY OF THE CELLULAR SYSTEMS

5.0 Introduction

The dispersion observed in percolation systems has received attention from both experimentalists and theoreticians for a long time. The results obtained from its study are complex and the search for theoretical models to explain the results observed in certain frequency ranges for some systems is ongoing.

This chapter reports on the AC conductivity studies made on systems comprising of Graphite, Graphite-Boron Nitride (15%), ground and raw (unground) Carbon Black, Niobium Carbide and Magnetite (Fe_3O_4) as conducting components in a common insulating matrix of Talc-wax. The Graphite-Boron Nitride-Talc-wax is a three-component system in which the Talc-wax is always coated by a mixture of Graphite and Boron Nitride powders whose combined volume fraction (ϕ) is fixed at $\phi = 0.15$. Details regarding the preparation of these systems were given in sections 3.2.2. Measurements were done on pellet (discs) samples in the insulating ($\phi < \phi_c$) as well as the conducting region ($\phi > \phi_c$) in the frequency range 10^{-2} to 10^9 Hz, in order to test for the power laws (which give the exponents x , y and q) given in section 2.4. The pellets or disc samples (26mm diameter) were used up to 10^6 Hz while 10mm diameter disc samples (cut from the bigger discs) were used for the high frequency measurements in order that they could fit onto the sample holder of the high frequency instrument (see section 3.2.2.2).

The AC conductivity results are presented as log-log plots of the real part of the complex conductivity ($\sigma_m(\phi, \omega)$) against frequency (ω). Scaling plots, where the reduced conductivity ($\sigma_{mr}(\phi, \omega)/\sigma_m(\phi, 0)$) is plotted against the reduced frequency (ω/ω_c), enabled the conductivity results of different samples of a particular system to be collapsed onto a single curve (see for example Laibowitz and Gefen 1984, Clerc *et al.* 1990, Chakrabarty *et al.* 1993, Connor *et al.* 1998, Wu and McLachlan 1998, McLachlan *et al.* 1998). Linear fits to the scaled plots (in the region where $\log(\omega/\omega_c) > 1$) give the scaling exponent x . The real part of the dielectric constant ($\epsilon_{mr}(\phi, \omega)$) close to ϕ_c , when plotted versus the frequency (ω), is found to be dispersive, with a characteristic exponent y . In the present study, the dielectric constant exponent y is obtained from the log-log plot of the imaginary part of the AC conductivity versus frequency (Wu 1997). The exponent q , obtained from the scaling frequency (ω_c) and the DC conductivity ($\sigma_m(\phi, 0)$) (as given in eqn. (2.35) in section 2.4) as well as the exponent z (Chen and Johnson 1991, Chakrabarty *et al.* 1993), obtained from a log-log plot of $\tan \delta$ against frequency, are also given for these systems. The results are analysed in terms of the intercluster polarisation model using the scaling exponents x , y and q as well as the DC conductivity exponents s and t (Table 4.1).

5.1 AC conductivity results

The AC conductivity results of three representative systems are shown in Figs. 5.1 – 5.3, where the real part ($\sigma_{mr}(\phi, \omega)$) of the complex conductivity $\sigma_m(\phi, \omega)$ is plotted as a function of frequency. These results show clearly the difference in behaviour between the insulating and conducting samples. Samples above the percolation threshold show a frequency-independent behaviour at low frequency. This frequency-independent behaviour is illustrated in the above figures through a constant DC conductivity (flat response to changing frequency), the magnitude of which depends only on the volume fraction (ϕ) of the conducting component. This behaviour of the conductivity is ascribed to the many percolating paths of well-connected conducting clusters

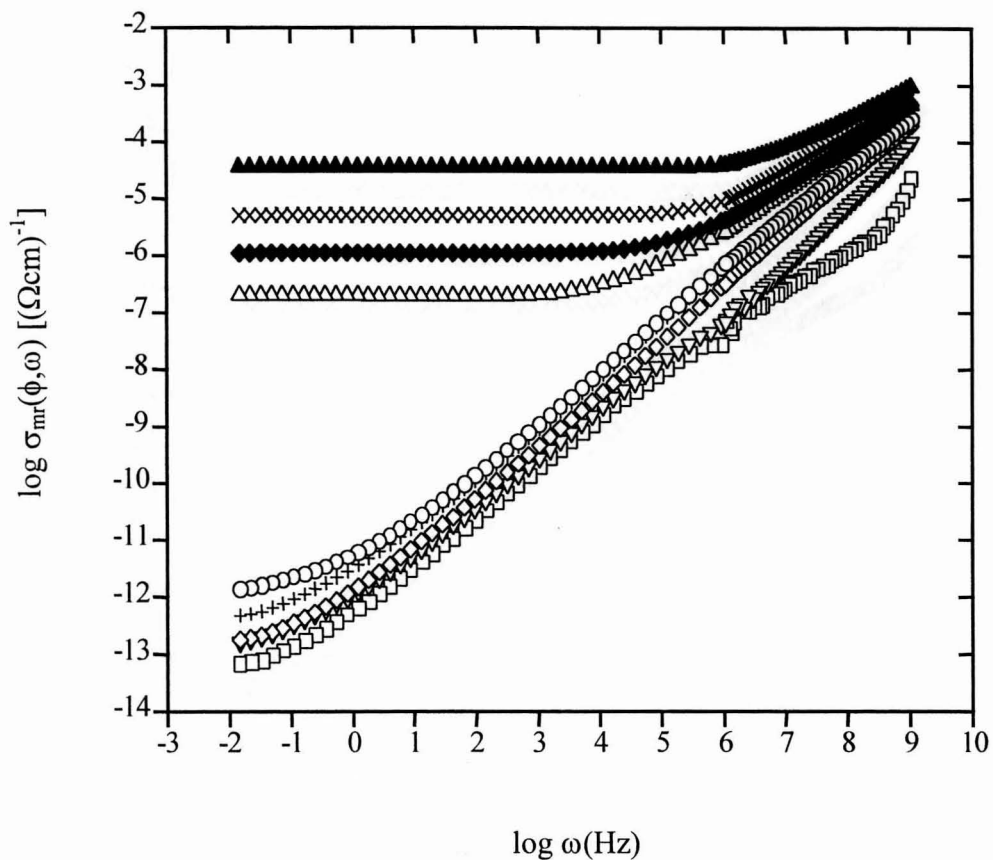


Figure 5.1: A log-log plot of AC conductivity versus frequency for the raw Carbon Black system. [$\phi = 0.0000$ ($\square$), $\phi = 0.0051$ (∇), $\phi = 0.0108$ ($\diamond$), $\phi = 0.0122$ ($+$), $\phi = 0.01291$ ($\circ$), $\phi = 0.0133$ (Δ), $\phi = 0.0136$ ($\blacklozenge$), $\phi = 0.0145$ ($\times$), $\phi = 0.0169$ ($\blacktriangle$), $\phi_c = 0.0131 \pm 0.0006$]. The samples $\phi = 0.0038, 0.0066, 0.0104, 0.0109, 0.0113, 0.01290, 0.0134, 0.0135, 0.0136$ and 0.0158 have been left out in order to avoid congestion.

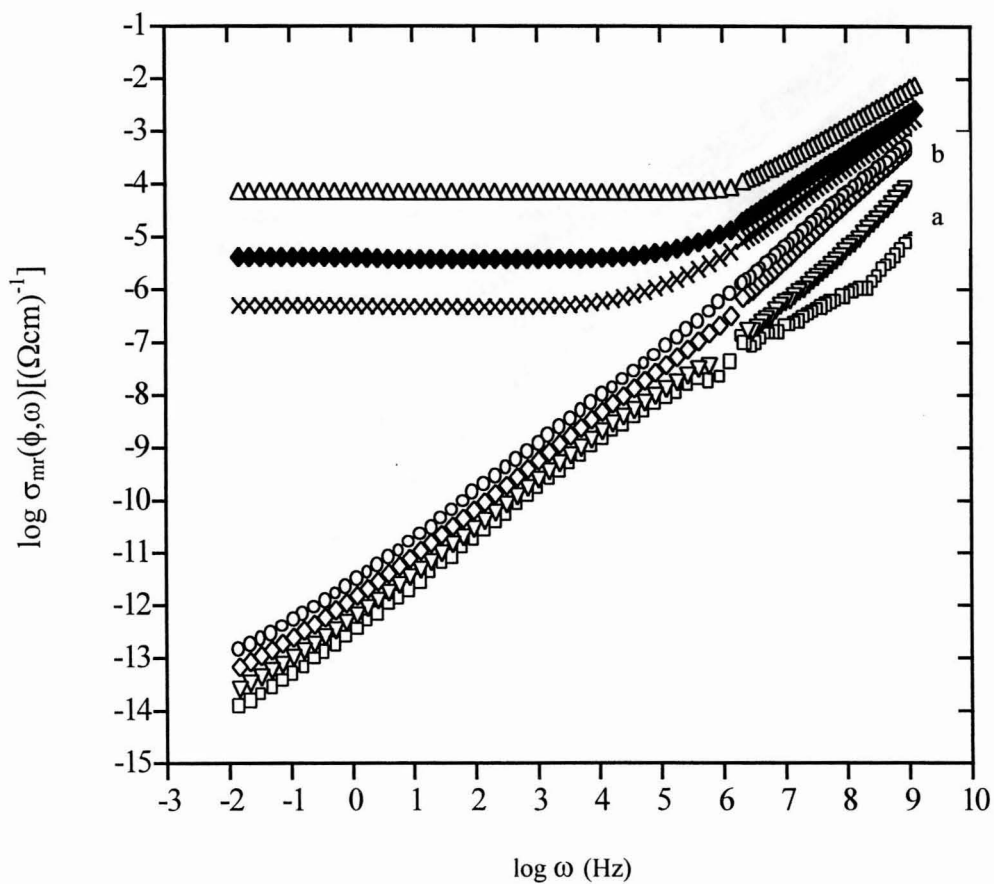


Figure 5.2: A log-log plot of AC conductivity versus frequency for the Graphite-Boron Nitride system over the full experimental frequency range used. [$\phi = 0.0000$ ($\square$), $\phi = 0.0169$ (∇), $\phi = 0.0270$ ($\diamond$), $\phi = 0.0319$ ($\circ$), $\phi = 0.0333$ ($\times$), $\phi = 0.0336$ ($\blacklozenge$), $\phi = 0.0345$ (Δ), $\phi_c = 0.033 \pm 0.001$]. The samples $\phi = 0.0167$, 0.0176 , 0.0299 and 0.0351 have been left out in order to avoid congestion.

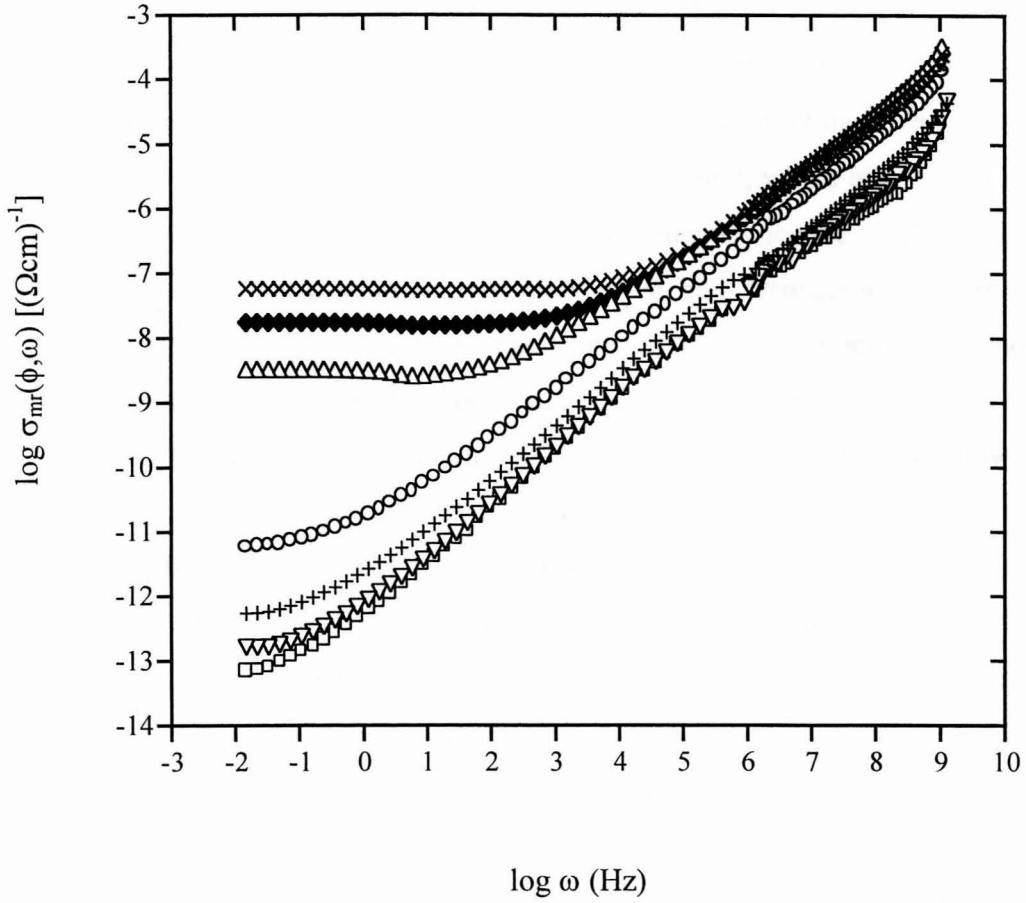


Figure 5.3: A log-log plot of AC conductivity versus frequency for the Niobium Carbide system over the full experimental frequency range. [$\phi = 0.0000$ ($\square$), $\phi = 0.0080$ (∇), $\phi = 0.0653$ ($+$), $\phi = 0.0742$ ($\circ$), $\phi = 0.0799$ (Δ), $\phi = 0.0831$ ($\blacklozenge$), $\phi = 0.0874$ ($\times$), $\phi_c = 0.065 \pm 0.006$]. Notice the upward hooks in the data at high frequency for this system. The samples $\phi = 0.0187, 0.0210, 0.0329, 0.0485, 0.0610, 0.0670, 0.0714$ and 0.0733 have been left out in order to avoid congestion.

(Laibowitz and Gefen 1984, Song *et al.* 1986, Chen and Johnson 1991, Smilauer 1991, Wu 1997, Wu and McLachlan 1998) existing in the samples above ϕ_c .

As the frequency of the applied signal is increased above a certain value ω_c , referred to here as the crossover frequency, the conductivity starts to increase (from its constant DC value) due to the extra contribution from the capacitive regions, which offer ever-decreasing impedance to current flow. The actual value of ω_c depends on the concentration (ϕ or $(\phi - \phi_c)$) of the conducting component, which also determines its DC conductivity (Song *et al.* 1986). There is also a tendency for the results in some systems (NbC and Fe_3O_4) to show an upward hook at high frequencies. Figure 5.3 shows this phenomenon in the NbC system as an example but the effect is even more pronounced in the Fe_3O_4 system. It is not clear whether the high t exponents of the systems have anything to do with “the hooks”. Similar but less pronounced upward hooks in the dispersion plots are also observed in the Graphite-Talc-wax system (refer to Fig. 5.5), which has a t exponent of 1.93 ± 0.06 , very close to the universal value of 2.00. McLachlan and Heaney (1999) also observed the upward hooks in a Carbon Black-polyethylene system, with $t = 2.9 \pm 0.1$ (Heaney 1995). These results seem to indicate a correlation between the t exponent and the hooks in the AC conductivity at high frequency, as the hooks tend to be more pronounced in high t systems.

Some common features that are observed in all the AC results studied in this thesis (close to ϕ_c and in the insulating region) can be explained as follows. Close to but above the percolation threshold, only tortuous fisherman’s net conducting paths or backbones exist. However, the conducting paths are also connected by a network of capacitive junctions, which offer high impedance to current flow at low frequency. Therefore at the low frequencies, the current is restricted to the conducting backbones (Song *et al.* 1986, Smilauer 1991). As the frequency increases, the impedance of the capacitive junctions decreases, such that the impedance of the whole sample decreases from its ‘DC’ value. Consequently, at high frequencies and in the immediate neighbourhood of the percolation threshold, there is very little difference between the conducting and insulating samples as their response is nearly the same owing to the

large effect of the capacitive junctions. The log-log plots of the conductivity against frequency are almost parallel to each other at the highest frequencies, as can be seen in the above three figures, for all samples near ϕ_c .

Insulating samples (well below ϕ_c) do not contain any DC percolation paths because the conducting clusters are separated by a large number of insulating regions, which offer high impedance to current flow at zero and low frequencies. The real conductivity of the insulating samples therefore continues to increase with frequency as the inter-cluster capacitive junctions offer less impedance to current flow with increasing frequency. The raw or insulating sample ($\phi = 0.00$) also shows a decrease in slope with frequency between 10^5Hz and 10^8Hz , after which the slope increases again on approaching 10^9Hz . This behaviour gradually changes as more conducting material is added (increasing ϕ), causing the curves to become linear up to 10^9Hz (except those showing the upward hooks).

The slopes of the conductivity curves for the samples below ϕ_c (Figs. 5.1-5.3) can be explained in terms of the dielectric loss in the samples (McLachlan *et al.* 1998 and 2000). Below ϕ_c , there are two dielectric loss terms contributing to $\epsilon_{mi} = \sigma_{mr}/\epsilon_0\omega$. One is due to the insulator (Talc-wax) and the other contribution is from the conducting clusters. Well below ϕ_c and at low frequencies, the dielectric loss term of the conducting clusters (which has a slope just greater than one) is not easy to detect, as it is masked by the dielectric loss of the insulator (with a slope of ~ 0.90). However, as the frequency increases, the dielectric loss due to the insulator has a slope lower than 0.90 (curve **a** in Fig. 5.2), which allows the loss due to the conducting clusters ($\sigma_{mr} \sim \omega^{(1+t)/t}$) to be clearly visible (curve **b** in Fig. 5.2 for the Graphite-Boron Nitride system). The results for this system have been modeled with reasonable success in an article by McLachlan *et al.* (2000).

Another noticeable feature of the insulating samples is the leveling off of the conductivity curves at low frequencies in the systems, indicating a small but finite DC conductivity (Figs. 5.1-5.3) even in the raw/insulating component. As all necessary

precautions were taken to avoid moisture contamination of the samples (by storing both the powders and compressed samples in dessicators with silica gel), this finite conductivity is almost certainly not due to moisture. Therefore, as it is also present in the $\phi = 0.00$ sample, the finite DC conductivity must be a fundamental property of the insulating component. The only exception to this behaviour is observed in the three-component system of Graphite, Boron Nitride and Talc-wax, where the Talc-wax is coated by 0.15 volume fraction of Boron Nitride in the $\phi = 0.00$ sample. Boron Nitride has a higher resistivity ($1 \times 10^{16} \Omega \text{cm}$ in the axial (pressure) and $4.2 \times 10^{14} \Omega \text{cm}$ in the transverse direction, as determined by Wu and McLachlan (1997)) than Talc-wax, which has a mean resistivity value of about $1.0 \times 10^{14} \Omega \text{cm}$ in the compression direction. As the Boron Nitride is a better insulator, coating the Talc-wax with this powder results in even more insulating samples, which do not indicate a finite DC conductivity in the frequency range used in the present study.

5.1.1 The scaling exponents x and y

The scaling function $F_{\pm}$, given in section 2.4, is a function of the ratio ω/ω_c , where ω_c is the frequency at which the frequency independent conductivity plateau (for samples close to but above the percolation threshold) ends (see Figs. 5.1 – 5.3). Several authors (Laibowitz and Gefen 1984, Connor *et al.* 1998, Wu and McLachlan 1998, McLachlan *et al.* 1998 and the present work) have reported on experimental evidence suggesting that the log-log plot of the real conductivity ($\sigma_{mr}(\phi, \omega)$) versus the frequency (ω) curves are parallel to each other above the frequency ω_c for conductor concentration ϕ greater than but close to ϕ_c . Assuming that the shape of the conductivity curve is independent of ϕ and that only the value of $\sigma_m(\phi, 0)$ and ω_c depend on ϕ , it is possible to construct an AC scaling curve (which is independent of ϕ) of the normalised conductivity ($\sigma_{mr}(\phi, \omega)/\sigma_m(\phi, 0)$) versus the reduced frequency (ω/ω_c). One advantage of a scaling curve is that it allows extrapolation of the

conductivity behaviour of a specific conductor-insulator composite over a frequency range that is not experimentally attainable.

Shown in Figs. 5.4 – 5.6 are the scaled results for the raw Carbon Black, Graphite and Niobium Carbide systems respectively. The value of ω_c for each sample was determined as the point where the high frequency conductivity curve intersected the $\log(\sigma_{mr}(\phi, \omega)/\sigma_m(\phi, 0)) = 0$ axis on a plot of $\log(\sigma_{mr}(\phi, \omega)/\sigma_m(\phi, 0))$ versus $\log(\omega)$. These values of ω_c were then used to scale the conductivity results of each sample on the $\log(\omega)$ axis. The results of this are shown in Figs. 5.4 – 5.6. The scaling exponent (x) was obtained from a linear fit to the regions of the scaled plots where $\log(\omega/\omega_c) > 1$. Table 5.1 gives the experimental values of x (denoted x_{exp}) for all the systems studied except for the Nickel system, in which the large conductivity of the Nickel made it difficult to fabricate samples in the crossover region. The inter-cluster polarisation model (section 2.4, eqn. (2.39)), predicts that $x = t/(s + t)$, where s and t are the dielectric and conductivity exponents respectively. Using the DC values of s and t given in Table 4.1, a theoretical exponent (x_{calc}) was calculated from the above expression and the values are given in Table 5.1. For comparison, x_{calc}' , obtained when s is replaced by s' (measured at 1kHz and found to be different from s as shown in Table 4.2), is also included. Note that because of the decrease in s' with frequency in the cellular systems, the values of x_{calc}' at 1MHz are found to be greater than those calculated using s' at 1kHz (Table 5.1), and hence show more disagreement with x_{exp} values than the 1kHz results.

Experimental values of x obtained from the scaled plots for all the systems studied in this thesis are in the range 0.71 - 0.85. The high t systems (containing Fe_3O_4 and Niobium Carbide) give the lowest values of x_{exp} (0.73 ± 0.01 and 0.71 ± 0.01 respectively) which are in serious disagreement with the values of x_{calc} (which are 0.90 ± 0.67 and 0.93 ± 0.47 respectively), calculated using the inter-cluster polarisation model expression. However, the experimental values lie within the large error bars of the calculated values. The other four systems (the two Carbon blacks and the two Graphite-containing systems) also have x_{exp} values somewhat greater than the

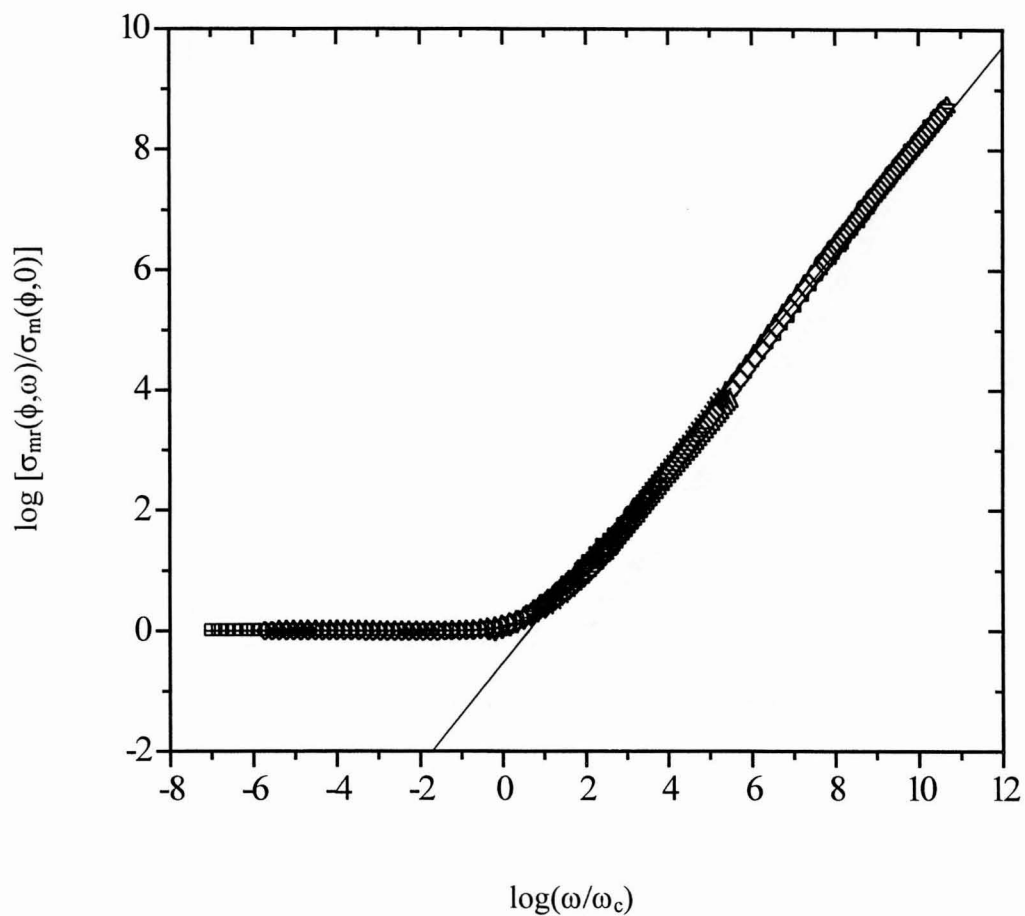


Figure 5.4: The scaled plot of the AC conductivity versus frequency for the raw Carbon Black system. The solid line is a linear fit to the data from which the exponent x (from the relation $\sigma_m(\phi, \omega) \propto \omega^x$) is found to be $x = 0.85 \pm 0.01$. [$\phi = 0.01225$ (Δ), $\phi = 0.01291$ (ϕ), $\phi = 0.01334$ ($+$), $\phi = 0.01343$ (x), $\phi = 0.01363$ (O), $\phi = 0.01447$ ($\square$)].

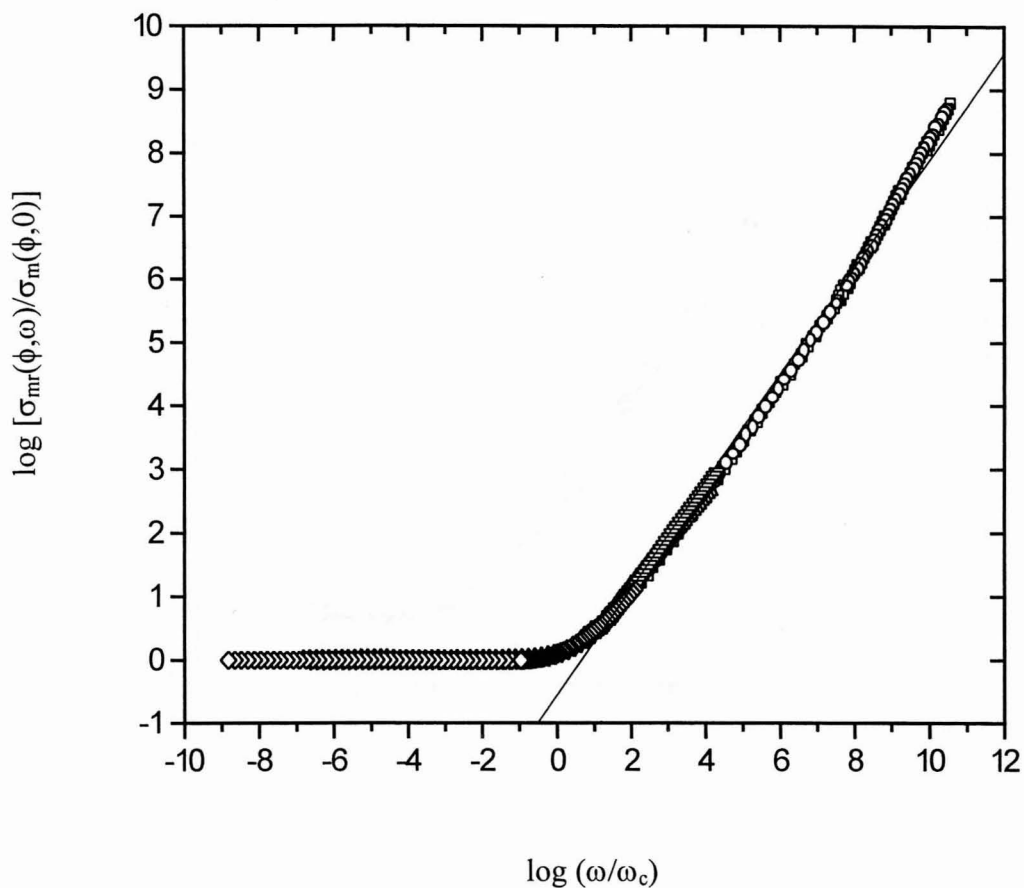


Figure 5.5: The scaled plot of the AC conductivity versus frequency for the Graphite system. The solid line is a linear fit to the data from which the exponent x (from $\sigma_m(\phi, \omega) \propto \omega^x$) is found to be $x = 0.84 \pm 0.01$. [$\phi = 0.03126$ ($\square$), $\phi = 0.03275$ ($\circ$), $\phi = 0.03528$ ($+$), $\phi = 0.03531$ (Δ), $\phi = 0.03613$ ($\diamond$)]. The reason for the up-turn at the high frequency end is not known.

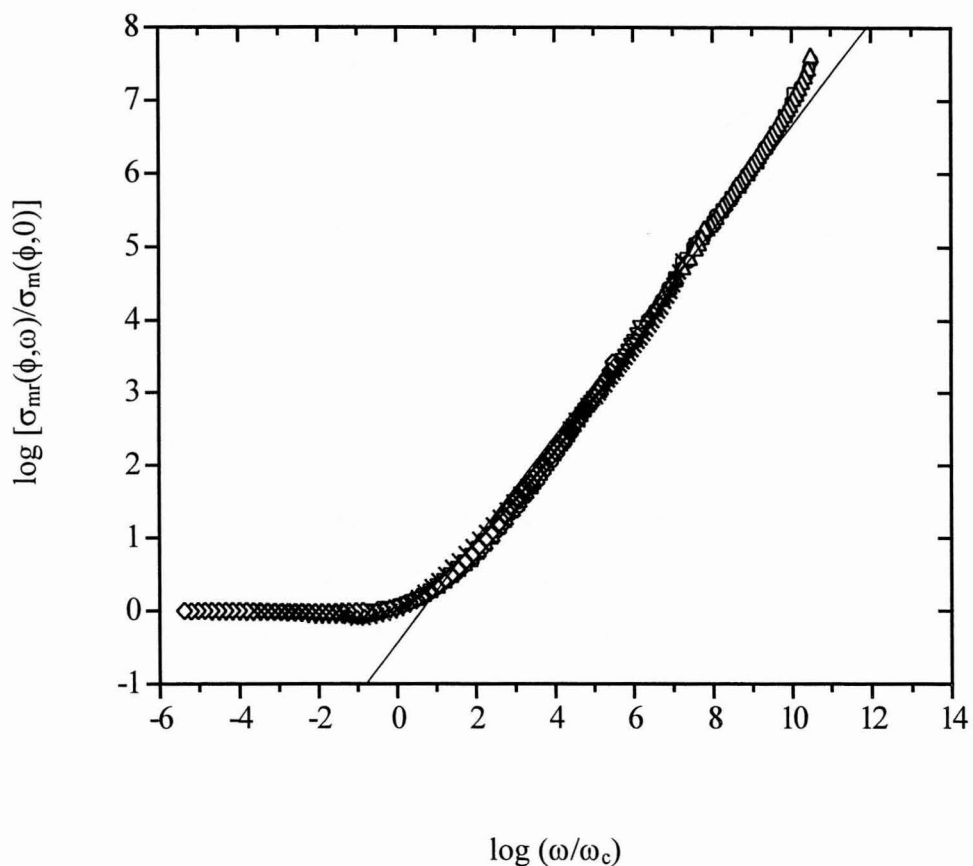


Figure 5.6: The scaled plot of the AC conductivity versus frequency for the Niobium Carbide system. The solid line is a linear fit to the data from which the exponent x (from the relation $\sigma_m(\phi, \omega) \propto \omega^x$) is found to be $x = 0.71 \pm 0.01$. [$\phi = 0.07145$ (O), $\phi = 0.07333$ ($\square$), $\phi = 0.07425$ (Δ), $\phi = 0.07987$ (+), $\phi = 0.08313$ (∇), $\phi = 0.08742$ ($\diamond$)]. Notice the upward hooks in the data at high frequency for this system.

Table 5.1: The exponent x from scaled AC conductivity plots

Composite System	x_{exp}	$x_{\text{calc}}=t/(s+t)$	$x'_{\text{calc}}=t/(s'+t)$
Ground Carbon Black	0.78 ± 0.01	0.66 ± 0.19	0.85 ± 0.14
Raw Carbon Black	0.85 ± 0.01	0.72 ± 0.20	0.84 ± 0.10
Ground Graphite	0.84 ± 0.01	0.74 ± 0.19	0.79 ± 0.06
Graphite-BN(15%)	0.77 ± 0.01	0.66 ± 0.13	0.82 ± 0.10
Nickel		0.58 ± 0.37	0.80 ± 0.12
Magnetite	0.73 ± 0.01	0.90 ± 0.67	$0.98 \pm 0.15^*$
Niobium Carbide	0.71 ± 0.01	0.93 ± 0.47	$0.96 \pm 0.17^*$

*Note that the high t systems give high values of the exponents x_{calc} and x'_{calc} , which are larger than and in disagreement with x_{exp} . Coincidentally, the x_{exp} for the high t systems are in good agreement with $x = 0.72$, obtained when the universal values of s and t are used in eqn. (2.39).

x_{calc} exponents but not x'_{calc} (as defined above and given in Table 5.1). The values of x'_{calc} are closer to x_{exp} than x_{calc} in these four systems. The raw Carbon Black and the Graphite systems also give values of x_{calc} very close to 0.72 (a value which is obtained when the universal values of s and t for 3D continuum systems (Song *et al.* 1986) are used in the inter-cluster polarisation model expression). This is not surprising as the systems have s and t exponents (Table 4.1) close to the universal values.

Despite the above disagreements between x_{exp} , x_{calc} and x'_{calc} , experimental values of x (x_{exp}) measured on the cellular systems are in reasonable agreement with previous studies on 3D continuum percolation systems. Wu and McLachlan (1998) obtained $x_{\text{exp}} = 0.82 \pm 0.02$, 0.94 ± 0.02 and 0.87 ± 0.01 for the compacted Graphite-Boron Nitride disc samples, 50% -50% and 55% - 45% powder mixtures of Graphite and Boron Nitride respectively. Using the measured DC conductivity and dielectric exponents, the corresponding values of x_{calc} (x'_{calc}) for the same systems are: 0.72 ± 0.01 (0.83 ± 0.06), 0.92 ± 0.11 (0.89 ± 0.01) and 0.91 ± 0.04 (0.87 ± 0.04) respectively. The value of x_{exp} obtained in the Graphite Boron Nitride disc samples agrees particularly well with the values of the two Graphite containing systems in the present study. In addition, the results from the Graphite-Boron Nitride disc samples show that $x_{\text{exp}} > x_{\text{calc}}$ and that x'_{calc} is very close to x_{exp} , a trend which is evident in the Graphite and Carbon Black systems shown in Table 5.1. The powder systems studied by Wu and McLachlan (1998) show good agreement of all the exponents (x_{exp} , x_{calc} and x'_{calc}). McLachlan and Heaney (1999) studied the AC conductivity of a Carbon Black-polyethylene composite and measured $x_{\text{exp}} = 0.94$. Using their measured t exponent and assuming a minimum s value of 0.50, the same authors found $x_{\text{calc}} = 0.85$, again showing x_{exp} is probably greater than x_{calc} .

Chen and Johnson (1991) studied the AC conductivity of three different random metal-insulator composites near their respective percolation thresholds. The systems consisted of filamentary and nodular shaped Nickel particles embedded in a polypropylene matrix and Silver particles in a Potassium Chloride matrix. The experiments covered a frequency range from 5Hz to 13MHz. Values of the exponent

x_{exp} obtained were 0.88 ± 0.01 and 0.81 ± 0.01 for the filamentary and nodular Nickel systems respectively and 0.77 ± 0.01 for the Ag-KCl system. Using the DC t and s exponents ($t = 3.1 \pm 0.3$, 2.2 ± 0.1 and $s = 0.55 \pm 0.10$, 0.62 ± 0.10), the calculated values of x are 0.85 ± 0.24 and 0.78 ± 0.16 for the filamentary and nodular Nickel systems respectively. Again the experimental values of the Nickel systems lie within the large error bars of the calculated x exponents. The exponent x for the Ag-KCl system agrees well with the experimental values obtained in the ground Carbon Black and the three-component Graphite-Boron Nitride system. Chen and Johnson's experiments (1991), showed agreement between x_{exp} and x_{calc} while those of Wu and McLachlan (1998), illustrate that agreement between theory (inter-cluster model) and experiment (x_{exp}) occurs only if the experimental (non-universal) values of s and t are used to determine exponent x_{calc} . The results presented in Table 5.1 show disagreement between x_{exp} and x_{calc} for all systems while x_{exp} and x_{calc} are reasonably close, only for the low t systems.

Song *et al.* (1986) measured $x = 0.86 \pm 0.06$ in a 3D compacted mixture of Carbon and teflon in the frequency range 10Hz to 13MHz, a value which was also in disagreement with the universal 3D value of 0.72. Unfortunately no measurements were done to obtain the experimental values of the exponents s and t to compute x_{calc} using the inter-cluster model expression for comparison with their experimental x value. Chakrabarty *et al.* (1993) measured the AC conductance of Carbon-paraffin wax mixtures in the low frequency regime of 7Hz to 100kHz close to the percolation threshold and reported a value of $x = 0.72 \pm 0.01$, which is in excellent agreement with the interacting cluster model value obtained using the universal values of s and t in three dimensions. However, their result could not be verified, as they did not measure the DC s and t in the same system.

More recently, Connor *et al.* (1998) obtained $x = 0.72$ in a Carbon Black in polyethylene terephthalate (PET) composite. A t exponent of 2.17 was measured in the system. Unfortunately, no value for the exponent s was measured so as to correlate the result with the predictions of the inter-cluster polarisation model ($x = t/(s + t)$).

However, their experimental x value is in very good agreement with the interacting cluster model prediction when the universal values of s and t in three dimensions are used in the above expression.

Below ϕ_c , the exponent y is obtained from the log-log plot of the imaginary AC conductivity ($\omega\epsilon_{mr}(\phi, \omega)$) against frequency using the relationship $\omega\epsilon_{mr}(\phi, \omega) \propto \omega^{1-y}$. Alternatively, the exponent y can be obtained from the log-log plot of the real dielectric constant against frequency (ω) using the relation $\epsilon_{mr}(\phi, \omega) \propto \omega^{-y}$. Examples of the latter plots are presented in section 5.1.3 but were not used to find the exponent y . Values of the exponent y were determined from the relation ($\omega\epsilon_{mr}(\phi, \omega) \propto \omega^{1-y}$). Some representative plots based on this relation are given in Figs. 5.7 and 5.8, which show the results for the raw Carbon Black and Niobium Carbide systems respectively. The experimental values of y for these and the rest of the systems are shown in Table 5.2. These values range from 0.04 to 0.12, with the lowest values being obtained from the high t -low s systems, with Fe_3O_4 and Niobium Carbide powders. These experimental values are all lower than values obtained from calculations, based on the inter-cluster polarisation model. The interacting cluster model also predicts that x and y should satisfy the relation; $x + y = 1$ (eqn. (2.38)).

Using the experimental values of x and y in Tables 5.1 and 5.2 respectively, only the ground Graphite ($x_{\text{exp}} + y_{\text{exp}} = 0.95 \pm 0.02$), ground Carbon Black ($x_{\text{exp}} + y_{\text{exp}} = 0.90 \pm 0.02$) and raw Carbon Black ($x_{\text{exp}} + y_{\text{exp}} = 0.92 \pm 0.02$) have values reasonably close to unity. It is worth noting that these systems have s and t values (Table 4.1) close to the universal values. The rest of the systems have the sum of the x and y exponents well below unity, even when the errors are taken into account. This is a rather different and perplexing result when comparison is made with previous studies (for instance Song *et al.* 1986, Chen and Johnson 1991, Chakrabarty *et al.* 1993, Wu and McLachlan 1998). It is interesting to note that the high t systems show the largest discrepancy with $x_{\text{exp}} + y_{\text{exp}} = 1$.

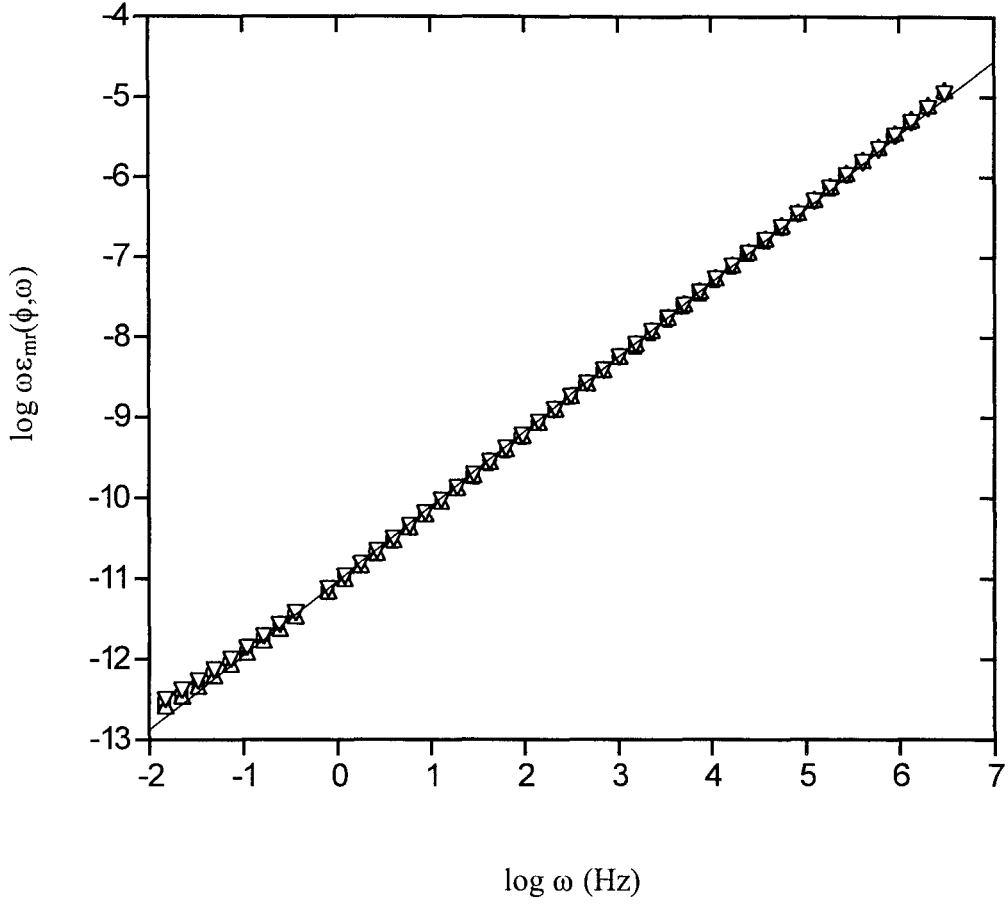


Figure 5.7: A log-log plot of the imaginary AC conductivity ($\omega\epsilon_{mr}(\phi, \omega)$) against the frequency (ω) for the raw Carbon Black system. The solid line is a linear fit to the data from which the value of the exponent y (from $\omega\epsilon_{mr}(\phi, \omega) \propto \omega^{1-y}$) is found to be $y = 0.074 \pm 0.003$ [$\phi = 0.01044$ ($\square$), $\phi = 0.01088$ ($\circ$), $\phi = 0.01077$ ($\triangle$), $\phi = 0.01134$ (∇), $\phi_c = 0.0131 \pm 0.0006$].

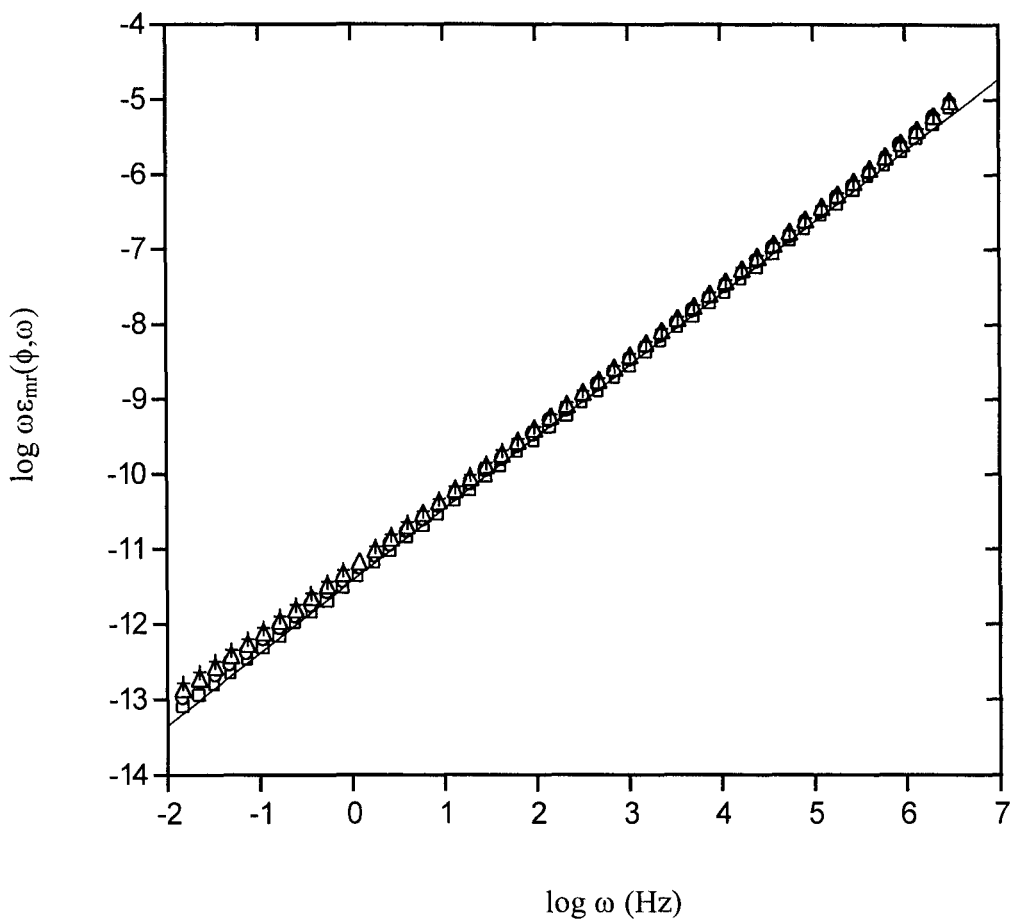


Figure 5.8: A log-log plot of the imaginary AC conductivity ($\omega\epsilon_{mr}(\phi, \omega)$) against the frequency (ω) for the Niobium Carbide system. The solid line is a linear fit to the data from which the value of the exponent y (from $\omega\epsilon_{mr}(\phi, \omega) \propto \omega^{1-y}$) is found to be $y = 0.042 \pm 0.002$ [$\phi = 0.0329$ ($\square$), $\phi = 0.0610$ ($\circ$), $\phi = 0.06528$ (Δ), $\phi = 0.06705$ ($+$), $\phi_c = 0.065 \pm 0.006$].

Table 5.2: The exponent y from AC conductivity plots

Composite System	y_{exp}	$*y_{\text{calc}}$	$*y_{\text{calc}}'$
Ground Carbon Black	0.119 ± 0.004	0.34 ± 0.10	0.15 ± 0.02
Raw Carbon Black	0.074 ± 0.003	0.28 ± 0.08	0.16 ± 0.02
Ground Graphite	0.106 ± 0.004	0.25 ± 0.06	0.21 ± 0.01
Graphite-BN(15%)	0.059 ± 0.002	0.34 ± 0.07	0.18 ± 0.02
Nickel	0.078 ± 0.003	0.42 ± 0.27	0.20 ± 0.03
Magnetite	0.051 ± 0.003	0.10 ± 0.07	0.020 ± 0.003
Niobium Carbide	0.042 ± 0.002	0.07 ± 0.04	0.040 ± 0.007

Composite System	x_{exp}	y_{exp}	$**x_{\text{exp}} + y_{\text{exp}}$
Ground Carbon Black	0.78 ± 0.01	0.119 ± 0.004	0.90 ± 0.01
Raw Carbon Black	0.85 ± 0.01	0.074 ± 0.003	0.92 ± 0.01
Ground Graphite	0.84 ± 0.01	0.106 ± 0.004	0.95 ± 0.01
Graphite-BN(15%)	0.77 ± 0.01	0.059 ± 0.002	0.83 ± 0.01
Nickel		0.078 ± 0.003	
Magnetite	0.73 ± 0.01	0.051 ± 0.003	0.78 ± 0.01
Niobium Carbide	0.71 ± 0.01	0.042 ± 0.002	0.75 ± 0.01

* The y_{calc} and y_{calc}' values were calculated from $y = s/(s + t)$ using the DC s and t exponents and s' (measured at 1kHz) respectively.

**Note that these values are supposed to be equal to unity as expected from eqn. (2.38).

Values of the exponent y reported in the literature range from 0.10 to 0.24. From the present study, only the ground Carbon Black and Graphite systems have values within this range. Wu and McLachlan (1998) measured $y_{\text{exp}} = 0.14 \pm 0.02$, 0.07 ± 0.01 and 0.10 ± 0.01 in the compacted Graphite-Boron Nitride, 50-50% and 55-45% Graphite-Boron Nitride powder mixtures respectively. In the same systems, values of $y_{\text{calc}}(y'_{\text{calc}})$ were 0.28 ± 0.02 (0.17 ± 0.01), 0.08 ± 0.01 (0.11 ± 0.01) and 0.09 ± 0.05 (0.13 ± 0.01) respectively. The powder systems showed reasonably good agreement for all the y exponents. For the compacted Graphite-Boron Nitride system, the y_{calc} exponents are greater than y_{exp} . McLachlan and Heaney (1999) measured $y_{\text{exp}} = 0.10$ and calculated $y_{\text{calc}} = 0.15$ in a Carbon Black-polyethylene system. Song *et al.* (1986) obtained $y_{\text{exp}} = 0.12 \pm 0.04$ in a 3D Carbon-teflon mixture. Chakrabarty *et al.* (1993) reported $y_{\text{exp}} = 0.23 \pm 0.05$ in a Carbon-paraffin wax 3D system. In three systems containing nodular and filamentary Nickel in a polypropylene matrix and Silver particles in a Potassium Chloride matrix, Chen and Johnson (1991) measured $y_{\text{exp}} = 0.14 \pm 0.01$, 0.13 ± 0.04 and 0.22 ± 0.01 respectively. In all these systems, fairly good agreement is shown with the relation $x + y = 1$.

Measurements have also been done in two dimensions to determine the exponents x and y . Laibowitz and Gefen (1984) studied the AC conductivity of thin Gold films in the frequency range of 100Hz to 10MHz. They obtained $x = 0.95 \pm 0.05$ and $y = 0.13 \pm 0.05$, which were in disagreement with the theoretical prediction of $x = y = 0.50$ (for the interacting cluster model) obtained using the universal values of s and t ($s = t = 1.3$) in two dimensions (Clerc *et al.* 1990, Nan 1993). However, the exponents sum to 1.08 ± 0.10 , in good agreement with $x + y = 1$. Hundley and Zetl (1988) reported measurements of the AC conductivity of percolating thin gold films at temperatures between 300K and 4.2K within the frequency range of 100Hz and 1GHz. They observed that the conductivity $\sigma_m(\phi, \omega)$ of their samples was highly temperature-dependent below 100K. For a particular sample with DC resistance around 2k Ω , the conductivity was found to scale with an exponent $x_{\text{exp}} = 1.00 \pm 0.05$ between 60kHz and 3MHz but the exponent x dropped to $x_{\text{exp}} = 0.32 \pm 0.05$ above 3MHz. Within

these frequency ranges, the exponent y varied from $y_{\text{exp}} = 0$ to $y_{\text{exp}} = 0.80 \pm 0.05$ respectively. It can be noted that in both frequency ranges the exponents obeyed the relation; $x_{\text{exp}} + y_{\text{exp}} = 1$.

In a two-dimensional lattice percolation system, Yoon and Lee (1990) measured $x_{\text{exp}} = 0.996 \pm 0.050$ and $y_{\text{exp}} = 0.024 \pm 0.005$ in good agreement with the results of Laibowitz and Gefen on thin Gold films. The samples of Yoon and Lee were generated on an Aluminum film by means of a computer controlled x-y plotter. The AC conductivity and dielectric constant of these samples were measured in the frequency range of 10Hz to 1MHz. Although these results and those given above obey the relation $x + y = 1$, the exponents are far from the predictions of both the inter-cluster polarisation and the anomalous diffusion models. However, the consistent values of x_{exp} and y_{exp} giving $x_{\text{exp}} + y_{\text{exp}} < 1$ observed in the results from the different systems, exposes the shortcomings of the models. A unified theory, which takes into account both the interacting cluster and anomalous diffusion on the percolation clusters, may provide an explanation of these results but such a theory is not yet available.

5.1.2 Scaling Properties of the AC Conductivity above the Percolation Threshold

As noted earlier in section 5.1.1, scaling laws require that the scaled experimental results of the complex AC conductivity on the conducting side of the percolation threshold ($\phi > \phi_c$) depend only on ω/ω_{c+} , where ω_{c+} is as defined in section 2.4. Plots of the reduced AC conductivity ($\sigma_{\text{mr}}(\phi, \omega)/\sigma_{\text{m}}(\phi, 0)$) versus reduced frequency (see for instance Laibowitz and Gefen (1984), Song *et al.* (1986), Connor *et al.* (1998), Wu and McLachlan (1998), McLachlan *et al.* (1998), McLachlan and Heaney (1999)) were given for some of the systems studied in this thesis, in Figs. 5.4 - 5.6, from which the exponent x was determined. Figures 5.9 – 5.11 show the same results for the raw

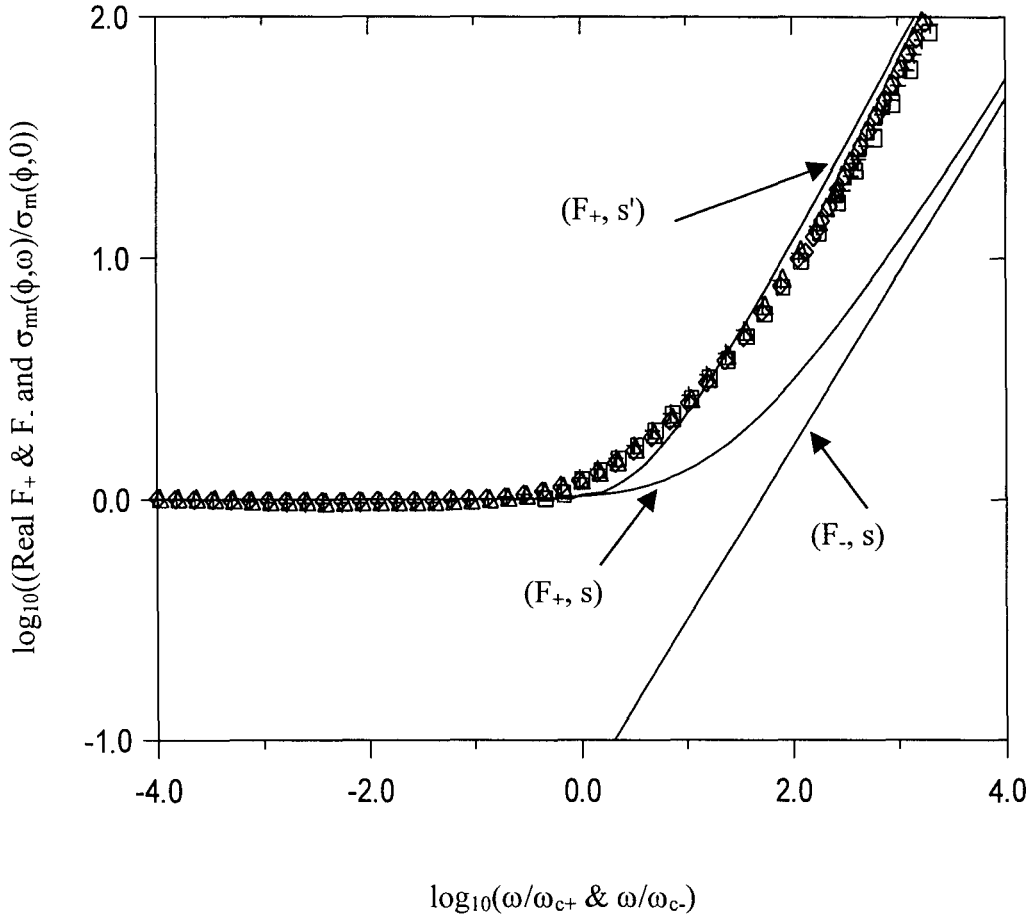


Figure 5.9: Log-log plot of the reduced AC conductivity versus reduced frequency for the raw Carbon Black system for the samples $\phi = 0.01291$ ($\square$), $\phi = 0.01343$ (Δ), $\phi = 0.01351$ ($\diamond$) and $\phi = 0.01334$ (+). The scaling functions F_+ and F_- (solid lines) are obtained using the DC parameters $\sigma_c = 6.166(\Omega\text{cm})^{-1}$, $\sigma_i = 9.120 \times 10^{-15}(\Omega\text{cm})^{-1}$, $\phi_c = 0.0131 \pm 0.0006$, $s = 0.90 \pm 0.20$ and $t = 2.26 \pm 0.11$). F'_+ is obtained using the same parameters but with s replaced by $s' = 0.43 \pm 0.03$. Note the close agreement between F'_+ and the experimental results.

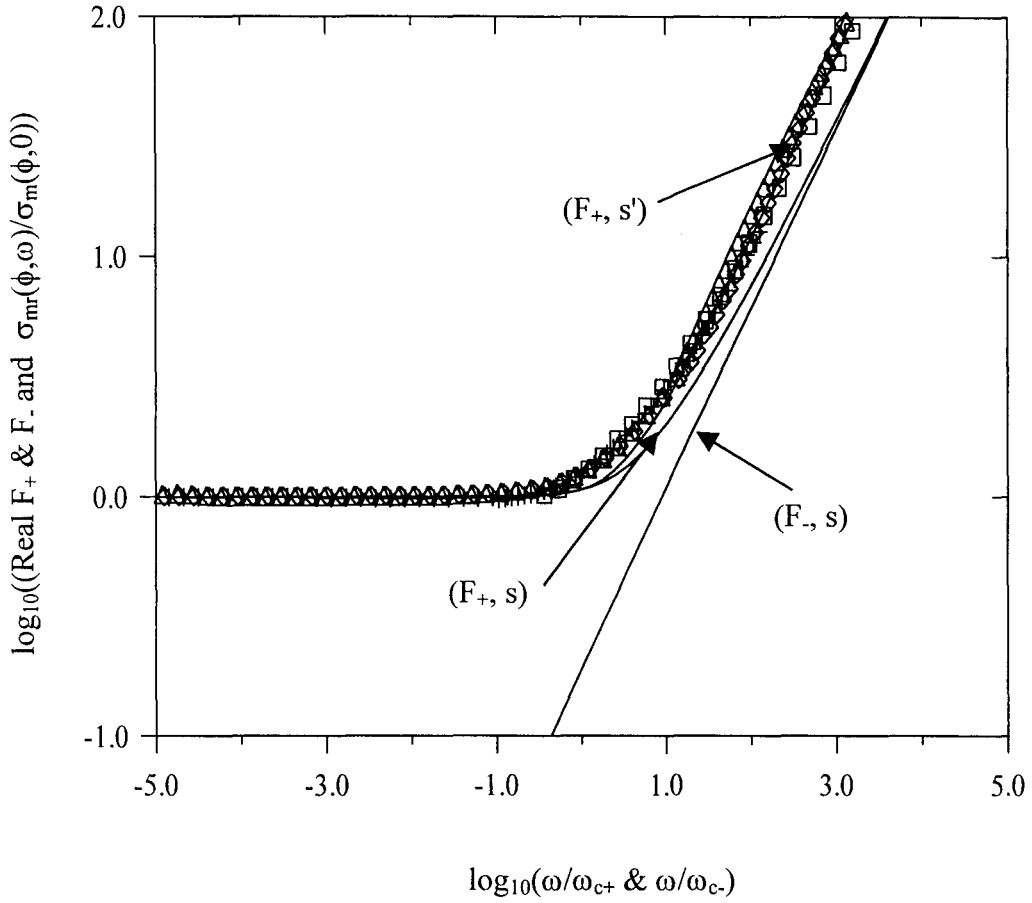


Figure 5.10: Log-log plot of the reduced AC conductivity versus reduced frequency for the Graphite system for the samples $\phi = 0.03275$ ($\square$), $\phi = 0.03531$ (Δ), $\phi = 0.03528$ ($\diamond$) and $\phi = 0.03613$ (+). The scaling functions F_+ and F_- (solid lines) are obtained using the DC parameters $\sigma_c = 251(\Omega\text{cm})^{-1}$, $\sigma_i = 1.100 \times 10^{-14}(\Omega\text{cm})^{-1}$, $\phi_c = 0.035 \pm 0.002$, $s = 0.66 \pm 0.15$ and $t = 1.93 \pm 0.06$. F'_+ is obtained using the same parameters but with s replaced by $s' = 0.50 \pm 0.02$.

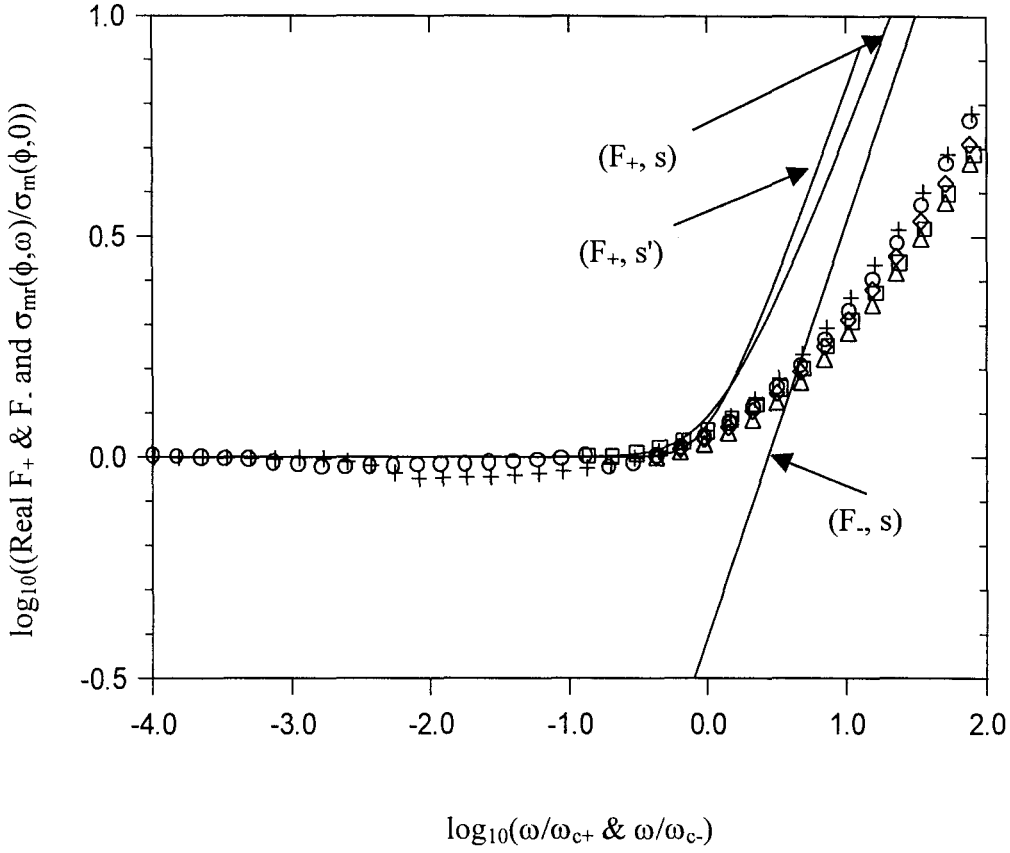


Figure 5.11: Log-log plot of the reduced AC conductivity versus reduced frequency for the Niobium Carbide system for the samples $\phi = 0.0714$ (Δ), $\phi = 0.0733$ ($\square$), $\phi = 0.0742$ ($\diamond$), $\phi = 0.0831$ (+) and $\phi = 0.0874$ ($\circ$). The scaling functions F_+ and F_- (solid lines) are obtained using the best-fit DC parameters $\sigma_c = 107.2(\Omega\text{cm})^{-1}$, $\sigma_i = 3.5481 \times 10^{-15}(\Omega\text{cm})^{-1}$, $\phi_c = 0.065 \pm 0.006$, $s = 0.37 \pm 0.14$ and $t = 5.25 \pm 0.67$. F'_+ is obtained using the same parameters but with s replaced by $s' = 0.21 \pm 0.01$. Note the disagreement between F_+ , F'_+ and the experimental results.

Carbon Black, Graphite and Niobium Carbide systems respectively, plotted together with the curves for F_+ and F_- given in section 2.4 (eqns. (2.45)). The curves were calculated from the fitted DC conductivity parameters of σ_c , σ_i , ϕ_c , s and t . The F_+ curve obtained using s' (as determined from dielectric measurements at 1kHz) and denoted F'_+ , is also included for comparison. The theoretical curves were generated by varying the frequency (ω) and volume fraction (ϕ) in order to build the curves over a large range of ω/ω_c .

The results shown in Figs. 5.9 – 5.11 have some common features. According to theory, the curves (F_+) should have a slope of $t/(s + t)$ for $\omega/\omega_{c+} > 1$ and the experimental results are expected to lie on these curves. However, the experimental results obtained from the cellular systems do not scale onto the F_+ theoretical curves, as can be seen in the above figures. Instead, the experimental results are found to lie closer to the F'_+ curves whose slopes are given by $t/(s' + t)$. This shows that s' gives better agreement with scaling theory than the exponent s . The curves for both F_+ and F'_+ coincide for small ω/ω_{c+} and only separate above $\omega/\omega_{c+} = 1$. Since the systems show better agreement with the F'_+ curve, obtained when s' (measured at 1kHz) is used to calculate the scaling curve instead of the DC s , this underscores the need to measure both s and s' in percolation systems. The high t systems of Niobium Carbide and Fe_3O_4 belong to a different category, as the experimental results do not scale close to either the F_+ or F'_+ curves (refer to Fig. 5.11). This is immediately obvious from Table 5.1, where the values of x_{exp} , x_{calc} and x'_{calc} for the systems are very different.

Note that in all the above scaling plots, the scaled experimental results can be moved a small amount backwards and forward along the $\log_{10}(\sigma_{\text{mr}}(\phi, \omega)/\sigma_{\text{m}}(\phi, 0)) = 0$ axis by varying ω_{c+} slightly for each curve. Even if this is done, the results always show disagreement with the theoretical (F_+ and F'_+) scaling curves.

5.1.3 The Dielectric Constant as a function of frequency

The real dielectric constant $\epsilon_{mr}(\phi, \omega)$ results of the cellular systems are illustrated by three representative plots of $\epsilon_{mr}(\phi, \omega)$ versus frequency ($10^{-2} - 10^9$ Hz). Figures 5.12 – 5.14 give log-log plots for the Graphite-Boron Nitride, ground Carbon Black and Fe_3O_4 systems respectively. The respective dielectric constants all decrease with frequency and appear to be converging towards the same value at very high frequencies (see for instance the results for the ground Carbon Black system in Fig. 5.13). The dielectric behaviour below the percolation threshold (ϕ_c) is dominated by the Talc-wax insulating component, which is highly dispersive as can be seen in the plots of Figs 5.13 and 5.14. The three-component system, containing some Boron Nitride, shows less dispersion than the other systems. This is not unexpected because as noted earlier for the three component system, the Talc-wax in the $\phi = 0.00$ sample is always coated by the more insulating and less dispersive Boron Nitride. Recall that the conducting Graphite progressively replaces the Boron Nitride coating as the volume fraction of the former is increased from 0.00 to 0.12.

In all the systems, the dielectric constant increases slowly at low volume fractions of the conducting component (ϕ). In this regime/region, the dielectric behaviour is dominated by the insulating component. As ϕ increases towards ϕ_c , due to the addition of the conducting component, the dielectric constant increases because of the effect of the conducting clusters. The dielectric constant continues to increase until it becomes unmeasurable just beyond ϕ_c as a result of the high conductivity of the conducting components. Results of the dielectric constant plotted against the volume fraction of the conducting component (just above ϕ_c) have already been presented in Chapter four.

The high t system of Magnetite (Fe_3O_4) shows unusual and interesting features of the dielectric constant behaviour as it is the only system in which the real dielectric constant could be measured well above the DC percolation threshold. As can be seen

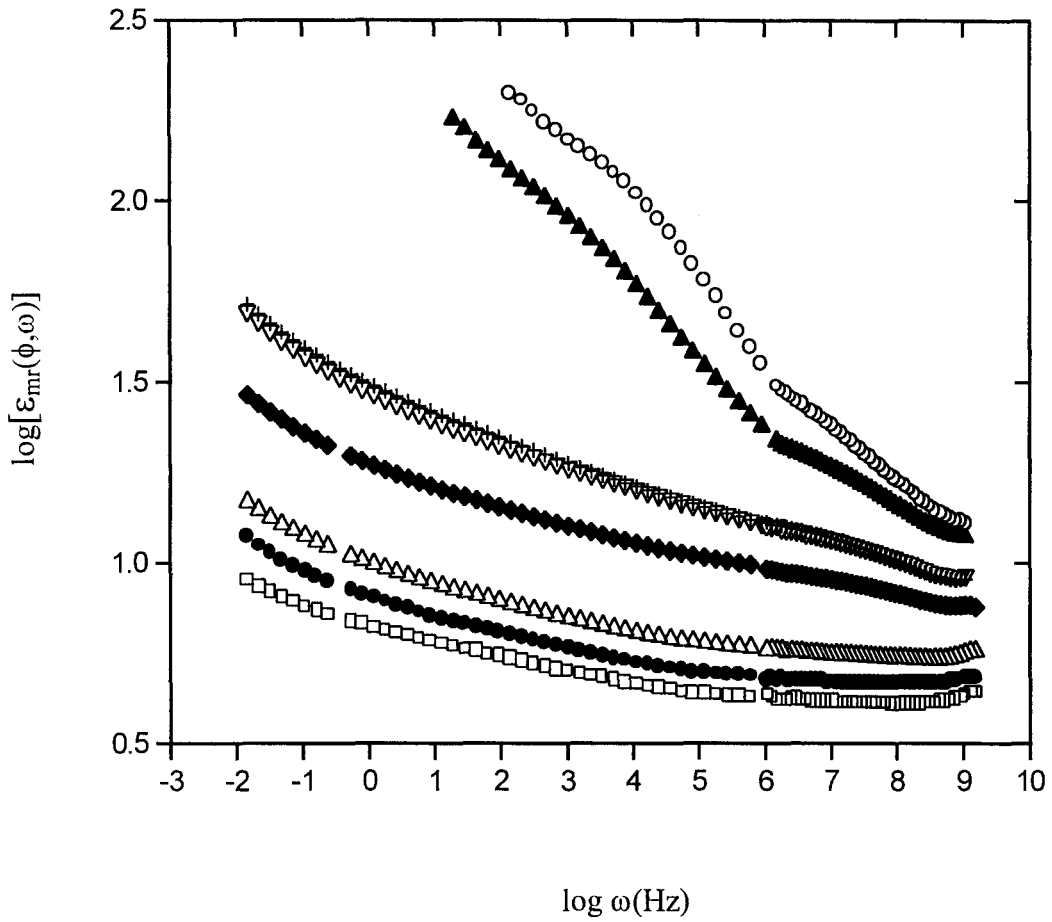


Figure 5.12: A log-log plot of the real dielectric constant of the composite ($\epsilon_{mr}(\phi, \omega)$) against the frequency (ω) for the Graphite-Boron Nitride system [$\phi = 0.0000$ ($\square$), $\phi = 0.0167$ ($\bullet$), $\phi = 0.0169$ (Δ), $\phi = 0.0270$ ($\blacklozenge$), $\phi = 0.0299$ (∇), $\phi = 0.0319$ ($+$), $\phi = 0.0333$ ($\blacktriangle$), $\phi = 0.0336$ ($\circ$)]. The percolation threshold, $\phi_c = 0.033 \pm 0.001$.

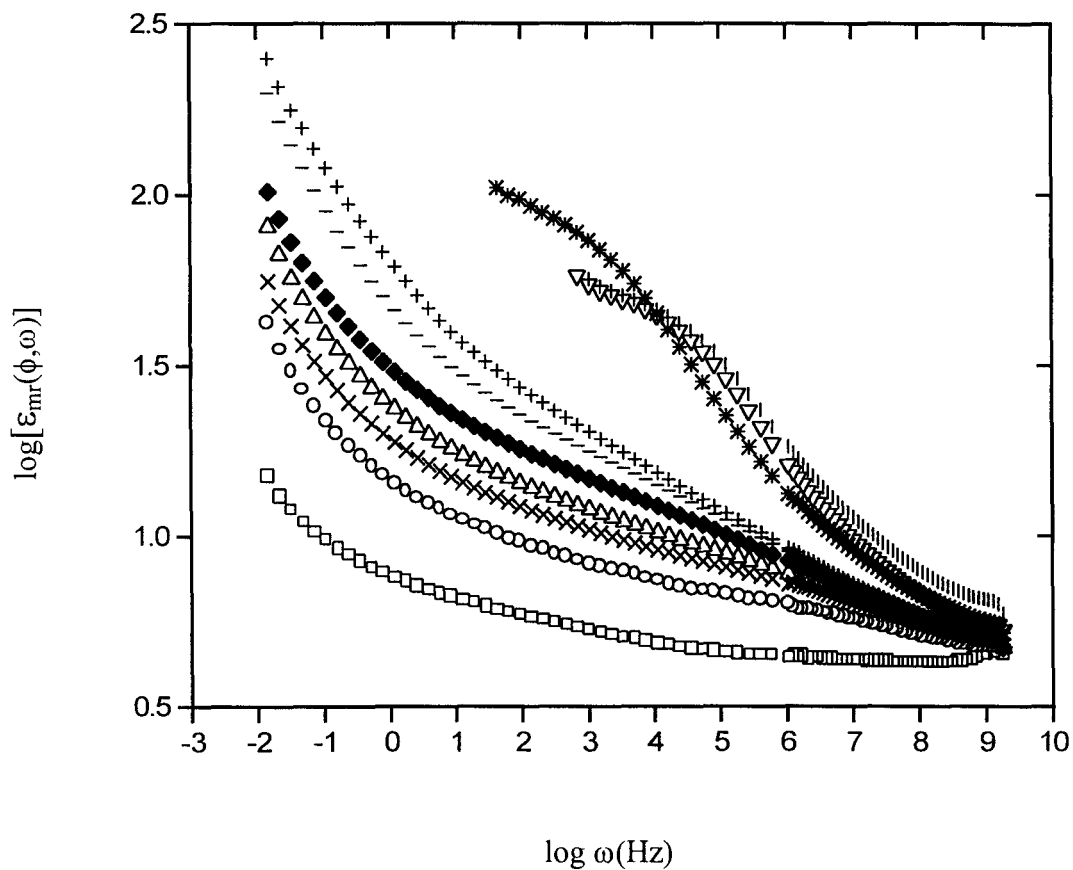


Figure 5.13: A log-log plot of the real dielectric constant of the composite ($\epsilon_{mr}(\phi, \omega)$) against the frequency (ω) for the ground Carbon Black system [$\phi = 0.0000$ ($\square$), $\phi = 0.00901$ ($\circ$), $\phi = 0.00914$ ($*$), $\phi = 0.0108$ (Δ), $\phi = 0.01221$ ($\blacklozenge$), $\phi = 0.01222$ ($-$), $\phi = 0.01223$ ($+$), $\phi = 0.01265$ ($*$), $\phi = 0.01333$ (∇), $\phi = 0.01360$ ($\circ$)]. The percolation threshold, $\phi_c = 0.0122 \pm 0.0007$.

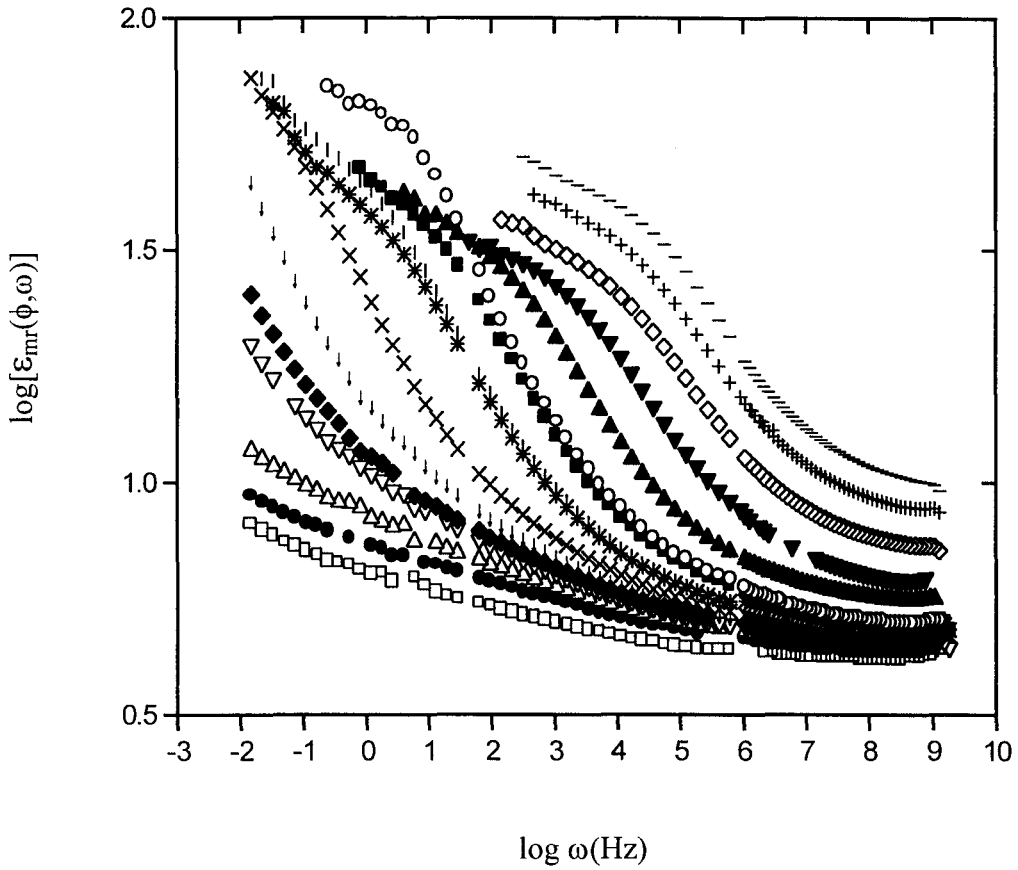


Figure 5.14a: A log-log plot of the real dielectric constant of the composite ($\epsilon_{mr}(\phi, \omega)$) against the frequency (ω) for the Magnetite (Fe_3O_4) system [$\phi = 0.0000(\square)$, $\phi = 0.0128(\bullet)$, $\phi = 0.0251(\Delta)$, $\phi = 0.0281(\nabla)$, $\phi = 0.0294(\blacklozenge)$, $\phi = 0.0344(\downarrow)$, $\phi = 0.0364(\times)$, $\phi = 0.0485(l)$, $\phi = 0.0498(*)$, $\phi = 0.0601(\blacksquare)$, $\phi = 0.0627(o)$, $\phi = 0.0871(\blacktriangle)$, $\phi = 0.1264(\blacktriangledown)$, $\phi = 0.1720(\diamond)$, $\phi = 0.2089(+)$, $\phi = 0.2310(-)$]. The percolation threshold, $\phi_c = 0.025 \pm 0.003$.

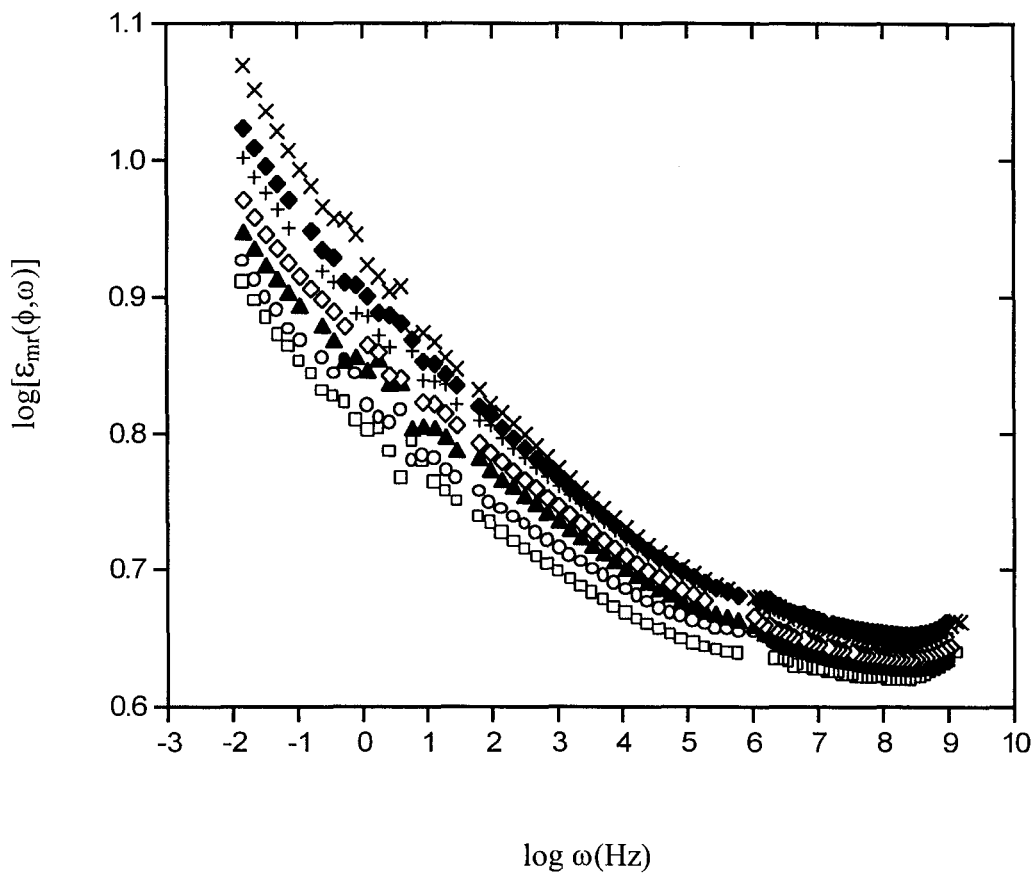


Figure 5.14b: A log-log plot of the real dielectric constant of the composite ($\epsilon_{mr}(\phi, \omega)$) against the frequency (ω) for the Magnetite (Fe_3O_4) system [$\phi = 0.0000$ ($\square$), $\phi = 0.0052$ ($\circ$), $\phi = 0.0077$ ($\blacktriangle$), $\phi = 0.0128$ ($\diamond$), $\phi = 0.0176$ ($+$), $\phi = 0.0219$ ($\blacklozenge$), $\phi = 0.0251$ ($\times$)]. The percolation threshold, $\phi_c = 0.025 \pm 0.003$.

in Figs. 4.9, 4.12 and 5.14 for this system, $\epsilon_{mr}(\phi, \omega)$ continues to increase even more rapidly (than the other systems studied in this thesis) above the percolation threshold, especially at low frequencies. Above ϕ_c , three distinct regions of different slopes can be identified in the more conducting samples, where the dielectric constant is still measurable across the whole frequency spectrum used in the experiments. Examples are the two samples represented by open circles and solid upright triangles in Fig. 5.14. Note that the results of some samples have also been omitted in this figure in order to avoid congestion.

5.1.4 The crossover frequency (ω_c) and the exponent q

The frequency ω_c , which characterises the region where the conductivity starts to deviate from the DC plateau to the region where it increases linearly with frequency, is supposed to scale with the DC conductivity as $\omega_c \propto \sigma_m(\phi, 0)^q$ (Hundley and Zettl 1988, Chakrabarty *et al.* 1993, Wu 1997, Wu and McLachlan 1998, McLachlan and Heaney 1999), where q is an exponent (section 2.4, eqn. (2.35)). The inter-cluster polarisation model, gives the exponent q in terms of the conductivity exponent t and the dielectric exponents s and s' as $q = (s + t)/t$ and $q' = (s' + t)/t$ on the conducting side ($\phi > \phi_c$). These theoretical expressions for q show that the exponent should never be less than unity. Experimental values of q (q_{exp}), were obtained from a log-log plot of the experimentally determined ω_c against $\sigma_m(\phi, 0)$. Figures 5.15 and 5.16 show such plots for the Graphite and Fe_3O_4 systems respectively. Table 5.3 gives the experimental values of q (q_{exp}) for all the systems studied. No q_{exp} value is given for the Nickel system due to the scarcity of data for $\omega/\omega_{c+} > 1$ arising from the high ω_c of the samples. Calculated values of q (denoted q_{calc}) were obtained using the DC s and t values (shown in Table 4.1) in the theoretical expression for q given above. The exponent q_{calc}' was obtained when the exponent s was replaced by s' (1kHz).

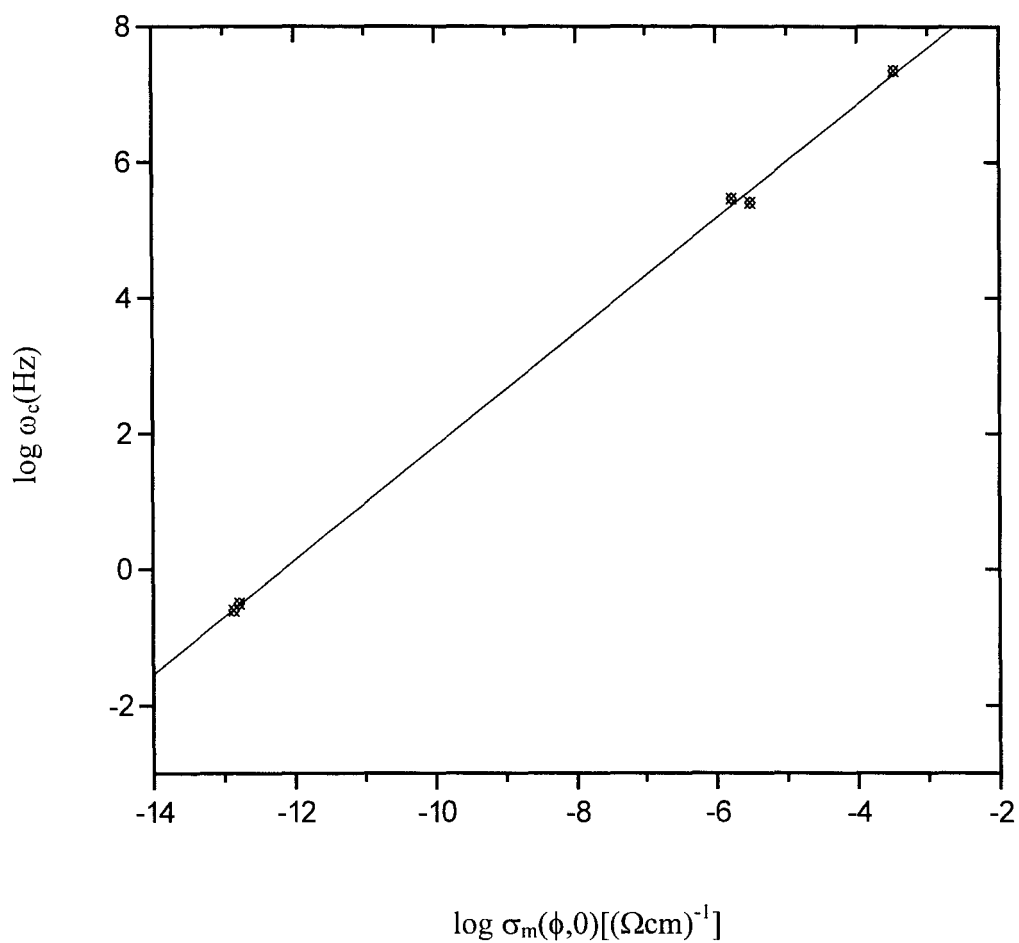


Figure 5.15: A log-log plot of ω_c against DC conductivity ($\sigma_m(\phi, 0)$) for the Graphite system. The solid line is a linear fit to the data from which the value of the exponent q (from $\omega_c \propto \sigma_m(\phi, 0)^q$) is found to be $q = 0.84 \pm 0.01$.

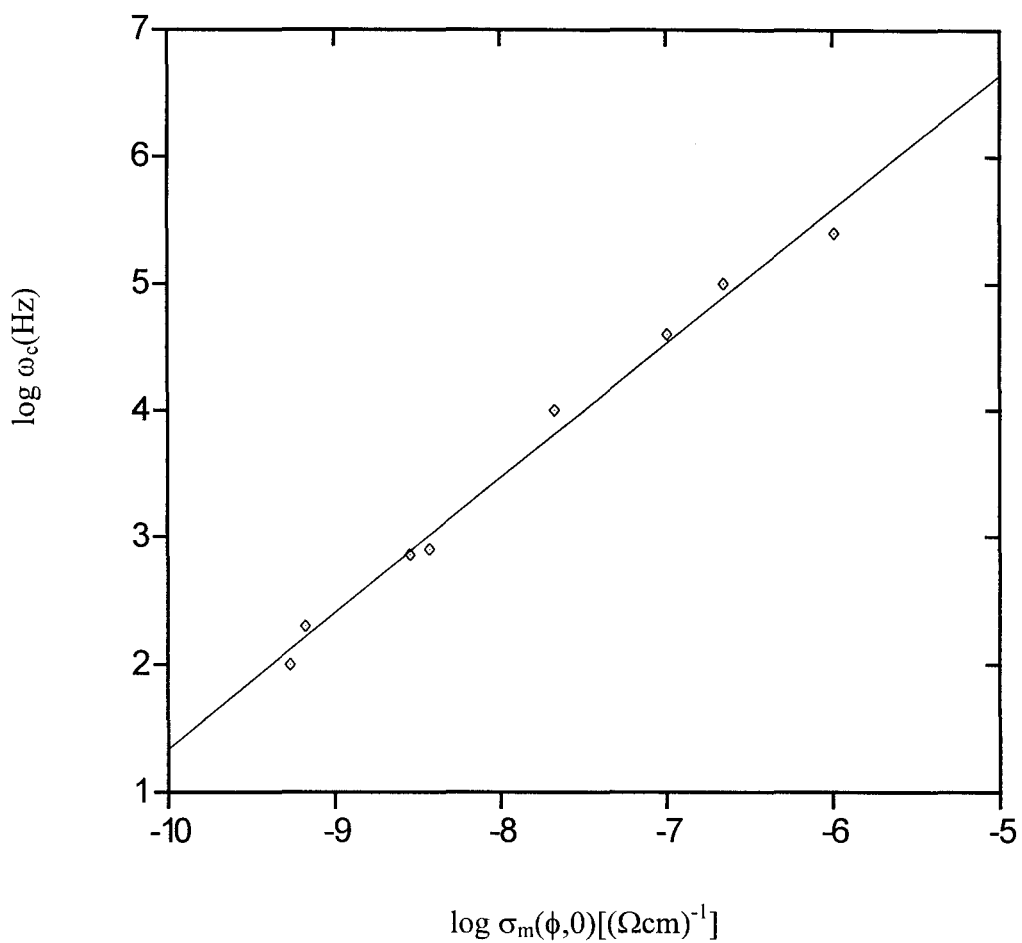


Figure 5.16: A log-log plot of ω_c against DC conductivity ($\sigma_m(\phi, 0)$) for the Fe_3O_4 system. The solid line is a linear fit to the data from which the value of the exponent q (from $\omega_c \propto \sigma_m(\phi, 0)^q$) is found to be $q = 1.06 \pm 0.04$.

Table 5.3: The exponent q results

Composite System	q_{exp}	$q_{\text{calc}} = (s+t)/t$	$q_{\text{calc}}' = (s'+t)/t$
Ground Carbon Black	1.47 ± 0.09	1.51 ± 0.44	1.17 ± 0.19
Raw Carbon Black	1.40 ± 0.03	1.40 ± 0.38	1.19 ± 0.14
Ground Graphite	0.84 ± 0.01	1.34 ± 0.35	1.26 ± 0.09
Graphite-BN(15%)	0.96 ± 0.05	1.51 ± 0.30	1.22 ± 0.15
Nickel		1.73 ± 1.10	1.25 ± 0.19
Magnetite (Fe_3O_4)	1.06 ± 0.04	1.11 ± 0.82	1.03 ± 0.16
Niobium Carbide	1.67 ± 0.13	1.07 ± 0.54	1.04 ± 0.18

Note that for the Carbon Black systems, $q_{\text{calc}} \sim q_{\text{exp}} > q_{\text{calc}}'$, while for the Graphite systems $q_{\text{calc}} > q_{\text{calc}}' > q_{\text{exp}}$. For the high t systems of Fe_3O_4 and NbC, $q_{\text{exp}} > q_{\text{calc}}' \sim q_{\text{calc}}$. Values of s, s' and t used to calculate q_{calc} and q_{calc}' are from Table 4.1.

The experimental values of the exponent q for the cellular systems can be sorted into two categories. Values greater than unity (in qualitative agreement with the theoretical predictions given by the inter-cluster polarisation model) and the q values less than unity, which show a more serious discrepancy with the inter-cluster model. The first category includes the two Carbon Black systems whose q_{calc} and q_{exp} values are in very good agreement. This is the first time that such an agreement is observed in real continuum systems. Taking the universal values of s and t as 0.87 and 2.00 respectively, the calculated value of q is 1.44. This value is also in good agreement with both q_{calc} and q_{exp} for the two Carbon Black systems. Systems with q_{exp} values less than unity include the two Graphite systems, with the lowest q value being observed in the Graphite system and the three-component (Graphite-Boron Nitride-Talc-wax) system, which gives a slightly higher q value, probably because of the influence of the Boron Nitride.

The high t systems of Fe_3O_4 and Niobium Carbide give q_{exp} values greater than unity. However, from the experimental results it can be seen that the Niobium Carbide system gives the largest experimental value of q . The other high t system of Fe_3O_4 -Talc-wax, has a lower q value but in good agreement with the cluster model for both s and s' . It can be noted that theoretically, the smaller the t value, the larger the q exponent should be for a given system. Note that both the Niobium Carbide and Fe_3O_4 systems give q_{calc} and q_{calc}' values that are very close to each other because of the high and small s (s') values. In addition, only the Niobium Carbide system gives $q_{\text{exp}} > q_{\text{calc}}$, which seems to indicate that this high t system is itself unique. This is the first time that such a result has been observed. However, this is probably not surprising as the experimental values of x and y show the largest disagreement with $x + y = 1$ as well.

The values of q_{calc} and q_{calc}' obtained in the high t systems agree with values calculated for the Graphite-Boron Nitride powder systems (Wu 1997, Wu and McLachlan 1998). These values of q_{calc} (q_{calc}') are 1.09 ± 0.12 (1.12 ± 0.13) and 1.10 ± 0.05 (1.15 ± 0.06) for 50%-Graphite and 55%-Graphite powder systems respectively.

However, the experimental values from the same powder systems are 0.84 ± 0.01 and 0.82 ± 0.01 respectively. The compacted Graphite-Boron Nitride system studied by Wu and McLachlan (1998), gives $q_{\text{exp}} = 1.03 \pm 0.01$ with q_{calc} and $q_{\text{calc}'}$ equal to 1.38 ± 0.22 and 1.20 ± 0.09 respectively. It is interesting to note that these Graphite systems appear to have the same behaviour as the Graphite systems studied in this thesis, where $q_{\text{calc}}(q_{\text{calc}'}) > q_{\text{exp}}$. In some of the systems studied (Benguigui 1985, Hundley and Zettl 1988, Chakrabarty *et al.* 1993, Wu and McLachlan 1998, McLachlan and Heaney 1999 and some results from this thesis), values of q greater than and some less than 1 were observed. However, these values are usually less than the theoretical predictions according to the interacting cluster model or $q = (s + t)/t$. Although insufficient data has been given as a reason for the discrepancy (Chakrabarty *et al.* 1993), systems in which this limitation does not apply (Hundley and Zettl 1988, Wu and McLachlan 1998, McLachlan and Heaney 1999 and this work) still give the same trend ($q_{\text{exp}} < q_{\text{calc}}$) for all q . These results appear to suggest that some important considerations, which may be playing a significant role in determining the exponents, might have been possibly omitted from the inter-cluster polarisation model. As noted earlier, the Niobium Carbide system studied in this thesis is the only system, which gives the unusual result of $q_{\text{exp}} > q_{\text{calc}}$. More experiments, where both s and s' are measured in conjunction with x and y , are therefore necessary to get further insight into the interrelation among these exponents, especially in the high t (low s) systems.

The q_{exp} values given Table 5.3 were all obtained from plotting the experimentally determined values of ω_c versus the DC conductivity ($\sigma_m(\phi, 0)$). Values of ω_c can also be calculated using eqn. (2.35) and the DC experimental values of σ_c , ϕ_c , s and t . Since the relative dielectric constant (ϵ_i) of the insulator or Talc-wax is frequency dependent, an average value of 7.00 was assumed for ϵ_i in the frequency range $10^0 - 10^6$ Hz, where most of the experimental ω_c values lie. Tables 5.4 and 5.5 show the calculated (ω_{ccalc}) and experimental values of ω_c (ω_{cexp}) for the raw Carbon Black and Fe_3O_4 systems respectively. The rest of the systems studied in this thesis are not shown. The results from the present study fall into two classes. Systems with low t exponents (close to the universal value) have their ω_c values obeying $\omega_{\text{cexp}} > \omega_{\text{ccalc}}$

Table 5.4: The ω_c results for the raw Carbon Black system

ω_{cexp} (Hz)	ω_{ccalc} (Hz)
1.995×10^4	3.300×10^2
3.388×10^4	6.175×10^2
5.012×10^4	1.043×10^3
1.585×10^5	2.768×10^3
6.310×10^5	1.892×10^4

Table 5.5: The ω_c results for the Fe_3O_4 system

ω_{cexp} (Hz)	ω_{ccalc} (Hz)
1.000×10^2	1.640×10^2
1.995×10^2	2.073×10^2
7.244×10^2	1.034×10^3
7.943×10^2	1.404×10^3
1.000×10^4	9.573×10^3
3.981×10^4	5.422×10^4
1.000×10^5	1.296×10^5
2.512×10^5	7.042×10^5

whereas the opposite ($\omega_{\text{cexp}} < \omega_{\text{ccalc}}$) is true for the high t systems of Fe_3O_4 and Niobium Carbide. In addition, ω_{cexp} and ω_{ccalc} are numerically very different for the low t systems and the high t system of Niobium Carbide, in agreement with Wu's results on Graphite Boron Nitride powder systems (Wu 1997, Wu and McLachlan 1998). It is interesting to note that Wu's results on Graphite Boron Nitride powder systems with high t exponents also have $\omega_{\text{cexp}} < \omega_{\text{ccalc}}$, in agreement with the present high t systems. It is not clear how the high t exponent causes this behaviour in these systems. It is also worth noting that the calculated and experimental values of ω_c for the high t Fe_3O_4 system (Table 5.5) are reasonably close in comparison with the other systems studied in this thesis. A similar result was observed in Wu's Graphite-Boron Nitride disc system (Wu 1997, Wu and McLachlan 1998).

5.2 The loss tangent: $\tan \delta$

The loss angle (δ) for a material with complex AC conductivity is given by the relation; $\tan \delta = \sigma_{\text{mr}}(\phi, \omega) / \epsilon_{\text{mr}}(\phi, \omega)$. Figures 5.17 - 5.19 show log-log plots of the loss tangent $\tan \delta$ versus frequency for some samples very close to the percolation threshold. It has been observed from the present results that $\tan \delta$ decreases with frequency above and below the percolation threshold. Numerical simulations using Bruggeman symmetric media theory done on the conducting side of the percolation threshold (Clerc *et al.* 1990) give the same qualitative result. In the present systems, for ϕ below ϕ_c , $\tan \delta$ is less frequency-dependent, in agreement with inter-cluster polarisation predictions. For samples close to but below ϕ_c , the Graphite containing systems show a subtle minimum in $\tan \delta$, between 10^5 and 10^6 Hz for the Graphite system and 10^6 and 10^7 Hz for the three-component Graphite Boron Nitride system. This is in qualitative agreement with the results of Wu (1997) and Wu and McLachlan (1998) on the compacted Graphite-Boron Nitride composite. The Carbon Black systems do not show any clear minimum in $\tan \delta$ but the raw Carbon Black system shows a gentle hump (maximum) between 10^4 and 10^8 Hz for samples very close to

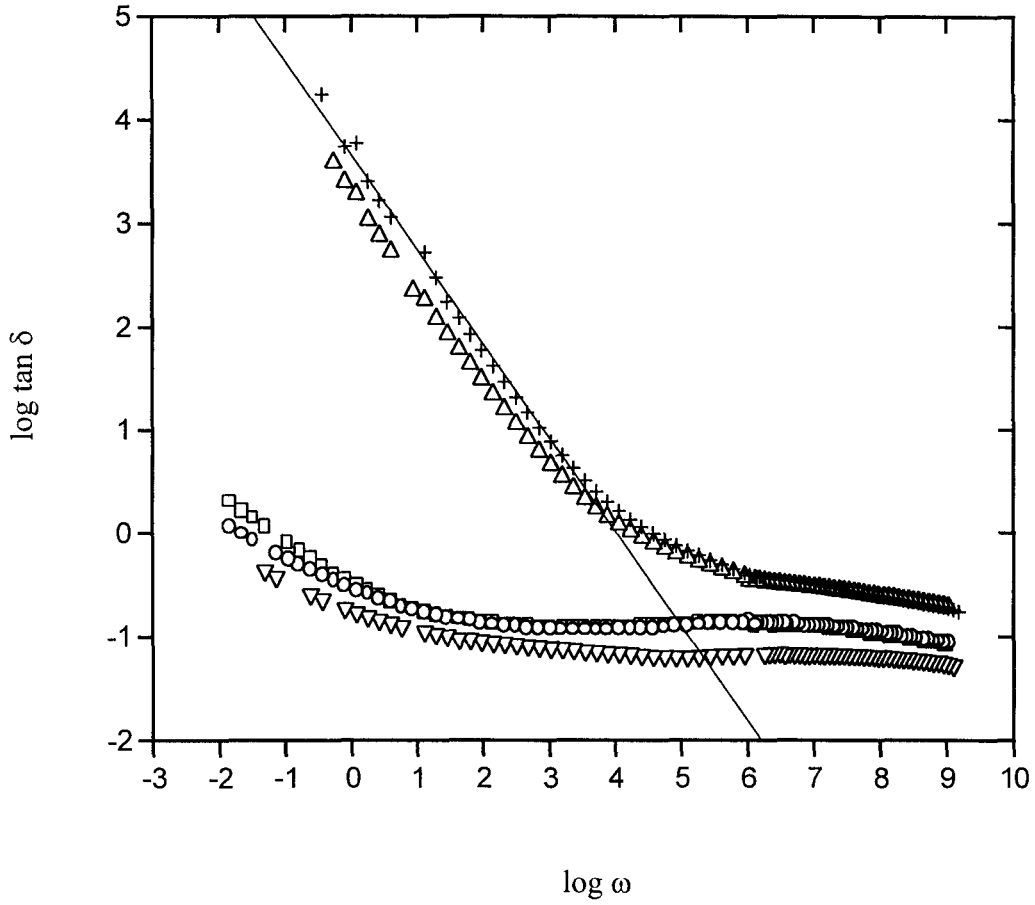


Figure 5.17: A log-log plot of $\tan \delta$ against ω for the raw Carbon Black system. The solid line is a linear fit to the data from a sample above ϕ_c which gives the value of the exponent z (from $\tan \delta \propto \omega^{-z}$) to be $z = 0.91 \pm 0.02$ [$\phi = 0.01044$ (∇), $\phi = 0.01290$ ($\circ$), $\phi = 0.01291$ ($\square$), $\phi = 0.01334$ (Δ), $\phi = 0.01343$ ($+$), $\phi_c = 0.0131 \pm 0.0006$].

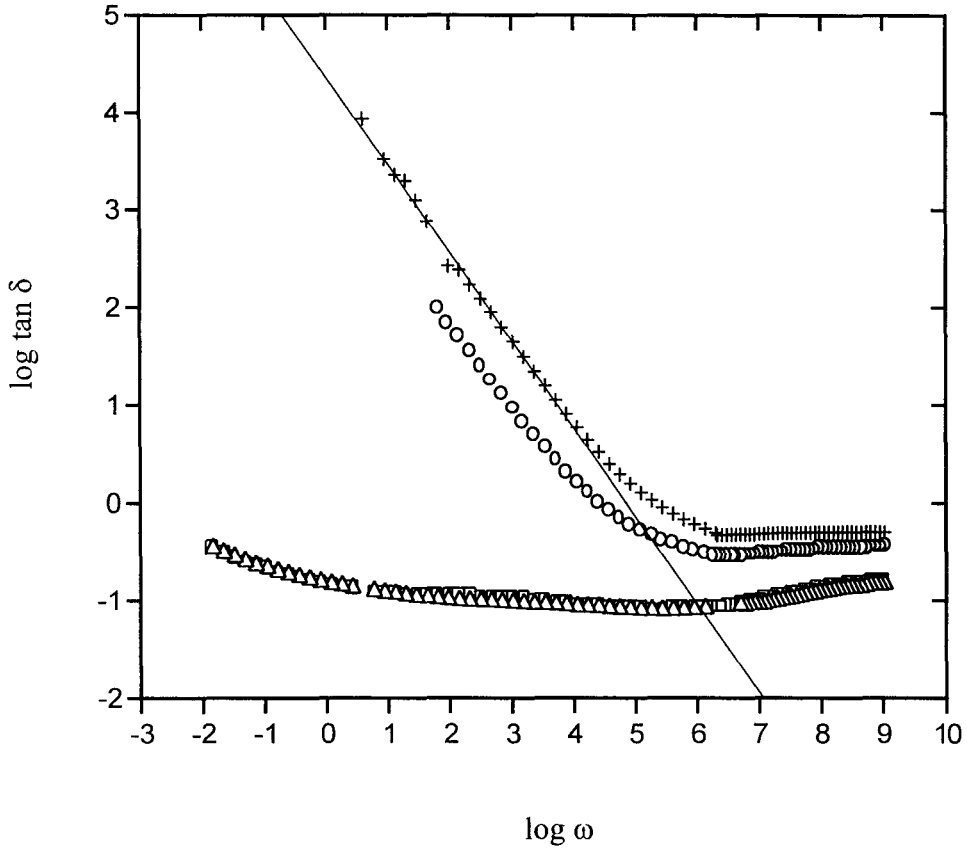


Figure 5.18: A log-log plot of $\tan \delta$ against ω for the Graphite-Boron Nitride system. The solid line is a linear fit to the data from a sample above ϕ_c which gives the value of the exponent z (from $\tan \delta \propto \omega^{-z}$) as $z = 0.90 \pm 0.01$ [$\phi = 0.0299$ ($\square$), $\phi = 0.0319$ ($\circ$), $\phi = 0.0333$ (Δ), $\phi = 0.0336$ (+), $\phi_c = 0.033 \pm 0.001$].

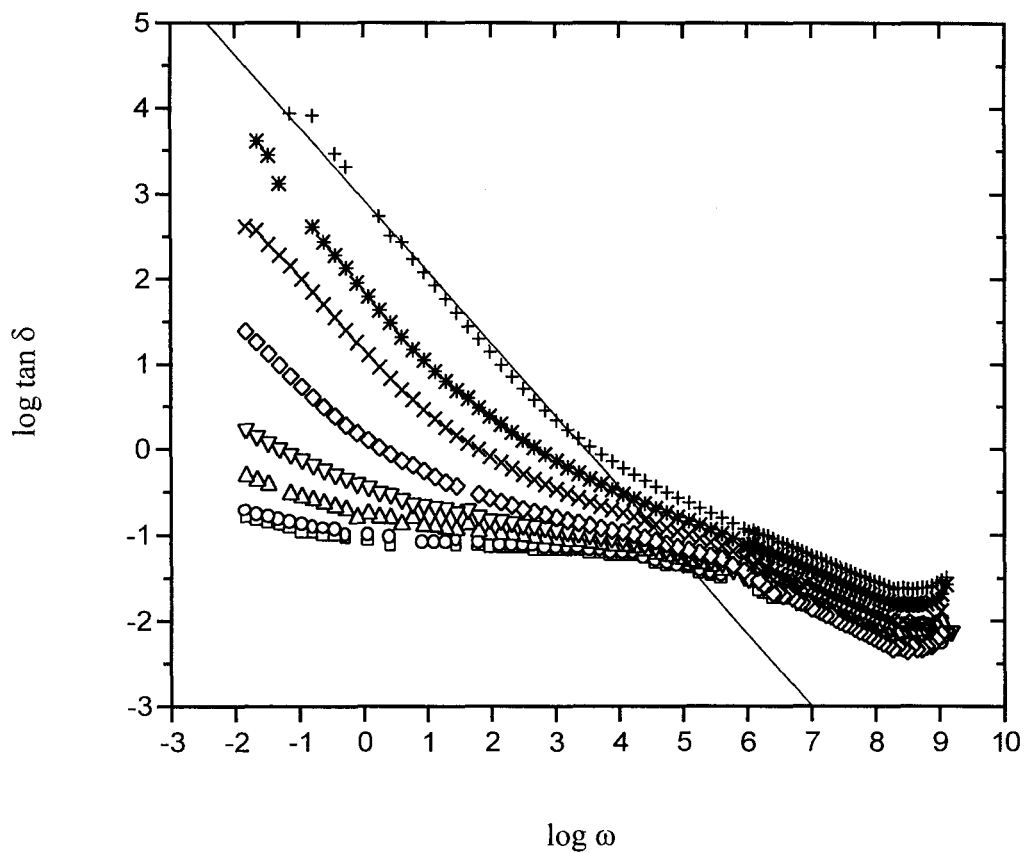


Figure 5.19: A log-log plot of $\tan \delta$ against ω for the Fe_3O_4 system. The solid line is a linear fit to the data from a sample above ϕ_c which gives the value of the exponent z (from $\tan \delta \propto \omega^{-z}$) as $z = 0.85 \pm 0.02$ [$\phi = 0.0219$ ($\square$), $\phi = 0.0251$ ($\circ$), $\phi = 0.0281$ (Δ), $\phi = 0.0344$ (∇), $\phi = 0.036$ ($\diamond$), $\phi = 0.0485$ ($\times$), $\phi = 0.0627$ ($*$), $\phi = 0.0840$ ($+$), $\phi_c = 0.025 \pm 0.003$].

but above ϕ_c (Fig. 5.17). The high t systems of Fe_3O_4 and Niobium Carbide show a more complex frequency dependence of $\tan \delta$ even for samples very close to the percolation threshold. The high t systems show a minimum in $\tan \delta$ between 10^8 and 10^9Hz , after which the curves show upward hooks, similar to those observed in the AC conductivity plots in the same frequency range (see for example Fig. 5.3 and 5.19 for the Niobium Carbide and Fe_3O_4 systems respectively). There is no available explanation for this result.

Above ϕ_c , $\tan \delta$ is highly frequency dependent for all systems and obeys $\tan \delta \propto \omega^{-z}$. Chen and Johnson (1991) calculated that for a sample above ϕ_c and in the low frequency regime $\omega < \omega_c$, $\tan \delta$ varies as $\tan \delta \propto 1/\omega RC$, thus predicting a slope of -1 (or $z = 1$). In this calculation, it was assumed that the energy loss in the dielectric was only due to conduction along the backbone, which is known not to be true (McLachlan *et al.* 1998 and 2000). Results obtained in the cellular systems, for samples just above the percolation threshold, give the slopes from -0.92 to -0.79 (or $z = 0.79$ to 0.92) as shown in Table 5.6, which do not agree with the prediction of Chen and Johnson (1991). The results from the cellular systems also show that the low t systems give higher values of z than those with high t .

Wu (1997) obtained $z = 0.80$ and 0.84 in the disc samples of a Graphite-Boron Nitride system and a 50%Graphite-50%Boron Nitride powder mixture respectively. These results are in reasonable agreement with the z exponent results of the two Graphite systems presented in this work (Table 5.6). Chen and Johnson (1991) obtained $z = 0.71 \pm 0.01$ and 0.86 ± 0.01 in filamentary and nodular Nickel systems respectively and suggested that the z values less than 1 were probably caused by an incomplete conductor-insulator transition in the systems.

The loss angle at ϕ_c (δ_c , see eqn. (2.32)), has been found experimentally for the systems. For those systems showing a minimum in $\tan \delta$, δ_c has been taken at this point for a sample close to but below ϕ_c . In systems with no minimum in $\tan \delta$

Table 5.6: Values of the exponent z from $\tan \delta \propto \omega^{-z}$. The results are obtained from samples above ϕ_c .

Composite System	z
Ground Carbon Black	0.92 ± 0.01
Raw Carbon Black	0.91 ± 0.02
Ground Graphite	0.92 ± 0.01
Graphite-BN(15%)	0.90 ± 0.01
Nickel	
Magnetite (Fe_3O_4)	0.85 ± 0.02
Niobium Carbide	0.79 ± 0.01

Note that the low t systems give higher values of the exponent z .

(Carbon Black systems), values of δ_c have been quoted at 10^5 Hz. These results are shown in Table 5.7a. According to the predictions of Clerc *et al.* (1984, 1990), δ_c is given by the expression; $\delta_c = (\pi/2)(1 - x) = (\pi/2)y = (\pi/2)[s/(s + t)]$, for $\omega \ll \omega_0 \equiv \sigma_c/2\pi\epsilon_i$. Using the experimental DC exponents given in Table 4.1, values of δ_c were calculated for the systems as shown in Table 5.7a. Values of δ_c' were obtained when s' (measured at 1kHz) was used in place of s in the expression for δ_c . According to Clerc *et al.* (1990), the value of δ_c should depend only on the dimensionality of the system and has a value of 0.54 in three dimensions. The experimental values of δ_c (δ_{cexp}) for the cellular systems are all greater than the calculated values of δ_c and δ_c' as well as the predicted value (0.54) in three dimensions. It is not clear what gives rise to such a serious discrepancy between the calculated and the experimental results. The results are also in serious disagreement with previous results on Graphite-Boron Nitride systems studied by Wu and McLachlan (1998). They obtained $\delta_c = 0.22 \pm 0.02$, 0.13 ± 0.02 and 0.09 ± 0.02 for the Graphite-Boron Nitride discs, 50%Graphite and 55%Graphite Boron Nitride powder mixtures respectively. Only the Fe_3O_4 system has a value close to the Graphite-Boron Nitride disc system. Using the universal values of s and t in 3D (0.87 and 2.00 respectively) gives a universal value of δ_c : $\delta_{cun} = 0.48$, which is in reasonable agreement with the calculated δ_c in the Graphite and Carbon Black systems. The extreme values of δ_c calculated in the Fe_3O_4 and Niobium Carbide systems are a result of the extreme values of the s and t exponents.

Table 5.7b shows the values of δ_c calculated from the measured x_{exp} and y_{exp} . These values are still less than δ_{cexp} , δ_c and δ_c' in Table 5.7a. The lowest values of δ_c are obtained from y_{exp} . This shows that the y_{exp} values measured in the systems are too low to give $x_{exp} + y_{exp} = 1$. This might be a characteristic of the cellular systems or a result of the complex dielectric properties of the Talc-wax insulating component.

Table 5.7a: Values of the loss angle, δ_c

Composite System	δ_{cexp}	δ_c	δ_c'
*Ground Carbon Black	5.09 ± 0.15	0.53 ± 0.16	0.23 ± 0.04
*Raw Carbon Black	3.61 ± 0.12	0.45 ± 0.12	0.25 ± 0.07
Ground Graphite	3.45 ± 0.10	0.40 ± 0.10	0.32 ± 0.08
Graphite-BN(15%)	4.75 ± 0.10	0.53 ± 0.10	0.28 ± 0.05
Nickel		0.66 ± 0.42	0.31 ± 0.20
Magnetite (Fe_3O_4)	0.29 ± 0.05	0.16 ± 0.12	0.04 ± 0.03
Niobium Carbide	1.14 ± 0.05	0.10 ± 0.05	0.06 ± 0.03

Table 5.7b: Values of the loss angle, δ_c , from x_{exp} and y_{exp} .

Composite System	δ_{cexp}	$\delta_c = (\pi/2)(1-x_{exp})$	$\delta_c = (\pi/2)y_{exp}$
*Ground Carbon Black	5.09 ± 0.15	0.345 ± 0.004	0.187 ± 0.006
*Raw Carbon Black	3.61 ± 0.12	0.236 ± 0.003	0.116 ± 0.004
Ground Graphite	3.45 ± 0.10	0.251 ± 0.003	0.166 ± 0.006
Graphite-BN(15%)	4.75 ± 0.10	0.361 ± 0.005	0.093 ± 0.05
Nickel			0.122 ± 0.005
Magnetite (Fe_3O_4)	0.29 ± 0.05	0.424 ± 0.006	0.080 ± 0.005
Niobium Carbide	1.14 ± 0.05	0.456 ± 0.006	0.066 ± 0.003

Note that in Table 5.7a, the experimental values of δ_{cexp} given were obtained from samples very close to ϕ_c . Values correspond to a minimum in $\tan \delta$ for the samples. For those samples marked *, which have no clear minimum value of $\tan \delta$, the values were read at 10^5 Hz. In Table 5.7b, the values of δ_c calculated from the measured x_{exp} and y_{exp} are different from δ_{cexp} , δ_c and δ_c' in Table 5.7a.

5.3 Summary

The AC properties (complex AC conductivity, dielectric constant and loss tangent) of a number of percolation systems with a cellular microstructure have been investigated experimentally and the results presented. The exponents obtained from the AC measurements on the cellular systems are in semi-quantitative agreement with previous studies on 3D continuum systems. The conducting samples ($\phi > \phi_c$) all show the expected low frequency independent plateau followed by a frequency-dependent conductivity at high frequencies. A plot of the normalised real AC conductivity ($\sigma_{mr}(\phi, \omega)/\sigma_m(\phi, 0)$) of the conducting samples close to ϕ_c against the normalised frequency (ω/ω_c) show that the scaling exponents x_{exp} , all lie between 0.70 to 0.86 in the systems studied. The x values (x_{calc}) calculated using the inter-cluster polarisation model and the separately measured t and s , disagree with the experimental x values for all the systems. However, values of x (x_{calc}') calculated using s' in place of s (in the inter-cluster model expression) give better agreement with the experimental values for the Carbon Black and Graphite systems. These systems show reasonable agreement with AC scaling theory provided s' is used to calculate the scaling function (F_+). Experimental values of x for the high t systems of Fe_3O_4 and Niobium Carbide, are less than the corresponding values calculated using the experimental DC s and t exponents, whereas the opposite is true (i.e. $x_{exp} > x_{calc}$) in the Carbon Black and Graphite (lower t) systems. The high t (low s) systems show that the experimental results scale, but disagree with the theoretical scaling curves calculated from t and s or s' . Most of the experimentally determined x exponents are close to those observed in previous studies. However, values of the exponent y (obtained from the log-log plot of the imaginary conductivity versus frequency) lie in the range 0.04 to 0.12, which is lower than those usually observed in the literature. In most of the systems studied in this work, the respective experimental x and y exponents do not sum up to unity (as they should according to the scaling relation of section 2.4, eqn. (2.38)) and are therefore in serious disagreement with the interacting cluster model.

The exponent q (q_{exp}), defined in sections 2.4 and 5.1.4, lies between 0.84 and 1.70 in the cellular systems. Only the Graphite-containing systems have q_{exp} less than 1, as previously observed by Wu (1997) and Wu and McLachlan (1998) in the Graphite-Boron Nitride powder systems. The Carbon Black systems gave q_{exp} values close to $q = 1.44$ (obtained using the universally accepted values of s and t for 3D continuum systems in the expression for q). This value is in good agreement with the q_{calc} values obtained using the measured DC s and t exponents. This is the first time that such agreement is observed between q_{exp} and q_{calc} in real continuum systems. A q value higher than the one calculated from the measured DC s and t or their universal values was measured in the Niobium Carbide system, which is rather unusual. However, the other high t system of Fe_3O_4 gave a q value lower than the corresponding calculated or universal value. In the log-log plot of the loss tangent (of the samples just above ϕ_c) against frequency, the exponent z was found to vary from 0.88 to 0.93, in agreement with previous studies on Graphite-Boron Nitride composites (Wu 1997, Wu and McLachlan 1998). The experimental values of δ_c from the cellular systems are in serious disagreement with theory and previous studies on Graphite-Boron Nitride systems (Chen and Johnson 1991, Wu and McLachlan 1998).

Table 5.8 shows the ratios of the calculated and experimental AC exponents obtained in this thesis as well as those from the Graphite-Boron Nitride systems studied by Wu (1997) and Wu and McLachlan (1998).

Table 5.8 The ratios of the calculated and experimental AC exponents

System	$x_{\text{exp}} + y_{\text{exp}}$	$x_{\text{calc}}/x_{\text{exp}}$	$x_{\text{calc}}'/x_{\text{exp}}$	$y_{\text{calc}}/y_{\text{exp}}$	$y_{\text{calc}}'/y_{\text{exp}}$	$q_{\text{calc}}/q_{\text{exp}}$	$q_{\text{calc}}'/q_{\text{exp}}$
Ground Carbon Black	0.90 ± 0.01	0.85	1.09	2.86	1.43	1.02	0.80
Raw Carbon Black	0.92 ± 0.01	0.85	0.99	4.00	2.28	1.00	0.85
Ground Graphite	0.95 ± 0.01	0.88	0.94	2.36	1.98	1.60	1.50
Graphite/Boron Nitride	0.83 ± 0.01	0.85	1.06	5.76	3.05	1.57	1.27
Nickel				5.38	2.56		
Fe_3O_4	0.78 ± 0.01	1.23	1.35	1.96	0.39	1.05	0.97
Niobium Carbide	0.75 ± 0.01	1.32	1.35	1.67	0.95	0.64	0.62
GBN DISCS (Wu 1997)	0.96 ± 0.04	0.88	1.01	2.00	1.21	1.34	1.16
50-50 GBN Powder (Wu 1997)	1.01 ± 0.03	0.98	0.94	1.14	1.57	1.30	1.33
55-45 GBN Powder (Wu 1997)	0.97 ± 0.02	1.04	1.00	0.90	1.30	1.34	1.40

The high t systems (except the 50-50% GBN powder) have $x_{\text{calc}}/x_{\text{exp}} > 1$. In these systems, only an increase in s relative to t , will bring x_{calc} closer to x_{exp} . For all the other cases, a decrease in s is required. Note also the inverse relation between $x_{\text{calc}}/x_{\text{exp}}$ ($x_{\text{calc}}'/x_{\text{exp}}$) and $q_{\text{calc}}/q_{\text{exp}}$ ($q_{\text{calc}}'/q_{\text{exp}}$), which is expected from the RC model. The huge discrepancy (large ratios) between y_{calc} (y_{calc}') and y_{exp} , means that a larger experimental t relative to s is required to bring y_{calc} (y_{calc}') closer to y_{exp} . The low y_{exp} values are thought to be responsible for $x_{\text{exp}} + y_{\text{exp}} < 1$.

CHAPTER SIX

1/F OR FLICKER NOISE IN THE CELLULAR SYSTEMS

6.0 Introduction

This chapter gives the experimental $1/f$ noise results from measurements done on four of the cellular systems where the conducting components of Graphite, Graphite-Boron Nitride (15%), ground and raw Carbon Black are mixed with a common insulator of Talc-wax. Noise measurements done on Nickel and Niobium Carbide systems were found to be inconsistent as a function of $\phi - \phi_c$ and DC resistance and are therefore not presented in such plots. However, the individual samples did give a $1/f$ -spectrum as illustrated in Fig. 6.1 for a Niobium Carbide-Talc-wax sample. No measurements were done on the Fe_3O_4 system because the resistance of the samples was too high to be measured using the available apparatus. All samples (in the form of 26mm diameter discs or pellets) used in the measurements were in the conducting region ($\phi > \phi_c$), some very close to the percolation threshold and others further into the conducting region. These measurements provided a further method of characterising the systems from very close to the percolation threshold to well into the conducting region. The samples used in all four systems spanned at least three decades in DC resistance. All measurements were taken in the axial (compression) direction within the frequency range of 1.2 - 1001.2Hz. Details of the experimental procedures were presented in section 3.2.3 and the measurement set-up for $1/f$ noise used in this thesis was shown in Fig. 3.4.

The measured noise spectra were characterised using Hooge's empirical formula (eqn. (2.16), Hooge 1969), in particular the frequency and current dependence of the noise (S_v) were first examined. The noise dependence on the DC voltage was investigated by passing several currents (at least five) through each sample so that a plot of S_v versus the DC voltage across the sample could be made. All measurements were done in the linear or ohmic range. The noise dependence on the DC voltage was studied to obtain the exponent m (eqn. (2.16)). According to the criteria used by Nandi *et al.* (1996), $m \approx 2$ is given by systems in which equilibrium resistance fluctuations are the sole source of the noise. Values of m greater or smaller than 2 would therefore imply the coexistence of other mechanisms. The resistance and conductor concentration dependence of the normalised noise (S_v/V^2) was investigated using the power laws: $S_v/V^2 \propto (\phi - \phi_c)^{-k}$ and $S_v/V^2 \propto R^w$. According to Rammal *et al.* (1985), the exponents w and k are related by $w = k/t$, where t is the DC conductivity exponent. Results obtained in this study show the occurrence of two values of k (k_1 and k_2) and two values of w (w_1 and w_2) in all the four systems. Calculations of the ϕ values for the upper and lower limits of the crossover regions (eqn. (2.2a)), using DC conductivity data, show that none of the samples used for the noise measurements were in the crossover region.

The experimental results are discussed primarily in terms of the Random Void (Swiss cheese) model (Halperin *et al.* 1985, Tremblay *et al.* 1986, Lee *et al.* 1986 and Feng *et al.* 1987) and the Balberg model (1998a and 1998b), which gives new limits for the non-universal noise exponents and allows for very high values of the resistance exponent (t). The results are presented and discussed in section 6.1 while section 6.2 gives a summary and some conclusions drawn from the results.

6.1 1/f Noise Measurement Results

6.1.1 S_v as a function of frequency

To investigate the 1/f nature of the noise spectra, the measured noise (S_v) was plotted on a log-log scale against the frequency (f) in order to determine the slope γ from Hooge's formula (section 2.3, eqn. (2.16)). Figure 6.1 shows this plot for a Niobium Carbide-Talc-wax sample. As indicated on the figure, the slope $\gamma \sim 1$ is obtained, thus verifying that the spectra is indeed 1/f. The values of γ (obtained by linear fitting) for all the samples measured in all four systems were in the range 0.97 - 1.09, and give a mean value of 1.02 ± 0.01 .

Previous measurements (Mantese and Webb 1985, Rudman *et al.* 1986, Octavio *et al.* 1987, Pierre *et al.* 1990b, Bruschi *et al.* 1994, Nandi *et al.* 1996, Wu 1997, Wu and McLachlan 1997) have reported various ranges of the exponent γ . Wu and McLachlan (1997) measured γ values in the range 0.95 – 1.08 with mean values of $\gamma = 1.01 \pm 0.01$ in the axial (compression) direction and $\gamma = 1.06 \pm 0.01$ in the transverse direction of the Graphite-Boron Nitride disc samples. In a Carbon-wax composite, Nandi *et al.* (1996) measured γ values within the range 0.9 – 1.3 and state that they could not find any correlation between their values of γ and the sample resistances or voltages. Pierre *et al.* (1990b) obtained γ exponent values between 1.0 and 1.4 for all samples they studied but noted that for their high resistance samples ($>10^6 \Omega$), the exponent γ tended to be closer to 1 ($\gamma = 1.00 \pm 0.01$). Rudman *et al.* (1986) obtained $\gamma = 1.30 \pm 0.15$ in a Ag/Pt-tetrafluoroethylene composite. Bruschi *et al.* (1994) measured 1/f-noise in polypyrrole thin film resistors at frequencies between 0.01Hz and 10Hz and obtained values of γ within the range $0.8 < \gamma < 1.4$. Octavio *et al.* (1987) obtained $\gamma = 1.10 \pm 0.06$ in 2D thin silver films which had been ion-milled at liquid nitrogen temperature. Mantese and Webb (1985) studied the noise in Pt-Al₂O₃ composite films and observed γ values in the range $0.8 < \gamma < 1.2$ at temperatures between 7K and 300K. In

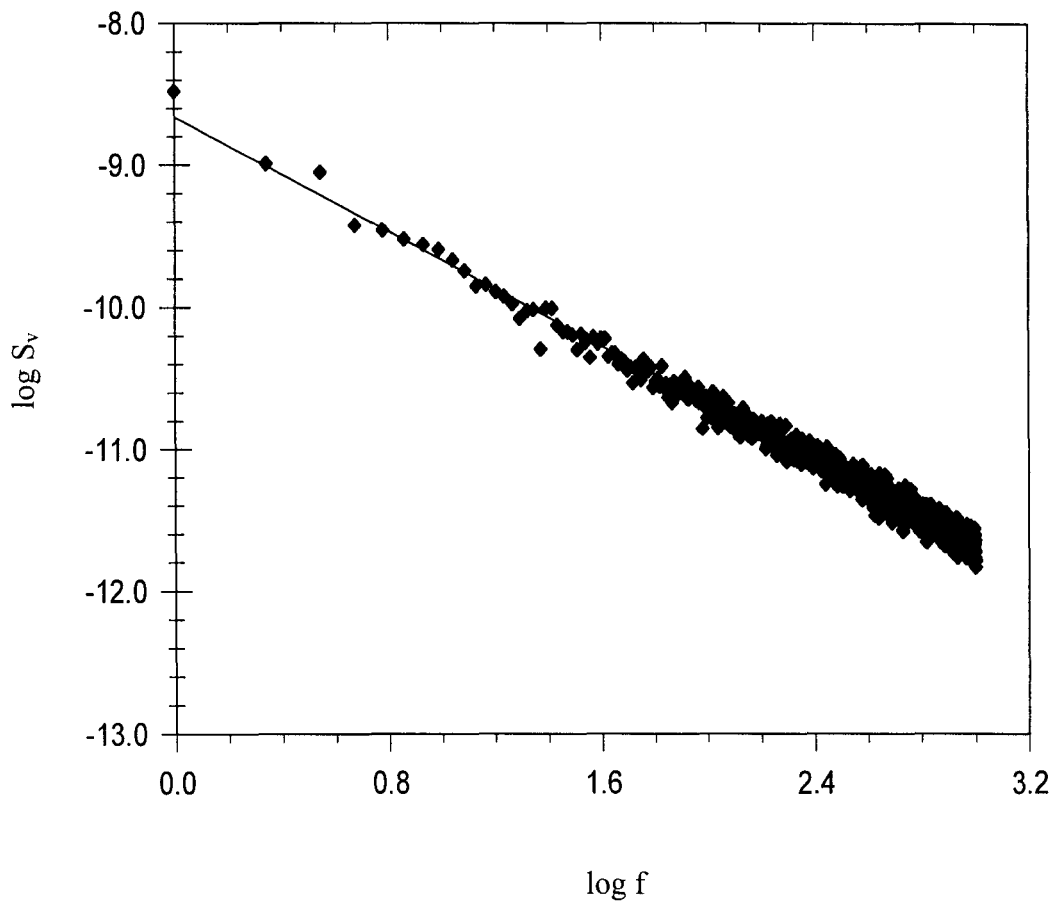


Figure 6.1: A log-log plot of the noise (S_v) versus frequency (f) for a Niobium Carbide-Talc-wax sample ($\phi = 0.117$) above the percolation threshold ($\phi_c = 0.065 \pm 0.006$). The solid line is a linear fit to the data and gives the noise exponent $\gamma = 1.01 \pm 0.06$ (from $S_v \propto f^{-\gamma}$).

general the values of γ usually reported in the literature and accepted to arise from $1/f$ noise are in the range $0.8 < \gamma < 1.4$ (Rudman *et al.* 1986), which is much wider than the range of experimental values (0.97 - 1.09) obtained in this study.

6.1.2 S_v as a function of sample voltage

The current dependence of the noise power was examined using a log-log plot of the noise at 10Hz ($S_{v10\text{Hz}}$) versus the resulting DC voltage (V) across each sample. Figures 6.2 and 6.3 show the plots for two samples from the raw Carbon Black system. Similar plots were done for all the samples upon which the measurements were made in order to obtain a value of m for each sample from $S_v \propto V^m$ (section 2.3, eqn. (2.16)). The values of m obtained for each sample, characterised here by the resistance (R_s), of the four systems studied are shown in Tables 6.1 – 6.4. To the best of the author's knowledge, this is the first time that the noise dependence on voltage has been investigated across such a wide range of sample resistance, which justifies the presentation of some detailed results, as shown in the Tables 6.1- 6.4.

Tables 6.1- 6.4 show the values of m lie between 1.00 and 2.13 with the lower resistance samples (larger $(\phi - \phi_c)$) generally giving higher values of the exponent. The variation of the exponent m with R_s indicates that the mechanism producing noise in the samples close to and further away from the percolation threshold is different. Samples close to the percolation threshold give values of m lower than 2, implying that the noise here is not solely generated by equilibrium resistance fluctuations (Bruschi *et al.* 1994). As the resistance of the samples decreases, m approaches 2, giving the expected quadratic dependence of the noise on the DC voltage (Rammal *et al.* 1985, Rudman *et al.* 1986, Pierre *et al.* 1990b, Bruschi *et al.* 1994, Nandi *et al.* 1996), implying equilibrium resistance fluctuations are probably the sole contributor to the noise. It is worth noting at this point that the DC conductivity of all the samples above ϕ_c , was fitted using a single t exponent. Different values of m and the two values of the exponents k and w (see later) show that the noise (which measures the

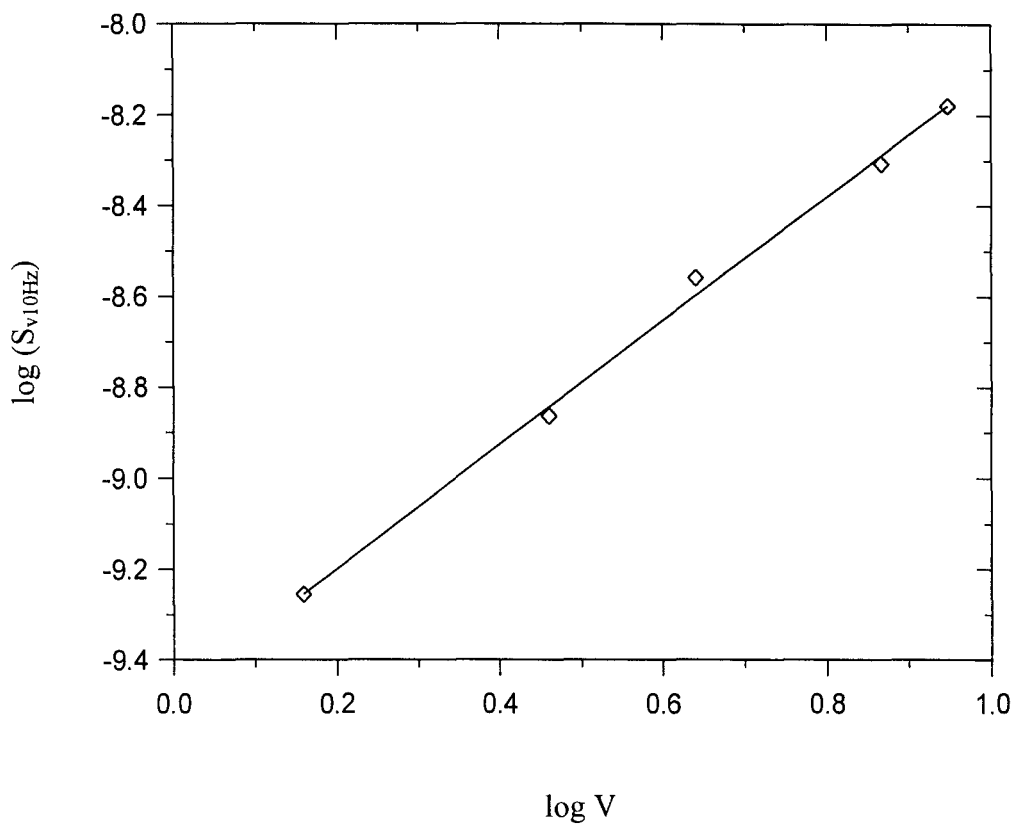


Figure 6.2: A log-log plot of the noise ($S_{v10\text{Hz}}$) versus DC voltage (V) across the sample for a raw Carbon Black-Talc-wax sample ($\phi = 0.0135$) close to the percolation threshold ($\phi_c = 0.0131 \pm 0.0006$). A linear fit to the data gives the exponent $m = 1.36 \pm 0.03$, much lower than the expected value of $m = 2$.

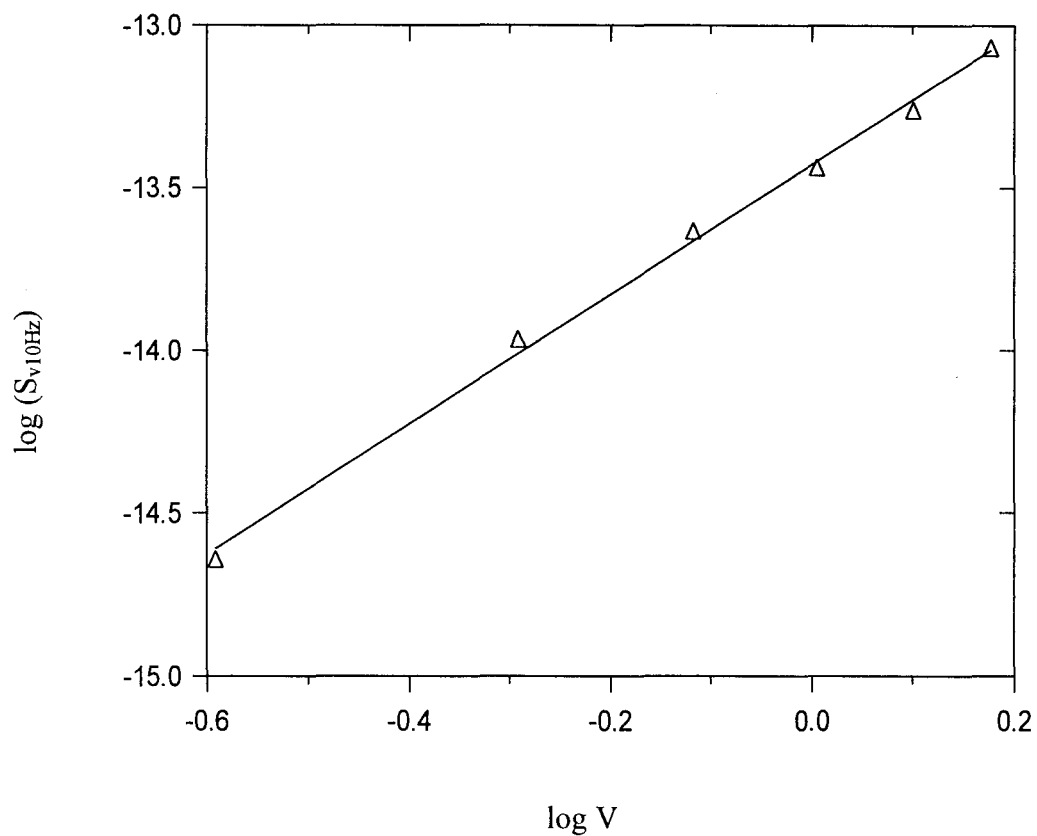


Figure 6.3: A log-log plot of noise ($S_{v10\text{Hz}}$) versus DC voltage (V) across the sample for a raw Carbon Black-Talc-wax sample ($\phi = 0.0249$) further into the conducting region. A linear fit to the data gives the exponent $m = 2.00 \pm 0.04$. For this system, $\phi_c = 0.0131 \pm 0.0006$.

Table 6.1: Variation of the exponent m with sample resistance for the ground Carbon Black system ($\phi_c = 0.0122 \pm 0.0007$).

ϕ	$\phi - \phi_c$	$\log(\phi - \phi_c)$	Sample resistance (Ω)	Exponent m
0.01265	0.00045	-3.35	1.8710×10^5	1.28 ± 0.04
0.01332	0.00112	-2.95	1.7620×10^5	1.60 ± 0.04
0.01360	0.00140	-2.85	1.2950×10^4	1.66 ± 0.04
0.01408	0.00188	-2.72	6.1700×10^3	1.88 ± 0.03
*0.01420	0.00200	-2.70	5.4100×10^3	1.94 ± 0.04
0.01556	0.00336	-2.47	1.8140×10^3	1.80 ± 0.04
0.01800	0.00580	-2.24	5.9800×10^2	2.05 ± 0.05
0.02180	0.00960	-2.02	2.0500×10^2	2.13 ± 0.02

*Note that the samples can be separated into two groups, as shown in the table, according to exponents k_1 (w_1) and k_2 (w_2) (see later). The first group generally has values of m lower than 2 (probably implying the existence of additional noise mechanisms) and the second group with $m \sim 2.0$ as expected from the theory of equilibrium resistance fluctuations.

Table 6.2: Variation of the exponent m with sample resistance for the raw Carbon Black system ($\phi_c = 0.0131 \pm 0.0006$).

ϕ	$\phi - \phi_c$	$\log(\phi - \phi_c)$	Sample resistance (Ω)	Exponent m
0.01334	0.00024	-3.62	2.9600×10^5	1.03 ± 0.02
0.01343	0.00033	-3.48	1.9285×10^5	1.33 ± 0.02
0.01351	0.00041	-3.39	1.2770×10^5	1.36 ± 0.03
0.01355	0.00045	-3.35	1.2440×10^5	1.25 ± 0.03
0.01447	0.00137	-2.86	1.2880×10^5	1.35 ± 0.02
0.01363	0.00053	-3.28	5.3400×10^4	1.60 ± 0.03
*0.01475	0.00165	-2.78	8.0500×10^3	1.66 ± 0.03
0.01483	0.00173	-2.76	7.4150×10^3	1.76 ± 0.04
0.01585	0.00275	-2.56	3.3200×10^3	1.82 ± 0.02
0.01692	0.00382	-2.42	1.6050×10^3	1.83 ± 0.01
0.01839	0.00529	-2.28	8.8000×10^2	1.87 ± 0.03
0.02307	0.00997	-2.00	2.5800×10^2	1.92 ± 0.03
0.02329	0.01019	-1.99	2.4500×10^2	2.13 ± 0.03
0.02490	0.01180	-1.93	1.7700×10^2	2.00 ± 0.04
0.02728	0.01418	-1.85	1.2500×10^2	2.05 ± 0.06

*Note that the samples can be separated into two groups, as shown in the table, according to exponents k_1 (w_1) and k_2 (w_2) (see later). The first group has values of m lower than 2 (perhaps implying the existence of additional noise mechanisms) and the second group with $m \sim 2.0$ as expected from the theory of equilibrium resistance fluctuations.

Table 6.3: Variation of the exponent m with sample resistance for the Graphite system ($\phi_c = 0.035 \pm 0.002$).

ϕ	$\phi - \phi_c$	$\log(\phi - \phi_c)$	Sample resistance (Ω)	Exponent m
0.0352	0.0002	-3.70	2.6500×10^5	0.92 ± 0.03
0.0353	0.0003	-3.52	1.9610×10^4	1.49 ± 0.06
0.0354	0.0004	-3.40	2.5000×10^3	1.19 ± 0.06
0.0360	0.0010	-3.00	2.0600×10^2	1.51 ± 0.04
0.0361	0.0011	-2.96	1.7900×10^2	1.66 ± 0.07
*0.0365	0.0015	-2.82	7.6200×10^1	1.76 ± 0.04
0.0367	0.0017	-2.77	6.6300×10^1	1.70 ± 0.03
0.0368	0.0018	-2.74	5.8000×10^1	1.80 ± 0.08
0.0369	0.0019	-2.72	5.3300×10^1	1.90 ± 0.01
0.0388	0.0038	-2.42	1.2300×10^1	2.05 ± 0.02

*Note that the samples can be separated into two groups, as shown in the table, according to exponents k_1 (w_1) and k_2 (w_2) (see later). The first group has values of m much lower than 2 (probably implying the existence of additional noise mechanisms) and the second group with $m \sim 2.0$ as expected from the theory of equilibrium resistance fluctuations.

Table 6.4: Variation of the exponent m with sample resistance for the Graphite-Boron Nitride system ($\phi_c = 0.033 \pm 0.001$).

ϕ	$\phi - \phi_c$	$\log(\phi - \phi_c)$	Sample resistance (Ω)	Exponent m
0.03358	0.00058	-3.24	1.6820×10^4	1.15 ± 0.04
0.03447	0.00147	-2.83	9.0300×10^2	1.45 ± 0.05
0.03501	0.00201	-2.70	4.2200×10^2	1.38 ± 0.07
0.03509	0.00209	-2.68	3.7400×10^2	1.50 ± 0.01
*0.03578	0.00278	-2.56	1.7150×10^2	1.67 ± 0.05
0.03996	0.00696	-2.16	1.6400×10^1	2.03 ± 0.02
0.04009	0.00709	-2.15	1.5400×10^1	2.04 ± 0.08
0.04143	0.00843	-2.07	1.0100×10^1	1.98 ± 0.06

*Note that the samples can be separated into two groups, as shown in the table, according to exponents k_1 (w_1) and k_2 (w_2) (see later). The first group has values of m much lower than 2 (probably implying the existence of additional noise mechanisms) and the second group with $m \sim 2.0$ as expected from the theory of equilibrium resistance fluctuations.

fourth moment of the current distribution) is more sensitive to changes in the microstructure than the resistance (which only measures the second moment of the current distribution). Note that the Ag/Pt-TFE composite samples, studied by Rudman *et al.* (1986), show that for over three decades of voltage change the noise scales approximately as V^2 with an mean exponent $m = 2.01 \pm 0.05$. The range of m values obtained in this study is not given. In the Graphite-Boron Nitride disc samples studied by Wu (1997) and Wu and McLachlan (1997), a mean value of $m = 1.96 \pm 0.01$ and $m = 1.93 \pm 0.02$ were measured in the axial (compression) and transverse directions respectively, in reasonable agreement with the expected quadratic dependence. The lowest m values observed were 1.87 ± 0.04 and 1.81 ± 0.07 in the axial and transverse directions respectively (Wu 1997).

To the best of the author's knowledge, the only study to have reported values of m much lower than 2 is that of Bruschi *et al.* (1994) in which they measured $1/f$ noise on single component conducting polymer 2D thin film resistors. The polypyrrole thin film resistors were prepared by chemical-vapour deposition onto copper chloride precursors. In spite of their single component nature, the samples were found to give different values of m at four different frequencies. For the same sample and over the same range of voltage (-0.4V to 0.8V), Bruschi *et al.* (1994) obtained m values of 1.38 (62.5mHz), 1.54 (109mHz), 1.73 (0.5Hz) and 1.73 (1Hz), from which they concluded that equilibrium resistance fluctuations do not completely explain the noise spectra in their samples. Note that their values of m are close to those obtained, for samples close to the percolation threshold, at 10Hz in all four cellular systems studied in this thesis.

6.1.3 S_v/V^2 as a function of $(\phi - \phi_c)$

The log-log plots of the normalised noise (S_{v10Hz}/V^2) as a function of concentration $(\phi - \phi_c)$ for the four cellular systems are shown in the Figs. 6.4 – 6.7. These plots were

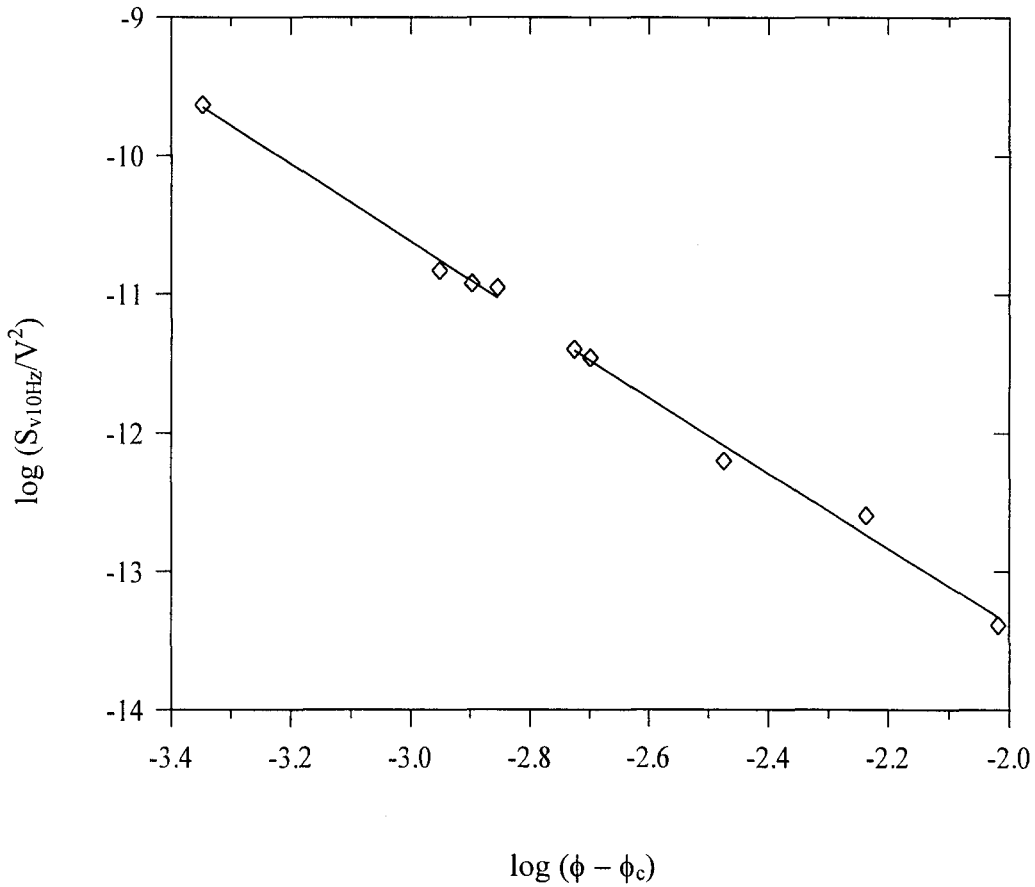


Figure 6.4: A log-log plot of the normalised noise versus the concentration of Carbon Black for the ground Carbon Black system ($\phi_c = 0.0122 \pm 0.0007$). The solid lines are linear fits to the data, which give the exponents, $k_1 = 2.80 \pm 0.08$ for the high resistance samples and $k_2 = 2.71 \pm 0.11$ for the low resistance samples. Note that the points on the graph can basically be fitted by a single line but are separated according to the value of m as is done for the other systems.

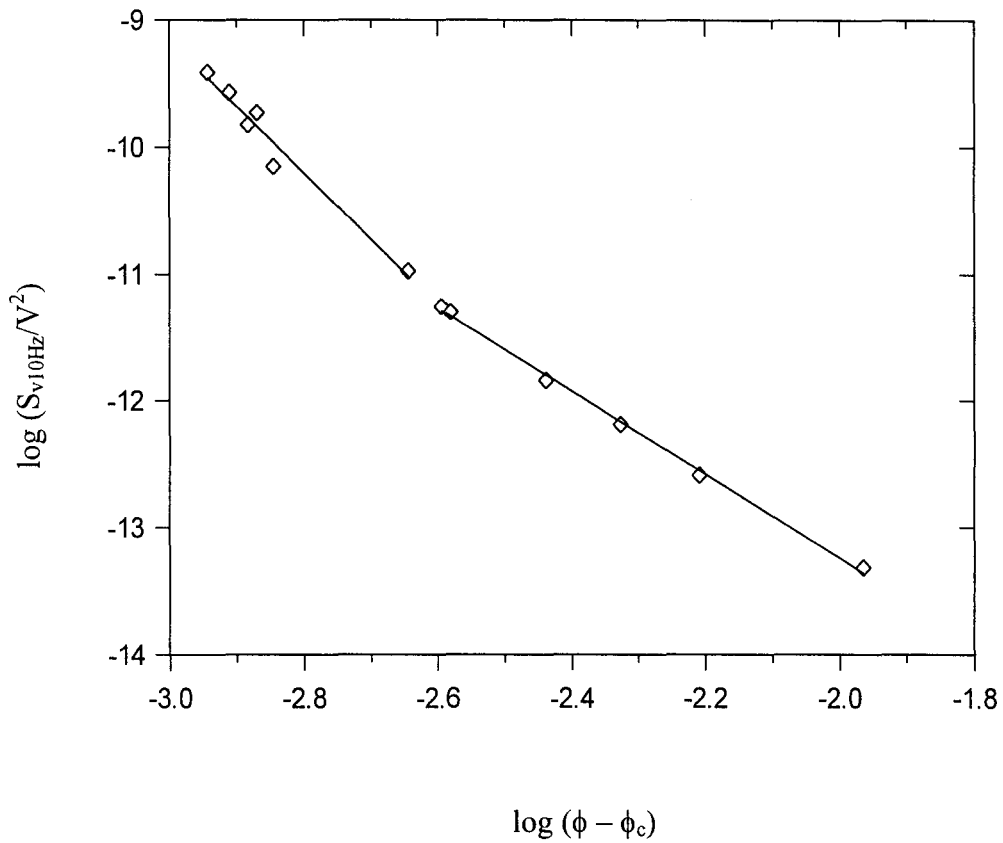


Figure 6.5: A log-log plot of the normalised noise versus the concentration of Carbon Black for the raw Carbon Black system ($\phi_c = 0.0131 \pm 0.0006$). The solid lines are linear fits to the data, which give the exponents, $k_1 = 5.23 \pm 0.12$ for the high resistance samples and $k_2 = 3.29 \pm 0.04$ for the low resistance samples.

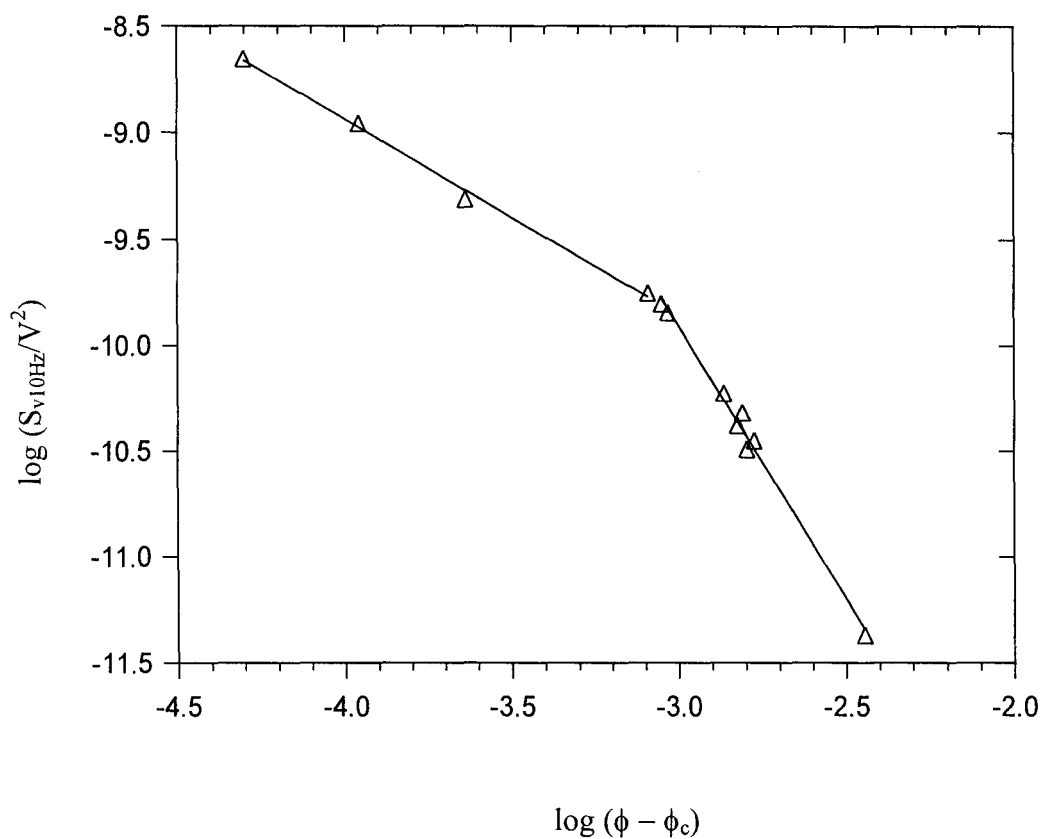


Figure 6.6: A log-log plot of the normalised noise versus the concentration of Graphite for the Graphite system ($\phi_c = 0.035 \pm 0.002$). The solid lines are linear fits to the data, which give the exponents, $k_1 = 0.92 \pm 0.03$ for the high resistance samples and $k_2 = 2.58 \pm 0.05$ for the low resistance samples.

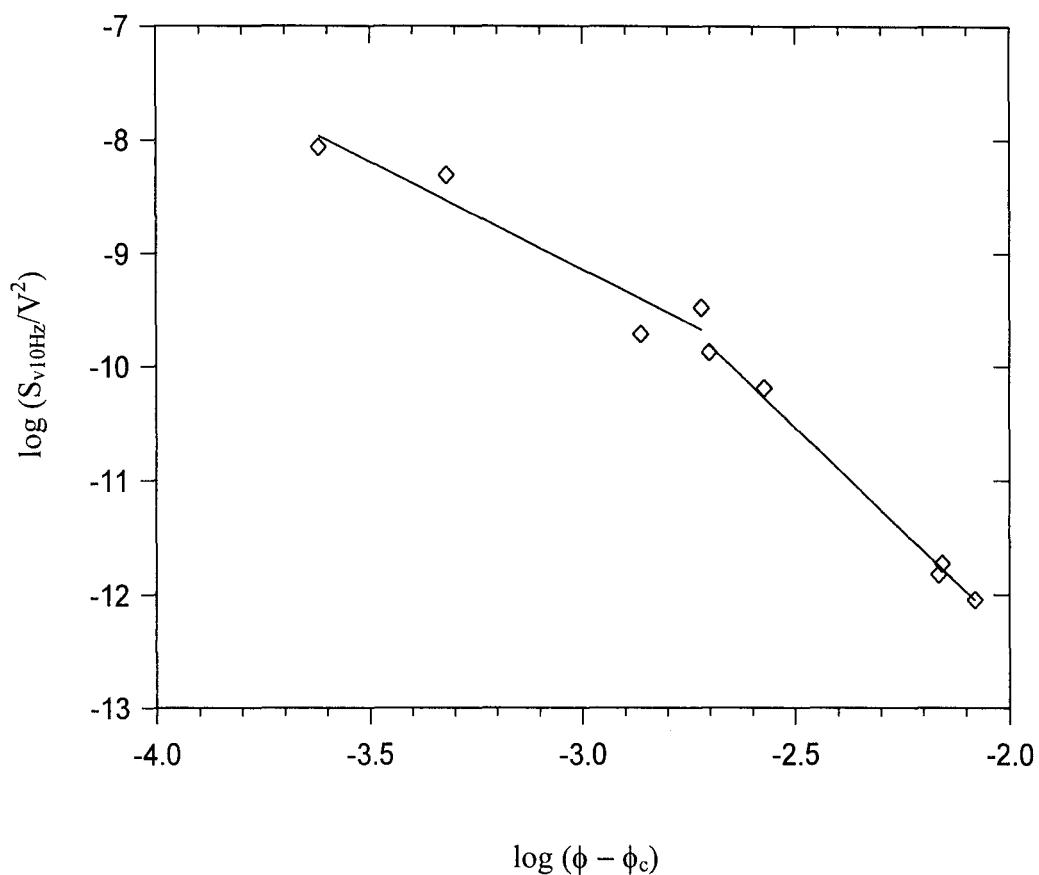


Figure 6.7: A log-log plot of the normalised noise versus the concentration of Graphite for the Graphite-Boron Nitride system ($\phi_c = 0.033 \pm 0.001$). The solid lines are linear fits to the data, which give the exponents, $k_1 = 1.90 \pm 0.31$ for the high resistance samples and $k_2 = 3.60 \pm 0.08$ for the low resistance samples.

Table 6.5: Experimental Noise Exponents for the Cellular Systems

Composite System	k_1	k_2	k_1/k_2
Ground Carbon Black	2.80 ± 0.08	2.71 ± 0.11	1.033 ± 0.07
Raw Carbon Black	5.23 ± 0.12	3.29 ± 0.04	1.580 ± 0.04
Ground Graphite	0.92 ± 0.03	2.58 ± 0.05	0.356 ± 0.05
Graphite-BN(15%)	1.90 ± 0.31	3.60 ± 0.08	0.528 ± 0.18

Table 6.6: The k exponents calculated from experimental t values for the Cellular Systems

Composite System	t	ω'	k_{calc}
Ground Carbon Black	2.06 ± 0.10	-0.42 ± 0.02	4.33 ± 0.21
Raw Carbon Black	2.26 ± 0.11	-0.19 ± 0.01	4.66 ± 0.24
Ground Graphite	1.93 ± 0.06	-0.61 ± 0.02	4.11 ± 0.13
Graphite-BN(15%)	2.51 ± 0.12	0.0100 ± 0.0005	5.08 ± 0.25
Nickel	1.52 ± 0.15	-1.88 ± 0.18	3.43 ± 0.34
Fe_3O_4	4.12 ± 0.23	0.52 ± 0.03	7.78 ± 0.43
Niobium Carbide	5.25 ± 0.67	0.65 ± 0.08	9.70 ± 1.25

Note: The experimental t exponents were used to find the corresponding ω' values (eqn. (2.10)) and k_{calc} was calculated from the **new Balberg** expressions (eqn. (2.24)). Note that even Balberg's new model does not account for the change in k with sample resistance R_s as observed in the systems studied in this work. The Graphite-Boron Nitride system gives a very small ω' (close to $\omega' = 0$, corresponding to the original random void model).

made in order to obtain k from the relation $S_{v10Hz}/V^2 \propto (\phi - \phi_c)^{-k}$. From the graphs, two regions of different slopes can be identified, yielding the exponents labeled as k_1 and k_2 for samples close to and further away from the percolation threshold respectively. The only exception is the ground Carbon Black system, where the change in slope is not very distinct. Interestingly, the exponent k_1 is given by samples with lower values of m while k_2 arises from samples with $m \approx 2$, the latter claimed to be a result of equilibrium resistance fluctuations by Nandi *et al.* (1996). The samples are separated accordingly as shown in Tables 6.1 – 6.4. The values of k_1 and k_2 obtained for all the systems are summarised in Table 6.5. It is the first time that the occurrence of two values of the exponent k has been observed and reported in any real continuum system. However, a w_1 and w_2 (see section 6.1.4) have been reported experimentally (Rudman *et al.* 1986 and Pierre *et al.* 1990b). The effect (k_1 and k_2 or w_1 and w_2) is perhaps most likely to occur in 3D continuum systems where the microstructure is more complex than in 2D systems. To the best of the author's knowledge, no 2D experiment (or simulation) has ever reported the occurrence of a k_1 and k_2 or w_1 and w_2 .

The experimental values of k_1 and k_2 in Table 6.5 cover quite a wide range (0.90 – 5.30), with the Carbon Black systems giving higher values than the Graphite systems. While the values of k_1 for the systems are very different (0.90 – 5.30), the k_2 values are relatively close to each other (2.58 – 3.60). The raw Carbon Black system has a particularly high value for k_1 (5.23 ± 0.12), which is almost twice that observed in the ground Carbon Black system ($k_1 = 2.80 \pm 0.08$). The more 'rounded' contacts of the ground Carbon Black might be the cause for the difference in behaviour of the two systems. Furthermore, the Carbon Black systems have k_1 values greater than the corresponding k_2 exponents whereas the reverse is true for the Graphite-containing systems. This can be seen clearly through the ratio k_1/k_2 included in Table 6.5. The k_1/k_2 ratio is greater than 1 for the Carbon Black systems but $k_1/k_2 < 1$ for the Graphite systems. This behaviour of the k_1 and k_2 exponents probably reflects some characteristic of the conducting components, possibly different inter-particle contacts for the Carbon Black and Graphite. Unfortunately, no noise results were obtainable

for the other three systems with extreme values of the exponent t (Niobium Carbide, Fe_3O_4 and Nickel) to allow similar plots to be made.

The Random Void and Inverted Random Void models (Halperin *et al.* 1985, Feng *et al.* 1987 and Tremblay *et al.* 1986, Lee *et al.* 1986) have been previously used to model noise in percolation systems (Tremblay *et al.* 1986). Recently Balberg (1998a and 1998b) introduced some extensions to the above models, in an attempt to accommodate the high values of the noise exponents (outside of the original Random Void and Inverted Random Void limits) observed in some percolation systems. As previously noted, the cellular systems studied in this work are more likely to be described by the Random Void model. The small conductor particles may be seen as forming the conducting medium or links, while the large Talc-wax particles are the voids. The new Balberg model (1998a and 1998b) predicts that the value of k for 3D continuum systems should be given by $k = k_{\text{un}} + (v + 1 - \omega')/(1 - \omega')$ (section 2.3, eqn. (2.24)). The universal value of k (k_{un}) for a 3D system is 1.56 and ω' is a parameter characterising the resistance distribution function as defined in section 2.1.4 (eqn. (2.10)). For a 3D Random Void system, $v = d - \frac{1}{2}$ (Halperin *et al.* 1985, Tremblay *et al.* 1986, Balberg *et al.* 1988), where d is the dimensionality of the system under study ($d = 3$ in this case). The Balberg model gives the value of k for the Random Void system to be $k = 1.56 + ((3.5 - \omega')/(1 - \omega'))$. The value of k is therefore largely dependent on the parameter ω' in this model. Substitution of $\omega' = 0$ in this expression gives $k = 5.06$, a value which is reasonably close to the k_1 (5.23 ± 0.12) measured in the raw Carbon Black system (with $t \sim 2.0$). It should be remembered that the $\omega' = 0$ case gives the original Halperin, Feng and Sen (HFS) and Tremblay, Feng and Breton (TFB) models (Halperin *et al.* 1985, Tremblay *et al.* 1986, Feng *et al.* 1987) and a k of 5.06. Therefore, the result obtained for the Carbon Black system shows that the original random void system may still be used to successfully model noise in some percolation systems. However, the slightly larger k_1 (compared to 5.06 from the original RV model) for the raw Carbon Black system implies values of k beyond the RV model prediction can occur, which justifies the extensions of the original RV and IRV models.

The **new Balberg** model gives the expressions for the conductivity exponent t and the noise exponent k in terms of ω' (eqn. (2.10)). Using $t_{un} = 2.00$ for 3D ($d = 3$) systems and $u = d - 3/2$ from the Random Void model (Halperin *et al.* 1985, Balberg *et al.* 1988), the expression becomes $t = 2 + ((0.5 + \omega')/(1 - \omega'))$. Using the experimental values of t from Table 4.1, values of ω' were calculated for each of the four systems. These values of ω' were in turn used to calculate k as given in Table 6.6. Unfortunately the values of ω' obtained from the experimental t values do not give k_{calc} values close to those measured experimentally. The values of k_{calc} in Table 6.6 range from 3.4 to 9.7, some of which are beyond the original RV and IRV model predictions (Tremblay *et al.* 1986, Balberg *et al.* 1988) of $k = 5.06$. Note also that the calculated (k_{calc}) values result from a single t exponent obtained for each system as shown in Table 4.1, which leads to a single ω' and a single k value, unlike the present experimental results. Values of k_{calc} increase with exponent t , in agreement with the experimental values of k_2 (Fig. A9). However, the k_{calc} values are always greater than the corresponding k_2 .

Apart from the work of Chen and Chou (1985), very few experiments have reported direct measurements of the exponent k in real 3D continuum systems. In a number of experiments (see for instance Wu and McLachlan 1997, Nandi *et al.* 1996, Rudman *et al.* 1986), values of t and w have been measured and values of k calculated from the relationship $w = k/t$ introduced by Rammal *et al.* (1985). Chen and Chou (1985) measured noise in a Carbon-wax mixture, in which the authors claim to observe tunneling conduction. The samples were made by mixing the Carbon powder (with individual particles of $1\mu\text{m}$ in diameter) and white wax at a temperature slightly higher than the melting point of wax ($T_m = 58^\circ\text{C}$). Rectangular samples made from the mixture were annealed at 54°C to smooth out any irregularities in their structure. Resistance and noise measurements were made by the four-probe method, using indium wires for electric contact. The measured noise spectra was observed to follow a power law of the form $S_v(f) \propto (\phi - \phi_c)^{-k}$ with $k = 5.0 \pm 1.0$ in good agreement with k_1 (and not k_2) for the raw Carbon Black system ($k_1 = 5.23 \pm 0.12$). Chen and Chou attributed this strong dependence of the noise on $(\phi - \phi_c)$ to the fluctuations in the

number of charge carriers in the system but this is highly unlikely considering the size of their samples and the fact that in noise, it is only the links that count. In a compacted system of Graphite and Boron Nitride, Wu (1997) calculated $k_{\text{calc}} = 3.87 \pm 0.07$ and $k_{\text{calc}} = 4.61 \pm 0.43$ in the axial (pressure) and transverse directions respectively, from $w = k/t$, using the corresponding measured w and t exponents ($w = 1.47 \pm 0.08$, $t = 2.63 \pm 0.07$ and $w = 1.72 \pm 0.08$, $t = 2.68 \pm 0.13$) respectively. The value calculated in the axial direction is close to k_2 obtained in the Graphite-Boron Nitride system studied in this thesis (Table 6.5). In a Carbon-wax system, Nandi *et al.* (1996), no normalised noise (S_v/V^2) versus $(\phi - \phi_c)$ plots were given and no such results quoted. However, Nandi and his coauthors calculated $k_{\text{calc}} = 3.6$ by using their measured $w = 1.7 \pm 0.2$ and $t = 2.1$. The samples used in Nandi's study had resistances between a few tens of kilo-ohms and 1mega-ohm. Rudman *et al.* (1986) calculated $k = 5.64$ using their measured value of $w = 3$ and a value of $t = 1.88$ (obtained using the nodes, links and blobs model together with the Inverted Random Void model). In most of the above previous experiments, there is no complete set of exponents (t , w and k) measured directly in the systems in order to check for consistency through the relationship $w = k/t$, as will be done in this thesis. Note that the results presented in this thesis seem to be the first complete work on noise measurements in which the exponents t , k and w have all been determined experimentally.

From simulations on 3D lattice systems, Wright *et al.* (1986) proposed some rigorous bounds for the exponent k of $1.53 < k < 1.60$ but these limits are too small to be applicable to 3D continuum systems, where experimental k values in the range 3.0 – 6.0 are usually observed. However, their simulations on 2D lattice systems, yielding bounds for the exponent k of $1.12 < k < 1.37$, tend to agree with the corresponding experiments on continuum systems. Such experiments include the work of Octavio *et al.* (1987), who studied thin silver films evaporated and ion-milled at liquid Nitrogen temperature and measured $k = 1.2 \pm 0.3$ in the evaporated films, in good agreement with the theoretical bounds as given by Wright *et al.* (1986). On the other hand, Dubson *et al.* (1989) used third harmonic measurements to obtain $k = 1.49 \pm 0.06$ and

$k = 2.6 \pm 0.2$, respectively for 2D computer simulations on lattice and measurements on model continuum samples, but both values are outside the proposed 2D bounds as given by Wright *et al.* (1986). Dubson *et al.* (1989) attributed the discrepancy to the size of the sample, which they felt was too small to give reliable values of the critical exponents. Calculations done by the same authors for their model continuum samples gave $k_{\text{calc}} = 3.4 \pm 0.3$ which is higher than the measured value of 2.6 ± 0.2 . However a value of $k = 2.7 \pm 0.3$, measured after the films had been ion-milled, was lower than their calculated result. The above quoted experiments and simulations show that there is still a lot of discrepancy between experiment and theory concerning $1/f$ noise studies in both 2D and 3D systems.

6.1.4 S_v/V^2 as a function of sample resistance

The normalised noise power at 10Hz ($S_{v10\text{Hz}}/V^2$) was plotted on a log-log scale against the sample resistance, as shown in Figs. 6.8 - 6.11, for the ground Carbon Black, raw Carbon Black, Graphite and Graphite-Boron Nitride systems respectively. The results for the last three systems again clearly show two linear regions, corresponding to two exponents given as w_1 and w_2 (see the graph captions). The exponent w_1 arises from samples closer to ϕ_c while w_2 is obtained from samples further into the conducting region, from which one can again infer the existence of different noise regions for the high and low resistance samples. Note that the w_1 and w_2 correspond to k_1 and k_2 exponents respectively, and mentioned earlier, arise from samples with $m < 2$ and $m \cong 2$ respectively. The $m < 2$ (k_1 , w_1) implies the existence of a noise process arising from mechanisms other than equilibrium resistance fluctuations. The values of w_1 and w_2 for all the systems studied in this thesis are given in Table 6.7.

Again the difference between the two exponents is probably due to the changes in microstructure on moving from close to the percolation threshold (with only a few filamentary conducting paths or links) to the more conducting region (characterised by a thicker network of conducting paths, consisting of many more links, nodes and

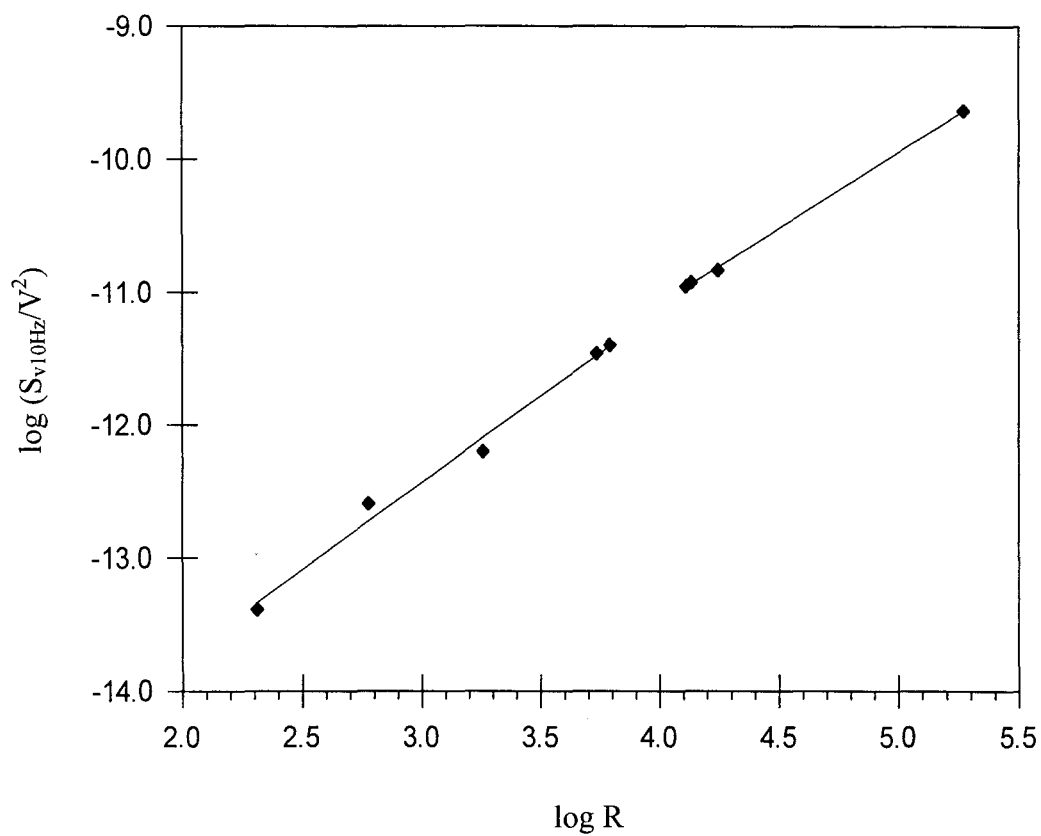


Figure 6.8: A log-log plot of the normalised noise versus the sample resistance for the ground Carbon Black system. The solid lines are linear fits to the data, which give the exponents, $w_1 = 1.10 \pm 0.02$ for the high resistance samples and $w_2 = 1.28 \pm 0.11$ for the low resistance samples.

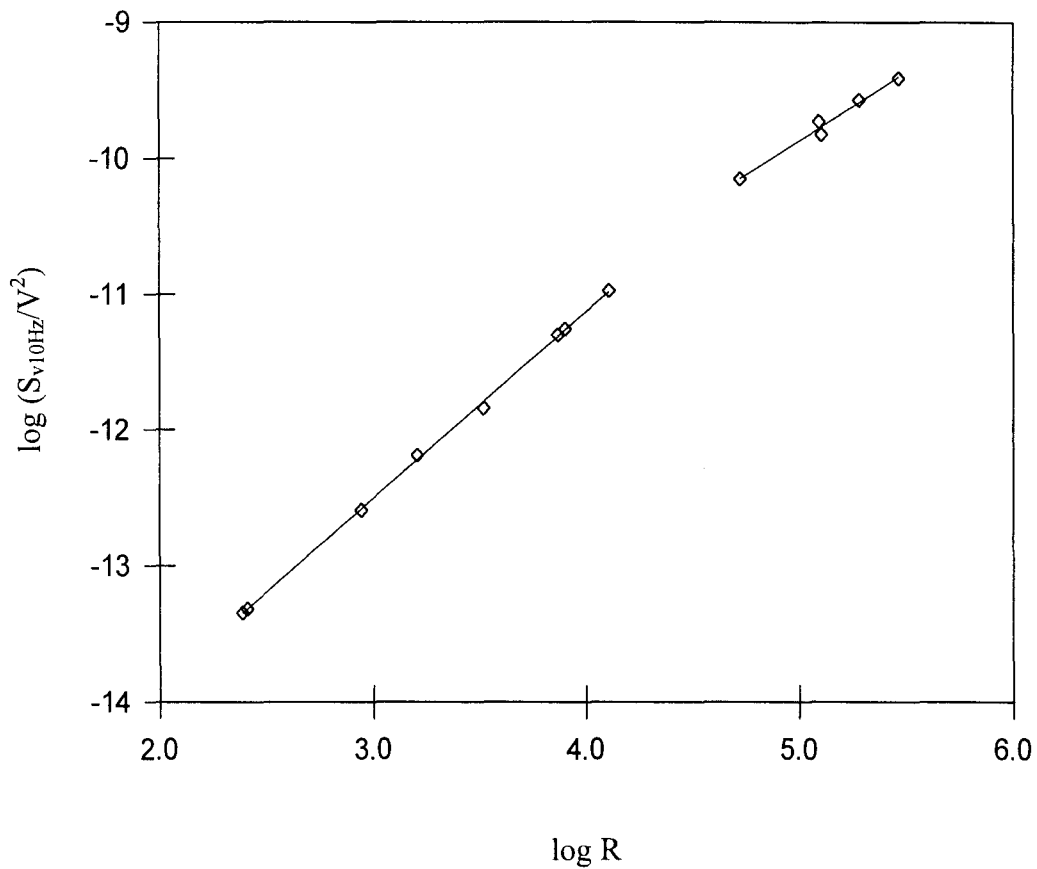


Figure 6.9: A log-log plot of the normalised noise versus the sample resistance for the raw Carbon Black system. The solid lines are linear fits to the data, giving the exponents, $w_1 = 1.00 \pm 0.04$ for the high resistance samples and $w_2 = 1.37 \pm 0.02$ for the low resistance samples.

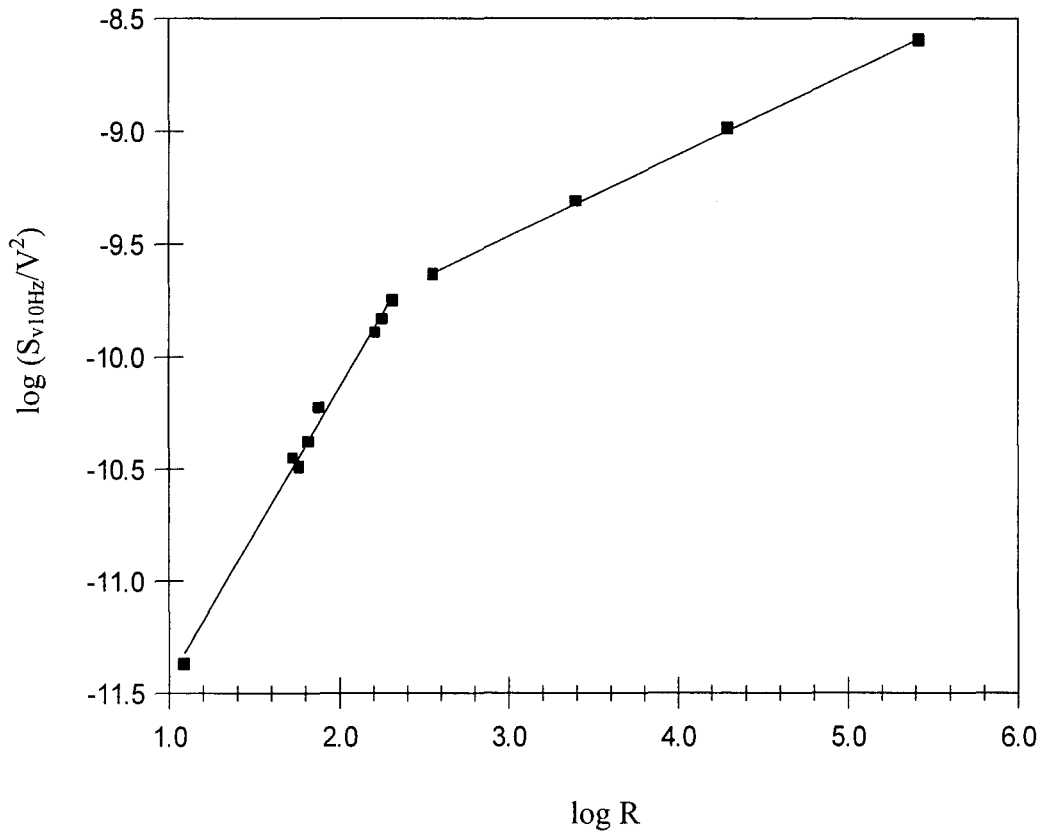


Figure 6.10: A log-log plot of the normalised noise versus the sample resistance for the Graphite system. The solid lines are linear fits to the data, giving the exponents, $w_1 = 0.36 \pm 0.01$ for the high resistance samples and $w_2 = 1.30 \pm 0.06$ for the low resistance samples.

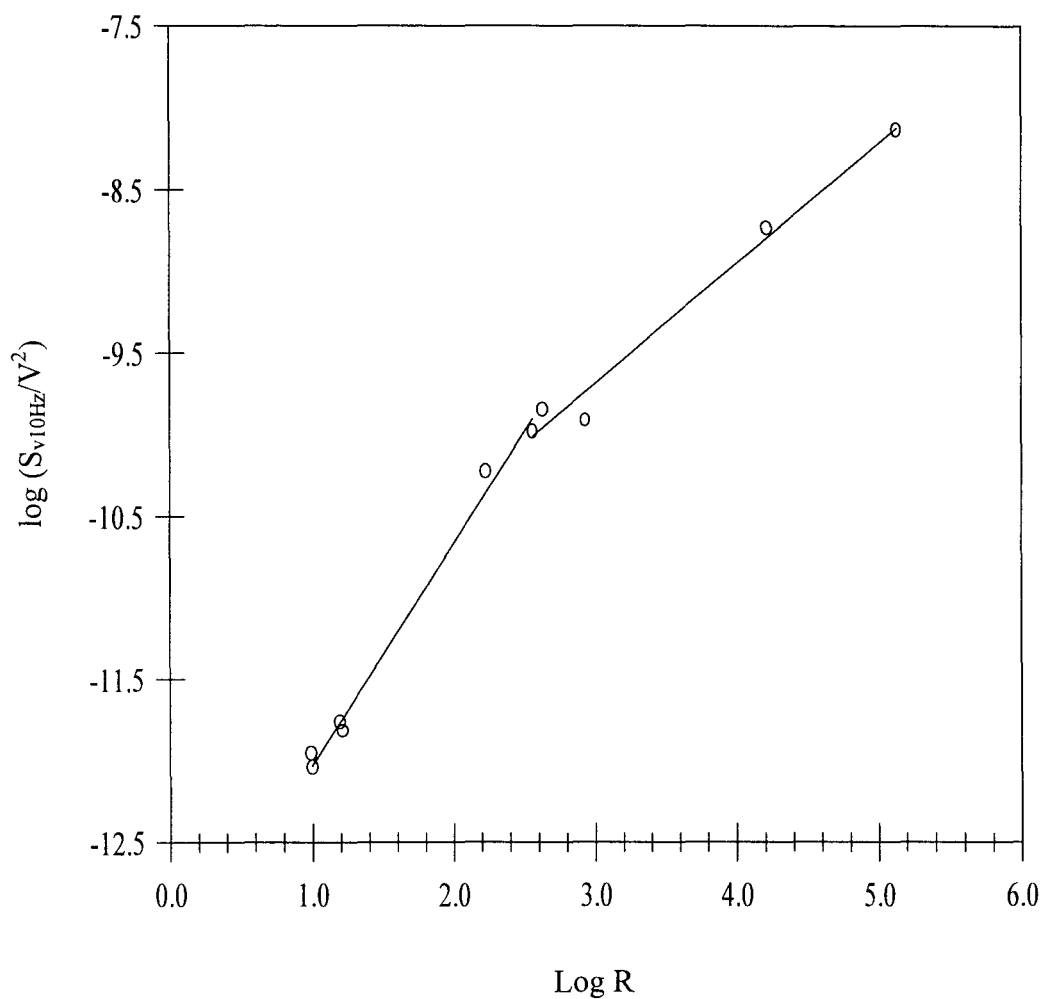


Figure 6.11: A log-log plot of the normalised noise versus the sample resistance for the Graphite-Boron Nitride system. The solid lines are linear fits to the data, which give the exponents, $w_1 = 0.74 \pm 0.13$ for the high resistance samples and $w_2 = 1.36 \pm 0.09$ for the low resistance samples.

Table 6.7: Experimental Noise Exponents (w_1 and w_2) for the Cellular Systems

Composite System	w_1	w_2	w_1/w_2
Ground Carbon Black	1.10 ± 0.02	1.28 ± 0.11	0.86 ± 0.09
Raw Carbon Black	0.93 ± 0.05	1.38 ± 0.03	0.67 ± 0.05
Ground Graphite	0.36 ± 0.01	1.30 ± 0.06	0.28 ± 0.02
Graphite-BN(15%)	0.74 ± 0.13	1.36 ± 0.09	0.54 ± 0.13

Table 6.8: Calculated Noise Exponents (w_{1calc} and w_{2calc}) for the Cellular Systems

Composite System	t	k_1	$w_{1calc}=k_1/t$
Ground Carbon Black	2.06 ± 0.10	2.80 ± 0.08	1.36 ± 0.10
Raw Carbon Black	2.26 ± 0.11	5.23 ± 0.12	2.31 ± 0.16
Ground Graphite	1.93 ± 0.06	0.92 ± 0.03	0.48 ± 0.03
Graphite-BN(15%)	2.51 ± 0.12	1.90 ± 0.31	0.76 ± 0.16

Composite System	t	k_2	$w_{2calc}=k_2/t$
Ground Carbon Black	2.06 ± 0.10	2.71 ± 0.11	1.32 ± 0.12
Raw Carbon Black	2.26 ± 0.11	3.29 ± 0.04	1.46 ± 0.09
Ground Graphite	1.93 ± 0.06	2.58 ± 0.05	1.34 ± 0.07
Graphite-BN(15%)	2.51 ± 0.12	3.60 ± 0.08	1.43 ± 0.10

Note that the calculated values of w in Table 6.8 are close to but are usually greater than the experimental values in Table 6.7. The only exception is w_{1calc} for the raw Carbon Black, which is more than twice the experimental value of w_1 .

blobs). As previously indicated, this sensitivity to the changing microstructure or connectivity is detected only through the measurement of noise, which measures a higher moment of the current distribution than the lower order moment obtained from conductivity measurements. Recall that a single t exponent, as shown earlier in Chapter four, fits the DC conductivity results for each of the systems.

Note that the two Carbon Black systems have very similar values of w_1 and w_2 but very different k_1 and k_2 exponents, which indicates that plotting the noise as a function of $\phi - \phi_c$ is more sensitive to changes in microstructure than the same data plotted versus the sample DC resistance. It appears that closely related systems may give very different values of k exponents but very similar w values. Recall also that in theory $w = k/t$, which means that a range of k and t values may give the same w . The difference in the noise exponents (k) for the two Carbon Black systems could also be attributed to the difference in the mean size of their particles (as one of them was ground in a planetary mill with agate balls) but this is considered unlikely as this difference is not very big (Table 3.1). However, as previously noted, the grinding might cause the ground system to have somewhat more “rounded” contacts than the raw system, which could lead to slightly different inter-particle contact resistances in the two systems. The raw system gives a relatively bigger change from w_1 to w_2 than the ground Carbon Black. Recall that the same trend was also observed with the k exponents presented earlier and that the t exponents are also slightly different.

The w_2 values for all the systems are very close (Table 6.7). This is probably because far above ϕ_c , where the conductor content is higher, the conductor-conductor bonds are relatively stronger and more uniformly distributed than in the just percolating high resistance samples. Therefore the systems are becoming more similar in the high concentration regime where, as previously noted, there are many more blobs and a denser net of conducting links than closer to the percolation threshold. The w_2 results also show better agreement with the Balberg limits (see Table 6.9 later). The above results appear to indicate that the Balberg model is more applicable to the w_2 values than w_1 .

Similar to the t exponent, the w_1 and w_2 values of the three-component system (Graphite-Boron Nitride-Talc-wax) are again larger than the corresponding exponents in the Graphite system. The w_1 values are markedly different, with the Graphite giving a w_1 value about half that measured in the three-component system. For a given ϕ value, the noise is higher in the three-component system of Graphite, Boron Nitride and Talc-wax than in a system with only Graphite mixed with Talc-wax. One would expect that in the three-component system, there are less Graphite-Graphite contacts at a given volume fraction than in the system without the Boron Nitride. This observation is supported by the DC conductivity results, where for a given ϕ value, the conductivity of the Graphite system is higher than the three-component system. Fewer contacts among the conductor particles lead to fewer conducting paths, which lead to an increase in noise according to Wright *et al.* (1986). Nandi *et al.* (1996) showed theoretically that the addition of a single resistor to an existing network leads to a decrease in the total noise of the network. Therefore it is not surprising that the three-component Graphite/Boron Nitride system has higher noise exponents (both k and w) than the Graphite system as borne out by the experimental results. The results also show that the noise amplitude decreases on moving further into the conducting region as the conducting network becomes dense (more conducting paths).

Recall that the DC conductivity exponent (t) of the three-component and Graphite systems is also different. The three-component system gives $t = 2.51 \pm 0.12$ (in close agreement with the original random void prediction) and the Graphite system has $t = 1.93 \pm 0.06$, very close to the universal value of 2.00. Therefore there seems to be a correlation between the magnitudes of the noise exponents (k_1 and k_2 , w_1 and w_2) and the t exponent in these two systems, where the only difference seems to be the manner in which the Graphite particles are distributed on the Talc-wax particles.

Rammal *et al.* (1985) showed theoretically that the exponent w should be related to the noise and conductivity exponents by $w = k/t$. Using the experimental values of t and k , values of w were calculated based on this relationship. These are denoted as w_{1calc} and w_{2calc} and the corresponding values are shown in Table 6.8. Both these

calculated values are very close to the corresponding w_1 and w_2 exponents measured directly in the four cellular systems. The only exceptions are in the w_1 values where the Graphite and raw Carbon Black systems respectively, give w_1 below the lower limit and w_{1calc} above the upper limit proposed by Balberg for the random-void like systems (Table 6.9). The cause for these differences is not immediately clear but the results do show that the w_2 exponents are self-consistent and perhaps more reliable than w_1 . According to the new expressions proposed for t and k by Balberg (section 2.3, eqns. (2.10) and (2.24) respectively), the exponent w is expressed as $w = k/t = [k_{un} + (v + 1 - \omega')/(1 - \omega')]/[t_{un} + (u + \omega' - 1)/(1 - \omega')]$. Using the values of ω' in Table 6.6 (obtained by substituting the measured t exponents in eqn. (2.10)), values of w calculated from the Balberg expression (and denoted w_b) are shown in Table 6.10. These values of w_b are in good agreement with the original Random Void model of Tremblay *et al.* (1986) but are different from the experimental values obtained for the cellular systems. The values of w_b for the extreme t systems (with no experimental values of w) have been included just for comparison.

The self-consistency of the experimental k and w exponents obtained in this thesis has been tested through the relation $w = k/t$ given by Rammal *et al.* (1985). Values of t calculated from the noise exponents using this relation are shown in Tables 6.11 and 6.12. The results clearly show that the k_2 and w_2 are self-consistent, as they give t values close to those measured experimentally (t_{exp}) in Chapter four. The corresponding exponents k_1 and w_1 , measured very close to the percolation threshold, give t values greater than t_{exp} and are therefore not self-consistent. From this observation, one can conclude that the k_2 and w_2 are more fundamental than k_1 and w_1 .

Unlike k_1 and k_2 , the two values of the w exponent arising from plotting the normalised noise versus the sample resistance have also been observed in two previous studies on continuum systems (Rudman *et al.* 1986, Pierre *et al.* 1990b). Rudman *et al.* (1986) obtained $w_1 \sim 3$ and $w_2 \sim 1$ (i.e. $w_1 > w_2$) closer to and further away from ϕ_c respectively in Ag/Pt-TFE composites and proposed that the transition

Table 6.9: Limits of w for 3D continuum systems

MODEL	TFB	BALBERG(1998)
Random Void	2.02	$0.78 \leq w \leq 2.1$
Inverted Random Void	2.29	$0.78 \leq w \leq 3$

Table 6.10: Calculated w exponents for the Cellular Systems from the new Balberg’s expression.

Composite System	t	ω'	w_b
Ground Carbon Black	2.06 ± 0.10	-0.42 ± 0.02	2.10 ± 0.10
Raw Carbon Black	2.26 ± 0.11	-0.19 ± 0.01	2.06 ± 0.11
Ground Graphite	1.93 ± 0.06	-0.61 ± 0.02	2.13 ± 0.07
Graphite/BN(15%)	2.51 ± 0.12	0.0100 ± 0.0005	2.02 ± 0.10
Nickel	1.52 ± 0.15	-1.88 ± 0.18	2.25 ± 0.22
Fe ₃ O ₄	4.12 ± 0.23	0.52 ± 0.03	1.88 ± 0.11
Niobium Carbide	1.93 ± 0.06	0.65 ± 0.08	1.84 ± 0.23

Note: In obtaining the w values in Table 6.10, the exponent t was used to calculate ω' (eqn. (2.10)), which was in turn used in the Balberg expression (eqn. (2.25)) to find w_b . Note that the ω' values are generally very small. It is interesting to note that these w_b values are very similar. The w_b values are also close to but higher than the experimental w_2 values. As the single t exponent gives a single ω' and w_b for each of the systems, the occurrence of w_1 and w_2 is not taken into account by the model. Note again that the model gives w values closer to w_2 and that w_b values decrease with increasing t.

Table 6.11: Exponent t from Experimental Noise Exponents for the Cellular Systems

Composite System	k_1	w_1	$t = k_1/w_1$	t_{exp}
Ground Carbon Black	2.80 ± 0.08	1.10 ± 0.02	2.54 ± 0.12	2.06 ± 0.10
Raw Carbon Black	5.23 ± 0.12	0.93 ± 0.05	5.62 ± 0.43	2.26 ± 0.11
Ground Graphite	0.92 ± 0.03	0.36 ± 0.01	2.56 ± 0.15	1.93 ± 0.06
Graphite-BN(15%)	1.90 ± 0.31	0.74 ± 0.13	2.57 ± 0.63	2.51 ± 0.12

Table 6.12: Exponent t from Experimental Noise Exponents for the Cellular Systems

Composite System	k_2	w_2	$t = k_2/w_2$	t_{exp}
Ground Carbon Black	2.71 ± 0.11	1.28 ± 0.11	2.12 ± 0.27	2.06 ± 0.10
Raw Carbon Black	3.29 ± 0.04	1.38 ± 0.03	2.38 ± 0.08	2.26 ± 0.11
Ground Graphite	2.58 ± 0.05	1.30 ± 0.06	1.98 ± 0.13	1.93 ± 0.06
Graphite-BN(15%)	3.60 ± 0.08	1.36 ± 0.09	2.65 ± 0.08	2.51 ± 0.12

observed in the w exponent was due to volume fraction-dependent changes in the distribution of inter-particle resistance. The samples used in their experiments were rods of 3.1mm in diameter and 20.0mm in length with resistance values in the range 0.5Ω to $30\text{ k}\Omega$. The mean diameter of the Ag/Pt powder was $1\mu\text{m}$ while the teflon particles had a mean diameter of $0.5\mu\text{m}$ such that $R_i/R_c = 1/2$. The noise results reported in their experiments were analysed at a frequency of 10Hz, the same as in the present study. The most obvious difference between this result and those obtained in the cellular systems studied in this thesis is the fact that $w_1 > w_2$ in the Ag/Pt-TFE composite as opposed to $w_1 < w_2$ observed in the cellular systems. Recall that $R_c \ll R_i$ for all the cellular systems studied in this thesis while R_c is slightly greater than R_i in the Ag/Pt-TFE system.

Pierre *et al.* (1990b) studied $1/f$ noise in copper particle-polymer composites as a function of frequency ($10^{-2} - 10^4\text{Hz}$) and resistance ($10^1 - 10^9\Omega$). They observed two values of w ; with $w_1 = 1.0 \pm 0.3$ for the high resistance ($10^5 - 10^9\Omega$) and $w_2 = 1.5 \pm 0.2$ for the low resistance ($10^1 - 10^6\Omega$) samples, in qualitative agreement with the results obtained from the cellular systems. Pierre and his colleagues (1990b) attributed the $S_v \sim R^{1.5}$ behaviour to conduction in the Sharvin limit and $S_v \sim R^{1.0}$ as arising from a noisy contact limited by intrinsic conduction through a dirty oxide layer, given the high oxygen affinity of the copper powder. Unfortunately from this study, no experimental values for the exponents t and k were given for one to calculate the corresponding k values from $k = wt$, so as to check on the consistency of the results and to make a thorough comparison with the present study. Also no DC ϕ_c result was given in this study. However, the results on Copper particle-polymer composites were among the first to reveal and propose the dependence of the noise exponents on different types of contacts existing above the percolation threshold in real continuum systems. However, the mechanism of intrinsic conduction through a dirty oxide layer does not apply in the cellular systems, as none of the conductors used (Carbon and Graphite) will form an oxide layer. Based on Pierre *et al.*'s interpretation, the w_2 values in Table 6.7 could be explained by conduction in the Sharvin limit, which occurs when the mean free path is much smaller than the contact radius between two

contacting metallic and spherical particles to give a $3/2$ -law ($\equiv w = 1.5$) dependence of the noise power on contact resistance (Pierre *et al.* 1990a and 1990b). However, it is difficult to define a contact ‘radius’ for the Graphite particles used in the present study because of their irregular shape (Fig. 3.1a).

In a compacted Graphite-Boron Nitride system (where the insulator and conductor particle “radii” were nearly equal, i.e. $R_i \cong R_c$), Wu and McLachlan (1997) obtained a single $w = 1.47 \pm 0.05$ in the axial direction and 1.72 ± 0.08 in the transverse direction. The axial w exponent is in reasonable agreement with the w_2 exponents shown in Table 6.7 for the cellular systems. The powders used in Wu’s study had mean diameters of $18.8 \pm 2.5 \mu\text{m}$ for Graphite and $12.4 \pm 1.8 \mu\text{m}$ for the Boron Nitride (Wu 1997). The occurrence of two values of w was not observed in this system probably because of the limited range of resistance (between 1Ω and $1\text{k}\Omega$) covered by the samples used in the measurement (axial direction). It is interesting to note that the w_2 exponents of the cellular systems were obtained from samples whose resistances were of the same order of magnitude as those used in the Graphite-Boron Nitride composite studied by Wu (1997) and Wu and McLachlan (1997). Recall that the samples from the cellular systems had DC resistances from 10Ω (120Ω) to $200\text{k}\Omega$ ($1\text{M}\Omega$) and the estimated insulator to conductor radius ratios (R_i/R_c) varied from 15 to 40. The ratio of the particle size of the powders used by Wu is also too small for the system to be described by random void-like models. The ratio ($R_i/R_c \cong 1$) could also be the cause for the non-occurrence of two w values in Wu’s samples but this is probably not the case as another system (Rudman *et al.* 1986), discussed above, with a smaller ratio ($R_i/R_c = 1/2$) gave two values of the exponent w .

Note that some systems showing two values of the exponent w have different sizes of the insulator and conductor particles (Rudman *et al.* 1986 and this work). Therefore one could speculate that the relative size of the insulator to conductor particles in the systems might be playing a role in the occurrence of w_1 and w_2 and the reason why the Ag/Pt-TFE system gives $w_1 > w_2$ is probably because R_i is slightly less than R_c . However, in Pierre *et al.*’s experiment (1990b), which also gives two values of w , it is

impossible to tell the size of the insulator (polymer) particles relative to that of the conductor, so the system may or may not belong to any of the random void-like models. It would be of interest to do noise measurements in definite inverted random void-like systems (with $R_i \ll R_c$) in order to investigate these observations.

6.2 Summary

Experimental results for $1/f$ -noise studies in several cellular percolative systems have been presented in this chapter. All results were obtained from measurements on samples close to but on the conducting side ($\phi > \phi_c$) of the percolation threshold. The noise power spectrum was measured in the axial (compression) direction. Some predicted aspects of the noise were verified; namely the $1/f$ behaviour ($\equiv \gamma \sim 1$), the power law dependencies on resistance and $(\phi - \phi_c)$. The V^2 -dependence, which is evidence of the noise originating from resistance fluctuations, was observed in the low resistance (more conducting) samples. The high resistance (less conducting) samples gave lower values (1.00 – 1.60) for the exponent m , probably indicating the existence of mechanisms other than equilibrium resistance fluctuations. The normalised noise power was plotted on a log-log scale against $(\phi - \phi_c)$ and resistance to give the exponents $k_1(w_1)$ and $k_2(w_2)$, one close to and the other further away from the percolation threshold respectively. The exponent $k_1(w_1)$ arises from the high resistance samples, with the lower m values, and the samples with $m \approx 2$ gave $k_2(w_2)$. For all the systems, $w_2 > w_1$ while $k_1 > k_2$ for the Carbon Black systems and $k_2 > k_1$ for the Graphite systems.

The occurrence of two values of the exponents k and w for different values of $(\phi - \phi_c)$ and sample resistance respectively confirm that $1/f$ noise is more sensitive to the changes in microstructure or distribution of the contact resistances than the resistance (or conductivity). Note that a single t exponent could fit the conductivity results above ϕ_c for all the systems studied and none of the samples used for the noise

measurements were in the crossover region. As noted earlier, noise measurements measure the fourth moment of the current distribution while resistance measurements account for the second order moment of the current. The most striking feature of the results is the differences in the k_1 and w_1 values and the similar values for all the w_2 exponents. The similarity in the w_2 exponents show that all the systems are evolving to a more similar links, nodes and blobs structure at higher ϕ 's of the conducting component but probably have different links, nodes and blobs structures close to the percolation threshold. Note that the presence of these different links, nodes and blobs structures cannot be detected by conductivity measurements. The experimental w_2 values agree well with the calculated values (Table 6.8), obtained from the measured values of k and t , in accordance with Rammal *et al.*'s (1985) prediction of $w = k/t$. This relationship is better obeyed by samples with $m \sim 2$ for which the noise exponent (w_2) also falls within the new Balberg limits for 3D random void-like continuum systems (Table 6.9). Samples with $m < 2$, giving rise to k_1 and w_1 , imply the existence of other noise mechanisms in the region close to the percolation threshold, where the conducting paths are more tenuous than well above ϕ_c .

Note also that continuum systems in which two values of the exponent w have been observed (from the present study and those from the literature) may possibly be put into two categories. In the first category we have systems in which $w_2 > w_1$. Such systems are observed to have $R_i > R_c$ (i.e. random void-like systems), where R_i is the insulator radius and R_c the conductor particle radius. This category includes systems studied in this thesis. In the second category, $w_2 < w_1$ and $R_i < R_c$ (i.e. inverted random void-like system). Unfortunately, the only system in this class, the Ag/Pt-TFE composite studied by Rudman *et al.* (1986), has R_i/R_c too small for the system to be considered inverted random-void like (where ideally $R_i \ll R_c$). More noise experiments need to be conducted on both random-void and inverted random void-like systems before one can draw a conclusion on the above trends observed in the noise exponents. Note also that in Copper particle-polymer composite studied by Pierre *et al.* (1990b), $w_2 > w_1$ was observed, but it is not possible to tell whether $R_i > R_c$ in this system.

The noise measurements presented in this Chapter seem to be the only complete work to have determined the different noise exponents (k and w) and the related conductivity parameter (t). This is borne out by the results shown in Table 6.13, which includes results from some of the most referenced noise articles.

Table 6.13: Summary of Noise Exponents and Related Parameters Measured in some 3D Continuum Systems

System	t	k ₁	**k ₂ (k)	w ₁	**w ₂ (w)
Ground CB	2.06 ± 0.10	2.80 ± 0.08	2.71 ± 0.11	1.10 ± 0.02	1.28 ± 0.11
Raw CB	2.26 ± 0.11	5.23 ± 0.12	3.29 ± 0.04	0.93 ± 0.05	1.38 ± 0.03
Graphite	1.93 ± 0.06	0.92 ± 0.03	2.58 ± 0.08	0.36 ± 0.01	1.30 ± 0.06
Graphit-BN	2.51 ± 0.12	1.90 ± 0.31	3.60 ± 0.08	0.74 ± 0.13	1.36 ± 0.09

Previous Studies

System	t	k ₁	k(k ₂)	w ₁	w(w ₂)
Graphite-Boron Nitride: Wu 1997	2.63 ± 0.07		*3.87 ± 0.07		1.47 ± 0.05
Carbon-wax: Nandi <i>et al.</i> 1996					1.7 ± 0.2
Copper-polymer: Pierre <i>et al.</i> 1990b				1.0 ± 0.3	1.5 ± 0.2
Ag/Pt-TFE: Rudman <i>et al.</i> 1986				3.0	1.0
Carbon-wax: Chen & Chou 1985	2.3 ± 0.4		5.0 ± 1.0		*2.2 ± 0.8

*Denotes values that have been calculated from the measured values using the relationship $w = k/t$. As is clearly seen from the Table, most previous studies never directly measured all the relevant parameters required to interpret and correlate the noise measurements. Note: CB-Carbon Black, BN-Boron Nitride.

**The k_2 and w_2 exponents are comparable to k and w from previous studies, as they have been determined in the region well above ϕ_c .

CHAPTER SEVEN

MAGNETIC PROPERTIES OF THE NICKEL AND MAGNETITE SYSTEMS

7.0 Introduction

A considerable amount of experimental electrical conductivity measurements have been made to which percolation and effective media theories have been applied to analyse the results. In theory, the same equations (but with different parameters) can also be applied for the magnetic permeability of mixtures or heterogeneous media, but very little has been done so far in this field. One of the reasons for this gap could be that magnetic percolation transition is not as sharp as its electrical counterpart because of the small contrast between the permeability of the samples below and above the percolation threshold (ϕ_c). Increasing the contrast would require a high permeability filler/magnetic component, which is not readily available in an appropriate (powder) form.

The present chapter gives the results of the magnetic properties measured in composites consisting of Nickel (conducting ferromagnet) and Fe_3O_4 (semi-conducting ferromagnet) in a common insulating matrix of Talc-wax. The DC magnetic properties, which include saturation magnetisation (M_s), coercive field (H_c or B_c) and remnant magnetisation (M_r) were studied as a function of the volume fraction (ϕ) of the magnetic component. The AC susceptibility (ACS, χ) of the two systems was also studied as a function of volume fraction of the magnetic

component. The results are compared to the variation (as a function of ϕ) of the DC conductivity and dielectric constant measured in the same systems, which were presented in Chapter four. The permeability results (obtained from $\mu_{mr} = 1 + \chi_{mr}$, where the subscript 'm' denotes parameters for the composite) were fitted to the two exponent phenomenological equation, using the s and ϕ_c (Table 4.1) obtained from DC conductivity results as fixed parameters, while t and μ_h were treated as variables. The fits yield estimates of μ_h for Fe_3O_4 and Nickel, which are much lower than expected. The results in this chapter are presented primarily in graphical form. Section 7.1 deals with the DC magnetic results while in section 7.2, the AC results are presented. Section 7.3 summarises and gives some concluding remarks on the results in this chapter.

7.1 DC Magnetometer Results

Magnetisation curves (magnetisation (M) versus external field (H)) were plotted for the samples as shown in Figs. 7.1 – 7.3, from which M_s , H_c and M_r , were determined. The curves show hysteresis loops, which are typical of ferromagnetic materials. The Magnetite (Fe_3O_4) system has a larger area hysteresis loop than the Nickel system for the same ϕ value. The quantities H_c and M_r (refer to Fig. 7.1) were obtained from the magnetisation curve for each sample in the two systems. Note that the actual values of H_c and M_r were obtained from the more blown up versions of the curves shown in Figs. 7.1 and 7.3.

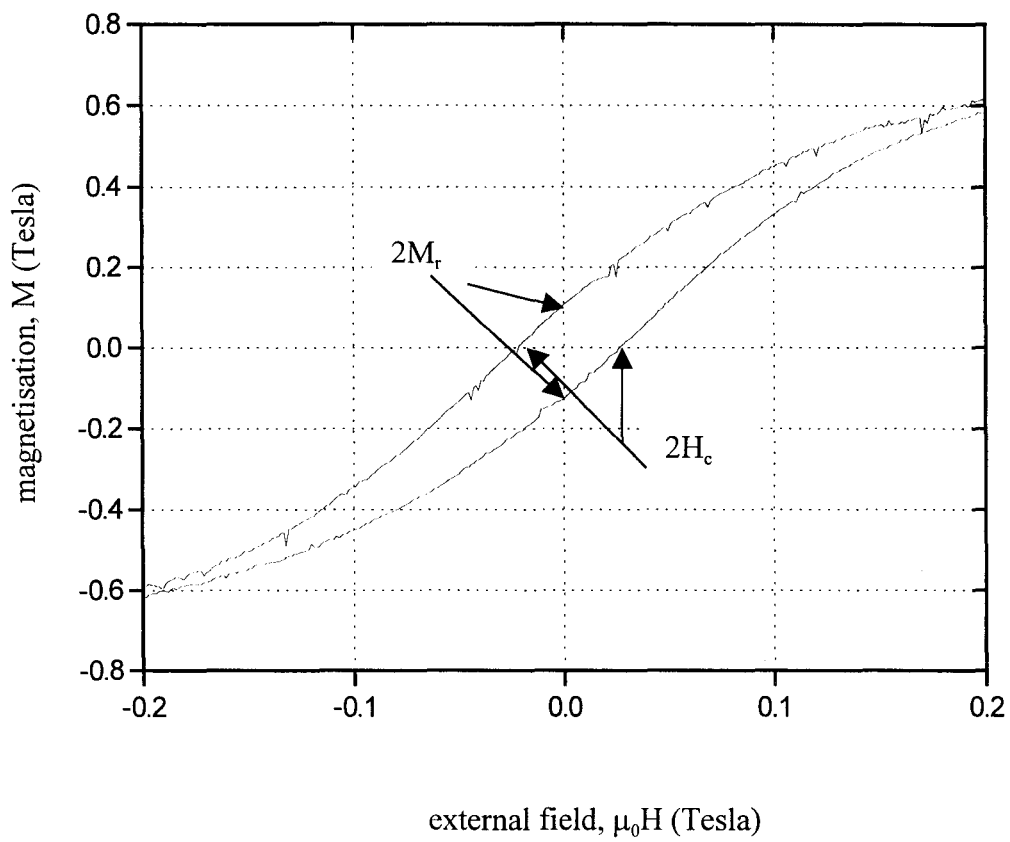


Figure 7.1: A partial Magnetisation curve for a Fe_3O_4 -Talc-wax sample ($\phi = 0.1718$) above the percolation threshold ($\phi_c = 0.025 \pm 0.003$).

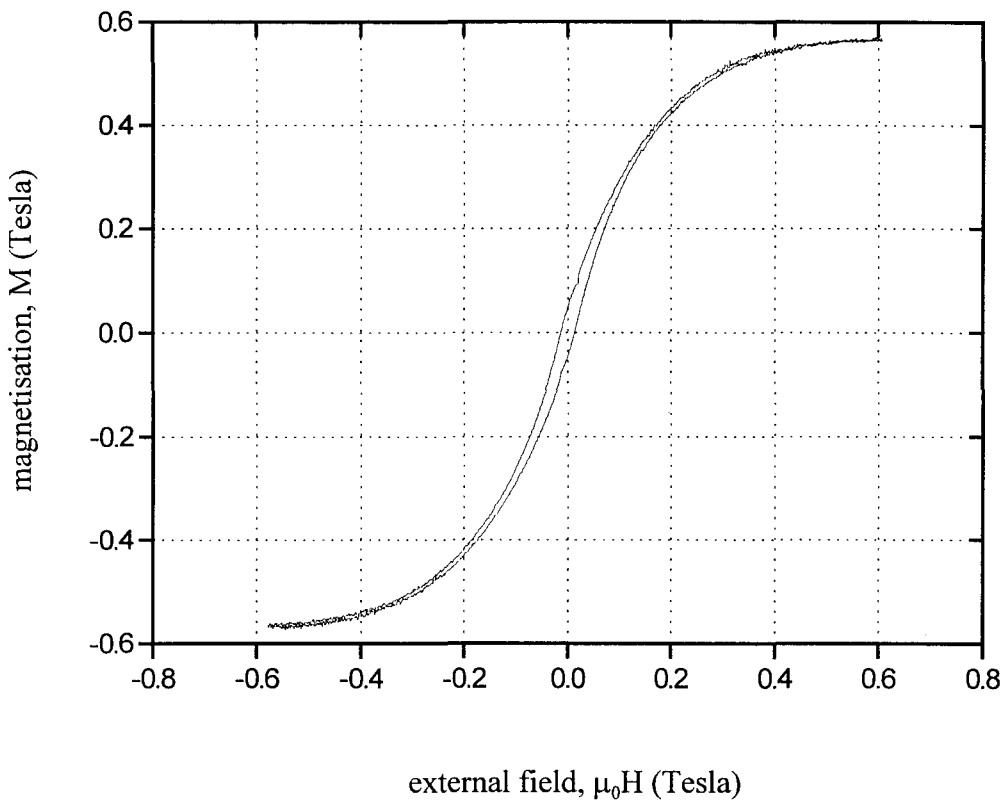


Figure 7.2: Magnetisation curve for a Nickel-Talc-wax sample ($\phi = 0.1173$) above the percolation threshold ($\phi_c = 0.025 \pm 0.003$). The results indicate that the saturation magnetisation (M_s) is not attained in the measurement.

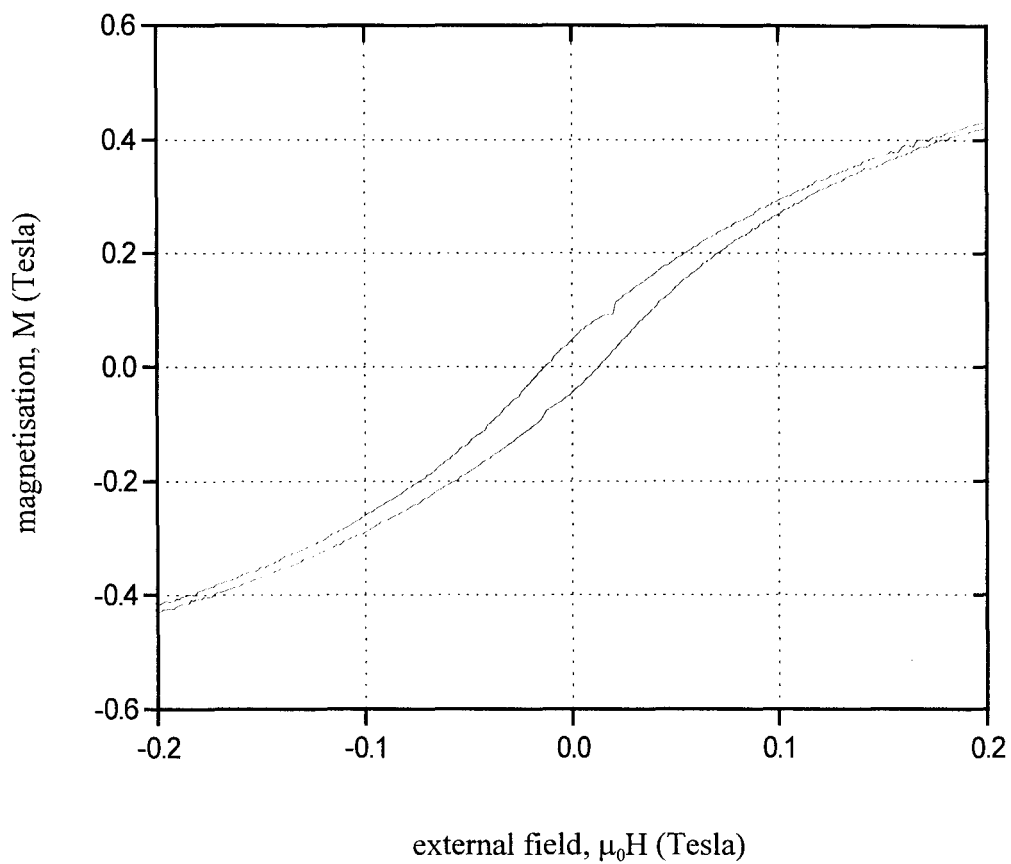


Figure 7.3: A partial Magnetisation curve for a Nickel-Talc-wax sample ($\phi = 0.1173$) above the percolation threshold ($\phi_c = 0.025 \pm 0.003$).

7.1.1 Coercive field (H_c) as a function of volume fraction

Figure 7.4 shows the results of the coercive field plotted as a function of volume fraction of Fe_3O_4 for the Fe_3O_4 system. The results have a lot of scatter at low volume fractions but show a broad peak in H_c located between $\phi = 0.06$ and $\phi = 0.15$. Note that the percolation threshold (ϕ_c) obtained from DC conductivity measurements is 0.025 ± 0.003 for the Fe_3O_4 system. The location of the peak is in qualitative agreement with that observed for the real dielectric constant (ϵ_{mr}) as they both occur beyond the ϕ_c obtained from DC conductivity measurements. There is no apparent reason for these results as ϵ_{mr} is a first order term below ϕ_c and second order above ϕ_c . The results for H_c plotted against the volume fraction of Nickel for the Nickel system are shown in Fig. 7.5. The Nickel system shows an H_c peak at a lower volume fraction than the Fe_3O_4 system. The results show a hump-like feature around 5% volume fraction of Nickel ($\phi = 0.05$), which is double the critical volume fraction ($\phi_c = 0.025 \pm 0.003$) obtained through DC conductivity measurements. The change in H_c with volume fraction is a result of the change in magneto-reluctance of the composite.

The only work the author found in the literature in which the variation of H_c with volume fraction of the magnetic component has been studied extensively (in magnetic–nonmagnetic composites) is that of Xiao and Chien (1987) and Liou and Chien (1988) in granular Fe-SiO₂ films. However, the magnetic particles used in these studies had sizes between 10Å and 170Å, which are less than the critical size (200Å) of a single domain in Fe particles at room temperature, and therefore were in the superparamagnetic state. However, measurements done on the Fe-SiO₂ samples at room temperature also show a peak in H_c , in semi-qualitative agreement with the results obtained in this thesis.

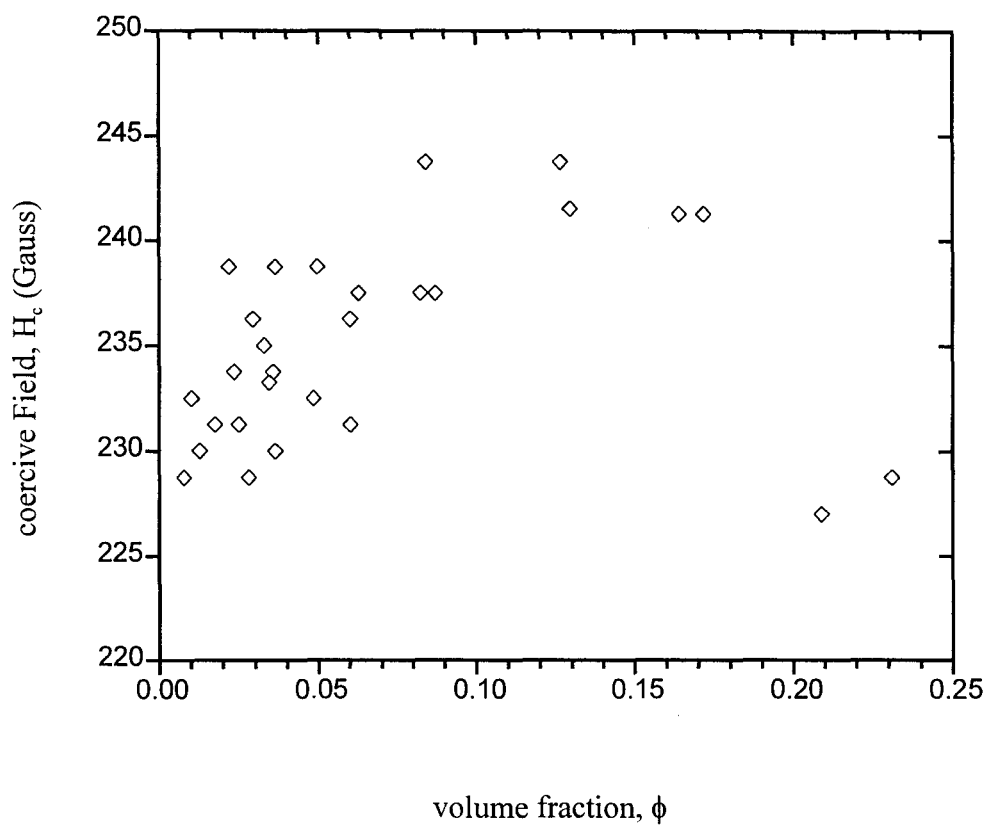


Figure 7.4: The coercive field (H_c) plotted versus the volume fraction (ϕ) for the Fe_3O_4 -Talc-wax samples. The percolation threshold from DC conductivity measurements for the system is; $\phi_c = 0.025 \pm 0.003$. Notice the broad peak located from $\phi = 0.08$ to 0.13 .

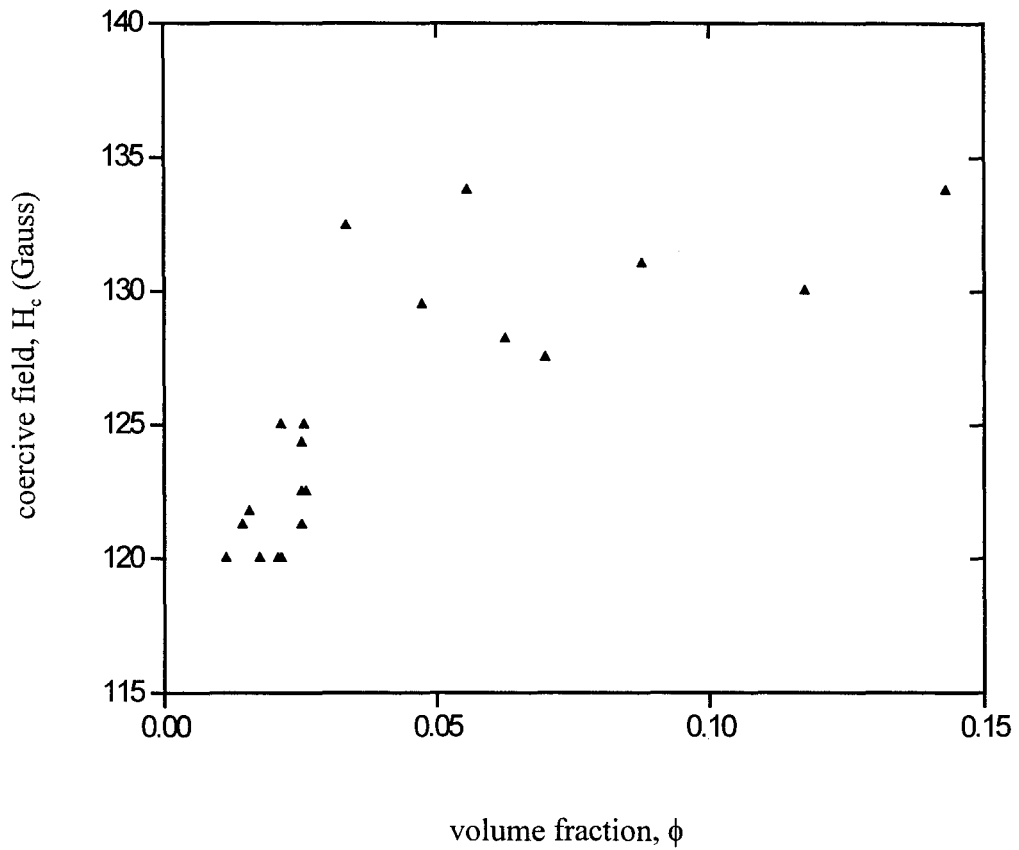


Figure 7.5: The coercive field (H_c) plotted versus the volume fraction (ϕ) for the Nickel-Talc-wax samples. The percolation threshold from DC conductivity measurements for the system is $\phi_c = 0.025 \pm 0.003$. Note also the up-turn shown by the last point at high ϕ . In the absence of more points at higher ϕ 's, it is difficult to tell whether this is a real effect or not.

Xiao and Chien (1987) observed that the coercive field (H_c) was greatly enhanced on approaching the percolation threshold (ϕ_c) from below and dropped precipitously at ϕ_c due to percolation effects. According to Xiao and Chien, as ϕ_c is approached from below, the granules start to form a connecting network, which becomes infinite at ϕ_c . At this point, the granules would prefer a magnetic-closure domain structure due to dipolar interaction and so H_c decreases. H_c was also observed to increase as the temperature was lowered from 400K to 2K during the measurements. Furthermore, the coercive field was observed to be very sensitive to the size of their particles and decreased drastically at room temperature (in comparison to the low temperature results) in their samples consisting of the largest particles.

The results of H_c versus volume fraction of the two systems studied in this thesis (Figs. 7.4 and 7.5) are different from those observed in the previous studies on Fe-SiO₂ films. No sharp peaks in H_c for the two systems were observed. H_c does not decrease at ϕ_c in the Fe₃O₄ and Nickel systems as was indicated in the Fe-SiO₂ films. Instead, the coercive field continues to increase with ϕ , showing some broad peak at a ϕ well beyond ϕ_c . In the work of Xiao and Chien (1987), ϕ_c was not measured directly through DC conductivity results, but estimated on the basis of previous studies on other granular composites. The mean diameter of the Fe₃O₄ particles used in the present study is about 10 μ m, which is much larger than the critical domain size. Therefore H_c is relatively small in comparison to that measured in the Fe-SiO₂ films.

7.1.2 The Remnant Magnetisation (M_r) as a function of magnetic volume fraction

Figures 7.6 and 7.7 show the results of M_r (refer to Fig. 7.1) plotted as a function of volume fraction of Fe₃O₄ and Nickel respectively. The Fe₃O₄-Talc-wax results clearly show a minimum, which appears to coincide with the H_c peak of Fig. 7.4, possibly

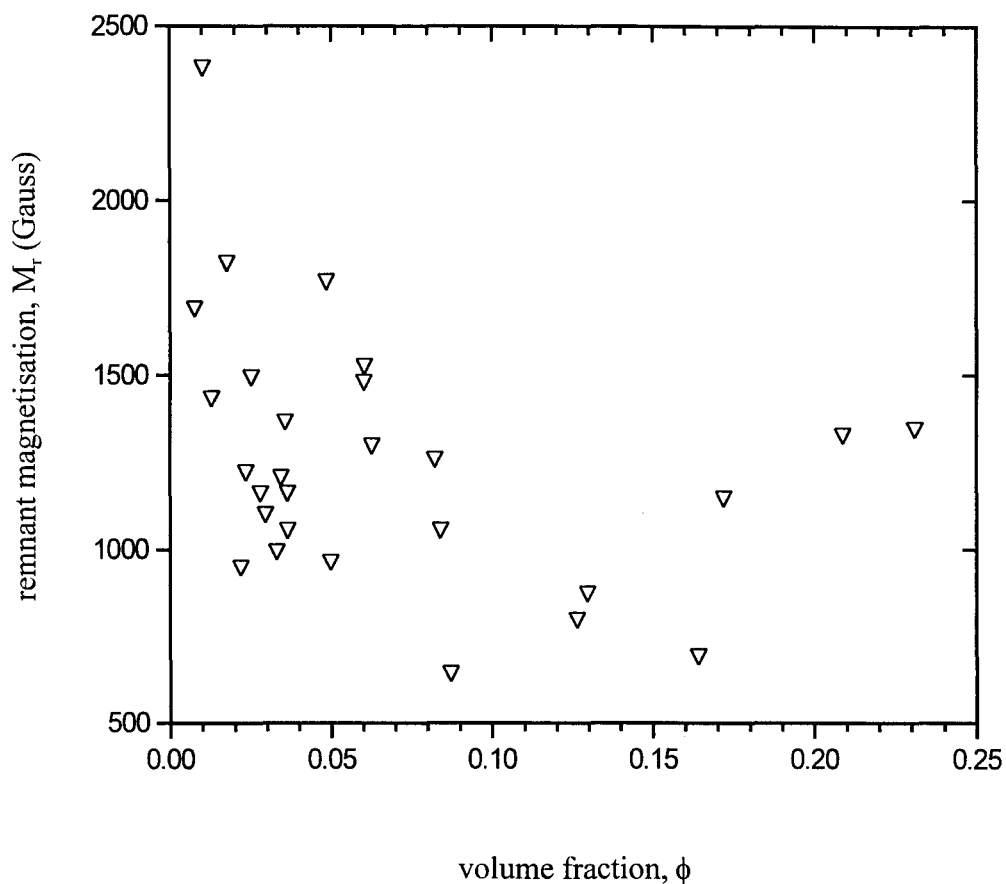


Figure 7.6: The remnant magnetisation (M_r) plotted versus the volume fraction (ϕ) for the Fe_3O_4 -Talc-wax samples. The percolation threshold from DC conductivity measurements for the system is; $\phi_c = 0.025 \pm 0.003$. Note the minimum in the graph, which occurs around the volume fractions corresponding to the H_c peak.

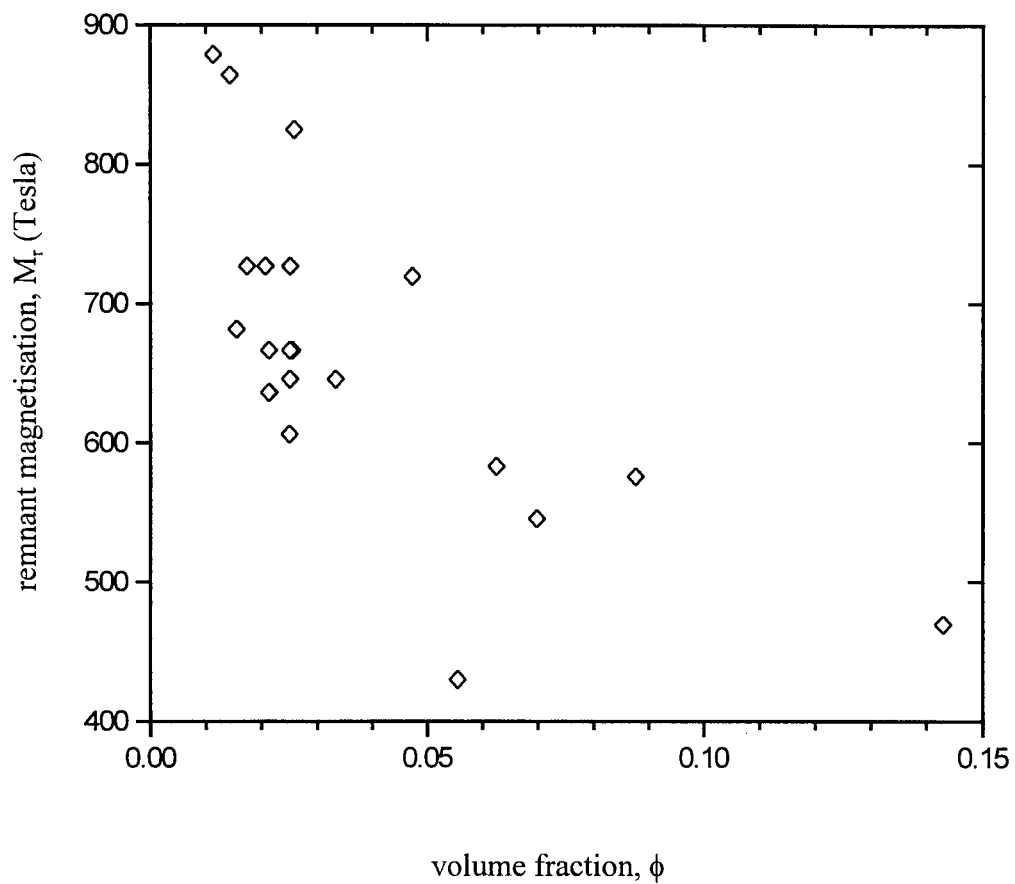


Figure 7.7: The remnant magnetisation (M_r) plotted versus the volume fraction (ϕ) for the Nickel-Talc-wax samples. The percolation threshold from DC conductivity measurements for the system is; $\phi_c = 0.025 \pm 0.003$.

implying an inverse relation between H_c and M_r . The reason for this coincidence is not immediately obvious. For the Nickel system, M_r decreases with volume fraction (ϕ) but without a clear minimum in the ϕ range covered (Fig. 7.7). In addition, the Nickel system does not show a clear maximum in H_c , unlike the Fe_3O_4 system.

In Figs. 7.6 and 7.7, M_r is observed to decrease, initially, with increasing volume fraction (ϕ). Note also that the Fe_3O_4 system has higher values of M_r for the same ϕ than the Nickel system. At low values of ϕ , isolated or non-interacting magnetic particles give high values of M_r . As ϕ increases, the particles start interacting and M_r decreases. Unfortunately, it is not clear what causes the small increase in M_r at higher volume fractions ($\phi > 0.16$) in the Fe_3O_4 -Talc-wax system. Figures 7.8 and 7.9 show the same M_r results (in Figs. 7.6 and 7.7) normalised by the volume fraction (ϕ) and then plotted versus ϕ . The ratio M_r/ϕ ($\equiv M_r/M_s$) decreases with ϕ for the two systems. In both systems, the decrease in M_r/ϕ is dramatic towards ϕ_c . The lines (arrows) in Figs. 7.8 and 7.9 are the best straight line fits that pass through the percolation threshold. Therefore, these lines show that, with a prior knowledge of ϕ_c , one can extrapolate the experimental points (below ϕ_c) through the percolation threshold. Unfortunately, the author could find no previous experimental or theoretical results for comparison and theories that incorporate the hysteresis of percolation systems have not yet been developed. Further studies are necessary to investigate the behaviour of M_r with magnetic volume fraction in percolation systems.

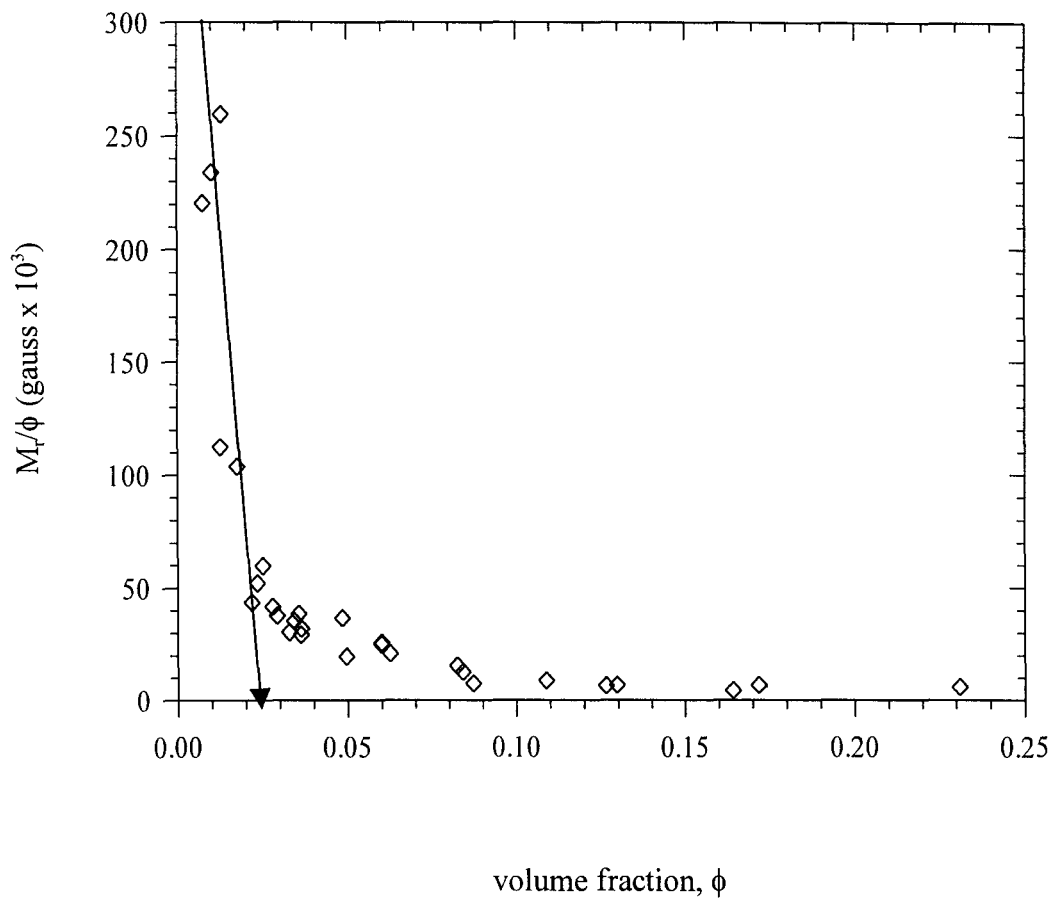


Figure 7.8: The normalised remnant magnetisation (M_r/ϕ) versus volume fraction (ϕ) of Fe_3O_4 for the Fe_3O_4 system. The line (arrow) in the figure indicates the position of ϕ_c .

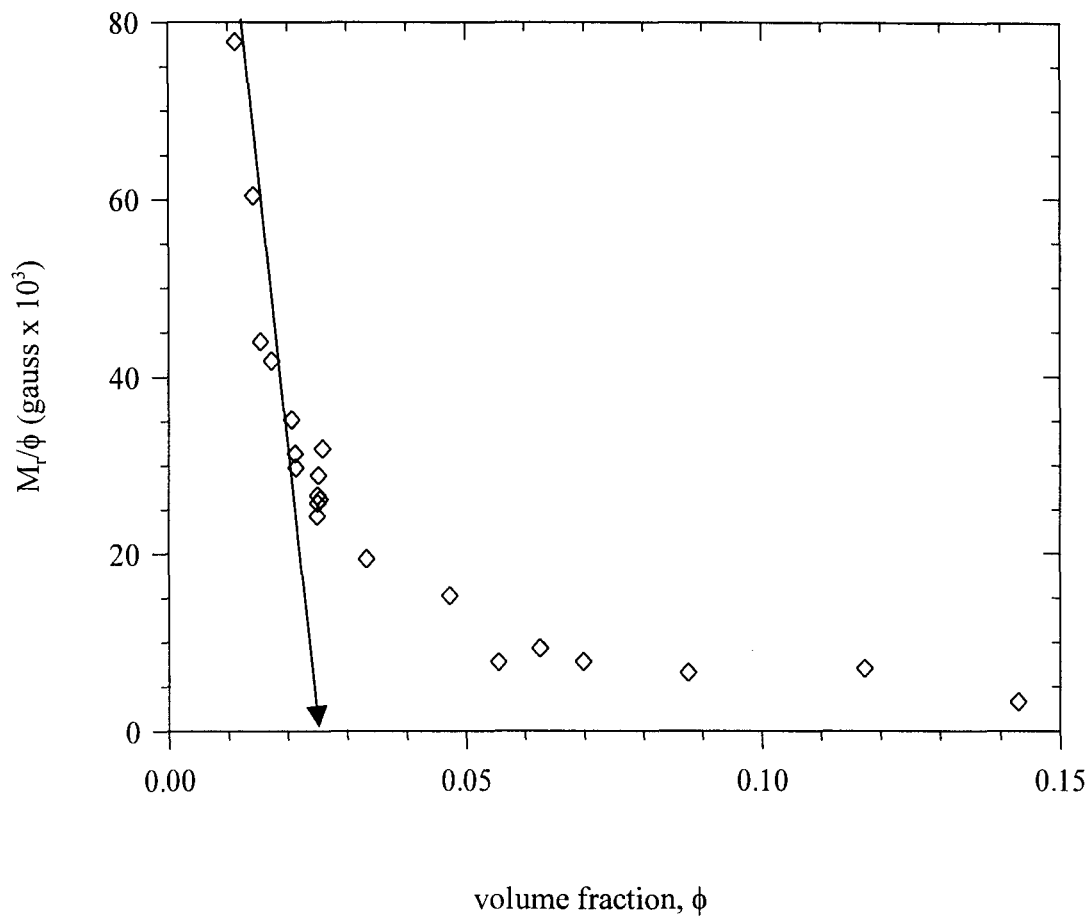


Figure 7.9: The normalised remnant magnetisation (M_r/ϕ) versus volume fraction (ϕ) of Nickel for the Nickel system. The line (arrow) in the figure indicates the position of ϕ_c .

7.2 AC Magnetic Results

This section presents AC magnetic results for the real permeability and susceptibility, measured at a frequency of 32.1Hz, as described in section 3.2.5.2. The permeability and susceptibility of the samples are related through the relation: $\mu_{mr} = \chi_{mr} + 1$. The values of μ_{mr} are plotted against the magnetic volume fraction in Figs. 7.10 and 7.11 for the Magnetite (Fe_3O_4) and Nickel systems respectively. The permeability results were fitted to the two exponent phenomenological equation as shown in the same figures. Note that these results could not be fitted to the percolation equations as a quarter of the data points are in the crossover region given by $(\mu_l/\mu_h)^{1/(s+t)}$, where μ_l and μ_h are the permeabilities of the low and high permeability components respectively, while s and t are the DC conductivity exponents.

7.2.1 Permeability as a function of magnetic volume fraction

The permeability (μ_{mr}) increases with volume fraction of the magnetic component as shown in Figs. 7.10 and 7.11 for the Fe_3O_4 and Nickel systems respectively. In both figures, the permeability undergoes a slight increase around the percolation threshold (obtained from DC conductivity measurements) but this is not very conspicuous because of the noise in the results and the fact that the permeability continues to increase almost linearly after the percolation threshold. However, at higher volume fractions, the rate of increase of μ_{mr} with magnetic volume fraction decreases. Hence the data cannot be fitted by a linear relationship across the entire range of volume fraction. The theory of non-interacting particles (Fiske *et al.* 1997 and references therein) is not applicable to these systems.

Fiske *et al.* (1997) measured the permeability of composites made from ferromagnetic particles of Ni-Fe- Molybdenum alloy (or Hy Mu), MnZn and NiZn embedded in low-

density-polyethylene (LDPE). The Hy Mu particles were about $10\mu\text{m}$, while the NiZn and MnZn ferrites consisted of particles of about $50\mu\text{m}$ and $100\mu\text{m}$ respectively. Complementary DC conductivity measurements (of a few samples) estimated the ϕ_c for the Hy Mu metal system to be between 0.10 and 0.25 compared to between 0.25 and 0.50 for the ferrite systems. Toroidal samples of 76.2mm outer diameter, 63.5mm inner diameter and 6.35mm thick were used for the magnetic measurements. The permeability results for the systems were plotted as a function of the magnetic volume fraction and observed to increase with ϕ , without any dramatic changes indicating a percolation threshold, in agreement with the results obtained in this thesis. Fiske *et al.* observed that their experimental results deviated significantly from the linear behaviour expected purely on the basis of non-interacting particles below ϕ_c , with the permeability increasing more rapidly at the higher volume fractions. They attributed the deviation from linearity to the increase in interaction among the magnetic particles, as their mean separation distance decreases dramatically at the high volume fractions. In addition to the permeability, Fiske *et al.* (1997) also measured the dielectric constant in their samples at 100kHz. The dielectric constant was also observed to increase with ϕ , beyond their estimated ϕ_c 's, in agreement with results obtained in the Fe_3O_4 system at 1MHz in section 4.1.4.

In other experiments, McLachlan and White (1987) reanalysed the susceptibility (permeability) results (from earlier work) of molybdenum-coated permalloy and iron cylinders in a non-magnetic matrix. They observed that these results could be fitted accurately by a single-exponent effective media equation (eqn. (2.45)), given in section 2.5.

As shown in Figs. 7.10 and 7.11, the permeability results for the Fe_3O_4 and the Nickel systems were fitted to eqn. (2.3). In order to generate the fitted curves (solid lines in the figures), the parameters μ_h (the permeability of the conducting/magnetic component) and t were treated as variables, while s and ϕ_c were fixed at the values determined from DC conductivity measurements. The permeability of the

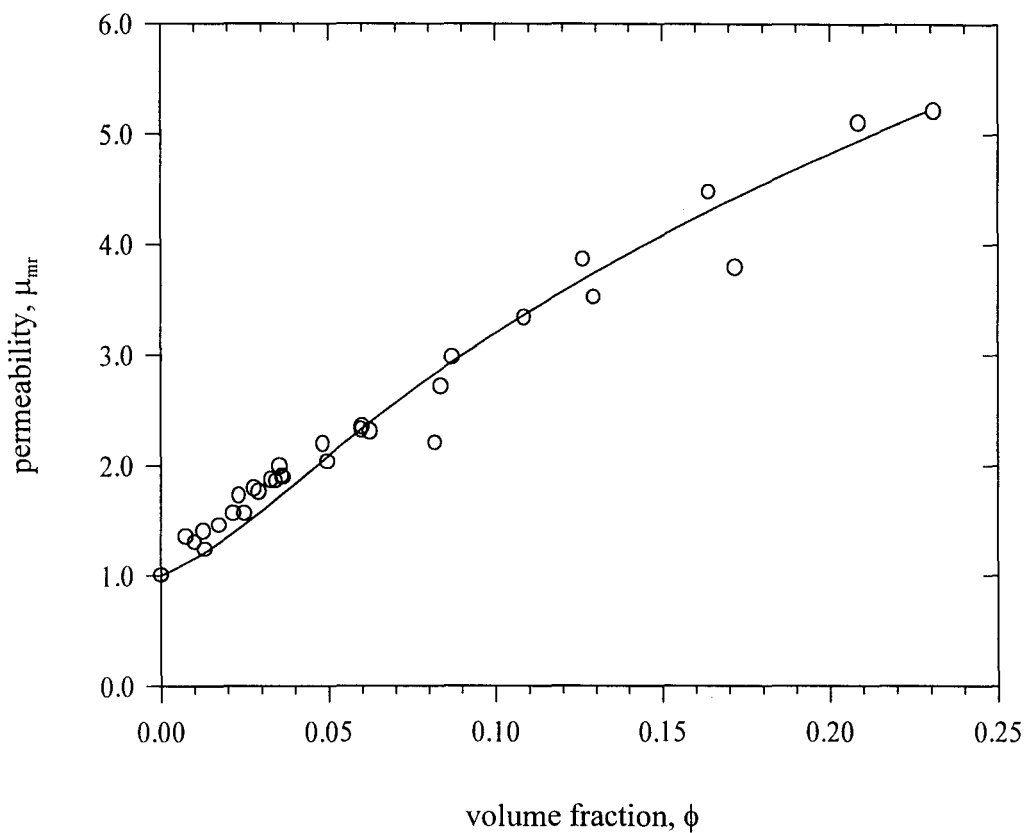


Figure 7.10: Permeability (μ_{mr}) plotted versus the volume fraction (ϕ) for the Fe_3O_4 -Talc-wax samples. The critical volume fraction from DC conductivity measurements for the system is; $\phi_c = 0.025 \pm 0.003$. The solid line is a fit from eqn. (2.3), with the best-fit parameters; $\mu_h = 12 \pm 3$, $\mu_l = 1.00$, $t = 0.53 \pm 0.19$, $s = 0.45 \pm 0.31$ and $\phi_c = 0.025 \pm 0.003$.

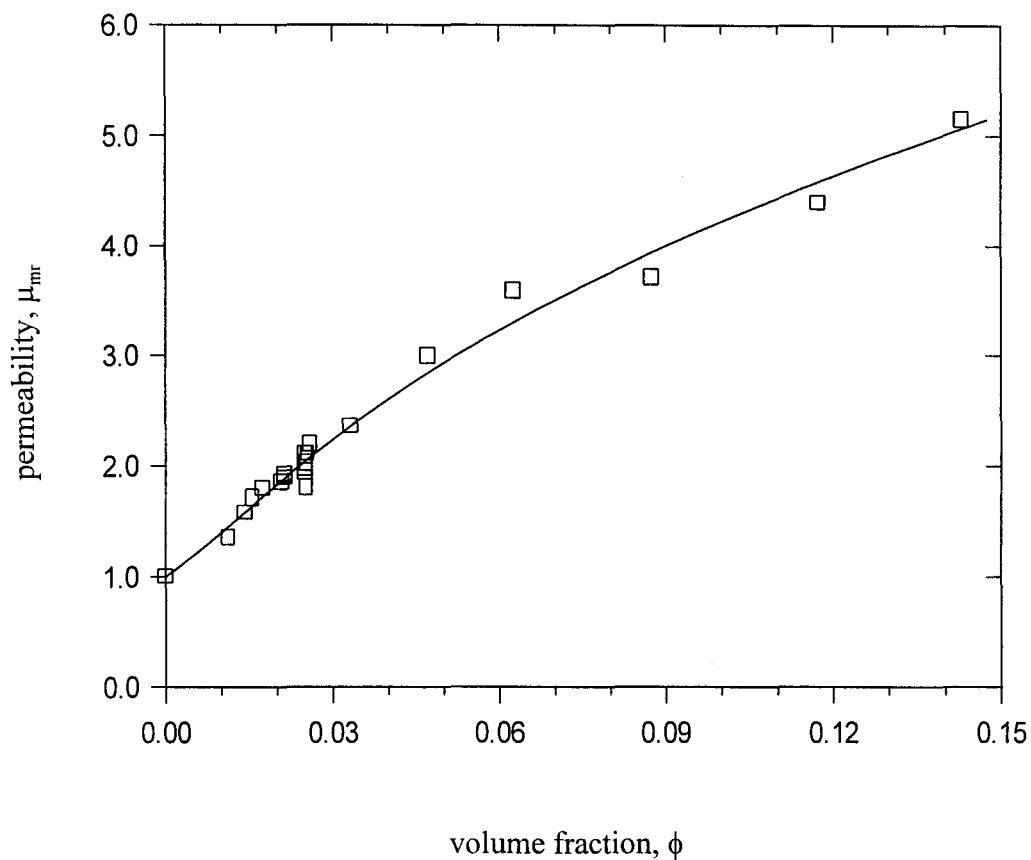


Figure 7.11: Permeability (μ_{mr}) plotted versus the volume fraction (ϕ) for the Nickel-Talc-wax samples. The critical volume fraction from DC conductivity measurements for the system is; $\phi_c = 0.025 \pm 0.003$. The solid line is a fit from eqn. (2.3), with the best-fit parameters; $\mu_h = 13 \pm 8$, $\mu_l = 1.00$, $t = 0.52 \pm 0.46$, $s = 1.11 \pm 0.60$ and $\phi_c = 0.025 \pm 0.003$. Note that two anomalous points, which are far off the trend, have been left out of the fit.

insulating/nonmagnetic component (μ_i) was fixed at 1.00 during the fitting. An attempt to let both s and t vary during the fitting process yielded unreasonable values of s . In addition, attempts to fit the permeability results with all the parameters fixed at the DC values were also not successful. Hence, it can be concluded that, based on these results, the DC s , t and ϕ_c cannot be used to fit magnetic permeability data. Unfortunately, there are no previous results available for comparison except for the study by McLachlan and White (1987), where the single exponent equation (eqn. (2.45)) appears to fit the results with similar accuracy.

The values of the exponent t obtained from the fits are much lower than the values measured from DC conductivity experiments for both the Fe_3O_4 and Nickel systems. The estimated value of μ_h for Nickel obtained from the fit is 13 ± 8 . This value is much lower than the value of $\mu_{h\text{Ni}} = 40.5$ reported by Deprez *et al.* (1988) on sintered Nickel samples. Unfortunately, as no previous value of μ_h is available for the Fe_3O_4 powder, comparison cannot be made with the estimate $\mu_h = 12 \pm 3$, obtained from the fit.

The results presented in this section confirm the difference between electrical and magnetic percolation, as observed by Fiske *et al.* (1997). The experimental results of Figs. 7.10 and 7.11 for the Fe_3O_4 and Nickel systems agree with Fiske *et al.*'s results in that the permeability (μ_{mr}) increases with volume fraction (ϕ) of the magnetic component. However, the small contrast in μ_{mr} between the samples below and above the percolation threshold (ϕ_c) causes the changes in the μ_{mr} curves to be less pronounced than in the DC conductivity curves. More experimental studies, where both DC electrical conductivity and magnetic properties (in systems where μ_i/μ_h is very small, i.e. $\mu_i/\mu_h \ll 1$) are measured, should be done to study this phenomenon.

Figures 7.12 and 7.13 show results of the loss factor (which is the ratio of the imaginary component to the real component of the permeability, $\tan \delta$ in chapter five) plotted against the volume fraction (ϕ) for the Fe_3O_4 and Nickel systems respectively.

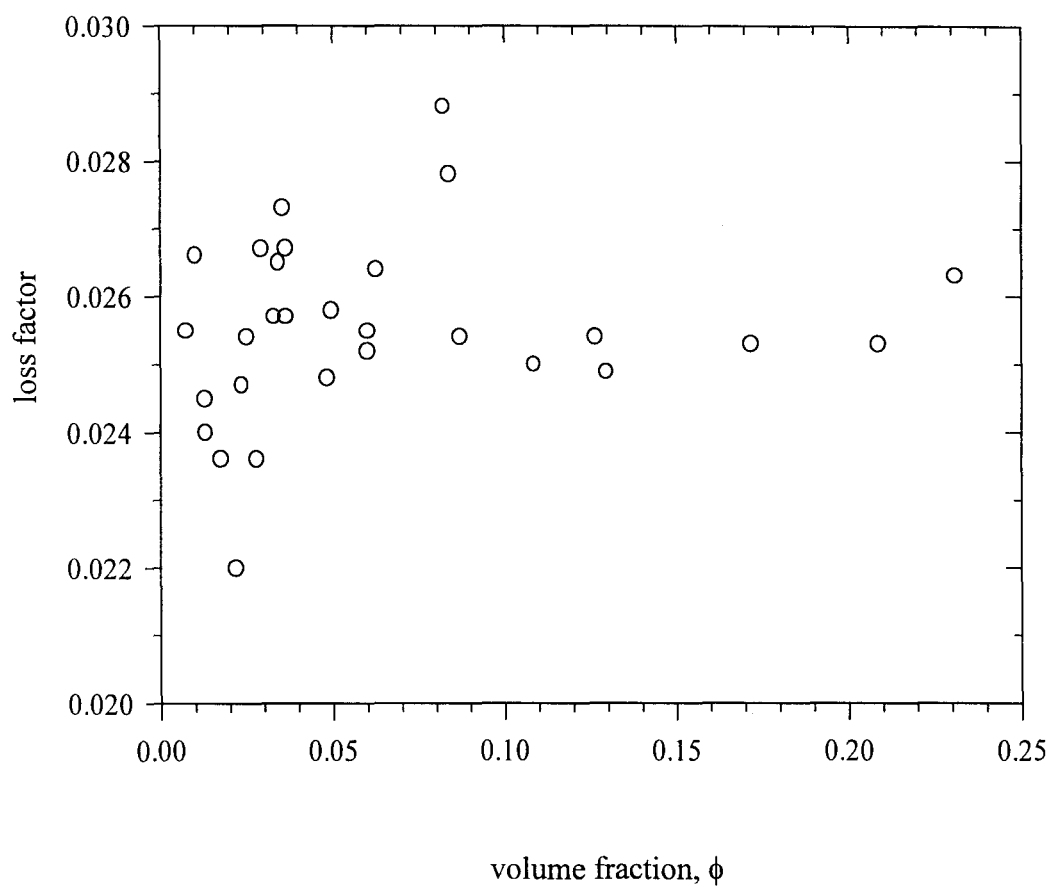


Figure 7.12: Loss factor plotted against volume fraction of Fe_3O_4 for the Fe_3O_4 -Talc-wax system.

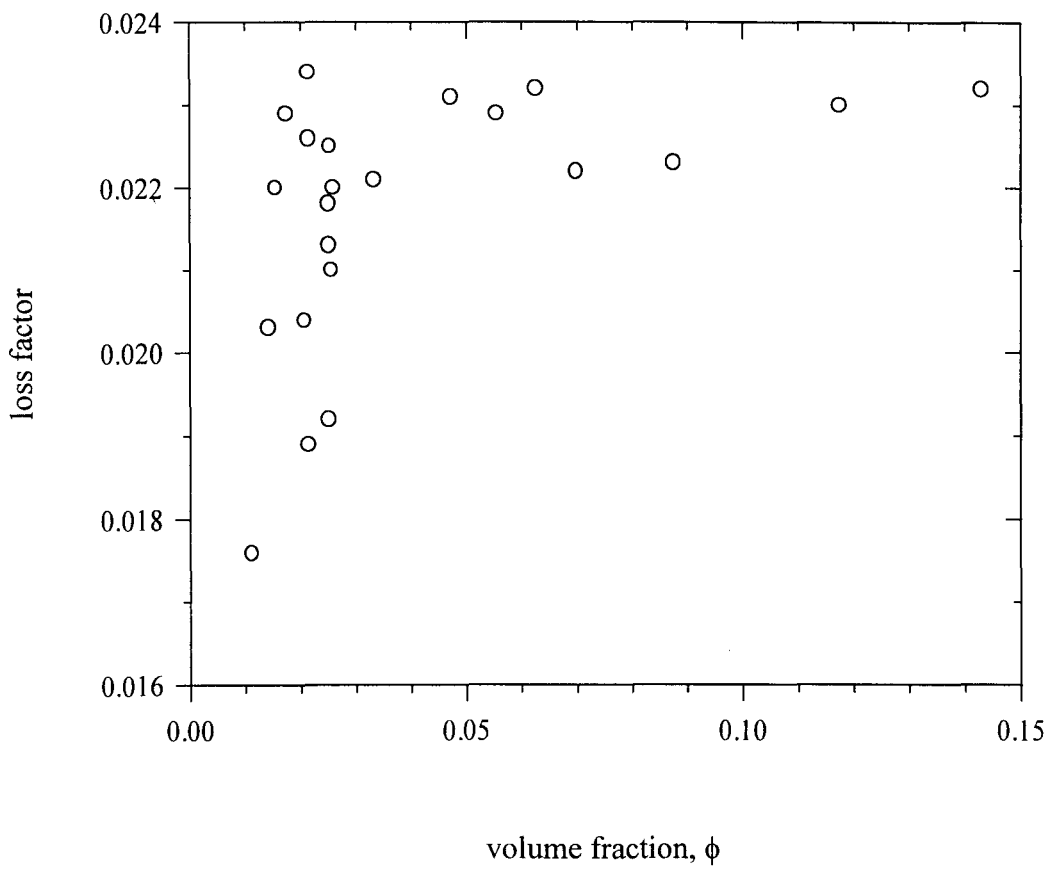


Figure 7.13: Loss factor plotted against volume fraction of Nickel for the Nickel-Talc-wax system.

The loss factor for the Fe_3O_4 system increases rapidly with ϕ , to what appears to be a broad peak between $\phi = 0.05$ and 0.10 , after which the loss factor drops to a constant value between 0.024 and 0.026 . The Nickel system shows similar behaviour of the loss factor, but there is no clear peak and has a constant value between 0.022 and 0.024 . There are no previous results or theory for comparison with the present study.

7.3 Summary

Magnetic properties of the two systems consisting of Fe_3O_4 and Nickel have been presented. DC properties, which include the coercive field and remnant magnetisation, have been observed to change as a function of the volume fraction of the magnetic component. Although the results are generally noisy, the coercive field shows a broad peak at a volume fraction beyond the percolation threshold obtained from DC electrical conductivity measurements. The remnant magnetisation shows a minimum at the volume fraction that corresponds to the broad coercive field peak for the Fe_3O_4 system, which appears to indicate an inverse or near inverse relation between M_r and H_c . For the Nickel system, the remnant field continues to decrease with volume fraction of Nickel (up to the highest ϕ used) in agreement with the theory of interacting particles (Fiske *et al.* 1997). The permeability results of the two systems can be fitted to eqn. (2.3) only with a t exponent much lower than that obtained from DC conductivity measurements.

The results presented in this Chapter indicate that the coercive field (H_c) shows a broad peak when plotted as a function of volume fraction of the magnetic component. No dramatic decrease of H_c is observed at ϕ_c . In the earlier work of Xiao and Chien (1987), H_c was reported to decrease precipitously at the percolation threshold, but the percolation threshold they refer to was never directly determined on their samples through DC conductivity measurements. Instead, their ϕ_c was based on previous measurements on other granular systems. More experimental studies, where both DC

electrical conductivity and magnetic properties are measured, should be done to further explore this observation.

An instrument to measure AC susceptibility and permeability at low frequencies for disc shaped samples, was fabricated in our laboratory. Measurements done on the Nickel and Fe_3O_4 systems, using this instrument, show that μ_{mr} (χ_{mr}) increases with volume fraction of the magnetic component and is best fitted by the two exponent phenomenological equation (eqn. (2.3)). While the change is definitely not linear, no dramatic change occurs at the DC percolation threshold. The only comparable study using micron-sized particles is that of Fiske *et al.* (1997) for which reasonable agreement with the present study was observed. However, Fiske *et al.*'s results show that the permeability increases more rapidly at high values of magnetic volume fraction, which is different from the present results.

The objective in the present study was to correlate the magnetic properties with the DC electrical conductivity, measured as a function of the volume fraction of the magnetic/conducting components. The results indicate that there are differences between the behaviour of some electrical and magnetic properties as a function of ϕ . Perhaps future experiments could look at measuring the magnetic properties as a function of variables such as magnetic field, temperature and frequency, to allow for better comparison with other data in the literature. The signal-to-noise ratio in susceptibility experiments could also be improved so that the imaginary component can be measured with better accuracy.

CHAPTER EIGHT

SUMMARY, DISCUSSION AND CONCLUSION

As described in the previous chapters, a number of percolation-type measurements were made on cellular systems. The measurements include the DC and AC conductivity, dielectric constant, $1/f$ noise and magnetic properties. The properties of all the systems were studied as a function of volume fraction of the conducting component. Flicker or $1/f$ -noise measurements were successfully done on only four of the systems, namely the raw (unground) and ground Carbon Black, Graphite and Graphite-Boron Nitride (15%) systems. Magnetic measurements were made on the Nickel and Fe_3O_4 systems and the magnetic properties were studied as a function of volume fraction of the magnetic component, in order to try to correlate them with the DC electrical conductivity results. A large amount of experimental parameters, mostly critical exponents obtained using the various percolation scaling laws, were obtained. The results have been tested against a number of theoretical models, as well as compared with previous experimental results. The relationship among the critical exponents obtained from this work cannot be explained using a single model, although a number of the exponents obtained from AC conductivity results (x , y and q) agree better with the inter-cluster polarisation model than the diffusion on percolation clusters theory. The remainder of this chapter discusses some of the results mentioned above in terms of the various models outlined in the preceding chapters.

The critical volume fractions or percolation thresholds (obtained from the DC electrical conductivity studies), were all in the range 0.01 - 0.07, in reasonably good agreement with the Kusy model, which predicts very low percolation thresholds in small conductor-large insulator particle composites. Predictions of ϕ_c values advanced

by the Kusy model (Kusy 1977) assume a spherical geometry and that monosize particles make up the composite. However, electron micrographs obtained on the particles used in the present study show that, as the real particles have such irregular shapes and size distributions, adopting this model is an oversimplification. This simplification inevitably leads to disagreement between the measured and the predicted values of ϕ_c . The assumption of mono-sized particles used by Kusy in his model is not easily realisable in practice. In fact, some powders used in this work showed a bimodal distribution of size as shown from the particle size analysis (see Fig. 3.2a for reference), leading to a further deviation from the assumptions of the theoretical model. It can be concluded from the present results that the harder and/or heavier Niobium Carbide particles have a tendency of being knocked deep into the surface of the soft Talc-wax particles, reducing the probability of contact among the conductor particles, consequently increasing the critical volume fraction beyond the value predicted by the Kusy model. This is despite the seemingly gentle “waterfall” mixing method used for these powders during sample preparation. For all the systems, the ϕ_c values calculated from the mean diameter values (ϕ_{cM}) are always less than the sauter diameter ϕ_c 's (ϕ_{cS}) as shown in Table 4.2 and Fig. A10, which also show how the calculated ϕ_c values correlate with the experimental value.

The extremely small ϕ_c values (~ 0.01) obtained for the Carbon Black systems agree with previous studies on Carbon Black-polymer systems, showing that the Carbon Black particles in polymers probably form similar 3-dimensional conducting networks to those in the cellular composites. Balberg (1987a) noted that there is a correlation between the structure of the Carbon Black particles and the corresponding percolation threshold (ϕ_c). The less ‘spherical’ or high structure Carbon Black particles give lower percolation thresholds than the more ‘spherical’ or low structure particles (Rubin *et al.* 1999). Previous results of Connor *et al.* (1998) in highly structured Carbon Black-polyethylene terephthalate composites (in which $\phi_c = 0.011$) are also in agreement with this observation. The high structure particles are assumed to have more connection points such that they form conducting networks (on the surface of the insulating particles) at a lower ϕ_c than the low structure particles. This argument

appears to support the results for ϕ_c obtained in the Graphite and Carbon Black systems with irregular (non-spherical) particles (refer to Figs. 3.1a and 3.1b for the structure of the particles). Rubin *et al.* (1999) measured $\phi_c = 0.39 \pm 0.02$ in a low structure (more spherical) Carbon Black-polymer composite, which, as it exceeds 0.16, also agrees with the above ϕ_c – powder structure correlation. Unfortunately, there are very few systems in the literature to conclusively validate these claims.

The conductivity exponent t (obtained by fitting the DC conductivity data to the two exponent phenomenological equation, eqn. (2.3)) shows a wide range of values for the cellular systems (see Table 4.1). For the purposes of discussion, the systems have been grouped into the low- t ($t < t_{un}$), universal- t ($t \sim t_{un}$), medium- t ($t > t_{un}$) and high- t systems (where $t > 2t_{un}$). In contrast to the $1/f$ noise, it was possible to fit the conductivity data above the percolation threshold with a single t exponent for all the systems, in spite of the complexity of the inter-particle contacts. A t exponent less than the universal value (measured in the Nickel system) cannot be explained by any of the existing models. The t values close to the universal value observed in some systems (ground Graphite, raw and ground Carbon Black) imply that the inter-particle contacts in these systems give a narrow range of inter-particular conductance, which is believed to lead to universal values of the exponent t (Straley 1979). It is not clear why these particular systems have a narrow range of conductance distribution. However, it is speculated that the narrow conductance range may be a result of the type of inter-particle contacts of the conductor particles i.e. the conductor-conductor contacts can be described as ‘good’, as opposed to ‘bad’ contacts which can give rise to a wide range of conductance. A common feature of the conducting powders used in the systems with close to the universal t is that they are ‘light’ (density $\sim 1.80 - 2.25\text{g/cm}^3$), which could play a role in determining the way these particles distribute themselves on the surface of the large insulator particles during sample preparation.

In addition to the previously mentioned ϕ_c –powder structure correlation, Balberg (1987a) also noted that there is a correlation between the structure of the Carbon Black particles and the corresponding conductivity exponent (t). The high structure or

less ‘spherical’ particles give values of t close to the universal values (and, as mentioned earlier, lower values of ϕ_c). According to Balberg (1987a), the aggregates (of the high-structure Carbon Black particles) have “arms” that get entangled while their centres still maintain a random distribution. The distances between the closest points of adjacent particles in this case have a conductance distribution, which is much narrower than that for spherical conductor (low structure) particles. The narrow conductance distribution yields a resistor network, which can be approximated by a system of equal resistors having some average value, and hence leads to universal behaviour. The t exponents close to the universal value obtained in the Graphite and Carbon Black systems with less ‘spherical’ particles are in agreement with Balberg’s observation. Previous results of Connor *et al.* (1998) in highly structured Carbon Black-polyethylene terephthalate composite (in which $\phi_c = 0.011$ and $t = 2.17$ were measured) are also in very good agreement with the ϕ_c and t measured in the present Carbon Black systems.

The three-component system of Graphite, Boron Nitride and Talc-wax gave a t exponent, which is close to the predictions of the original random void model ($\omega' = 0$ in the new Balberg model, section 2.1.4). Complementary noise measurements show that ω' for this system is indeed very small (Table 6.6). However, the fact that $\omega' \neq 0$ in this system is probably because the conducting “necks” in the three-component system are made up of an independent percolation system consisting of the Graphite and Boron Nitride powders, which makes them far more complex than those of the random void model. The value of the t exponent in the three-component system is in very good agreement with the t values measured in the axial and transverse directions of the compacted Graphite-Boron Nitride composite (Wu 1997, Wu and McLachlan 1997). Note that the Graphite/Boron Nitride coating, taken as an independent percolation system also gives a t value close that of the “parent” system. The similar values of t exponents in all these systems appear to highlight the role played by the Graphite-Graphite contacts in influencing the conductivity exponent.

The random void model can, in principle, be applied to all the cellular systems used in the present study as the large insulating Talc-wax particles can be considered as voids in a conducting medium, consisting of the small conducting particles. However, the microstructures resulting from the different links, nodes and blobs formed by the conducting powders are far more complex than the 'necks' making up the uniform conducting medium in the random void model, as evidenced by the wide range of t exponents measured in these systems. Note that the links, nodes and blobs structure is even more complex in the three-component system, where the 'necks' form an independent percolation system consisting of the Graphite and Boron Nitride powders (refer to Fig. 4.5).

The high values of t obtained in the Fe_3O_4 and Niobium Carbide (NbC) systems (Table 4.1) are not that unusual in continuum systems, where t values as high as 6.4 (Pike 1978, Rubin *et al.* 1999) have been reported. However, the exact distributions of inter-grain contacts that give rise to such extreme values of t are still not clearly understood. All existing models (section 2.1.4) explain the existence of high t values in terms of a wide range of conductance or divergence of the resistance distribution function. In the Fe_3O_4 and NbC systems, the very wide range of conductance is assumed to arise from the inter-particle contacts (mostly in the form of point contacts) between the angular conductor particles. Note that the t exponent in the Fe_3O_4 system was also observed to decrease with temperature (Table 4.4), showing that perhaps the inter-particle contact distribution decreases with temperature. It is unfortunate that noise measurements could not be done on these two systems, from which the ω' values (as well as experimental values of w and k) could have been determined and the corresponding t exponents calculated from eqn. (2.10).

The extended random void model (Balberg 1998a and 1998b) can accommodate the high t exponents measured in the Fe_3O_4 and Niobium Carbide systems. In the new Balberg models, a parameter ω' ($-\infty < \omega' < 1$) was introduced in the resistance distribution function to obtain an expression for a non-universal value of t (eqn. (2.10)). For $\omega' = 0$, the expression gives the original Halperin, Feng and Sen (1985) or

Tremblay, Feng and Breton (1986) ($d = 3$) random void model, which yields $t = 2.5$, using $t_{un} = 2.00$ and $u = d - 3/2$. The various t values observed in the systems (Table 4.1) suggest that there are different values of ω' arising from the different inter-particle contact distributions within the various systems. As noted earlier, $1/f$ noise provides an independent method of finding the ω' values. Systems on which noise measurements could be made gave different values of ω' ranging from -125 to 0.07 . In theory, these ω' values can be used in the Balberg expression for exponent k (eqn. (2.24)) to find the corresponding t values (referred to as $t_{\omega'}$) using eqn. (2.10). Using the k_1 noise results given in Table 6.5, the values of $t_{\omega'}$ calculated from these expressions were 1.14 ± 0.03 and 2.46 ± 0.05 for the ground and raw Carbon Black systems respectively. The value calculated for the ground Carbon Black system is well below the universal t exponent of 2.00 and the measured value of 2.06 ± 0.10 (despite the ω' value being within the specified range). However, the $t_{\omega'}$ value for the raw Carbon Black system (with a high k_1 exponent), seems to be reasonable when comparison is made with the experimental value of $t = 2.26 \pm 0.11$. Note that the ω' values calculated from k_1 for the Graphite and Graphite/Boron Nitride systems ($\omega' = 2.52 \pm 0.08$ and $\omega' = 4.79 \pm 0.78$ respectively) were outside the range required by the Balberg model and it is not surprising that the resultant $t_{\omega'}$ values are unreasonably small. Calculations done using k_2 exponents for all the four systems (Table 6.5) gave $t_{\omega'}$ values in the range $1.01 - 1.65$ despite the ω' values for all the systems lying within the correct range. The results show a serious discrepancy between the experimental results and the theoretical expressions from the Balberg model, indicating that even the new Balberg model is not adequate in giving quantitative interrelation of the exponents in all cases.

The values of t were also calculated from $t = k/w$ (with k and w given by eqns. (2.18) and (2.19)) using the experimental values of k_1 and k_2 (Table 6.5), and w_1 and w_2 (Table 6.7). These values of t ($t_{k/w}$) are shown in Tables 6.11 and 6.12. The values of $t_{k/w}$ from k_1 and w_1 are generally larger than the experimental values (Table 6.11). The only exception is the Graphite-Boron Nitride system, where the $t_{k/w}$ value is close to

the measured t (t_{exp}). The results in Table 6.11 appear to cast a shadow on the self-consistency of the k_1 and w_1 exponents. In contrast the t values calculated from k_2 and w_2 are very close (within the error bars) to those observed experimentally (Table 6.12). This is the first time that the t exponent is found independently from noise measurements (k from noise versus $(\phi - \phi_c)$ and w from noise versus resistance), which experimentally verifies the self-consistency of the results. Any valid theoretical model is expected to incorporate this self-consistency. The results clearly show that the k_2 and w_2 are self-consistent, whereas the corresponding exponents k_1 and w_1 , measured very close to the percolation threshold, are not. No theoretical explanation exists for this difference in the results as the present study is the first work to report the occurrence of two k values (k_1 and k_2). Since no noise data was available to evaluate ω' for the high t systems of Niobium Carbide and Fe_3O_4 , as well as the small t system of Nickel, similar calculations could not be done for these systems.

The range of values of the dielectric exponent s obtained in the systems is also quite broad. Again the Carbon Black and Graphite systems gave s exponents close to the universal value, while the high t Fe_3O_4 and NbC systems gave very small values of the exponent s (and s' , see section 4.1.3). Very little theoretical and experimental work has been done on the exponent s to date, mainly because most previous conductivity experiments never extended their measurements in the insulating or dielectric region. Some previous experimental work (see for instance Chen and Johnson 1991) implied that the value of s' (measured at 1kHz) was the same as the s value obtained from DC conductivity measurements. The values of the dielectric exponent s' , obtained from the low frequency AC measurements in this study, are different from the corresponding s values in agreement with the Wu (1997) and Wu and McLachlan (1997) results on Graphite-Boron Nitride systems), but show a definite trend towards s as the frequency is lowered. An attempt to extrapolate the s' values down to zero frequency was not successful. This work and that of Wu (1997) establish the fact that the exponents s and s' (as defined in this thesis) are not the same, this work being the more detailed study (refer to Tables 4.3). There is no theoretical work available for comparison with these results.

The real part of the low frequency dielectric constant of the cellular systems was studied as a function of the volume fraction (ϕ) of the conducting component. Instead of showing a peak at ϕ_c (as predicted by the original Percolation Theories), the dielectric constant continues to increase beyond the percolation threshold, suggesting that previous experiments claiming a result to the contrary might have suffered from inadequate instrumentation or an incorrect identification of ϕ_c . The amplitude and position of the dielectric constant peak was observed to be frequency-dependent, occurring at a higher volume fraction of the conducting component (ϕ) as the frequency increases (see for instance Figs. 4.7 and 4.8). The behaviour of the dielectric constant data as a function of conductor volume fraction (for the Fe_3O_4 system) has been modeled fairly well using the two-exponent phenomenological equation (eqn. (2.3)), with some modifications using eqns. (2.11) and (2.14) (Heiss *et al.* 2000), as outlined in section 2.2 and shown graphically in section 4.1.4 and 4.1.6. DC scaling was investigated in the Fe_3O_4 -Talc-wax system through changing the conductivity ratio (σ_i/σ_c) of the components by varying the temperature. This is the first time that DC scaling for different σ_i/σ_c values has been done on a real composite system. Small variations in the exponent t were observed as a function of temperature. The results shown in Table 4.4 show that the exponent t decreases slightly with temperature or the σ_i/σ_c ratio in the Magnetite (Fe_3O_4)-Talc-wax composite. The change in the exponent t observed in this system is in qualitative agreement with Lin's observation (1991) in a $\text{PrBa}_2\text{Cu}_3\text{O}_7$ -Ag percolation system. The changes in the t exponent have a very small effect on the scaling of the results (Fig 4.11).

At high frequency and close to the percolation threshold, it is well established that the AC conductivity and dielectric constant follow the power laws; $\sigma_m(\phi, \omega) \sim \omega^x$ and $\epsilon_m(\phi, \omega) \sim \omega^{-y}$ respectively. However, contrary to expectations, none of the exponents x_{exp} and y_{exp} obtained from the cellular systems through these power laws obey the relationship $x_{\text{exp}} + y_{\text{exp}} = 1$ (refer to Table 5.1). Note that many previous experiments (e.g. Song *et al.* 1986, Chen and Johnson 1991, Chakrabarty *et al.* 1993, Wu and McLachlan 1998) have found that $x_{\text{exp}} + y_{\text{exp}} = 1$. In some of the systems, $x_{\text{exp}} + y_{\text{exp}}$ tends to be lower than 1 but the result agrees with $x_{\text{exp}} + y_{\text{exp}} = 1$ within the error bars.

The x_{exp} exponents obtained in the present study are generally in agreement with those from previous studies on 3D continuum systems. However, the values of the exponent y_{exp} (from $\omega \epsilon_m(\phi, \omega) \propto \omega^{1-y}$) are less than both the theoretical prediction of the interacting cluster model (where $y = s/(s + t)$) and previous studies and are probably responsible for $x_{\text{exp}} + y_{\text{exp}}$ being less than 1. As mentioned earlier, this may be a characteristic of the low ϕ_c cellular systems or the complex dielectric properties of the Talc-wax. Only the two Carbon Black systems and the Graphite system, with $t \approx 2$, are close to obeying $x_{\text{exp}} + y_{\text{exp}} \sim 1$. The present results and those from previous experiments (Wu 1997, Wu and McLachlan 1998) show that when the experimental DC exponents are used in the interacting cluster model expressions (section 2.4), the relation $x_{\text{calc}} + y_{\text{calc}} = 1$ is always obeyed. The results in Table 5.1 show that using s or s' in the inter-cluster model expressions makes a big difference to the calculated result for x_{calc} or x'_{calc} and y_{calc} or y'_{calc} , which underscores the necessity to give both s and s' when presenting experimental results. There is relatively good agreement between the experimental values of exponent x and the calculated values for some systems but only if s' (measured at 1kHz) is used in the inter-cluster model expression. This agreement is well illustrated by the Carbon Black and Graphite systems (Table 5.1). Scaling of the AC conductivity (shown in Figs. 5.9 and 5.10), for samples above the percolation threshold, shows s' gives better agreement with the experimental results than the s from DC measurements. This is probably to be expected given that AC scaling is a high frequency phenomenon. The slopes of the scaled experimental results (x_{exp}) of the high t systems do not show agreement with the inter-cluster polarisation (RC) model, whether t and s or t and s' are used to generate the theoretical scaling curves (see for instance Fig. 5.11).

Values of the crossover frequency ω_c (the frequency at which the conductivity of a sample above the percolation threshold deviates from its DC behaviour and the conductivity becomes frequency-dependent) and the related exponent q have also been measured in the systems, using the power law $\omega_c \propto \sigma_m(\phi, 0)^q$. The measured q (q_{exp}) values are always (except in one case) less than the predictions of the inter-cluster polarisation model. The best agreement between the experimental and

theoretical values is again obtained in the two Carbon Black systems as well as the high t system of Magnetite (Fe_3O_4). The Graphite-containing systems have values less than unity, in disagreement with $q = (s + t)/t$, but in agreement with Wu's results (1997) on systems containing the same Graphite powder. From these results, the $q_{\text{exp}} < 1$ appears to be a characteristic of the Graphite powder. In the other high t system of Niobium Carbide, a large discrepancy is observed between the experimental and theoretical value of q , even though both values are greater than unity. The Niobium Carbide system is the first and only system to give the result of $q_{\text{exp}} > q_{\text{calc}}$. The various AC exponents (x , y and q), measured experimentally and their corresponding values calculated from theory, have been plotted against the DC exponents s and t to check for possible correlations. These plots are given in the appendix section of the thesis. In general, the experimental values of the exponents (q_{exp}) tend to scatter but the exponents calculated using s' (at 1kHz and 1MHz) instead of s , show a somewhat better correlation with both DC exponents s and t .

Another result of interest obtained from the AC section is the variation of the loss angle $\tan \delta$ with frequency, especially for samples close to the percolation threshold. The results from the cellular systems have been observed to obey the power law $\tan \delta \propto \omega^{-z}$, with z values between 0.78 and 0.93. The Carbon Black systems give the highest values of z . Note that Chakrabarty *et al.* (1993) claim that the exponent z is expected to be 1 for a pure electronic conductor. The lowest value of z was measured in the Niobium Carbide system, which has an exceptionally high t exponent.

The $1/f$ or flicker noise results obtained from the cellular systems are arguably some of the most striking results from this work. The values of the exponent γ indicate that the noise is indeed $1/f$. The voltage dependence of the noise gave values of m (sections 2.3 and 6.1.2) close to the predicted value of 2, for the low resistance (small $(\phi - \phi_c)$) samples, and smaller values of the exponent m ($m < 2$) for the relatively high resistance (very small $(\phi - \phi_c)$) samples. Note that none of the latter samples were in the crossover region (eqn. (2.2a)). The different values of m ($m < 2$ and $m \leq 2$) gives two categories of samples which lead to two noise regimes (as shown by the results in

sections 6.1.3 and 6.1.4 and discussed below) in the systems. Equilibrium resistance fluctuations are probably the sole contributor to the noise in the low resistance samples showing a V^2 -dependence as noted by Nandi *et al.* in 1996. Deviation from the V^2 -behaviour is taken to imply the coexistence of other mechanisms, which in our case, applies to samples close to ϕ_c .

The normalised noise (S_v/V^2) plotted against $(\phi - \phi_c)$ gave two exponents, k_1 and k_2 as shown in Table 6.5 for the four systems studied. This is the first time that the occurrence of two values of k has been observed and reported in percolation systems. As noted before, the exponent k_1 arises from samples with $m < 2$ (very small $(\phi - \phi_c)$) and k_2 from samples having $m \sim 2$ (small $(\phi - \phi_c)$). In the two Carbon Black systems, the exponent $k_1 > k_2$ while the opposite is true for the two Graphite-containing systems. It is suggested that the phenomenon might be a characteristic of the conducting component. Corresponding to the k exponents are the w exponents (w_1 and w_2) obtained through plotting the normalised noise versus the DC resistance of the samples, again indicating the existence of two noise regimes. Recall that a single t exponent could fit the DC conductivity of the samples in the different noise regimes. $1/f$ -noise measurements, which measure the fourth order moment of the current distribution, are more sensitive to small variations in the percolation path than the conductivity measurements, which only measure the second order moment of the current distribution. Values of k_1 and w_1 vary from system to system, while the w_2 exponents for all the four systems are very close, perhaps showing that the systems are becoming similar at higher values of the conductor concentration. Note that the k_2 exponents are also relatively close to each other than the k_1 values and that the systems had similar t values.

In the high conductor concentration regime (characterised by increased blob formation and a large number of parallel conducting paths), the noise results (w_2 and k_2) have been shown to be consistent with the measured t value (Table 6.12), whereas the k_1 and w_1 are generally not (Table 6.11). Unlike the difference shown by the k exponents in the Carbon Black ($k_1 > k_2$) and Graphite ($k_1 < k_2$) systems, the w

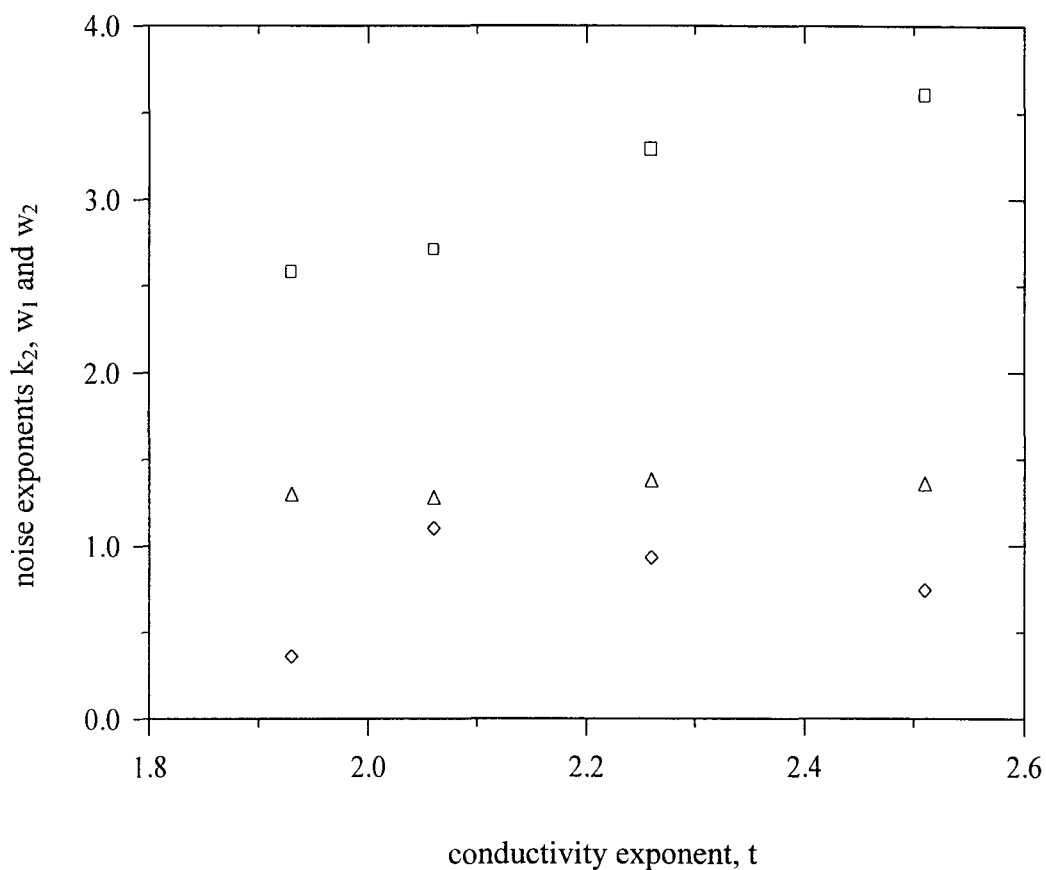


Figure 8.1: The noise exponents ($k_2(\square)$, $w_2(\Delta)$ and $w_1(\diamond)$) plotted against the DC conductivity exponent for the Carbon Black and Graphite systems. From left to right, the symbols in the figure represent the Graphite, ground Carbon Black, raw Carbon Black and Graphite Boron Nitride systems.

exponents all obey the relation $w_1 < w_2$. The w_1 and w_2 exponents generally lie within the limits proposed by Balberg (1998a and 1998b) for the Random Void model. The only exception is the w_1 exponent for the Graphite system, which is well below the lower limit of w proposed by Balberg (Table 6.9). This w_1 value also appears to be off the trend in Fig. 8.1, where the noise exponents have been plotted versus the conductivity exponent t . The w_2 exponents agree reasonably well with previous experiments, for instance, those on Copper particle-polymer composites studied by Pierre *et al.* (1990b) and Wu's result on Graphite-Boron Nitride disc samples (1997). A plot of k_2 and w_2 versus the DC conductivity exponent (t) for the four cellular systems (Fig. 8.1) shows that w_2 (in which the exponent t has obviously been eliminated through the relation $w = k/t$) hardly changes with t but that k_2 steadily increases with t . However, k_1 (not shown) does not show any correlation with the t exponent. The plot of w_1 shows the latter decreases rapidly with t if the value for the Graphite system is ignored. The w_1 results show that there is a different 'nodes-links-blobs' pattern close to the percolation threshold for each system, which gives rise to different noise mechanisms.

Experimental values of the t exponents have been used to calculate values of ω' (eqn. (2.10)) for all systems as shown in Table 6.6. The ω' values are all within the range ($-\infty < \omega' < 1$) required by Balberg's extended random void model (Balberg 1998a and 1998b). These values of ω' were used to calculate k from eqn. (2.24). The calculated values of k (Table 6.6) expected from the measured t exponents are generally larger than those directly measured in the noise experiments (k_1 or k_2 in the present study) and well beyond the universal value of 1.56 for k (Balberg 1998a). The raw Carbon Black is the only system with a measured k_1 larger than the calculated value. The results in the table also show that high t systems give large k values. Note also that only one value of k can be calculated from a single t exponent, whereas the experimental results give two k (w) values, making it rather difficult to compare the results. Hence the Balberg theory cannot model the occurrence of two exponents k_1 (w_1) and k_2 (w_2). The noise results obtained in this thesis show that there is need for

more experimental (in both high and low t systems) and theoretical investigation, if the mysteries surrounding $1/f$ noise, in percolation systems, are to be solved.

The magnetic properties of the two systems consisting of Fe_3O_4 and Nickel have been presented in Chapter seven. Both DC properties, which include the coercive field and remnant magnetisation, and AC properties (susceptibility and permeability) have been observed to change as a function of the volume fraction of the magnetic component (Figs. 7.4 – 7.13). Although the results are generally noisy, the coercive field and remnant magnetisation, show a broad peak (more pronounced in the Fe_3O_4 system) and a minimum respectively at a volume fraction beyond the percolation threshold obtained from DC electrical conductivity measurements, which indicates that there are differences between electrical and magnetic percolation. The position of the H_c peak is in disagreement with previous work, where H_c was reported to decrease precipitously at the percolation threshold (Xiao and Chien 1987, Liou and Chien 1988). However, the percolation threshold referred to in these studies was never obtained directly from DC conductivity measurements on the samples but was simply estimated on the basis of previous studies on other granular composites. It is also not clear whether the size of the magnetic particles used in the present study had an effect on these results, because all previous studies which measured H_c (to the author's best knowledge) used magnetic particles from 10 to 170 angstroms in size. This differs significantly from the present study, where the magnetic particles used are of the order of microns. More experimental studies, where both DC electrical conductivity and magnetic properties are measured, should be done to further explore these observations.

The AC magnetic properties (μ_{mr}), measured at 32.1Hz on the magnetic systems discussed in the previous paragraph, increase with volume fraction of the magnetic component. While the change is definitely not linear, no dramatic change occurs at the percolation threshold. The results agree with those of Fiske *et al.* (1997) on Ferrites embedded in low-density polyethylene, in which a nonlinear dependence of permeability on magnetic volume fraction was also observed. The permeability results

were fitted to the two exponent phenomenological equation (eqn. (2.3)) using some of the parameters obtained from DC conductivity measurements. The fits, with s and ϕ_c fixed at their DC values (Table 4.1), yielded $\mu_{rNi} = 13 \pm 8$ and $\mu_{rFe_3O_4} = 12 \pm 3$ ($\equiv$ high σ_i/σ_c in DC conductivity experiments). The value for Nickel is much less than the expected value of 40.5 (Deprez *et al.* 1988). The lower volume fractions of Nickel used in the present experiment (and the subsequent large extrapolation to 100% volume fraction) may be one of the reasons for this discrepancy. The t exponent was treated as a variable parameter in the permeability fits and the resulting values of t are much lower than the corresponding DC conductivity values for both systems. Based on these results, it can be concluded that the DC conductivity parameters cannot be used directly to fit magnetic data.

One of the problems encountered when comparing results from this thesis with those from previous experiments is that very few of the experiments, reported in the literature, measured all the related exponents s , t , w , k , x , y , q and z (as defined in this thesis) in a single system. As a result, it is very clear (even in systems where some agreement with theory has been reportedly observed) that the interrelation among all the exponents from various laws of percolation were not tested in previous experiments. The only other extensive study of experimental relations between exponents is that of Wu (1997) and Wu and McLachlan (1997, 1998) on the Graphite-Boron Nitride systems, where a large number of percolation exponents were obtained. However, despite the shortcomings of previous experiments, the following trends can be established in the present results in conjunction with previous experiments. Note that the following paragraphs reiterate some of the points already mentioned in this chapter.

Better agreement between theory and experiment for some percolation exponents is observed in a number of systems provided the experimentally determined exponents (s or s' , t), and not their universal values, are used in the theoretical expressions to determine the AC exponents x and y . The ratios of the measured and calculated exponents (x , y and q) do not show any discernible pattern (Table 5.8). Furthermore,

it is not clear whether s or s' should be substituted in the expressions for x and y as the results obtained in this thesis show the two exponents are different, which was not allowed for in the above models. However, as noted earlier, scaling of the AC conductivity results from this study give better agreement with s' (1kHz) and since x and y are measured at high frequency, s' should probably be used in the calculations than s .

Systems with extremely high values of the exponent t ($t > 2t_{un}$) have all so far had small values of the s exponent. The Niobium Carbide and Fe_3O_4 systems and the Graphite-Boron Nitride powder systems (Wu 1997, Wu and McLachlan 1997) are examples. The Fe_3O_4 system clearly shows the dielectric hump given in Fig. 4.9. The Niobium Carbide system also shows a dielectric hump but less clearly so than the Fe_3O_4 system. The scaled AC results for the two systems have slopes different from that predicted by the RC model and the x_{exp} values have a very poor correlation with t (Fig. A2).

$1/f$ -noise measurements should be more sensitive to changes in the 'nodes-links and blobs' structure of the conducting powders on Talc-wax than conductivity measurements. This is because $1/f$ noise measures the fourth moment of the current distribution while the conductivity measures only the second moment, which shows that $1/f$ noise measurements provide an independent method of characterising the conducting region close to and above ϕ_c . This is illustrated by the fact that two values (k_1 and k_2) of the noise exponent k have been observed and reported in real continuum systems, in different $(\phi - \phi_c)$ regions. Corresponding resistance noise exponents, w_1 and w_2 , were also reported in the systems. Note that the samples in the different noise regions could be fitted by a single DC conductivity exponent t . The systems studied in this thesis have $R_i \gg R_c$ (i.e random void-like) and gave $w_2 > w_1$. Only one system (to the author's best knowledge) was studied where $R_i < R_c$ and $w_2 < w_1$ was observed (Rudman *et al.* 1986) and so one cannot say whether $w_2 < w_1$ is caused by $R_i < R_c$. In addition, the ratio R_i/R_c in this system was very small (0.5) in comparison with those used in the cellular systems. It is therefore necessary to do more noise measurements

in definite inverted random void-like systems (i.e. $R_i \ll R_c$) so that better correlation can be made between the w exponents and the particle size ratio.

While good agreement (both qualitative and semi-quantitative) has been observed between the experimental results and the percolation power laws (eqns. (2.1a) and (2.1b)) as well as eqn. (2.3) used in this thesis, it is clear that the theoretical models (for exponents) are not sufficient to explain all the current experimental results and the interrelations among the exponents. However, further progress can certainly be made when more experiments are designed, where the systems have specific microstructures, such that the effect of the microstructure on the various exponents can be more systematically studied, and the necessary correlations made. The work presented in this thesis has moved our knowledge a step towards achieving this objective and hopefully will inspire further work in the field of percolation, the universality/non-universality of percolation exponents and their effect on the electrical transport properties of percolation systems.

APPENDIX

Throughout the discussions of the experimental results obtained in this thesis in the preceding chapters, attempts have been made to find correlations among the various parameters measured. Unfortunately, there has been very little in terms of obvious trends in the results. However, the various parameters are plotted against each other in the following sections so they are available for future reference.

A.1: Correlations between the Exponents

In this section, the exponents (x_{exp} , x_{calc} , x_{calc}' , y_{exp} , y_{calc} , y_{calc}' , q_{exp} , q_{calc} , q_{calc}' , k_1 , k_2 , w_1 and w_2 , as defined in the preceding chapters in this thesis), and obtained from the various percolation power laws, are plotted against the DC exponents s and t to look for possible correlations among them.

The symbols x_{exp} , y_{exp} , q_{exp} , k_1 , k_2 , w_1 and w_2 denote the experimentally determined values of the exponents, while x_{calc} , y_{calc} and q_{calc} are the values of the exponents calculated from the experimentally measured values of the DC conductivity exponents s and t , using the inter-cluster polarisation model expressions (eqns. (2.39)). Using the same DC exponent t and an s' (measured from low frequency dielectric measurements at 1kHz and 1MHz), corresponding values of x_{calc} , y_{calc} and q_{calc} (denoted x_{calc}' , y_{calc}' and q_{calc}') were also calculated from eqns. (2.39). These calculated AC exponents are expected to correlate with s and t .

Figure A1 shows the DC exponent s (s_{dc}) and s' (at 1kHz and 1MHz) plotted versus the DC conductivity exponent t for the cellular systems. For the low values of t (1.5-2.6), the s exponents (s_{dc} , $s'_{1\text{kHz}}$, $s'_{1\text{MHz}}$) show no correlation with t . For the extreme t

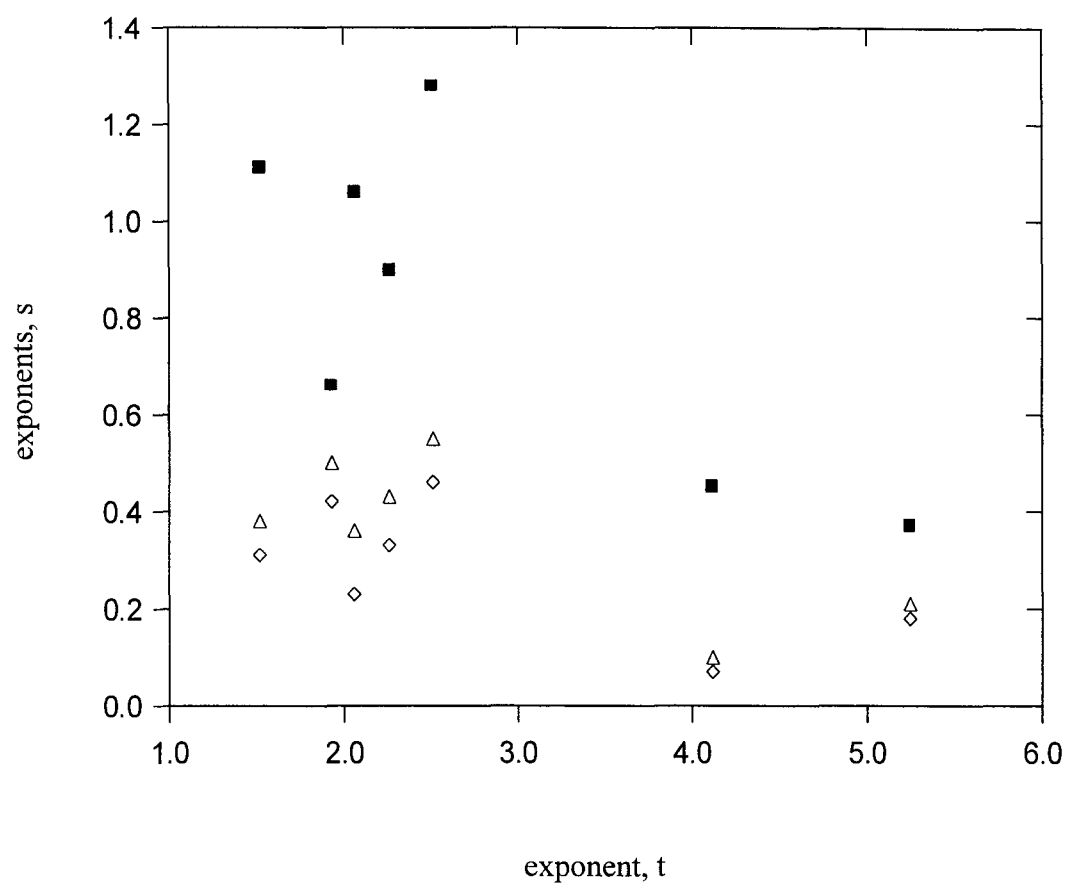


Figure A1: The s exponents (s_{dc} (■), s_{1kHz} (Δ), s_{1MHz} (◇)) plotted versus the DC conductivity exponent t . From left to right, the symbols are for Nickel, Graphite, ground Carbon Black, raw Carbon Black, Graphite Boron Nitride, Fe_3O_4 and Niobium Carbide systems.

systems, s_{dc} decreases as t increases. Note also that at high values of t , the gap (discrepancy) between s_{dc} and s' generally narrows.

In Fig. A2, all the x exponents for the systems are plotted as a function of the DC exponent t . The x values for systems with close to the universal value of t show no discernible pattern, except that the x_{calc} values are lower than the other exponents (x_{exp} , x_{calc}'). For the high t systems (Fe_3O_4 and Niobium Carbide), the x_{exp} values decrease with increasing t , which is inconsistent with the line $t/(s_{un} + t)$. Note that the dispersion results for these high t systems showed the largest differences with the RC model as previously mentioned. The calculated values (x_{calc} , x_{calc}' (1kHz) and x_{calc}' (1MHz)) also cluster around $t = 2$ but increase as t increases, almost showing the same curvature as $x = t/(s_{un} + t)$.

Figure A3 shows the y exponents plotted versus the DC conductivity exponent t . All the y exponents (y_{exp} , y_{calc} , y_{calc}' (1kHz) and y_{calc}' (1MHz)) generally decrease as t increases. The more pronounced decrease of y , for $t > 2.5$, with t is due to the fact that the high t systems are associated with very small s (s') values.

Figure A4 shows the q exponents plotted versus the exponent t . The q_{exp} values show no correlation with the exponent t , with q_{exp} for the Niobium Carbide possibly separated from the rest of the systems. Recall that this is the only system to have given $q_{exp} > q_{calc}$. The calculated q exponents (q_{calc} , q_{calc}' (1kHz) and q_{calc}' (1MHz)) generally decrease with t . Similar to the behaviour of their y counterparts, the q_{calc}' (1kHz) and q_{calc}' (1MHz) show less scatter at lower values of t than q_{calc} . The decrease of the calculated q values (from q_{calc} down to q_{calc}' (1MHz)) is a result of the decrease of s' with frequency.

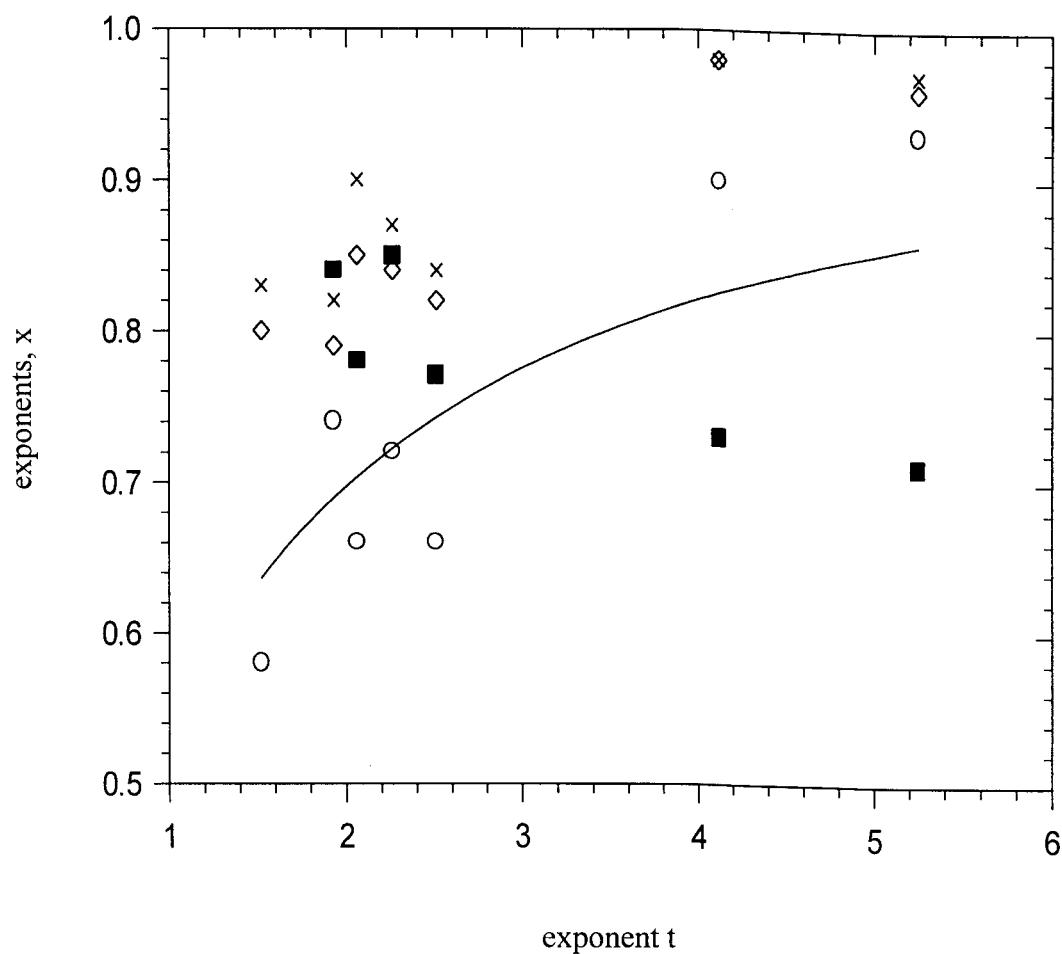


Figure A2: The x exponents (x_{exp} (■), x_{calc} (○), x_{calc} at 1kHz (◇) and x_{calc} at 1MHz (×)) plotted versus the DC conductivity exponent t . From left to right, the symbols are for Nickel, Graphite, ground Carbon Black, raw Carbon Black, Graphite Boron Nitride, Fe_3O_4 and Niobium Carbide systems. The solid line is $x = t/(s_{um} + t)$, where s_{um} is taken to be 0.87. Note that there is no x_{exp} for the Nickel system because of the large ω_c .

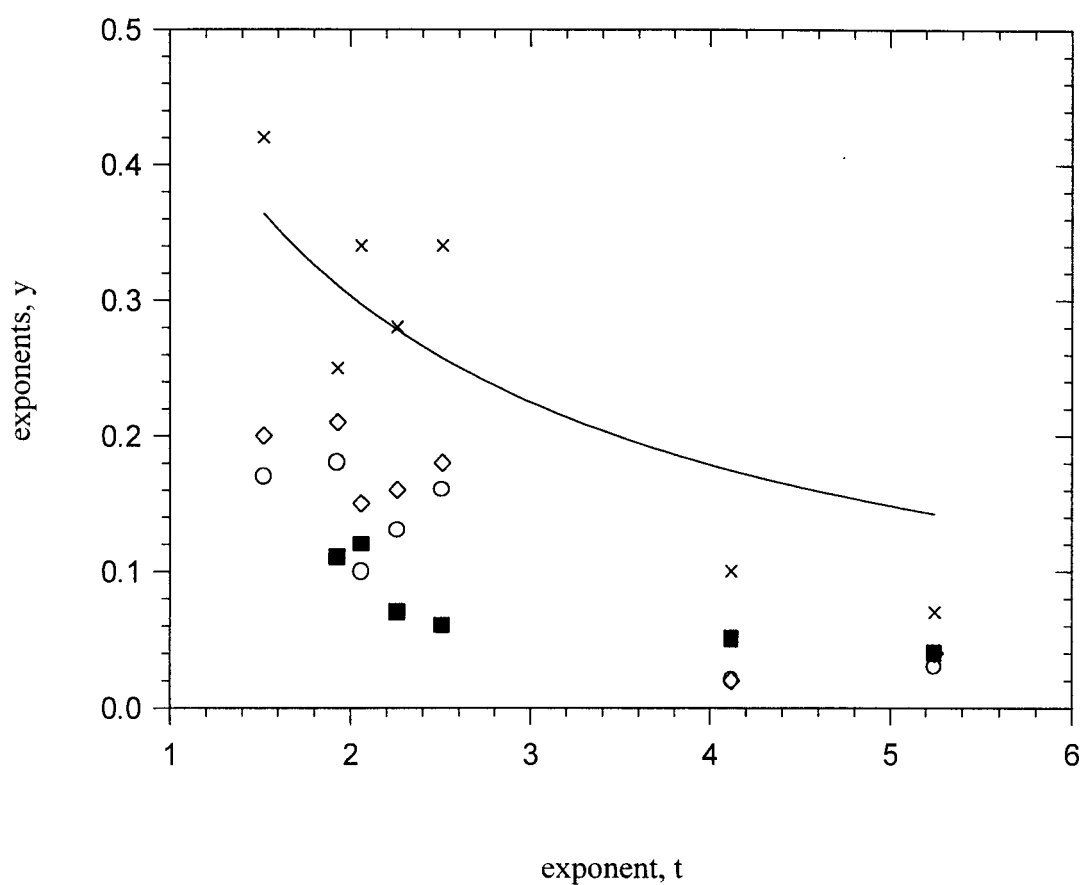


Figure A3: The y exponents (y_{exp} (■), y_{calc} (×), y_{calc} ' at 1kHz (◇) and y_{calc} ' at 1MHz (○)) plotted versus the DC conductivity exponent t. From left to right, the symbols are for Nickel, Graphite, ground Carbon Black, raw Carbon Black, Graphite Boron Nitride, Fe_3O_4 and Niobium Carbide systems. The solid line is $y = s_{\text{un}}/(s_{\text{un}} + t)$.

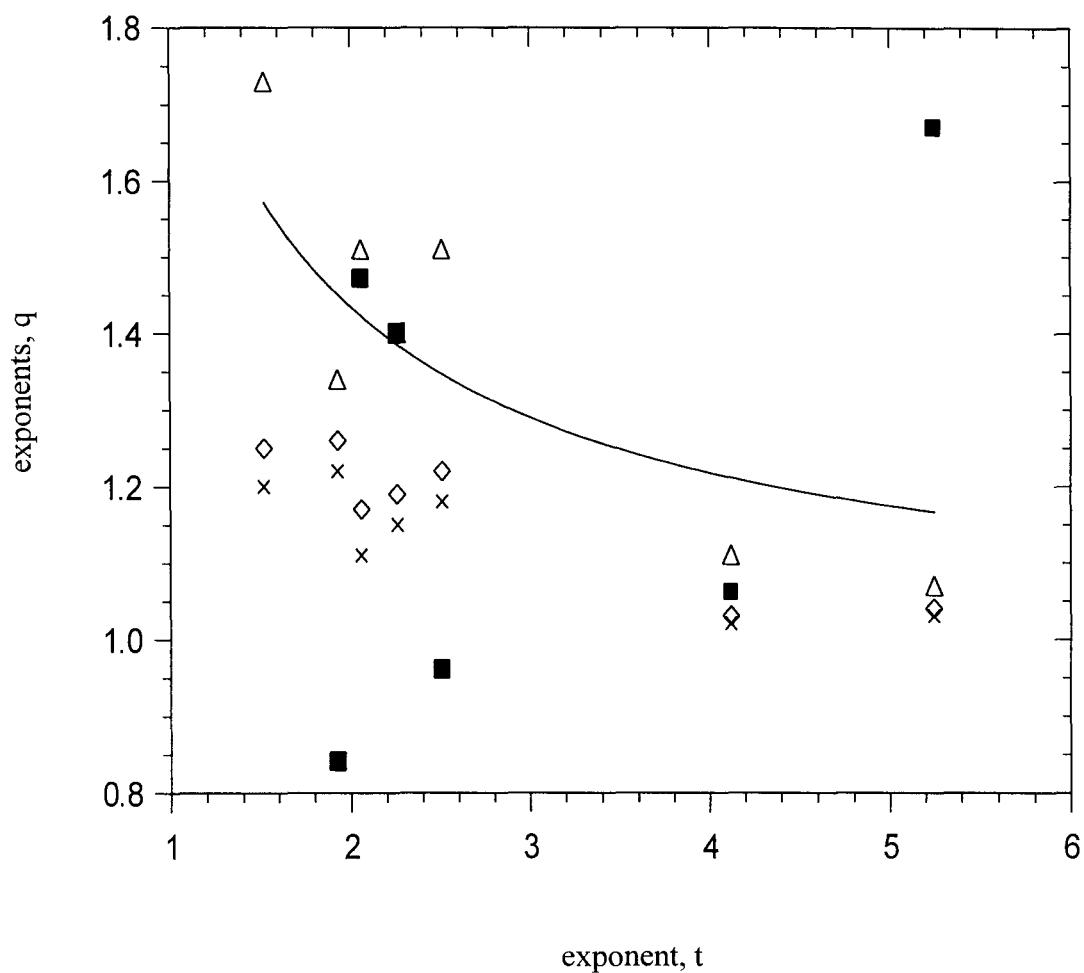


Figure A4: The q exponents (q_{exp} (■), q_{calc} (Δ), q_{calc} at 1kHz (◇) and q_{calc} at 1MHz (×)) plotted versus the DC conductivity exponent t . From left to right, the symbols are for Nickel, Graphite, ground Carbon Black, raw Carbon Black, Graphite Boron Nitride, Fe₃O₄ and Niobium Carbide systems. The solid line, which is a guide to the eye, is $q = (s_{\text{um}} + t)/t$.

Figure A5 shows the x exponents plotted versus the DC conductivity exponent s . The experimental values of x (x_{exp}) increase with exponent s and appear to show a peak between $s = 0.7$ and 0.9 , after which the x_{exp} values decrease with increasing s . The calculated x_{calc} exponents do not show any discernible trend with s . The x_{calc} values, however generally decrease as s increases, with some points close to the $t_{\text{un}}/(t_{\text{un}} + s)$ curve, showing a reasonable correlation with s .

In Fig. A6, the y exponents are plotted as a function of s (s_{dc}). The y_{exp} and y_{calc} values show no correlation with s . The y_{calc} values increase with s and the points approximate the curvature of $y = s/(t_{\text{un}} + s)$, again showing reasonable correlation with the s exponent.

Figure A7 show the q exponents (q_{exp} , q_{calc} , q_{calc} (1kHz) and q_{calc} (1MHz)) plotted against s . The q_{exp} and q_{calc} values show no correlation with s . The two systems (Niobium Carbide and Graphite-Boron Nitride) with the lowest and highest s respectively, have their q_{exp} values separated from the rest. The q_{calc} values generally increase with s , showing the best correlation so far compared with the other AC exponents. Note also the agreement between q_{exp} and q_{calc} for the Carbon Black systems and their proximity to the $q = (t_{\text{un}} + s)/t_{\text{un}}$ line.

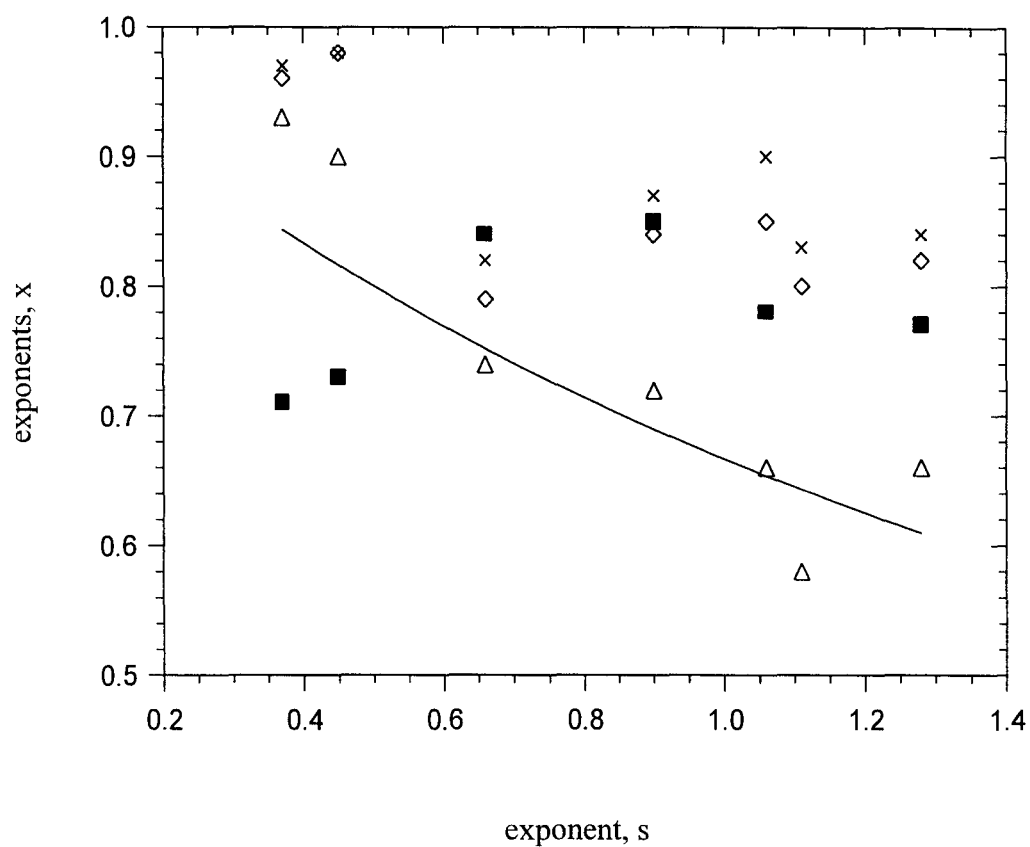


Figure A5: The x exponents (x_{exp} (■), x_{calc} (Δ), x_{calc} at 1kHz (◇) and x_{calc} at 1MHz (×)) plotted versus the DC conductivity exponent s . From left to right, the symbols are for Niobium Carbide, Fe_3O_4 , Graphite, raw Carbon Black, ground Carbon Black, Nickel and Graphite Boron Nitride systems. The solid line, which is a guide to the eye, is $x = t_{un}/(t_{un} + s)$.

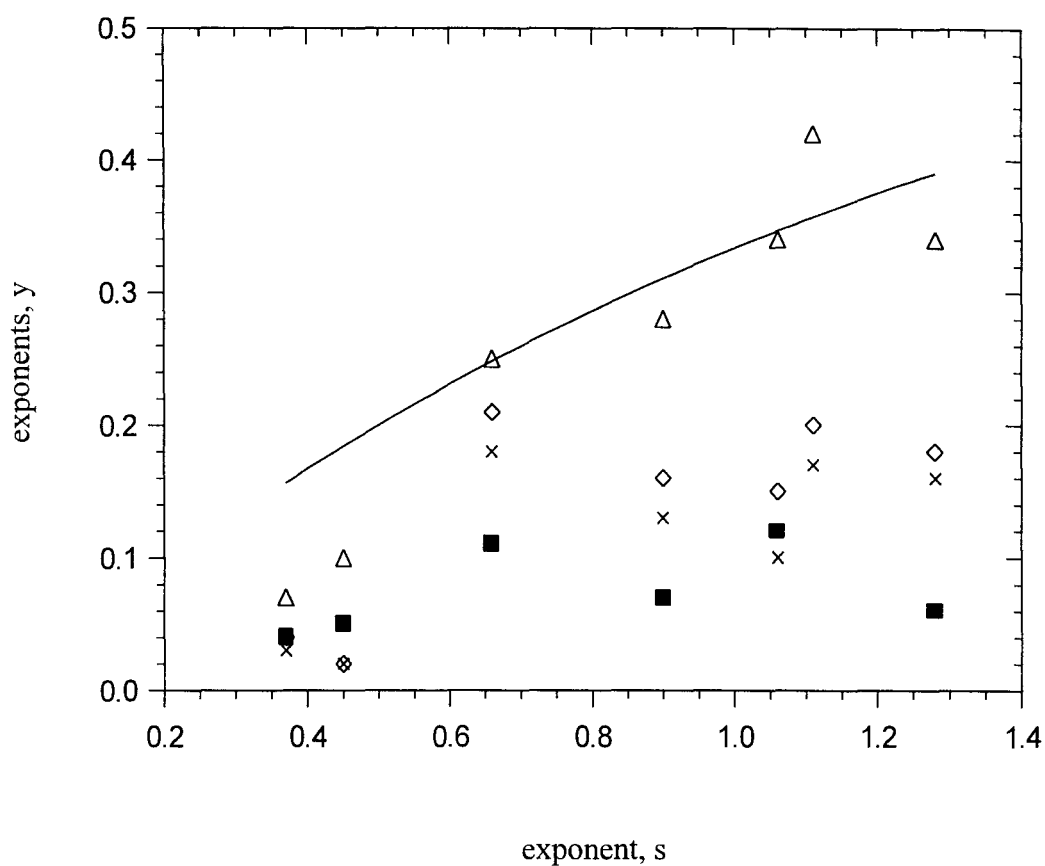


Figure A6: The y exponents (y_{exp} (■), y_{calc} (Δ), y_{calc} at 1kHz ($\diamond$) and y_{calc} at 1MHz ($\times$)) plotted versus the DC conductivity exponent s . From left to right, the symbols are for Niobium Carbide, Fe_3O_4 , Graphite, raw Carbon Black, ground Carbon Black, Nickel and Graphite Boron Nitride systems. The solid line, which is a guide to the eye, is $y = s/(t_u + s)$.

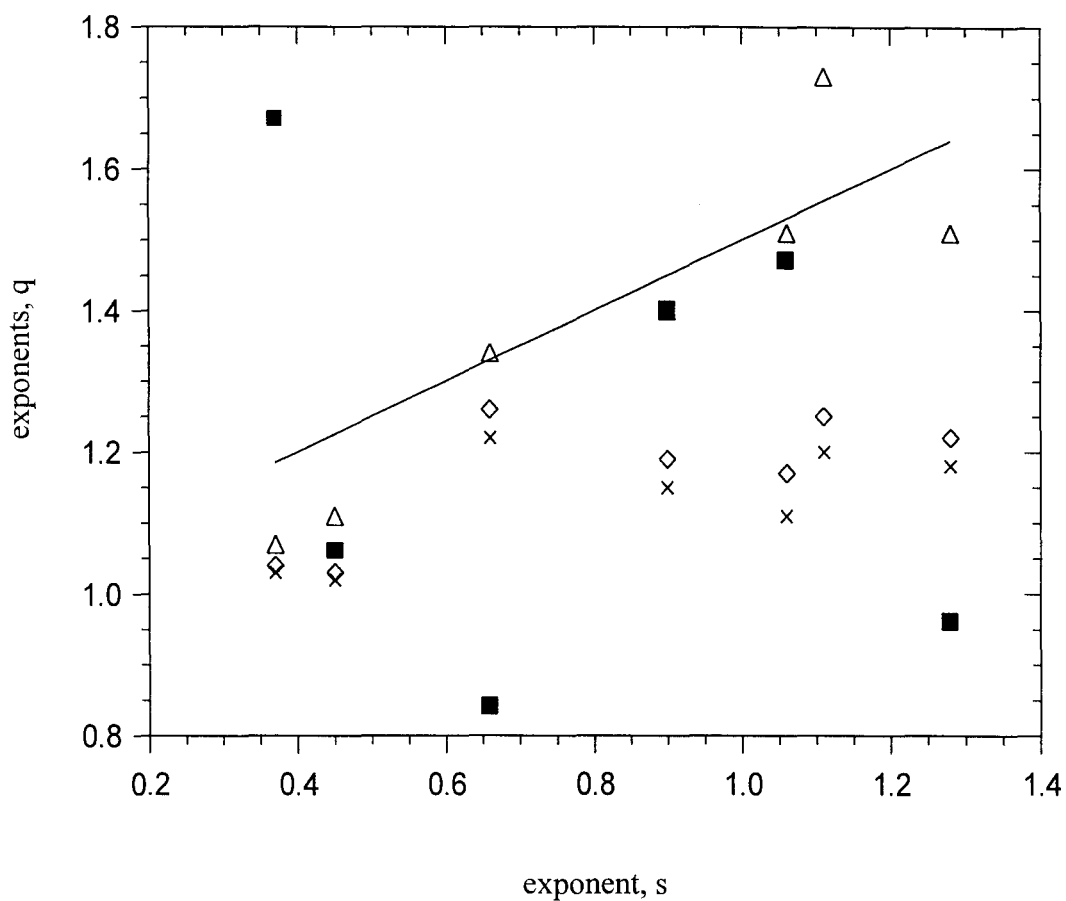


Figure A7: The q exponents (q_{exp} (■), q_{calc} (△), q_{calc} at 1kHz (◇) and q_{calc} at 1MHz (×)) plotted versus the DC conductivity exponent s . From left to right, the symbols are for Niobium Carbide, Fe_3O_4 , Graphite, raw Carbon Black, ground Carbon Black, Nickel and Graphite Boron Nitride systems. The solid line is $q = (t_{un} + s)/t_{un}$.

Figure A8 shows a plot of the experimental values of the noise exponents (k_2 , w_1 and w_2) versus the DC conductivity exponent t . Note that the exponent k_1 has been left out of this plot because it jumps from a small value (0.92) for the Graphite system to a large value (5.23) in the raw Carbon Black system. Therefore, including k_1 in Fig. A8 would make the variations of the other exponents less clear. The k_2 exponent increases steadily with t whereas the resistance exponent (w_2) hardly changes across the t range covered. In contrast, most w_1 exponents (measured very close to the percolation threshold) decrease with t , the w_1 exponent for the Graphite system being off this general trend. The very close values of the w_2 exponents in the systems (for different t exponents) shows that the systems are becoming more similar in their nodes-links and blobs structures at higher values of the conductor concentration. Note that no plot was done versus the DC exponent s as the noise measurements were done only on samples above the percolation threshold, where it is the exponent t , which principally characterises the conductivity behaviour.

Values of the exponent k (k_{calc}) have been calculated for all the cellular systems using the experimental values of the exponent t and the Balberg expressions (eqns. (2.10) and (2.24)). These values k_{calc} are given in Table 6.6 and are shown plotted versus the exponent t in Fig. A9. For comparison, the values of k_2 (for those systems in which they could be measured) are also included. Note that k_1 is left out because the noise results obtained in this thesis appear to indicate that the Balberg model (1998a and 1998b) is more applicable to the k_2 (w_2) than the k_1 (w_1) exponents (refer to chapter eight). The calculated and experimental k exponents in Fig. A9 have similar slopes and hence a very good correlation between them. However, the experimentally determined k_2 are always less than the corresponding k_{calc} from the Balberg model.

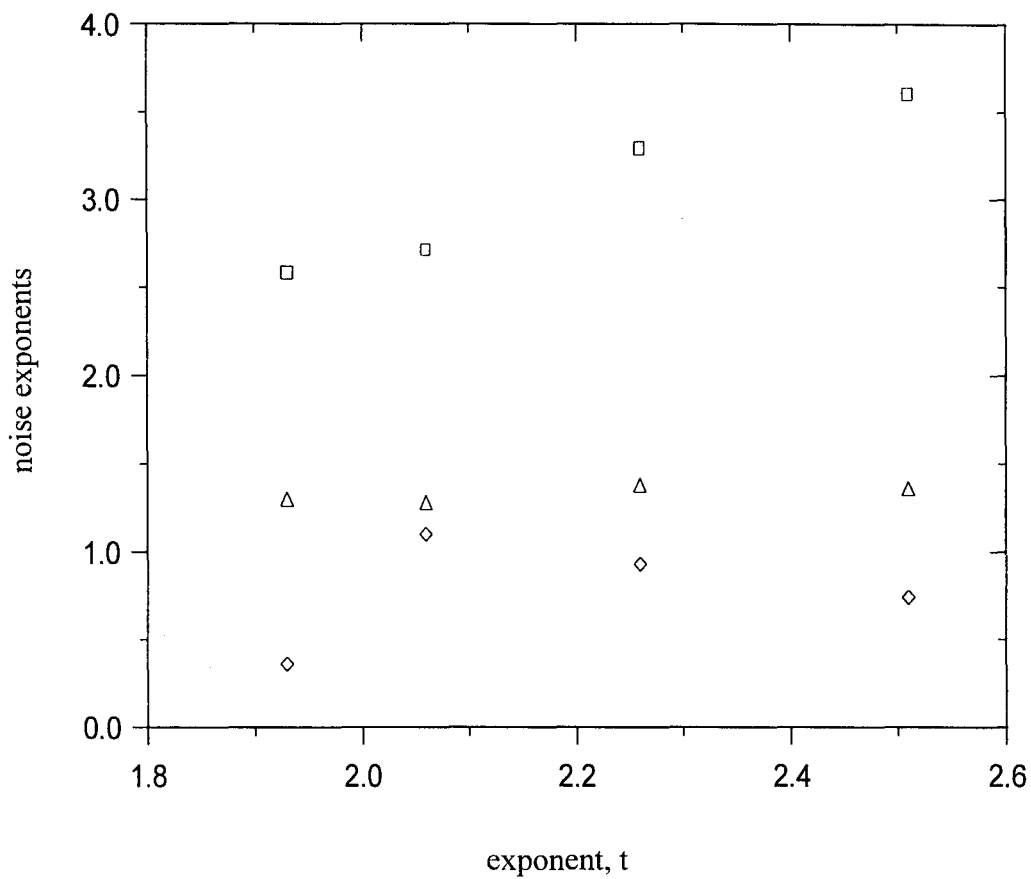


Figure A8: The noise exponents (k_2 (□), w_2 (Δ), w_1 (◇)) plotted versus the DC conductivity exponent t . From left to right, the symbols are for Graphite, ground Carbon Black, raw Carbon Black and Graphite-Boron Nitride systems.

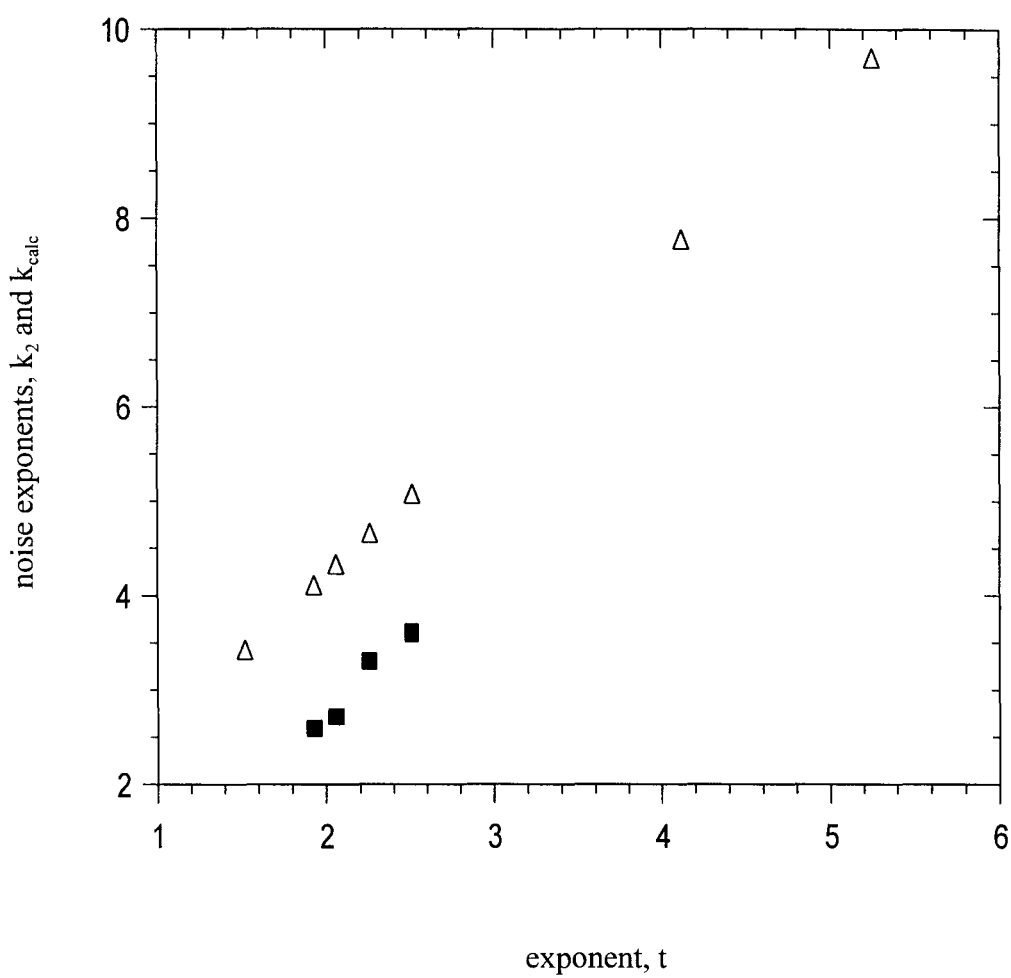


Figure A9: The noise exponents k_2 (■) and k_{calc} (Δ) plotted versus the DC conductivity exponent t . From left to right, the symbols for the experimental values (■) are for Graphite, ground Carbon Black, raw Carbon Black and Graphite-Boron Nitride systems.

A.2: Correlations involving the Critical Volume fractions

Figure A10 shows the predicted values of the critical volume fractions (according to the Kusy model, section 2.1.1) plotted versus the experimental values determined from DC conductivity measurements. The plotted values are those given in Table 4.2. The diameters (mean and sauter, as measured on the Malvern size analyser) of the powder particles were used to calculate the predicted values of ϕ_c as discussed in section 4.1.1.

The results in Fig. A10 show that for any given system, the mean calculated diameter ϕ_c (ϕ_{CM}) is always less than the corresponding calculated sauter diameter values (ϕ_{CS}). Note that the points for all the systems (except the Niobium Carbide system) are either very close to or above the line ($\phi_{CE} = \phi_{CM} = \phi_{CS}$). The calculated values increase with the experimental ϕ_c values (ϕ_{cE}) for all but the Niobium Carbide system, which also shows the biggest discrepancy between ϕ_{CS} and ϕ_{cE} . This is probably because, as mentioned earlier, the hard and angular Niobium Carbide particles are knocked into the surfaces of the relatively soft Talc-wax particles, which reduces the probability of contact among the conductor particles, thereby increasing ϕ_{cE} . The pronounced bimodal distribution in the Niobium Carbide particle size profile (Fig. 3.2a) may also have contributed to this apparent deviation. Recall that no superconductivity was detected in Niobium Carbide-Talc-wax samples, even those well above the percolation threshold.

In Fig. A11, the measured DC conductivity exponents (s and t) are plotted against the critical volume fractions as determined from fitting the conductivity data to the two exponent phenomenological equation (eqn. (2.3)). The values were given in Table 4.1. The results in Fig. A11 show that the DC conductivity exponents s and t are not correlated with ϕ_c . The high t systems consisting of Fe_3O_4 and Niobium Carbide

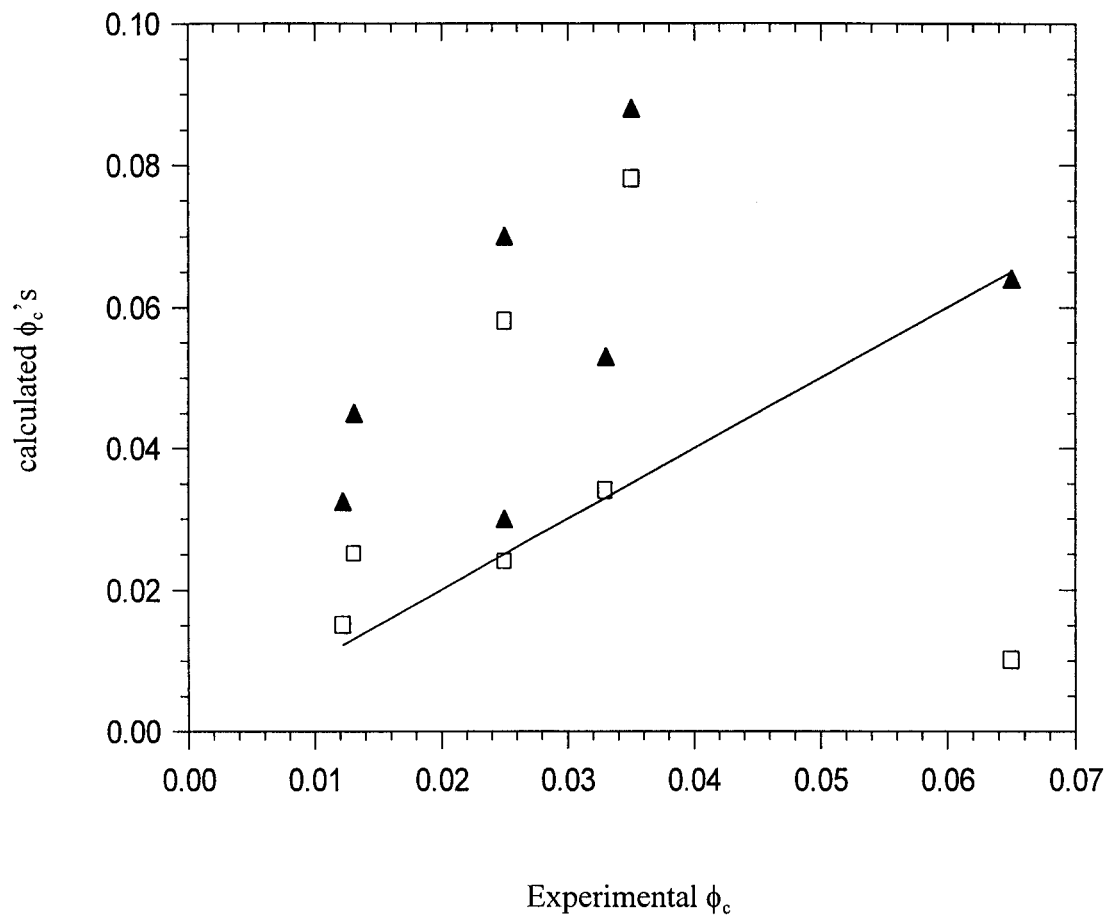


Figure A10: Calculated values (ϕ_{CM} and ϕ_{CS}) of the critical volume fraction versus the experimentally determined values (ϕ_{CE} , from DC conductivity measurements). The predicted values were calculated using the Kusy model and the measured mean ($\square$) and sauter ($\blacktriangle$) diameter values of the powders. The solid line represents ($\phi_{CE} = \phi_{CM} = \phi_{CS}$) just as a guide to the eye.

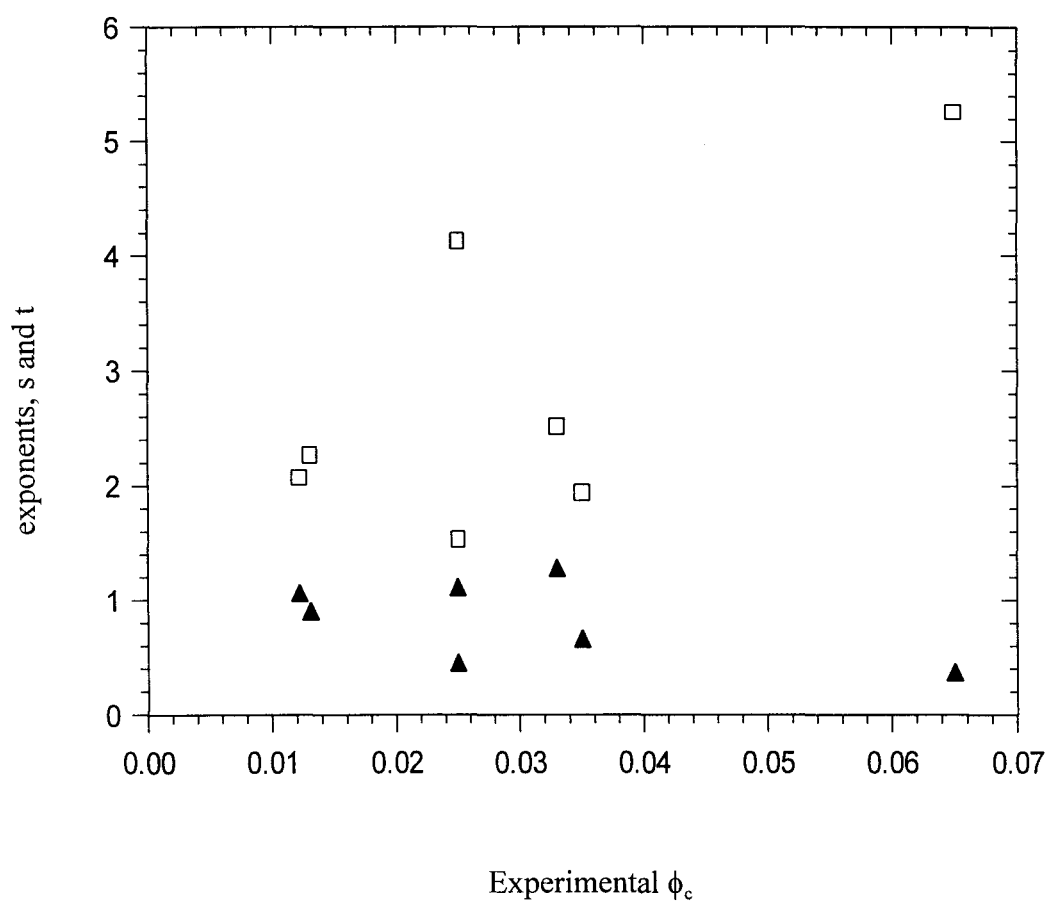


Figure A11: DC conductivity exponents (s ($\blacktriangle$) and t ($\square$)) versus the experimentally determined ϕ_c values (from DC conductivity measurements).

powders and have very small s values, seem to indicate that t increases with ϕ_c . However, there are very few points to support this claim.

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