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Charge transport and morphology in nanofillers and polymer nanocomposites

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Cover: Hopping on a random percolating structure of aggregates
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Chapter 1

Introduction

1.1 Nanocomposites and their conductivity

Many modern products are made of polymers. Often the materials are not pure polymers, but other components are added to give the final product better properties. The combination of a polymer with such additives (and sometimes also the pure polymer) is known as a ‘plastic’. Additives that are commonly used are pigments, flame retardants, stabilizers, conductive particles, lubricants, and antioxidants. Nanoparticles, which are particles with sizes well below $1 \mu m$, are sometimes used as additives, because, when distributed in a smart way throughout a polymer, they add functional properties to the polymer. Such a material, filled with nanoparticles, is called a ‘nanocomposite’. The term ‘matrix’ is used for the material (in this case, a polymer) in which the particles are embedded. The particles are called ‘fillers’ or ‘filler particles’. This thesis concentrates on polymer nanocomposites that can conduct an electrical current thanks to (semi)conductive filler particles.

Before continuing talking about the conductivity of such nanocomposites, we will first elaborate on electrical conductivity in general and on different kinds of conductivity levels. The electrical conductivity $\sigma$ is a material property that gives a measure for the magnitude of the current that runs under the application of a certain electric field. Its definition\footnote{This is the definition for isotropic materials; for anisotropic materials, the conductivity is a tensor, see also section 2.2.1 and 2.3.} is

$$\vec{j} = \sigma \vec{E},$$

with $\vec{j}$ being the current density and $\vec{E}$ the electric field. The unit that is
most often used for $\sigma$ is Siemens per centimeter, abbreviated as ‘S/cm’. The unit Siemens (S) is equal to $\Omega^{-1}$, where $\Omega$ (ohm) is a better known unit, because most people learned at high school that it is the unit of resistance. Actually, $\sigma$ is just equal to $1/\rho$, with $\rho$ being the resistivity (i.e. the resistance of a piece of material times its cross-section in the direction of the current, divided by its length in the direction of the current).

The conductivities of all materials vary over many orders of magnitude. A division is made between materials that conduct currents very well, materials that do not (or hardly) conduct any current, even at high temperatures, and materials that have a conductivity in between these two extremes. The first class of materials are called ‘conductors’ or ‘metals’. They have a conductivity $\sigma$ that is typically higher than $10^2$ S/cm at room temperature. The second class of materials are called ‘insulators’. Their conductivity is lower than $10^{-8}$ S/cm at room temperature. The materials with conductivities that lie in between these two values are called ‘semiconductors’. A material is said to be ‘permanent antistatic’ when its conductivity is between $10^{-11}$ and $10^{-6}$ S/cm. The division in conductivities is shown in figure 1.1. This division can be seen as a rough classification. However, the real distinction between insulators, semiconductors, and metals has a more physical ground: In a metal, electrons can move almost freely through the material; at room temperature, they are usually only hindered by the vibrations of the atom cores. As the vibrations increase when the temperature becomes higher, the conductivity of metals decreases with increasing temperature. In semiconductors, the charge carriers have to overcome an energy barrier before they can contribute to the charge transport. It is easier to overcome this barrier at a higher temperature. Therefore, the conductivity increases with temperature in semiconductors. At a temperature of 0 K, none of the charge

Figure 1.1: Division of materials according to their conductivity levels at room temperature. The conductivities are given in S/cm. The division in conductivity levels is only rough; the real distinction between insulators, semiconductors, and conductors/metals is based on the origin of the charge carrier transport, see text.
carriers can overcome the barrier, leading to a conductivity that is zero. In insulators, the energy barrier is so large, that even at high temperatures there is hardly any charge transport.

Most polymers are insulators with a conductivity below $10^{-13}$ S/cm. This is undesirable for many applications, as static electricity will build up and generally dust particles are attracted to such materials. These problems can be solved by adding (semi)conducting fillers to the insulating polymers. Under certain conditions (discussed below), the material will then become semiconductive. Sometimes we refer to it as ‘conductive’. This would suggest a metallic conductivity level. However, mostly, the conductivity of a nanocomposite is orders of magnitude lower than the conductivity of the filler particles [1, 2, 3, 4], which makes the conductivity of the nanocomposite being only in the antistatic or low-semiconductive range. Applications for such permanent antistatic materials are for example floors in hospitals and factories with electronic devices, safety garment and shoes, and the upper layer of the paper-transport roll in printers and copying machines.

The conductivity of a material only changes from insulating to semiconductive if the fillers form a continuous path through the material, from one side to the other. The term ‘percolation threshold’ or ‘critical filler fraction ($\phi_c$)’ is used for the lowest filler fraction ($\phi$) at which this happens (i.e. the fillers just ‘percolate’). Below this fraction the material is insulating, above this fraction it is semiconducting with a conductivity at direct current ($\sigma_{\text{DC}}$) that saturates to a level $\sigma_{\text{max}}$ for the highest filler fractions. This behavior and the definitions are explained in figure 1.2.

Polymer nanocomposites will get many more applications, if it is possible to increase the conductivity to a metallic or almost metallic level. Still, this higher conductivity level should be achieved at low filler fractions, because only when the filler fraction is at most a few per cent (in volume), the favorable properties of the matrix like its transparency, the ability of easy processing, and the mechanical properties are preserved.

Polymer nanocomposites with very low critical filler fractions have been prepared [5, 6, 7, 8, 9, 10, 11, 12, 2, 13, 14, 15, 16, 17, 18, 19], even down to a critical volume fraction $\phi_c$ of 0.03 vol% [12]. This is much lower than the theoretical 16 vol% for randomly placed spherical filler particles [20]. There are several ways to obtain a material with $\phi_c < 16$ vol%. One of them is usage of a filler with a high aspect ratio (i.e. a filler with a length

\[\text{\footnotesize Some of these references report on nanocomposites with the frequently used filler carbon black. The conductivity of carbon black is approximately } 10^7 \text{ S/cm.}\]

\[\text{\footnotesize We will come back to the value of 16 vol\% in section 2.2.2.}\]
Figure 1.2: $\sigma_{\text{DC}}$ as a function of filler fraction $\phi$. A steep increase in conductivity is observed at a critical filler fraction $\phi_c$. For $\phi < \phi_c$ the filler fraction is too small to form a continuous network through the sample, as shown in the left drawing of the nanocomposite, whereas for $\phi > \phi_c$ such a continuous network exists (right drawing).

that is much larger than its width). A random distribution of such fillers throughout a matrix leads purely on geometrical grounds to a low value of $\phi_c$ [21, 22]. Another way to get a material with $\phi_c << 16$ vol% is to create some kind of inhomogeneity in the matrix, for example by using a matrix made of a mixture of two polymers. If in such a structure the particles are preferably in one of the two polymers or on the interface between the two polymers, $\phi_c$ can be reduced, provided that the host polymer of the particles (or the interface respectively) forms a percolating path through the material [3]. A similar idea is compression of insulating spheres that are coated with a conducting material [23] or compression molding of a mixture of large insulating particles and smaller conductive particles [24, 25, 26]. The use of porous fillers, like some kinds of carbon black, can also help in reducing $\phi_c$ [27, 28]. Finally, a low $\phi_c$ can be created by the formation of a fractal particle network [10, 12, 15, 18, 19]. A fractal structure is a structure that
is self-similar: it looks similar on different length scales. Examples from nature are the shapes of a cauliflower, a fern, and a snowflake, see figure 1.3a, b and c. A picture of one of the samples we used in our experiments is shown in figure 1.3d. It has also fractal features. A fractal particle network is “airy”; the particles do not fill up the total space. When fractal building blocks are used to form a larger network, this network is even more “airy”. In that way, a percolating network arises with a critical filler fraction that is (much) lower than 16 vol%. This thesis concentrates on nanocomposites with a low $\phi_c$ thanks to the formation of a fractal particle network.

As examples a, b, and c in figure 1.3 show, fractals can be formed in nature, without human intervention. This is also the case for the fractal structures of particle networks in some nanocomposites (like in figure 1.3d).
The finally formed structure depends on the interfacial tension between the matrix and the particles and on the processing conditions like how well the particles are separated in the starting dispersion and the curing time and temperature. When those factors are chosen well, a fractal particle network will be formed automatically during processing. Although we mentioned above that reducing $\phi_c$ can be done by using a porous filler, it must be said that the interfacial tension between the filler and the matrix and the processing conditions (which together determine the structure of the particle network) are more important for the value of $\phi_c$ than the porosity of the fillers [16].

1.2 Questions underlying the research in this thesis

As mentioned above, both a low critical filler fraction $\phi_c$ and a high saturation conductivity $\sigma_{\text{max}}$ are desired for many applications. In this thesis, we try to find out whether it is possible to raise $\sigma_{\text{max}}$ in a nanocomposite with a $\phi_c$ much lower than 16 vol%, where a fractal structure is the cause of the low $\phi_c$. If this is possible, we want to know how this can be done.

To answer these questions it is important to know more about the morphology of the nanocomposites and how the charge carriers move within the material. Therefore, we will try to visualize the structure of the particle network and find out what the charge-transport mechanism is.

It will become clear in this thesis, that the conductivity of the filler particles in the nanocomposites that we study is of the utmost importance for the conductivity of the nanocomposites. Therefore, we also extensively study the conductivity of filler particles themselves. The questions that we have concerning the filler particles are:

1. What is the charge-transport mechanism in a densely packed powder of the particles?
2. What is the role of the barrier between two particles for the charge transport?
3. Is the conduction inside the filler particles under investigation isotropic (i.e. equal in all directions)?

To answer the second question, we try to distinguish the interparticle transport (i.e. charge transport from one particle to another) from the intraparticle transport (i.e. the charge transport within the bulk material of a
large crystal). The third question is important because a large anisotropy in the conductivity of a crystal (which means that the charge transport in one or two directions of the crystal is much slower than in the other direction(s)) will influence the conductivity of a powder of the crystals and also of a nanocomposite where the crystals are used as fillers. Compared to a 3-dimensional densely packed powder of crystals, the influence will be larger when the crystals are used as fillers in a nanocomposite, because in more or less 1-dimensional channels of particles in the nanocomposite, a particle with an unfavorable orientation cannot be bypassed.

1.3 Materials used for the investigation

Instead of studying and comparing several kinds of nanocomposites on their effective conductivity, we chose to study one kind of nanocomposites in detail. The set of nanocomposites we studied can be seen as a model system for nanocomposites with a similar particle-network formation mechanism. We chose to study coatings of so-called ‘Phthalcon-11’ particles [29, 19, 30] in a crosslinked epoxy polymer matrix. Phthalcon-11 is a phthalocyanine with one CN and one H$_2$O ligand per molecule (for the molecular and crystal structure, and for background information on phthalocyanines, see chapter 7). The Phthalcon-11 particles are blue semiconductive crystals. They can be made in several sizes. We used crystals of about 200 nm with an aspect ratio of 0.2. The crosslinked epoxy matrix is made out of prepolymer Epikote 828 and crosslinker Jeffamine D230. These two low-viscous components are a diepoxy and a diamine, respectively. For the preparation of the coating, first a dispersion of Phthalcon-11 in m-cresol is made (i.e. the Phthalcon-11 particles are separated into small clusters, dissolved in m-cresol). This dispersion is mixed with Epikote 828 and Jeffamine D230. The mixture is put in an oven, where the prepolymer reacts with the crosslinker, forming a hard crosslinked polymer network. Before the mixture has become highly viscous, the Phthalcon-11 particles have already formed a particle network via Brownian aggregation. For thick-enough coatings [30] this network already percolates at a filler fraction of 0.55 vol%. The system thus indeed has a $\phi_c$ much lower than 16 vol%. It also turns out to have a saturation conductivity $\sigma_{\text{max}}$ much lower than the conductivity of the filler; the difference is a factor $10^4$ (see chapter 3 and refs [19, 30]). This system can therefore be used to investigate how a low $\phi_c$ can be created and why the conductivity is so low.

One reason to choose for this system instead of for another system with
a low $\phi_c$ and a $\sigma_{\text{max}}$ much smaller than the conductivity of the filler is that the experience to prepare these nanocomposites was already present at the Eindhoven University of Technology. The filler particles can be made with high purity at the university, too. In addition, by dissolving them in m-cresol, the particles can be separated into clusters of less than a micrometer, which makes the starting dispersion for the preparation of the coating well-defined. Other advantages of Phthalcon-11 particles are that they are very stable, non-toxic, non-irritating, and environment-friendly [31]. In the preparation of the coating, the viscosity of the prepolymer mixture hardly depends on the filler fraction. Therefore a similar particle-network formation is expected for all filler fractions, which is an additional advantage. A disadvantage of the use of Phthalcon-11 crystals might be their assumed large anisotropy in the conductivity\[32]\. As explained in the previous section, this would influence the conductivity of the nanocomposite dramatically.

As mentioned before, we also studied the conductivity of the filler particles as such. We did so not only for densely packed Phthalcon-11 particles, but also for antimony-doped tin oxide (ATO). Just like Phthalcon-11, ATO particles can be used to make insulating polymers semiconductive [33]. An important difference with Phthalcon-11 particles is that ATO particles are much smaller, namely approximately 7 nm. The ATO particles were used to investigate the influence of this size aspect in the transport mechanism [34]. In addition, they gave us more information on how to distinguish between interparticle and intraparticle charge transport.

1.4 Methods used for the investigation

When measuring the frequency dependence of charge transport in a material, an increase in conductivity with increasing frequency is expected, because at higher frequencies, charge carriers travel shorter distances, which results in lower barriers to take. This can be understood as follows. In a disordered material, like a nanocomposite, a charge carrier will encounter energy barriers of various heights. Consider a charge carrier in such an energy landscape (see figure 1.4). For simplicity, the energy landscape is 1-dimensional (which is a reasonable assumption for the quasi-1-dimensional channels in a nanocomposite), but a similar explanation holds in higher dimensions. For a constant electric field, the charge carrier is forced to take all the barriers in order to induce a current. On the other hand, when an

\[32\]Kramer et al. [32] concluded from their ab-initio calculations that the anisotropy in the conductivity of Phthalcon-11 is large. This will be reinvestigated in chapter 7.
Figure 1.4: Charge transport over an energy landscape with a spread in energies ($E$). At a constant electric field, the charge carrier moves all the way from $a$ to $f$ (green), thus all barriers have to be crossed. At an alternating field, the charge carrier moves a shorter distance, for example between $c$ and $e$ (red), to and fro, so it does not have to take the highest barriers.

An alternating electric field is applied, the charge carriers can move to and fro between two barriers. In that way, high barriers can be avoided. As each frequency ($f$) corresponds to transport over a certain length scale, $\sigma(f)$ gives information on important length scales in the system and makes it possible in particular to distinguish between the inter and intraparticle transport. It also gives information on the effective density of states belonging to the important length scales and on the number of charge carriers involved in the charge transport. Notice that in a nanocomposite, non-percolating clusters or channels of particles do not contribute to the DC conductivity, whereas, for high-enough frequencies, they do contribute to the alternating-current (AC) conductivity.

Up to 1 GHz, the frequency dependence of the conductivity of both the specific [35] Phthalcon-11/epoxy nanocomposite and the Phthalcon-11 and ATO filler powders were measured by dielectric spectroscopy. Measuring the conductivity at frequencies higher than 100 GHz directly is impossible (or at least very inaccurate), but optical-transmission and -reflection measurements can be used to derive the conductivity. This was done for the filler powders at THz and infrared frequencies.

Apart from measuring the conductivity as a function of frequency, some other experiments were performed:

The electric-field dependence and the temperature dependence of the DC conductivities of the specific [35] Phthalcon-11/epoxy nanocomposite and the Phthalcon-11 and ATO filler particles were measured to get insight in the conduction mechanism(s).
The conductivity of the nanocomposite was measured locally with conducting atomic force microscopy (C-AFM). This gives insight in the morphology of the particle network.

One thing that could not be determined experimentally was the anisotropy in the conductivity of a single submicron-sized Phthalcon-11 crystal. Fortunately, computer programs exist that are able to calculate energy-band structures based on first principles. Such calculations are called ‘ab-initio’ calculations, which means that they only need the molecular and crystal structure of a material, without any further experimental data, to calculate the band structures from the Schrödinger equation. The ab-initio method we used was based on density-functional theory (DFT). With the use of the calculated band structures, the mobilities of the charge carriers in different directions could be compared.

1.5 Structure of this thesis

This thesis is constructed as follows: The next chapter gives background information on several topics that will appear in the chapters that follow. Chapter 3 treats the electric-field, temperature, and frequency dependence of the conductivity of the specific Phthalcon-11/epoxy coatings that we analyzed. In chapter 4 the conductivity of Phthalcon-11 powder is investigated in more detail with dielectric-spectroscopy and a comparison is made with the charge transport in the smaller ATO particles. Chapter 5 treats AFM measurements on the Phthalcon-11 crystals and the specific Phthalcon-11/epoxy coatings. It also includes the locally measured conductivity of the coatings with C-AFM. When the results of these measurements are combined with the results of the previous chapters, we can draw conclusions on the structure of the particle network in the specific Phthalcon-11/epoxy coatings. With these conclusions, we are able to construct a model for the morphology of nanocomposites with a certain kind of network formation. This model is described in chapter 6 and used to give quantitative information on the conductivity in such nanocomposites. In chapter 7, the anisotropy of the conductivity inside Phthalcon-11 particles is investigated by using computer simulations based on DFT. The conclusions of the research described in this thesis are given in chapter 8.
Chapter 2

Background information

2.1 Introduction

This chapter gives background information for the remainder of the thesis. Section 2.2 summarizes existing theories that are most relevant to our subject. These theories will come back in several chapters of the thesis, or are needed for understanding of other theoretical explanations that will be discussed. Section 2.3 comments on the use of the theories for real materials. In section 2.4 the experimental methods that we will use are described.

2.2 Theories

We start in section 2.2.1 with general equations for the conductivity. The previous chapter showed that percolation and fractality play an important role in polymer nanocomposites; section 2.2.2 explains the concepts of percolation and fractality in more detail and gives the most relevant outcomes of percolation theory. In section 2.2.3 several charge-transport mechanisms that are important in the investigated materials are discussed.

2.2.1 Conductivity in general

As mentioned in the previous chapter, the conductivity $\sigma$ is defined as

$$\vec{j} = \sigma \vec{E},$$

where $\vec{j}$ is the current density and $\vec{E}$ the electric field. Since, in principle, the conductivity may depend on the direction of the electric field in the material, the conductivity is actually a tensor. However, for now, we restrict
ourselves to a scalar conductivity, which implies that the conductivity of the material is isotropic (i.e. the same in all directions). In section 2.3 we will come back on this aspect.

Since the charge carriers in a material do not react instantaneously to a change in the electric field, the conductivity depends on how fast the electric field changes. In addition, as explained in section 1.4, the morphology of an inhomogeneous material may cause its conductivity to depend on the rate of change of the electric field. To specify the time dependence of the conductivity of a material, its response to a harmonically oscillating field with angular frequency $\omega$ is given as a function of $\omega$. For convenience, the complex exponential is used instead of sine and cosine. We write the applied electric field as $\vec{E}(t) = \vec{E}_0 \exp i\omega t$, where $t$ is the time, and $i$ is equal to $\sqrt{-1}$. When the current density is defined as $\vec{j} = j_0 \exp(i\omega t + i\theta)$, where $\theta(\omega)$ is the angle that denotes how far the current lags behind, then equation (2.1) gives

$$
\sigma(\omega) = \frac{|j_0| \exp i\theta}{|E_0|} = \sigma_0(\omega) \exp i\theta = \sigma_0(\cos(\theta) + i\sin(\theta)) \equiv \sigma' + i\sigma'', \quad (2.2)
$$

where we defined $\sigma'$ as the real part of $\sigma$ and $\sigma''$ as the imaginary part of $\sigma$. Both $\sigma'$ and $\sigma''$ depend on $\omega$. For $\omega = 0$, time lag is not applicable. Hence, $\theta$ equals 0, leading to $\sigma(0) = \sigma_0(0) = \sigma_{DC}$, where ‘DC’ stands for ‘direct current’.

$\sigma''$ is related to energy that is stored in the system by some kind of polarization. Therefore, there is a connection between $\sigma''$ and the real part of the dielectric constant $\epsilon_r'$. Similarly, $\sigma'$ is related to the imaginary part of the dielectric constant $\epsilon_r''$. When we define the relative dielectric constant ($\epsilon_r$)\(^1\) as

$$
\epsilon_r(\omega) = \epsilon_r'(\omega) - i\epsilon_r''(\omega), \quad (2.3)
$$

then the relation between $\epsilon_r$ and $\sigma$ is given by

$$
\sigma' = \omega \epsilon_0 \epsilon_r'' \quad (2.4)
$$

and

$$
\sigma'' = \omega \epsilon_0 (\epsilon_r' - 1), \quad (2.5)
$$

with $\epsilon_0$ being the permittivity of vacuum.

\(^{1}\)The actual dielectric constant is the relative dielectric constant times the permittivity of vacuum ($\epsilon_0$).
Another property that is related to $\sigma$ is the mobility $\mu$ of the charge carriers. The mobility is a measure for how fast charge carriers in a material on average move per unit electric field:

$$\mu = \frac{|\vec{v}_D|}{|\vec{E}|},$$  \hspace{1cm} (2.6)

where $\vec{v}_D$ is the average, or ‘drift’, velocity of a charge carrier ($\vec{v}_D = \langle j \rangle / (nq)$, with $n$ being the charge-carrier density and $q$ the charge of a charge carrier). As a result, the relation between $\sigma'$ and $\mu$ is

$$\sigma' = nq \mu.$$  \hspace{1cm} (2.7)

### 2.2.2 Percolation theory and fractals

In chapter 1, we already mentioned that the particle networks in the nanocomposites under investigation are fractal and that there can only be a conductivity significantly larger than that of the matrix if the particle network percolates. Extensive theories exist on the topics fractality and percolation, see for example refs [36] and [37]. This section discusses percolation in general, conduction in percolating systems, features of fractals, and their role in percolation theory.

Percolation theory describes structures originating from random processes. At least in a certain range of length scales, these structures turn out to be fractal (i.e. they look similar on different length scales, as explained at the end of section 1.1). Originally, to derive equations or scaling exponents in percolation theory (analytically or by simulations), the structure was often built on a lattice (denoted as “lattice percolation”). However, in most practical cases, no lattice underlies the percolating structure, leading to so-called “continuum percolation”. Theories on continuum percolation also exist. We will first concentrate on lattice percolation and in particular on a so-called “random percolating network”, and we will subsequently discuss continuum percolation.

A percolating structure in a lattice can be obtained, when each site (or each bond between two sites) is made occupied with a probability $p$ and unoccupied with a probability $1 - p$. When the network is constructed in this way, the associated structure formation is referred to as “random percolation”, because the occupied sites (or bonds) are randomly distributed over the system. An example is shown in figure 2.1. The percolation threshold $p_c$ is defined as the lowest probability for which the occupied sites (resp.
Figure 2.1: Square lattice where occupied sites are black and empty sites white. Under the restriction that touching of two sites only at the corners is not enough for connection, the chosen probability of the occupation of a site is less than the percolation threshold. On the contrary, the empty sites do form a percolating path (which percolates both from left to right and from top to bottom).

Bonds) form a connected path\(^2\) that percolates (i.e., that spans the total lattice). \(p_c\) depends on the type of percolation (site or bond percolation), the kind of lattice (e.g., a triangular lattice, a honeycomb lattice, a square lattice, a simple cubic lattice, etc.), on the Euclidean dimension \(d\), and on the size of the lattice \(L\). Generally, an infinite system \((L = \infty)\) is considered. In that case, for example, the percolation threshold for bond percolation in a square lattice is 1/2, while for site percolation it is 0.593. In a simple cubic lattice, these values are 0.249 and 0.312, respectively (the values were taken from ref. [37]).

Around the percolation threshold, several properties of the random percolating network show a so-called “universal behavior”. This means that

\(^2\)Usually two sites are defined to be connected when they are nearest neighbors and are both occupied, or when there is a path of nearest-neighbor occupied sites from one site to the other.
the behavior does not depend on the type of percolation (site or bond), nor on the kind of lattice, but only on the Euclidean dimension \( d \). A network property \( \Upsilon \) that follows universal behavior can be described by

\[
\Upsilon \propto |p - p_c|^u
\]

with \( u(d) \) being the universal exponent (\( u \) above \( p_c \) may differ from \( u \) below \( p_c \)). The universality originates in the fractal behavior of the structure: A group of neighboring sites can be seen as a new site, which is either occupied or empty. These new (larger) sites form a new lattice. The lattice is thus redefined. Again, neighboring sites on this new lattice can be seen as an even larger site, and so on. It is shown in the next paragraph that at and close to the percolation threshold this redefining of the lattice can be done many times and still the new structure looks like the original one. This phenomenon gives rise to universality. We will now discuss the universal exponents that will come back in the remainder of this thesis. Other universal exponents in percolation theory can be found for example in refs [36] and [37].

The correlation length \( \xi \) of a structure is defined as some average distance between two sites belonging to the same cluster:

\[
\xi^2 = \frac{2 \sum_s R_s^2 s^2 n_s}{\sum s^2 n_s},
\]

with \( s \) being the number of sites (or bonds) belonging to the cluster, \( R_s \) the average radius of gyration\(^3\) of a cluster with \( s \) sites (resp. bonds), and \( n_s \) the number of clusters with \( s \) sites (resp. bonds). \( \xi \) is one of the network properties that shows universal behavior; it follows the relation

\[
\xi \propto |p - p_c|^{-\nu},
\]

where \( \nu \) is a universal exponent, equal to 0.88 for random percolation in 3 dimensions. Equation (2.10) shows that at the percolation threshold (\( p = p_c \)), the correlation length is infinite and it decreases for increasing as well as for decreasing \( p \) from \( p_c \). The correlation length \( \xi \) is also a measure for the fractality of the structure: the structure is homogeneous on length scales larger than \( \xi \), while it is fractal at shorter length scales.

The percolation probability \( P_\infty \) is defined as the fraction of occupied sites attached to the infinite cluster. It is, of course, equal to zero below the

\(^3\) The radius of gyration is the root mean square distance of the parts of a structure with respect to the centre of mass.
percolation threshold. Near the percolation threshold, above $p_c$, also this property shows universal behavior, expressed as

$$P_\infty \propto (p - p_c)^\beta,$$

(2.11)

where $\beta$ is a universal exponent equal to 0.42 for the random percolating cluster in 3 dimensions [36, 37].

Before we can go on, we have to explain the term “fractal dimension”, $d_f$. To explain what $d_f$ is, a homogeneous and a fractal structure are drawn in figure 2.2. In a homogeneous structure, the mass $M$ inside a box with sides $L$ is proportional to $L^d$, with $d$ the Euclidean dimension (i.e. 2 in a 2-dimensional (2D) system, 3 in a 3-dimensional (3D) system, etc.) On the other hand, the mass of a fractal structure follows the relation

$$M \propto L^{d_f}.$$

(2.12)

Generally $d_f$ is smaller than the Euclidean dimension of the system. Hence, the material in the outer regions is less dense than close to the center of mass. It can be shown [36, 37] that the fractal dimension of a random percolating structure is given by

$$d_f = d - \beta/\nu.$$

(2.13)

$^4$An exception are dendrimeric structures, which can have $d_f > d$. However, in this thesis we will concentrate on structures with $d_f < d$. 

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For a random percolating structure, the fractal dimension $d_f$ around the percolation threshold is 2.5 in 3D.

Of course, we are interested in the conductivity $\sigma$ of a fractal structure. In the discussion below, we will talk about bonds. This seems to indicate that we are only talking about bond percolation. However, when two neighboring sites are occupied, it can be seen as a bond being present between the two sites. Therefore, the discussion below also holds for site percolation.

When a voltage is applied over a fractal structure, only part of the percolating cluster will carry the current; the branches that lead nowhere (these are called “dead ends” or “dangling chains”) will not. The part of the percolating cluster that does carry a current is called the “backbone”. Some parts of the backbone carry the whole current. These are the singly connected bonds, also called “red bonds”. The rest of the backbone carries only part of the total current. This happens in the so-called “loops”. These definitions are shown in figure 2.3.

![Figure 2.3](image-url)

Figure 2.3: When a voltage is applied, the dead ends (green) of a conductive network will carry no current, the singly connected (or ‘red’) bonds (red) will carry the total current, and the loops (blue) will carry only part of the current. The red and blue bonds together form the backbone.

The conductivity of such a structure can be calculated with the use of Kirchhoff’s rules: for every loop of conductors, the sum of the voltages is zero, and at every knot, the sum of the currents is zero. When each bond has the same conductance, the DC conductivity of the structure is, for small
positive values of \( p - p_c \), given by

\[
\sigma_{\text{DC}} \approx \sigma_0 (p - p_c)^t,
\]

where \( \sigma_0 \) is the conductivity of one bond and \( t \) is a universal constant.

We will now show how the value for \( t \) can be derived when all bonds have the same resistance. The DC conductivity \( \sigma_{\text{DC}} \) is known to follow Einstein’s diffusion equation:

\[
\sigma_{\text{DC}} = \frac{q^2 n}{k_B T} D,
\]

with \( q \) being the charge of a charge carrier, \( n \) the charge-carrier density, \( k_B \) Boltzmann’s constant, \( T \) the temperature, and \( D \) the diffusion constant. The latter is given by

\[
D = \lim_{\tau \to \infty} \frac{\langle r^2(\tau) \rangle}{2d\tau},
\]

where \( \langle r^2(\tau) \rangle^{1/2} \) is the root mean square displacement of the charge carrier after time \( \tau \), \( d \) is the dimension, and the motion of the charge carrier is assumed to be a random walk. For a random walk on a fractal cluster, the Brownian law (\( \langle r^2(\tau) \rangle \propto \tau \)), which is valid for a homogeneous structure, has to be adapted:

\[
\langle r^2(\tau) \rangle \propto \tau^{2/d_w},
\]

where \( d_w \) is the so-called “random-walk dimension”. As a result, the time \( \tau \) a random walker takes to travel a distance \( L \) scales as

\[
\tau \propto L^{d_w}.
\]

Combining equations (2.16), (2.17), and (2.18) gives

\[
D \propto \tau^{2/d_w - 1} \propto L^{2-d_w}.
\]

In addition, the charge-carrier density \( n \) is proportional to the mass of the network divided by its volume, and thus \( n \) scales with \( L \) according to

\[
n \propto L^{d_f - d}.
\]

As a consequence, equation (2.15) gives

\[
\sigma_{\text{DC}} \propto L^{d_f - d + 2 - d_w}.
\]
ξ. The influence of the fractality on $\sigma_{DC}$ of a material with dimensions equal to or larger than $\xi$ can thus be found by setting $L$ equal to $\xi$. Combination of equation (2.10) and (2.22) then gives

$$\sigma_{DC} \propto (p - p_c)^{-\nu(d_f - d + 2 - d_w)}$$

and thus

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

For random percolation in 3D, $d_w$ is (at least numerically) equal to $3d_f/2$ [38]. Together with the values of $d_f$ and $\nu$ given above, this yields $t = 2.0$. This value for $t$ is often seen as the universal value. Notice however, that in the derivation, all bonds had the same conductance. When there is a large spread in the conductances of the bonds (either on a lattice, or without a lattice, as will be discussed below), $t$ can differ from 2.0. In particular, Kogut and Straley [39] showed that when the bonds are conducting with probability $p$ and insulating otherwise, and when in addition the conducting bonds have conductivities that follow a distribution behaving as $\sigma^{-\alpha}$ for $0 < \sigma < 1$ and which is zero otherwise, the system shows universal behavior ($t = 2.0$) for $\alpha < 0$ and non-universal behavior with $t > 2.0$ in the case $0 \leq \alpha < 1$. The non-universality of $t$ has been seen in experiments (see for example refs. [40, 41, 42]) and has been studied theoretically in detail [39, 43, 44, 45, 46].

Like for $t$, values for other exponents do not hold universally: values can depend on the kind of network when the (fractal) network is not constructed according to the method for random percolation. In that sense, they are not totally universal. There exist many ways to construct fractal networks. Some of them are described in refs [36] and [37]. An important one for our research is network formation by diffusion-limited cluster aggregation (DLCA). In DLCA particles or clusters of particles move by diffusive motion and when they meet another cluster or particle, they irreversibly stick. The mechanism will be described in more detail in chapter 6. A 3-dimensional network formed by DLCA has a local fractal dimension of 1.8 [47, 48, 49, 50]. This value differs from the value of 2.5 for a randomly percolating cluster on a lattice. It is to be expected that $d_w$ will also differ for a structure formed by DLCA. We will come back to this value for $d_w$ in chapter 6.

Through the random-percolation and DLCA mechanisms, networks can be constructed on a lattice or in absence of a lattice; the latter corresponds to most situations in reality. To denote network percolation that is not based
on a lattice, the term “continuum percolation” is used\textsuperscript{5}. In the continuum, the original definition of $p$, being the chance for a certain site or bond to be occupied, cannot be used. Usually $p$ is replaced by the volume fraction $\phi$ or weight fraction $w$ of the ‘objects’ in the material. As mentioned in chapter 1, the percolation threshold can then also be called the “critical filler fraction” ($\phi_c$ or $w_c$, respectively). The objects can have all kind of shapes, like spheres, cubes, or sticks.

A structure in the continuum built by randomly placing objects, will have a fractal dimension similar to a random percolating structure on a lattice. Also, exponents like $\beta$ and $\nu$ will have the same values, because they refer to the large-scale geometry of the structure, irrespective of lattice details. This does not need to be the case for the exponent $t$ for charge transport. For example, when the charge carriers move from one object to the next by tunneling, the “bond resistances” between the objects may show a large variation, because the tunneling probability depends strongly on the distance that has to be tunneled (see section 2.2.3) and this distance may strongly vary in a structure that is not based on a lattice. As a result, as explained above, in such a case often a value of $t$ that differs from 2.0 is seen.

It has often been tried to find a general formula for the critical filler fraction $\phi_c$ in random continuum percolation. In the remainder of this section, some of the work that has been done on that subject will be discussed. We will only consider systems with one type of objects, e.g. a system with only spheres, or a system with only rods. In addition, unless stated otherwise, only systems with equally sized objects will be considered.

First of all, we must notice that percolation for conduction is different from the usual percolation where the objects of the percolating path are in contact with each other; thanks to tunneling (see section 2.2.3), there can still be a current between two conducting particles that do not touch. To take this into account, the objects are usually given a hard core and a soft shell, as depicted in figure 2.4 for a 2D situation. The hard cores are the actual conducting particles, while the charge carriers can tunnel over a distance of maximally twice the thickness of the soft shells. Hence, there is percolation for conduction when the combinations of the particles with their shells form a continuous path spanning the whole sample. These systems have been simulated by computers \cite{21, 51, 52, 53, 54}, but no general formula for the

\textsuperscript{5}Sometimes the term “continuum percolation” is also used to denote a network on a lattice with a spread in bond conductances. However, we will only use the term for a network that is not based on a lattice.
critical filler fraction could be derived; $\phi_c$ depends on the kind of objects, their aspect ratio, and the thickness of the shells.

Simulations on fully permeable objects were more successful in that respect, at least when $\phi_c$ is defined as $\phi_c = N_c V$, with $N_c$ the critical number density of the objects and $V$ the volume of each object\(^6\). In 1973, Skal and Shklovskii\(^{[55]}\) showed that for fully permeable parallel-aligned 3-dimensional objects like spheres, cubes, or ellipsoids, $N_c V$ equals 0.35. Analogously, in 2D, $N_c V = 1.10$, where $V$ is the object’s area. When the objects have another alignment, $N_c V$ does not have such an invariant value in each dimension. However, Balberg \textit{et al}.\(^{[56]}\) showed that it is still possible to give a general formula for $\phi_c$ when only one type of objects and a fixed degree of alignment (for example a certain fraction of the objects parallel to each other and the rest perpendicular to it (figure 2.5b), or randomly oriented objects (figure 2.5c)) is considered. An important parameter in that respect is the total excluded volume $V_{t,ex}$ (where the ‘t’ stands for ‘total’ and ‘ex’ for ‘excluded’). The total excluded volume is defined as the average excluded volume $\langle V_{ex} \rangle$ around one object times the number density $N$ of the

\(^6\)Notice that for this definition of $\phi_c$, a partial volume of an object that overlaps with another object is taken into account twice.

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objects. Hence, at the critical filler fraction we have

\[ V_{t,\text{ex},c} = N_c \langle V_{\text{ex}} \rangle, \tag{2.24} \]

where the subscript ‘c’ stands for ‘critical’. The excluded volume \( V_{\text{ex}} \) of an object is defined as the volume (or area for 2D) around the center of that object in which the center of another object cannot be when the objects are NOT allowed to overlap\(^7\). Figure 2.6 shows the excluded volume of a sphere and the excluded ‘volume’ (which is actually an excluded area) of a 2-dimensional stick. \( V_{\text{ex}} \) depends on the orientation of the objects with respect to each other. Therefore, the average of \( V_{\text{ex}} \) over the orientation angles is taken in equation (2.24). The earlier results found for parallel-aligned objects give in 3D: \( V_{t,\text{ex},c} = N_c \langle V_{\text{ex}} \rangle = 8N_c V = C_3 \) with \( C_3 \approx 2.8 \) (and hence \( \phi_c = C_3/8 \approx 0.35 \)), and in 2D: \( V_{t,\text{ex},c} = N_c \langle V_{\text{ex}} \rangle = 4N_c V = C_2 \) with \( C_2 \approx 4.4 \) (and hence \( \phi_c = C_2/4 \approx 1.1 \)). For other arrangements, \( V_{t,\text{ex},c} = C_x \), where \( C_x \) is always smaller than \( C_3 \) in 3D or \( C_2 \) in 2D and \( C_x \) is invariant under a given degree of alignment and a given type of objects \([56]\). When the arrangement and type of objects are fixed, \( C_x \) is even independent of the size distribution of the objects, when this distribution is taken into account properly in the calculation of \( \langle V_{\text{ex}} \rangle \) \([56]\). In addition, \( C_x \) is independent of the aspect ratio of the objects. Hence, the parameter \( V_{t,\text{ex},c} \) is useful to determine the relation between \( \phi_c \) and the objects’ aspect ratio.

\(^7\)Notice that in the simulations discussed in this paragraph, the objects ARE allowed to overlap. Still the excluded volume as defined for non-overlapping objects gives a handle to calculate the critical filler fraction. 

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Figure 2.5: Several manners of alignment: (a) parallel, (b) a certain fraction parallel and the rest perpendicular to it, (c) randomly oriented.
Figure 2.6: Excluded volume (or area) of objects given by the dashed lines for a sphere (left) and a stick (right), where for the latter the angle between the stick and a second stick is fixed and given by the angle between de dark grey and the light grey stick. The excluded volumes of the dark grey objects are shown, while the light grey objects are a guide to the eye.

The simulations described above (both the simulations on fully permeable objects and those on objects with a hard core and a soft shell) revealed that $\phi_c$ decreases when the aspect ratio deviates from 1. This is a result that already followed from a very old theory called the “effective-medium approximation” (EMA) [57]. In the EMA, locally fluctuating fields due to the distributed heterogeneity of the material are treated as effective homogeneous fields acting on a single heterogeneity. By using this approximation, a self-consistent solution for the effective field - and therewith for the macroscopic material property such as the effective conductivity - is found. The effective-medium approximation is bad in predicting $\phi_c$ quantitatively (it gives $\phi_c = 0.33$ for conductivity via impermeable spheres, which should be $\phi_c \approx 0.16$, see below), but can be used to demonstrate the influence of the aspect ratio for ellipsoidal objects of arbitrary aspect ratio [58]. Spherical objects give the highest critical filler fraction, while $\phi_c$ decreases when the objects become flatter or more oblong; $\phi_c = 0$ is obtained in the limit of infinitely thin needles or flat disks.

The first simulations that were performed to determine a 3D critical filler fraction in the continuum for impermeable objects more precisely than the

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8for example the electric field, but the EMA can also be applied to the problem of linear mechanical deformation.

9“Impermeable” here means that the objects are not allowed to overlap and they do not have a soft shell.
EMA did, were done on systems filled with spheres [59, 60, 20]. Actually, the simulations by Scher and Zallen [59] were performed on lattices. They noticed that for the various lattices, \( p_c \) varied by a factor of 2, while the variation in \( p_c \) times the packing factor \( f_p \) was only about 10%. This product is thus in good approximation lattice invariant. The values found for \( p_c f_p \) in lattices and the values found later for \( \phi_c \) in the continuum, all ranged between 0.14 and 0.18 [59, 60, 20]. We will show in this thesis, that, in the materials studied by us, the ‘objects’ that randomly percolate are approximately spherical and have a negligible tunneling distance compared to their size. Hence, we can approximate them by impermeable spheres. Throughout the thesis, we will use \( \phi_c = 0.16 \) [20] as the critical filler fraction for randomly placed impermeable spheres.

### 2.2.3 Charge-transport mechanisms

This section describes several charge-transport mechanisms that are important for understanding the conductivity in the nanocomposites that we study. Since ion conduction can be neglected in our materials, the theories that will be treated in this section concentrate on electron or hole transport. The charge-transport mechanisms that will be described are: Drude transport, activated transport, tunneling, and hopping. Concerning hopping, Mott variable-range hopping and Efros-Shlovskii variable-range hopping are treated, followed by a discussion on hopping in systems with another geometry than homogeneously distributed point sites.

#### Drude transport

The Drude model (see for example refs [61, 62, 63]) was developed in the 1900s by Paul Drude. His model is usually applied to materials in which the charge carriers have delocalized wave functions. This means that the charge carriers can move more or less freely through the material, like in a metal. If the movement of the charge carriers were not hampered by anything, Newton’s equation \( \vec{F} = m \vec{a} \) (with \( \vec{F} \) being the force on an object, \( m \) its mass, and \( \vec{a} \) its acceleration) would give \( \vec{a} = q\vec{E}/m \), and thus a constant acceleration, leading to a continuously increasing speed. In reality, however, the movement of a charge carrier is hampered by collisions, for example collisions with phonons. At each collision, the charge carrier is scattered, which leads to damping. For Drude transport, the damping force \( F_D \) is assumed...
to depend on the velocity $\vec{v}$ of the charge carrier and on a characteristic time between two collisions $\tau$ in the following way:

$$\vec{F}_D^\tau = -\frac{\vec{v}}{\tau}. \quad (2.25)$$

Newton’s equation then becomes

$$m \frac{d\vec{v}}{dt} + m \Gamma \vec{v} = q \vec{E}(t). \quad (2.26)$$

where $\Gamma = 1/\tau$.

For a harmonically oscillating electric field with angular frequency $\omega$, the solution is

$$\sigma = \frac{\sigma_{DC}}{1 + i\omega\tau} = \frac{\omega_{pd}^2 \epsilon_0 \tau}{1 + i\omega\tau}, \quad (2.27)$$

where $\omega_{pd}$ is the Drude frequency, given by

$$\omega_{pd} = \sqrt{\frac{nq^2}{\epsilon_0 m}}. \quad (2.28)$$

Combination of equations (2.4) and (2.5) with equations (2.27) and (2.28), yields that the real and imaginary parts of the relative dielectric constant in the Drude model are given by

$$\epsilon'_r = 1 - \frac{\omega_{pd}^2 \tau^2}{1 + \omega^2 \tau^2} \quad (2.29)$$

and

$$\epsilon''_r = \frac{\omega_{pd}^2 \tau}{\omega (1 + \omega^2 \tau^2)}, \quad (2.30)$$

Sometimes $\omega_{pd}$ is called the “plasma frequency”. However, we use the word ‘plasma frequency’ for the frequency $\omega_p$ where $\epsilon'_r$ is equal to 0. The relation between $\omega_p$ and $\omega_{pd}$ is

$$\omega_p = \sqrt{\omega_{pd}^2 - \Gamma^2}. \quad (2.31)$$

When the Drude theory is applied to semiconductors, the mass $m$ should be replaced by the effective mass $m^*$ [64] of the charge carriers.

**Activated transport**

To explain activated transport (see for example ref. [64]), we use the example of the conduction in classical semiconductors. Classical semiconductors like
Si, Ge, and GaAs have a bandgap $E_{\text{gap}}$ (the difference in energy of the valence band and the conductance band) of the order of 1 eV and band widths of several eV [64]. The electrons have to overcome the energy $E_{\text{gap}}$ before the electrons and/or holes can contribute to the conduction. When the energy to overcome $E_{\text{gap}}$ is provided by the lattice vibrations (i.e. the thermal energy), then the temperature dependence of the conductivity is given by

$$\sigma \propto \exp \left( -\frac{E_a}{k_B T} \right),$$

(2.32)

where $E_a$ is an activation energy, $k_B$ is Boltzmann’s constant and $T$ is the absolute temperature. This kind of transport is called “activated” or “Arrhenius”-like. For the classical non-doped semiconductors discussed here (which have delocalized wave functions), with the Fermi level in the middle of the band gap, $E_a$ is equal to $E_{\text{gap}}/2$. The Arrhenius temperature dependence is also seen in semiconductors with localized wave functions at high temperatures, see the discussion on Mott variable-range hopping below.

**Tunneling**

Tunneling is a general concept in quantum mechanics (see for example ref. [65]). At locations where it is energetically unfavorable for a particle to be, its wave function will fall off exponentially with distance. This is illustrated in figure 2.7. In the figure, two sites with their wave functions are

![Figure 2.7: Illustration of the exponential fall off of wave functions ($\Psi$) at places with an unfavorable energy ($E$). Two sites are shown. Since the wave functions of the two sites overlap, it is possible to tunnel from one site to the other.](image)

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drawn. Although the probability is small, it is possible to switch from one site to the other, because the wave functions overlap. Such a switch is called “tunneling”. Thanks to this principle (or hopping, see next paragraph) it is possible that charge carriers in a nanocomposite pass a contact barrier or a barrier of the insulating matrix between two conducting particles.

Hopping

In many disordered materials, the wave functions are localized (i.e. they show an exponential decay as discussed in the previous paragraph) and the energies of the sites vary from site to site. This is illustrated in figure 2.8. The difference with tunneling is that the chance to switch from site \(i\) to site \(j\) not only decreases with increasing distance between the sites, but it also decreases with an increasing energy difference between the sites (at least when the site to switch to has a higher energy than the original site). Switching from one site to another in such a system is called “hopping”. Sometimes the term “tunneling” is used for this process as well.

Under the assumption that the energy is provided by phonons, the probability \(W_{ij}\) to hop from site \(i\) to an unoccupied site \(j\) with the energy \(E_j\) of site \(j\) being larger than the energy \(E_i\) of site \(i\) is given by [66]

\[
W_{ij} = f_{ph} \exp(-\alpha R_{ij} - \frac{E_{ij}}{k_B T})
\]

(2.33)

and, for \(E_j < E_i\) under the assumption that the phonons can easily absorb
the excess energy, the probability to hop from site \(i\) to site \(j\) is at low electric-field strengths given by

\[
W_{ij} = f_{ph} \exp(-\alpha R_{ij})
\]  

(2.34)

where \(f_{ph}\) is the phonon attempt frequency, \(R_{ij}\) is the distance between site \(i\) and site \(j\), \(E_{ij}\) is their energy difference \((E_{ij} = E_j - E_i)\), and \(\alpha\) is a measure for the decay of the wave function:

\[
|\Psi|^2 \propto \exp(-2\alpha r),
\]  

(2.35)

with \(r\) being the distance measured from the site under consideration. \(\alpha^{-1}\) is the localization length.

Miller and Abrahams [66] were the first to give the relations (2.33) and (2.34). Transport that follows these relations is therefore sometimes called “Miller-Abrahams hopping”.

**Mott VRH**

Mott [67] used the expressions for the hopping probability (see previous paragraph) to derive an expression for the temperature dependence of the low-temperature conductivity of a disordered material with a constant density of states (DOS) around the Fermi level. He assumed that there exist a typical distance \(R_M\) and a typical energy \(E_M\) that determine the conductivity. \(R_M\) and \(E_M\) can be interpreted as the maximum distance and energy difference between two sites that are at least needed to obtain a percolating path (i.e. by including all sites with \(\alpha R_{ij} + E_{ij}/(k_B T) \leq \alpha R_M + E_M/(k_B T)\) a sample-spanning path is just formed). Another important assumption that Mott made is that, in order for a current to keep flowing, the number of states with \(R_{ij} \leq R_M\) and \(E_{ij} \leq E_M\) must be of the order of 1. This assumption is known as the Mott condition. In a formula, it is given by

\[
\int_{R_{ij} \leq R_M} dR_{ij} \int_{E_{ij} \leq E_M} dE_{ij} g(E_{ij}) = p,
\]  

(2.36)

with \(g\) being the density of states and \(p\) a constant of the order of unity. For a constant DOS \(g_F\) (where the ‘F’ refers to the Fermi level) and point sites (i.e. sites of an infinitely small size), equation (2.36) simply becomes

\[
R_M^d E_M \approx p/g_F,
\]  

(2.37)

where \(d\) is the systems’ dimension.
By using equation (2.37), Mott optimized equation (2.33). The derivation is written in more detail for a more general case in appendix A, section A.1. The result is that

\[ R_M = \left( \frac{pd}{k_B T \alpha g_F} \right)^{1/(d+1)}, \]  

(2.38)

\[ E_M = \left( \frac{p}{g_F} \right)^{1/(d+1)} \left( \frac{k_B T \alpha}{d} \right)^{d/(d+1)}, \]  

(2.39)

and the temperature dependence of the conductivity is given by

\[ \sigma \propto \exp \left[ - \left( \frac{T_0}{T} \right)^\gamma \right], \]  

(2.40)

with

\[ \gamma = \frac{1}{d+1} \]  

(2.41)

and

\[ T_0 = \frac{\beta \alpha^d}{g_F k_B}, \]  

(2.42)

where \( \beta \) is a constant. Values of \( \beta \) have been found analytically, experimentally, and by simulations, see for example refs [68, 69, 70]. The 3D values range between 11.5 and 27.

Equation (2.38) shows that \( R_M \) increases with decreasing temperature. This can easily be understood: At low temperatures, there is (by definition) little thermal energy. Since thermal energy is needed to overcome the energy difference between two states, the transport will then be dominated by hops to sites that have energies close to the energies of the sites from which the hops take place. Such sites are generally relatively far away. Hence, at low temperatures, the dominating hops overcome a small energy difference, but this goes at the expense of the average distance traveled per hop; this distance becomes large. On the other hand, at high temperatures, energy barriers are easily taken thanks to the large kinetic energy. Hence, the distance between the sites is the decisive factor. As a consequence, at high temperatures, the charge carriers only hop to sites that are close by. This transport mechanism is called “variable-range hopping (VRH)”, because the range of the dominant hops varies with temperature. To distinguish it from the kind of VRH treated in the next paragraphs, we will refer to it as “Mott VRH”. When the temperature is above a certain critical value, \( E_{ij}/(k_B T) \) in equation (2.33) is for (almost) all combinations of \( i \) and \( j \) much smaller than \( R_{ij} \), even when site \( i \) and site \( j \) are nearest neighbors. Hence, only hops to nearest neighbors will take place and \( R_{ij} \) cannot decrease any further with
increasing temperature. The temperature dependence is then not given by equation 2.40, but it is Arrhenius-like (equation (2.32)) [68]. The transport at such high temperatures is referred to as “nearest-neighbor hopping”.

**ES VRH**

The theory of variable-range hopping was revised by Efros and Shklovskii [71, 69] for a temperature regime in which the interaction between an electron that has hopped to another site and the hole it has left behind is not negligible. In materials with a finite bare density of states around the Fermi level (like in doped semiconductors), this interaction turns out to create a gap around the Fermi level in the effective DOS for hopping (i.e. \( g \) in equation (2.36)). This can be understood as follows: There is an attractive Coulomb force between an electron that has jumped from site \( i \) to site \( j \) and the hole it has left behind at site \( i \). For an energetically favorable hop, the energy gain \( E_{ij} \) should therefore be larger than the Coulomb energy \( E_{\text{Coulomb}} = e^2/(4\pi\epsilon_0\epsilon_r R_{ij}) \). For small distances \( R_{ij} \) or small energy differences \( E_{ij} \), this condition will not be fulfilled. Hence, hops from a state close to the Fermi level to another state close to the Fermi level, with a small separation in space will not take place. In three dimensions, the gap in the density of states \( (g) \) that is created as in this way, is quadratic in the energy \( E \), because for a small energy interval \( E \) around \( E_F \), the mean distance \( R \) between two states is determined by the condition \( gR^3E \approx 1 \). Substituting for \( R \) the expression that follows from the Coulomb energy \( R = e^2/(4\pi\epsilon_0\epsilon_r E) \) gives \( ge^6/(e_{\text{Coulomb}}^3E^2) \approx 1 \), and thus, \( g(E) \approx e_{\text{Coulomb}}^3E^2/e^6 \propto E^2 \). Since the gap depends quadratically on \( E \) it is called a “soft gap”, as opposed to a so-called “hard gap”, which is a gap where \( g(E) \) is not only zero at \( E_F \), but also in the vicinity of \( E_F \).

The derivation of the temperature dependence in this case is analogous to the one for Mott VRH. Appendix A gives the derivation for a more general case. The results is

\[
\sigma \propto \exp \left[-\left(T_0/T\right)^\gamma\right], \tag{2.43}
\]

with \( \gamma = 1/2 \) in all dimensions. Since Efros and Shklovskii were the first to derive these equations, this kind of transport is referred to as Efros-Shklovskii (ES) VRH. It is only observed at low temperatures, because at high temperatures the Coulomb energy becomes negligible compared to the thermal energy, so the gap disappears.

Zhang and Shklovskii [34] argue that in a system of small\(^{11}\) particles,
granular metals, or quantum dots, the gap in \( g(E) \) is a hard gap under the assumption that the surrounding material does not influence \( g(E) \). This is caused by the Coulomb charging energy \( (E_C) \) of a particle, granule, or dot. \( E_C \) is in first approximation given by

\[
E_C = \frac{e^2}{2\pi\epsilon_0\epsilon_r a},
\]

where \( a \) is the radius of the particle, granule or dot. In chapter 4, we will come back to the density of states in a powder of small particles.

**VRH in other geometries - I Superlocalization**

In the discussion of Mott VRH and ES VRH above, the sites were assumed to be distributed homogeneously and, in addition, they were assumed to be point sites\(^{12}\). In the remainder of this section two other geometries are discussed.

When the material has a fractal structure (see section 2.2.2), the number of sites available within a distance \( r \) increases only with \( r^{d_f} \) instead of with \( r^d \), where \( d_f \) is the fractal dimension and \( d \) is the Euclidean dimension. Mathematical analysis showed that, when the structure is fractal on the scale of the localization length (i.e. \( \alpha^{-1} \leq \xi \), with \( \xi \) being the correlation length), the wave function should be described with an extra exponent \( \zeta \) \((\zeta > 1)\) \[^{[72]}\):

\[
|\Psi(r)|^2 \propto \exp[-2(\alpha r)\zeta].
\]

The consequences for the temperature dependence of the conductivity will be discussed extensively in section 3.4.2 and appendix A.

**VRH in other geometries - II Cotunneling**

The localization length \((\alpha^{-1})\) is generally of the order of a few Å. Direct hops to sites that are several nanometers or even further away are therefore very unlikely, and will only occur if nearby hops are impossible. As a consequence, in a material that consists of particles\(^{13}\) of a nanometric size or larger, direct hops will only occur between nearest-neighbor particles. This is illustrated in figure 2.9. With only hops to nearest-neighbors, an Arrhenius temperature dependence would be expected. However, in practice, often a conductivity

---

\(^{12}\)We define point sites as sites with no spatial extension, apart from the decay in wave function.

\(^{13}\)The same argument holds for quantum dots or granular metals.
Figure 2.9: Nanometric-sized particles (grey squares) with an interparticle distance $R$ between nearest neighbors and a localization length ($\alpha^{-1}$) of the order of a few Å. The distance between non-nearest neighbors is automatically much larger, which makes a direct hop very unlikely.

The distance between non-nearest neighbors is automatically much larger, which makes a direct hop very unlikely.

proportional to $\exp((T_0/T)^\gamma)$ with $\gamma = 1/4$ or $\gamma = 1/2$ is observed in such materials, indicating some form of variable-range hopping.

In 1990, Averin et al. [73] showed that tunneling over two distant junctions can take place by using a virtual state of conducting material that is in between the two junctions. This process is called “cotunneling”. There exist two forms of cotunneling: elastic cotunneling and inelastic cotunneling. In elastic cotunneling, the energy in all the steps\textsuperscript{14} is conserved, whereas in inelastic cotunneling an excited state arises in the material between the junctions. The latter is only possible when more than one electron in involved in the process. The electrons involved simultaneously change state; one electron hops over the first junction to the conducting material between the two junctions and another electron hops at the same time from this conducting material over the second junction. For inelastic cotunneling, the former electron hops to a state that has an energy that differs from the energy of the state from which the latter electron comes, while for elastic cotunneling these energies are equal. Cotunneling needs not to be restricted to two

\textsuperscript{14}Here we refer to the simultaneously occurring electron transfers to nearest neighbors, as explained in the remainder of this paragraph.
junctions; it can also cover three or more junctions. Thanks to cotunneling, large distances can be hopped to states with favorable energies. Therefore, in materials like semiconductive nanocrystals, granular metals, or quantum dots the temperature dependence typical for variable-range hopping can be observed. Recently, several articles were published on this subject, see for example refs [74, 75, 76, 77].

At high temperatures, the contribution of elastic cotunneling is negligible compared to the inelastic contribution [73, 75]. The electric-field dependence of the conductivity due to inelastic cotunneling in an array of quantum dots is given by [76]

$$\sigma = \left( \frac{\sigma_t}{\hbar/e^2} \right)^j \left( \frac{(eV)^2 + (k_BT)^2}{E_C^2} \right)^{j-1}, \quad (2.46)$$

with $\sigma_t$ being the tunnel conductance of a single junction, $\hbar$ Planck’s constant, $j$ the number of junctions crossed per hop, $V$ the potential difference over $j$ junctions, and $E_C$ the Coulomb charging energy of the conducting component of the system (i.e. the nanocrystal, granule, or quantum dot). $E_C$ is in first approximation given by equation (2.44). At low temperatures, where the contribution of elastic cotunneling may not be negligible, the conductivity due to elastic cotunneling is ohmic [73]. Therefore, for the field dependence in a system with both inelastic and elastic cotunneling, an ohmic term has to be added to equation (2.46).

### 2.3 Theories in practice

For real materials, it is often not possible to apply the theories discussed in section 2.2 straightforwardly. In this section, we discuss some complications for the use of the theories in practice.

In section 2.2.3 we concentrated on electron and hole transport. The conductivity may also (partly) be caused by ions. Apart from systems like fuel cells, which are based on ion transport and where the ion concentration is regulated by an electrolyte, the ion conductivity drops in time under the application of a constant electric field. Hence it is possible to distinguish between the ion contribution and the electron or hole contribution to the conductivity. Insulators, which are, on the basis of the energy gap between the valence and conductance band, expected to have a negligible conductivity at room temperature, usually contain ions (for example originating from catalysts or precursors used in the preparation). These ions give a nonzero conductivity. The ion conductivity might not be negligible.
in polymer nanocomposites below the percolation threshold. However, in this thesis, we only investigated nanocomposites (far) above the percolation threshold, and semiconducting particles. For these materials, the ionic conductivity can be neglected.

In sections 2.2.1, 2.2.2, and 2.2.3, we discussed “conductivity”. What we actually meant was “volume conductivity”: the conductance of a material times the length of the material in the direction of the current, divided by the cross-section in that direction. It is an intrinsic material property, generally expressed in the units S/cm (= Ω$^{-1}$/cm) or S/m. On the other hand, sometimes the notion of “surface conductivity” is introduced. The surface conductivity is defined as the conductance of a surface for a current along the surface, measured over a certain area at the surface. The values are generally given in S/$\Box$ and depend on the thickness of the measured layer. It is not an intrinsic material property. Still surface conductivity is often used in a commercial environment and specific ASTM methods are used to compare the different results. In polymers, the surface conductivity is often enhanced by the presence of antistatic agents. Antistatic agents are molecules that increase the polar and/or ionic concentration at the surface. These ions and polar groups at the surface attract moisture from the air, which influences the transport of charges. Hence, the level of surface conductivity is not permanent and strongly depends on the moisture in the air. The materials used for the experiments discussed in this thesis did not contain antistatic agents and they were dried before the experiments. We will concentrate on the volume conductivity (which we simply call “conductivity”).

A material like a nanocomposite is a highly inhomogeneous material; on the scale of the filler-particle size, the conductivity is high at the positions of the particles and low in the matrix. Although there is a method to probe the conductivity locally (see section 2.4.2), normally, it is measured over a length and area that are much larger than the size of the particles. In such a macroscopic measurement, the ‘average’ conductivity is found in the sense that the measured current (which will (mainly) flow through the particles and not through the matrix) is treated as if it were flowing through the total material with a constant current density.

Most equations of percolation theory hold for infinite systems. Of course, in practice, infinite materials do not exist. Still, the equations will be good when the dimensions of the material are much larger than the correlation length $\xi$, because on such length scales, the morphology of the material can be seen as homogeneous. The conductivity as a function of filler fraction of the 40 µm-thick coatings investigated in this thesis is close to the extrapolated bulk values of infinitely thick coatings [30]. However, there is still
some thickness dependence [30], which is expected to be due to the fact that $\xi$ is not much smaller than the coating thickness.

We already mentioned in section 2.2.1 that actually the conductivity is not a scalar ($\sigma$), but a tensor ($\bar{\sigma}$), because the electric field may induce a current in a direction that is not parallel to the field direction and depend on the direction of the field with respect to the orientation of the material. Materials that show this behavior are said to have an “anisotropic conductivity”. On the other hand, for isotropic materials, the current is always parallel to the electric field and it is independent of the direction of the field with respect to the orientation of the material. In that case, the off-diagonal elements of $\bar{\sigma}$ are zero and the diagonal elements are equal. The value of the diagonal elements is taken to be the constant $\sigma$. In this thesis, we study three kinds of materials: antimony-doped tin-oxide (ATO) crystallites, Phthalcon-11 crystallites, and a specific set of Phthalcon-11/epoxy coatings. Based on experiments that revealed that the structure of the specific ATO crystallites studied in this thesis is quite homogeneous [31], no anisotropy in the conductivity can be expected inside the crystallites nor in their compressed powder. This cannot, in advance, be said about Phthalcon-11, because its molecular and crystal structure is not isotropic. However, we will show in chapter 7 that also in Phthalcon-11 crystals, the anisotropy in the conductivity is negligible. Finally, anisotropy in the Phthalcon-11/epoxy coatings is conceivable due to the smearing of the pre-coating formulation on the substrate, or possible sedimentation of Phthalcon-11 particles or clusters during the preparation of the coating under the influence of gravity. However, the conductivity that we measure for an electric field applied perpendicular to the substrate turns out to be of the same order of magnitude as the conductivity measured parallel to the substrate by Chen et al. [19], see chapter 3. In addition, Chen et al. [19] showed with the use of confocal microscopy that the particles on a macroscopic scale are homogeneously distributed throughout the coating. Hence, for all the materials that we investigate in this thesis anisotropy effects can be neglected. We will therefore only talk about the scalar $\sigma$ instead of the tensor $\bar{\sigma}$ (except for chapter 7, where the anisotropy of Phthalcon-11 crystals is explicitly investigated).

Some materials degrade, leading (among other things) to a conductivity that changes in time. The materials discussed in this thesis are very stable. Even after two to three years, the measurements were reproducible. In addition, several batches of Phthalcon-11 powder were studied and turned out to give approximately the same results.


2.4 Experimental methods

This section is divided into two parts: in section 2.4.1 we explain how charge-transport properties can be measured in the total frequency range from direct current (DC) to infrared frequencies and in section 2.4.2 the working of atomic force microscopy (AFM) and in particular conducting atomic force microscopy (C-AFM) is discussed.

2.4.1 Charge-transport measurements from DC till the infrared

As explained in section 1.4, measuring the conductivity as a function of frequency \( f \) can give information on important length scales in the samples. In practice, determining \( \sigma(f) \) directly by measuring the current when a voltage is applied (or measuring the voltage when a current is imposed) becomes very inaccurate at frequencies higher than 100 GHz when (coax) cables are used in the set-up, because the electromagnetic waves are then strongly damped in the cables. This problem can be circumvented by using optical methods to determine the conductivity, because \( \sigma \) is related to the optical complex index of refraction \( n^* \). \( n^* \) is a material property that shows the influence of a material on an electromagnetic wave \( \vec{\psi} \). Within the material \( \vec{\psi} \) in the \( \vec{x} \)-direction is given by

\[
\vec{\psi}(x, t) = \vec{\psi}_0 \exp\left(i \omega \left( \frac{x n^*}{c} - t \right) \right) \exp(-x/\delta), \quad (2.47)
\]

where \( \omega \) is the angular frequency, \( c \) is the speed of light in vacuum, \( t \) is the time, and \( \delta \) is the so-called ‘skin depth’. \( n^* \) may depend on the orientation of the material with respect to the electromagnetic wave. Under the definitions that \( n \) is the real part of \( n^* \) and \( k \) the imaginary part (thus \( n^* = n + ik \)), the relations between \( n^* \) and \( \epsilon_r \) are

\[
\epsilon_r' = n^2 - k^2, \quad (2.48)
\]

\[
\epsilon_r'' = -2nk, \quad (2.49)
\]

and

\[
k = \sqrt{-\frac{\epsilon_r'}{2} + \frac{1}{2} \sqrt{\epsilon_r'^2 + \epsilon_r''^2}}; \quad (2.50)
\]

\( n \) in terms of \( \epsilon_r' \) and \( \epsilon_r'' \) easily follows from these relations, while \( \sigma \) is related to \( \epsilon_r \) via equations (2.4) and (2.5).
The reflectance, transmittance, and absorbance of light shone on a piece of material depend on its refractive index $n^*$. Hence, by measuring these quantities, the conductivity of the material can be derived. We define the reflectance $R$ as

$$R = 1 - I_0'/I_0,$$  \hspace{1cm} (2.51)

where $I_0$ is the light intensity of the wave just in front of the sample and $I_0'$ is the light intensity just behind the sample interface (where the beam enters the material). $R$ is related to $n^*$ by

$$R = \frac{(n-1)^2 + k}{(n+1)^2 + k}.$$  \hspace{1cm} (2.52)

Inside the material, the light will be absorbed and scattered. The influence of these processes on the light intensity $I$ in the sample at a distance $x$ from the surface in the direction of the incoming beam is given by the extinction coefficient $\gamma_e$, defined as

$$I = I_0' \exp(-\gamma_e x) = I_0' \exp(- (\gamma_a + \gamma_s) x),$$  \hspace{1cm} (2.53)

with $\gamma_a$ and $\gamma_s$ being the absorption and scattering constant respectively. $\gamma_e$ is per definition a factor 2 lower than the earlier defined skin depth $\delta$.

The relation between the absorption coefficient $\gamma_a$ and the refractive index $n^* = n + ik$ is

$$\gamma_a = \frac{4\pi k}{\lambda},$$  \hspace{1cm} (2.54)

where $\lambda$ is the wavelength of the light in the sample. The transmitted light through a sample is what is left after the reflection, absorption and scattering. The transmittance $T$ is defined as

$$T = I_T/I_0,$$  \hspace{1cm} (2.55)

with $I_T$ being the light intensity just behind the sample.

In an experiment where scattering is negligible, transmission and reflection measurements give information on $n^*$ via the relations above. In practice, however, in transmission and reflection measurements not only the transmitted and reflected light is measured, but there is also a contribution of the scattered light.

For DC and frequencies up to 1 GHz, the conductivity can be directly derived from the voltage applied to the sample and the resulting current. For the DC measurements, a Keithley 237 source-measure unit was used for the measurements at room temperature and a Keithley 617 electrometer was used for the measurements as a function of temperature. For the
latter measurements, the sample was cooled with liquid helium, down to temperatures of 4 K. Resistances could be measured accurately up to $10^{16}$ Ω. From 20 Hz till 1 MHz, a Hewlett Packard 4284A impedance meter was used and from 1 MHz till 1 GHz the measurements were performed with an Agilent E4991A RF. For these measurements, the sample was cooled or heated by a Novocontrol Quatro Cryosystem with liquid nitrogen, and the lowest temperature that could be reached was about 115 K. Both amplitude and phase were measured. For higher frequencies, the switch to optical measurements had to be made, as explained above. Between 200 and 500 GHz, an ABmm MVNA (millimeter vector network analyzer) was used for measuring the transmittance, amplitude as well as phase. The set-up is schematically shown in figure 2.10. The samples used for these measurements were pure filler powders (the sample thickness was 3 mm), put between two quartz plates of 4 mm thick. Quartz was used, because it is almost transparent in the measured frequency range. Higher frequencies are according to the practice in the field given in cm$^{-1}$, where 1 cm$^{-1}$ = 30.0 GHz. Reflection measurements on pure filler powders were performed from 150 cm$^{-1}$ till 6000 cm$^{-1}$ with a Bruker IFS 113v Fourier-transform infrared (FT-IR) spectrometer, where approximately all the light that comes back from the sample (i.e. not only the light that comes back under a certain angle) is detected. It was not possible to measure the phase at these high frequencies. More-detailed information on this set-up and the set-up for the subTHz transmission measurements with the ABmm MVNA can be found in refs [78, 79].

Between 400 cm$^{-1}$ and 6000 cm$^{-1}$ transmission measurements were performed with

![Figure 2.10: Schematic drawing of the ABmm-MVNA set-up. The sender horn sends light to a lens, which focuses the light on the sample. The transmitted light is focused by another lens to the receiver horn.](image-url)
a BioRad Excalibur Series FT-IR spectrometer. For these measurements, the samples were prepared by mixing a small amount of filler powder with KBr (resulting in a weight fraction of approximately 1% of filler particles) and a compressed pellet was made from this mixture. The mixing with KBr was done to make the pellet sufficiently transparent for the wavelengths measured.

### 2.4.2 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is a technique to measure several properties of a sample on a very small (see below) scale.\(^{15}\) It works with a tip that scans the surface. The distance between the tip and the surface of the sample is controlled by their Van der Waals interaction; by keeping the Van der Waals force constant, the distance between surface and tip is approximately fixed. In this way, the height profile of the sample can be measured. Simultaneously, the bending forces on the tip in the scanning direction can be measured, which gives a measure for the local friction of the sample. When a conductive tip is used and a voltage is applied between the tip and the substrate, the local current that arises can be measured, see figure 2.11. This measuring method is called “conducting atomic force microscopy (C-AFM)”.

![Figure 2.11: Schematic set-up of a C-AFM measurement. \(R\) is the radius of curvature of the tip.](image)

The force on the tip is derived from the deflection of the cantilever to which it is attached. The deflection of this cantilever is usually determined with the use of a laser beam. This beam shines on the cantilever and the

\(^{15}\) General information on AFM can for example be found in ref. [80].
reflected beam is detected with an array of photodiodes. The difference in intensity on the different photodiodes gives information on the deflection of the cantilever. There exist cantilevers that bend easily and there exist stiffer ones. The choice of the cantilever depends on the mechanical properties of the material under investigation. The stiffness of each cantilever is given by the spring constant, which is normally specified by the manufacturer.

Cantilevers with different spring constants also have different eigenfrequencies. The eigenfrequency comes into play when so-called “tapping mode” is used. In tapping mode, the tip is forced to oscillate. It is different from “contact mode”, where the surface-to-tip distance remains fixed. In contact mode, a soft sample will easily get damaged, as the tip ‘penetrates’ the sample. In tapping mode, this is normally not the case. As will become clear in chapter 5, in contact mode, particles that are loosely attached to the substrate may be swept away. This is usually prevented by using tapping mode. Similarly, dust particles can easier attach to the tip in contact mode. In addition, the difference in phase between the imposed oscillation and the actual oscillation of the cantilever in tapping mode gives information on the error\textsuperscript{16} in the measurement. Apart from these advantages, there is also a drawback of tapping mode compared to contact mode: conducting AFM does not work in tapping mode; contact mode is needed for a good current signal.

The resolution of AFM in the directions parallel to the surface is determined by the radius of curvature $R$ of the tip (see figure 2.11). It is of the order of tens of nanometers or even smaller. The resolution in the direction perpendicular to the sample is of the order of 1 nm.

AFM is often confused with scanning tunneling microscopy (STM). Both AFM and STM are scanning-probe-microscopy (SPM) techniques. The main difference between STM and AFM is the steering mechanism for the distance between sample surface and tip: STM does not use the Van der Waals force, but it tries to keep the tunneling current constant. The tunneling current falls off steeper with distance than the Van der Waals force. As a consequence, the resolution of STM is higher than the resolution of AFM; STM can really show individual atoms. A disadvantage of STM is that the whole sample needs to be (semi)conductive. This can be understood as follows: The tunneling current becomes zero when an insulating part of the sample is probed. Then, in order to keep the current constant, the STM tip moves closer to the surface, but as the part of the sample is insulating, this

\textsuperscript{16}The error depends on the measuring conditions like the pressure of the tip on the sample and the scanning speed.
does not help and finally the tip penetrates the sample, damaging either the sample, or the tip, or both of them. Since our nanocomposites have an insulating matrix, STM is not possible for our materials. In AFM, a (partly) insulating sample is not a problem.

For our measurements, a Digital Instruments Dimension 3100 AFM with a Nanoscope IIIa controller was used. It was combined with different kinds of silicon cantilevers:

- MikroMash CSC12/Ti-Pt/4 cantilevers: Ti-Pt coating, radius of curvature $\approx 40$ nm, spring constant $\approx 1.75$ N/m.
- Olympus OMCL-AC240TM-B2 cantilevers: Pt coating, radius of curvature $\approx 15$ nm, spring constant $\approx 2$ N/m.
- NT-MDT CSG11/Pt cantilevers: Pt coating, radius of curvature $\approx 35$ nm, spring constant $\approx 0.1$ N/m.
Chapter 3

Conductivity of Phthalcon-11/epoxy coatings

3.1 Abstract

A crosslinked epoxy coating with semiconductive Phthalcon-11 crystallites as fillers is a nanocomposite that can have a percolation threshold as low as 0.55 vol% [30]. To get more insight in the conduction mechanism and the filler particle network structure, the macroscopic electrical conductivity of this nanocomposite with a filler fraction well above the percolation threshold was measured as a function of frequency, temperature, and electric field. The DC conductivity at room temperature was $3 \cdot 10^{-8}$ S/cm. The frequency dependence showed a behavior that is common for disordered solids. From the critical frequency a typical length scale for local transport of 0.4 µm was calculated. The temperature and field dependence indicated that the conduction mechanism in this material is variable-range hopping by cotunneling with an average number of junctions per hop of 1.75.

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3.2 Introduction

When (semi)conductive spherical particles are randomly distributed throughout a matrix, the theoretical value for the critical filler fraction $\phi_c$ to obtain a semiconductive material (under the assumption that transport takes place
via nearest neighbors\(^1\)) is 16 vol\% (see ref. [20] and section 2.2.2). As was mentioned in chapter 1, materials with much lower critical filler fractions have been prepared by many authors [5, 6, 7, 8, 9, 10, 11, 12, 2, 13, 14, 15, 16, 17, 18, 19]. When fillers with a high aspect ratio are used, this can be explained purely on geometrical grounds, already for a simple random distribution of the fillers [21, 22]. For several fillers with low aspect ratios, the explanation lies in the formation of fractal aggregates [6, 10, 12, 15, 16, 18, 19]\(^2\). Although intensive research has been done on the electrical conductivity of nanocomposites with low filler fractions, the variety of fillers that has been used is relatively small. The majority of the studies concentrate on carbon black, see e.g. refs. [7, 8, 12, 2, 16, 17]. Other fillers that are becoming increasingly important are carbon fibers [13, 17], carbon nanotubes [13, 14], doped conjugated polymers [9, 11], inorganic semiconducting nanoparticles [82, 16, 33], and metal particles [83]. In this chapter, we will report on organic crystals that can also give semiconducting nanocomposites with a low percolation threshold.

Nanocrystals of aquocyanophthalocyaninatocobalt (III), also called Phthalcon-11, can be used in very low amounts to make insulating thermoplastic as well as thermoset polymers semiconducting [29, 19]. Phthalcon-11 nanocrystals are very stable, non-toxic, non-irritating, and environment-friendly [31]. They have an aspect ratio between 3 and 5 (see also chapter 5), where the length of the long side can be tuned between 50 nm and 700 nm by varying the processing conditions [31]. In this chapter and in previous work [19, 30] crystals with a typical size of the long side of 200 nm were used. Their molecular build-up is shown in figure 3.1. More background information on Phthalcon-11 crystals will be given in chapter 7.

One of the polymer matrices in which Phthalcon-11 particles have been dispersed [19, 30] is a crosslinked epoxy matrix made of Epikote 828 and Jeffamine D230. The structural formulas of Epikote 828 (a diglycidyl ether of bisphenol A) and Jeffamine D230 (a bi-functional primary amine) are shown in figure 3.2. When these two liquid components are mixed, they react with each other and form a solid crosslinked polymer network (for more information on the reaction, see section 3.3). It is a glassy polymer with a glass-transition temperature well above room temperature. As a consequence, when it is used as a matrix for a nanocomposite, the particle network becomes fixed. Coatings of Phthalcon-11 particles in this matrix

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\(^1\)This holds for the case that the particles are much larger than the localization length, so that direct tunneling to next nearest neighbors is impossible [81].

\(^2\)Other explanations for low critical filler fractions are given in chapter 1.
Figure 3.1: Crystal structure of Phthalcon-11. Right: More detailed structure of the unit in the grey circle.

have been produced with thicknesses between 9 \( \mu \)m and 150 \( \mu \)m [30]. The critical filler fraction \( \phi_c \), for conduction measured along the lateral film direction, decreases with increasing coating thickness, approaching a value of 0.55 vol% for bulk percolation [30].

So far, the electrical properties of Phthalcon-11/epoxy composites were only studied by four-point direct-current (DC) measurements at room temperature in the ohmic regime [19, 30]. In this chapter we show results for the conductivity as a function of frequency (\( f = \omega/2\pi \)), temperature (\( T \)), and electric field (\( E \)). These measurements give more information on the morphology of the particle network and the conduction mechanism. The measurements were performed on coatings with a filler fraction \( \phi \) of 12 vol%. This particle fraction is far above \( \phi_c \), as shown in figure 3.3 [30]. We believe that the conclusions to be drawn will draw from the experiments treated in this chapter concerning the kind of conduction mechanism, will also hold for
Epikote:
\[
H_2C-\text{CH-CH}_2-O-\text{C-CH}_2-\text{O-CH}_2-\text{CH}_2-O
\]

Jeffamine:
\[
H_2N-\text{CH-CH}_2-\left(\text{O-CH-CH}_2\right)_{\text{n}}\text{NH}_2
\]
\[m=1.2\text{ for Epikote 828}\]
\[n=2.7\text{ for Jeffamine D230}\]

Figure 3.2: Structural formulas of Epikote and Jeffamine.

composites prepared in the same way, but with a lower amount of Phthalcon-11 filler particles.

3.3 Experimental

3.3.1 Materials

For the preparation of Phthalcon-11/epoxy coatings, we used the following materials:
- Phthalcon-11: The semiconductive Phthalcon-11 crystals were prepared by Chen as described in ref. [19]. The purity was approximately 95% [31], where the main impurity consisted of \(\beta\)-PcCo [84] particles. The density of Phthalcon-11 is 1.65 g/l [19]. The batch contained particles with rib sizes approximately between 40 and 200 nm (see also chapter 5).
- Epikote 828: The epoxy resin Epikote 828 (see figure 3.2) was bought from Resolution Nederland BV.
- Jeffamine D230: The diamine hardener Jeffamine D230 (see figure 3.2) was bought from Huntsman BV, Belgium.
- m-cresol: Solvent m-cresol was purchased from Merck.

All materials were used without further purification.

3.3.2 Coating preparation

For the preparation of the Phthalcon-11/epoxy coatings we followed the procedure of refs [19, 30]: Phthalcon-11 powder was dried for two days at 353 K in a vacuum oven. A dispersion of the dried Phthalcon-11 in m-cresol
Figure 3.3: $\sigma_{\text{DC}}$ as a function of weight fraction $w$ (lower axis) and volume fraction $\phi$ (upper axis) of Phthalcon-11 crystals, for a coating with a thickness of 47 $\mu$m. The data were taken from refs [19, 30].

was made by magnetic stirring for 1 h, followed by ultrasonic mixing for 1 h, both at ambient temperature. The epoxy prepolymer and the hardener were added to this dispersion. As one amine group can react with two epoxy groups [85] (see figure 3.4) the overall ratio NH$_2$/epoxy used was 0.5 (this is the molar ratio of the NH$_2$ and epoxy groups present in the prepolymer formulations) in order to optimize the crosslink density of the polymer matrix. The mixture was magnetically stirred for 5 min and degassed in an ultrasonic bath for another 5 min at ambient temperature. Subsequently, the mixture was cast on substrates with a square applicator. Finally, the coatings were cured in a vacuum oven at 373 K for 4 h and postcured at 393 K for 8 h. After evaporation of the solvent m-cresol, the coatings contained 12 vol% Phthalcon-11.

3.3.3 Sample preparation

For the different kinds of measurements, samples were prepared in different ways.

For the measurement in which the electric-field dependence of the con-
Figure 3.4: Basic reaction steps that take place when an epoxy resin is cured with an amine hardener [85]. Since Epikote 828 has two epoxy groups and Jeffamine D230 is a diamine, rest group R’ contains another epoxy group and rest group R” contains another amine group in the mixture used to prepare the coatings. These groups can react further. In that way, a crosslinked network is formed.

The conductivity of the coating was measured, a glass substrate was used. A 100 nm thick layer of gold was evaporated on the substrate. Before use, a scratch with a width of 0.1 mm was made in the gold layer, which separated the gold in two parts. These two parts, with an area of about 5 cm² each, served as two electrodes. The Phthalcon-11/epoxy prepolymer mixture was cast on top of the separated gold layer and cured as described above. The sample was prepared as such, because in that way the electric field could be applied over a coating length of 0.1 mm and a thickness of 40 µm, which corresponds with a resistance that is suitable for the measurement range of our equipment. In addition, contact resistance was reduced by the large area of the electrodes.

For the other measurements treated in this chapter, two 0.7 mm thick zinc substrates were used. On each substrate, a coating of 7 cm x 5 cm x 40 µm was made as described above (the thicknesses of the coatings were measured with a digital tip micrometer). From the coatings, several samples were cut. The coatings were then peeled off the zinc substrates and 100 nm of gold was evaporated on both sides of the film to decrease the contact resistance with the electrodes. For the conducting-atomic-force-microscopy measurements treated in chapter 5, the coatings were not removed from the zinc substrates and no gold was evaporated on the coatings, but the unwrought cut samples were used.

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3.3.4 Equipment and measurement conditions

The frequency dependence of the conductivity for frequencies between 40 Hz and 1 MHz was measured by using a Hewlett Packard 4284A impedance meter. Measurements in the frequency range of 1 MHz to 1 GHz were performed with an Agilent E4991A RF (for more information, see section 2.4). These devices measure the real ($\sigma'$) as well as the imaginary ($\sigma''$) part of the conductivity, but in this chapter we will mainly discuss $\sigma'$. The amplitude of the AC voltage was 0.1 V, low enough to be in the ohmic regime. We did not go beyond a temperature of 326 K to be sure to measure below the glass-transition temperature of the matrix material ($T_g = 333$ K [86]), in order to keep the particle network fixed.

The temperature dependence of the DC conductivity was measured with a Keithley 617 electrometer. The temperature was varied from room temperature down to 23.4 K.

A Keithley 237 ‘source and measure unit’ was used to measure the influence of the electric field at room temperature.

3.4 Results and discussion

3.4.1 Frequency dependence

Figure 3.5 shows $\sigma'$ of a 12 vol% cured Phthalcon-11/epoxy coating as a function of frequency for different temperatures. For all curves, $\sigma'$ is approximately constant at low frequencies till a critical frequency $f_c$. At the lowest frequencies ($f < f_c$), $\sigma'$ approaches its DC value $\sigma_{DC}$. From figure 3.5 we deduced $\sigma_{DC} = 3 \cdot 10^{-8}$ S/cm at room temperature, which is within a factor of two equal to previously reported values [30]. Above $f_c$ the conductivity increases with frequency. This increase originates in the presence of a network that is not homogeneous on all length scales. At higher frequencies, the electrons travel shorter distances and therefore encounter fewer (and lower) barriers. The typical length where the inhomogeneity starts to be felt can be calculated by using the well-known Einstein diffusion equation:

$$\sigma = ne\mu = \frac{ne^2D}{k_BT}, \quad (3.1)$$

where $n$ is the number of electrons or holes per unit volume, $e$ the electronic charge, $k_B$ Boltzmann’s constant and $D$ the diffusion coefficient. This equation is valid in a homogeneous structure. The frequency at which the
conductivity starts to deviate from $\sigma_{DC}$ is the point at which the equation starts to be invalid in its simple form, with a constant $D^3$. At that point, the mean-square typical distance that marks the transition from an inhomogeneous to a homogeneous network, $l^2$, and the critical number of transitions per second, $W_c$, determine the diffusion constant ($D = l^2/W_c$, where $W_c$ equals $f_c/(2d)$ [70], with $d$ being the relevant dimension). The typical distance is therefore given by

$$l^2 = \sigma_{DC}k_B T/(ne^2W_c).$$

(3.2)

Using $n = 2 \cdot 10^{15}$ cm$^{-3}$ at room temperature, derived in chapter 4, the calculated length scale is found to be 0.4 $\mu$m. This is close to the 0.45 $\mu$m found in ref. [30] for the cluster size of a few crystals that stick together, possibly by chemical bonding.

The increase in conductivity above $f_c$ can be expressed as $\sigma' \propto f^s$. Figure 3.6 shows $s$ for three frequency regimes as a function of temperature. The exponent $s$ increases with increasing $f$ and decreasing $T$. Its maximum value, measured at the highest frequencies and lowest temperatures, is 1.0.

\footnote{In appendix B, a more extensive form of the diffusion equation is given, which is valid above $\omega_c$ in nanocomposites like ours.}
This behavior is often seen in disordered materials [87, 70, 88, 89, 90]. It is an indication of phonon-assisted hopping [70, 91]. Photon-assisted hopping would lead to $\sigma \propto f^2$ [92, 70, 91]. The theoretical value of $s = 1.0$ for phonon-assisted hopping (and also the value of $s = 2.0$ for photon-assisted hopping), was derived in the pair approximation [93]. The pair approximation is valid when the frequency is so high that hops only occur between pairs of sites. For lower frequencies, $s$ generally differs from 1 (or 2). More details on phonon and photon-assisted hopping are given in chapter 4. In reference [12], two frequency regimes with different slopes of $\sigma(f)$ could be distinguished for $f > f_c$, from which different fractal dimensions of the particle network in the nanocomposite were derived. In our case, the slope of the master curve shows a more gradual course, making distinction between fractal regimes impossible.

By multiplying $f$ with $f_c(T_{\text{fixed}})/f_c(T)$ and $\sigma'(T)$ with $\sigma'_c(T_{\text{fixed}})/\sigma'_c(T)$ (i.e. scaling of $f$ and $\sigma'$), where $T_{\text{fixed}}$ is a fixed temperature (we used $T_{\text{fixed}} = 326$ K) and $\sigma'_c = \sigma'(f_c)$, the frequency dependence of $\sigma'$ at all temperatures can be represented by one curve, the so-called master curve (figure 3.7). The existence of a master curve after scaling is seen in various kinds of disordered materials, like polycrystalline and amorphous semiconductors, ionic conductive glasses, and ionic or electronic conducting poly-
It is known under the name ‘time-temperature superposition principle (TTSP)’. The existence of TTSP in disordered systems has been explained in various ways [94, 97, 12, 95, 98]. One of them is by using the diffusion equation (equation (3.1)) with a frequency-dependent diffusion constant. In appendix B, we use this equation to explain TTSP in a nanocomposite like the one treated in this chapter. The conclusion is that TTSP takes place when $\sigma_{DC}$ is governed by a time constant that is connected with $f_c$. The time constant is the time associated with a hop. In appendix B, it also becomes clear that

$$\sigma_{DC} \propto n_\infty e^{2a^2f_c/k_BT},$$

(3.3)

with $n_\infty$ the electron density contributing to the conduction in the percolating network. Since often $n_\infty(T)$ is constant or increases linearly with $T$, equation (3.3) explains why in many cases a master curve is obtained by scaling the frequency in the experimental results with $\sigma_{DC}T$ or $\sigma_{DC}$ (see for example [94, 88] for scaling with $\sigma_{DC}T$ and [99, 100, 101] for scaling with $\sigma_{DC}$).

Equation (3.3) also shows that by plotting $\sigma_{DC}T/f_c$ versus $T$, the temperature dependence of $n_\infty$ can be derived. This is done in figure 3.8.
The vertical axis is logarithmic and the horizontal axis shows $T^{-1}$, in order to show the proportionality of $n_{\infty}$ to $\exp(-E/k_B T)$. The slope of the fit yields $E = 37$ meV. For intrinsic semiconductors, the electron density is proportional to $\exp(-E/2k_B T)$, with $E_g$ the energy gap. The energy gap of Phthalcon-11 is, however, much larger than 74 meV ($E_g \approx 1.2$ eV, see chapter 7). Strikingly, the value of only 37 meV corresponds very well with the donor ionization energies of deficit semiconductors. For example, silicon has an donor ionization energy of 29.8 meV [64]. Although the Phthalcon-11 crystals were not intentionally doped, it is possible that they contained some impurities. The Phthalcon-11 batch that was used had a purity of approximately 95% [31]. $\beta$-PcCo [84] crystals turned out to cause the main impurity [31]. However, it had been impossible to determine whether there existed also impurities inside the Phthalcon-11 crystals, like built in Phthalcon-11 molecules with the CN ligand replaced by another H$_2$O ligand, the H$_2$O ligand replaced by another CN ligand, or with only a CN ligand$^4$. The small energy determined from figure 3.8 might be an indication for the existence of such impurities inside the Phthalcon-11 crystals.

The contact resistance between the electrodes and a polymer nanocomposite may influence the actually measured values of $\sigma'$, especially at low $T^{-1}$.

Figure 3.8: $\log(\sigma_{DC} T)$ (which is proportional to $n_{\infty}$) versus $T^{-1}$. The energy derived from the slope of the fit is 0.037 eV.

$^4$These molecules have charges of +1, -1, and 0 respectively when the metal ion is Co(III). The metal ion can also be Co(II). There is enough space in the lattice for an interchange of CN and H$_2$O [31].
frequencies. The fact that our results could be scaled is a strong indication that contact problems with the electrodes were negligible.

For the same kinds of materials as for which the time-temperature superposition principle holds, the BNN relation:

$$\sigma_{DC} \propto p \Delta \epsilon \epsilon_0 2\pi f_c,$$  

holds. In this relation, \(p\) is a numerical constant of the order of 1, \(\Delta \epsilon\) is the difference between the DC relative dielectric constant, \(\epsilon_{DC}\), and the relative dielectric constant for \(f \to \infty\), and \(\epsilon_0\) is the permittivity of vacuum. The BNN relation was initially an empirical relationship, named after the findings of Barton (1966) [102], Nakajima (1972) [103], and Namikawa (1975) [104], based on experiments on various materials performed by different researchers. Only in 1999, a theoretical validation for the BNN relation appeared [95]. In the validation, the hop of a charge carrier was compared with a rotation of a permanent dipole, which enables the use of the Debye model [105] to approximate the permittivity change. Together with the use of the Einstein diffusion equation for the conductivity (equation (3.1)), the BNN relation was derived. One year later, Schröder and Dyre showed by using simple mathematics that in a first order approximation the existence of scaling according to the time-temperature superposition principle automatically leads to the BNN relation [96]. To check whether the BNN relation holds for our coatings, the factors \(\sigma_{DC}(326\, \text{K})/\sigma_{DC}(T)\) and \(f_c(326\, \text{K})/f_c(T)\) that were used to obtain the master curve are plotted in figure 3.9. They are well described by equation \(\sigma_{DC} \propto f_c^b\), where \(b = 1.20 \pm 0.04\). At first sight, the power 1.20 disagrees with the BNN relation. However, it appears that \(\epsilon\) is temperature dependent and therefore is a function of \(f_c\). If the relationship \(\Delta \epsilon \propto f_c^{-0.20}\) is fulfilled, the BNN relation would still be satisfied. This relation could not be verified, because the measurements were hampered by electrode polarization [106], leading to unrealistically high values of \(\epsilon\) at low frequencies.

### 3.4.2 Temperature dependence

Figure 3.10 shows the temperature dependence of \(\sigma_{DC}\). \(\log(\sigma_{DC})\) is plotted versus \(1/T^\gamma\), with \(\gamma = 1, 1/2, \text{ and } 1/4\). The reason for this is that several theories for conduction in disordered solids exist that predict \(\sigma \propto \exp[-(T_0/T)^\gamma]\), and hence they predict straight lines in such plots. A value of \(\gamma = 1\) corresponds to activated (Arrhenius) behavior (see section 2.2.3). A value considerably smaller than 1 indicates some form of variable-range hopping (VRH). In particular, a value of \(\gamma = 1/2\) can be interpreted as Mott
VRH in a 1-dimensional system or as VRH with a Coulomb gap (Efros-Shklovskii (ES) VRH) in a 3-dimensional system, and a value of $\gamma = 1/4$ normally hints to Mott-VRH in a 3-dimensional system (see also section 2.2.3 or refs [67, 69]).

From the figure we can exclude $\gamma = 1$ for our materials. A straight line is followed best for $T^{-1/2}$ on the horizontal axis. This indicates some form of VRH instead of activated charge transport. Section 2.2.3 explains that variable-range hopping in a system with sites that are large compared to the localization length ($\alpha^{-1}$) and to the site-to-site separation implies so-called cotunneling, i.e. hopping to crystals that are no nearest neighbors by using virtual excited states in nearest-neighbor crystals [77, 75, 74, 76, 108]. The Phthalcon-11 particles are much larger than $\alpha^{-1}$ and the site-to-site distance (see chapter 5). Hence, the temperature dependence indicates that cotunneling takes place.

We will now elaborate on what we expect for the value of $\gamma$. It will depend on several factors. First of all on the size of the particles. As discussed in section 2.2.3, for particles that are “small enough”, Coulomb and quantum size effects influence the conduction. The standard theory of Mott VRH was derived for a constant density of states (DOS) near the Fermi

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5 The situation where the localization length is much smaller than the site-to-site distance is worked out in ref. [107].
Figure 3.10: \( \sigma_{DC} \) of a Phthalcon-11/epoxy coating versus (a) \( T^{-1} \), (b) \( T^{-1/2} \) and (c) \( T^{-1/4} \).

level. However, Coulomb interactions between localized electrons create a soft gap in the density of states near the Fermi level, giving rise to ES VRH for small particles at low temperatures [71]. In addition, quantum size effects lead to discrete energy levels around the Fermi level, which may also result in an energy dependent DOS and therefore a value of \( \gamma \) that differs from 1/4 or 1/2. Finally, the fractal dimension \( d_f \) of the network influences \( \gamma \). These aspects were already explained in section 2.2.3. Below, they are shortly repeated and discussed for the case of the Phthalcon-11/epoxy coating. In the arguments, it is assumed that the influence of the matrix is negligible for the conduction process (meaning that the current is governed by hopping from particle to particle), which is justified, as will be shown in the next chapters.

The influence of quantum size effects is estimated by calculating the energy difference between consecutive energy levels. As a first approximation, the situation where a single electron or hole is inside a crystal with dielectric properties that are the same as those from the surrounding medium is considered. Polarization of the medium by the presence of an electron charge [109, 110] is thus neglected. In such a situation, the energy levels \( \varepsilon \) are given by

\[
\varepsilon_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2}{2m^*_e} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right),
\]

(3.5)
where $\hbar$ is the reduced Planck’s constant, $m^*_e$ the effective electron mass, $L_x$, $L_y$, and $L_z$ are the dimensions of the crystal in the x-, y-, and z-direction and $n_x$, $n_y$, and $n_z$ are 1, 2, 3,... As a measure for the energy spacing in Phthalcon-11 single crystals, we take $L_x = 200$ nm, $L_y = L_z = 50$ nm, we approximate $m^*_e$ with the electron mass $m_e$ and calculate the difference $\varepsilon_{2,1,1} - \varepsilon_{1,1,1}$. It gives a spacing of $3 \cdot 10^{-5}$ eV, corresponding with a temperature of 0.3 K. This temperature is much lower than the temperatures in the experiment. Hence the discretization of energy levels is negligible.

A method to calculate whether the transport is influenced by the Coulomb effect is to determine $T_{\text{cross}}$: below $T_{\text{cross}}$, the Coulomb gap affects the conduction and above $T_{\text{cross}}$, the Coulomb effect is negligible compared to $k_B T$. However, the standard equations for $T_{\text{cross}}$ [111, 76] were derived for standard ES VRH and Mott VRH, with $\gamma$ equal to 1/2 and 1/4, respectively. We will show in the remainder of this section that these standard theories are not appropriate for our samples and that a theory that fully describes the transport in a material with a morphology similar to our Phthalcon-11/epoxy coatings does not exist yet. Therefore, $T_{\text{cross}}$ cannot be determined theoretically. In addition, within the uncertainty of the measurement, all data in figure 3.10b are described by one single straight line and most of the data in figure 3.10c also follow a straight line fairly well. Determining $T_{\text{cross}}$ by the point of intersection between the line that fits the data of the highest temperatures and the line that fits the data of the lowest temperatures would therefore be very inaccurate. Hence, it is impossible to determine $T_{\text{cross}}$ from these experimental data. Another method to determine whether the Coulomb effect will play a role is by estimating the Coulomb charging energy of a single crystal. This method is worked out extensively in chapter 4. It turns out that the Coulomb charging energy plays no measurable role in the transport for Phthalcon-11 crystallites.

However, there is one known aspect of the experimental system for which the standard VRH description needs to be corrected. The network of filler particles is fractal, with a fractal dimension $d_f = 1.77$ on the micronscale [30]. A network with a fractal dimension that differs from the Euclidean dimension gives rise to superlocalization if the localization length is in the same range of the length scales [72]. The wave function $\Psi$ is then given by

$$|\Psi(r)|^2 \propto \exp[-2(\alpha r)^{d_f}] \quad (3.6)$$

As a consequence, the standard expressions for $T_0$ and $\gamma$ derived by Mott and by Efros and Shklovskii are not valid. Some work to adapt the expressions or to find the appropriate value of $\gamma$ has been performed [72, 112, 113, 114, 8],
but the derivations are only published quite scantily. Appendix A shows the full derivation for the temperature dependence of the conductivity with superlocalization for a constant DOS as well as for a Coulomb gap. The derivation is valid for point sites. In our case, the conductive particles are much larger than the localization length, so that variable-range hopping must take place by cotunneling. Cotunneling effectively changes the wavefunction, giving it a more complex form. This will probably have consequences for the expression for \( T_0 \), but we assume that the expression for \( \gamma \) will still be valid as long as the coherence in the hopping probability to sites of different crystals extends over several particle diameters\(^6\). As shown in the appendix,

\[
\gamma = \frac{\zeta}{\zeta + 1}
\]

in the case of a Coulomb gap and

\[
\gamma = \frac{\zeta}{d_f + \zeta}
\]

in the case of a constant DOS. Aharony and Harris \([112, 113, 114]\) showed that \( \zeta = d_{\text{min}} \), with \( d_{\text{min}} \) the dimension of the minimal path length (being the minimal length between two sites via the network). For the 3D fractal percolating cluster of random percolation \( d_{\text{min}} \) is equal to 1.36 \([115, 113, 114]\). However, it was found that in Phthalcon-11/epoxy coatings prepared under the same conditions as our coatings, the fractal dimension is equal to \( d_f = 1.77 \) on length scales below 20 \( \mu \)m \([30]\), corresponding with diffusion-limited cluster aggregation (DLCA; this mechanism of network formation will be explained in chapter 6). The particle network is therefore not just a random percolating network \( (d_f = 2.49 \ [115]) \). We will explain in chapter 6 that the morphology of the particle network is expected to be a combination of DLCA-like structures and random percolation. For a cluster formed by DLCA, \( d_{\text{min}} \) equals 1.25 \([116]\). Substituting the values for \( d_{\text{min}} \) in equation (3.7), gives that, when the Coulomb gap plays a role, \( \gamma = 0.58 \) for a random percolating network and \( \gamma = 0.56 \) for a cluster formed by DLCA. When there is no Coulomb gap, \( \gamma \) is given by equation (3.8), which contains \( d_f \). Zvyagin and Keiper \([117]\) argue that, when cotunneling dominates the transport over direct hopping between non-nearest neighbors (as it does in our materials), the fractal dimension \( d_b \) of the backbone cluster (i.e. the cluster without dangling ends, see figure 2.3) should be used in equation (3.8) instead of the fractal dimension \( d_f \) of the total network. For random percolation \( d_b \) is approximately equal to 1.87 \([118, 119]\), leading with \( \zeta = d_{\text{min}} = 1.36 \) to

\(^6\)Ref. \([72]\) treats the influence of the sizes of grains, but not in accordance with the theory of cotunneling, which was unknown at that time.
$\gamma = 0.42$ for hopping without a Coulomb gap. To our knowledge, $d_b$ of a structure formed by DLCA has never been determined. As the relation $d_{\text{min}} \leq d_b \leq d_f$ holds for all fractal structures (where the first equals sign counts for all aggregates without loops and branches, and the second one only for aggregates without dead ends), equation (3.8) gives that $0.41 < \gamma < 0.5$ for hopping without a Coulomb gap in a structure formed by DLCA.

The experimental data of figure 3.10 showed that $\gamma \approx 0.5$ with an uncertainty in the value for $\gamma$ of at least 0.1. The uncertainty is therefore too large to exclude either hopping with or without a Coulomb gap. In addition, it cannot directly be inferred from the data whether the local DLCA-like structure or the long-range random percolating structure dominates the temperature dependence of the conductivity. For that purpose, a comparison should be made between the average hopping distance and the aggregate size.

### 3.4.3 Electric-field dependence

The influence of the electric field on $\sigma_{\text{DC}}$ is shown in figure 3.11. Many theories for disordered materials predict (at least in a certain range of electric fields) $\sigma(E) \propto \exp(E)$ or $\sigma(E) \propto \exp(E^{1/2})$ [120, 121, 122, 123]. As a result, when a conductivity that follows one of these theories is plotted on

![Figure 3.11: $\sigma(E)$ versus $E$ (a) and $E^{1/2}$ (b). The solid line is a fit that follows the theory for cotunneling.](image)

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a logarithmic scale versus $E$ or versus $E^{1/2}$, a straight line is obtained. To find out whether the conduction in our materials can be described by one of the theories, we plotted our results in both ways. A fit that follows the theory for cotunneling was also added. For the latter, we used the equation (2.46) with an ohmic term added for the elastic-cotunneling contribution (see section 2.2.3). The three data points at the highest electric fields follow an almost straight line in both plots and the fit for cotunneling describes all data points fairly well. We can therefore, only on grounds of the electric field dependence, not exclude any of the theories. However, we concluded from the temperature dependence of the conductivity (combined with the size of the particles in comparison with the localization length) in the previous section that variable-range hopping by cotunneling is the expected conduction mechanism. The fit of equation (2.46 for this process yields that the average number $j$ of junctions included in a hop is equal to 1.75. This means that at room temperature often a virtual state of a neighboring crystal is used to reach a farther (next nearest neighbor) crystal.

### 3.5 Conclusions

The frequency, temperature and electric-field dependencies of the conductivity of a Phthalcon-11/epoxy coating were measured over broad ranges of these variables. The DC conductivity at room temperature of this coating was $\sigma_{\text{DC}} = 3 \cdot 10^{-8}$ S/cm. The frequency dependence of the conductivity measured at different temperatures showed a behavior that is common for disordered materials. By scaling the curves, a master curve could be constructed. This is an indication that contact problems between the nanocomposite and the electrodes were negligible. From the critical frequency, where the conductivity starts to increase above its DC value, a typical length scale representing the transition from an inhomogeneous to a homogeneous conducting network was calculated. Its value was 0.5 $\mu$m, which matches with the length scale found in ref. [30] for the size of a few, possibly chemically bound, Phthalcon-11 crystals. From the temperature dependence of the conductivity we concluded that variable-range hopping by cotunneling takes place. The fit for the electric-field dependence of this process yields an average number of junctions passed per hop of 1.75 at room temperature.
Chapter 4

Conductivity of filler particles

4.1 Abstract

Investigating the conductivity of the filler particles can give information on which effects in the nanocomposite’s conductivity can be attributed to the filler. Therefore, we studied the conductivity of Phthalcon-11 powder and compared it with the conductivity of the Phthalcon-11/epoxy coatings studied in chapter 3. Indications were found that the matrix has no influence on the transport mechanism inside the coatings. Since powders of particles have a more suitable form to study with optical measurements than nanocomposites, it was possible to study them in more detail. Generally, the conductivity within the particles is higher than the conductivity over several or many particles due to bad electrical contact between the particles. For very small particles, another effect is also expected: the density of states (DOS) for the interparticle transport is effectively reduced compared to the DOS inside a large crystal due to the Coulomb charging energy. By measuring the response of a powder over the total frequency range from direct current (DC) to the infrared, we were able to discriminate between these densities of states and the conductivities associated with them. We studied Phthalcon-11 and also smaller antimony-doped tin-oxide (ATO) filler particles, with a diameter of 7 nm. The Phthalcon-11 particles turned out to be large enough, but for the ATO particles, the DOS for interparticle transport is dramatically reduced by the small size of the particles.

The contents of this chapter were or will be published in the following articles:

- L. J. Huijbregts, H. B. Brom, J. C. M. Brokken-Zijp, M. A. J. Michels, M.
4.2 Introduction

To investigate to which extent the conductivity of the filler particles influences the conductivity of a nanocomposite, the filler particles are studied separately in this chapter. Therefore, similar measurements as discussed in chapter 3 for specific [35] Phthalcon-11/epoxy coatings are performed on Phthalcon-11 powder and the results are compared. In addition, we try to discriminate between intra- and interparticle transport for touching particles, where we define the intraparticle transport as the transport within a crystal if the crystal would be very large and the interparticle transport as the transport over more than one crystallite (with the crystallites of the real size). One way to do this is of course to measure the conductive properties of a powder of crystals and compare it with those of a single crystal. Unfortunately, the filler particles that we want to investigate cannot be produced in sizes of a micron or larger. Measuring the conductivity of a submicrometer- or nano-sized single crystal is still a challenge (and this would of course lead to a slightly different definition of intraparticle transport). One can think of attaching wires to the crystallite, or measuring the conductivity with conducting atomic-force microscopy (C-AFM). We tried the latter, but that gave no measure for the single-crystal conductivity, see chapter 5. There is however, another method to distinguish the inter- from the intraparticle transport, which uses the response of a powder of particles from direct current (DC) till infrared frequencies. For practical reasons, it is hard to use this method directly on nanocomposite coatings, but it will become clear in this thesis that using the more suitable powder of particles makes sense\footnote{The contact between crystals inside the studied nanocomposite coatings is similar to that in pressed powder, as will be shown in section 4.4 and chapter 5.}.

The interparticle conductivity can be lower than the intraparticle transport due to bad electrical contact between touching particles and/or a non-negligible Coulomb charging energy. The latter effect, which will be explained below, will only play a role in very small particles. To investigate its influence, we will study Phthalcon-11 as well as antimony-doped tin-oxide (ATO) crystallites, with a size of only 7 nm. Just like Phthalcon-11, ATO...
particles can be used to make insulating polymers conductive already at a filler fraction below 1 vol % [124, 33, 125].

Usually a system with only neutral crystals will have a lower energy than a system with charged crystals due to the Coulomb force between the atom cores and the electrons. When a large crystal is charged by an extra electron, the other electrons will shift a little to other locations in order to minimize the energy. In that way, the extra charge is “screened”. However, in small crystals, the movement of the other electrons is restricted by the boundaries of the crystals. Hence, their shift can only be minimal resulting in a higher energy than in the case of large crystals. As a result, the energy barrier to charge small crystals is higher than the barrier to charge large crystals. A hop of an electron from one neutral crystal to another is thus hindered by the so-called “(Coulomb) charging energy” $E_C$.

The charging energy is given by

$$E_C = \frac{e^2}{2\pi\epsilon_{\text{eff}} R},$$  \hspace{1cm} (4.1)

where $R$ is the radius of the crystals and $e$ is the electron charge. In the dilute limit, i.e. for a system in which the distance between the crystals is so large that the Coulomb force between charged crystals can be neglected, $\epsilon_{\text{eff}}$ is equal to $\epsilon$, the dielectric constant of the surrounding medium. When the crystals are more densely packed, an adapted value for $\epsilon$ should be used in equation 4.1. For a regular array of crystals $\epsilon_{\text{eff}}$ equals [34]

$$\epsilon_{\text{eff}} \approx \epsilon R / d,$$  \hspace{1cm} (4.2)

where $d$ is the spacing between the crystals. The reason to use an effective dielectric constant that differs from the normal $\epsilon$ is that the electrons in the surrounding crystals also shift a little when a certain crystal is charged and they therefore contribute to the screening of the charge.

For a hop of an electron to take place, the energy $E_C$ has to be overcome. Therefore, an otherwise constant density of states (DOS) effectively becomes split up, as shown in figure 4.1a for undoped equally sized crystals. This energy splitting leads to a hard gap in the effective DOS at the Fermi level $E_F$. As the temperature dependence of Efros-Shklovskii variable-range hopping (see section 2.2.3) -which needs a nonzero DOS at $E_F$- is often seen in a system of crystals (or quantum dots or granular metals, for which the same arguments hold) that are not intentionally doped and for which $E_C$ is not negligible, Zhang and Shklovskii [34] argue that these systems are still doped, for example by the surrounding material. In such a doped system,
Figure 4.1: Splitting of the DOS in a system of equally sized crystals by the effect of the Coulomb charging energy for an otherwise constant DOS. The occupied states are shown in grey. (a) Without doping. (b) With doping. Doping is needed to create a non-zero DOS at the Fermi level $E_F$ [34]. A broadening of the peaks, as shown in (b), can also be caused by a distribution in the crystal sizes.

the peaks in the effective DOS get broadened and the Fermi level shifts, leading to a non-zero DOS at $E_F$, see figure 4.1b. When the crystals do not all have the same size, but there is a distribution in their sizes, a similar broadening of the peaks takes place.

When $E_C$ is not negligible compared to the thermal energy, the effect of a changed DOS due to the charging energy will play a role in the interparticle charge transport, while for the intraparticle charge transport, the DOS is unaffected. In this chapter, we will try to show by experiments on powders whether the conductivity and the effective DOS for inter- and intraparticle transport differ. This is done in section 4.5 for Phthalcon-11. In section 4.6 a comparison is made with the smaller ATO crystallites, which shows the influence of the particle size on the reduction of the DOS due to the charging energy. However, we will start (after the experimental section) with a section in which the conductivity of Phthalcon-11 powder is compared with that of the Phthalcon-11/epoxy coatings discussed in chapter 3.

4.3 Experimental

Phthalcon-11 powder was prepared by Ming Yuan at the Eindhoven University of Technology as described in ref. [19]. The batch had crystal sizes of
about 200 nm with an aspect ratio of 0.25. ATO powders were obtained from Nano Specials (Geleen, the Netherlands). They were made from ATO/water dispersions by evaporating the water at 100°C and drying the obtained powder at reduced pressure at room temperature. Special care was taken during preparation to minimize surface pollution. More details on the bulk and surface composition of the materials are given in chapter 7 for Phthalcon-11 and in section 4.6 and ref. [125] for ATO. In most experiments compressed powder was used with a sample thickness of typically a few mm, but for the reflection measurements on ATO we used precipitated films with a thickness of about 1 mm. These films were made by slowly evaporating the water from the same ATO/water dispersions as used for the preparation of the powder at 323 K. For the infrared transmission measurements, pellets were made of a KBr/ATO mixture. Mixing with KBr was done to make the sample sufficiently transparent. The pellets contained only 1 wt% of filler powder (the density of Phthalcon-11 is 1.65 [19] and of ATO 6.99 [125] g/cm³). In all other measurements, the pure filler powder was used. The Phthalcon-11 powder was always dried for two days at 353 K in a vacuum oven and the ATO powder was kept under vacuum at room temperature.

Except for the field-dependence measurements, all data were taken in the ohmic regime. The DC conductivity measurements were performed in the dark under helium atmosphere with a Keithley 617 electrometer, except for the field-dependence measurements on Phthalcon, which were performed with a Keithley 237 ‘source and measure unit’ under ambient conditions in the dark. For frequencies \( f \) between 20 Hz and 1 MHz, a Hewlett Packard 4284A impedance meter was used. For \( 1 \text{ MHz} \leq f \leq 1 \text{ GHz} \) the measurements were performed with an Agilent E4991A RF impedance/material analyzer. The device for frequencies between 200 GHz and 500 GHz was an ABmm MVNA (millimeter vector network analyzer). In the infrared regime we used a Bruker IFS 113v Fourier-transform infrared (FT-IR) spectrometer for the reflection measurements and a BioRad Excalibur Series FT-IR spectrometer for the transmission measurements. More information on the experimental methods can be found in section 2.4.

Although the powders can be compressed only till a packing factor of about 0.5, we use the total sample thickness (or effective thickness of the filler in the case where the powder was mixed with KBr) in the calculations, without correcting for the factor of 2. In addition, a variation in the packing factor due to shrinkage for the temperature-dependent measurements is neglected.
4.4 Conductivity of Phthalcon-11 powder vs Phthalcon-11/epoxy coatings

This section shows the results of temperature-, electric-field-, and frequency- ($f < 1 \text{ GHz}$) dependence measurements of the conductivity of Phthalcon-11 powder. The measurements are similar to the ones discussed in chapter 3 on Phthalcon-11/epoxy coatings. Hence, we can make a comparison between the conductivity of those Phthalcon-11/epoxy nanocomposite coatings and that of Phthalcon-11 powder.

At room temperature, we measured a DC conductivity ($\sigma_{\text{DC}}$) of compressed Phthalcon-11 powder of $2 \cdot 10^{-4} \text{ S/cm}$ in the ohmic regime. However, based on the low-frequency ($f < 1 \text{ MHz}$) measurements as well as the electric-field-dependence measurements, we believe that the real DC conductivity is higher by a factor of 1.5 to 2. Both measurements showed a step from $2 \cdot 10^{-4} \text{ S/cm}$ to $(3 - 4) \cdot 10^{-4} \text{ S/cm}$ by increasing respectively the frequency or the electric field (see figure 4.2 and 4.3). The step in

![Figure 4.2: $\sigma'$ of compressed Phthalcon-11 powder at several temperatures as a function of frequency for frequencies between 20 Hz and 1 MHz.](image)

the frequency domain did not satisfy the time-temperature superposition principle (i.e. the conductivity-frequency curves at different temperatures could not be brought onto one single curve (a master curve) by scaling), described in chapter 3 and appendix B. Therefore, we conclude that the
measurements at low frequencies (< $10^4$ Hz) suffered from contact problems with the electrodes. The step in the electric-field domain might be due to an increase in effective contact area. The regime of electric fields after the step is too small for a fruitful comparison with a model. For frequencies above 1 MHz, a master curve of $\sigma'(f)$ can be made (see below), indicating that the contact problems are negligible for these frequencies. It is thus reasonable to assume that $4 \cdot 10^{-4}$ S/cm is the actual DC value of the conductivity at room temperature. Compared with $\sigma_{\text{DC}} = 3 \cdot 10^{-8}$ S/cm for the nanocomposite Phthalcon-11/epoxy coatings discussed in chapter 3, the DC conductivity of the filler powder is 4 orders of magnitude larger.

Figure 4.4 shows the temperature ($T$) dependence of $\sigma_{\text{DC}}$ of Phthalcon-11 powder, measured till temperatures down to 4 K. Since the data follow a straight line best when plotted logarithmically versus $T^{-1/4}$, they are well represented by

$$\sigma_{\text{DC}} \propto \exp\left(\frac{T_0}{T}\right)^\gamma,$$

with $\gamma$ being equal to 1/4; this indicates Mott variable-range hopping (Mott VRH), see chapter 2, which was also suggested to be the conduction mechanism in the nanocomposite coatings (see chapter 3). For the exponent $\gamma$ of the coatings, the fractal particle-network structure had to be taken into account.
Figure 4.4: $\sigma_{DC}$ of compressed Phthalcon-11 powder versus $T^{-1/2}$ (a) and $T^{-1/4}$ (b).

account, while compressed powder is just 3-dimensional. Again, apparently cotunneling takes place, because this is needed for variable-range hopping in a system with large particles (as compared to the localization length and the interparticle distance), see section 2.2.3.

$\sigma'(f)$ of compressed Phthalcon-11 powder is plotted in figure 4.5 for frequencies between $10^6$ and $10^9$ Hz. $\sigma'$ is approximately constant until a frequency $f_c(T)$ ($f_c \approx 1 \cdot 10^8$ Hz at room temperature). For $f > f_c$, the conductivity increases as a function of frequency according to $\sigma'(f) \propto f^s$, where $s$ slightly increases with increasing frequency and decreasing temperature. In figure 4.5 $s$ reaches a value of 0.6 at the highest frequencies and the lowest temperatures shown in this figure. In section 4.5, we will show that $s$ increases further for higher frequencies. The origin of the increase was already partly discussed in sections 1.4 and 3.4.1 and will be discussed further in sections 4.5 and 4.6. Like for the coatings discussed in chapter 3, a length scale $L_{hom}$ corresponds to the critical frequency $f_c$. At lower frequencies, the charge carriers move over longer distances than $L_{hom}$ and the system can on those length scales be seen as homogeneous, whereas at higher frequencies the charge carriers move shorter distances, where they feel the inhomogeneity of the system. The reason to use a subscript (‘hom’) to denote this length scale will become clear in section 4.5. $L_{hom}$ can be
calculated by using

\[ L_{\text{hom}}^2 = \frac{\sigma_{\text{DC, hom}} k_B T}{n_{\text{hom}} e^2 f_c / (2d)}, \quad (4.4) \]

which was derived in section 3.4 (see equation 3.2). In the equation, \( n \) is the charge-carrier density and \( d \) is the dimension (equal to 3 in the compressed powders). Since both \( f_c \) and \( \sigma_{\text{DC, hom}} \) in the powder are a factor \( 10^4 \) higher than in the coating, equation 4.4 gives the same typical length scale (0.3 \( \mu \)m; the size of some particles stuck together [30]) as found for the coating (chapter 3). The charge-carrier density of \( n = 2 \cdot 10^{15} \) cm\(^{-3} \) used in the calculations of \( L_{\text{hom}} \) is derived below (section 4.5)\(^2 \).

As mentioned before, in contrast to the data for \( f < 1 \) MHz, the data for \( f > 1 \) MHz, do follow a master curve after proper scaling, see figure 4.6. The scaling factors are shown in figure 4.7. They are well described by equation \( \sigma_{\text{DC}} \propto f_c^b \), where \( b = 0.9 \pm 0.1 \). This is within the uncertainty in accordance with the BNN relation (equation 3.4). Again (see also section 3.4.1), we can determine the temperature dependence of the charge-carrier density \( n \) from the scaling factors. A plot similar to figure 3.8 is shown in figure 4.8. The figure shows that \( n \propto \exp(-E/k_B T) \), where \( k_B \) is Boltzmann’s constant and

\(^2\)We used \( n_{\text{hom}} = n_{\text{crys}} \) (see section 4.5), which seems to be a reasonable assumption, as explained in section 4.5.3.
the best-fit value of $E$ is 0.029 eV, which is of the same order of magnitude as the value of 0.037 eV, found for the coating. In chapter 3 we explained that this energy, which is much lower than the energy gap of about 1.2 eV (see chapter 7), may be a result of unintentional doping.

The fact that the typical length scale, the transport mechanism, and the found energy of the Phthalcon-11 powder all appeared to be similar to those of the specific [35] Phthalcon-11/epoxy coatings discussed in chapter 3 might be a coincidence. They could also indicate that the matrix of the crosslinked coatings has a negligible influence on the conductivity in these coatings. We will show in chapter 5 that there are two other reasons to assume the latter explanation: at room temperature, the absolute value of the DC conductivity of the particle channels in the coatings is approximately equal to the DC conductivity of Phthalcon-11 powder and the electric-field dependence of the DC conductivity of the particle channels shows a similar behavior as the macroscopically measured electric-field dependence of the coating conductivity. We conclude that the particles inside the specific coatings really touch; they are not separated by, even a very thin, layer of the epoxy matrix. As a consequence, the conductivity shows similar features as the conductivity of the filler powder. It is thus obvious that further investigation of the conductivity of filler particles (which is for practical rea-
Figure 4.7: Relation between $\sigma_{DC}'$ and $f_c$ derived from the construction of the master curve (figure 4.6) of compressed Phthalcon-11 powder. The fit follows equation $\sigma_{DC} \propto f_c^{0.9}$.

4.5 Inter- and intraparticle transport in Phthalcon-11

A powder of particles has a more suitable form than a nanocomposite coating for measuring the conductivity at even higher frequencies than discussed in the previous section. The conductivity at frequencies higher than 1 GHz is measured indirectly, by using the reflectance and transmittance, as discussed in section 2.4.1. The idea behind going to higher frequencies is that, when the frequency is high enough, the movement of the charge carriers is only back and forth within the crystallites, without hopping from one crystal to another. In this way, it is possible to discriminate between inter- and intraparticle transport. Such an analysis is made in this section. In addition, a powder of particles is not fractal, like the particle network in the nanocomposite coating. The fractality of the particle network in the coating made further analysis of the temperature dependence of the conductivity difficult, because the exponent for superlocalization $\zeta$ was unknown. For a simple 3-dimensional powder, this problem does not exist. Hence, in this section
Figure 4.8: $\log(\sigma_{DC}T/f_c)$ (which is proportional to $n_\infty$) versus $T^{-1}$ for compressed Phthalcon-11 powder. The energy derived from the slope of the fit is 0.029 eV.

the temperature dependence of the conductivity (already shown in figure 4.4) will be analyzed in more detail. It gives, just like the high-frequency measurements, information on an important length scale $L$ and the density of states $g$ for the transport (although here $L$ and $g$ belong to different processes than the $L$ and $g$ found from the high-frequency measurements). As explained in reference [34], the effective density of states used in the transport needs not to be the same at all length scales. In particular, for a hop of an electron from an initially neutral crystal to another initially neutral crystal (resulting in crystals with charges $+e$ and $-e$ (with $e$ being the electron charge), respectively) the Coulomb charging energy $E_C$ has to be overcome, which can lead to a reduction of the effective density of states (DOS) as compared to the DOS for charge transport inside a crystallite, as explained in section 4.2. We divide the system in three regimes based on different length scales: The homogeneous regime (index 'hom'), where the packing of the crystallites can be seen as homogeneous, the hopping regime (index 'hop'), where phonon- or photon-assisted hopping between two crystallites is important, and the crystal regime (index 'crys'), which gives the transport in the bulk material for a large crystal.
4.5.1 Additional information from $\sigma_{\text{DC}}(T)$

Further exploitation of the results obtained for the temperature dependence of the Phthalcon-11 powder conductivity (shown in figure 4.4) is possible. As discussed in section 2.2.3, Mott VRH leads to a conductivity given by equation 4.3, with $\gamma$ being equal to $1/4$ and $T_0$ given by

$$T_0 = \frac{\beta \alpha^3}{k_B g_{\text{hom}}(E_F)}, \quad (4.5)$$

where $\beta \approx 2 \cdot 10^1 [70]$ is a numerical parameter, $1/\alpha$ the typical decay length of the electron density, and $E_F$ the Fermi energy. A fit of the data in figure 4.4b yields $T_0 = 2 \cdot 10^8$ K, and thus $\alpha^3/g_{\text{hom}}(E_F) = 7 \cdot 10^2$ eV. We come back to this value in section 4.5.3.

4.5.2 $\sigma(f)$ till the infrared

The subTHz transmission (amplitude as well as phase) and infrared transmittance and reflectance data are shown in figures 4.9 and 4.10. They were fitted simultaneously. The fit (shown in the figures) was limited to the data for frequencies up to $2000 \text{ cm}^{-1}$, because of the increasing influence of scattering with increasing frequency.

![Figure 4.9: Transmittance and phase of Phthalcon-11 powder between 300 and 500 GHz (squares). A phase angle of 63 means that the phase has accumulated 10 multiples of $2\pi$. The lines are a fit, discussed in the text.](image-url)
Figure 4.10: Reflectance (left) and transmittance (right) of Phthalcon-11 powder in the infrared (black squares). The grey lines are a fit, discussed in the text.

The data could not be fitted with only a Drude contribution. Therefore, a harmonic oscillator was added\(^3\). For such an oscillator, the relative dielectric constant \(\epsilon = \epsilon' - i\epsilon''\) is given by

\[
\epsilon' - 1 = \frac{N_{\text{osc}}\epsilon^2}{\epsilon_0 m^*} \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + \Gamma_{\text{osc}}^2 \omega^2},
\]

and

\[
\epsilon'' = \frac{N_{\text{osc}}\epsilon^2}{\epsilon_0 m^*} \frac{\Gamma_{\text{osc}} \omega}{(\omega_0^2 - \omega^2)^2 + \Gamma_{\text{osc}}^2 \omega^2},
\]

where \(\omega\) is the angular frequency, \(N_{\text{osc}}\) the concentration of oscillators, \(\epsilon_0\) the permittivity of vacuum, \(m^*\) the effective mass of the charge carriers, \(\omega_0\) the resonant angular frequency, and \(\Gamma_{\text{osc}}\) the damping coefficient. The Drude conductivity was already explained in section 2.2.3. For a powder of crystallites, it gives a conductivity \(\sigma_{\text{crys}}\) of

\[
\sigma_{\text{crys}}(\omega) = \frac{\sigma_{\text{DC,crys}}}{1 + i\omega\tau} = \frac{\omega_{\text{PD}}^2 \epsilon_0 \tau}{1 + i\omega\tau},
\]

\(^3\)This is done by adding \(\epsilon(\omega) - 1\) for the Drude conductivity, \(\epsilon(\omega) - 1\) for the oscillator, and \(\epsilon_{\text{DC}}\) (which is actually the dielectric constant in the Drude regime; we used \(\epsilon_{\text{DC}} \approx 3\) for Phthalcon).
where $\sigma_{\text{DC,crys}}$ is the conductivity of the bulk material for a large crystal, $\omega_{\text{pD}}$ the Drude plasma resonance frequency and $\tau$ is equal to $1/\Gamma$, with $\Gamma$ being the damping rate. The Drude plasma frequency is related to the number of carriers per unit of volume $n_{\text{crys}}$ and the effective mass $m^*$ as

$$\omega_{\text{pD}}^2 = \frac{n_{\text{crys}}e^2}{\epsilon_0 m^*}. \quad (4.9)$$

For damping rates comparable to the Drude plasma frequency, the real plasma frequency, where the dielectric constant becomes zero, will be larger than $\omega_{\text{pD}}$. The Drude theory can be applied in the infrared regime, because at such high frequencies the short period of the radiation is expected to restrict the motion of the carriers to the crystallite. The scattering time $\tau$ is determined by the boundaries of the nanoparticle and additional (ionized impurity) scattering:

$$\Gamma = 1/\tau = v/L_{\text{crys}}, \quad (4.10)$$

where $1/L_{\text{crys}}$ is the sum of the inverse size of the particle and the inverse phonon scattering length and $v$ is the velocity of the charge carriers. In organic semiconductors with small energy-band widths, like Phthalcon-11 (see chapter 7), $v$ is set by the thermal energy ($\frac{3}{2}k_B T = \frac{1}{2}mv^2$), whereas in inorganic semiconductors like ATO (discussed in section 4.6), $v$ is equal to the Fermi velocity $v_F$ ($v_F \approx 10^8 \text{ cm/s}$), which is almost independent of temperature.

The fit shown in figures 4.9 and 4.10, for which a Drude term and one oscillator are used, does not follow the data perfectly. A better fit can be obtained by adding more oscillators. It is unclear what the physics behind these oscillators is. Another way of getting a reasonable fit is by using a frequency-dependent $\tau$ in the Drude term instead of oscillators [126]. Which of the two manners of fitting corresponds best with the physical transport mechanism is unknown.

Even if we restrict ourselves to only one oscillator, there is still some freedom in the fit parameters for obtaining an acceptable fit through the data of figures 4.9 and 4.10. However, it can be concluded that the Drude contribution is small compared to the contribution of the oscillator and that the DC conductivity $\sigma_{\text{DC,crys}}$ and charge-carrier density $n_{\text{crys}}$ within the crystallites, which follow from the Drude term (equations (4.8) and (4.9)), are approximately $2 \cdot 10^{-2} \text{ S/cm}$ and $2 \cdot 10^{15} \text{ cm}^{-3}$ respectively.

Already at lower frequencies, the incoherent hopping process can be either by phonon-assisted or photon-assisted hopping, where in the latter

\[\text{See the error bars in the Drude conductivity shown in figure 4.11.}\]
case the energy difference between the sites is supplied by photons instead of phonons [70]. When the frequency is high enough to be in the pair limit (i.e. the regime where the major contribution to the conductivity is due to hopping between localized states at neighboring sites), the phonon-assisted contribution to the conductivity is given by [70]

$$\sigma_{\text{phonon}}(\omega) = \frac{\pi^2 e^2}{192} \omega k_B T L_{\text{hop}}^5 g_{\text{hop}}^2 \ln^4 \left( \frac{\omega_{\text{ph}}}{\omega} \right), \quad (4.11)$$

with $L_{\text{hop}}$ the decay length of the electronic state outside the particles, $g_{\text{hop}}$ the relevant DOS at the Fermi energy $E_F$ and $\omega_{\text{ph}}$ the phonon ‘attempt’ frequency [70]. This formula is valid when $\omega < \omega_{\text{ph}}$; at higher $\omega$, where the contribution of phonon-assisted hopping to $\sigma$ becomes constant, photon-assisted processes take over, with a conductivity $\sigma_{\text{photon}}$ given by

$$\sigma_{\text{photon}}(\omega) = \frac{\pi^2 e^2}{6} \hbar \omega^2 L_{\text{hop}}^5 g_{\text{hop}}^2 \ln^4 \left( \frac{2I_0}{\hbar \omega} \right). \quad (4.12)$$

The energy $k_B T$ in eq. (4.11) is in eq. (4.12) replaced by $\hbar \omega$ and the phonon attempt frequency $\omega_{\text{ph}}$ by $2I_0$, with $I_0$ being the ‘overlap’ pre-factor for the energy levels of two neighboring sites. In analogy with $\omega_{\text{ph}}$, $I_0/\hbar$ can be interpreted as the attempt frequency for photon-assisted hopping. Equation (4.12) is only valid when $\omega \ll I_0/\hbar$. As in phonon-assisted hopping, $\sigma$ is expected to become constant at high $\omega$.

The data of figure 4.5 are shown together with data measured at higher frequencies in figure 4.11. The figure also shows $\sigma_{\text{DC,cryst}}$ (derived from the Drude fit above) and fits for phonon- and photon-assisted hopping. The fit with $\sigma_{\text{phonon}}(\omega)$ (dash-dot-dot line in figure 4.11) gives $g_{\text{hop}}^2 L_{\text{hop}}^5 = 2.5 \cdot 10^3$ eV$^{-2}$cm$^{-1}$. In the fit for $\sigma_{\text{photon}}(\omega)$, $L_{\text{hop}}^5 g_{\text{hop}}^2$ is kept fixed to the value found from $\sigma_{\text{phonon}}(\omega)$, while the impact parameter $I_0$ is optimized, resulting in $I_0/\hbar = 2\pi \times 3 \cdot 10^{12}$ (dash-dot line in figure 4.11). An estimate of $I_0$ using the ratio of the width of the crystallite and the average thermal velocity agrees with the value found from the fit.

### 4.5.3 Discussion

In this subsection, we use the values derived in the previous subsections to get an insight in the parameters that are important for charge transport on the different length scales, indicated with ‘hom’, ‘hop’, and ‘cryst’.

An implication of $n_{\text{cryst}}$ being equal to $2 \cdot 10^{15}$ cm$^{-3}$ is that the number of carriers per crystallite is about 1 at room temperature. This low
Figure 4.11: $\sigma$ of Phthalcon-11 as function of frequency at room temperature, reconstructed from the dielectric data. The symbols give the conductivity calculated from the measurements with frequencies below 1 GHz (circles), in the GHz till THz regime (square) and in the infrared (triangles). The uncertainty in the calculated (Drude) conductivity from the infrared measurements is given by the error bars. For the other measurements the uncertainty was of the order of the symbol size. The contributions by phonon- and photon-assisted hopping ($\sigma_{\text{phonon}}$ and $\sigma_{\text{photon}}$) and Drude are indicated by respectively dashed-dot-dot, dashed-dot and dashed lines.

The charge-carrier density is probably caused by surface doping. At such a low charge-carrier density the energy scale is set by $k_B T$, and the corresponding $g_{\text{crys}}(E_F)$ is estimated from $g_{\text{crys}}(E_F)k_B T \sim n_{\text{crys}}$ to be $10^{17} \text{eV}^{-1}\text{cm}^{-3}$. This value of $g_{\text{crys}}$ is the upper limit for $g_{\text{hop}}$ and $g_{\text{hom}}$ and will be used in the following calculations.

From $g_{\text{hop}}^2 L_{\text{hop}}^5 = 2.5 \cdot 10^3 \text{eV}^{-2}\text{cm}^{-1}$ and using $g_{\text{hop}} = 10^{17} \text{eV}^{-1}\text{cm}^{-3}$, we find that the localization length $L_{\text{hop}}$ equals 8 nm. From $\alpha^3/g_{\text{hom}}(E_F) = 7 \cdot 10^2 \text{eV}$, with $g_{\text{hom}} = 10^{17} \text{eV}^{-1}\text{cm}^{-3}$, we find a decay length $1/\alpha$ of 3 nm. The decay length $1/\alpha$ is generally assumed to be equal to the localization length $L_{\text{hop}}$. The found difference between the values of $L_{\text{hop}}$ is likely due to the approximation of a homogenous charge distribution underlying the formula for phonon-assisted hopping. In the dilute limit the electron density decays with a characteristic length of a few Ångstrom. In closely packed crystallites, the localization length will be enhanced due to cotunneling by
the ratio between particle diameter and spacing [127, 34] being of the order of 10, which explains the found value of a few nm.

The consistency of the values shows that in the particular case of Phthalcon-11 the number of carriers involved in the hopping process is similar to the number of carriers that determines a Drude-like contribution in the crystallites. In other words, the Phthalcon-11 crystallites are large enough in order not to induce a reduction of the DOS for interparticle transport compared to intraparticle transport at room temperature. This could be expected, because the charging energies are only of the order of 3 meV, which is 8 times smaller than $k_B T$.

Still, the value of the powder conductivity ($\sigma_{\text{DC, hom}} = 4 \cdot 10^{-4}$ S/cm) is two orders of magnitude lower than the intrinsic conductivity ($\sigma_{\text{DC, crys}} = 2 \cdot 10^{-2}$ S/cm). This can be due to surface barriers, for example caused by the difference in valency between bulk and surface metal atoms, a shift in crystal structure of the particles with respect to each other, or to adhesion of surface ions, like in catalysts and cluster materials. Figure 4.11 shows that even at high frequencies this electrical contact between the crystallites is the limiting factor: the phonon- and photon fits both have a maximum that is lower than the Drude conductivity. In a powder, the surface barriers can often be removed by annealing the sample. However, when the particles are used as fillers in polymer composites, an annealing step is not possible because of the risk of other unwanted processes like decomposition of the polymer matrix during heating. Notice that the quality of the electrical contact between two crystals may even depend on which sides of the crystals touch each other, because at different sides, different end groups stick out (see figure 7.15). However, we will explain at the end of section 7.9 that the difference in ease to leave the crystal\textsuperscript{5} from different sides is expected to be small. Another factor that diminishes the electrical contact between the crystallites is the packing factor of approximately 0.5; because of the exponential decay of the wave functions of the charge carriers, this can have a large effect, as illustrated in figure 4.12.

If the number of charge carriers can be increased by intrinsic doping of the Phthalcon-11 particles, this will probably lead to an improved conductivity, both in the powder and in Phthalcon-filled nanocomposites.

\textsuperscript{5}The ease to leave the crystal is expressed in the so-called “exit potential”
Figure 4.12: Influence of the packing factor illustrated in 2D. a: ideal packing (i.e. the packing factor is equal to 1). b: packing with a packing factor smaller than 1. In the right drawing, two particles only touch at one point. There will be an area around that point that contributes to the interparticle conduction, because the wave functions of the charge carriers on the different crystals still have a considerable overlap. However, further from the point of mechanical contact, the separation between the two crystals is larger, which will significantly decrease the transport because of the exponential decay of the wave functions.

4.6 Influence of the particle size

Equation 4.1 shows that the charging energy $E_C$ increases with decreasing particle size. For Phthalcon-11, a reduction in the density of states for interparticle transport (compared to intraparticle transport) due to the charging energy could not be observed at room temperature (see section 4.5). Apparently, the crystallites were large enough for $E_C$ to be neglected in the interparticle transport. In this section, we analyze the charge transport in smaller particles (antimony-doped tin oxide (ATO) with a diameter of approximately 7 nm) in the same manner as we did for Phthalcon-11 to see whether a reduction of the effective density of states can be observed for ATO particles.

In section 4.6.1, information is given on the ATO particles used here and some results from literature where ATO or related particles were investigated. Section 4.6.2 shows our own experimental results on ATO. In section 4.6.3, the results are discussed.

4.6.1 Information on ATO and related particles

ATO particles are semiconductive, and generally spherical nanometric, particles. They can be used as fillers in polymeric materials like acrylates to
make these materials semiconductive, already at a filler fraction below 1 vol % [124, 33, 125]. Details of the chemical preparation and characterization of the ATO particles that we used for our experiments are given in ref. [125]. For this preparation method, antimony is incorporated in the cassiterite SnO$_2$ lattice up to the highest doping level. The doping level $D$ is expressed by the ratio of the atomic antimony concentration and the total atomic concentration of antimony and tin, i.e. $D = [\text{Sb}] / ([\text{Sn}] + [\text{Sb}])$. For $D \leq 0.07$, (almost) all the antimony is present in the form of Sb$^{5+}$. For $D \geq 0.09$, there is also Sb$^{3+}$ substituting Sn$^{4+}$ [125]. Our experiments were performed on ATO particles with doping levels of 0, 2, 5, 7, 9, and 13 at%. Unless indicated otherwise, the data shown are for $D$ equal to 0.07. Except for the absolute values of the powder conductivity measured at low frequencies, the data for the various doping levels showed similar results. The average size of the particles for $D = 0.07$ is 7.1 nm, while the average particle size in the measured range of $0 \leq D \leq 0.13$ ranged from 8.2 to 6.6 nm [125]. A transmission-electron-microscopy (TEM) image (taken from ref. [125]) of the ATO particles is shown in figure 4.13. X-ray-diffraction (XRD) and TEM measurements show that the particles are likely to be monocrystals.

Now we will elaborate on some results on ATO and related particles (indium tin oxide (ITO)) from literature, where the Drude analysis is also applied. They are summarized in table 4.1, together with our results, which will be derived in section 4.6.2. The experiments from literature (with ATO particles prepared in a different way than the particles we used) are discussed in the remainder of this section. We will compare the data with our results in section 4.6.2.

The Sb-doped SnO$_2$ films of Shanthi et al. [128] cover a carrier concentration range from $10^{19}$ cm$^{-3}$ to $10^{21}$ cm$^{-3}$. The minimal value of the resistivity is reached for a carrier concentration of a few times $10^{20}$ per cm$^3$, with an almost $T$-independent mobility (and resistivity) of 12 cm$^2$/V$s$ ($2 \cdot 10^{-3}$ $\Omega$cm). At that doping level $\omega_{PD}$ is of the order of $10^{15}$ s$^{-1}$ (being $3 \cdot 10^{14}$ s$^{-1}$ for undoped films) with a damping rate $\Gamma = 0.8 \cdot 10^{15}$ s$^{-1}$. The effective mass grows with carrier concentration from 0.1 to 0.3 electron mass ($m_e$).

In the analysis of thin films of In$_2$O$_3$:Sn of Mergel and Qiao [126], the Drude model is refined with a frequency-dependent damping. A fit of similar quality was obtained by the standard Drude expression combined with a harmonic oscillator, where the oscillator frequency was $0.6\omega_{PD}$. As mentioned before, it is unknown which of the two manners of fitting corresponds best with the physical transport mechanism. The optical mobilities are considerably higher than the DC mobilities and reach values of $10^2$ cm$^2$V$^{-1}$s$^{-1}$,
similar to the values cited in ref. [128] for ATO films. Transmission and reflection data can also be found in ref. [130].

The conductivities of dried spin-coated composites of n-doped SnO$_2$:Sb nanoparticles of Nütz et al. [129] are orders of magnitude lower than the film results of Shanthi et al.[128]. Typical values for the DC resistivity are $10^6$ Ωcm or higher in the investigated atom ratio ([Sb]/[Sn]+[Sb])-range up to 0.06. By annealing of the samples at 900 °C the resistivity dropped to 10 Ωcm, still four orders of magnitude higher than reported for bulk SnO$_2$:Sb films. This is in accordance with XRD data, showing that the nanocrystalline structure of the sample is preserved. From $\omega_{pD} = 2.2 \cdot 10^{15}$ s$^{-1}$ and $\Gamma = 5.9 \cdot 10^{14}$ s$^{-1}$ the number density of dopants is calculated to amount to $n_{crys} = 1.6 \cdot 10^{21}$ per cm$^3$. Using equation (4.10) and an estimated Fermi velocity of $10^6$ m/s, a mean particle diameter of 4.3 nm is obtained, roughly in accordance with the particle diameter seen in TEM (4-6 nm) and determined from XRD.
Table 4.1: Transport parameters obtained for ATO and ITO (second row) at doping levels of $10^{20}$ to $10^{21}$ per cm$^3$. The parameters that are given are the charge-carrier density $n$, the (directly measured) conductivity $\sigma_{\text{DC, hom}}$, the Drude frequency $\omega_{pD}$, the damping $\Gamma$, and the effective mass $m^*$. The first and second row are obtained for films of ATO [128] and ITO [126] resp., the last two rows contain the data on powders of nanoparticles of Nütz et al. [129] and our data (labeled with ‘pw’ for ‘present work’), discussed in section 4.6.2. For a bulk material with a Drude frequency of $10^{15}$ Hz, a scattering time of $10^{-14}$ s and a carrier mass of $0.3 m_e$ a DC conductivity is expected of $10^3$ S/cm (this will be the intraparticle conductivity $\sigma_{\text{DC,crys}}$).

<table>
<thead>
<tr>
<th>sample</th>
<th>$n$ (cm$^{-3}$)</th>
<th>$\sigma_{\text{DC, hom}}$ (S/cm)</th>
<th>$\omega_{pD}$ (THz)</th>
<th>$\Gamma$ (s$^{-1}$)</th>
<th>$m^*$ ($m_e$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATO film [128]</td>
<td>$2 \cdot 10^{20}$</td>
<td>$10^2$</td>
<td>$10^{15}$</td>
<td>$8 \cdot 10^{14}$</td>
<td>0.3</td>
</tr>
<tr>
<td>ITO film [126]</td>
<td>$10^{21}$</td>
<td>$?</td>
<td>$5 \cdot 10^{14}$</td>
<td>$3 \cdot 10^{14}$</td>
<td>0.35</td>
</tr>
<tr>
<td>ATO powder [129]</td>
<td>$2 \cdot 10^{21}$</td>
<td>$10^{-6}$</td>
<td>$10^{15}$</td>
<td>$6 \cdot 10^{14}$</td>
<td>0.27</td>
</tr>
<tr>
<td>ATO powder (pw)</td>
<td>$10^{21}$</td>
<td>$10^{-2}$</td>
<td>$4 \cdot 10^{14}$</td>
<td>$10^{14}$</td>
<td>0.3</td>
</tr>
</tbody>
</table>

4.6.2 Experimental results

Figure 4.14 shows our results for $\sigma$ as a function of the doping concentration $D$, at DC and for a frequency of 4000 cm$^{-1}$. The conductivity at 4000 cm$^{-1}$, which gives the conductivity within the bulk material, is seen to be only slightly concentration dependent (it is approximately constant within the uncertainty of the measurement). The dependence is clearly different from the DC results, where especially the loss in $\sigma$ at low doping concentrations is significant. The explanation of this difference is probably two-fold: With increasing doping level the Fermi level within the crystallites will shift into more degenerate levels and hence the chance to find an equal energy on a neighboring site in the hopping process will increase. Secondly, the higher the doping level, the better the screening of the charges. The latter is important because for ATO the charging energy has a considerable influence on the conductivity, as will become clear in the remainder of this chapter. The measured DC conductivity $\sigma_{\text{DC, hom}}$ for $D = 0.07$ is approximately $10^{-2}$ S/cm. It is compared with the values from literature in table 4.1. The value for $\sigma_{\text{DC, hom}}$ found by Nütz et al. [129] is much lower than the value we found. This can probably be explained by the different preparation method,
Figure 4.14: Normalized conductivity of ATO at DC and 4000 cm$^{-1}$ as a function of the doping concentration at room temperature. The DC data are published in ref. [125]. The D-dependence in the infrared is clearly weaker than for $\sigma_{\text{DC}}$, especially at low doping levels.

which may lead to a different chemical composition at the surface and/or in the bulk of the ATO particles. Another factor may be the number of particles that is chemically connected in the powder. For our ATO materials probably 4 to 10 particles are connected [125]. However, the structure is such that the particles are still almost separated (see ref. [125] and the TEM image of figure 4.13). Unfortunately, Nütz et al. did not provide any information on these aspects in their materials. On the other hand, Shanthi et al. [128] found a much higher value of $\sigma_{\text{DC, hom}}$. Their films were prepared at much higher temperatures (613 - 813 K). The particles observed in the films were considerably larger (0.4 - 0.7 µm). As a result, the charging energy is negligible and the density of particle-particle contacts is lower, which leads to a higher conductivity.

The $T$ dependence of 7 %-doped ATO is given figure 4.15. For the $T$ dependence of $\sigma$, the data can be fitted with $\gamma = 1$ in equation (4.3) if the fit is restricted to $T \geq 50$ K and with $\gamma = 0.5$ for $T \leq 50$ K. This indicates a transition from Efros-Shklovskii (ES) VRH at low temperatures to activated behavior at high temperatures (see section 2.2.3). The $\gamma = 1$ fit gives an activation energy of $10^2$ K

\footnote{Due to the larger distance between the conductive particles, the activation energies in the deposited films of CdSe nanoparticles found by Balberg et al. [131] are larger than the one we find.}.
Figure 4.15: DC conductivity as function of $T$ for compressed 7 %-doped ATO. For $T \leq 50$ K the data can be fitted by equation (4.3) with $\gamma = 1/2$ (a), while for $T \geq 50$ K the $T$ dependence is activated (b).

by

$$T_0 = 2.8e^2\alpha/(4\pi\epsilon\epsilon_0k_B). \quad (4.13)$$

$1/\alpha$ is the typical decay length of the electron wave function outside the crystallites (the ‘localization length’). For randomly packed spheres of radius $R$ and spacing $s$, the localization length in the dilute limit (typically about 2 Å) has to be multiplied by the ratio between diameter and spacing $2R/s$ to obtain the real localization length [127, 34]. In the temperature regime where the data of figure 4.15 can be fitted with $\gamma = 0.5$, the value of $T_0$ of $0.6 \cdot 10^4$ K yields $a = 3$ nm. This is in good agreement with the value of approximately 2 nm, obtained for an estimated ratio $(2R/s)$ of 10.

Figure 4.16 shows the frequency dependence of the conductivity for frequencies up to 1 GHz, measured at several temperatures. Like for Phthalcon-11, at the critical frequency $f_c$, where the conductivity starts to increase, the charge carriers start to feel the inhomogeneity of the underlying structure. The accompanying typical length scale is $L_{\text{hom}}$. Substitution of the room-temperature values $f_c = 3 \cdot 10^8$ Hz and $\sigma_{\text{DC, hom}} = 10^{-2}$ S/cm in equation (4.4) gives $L_{\text{hom}}^2 n_{\text{hom}} = 10^8$ cm$^{-1}$. To find the typical length scale $L_{\text{hom}}$, the approximation $g_{\text{hop}}(E_F)k_B T \approx n_{\text{hom}}$ can be used. We will show below that $g_{\text{hop}}(E_F)$ is approximately $3 \cdot 10^{18}$ eV$^{-1}$cm$^{-3}$ at room temperature. Hence, $n_{\text{hom}}(293$ K) is equal to $7 \cdot 10^{16}$ cm$^{-3}$, yielding an $L_{\text{hom}}$ of 360 nm; about 50
times larger than the diameter of the crystallites. The relatively large length scale for homogeneity might indicate the presence of physically connected aggregates.

In figure 4.17 the transmission and reflection data measured at infrared frequencies are shown. They are fitted simultaneously with the amplitude and phase of the subTHz transmission data (not shown; the resulting conductivity is shown in figure 4.18). Only a Drude term (without any oscillators) was sufficient to get an acceptable fit (shown in the figure). The oscillations in the fit to the transmittance are an artefact, because the effective ATO film thickness of 0.005 mm is much smaller than the real thickness of the compressed KBr/ATO pellet which was used for the experiment due to the fraction of only 1 wt% ATO. The parameters for the Drude fit are $\omega_{pD} = 11000 \text{ cm}^{-1}$ and $\tau = 3300 \text{ cm}^{-1}$, together with a dielectric constant of 4.0. According to equations (4.8) and (4.9), they lead to $\sigma_{DC,\text{crys}} = 1 \cdot 10^{2}$ and $n_{\text{crys}} = 10^{21} \text{ cm}^{-3}$. In table 4.1 the fit parameters are given and compared with the values from literature. The values of $\omega_{pD}$ agree within a factor 2, while the spread in the scattering rates is larger. In addition, the value for $\tau$ can be used as a consistency check: We expect that the scattering time is set by the crystal boundaries. Combing the estimated Fermi velocity of $0.8 \cdot 10^{8} \text{ cm/s}$, with $m^* = 0.3m_e$ [129] and the crystallite size of 7 nm, gives $\tau = 10^{-14} \text{ s}$, in agreement with the data.

Again we can try to fit the phonon- and photon contribution to the
conductivity, like we did for Phthalcon in figure 4.11. Figure 4.18 shows the result. The linear frequency dependence of the conductivity at 7 K in the double logarithmic plot is in agreement with equation (4.11). The linear dependence of the conductivity on frequency points to phonon-assisted tunneling. In the range of 10 - 100 cm$^{-1}$ photon-assisted processes take over. Applying equation (4.11) for the 293 K conductivity of $10^{-3}$ S/cm at $10^9$ Hz and taking the usual value for the phonon frequency in solids of $\omega_{ph} = 10^{12}$ s$^{-1}$ [70, 88], we find $L_{\text{hop}}^5 g_{\text{hop}}^2 = 2 \cdot 10^4$ eV$^{-2}$cm$^{-1}$. Using $L_{\text{hop}} = \alpha^{-1} = 3$ nm derived from $T_0$ (see above), we find that $g_{\text{hop}}$ is equal to $3 \cdot 10^{18}$ eV$^{-1}$cm$^{-3}$. The value for $L_{\text{hop}}^5 g_{\text{hop}}^2$ that we find for the fit of data measured at 7 K is a factor of 80 smaller than the room-temperature value. This indicates that the density of states is curved around the chemical potential.

4.6.3 Discussion

At room temperature, the directly measured DC conductivity $\sigma_{\text{DC, hom}}$ is a factor $10^4$ lower than the intrinsic conductivity of 7 at%-doped ATO ($\sigma_{\text{DC,crys}}$, which followed from the Drude fit). This difference is for a large
Figure 4.18: The various contributions to the conductivity of 7 at% doped ATO as function of frequency. The uncertainty in the measurements is of the order of the symbol size. At room temperature at the lowest frequencies the conductivity is dominated by charging energies, at intermediate frequencies phonon- and photon assisted hopping processes describe the frequency dependence, and in the infrared the Drude conductivity inside the bulk material is seen.

part caused by the reduction in the DOS for interparticle transport compared to the DOS for intraparticle transport; \( g_{\text{hop}} \) is a factor \( 10^3 \) lower than \( g_{\text{crys}} \). The fact that \( g_{\text{hop}} \) is considerably smaller than \( g_{\text{crys}} \) could be expected, because the estimated charging energy is of the order of 50 meV (\( \approx 2k_B T \) at room temperature). The remedy - an increase of the crystal size - is easy to indicate but might be hard to realize in practice.

The dielectric response of the individual ATO particles seen at high frequencies is clearly different from the behavior at low frequencies, where many particles are involved. Still the two behaviors are coupled to the same density of states (and can therefore be called intrinsic), be it that the disorder in packing is responsible for the smearing (which is an extrinsic effect).

Although the measurement results of ATO particles with higher or lower doping levels than 7 at% still have to be analyzed, they look very similar to the results for \( D = 0.07 \). We therefore expect that the conductivities and
densities of states at the different length scales for those doping levels show a comparable trend.

Let us address possible complications in the analysis of the ATO data. It is sometimes seen, like in Ketjen-Black [8], that nanoparticles form aggregates that survive the preparation stage. Likely aggregates of 4 to 10 chemically connected particles exist in ATO powder. Because of the type of chemical bonding [125] we expect that they have only a small effect on the conductivity compared to the conductivity of ATO powder without chemical connections between the particles. Further fine-tuning is outside the accuracy of the present analysis. Also the value of $g_{\text{crys}}$ has to be seen as an average, as inhomogeneities in the doping of ATO might be present as well.

When used as fillers in nanocomposite coatings for high-frequency shielding, the effects of the reduced conductivity compared to the intrinsic conductivity of the fillers are less pronounced. The geometrical constraints are released because only short segments of the fractal structure matter, while regarding the density of states phonon- and photon-mediated transport between nearest neighbors increase the conductivity considerably above the DC level, see figure 4.18.

4.7 Conclusions

To sum up, the powder of Phthalcon-11 crystallites has a $\sigma_{\text{DC}}$ value of $4 \cdot 10^{-4}$ S/cm at room temperature, which is a factor $10^4$ higher than the conductivity of the Phthalcon-11/epoxy coatings discussed in chapter 3. The temperature dependence of $\sigma_{\text{DC}}$ showed that the conduction mechanism in Phthalcon-11 powder is (Mott) variable-range hopping by cotunneling, just like in the nanocomposite coatings. The typical length scale of homogeneity ($L_{\text{hom}} \approx 0.3 \mu\text{m}$, of the order of size of a cluster of a few crystallites stuck together) is also similar to the one found in the coating. $\sigma(f)$ shows familiar scaling behavior. From the scaling factors, the temperature dependence of the charge-carrier density could be derived, which gave an energy scale similar to the one found in the Phthalcon-11/epoxy coatings. All these similarities between the specific [35] coatings and their filler powder already indicate that the matrix hardly influences the charge transport inside the particle network of the coatings. In chapter 5, this assumption will be verified. The importance for the investigation of the conductivity of filler particles -in many aspects easier to measure than the conductivity of a nanocomposite- is therefore obvious.

By combining data of sub-THz transmission with infrared transmis-
sion and reflection we were able to explain the full frequency response of Phthalcon-11 and also of even smaller antimony-doped tin-oxide crystallites. All parameters relevant for the conduction could be quantified. When conclusions are drawn about consistency of parameters in the evaluation of the different contributions to the conductivity, it is crucial to differentiate between the various involved length scales and densities of states.

For Phthalcon-11 the very low number of carriers involved in the hopping process is similar to the number of carriers that determines the Drude contribution in the crystallites. This could be expected, because the charging energies are negligible at room temperature. Still, the intrinsic conductivity of Phthalcon-11 is a factor $10^2$ higher than the DC powder conductivity. This is caused by the electrical contact between the particles, which is not optimal, even when the particles touch.

For 7 at%-doped ATO particles, the charging energy is larger than the thermal energy at room temperature. As a result, the density of states for interparticle transport is reduced by a factor $10^3$ compared to the DOS for intraparticle transport. Increasing the particle size (which may be hard to realize in practice) would directly increase the DC conductivity, which is a factor $10^4$ lower than the intrinsic conductivity. An increase of the diameter with a factor 10 will probably be enough to make the difference in DOS for inter- and intraparticle transport negligible. When the particles are used in nanocomposites, a fractal particle network (needed to obtain a low percolation threshold), will likely still form at this particle size.

Notice that the analysis of the experiments discussed in this chapter only give an averaged density of states involved in transport. They do not take into account inhomogeneities or anisotropy within the crystallites nor the problem of a side-dependent exit potential; these effects are averaged out.

We will show in chapter 6 that, even when the filler particles in a nanocomposite touch, the morphology of the particle network is responsible for a huge reduction of the conductivity of the nanocomposite as compared to that of the filler-particle powder when the network is formed by so-called ‘diffusion-limited cluster aggregation’ and the critical filler fraction $\phi_c$ is low; for $\phi_c = 0.0055$, the conductivity of the nanocomposite is 3 to 4 orders lower than the conductivity of the filler powder. We showed in the present chapter that for Phthalcon-11 or ATO as filler an additional 2 (for Phthalcon-11) or 4 (for 7 at%-doped ATO) orders of magnitude are lost compared to the intrinsic conductivity of these fillers, the main causes being probably surface-barrier effects (for Phthalcon-11) and nanosize charging effects (for ATO).
Chapter 5

(Conducting) Atomic Force Microscopy of thin composite films

5.1 Abstract

Conducting atomic force microscopy (C-AFM) is a technique to measure conductances on a very small scale. Phthalcon-11/epoxy coatings proved to be an ideal system to characterize with C-AFM. The method was used to obtain information on the distribution and conductivity of conducting channels inside the coating. We found that a substantial fraction of the dispersed Phthalcon-11 particles takes part in conducting percolating channels and that the electrical contact between the particles in many of these channels is close to optimal. With AFM we also obtained information on the size of the particles.

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5.2 Introduction

Atomic force microscopy (AFM) is a suitable technique to obtain images with a high resolution. The resolution depends on the tip radius and can be of the order of a few nanometers. Apart from height profiles, also other aspects like friction or conduction can be measured. For the latter case the term conducting-AFM (C-AFM) is used. In C-AFM the current is measured while a voltage is applied between the tip and the substrate. It
is a relatively new technique (1993 [132]), which is widely used on inorganic semiconductors, but rarely on polymeric materials. The reason for this is that most polymers are soft and therefore easily damaged by the AFM tip, especially because in C-AFM the contact mode is needed to measure the current (see section 2.4). Nevertheless, some experiments with C-AFM on polymers have been performed, see for example refs [133, 134, 135, 136, 137, 138, 139].

In C-AFM, the material under investigation is attached to a conducting substrate. This substrate and the tip act as two electrodes. The current is measured while a voltage is applied between the tip and the substrate. When C-AFM is performed on a nanocomposite coating, the current will only be nonzero when a channel of conducting particles connects the surface of the coating with the bottom (see figure 5.1). The tip can either scan the surface at a constant voltage, or focus on a certain location and measure the current as a function of voltage.

![Figure 5.1: Sketch of a measurement with C-AFM. The black lines inside the coating depict channels of conducting particles. A current will flow through the left one, whereas the right one will not be detected, because it does not reach the substrate.](image)

In the following sections, the results of (C-)AFM measurements on Phthalcon-11 particles and the cross-linked Phthalcon-11/epoxy coating of chapter 3 are presented. This coating contained 12 vol% Phthalcon-11, which is well above the percolation threshold (see chapter 3 and ref. [30]). We showed in chapter 3 that probably the conduction in the coating takes place by variable-range hopping through cotunneling. In the present chapter, we will
show that the images of the coating perfectly show where the channels of particles are that contribute to percolation. In addition, we are able to draw conclusions on the quality of the electrical contact between the particles in these channels. The dimensions of Phthalcon-11 particles were determined by measuring them separately (i.e. not in a coating) with AFM.

5.3 Experiment

The experiments in this chapter were performed with a Digital Instruments Dimension 3100 AFM with a Nanoscope IIIa. For the conduction measurements, three different kinds of silicon cantilevers were used: MikroMash CSC12/Ti-Pt/4 cantilevers (Ti-Pt coating, radius of curvature $\approx 40$ nm, spring constant $\approx 1.75$ N/m), Olympus OMCL-AC240TM-B2 cantilevers (Pt coating, radius of curvature $\approx 15$ nm, spring constant $\approx 2$ N/m) and NT-MDT CSG11/Pt cantilevers (Pt coating, radius of curvature $\approx 35$ nm, spring constant $\approx 0.1$ N/m). In the current ($I$) - voltage ($V$) measurements the applied voltages between tip and zinc substrate were between 0 to 12 V. $I-V$ characteristics were only measured if pushing the tip harder onto the coating did not change the current.

5.4 Phthalcon-11 crystals

To determine the dimensions and possibly the conduction of Phthalcon-11 particles, they were distributed on a substrate. For that purpose, a 0.1 wt% dispersion was made in m-cresol by stirring the powder in the solution magnetically for 1 h followed by ultrasonic mixing for 1 h. Both mixing steps were performed at ambient temperature. After mixing, a droplet of the dispersion was put on a substrate and the m-cresol was evaporated from the dispersion in a vacuum oven (353 K, 8 h). As a substrate we used highly ordered pyrolytic graphite (HOPG), because it has a very smooth surface and because it is conductive, which makes it suitable for C-AFM measurements.

A representative height profile of such a sample, obtained with AFM in tapping mode, is shown in figure 5.2. Most Phthalcon-11 crystals in figure 5.2 and in the other images that we obtained with AFM (not shown) have one long side of about 200 nm and two short sides of 40 to 70 nm. However, some TEM images\(^1\), as the one of figure 5.3, seem to show also particles

\(^1\) taken from work of Ming Yuan and Joachim Loos, Eindhoven University of Technology, the Netherlands.
Figure 5.2: Left: Image of Phthalcon-11 particles obtained with AFM in tapping mode. It represents a surface of 900 nm \times 900 \text{ nm}. The measured heights follow from the grey scale legend. Right: Height profiles along the white lines in the left image.

with two long sides. The Phthalcon-11 particles used for the TEM-images were from a different batch, prepared under slightly different conditions.

Although the interpretation of a conduction measurement with C-AFM on a single Phthalcon-11 particle might be difficult due to the contact resistances between tip and particle and between particle and substrate, we tried to perform C-AFM on the sample. Unfortunately, the attempts failed, because C-AFM works in contact mode, by which the particles were swept from the substrate.
5.5 Phthalcon-11/epoxy coating

As mentioned in the introduction of this chapter, polymers are often too soft for AFM in contact mode, as soft polymers are penetrated by the tip (unless much effort is put in adjusting parameters like tip load carefully). C-AFM is therefore inadequate for many polymers. The epoxy of our coating is a relatively hard polymer and turned out to be hard enough to measure in contact mode, without problems. Also the conductances of the channels formed by the particles through the Phthalcon-11/epoxy coatings, turned out to be perfectly in the range of what is possible to measure with C-AFM without any adjustments.

In most of our measurements, current and height were measured simultaneously. Figure 5.4 is an example of such a measurement. A correlation between the two images can be seen: the bright spots in the current image, appear as dark spots in the height image. We captured more images (not shown) that showed the same correlation. However, especially for images that covered a larger area, the roughness of the coating was dominant, which made it hard to observe a correlation between the height and the current images. Even on small scales, the images were sometimes uncorrelated. An example is shown in figure 5.5. The upper halves of the images seem to cor-
Figure 5.4: Current (left) and height (right) of an area of 500 nm × 500 nm of a Phthalcon-11/epoxy coating at a bias of 3.5 V. A correlation between the two images is visible.

relate, but the bright spots in the lower half of the current image do not show up in the height image. The opposite case (i.e. spots in the height image that do not appear in the current image) would be explicable, because it is very well possible that not all the particles at the surface belong to particle channels that percolate through the coating to the substrate. Comparison of the lower halves of the images in figure 5.5 suggests that particles lying at (or near)\(^2\) the surface sometimes have a negligible effect on the surface height. It is therefore impossible to conclude only from the height image where the particles are located at (or near) the surface.

Notice also that, according to the height image of figure 5.4, the particles lie deeper than the surrounding matrix, while according to the (upper half of) the height image of figure 5.5, they stick out. This difference could be due to different AFM settings, leading (unwished) to negative values in one of the two cases. Assuming that it is indeed a matter of AFM settings, we cannot say which of the two cases (particles deeper than the matrix, or particles sticking out of the matrix) reflects the real situation. As the surface

\(^2\)The words "or near" are added, because in principle it is possible that the spots in the current images originate from particles that are covered by a thin layer of the matrix, through which tunneling takes place.
tension of Phthalcon-11 is higher than that of the matrix, it is, purely based on surface tensions, not expected that the particles would stick out. On the other hand, the curing of the matrix is a complex process: the mixture of the prepolymer and the crosslinker first expands while it is heated up in a low-viscous state, it then starts reacting at several points at the same time, leading to a rough surface after curing, and it is then cooled down, giving rise to considerable shrink. It is unknown how the positions of the particles near the surface are influenced by this process; they may either become higher or lower at the surface than the surrounding matrix.

Figure 5.6 shows an AFM image of friction, together with a C-AFM image. A correlation between the left and right figure can be seen, but is not obvious. Also from other friction images we conclude that these images cannot be used to determine the positions of particles at the surface. C-AFM (current) images appear to be much more useful for that purpose. However, the C-AFM images only show the particles that are part of conducting channels connecting the surface with the substrate. Isolated particles or clusters of particles that are not connected with the substrate are not detected.

It would be nice to compare the C-AFM images with images that show all the particles at the surface, to determine the fraction of particles at
the surface belonging to percolating channels and the fraction of particles isolated from the substrate. As explained above, height and friction images can not be used for that purpose. Possible methods to detect all particles at the surface are Kelvin Probe Microscopy (see for example ref. [141] and [142]) and Scanning Electrochemical Microscopy (see for example ref. [143] and [144]). Nevertheless, we did not perform these measurements, because it is hardly possible to find exactly the same locations on the samples as captured with C-AFM, so a real comparison would be impossible.

The C-AFM image of figure 5.6 shows that the current distribution on a conducting area is quite homogeneous (apart from the time-lag, which is visible in this image, and which is due to the high scanning frequency; it disappears by lowering the scanning frequency). On the other hand, in the C-AFM image of figure 5.4 the current is far from constant over the conducting areas. For this image, increasing the voltage that regulates the pressure of the tip on the surface (the so-called “inflection voltage”) led to higher currents and a more homogeneous distribution over the conducting areas. In other words: the resistance between tip and coating was not negligible in figure 5.4 and decreased by pressing the tip harder onto the surface. In the remainder of this chapter, quantitative information is reported from the magnitude of the currents measured with C-AFM. In those measurements, we always made sure that a further increase of the inflection voltage did not
Although the current distribution on the conducting areas of figure 5.6 is quite homogeneous, it is unlikely that each area corresponds to only one particle at the surface, because the size of the areas is larger than the size of the individual particles; the three spots in the middle have a width and height between 400 and 450 nm, while the sizes of the particles range between 40 and 200 nm (see previous section). Also their shape is "rounder" than the more rectangular crystal shape. Although the tip with the largest radius of curvature (MikroMash CSC12/Ti-Pt/4 cantilever, radius of curvature ≈ 40 nm) was used to obtain the images of figure 5.6, we do not think that this causes the differences. Probably clusters of particles lie at the surface that are partly covered with the matrix. Notice that, in contrast to the spots in figure 5.6, the spots in figure 5.5 have sizes that are comparable to the Phthalcon-11 crystal sizes.

The images of figure 5.7 cover an area that is large enough to be representative for the sample, which can be concluded from the fact that scans of similar size captured on other places of the coating gave similar images (not shown). Deriving quantitative information from the left image of figure 5.7 thus makes sense. This will be done below.

Figure 5.8 gives the current profile along the black line shown in figure 5.7.

Figure 5.7: Current (left) and height (right) of an area of 20 µm × 20 µm of a Phthalcon-11/epoxy coating at a bias of 5 V. The black line in the middle of the left image is used for figure 5.8.
5.7. It shows that the bright spots in figure 5.7 have a current that can clearly be distinguished from the grey background; the currents in the bright spots are several tens of pA, whereas the current in the grey background is less than 2 pA. In addition, the transition from background to bright spot is sharp. Thanks to this sharp crossover, the total area of the bright spots in figure 5.7 can be determined and hardly depends on the chosen threshold value used to distinguish between background and bright spot. We find that the bright spots cover 4 % of the total area. For a coating with 12 vol% particles evenly distributed, the surface fraction of particles is expected to be 0.12. One cause of the fact that the total area of the bright spots is lower might be that there are fewer particles near the surface than in the bulk of the coating, due to segregation by gravity or surface energies. In that case, there will be an excess of particles in the bulk (see figure 5.9 (a)) that is hardly contributing to the conductivity of the coating, because the conduction at the surface of the coating forms the bottleneck. Another cause may be that a fraction of the particles at the surface are not connected to a path percolating to the substrate (figure 5.9 (b)), so that they are not seen with C-AFM. From the 4 % of the surface area contributing to the current, it can be concluded (with either argument) that not all particles in the coating belong to ideal paths (figure 5.9 (c)) for conduction in the direction perpendicular to the surface. Since the difference between the measured 4 % area at the surface belonging to percolating paths and the theoretical 12 % for evenly distributed particles throughout the matrix is less than an order of magnitude, the gain in conductivity for a more ideal distribution will,
Figure 5.9: Illustrative sketch of the particle network inside the coating. For clarity, paths percolating in the direction parallel to the surface are not shown. For a discussion, see text.

purely on geometrical grounds, only be modest$^3$.

In the comparison above of the conducting area at the surface observed with C-AFM and the one calculated from the volume fraction of particles, we implicitly assumed that there is no preferential orientation of the particles at the surface, or that their aspect ratio is 1. However, on the basis of surface energy (the surface energy of Phthalcon-11 is substantially higher than that of epoxy) it can be expected that the particles at the surface rotate when the coating is still in a liquid state and orient their smallest side towards the surface. Taking this into account, the conducting area at the surface calculated from the volume fraction of particles would be less than 12%. The observed 4 vol% is then even closer to the ideal distribution.

It is possible to estimate the macroscopic conductivity of the coating from the C-AFM image (figure 5.7, left). First the current $I$ is determined by adding the average current of each bright spot. The current of the background is neglected, which is justified because it is much smaller than the currents measured in the spots (see figure 5.8). Subsequently, the conductivity is calculated from the current by using $\sigma = (I/V)(l/A)$ (with $V$ being the voltage, $l$ the length, and $A$ the area through which the current

$^3$At least for the concentration used here. It might have more influence when the concentration is closer to the percolation threshold.
flows). For the macroscopic coating conductivity, the total area of the image \((A = 20 \times 20 \, \mu\text{m}^2)\) is used and \(l\) is equal to the thickness of the coating \((40 \, \mu\text{m})\). Ohmic \(I/V\) values were obtained by correcting for the enhancement by the field (see next paragraph). In this way, the conductivity becomes \(\sigma = 3 \cdot 10^{-7} \, \text{S/cm}\), which is factor of 10 higher than the one directly measured in the macroscopic measurements on the coatings (reported in chapter 3). This difference can be explained when many paths, which are separated at the surface, come together inside the coating (figure 5.9(d)). The C-AFM image then gives an overestimation of the conductivity, as the currents through channels are measured one by one instead of simultaneously. The channels of particles thus have numerous branches. This is consistent with the fractal network observed by Zhe Chen et al. [19, 30] in their microscopic and TEM images. Another reason why they concluded that the network is fractal, was the fact that the critical exponent deduced from their conductivity measurements as a function of filler fraction equals the one expected from percolation theory [19, 30]. Part of the difference between the macroscopic conductivity deduced from the AFM image (treated in the present chapter) and the one directly measured with dielectric spectroscopy (discussed in chapter 3) may also be explained by the possible presence of microcracks in the films of the latter measurements, due to the removal of the coating from the zinc substrate, leading to breaks in the particle network and thus a lower conductivity.

In other scans, the tip of the AFM was focused on places that would appear as bright spots in C-AFM-images and the currents were measured as functions of the applied voltage. The conductivity was calculated with the formula above, by using the simplification that a channel of particles is a straight pile of single blocks with ribs of the order of the size of the single crystals \((10^{-7} \, \text{m})\). This leads to an area \(A = 10^{-7} \times 10^{-7} \, \text{m}^2 = 10^{-2} \, \mu\text{m}^2\) and a length \(l\) equal to the thickness of the coating \((40 \, \mu\text{m})\). The conductivities in the ohmic regime varied between \(5 \cdot 10^{-6}\) and \(2 \cdot 10^{-4} \, \text{S/cm}\) (see figure 5.10). From the expectation that the channels are not straight, but have numerous bends (see also next chapter), and are therefore longer than the length used for the calculation of their conductivities, we conclude that the calculated conductivity values are underestimates. This makes, at least for the most conducting channels, the actual conductivities as derived from the channels really comparable to the conductivity as derived from pressed Phthalcon-11 powder \((4 \times 10^{-4} \, \text{S/cm}, \text{see chapter 4})\). This indicates that the electrical contact between the particles inside the coating (at least in the most conducting channels) is as good as in pressed powder.

Moreover, in figure 5.10, the slopes of the curves measured with C-AFM
Figure 5.10: $\sigma_{\text{DC}}$ of Phthalcon-11 powder (black circles) and local conductivity measured with C-AFM on the coating (colored symbols) as a function of the electric field. The logarithm of $\sigma$ is plotted versus $E$ (activated behavior, panel (a)) and $E^{0.5}$ (panel (b)), see also text. The differently colored symbols are measurements on different samples and on different places within those samples. The black line is a fit for cotunneling (see section 2.2.3).

on the coating are comparable to the slope of the curve of the powder conductivity (after the step). This indicates that the conduction mechanism in the coating is equal to that in the pure filler powder. From comparison of the temperature dependence of the conductivity of the powder (chapter 4) with that of the coating in the macroscopic measurement (chapter 3), the same conclusion could be drawn.

To compare the field dependence of the conductivities with existing theories, we plotted in figure 5.10 log($\sigma$) versus $E$ and $E^{1/2}$ (straight lines in these plots correspond to the theories of refs [120, 121] and refs [122, 123, 121], respectively). There is some spread in the data, because the various channels do not have precisely the same conductivity. We added in both plots a fit describing variable-range hopping (VRH) by cotunneling (see equation
as has been discussed in chapters 3 and 4, this may be the conduction mechanism explaining the temperature dependence of the conductivities of both Phthalcon-11/epoxy coatings (chapter 3) and Phthalcon-11 powder (chapter 4). Since the curves of the C-AFM measurements are almost straight in both parts a and b of figure 5.10, and since furthermore the fit for cotunneling describes the data qualitatively as well as quantitatively very well, none of the theories can be excluded. If the theory for cotunneling applies, information on the average number $j$ of junctions in a row through which inelastic cotunneling takes place can be obtained from the fit. The value of $j$ thus obtained is 1.75. This is the same value as found in the macroscopic measurement on the coating (see chapter 3).

5.6 Conclusions

AFM-measurements were performed on Phthalcon-11 particles and on a crosslinked Phthalcon-11/epoxy coating containing 12 vol% Phthalcon-11 particles. The images of the particles showed that the size of the ribs of the crystals ranged between 40 and about 200 nm. Unfortunately no single-particle conductances could be measured, because -apart from the fact that such a measurement with C-AFM would not be easy to interpret- the particles were swept away by the tip in the contact mode necessary to measure the current. On the other hand, the hardness of the epoxy polymer matrix and the conductances of the channels formed by the particles through the coating, turned out to be perfectly in the range of what is possible to measure with C-AFM. Compared with friction and height profiles, the current even turned out to be the best method to detect the particles at the surface (at least for those particles that are part of a conducting channel to the substrate). The area at the surface of the coating that plays a role in the conduction is not the ideal 12 % of the total area (based of the filler amount), but is 4 %. This difference is less than an order of magnitude, so we conclude that a substantial fraction of all particles takes part in conducting percolating channels and that the gain in conductivity with a better particle distribution will only be modest for the concentration of Phthalcon-11 particles used here. From the electric-field dependence alone no conclusions can be drawn on which charge-transport theory is valid for our system, but we can conclude that if variable-range hopping by cotunneling takes place (which was deduced from the temperature dependence of the conductivities of the coatings and the filler, see chapters 3 and 4), the average number

\[ (2.46)^4 \]

An ohmic term was added for the elastic-cotunneling contribution.
of junctions per hop is 1.75, which is equal to the value found in chapter 3. The slopes of the conductivities of the particle channels inside the coating as a function of the electric field, as well as the magnitudes of these conductivities, are comparable to the ones found for pressed Phthalcon-11 powder. This indicates that the electrical contact between the particles in the conducting channels in the coating is as good as in pressed powder.
Chapter 6

Conductivity difference between nanocomposite and filler: explanation from filler-network geometry

6.1 Abstract

The conductivity of a nanocomposite is generally orders of magnitude lower than that of its conductive filler. An example of such a nanocomposite is a specific set of Phthalcon-11/epoxy coatings, studied in detail by us. Experiments on these coatings revealed that they have a very low percolation threshold, a fractal particle network with a fractal dimension that hints to diffusion-limited cluster aggregation (DLCA), and good contact between the particles. In this chapter, we used these characteristics to construct a model that quantitatively predicts the optimal conductivity as a function of filler fraction for such composites. According to the model, the particles form fractal aggregates during preparation, with a random aggregate distribution throughout the material. The model can explain a low percolation threshold as well as a saturation conductivity that is much lower than the conductivity of the filler. These features turn out to be linked in a non-trivial way, giving a lower maximum conductivity with a lower percolation threshold. The model also shows that for the specific Phthalcon-11/epoxy coatings the conductivity is close to the maximum conductivity that can be obtained for the assumed network-formation mechanism and the observed low percolation threshold.
6.2 Introduction

When comparing the DC conductivity level of the Phthalcon-11/epoxy nanocomposite ($3 \cdot 10^{-8}$ S/cm at room temperature, chapter 3) with that of the pure Phthalcon-11 powder ($4 \cdot 10^{-4}$ S/cm at room temperature, chapter 4), the huge difference is very remarkable. However, the fact that the conductivity of a nanocomposite is much lower than that of its filler is very common (see for example refs [1, 2, 3, 4]) and is up to now not fully understood. It is often assumed that the large difference is created by insulating layers of the matrix between the filler particles [1, 145, 15, 33].

In the previous chapters, we came to the following conclusions: The temperature and electric-field dependencies of the conductivities of Phthalcon-11 powder and the specific [35] Phthalcon-11/epoxy coatings indicate that the conduction mechanisms in these materials are the same (see chapter 3, 4, and 5). From their frequency dependencies, similar typical length scales follow for the heterogeneity that determines the effective conductivity (chapter 3 and 4). Finally, conducting-atomic-force-microscopy measurements revealed that the magnitude of the DC conductivity of the particle channels inside the coating is approximately equal to that of pressed Phthalcon-11 powder (chapter 5). These results are a strong indication that the Phthalcon-11 crystals inside the coating are in good contact with each other. The measurement results of Chen et al. [19] gave an extra indication for this assumption. Their conductivity data on the specific [35] Phthalcon-11/epoxy coatings were fitted with $\sigma_{DC} \propto (\phi - \phi_c)^t$ (equation (2.14), with the occupation probability $p$ replaced by the filler fraction $\phi$). The fit, which followed the data well over the total range of volume fractions ($0.01 \leq \phi \leq 0.12$), gave $t = 2.1$. This is within the uncertainty of the measurement equal to the “semi-universal” value of 2.0, which can only be found when the spread in local conductances is small (see refs [39, 43, 44, 45, 46] and section 2.2.2).

As a consequence, the spread in the distances between nearest-neighbor particles inside the coatings must be small. This is indeed the case for touching particles. We conclude from all the indications mentioned above that insulating polymer layers between the filler particles cannot be the cause of the large difference between the conductivity of the nanocomposite and that of

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1Some of these references report on nanocomposites with carbon black as filler particles. The powder conductivity of carbon black is approximately $10^2$ S/cm.
In the present chapter, we introduce a model that explains such a large difference for filler particles in good contact with each other in a network through the nanocomposite. The model is based on several features of the specific [35] Phthalcon-11/epoxy coatings, but may have a more general application, because these features may also hold for similarly processed composite materials. In the next section, the features are summed up. Section 6.4 gives the model that we propose for the particle network on the basis of these features. Within the context of the model, section 6.5 derives equations for the DC conductivity as a function of filler fraction. The consequences of the model are given in section 6.6. The chapter ends with conclusions.

6.3 Features of Phthalcon-11/epoxy nanocomposites

An important characteristic of the Phthalcon-11/epoxy nanocomposite that we studied is that its critical filler fraction is low: in thick coatings, a percolating particle network is already formed at 0.55 vol% [30], which is much lower than the theoretical 16 vol% for randomly placed spheres (see ref. [20] and section 2.2.2). There are several ways to explain such a small value of the critical filler fraction, see chapter 1. In the case of Phthalcon-11/epoxy nanocomposites, it is attributed to the formation of fractal aggregates. Transmission Electron Microscopy (TEM) and Optical Microscopy (OM) images of Phthalcon-11/epoxy coatings indeed showed a fractal structure [19, 30].

From the OM images the fractal dimension $d_f$ of the particle network was determined to be 1.77 [30] on length scales below 20 $\mu$m. This value of $d_f$ is characteristic for a particle network formed by diffusion-limited cluster aggregation (DLCA) [146, 147, 48, 49, 148, 50]. In DLCA particles and clusters of particles move (by diffusive motion) and when they touch another particle or cluster, they irreversibly stick to that particle or cluster, forming a (larger) cluster, which moves on and to which again other particles and other clusters can stick. Since in DLCA clusters immediately stick to each other as soon as they touch, the resulting aggregates have quite a low density and little loops, because the clusters mainly touch with their exteriors. Simulations [48, 49, 50] and experiments [47] revealed that, at low concentrations, aggregates formed in this way have a fractal dimension of 1.8. As the clusters grow, their velocity decreases because of the increasing Stokes
drag, which is proportional to the radius of the object (the self diffusion coefficient for isolated Brownian spheres is given by \( D = \frac{k_B T}{6 \pi \eta a} \), with \( k_B \) being Boltzmann’s constant, \( T \) the temperature, \( \eta \) the viscosity of the medium and \( a \) the radius of the sphere). The process yields, at a fixed point in time, clusters that have all about the same size [47, 50].

A mechanism opposed to DLCA is reaction-limited cluster aggregation (RLCA). In RLCA the diffusion time, which is a measure for the time between two collisions of clusters, does not form the bottleneck in the formation of the clusters, but the “reaction time” is the decisive factor. The word “reaction” here refers to irreversible sticking. For DLCA the chance of sticking after a collision is 1, whereas for RLCA it is considerably smaller than 1. As a consequence, clusters will statistically penetrate each other more before they get stuck, leading to denser clusters and thus a higher fractal dimension. In 3D the \( d_f \) of an aggregate formed by RLCA is 2.1 [50]. In addition, in RLCA, the aggregate size distribution is not monodisperse [50].

The influence of attrition and reaggregation of primary particles that had already stuck to an aggregate was investigated in reference [149]. This process is called “aging”. It turned out to reduce the fractal dimension of the aggregates with 0.2 for low concentrations.

For the specific [35] Phthalcon-11/epoxy coatings, aggregate formation takes place during the preparation of the prepolymer formulation and/or during the cure of this formulation. Initially, when the monomers (Epikote 828 and Jeffamine D230) and filler particles in the m-cresol dispersion are put together, the coating is in a low-viscosity liquid state. Epikote 828 and Jeffamine D230 then start crosslinking and m-cresol starts evaporating. Rheology measurements show that for this system it takes several hours (at a curing temperature of 373 K) to reach the gel point, at which the coating becomes highly viscous. In the meantime, when the coating is still in a low-viscosity liquid state, diffusion-limited cluster aggregation takes place. At the gel point of the matrix, the movement of the (clusters of) particles stops. In order to have a DC conductivity higher than that of the matrix, the formed aggregates must then form a percolating path through the coating.

Apart from a low percolation threshold and a network formed by DLCA we will use another feature of the specific [35] Phthalcon-11/epoxy coatings to come to a model in the next section: As we already mentioned in the introduction of this chapter, the electrical contact between the particles in many channels inside the coating is good and the matrix has a negligible influence on the conductance through the channels.
6.4 Model for the particle network

The features of the specific [35] Phthalcon-11/epoxy coatings summed up in the previous section will be used in this section as input to come to a model. The model may also hold for other nanocomposites with other matrix and/or other filler particles prepared in a similar way. It can be used to calculate the maximum conductivity of a nanocomposite that is formed by DLCA, with a known critical filler fraction. In section 6.6, we come back to the Phthalcon-11/epoxy coatings and compare some of the consequences of the model with experimental results of these coatings.

As explained in the previous section, in DLCA the distribution of the aggregate sizes at a certain time after the process started has a low spread. Therefore, when the matrix becomes solid and the particle network gets fixed, all aggregates will have approximately the same size. In our model, we approximate the aggregates as being spherical with the same radius, \( R_a \) (subscript ‘\( a \)’ stands for aggregates, while we refer to the particles with subscript ‘\( p \)’). In our approximation, the particles are also spherical and equal in size, with radius \( R_p \). In addition, we assume that the aggregates are placed randomly throughout the material and are impermeable (i.e. they cannot penetrate each other). As explained in the previous section, this is justifiable, because the clusters touch each other mainly at the exteriors and get stuck immediately. A schematic picture of the morphology of the particle network according to this model is shown in figure 6.1. The aggregates are

![Figure 6.1: Schematic drawing of a random percolating network built of fractal aggregates.](image-url)
the (spherical) building blocks for which normal percolation theory holds. They will therefore have a critical filler fraction \( \phi_{a,c} \) of 16 vol\%. As these building blocks are not completely filled with particles, \( \phi_{p,c} \) will be lower.

We assume that the structure is optimal for the conductivity in the sense that neighboring particles inside an aggregate touch and also that the aggregates are rotated in such a way that particles of adjacent aggregates touch. The fact that in DLCA the particles get stuck as soon as they touch, makes the assumption of the proper rotation of the aggregates tenable.

The mobilities of charge carriers inside the filler particles and between contacting filler particles in the nanocomposite are assumed to be equal to these mobilities in pressed filler particle powder. Hence, the temperature dependence, possible contact problems between touching particles, and the possible reduction of the density of states as described in chapter 4 are accounted for in the conductivity of the particles, \( \sigma_p \) (which in this chapter is thus the powder conductivity). In addition, we assume that the contribution of tunneling between particles that do not touch is negligible.

Finally, the matrix is assumed to be a perfect insulator, i.e. its conductivity is 0.

### 6.5 DC conductivity on the aggregate network

For randomly placed conducting spheres in an insulating matrix, the following relation between the DC conductivity \( \sigma \) and the fraction \( \phi \) of spheres is known from percolation theory (above the percolation threshold): [36, 150, 151]

\[
\sigma = \sigma_0 |\phi - \phi_c|^t,
\]

where \( \phi_c \) is the percolation threshold (\( \phi_c \approx 0.16 \)) [20], \( t \approx 2.0 \) and \( \sigma_0 \) is approximately equal to the conductivity of the spheres. When the building blocks of the network are fractal aggregates instead of solid spheres, the equation should be written as

\[
\sigma = \sigma_a |\phi_a - \phi_{a,c}|^t,
\]

with \( \sigma_a \) remaining to be determined and \( \phi_{a,c} \) being the effective volume fraction, 0.16.

As \( \sigma_a \) and \( \phi_a \) are not known beforehand, we want to write equation (6.2) in terms of \( \sigma_p \) and \( \phi_p \):

\[
\sigma = \tilde{\sigma}_0 |\phi_p - \phi_{p,c}|^{t'}.
\]
In order to determine \( \tilde{\sigma}_0, \phi_{p,c}, \) and \( t', \) the following equations are used. From conservation of mass, it follows that

\[
N_a m_a = N_p m_p, \quad (6.4)
\]

with \( N \) being the number and \( m \) the mass of the aggregates and particles. In addition

\[
\phi_a / \phi_p = r^3 N_a / N_p, \quad (6.5)
\]

with \( r = R_a / R_p \), the ratio of the radii of the fractal aggregates and the particles, respectively. The definition of the fractal dimension \( d_f \) (here \( d_f \) is the fractal dimension of the aggregates, not of the percolating network) gives

\[
m_a / m_p = r^{d_f}. \quad (6.6)
\]

Elimination of \( N \) and \( m \) from equations (6.4) - (6.6) yields

\[
\phi_a = \phi_p r^{3-d_f}. \quad (6.7)
\]

The conductivity of the single aggregates must scale with \( r \) as well. As long as the size of the aggregate is appreciably smaller than the distance between the electrodes, the conductivity will become lower with increasing size of the aggregate (for the consequences of a relatively small distance between the electrodes see e.g. Pollak and Hauser [152], Raikh and Ruzin [153], and Chen et al. [30]). We will show below that it can be expressed as

\[
\sigma_a = \sigma_p r^{-\mu}, \quad (6.8)
\]

with \( \mu \) being positive and to be determined later. Substitution of equations (6.7) and (6.8) into equation (6.2) yields equation (6.3) with

\[
t' = t, \quad (6.9)
\]

\[
\tilde{\sigma}_0 = \sigma_p r^{(3-d_f)-\mu}, \quad (6.10)
\]

and

\[
\phi_{p,c} = \phi_{a,c} r^{d_f-3} = 0.16 r^{d_f-3}. \quad (6.11)
\]

When \( \phi_{p,c} \) is known from experiments, \( r \) can be calculated by using the rewritten form of equation (6.11):

\[
r = \left( \frac{0.16}{\phi_{p,c}} \right)^{1/d_f}. \quad (6.12)
\]
Finally, the expression for the conductivity of the nanocomposite in terms of $\sigma_p$ and $\phi_p$ is found by substituting equation (6.12) into equation (6.10) and substituting that equation into equation (6.3):

$$\sigma = \sigma_p \left( \frac{\phi_{p,c}}{0.16} \right)^{\frac{\mu}{3 - df}} |\phi_p - \phi_{p,c}|^t. \quad (6.13)$$

Elimination of $r$ from equation (6.8) by using equation (6.12) gives the ratio between the conductivity of the aggregates and the conductivity of the particles from which they are built in terms of $\phi_{p,c}$:

$$\frac{\sigma_a}{\sigma_p} = (\phi_{p,c}/0.16)^{\mu/(3 - df)}. \quad (6.14)$$

The saturation value of the conductivity, $\sigma_{\text{max}}$ is the conductivity that is approached for the maximum amount of fillers in the sample. Since we assumed that the aggregates are randomly placed and impermeable, the maximum amount of fillers corresponds to the amount of fillers for a random close packing of the spherical aggregates. The random close packing of spheres is 64 % [154]. Equation (6.2) thus gives

$$\sigma_{\text{max}} = \sigma_a |\phi_a - \phi_{a,c}|^t = \sigma_a |0.64 - 0.16|^{2.0}. \quad (6.15)$$

After substitution of $\sigma_a$ (equation (6.14)), we find

$$\frac{\sigma_{\text{max}}}{\sigma_p} = 0.23 \left( \frac{\phi_{p,c}}{0.16} \right)^{\mu/(3 - df)}. \quad (6.16)$$

The conductivity exponent $\mu$ follows from the Einstein diffusion equation [150]:

$$\sigma_a \propto n_a D_a, \quad (6.17)$$

where $n_a$ is the charge-carrier density within the sphere of the aggregate, $n_a \propto m_a / x^3 \propto x^{d_f - 3}$ (with $x$ being the linear distance from the middle of the aggregate$^2$), and $D_a$ is the diffusion constant of a charge carrier, $D_a \equiv dx^2 / d\tau$, with $\tau$ being the time. Since the diffusion takes place on a fractal structure instead of in a homogeneous medium, a so-called random-walk dimension $d_w$, defined as

$$x^{d_w} \propto \tau \quad (6.18)$$

is introduced. It follows that

$$D_a \propto x^{2 - d_w}. \quad (6.19)$$

$^2$For convenience we left out the brackets indicating the expectation value of $x$. 

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Substituting this, together with \( n_a \propto x^{d_f - 3} \), in equation (6.17) yields
\[
\sigma_a \propto x^{-(1+d_w-d_f)},
\]
and thus
\[
\mu = 1 + d_w - d_f. \tag{6.21}
\]

In general \( d_w \geq 2 \) holds, which gives \( \mu \geq 3 - d_f \). As a consequence, the exponent in equation (6.16) is larger than 1; the relationship between \( \sigma_{\text{max}} \) and \( \phi_c \) is superlinear.

An analytical expression for \( d_w \) can be derived only for special networks. For example, the upper bound of \( d_w/d_f \) is obtained for an aggregate without loops and branches. In that case, \( l^2 \propto \tau \), \( (l \) is the distance traveled by a charge carrier along an arm of the aggregate) and \( l \propto x^{d_f} \), yielding \( d_w = 2d_f \) \([150]\) and thus \( \mu = 1 + d_f \). The random percolating cluster has many loops and branches, and may be taken as an opposite case. No analytical derivation for \( d_w \) of such a structure is known. However, Alexander and Orbach postulated that in any dimension \( d_w/d_f = 3/2 \) at the percolation threshold \([38]\). Their postulation is known under the name “Alexander-Orbach conjecture” and we will abbreviate it with “AO”. It is indeed consistent with the values for \( d_w \) found in many simulations. For the intermediate case of tree-like networks (branches, but no loops) one can rigorously prove \([155]\) \( d_w = d_f + d_{\text{min}} \) and hence \( \mu = 1 + d_{\text{min}} \), with \( d_{\text{min}} < d_f \) the shortest-path dimension. Calculations by Meakin et al. \([116]\) indicate that in DLCA clusters, rings are probably irrelevant; \( d_{\text{min}} \) in this case is found to be 1.25. This would then imply \( d_w = 3.0 \) and \( d_w/d_f = 1.7 \).

### 6.6 Consequences of the model

In the following, we will call the matrix of a composite “phase 1” and the objects that are randomly placed in the matrix “phase 2”. They are denoted by subscripts ‘1’ and ‘2’, respectively, and \( \sigma_1 \) equals zero. For the model discussed in sections 6.4 and 6.5, phase 2 are fractal aggregates. Figure 6.2 shows the conductivity \( \sigma \) of a composite normalized by the particle powder conductivity \( \sigma_p \) as a function of the particle filler fraction \( \phi_p \). The dotted black and dotted dark grey lines give the conductivity according to the model, for aggregates without loops and branches, and aggregates that obey the AO conjecture, respectively. To construct the lines in the figure, we used the values of \( d_f \) and \( \phi_{p,c} \) measured on the Phthalcon-11/epoxy coatings \((d_f = 1.77 \) and \( \phi_{p,c} = 0.0055)\). As discussed in the previous section, for
Figure 6.2: Upper bounds and expected value of $\sigma$ (scaled by the conductivity of particles $p$) as function of the volume fraction of the particles for a material consisting of particles embedded in a matrix with $\sigma = 0$. For the light grey lines the building blocks used in the theories are single particles, for the dark grey lines those building blocks are fractal aggregates that fulfil the Alexander-Orbach conjecture ($d_w/d_f = 3/2$), and for the black lines they are fractal aggregates without loops and branches ($d_w/d_f = 2$). The solid lines are Wiener bounds, the dashed lines are HS bounds and the dotted lines show the percolation theory. The lower bounds are zero.

Fractal aggregates formed by DLCA, a line in between the black and dark grey dotted lines will be obtained, because those aggregates have branches but little loops. Figure 6.2 also shows the result from normal percolation theory, with massive particles as phase 2 (dotted light grey line). It is obvious from the figure that the latter theory has a higher percolation threshold and leads to a much higher conductivity than our theory for random percolation of fractal aggregates. Both predictions (and thus all three dotted lines) must lie between the lower and upper bounds of other theories, like the Wiener bounds [156, 157] and the bounds found by Hashin and Shtrikman [158, 159] (further abbreviated as HS). The Wiener bounds give the lowest and the highest conductivity possible for any material made of two components. They are reached when the components (i.e. phase 1 and phase 2)
are placed in series or parallel, respectively. The parallel case is equal to the simple linear rule of mixtures. For $\sigma_1 = 0$, the lower Wiener bound is $\sigma/\sigma_2 = 0$ and the upper Wiener bound is $\sigma/\sigma_2 = \phi_2$. The HS bounds lie within the Wiener bounds. They have an extra criterion that the material is statistically isotropic. In the derivation of the HS bounds, the material is assumed to be built out of spheres of one component with shells of the other component. To fill the space, spheres of all kinds of sizes are used, but the ratio of the radii of the inner sphere and the outer sphere is constant. The result is that for $\sigma_1 = 0$, the lower HS bound is again $\sigma/\sigma_2 = 0$ and the upper HS bound is $\sigma/\sigma_2 = \frac{2}{3} \phi_2/(1 - \frac{1}{3} \phi_2)$. In figure 6.2 the upper Wiener bounds (solid lines) and upper HS bounds (dashed lines) are shown, both for fractal aggregates (black and dark grey line) and for massive particles (light grey line) as phase 2. Indeed, the predictions for random percolation are below the accompanying upper Wiener and HS bounds.

Notice that the lines in Figure 6.2 are only shown until limited values of $\phi_p$ due to (random) maximum packing densities of the spherical particles or aggregates. The random close packing density of 0.64 [154] for the aggregates corresponds, for $\phi_{p,c} = 0.0055$ and $d_f = 1.77$, to $\phi_p = 0.022$. Therefore, the theory can in principle only be applied to filler fractions up to 2.2 vol%.

Figure 3.3 shows that, for the specific [35] Phthalcon-11/epoxy coatings, at this filler fraction, the conductivity has almost reached the plateau value $\sigma_{\text{max}}$.

Apparently, adding more filler particles does not have much influence on the conductivity. Therefore, although our experiments were performed on coatings with a filler fraction larger than 2.2 vol%, we think that they are still useful to compare with the model.

The dark grey and black dotted lines in figure 6.2 correspond to our model described above. They show that, according to the model and with the values of $\phi_{p,c}$ and $d_f$ found for the specific [35] Phthalcon-11/epoxy coatings, $\sigma_{\text{max}}$ is a factor between $1 \cdot 10^3$ and $1 \cdot 10^4$ (valid for aggregates that follow the AO conjecture and for aggregates without loops and branches, respectively) smaller than $\sigma_p$. This would be in the optimal situation, where all particles within the aggregates are in good contact with each other and the aggregates are rotated in such a way that the particles of adjacent aggregates also touch. Using the conductivities of our Phthalcon-11/epoxy coating...
ings (\(\sigma = 3 \cdot 10^{-8} \text{S/cm (chapter 3)}\)) and Phthalcon-11 powder (\(\sigma_p = 4 \cdot 10^{-4} \text{S/cm (chapter 4)}\)), we find that \(\sigma = 8 \cdot 10^{-5} \sigma_p\). This is very close to the optimal situation for aggregates without loops and branches.

We will now elaborate on the influence of \(\phi_{p,c}\) according to the model. Equation (6.16) already shows that \(\sigma_{\text{max}}\) increases with increasing \(\phi_{p,c}\). The dependence grows with an exponent of \(\mu/(3 - d_f)\). At the end of section 6.5, we showed that \(\sigma_{\text{max}}\) increases stronger than linearly with \(\phi_{p,c}\) and in particular that for aggregates formed by DLCA, \(\mu \approx 1 + d_{\text{min}} \approx 2.25\), which yields for the exponent in equation (6.16) \(\mu/(3 - d_f) \approx 1.85\). Hence, a low value of \(\phi_{p,c}\) will lead to a value of \(\sigma_{\text{max}}\) that is much lower than \(\sigma_p\).

Figure 6.3 shows the influence of \(\phi_{p,c}\) on \(\sigma\) (normalized by \(\sigma_p\)) as a function of \(\phi_p\) and \(\phi_a\). Of course, for \(\phi_a\) on the horizontal axis, the conductivity starts to be nonzero from \(\phi_{a,c} = 0.16\) and the model holds till \(\phi_a = 0.64\), which corresponds with the random close packing of spherical aggregates. The right picture is obtained from the left picture by calculating \(\phi_p\) from \(\phi_a\) using equation (6.7) with substitution of \(r\) (equation (6.12)). It shows that with lower \(\phi_{p,c}\), the fraction of particles at which the material is saturated

![Figure 6.3](image-url)

**Figure 6.3:** Normalized \(\sigma\) as a function of \(\phi_a\) (left) and \(\phi_p\) (right) for several values of \(\phi_{p,c}\). For the calculation of the curves, \(\mu = 1 + d_{\text{min}} = 2.25\) was used, which holds in good approximation for aggregates formed by DLCA (see text). In addition, we used the experimentally found value for \(d_f\) (\(d_f = 1.77\)).
becomes lower as well, leading to a lower $\sigma_{\text{max}}$. This is logical, because in order to obtain a low $\phi_{p,c}$, the aggregates must have a low average density. The local density in an aggregate decreases with increasing distance from the midpoint of the aggregate. Therefore, for a constant $d_f$, aggregates with a low average density are formed when the aggregates are large. Equation (6.12) clearly shows that indeed larger aggregates lead to a lower $\phi_{p,c}$. The fact that larger aggregates also give a lower $\sigma_{\text{max}}$ is also understandable: Large aggregates are sparse at the outside. Under the assumption made that the aggregates are impermeable, the contact between the aggregates is via the exterior of the aggregates. The low conductivity of the exterior of the aggregates due to the low surface density forms the bottleneck in the conductive path through the material. As a consequence, the conductivity is low.

In practice, aggregates can grow large when the concentration is low and there is enough time to diffuse. There are two opposing aspects that determine whether there is “enough time to diffuse”: the time till the gel point is reached, which decreases with increasing curing temperature, and the velocity of the particles, which increases with increasing temperature. This subject is studied for Phthalcon-11/epoxy coatings by Ming Yuan at the Eindhoven University of Technology.

As explained above, large aggregates give a low percolation threshold $\phi_{p,c}$ and a low value of the saturation value of the conductivity $\sigma_{\text{max}}$. The model was based on an infinitely large material, or, at least a material with sample sizes much larger than the aggregate size. In practice, the sample has a finite size. When the aggregates grow till a size comparable with the sample size, the statistics for the random percolating network become poor. For our Phthalcon-11/epoxy samples, the radius of the aggregates is, according to equation (6.12), 15 times larger than that of the particles, giving $R_a \approx 1.5 \mu m$. The thickness of our coatings was 40 $\mu m$. The difference of more than an order of magnitude seems to be enough for the model to be valid. However, reference [30] shows that the bulk value for $\phi_{p,c}$ of Phthalcon-11/epoxy coatings is not yet reached for a 40 $\mu m$ thick coating. In addition, it is not obvious whether aggregates with a radius 15 times larger than the radius of the particles are large enough for good fractal statistics.

Figure 6.4 shows what the model predicts when the fractal dimension of the aggregates differs from 1.77. Notice that for a higher or lower value, the aggregates have to be formed not by DLCA, but that another mechanism like RLCA; also aging can play a role (see section 6.3). As mentioned in section 6.3, the fractal dimension of the clusters formed by RLCA is higher
than in DLCA (2.1 versus 1.8 in 3D), while aging reduces $d_f$. In RLCA, the aggregate size distribution is polydisperse, which makes our model less applicable. For the calculation of the curves in figure 6.4 we only changed the value of $d_f$ and just used a $d_w$ proportional to $d_f$ (namely $d_w = 1.7d_f$), which is a questionable assumption. Figure 6.4 reveals that $\sigma_{\text{max}}$ increases with a decreasing fractal dimension. This seems counterintuitive: a lower value of $d_f$ gives sparser aggregates at the exterior, and thus a lower expected conductivity. However, the latter consideration only holds when the aggregate size is constant. It follows from equation (6.12) that, for a constant $\phi_{p,c}$ (which was the case for the calculation, where $\phi_{p,c} = 0.0055$ was used), $r$ decreases with decreasing $d_f$, which enhances the density at the exterior. Thus, in a simple theory where the relation between $d_w$ and $d_f$ does not change and where the final aggregates are impermeable and percolate randomly through the material, aggregates with a lower fractal dimension will lead to a higher value of $\sigma_{\text{max}}$. To lower $d_f$ one can think of the process of aging. However, this process will complicate the theory, because for example the relation between $d_w$ and $d_f$ changes or the aggregates may start penetrating each other during aging. Therefore, it might be impossible to increase $\sigma_{\text{max}}$ by decreasing $d_f$. 

Figure 6.4: Normalized $\sigma$ as a function of $\phi_p$ for several values of $d_f$, with $d_w = 1.7d_f$. The critical volume fraction of particles is taken equal to the experimental value $\phi_{p,c} = 0.0055$. 

\[ \frac{\sigma}{\sigma_p} \]
6.7 Conclusions

The Phthalcon-11/epoxy coatings treated in the previous chapters have a low percolation threshold, a fractal particle network with a fractal dimension that corresponds to diffusion-limited cluster aggregation (DLCA), and particles that are in good contact with each other. Despite the latter feature, their conductivity is orders of magnitude lower than the conductivity of pressed Phthalcon-11 powder. All features of the Phthalcon-11/epoxy coatings were used to construct a model for the morphology of the particle network. The model can quantitatively predict the DC conductivity of the composites at hand. In this model, the particles have formed fractal aggregates by DLCA during the preparation, when the coating is in a low-viscosity state. The aggregation stops when the coating becomes highly viscous. The formed aggregates will then be distributed randomly throughout the material. For these aggregates, standard percolation theory holds. By combining the fractal structure with conservation of mass, an expression for the conductivity of the nanocomposite could be derived. It turned out that, in this model, a low percolation threshold automatically leads to a conductivity that is orders of magnitude lower than the conductivity of the filler. The percolation threshold and the maximum conductivity are linked, because large aggregates give rise to a low percolation threshold, but also to a low saturation value of the conductivity. As a consequence, in practice, one has to make a compromise between a low critical filler fraction and a high conductivity. Our model shows that for the Phthalcon-11/epoxy coatings, the conductivity is already close to the maximum value that can be reached with the observed low percolation threshold under the present DLCA processing mechanism. When the critical filler fraction is desired to remain as low as it was for our coatings, a drastic increase in conductivity can therefore only be obtained by the use of a better-conducting filler.
Chapter 7

Molecular, crystal, and energy-band structure of Phthalcon-11

7.1 Abstract

Based on earlier ab-initio calculations, Phthalcon-11 crystals are believed to have a large anisotropy in the conduction. Since this would strongly influence the conductivity of a nanocomposite with Phthalcon-11 crystals as conductive filler, we investigated this aspect further. This was done by performing density-functional-theory (DFT) calculations. For such calculations, the molecular and crystal structure of the material under consideration has to be known. In the past, much research was done at the Koninklijke/Shell Laboratorium Amsterdam (KSLA) to unravel the structure of Phthalcon-11. In this chapter, we summarize some of the results of the experiments performed at the KSLA. The Rietveld analysis on the X-ray and neutron powder-diffraction spectra was repeated, because the original outcome of the KSLA was not well-documented. The found structure was used as input for DFT calculations on the bulk Phthalcon-11 material. A band gap of 0.7 eV was found, which is considerably lower than the experimentally determined value of 1.2 eV [160]. This amount of underestimation is expected for DFT calculations with the local-density approximation as used here. Straightforward calculations based on the dispersion of the energy bands indeed show that the conduction along the $b$-axis of the unit cell would be much smaller than in the other two lattice-vector directions, in accordance with the conventional idea. However, when the band struc-
tures along more logical charge-transport directions within the unit cell are calculated, the mobility in the effective $\vec{b}$ direction turns out to be at least as high as in the other directions, with a resulting small anisotropy in the conduction of the Phthalcon-11 crystals.

The contents of this chapter will be published in an article on the analysis of the structure of Phthalcon-11.

7.2 Introduction

It became clear in the previous chapter that the conductivity level of the filler particles is of the utmost importance for the final conductivity of the nanocomposite. Therefore, we want to study the conductivity of the Phthalcon-11 filler particles in more detail. We are especially interested in the anisotropy of this conductivity. Up till now, it had been assumed, based on earlier ab-initio calculations [32], that the conductivity within the Phthalcon-11 is crystals in one direction about a factor of 100 smaller than along a perpendicular direction. If that is indeed the case, it will have a large influence on the conductivity of the nanocomposite. The influence of the anisotropy will be more distinct in a nanocomposite than in pure pressed filler powder, because in a nanocomposite the particle channels are mainly 1-dimensional (see chapter 6) so that crystals with an unfavorable orientation cannot be avoided in the charge transport. However, we concluded in the previous chapters that there is hardly any difference between the conductivity of the particle channels inside the specific [35] Phthalcon-11/epoxy coatings and that of the Phthalcon-11 powder. This is in contradiction with the considerable anisotropy found in the earlier ab-initio calculations.

C-AFM measurements on single crystals with different orientations might give more information about anisotropy in the conductivity, provided that the contact with neither the AFM tip nor the substrate is the decisive factor for the conductivity. However, as mentioned in chapter 5, we did not succeed in performing C-AFM measurements on single crystals. Also, attaching wires to nanocrystals is still a challenging activity. Therefore, we try to determine the anisotropy with ab-initio calculations, namely with density-functional theory (DFT) calculations. Therefore, we need to know approximately the molecular and crystal structure of Phthalcon-11. In the previous decade, much research was done at the Koninklijke/Shell Laboratorium Amsterdam (KSLA) to unravel the molecular and crystal structure. It turned out to be different from the conventional idea proposed by Hanack et al. [161, 162].
The next section will give general information on phthalocyanines, also showing the idea of the structure proposed by Hanack. Section 7.4 reports on the experiments performed at the KSLA. In section 7.5 experimental data of the KSLA were used to determine the structure of Phthalcon-11. Section 7.6 shows the final structure that follows from the experiments and the analysis discussed in section 7.4 and section 7.5. In section 7.7 the principle of DFT calculations is drawn up. Information on the computer program and the parameters that we used for the DFT calculations are given in section 7.8. The results on the energy-band structure and the ensuing conduction anisotropy are discussed in section 7.9. The chapter ends with the conclusions.

7.3 Phthalocyanines

Phthalcon-11 belongs to a group of materials called “phthalocyanines”. In 1907, the first known occurrence of a phthalocyanine was reported. Twenty years later, a patent was filed describing the manufacturing process. In the past, phthalocyanines were mainly used as (blue) pigments and as catalysts. In the last decade, the interest in phthalocyanines has grown, because of their (possible) applications in solar cells [163], light emitting diodes [164], transistors [165, 166], and light-absorbing coatings on recordable CDs [167, 168].

A material is called a phthalocyanine when the molecules contain the ring structure that is depicted in figure 7.1. The cavity in the center can contain a metal ion, two H\(^+\) ions, or it can be empty. In the latter case, the phthalocyanine ring has a charge of -2. Many different metal atoms can be placed in the cavity. The most common ones are Cu\(^{2+}\), Fe\(^{2+}\), and Co\(^{2+}\); these materials are called “metal phthalocyanines” and are abbreviated with CuPc, FePc, CoPc, etc. Frequently, also parts of the hydrogen atoms on the phenyl rings are replaced by substituents, such as Cl or Br.

When the charge of the metal ion is higher than 2+, ligands can easily bind to the transition-metal ion in phthalocyanines. They usually arrange themselves approximately perpendicular to the phthalocyanine ring structure. Phthalocyanine molecules without ligands can self-assemble in several ways [84, 169, 170]. One way of self-assembling is the formation 1-dimensional stacks with an intermolecular distance of about 3 Å (caused by the Van-der-Waals interaction between the \(\pi\)-orbitals of the phthalocyanine rings) [171], which can lead to nanofibers [169, 170]. Ligands will generally change the way of stacking or increase the distance between the phthaloc-
Figure 7.1: Characteristic structure of a phthalocyanine. In the figure, the cavity is filled with a metal ion ('M'), like copper, iron, or cobalt. For a phthalocyanine without ligands (as depicted here), the metal ion has to have a valence of 2+ to make the total molecule neutral. The cavity can also contain two H\(^+\) ions, or it can be empty. In the latter case, the molecule has a negative charge (2-).

cyanine rings. A structure for phthalocyanines with ligands that is often cited is the one proposed by Hanack [161, 162]. According to Hanack, the phthalocyanine molecules form a 1-dimensional chain of which the metal atoms and the ligands form the backbone, see figure 7.2.

Figure 7.2: Stacking of metal ('M') phthalocyanines (depicted as squares) with ligands ('L') as proposed by Hanack [161, 162].

The conduction in such a structure was supposed to take place along the backbone. It will become clear in section 7.4 - 7.6 that the structure of
Phthalcon-11 differs from this structure. The unit cell dimensions are also very different. For example, the unit cell of \([\text{PcCoCN}]_n\) with a Hanack structure is monoclinic with axes lengths \(|\vec{a}| = 13.21 \text{ Å}, |\vec{b}| = 13.72 \text{ Å}, \text{ and } |\vec{c}| = 15.37 \text{ Å}| \text{ and angle } \beta = 126.3^\circ | [172] (the values for Phthalcon-11 are given in section 7.6). In literature, stackings of phthalocyanines with ligands that differ from the Hanack stacking are also proposed [173, 174], like the ones schematically shown in figure 7.3.

![Figure 7.3](image)

**Figure 7.3:** Three kinds of possible stackings for phthalocyanines (depicted as disks) with two ligands (depicted as bars). The picture was taken from ref. [173].

### 7.4 Structural information on Phthalcon-11 as determined at the KSLA

In the past, many experiments were performed at the KSLA to unravel the molecular and crystal structure of Phthalcon-11. The results were only published in a very limited form [29]. In this section, we will give more information about these experiments and results. We will mainly focus on the experiments that were performed to determine the crystal structure of Phthalcon-11, i.e. transmission-electron-microscopy (TEM) and electron-diffraction (ED) measurements, which will be discussed in section 7.4.1, and X-ray and neutron-diffraction measurements, which will be described in section 7.4.2.

Before the molecular structure of Phthalcon-11 was studied in detail, the
structures shown in figure 7.4 had been proposed at the KSLA.

Figure 7.4: Molecular structures that were proposed for Phthalcon-11 before its structure was analyzed in detail. Everywhere where “H$_2$O” is written, it refers to lattice H$_2$O. The arrows denote “bonds” that are not real covalent bonds, because the distance between the atoms is a little larger than expected for a covalent bond. Structure (a) is the Hanack structure, see section 7.3.

Many experiments were performed to decide which of the molecular
structures is right, among them pyrolysis-combustion mass-spectrometry elemental analysis (PCME), extended X-ray-absorption fine-structure (EX-AFS) spectroscopy, ultraviolet-visible (UV-VIS) spectroscopy, infrared spectroscopy, röntgen fluorescence and elemental analysis, liquid and solid-state nuclear magnetic resonance (NMR) spectroscopy, field-desorption mass spectrometry, X-ray diffraction, and neutron diffraction. The Phthalcon-11 powder used in these experiments had a purity of at least 99.5 %. Often Phthalcon-11 powder labeled with $^{13}$CN, D$_2$O, or C$^{15}$N was used. On the basis of the experiments, all proposed structures except for structure (c) (see figure 7.4) were excluded.

In section 7.4.1 and 7.4.2 the experiments used to determine the crystal structure of Phthalcon-11, which is monocrystalline, are discussed.

### 7.4.1 TEM and ED

Figure 7.5 shows a TEM image of Phthalcon-11 captured at the KSLA.

![Figure 7.5: TEM image of a Phthalcon-11 crystal captured at the KSLA. Regular lattice fringes are clearly visible. Unfortunately the scale is not depicted in the image. According to a Shell research note, the width of the particle is approximately 50 nm and the distance between the fringes is approximately 11 Å. Parallel dark lines with regular spacings are clearly visible. These lattice fringes are due to diffraction by the crystal lattice. The separation between

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the lines could not be determined very accurately. A value of 11.2 Å was calculated from the image to be the distance between the fringes.

In order to determine this distance more accurately, electron-diffraction pictures were taken. It was impossible to perform ED on a single crystallite, because there was not enough time to bring it into the zone-axis orientation without damage caused by the electron beam. Therefore, a dense population of crystallites was slowly moved across the electron beam. A recorded diffraction pattern is shown in figure 7.6. A few double peaks are observed due to a second crystallite that is partially present in the sampled area. The characteristic (real space) distance calculated from the distance between the spots on a horizontal line in the image was 12.4 Å. The distance of 12.4 Å is likely a better approximation for the distance between the lattice fringes than the approximation obtained directly from the TEM image of figure 7.5. It will become clear in section 7.6, that this distance perfectly matches with the unit-cell dimensions determined by X-ray and neutron diffraction: it corresponds to half of the length of the b-vector. The factor one half comes into play because there are two Phthalcon-11 molecules placed along the b-direction in a unit cell (see section 7.6). From the distance between the fringes, we can therefore conclude that in figure 7.5 the b-direction is in the plane of the picture, perpendicular to the fringes. Since the \( \vec{a} \), \( \vec{b} \), and \( \vec{c} \)-axes (see section 7.6) as well as the sides of the crystals are approximately perpendicular to each other, the lattice vectors approximately correspond

Figure 7.6: Pattern obtained by electron diffraction (KSLA). A few double peaks are due to a second crystallite that is partially in the sampled area. The characteristic (real space) distance calculated from the distance between the spots on a horizontal line in the image was 12.4 Å.
to the crystal axes.

### 7.4.2 Neutron and X-ray diffraction

In order to obtain accurate information on the unit-cell dimensions, the orientation of the Phthalcon-11 molecules in the unit cells, and the atomic positions within the molecules, Rietveld analysis was performed. In Rietveld analysis, a measured diffraction spectrum is compared with the theoretical line profile belonging to a prediction of the structure of the material. The positions of the atoms in the unit cell and/or the dimensions of the unit cell of the predicted structure are then adapted and the theoretical line spectrum that belongs to this new structure is again compared with the experimentally determined spectrum. This step is repeated many times till the theoretical spectrum matches the experimental one as well as possible. In such a way, the predicted structure is optimized.

For the Rietveld analysis two kinds of diffraction spectra were measured: X-ray and neutron powder-diffraction spectra, with wavelengths of 1.041 Å and 2.572 Å respectively. Both X-ray and neutron spectra were used, because the X-ray spectrum had sharp peaks but X-ray spectra lack information on hydrogen atoms, whereas the neutron spectra do contain information on hydrogen atoms but have a lower signal to noise ratio.

A better signal-to-noise ratio in the neutron spectrum was obtained with H$_2$O replaced by D$_2$O in the Phthalcon-11 molecules. Therefore, deuterium-labeled material was used for the neutron powder-diffraction measurement. For the X-ray diffraction, separate measurements on unlabeled Phthalcon-11 and on Phthalcon-11 labeled with D$_2$O were performed to make sure that they had the same structure. The labeled Phthalcon-11 contained 98% D$_2$O.

The X-ray measurement was performed at the Daresbury synchrotron, the neutron measurement at the High Flux Reactor of the Energie Centrum Nederland (ECN).

For the Rietveld analysis the total range of the X-ray spectrum was used, but in the neutron spectrum the data between $72.3^\circ \leq 2\theta \leq 77.6^\circ$ and $89.4^\circ \leq 2\theta \leq 92.6^\circ$ (with $\theta$ the angle of diffraction) were excluded, because vanadium, which was used in the container for the experiment, disturbs the signal in these regimes.

The positions of the atoms, which resulted from the Rietveld analysis, were not well-documented. Therefore, we repeated the analysis. The outcome is described in the next section.
7.5 Rietveld analysis revisited

The main reason to repeat the Rietveld analysis was that the positions of the atoms derived at the KSLA were not well-documented. Besides, Rietveld-analysis software has improved since 1992 (the year in which the analysis was performed at the KSLA).

We used the X-ray and neutron powder-diffraction spectra measured at the KSLA and followed exactly the same procedure concerning the exclusion of the two diffraction-angle regimes (see section 7.4.2). For the Rietveld analysis two computer programs were used: First FOX (Free Objects for Xtallography) as structure-solution program and subsequently GSAS (General Structure Analysis System) as structure-refinement program.

The structure of Phthalcon-11 that follows from the Rietveld analysis is presented in section 7.6. Figure 7.7 shows the measured neutron and X-ray spectra and their respective theoretical spectra for the determined structure. The peaks of both experimental spectra correspond very well to the theoretical ones. The figure also clearly shows that after horizontal scaling the peak positions of the X-ray spectra coincide with those of the neutron spectra.

7.6 Final structure

The final structure that follows from the experiments and the analysis discussed in section 7.4 and section 7.5 has a monoclinic $P_{21}$ unit cell with $|\vec{a}| = 7.2841(4)$ Å, $|\vec{b}| = 24.7487(17)$ Å, and $|\vec{c}| = 7.1579(6)$ Å while the angle $\beta$ between $\vec{a}$ and $\vec{c}$ is $103.659(5)^\circ$. The unit cell contains two molecules that are rotated relative to each other. Several views of the structure are shown in figures 7.8 to 7.10. The coordinates of the atoms are given in appendix C.

The positions of the hydrogen atoms in the H$_2$O ligand followed from the Rietveld analysis. They are not totally in line with the Co-O-H angles as determined with NMR at the KSLA [175]. Still, the existence of a hydrogen bond between one of the two hydrogen atoms with the nitrogen atom of the next molecule in the stack (which followed from the deuterium NMR and also from infrared-spectroscopy experiments) is reproduced by the Rietveld analysis; the distance between the two atoms is 1.871 Å, which is in the range of a typical hydrogen-bond distance (1.6 - 2.0 Å). In appendix C more bond

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1 provided by J. v. Mechelen, University of Amsterdam, the Netherlands
2 For a monoclinic unit cell, $\alpha = \gamma = 90^\circ$
Figure 7.7: Experimental (grey squares) and theoretical (black lines) X-ray (upper graph) and neutron (lower graph) powder diffraction spectra for the determined structure of Phthalcon-11. Note that the diffraction angle $2\theta$ of the X-ray spectra is shown on the upper axis, while for the neutron spectra it is shown on the lower axis. The scale on the upper axis differs from the scale on the lower axis in order to show that after scaling the peak positions of the X-ray spectra coincide with those of the neutron spectra. Inset: magnification of the X-ray spectra for $2\theta \leq 22^\circ$.

distances and angles are given. The distance between the phthalocyanine rings of two adjacent molecules with the same orientation (best shown in figure 7.9) is 3.35 Å. This is equal to the distance between the planes in graphite [176], caused by Van der Waals bonding. A $\pi - \pi$ orbital interaction between the phthalocyanine rings in Phthalcon-11 is expected. The ligands
Figure 7.8: One unit cell of Phthalcon-11. It contains two molecules, which are rotated relative to each other. $\vec{a}$ is the red edge, $\vec{b}$ the green edge, and $\vec{c}$ the blue edge. The rest of the unit cell is shown with black lines. All carbon atoms (and half of the corresponding bondings) are depicted in red, the nitrogen atoms in green, the oxygen atom in black, the cobalt atom in blue, and the hydrogen atoms in grey.

are small enough to fit in the open spaces that arise when the molecules are arranged as shown in figure 7.8 to 7.10, with the typical Van der Waals distance between the phthalocyanine rings.

7.7 Principle of density-functional theory (DFT)

When a molecular or band structure is obtained without using experimental results, but purely by calculations based on the Schrödinger equation, the method is called ‘ab initio’ or ‘derived from first principles’. An example is density-functional theory (DFT). In this section, we shortly describe the idea behind DFT and how it is used in practice to determine a molecular or band structure.
The basis of DFT forms the Schrödinger equation:

\[ H \Psi = E \Psi, \tag{7.1} \]

with \( \Psi \) being the wave function of the system, \( E \) its energy, and \( H \) the Hamiltonian. We consider a system of \( M \) nuclei that are assumed to be fixed in space at positions \( \vec{R}_1, \vec{R}_2, \ldots, \vec{R}_M \) and \( N \) electrons with (variable) positions \( \vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N \). For such a system, \( H \) is given by

\[ H = \sum_{i=1}^{N} \left( -\frac{\hbar^2}{2m} \nabla_i^2 - \sum_{j=1}^{M} \frac{Z_j e^2}{|\vec{r}_i - \vec{R}_j|} \right) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}, \tag{7.2} \]

where \( \hbar \) is the reduced Planck constant, \( m \) the electron mass, \( e \) its charge, and \( Z \) the charge of a nucleus. Since \( \Psi \) is the wave function of all electrons together (i.e. \( \Psi = \Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \)), equation 7.1 is hard to solve.

Fortunately, Hohenberg and Kohn [177] proved that, provided that the state is non-degenerate, the total ground-state energy \( E_0 \) of a system with
fixed nuclei and electron density $n(\vec{r})$ is a unique function of $n(\vec{r})$. This means that not only $E_0$ can be derived from $n(\vec{r})$ (with only one solution), but also that $n(\vec{r})$ can be derived from $E_0$ (with only one solution). Subsequently, Kohn and Sham [178] showed that it is possible to replace the many-electron problem by an exactly equivalent set of self-consistent one-electron equations. Thanks to these two theorems, the total energy $E$ of the system under consideration can be written as a function of $n(\vec{r})$:

$$E = \int V_{\text{ion}} n(\vec{r}) d\vec{r} + \frac{1}{2} \int \int \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + T_0 + E_{xc}, \quad (7.3)$$

where $T_0$ is the kinetic energy of a system with non-interacting electrons, $E_{xc}$ the exchange-correlation energy, which contains all remaining electronic
effects (see below), and $V_{\text{ion}}$ is the Coulomb energy resulting from the interaction of the electrons with the ions. It is given by

$$V_{\text{ion}} = -\sum_{j=1}^{M} \frac{Z_{j}e^{2}}{|\vec{r} - \vec{R}_{j}|}. \quad (7.4)$$

The exchange-correlation energy $E_{\text{xc}}$, which was introduced in equation 7.3, takes care of all electron-electron interactions other than the Coulomb interaction: the Pauli-exclusion principle, and the difference in kinetic energy of a system with and without interacting electrons.

Since the minimum of equation 7.3 gives the ground state of the system [177], the ground-state electron density can in principle be determined by minimizing this equation with the help of a computer program.

Apart from the electron densities, the equilibrium positions of the atom cores can also be determined by DFT. Each time when the electron density is updated in a computer program, the force $\vec{F}_{j}$ on the $j^{\text{th}}$ nucleus can be calculated by using

$$\vec{F}_{j} = -\frac{dE}{dR_{j}}. \quad (7.5)$$

This gives a handle to bring the position of the atom core closer to the equilibrium position.

For the calculations of the ground-state electron density and the equilibrium atom-core positions, computer programs have to use some approximations and tricks. These are treated in the remainder of this section.

$E_{\text{xc}}$ of molecules is not exactly known. It can be approximated in several ways. One method is the local-density approximation (LDA). LDA approximates the exchange-correlation energy at each point with the exchange-correlation energy of a homogeneous electron gas (for which good estimations exist) having the same overall density. Another method is the generalized gradient approximation (GGA), which also takes into account the gradient in the local density. GGA is more accurate than LDA, but it has the disadvantage of using more computer time and memory.

Crystalline solids have a molecular structure that consists of a unit cell that is repeated in the directions of the unit cell vectors. This is exploited in computer programs for DFT calculations by imposing periodic boundary conditions and making the calculations only for one Brillouin zone.

In principle, the density should be known everywhere in the Brillouin zone. This is, however, impossible in practice. Therefore, computer programs only use a discrete set of points in the Brillouin zone. These points
are called ‘k-points’. Making the grid of k-points denser increases the accuracy, but it also increases the memory and time needed for the calculation. Smart ways for the choice of k-points exist, like the method of Monkhorst and Pack [179]. Also, the symmetry of the unit cell can be used to reduce the number of k-points. The number of k-points that remain after using the symmetry is referred to as the number of ‘irreducible k-points’.

Another method to facilitate the computer calculations is the use of pseudopotentials. The real electronic wave functions are hard to work with, because they oscillate heavily close to the nuclei. However, it is known that most material properties are governed by the valence electrons. Hence, in practice it is convenient to use pseudopotentials: a pseudopotential resembles the real potential at the distance of the valence electrons and distances farther from the nucleus\(^3\), but near the nucleus it is soft (i.e. it does not oscillate).

### 7.8 Computational Details

For our DFT calculations, we used the Vienna Ab-initio Simulation Package (VASP)\(^4\). The allowed error in the total energy had the default value of \(10^{-4}\) eV, which is \(10^6\) times smaller than the total energy. The ultra-soft pseudo potentials supplied with VASP and a mesh of 54 irreducible k-points were used. For the approximation of the exchange-correlation energy, we did one check with GGA. It turned out to give the same results as LDA for our material and the accuracy described above. We then continued by performing the calculations with LDA. As input, we used the structure described in section 7.6 and appendix C. Equilibrating the structure with VASP did not alter the positions of the atom cores.

### 7.9 Results of DFT for Phthalcon-11

Normally, in band-structure calculations, the energy bands are calculated along high-symmetry lines. In particular, often the directions of the unit-cell axes are used. Following this procedure, we find the band energies (of the bands around the Fermi level) in the \(\vec{a}\), \(\vec{b}\), and \(\vec{c}\) directions as shown in figure 7.11. For the calculations, the encircled atom in figure 7.12 was taken as a reference atom: the lines in the \(\vec{a}\), \(\vec{b}\), and \(\vec{c}\) directions along which

\(^3\)At least until a certain cut-off distance.

\(^4\)VASP has been developed by G. Kresse and J. Furthmüller, Institut für Materialphysik, Universität Wien, Wien, Austria.
the band structures were calculated had this atom in common as a starting point. The reason for this was to make sure that we did not calculate band structures far away from the Phthalcon-11 molecules in the unit cell.

Figure 7.11: Bands around the Fermi level in the $\vec{a}$, $\vec{b}$, and $\vec{c}$ directions, along lines through the encircled atom in figure 7.12. The Fermi level is between the second and the third band from below.

From a figure with a band structure, like figure 7.11, information can be obtained on the band gap and on the anisotropy of the conduction.

For DFT calculations that use LDA (like our calculations), the band gap cannot be determined accurately; it generally gives a considerable underestimation, see for example refs [180, 181, 182, 183, 184]. Usually, an underestimation of 30 to 50 % is found [185]. The band gap (shown as the difference between the second band from below (the HOMO) and the third band from below (the LUMO) in figure 7.11) in all three directions has value of 0.7 eV. This value can be compared with the experimentally determined value of 1.2 eV, found by absorption spectroscopy at a temperature of 1.2 K at the KSLA [160]. The value obtained by the DFT calculations is 42 % lower than the experimentally determined value, which is in agreement with the expected underestimation.

At low temperatures, the anisotropy in the conduction can be derived from the band structure, because the mobility of a charge carrier in a band
Figure 7.12: Visualization of the directions A, B and C (purple lines) that were used for the non-standard (see text) DFT calculations. The line through the encircled atom, perpendicular to the phthalocyanine ring structure was used in these calculations too, but is not shown in this figure. The atom in the circle is also the starting point for the calculations in the $\vec{a}$, $\vec{b}$, and $\vec{c}$ directions. The molecules shown lie in different unit cells; they differ by a vector $\vec{c}$.

is then inversely proportional to its effective mass $m^*$ [64], which is given by [64]

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2\varepsilon}{dk^2},$$

(7.6)

with $\hbar$ being the reduced Planck constant, $\varepsilon$ the energy and $\vec{k}$ the position in the reciprocal space. As a consequence, charge carriers in a band with a largely fluctuating dispersion are more mobile than charge carriers in a band with a low variation in dispersion, which leads to a higher conduction in the former case\(^5\). This argument is based on the Drude theory, discussed in

\(^5\)The charge-carrier density, with which the mobility should be multiplied to obtain the conductivity, is expected to be independent of the direction.
section 2.2.3. In organic semiconductors like Phthalcon-11, the band width is only of the order of 0.1 eV (see figure 7.11), which is at room temperature comparable to the thermal energy (0.04 eV). For such materials, the Drude theory is not appropriate at room temperature, because then the electrons cannot be seen as extended wave packages, but they are localized in the minima of the bands due to the electron-phonon coupling. Obtaining quantitative information on the anisotropy in the conduction is not straightforward in such a case, but requires a tedious analysis [186]. We will not analyze our results that thoroughly and we can therefore not give quantitative information on the anisotropy in the conductivity of a Phthalcon-11 crystal. Still, also at room temperature, a large fluctuation in $\varepsilon(k)$ leads to a higher mobility than a constant $\varepsilon(k)$, which allows us to give a qualitative analysis.

Figure 7.11 shows that the variation in dispersion of all energy bands, in particular of the HOMO (used for hole transport) and the LUMO (used for electron transport), is much lower in the $\vec{b}$-direction than in the other two directions. This would give the conclusion that the mobility along $\vec{b}$-direction is much lower than along the other directions. In addition, hole transport along the $\vec{c}$-direction is less efficient than along the $\vec{a}$-direction due to less variation in dispersion of the HOMO. These results are in accordance with the old ab-initio calculations at the KSLA, from which it was claimed that the conductivity along the $\vec{b}$-direction is a factor 10 smaller than along the $\vec{c}$-direction, which on its turn is a factor 10 smaller than along the $\vec{a}$-direction [32].

However, inspection of the unit cell (see for example figure 7.8) shows that a direct conduction along the $\vec{b}$-direction is indeed not expected, because the phthalocyanine rings in the Phthalcon-11 molecules are slightly tilted with respect to the b-axis. A more logical way of conduction would be along the direction of the phthalocyanine rings. This can effectively result in a conduction in the $\vec{b}$-direction when conduction can also take place from a molecule in one stack to a molecule in the adjacent stack (tilted with respect to the former stack).

In order to get a more realistic insight in the anisotropy of the conduction, we calculated the band structure along directions that are non-standard for DFT calculations, but that are more logical for charge transport in Phthalcon-11. Figures 7.12 and 7.13 show these non-standard directions. They are

- In the plane of a phthalocyanine ring structure, pointing towards the adjacent (tilted) stack. This direction is denoted with the letter 'A' in figures 7.12 and 7.13.
Figure 7.13: Visualization of the directions (in purple) that were used for the DFT calculations. The directions are equal to those in figure 7.12, but shown from another side and with the circle omitted.

- In the plane of a phthalocyanine ring structure, perpendicular to the previous direction. This direction is denoted with the letter ‘B’ in figures 7.12 and 7.13.
- The direction perpendicular to the plane of the phthalocyanine ring structure. This direction is not shown in figures 7.12 and 7.13.
- The direction for transport from one phthalocyanine ring to an adjacent ring, which is tilted with respect to the former ring and lies in the unit cell next to the unit cell of the former ring, displaced in the $\vec{c}$-direction (this molecule appeared to have the best overlap with the original molecule). This direction is denoted with the letter ‘C’ in figures 7.12 and 7.13.

A combination of lines A, C, and again A (but then for the second molecule) effectively gives transport in the $\vec{b}$-direction. The result of the calculations is shown in figure 7.14.

In can be concluded from figure 7.14 that transport along the phthalocyanine rings (inclusive the transport from two adjacent rings), giving an
effective conduction in the $\vec{b}$ direction, is quite efficient: the fluctuations in the dispersion of the corresponding bands is even somewhat higher than that along the direction denoted with the letter ‘B’ in figures 7.12 and 7.13. In order of magnitude, the variations in the dispersions (and thus the conduction) of all four directions are equal. For the old ab-initio result that gave a factor of 100 difference [32], the logical transport directions had not been taken into account. Notice that the HOMO (used for hole transport) and for the LUMO (used for electron transport) have in all four directions a variation in dispersion of the same order of magnitude.

The remainder of this section gives a few remarks on the validity of the results.

The DFT calculations of VASP are bulk calculations: they use periodic boundary conditions, which effectively makes the material infinitely large. One might wonder whether this is justified for transport in Phthalcon-11 crystallites. A simple calculation based on the unit-cell vectors reveals that...
a Phthalcon-11 crystal with a typical size of 200 nm x 50 nm x 50 nm contains $4 \cdot 10^5$ unit cells. As this is a huge number, a large part of every crystal indeed will show bulk behavior.

Due to the periodic boundary conditions, the calculations are not correct for the outer layers of the crystals. Even under the assumption that the results are also good predictions for the outer layers, there is another problem: The calculations do not give any information on the transport between crystallites. Experiments at the KSLA revealed that each crystal contains two sides were CN, H$_2$O and OH groups stick out, whereas the other sides have the benzene rings of the phthalocyanine ring structure at the outside [31], see figure 7.15. As a consequence, the exit potential may depend on the side of the crystal. The charge transport between two crystals will then be influenced by the orientation of the crystals with respect to each other. As shown in chapter 4, the contact between particles plays an important role in the final DC conductivity. When indeed the exit potential depends strongly on the side of the crystal, this would have a larger influence in the nanocomposite coatings than in compressed powder; in the 3-dimensional powder the charge carriers can circumvent bad electrical crystal contacts caused by an unfavorable orientation by taking another route, along crystals that have a favorable orientation with respect to each other, whereas in the quasi-1-dimensional channels in the coatings, all bad electrical contacts have to be passed. However, we saw in the experiments discussed in the pre-

![Figure 7.15: Schematic picture of the kind of groups that stick out on different sides of the Phthalcon-11 crystals. The ellipses denote benzene rings. The groups are not drawn on scale with respect to the crystal size; in reality many more groups stick out.](image)
vious chapters that the difference between the channel conductivity inside the coatings and the powder conductivity is negligible. Hence, we believe that the influence of the difference in exit potentials on the various sides of the Phthalcon-11 crystallites is small.

The calculations treated in this chapter do not take into account imperfections. The measurements of section 3.4.1 showed that imperfections are likely present in the batch of Phthalcon-11 crystals used for our experiments of chapter 3, 4, and 5.

As discussed earlier in the present section, the analysis of the conductivity by using the variation in the dispersion holds strictly speaking only for low temperatures. At higher temperatures (like at room temperature) the analysis becomes more complicated.

7.10 Conclusions

In the past, many (non-published) experiments were performed at the KSLA from which the molecular and crystal structure of Phthalcon-11 followed. We used these data and repeated the Rietveld analysis of the crystal structure, which gave the positions of the atoms in a monoclinic $P2_1$ unit cell with $|\vec{a}| = 7.2841(4)$ Å, $|\vec{b}| = 24.7487(17)$ Å, $|\vec{c}| = 7.1579(6)$ Å and $\beta = 103.659(5)^\circ$. The unit cell contains two molecules, tilted with respect to each other.

The found structure was used for DFT calculations to determine the band structure. Contact problems between different crystals and imperfections were not taken into account in the calculations; the calculations only hold for the bulk conductivity inside the crystals.

Since DFT calculations usually give an underestimation of 30 to 50 % for the band gap, the obtained value of 0.7 eV is in line with the experimental value of 1.2 eV, determined at the KSLA.

Our straightforward calculations of the band dispersions would suggest that the conduction along the $\vec{b}$-direction is much lower than in the other lattice-vector directions. This is in accordance with earlier ab-initio calculations at the KSLA. However, when the band structures along more logical charge-transport directions are calculated, the mobility in the effective $\vec{b}$-direction turns out to be at least as high as in the other directions. We therefore conclude that the anisotropy in the crystal conduction is small.

The batch of Phthalcon-11 used for the measurements discussed in chapters 3, 4, and 5 had a purity of 95 %, while the one for the KSLA measurements (chapter 7) had a purity of at least 99.5 %.
Chapter 8

Conclusions

A specific set of Phthalcon-11/epoxy coatings was investigated in order to get insight in two remarkable and general aspects of a wider class of conducting polymer nanocomposites that are made by filler aggregation during matrix curing:

- a critical filler fraction \( \phi_c \) much lower than 16 vol\% 
- a saturation conductivity level \( \sigma_{\text{max}} \) orders of magnitude lower than the conductivity of the filler particles \( \sigma_f \).

By analyzing the conductivity of the specific Phthalcon-11/epoxy coatings as a function of electric field, temperature, and frequency, and locally (with C-AFM), and comparing with the conductivity of the Phthalcon-11 powder -also measured as a function of electric field, temperature, and frequency-, the following results were found:

- The Phthalcon-11/epoxy coatings as well as the Phthalcon-11 powder showed an electric-field and temperature dependence that indicates that variable-range hopping by cotunneling over the filler network is the charge-transport mechanism.
- From the critical frequencies for the onset of enhanced AC conductivity of the nanocomposite coating and the powder, the same typical microstructure length scale follows.
- The conductivity of the particle channels inside the Phthalcon-11/epoxy coatings is of the same order of magnitude as the filler-powder conductivity.

From these three results, we conclude that **the morphology of the Phthalcon-11/epoxy coatings is optimal in the sense that the Phthalcon-11 crystals really touch each other** as they do in pressed powder. The large reduction of \( \sigma_{\text{max}} \) compared to \( \sigma_f \) is therefore not caused by insulating
layers of the matrix between the particles.

This conclusion was used in combination with the results of Chen et al. [19], who measured the fractal dimension of the Phthalcon-11 aggregates in the epoxy coatings and determined the critical filler fraction, to construct a microscopic model from which quantitative information on the conductivity as a function of filler fraction for the relevant class of polymer nanocomposites can be derived. The model was based on the fact that the measured fractal dimension indicated diffusion-limited cluster aggregation (DLCA) as the network-formation mechanism. We assumed that the aggregates formed in this way are randomly distributed throughout the material and that neighboring particles inside the aggregates and between the aggregates touch. The model yields that the saturation conductivity of a polymer nanocomposite decreases with decreasing critical filler fraction and this decrease is disproportional, i.e., stronger than linearly. As a result, for applications, a compromise has to be made between a low critical filler fraction and a high $\sigma_{\text{max}}$. Of course, this may not hold for composites for which the model does not apply, but it is true for composites with a particle network formed by DLCA, provided that other limitations (discussed below) are not the decisive factor. For the investigated Phthalcon-11/epoxy coatings, the model yields that the fractal geometry will give a saturation conductivity $\sigma_{\text{max}}$ that is a factor $10^4$ lower than the conductivity of the filler powder, in agreement with our measurements.

The measurements on the Phthalcon-11 particles also showed that there is a difference of a factor 100 between the conductivity of the Phthalcon-11 powder and the intrinsic conductivity of a Phthalcon-11 crystal. Thus, even when the particles touch, the conductivity is limited by the interparticle tunneling transport.

Moreover, measurements on much smaller antimony-doped tin oxide (ATO) particles revealed that the difference between the powder conductivity and the intrinsic particle conductivity becomes even larger with decreasing particle size. This is caused by the Coulomb charging energy, which is larger for smaller particles and which reduces the effective density of states for the tunneling transport. Phthalcon-11 crystals ($\sim 100 \text{ nm}$) turned out to be large enough to neglect the loss in conductivity due to a reduction of the effective density of states, whereas ATO particles ($\sim 7 \text{ nm}$) are not.

When the conductivity of filler particles depends on the direction in the crystal, this would have a large influence for the conductivity of the nanocomposite -more than in the pure (3-dimensional) filler powder- because in the quasi 1-dimensional particle channels in the nanocomposite un-
favorably oriented particles cannot be circumvented in the charge transport. Using density-functional theory (DFT), we calculated that the anisotropy in the conductivity of a Phthalcon-11 crystal is negligible.

In conclusion, for the investigated Phthalcon-11/epoxy coatings the conductivity is much lower than the intrinsic conductivity of the Phthalcon-11 crystals due to

- bad electrical contact between the crystals, even though the mechanical contact between the crystals is good. This reduces $\sigma$ with a factor $10^2$.
- the geometry of the particle network. This reduces $\sigma$ with a factor $10^4$.

Other factors that can reduce the conductivity of a nanocomposite compared to the intrinsic conductivity of its filler, but which were excluded (or can be neglected) for the investigated Phthalcon-11/epoxy coatings are

- the size of the particles; when they are too small, the effective density of states is reduced due to charging effects
- insulating layers of the matrix between the particles
- anisotropy in the conductivity of a particle.
Appendix A

Derivation of VRH parameters $T_0$ and $\gamma$ in the case of superlocalization

In this appendix, we derive equations for the VRH parameters $T_0$ and $\gamma$ in the case of hopping on a fractal structure (see sections 2.2.3 and 3.4.2). We use the same method as Mott [67], but include superlocalization of the electronic wave function on a fractal. References [72, 112, 113, 114, 8] also treat the temperature dependence of the conductivity on a fractal structure, but these papers discuss the derivation less extensively than we do.

Our derivation below is written as if we are dealing with point sites. However, there is a subtle analogy with the case of cotunneling in a network with large (compared to the localization length and the site-to-site distance) crystals. Since in the latter case there is a coherence between hopping probabilities extending over several crystals, it corresponds to the case of superlocalization in a network of point sites when the localization length is replaced by an effective length scale that is a measure for the coherence length.

Section A.1 treats a derivation of $T_0$ and $\gamma$ for a constant DOS, and section A.2 deals with a derivation for a DOS with a Coulomb gap, which can be the consequence of the interaction between hopping electrons and the holes that they leave behind (see section 2.2.3 or ref. [71]). In the last section, the crossover temperature between the two regimes is calculated.

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A.1 Constant DOS

On a fractal structure the wave functions $\Psi$ of the charge carriers as a function of the distance $r$ are given by

$$|\Psi(r)|^2 \propto \exp[-2(\alpha r)^\zeta], \quad (A.1)$$

where the exponent $\zeta > 1$ enters because of superlocalization and $\alpha$ is the inverse localization length. The probability $W_{ij}$ to hop from an occupied site $i$ to an empty site $j$ with a higher energy is then given by

$$W_{ij} \propto \exp[-(\alpha r)^\zeta - \beta E_{ij}], \quad (A.2)$$

where $\beta = 1/(k_B T)$ ($k_B$ is Boltzmann’s constant and $T$ is the temperature) and $E_{ij}$ is the energy difference between site $i$ and site $j$. Mott stated that there exist a typical distance $R_M$ and a typical energy $E_M$ that mainly determine the conductance (see also chapter 2). The general form of the Mott condition is

$$\int_{|\vec{r}|<R_M} dr \int_{E<E_M} dE g(E) = p, \quad (A.3)$$

where $p$ is a constant of order one and $g$ the density of states. On a fractal with fractal dimension $d_f$ and for a constant density of states $g_F$ near the Fermi level, the Mott condition gives

$$E_M = \frac{p}{g_F} R_M^{-d_f}. \quad (A.4)$$

To determine $E_M$ and $R_M$, the expression for $E_M$ (equation (A.4)) is substituted for $E_{ij}$ in equation (A.2), where $R_M$ is still taken to be a variable $r$. Then, the optimum of equation (A.2) is found by setting the derivative to $r$ to zero.

$$\alpha \zeta r^{\zeta-1} - \beta \frac{pd_f}{g_F} r^{-d_f-1} = 0. \quad (A.5)$$

The solution of this equation gives $R_M$:

$$R_M = \left(\frac{\beta pd_f}{\alpha \zeta g_F}\right)^{1/(d_f+\zeta)}. \quad (A.6)$$

Subsequently, equation (A.4) gives

$$E_M = \left(\frac{p}{g_F}\right)^{\zeta/(d_f+\zeta)} \left(\frac{\alpha \zeta}{\beta d_f}\right)^{d_f/(d_f+\zeta)}. \quad (A.7)$$
Substituting the expressions for $R_M$ and $E_M$ (equations (A.6) and (A.7)) for $r$ and $E_{ij}$ respectively in equation (A.2) yields

$$W_{ij} \propto \exp \left[ - \left\{ \frac{\beta p \alpha d_f}{g_F} \left( \frac{d_f}{\zeta} + \left[ \frac{\zeta}{d_f} \right]^{d_f/\zeta} \right)^{\zeta/(d_f+\zeta)} \right\} \right]$$

as the probability for the hops that determine the conductivity $\sigma$. Hence,

$$\sigma \propto W_{ij} \propto \exp \left[ - (T_0/T)^\gamma \right],$$

with

$$\gamma = \zeta/(d_f + \zeta)$$

and

$$T_0 = \frac{pe^{d_f}}{g_F k_B} \left( \frac{d_f}{\zeta} + \left( \frac{\zeta}{d_f} \right)^{d_f/\zeta} \right).$$

Notice that the original equations of Mott (see section 2.2.3) are found by substituting $\zeta = 1$ and $d_f = d$, with $d$ the Euclidean dimension.

### A.2 Coulomb gap

In the case of a Coulomb gap, the density of untrapped states is given by (see section 2.2.3 and refs [71, 69]):

$$g(E) = ce^{d_f} E^{d_f-1}/e^{2d_f},$$

where $c$ is an unknown numerical coefficient, $\epsilon$ is the the dielectric constant equal to $\epsilon_0\epsilon_r$, and $e$ is the electron charge. The Mott condition (equation (A.3)) then gives

$$E_M = \left( \frac{d_f p}{c} \right)^{1/d_f} \frac{e^2}{R_M \epsilon}. $$

Like in section A.1, equation (A.13) is substituted in equation (A.2) and the optimal hop is found by setting the derivative to $r$ to zero. The solution gives $R_M$:

$$R_M = \left( \frac{\beta e^2}{\zeta \alpha \epsilon} \left( \frac{d_f p}{c} \right)^{1/d_f} \right)^{1/(\zeta+1)}. $$

Substitution in equation (A.13) results in

$$E_M = \frac{e^2}{\epsilon} \left( \frac{d_f p}{c} \right)^{\frac{\zeta}{\zeta+1}} \left( \frac{\beta e^2}{\zeta \alpha \epsilon} \right)^{-1/(\zeta+1)}. $$

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Finally, substituting in equation (A.2) for \( r \) the expression for \( R_M \) (equation (A.14)) and for \( E_{ij} \) the expression for \( E_M \) (equation (A.15)) leads to

\[
\sigma \propto W_{ij} \propto \exp \left[ - \left( \frac{T_0}{T} \right)^{\gamma} \right], \quad (A.16)
\]

with

\[
\gamma = \frac{\zeta}{\zeta + 1} \quad (A.17)
\]

and

\[
T_0 = \frac{e^2 \alpha}{k_B \epsilon} \left( \frac{d_J \rho}{e} \right)^{1/d_J} \left( \frac{\zeta^{-1} + 1}{\zeta} \right)^{1/\zeta}. \quad (A.18)
\]

Efros and Shklovskii [71] considered the case with \( \zeta = 1 \) and \( d_J = d \). In that case \( \gamma = 1/2 \).

### A.3 Crossover temperature

The crossover temperature \( T_{\text{cross}} \) between a regime where the Coulomb gap is felt and a regime where the DOS at the Fermi level can be approximated by a constant is found by equalling the factor \( (T_0/T)^\gamma \) of section A.1 with that of section A.2. Let subscripts ‘CG’ and ‘cDOS’ used in combination with \( T_0 \) and \( \gamma \) denote the values of \( T_0 \) and \( \gamma \) in the case of a Coulomb gap and a constant density of states, respectively. The calculation of \( T_{\text{cross}} \) then follows as:

\[
\left( \frac{T_{0,\text{cDOS}}}{T_{\text{cross}}} \right)^{\gamma_{\text{DOS}}} = \left( \frac{T_{0,\text{CG}}}{T_{\text{cross}}} \right)^{\gamma_{\text{CG}}} \quad (A.19)
\]

\[
T_{\text{cross}} = \left( \frac{T_{0,\text{CG}}}{T_{0,\text{cDOS}}} \right)^{\gamma_{\text{CG}}/\gamma_{\text{DOS}}} \left( \frac{\gamma_{\text{CG}}}{\gamma_{\text{DOS}}} \right)^{1/(\gamma_{\text{CG}} - \gamma_{\text{DOS}})} \quad (A.20)
\]
Appendix B

Explanation of time-temperature scaling in nanocomposites

In this appendix an explanation for the time-temperature superposition principle (TTSP) is given. This principle means that, after scaling both the conductivity of a material and the frequency, a master curve of the conductivity versus the frequency exists, see chapter 3. Our explanation of the TTSP is based on the Einstein diffusion equation:

\[ \sigma' = n e \mu = \frac{n e^2 D}{k_B T}, \]  

(B.1)

where \( n \) is the number of electrons or holes per unit volume, \( e \) the electronic charge, \( \mu \) the mobility, \( D \) the diffusion coefficient, \( k_B \) Boltzmann’s constant, and \( T \) the temperature. When the charge carriers are ions, \( n e^2 \) should be replaced by \( n_{ion} q^2 \), with \( n_{ion} \) the density of the mobile ions and \( q \) the charge of an ion. For convenience, we consider the case where the charge carrier is a hole or an electron. We follow the reasoning of Adriaanse et al. [12]. They considered a nanocomposite in which the conductive fillers form a percolating network, indicated with symbol “\( \infty \)”, as the percolating network in a sample is quasi infinite. In addition, the network contains smaller, finite clusters, denoted by the subscript “\( f \)”. Their contribution to the direct-current (DC) conductivity is zero, but they do have a non-zero contribution to the alternating-current (AC) conductivity. They are assumed to be smaller than the percolation length \( \xi \). This picture is totally consistent with the model we have for our nanocomposites (see chapter 6).
The total conductivity is the sum of the conductivity of the percolating network and that of the finite clusters\(^1\):

\[
\sigma' (\omega) = \sigma'_{\infty} (\omega) + \sigma'_f (\omega). \tag{B.2}
\]

The frequency dependent diffusion coefficient of a network is given by

\[
D (\omega) = \frac{a^2}{\tau} \left( \frac{R (\omega)}{a} \right)^{2-d_w}, \tag{B.3}
\]

where \(a\) is the typical hopping length, \(\tau(T)\) the typical (temperature-dependent) time between the hops of a single charge carrier, and \(R\) the frequency dependent average displacement of the charge carrier, defined as

\[
R^2(t) \propto t^{2/d_w}, \tag{B.4}
\]

with \(d_w\) being the random-walk dimension, discussed in chapter 6.

When the frequency is so small that the charge carriers, within one period, travel distances that are larger than \(\xi\), the Einstein diffusion equation (equation (B.1)) gives the following conductivity:

\[
\sigma' = \sigma'_\infty = \frac{n_\infty e^2}{6 k_B T} \frac{a^2}{\tau} \left( \frac{\xi}{a} \right)^{2-d_w,\infty} := \sigma_{\text{DC}}, \quad \text{for } \omega < \omega_\xi, \tag{B.5}
\]

with \(n_\infty\) being the charge carrier density contributing to the current on the percolating network, \(d_w,\infty\) the random-walk dimension of the percolating network, and \(\omega_\xi\) the frequency at which the charge carriers travel a distance \(\xi\) during one period. Since the expression for \(\sigma'\) in equation (B.5) is independent of \(\omega\) and also gives the conductivity at \(\omega = 0\), we call it “\(\sigma_{\text{DC}}\)”.

At frequencies higher than \(\omega_\xi\), but lower than \(\tau^{-1} = \omega_\tau\), the transport on the percolating network depends on the ratio between \(\omega\) and \(\omega_\tau\). Since \((R/a)^{d_w} = t/\tau = (\omega/\omega_\tau)^{-1}\), the conductivity on the percolating network for frequencies between \(\omega_\xi\) and \(\omega_\tau\) becomes

\[
\sigma' = \frac{n_\infty e^2}{6 k_B T} \frac{a^2}{\tau} \left( \frac{\omega}{\omega_\tau} \right)^{1-2/d_w,\infty}, \quad \text{for } \omega_\xi < \omega < \omega_\tau. \tag{B.6}
\]

For the conductivity on the finite clusters, a similar equation holds, but with \(n_\infty\) replaced by \(n_f\) (the charge carrier density on the finite clusters)

\(^1\)To avoid confusion between the frequency \(f\) and the subscript \(f\) used to denote the finite clusters, we used the symbol \(\omega\) for the frequency. In the rest of the thesis, \(\omega\) was defined as the angular frequency. The difference of a factor \(2\pi\) is irrelevant for the explanation in the present appendix.
and $d_{w,\infty}$ replaced by $d_{w,f}$, which may be another random-walk dimension than on the percolating cluster. This results in the following equation:

$$\sigma' = \sigma_{\infty} + \sigma_f = \sigma_{\infty} + n_f \frac{e^2 a^2}{6k_B T \tau} \left( \frac{\omega}{\omega_T} \right)^{1-2/d_{w,f}}, \text{ for } \omega < \omega_T. \quad (B.7)$$

Using the equations in the text above, the total conductivity ($\sigma' = \sigma_{\infty} + \sigma_f$) can be expressed in terms of $\sigma_{DC}$:

$$\sigma' = \sigma_{DC}, \text{ for } \omega < \omega_\xi \quad (B.8)$$

and

$$\sigma' = \sigma_{DC} \left\{ \left( \frac{\omega}{\omega_T} \right)^{1-2/d_{w,\infty}} \left( \frac{a}{\xi} \right)^{2-d_{w,\infty}} + \frac{n_f}{n_\infty} \left( \frac{\omega}{\omega_T} \right)^{1-2/d_{w,f}} \left( \frac{a}{\xi} \right)^{2-d_{w,\infty}} \right\}, \quad (B.9)$$

for $\omega_\xi < \omega < \omega_T$.

In general, it is possible to scale data when

$$\frac{\sigma'}{\sigma_0} = F \left( \frac{\omega}{\omega_0} \right), \quad (B.10)$$

where $\sigma_0'$ and $\omega_0$ are independent of $\omega$, but may depend on $T$. $F(x)$ is a function of $x$ only. When defining $\sigma_0' = \sigma_{DC}$ and $\omega_0 = \omega_T$, it is easy to see that equations (B.8) and (B.9) have the form of equation (B.10) if $a/\xi$, $d_{w,\infty}$ and $n_f/n_\infty$ are independent of frequency and temperature. $a$, $\xi$ and $d_{w,\infty}$ are properties of the fixed network and are therefore indeed independent of $\omega$ and $T$. In addition, we expect $n_f$ to be proportional to $n_\infty$, which makes the ratio of $n_f$ and $n_\infty$ also independent of $\omega$ and $T$. Therefore, scaling is possible. Moreover, as the expression for $\sigma_{DC}$ contains $\tau^{-1} = \omega_T$, a scaling of $\omega$ with $\sigma_{DC}$ is possible. The exact scaling depends on the temperature dependence of $n_\infty$. For example, if $n_\infty$ is constant, equation (B.5) gives that $\omega_T \propto \sigma_{DC} T$, and if $n_\infty \propto T$, then $\omega_T \propto \sigma_{DC}$. These two manners of scaling are often seen in experiments (see for example [94, 88] for scaling with $\sigma_{DC} T$ and [99, 100, 101] for scaling with $\sigma_{DC}$). Some of the materials in those experiments, were disordered solids, other than nanocomposites. This is because the TTSP can actually be derived in a more general way than it was done above. In systems where hopping is the conduction mechanism, the Einstein diffusion equation (equation (B.1)) is valid. In the special case of a nanocomposite with an infinite particle network and finite particle aggregates, the Einstein diffusion equation yields equations (B.8) and (B.9).
More generally, for other disordered systems, a derivation analogous to the one above would yield equation (B.10) with $\omega_0 = \omega_\tau$ and
\[
\sigma'_0 = \sigma_{DC} = \frac{ne^2}{6k_B T} \frac{a^2}{\tau} G \left( \frac{\omega}{\omega_0} \right),
\]  
where $G(x)$ is a function of $x$ only. As already mentioned, similar equations hold when the charge carriers are ions instead of electrons or holes. For example, Sidebottom [95] uses the Einstein diffusion equation to prove the existence of scaling in glasses with ionic motion. In his derivation, the diffusion coefficient had a simpler form than the one treated here. The reason for is that the glasses were assumed to have a homogeneous (not a fractal) structure. The TTSP has also been proven by other means than the Einstein diffusion equation [94, 97, 98].

We remark that scaling for $\omega > \omega_\tau$ is in general not possible.
Appendix C

Atomic positions in Phthalcon-11

The coordinates of the atoms in Phthalcon-11 that we used for the DFT calculations are given in table C.1. The positions ($\vec{r}$) are given in relative coordinates: $\vec{r} = a\vec{a} + b\vec{b} + c\vec{c}$, with $\vec{a}$, $\vec{b}$, and $\vec{c}$ being the unit-cell vectors and $a$, $b$, and $c$ the coordinates. The names of the atoms correspond to the labels shown in figure C.1. Table C.2 contains several bond angles and distances.

Figure C.1: Labeling of the atoms in Phthalcon-11.
Table C.1: Relative coordinates (see text) of the atoms in the Phthalcon-11
unit cell, as used for the DFT calculations.

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<th>b</th>
<th>c</th>
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Table C.2: Bond angles and distances. “H(62)•••N′(43)” refers to the hydrogen bond between two molecules.

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<td>N(43)-C(42)-CO(41)</td>
<td>156.85°</td>
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Bibliography


[35] The specific set of coatings prepared as described in section 3.3 and ref. [19] is meant.


[140] taken from work of Ming Yuan and Joachim Loos, Eindhoven University of Technology, the Netherlands.


List of Publications


Articles on the following topics are in preparation:

• scaling behavior for DC conduction in disordered materials, investigated by computer simulations

• the influence of particle size and chemical composition of Phthalcon

• the analysis of the structure of Phthalcon-11.
Summary

Charge transport and morphology in nanofillers and polymer nanocomposites

An insulating polymer can be made semiconductive by mixing it with (semi)conducting nanoparticles. Even for filler particles with a low aspect ratio, in some cases, the polymer can already be made semiconductive with a filler amount of less than 1 vol%. These nanocomposites generally have a conductivity that is orders of magnitude lower than the conductivity of the particles, also when the filler fraction is high. In this thesis it is investigated why the conductivity remains so low in such nanocomposites, and what the relation is with the filler distribution and filler properties. We try to find out whether the conductivity can be improved and which properties the filler particles should meet for this purpose.

A specific kind of nanocomposite is investigated in detail: a crosslinked epoxy polymer coating filled with crystalline Phthalcon-11 particles, prepared under conditions that give a critical filler fraction (i.e. the first fraction at which a sample-spanning particle network is formed, marking also the onset of a steep increase in the conductivity as function of filler fraction) of 0.55 vol%. In addition, the conductivity of the Phthalcon-11 particles (∼ 100 nm) is studied separately and compared with the conductivity of much smaller antimony-doped tin-oxide (ATO) particles (∼ 7 nm).

Several techniques are used. The conductivities of the composite and filler materials are measured as a function of frequency, temperature and electric field. For the filler particles the high-frequency transmittance and reflectance are measured too. With conducting atomic-force microscopy (C-AFM) the conductances of the particle channels inside the nanocomposite coatings are measured locally. Density-functional-theory (DFT) calculations are used to determine the energy-band structures in Phthalcon-11, which gives information on the anisotropy in the conductivity within these particles.
We find that the low conductivity of the Phthalcon-11/epoxy nanocomposite is not caused by insulating layers of the polymer matrix between the particles, nor by anisotropy in the intrinsic conductivity of the Phthalcon-11 crystallites. It is the structure of randomly distributed fractal aggregates that causes the conductivity to be much lower than the filler-particle conductivity. With a theoretical model we show that for such a geometry, which is formed by diffusion-limited cluster aggregation during processing, the maximal obtainable conductivity decreases with decreasing critical filler fraction in a non-trivial way.

The conductivity can obviously be improved by using fillers with a higher intrinsic conductivity level. However, our study reveals that the size of the fillers is also important: when they are too large, a particle network will probably not be formed and/or it will suffer from sedimentation by gravity; when they are too small, the Coulomb charging energy (the energy increase from charging a crystal with an extra charge) will hinder the charge transport. Phthalcon-11 particles of about 100 nm turned out to have the right size, while ATO particles with a diameter of 7 nm are too small; the nanosize of these particles causes a drastic reduction of the conductivity due to charging in densely packed ATO powder.
Dankwoord

Bij deze wil ik nog een aantal mensen bedanken die direct een rol hebben gespeeld in de totstandkoming van dit proefschrift of die de laatste jaren belangrijk voor me zijn geweest.

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