Moving charged particles in fluctuating and disordered energy landscapes

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MOVING CHARGED PARTICLES IN FLUCTUATING AND DISORDERED ENERGY LANDSCAPES

WIJNAND GERMS
Moving charged particles in fluctuating and disordered energy landscapes

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de rector magnificus, prof.dr.ir. C.J. van Duijn, voor een commissie aangewezen door het College voor Promoties in het openbaar te verdedigen op woensdag 16 januari 2013 om 16.00 uur

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1 Introduction
In this thesis various experiments are performed that concern the motion of charged particles in fluctuating and disordered energy landscapes at a nanometer scale. In particular, particle ratchets (Chapters 2 and 3), the Seebeck effect in disordered semiconductors (Chapter 4, 5 and 6), and admittance spectroscopy on organic disordered semiconductors (Chapter 7 and 8).

Out-of-equilibrium systems can show qualitatively different behavior than the same systems at equilibrium. For instance, the second law of thermodynamics prescribes that in equilibrium no work can be extracted from the thermal energy in the system. When an isolated system performs work the entropy of that system has to increase. In thermal equilibrium the entropy of an isolated system is at its maximum, therefore it cannot perform work. In ratchets thermal motion can be rectified, delivering power by e.g., creating directed motion of particles in a viscous system. In order to function, ratchets therefore require that the system is taken out-of-equilibrium by e.g., applying an oscillating potential to ionized particles or applying a temperature difference. Likewise, the Seebeck effect converts thermal energy into (electrical) power provided the system is subject to a temperature gradient. Parallel to the ratchet, a thermoelectric device in equilibrium, i.e., having a constant temperature, will generate no power.

In disordered semiconductors an out-of-equilibrium situation can be achieved by applying a time-varying electrical potential, which e.g., is done in admittance spectroscopy. A time-varying electrical potential can be applied using admittance spectroscopy. Admittance spectroscopy is a near-to-equilibrium experiment, but it allows to investigate the injection of far-from-equilibrium charge carriers. The slow relaxation of charge carriers, i.e., thermalization, with time gives rise to a strongly time and therefore frequency dependent mobility that can be orders of magnitude larger than for the same system in a steady state situation.

In this chapter these subjects are further introduced in the same order as mentioned above. Theory on charge transport in disordered semiconductors is important for both the Seebeck effect and the admittance spectroscopy studies. It is therefore introduced in a separate section before we move to the Seebeck effect.

### 1.1 Brownian Ratchets

#### 1.1.1 What are Brownian Ratchets?

The Brownian ratchet concept was invented in 1912 by Marian von Smoluchowski.¹ What is now called the Feynman-Smoluchowski ratchet was a Gedankenexperiment, which von Smoluchowski came up with in the course of solving another well-known Gedankenexperiment, Maxwell’s Demon.² With the
development of thermodynamics in the 19th century the second law of thermodynamics was formulated. It postulates that the entropy of an isolated system cannot decrease, and attains its maximum when thermal equilibrium has been reached. Another more comprehensible formulation of that law is that a system in thermal equilibrium cannot perform useful work. The Feynman-Smoluchowski ratchet, displayed in Fig. 1, has the looks of a perpetual motion machine and was invented to test the second law of thermodynamics.

The device is supposed to lift the weight, hanging on a rope in the middle of the axis, by rectifying the (undirected) Brownian motion of molecules in the surrounding gas. Molecules colliding with the paddles on the right will exert forces on the axis in both directions. However, at the left the pawl prevents the ratchet wheel to turn counterclockwise, resulting in a net clockwise rotation of the axis, thereby lifting the weight and violating the second law.

The solution to the problem lies in the fact that the system has to be very small for the molecules to be able to rotate the paddle wheel. In such a small system the pawl will be small enough to start oscillating itself due to its own Brownian motion. Regularly the pawl will move up enough allowing the wheel to rotate back, and therefore no net rotation is expected over a large period of time. In this way Smoluchowski demonstrated that also in this setup the second law of thermodynamics holds.\textsuperscript{1,4}

The Feynman-Smoluchowski ratchet was discussed in the Feynman
Lectures on Physics$^4$ where Feynman modified the device to make it perform work under out-of-equilibrium conditions, not violating the second law of thermodynamics. By placing the paddles in a bath of a higher temperature than the pawl and ratchet wheel the paddles experience strong collisions while the pawl hardly oscillates, allowing the device to lift the weight. The device works, and thermodynamics still lives.

This device has been the inspiration to many other devices that are called Brownian ratchets. What all Brownian ratchets have in common is that they are devices that use some kind of asymmetry to rectify Brownian motion. The common asymmetry used is a spatially periodic potential with asymmetric potential wells comparable to the shape of the ratchet wheel. In the last decades a wide variety of Brownian ratchets has been realized,$^5$ which can usually be classified as either on/off or rocking ratchets. Both are explained below.

**On/off Ratchet**

In on/off ratchets the particles that experience random (thermal) motion are subjected to a time-dependent asymmetric potential, which is displayed in the
Moving Charged Particles in Fluctuating and Disordered Energy Landscapes

cartoon of Fig. 1.2(a). The cartoon shows a periodic, saw tooth-shaped potential, \( V \), as a function of position, \( x \), at three different moments in time, \( t \). At time \( t_0 \) the particles are trapped in one of the asymmetric potential wells. At \( t_1 \) the potential is switched off, the particles diffuse without a preferential direction. After a certain time the potential is switched on again. The asymmetry of the potential wells leads to an asymmetry in the retrapping. More particles have diffused over the short distance in the asymmetric repeat unit, i.e., to the left trap, than over the long distance to the right. Hence, the asymmetry results in a net particle current.

**Rocking Ratchet**

In the rocking ratchet the periodic asymmetric potential is constant in time. In addition to the ratchet an oscillating force, \( F_{\text{ext}} \), is superimposed on the particles, which changes the effective potential experienced by the particles. This is displayed in Fig. 1.2(b). Even when the oscillating force has a zero time averaged magnitude, like e.g., a sinusoid, this can result in a nonzero average movement of particles. With the right force magnitude, \( F_x \), the particle remains trapped when the force has a negative value, pictured in the second potential profile for \( F_{\text{ext}} = -F_x \). When the force has an equally large positive value, \( F_{\text{ext}} = +F_x \), the particle is able to move to the potential well to the right, resulting in a non-zero time averaged particle displacement.

**1.1.2 Ratchets in Literature**

In the last decades ratchets received a revived interest with publications both theoretical\(^6\)-\(^8\) and experimental in nature. The experimental realizations of Brownian ratchets found in literature are very diverse and demonstrate directed transport of charges,\(^9\),\(^10\) Leidenfrost droplets,\(^11\),\(^12\) and granular gasses.\(^13\) A recent overview of the field is given by Hänggi and Marchesoni.\(^5\)

Apart from being a scientific curiosity there are other more practical reasons to investigate these systems. For example the myosin-actin system, responsible for muscle contraction, can be explained by a ratchet-like mechanism.\(^14\) The main practical application foreseen for ratchets is the separation of particles, molecules, or even living cells.\(^15\)-\(^26\) It has been shown in different ratchet systems that current reversals can occur upon minute changes in one of the system parameters.\(^5\),\(^9\),\(^10\) Achieving a current reversal for suspended particles (or molecules, cells) would allow one to have any two types of particles moving in opposite direction, which would open the way to highly selective and small sized particle separators.

Why current reversals occur is system-dependent, and the exact reason can sometimes be difficult to grasp. One possible explanation is that two different driving mechanisms with opposite direction are active in the same system.\(^9\) A
simple example of this is given here for a marble on a washboard in Fig. 1.3. Shaking the washboard in the horizontal direction is prone to give a net movement of the marble to the right. Shaking the washboard vertically is likely to make the marble move left as small lateral components in mainly vertical jumps are more likely to make the marble surpass the left-hand barrier than on the right-hand one. When allowing the washboard to simultaneously shake in both directions it is not a priori clear in which direction the marbles move. If the amplitudes in horizontal and vertical directions can be controlled separately a point can be found where zero particle current is found. This is where the current reversal is occurring.

Different sorts of ratchets for suspended particles have been employed, and include structured arrays for moving molecules and cells, \textsuperscript{15-17} optical ratchet traps for moving microspheres, \textsuperscript{18,19} magnetic ratchets for moving superparamagnetic beads, \textsuperscript{20-22} and electrostatic ratchets for moving microspheres and molecules.\textsuperscript{23-28}

Detailed knowledge of the different driving forces is needed in order to find the optimal device parameters for a particle separator. In this thesis a quasi-electrostatic ratchet is studied for suspended polystyrene particles, opportunities and limitations of the system are explored. Previous work shows that experiments with suspended particles in electric fields can be very complex to analyze.

Two examples of ratchets studied earlier are shown in Fig. 1.4. In Fig 1.4(a) a structured ‘Christmas tree’-shaped channel is shown with which Marquet \textit{et al.}\textsuperscript{26} created a dielectrophoretic ratchet using an oscillating electric field (2 Hz) along the channel. The channel shape causes increased electric fields at the necks, as shown below the photo. The difference in polarizability between a (latex) particle in the channel and the fluid results in a difference in electrostatic energy density. Whether the energetically favorable position for a particle is at the
maximum or the minimum of the field can be difficult to determine theoretically for low frequencies,\textsuperscript{26,28} as it depends on the dielectric constants and the conductivities of both materials and the frequency of the field oscillation.\textsuperscript{29}

Next to dielectrophoresis Marquet \textit{et al.} mention the presence of electrophoresis and electro-osmosis. Electrophoretic forces are caused by the interaction between the ionized surface of the particle and the local electric field. With electro-osmosis the particles move due to the movement of the surrounding fluid. Intrinsic charge at the channel walls creates an ionic double layer in the fluid. The ionic double layer responds to the electric field and drags the particles along. Due to the combination of these three effects the system works as a rocking ratchet. The periodic potential in Fig. 1.2(b) is created by the dielectrophoretic forces. Electrophoresis and electro-osmosis work as the external force, $F_{\text{ext}}$, tilting the ratchet periodically.

Figure 1.4: Two ratchets for suspended particles described in literature. (a) A dielectrophoretic rocking ratchet for latex particles, driven by an oscillating electric field in a ‘Christmas tree’ shaped microchannel,\textsuperscript{26} and (b) an electrophoretic on/off ratchet formed by interdigitated finger electrodes, with the movement of fluorescently labeled DNA molecules shown by three pictures at the right.\textsuperscript{24}
The three different effects present make it difficult to understand what happens at a microscopic scale. The authors observe the particles being trapped in the high field necks in the channel, but another force seems to push the particles away which they attribute to electrophoresis. This shows that experiments in which suspended particles are actuated by electric fields can be very complex to analyze.

In Fig. 1.4(b), an on/off ratchet is shown that looks very similar to the ratchet used in this thesis. Bader et al. fabricated a device with interdigitated finger electrodes that are placed asymmetrically to create an asymmetric electrostatic potential profile. Ionized fluorescently labeled DNA molecules are attracted to the positive electrode by electrophoretic forces. Switching the potentials on and off creates the ratchet behavior shown by the pictures on the right, which displays the fluorescence of the particles at three moments in time. It shows an average movement to the right while the width of the particle distribution increases. The movement is assumed to take place due to electrophoretic interactions. Other effects are not considered, and the paper mainly describes the experiments without taking the exact nature of the forces into account. In the previous paragraph dielectrophoresis and electro-osmosis appeared to play a significant role in the experiments by Marquet et al. The question can be raised whether these two effects also play a role in the ratchet created by Bader et al. Is the microscopic behavior indeed simply determined by electrophoretic interactions only? We will study a very similar device using polystyrene spheres of 300 nm and 500 nm in diameter and encounter complex microscopic behavior.

1.1.3 Ratchets in this Thesis

As discussed in the previous section detailed knowledge is needed to find optimal device parameters for an effective particle separator. In chapters 2 and 3 an on/off ratchet device with interdigitated finger electrodes is investigated for transporting suspended polystyrene spheres. This device is very similar to the device studied by Bader et al. shown in Fig. 1.4(b). Chapter 2 focuses on the driving forces in the ratchet. From experimental results and simulations methods a strong dependence on dielectrophoretic forces is shown for polystyrene spheres, which is unlike what Bader et al. show for DNA molecules. This knowledge is used to manipulate the speed with which the particle distribution moves.

In chapter 3 we discuss the broadening of the distribution of particles in an on/off ratchet. The broadening is important for particle separation purposes, since broader distributions make the separation of distributions more difficult. An experimental observation of an increased effective diffusion is supported by the results from a numerical Master-equation model. Using the same model we show that the observed diffusion enhancement can be described by a master curve whose shape only depends on the asymmetry of the ratchet repeat unit.
Furthermore we will discuss the usage of this numerical model to determine the optimal driving parameters for particle separation.

1.2 Transport Models for Disordered Semiconductors

Before we move to the Seebeck effect and admittance spectroscopy an introduction is given to charge transport in disordered semiconductors. Charge transport models are usually first developed using the current response to a quasi-static potential difference, i.e., $I-V$ measurements. Once a model can describe $I-V$ measurements, the validity can be examined further by measuring other transport related properties, e.g., the Seebeck coefficient, and measuring under other conditions, e.g., using admittance spectroscopy.

Charge transport in disordered semiconductors is a subject of large technological relevance. Actual applications include e.g., active matrix organic light emitting diode (AMOLED) displays for transportable electronic devices such as mp3-players, smartphones and tablets, cheap ‘low’ speed electronics like display pixel switches, the logic and memory in electronic tags and labels, and organic photovoltaic cells. In the past decade, much progress in the understanding of the charge-carrier transport in disordered semiconductors has been realized.

Apart from having a lower mobility than their crystalline counterparts, the physics of the charge transport in disordered materials is different. Charge transport in crystalline materials is typically described by an electron gas in a band of extended states. Anderson$^{30}$ showed that in the presence of sufficiently strong energetic disorder in a periodic array of states, localized tail states develop at the edges of the band, as shown in Fig. 1.5(a) and (b). Between the localized and extended states a sharp separation is assumed, the so-called mobility edge.$^{31}$ The localized states were assumed to be trapping states. In order to have charge transport, charge carriers need to be thermally activated to the extended high energy states. This description of the charge transport is called the mobility edge (ME) model.

Later, Mott$^{32}$ demonstrated that charge transport can also result from hopping processes between two localized sites. Hopping also requires thermal activation. It results in thermally activated tunneling to another localized state instead of to an extended state. Hopping can occur to the nearest neighboring state, but it can also occur to a state further away. In that case we refer to the process as variable range hopping (VRH). In literature the charge transport in disordered materials is often described by either the bandlike ME model or by (variable range) hopping. The two are seen as two different types of charge transport models, but in principle bandlike transport and hopping can co-exist.
In this thesis, we show how a distinction can be made between both models by using Seebeck effect measurements. We further show, using admittance measurements, how in the case of transport as described within the VRH model the effective energy of the high-energy states at which the transport takes place (“transport level”) can be determined. In the next two subsections, we give a basic description of the ME and VRH models. An introduction to the Seebeck and admittance studies is given in the next sections.

1.2.1 Mobility Edge Model

When we talk about a ME model we assume that hopping between two localized states will have a negligible contribution to the charge transport. Due to the disorder, the density of states (DOS), \( G \), contains a tail of localized states which is formed at the edges of the band. Typically the shape of the DOS in the conduction band is expected to resemble the curve shown in Fig. 1.5(b). The density of states below the mobility edge, \( E_C \), is often taken as an exponential function. In this thesis the DOS above \( E_C \) is approximated as being constant. The DOS used is shown in Fig. 1.5(c) and described as

\[
G(E) = \begin{cases} 
\frac{N_{\text{loc}}}{k_B T_0} \exp \left( -\frac{E}{k_B T_0} \right) & \text{and } \mu = 0 \text{ if } E < E_C, \\
\frac{N}{k_B T_0} & \text{and } \mu \neq 0 \text{ if } E \geq E_C,
\end{cases}
\]  

\( (1.1) \)
with \(k_B\) the Boltzmann constant, \(T_0\) the width of the exponential tail, \(N_{\text{loc}}\) the number of localized states, \(N\) a constant, and \(\mu\) the corresponding mobility. For the DOS above \(E_C\) the \(N\) is divided by \(k_B T_0\) for dimensional reasons. The dark grey area in the DOS tail in Fig. 1.5(c) represents the occupied states. This occupation is determined by the Fermi-Dirac distribution.

As long as the model is still able to describe the physics the advantage of taking a constant DOS for \(E \geq E_C\) is that it minimizes the number of free parameters. Importantly, this reduces the probability of having multiple solutions for the same set of experiments. When the Fermi level lies below the mobility edge, charge carriers are thermally activated to \(E_C\), reflected by presence of occupied states in Fig 1.5(c). Most of the transport will take place at the mobility edge. The shape far above \(E_C\) is then of minor importance, provided it does not depend stronger than algebraically on energy.

The device mobility is determined by the relative number of charge carriers in the extended states, \(n_{\text{ext}}\)

\[
\mu_{\text{meas}} = \frac{n_{\text{ext}}}{n_{\text{ext}} + n_{\text{loc}}} \mu(T) = \frac{\int_{-\infty}^{E_C} G(E) f_{\text{FD}}(E) dE}{\int_{-\infty}^{\infty} G(E) f_{\text{FD}}(E) dE} \mu(T),
\]

with \(n_{\text{ext}}\) and \(n_{\text{loc}}\) the number of extended and localized states respectively, and \(f_{\text{FD}}\) the Fermi Dirac distribution. The mobility in the band is often approximated to have a temperature independent value. However, especially for organic semiconductors, thermally driven molecular vibrations can give rise to a significant temperature dependence of the mobility above the mobility edge.

### 1.2.2 Variable Range Hopping Model

When the Fermi level is not located close to a mobility edge, the charge transport can be dominated by charge carriers tunneling from one localized state to the next. When this process is thermally assisted it is called variable-range hopping (VRH). Hopping was first demonstrated by Mott, who studied hopping in a uniform DOS. The conductivity shows then the famous \(T^{-1/4}\) dependence. In recent literature VRH hopping transport has been studied for two other shapes of the DOS. One is the exponential DOS, as in the ME model described as
\[ G_{\text{exp}}(E) = \begin{cases} \frac{N_{\text{loc}}}{k_B T_0} \exp\left(-\frac{E}{k_B T_0}\right) & \text{if } E \leq 0, \\ 0 & \text{if } E > 0, \end{cases} \]  

(1.3)

with \( N_{\text{loc}} \) the total density of localized states. The other is the Gaussian DOS

\[ G_{\text{Gauss}}(E) = \frac{N_{\text{loc}}}{\sigma \sqrt{2\pi}} \exp\left(-\frac{E^2}{2\sigma^2}\right), \]  

(1.4)

with \( \sigma \) the width of the distribution.

Whether an exponential or a Gaussian gives the correct description of the DOS is often not \textit{a priori} known. From the Anderson localization picture, the complete absence of extended states would not be expected for a low degree of disorder. For high disorder the absence is possible; the mobility edges in Fig. 1.5(b) shift to the middle of the band, and no extended states remain. In view of the central limit theorem a Gaussian is often a very reasonable shape of the DOS, e.g., for the DOS resulting from the presence of a small concentration of guest molecules in a host material.

In the presence of disorder, charge carrier hops are in general between sites with different energies. Hopping from a lower to a higher energy state requires thermal activation. In this thesis the Miller-Abrahams hopping rates are used. Within this formalism the hopping rate \( \nu_{ij} \) for a hop between sites \( i \) and \( j \), with energy \( E_i \) and \( E_j \), is given by\(^{39} \)

\[ \nu_{ij} = \begin{cases} \nu_0 \exp\left(-2\alpha R_{ij} - \frac{E_j - E_i}{k_B T}\right) & \text{if } E_j > E_i, \\ \nu_0 \exp(-2\alpha R_{ij}) & \text{if } E_j > E_i, \end{cases} \]  

(1.5)

with \( R_{ij} \) the distance between sites \( i \) and \( j \), \( \alpha \) the inverse of the decay length of the localized wave function, and \( \nu_0 \) an attempt rate.

**Hopping Mobility**

Several VRH-expressions exist for the conductivity and mobility.\(^{39} \) Here we will introduce only two of them that are used in this thesis, a Mott-Martens\(^{39,40} \) type of conductivity that can be used for any shape of the DOS and an expression found by Pasveer \textit{et al.}\(^{41} \) for the mobility in a Gaussian DOS.
The Mott-Martens expression for the conductivity is written as\textsuperscript{32,40}

\[
\sigma = \sigma_0 \exp \left( -2\alpha R^* - \frac{E^* - E_F}{k_B T} \right),
\]

with \(\sigma_0\) a prefactor, and where \(R^*\) and \(E^*\) follow from percolation theory. \(E^*\) is called the transport energy. The hop from \(E_F\) to the energy \(E^*\) is the most difficult but still necessary hop within the percolating network. Therefore this hop dominates the total conductivity. The position of this level and the typical hopping distance \(R^*\) are connected via a percolation argument\textsuperscript{39,40}

\[
B_C = \frac{4}{3} \pi R^*^3 \int_{E_F}^{E^*} G(E) dE,
\]

with \(B_C = 2.8\) the critical number of bonds. The right-hand side of Eq. (1.7) represents the volume of a four-dimensional region, formed by three spatial dimensions and one energy dimension. This region should contain 2.8 hopping sites to have conduction. \(R^*\) and \(E^*\) are subsequently calculated by using Eq. (1.7) and by optimizing Eq. (1.6) such that

\[
2\alpha \frac{dR^*}{dE^*} + \frac{1}{k_B T} = 0.
\]

The calculation of \(R^*\) and \(E^*\) can be performed numerically for any shape of the DOS. When the carrier concentration is known the mobility follows from \(\mu = \sigma / (e n)\).

An analytical description of the mobility for a Gaussian DOS was found by Pasveer\textit{et al.}\textsuperscript{41} from numerical modeling. From a three-dimensional Master-equation model Pasveer determined a temperature, electric field, and carrier density dependent expression for the mobility,\textsuperscript{41}

\[
\mu(T, p) = \mu_0(T) \exp \left( \frac{1}{2} (\hat{\sigma}^2 - \hat{\sigma})(2na^3)^{\delta} \right),
\]

\[
\mu_0(T) = \frac{a^2 v_0 e}{\sigma} c_1 \exp (-c_2 \hat{\sigma}^2),
\]

\[
\delta \equiv 2 \frac{\ln(\hat{\sigma}^2 - \hat{\sigma}) - \ln(4)}{\hat{\sigma}^2},
\]

\[
(1.9)
\]

\[
(1.8)
\]
with \( n \) the charge carrier density, \( a \) the lattice constant, \( e \) the elementary charge, \( \tilde{\sigma} \) equal to the width of the Gaussian divided by \( k_B T \), \( c_1 \) equal to \( 1.8 \times 10^{-9} \), and \( c_2 \) equal to 0.42.

The expressions from the two discussed approaches seem very different. However, Coehoorn et al.\(^3\) showed that when the Mott-Martens approach is applied to a Gaussian DOS the two models give comparable results for a wide parameter range. Only at very high concentrations, when the Gaussian DOS decreases with increasing \( E \), does the Mott-Martens expression seem to underestimate the mobility. This is caused by not taking the states below the Fermi level into account as final states.\(^3\)

Recently, deeper insight has been obtained in the percolative transport in a Gaussian DOS, and its dependence on the temperature and carrier concentration,\(^4\) revealing that the effective critical energy up to which hops occur that contribute to the mobility is approximately \(-0.5 \sigma\), depending on the details of the transport model. The expression for the steady-state mobility, given by Eq. (1.9) and obtained from a numerical study, does not contain this critical (or “transport”) energy. We will show that the effective transport energy can be obtained from admittance experiments, from which we find a value which is close to the value obtained in Ref. 42.

### 1.3 Thermoelectricity

#### 1.3.1 The Seebeck effect

The thermoelectric effect is another out-of-equilibrium effect by which work can be extracted from thermal energy. When applying a temperature difference to a thermoelectric module, thermal energy can be converted into electricity. Applying a temperature difference, \( \Delta T \), to a material containing free charges will in general generate a thermovoltage, \( \Delta V \). This is called the Seebeck effect, see Fig. 1.6(a). The ratio of the thermovoltage and the temperature difference is referred to as the Seebeck coefficient,

\[
S = \frac{\Delta V}{\Delta T}. \tag{1.10}
\]

This equation satisfies the second law of thermodynamics: Under equilibrium conditions, \( \Delta T = 0 \), no voltage will be generated, \( \Delta V = 0 \), and the generated power
Figure 1.6: (a) Schematic of a thermovoltage measurement of a material with an applied temperature difference. (b) The Fermi-Dirac distribution and the occupied DOS (in grey) for the cold (left) and the hot (right) side of the material. The areas of the grey surfaces in the log DOS-plots are equal since they represent equal carrier concentrations. The difference in Fermi level explains the Seebeck effect. (c) The Peltier effect, occurring due to the charge carriers transporting heat from left to right.

will be equal to zero, \( P = V \times I \), with \( I \) the current. Similar to the Feynman-Smoluchowski ratchet in Fig. 1.1 a thermoelectric module requires a difference in temperature to perform work. However, it will be shown that the Seebeck effect is described as a linear response to the temperature difference indicating that the experiments are performed near equilibrium. A review of the field of thermoelectrics can be found in Ref. 51.

A qualitative understanding of why the Seebeck effect occurs can be obtained by considering a material with a fixed concentration of electrons, across which a temperature difference is applied. When the DOS is not constant, but for example an exponentially increasing function of the energy (Fig. 1.6(b)) the Fermi level will be temperature dependent in order to maintain a constant concentration of charge carriers. This difference in Fermi level can be measured as the thermovoltage. Due to their polarity holes are associated with a positive \( S \) and electrons with a negative \( S \). For a decreasing DOS the sign of \( S \) also inverts. From
the empirical relations of Ohm’s law and the Seebeck effect the current density is written as, \(^{43}\)

\[ J = \sigma \vec{E} - \sigma S \vec{V} T, \]  

(1.11)

with \(\sigma\) the conductivity, \(\vec{E}\) the electric field, and \(\vec{V} T\) the temperature gradient.

The Peltier effect can be seen as the reverse of the Seebeck effect. When a charge current is sent through a material one side cools down and the other side heats up. The Peltier effect occurs due to the charge carriers not only carrying charge but also heat from one side of the material to the other, as displayed in Fig. 1.6(c). Therefore the current flow leads to a cooling at one side and heating at the other side of the material. The heat carried per unit charge is called the Peltier coefficient and can be written as \(^{44}\)

\[ \Pi = \int (E - E_F) \sigma(E) dE \quad e \int \sigma(E) dE, \]  

(1.12)

with \((E - E_F)\) the heat carried by a charge carrier at the energy level \(E\), and \(\sigma(E)\) the contribution to the conductivity at that energy level. From the empirical relations of the Peltier effect and Fourier’s Law, the heat current density can be written as \(^{43}\)

\[ W = \sigma \Pi E - \kappa \vec{V} T, \]  

(1.13)

with \(\kappa\) the thermal conductivity.

Lord Kelvin (Thomson) discovered in the 19th century that \(S\) and \(\Pi\) are related to each other by \(S = \Pi / T\). This could later be derived from the Onsager reciprocity relations, \(^{45}\) which were published in 1931. The Onsager reciprocity relations give a general mathematical description of a system returning to equilibrium after being taken out of equilibrium. The fluxes of two quantities, \(J_1\) and \(J_2\), are driven by two forces \(X_1\) and \(X_2\) and are described by

\[ J_1 = L_{11}X_1 + L_{12}X_2, \]
\[ J_2 = L_{21}X_1 + L_{22}X_2, \]  

(1.14)

with the important relation \(L_{12} = L_{21}\). For thermoelectrics the two fluxes are a heat and a charge flux, and the forces arise due to gradients in temperature and electric potential. The two fluxes are then described by \(^{46}\)
Moving Charged Particles in Fluctuating and Disordered Energy Landscapes

\[
J = L_{11} \frac{E}{T} - L_{12} \frac{\nabla T}{T^2},
\]

\[
W = L_{21} \frac{E}{T} - L_{22} \frac{\nabla T}{T^2}.
\]

(1.15)

From Eqs. (1.15), (1.11), and (1.13), Kelvin’s law follows to be

\[
S = \frac{\Pi}{T}.
\]

(1.16)

Using Kelvin’s law and the expression for the Peltier coefficient (1.12) the Seebeck coefficient can be expressed as

\[
S = \frac{\int (E - E_F) \sigma(E) dE}{eT \int \sigma(E) dE}.
\]

(1.17)

The Seebeck coefficient is an interesting parameter when studying charge transport, as it gives additional information about the DOS and the energetics in the system. The expression of the Seebeck coefficient in Eq. (1.17) shows that \( S \) is determined by the energy of the conductive states. A low Seebeck coefficient thus implies that little thermal activation is required to have charge transport.

Seebeck coefficient measurements have been used before to study charge transport in organic semiconductors. Maennig et al.\textsuperscript{47} and Menke et al.\textsuperscript{48} studied the doping dependence of charge transport in zinc phthalocyanine and C\textsubscript{60}, respectively. The Seebeck coefficient was used to make statements about the magnitude of the thermal activation.

Pernstich et al.\textsuperscript{49} studied pentacene thin films and rubrene single crystals in the framework of a ME model. The Seebeck coefficient measurements confirmed the consistency of the charge transport model used. However, the pentacene measurements were performed only at room temperature, and the contribution of the extended states above \( E_C \) was left as a free parameter. For a parameterized DOS above \( E_C \) this contribution can be calculated. Furthermore, the charge transport in pentacene thin film transistors (TFTs) is also frequently modeled in the context of VRH. Hopping is mentioned in the work by Pernstich et al.,\textsuperscript{49} but no analysis using hopping is shown.

In this thesis the Seebeck coefficient is used in studies of charge transport in disordered materials, to make a distinction between bandlike charge transport and VRH. According to the ME model \( S \) is determined by a fixed transport level at the mobility edge, \( E_C \). According to the VRH model \( S \) is determined by a temperature and density dependent transport level \( E^* \). Nonetheless it is not
straightforward to distinguish the models on basis of the transport level alone, since the Fermi level is also temperature and charge carrier density dependent.

1.3.2 Figure of Merit

In this thesis the prime goal of using the thermoelectric effect is to investigate the nature of the charge transport in disordered materials. However, we will also address the possible practical applicability of the materials which are investigated. The two materials that will be discussed, pentacene and amorphous InGaZnO (IGZO), have a high mobility compared to other disordered materials used in thin film transistors (TFT). From the thermoelectric figure of merit\(^51\)

\[
ZT = \frac{S^2 \sigma}{\kappa} T, \quad (1.18)
\]

a high mobility can indicate that the material could be a feasible candidate for power generation. Furthermore a highly disordered structure usually results in a relatively low thermal conductivity due to the strong scattering of phonons. Because of the importance of sustainable sources of energy we will briefly look at the figure of merit, and discuss the likelihood of achieving high \(ZT\)'s with disordered semiconductors. A review on organic materials focusing on their thermoelectric performance can be found in Ref. 50

Attractive features of thermoelectric devices are their small size and absence of moving parts. However, the power generation efficiency is lower than conventional steam operated heat engines.\(^51\) Eq. (1.18) shows that for efficient transformation of heat into electricity a high \(S\) and conductivity \(\sigma\) are required. A low thermal conductivity reduces losses due to heat flow. This immediately shows one problem in achieving a high \(ZT\). For free-electron metals the electrical and thermal conductivity are directly related, which is expressed by the Wiedemann-Franz law\(^52\)

\[
\frac{\kappa}{\sigma} = LT, \quad (1.19)
\]

with \(L\) the Lorenz number, derived to be

\[
L = \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2 \approx 2.44 \times 10^{-8} \text{ } \text{W} \Omega \text{K}^{-2}. \quad (1.20)
\]
Due to the high electrical conductivity in metals the heat transported by the mobile charge carriers is higher than the heat transported due to lattice vibrations. For a metal an increase in $\sigma$ therefore results in a proportional increase in $\kappa$, and no increase in $ZT$ is achieved.

The second difficulty, and maybe even more important than the first, is that in general a material with lower $\sigma$ shows a higher $S$, which is displayed in Fig. 1.7. Metals show a high $\sigma$, but $S$ is very low because the transport takes place close to the Fermi level, reducing $(E - E_F)$ in Eq. (1.17). For insulators mobile charge carriers require a large thermal activation leading to a high $S$, but here the conductivity is the limiting factor. The optimum in $ZT$ is therefore found for semiconductors, shown by the power factor $S^2\sigma$ in Fig 1.7.

Presently the best commercially available thermoelectric material is Bi$_2$Te$_3$ with $ZT \approx 1$ with typically $S \approx 225$ $\mu$V K$^{-1}$. The advantage of amorphous semiconductors is that the phonon contribution to the thermal conductivity is reduced. It can be shown that when the heat current density, $P_Q$, is only determined by the charge carriers

$$P_Q = \Pi J,$$  \hfill (1.21)

and $\Delta T$ approaches zero, the efficiency equals the Carnot efficiency,

$$\frac{P_{el}}{P_Q} = \frac{J\Delta V}{J\Pi} = \frac{JS\Delta T}{JST} = \frac{\Delta T}{T},$$  \hfill (1.22)

with $J$ the current density and $P_{el}$ the generated electrical power. However, in deriving Kelvin’s law, $\Pi = S T$, the system is assumed to be close to its
Figure 1.8: Plot of the electrical conductivity that is needed to achieve a figure of merit $ZT = 1$ at $T = 300$ K vs. thermal conductivity for three different Seebeck coefficients indicated in the legend (solid lines). The mobility (right axis) follows from the electrical conductivity assuming a charge carrier density of $10^{25}$ m$^{-3}$. The vertical dotted lines correspond to the thermal conductivity of various materials mentioned at the right. The dashed line corresponds to the Wiedemann-Franz law, with the grey area up to $L = 10^{-8}$ W K$^{-2}$. The star indicates the $\kappa$ and $\sigma$ values of the $ZT = 0.25$ PEDOT-Tos device.

Several studies determined a figure of merit or a power factor (denominator of Eq. (1.18)) of organic materials. Studies have been performed on polyaniline films, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) PEDOT:PSS, and poly(2,7-carbazole) derivatives. In a study on poly(3,4-ethylenedioxythiophene)–tosylate (PEDOT–Tos), Bubnova et al. found $ZT \approx 0.25$. This material has a much higher conductivity than the typical organic TFT and can even reach $10^5$ S m$^{-1}$. The Seebeck coefficient, electrical conductivity, and thermal conductivity of the record device equal $\sim 220$ $\mu$V K$^{-1}$, $\sim 7 \times 10^3$ S m$^{-1}$, and 0.37 W m$^{-1}$ K$^{-1}$ respectively. Furthermore PEDOT–Tos is an air stable material, which makes the achievement even more interesting as a step towards commercial application.

For the materials investigated here it seems difficult to compete. Fig. 1.8 shows the required $\kappa$ and $\sigma$ to achieve $ZT = 1$ for three $S$ values. A star indicates the values found for the PEDOT–Tos device discussed above. Evaporated pentacene, a high mobility disordered organic semiconductor, shows a mobility of approximately $0.1$ cm$^2$ V$^{-1}$ s$^{-1}$ ($\mu$ on right y-axis). For a Seebeck coefficient of 500 $\mu$V K$^{-1}$ Fig. 1.8 shows that the thermal conductivity has to be far below $10^{-2}$ W m$^{-1}$ K$^{-1}$. In view of the thermal conductivity of other materials (see dotted
lines) such a thermal conductivity is extremely low and therefore not likely. For amorphous InGaZnO the mobility is higher and gets to approximately 10 cm$^2$ V$^{-1}$ s$^{-1}$, however, the Seebeck coefficient is lower, around 200 $\mu$V K$^{-1}$. Its thermal conductivity too has to be very low, close to that of cork, to reach $ZT = 1$.

To further picture the challenge of finding better thermoelectric materials, Fig. 1.8 also displays the Wiedemann-Franz relation, Eq. (1.19), by the dashed line. For metals the thermal conductivity is determined by the heat carried by the free charge carriers, i.e., the phonon contribution can be neglected. For non-metals one likely finds the combination of $\sigma$ and $\kappa$ below this dashed line. At the same time one wants to find the point above the solid line of the corresponding Seebeck coefficient. It is clear that there is not much room in between the solid and the dashed lines.

In view of the above the high conductivity materials, like the PEDOT-Tos by Bubnova et al., seem more promising than the disordered materials we investigate in this thesis. Obtaining very high conductivities in a disordered material is more likely when the charge transport takes place in the extended states above a mobility edge that is not too far away from the Fermi level. In that case both the mobility and the number of mobile charge carriers are high, resulting in a high conductivity. Although some distance between the Fermi level and the mobility edge is still needed for a high enough Seebeck coefficient. With the $ZT \approx 0.25$ for PEDOT-Tos disordered organic materials are getting closer to the inorganic Bi$_2$Te$_3$. However, every additional increase in $ZT$ is more and more challenging.

### 1.3.3 Thermoelectric Effect in Disordered Semiconductors in this Thesis

In this thesis, the Seebeck coefficient is used to study three different materials in the framework of different charge transport models. In chapter 4, polytriarylamine (PTAA) in TFT geometry is investigated using both the ME model and a variable range hopping model. We will show that the two models show very comparable results but that they differ in the predicted temperature dependence of $S$.

In chapter 5, the measurements on a TFT with pentacene on a fluoropolymer dielectric, is discussed. The Seebeck coefficient shows an unexpected carrier density dependent behavior. We explain this behavior by a transition from hopping dominated transport to more bandlike charge transport.

In chapter 6, inorganic amorphous-InGaZnO is investigated. Two charge transport models are discussed, a band percolation model used frequently for a-InGaZnO, and a mixed hopping-ME-model. Three different measurement techniques are used, thermoelectric measurements, mobility measurements, and a scanning Kelvin probe technique. The surprising result is that we find a hopping
dominated charge transport, while bandlike transport was expected based on the available literature on a-InGaZnO.

1.4 Admittance Spectroscopy on Organic Semiconductors

1.4.1 Admittance

In disordered semiconductors an out-of-equilibrium situation can be achieved by applying a time-varying electrical potential, which is done with admittance spectroscopy. Admittance spectroscopy is a small-signal experiment and therefore not far-from-equilibrium. However, electrical potential oscillations result in a non-thermalized charge carrier distribution, as opposed to more common steady-state transport experiments, and can therefore give more insight in far-from-equilibrium processes. When a sudden increase in the number of charge carriers is described as carrier injection at the transport level, the occupation of states around the transport level will be higher than derived from Fermi-Dirac statistics. In view of the thermal activation required this could lead to an increase in conductivity. With the insight on these injected non-thermalized charge carriers relaxation, one could think about the extrapolation to a far-from-equilibrium experiment, where the number of added charge carriers is very high. Would this lead to an increased the Seebeck coefficient?

Charge transport models that describe steady state situations do not by definition describe the thermalization correctly. In this thesis we will study a disordered organic semiconductor using admittance spectroscopy in the context of hopping transport. From the description of the thermalization and the admittance experiments we come to a new derivation of the transport level.

With admittance spectroscopy a small signal current response to a small sinusoidal voltage is investigated. The small sinusoidal voltage is added to a constant voltage \( V_{DC} \),

\[
V(t) = V_{DC} + V_{AC} \exp(i \omega t),
\]

with \( \omega \) the angular frequency and \( V_{AC} < V_{DC} \), except when \( V_{DC} = 0 \) V. The current density response will have the same frequency, but shows a phase difference \( \phi \),

\[
J(t) = J_{DC} + J_{AC} \exp(i(\omega t + \phi)).
\]
The current density response can be expressed in terms of the admittance, $Y$, which is defined as the ratio of the AC components of the current density and the voltage

$$Y = \frac{J_{AC} \exp(i(\omega t + \phi))}{V_{AC} \exp(i\omega t)} = G + i\omega C,$$

with $G$ the differential conductance and $C$ the differential capacitance. Admittance measurements provide a powerful tool to assess the validity of charge transport models. However, unexpected results can be very difficult to analyze.

The experimental values for the admittance can be obtained through impedance measurements. The impedance $Z$ is equal to the inverse of the admittance $Y$. Typical frequencies used in organic semiconductor experiments are between 10 and 1000 Hz. At frequencies much higher than 1000 Hz the charge carriers will not be able to respond, and only a displacement current is measured, telling little about the charge carrier response. At frequencies below 10 Hz the measurement will take a lot of time, since a measurement is preferably done over a large number of oscillations.

### 1.4.2 Capacitance of Organic Semiconductors

In many admittance studies the analysis is focused on the differential capacitance, where the dependence on $V_{DC}$ or the frequency is investigated. Some examples from literature relevant for this thesis are given below.

**Studying Built-in Voltage and Injection Barriers**

Van Mensfoort et al. $^{58}$ have described how the $V_{DC}$ dependence of the differential capacitance can be used to investigate the built-in voltage and the injection barriers. Fig. 1.9 shows an experimental differential capacitance curve for a frequency of 200 Hz of a 100 nm polyfluorene based copolymer hole-only sandwich-type device at room temperature.$^{58}$ The differential capacitance is expressed in terms of the geometrical capacitance, $C_{geom} = \varepsilon A / L$, with $\varepsilon$ the dielectric constant, $A$ the area of the organic layer, and $L$ the layer thickness. The increase below the built-in voltage was explained by charge accumulation with increasing voltage. With more charge present in the device the effective distance between the positive charge in the organic layer and the negative image charge on the electrode will become smaller. In analogy with a parallel plate capacitor the differential capacitance increases when the distance between the plates decreases. At a certain voltage charge will start to flow. The phase lag of the current response has a negative contribution to the differential capacitance, decreasing the total
Figure 1.9: Capacitance-voltage measurements by Van Mensfoort et al.\textsuperscript{58} for a polyfluorene device at 200 Hz. The differential capacitance is expressed in the geometrical capacitance. $T = 295$ K. The peak in the capacitance is shown to occur below $V_{bi}$.

For many double carrier devices the negative contribution is so large that it even leads to a negative capacitance.\textsuperscript{59-61} Taken the two effects together one could say that the increase of the differential capacitance is an effect of the charge near the electrode, and that the decrease is by the charge far away from the electrodes. The latter becomes dominant beyond the voltage of the differential capacitance peak. With this theory for the differential capacitance peak it was thought before that the capacitance peak should be at the built-in voltage, because from that point on a drift current will start to flow. Later it was realized that due to the charge accumulation and the diffusion enhancement in disordered organic materials\textsuperscript{62} a significant diffusion current already starts to flow just below the built-in voltage.

Van Mensfoort et al.\textsuperscript{58} determined the magnitude of this peak shift for single carrier devices,

$$V_{bi} - V_{peak} = \left( \ln \left( 1 - \gamma \right) \right) \frac{k_B T}{e},$$

with $a$ the inter site distance and

$$\gamma = \frac{n_{loc} \exp \left( - \frac{\phi}{k_B T} \right)}{n_0},$$

with $\phi$ the injection barrier and $n_0 = \varepsilon k_B T / (e^2 L^2)$. These equations show that the peak shift depends among others on layer thickness, temperature and depends
strongly on the injection barriers at the electrodes. This is important if one wants to deduce the injection barriers from a differential capacitance measurement.

In the derivation of Eq. (1.26) van Mensfoort assumed that the semiconductor had a low degree of disorder. The disorder dependence of this peak position is one of the topics in this thesis. We will also study the differential capacitance beyond this peak where we will take charge carrier relaxation effects into account. The effect of charge carrier relaxation on the mobility was studied before by Martens et al. using the frequency dependence of the capacitance.

**Studying Mobility from Frequency Dependence**

By measuring the frequency dependence of the differential capacitance the mobility in a sandwich device can be investigated. Martens et al. used the frequency dependence to investigate charge carrier relaxation effects on the mobility in a PPV layer. The small signal potential oscillations result locally in small oscillations in charge carrier density. When the charge carrier density locally increases the injected carriers are not injected at the quasi Fermi level, but at slightly higher energy states. The energy level of these high energy states can be called a transport level. Such a definition of a transport level does not necessarily result in the same value as the definition used in Eq. (1.6) of the Mott-Martens hopping model. For the mobility the precise energy of the injected charge carriers is important in view of the thermal activation required for hopping transport. When charge carriers are injected at a high energy the first few hops are likely to lower energy states, until the charge carriers have thermalized. The Miller-Abrahams hopping rates in Eq. (1.5) show that hops down in energy have relatively high hop rates, therefore an increase in the effective mobility can be expected as long as the injected charge carriers have not completely thermalized. The thermalization is a time dependent process leading to a time dependent mobility. This time dependence can be expressed in a frequency dependence of the mobility. Martens et al. used a phenomenological expression for the mobility

\[
\mu(\omega) = \mu_{DC} \left( 1 + M(i\omega\tau)^{1-\alpha} \right),
\]

with \( \omega \) the angular frequency and \( \tau \) the transit time that would be obtained in a simple drift-only model with a constant mobility,

\[
\tau = \frac{4}{3\mu V},
\]

Here \( M \) and \( \alpha \) need to be fitted to the experimental data.

In addition to the charge carrier relaxation the relaxation of the permanent dipoles is described by a frequency dependent dielectric constant.
\[ \frac{\varepsilon(\omega)}{\varepsilon_0} = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau_0)^{1-\beta}}, \tag{1.30} \]

where \(\varepsilon_\infty, \varepsilon_s, \tau_0,\) and \(\beta\) also need to be fitted to the data.

Although Martens was capable of fitting his model well to his experimental data, there were a number of constants that are not known beforehand. The necessity of fitting the model to the experimental data makes \textit{ab initio} simulations impossible.

### 1.4.3 Admittance Spectroscopy in this Thesis

In chapters 7 and 8 admittance spectroscopy is applied to investigate the extended Gaussian disorder model for a sandwich-type device with a polyfluorene-(triarylamine) (PF-TAA) co-polymer. In chapter 7 we show that the capacitance peak shift expressed in Eq. (1.26) is actually dependent on the disorder of the semiconductor layer. Measurements at voltages beyond the capacitance peak are shown in chapter 8, where the capacitance curve shows a second increase. This increase is explained by charge carrier relaxation effects, which increase the mobility of injected charge carriers. By combining Monte Carlo simulations and a simple ‘multiple trapping and release’ (MTR) model a transport level is determined at which the charge carriers are locally injected. With this transport level, the MTR model is used to calculate a frequency dependent mobility. Applying this frequency dependent mobility in the model gives a fair description of the measured increased differential capacitance.

For high disorder materials the increase in mobility of the injected charge carriers can be a few orders in magnitude, and the thermalization time can be in the order of 1 s. For the just-injected charge carriers a higher average energy is expected than for the thermalized charge carriers. Therefore an increase in the Seebeck coefficient can be expected when the number of injected charge carriers is in the order of the total charge carrier density. An attempt to measure this in an AC Seebeck experiment, with an oscillating charge carrier density in a TFT structure unfortunately failed. The potential modulations resulted in increased noise, and no increased Seebeck coefficient could be found.

### References

Brownian ratchets enable the use of thermal motion in performing useful work. They typically employ spatial asymmetry to rectify non-directed external forces that drive the system out of equilibrium, cf. running marbles on a shaking washboard. The major application foreseen for Brownian ratchets is high-selectivity fractionation of particle or molecule distributions. Here, we investigate the functioning of an important model system, the on/off ratchet for water-suspended particles, in which interdigitated finger electrodes can be switched on and off to create a time-dependent, spatially periodic but asymmetric potential. Surprisingly, we find that mainly dielectrophoretic rather than electrophoretic forces are responsible for the ratchet effect. This has major implications for the (a)symmetry of the ratchet potential and the settings needed for optimal performance. We demonstrate that by applying a potential offset the ratchet can be optimized such that its particle displacement efficiency reaches the theoretical upper limit corresponding to the electrode geometry and particle size. Efficient fractionation based on size selectivity is therefore not only possible for charged species, but also for uncharged ones, which greatly expands the applicability range of this type of Brownian ratchet.

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2.1 Introduction

Ratchet devices are made up of repeated asymmetric units that give rise to an (asymmetric) potential landscape that resembles a washboard or a factory rooftop. Particles that are subjected to both this potential and some unbiased, periodic or random time-dependent force can show a net average motion: The unbiased force is rectified by the ratchet asymmetry and drives a particle current. The ‘particle’ can be an electron or hole, a suspended bead, a marble, a droplet or even a living cell. In a Brownian ratchet random thermal forces are rectified. Hence, in such devices thermal motion is not a disruptive element, but is used to perform useful work. Brownian ratchets were first introduced in a thought experiment by von Smoluchowski. Later, Feynman showed that ratchets can only perform work using Brownian motion when the system is taken out of thermal equilibrium. A recent overview of the field is given in Ref. 1.

The first and main practical application foreseen for ratchets is the separation of particles, molecules, or even living cells. It has been shown in different ratchet systems that current reversals can occur upon minute changes in one of the system parameters. Achieving this for suspended particles (or molecules, cells) would allow one to have any two types of particles being transported in opposite directions, which would open the way to highly selective and small sized particle separators. The typical ‘Drosophila system’ is formed by water suspended particles that are subjected to a time-dependent ratchet-shaped potential – the example of the on/off ratchet is explained in the next section. Different sorts of ‘wet ratchets’ have been employed, and include structured arrays for moving molecules and cells, optical ratchet traps for moving micro spheres, magnetic ratchets for moving superparamagnetic beads, and electric ratchets for moving micro spheres and molecules.

Of the above realizations of wet ratchets, the electric ratchets impose the least constraints on the particle to displace as they can potentially use both electrophoretic and dielectrophoretic forces and are not restricted to (superparamagnetic) magnetic particles. The electrophoretic forces result from the direct interaction between the electric field in the medium and the charge on the particles. Dielectrophoretic forces occur due to the difference in (effective) relative dielectric constant \( \epsilon_r \) between the particle and the medium and the difference in electrostatic energy density \( u \),

\[
\Delta u = \frac{1}{2} \epsilon_0 (\epsilon_{r1} - \epsilon_{r2}) |E|^2
\]

that follows from this. In Eq. (2.1) \( E \) is the local electric field. For particles in conductive media the dielectrophoretic forces are not only determined by the
polarizability. Free charge can flow to the bound charge at the interface between two materials with different $\varepsilon_r$, changing the effective polarizability, which is known as the Maxwell-Wagner mechanism.\(^{23}\) As a consequence of the finite time required for this flow, the effective polarization becomes frequency dependent. The dielectrophoretic force is then written as\(^{24}\)

$$\langle F_{\text{DEP}} \rangle = \pi \varepsilon_m \alpha^3 \text{Re} \left( \frac{\tilde{\varepsilon}_p - \tilde{\varepsilon}_m}{\tilde{\varepsilon}_p + 2 \tilde{\varepsilon}_m} \right) \nabla |E|^2,$$

with $\alpha$ being the particle radius, $\tilde{\varepsilon} = \varepsilon - i\sigma / \omega$ the complex permittivity of the particle (p) and medium (m) with $\varepsilon = \varepsilon_0 \varepsilon_r$, $\omega$ the frequency and $\sigma$ the conductivity. The Clausius-Mossotti factor, Re(), describes the frequency dependence and can have values between +1 and $-1/2$.\(^{23}\) For non-conductive particles as discussed here, Eq. (2.2) implies that for low $\sigma_m / \omega$ the dielectrophoretic force is dominated by its static component (cf. Eq. (2.1)) and can be either positive or negative, depending on the sign of $(\varepsilon_{r,p} - \varepsilon_{r,m})$. For high $\sigma_m / \omega$ the force is dominated by the free charges at the particle-fluid interface giving rise to negative dielectrophoresis.

In a general electrically driven wet ratchet, the dominance of electrophoretic or dielectrophoretic forces depends on subtle, and sometimes hard to control details of the system such as the surface charge of particles or the ion concentration in the medium. This issue is particularly relevant as one and the same driving signal can lead to rather different net forces on the particle, depending on which force dominates; below it will be shown that a potential that is highly asymmetric for electrophoretic interactions may actually be completely symmetric for dielectrophoretic interactions. In previous works, dominance of dielectrophoresis was enforced using modulated high frequency potentials.\(^{19,21}\) In contrast, when low frequency potentials were employed electrophoresis was assumed dominant.\(^{18}\)

Here, we use an on/off ratchet, consisting of asymmetrically spaced interdigitated electrodes on a planar substrate, to displace suspended polystyrene spheres. A major advantage of this design is that the magnitude of the potential minima and maxima, and hence the symmetry of the drive, can be independently tuned. Using both simulations and experiments we show that also at low frequency drive the potential profile experienced by the particle is dominated by dielectrophoresis. Being able to qualitatively explain the observed behavior, this knowledge can be exploited to optimize the particle displacement, bringing it to the theoretical maximum expected for this device layout and particle size: displacement data match calculations without free parameters.
Figure 2.1: (a) Schematic overview of the ratchet device consisting of interdigitated finger electrodes on a silicon wafer with a 200 nm isolating thermal silicon dioxide layer on top. A patterned slab of PDMS is placed on top creating a 25 μm × 100 μm micro channel for the suspended particles. (b) Schematic electrostatic potential along the micro channel at three subsequent moments in time explaining the ratchet mechanism. At time \( t_1 \) all particles are in the same trap. At \( t_2 \) the electrodes are switched off allowing (undirected) diffusion. At \( t_3 \) the electrodes are switched on again, due to the asymmetry a net displacement of particles results. The cartoon assumes electrophoresis to be dominant over dielectrophoresis. The asymmetry parameter \( \alpha \) is explained in the final ratchet trap.
2.2 Device Principle and Experimental Details

The ratchet used here, the electrical on/off ratchet, is explained in Fig. 2.1(a). Two sets of asymmetric interdigitated finger electrodes, AF1 and AF2, are placed on an insulating surface. When these finger electrodes are biased with different polarity, suspended charged particles present in the micro channel are trapped in the resulting asymmetric potential wells (Fig. 2.1(b)). When the potential on the electrodes is switched off, the particles diffuse without a preferential direction. After a certain time the potential is switched on again. The asymmetry of the potential wells leads to an asymmetry in the retrapping. More particles have diffused over the short distance in the asymmetric repeat unit, i.e., past the electrode on the right, than over the long distance to the left. Hence, a larger fraction of particles becomes retrapped in the nearest neighbor trap on the right, than in the nearest neighbor trap on the left. The asymmetry therefore results in a net particle current. Also, when other than electrophoretic forces are present or even dominant, the device remains a ratchet as long as a spatial asymmetry in the forces is maintained.

The parameter \( \alpha \) indicates the asymmetry, and is defined as the location of the trapping position over the total length of the repeat unit, shown in Fig. 2.1(b); hence \( \alpha = 1/2 \) corresponds to a symmetric device.

The ratchets sketched in Fig. 2.1(a) were fabricated on Si-SiO\(_2\) substrates. The finger electrodes have a width of 1 \( \mu \)m, a length of 1 mm, and a thickness of 30 nm (5 nm Ti, 25 nm Pt). The short distance between the fingers is 1 \( \mu \)m and the long distance is 4 \( \mu \)m. The electrodes are defined using conventional UV photolithography and lift off. A patterned poly(dimethylsiloxane) (PDMS) slab with the micro channel is fabricated from a SU8 mold fabricated using photolithography.

Measurements are performed for 300 nm (Ademtech, Standard Carboxyl-Adembeads 0213) and 500 nm (Ademtech, MasterBeads Carboxylic Acid 0215) polystyrene spheres functionalized with carboxylic acid. Suspended in a \( 10^4 \) times diluted phosphate buffered saline (PBS) solution (0.015 mM) with \( \text{pH} \ 7.4 \), the particles are negatively charged. An optical microscope (Leica CTR6000M) with immersion objective (Leica HXC APO L63X/0.90W U-V-I) and a high speed camera were used to record the particle motion at 50 frames s\(^{-1}\) and a pixel size of 91 nm. The images were analyzed using home-written software in MatLab from which the particle position and subsequently their movement could be determined with subpixel precision.

2.3 Results

Typical ratchet behavior was measured for the negatively charged 300 and 500 nm polystyrene spheres. When the electrodes are turned on, electrode AF1 is biased to
375 mV and AF2 to –375 mV, defined with respect to a reference electrode outside the channel. On periods are marked by the shaded areas in Fig. 2.2(a). When turned off both AF1 and AF2 are set to 0 V. During the ‘off’ period of 6 s there is little average movement and it is undirected, showing the absence of convective or other background fluid motion. The diffusive spread of the initially highly localized particle distribution does not show up in this ensemble-averaged graph of approximately 200 particles. Upon switching on the potential, the particles show an average movement (marked by a 1) which saturates when most particles reach their respective equilibrium or ‘trap’ location. This behavior closely follows the expected on/off ratchet behavior discussed in Fig. 2.1(b). After 2 s, when the ratchet potential is turned off again, the particles show a short, sudden movement, marked by a 2. We tentatively attribute this unexpected motion to transient electric fields arising due to the delayed rearrangement of ions in the electrostatic double layers after the sudden change in electrode potential: Upon removal of the positive bias on AF1 the screening anions cause a repulsive force for the negatively charged beads, driving them towards AF2, i.e., in the positive x-direction. Alternatively, drag forces due to redistributing ions could have a similar effect. In either case, the associated displacement is smaller than the electrode width and will therefore not break down the ratchet mechanism and convert the device to a ‘plain’ pumping device. Actually, feature 2 turns out to be decoupled from the ratchet effect No. 1 in which we are interested and will be disregarded in the remainder of this chapter: All displacements shown below refer to feature 1 only.

Fig. 2.2(b) shows that going from forward drive to reverse drive, i.e., switching the polarity of the electrodes, results in the same behavior but in the

![Figure 2.2: Average position during one driving cycle determined from approximately 200 particles (500 nm). Shaded areas indicate the electrodes being switched on. With (a) forward drive, (b) reverse drive, achieved by changing polarity. The insets show the driving potentials on the two electrodes.](image-url)
moving charged particles in fluctuating and disordered energy landscapes 39

Figure 2.3: (a) Average displacement after switching the electrodes on vs. the potential of the positive electrode. The potential difference between AF1 and AF2 remains 750 mV and the on (off) time is equal to 2 (6) seconds. The black and the grey points are two sets of nominally identical measurements taken on two different days. (b) Average displacement vs. the off time for two sizes of particles with electrode AF1 = 50 mV and AF2 = –700 mV. Measurements are indicated by the squares, calculations by the solid lines. Dashed lines indicate other asymmetries for 500 nm particles.

opposite direction. This is expected from a ratchet. In the direction parallel to the electrodes no notable features could be found, which is shown in Appendix A.

Fig. 2.3(a) shows two sets of measurements in which we varied the central potential offset of the finger electrodes, while keeping the potential difference at 750 mV (see inset). The electrode potentials in the off state are still equal to 0 V. In Fig. 2.3(a) the average displacement is plotted versus the potential of the positive electrode. Although the figure shows that the reproducibility between sets of nominally identical experiments is still an issue, the reproducibility within each experimental run is good which is demonstrated by the magnitudes shown in Figs. 2.2(a) and (b). As standard cleaning procedures were used, the differences between the two sets of experiments are most likely due to variations in the amount of surface charges on the SiO$_2$ substrates, which are notoriously hard to control in humid or wet environments. For the present purposes this is not problematic but for real applications improved surface control is mandatory.

The experimental results in Fig. 2.3(a) can be considered surprising if one expects the ratchet to work due to electrophoretic forces only, as in this case the asymmetry should hardly change when only changing the offset of the electrodes. The explanation of the measurements will follow in the next section.

All the measurements up to now are done with an off time of 6 s. Fig. 2.3(b) shows measurements of the displacement as a function of the off time using two sizes of beads. In view of the results in Fig. 2.3(a) the measurements are performed with an offset of –325 mV, i.e., with the positive (AF1) and negative (AF2) electrodes at 50 and –700 mV when on, respectively. The off time dependence found is what would be expected for this type of ratchet.$^{15,18,21,25}$ For
short off times, where the time to diffuse is the limiting factor of the displacement per cycle, the 300 nm particles have a larger average displacement than the 500 nm particles. This is a direct consequence of the larger diffusion constant of the smaller particles: More particles have been able to diffuse to the capture area of the nearest neighbor trap.

From the size and off-time dependence in Fig. 2.3(b) we conclude that applying the potential offset did not break down the ratchet mechanism. In the next section we will discuss the origin of the offset dependence found in Fig. 2.3(a).

2.4 Discussion

2.4.1 Driving Forces

Figs. 2.2(a) and (b) seem to correspond to the model described in Fig. 2.1(b). However, the potential offset dependence of the average displacement cannot directly be explained by this model. Upon closer inspection we observed that the equilibrium trapping position in the experiments is not located above the positive electrode as expected from a dominant electrophoretic interaction. Rather, the particles accumulate in the 1 μm gap between the two electrodes (Fig. 2.4(a)). An experiment with an identical device layout, but for a short inter-electrode distance of 2 μm instead of 1 μm showed that the particles are in fact attracted to the edge of the positive electrode (Fig 2.4(b)).

This accumulation position cannot be explained by electrophoresis. Also electro-osmosis could, potentially, play a role in fluid motion and hence particle displacement, but cannot explain the observed static accumulation position after the particles have reached their equilibrium positions. This leaves dielectrophoresis as the explanation for the off-electrode accumulation position.

It has been shown that particles subjected to non-uniform AC-electric fields are often driven by dielectrophoretic forces.\textsuperscript{19,23} Whether electrophoretic or dielectrophoretic forces dominate in quasistatic situations like considered here depends on subtle details of the experimental system.\textsuperscript{23,24} As mentioned in the introduction, dielectrophoretic forces occur due to the different effective dielectric constants of polystyrene and water which depend on the static dielectric constants (\(~2.7\) and \(~80\), respectively) and on the conductivity of the buffer solution. Depending on the frequency and the system parameters a particle will therefore be attracted to either the field maximum or the field minimum. Intuitively one might expect a high instead of a low electric field at the side of an electrode. However, in Figs. 2.4(c) and (d) we show two-dimensional finite element simulations of the static electric field in the solution along one repeat unit of the micro channel. The calculations represent the fields in the on state when the particles are trapped.
These simulations were performed using COMSOL Multiphysics 3.4. When the particles are trapped and have reached their steady state positions, no current of any kind flows and we can assume local equilibrium holds and Boltzmann statistics can be applied. The charge carrier density is then calculated using the Boltzmann equation

$$\rho = eN_A \sum_i z_i M_i \exp \left( \frac{-z_i e V}{k_B T} \right),$$  \hspace{1cm} (2.3)$$

with $N_A$ being Avogadro’s number, $z_i$ the valency of the ion species, $M_i$ its molarity in mol dm$^{-3}$, $k_B$ the Boltzmann constant, and $T$ the temperature. The surface charge on the SiO$_2$ was calculated to be $-5.4$ C m$^{-2}$ from a generalized Grahame equation

$$\sigma_{\text{surface}} = \sqrt{4 \varepsilon_0 \varepsilon_r k_B T \sum_i \left( n_{0i} \exp \left( - \frac{ez_i V_0}{k_B T} \right) - 1 \right)},$$  \hspace{1cm} (2.4)$$

with $n_0$ the ion concentration and $V_0$ the SiO$_2$ surface potential. More details can be found in Appendix B. Figs. 2.4(e) and (f) show the electric field magnitude $|E|$ over a cross-section at a height of $z = 1 \mu$m. The finger electrodes are biased at $375$ mV (AF1, left) and $-375$ mV (AF2, right), i.e., with zero central offset. The field minima at the sides of the positive electrode occur due to the presence of a negative surface charge on the silicon dioxide at pH 7.4. The perpendicular component of the electric field $E_z$ of the silicon dioxide surface is opposite to that of the positive electrode and there the superposition results in a minimum in the electric field magnitude $|E|$. Hence, dielectrophoretic interactions are expected to lead to a pileup of beads either beside the positive electrode, i.e., in the field minimum, or on top of the electrodes, i.e., in the field maxima. Electrophoresis would still pile up (negatively charged) beads on top of the positive electrode. Since the beads pile up in the field minimum we conclude that the equilibrium trapping position in the present system is dominated by negative dielectrophoresis. By disregarding the silicon dioxide surface charge the field minimum is found exactly in the middle between AF1 and AF2. This does not correspond to the trap position observed in Fig. 2.4(b). However, we confirmed the dominance of dielectrophoresis over electrophoresis in determining the particle trapping position by applying a fast AC (100 Hz) instead of DC potential to the electrodes, which led to a pile up of beads at the same positions as shown in Fig. 2.4.

Having established negative dielectrophoresis as being responsible for the
equilibrium position of the beads when the electrodes are biased might suggest that the beads should move away from the bottom surface, in the direction of lower electric field, see Figs. 2.4(c, d). However, gravitational forces counteract this, leading to an equilibrium position in close vicinity of the SiO₂ surface.

Although essential to explain the trap position, the field calculation in Fig. 2.4 cannot explain the preferential pile up of virtually all beads on the right-hand side of the left electrode, since many particles have to pass the high field region above the left electrode to get there after switching on. This high field region is dielectrophoretically ‘repelling’. We tentatively attribute this to transient
electrophoretic forces during switching and electro-osmosis. Due to the static screening of the electric field, Fig. 2.4 shows negligible potential gradients between $x = 0$ and 1 $\mu$m and between $x = 6$ and 7 $\mu$m, i.e., over most of the long distance in the asymmetric repeat unit. However, in the experiments the fast motion directly after switching the potential on shows that the beads do experience a significant force in those regions shortly after switching. When the potential is switched on, the (changes in the) screening double layers need some time to form, during which the field penetrates further into the fluid, attracting the beads towards the positive electrode. Furthermore electro-osmosis can play an important role as the double layer ions can create a fluid motion that drags the particles along. Although this effect can assist particles in overcoming dielectrophoretically ‘repelling’ regions, it cannot explain the lack of diffusive motion once the particles have reached their equilibrium position.

The importance of transient electric fields makes it extremely difficult to predict the particle displacement from field calculations. It becomes even more complicated due to the spread in particle height, estimated to be 0.6 – 6 $\mu$m (Appendix C), making it virtually impossible to even define one asymmetry $\alpha$ on the basis of steady state calculations.

In the next section it will be shown that an ‘effective asymmetry’ can nonetheless be determined from experimental results.

### 2.4.2 Symmetry Considerations

We started out explaining the device using Fig. 2.1(b), displaying the position dependent potential, relevant for electrophoresis. Whereas the electrophoretic force is proportional to the gradient of the potential,

$$ F_E \propto \nabla V, \quad (2.5) $$

the dielectrophoretic force is proportional to the gradient of the squared electric field,

$$ F_D \propto \nabla|E|^2 = \nabla|\nabla V|^2. \quad (2.6) $$

The dielectrophoretic analog of the ratchet potential in Fig. 2.1(b) would therefore show the square of the electric field magnitude $|E|^2$ i.e., $|\nabla V|^2$. This we will use to look at the asymmetry of the dielectrophoretic ratchet.

With Fig. 2.5 we can explain that using equal potential amplitudes on the positive and the negative electrodes (solid lines), and disregarding the SiO$_2$ surface charge, results in a perfectly symmetric dielectrophoretic ‘ratchet’, from
which no net particle current is to be expected. Fig. 2.5(a) shows the corresponding potential; the shaded areas represent the electrode positions. Clearly, the maximum and the minimum in the potential have an equal magnitude but different sign. The field directed along the micro channel $E_x$ is simply the derivative of this potential curve and is displayed in Fig. 2.5(b). Note that $E_x = dV/dx$ is inversion symmetric in $x = 3.5 \mu m$. Fig. 2.5(c) shows that the field perpendicular to the SiO$_2$ surface, $E_z$, is not symmetric. However, the magnitude of $E_z$ is symmetric. The total field squared (Fig. 2.5(d)) will therefore also be symmetric in $x = 3.5 \mu m$. Inversion asymmetry can be induced by applying an offset to the finger potentials in the on state as illustrated in the inset of Fig. 2.3(a). An (unintended) potential offset can also result from the SiO$_2$ surface charge, or from electrochemical processes at the (reference) electrode(s). To investigate the consequences of an offset to the electrode potentials the dashed line in Fig. 2.5 shows the potential and field if one applies an equal offset to both electrodes when turned on. Figs. 2.5(b) and (c) show that the field magnitudes in the $x$ and $z$ directions are no longer symmetric in $x = 3.5 \mu m$. The latter can be understood from the three-dimensional geometry and the screening by the water: The perpendicular field $E_z$ goes nonlinearly to zero when moving away from $z = 0$. Hence, at any given height, $E_z$ will depend on offset; in particular, the magnitude of $E_z$ will be different if the positive and negative electrodes have an unequal bias magnitude due to a nonzero offset. As a consequence the square of the field magnitude does have a ratchet shape now, i.e., it lacks inversion symmetry. This result tells us that asymmetric biasing of the electrodes while keeping the potential difference equal should alter the particle displacement efficiency in a dielectrophoretic ratchet. Here, we use the average displacement per on/off cycle as a measure for the displacement efficiency – a real (dimensionless) efficiency can be obtained by e.g., normalization by the ratchet period. Although the magnitudes of the electrostatic potential change, the (a)symmetry of the electrostatic potential is virtually unaffected by the asymmetric biasing.

Both data sets in Fig. 2.3(a) indeed show that the average displacement depends monotonically on the asymmetry in the on bias on AF1 and AF2, as anticipated for a dielectrophoretic ratchet. Unfortunately, the workable bias interval is insufficient to observe the anticipated minimum where the net potential turns symmetric and dielectrophoretic driving will be absent. Using more positive or negative biases first results in undesired fluid motion and later in hydrolysis. Apart from the SiO$_2$ surface, also the Au electrode may carry a basically unknown surface charge. This makes it hard to predict whether an increase or a decrease in displacement efficiency is to be expected upon increasing the asymmetry in the on biases.

Summarizing this discussion, both the observed accumulation position and the dependence of the average displacement on the potential offset can be explained by dielectrophoresis.
2.4.3 Particle Displacement

The solid lines in Fig. 2.3(b) show the expected average displacement per cycle for the two types of polystyrene particles in this geometry, i.e., with short and long distances of 2 and 5 μm and a total repeat unit length of 7 μm. Geometrically, $\alpha = 2/7$ is expected for our geometry and this value is used in the calculations; other, potentially height-dependent values can result from the interplay between surface charges and screening and from the dynamic competition between electrophoretic and dielectrophoretic interactions, as discussed above. The calculation is very similar to those in Refs. 15, 18, and 25, and evaluates the fraction of charges that, after diffusion from a given starting position for a time $t_{\text{off}}$, ends up above neighboring potential minima. This is calculated by integrating the Gaussian particle distribution at the potential well. Further details of the calculation are given in Appendix D, but it should be stressed that it contains no freely adjustable parameters. The agreement between calculation and experiment is striking, and indicates that the used bias parameters, which are at the edge of the window for stable operation, are close to optimal.

In spite of being practically impossible to determine from electric field calculations, the measurements show that the device does operate with an effective asymmetry parameter that is very close to the geometrically expected value of $\alpha = 2/7$. Even more remarkable is the fact that Fig. 2.3(a) suggests that decreasing the offset further, i.e., to negative values, can increase the particle
displacement efficiency beyond the 1.5 μm that is expected from this electrode configuration. If this would indeed be the case, one could speculate that the most likely cause is transient effects related to ionic motion upon switching.

2.5 Conclusion

We fabricated electrical ratchets for suspended particles in water. A detailed analysis of equilibrium particle positions showed that even for low frequency driving dielectrophoretic rather than electrophoretic forces determine the particle trapping. The combination of a negative SiO₂ surface charge and a positively charged electrode creates a field minimum at the side of the positive electrode, making this the dielectrophoretical equilibrium position for the polystyrene spheres. Particle motion, in contrast, appears to be driven by dielectrophoretic, electrophoretic, and electro-osmotic interactions which we attribute to the finite time required by ions in the solution to reach equilibrium. The dominance of dielectrophoretic forces qualitatively changes the biasing scheme. However, by varying the asymmetry in the on bias applied to the interdigitated electrodes the particle displacement efficiency of the device can be tuned to its theoretically predicted maximum value. There are indications that the efficiency can go beyond this value.

References


We show a diffusion enhancement of suspended polystyrene particles in an electrical on/off ratchet. The enhancement can be described by a simple Master-equation model. Furthermore, we find that the diffusion enhancement can be described by a general curve whose shape is only determined by the asymmetry of the ratchet repeat unit. The scaling of this curve can be explained from an analytical expression valid for small off-times. We demonstrate how the Master-equation model can be used to find the driving parameters for optimal particle separation. The device as used in the experiments is very slow when a separation quality is desired comparable to the size dispersion in commercially available particles. However, calculations show that miniaturizing the device tenfold can enhance the separation speed to acceptable values.
3.1 Introduction

In a Brownian ratchet the random thermal motion of particles is used to create directed transport. By subjecting the particles to an asymmetric periodic potential and driving the system out of equilibrium, e.g., by superposing an oscillating force, the random motion is rectified into directed motion. Many different types of Brownian ratchets have been realized.\(^1\) For example, ratchets have been demonstrated for suspended particles using structured arrays,\(^2-4\) optical fields,\(^5,6\) magnetic fields,\(^7-9\) and electric fields.\(^10-13\) Here we focus on the on/off ratchet for suspended particles, where the periodic potential itself is oscillating in time, as explained in Fig. 3.1(a).

Ratchets have been proposed as possible separators of different types of particles.\(^11-14\) When using a ratchet as a particle separator there are two important factors. One is the difference in average velocity of different types of particles, which is preferably as large as possible. Second, the spread of an ensemble of equal particles should be as small as possible. As depicted in Fig. 3.1(b), a mixture of two types of particles can then eventually be extracted from a microchannel as two separated particle distributions.

A sufficient difference in average velocity can be achieved when the particles have a large enough difference in size. However, the second criterion can be more problematic. A ratchet can enhance the spreading of particles compared to the diffusion derived from the Einstein relation. This can be seen in Fig. 3.1(a) where at time \(t_2\), when the potential has been restored, the spreading has increased as compared to thermal diffusion at \(t_1\). This increase can be expressed as an increased effective diffusion constant, \(D_{\text{eff}}\), of the whole ensemble of particles. For rocking ratchets this has been calculated\(^15-19\) and has experimentally been confirmed.\(^20,21\) A similar increased diffusion is calculated\(^22\) and measured\(^23\) for particles between oscillating potential barriers of a non-ratchet device. However, apart from an anomalous increased diffusion perpendicular to the transport direction,\(^8\) the enhanced diffusion along the transport direction has not been shown for on/off ratchets, even though \(D_{\text{eff}}\) is one of the critical parameters for successful particle separation.

Here we demonstrate the diffusion enhancement for water-suspended polystyrene particles in an electrical on/off ratchet.\(^24\) We develop a Master-equation model with which the average movement and effective diffusion constant can readily be calculated numerically for on/off ratchets of arbitrary shape. We compare the results with measurements of the effective diffusion of suspended polystyrene particles. The model and the experiment show good agreement. For every asymmetry, the diffusion enhancement can be described by a master curve. The scaling of this curve will be explained using an analytical expression of \(D_{\text{eff}}\).
Figure 3.1: (a) Particles in an on/off ratchet potential for three moments in time, showing the principle of an on/off ratchet. (b) The ratchet as a particle separator. Two types of particles are injected as a mix and extracted as two separated distributions. The effective diffusion coefficient, $D_{\text{eff}}$, is defined at the distribution on the utmost right, with $n$ the number of on/off cycles and $t_{\text{off}}$ the time per cycle for free diffusion.

valid for low off-times. Furthermore we apply the Master-equation model to calculate the optimum switching time for the separation of the two particles sizes used in the experiment. The separation quality is expressed in terms of a measure of the resolution that is used in the field of chromatography. As a final test of the separation quality of the ratchet device we calculate the separation of two particle species with a relatively small size difference that is comparable to the size dispersion in commercially available particles.

### 3.2 Effective Diffusion of Suspended Particles

The water-suspended polystyrene particles are measured in a microchannel above asymmetrically placed interdigitated finger electrodes. The ratchet has a spatial period of $L = 7 \ \mu\text{m}$; geometrically, the short side of the ratchet unit equals $x_{\text{short}} = 2 \ \mu\text{m}$. Particle displacement is recorded with an optical microscope and a high speed camera. A full description of the on/off ratchet and measurement setup
is given in Ref. 24, which focuses on the interaction forces. We reanalyze the experimental data which was used to determine the average displacement of 300 and 500 nm particles vs. \( t_{\text{off}} \) in our previous work. Here we calculate the effective diffusion coefficient, \( D_{\text{eff}} \), using

\[
D_{\text{eff}} = \frac{\sigma_{\text{eff}}^2}{2n_{\text{cycl}}t_{\text{off}}}, \quad \text{with} \quad \sigma_{\text{eff}}^2 = \sum_i p_i (x_i - \bar{x})^2, \tag{3.1}
\]

where \( n_{\text{cycl}} \) is the number of on/off cycles and \( \bar{x} \) the average position of the particles. Fig. 3.2 shows \( D_{\text{eff}} \) normalized by the Einstein-Stokes diffusion constant as symbols.

### 3.3 Master-Equation Model

To describe on/off ratchet measurements we developed a rather simple Master-equation model. The driving of the particles in the experiment has been shown to be dielectrophoretic in nature;\(^{24}\) however, the model does not require any assumptions on the nature of the driving. It only assumes well defined locations of the potential well boundaries and potential minima. The time dependence of the ratchet potential is modeled as a block function, which is consistent with the experimental realization. The on-time is assumed to be long enough to trap all particles to a distribution that can be approximated as a delta function.

We define a probability, \( p_i \), of finding a particle in a trap \( i \), which is equal to the number of particles in the trap, \( n_i \), divided by the total number of particles present in the device, \( N \), hence
\[ p_i \equiv \frac{n_i}{N}. \]  
(3.2)

After switching the ratchet potential off the particles diffuse from a delta-shaped distribution to a Gaussian distribution. The rate per on/off cycle, \( \gamma_{ij} \), at which a particle displaces from trap \( i \) to \( j \) is calculated from the integral of the Gaussian distribution of particles as

\[ \gamma_{ij} = \frac{1}{\sigma_{\text{ES}} \sqrt{2\pi}} \exp \left( -\frac{(x - X_j)^2}{2\sigma_{\text{ES}}^2} \right) \text{d}x, \]  
(3.3)

with \( x_{j,j+1} \) and \( X_j \) defined in Fig. 3.1(a). The width of the distribution is calculated as \( \sigma_{\text{ES}} = \sqrt{2D_{\text{ES}} t_{\text{off}}} \), with \( t_{\text{off}} \) the time of the ratchet being in the off-state, and \( D_{\text{ES}} = k_B T / 6\pi r \eta \) the Einstein-Stokes diffusion coefficient with \( k_B T \) being the thermal energy, \( \eta \) the viscosity, and \( r \) the particle radius.

For the Master-equation model the rate at which the trap occupation changes is written as

\[ \frac{dp_i}{dt} = \sum_j (\gamma_{ji} p_j - \gamma_{ij} p_i). \]  
(3.4)

The change per cycle in occupation for a whole array of traps can be calculated as

\[
\begin{pmatrix}
\Gamma_1 & \gamma_{21} & \gamma_{31} & \cdots \\
\gamma_{12} & \Gamma_2 & \gamma_{21} & \\
\gamma_{13} & \gamma_{12} & \ddots & \\
\vdots & \vdots & \ddots & \Gamma_{\text{final}}
\end{pmatrix}
\begin{pmatrix}
p_1 \\
p_2 \\
p_3 \\
p_{\text{final}}
\end{pmatrix}
= \begin{pmatrix}
\delta p_1 \\
\delta p_2 \\
\delta p_3 \\
\delta p_{\text{final}}
\end{pmatrix},
\]  
(3.5)

with \( \Gamma_i = -\sum_j \gamma_{ij} \), from the right hand side of the sum in Eq. (3.4). Note that, apart from the middle diagonal, the matrix consists out of diagonals of the same value, since \( \gamma_{12} = \gamma_{23} = \gamma_i i+1 \). By taking \( p_{\text{final/2}} \) equal to one and all other traps empty, the average displacement per cycle and the effective diffusion coefficient of the entire particle distribution can be calculated by evaluating Eq. (3.5) only once. A few hundred subsequent evaluations for an array of a few hundred traps can easily be performed as well. Comparable to ‘normal’ free diffusion, the calculations show
that the width of the distribution $\sigma_{\text{eff}}$ changes with $\sqrt{n_{\text{cycl}}}$, and $D_{\text{eff}}$ is independent of $n_{\text{cycl}}$, i.e., independent of time.

Fig. 3.2 shows the results of the Master-equation calculations as lines for two different ratchet asymmetries, $\alpha = x_{\text{short}} / L = 1.5/7$ and $\alpha = 2/7$, with $T = 298$ K and $\eta = 8.9 \times 10^{-4}$ Pa s. For the 500 nm particles and an asymmetry of $\alpha \approx 1.5/7$ a good agreement between experiments and calculations is obtained. Both clearly show a peak in $D_{\text{eff}}$ for intermediate $t_{\text{off}}$. The agreement for the 300 nm particles is of somewhat lower quality. The low $D_{\text{eff}}$ at low $t_{\text{off}}$ is due to the very limited diffusive spread ($<< x_{\text{short}}$) of the particles for low $t_{\text{off}}$. This reduction of $D_{\text{eff}}$ becomes smaller with increasing $t_{\text{off}}$, where at intermediate $t_{\text{off}}$ we observe a $D_{\text{eff}}$ that is larger than the Einstein-Stokes diffusion. This diffusion enhancement is explained by the process displayed in Fig. 3.1(a), where the ratchet potential displaces particles during the retrapping process, increasing the width of the total distribution. Finally, when $t_{\text{off}}$ becomes very large, $D_{\text{eff}} / D_{ES}$ approaches 1, since the average displacement by the retrapping becomes small compared to the width $\sigma_{ES}$. The shape of the diffusion enhancement curve is very similar to the diffusion enhancement vs. tilting force in rocking ratchets, where the enhancement can be explained by similar reasoning.

Finally, we remark that the effective asymmetry $\alpha \approx 1.5/7$ found here on basis of the effective diffusion constant is rather close to $\alpha \approx 2/7$ found in Ref. 24 by analyzing the average displacement of the beads.

### 3.4 Scaling of the Diffusion Enhancement

The number of particles that moves from trap $i$ to trap $j$ is described in Eq. (3.3) to depend on the width of the diffused particle distribution originating from trap $i$. Therefore the diffusion enhancement curve can be generalized to a curve that depends on this width, $\sqrt{2D_{ES}t_{\text{off}}}$. In fact for each asymmetry $\alpha$ a master curve can be found that describes the effective diffusion enhancement. These curves are shown as a function of the width relative to the trap length $L$ and the asymmetry $\alpha$ for five different asymmetries in Fig. 3.3(a). The shape of the curve only depends $\alpha$, all other parameters are contained in the scaled axis variables which include the temperature, viscosity, and particle radius. The scaling can be explained from describing the diffusion using an analytical expression for the fraction of particles, $s$, that is displaced to the spatially nearest trap, for $t_{\text{off}} << (1 - \alpha)^2 L^2 / 2 D_{ES}$, as

$$s = \frac{1}{2} \text{erfc} \left( \alpha L / \sqrt{4 D_{ES} t_{\text{off}}} \right)$$  \hspace{1cm} (3.6)

from which the width of the distribution can be approximated as\textsuperscript{11}
\[ \sigma^2 = n_{\text{cyl}} L^2 s (1 - s), \tag{3.7} \]

where \( \text{erfc} \) is the complementary error function. Using Eq. (3.1), the effective diffusion constant becomes

\[
D_{\text{eff}} = \frac{L^2}{4 t_{\text{off}}} \text{erfc} \left( \frac{\alpha L}{\sqrt{4 D_{\text{ES}} t_{\text{off}}}} \right) \left[ 1 - \frac{1}{2} \text{erfc} \left( \frac{\alpha L}{\sqrt{4 D_{\text{ES}} t_{\text{off}}}} \right) \right], \tag{3.8}
\]

which can be rewritten as

\[
\frac{\alpha^2}{D_{\text{ES}}} D_{\text{eff}} = \frac{\alpha^2 L^2}{4 D_{\text{ES}} t_{\text{off}}} \text{erfc} \left( \frac{\alpha L}{\sqrt{4 D_{\text{ES}} t_{\text{off}}}} \right) \left[ 1 - \frac{1}{2} \text{erfc} \left( \frac{\alpha L}{\sqrt{4 D_{\text{ES}} t_{\text{off}}}} \right) \right]
= \frac{1}{2 \chi^2} \text{erfc} \left( \frac{1}{\chi \sqrt{2}} \right) \left[ 1 - \frac{1}{2} \text{erfc} \left( \frac{1}{\chi \sqrt{2}} \right) \right], \tag{3.9}
\]

explaining the choice of the \( x \)- and \( y \)-axis scaling. Eq. (3.9) is displayed in Fig. 3.3(a) as the dashed line and is almost overlapping the low \( \alpha \) curve. The \( \chi \) value where Eq. (3.9) breaks down scales roughly with \( \alpha^1 \), leading to comparable \( t_{\text{off}} \) values for the break down. Even though the expression is valid for \( \alpha \to 0 \), the choice of the \( x \)-axis makes it impossible to actually display the curve for \( \alpha = 0 \). For \( \alpha = 0 \), Eq. (3.8) reduces to the simple size independent expression

\[
D_{\text{eff}, \alpha=0} = \frac{L^2}{8 t_{\text{off}}}, \tag{3.10}
\]

which predicts the numerical results within 10% accuracy as long as \( \sqrt{2 D_{\text{ES}} t_{\text{off}}} < 0.4 L \). Eq. (3.10) is displayed in Fig. 3.3(b) together with numerical calculations for three different particle sizes. For large \( t_{\text{off}} \) all asymmetries have \( D_{\text{eff}}/D_{\text{ES}} \) approaching 1, therefore the curves in Fig 3.3(a) approach \( \alpha^2 \). The peak in the diffusion enhancement remains at the same coordinates for low \( \alpha \). We determined that for \( \alpha \leq \frac{1}{4} \) the diffusion peak sits at \( \chi = 0.78 \pm 0.01 \) with a height of \( \alpha^2 D_{\text{eff}}/D_{\text{ES}} = 0.148 \pm 0.001 \), which corresponds to the value found with Eq. (3.9). We therefore conclude that for intermediate and strong asymmetries, \( \alpha \leq \frac{1}{4} \), the effective diffusion peak occurs at
\[ t_{\text{off, peak}} = \frac{(0.78 \alpha L)^2}{2D_{\text{ES}}} = \frac{3\pi \eta r (0.78 \alpha L)^2}{k_B T}, \tag{3.11} \]

with

\[ D_{\text{eff, peak}} = \frac{0.148 D_{\text{ES}}}{\alpha^2} = \frac{0.148 k_B T}{\alpha^2 6\pi\eta r}. \tag{3.12} \]

Figure 3.3: (a) Calculations (solid lines) of the effective diffusion master curves for different asymmetries \( \alpha \). All other parameters are contained in the \( x,y \)-variables. The dashed line is calculated from Eq. (3.9). The measurements (symbols) are the same results as displayed in Fig. 3.2, the dotted line is calculated with \( \alpha = 1.5/7 \). (b) The analytical expression Eq. (3.10) (thick line) and the numerical calculations of the effective diffusion constant for three particle sizes (thin lines), all with \( L = 7 \, \mu m \) and \( \alpha = 0 \).
3.5 Practical Implications

We mentioned in the Introduction that for particle separation the effective diffusion is preferably as small as possible. In that view the diffusion enhancement is no good news. Irrespective of a diffusion enhancement, for having a particle separation as effective as possible one has to find the device and driving parameters for the best combination of a low effective diffusion and a large average velocity difference between the particles. These parameters can be found using the same Master-equation model, which we will apply to calculate the optimal $t_{\text{off}}$ for the system used here. The calculations are fast and therefore a whole range of $t_{\text{off}}$ can be calculated to find a maximum purity. Fig. 3.4 shows a calculation for the two particle sizes used in Fig. 3.2 with $\alpha = 1.5/7$ and $t_{\text{off}} = 0.32$ s. The solid lines are the average positions of the particle distributions after $n_{\text{cycl}}$ cycles. The short dashed lines indicate the $\pm \sigma$ points. If enough cycles are allowed, any two particle sizes can in principle be separated, since the difference in position is linear in $n_{\text{cycl}}$ while $\sigma \sim \sqrt{n_{\text{cycl}}}$.

The long dashed line shows the purity. The coordinate of separation is taken such that on each side of this coordinate both distributions have the same purity $n_1 / (n_1 + n_2)$. The inset of Fig. 3.4 displays the purity after 5 min. as a function of $t_{\text{off}}$. The highest purity was found for $t_{\text{off}} = 0.32$ s. For a realistic trapping time of 2 s, a 5 minute interval is equal to 130 cycles, at which a purity of 0.87 can theoretically be obtained. Evidently, for larger (smaller) size differences the same separation can be performed faster (slower). For example, separating 100

![Figure 3.4: Position of 300 and 500 nm (diameter) particle distributions as a function of number of on/off cycles (left axis). The solid lines are the average positions and the short dashed lines the $\pm \sigma$ position. The long dashed line (right axis) shows the purity if the distributions are separated. Here $t_{\text{off}} = 0.32$ s, determined to be the optimal value after 5 minutes, as shown in the inset.](image-url)
and 700 nm particles for 5 min. with $t_{\text{off}} = 0.25$ s, a purity better than 0.9999 is calculated.

In the remaining paragraphs we shall briefly discuss some quantitative measures for the performance of particle separating on/off ratchets. The Péclet number is often used as a figure of merit for ratchets\textsuperscript{25} and is defined as

$$\text{Pe} \equiv \frac{\langle v \rangle l}{D_{\text{eff}}}, \quad \text{(3.13)}$$

with $\langle v \rangle$ the average velocity and $l$ a characteristic length. A high $\text{Pe}$ indicates a high average velocity with a small diffusion coefficient, which is usually desired. Using Eqs. (3.6) and (3.8), and taking $l$ as the length of one ratchet period, the Péclet number can be written as

$$\text{Pe} = \frac{4}{1 + \text{erf} \frac{\alpha l}{\sqrt{4D_{\text{ES}} t_{\text{off}}}}}. \quad \text{(3.14)}$$

This expression is not particularly helpful for particle separation since Eq. (3.14) gives information on only one of the two particles and doesn’t show a maximum: It has its minimum value of $\text{Pe} = 2$ at $t_{\text{off}} = 0$ and then continuously increases to $\text{Pe} = 4$ for $t_{\text{off}} \to \infty$. However, Eq. (3.14) is only valid for small $t_{\text{off}}$, for large $t_{\text{off}}$ $\text{Pe}$ is expected to decrease to 0.

In chromatography the resolution is used as an indication of the separation quality. It is defined as\textsuperscript{26}

$$R \equiv 2 \frac{t_{\text{ra}} - t_{\text{rb}}}{W_a + W_b}, \quad \text{(3.15)}$$

with $t_{\text{ra}}$ the retention time, i.e., the time required for a substance “a” to give its maximum signal and $W_a$ the width at the base (in time) of the corresponding signal. Both parameters are visualized for the 300 nm particles in Fig. 3.5(a), which shows results from the Master-equation calculation. The calculation is adapted such that all particles moving to the 15\textsuperscript{th} trap from the start point or beyond are taken from the system as if it is the end of a chromatograph tube. In the geometry used the fifteen traps corresponds to a channel length of 105 μm, according to the calculations shown in Fig 3.5(a) it takes approximately 30 minutes for the 500 nm particles to move beyond this point. A resolution equal to 1 is regarded as reasonable and corresponds to a 0.94 purity,\textsuperscript{26} and for a resolution of 1.5 two Gaussian signals show separated bases, corresponding to a 0.98 purity.\textsuperscript{26}
Figure 3.5: (a) Normalized number of particles $\delta n / N$ exiting the microchannel at 105 μm (15th ratchet trap) vs. no. of on/off cycles (lower axis) and time (upper axis). Calculated from the Master-equation model for three particle diameters with $L = 7 \mu$m, $\alpha = 1.5/7$, $t_{\text{on}} = 2$ s, and $t_{\text{off}} = 0.32$ s. The figure shows how $t_{300}$ and $W_{300}$ (using the dotted line) are defined. (b) Purity vs. time calculations for high selectivity separations with $\alpha = 1.5/7$ and optimal $t_{\text{off}}$.

Taking the same geometry and $t_{\text{off}}$ as in Fig. 3.4 we calculate a resolution of $0.79 \pm 0.02$ for the separation of 300 and 500 nm particles, which is below reasonable. Similar to chromatography, this can be increased by increasing the channel length and operation time. For separating 100 and 500 nm particles the resolution found is $1.31 \pm 0.02$. Although this resolution is below 1.5, the signals seem separated in Fig. 3.5(a).

As a final test of the separation quality we compare numerical calculations to the size dispersion in commercially available particles. According to the specifications of the 500 nm particles used in the experiments the size distribution has a standard deviation of $\pm 20$ nm. To achieve comparable accuracy we aim for a relatively fast separation (< 30 min) of 450 and 500 nm particles with a reasonable purity (> 0.94). From the Master-equation calculations an optimum $t_{\text{off}}$ is determined to be 0.38 s. Fig. 3.5(b) shows the purity as a function of time. Apart from the limited throughput of the device, it is clearly too slow to meet the conditions we have set, obtaining a purity slightly above 0.7 after 30 minutes. Reducing the device dimensions, the particle diameters, and the trapping time, $t_{\text{ons}}$, tenfold gives a large improvement, as the dashed curve in Fig. 3.5(b) shows. However, without the assumed reduced trapping time an improvement of only a few percent would be achieved. Therefore we conclude that the calculations show that separation of already narrow dispersions is not straightforwardly achieved in on/off-type ratchets. The most important hindrance is the retrapping time required, which is constrained by the ratchet trap size and viscosity. Miniaturizing the device and thereby decreasing the retrapping time would greatly improve the
device performance. A large reduction in size does imply that the particles should also be reduced in size for the ratchet potential to be effective.

### 3.6 Conclusion

In conclusion, we have demonstrated the occurrence of diffusion enhancement in an electrical on/off ratchet for polystyrene particles. The experiments show good agreement with a simple Master-equation model. Furthermore we have shown that the diffusion enhancement can be described via a general curve whose shape only depends on the asymmetry. An analytical approximation was derived and found to be in good agreement with the numerical model; its limitations are discussed. Finally we have shown that the Master-equation model can be used to find the optimal driving setting for optimal particle separation and determine the corresponding resolution. However, in order to make a fast, high selectivity particle separator the retrapping time should be shortened. Shortening the retrapping time is severely limited by constraints of the system, but can be achieved by miniaturizing the particles and the system.

### References

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Seebeck coefficient measurements are used to investigate two types of charge transport models frequently used for disordered organic semiconductors. From the temperature dependence of the Seebeck coefficient in a polytriarylamine (PTAA) thin film transistor we conclude that both a mobility edge model and a Mott-Martens type of variable range hopping model cannot give an adequate description of the temperature dependence of the experiments. Further analysis suggests that the type of variable range hopping model overestimates the heat transported by the charge carriers. For the mobility edge model the mismatch seems to be of more fundamental nature. From the analysis of the temperature dependence we can show that a decreasing Seebeck coefficient with decreasing temperature, as measured for PTAA, is in general a strong indication of hopping transport.
4.1 Introduction

The research of organic semiconductors enjoys a high interest due to emerging technologies like organic light emitting diodes, organic photovoltaics, and organic thin film transistors (TFT). In these devices the organic semiconductor used is often a disordered layer, lacking long range crystallinity. The basis for the charge transport models in disordered semiconductors was already laid in the 1950s and 1960s. Anderson\(^1\) showed that sufficient energetic disorder in a crystal lattice can result in a conduction band with a mobility edge. Below this mobility edge the states have become localized and act as trap states to the charge carriers. When the Fermi level lies in the tail of localized states the charge carriers require thermal activation to reach the extended states above the mobility edge for charge transport to occur. Later Mott\(^2,\!^3\) demonstrated that charge transport between localized states was possible by hopping. Hopping is a thermally assisted tunneling process and is therefore temperature dependent and, in a non-uniform density of states, also carrier density dependent. Both processes can in general coexist, however, usually one of the two is dominant.

Comprehensive models exist for both types of charge transport,\(^4,\!^5\) nevertheless it is not always clear which of the two processes gives the best, i.e., physically most adequate description of charge transport for a specific material. Usually only one of the two processes is used for the characterization of organic materials in TFTs. For the description of a pentacene thin film transistor, Vissenberg and Matters\(^6\) describe the charge transport in the framework of variable range hopping (VRH), disregarding a mobility edge, while Völkel \textit{et al.}\(^7\) describe the charge transport in pentacene by a mobility edge (ME) model that does not take hopping into account. One of the problems lies in the fact that often both models allow for good fits of the mobility of a material, in particular when the experimental conditions have only been varied to a limited extent. To nevertheless distinguish between the two models, the experiments should be extended. For example Salleo \textit{et al.}\(^8\) investigated the transfer curves of poly(thiophene) devices with a varying degree of disorder. Another approach is to combine two different experimental techniques, e.g. Kemerink \textit{et al.}\(^9\) used for their analysis of poly(2,5-bis(3-alkylthien-2-yl)thieno[3,2-b]thiophene) devices both transfer curve and channel potential measurements.

When a temperature difference $\Delta T$ is applied over a semiconducting material, a thermovoltage is created which scales with the temperature difference as $\Delta V = S \Delta T$, with $S$ the Seebeck coefficient. The magnitude of the Seebeck coefficient is determined by the energy difference between the Fermi level and the states of the mobile charge carriers and will depend on the prevailing mechanism for charge transport.
Here we use experiments and modeling of the Seebeck effect on organic semiconductors in combination with the experimental and theoretical analysis of charge transport in a thin film transistor (TFT) configuration to possibly discriminate between and test the consistency of VRH and ME models for describing charge and energy transport. We investigate the Seebeck coefficient in simplified versions of both types of models. The models are applied to polytriarylamine (PTAA) and a polycrystalline pentacene film of which the charge transport and Seebeck coefficient are measured on the same device. PTAA, shown in the inset of Fig 4.3(a), is a p-type semiconductor which reaches mobilities above $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. It is an amorphous semiconductor, for which hopping transport is expected. Surprisingly, neither of the two models can give an adequate description of the experiments. We discuss the overestimation of heat displacement in the VRH model used. Analyzing the models we rationalize the difference the two models show in the predicted $T$ dependence of $S$. This difference can be used in measurements to make a distinction between the two types of charge transport, which is applied to both the PTAA and a polycrystalline pentacene TFT.

4.2 Experimental

4.2.1 Device Fabrication

The measurements are performed on a Si | 200 nm SiO$_2$ wafer, with the heavily doped Si layer being used as the common gate electrode. The source and drain electrodes have a thickness of 30 nm (5 nm Ti and 25 nm Au) and are defined by standard UV-lithography and lift-off. The channel length and width are equal to 100 $\mu$m and 7 mm respectively. A monolayer of hexamethyldisilazane (HMDS) is applied to the SiO$_2$. A 30 nm thick PTAA layer is applied by spin coating from toluene. Alternatively, a 40 nm thick pentacene layer is applied by evaporation at room temperature.

4.2.2 Measurement Setup

Both mobility and thermovoltage measurements are performed using a Keithley 4200 SCS source-measure unit. The linear field effect mobility is determined by sweeping the gate bias $V_g$ and applying

$$\mu = \frac{L}{C_i W V_d} \frac{\partial I}{\partial V_g},$$

(4.1)
with \( L \) the channel length, \( W \) the channel width, \( C_i \) the capacitance per unit area, \( I \) the source-drain current, and \( V_d \) the drain bias.

The source, drain, and gate electrode each have their own source-measure unit (SMU). For each electrode the voltage is applied relative to the ground. When a current runs from source to drain the two SMUs show equal current magnitude with opposite sign. A leakage current from the gate electrode is expected to be equal for both source and drain when the gate bias is significantly larger than both the source and drain bias, which is the case for almost all measurement points. By sweeping the drain voltage and measuring both the source and the drain current, the thermovoltage is taken as the point where source and drain current are equal, which, due to the leakage current from the gate electrode, is not always at 0 A.

The measurements are performed in a Janis Research ST-500 probe station with a built-in cryostat. In addition to the cryostat we placed two Peltier
elements on the sample holder in order to apply a temperature difference along the length of the transistor channel. Fig. 4.1(a) shows a drawing of the sample holder. The temperature difference is measured using two Si-diode sensors. The high thermal conductivity of the Si common gate electrode determines the shape of the temperature profile of the whole sample. The temperature gradient can be estimated as being zero above the Peltier elements, and having a constant gradient between the Peltier elements as depicted in Fig. 4.1(b). The temperature difference can then be calculated from the temperature difference between the Peltier elements $\Delta T_p$, the distance between the Peltier elements $x_p$ and the distance between the source (S) and drain (D) electrodes $x_{sd}$, $T_{sd} = \Delta T_p \times x_{sd} / x_p$. From finite element calculations we determined the range of temperature differences between the Peltier elements at which the assumed temperature gradient in Fig. 4.1(b) is still a good approximation. For a value of $\Delta T_p$ lower than 35 K and $x_p$ equal to 4 mm the accuracy of $T_{sd}$ stays within 10%. The validity of the assumption is verified by measuring the thermovoltage $V_{sd}$ for five different $T_{sd}$. With the assumption being correct the five measurement points should be on a line as displayed in Fig. 4.1(c). The slope of a linear fit through this point is taken as the Seebeck coefficient. This procedure takes out systematic offsets of the measurement equipment and reduces the effect of random errors. An example of a single thermovoltage measurement is shown in Fig. 4.1(d).

### 4.3 Theory

#### 4.3.1 Mobility Edge Model

In the ME model applied here, the density of states (DOS), $G(E)$, has the shape of a tail of localized states which is taken as a single exponential and, above the mobility edge $E_C$, a constant density of the extended states. An exponential shape of the tail is chosen because in organic TFTs the observed DOS can often be approximated (for a large part) as being exponential. The DOS is shown in Fig. 4.2(a) and expressed as

$$
G(E) = \begin{cases} 
\frac{N_{loc}}{k_B T_0} \exp \left( -\frac{E}{k_B T_0} \right) & \text{for } E < E_C, \\
\frac{N_{loc}}{k_B T_0} & \text{for } E \geq E_C,
\end{cases}
$$

(E_C = 0), \quad (4.2)
Figure 4.2: (a) Representation of the DOS for the ME model, with localized states below the mobility edge, $E_C$, and extended states above $E_C$. The lower grey area represents the occupied DOS, determined by $f_{FD}$. (b) Representation of the DOS for the VRH model. The cartoon to the right shows the transport energy ($E^*$) concept, which assumes that the transport is mainly determined by hops from $E_F$ up to energies of approximately $E^*$. The arrows at $E_F$ and $E^*$ show the shift direction upon decreasing the temperature.

with $N_{loc}$ the volume density of localized states, $k_B$ the Boltzmann constant, and $k_B T_0$ the width of the exponential DOS. The DOS above $E_C$ is chosen such that the DOS is a continuous function, giving as few fitting parameters as possible. Due to the sharp decrease of the Fermi-Dirac distribution above the Fermi level, $E_F$, the conductivity is mainly determined by the product of the mobility in the extended states and the magnitude of the DOS at $E_C$. The exact shape of the DOS above $E_C$ is expected to be of minor importance when the Fermi level is well below $E_C$.

Charge carriers in the localized states have no net contribution to the charge transport. Only after a thermally activated release process to the mobility edge, will charge carriers contribute. The number of charge carriers above the mobility edge is determined by the Fermi-Dirac distribution, $f_{FD}$. The charge carriers above the mobility edge have a finite mobility, $\mu_0$, which is assumed to be independent of the temperature, which results in a device mobility

$$
\mu_{ME} = \mu_0 \frac{n_{ext}}{n_{loc} + n_{ext}} = \mu_0 \left( \frac{\int_{-\infty}^{0} G(E) f_{FD}(E) dE}{\int_{-\infty}^{0} G(E) f_{FD}(E) dE} \right), \quad (4.3)
$$

with $n_{ext}$ and $n_{loc}$ the number of occupied extended and localized states respectively.
4.3.2 Variable Range Hopping Model

The DOS for the VRH model is assumed to be formed by only an exponential of localized states,

\[ G(E) \equiv \frac{N_{\text{loc}}}{k_B T_0} \exp \left( -\frac{E}{k_B T_0} \right) \quad \text{for } E \leq 0. \]  

(4.4)

The VRH conductivity is described by the Mott-Martens model,\textsuperscript{13,14} as described in section 1.2.2,

\[ \sigma_{\text{VRH}} = \sigma_0 \exp \left( -2\alpha R^* - \frac{E^* - E_F}{k_B T} \right), \]  

(4.5)

with \( \sigma_0 \) a prefactor, and where \( R^* \) and \( E^* \) represent the hopping distance and final energy of the critical hop in a percolating network. \( E^* \) is called the transport energy. It is explained in Fig. 4.2(b) and follows from optimizing Eq. (4.5) and using the percolation argument

\[ B_C = \frac{4}{3} \pi R^*^3 \int_{E_F}^{E^*} G(E) dE, \]  

(4.6)

which calculates the number of hopping sites, \( B_C \), in a four-dimensional region of energy and space. Here \( B_C \) is taken equal to 2.8.\textsuperscript{14} \( R^* \) and \( E^* \) have temperature dependent values, since an increasing temperature allows for a larger thermal activation, increasing \( E^* \). When hops to higher energies are allowed more states per unit volume become accessible, reducing \( R^* \). Once the parameters for the conductivity are known the mobility is calculated as

\[ \mu = \frac{\sigma_{\text{VRH}}}{e n_{\text{loc}}} = \frac{\sigma_{\text{VRH}}}{e \int_{-\infty}^{0} G(E) f_{\text{FD}}(E) dE}, \]  

(4.7)

with \( e \) the elementary charge.
4.3.3 Seebeck coefficient

The Seebeck coefficient for each model is calculated using the expression

$$S = \frac{\int (E - E_F) \sigma(E)dE}{eT \int \sigma(E)dE},$$  \hspace{1cm} \text{(4.8)}

which can be explained as the associated heat of a state, $E - E_F$, weighted by its contribution to the conductivity, $\sigma(E) = e n(E) \mu(E)$, and divided by the unit charge and the temperature.

For the ME model the states below the mobility edge, taken as the zero of energy, do not contribute, and Eq. (4.8) reduces to

$$S_{\text{ME}} = \frac{E_C - E_F}{eT} + A = -\frac{E_F}{eT} + A,$$  \hspace{1cm} \text{(4.9)}

with

$$A = \frac{\int_0^\infty \epsilon \sigma_{\text{ME}}(\epsilon)d\epsilon}{\int_0^\infty \sigma_{\text{ME}}(\epsilon)d\epsilon},$$  \hspace{1cm} \text{(4.10)}

where $\epsilon = E - E_C$. $A$ is the contribution from states above $E_C$ and always increases the value of $S$, but is often relatively small, in the order of $1\% - 20\%$.

For the VRH model, where the transport is dominated by the critical hops from the Fermi energy to a narrow region around $E^*$, we approximate the Seebeck coefficient as

$$S_{\text{VRH}} = \frac{E^* - E_F}{eT}.$$

\hspace{1cm} \text{(4.11)}

4.4 Results

4.4.1 Mobility Edge Model Results

Mobility measurements of the PTAA TFT were performed at four different temperatures. The fit to the measurement data is shown in Fig. 4.3(a), and the fit parameters are given in Table 4.1. At low gate bias the calculation does not fit
well to the measurement data, which we relate to leakage currents and the expression used for the mobility being valid for \(|V_d| >> |V_g - V_{th}|\), with \(V_{th}\) the threshold voltage.

Measurements of the gate bias dependent Seebeck coefficient are performed for two devices at three temperatures and are shown in Fig. 4.3(c). The solid symbols belong to the device used for the mobility measurements.

The measurement of the Seebeck coefficient is reproducible; two nominally identical devices show only a small quantitative difference. Both devices show a decreasing \(S\) with decreasing \(T\) for low temperatures. When increasing the gate bias, i.e., increasing \(E_F\), \(S\) decreases. Measurements at 250 K are not shown since they were not monotonous with gate bias and not reproducible. This is possibly related to the melting point of confined water being close to this temperature.\(^{16}\) Water is known to have a charge trapping effect at the SiO\(_2\) interface,\(^{17}\) which can affect the charge transport.

Using the ME model fit parameters, \(S\) values are calculated that are of the same order of magnitude, however, the values are too high and have the opposite temperature dependence, i.e., an increasing \(S\) with decreasing \(T\). These predictions for PTAA can therefore be regarded as relatively poor. The calculated gate bias dependence is correct and is explained by the increasing gate bias, which increases the charge carrier density. With the increased carrier density, \(E_F\) will be closer to \(E_C\), decreasing \(S\) in Eq. (4.9).

The calculated temperature dependence can be explained from the term \((E_C - E_F) / (eT)\) in Eq. (4.9). When decreasing the temperature the denominator decreases, which can increase \(S\). Nevertheless, \(S\) does not necessarily increase, since \(E_F\) is also temperature dependent. For an increasing DOS, the decrease of the temperature, under a constant charge carrier density requires \(E_F\) to increase, as shown in Fig. 4.2(a). For the parameters chosen \(E_F\) does not increase fast enough, \((1/e) |dE_F / dT| < 1\).

Another problematic aspect of the ME model in its present description is that at \(T = 0\) K, the Seebeck coefficient is calculated from Eq. (4.9) as being infinity when the number of localized states is larger than the number of charges induced by the gate, viz. \(e N_{loc} x_{al} > C_i V\), with \(x_{al}\) the accumulation layer thickness. To obtain the expected \(S = 0\) for \(T = 0\) one should either have a low enough

---

### Table 4.1 The ME model fit parameters for the calculations shown in Figs. 4.3(a) and (c).

<table>
<thead>
<tr>
<th>Fit parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\mu_0)</td>
<td>(2.3 \times 10^{-5} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1})</td>
</tr>
<tr>
<td>(T_0)</td>
<td>630 K</td>
</tr>
<tr>
<td>(N_{loc})</td>
<td>(3.7 \times 10^{26} \text{ m}^{-3})</td>
</tr>
</tbody>
</table>
density of localized states, such that $E_F$ increases into the band of extended states upon approaching zero temperature, i.e., the transport becomes metal-like, or one should allow transport in the localized states around $E_F$, e.g. via hopping. When $T \neq 0$ a third solution exists, namely adapting the DOS function parameterization such that for the relevant energy levels $|dE_F/dT| > e$.

It can be concluded that the ME model in its current form cannot consistently describe the charge and energy transport. Either the tail of localized states should be parameterized differently or the transport involving localized states should not be neglected. The latter is a reasonable explanation, in view of the amorphous structure of the PTAA layer a large number of localized states is likely to exist. Therefore the next section analyzes the measurements in the context of a VRH model.
4.4.2 Variable Range Hopping Model Results

The fit of the VRH model to the mobility of the PTAA TFT is shown in Fig. 4.3(b) with the fit parameters displayed in Table 4.2. The VRH mobility fit is of comparable quality as the ME model fit, with again a discrepancy at low gate bias.

The prediction of the Seebeck coefficient using the same fit parameters shows a somewhat better result than the ME model, although the values are still too high and with the wrong sign of the temperature dependence, though less pronounced. The gate bias dependence of $S$ is predicted correctly. Since the position of $E^*$ is not static, but depends, amongst others, on $E_F$ the explanation is different from that in the ME model. When $E_F$ increases with increasing charge carrier density, the DOS at and directly above $E_F$ increases. To reach the number of hopping sites required from the percolation argument in Eq. (4.6), the difference between $E_F$ and $E^*$ can be smaller, and therefore Eq. (4.11) will give a lower $S$ value for larger gate bias.

Table 4.2: The VRH model fit parameters for the calculations shown in Figs. 4.3(b) and (d) with $N_{loc}$ set at $1.0 \times 10^{27}$ m$^{-3}$.

<table>
<thead>
<tr>
<th>Fit parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_0$</td>
<td>$1.4 \times 10^6$ S m$^{-1}$</td>
</tr>
<tr>
<td>$T_0$</td>
<td>700 K</td>
</tr>
<tr>
<td>$\alpha^{-1}$</td>
<td>$3.5 \times 10^{-10}$ m</td>
</tr>
</tbody>
</table>

We hypothesize that the overestimation of $S$ is caused by using the transport level $E^*$ as being representative for all hops in the entire channel. According to Mott, the conduction through a conductive path is mainly determined by critical hops to an energy $E^*$, and the measured mobility is essentially governed by this specific hop. The calculated $S$, Eq. (4.11), corresponds to that hop. However, for all non-critical hops the charge carrier hops to states of lower energy with a lower associated $S$. Furthermore, hops to lower energies can take place over longer distances $R$, thus increasing the importance of these hops for the calculation of the total device Seebeck coefficient. The interdependence of the hopping distance and the thermal activation makes it complicated to calculate this effect, and it is therefore not further analyzed at this moment.

The incorrectness of the predicted temperature dependence is not as severe as for the ME model. In contrast to $E_C$, the value of $E^*$ is both $E_F$ and temperature dependent. When decreasing $T$ the thermal activation $E^* - E_F$ in Eq. (4.5) is reduced. A hop over a large distance becomes more probable than a hop that requires a large thermal activation, hence $R^*$ increases and $E^* - E_F$ decreases. $E^* - E_F$ decreases further due to the temperature induced increase of $E_F$, which
follows from the same line of reasoning as for the gate bias dependence of $E^*$ above.

To illustrate the difference in temperature dependence between $S$ in the ME model and the VRH model, we plotted the numerators of the expressions for $S$ in Eqs. (4.9) and (4.11) as a function of temperature. Figs. 4.4(a) and (b) show a normalized $-E_F$ and normalized $E^* - E_F$. Both numerators are normalized such that they equal 300 K when $T = 300$ K. Using this normalization they are easy to compare to the corresponding denominator, i.e., the temperature. Fitting the different models usually results in different $T_0$ and $N_{loc}$ values, therefore this comparison has its limitations. Nonetheless, Fig. 4.4(a) shows for a range of concentrations that using the parameters in Table 4.2 the temperature dependence of $E_F$ alone is too weak to predict the measured temperature dependence of $S$. In accordance with the calculations in Fig. 4.3(d) the temperature dependence of $E^* - E_F$ is almost equal to that of $T$ at high concentrations, $c = 0.05$, resulting in an almost $T$ independent $S$. Fig. 4.4(b) shows that a lower $T_0$ increases the temperature dependence of both $E_F$ and $E^* - E_F$. However, the temperature dependence of $E_F$ alone remains weak showing that a negative $dS/dT$ is rather persistent in the ME model. The measurement of a decreasing $S$ with decreasing $T$ in PTAA is easier to reconcile with VRH-type transport.

The influence of $T_0$ on the temperature dependence is an indication that also the choice for a specific shape of the DOS will be of influence on $S$. However, when the DOS remains an increasing function with energy, e.g. the increasing slope of a Gaussian, the above discussed temperature dependence of $E_F$ and $E^*$ remains qualitatively the same. A thorough analysis on the Seebeck coefficients for different shapes of the DOS is beyond the scope of the discussion here.

Figure 4.4: Comparison of the temperature dependence of $E_F$ and $E^* - E_F$, performed in view of the temperature dependence of $S$ in Eqs. (4.9) and (4.11). Calculations are performed for the parameters in Table 4.2 for (a) different concentrations, $c = n_{loc} / N_{loc}$, and (b) for different $T_0$ with $c = 0.05$. 

...
The discussions in this and the previous subsection show that for specific DOS values the ME and VRH models can show opposite temperature dependence of $S$. For a large enough tail of localized states, a decreasing $S$ with decreasing $T$ suggests VRH. A large density of localized states is expected for the amorphous PTAA TFT, therefore we relate the measured temperature dependence of the Seebeck coefficient to hopping transport.

### 4.4.3 Seebeck Effect in Pentacene

Pentacene is a widely used high mobility organic semiconductor, studied both in the context of VRH\textsuperscript{6} and ME\textsuperscript{7} models. Here we will measure the Seebeck coefficient in a polycrystalline pentacene TFT to see which type of transport is expected based on the temperature dependence of the Seebeck coefficient. The Seebeck coefficient in pentacene has been studied before; von Mühlenen \textit{et al.}\textsuperscript{18} measured Seebeck coefficients at different temperatures but with a rather large spread in measured values. From their measurements they concluded to observe transport in localized states in polycrystalline pentacene and for single crystal pentacene transport in delocalized states. Measurements by Pernstich \textit{et al.}\textsuperscript{19} on pentacene TFTs did not show the large spread in values, but they were only performed at room temperature. The results were analyzed in the context of a ME model. The same measurement results were later analyzed by Kim \textit{et al.}\textsuperscript{20} in the context of hopping in a Gaussian DOS. However, the dataset is too small to determine which analysis is superior. The published data are insufficient to give an analysis based on the temperature dependence of $S$.

Fig. 4.5 shows temperature and gate bias dependent Seebeck coefficient measurements of a pentacene TFT on a Si-SiO$_2$ substrate. The mobility measurements are not shown, since they did not show monotonous trends in temperature below 273 K. We relate this again to water at the SiO$_2$ interface acting as charge traps.\textsuperscript{17} Nonetheless, a measurement of the Seebeck coefficient at 200 K was performed successfully. The measurements show the expected decrease with increasing gate bias. Only at low gate bias a decrease in $S$ with decreasing $T$ is observed. For intermediate and high gate bias $S$ is practically independent of $T$.

Based on the discussion in the previous sections we conclude that the temperature independence at large gate bias suggests VRH transport rather than transport above a mobility edge. Due to the lack of mobility measurements or other experimental data this conclusion should be seen as a tentative prediction. To come to more conclusive evidence of VRH, more measurement data is needed of the pentacene TFT. In view of the (unexpected) difficulty in measuring these particular samples below 273 K, we suggest the use of a TFT with a dielectric other than SiO$_2$, for example a fluoropolymer. In such a device water is expected to be less of a disturbance.\textsuperscript{21}
4.5 Conclusions

We showed mobility and Seebeck coefficient measurements of a TFT with PTAA that cannot be described by either a ME model or a Mott-Martens type of VRH model. Calculations with both models overestimate the Seebeck coefficient and predict an incorrect sign of the temperature dependence. We rationalize how the calculation of the Seebeck coefficient within the VRH formalism can result in an overestimation of the heat transported by the charge carriers. For the ME model no explanation can be given for the overestimation of $S$. In view of the amorphous nature of PTAA, the VRH model can be expected to give a better description of the measurements. This is supported by the temperature dependence of the Seebeck coefficient. From an analysis of both models the measured decrease in $S$ with decreasing temperature is far more likely to be found from a VRH-type model, although the temperature dependence will ultimately depend on the specific DOS parameters. Applying the same principle to a polycrystalline pentacene TFT suggests that also in polycrystalline pentacene on SiO$_2$ the transport is dominated by VRH. We recommend the use of another dielectric than SiO$_2$ to reduce the charge trapping by water and improve the quality of the measurements to enable more conclusive statements.

References


An unusual increase in the Seebeck coefficient with increasing charge carrier density is observed in pentacene thin film transistors. This behavior is interpreted as being due to a transition from hopping transport in static localized states to bandlike transport, occurring at temperatures below ~250 K. Such a transition can be expected for organic materials in which both static energetic disorder and dynamic positional disorder are important. While clearly visible in the temperature and density dependent Seebeck coefficient, the transition hardly shows up in the charge carrier mobility.

Published as:
5.1 Introduction

The increasing performance of organic semiconductors over the past decades has increased the technological interest in these materials, and vice versa. Considerable efforts notwithstanding, fundamental aspects of the charge transport in organic semiconductors are still subject of debate. This holds in particular for the question to which extent the mobility, and its temperature and charge carrier density dependence, should be interpreted in terms of bandlike conduction. Because of energetic disorder, charge transport in organic semiconductors is often described within the framework of strong localization as developed by Anderson and Mott.\textsuperscript{1,2} Anderson showed that in presence of sufficiently strong static energetic disorder, localized tail states develop below a so-called mobility edge which separates them from delocalized states that are expected to dominate the charge carrier transport.\textsuperscript{1} Later, Mott demonstrated that charge transport can also result from hopping processes between localized sites.\textsuperscript{2,3} In organic semiconductors this picture is further complicated. Due to weak intermolecular bonding, thermally driven molecular vibrations give rise to significant dynamic disorder that limits the charge carrier mobility even in high-purity crystalline organic semiconductors where static disorder is minimized.\textsuperscript{4-6} In these crystalline organic semiconductors these vibrations freeze out at low temperature, giving rise to an increased mobility.\textsuperscript{7,8}

Polycrystalline and amorphous organic semiconductors behave differently. The increasing mobility with increasing temperature and charge density typically observed for these materials can be described in terms of either the mobility edge (ME) or multiple trapping and release (MTR) model,\textsuperscript{9-11} or by the variable range hopping (VRH) model.\textsuperscript{12-14} The ME model implies bandlike conduction, the VRH model does not.

In this chapter we measure the Seebeck coefficient $S$ of polycrystalline pentacene in a thin film transistor (TFT) configuration. The Seebeck coefficient shows a remarkable increase with increasing charge carrier density, originating from a transition from hopping to bandlike conduction. The simultaneously measured charge carrier mobility increases with temperature and charge carrier density, but shows no noticeable signatures associated with the hopping to bandlike transport transition.

5.2 The Seebeck Effect

Several techniques can be used to investigate charge carrier transport in organic semiconductors.\textsuperscript{15} Here we employ thermoelectric measurements which so far have hardly been applied to undoped organic semiconductors.\textsuperscript{16,17} In particular, we measure the Seebeck coefficient ($S$) of pentacene in a TFT configuration as a
function of temperature and gate bias. By tuning the gate bias, we control the charge density and Fermi level $E_F$ in pentacene. The Seebeck coefficient $^{18}$

$$ S = \frac{\int (E - E_F) \sigma(E) dE}{eT \int \sigma(E) dE}, \quad (5.1) $$

is determined by the difference between $E_F$ and the energy $E$ of the transporting states, i.e., the heat transported by the charge carriers. It therefore gives very direct insight in the energetics of the dominant charge transport processes. In (5.1), $\sigma(E)$ is the conductivity distribution function, $T$ the temperature, and $e$ the charge of the carrier. For bandlike transport within the ME model, where the current is carried by charges that are thermally excited over the mobility edge at energy $E_C$ as illustrated in Fig. 5.1(a), Eq. (5.1) reduces to $^{18}$

$$ S_{ME} = \frac{E_C - E_F}{eT} + A, \quad (5.2) $$

with

$$ A = \frac{\int_0^\infty \frac{\varepsilon}{eT} \sigma(\varepsilon) d\varepsilon}{\int_0^\infty \sigma(\varepsilon) d\varepsilon}, $$

where $\varepsilon = E - E_C$. In Eq. (5.2), the second term on the right-hand side accounts for excitations beyond the band edge and is typically 1% – 20% of $S_{ME}$. Similarly, within the VRH model, where the transport is assumed to be dominated by a characteristic hop from the equilibrium energy to a relatively narrow transport energy $^{19} E^*$ as illustrated in Fig. 5.1(b), Eq. (5.1) becomes

$$ S_{VRH} = \frac{E^* - E_F}{eT}. \quad (5.3) $$

The usual behavior for the Seebeck coefficient is to decrease with increasing charge carrier density. $^{20}$ For bandlike transport, Eq. (5.2), this is explained by the Fermi level shifting towards the band edge. Likewise, for hopping transport, Eq. (5.3), $E_F$ also shifts upward. Concomitantly, the number of unoccupied states near the Fermi level increases, and consequently the transport energy $E^*$ comes to lay closer to the Fermi level. To test this experimentally, we measured the Seebeck coefficient of pentacene in a TFT.
5.3 Seebeck Coefficient Measurements

TFTs were built on a p⁺-Si wafer, used as gate, with 100 nm of thermally grown SiO₂ and an additional spin coated layer of 130 nm Cytop (an amorphous fluoropolymer available from Asahi Glass Company) as gate dielectric. The pentacene layer was deposited by thermal evaporation at 0.4 Å s⁻¹ in a high vacuum system. Au source and drain top contacts are subsequently thermally deposited through a shadow mask to define the ~80 μm long and ~8 mm wide channel. Electrical characterization and Seebeck measurements were performed in a high vacuum probe station. The Seebeck coefficient at given temperature and gate bias was determined by linear fitting of the thermovoltage to \( V = S \Delta T \), where the temperature difference \( \Delta T \) across the channel of the TFT is generated by two Peltier elements.

By bringing the gate bias \( V_g \) to more negative potential, the charge density in the pentacene TFT is increased, and Fig. 5.2 shows that at room temperature this indeed results in the expected decrease of \( S \). Similar behavior was previously observed by Pernstich et al. and interpreted in terms of a ME model. The room temperature behavior of \( S \), i.e., to decrease with increasing hole density, is consistent with transport that is dominated by static energetic disorder. As explained above, depending on the model used, the decrease is explained by the shift of \( E_F \) to either the band edge \( E_C \) or the transport level \( E^* \). The (positive) sign of \( S \) is consistent with p-type transport.

Surprisingly, when decreasing the temperature to below room temperature, we see an increase of \( S \) with increasing charge carrier density at \( T = 250 \) K and even more pronounced at \( T = 200 \) K. Clearly, such an increase in \( S \) cannot be explained using VRH or ME alone, as both predict a strictly monotonously decreasing density dependence.
Enhancement of the Seebeck coefficient at lower temperatures could in principle be due to phonon drag effects which are typically observable below roughly a quarter of the Debye temperature $T_D$. Since $T_D$ is in the range $125$ K - $216$ K in pentacene, the onset of possible phonon drag effects is expected at far lower temperatures than observed.

### 5.4 Hopping and Bandlike Transport in a Hybrid Model

To explain the increase of $S$ with charge carrier density we developed a simplified hybrid model that incorporates both VRH and ME transport. It accounts for the contributions to the charge and energy transport by two processes that are treated as independent: VRH-type processes that occur within an exponential tail of localized states and transport by charges that are thermally excited to bandlike states above a mobility edge. For this model the DOS and transport parameters are determined by fitting to the temperature dependent field-effect mobility measured on the same sample (Fig. 5.3).

As indicated in Fig. 5.1(c) the DOS is simplified to a single exponential trap tail below the mobility edge and a constant density of extended states above $E_C$,
\[ G(E) = \begin{cases} 
\frac{N_{\text{loc}}}{k_B T_0} \exp\left(-\frac{E}{k_B T_0}\right) & \text{for } E < E_C, \\
\frac{N_0}{k_B T_0} & \text{for } E \geq E_C, 
\end{cases} \]

where \( N_0 \) is divided by \( k_B T_0 \) for dimensional reasons. The number of charge carriers above \( E_C \), \( n_\text{free} \), follows from the Fermi-Dirac distribution. The exact shape of the DOS above \( E_C \) can have some influence on the charge transport; however the small contribution of the second term \( A \) in Eq. (5.2) shows that this is usually of relatively minor importance. The conductivity in the ME-part of the model is calculated as \( \sigma_{\text{ME}} = e n_\text{free} \mu_\text{free}(T) \), with \( \mu_\text{free} \) the band mobility. In order to account for the inherently large thermal lattice fluctuations in molecular semiconductors we assume \( \mu_\text{free} \) to follow a power law dependence on temperature:\textsuperscript{4,6,8}

\[ \mu_\text{free}(T) = \mu_0 \left(\frac{T_0}{T}\right)^m \]  

The VRH-part is described by the Mott-Martens model that assumes transport to be dominated by hops from the Fermi level to the transport level \( E^* \).\textsuperscript{12,24} The position of this level and the typical hopping distance \( R^* \) are connected via a percolation argument\textsuperscript{12,24}

Figure 5.3: (a) The measured (symbols) and calculated (lines) linear mobility vs. gate bias with intervals of \( T = 20 \text{ K} \). The deviations at small gate voltage are attributed to leakage currents and the breakdown of the assumption that \( |V_g - V_{\text{th}}| \gg V_{\text{sd}} \) (\( V_{\text{sd}} = \) source-drain voltage). The inset shows \( \mu_\text{free} \times n_\text{free} \sim \sigma_{\text{ME}} \) vs. \( T \) for \( V_g - V_{\text{th}} = -30 \text{ V} \). (b) Activation plot of the measured (symbols) and calculated (lines) mobility for different gate bias, with intervals of 2 V.
with $B_C$ equal to 2.8, the critical number of bonds. The conductivity is subsequently calculated by optimizing a Miller-Abrahams-type expression\textsuperscript{3,24} $\sigma_{\text{VRH}} = \sigma_0 \exp[-2 \alpha R^* - (E^* - E_F) / (k_B T)]$, with $\alpha$ the inverse localization length, $k_B$ the Boltzmann constant, and $\sigma_0$ the conductivity prefactor. This implementation of the VRH-part is essentially identical to that of Ref. 14. The total conductivity of the hybrid model is simply the sum of the ME and VRH contributions, viz. $\sigma_{\text{hyb}} = \sigma_{\text{ME}} + \sigma_{\text{VRH}}$. Consistent with Eq. (5.1), the Seebeck coefficient of the hybrid model is calculated as the conductivity-weighted average of the two contributing transport channels:

$$S_{\text{hyb}} = \frac{S_{\text{ME}} \sigma_{\text{ME}} + S_{\text{VRH}} \sigma_{\text{VRH}}}{\sigma_{\text{ME}} + \sigma_{\text{VRH}}}$$ (5.7)

The mobility measurements and the fitting results are shown in Fig. 5.3; the used parameters are given in Table 5.1. No distinctive features are visible. The mobility increases with increasing (negative) gate bias and decreases with decreasing temperature. Both are consistent with earlier observations for polycrystalline pentacene\textsuperscript{13} and suggest (static) energetic disorder dominated transport over the entire measurement range. Unsurprisingly, bare VRH and ME models give rather accurate fits to the mobility data (see Appendix E Figs. E3-E6). The somewhat better fit quality of the hybrid model could, in the case of the mobility data, also be attributed to the larger number of free parameters.

In Fig. 5.3(b), the measured mobility might seem to show a slightly different activation behavior above and below 260 K, which is around the

<table>
<thead>
<tr>
<th>$N_{\text{trap}}$</th>
<th>$10^{26}$ m$^{-3}$</th>
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<tbody>
<tr>
<td>$T_0$</td>
<td>1000 K</td>
</tr>
<tr>
<td>$\sigma_0$</td>
<td>$2.3 \times 10^6$ S m$^{-1}$</td>
</tr>
<tr>
<td>$\alpha^{-1}$</td>
<td>9 Å</td>
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<tr>
<td>$\mu_0 N_0$</td>
<td>$5.3 \times 10^{20}$ m$^{-1}$ V$^{-1}$ s$^{-1}$</td>
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<td>$m$</td>
<td>6</td>
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transition temperature in the Seebeck behavior, but the effect is too small to make definitive statements. The calculated curves in Fig. 5.3(b) do show a slight bend which is due to the changing ratio of $\sigma_{VRH} / \sigma_{ME}$. The corresponding Seebeck coefficients are shown as lines in Fig. 5.2. Although the agreement with experiment is only qualitative, the characteristic features are well reproduced. In particular, the 200 K curve reproduces the unusual increase in the Seebeck coefficient curve beyond a gate bias of $-10$ V. The increase is explained by a shift from entirely hopping-dominated conduction at low gate bias to conduction in which bandlike states above the mobility edge play an important role. This is illustrated in Fig. 5.4.

At 200 K the heat transported at the mobility edge ($E_C - E_F$) and the heat transported at the transport level ($E^* - E_F$) both decrease with increasing charge carrier density, accounting for the downward trends in $S_{ME}$ and $S_{VRH}$ in Fig. 5.4(a). With increasing density the Fermi level moves towards the band edge. Since $E^*$ does, and $E_C$ does not shift up with $E_F$, the relative contribution from hopping conduction goes down, as is shown by the ratio $\sigma_{VRH} / \sigma_{ME}$ in Fig. 5.4(b). Consequently, the weight-averaged Seebeck coefficient $S_{hyb}$ shifts from the $S_{VRH}$ curve at small gate bias up towards $S_{ME}$ for large gate bias. The relatively large value of $S_{ME}$ at lower temperatures follows from Eq. (5.2) and the temperature independence of $E_C$. In contrast, $E^*$ decreases with $T$, making $S_{VRH}$, Eq. (5.3), relatively temperature independent (see also Figs. E1 and E2).

A remarkable consequence of these observations is that in the investigated temperature window, and at higher charge densities ($V_g - V_{th} < -20$ V), the contribution of VRH to the total conductivity actually decreases with decreasing temperature. The opposite would be expected from VRH hopping theory when applied to an energetically disordered inorganic semiconductor. In the present
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system, due to the freezing out of molecular vibrations in the pentacene, the band mobility $\mu_{\text{free}}$ increases strongly at lower $T$, shifting the balance in the charge transport to bandlike conduction despite the increasing energetic penalty for thermal activation over the mobility edge. The temperature dependence of the band mobility, $\mu_{\text{free}}(T) = \mu_0 \left( T_0 / T \right)^6$ that is plotted in the inset of Fig. 5.4(b) is, for the presently probed temperature window, not unrealistic in view of the calculations by Ortmann et al. It is, however, rather strong in comparison to experimental observations on p- and n-type single crystal devices. However, in the latter case typically the effective mobility is probed, which can be substantially below the free mobility due to the fact that only a fraction of the carriers contributes to the actual transport. We have therefore plotted the product $\mu_{\text{free}} \times n_{\text{free}}$ as inset to Fig. 5.3(a). Interestingly, the curve first shows an increase in mobility followed by a (stronger) decrease with decreasing temperature. Such behavior has been observed on a number of single crystal OFET devices and was actually interpreted in terms of a ME-model that is similar to what is used here. More details can be found in Figs. E7 and E8.

5.5 Conclusion

Summarizing, we have shown that at lower temperatures the Seebeck coefficient in a pentacene thin film transistor displays an unusual increase with increasing gate bias. The increase is explained by a transition from variable range hopping dominated transport at low gate bias to more pronounced bandlike transport at high gate bias. A simplified hybrid model that accounts for both types of charge transport gives a qualitative description of the observed thermoelectric behavior. These findings confirm that charge transport in polycrystalline organic semiconductors can simultaneously be affected by two types of disorder: static energetic disorder resulting from e.g., charges in the gate dielectric and dynamic positional disorder driven by molecular vibrations. Finally, the temperature and density dependence of the simultaneously measured charge carrier mobility shows no notable features, making it hard, if not impossible, to distinguish transport models on basis of such data alone.

References

We investigate the mechanism of charge transport in indium-gallium-zinc oxide (a-IGZO), an amorphous metal oxide semiconductor. We measured the field-effect mobility and the Seebeck coefficient (\(S = \Delta V / \Delta T\)) of a-IGZO in thin-film transistors as a function of charge carrier density for different temperatures. Using these transistors, we further employed a scanning Kelvin probe-based technique to determine the density of states of a-IGZO that is used as the basis for the modeling. After comparing two commonly used models, the band transport percolation model and a mobility edge model, we find that both cannot describe the full properties of the charge transport in the a-IGZO semiconductor. We therefore propose a model that extends the mobility edge model to allow for variable range hopping below the mobility edge. The extended mobility edge model gives a superior description of the experimental results. We show that the charge transport is dominated by variable range hopping below, rather than by bandlike transport above the mobility edge.

Published as:
6.1 Introduction

Amorphous oxide semiconductors (AOSs) are of interest for their use as transparent and flexible backplanes and electrodes in, among others, displays and photovoltaic cells. Consequently, the charge transport in AOSs received considerable attention. In recent literature two types of charge transport models can be found for AOS: a band transport percolation model\textsuperscript{1-4} and the mobility edge (ME) model,\textsuperscript{5,6} also known as the multiple trapping and release model. This situation is particularly unsatisfactory as these models are based on fundamentally different physical assumptions regarding the nature of the charge transport in AOS. In this chapter we confront the two types of models with an extensive set of thermoelectric measurements obtained on amorphous InGaZnO (a-IGZO) field effect transistors. a-IGZO was introduced by Nomura \textit{et al.}\textsuperscript{2} in 2004, and can reach charge carrier mobilities in excess of 10 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}. In the last decade several papers were published on the nature of the charge transport in a-IGZO. A recent review can be found in Ref. 7.

The percolation\textsuperscript{1} model assumes charge transport to take place in a conduction band with a square root energy dependence of the densities of states (DOS). Furthermore the presence of a Gaussian distribution of potential barriers is assumed that limit the contribution of low energy band states to the conductivity. The charge transport is then described in a manner that is similar to the standard Boltzmann transport formalism, but with the addition of the barriers. For the remainder of this chapter we refer to this model as the Kamiya-Nomura model.

By investigating the optical response in capacitance-voltage characteristics Jeon \textit{et al.} extracted a different DOS for a-IGZO, consisting of an exponential tail.\textsuperscript{8,9} When the exponential tails are assumed to be trap states that do not contribute to the conduction, this gives rise to a charge transport description in terms of a ME model. In a ME model, the Fermi level lies in a tail of localized states, and transport is assumed to take place by charges that are thermally excited over a mobility edge that separates localized and delocalized, or bandlike states. However, at low temperatures the charge transport in such systems is expected to occur via hopping-type processes.\textsuperscript{10} Only at sufficiently high temperatures is transport dominated by the mobility edge. So far, hopping has been assumed to be irrelevant in a-IGZO because of the observation of a well-developed Hall effect which implies the occupation of bandlike states.\textsuperscript{4,7} Therefore we extend the ME model to allow for variable range hopping (VRH) in the localized states in addition to the bandlike transport above the mobility edge.

Here, we compare the Kamiya-Nomura model to the extended mobility edge (eME) model. Both the Kamiya-Nomura and the eME model were used to simultaneously describe measured charge carrier mobilities and Seebeck coefficients ($S = \Delta V / \Delta T$) as a function of charge carrier density and temperature.
In order to constrain the degrees of freedom in the fitting procedure we used a scanning Kelvin probe microscopy (SKPM) based technique to determine the density of states on the same type of device\textsuperscript{11}. We find that in our devices the charge transport can only be consistently described by the eME model, and that over the entire investigated temperature and density range the transport is dominated by hopping processes.

In the next section we will give a description of the device fabrication, followed by a description of the thermoelectric measurement procedures in Sec. 6.3. In Sec. 6.4 we describe the theoretical framework used to interpret the experimental results in Sec. 6.5. Sec. 6.6 summarizes our findings.

6.2 Device Preparation

Thin-film transistors (TFTs) were prepared using a highly doped Si substrate as the gate electrode and 200 nm of thermally grown SiO\textsubscript{2} as the gate dielectric. This bottom contact, blanket gate approach allows for excellent heat transfer through the substrate and the device. Source and drain electrodes consisted of a 5 nm titanium adhesion layer followed by 25 nm of gold and were defined using UV lithography. The channel length and width of the used devices were 500 and 100 μm, respectively. A 10 nm thick a-IGZO layer was then deposited via RF-sputtering from an Advanced Nano Products IGZO target (2:2:1 In:Ga:Zn metal ratio, leading to a 1:1:1 Ga\textsubscript{2}O\textsubscript{3}:In\textsubscript{2}O\textsubscript{3}:ZnO oxide ratio) at 10\textsuperscript{-3} mbar pressure and room temperature. A partial pressure of oxygen in argon of 2% was maintained throughout the deposition in the sputter chamber. This is the same procedure as followed in Ref. 12, apart from the annealing step which was performed at 400 °C for 20 minutes in air.

6.3 Thermoelectric Measurement Procedures

When a temperature difference, \( \Delta T \), is applied to a material it will in general cause a thermovoltage, \( \Delta V \). The Seebeck coefficient is equal to the ratio between the thermovoltage and the temperature, \( S = \Delta V / \Delta T \).\textsuperscript{13} We will use Seebeck coefficient measurements to investigate different charge transport models.

The thermovoltage is measured using a Keithley 4200 SCS. The measurements are performed in a Janis ST-500 probe station, where, under high vacuum conditions (<10\textsuperscript{-5} mbar), the temperature of the sample holder and the TFT can be varied. Two Peltier elements are placed on the sample holder to apply a temperature gradient across the TFT channel. Fig. 6.1(a) schematically shows the sample holder. On top of the sample, above each Peltier element, a Si-diode temperature sensor is placed. The TFT is positioned between the two Peltier
Figure 6.1: (a) A drawing representing the sample and sample holder, with P being the Peltier elements and S (D) the source (drain) electrode. (b) The typical temperature vs. position for the sample in (a). (c) Representation of measured thermovoltage, vs. temperature difference. The derivative of the fitted line equals the Seebeck coefficient $S$.

The high thermal conductivity of the Si common gate electrode determines the shape of the temperature profile of the whole sample. The temperature gradient is assumed to be constant between the Peltier elements as depicted in Fig. 6.1(b). The temperature difference can then be calculated from the temperature difference between the Peltier elements $\Delta T_p$, the distance between the Peltier elements $x_p$, and the distance between the source (S) and drain (D)
electrodes $x_{sd}$, $\Delta T = \Delta T_p \times x_{sd} / x_p$. From finite element calculations we determined the range of temperature differences between the Peltier elements at which the assumed constant temperature gradient in Fig 6.1(b) was still a good approximation, and we found that for a $\Delta T_p$ equal to 35 K over a distance $x_p = 4$ mm the error in $\Delta T$ is smaller than 10%. The validity of the assumption is further verified by measuring the thermovoltage $\Delta V$ for different $\Delta T$, as shown in Fig. 6.1(c). The Seebeck coefficient has been determined from the gradient of a linear fit through these measurement points. By using the gradient we reduce both systematic and random errors. The above procedure is followed for each different gate bias and temperature.

By switching off the Peltier elements the same setup can be used to measure transfer and output curves just before or after a Seebeck measurement. From the transfer curves in the linear regime ($V_d = 2$ V) the temperature and gate voltage dependent mobility is calculated as

$$\mu = \frac{L}{CWV_d} \frac{\partial I_{sd}}{\partial V_g}, \quad (6.1)$$

with $L$ as the channel length, $W$ as the channel width and $C$ as the capacitance per unit area.

### 6.4 Theory

#### 6.4.1 The Kamiya-Nomura Model

The Kamiya-Nomura model is very similar to the standard Boltzmann transport formalism which can be found in for example Ref. 13. In addition to the usual description of band transport, the model assumes a Gaussian distribution of potential barriers in the band. These barriers are attributed to the Ga\(^{3+}\) and Zn\(^{2+}\) ions.\(^4,7\) The potential barriers can hinder conduction and thereby reduce the contribution of charge carriers in low energy states. A cartoon to visualize the model is given in Fig. 6.2. A typical conduction band is shown in Fig. 6.2(a). The Gaussian in Fig. 6.2(b) represents a distribution of potential barriers. To the right of the Gaussian a low energy electron in the conduction band is shown between the barriers; at higher energies, electrons become increasingly less hindered by the barriers. The mathematical description of the model is based on the paper by Adler et al.\(^14\) An extra term $p(E)$ is added to the transport equation representing a Gaussian distribution of barriers. The conductivity is given by\(^1\)
Figure 6.2: (a) The conduction band as a function of energy. (b) The Gaussian represents the position of the distribution of potential barriers in the conduction band. The cartoon at the right shows a low energy electron in the conduction band that is ‘trapped’ between two potential barriers.

\[
\sigma_{KN} = -\frac{e^2}{m_e^*} \int_{E_C}^{\infty} p(E) \tau(E) v_z(E) \frac{df_{FD}}{dE} D_C(E) dE, \quad (6.2)
\]

with \( e \) as the elementary charge, \( m_e^* \) as the effective mass, \( E_C \) as the conduction band onset, \( \tau \) as the relaxation time, \( v_z \) as the electron velocity, \( f_{FD} \) as the Fermi-Dirac distribution function, the conduction band DOS \( D_C(E) = D_{C0}(E-E_C) \), and

\[
p(E) = \left(2\pi\sigma_\phi^2\right)^{1/2} \int_{E_C}^{E} \exp\left[-\left(E'-\phi_0\right)^2/(2\sigma_\phi^2)\right]dE', \quad (6.3)
\]

as the ‘percolation factor’ running from zero to unity, describing the barrier effect. Furthermore, \( \phi_0 \) is the top of the Gaussian distribution of barriers, and \( \sigma_\phi \) is its width. It should be noted that in, Ref. 14, the conductivity is taken to be proportional to \((p - p_c)^2\) with \( p_c \) as the percolation threshold and 2 as the critical exponent, instead of just to \( p(E) \) as in Eq. (6.2). A more detailed description of the Kamiya-Nomura model is given in Ref. 1 and its supplementary information.

### 6.4.2 The Extended Mobility Edge Model

The extended mobility edge model (eME), meanwhile, assumes that with the presence of sufficiently strong energetic disorder a tail of localized states can develop below a mobility edge, \( E_C \). In order to contribute to the transport, charge carriers need to be thermally excited over the mobility edge. For transistor measurements the details of these tail states are very important, as they determine
which portion of the induced accumulation of charge carriers participates in the transport. In a ME model, the charge carriers in the localized tail states are typically assumed to be trapped and immobile. However, Mott showed that transport between localized states is possible by hopping.\(^{10,16}\) Hopping requires thermal activation to go from low- to high-energy localized states. Whether hopping and/or bandlike transport have a significant contribution to the total current depends on the shape of the DOS, the temperature, and the charge carrier density.\(^{17}\) So far, VRH was not considered to be relevant in a-IGZO because of the observation of a well-developed Hall effect.\(^{4,7}\) However, having bandlike transport above the mobility edge does not exclude VRH below the mobility edge to exist simultaneously.

The eME model applied in this chapter allows VRH below \(E_C\) to coexist next to the bandlike transport above \(E_C\). The DOS is defined as

\[
G(E) = \begin{cases} 
\frac{N_{\text{loc}}}{k_B T_0} \exp \left( - \frac{E}{k_B T_0} \right) & \text{for } E < E_C, \\
\frac{N_{\text{loc}}}{k_B T_0} & \text{for } E \geq E_C,
\end{cases} 
\quad (E_C = 0),
\]

(6.4)

with \(N_{\text{loc}}\) as the density of localized states, \(T_0\) as the width of the exponential tail of localized states, and \(k_B\) as the Boltzmann constant. The DOS above \(E_C\) is chosen such that the DOS is a continuous function with as few fitting parameters as possible. Due to the sharp decrease in the Fermi-Dirac distribution above the Fermi level, \(E_F\), the conduction is mainly determined by the value of the DOS at \(E_C\). The exact shape of the DOS above \(E_C\) is expected to be of minor importance when the Fermi level is well below \(E_C\).

The conductivity above the mobility edge is calculated by

\[
\sigma_{\text{ME}} = e \mu_{\text{free}} \int_{E_C}^{\infty} f_{\text{FD}}(E) G(E) dE,
\]

(6.5)

with the integral being the number of particles above \(E_C\) and \(\mu_{\text{free}}\) being the band mobility.

The VRH contribution to the conductivity is described by the Mott-Martens model.\(^{18,19}\) This model uses a percolation argument with a critical number of hops, \(B_C\), within a four dimensional region of the typical hopping distance \(R^*\) and energy difference between the \(E_F\) and an effective transport level \(E^*\),
Figure 6.3: The logarithm of the exponential DOS tail below $E_C$ and the bandlike states above $E_C$. The cartoon shows the concept of the transport level $E^*$. The homogeneously grey area indicates occupied localized states around $E_F$.

\[ B_C = \frac{4}{3} \pi R^* \int_{E_F}^{E^*} G(E) dE, \]  

(6.6)

with $B_C = 2.8$. Fig. 6.3 shows a representation of the DOS and the transport level $E^*$. The model is based on the assumption that charge transport is limited by a critical hop over an energy $E^* - E_F$ and distance $R^*$, such that the charge carriers have a sufficient number of unoccupied states ($B_C$) available within the four-dimensional volume set by $E^*$ and $R^*$. Therefore $E^*$ and $R^*$ both depend on the temperature and the DOS. With increasing temperature the increased thermal activation will increase $E^*$ and will decrease $R^*$; an increased DOS will decrease both $E^*$ and $R^*$. In the hybrid model presented here there is the extra constraint that $E^*$ should be smaller than $E_C$. The VRH conductivity is subsequently calculated by optimizing a Miller-Abrahams-type expression\textsuperscript{10,18}

\[ \sigma_{VRH} = \sigma_0 \exp\left[ -2\alpha R^* (E^* - E_F)/(k_B T) \right], \]  

(6.7)

with $\sigma_0$ being a conductivity prefactor and $\alpha$ being the inverse decay length of the localized state.

The total conductivity of the extended mobility edge model is a superposition of the VRH conductivity and the band conductivity, viz.

\[ \sigma_{eME} = \sigma_{ME} + \sigma_{VRH}, \]  

(6.8)
6.4.3 The Seebeck Coefficient

In order to calculate the Seebeck coefficient, the energy and the relative contribution to the charge transport of all relevant states have to be known. For the two charge transport models described above a fit to the transfer curves is sufficient to have all necessary parameters.

From the empirical charge and heat current relations and the Onsager reciprocity relations it follows that the Seebeck coefficient can be written as the Peltier coefficient, \( \Pi \), divided by the temperature.\(^{20,21,22} \) The Peltier coefficient equals the heat per unit charge that is transported by a charge current. From this the Seebeck coefficient follows as

\[
S = \frac{\Pi}{T} = \frac{\int (E - E_F) \sigma(E) dE}{eT \int \sigma(E) dE}, \tag{6.9}
\]

which is the heat carried by a charge carrier, \( E - E_F \), weighed by \( \sigma(E)/(\int \sigma(E) dE) \), the contribution to the conductivity by the states at energy \( E \).

For the Kamiya-Nomura model the calculation of \( S \) is quite straightforward. Using Eq. (6.2), \( S \) can be calculated as

\[
S_{KN} = \frac{\int (E - E_F) p(E) \tau(E) \nu_z(E) \frac{\partial f_{FD}}{\partial \nu_z} D_C(E) dE}{eT \int p(E) \tau(E) \nu_z(E) \frac{\partial f_{FD}}{\partial \nu_z} D_C(E) dE}. \tag{6.10}
\]

The Seebeck coefficient for the extended mobility edge model is calculated from a contribution from the VRH, \( S_{VRH} \), and a contribution from the transport above \( E_C \), \( S_{ME} \). For \( S_{ME} \), the states below the mobility edge can be ignored, and Eq. (6.9) reduces to\(^{23} \)

\[
S_{ME} = \frac{E_C - E_F}{eT} + A, \tag{6.11}
\]

with

\[
A = \int_{E_C}^{E} \int_{E_C}^{E} \sigma_{ME}(\varepsilon) d\varepsilon dE + \int_{E_C}^{\infty} \sigma_{ME}(\varepsilon) d\varepsilon, \tag{6.12}
\]
where \( A \) is the contribution from the states above the mobility edge and \( \sigma_{\text{ME}}(E) = e \mu \text{free} f_D(E) G(E) \). In practice \( A \) is relatively small although it cannot always be ignored altogether.

For the VRH part, where the transport is dominated by the critical hops from the Fermi energy to a narrow region around \( E^* \), the Seebeck coefficient is written as

\[
S_{\text{VRH}} = \frac{E^*-E_F}{eT}.
\]

(6.13)

For the total Seebeck coefficient of the extended mobility edge model Eq. (6.9) is again used to come to

\[
S_{\text{cME}} = \frac{S_{\text{ME}} \sigma_{\text{ME}} + S_{\text{VRH}} \sigma_{\text{VRH}}}{\sigma_{\text{ME}} + \sigma_{\text{VRH}}},
\]

(6.14)

i.e., \( S_{\text{cME}} \) is the conductivity-weighted average of the contributions from localized and delocalized states.

6.5 Experimental Results and Discussion

The experimentally determined charge carrier mobility and Seebeck coefficient of the a-IGZO transistors are plotted in Fig. 6.4 (symbols) as a function of gate bias for temperatures between 150 and 310 K. The experiments show that mobility increases with temperature and gate bias (Fig 6.4(a)). The Seebeck coefficient reduces with gate bias and is weakly temperature dependent (Fig. 6.4(b)). In the following sections we test the validity of the Kamiya-Nomura and extended mobility edge models for giving a consistent description of these experimental results on a-IGZO.

6.5.1 The Kamiya-Nomura Model

To obtain all the device parameters for the Kamiya-Nomura model we first extract mobilities from the transfer curves using Eq. (6.1) and then fit these mobilities with Eq. (6.2), where we derive the associated mobility by dividing the conductivity by the gate bias induced charge carrier density and the elementary charge. The calculated mobility vs. \( V_g \) results are shown in Fig. 6.4(a) together with the experimental results. The curves are calculated using the parameters in
Figure 6.4: (a) The measured (symbols) and calculated (lines) mobility vs. gate bias for different temperatures. The calculations are performed using the Kamiya-Nomura model and the fit parameters in Table 6.1. (b) The measured (symbols) and calculated (lines) Seebeck coefficients vs. gate bias for different temperatures. The inset shows the position of the Fermi level with respect to the band edge (dashed line).

Table 6.1. For a TFT with a SiO$_2$ dielectric, additional trapping states can be present in the SiO$_2$\textsuperscript{24,25} which could increase the subgap DOS. Nevertheless, the fitting parameters are very much comparable to those found for bulk a-IGZO in Ref. 1.

Without further fitting, the parameters in Table 6.1 enable the calculation of the Seebeck coefficient using Eq. (6.10). The calculated Seebeck coefficients
are shown as a function of gate bias and temperature in Fig. 6.4(b). Compared to the measured data, the calculated values for $S$ are too high, but the curves do show the correct gate bias and temperature dependence and can be regarded as a reasonable prediction of the experiment. The correct gate bias dependence follows from the increase in $E_F$ with increasing gate bias. With the Fermi level increasing it approaches the energy of the high energy states, reducing $E - E_F$ in Eq. (6.10). Moreover, it should be noted that the determined parameters imply that for most gate bias and temperature values the Fermi level lies in the conduction band ($E_F > E_C$) as shown in the inset of Fig. 6.4(b).

Predicting the correct temperature dependence from Eq. (6.10) is not straightforward. When $E_F$ is below a band or in an increasing DOS, $E_F$ increases with decreasing $T$ in order to maintain a constant charge carrier density. This decreases the term $E - E_F$. However, the denominator in Eq. (6.10) contains $T$, which decreases as well. A decrease in $S$ with decreasing $T$ can therefore not be intuitively explained on the basis of the above arguments.

Summarizing, the Kamiya-Nomura model gives a good fit to the mobility data with representative fitting parameters. These give rise to a reasonable prediction of the Seebeck coefficient. The calculations give a Fermi level that lies in the band of mobile states which is chosen to have a square root dependence on the energy. In the next section we will use an SKPM technique to measure the DOS shape at the Fermi level.

<table>
<thead>
<tr>
<th>Fit parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{C0}$</td>
<td>$18 \times 10^{26}$ m$^{-3}$ eV$^{-3/2}$</td>
</tr>
<tr>
<td>$T$</td>
<td>$1.02 \times 10^{-15}$ s</td>
</tr>
<tr>
<td>$m_e^*$</td>
<td>$0.35 \times m_0$</td>
</tr>
<tr>
<td>$\sigma_0$</td>
<td>0.05 eV</td>
</tr>
<tr>
<td>$\phi_0$</td>
<td>0.15 eV</td>
</tr>
</tbody>
</table>

### 6.5.2 Determining the DOS Using Kelvin Probe

In any transport model the DOS is a key ingredient. Consequently, when a transport model is assumed, information regarding the DOS can be extracted by fitting to transport measurements, as in the previous section where the characteristic parameters of a fixed DOS shape are fitted. For some transport models it is possible to extract the entire DOS from transport data without any a priori assumptions regarding the DOS shape. This was, for instance, done by Chen et al. for a-IGZO. However, for the present purpose of finding the actual
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transport mechanism, this method cannot be used, and the DOS should be determined by independent means.

Previously, Jeon et al. used capacitance-voltage ($C-V$) based methods to extract the DOS in different a-IGZO samples and found either a combination of an exponential and a Gaussian or, from a remarkably similar dataset, a tail of two exponentials. Such exponential tails seem reasonable in view of the Anderson localization model for disordered materials.

In this section, we measure the DOS of an a-IGZO TFT, using a scanning Kelvin probe microscopy technique described in Refs. 11 and 27. The technique uses a metallic atomic force microscopy (AFM) probe tip to analyze the potential at the a-IGZO surface and is explained in Fig. 6.5 which displays the band and energy levels for the different layers in the sample. With no electric field present between the gate and the a-IGZO no charges are accumulated and the energy levels are represented by the solid lines. The electric field between the AFM tip and the a-IGZO surface is nullified by applying a potential $V_{skpm}$ to the tip.

Applying a gate bias $V_g$ with respect to the source and drain electrode forms an accumulation layer in the a-IGZO. This fills the conduction band, and with the source and drain electrodes fixed at 0 V, $E_F$ does not move and, consequently, the conduction band needs to shift to a lower energy. The shift in the band $\Delta E_{\text{band}}$ at the sample surface equals $\Delta V_{skpm}$. Assuming a homogeneous DOS and permeability throughout the IGZO layer a DOS can be calculated.

For a homogeneous charge carrier density throughout the semiconductor layer with thickness $d_{IGZO}$, i.e., in the absence of band bending, the DOS at $E_F$ can be calculated from

$$G(E_F) = \frac{\Delta n(E_F)}{\Delta E_{\text{band}}(E_F)} = \left[ \left( \frac{dV_{skpm}}{dV_g} \right)^{-1} - 1 \right] \frac{C}{d_{IGZO} q^2}, \quad (6.15)$$

where $C$ is the areal gate capacitance.

However, the accumulation layer is mainly formed at the SiO$_2$/a-IGZO interface, and consequently the band bending displayed in Fig. 6.5 needs to be taken into account. Unfortunately, no analytical equivalent of Eq. (6.15) exists which does account for band bending. We therefore use the following procedure to extract $G$ from $V_{skpm}(V_g)$.

Starting from a trial DOS $G_{\text{trial}}$, one can numerically calculate the change in surface potential vs. gate voltage, i.e., $V_{skpm}(V_g)$. First, the gate voltage sets the total charge density in the channels as $N = \int n(z) dz = CV_g$. Then, the charge density distribution $n(z)$ in the channel follows from Poisson’s law,
using the boundary condition that the derivative of the electric field at the
a-IGZO/vacuum interface is zero, which follows from charge neutrality in the
entire system. Moreover, for each position in the active layer \( z \) one has

\[
n(z) = \int_{-\infty}^{\infty} G(E + eV(z)) f_{FD}(z) dE .
\]  

For each \( V_g \), Eqs. (6.16) and (6.17) can be solved by forward integration towards
the a-IGZO/vacuum interface. Using Eq. (6.15) the resulting \( V_{skpm}(V_g) \) curve can
be transformed into an apparent DOS, \( G_{app} \). The difference \( \Delta G = (G_{app} - G_{trial}) \) is
then taken as a measure for the error that is made by ignoring the band bending in
calculating \( G_{exp} \) from the experimental \( V_{skpm}(V_g) \) data with Eq. (6.15). A new trial
DOS is then calculated as \( G_{trial} = G_{exp} - \Delta G \). This procedure is iterated until self-
consistent is obtained and \( G_{\text{trial}} \) no longer changes. The stable function \( G_{\text{trial}} \) should then be a good approximation of the real density of states \( G(E) \) of the a-IGZO that underlies the band bending-affected SKPM measurement. In order to stabilize this procedure \( G_{\text{trial}} \) is approximated by an analytical expression with a number of free fitting parameters. Internal consistency is assured by validating that the final solution \( G(E) \) can indeed be well described by the chosen analytical expression. For the present purposes it turned out that \( G(E) \) can sufficiently be accurately approximated with a single exponential.

Measurements of the surface potentials as a function of gate bias are shown in Fig. 6.6(a) for five different locations in the channel of an a-IGZO TFT; an example of the derived DOS is shown in Fig. 6.6(b). The squares are calculated directly with Eq. (6.15), i.e., by ignoring band bending, the circles show the final result of the iterative procedure described above, i.e., including band bending, and the line is an exponential fit. The characteristic temperature \( T_0 \) of the exponential DOS,

\[
G(E) \propto \exp \left( \frac{E}{k_B T_0} \right),
\]

is given in Table 6.2. From these measurements we conclude that under the operational conditions employed here, the Fermi level \( E_F \) lies in an exponential tail of the a-IGZO DOS with \( T_0 \approx 800 \text{ K} \).

The obtained exponential DOS is inconsistent with the fitting result of the Kamiya-Nomura model in the previous subsection, where the fitting parameters imply that \( E_F \) lies in a band with an algebraic (square root) energy dependence. A tail of localized states was also shown by Kamiya et al.,\textsuperscript{28} but was assumed to be very small. In principle, incorporating the measured exponential tail states in the Kamiya-Nomura model is possible. However, this would lead to a model that is essentially equivalent to the eME model but with a far more complicated contribution of the band states due to the additional Gaussian distribution of

---

Table 6.2: Extracted values of the characteristic temperature of the exponential DOS of a-IGZO.

<table>
<thead>
<tr>
<th>Position</th>
<th>( T_0 ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>743</td>
</tr>
<tr>
<td>2</td>
<td>836</td>
</tr>
<tr>
<td>3</td>
<td>1231</td>
</tr>
<tr>
<td>4</td>
<td>758</td>
</tr>
<tr>
<td>5</td>
<td>836</td>
</tr>
</tbody>
</table>
bars. Moreover, the largely increased number of free parameters would make such a model underdetermined. In the following section the obtained DOS is therefore used in the extended mobility edge model.

6.5.3 The Extended Mobility Edge Model

For the eME model we use the DOS measurements in the previous subsection which yielded $T_0 = 800$ K for the exponential tail of the DOS in Eq. (6.4). For consistency with the DOS measurement analysis, band bending was included in
Figure 6.7: The measured (symbols) and the calculated (lines) (a) mobilities and (b) Seebeck coefficients vs. gate bias for different temperatures. The calculations are performed using the eME model and the parameters in Table 6.3.

the eME model by treating the channel as parallel quasi-two-dimensional sheets of which the densities are calculated as described at Eqs. (6.16) and (6.17). The measured and the fitted mobility data are shown in Fig. 6.7(a); the corresponding parameters are given in Table 6.3. The fit does not reflect the strong onset of the high temperature mobility as clearly as the Kamiya-Nomura model. The overall curvature by the Kamiya-Nomura model seems somewhat better, but the
Table 6.3: Device parameters used for the calculations of the eME model displayed in Fig. 6.7.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_0$</td>
<td>800 K</td>
</tr>
<tr>
<td>$\sigma_0$</td>
<td>$4.6 \times 10^4$ S m$^{-1}$</td>
</tr>
<tr>
<td>$\alpha^{-1}$</td>
<td>$4.8 \times 10^{-9}$ m</td>
</tr>
<tr>
<td>$\mu_{ME}$</td>
<td>78 cm$^2$ V$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$N_{loc}$</td>
<td>$3.4 \times 10^{19}$ cm$^3$</td>
</tr>
</tbody>
</table>

calculated eME model values still provide a rather accurate description of the measured values. Using the parameters obtained in the mobility fitting the Seebeck coefficient is calculated from Eqs. (6.11) – (6.14). Both measurements and calculations are shown in Fig. 6.7(b). The Seebeck coefficient calculations show very good agreement with the experiments. They show the correct gate bias dependence and the calculated small temperature dependence of the Seebeck coefficient agrees very well with the experiments. Only for low temperatures, do the experimental values show somewhat stronger temperature dependence than the calculated curves. The origin of the gate bias and temperature dependence follows from the same line of argument as in the discussion in Sec. 6.4.1 on the Kamiya-Nomura model.

Comparing the results from the Kamiya-Nomura model with the extended mobility edge model shows that the eME model gives a better description of the experimental Seebeck results. Furthermore the eME is consistent with the DOS measurement, which shows that $E_F$ lies in an exponential DOS.

The value obtained for the localization length, $\alpha^{-1} = 4.8$ nm, may appear surprisingly large, given that vacuum tunneling typically leads to values around 0.5 nm. However, it seems likely that the tunneling electrons use virtual states in the nearby conduction band ($E_F - E_C \approx 0.3 - 0.6$ eV for the parameters used), which leads to a significant enhancement in $\alpha^{-1}$.

On further inspection of the calculated results the contribution of hopping to the conductivity appears to be much larger than the contribution of bandlike transport above the mobility edge. In Fig. 6.8, the ratio between the two conductivities is shown for three temperatures. The contribution by bandlike transport is on the order of 1% at most, but usually is much less. However, we were reluctant to use a hopping-only model in view of an observed Hall effect. We should note that the values used are the best (mobility) fitting values, but there is definitely room to increase the contribution of the bandlike conduction above $E_C$ while still having a description of the experiments within the error margins. Furthermore, Ref. 1 mentioned the presence of localized states as an explanation for odd charge carrier density results obtained from Hall measurements. In that paper, the coexistence of hopping and bandlike transport was not considered, and hopping transport was discarded. However, when disallowing hopping conduction
in the eME model by setting $\sigma_0 = 0 \text{ S m}^{-1}$, the constraint of $T_0 \approx 800 \text{ K}$ results in extremely poor fits to the mobility curves – actually an opposite curvature of the gate voltage dependence is found. Note that this constraint turns the extended ME model into a pure ME model.

Finally, we should note that it is likely that the SiO$_2$ dielectric causes additional trap states in a-IGZO TFTs which are absent in bulk a-IGZO devices. These states would lead to an increased contribution of hopping-type transport relative to the bandlike transport in TFT devices. However, our results show that hopping transport cannot upfront be ruled out when interpreting the charge transport in amorphous oxide semiconductors.

![Figure 6.8 The ratio of the conduction by VRH and the conduction by bandlike transport above $E_C$ for the extended mobility edge model calculations.](image)

### 6.6 Conclusions

We combined three different experiments to investigate the charge transport mechanism in a-IGZO TFTs: an SKPM-based technique to measure the DOS, transfer curve measurements, and Seebeck coefficient measurements. We found that an extended mobility edge model that includes variable range hopping below the mobility edge gives a consistent and accurate description of the temperature and gate voltage dependent mobility and Seebeck coefficient. The extended mobility edge model is consistent with the Fermi level lying in an exponential DOS with a width of $T_0 = 800 \text{ K}$, which follows from the DOS measurements. The calculations show that the contribution of the variable range hopping to the overall charge transport is larger than that of the bandlike transport above the mobility edge.
References

Effects of Energetic Disorder on the Low-Frequency Differential Capacitance of Organic Light Emitting Diodes

It has recently been shown how the injection barriers at the electrode interfaces and the built-in voltage ($V_{bi}$) of organic light emitting diodes can be obtained from measurements of the differential capacitance at low frequencies, using the voltage and height of a distinct peak in the capacitance-voltages curves. In this chapter, we investigate the effects of Gaussian energetic disorder on the analysis, for single-carrier and double-carrier devices. We show how the disorder affects the peak position and height, and how from combined capacitance-voltage measurements and device modeling the injection barriers and $V_{bi}$ can be determined. As examples, hole-only and double-carrier devices are investigated based on a blue-emitting polyfluorene-triarylamine copolymer.

Published as:
7.1 Introduction

Measurements of the differential capacitance of single layer organic light emitting diodes (OLEDs) have been employed to determine the electron and hole mobilities in the organic semiconductor material and the energy barriers at the two electrode interfaces. Within these studies, use is made of the frequency ($f$) dependence of the differential capacitance ($C$), around frequencies corresponding to the inverse charge carrier transit time, and of the low-frequency voltage ($V$) dependence of the capacitance, respectively. In this chapter, we focus on the latter type of study. In Ref. 2, an analysis of low-frequency $C(V)$ measurements to determine the injection barriers was carried out assuming a constant mobility and diffusion coefficient, and for single-carrier devices only. It is the purpose of this chapter to analyze how the application of $C(V)$ measurements as a non-invasive technique for determining the energy barriers as well as the built-in voltage, $V_{bi}$, can be extended to single-carrier and double-carrier devices based on disordered organic semiconductors with a spatially uncorrelated Gaussian density of states. The charge carrier mobilities depend then on the charge carrier density and on the electric field.

The method makes use of the occurrence of a distinct low-frequency peak in the differential capacitance, which is observed when the energy barrier at the injecting contact is relatively small. In Fig. 7.1, the thick curves (“no disorder”) show the $C(V)$ curves of a single layer OLED for the case of a constant mobility and diffusion coefficient and with no injection barriers, already given in Ref. 2. For symmetric devices, with $V_{bi} = 0$ V, the peak in the capacitance is situated at $V = 0$ V (Fig. 7.1(a)). The effect may be understood as a result of charge carrier diffusion, which already at zero voltage leads to an appreciable space charge near the electrodes. This effectively lowers the distance between the electrode planes, so that the capacitance is larger than the geometrical capacitance, $C_{geom} = \varepsilon / L$, with $\varepsilon$ the electric permittivity of the organic semiconductor and $L$ the layer thickness. Upon the application of a voltage, the space charge in the bulk of the device increases. The finite charge-carrier transit time gives rise to a delayed response of this bulk space charge distribution to an applied voltage change, leading to a negative contribution to the capacitance. This is the predominant effect at high voltages, when the drift-contribution to the current density is much more important than the diffusion-contribution. For the case of a system with ideal contacts, the peak height is $C_{peak} / C_{geom} = 1.29$. The peak half-width, defined as the voltage at which $C = C_{geom}$, is equal to $16 k_b T / e$. This may be viewed as the crossover voltage between diffusion-dominated and drift-dominated AC transport. It follows from analytical drift-only theory that for high voltages the low-frequency differential capacitance is equal to $(3/4)C_{geom}$. 
Figure 7.1: Calculated $C(V) / C_{\text{geom}}$ curves for single-carrier devices with a thickness $L = 100$ nm, relative dielectric constant $\varepsilon_r = 3$, at $T = 300$ K and in the low-frequency limit, for (a) symmetric devices with ideal injection at both interfaces, so that $V_{\text{bi}} = 0$ V, and (b) asymmetric devices with ideal injection at one of the interfaces and a 2 eV injection barrier at the other interface, so that $V_{\text{bi}} = 2$ V. Thick curves show the results for the case of a constant mobility and diffusion coefficient (“no disorder,” with peak heights indicated by horizontal dashed lines), and the thin curves show the results for transport within a spatially uncorrelated Gaussian density of states with a site density $N_{\text{loc}} = 1 \times 10^{27}$ m$^{-3}$ and a width $\sigma / (k_B T) = 3$ and 6.

For asymmetric devices, with a finite value of $V_{\text{bi}}$, the formation of a significant space charge layer near the injecting electrode sets in above zero voltage, but already well below $V_{\text{bi}}$. The peak voltage, $V_{\text{peak}}$, may be several tenths of a Volt smaller than $V_{\text{bi}}$, depending on the injection barrier at the injecting contact. With increasing injection barrier, the peak shifts to $V_{\text{bi}}$, and the intensity decreases from a theoretical maximum of 1.41 (ideal contact) to zero, as was shown in Ref. 2. Fig. 7.1(b) (thick curve) shows the result for the case of an ideal contact. A study of this peak may thus be used to investigate the charge carrier injection conditions, and possible changes of these conditions during the operational lifetime.
The capacitance-peak has been observed for various systems,\(^2,8\) and a quantitative analysis has been given in Ref. 2 for the case of hole-only devices based on a blue-emitting polyfluorene-triarylamine (PF-TAA) copolymer. However, within the model used to analyze the effect a constant mobility was assumed, whereas it was found in a subsequent study that the hole transport in PF-TAA is strongly affected by Gaussian energetic disorder.\(^9\) In this chapter, we show that the introduction of Gaussian disorder leads to a significant increase of the peak shift, \(V_{bi} - V_{peak}\), for single-carrier and double-carrier devices, and to peak heights which are larger than for the case of a constant mobility and diffusion coefficient. The model used for calculating the frequency-dependent capacitance at any voltage is an extension of a recently developed one-dimensional Master-equation OLED device model,\(^10\) and employs a small-signal approach. Our findings can explain the 0.3 V difference between the value of \(V_{bi}\) for the abovementioned PF-TAA based devices as obtained in Ref. 9 from measurements of current density versus voltage (\(J(V)\)) curves using the Extended Gaussian Disorder model (EGDM), and as obtained in Ref. 2 from \(C(V)\) measurements assuming a constant mobility.

In Sec. 7.2, the device model used for calculating the differential capacitance is discussed. In Sec. 7.3, the disorder dependence of the capacitance peak height and position is discussed for single-carrier devices, and a comparison is made with experimental results obtained for PF-TAA based devices. In Sec. 7.4, a similar analysis is given for the case of double-carrier devices. It is furthermore shown that energetic disorder can lead to a negative differential capacitance, as has indeed been observed in various studies of double-carrier devices and for which various explanations were given in the literature.\(^11-15\) Sec. 7.5 contains the summary and conclusions.

### 7.2 Theoretical Model

The systems studied are devices within which a single organic layer with thickness \(L\) is sandwiched between two metallic electrodes. The charge transport in the organic layer takes place by hopping in between sites at which the energies are spatially uncorrelated, with a Gaussian density of states characterized by a width \(\sigma\) and a hopping site density \(N_{loc}\). The complex impedance is calculated by applying a small-signal analysis method, within which a linearization approach is used to calculate the response of the system to a small applied voltage modulation.

As a first step, the steady-state solution of the drift-diffusion-recombination problem is calculated using a recently developed one-dimensional Master-equation (1D-ME) OLED device model.\(^10\) The model describes charge transport along a linear chain of \(N\) equidistant sites, with the electrodes at sites 0
and $N$. The steady-state current density across the interval $m$ between sites $m-1$ and $m$ is given by

$$J_{DC} = \left( c_{m-1,DC} r_{m,DC}^+ - c_{m,DC} r_{m,DC}^- \right) \frac{e}{a^2},$$

(7.1)

with $r^+$ and $r^-$ the forward and backward hopping rates, respectively, $c$ the carrier concentration (occupation probability) at each site, $e$ the elementary charge, and $a \equiv N_{loc}^{-1/3}$ the average intersite distance in the organic semiconductor. The hopping rates depend on the local carrier density and electric field in a manner which is consistent with the mobility and diffusion coefficient as obtained within the EGDM. The distance between the grid points used may be viewed as the effective hopping distance. It is close to $a$, but increases slightly with the dimensionless disorder parameter $\hat{\sigma} \equiv \sigma/(k_B T)$, with $k_B$ the Boltzmann constant and $T$ the temperature, as expected from percolation theory. The solution for a given applied voltage is obtained after iteration until a uniform current density is obtained. The injection barriers determine the boundary conditions, i.e., the values of $c_0$ and $c_N$. When no injection barrier is present, the Fermi level is at the top of the Gaussian DOS and the concentration is equal to 1/2. When an injection barrier $\Phi$ is present, the Fermi level at the interfacial site is taken at $-\Phi$ and the occupation is smaller than 1/2. We note that in literature several alternative models describing the boundary conditions have been proposed. However, the application of these models is restricted to systems with high injection barriers (injection limited current limit) and/or to systems without energetic disorder. Support for the approach described above was obtained from a comparison with the results of three-dimensional Master-equation or Monte Carlo device simulations, carried out for a wide range of injection barriers and disorder parameters. For the case of PF-TAA based single-layer and single-carrier devices, the $J(V)$ curves as obtained from the 1D-ME model are in excellent agreement with the results from the continuum EGDM drift-diffusion model which was used to deduce the parameter values describing the shape of the DOS. In double-carrier devices the recombination rate in the limit of zero field is assumed to be given by the Langevin formula. For finite values of the field it is taken to be slightly larger, in a manner described in detail by Eq. (8) and Fig. 3 of Ref. 10 (“k = 4 model”).

The steady-state solution is fully characterized by the set of charge carrier concentrations $\{c_{m,DC}\}$ at all internal sites. The fields at all intersite intervals are equal to the sum of the effective applied field, $(V - V_{bi}) / L$, and a contribution from the space charge in the device. The hopping rates depend only on the local carrier concentration and field. Within the small-signal approximation, the time ($t$)
response to a small superimposed AC modulation voltage $\delta V = v_{AC} \exp(i\omega t)$ with angular frequency $\omega$ are an oscillatory AC current density $\delta J = \tilde{J}_{AC} \exp(i\omega t)$ and oscillatory local AC concentrations $\delta c_m = \tilde{c}_{AC,m} \exp(i\omega t)$. The tilde indicates that the concentration and current density amplitudes are complex, as they contain a phase factor. For single-carrier devices, the AC current density may be expressed as

$$J_{DC} + \delta J_m = [(c_{DC,m-1} + \delta c_{m-1})(r_m^+ + \delta r_m^+)$$
$$- (c_{DC,m} + \delta c_m)(r_m^- + \delta r_m^-)] \frac{e}{a^2} + e \frac{dF_m}{dt}, \quad (7.2)$$

where the final term is the displacement contribution. Writing $\delta r_m^{+(-)} = \tilde{r}_{AC,m}^{+(-)} \exp(i\omega t)$, it follows after linearization of Eq. (7.2) and after elimination of the steady-state contribution that the local current density amplitudes are given by

$$\tilde{J}_{AC,m} = (r_{m,DC}^+ \tilde{c}_{AC,m-1} - r_{m,DC}^- \tilde{c}_{AC,m} + c_{DC,m-1} \tilde{r}_m^+ - c_{DC,m} \tilde{r}_m^-) \frac{e}{a^2}$$
$$+ i\omega e \left( \sum_{k=1}^{N-1} \frac{dF_m}{dc_k} \tilde{c}_{AC,k} + \frac{v_{AC}}{L} \right). \quad (7.3)$$

The AC amplitudes of the hopping rates are given by

$$\tilde{r}_m^+ = \frac{d r_m^+}{d c_{m-1}} \tilde{c}_{AC,m-1} + \frac{d r_m^+}{d F_m} \left( \sum_{k=1}^{N-1} \frac{dF_m}{dc_k} \tilde{c}_{AC,k} + \frac{v_{AC}}{L} \right) \quad (7.4)$$

and

$$\tilde{r}_m^- = \frac{d r_m^-}{d c_m} \tilde{c}_{AC,m} + \frac{d r_m^-}{d F_m} \left( \sum_{k=1}^{N-1} \frac{dF_m}{dc_k} \tilde{c}_{AC,k} + \frac{v_{AC}}{L} \right). \quad (7.5)$$

The first terms in Eqs. (7.4) and (7.5) arise as a result of the charge carrier concentration dependence of the mobility. The second terms are due to the dependence of the hopping rates on the local field, and contain contributions from the AC space charge throughout the device and from the applied AC voltage. The concentration and field derivatives are calculated at the DC values of the local
concentration and the field, respectively. The requirement that the AC current density amplitudes $\tilde{j}_{AC,m}$ are equal for all intervals leads to a set of $N$ equations (Eq. (7.3)) which are linear in the concentrations $\tilde{c}_{AC,m}$. The coefficients are straightforwardly calculated using the formalism developed in Ref. 10. Solving this set of $N$ equations provides the values of $\tilde{c}_{AC,m}$ for $1 \leq m \leq N - 1$, as well as $\tilde{j}_{AC}$. The differential conductance $G$ and the differential capacitance $C$ are then obtained from the admittance, which is defined as

$$Y \equiv \frac{\delta j}{\delta V} = \frac{\tilde{j}_{AC}}{v_{AC}} = G + i\omega C. \quad (7.6)$$

An analogous method is used for deriving the capacitance of double-carrier devices. The $2(N - 1)$ electron and hole AC concentration amplitudes at the inner sites and the AC current density amplitude are determined from a set of $2N - 1$ linear equations, obtained from the requirement that the AC current density in all $N$ intervals is equal and the requirement of charge conservation upon recombination at each of the $N - 1$ internal sites.

### 7.3 Single-Carrier Devices

#### 7.3.1 Simulation Results

Using the model developed in the previous section, we calculated the voltage dependence of the capacitance of a system formed by an organic semiconductor sandwiched between two metallic electrodes, and varied the disorder parameter. Fig. 7.1(a) includes the low-frequency $C(V)$ curves for single-carrier devices at $T = 300$ K with a layer thickness $L = 100$ nm, for $V_{bi} = 0$ V, $N_{loc} = 10^{27} \text{ m}^{-3}$, a relative dielectric constant $\varepsilon_r = 3$, and no injection barriers, for the cases $\sigma / (k_B T) = 3$ and 6. Fig. 7.1(b) includes the results of otherwise identical devices for the case $V_{bi} = 2$ V. The frequency is chosen in the low-frequency limit, equal to $10^{15}$ Hz, far below the frequency above which the capacitance becomes frequency dependent. There is no practical limit imposed by the method to how low the frequency can be chosen.

The figures show that the peak height increases with increasing disorder parameter, and that it exceeds the values obtained for the case of a constant mobility. We find that for large $V_{bi}$ the peak voltage follows the built-in voltage, as for the case of a constant mobility, but at a distance which increases with increasing disorder parameter. $V_{peak}$ shifts from 1.65 V (constant mobility) to
Figure 7.2: Calculated effect on the disorder dependent peak voltage and peak height due to (a), (b) a variation of the layer thickness and (c), (d) a variation in the injection barrier, in all cases for devices studied in Fig. 7.1(b). The layer thickness and injection barrier are varied in 50 nm and 0.1 eV steps, respectively.
1.57 V for $\sigma / (k_B T) = 3$ and to 1.41 V for $\sigma / (k_B T) = 6$. The observed increase of the peak height and peak shift with respect to $V_{bi}$ indicate that with increasing disorder the role of diffusion becomes more important. This can be explained as a result of the disorder and charge carrier concentration dependent enhancement of the diffusion coefficient, described by the generalized Einstein equation. The diffusion coefficient enhancement results in a redistribution of the carrier density in the device, as may be seen from the simulation results for comparable devices shown in Fig. 4 in Ref. 23.

In Ref. 2, it was shown that in the absence of disorder, $V_{\text{peak}}$ and $C_{\text{peak}}$ depend only on the dimensionless carrier densities at the electrodes

$$\gamma_i = \frac{e^2 L^2}{\varepsilon k_B T n_i}, \quad (7.7)$$

with $n_i$ (for $i = 1, 2$) the carrier density at the injecting and exit electrodes. The factor which is used to normalize the carrier density is (apart from a numerical factor) equal to the carrier density in the device center at zero voltage and for the case of ideal contacts. For the case of such an ideal symmetric device, the $\gamma$-parameters are thus a dimensionless measure of the role of charge carrier diffusion from the electrodes toward the device center. For the case of an asymmetric device such as discussed in Fig. 7.2, with a large-built-in voltage resulting from a small and a large barrier at the injecting and exit electrodes, respectively, $V_{\text{peak}}$ is only determined by $\gamma_1$ and increases then with decreasing $\gamma_1$ (see Eq. (1) in Ref. 2) This may be understood from the decreasing role of carrier diffusion from the injecting contact, so that the current density onset voltage (and hence $V_{\text{peak}}$) shifts to a higher value, more close to $V_{bi}$. In such a case, $V_{\text{peak}}$ increases with a decrease of the layer thickness or an increase of the barrier at the injecting contact. Figs. 7.2(a) and 7.2(c) show that, qualitatively, such a trend is also obtained in the presence of energetic disorder, studied for systems with $V_{bi} = 2$ V. The effect of the boundary conditions on the peak height is somewhat more complicated, as may be seen from Fig. 3(c) in Ref. 2, which reveals that for a strongly asymmetric device $C_{\text{peak}}$ can decrease with increasing thickness and with an increase of the injection barriers at both interfaces. Figs. 7.2(b) and 7.2(d) show that such trends are also obtained in the presence of energetic disorder.

### 7.3.2 Comparison with Experiment

We apply the model to the PF-TAA based hole-only devices, already discussed in the Introduction, for which the $C(V)$ curve was analyzed in Ref. 2 assuming a constant mobility and diffusion coefficient. The hole-injecting layer is
Figure 7.3: (a) The structure of the PF and TAA monomer units. (b) $C(V)$ curves for PEDOT:PSS $|$ 97 nm PF-TAA(7.5%) $|$ Pd devices, measured at room temperature at various frequencies (left-hand scale) and simulated in the low-frequency limit (right-hand scale). The simulation was carried out using $\sigma = 0.13$ eV, $N_{loc} = 0.6 \times 10^{27}$ m$^{-3}$, $V_{bi} = 1.95$ eV, and $e_r = 3.2$.

poly(3,4-ethylendioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS), fabricated by spin-coating on a 100 nm indium-tin-oxide (ITO) layer on glass, while an evaporation deposited Pd cathode layer was used. The device structure is thus PEDOT:PSS $|$ PF-TAA $|$ Pd. The experimental method has been described in Ref. 2. The structure of the monomer units is shown in Fig. 7.3(a). The triarylamine units are randomly copolymerized with the fluorene units, and are present with a concentration of 7.5 mol %. With increasing TAA concentration, the mobility first decreases, when these units act as hole traps. A steep increase is observed beyond a TAA-concentration of approximately 2%, above which the transport takes place via the TAA units (with an ionization potential of approximately 5.1 eV), instead of via the polyfluorene highest occupied molecular orbitals (HOMO), at approximately 5.8 eV. As the ionization potential of PEDOT:PSS is approximately 5.1 eV, a large (~0.7 eV) injection barrier to the PF-HOMO states is present at the interface, so that the space charge density at the interface, related to the occupation of the PF-states, is expected to be very small. This explains why for PEDOT:PSS / PSF devices, containing poly(spirofluorene) (PSF) which is electronically very similar to PF and which contains no TAA units, no peak in the low-frequency differential capacitance has been observed.8
Fig. 7.3(b) shows for the PEDOT:PSS | 97 nm PF-TAA(7.5%) | Pd hole-only devices a series of $C(V)$ curves measured at low frequencies, taken from Ref. 2 (left axis, using the capacitance measured at $V = 0$ V, $C_{V=0}$, for normalizing the curve), and the simulated curve, obtained using the experimental parameters given in the figure caption (right axis). The parameters describing the hole density of states and the hopping mobility were taken from the analysis of the steady-state $J(V)$ curves, carried out in Ref. 9 within the EGDM for a wide range of layer thicknesses and temperatures. No evidence for the presence of spatially correlated (instead of random) energetic disorder was found. No injection barrier at the PEDOT:PSS interface was assumed, consistent with the excellent energy level alignment of the PEDOT:PSS electrode layer and the HOMO energy of the TAA units, as mentioned above. The analysis led to $V_{bi} = 1.95$ eV, a value which is much larger than would be expected on the basis of the vacuum work function of the Pd cathode. This points at the formation of a significant interfacial dipole layer.

Both curves show a distinct shift of $V_{peak}$ to a value below $V_{bi}$. The measurement shows a peak at 1.3 V, approximately 0.65 V below $V_{bi}$, whereas the simulation leads to $V_{peak} \approx 1.45$ V, corresponding to a peak shift of approximately 0.5 V. In view of the experimental uncertainty in the parameters used in the model calculation (±0.05 V for $V_{bi}$ and ±0.01 eV for $\sigma$, as stated in Ref. 9, the agreement may be regarded as good.

We remark that a recent experimental study of the same devices, carried out approximately two years after the work reported in Refs. 2 and 9, confirmed the values of the bulk transport parameters used and the approximately 0.65 V difference between $V_{bi}$ and $V_{peak}$, but revealed an approximately 0.3 V decrease of both voltages. This was attributed to a small time-dependent change of the dipole layer at the PF-TAA / Pd interfaces. As expected from the simulations, such a change has no effect on the peak shift. We also note that the same study revealed that $V_{peak}$ is very close to the voltage at which the signal as obtained from an electroabsorption (EA) experiment goes through zero (zero field-voltage, $V_{0,EA}$), and that for these devices $V_{0,EA}$ is consistent with predictions as obtained from an EGDM simulation. It was furthermore found that both voltages may be interpreted as an effective current density onset voltage.

The height of the experimental low-frequency capacitance peak shown in Fig. 7.3(b) is significantly (approximately a factor of three) smaller than as obtained from the simulation, and it is somewhat broader. Furthermore, the simulated capacitance decreases above the peak voltage to a value of 0.80 $C_{geom}$ at high voltages, whereas the experimental capacitance increases at high voltages with a rate which is larger for smaller frequencies. The smaller peak height and large peak width may, in part, be explained as a result of small lateral variations of the built-in voltage. The increase of the capacitance at higher voltages can be attributed to charge carrier relaxation. This is a low-frequency contribution to the
capacitance for which a phenomenological description was given by Martens et al.\textsuperscript{1} for the case of poly(p-phenylene vinylene) based devices. The effect is due to the effective time (or frequency) dependence of the mobility which arises in any transient experiment, in which after a sudden change of the carrier density in a certain volume the local energy distribution is not immediately equal to the steady-state distribution. The effect of charge carrier relaxation on the capacitance is expected to increase with increasing space charge, and hence with increasing voltage, consistent with the experimental results. Modeling of the effect of charge carrier relaxation on the capacitance within the framework of the EGDM shows that including the effect hardly affects $V_{\text{peak}}$, but that it can lead to a slight decrease of the peak height.\textsuperscript{27}

Another possible explanation of the reduced peak height would be the presence of an injection barrier at the PEDOT:PSS / PF-TAA interface. However, we find that a significant effect on the peak height is only expected when the injection barrier is at least 0.3 V, as also suggested by the simulation results shown in Fig. 7.2(d) for a system described by similar parameters, and that the introduction of such a barrier would give rise to a strong upward peak shift which is inconsistent with the measured value. We remark that it is, in fact, remarkable that from the analyses of the $J(V)$ and EA measurements no evidence for a (significant) injection barrier was found. It is well known, e.g., from an extensive study of metal / semiconductor / metal devices with aluminumtris-(8-hydroxy-quinoline) (Alq3) as the organic semiconductor,\textsuperscript{28} that in the case of excellent energy level alignment an effective injection barrier can arise as a result of charge transfer to the organic layer, leading to the formation of a dipole layer. Such an effect has indeed been obtained from phenomenological modeling, involving image charge stabilization of a dipole layer,\textsuperscript{29} as well as from \textit{ab initio} modeling using density functional theory (see, e.g., Ref. 30). On the other hand, experimental evidence of strongly weakened dipole layer formation at interfaces with PEDOT:PSS has been found by Tengstedt et al.\textsuperscript{31} Indeed, a weakening of image charge interactions might be expected from the structure of PEDOT:PSS, which is an inhomogeneous material consisting of conducting PEDOT segments in a matrix of non-conducting PSS, which is known to segregate to the surface.\textsuperscript{32} The complex structure of PEDOT:PSS has been shown to give rise to anisotropic conduction.\textsuperscript{33} The decreased height of the $C(V)$ peak suggests that it might be of interest to develop a refined model for simulating the hole injection at the PEDOT:PSS / PF-TAA interface, taking the effect of the inhomogeneous character of the PEDOT:PSS layer on the charge carrier density in PF-TAA at the interface with PEDOT:PSS layer into account.
7.4 Double-Carrier Devices

Fig. 7.4(a) shows simulated low-frequency $C(V)$ curves for 100 nm double-carrier devices which are otherwise identical to the single-carrier devices studied in Fig. 7.1(a) (no injection barriers, the same electron and hole mobility functions and $V_{bi} = 2$ V). The voltage differences between $V_{peak}$ and $V_{bi}$ increase with increasing disorder parameter, and are approximately a factor of two larger than for corresponding single-carrier devices, as may be seen from a comparison given in Fig. 7.4(b). Furthermore, the peak heights (also shown in Fig. 7.4(b)) are almost a factor of two larger. These results reflect the larger role of charge carrier diffusion in the double-carrier devices, in which due to diffusion near both interfaces a high charge density is present. The result is consistent with the current onset difference between otherwise identical single-carrier and double-carrier devices with varying Gaussian disorder, displayed in Fig. 4 of Ref. 10.

Fig. 7.4(c) shows the effect of the introduction of an electron injection barrier, $\phi_e$, on the $C(V)$ curves, for otherwise identical devices with $\sigma / (k_B T) = 3$. The built-in voltage is equal to $E_g - \phi_e$, where $E_g$ is the 2 eV gap energy taken. The figure shows clearly that the peak voltage varies nonlinearly with $V_{bi}$. In general, deducing the built-in voltage from the peak voltage will therefore require detailed device modeling. However, when the electron injection barrier is sufficiently large, so that the space charge density near the cathode is very small, no detailed modeling is needed for deducing injection barrier differences, as these are then equal to the measured peak voltage differences. This condition is met for the $\phi_e = 0.5$ and 0.7 eV cases studied, for which Fig. 7.4(c) reveals a shift of the peak voltage from 1.07 to 0.87 V. Furthermore, under these conditions the peak shift is seen to be very close to the peak shift for the corresponding single-carrier device (~0.42 V). If this peak shift is known from experiments and modeling of single-carrier devices ($\Delta V_{SC}$), the built-in voltage for the double-carrier device follows then from the measured peak voltage using

$$V_{bi,DC} = V_{peak,DC} + \Delta V_{SC}.$$  \hspace{1cm} (7.8)

This is a general result, irrespective of the disorder parameter.

As an application, Fig. 7.5 shows the measured low-frequency $C(V)$ curves for PF-TAA(7.5%) based double-carrier devices with Ba/Al and LiF/Ca/Al cathodes. Fig. 7.5(a) gives the energy level scheme. The barrier from the LiF/Ca/Al and Ba/Al cathodes to the lowest-occupied molecular orbital states of the copolymer, which are PF-derived, is approximately 0.4 and 0.5 eV, respectively (see below). For the case of a Ba/Al cathode (see Fig. 7.5(b)), a pronounced peak in the capacitance is observed at 2.39 V. Under the assumption that the barrier at the Ba/Al interface is sufficiently high, the ~0.65 eV peak shift
Figure 7.4: (a) Calculated $C(V) / C_{\text{geom}}$ curves for double-carrier devices based on a semiconductor with a gap energy $E_g = 2$ eV, a thickness $L = 100$ nm, relative dielectric constant $\varepsilon_r = 3$, at $T = 300$ K and in the low-frequency limit. The contacts are ideal, so that $V_{bi} = 2$ V. (b) Calculated dependence of the peak voltage and the peak capacitance on the disorder parameter, for the devices studied in figure (a). (c) Calculated effect of a finite electron injection barrier on the $C(V) / C_{\text{geom}}$ curves for devices which are otherwise identical to those studied in (a).
as observed from the analysis of single-carrier device experiments would imply that $V_{bi,DC} \approx 3.04$ eV. The somewhat smaller shift of $\sim 0.50$ V as obtained from the single-carrier device simulations would imply that $V_{bi,DC} \approx 2.89$ eV. Replacement of the Ba/Al cathode by a LiF/Ca/Al cathode is known to give rise to enhanced electron injection. The 0.13 eV higher peak voltage obtained for these devices, as shown in Fig. 7.5(c), implies that the injection barrier is 0.13 eV smaller than for Ba/Al electrodes, provided that for both electrodes the injection barrier is sufficiently large. The appropriateness of the latter criterion is supported by recent analyses of the steady-state current-voltage curves of single-carrier electron-only and double-carrier PF-TAA(7.5%)/LiF/Ca/Al-based devices, which yielded $\phi_e = 0.30 \pm 0.10$ eV (Ref. 35) and $\phi_e \approx 0.40$ eV, respectively. Using the latter value, the analysis of the $C(V)$ curves would imply that for the Ba/Al devices $\phi_e \approx 0.53$ eV.

Fig. 7.4(a) shows a strong disorder-related decrease of the capacitance for voltages beyond the capacitance peak, even to negative values for disorder parameters $\sigma/k_B T \geq 6$. A negative differential capacitance (NDC) at voltages close to the built-in voltage has been reported from several studies of double-carrier devices. These studies suggest that the effect results from the presence of a high-density nearly charge-compensated electron hole plasma in such devices. Various quantitative models have been proposed, involving a strong (more than one order of magnitude) reduction of the bimolecular recombination rate near the electrode interfaces, a non-equilibrium population of interface trap states, and trap-mediated recombination. Our simulation method can thus already account for the occurrence of a NDC, provided that sufficient energetic disorder is present.

We find that the capacitance at high voltages and low frequencies of the double-carrier devices studied in Fig. 7.4(a) is very sensitive to the recombination rate assumed. E.g., for the case $\sigma/(k_B T) = 3$ or 6 a reduction of the recombination rate by a factor of 2.5 already reduces the capacitance to approximately zero or $-2.3 \times 10^4$ respectively. Although it has been proposed that the recombination rate in organic semiconductors can be much smaller than as given by the Langevin formula, recent Monte Carlo calculations have indicated that the Langevin formula holds well, albeit that it should be applied using so-called “bipolar” mobilities. In double-carrier devices the mobility is smaller than the single-carrier mobility due to the interaction with the randomly distributed carriers of the other type. A quantitative analysis for specific systems should thus include the effect of Coulomb-interactions on the charge carrier mobility and recombination rate. Furthermore, also the role of electron trap states, at which hole capture followed by recombination can take place, should be taken into account. Giving such an analysis, and an analysis of the positive relaxation contribution at high voltages which is revealed by the experimental double-carrier $C(V)$ curves given in Fig. 7.5, would be beyond the scope of this chapter.
Figure 7.5: (a) Energy-level structure for the PF-TAA devices studied, and $C(V)$ curves measured at room temperature at various frequencies for (b) PEDOT:PSS | 101 nm PF-TAA(7.5%) | Ba | Al devices and for (c) PEDOT:PSS | 96 nm PF-TAA(7.5%) | LiF | Ba | Al devices.

### 7.5 Summary and Conclusions

A one-dimensional Master-equation model for transient charge transport has been developed that takes disorder into account according to the Extended Gaussian Disorder model. The current response to an infinitesimal oscillation on a DC voltage is calculated using the small signal approximation. Subsequently, the differential capacitance is calculated and used to study the influence of disorder on the peak in the differential capacitance versus voltage curve, which can be used to determine the injection barriers in OLEDs. The model showed a pronounced disorder dependence in the peak position and height, which indicates that disorder
cannot be neglected when this peak is used to determine the injection barriers. The capacitance peak voltage is more strongly shifted to a value below the built-in voltage than as expected in the absence of disorder. The shift is explained by the significant diffusion current below the built-in voltage, which becomes even more important with increasing disorder. For double-carrier devices, the peak in the $C(V)$ curve is shifted to lower voltages than for single-carrier devices, which is explained as a result of the increased charge carrier concentration giving rise to an enhanced diffusion current density and a reduced onset voltage.

For a small injection barrier at one of the contacts, a change in the barrier leads to a nonlinear shift in the peak voltage. Deducing the built-in from this type of measurements therefore requires detailed device modeling. Only at sufficiently large injection barriers, the built-in voltage varies linearly with the peak voltage. The model is applied successfully to single-carrier and double-carrier devices based on the blue-emitting polymer PF-TAA.

For double-carrier devices based on materials with a large width of the Gaussian density of states, the model also revealed a negative capacitance at voltages above $V_{\text{peak}}$. This indicates that disorder is one of the important parameters determining the observation of a negative capacitance. For single-carriers a negative capacitance was not found, consistent with the fact that the effect has (so far) only been observed in some double-carrier devices. We remark that in actual organic semiconductors the electron transport is often described by a more complex shape of the density of states, formed by a Gaussian and a superimposed exponential trap density of states. Future modeling studies of the negative capacitance should include this more refined description of the DOS.

At voltages well beyond the low-frequency capacitance peak the model starts to break down. The experimental capacitance shows then often a strong increase with the voltage, to values well above the geometrical capacitance. This effect is due to relaxation of injected charge carriers, related to the presence of energetic disorder, which is not taken into account in this work. For the case of single-carrier devices, an extension of the model to include this effect has been recently developed$^2$7 and is the subject of the next chapter.

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Modeling of the Transient Mobility in Disordered Organic Semiconductors With a Gaussian Density of States

The charge-carrier mobility in organic semiconductors is often studied using non-steady-state experiments. However, energetic disorder can severely hamper the analysis due to the occurrence of a strong time dependence of the mobility caused by carrier relaxation. The multiple-trapping model is known to provide an accurate description of this effect. However, the value of the conduction level energy and the hopping attempt rate, which enter the model as free parameters, are not a priori known for a given material. We show how for the case of a Gaussian density of states both parameters can be deduced from the parameter values used to describe the measured DC current-voltage characteristics within the framework of the extended Gaussian disorder model. The approach is validated using three-dimensional Monte Carlo modeling. In the analysis, the charge-density dependence of the time-dependent mobility is included. The model is shown to successfully predict the low-frequency differential capacitance of sandwich-type devices based on a polyfluorene-triarylamine copolymer.

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8.1 Introduction

The organic semiconductors which are used in organic light-emitting diodes (OLEDs) and organic field-effect transistors are often strongly disordered. The charge transport is then due to hopping between states which are localized on a molecule or on a conjugated segment in a polymer. Energetic disorder can give rise to a strong temperature \( T \), electric field \( F \), and charge-carrier density \( n \) dependence of the charge-carrier mobility \( \mu \), depending on the detailed shape of the density of states (DOS).\(^{1-5}\) However, the mobility function \( \mu(T,F,n) \) is only well defined under steady-state conditions. The transient electrical response can be severely affected by charge-carrier relaxation effects, caused by the slow and widely time-distributed hopping processes in between high-energy “conduction” states and low-energy states in the tail of the DOS which effectively act as trap states.\(^6\) Well known consequences are the anomalous transit-time dispersion observed in time-of-flight (TOF) mobility measurements\(^7-11\) or in transient photocurrent measurements,\(^12,13\) an anomalous low-frequency electrical admittance,\(^14-16\) and hysteresis or even long-time memory effects.\(^17\)

Transient effects in energetically disordered semiconductors have been studied by Monte Carlo modeling\(^1,18\) and using the multiple-trapping (MT) model,\(^6,14,19-27\) which is better suitable for long time scales or at low frequencies. Within the MT model, the transport is assumed to be due to the fraction of carriers in a high-energy conduction level \( E_C \), while the remaining carriers reside in a distribution of low-lying localized states in which they are immobile. The effect of a sudden spatially uniform increase of the carrier density is described as an instantaneous increase of the population of the conduction level, followed by multiple capture-and-release processes during which the average carrier energy decreases. The time dependence of the mobility is assumed to be equal to the average time fraction during which carriers reside at the conduction level times the mobility of carriers in the conduction level. The energetic relaxation process leads to a decrease of the mobility, in a manner which depends on the detailed shape of the DOS. For the case of an exponential DOS, no characteristic time constant is involved in the relaxation process, as it evolves to energetically ever deeper states. The DOS is then proportional to \( \exp(E/k_B T_0) \), with \( E \) the energy and \( k_B T_0 \) a characteristic energy, where \( k_B \) is the Boltzmann constant and \( T_0 \) is a characteristic temperature. If \( T \leq T_0 \), the time- \((t)\) and temperature-dependent \((T)\) mobility is to a good approximation proportional to \( t^{\alpha-1} \), with \( \alpha = T / T_0 \).\(^{20,21}\) In contrast, for the case of a Gaussian DOS with a width (standard deviation) \( \sigma \), the time dependence of the mobility is more complex and the relaxation process ends when the average carrier energy is equal to the thermal equilibrium energy, \( E_0 = -\sigma / (k_B T) \).\(^1\) The mobility relaxation time depends sensitively on the position of the conduction level with respect to the thermal equilibrium energy,\(^24,25\) viz. as


\[
t_{0,\text{mob}} = \frac{1}{v_0} \exp \left( \frac{E_C - E_0}{k_B T} \right),
\]

(8.1)

with \(v_0\) the hopping attempt frequency. The concept of a conduction (or “transport”) energy is well established in theories of the steady-state mobility\textsuperscript{24,28–30} and provides an excellent description of its carrier density dependence.\textsuperscript{30,31} However, it has been defined in various ways and it is not known which expression for \(E_C\) should be used when modeling relaxation processes. Furthermore, the hopping attempt frequency, which determines the capture-and-release rates, is in general not known. Therefore, MT models can so far only empirically describe charge-carrier relaxation in materials with a Gaussian DOS.

A second consequence of the multiple-trapping process, which becomes apparent when the charge carriers are introduced only in a spatially strongly confined region and in the presence of an electric field, is an anomalous broadening of the initially narrow package of charge carriers, leading to a diffusion coefficient along the field direction that is much larger than that expected from an application of the Einstein relation. This so-called anomalous dispersive transport effect may be understood as a result of the fact that at any time \(t\) those carriers which have been captured in deep trap states, defined as states from which the release time is (much) larger than \(t\), are essentially immobile so that equilibrium statistics is not applicable. A thermal equilibrium distribution has only been established (after multiple-trapping and release processes) for those carriers which reside in shallow trap states, defined as states from which the release time is (much) smaller than \(t\). This “demarcation-line picture,” involving a time-dependent energy which separates the shallow and deep trap states, has been found to provide a convenient basis for calculating the effects of the time-dependent mobility and anomalous dispersion on the transient current measured in TOF measurements. Measurements of the post-transit-time photocurrent response in such experiments may even be used to determine the shape of the deep part of the DOS, i.e., the part of the DOS within which no thermal equilibrium occupation has been established yet at the transit time.\textsuperscript{23} Again, also dispersive transport manifests itself in qualitatively different ways for the cases of an exponential DOS and a Gaussian DOS, viz. as a continuing process and a process which ends after a time

\[
t_{0,\text{disp}} = \frac{1}{v_0} \exp \left( \frac{E_C - 2E_0}{k_B T} \right),
\]

(8.2)
respectively, as shown by Nikitenko et al.\textsuperscript{25} The dispersion process will thus in general proceed long after the mobility has been relaxed. As already suggested by Eq. (8.2), Nenashev et al.\textsuperscript{26} showed recently theoretically that the most important sites determining this effect reside around the energy \( E_0 = -2 \sigma^2 / (k_B T) \) and that the effect almost disappears if sites with energies below the thermal equilibrium energy \( E_0 \) are eliminated. On the other hand, the mobility was found to be only weakly affected by taking away states below \( E_0 \). As the anomalous dispersion effect is thus sensitive to the presence of a very small fraction of deep tail states, it is expected to be less pronounced in small systems,\textsuperscript{26} e.g., systems containing thin layers, such as OLEDs. However, this has not been studied systematically. Relaxation effects have so far most intensively been studied for relatively thick devices, such as used in TOF experiments (typically 10 \( \mu \)m).

As far as is known to the author, all TOF analyses of relaxation and anomalous dispersive transport and all theoretical studies were carried out under the assumption that the carriers may be viewed as noninteracting. For the case of a Gaussian DOS, this corresponds to considering only systems with carrier concentrations within the Boltzmann regime. Whereas this is often a fair approximation when analyzing TOF experiments, a significant carrier density dependence of the transient charge transport processes is expected under space-charge-limited current (SCLC) transport conditions. In this chapter, we further develop the MT model for the case of semiconductors with a Gaussian DOS and show how it can be used to predictively model relaxation, viz. by (i) applying the MT formalism to relaxation at any arbitrary carrier density, also outside the Boltzmann regime, (ii) providing for \( E_C \) a simple relationship with \( \sigma \), and (iii) providing for \( v_0 \) a simple relationship with \( \sigma \) and the hopping site density \( N_{loc} \). Both parameters \( \sigma \) and \( N_{loc} \) can already be obtained from steady-state current density \( (J) \) versus voltage \( (V) \) measurements. Therefore, no additional parameters are involved. The expression for \( E_C \) is obtained from three-dimensional (3D) Monte Carlo calculations and is shown to be in good agreement with the results obtained recently independently from percolation theory.\textsuperscript{32} The approach is applicable to organic and inorganic semiconductors. We discuss how it leads to a time- or frequency-dependent mobility that can be used to model transients measured in any experiment, and we apply it to the case of the differential capacitance \( (C) \) of hole-only metal – organic semiconductor – metal (MOM) devices based on a blue-emitting copolymer. The devices studied operate under SCLC conditions, and the development and application of a charge-carrier density dependent model for the AC mobility is shown to be relevant.

In Sec. 8.2, the structure of the devices studied is presented, and it is discussed why measuring the angular frequency \( (\omega) \) dependence of \( C(V) \) characteristics of MOM devices is expected to be a particularly sensitive method for probing relaxation effects, as suggested earlier in Refs. 14 – 16. Sec. 8.3 contains the main results, including an expression for the hopping attempt
frequency, the conduction energy level for materials with a Gaussian DOS, and expressions for the AC mobility. In Sec. 8.4 an analysis is presented of the measured layer-thickness-dependent \( C(V) \) curves, which provides support for the method developed. Sec. 8.5 gives a summary and conclusions.

8.2 Device Structure

The devices studied are based on a blue-emitting polyfluorene-(7.5 mol % triarylamine) (PF-TAA) co-polymer, supplied by Sumation Co., of which the molecular structure is shown in Fig. 8.1(a). The layer structure of the devices is

\[
glass | \text{ITO} | \text{PEDOT:PSS} | \text{PF-TAA} | \text{Pd},
\]

with an indium tin oxide (ITO) / 100 nm poly(3,4-ethylenedioxythiophene): poly(styrene sulfonic acid) (PEDOT:PSS) anode and a 100 nm palladium cathode. Details on the device fabrication and measurement methods are given in Ref. 33.

Figure 8.1: (a) Schematic structure of PF-TAA. (b) Experimental \( C(V)/C_{V=0} \) curves (symbols) for a 97 nm device at \( T = 295 \) K for various frequencies\(^3^4\) and calculated 100 Hz curve without relaxation.
In PF-TAA, the hole transport takes place by hopping in between states localized on the TAA units. From an analysis of the steady-state \( J(V) \) curves, measured for a range of temperatures and PF-TAA layer thicknesses, it was found that the hole mobility of PF-TAA can be accurately described by assuming hopping transport in between spatially uncorrelated localized states with a Gaussian DOS.\(^{35,36}\) The carrier density and electric field dependence of the steady-state mobility are then given by the extended Gaussian disorder model (EGDM),\(^4\) and described by three parameters, viz. the width \( \sigma \approx 0.13 \text{ eV} \) of the Gaussian DOS, the hopping site density \( N_{\text{loc}} \approx 0.6 \times 10^{27} \text{ m}^{-3} \), and the mobility in the limit of zero carrier density and zero field, \( \mu_0(295 \text{ K}) = 5.2 \times 10^{-12} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1} \). The temperature dependence of \( \mu_0(T) \) is found to be described well by

\[
\mu_0(T) = \mu^*_{0,\text{EGDM}} \exp(-\chi \hat{\sigma}^2),
\]

with \( \hat{\sigma} = \sigma / (k_B T) \) and where \( \chi \) is in the range as expected within the scope of the EGDM, viz. \( \chi \approx 0.39 \). In the high-temperature and low-carrier-density limit, the zero-field mobility is equal to \( \mu^*_{0,\text{EGDM}} = 1.4 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1} \). The hole injection barriers at the anode and cathode are 0 and 1.9 eV, respectively.\(^35,37\)

The capacitance-voltage curves shown in Fig. 8.1(b) may be understood as follows. In Ref. 33, it was discussed how the voltage and height of a distinct low-frequency peak in the experimental \( C(V) \) curves can be used to determine the injection barriers at both interfaces. The peak voltage, 1.30 ± 0.05 V, may be viewed as an effective value of the conductance onset voltage.\(^38\) It is significantly smaller than the built-in voltage, \( V_{\text{bi}} \approx 1.9 \text{ V} \), as a result of the space charge near the anode due to charge-carrier diffusion. The full \( C(V) \) curve shows the result of a calculation for a frequency \( f = 100 \text{ Hz} \), using the \( f \)-independent EGDM mobility function.\(^39\) The calculated peak voltage, 1.40 ± 0.10 V, agrees well with the experimental value. However, the simulation predicts at high voltages a \( V \)-independent capacitance smaller than \( C_{f=0} \), resulting from the delayed response of the space charge in the bulk of the device, whereas the experimental \( C(V) \) curves show a pronounced \( f \)-dependent increase. A similar effect has been observed earlier for various other organic semiconductor systems and has been interpreted either as an intrinsic effect, resulting from the charge-carrier relaxation in the presence of energetic disorder,\(^15,40\) or due to the presence of extrinsic trap states.\(^16,41,42\) Martens et al. observed the effect for devices based on poly(p-phenylene vinylene), attributed it to charge-carrier relaxation within the Gaussian DOS, and analyzed the admittance in terms of a complex mobility of the form

\[
\mu(\omega) = \mu_{\text{DC}} \left[ 1 + M(i \omega \tau_t)^{-\alpha} \right],
\]

with \( \sigma \equiv \sigma / (k_B T) \) and where \( \chi \) is in the range as expected within the scope of the EGDM, viz. \( \chi \approx 0.39 \). In the high-temperature and low-carrier-density limit, the zero-field mobility is equal to \( \mu^*_{0,\text{EGDM}} = 1.4 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1} \). The hole injection barriers at the anode and cathode are 0 and 1.9 eV, respectively.\(^35,37\)
with $\mu_{\text{DC}}$ the DC mobility, $\tau_i$ the layer-thickness- and voltage-dependent average charge-carrier transit time, and $\alpha$ and $M$ phenomenological parameters. This approach was also adopted in more recent work. However, no relationship was established between these parameters and the shape of the DOS. We show that it is indeed possible to define a frequency-dependent mobility, but that it only depends on the EGDM parameters $\sigma$, $N_{\text{loc}}$, and $\mu_{0,\text{EGDM}}^*$ and on the local carrier density, and not on the layer thickness and voltage.

### 8.3 Modeling the AC Mobility

#### 8.3.1 Hopping Attempt Frequency $v_0$

Within the MT model, the relaxation dynamics is modeled as a local process, i.e., neglecting the spatial distribution of the sites, using a total DOS composed of a normalized Gaussian DOS with a width equal to the experimental value and a normalized $\delta$-function-shaped conduction level. Fig. 8.2 shows schematically the effect of relaxation on the current density $J(t)$ (Fig. 8.2(a)) due to a sudden small increase of the carrier density (Fig. 8.2(b)). Initially, $J$ is strongly enhanced, as all additional carriers occupy then the high energy conduction level (Fig. 8.2(c)). Upon relaxation, the occupation probability $p_c$ of the conduction states decreases to the dynamic equilibrium value. The current density is proportional to $p_c(t)$. The final current density is larger than the initial current density ($t < 0$) due to the larger final carrier density and, depending on the initial carrier density $n_0$, due to a density dependence of the mobility. The relaxation kinetics is described as follows. For downward hops (capture), the rate is equal to $r_{\text{cap}} = v_0(1 - p_f)$, with $v_0$ an attempt frequency and $p_f$ the occupation probability of the final state. The rate of upward hops to $E_c$ (release, a thermally activated process) is given by $r_{\text{rel}} = v_0 \exp(-E/k_BT)$, with $E$ the energy difference between the final and initial states. The energy-difference dependence of the rates is thus equal to that given by the Miller-Abrahams expression used in three-dimensional Master-equation (3D-ME) modeling of the mobility. Within our model, $v_0$ is taken to be equal to the value for nearest-neighbor (NN) hops in the 3D-ME model,

$$v_{0,\text{NN}} \equiv \mu_{0,\text{EGDM}}^* \frac{\sigma}{a^2 e},$$

(8.5)

with $a = N_{\text{loc}}^{-1/3}$ the average intersite distance and $e$ the elementary charge. The
parameter values of $\sigma$, $N_{\text{loc}}$, and $\mu^*_{\text{EGDM}}$ describing the mobility in PF-TAA, obtained from Ref. 35 and given in Sec. 8.2, yield $v_0 \cong 1.3 \times 10^{10}$ s$^{-1}$ at room temperature.

### 8.3.2 Conduction-level Energy $E_C$

We have determined $E_C$ by first carrying out a 3D-MC calculation of the time dependence of the zero-field mobility in the Boltzmann regime. Single carriers are randomly injected at $t = 0$ at sites with $E > 0$ in an otherwise empty cubic grid with periodic boundary conditions, containing $250^3 \cong 1.6 \times 10^7$ sites with a Gaussian energy distribution. By ensemble averaging, a relative accuracy of better than 10% was realized. Fig. 8.3 (solid curves) shows the resulting time-dependent mobility for various values of $\tilde{\sigma} = \sigma/(k_B T)$. For PF-TAA, with $\sigma = 0.13$ eV, we have $\tilde{\sigma} = 5.1$ at room temperature. Shortly after $t = 0$ the mobility is enhanced by a factor of $\sim 10^4$ as compared to the DC mobility in the Boltzmann limit, independent of the carrier density. In the Boltzmann regime, the entire relaxation process takes more than a second. However, at higher concentrations the steady state is reached more quickly. The approach includes thus in a natural way a decrease of the relaxation time with increasing carrier concentration ($c \equiv n/N_{\text{loc}}$) outside the independent-particle Boltzmann regime, i.e., when $c > \frac{1}{2} \exp(-\frac{1}{2} \tilde{\sigma}^2) \approx 10^{-6}$ for $\tilde{\sigma} = 5.1$. The effect of relaxation decreases strongly with decreasing disorder, as may be seen from Fig. 8.3 for $\tilde{\sigma} = 3$ and 4 (Boltzmann limit). For all cases an excellent fit to the Monte Carlo (MC) curves could be obtained using the MT model, using...
\[ E_C^{\text{MC}} (\hat{\sigma} = 3) = -(0.60 \pm 0.1)\sigma, \]
\[ E_C^{\text{MC}} (\hat{\sigma} = 4) = -(0.65 \pm 0.1)\sigma, \]
\[ E_C^{\text{MC}} (\hat{\sigma} = 5.1) = -(0.70 \pm 0.1)\sigma. \]

For the last case, the figure shows the MT results for \( E_C = -0.75\sigma \), and it includes for comparison also results for \(-0.5\sigma \) and \(-1.0\sigma \) as obtained for the Boltzmann limit. It may be seen that the mobility enhancement is very sensitive to the precise value of the conduction-level energy, making it possible to deduce \( E_C \) with an uncertainty of only \( \pm 0.1\sigma \).

It is of interest to compare these values for the effective conduction-level energy with the results of a recent analysis by Cottaar et al. \(^{32}\) of the transport in systems with a Gaussian DOS using percolation theory. The authors determined for various types of lattices and expressions for the hopping rates the energy \( E_{\text{crit}} \) of the critical sites, i.e., the sites with the highest energies which still contribute to the percolating path. For the case of simple cubic systems within which the hopping is described by Miller-Abrahams hopping rates (as in the Monte Carlo carried out in our work), it was found that \( E_{\text{crit}} = -0.49\sigma \), very close to the values of \( E_C \) obtained independently in our work from an analysis of the relaxation process. The finding of an effective conduction level energy and a critical energy which are both essentially independent of temperature is consistent with our

---

Figure 8.3: Calculated time dependence of the zero-field mobility relative to \( \mu_0 \) (the DC mobility in the Boltzmann limit, BL) for PF-TAA (\( \hat{\sigma} = 5.1 \), including results for various concentrations) and for systems with \( \hat{\sigma} = 4 \) and 3 (BL). Results from the MT model (solid spheres) with \( E_C = -0.75\sigma \), \(-0.65\sigma \), and \(-0.60\sigma \), respectively, are compared with the results from MC calculations (solid curves, smoothened). The dashed curves give the MT results for \( \hat{\sigma} = 5.1 \) (BL) with \( E_C = -0.5\sigma \) (I) and \(-1.0\sigma \) (II). For PF-TAA, the time range corresponds to 0.08 ns to 80 s.
observation that in the discrete lattice systems studied nearest-neighbor hopping processes are predominant, even for PF-TAA with $\tilde{\sigma} = 5.1$.

The work of Cottaar et al. shows that the critical energy depends on the type of lattice considered. For a face centered cubic (fcc) lattice it is lower than for a simple cubic (sc) lattice, viz., $\sigma \approx 0.84 \tilde{\sigma}$.32 Such a decrease may be understood qualitatively from percolation theory, from which it follows that in order to establish a percolating pathway each site must have on average at least a certain critical number of nearest neighbors to which it can be connected, i.e. with an energy below $E_{\text{crit}}$. In an fcc lattice, within which each site has 12 nearest neighbors, this criterion is already fulfilled for a lower value of $E_{\text{crit}}$ than for a sc lattice, within which each site has six nearest neighbors. As a consequence, one may expect that also the conduction-level energy for a material depends slightly on the (average) coordination number of the molecules. A study of this effect and more generally of the precise relationship between $E_C$ and $E_{\text{crit}}$ is beyond the scope of the present chapter. However, we note that it may be possible to obtain relevant experimental information about this issue from the temperature dependence of the mobility in the zero-field and zero-density limit, given by Eq. (8.3). Cottaar et al. found that in the range $2 \leq \tilde{\sigma} \leq 6$ the results for Miller-Abrahams hopping on sc and fcc lattices can be well described with $\chi = 0.44$ and $\chi = 0.40$, respectively. The smaller $\chi$ value for the fcc case arises from the somewhat smaller effective activation energy, resulting from the somewhat lower (more negative) value of the critical energy. For PF-TAA, with $\chi = 0.39 \pm 0.01$ as discussed in Sec. 8.2, it would be suggested by the formalism discussed above that the effective coordination number is relatively large and close to that in an fcc lattice.

We finally note that our results concerning $E_C$ are also applicable to systems in which a small low-energy trap (guest) DOS is superimposed on the Gaussian (host) DOS, as observed frequently in electron-transporting materials or in the emissive layers in OLEDs, since it follows from percolation theory that their presence does not affect $E_C$.$^{30}$

### 8.3.3 Time- and Frequency-dependent Mobility $\mu(t)$ and $\mu_{AC}(\omega)$

The expressions given for $r_{\text{cap}}$, $r_{\text{rel}}$, and $E_C$ make it possible to calculate $J(t)$ for any transient experiment, under the assumption that the time dependence is predominantly due to the time dependence of the mobility resulting from charge-carrier relaxation. We neglect here the effect of dispersive transport, related to the formation of a non-equilibrium occupation of deep trap states (see Sec. 8.1), which is relevant for large layer thicknesses, but which is likely to be of less relevance to the relatively thin devices investigated in this study. The time-dependent mobility is equal to
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\[ \mu(t) = \mu_{0,\text{EGDM}} f(F) \frac{\eta_c(t)}{\eta_{c,\text{BL}}}, \]  

(8.6)

with \( \mu_{0,\text{EGDM}} \) the DC mobility for \( F = 0 \) and \( n = 0 \), \( f(F) \) the field-dependent mobility enhancement in a Gaussian DOS (from Ref. 4), and \( \eta_c(t) \equiv p_c(t) N_{\text{loc}} / n \) and \( \eta_{c,\text{BL}} \) the time-dependent occupation of the conduction level per charge carrier and the occupation of the conduction level per charge carrier in the Boltzmann limit, respectively. For calculating \( p_c(t) \), standard drift-diffusion device modeling may be used in conjunction with the MT model.\(^6\)

In general, the calculation of \( p_c(t) \) at each position is an integral part of the calculation. However, in admittance experiments the density modulation is small and sinusoidal, so that the AC contribution to \( J \) follows already from the frequency-dependent mobility,

\[ \mu_{\text{AC}}(\omega, n_0) \equiv \frac{J_{\text{AC}}(\omega, n_0)}{en(\omega, n_0) F}. \]  

(8.7)

The functions \( J(\omega) \) and \( n(\omega) \) are the Fourier transforms of the current density \( J(t) = J(\infty) + J_{\text{AC}}(t) \) and the carrier density \( n(t) = n_0 + n_{AC}(t) \), respectively, for the case of an infinitesimal density increase at \( t = 0 \) in a uniform system.

8.4 Application: C(V) Curves of PF-TAA Based Devices

In Fig. 8.4, the approach developed in the previous section is applied to 97 and 121 nm thick PF-TAA-based devices. The \( C(V) \) curves were obtained using a small-signal AC extension\(^3\) of a drift-diffusion device model,\(^4,5\) within which the (generally complex) AC mobility as given by Eq. (8.7) has been added to the real DC mobility. Within the model, the current density includes a diffusion contribution as described by the generalized Einstein equation (see Appendix A of Ref. 45). We note that the use of small-signal methods for calculating \( C(V) \) curves is widespread (see, e.g., Ref. 46) and that the approach for including a frequency-dependent mobility such as that developed in this chapter can be used straightforwardly in conjunction with such methods.

For the 97 nm devices, the experimental results are well described using \( E_C = -0.75\sigma \), the value used in Fig. 8.3. The \( C(V) \) curves are quite sensitive to \( E_C \), as may be seen from the dashed curves in Fig. 8.4(a) which give the results at 100 Hz for \( E_C = -0.5\sigma \) and \( -1.0\sigma \). A fair agreement of the high voltage capacitance as a function of \( V \) and \( f \) with the model predictions is obtained, which
is remarkable in view of the large time scale covered by the $\mu(t)$ curves and their sensitivity to $\hat{\sigma}$ and $E_C$. The observed decrease of the relaxation-induced capacitance with increasing layer thickness is found as well from the model. The discrepancy concerning the low-voltage peak height might be due to lateral variations of $V_{bi}$, leading to peak widening, and indicates that, in future refined models of the electrode boundary conditions should be developed.

It is interesting to note that the modeled relaxation process extends over a time range up to approximately 1 s, for charge carriers in the Boltzmann limit, as may be seen from Fig. 8.3 or as may be calculated from Eq. (8.5). This implies that when measuring steady-state $J(V)$ curves great care should be taken concerning the rate of increase of the voltage, even at room temperature. We find that the current-density response to a sudden increase of the voltage can indeed give rise to a time dependent signal which only saturates after 1 s, depending on the detailed initial and final voltage values. The results of these “dark injection” experiments are presented elsewhere.

The relaxation-enhanced capacitance is the net result of various counteracting effects, as may be seen from Fig. 8.5. Fig. 8.5(a) shows that $\mu_{AC}$ increases with increasing frequency, but only relatively weakly, so that the capacitance (defined as the imaginary part of $J(\omega) / [\omega V(\omega)]$) decreases with increasing frequency. Fig. 8.5(b) gives for a representative example the
Moving Charged Particles in Fluctuating and Disordered Energy Landscapes

Figure 8.5: (a) Calculated concentration dependence of the real and imaginary components of $\mu_{AC}/\mu_0$ for PF-TAA. (b) Local relaxation contribution to the capacitance (normalized, solid curve) and carrier concentration (dashed) for a 97 nm device at 4 V and 250 Hz.

normalized position-resolved contribution to $C$, obtained by only including relaxation in an infinitesimal position range. We find that its integral is to an excellent approximation equal to the total relaxation contribution. The figure reveals that the relaxation contribution to $C$ is a bulk effect; it is small near the anode, where the carrier concentration is high but the relaxation very fast (see Fig. 8.5(a)), and near the cathode, where $c$ is small.

8.5 Summary and Conclusions

We have shown how the effect of charge-carrier relaxation on the time-dependent mobility in organic semiconductor devices based on materials with a Gaussian DOS may be predictively modeled. For that purpose, three-dimensional Monte Carlo modeling has been used to calculate the effective value of the conduction energy level which enters calculations of $\mu(t)$ within a multiple-trapping model. Assuming hopping in a simple-cubic lattice and assuming Miller-Abrahams hopping rates, we find values of $E_C$ in the range $-(0.5 - 0.8)\sigma$. A slight dependence on the disorder parameter $\sigma$ cannot be excluded. The carrier density dependencies of $\mu(t)$ as obtained from both approaches were found to be in excellent agreement. Quantitative modeling is then possible by making use of the values of the width of the Gaussian DOS and the hopping attempt frequency ($\sigma$ and $v_0$), which can be derived from an analysis of steady-state $J(V)$ curve measurements. The approach was demonstrated successfully for the specific case of the low-frequency differential capacitance of MOM devices based on the blue-emitting polymer PF-TAA. A fair description of the pronounced relaxation-related contribution to the capacitance was obtained using $E_C = -0.75\sigma$. It is thus in this case possible to describe the relaxation contribution to the capacitance as an intrinsic effect, which follows directly from considering multiple trapping in the
Gaussian DOS, without introducing additional parameters. Future studies should consider the additional contribution to the transient current density due to anomalous dispersive transport, which is expected to be most relevant in relatively thick devices. We envisage applications to the modeling of other transient effects, such as transient electroluminescence, dark current injection experiments, and hysteretic $J(V)$ measurements.

References


The barrier at the Pd electrode was obtained from the data given in Ref. 35 using the discrete drift-diffusion model employed in the present chapter.


From Eq. (3) in Ref. 4, with \( c_1 \) equal to the exponential rate reduction factor for nearest-neighbor hopping.


Summary

In this thesis various experiments are performed that concern the moving of charged particles in fluctuating and disordered energy landscapes. Systems under out-of-equilibrium conditions behave differently than at thermal equilibrium. The 2nd law of thermodynamics prohibits the extraction of useful work from thermal equilibrium situations. Despite the 2nd law Brownian ratchets and thermoelectric modules are able to convert thermal energy into a useful form of work, because the systems are in an out-of-equilibrium state. We examined a Brownian ratchet for suspended polystyrene particles, which can potentially be used as a particle separator. We wanted to find out how the ratchet works in detail and under which conditions we have the highest performance in particle separation. Second, we examined different charge transport models for disordered semiconductors using the thermoelectric effect. How does the Seebeck coefficient depend on temperature and charge density? Can we use this to make a distinction between different charge transport models? Finally we studied transient charge transport in an organic disordered semiconductor using admittance spectroscopy. What is the influence of the degree of disorder on the differential capacitance? Can we describe the charge carrier relaxation occurring in admittance spectroscopy experiments, and does this give an improved description of the measured differential capacitance?

Ratchets and Particle Transport

Brownian ratchets are out-of-equilibrium devices in which an asymmetry is used to extract work from thermal motion. The concept of the Brownian ratchet was conceived by Marian von Smoluchowski in a *Gedankenexperiment* to test the 2nd law of thermodynamics. Later Feynman adapted the imaginary device and applied a temperature difference to it. No longer constrained by the 2nd law the device was able to extract work from thermal motion. In the last decades several examples of ratchets have been realized performing work in different forms.

In Chapter 2 we studied a Brownian ratchet for suspended polystyrene particles in which the undirected thermal motion of the particles is used to create directed motion. This device can possibly be used as a particle separator, since particles of different sizes show a different magnitude of thermal motion, i.e., have a different diffusion coefficient. In order to increase the separation efficiency of the ratchet, detailed knowledge of the device is required. The ratchet was
constructed from asymmetrically placed interdigitated finger electrodes on a Si-
SiO₂ wafer, which create a periodic asymmetric potential that can be switched on
and off. From a similar experiment for DNA molecules, described in literature, the
driving was expected to be based on the interactions between the ionized surface
of the particles and the local electrostatic potential.

Surprisingly, we found that mainly dielectrophoretic rather than
electrophoretic forces are responsible for the ratchet effect. The negatively
charged particles are not attracted to the positive electrode, but rather to a field
minimum between the positive electrode and the negatively charged SiO₂
substrate. This has major implications for the asymmetry of the ratchet potential
and the settings needed for optimal performance. We demonstrated that by
applying a potential offset the ratchet can be optimized such that its particle
displacement efficiency reaches the theoretical upper limit corresponding to the
electrode geometry and particle size. Efficient fractionation based on size
selectivity is therefore not only possible for charged species, but also for
uncharged ones, which greatly expands the applicability range of this type of
Brownian ratchet.

In Chapter 3 we showed that during the ratchet operation a diffusion
enhancement of the suspended polystyrene particles occurs due to an additional
broadening of the distribution during the retrapping process. The enhancement can
be described by a simple Master-equation model. Furthermore, we found that the
diffusion enhancement can be described by a master curve whose shape is only
determined by the asymmetry of the ratchet repeat unit. The scaling of this curve
can be explained from an analytical expression valid for small off-times.

Finally, we demonstrated how the Master-equation model can be used to
find the driving parameters for optimal particle separation. For separating particles
with a large size difference an acceptable resolution can be achieved. However,
the device as used in the experiments is very slow when a separation quality that
is comparable to the size dispersion in commercially available polystyrene
particles is desired. Calculations showed that miniaturizing the device tenfold
enhances the separation speed to acceptable values for high selectivity
fractionation, caused mainly by the reduction in the retrapping time.

Thermoelectric Effects and Charge Transport
The thermoelectric effect is another effect by which work can be extracted from
an out-of-equilibrium situation. When applying a temperature difference to a
thermoelectric module thermal energy can be converted to electricity. The
Seebeck coefficient is equal to the ratio of the temperature difference and the
generated thermovoltage \( S = \Delta V / \Delta T \). Different charge transport models exist
for disordered semiconductors. The magnitude of the Seebeck coefficient depends
on the type of charge transport occurring in the material, and it depends on the
same materials parameters as the conductivity. In Chapters 4 to 6 of this thesis the
The thermoelectric effect was studied to make a distinction between various different models and to determine which type of charge transport is occurring.

Two important models frequently used for disordered semiconductors are the mobility edge model and the variable range hopping model. In the mobility edge model, the charge transport mainly takes place just above the fixed mobility edge, whereas in the variable range hopping model, the effective transport level is temperature and charge density dependent. The Seebeck coefficient is dependent on this level, and therefore the two models can show different temperature and charge density dependent behavior.

In Chapter 4, we measured the field-effect mobility and the Seebeck coefficient in a polytriarylamine (PTAA) thin film transistor (TFT). Both a mobility edge model and a Mott-Martens type of variable range hopping model cannot give an adequate description of the temperature dependence of the experiments. Further analysis suggests that the type of variable range hopping model used overestimates the heat transported by the charge carriers. For the mobility edge model, the mismatch seems to be of a more fundamental nature. From the analysis of the temperature dependence, we showed that a decreasing Seebeck coefficient with decreasing temperature, as shown for PTAA, is in general a strong indication of hopping-dominated transport.

In Chapter 5, an unusual increase in the Seebeck coefficient with increasing charge carrier density was observed in pentacene TFTs. This behavior was interpreted as being due to a transition from hopping transport in static localized states to bandlike transport above the mobility edge, occurring at temperatures below ~250 K. Such a transition can be expected for organic materials in which both static energetic disorder and dynamic positional disorder are important. The dynamical positional disorder, caused by molecular vibrations, is temperature dependent. While clearly visible in the temperature and density dependent Seebeck coefficient, the transition hardly shows up in the charge carrier mobility.

We investigated the mechanism of charge transport in indium-gallium-zinc oxide (a-IGZO), an amorphous metal oxide semiconductor, in Chapter 6. Apart from the field-effect mobility and the Seebeck coefficient, we employed a scanning Kelvin probe-based technique to determine the density of states of a-IGZO that was used as basis of the modeling. After comparing two models commonly used for a-IGZO, a band transport percolation model and a mobility edge model, we found that neither can describe the full properties of the charge transport in the a-IGZO semiconductor. We therefore proposed a model that extends the mobility edge model to allow for variable range hopping below the mobility edge. The extended mobility edge model gives a superior description of the experimental results. We showed that the charge transport is dominated by variable range hopping below, rather than by bandlike transport above the mobility edge.
In combination with the measurement of other parameters, the Seebeck coefficient was shown to be a helpful parameter in distinguishing between different charge transport models. Especially the temperature dependence of the Seebeck coefficient is useful in this respect, as the charge density dependence is often very similar for the different models.

**Transient Effects in Charge Transport**

Admittance spectroscopy is another out-of-equilibrium experiment by which the charge transport in disordered semiconductors can be studied. Admittance spectroscopy is a transient charge transport experiment, i.e., the electric potential and current are not constant in time, as opposed to steady state experiments. The admittance is defined as the ratio of the AC components of the current density and the voltage. The imaginary part of the admittance is equal to the product of the angular frequency and differential capacitance, and the real part is equal to the differential conductance.

It has been shown in literature how the injection barriers at the electrode interfaces and the built-in voltage of organic light emitting diodes can be obtained from measurements of the differential capacitance at low frequencies, using the voltage and height of a distinct peak in the capacitance-voltages curves. In Chapter 7 we investigated the effects of Gaussian energetic disorder on this analysis, for single-carrier and double-carrier devices. We showed how the disorder affects the peak position and height, and how from combined capacitance-voltage measurements and device modeling the injection barriers and the built-in voltage can be determined. As examples, hole-only and double-carrier sandwich-type devices based on a blue-emitting polyfluorene-triarylamine copolymer were investigated.

In highly disordered materials the thermalization, i.e., the energy relaxation, of charge carriers initially in a far-from-equilibrium distribution results in a strong time dependence of the mobility. The multiple-trapping and release model is known to provide an accurate description of this effect. However, the value of the conduction level energy and the hopping attempt rate, which enter the model as free parameters, are not *a priori* known for a given material. We showed in Chapter 8 how for the case of a Gaussian density of states both parameters can be deduced from the parameter values used to describe the measured DC current-voltage characteristics within the framework of the extended Gaussian disorder model. The approach was validated using three-dimensional Monte Carlo modeling. In the analysis, the charge-density dependence of the time-dependent mobility was included. The model was shown to successfully predict the low-frequency differential capacitance of sandwich-type devices based on a polyfluorene-triarylamine copolymer.
Synopsis

In conclusion, we elucidated several experiments in which charged particles were subject to fluctuating or disordered energy landscapes. We clarified the working of an on/off ratchet for suspended particles, studied its potential as a particle separator and determined its potential for improvement. We used the thermoelectric effect to study charge transport in disordered semiconductors, and determined how the temperature dependence relates to different charge transport models. Finally we used admittance spectroscopy to determine the effect of disorder on the differential capacitance and to study charge carrier relaxation.
Samenvatting

In dit proefschrift wordt de verplaatsing van geladen deeltjes in fluctuerende en wanordelijke energielandschappen op nanometerschaal onderzocht in drie verschillende systemen, te weten: (1) Brownse ratchets voor nanodeeltjes in een oplossing, (2) thermo-elektrische eigenschappen van wanordelijke halfgeleiders en (3) admittantiespectroscopie in wanordelijke organische halfgeleiders. Om de karakteristieke natuurkundige eigenschappen van deze drie systemen te verhelderen en hun onderlinge relatie te kunnen doorgronden volgt hieronder een korte beschrijving van de inhoud van dit proefschrift voor een algemeen publiek.

Brownse Ratchets

Systemen die zich in een toestand ver uit evenwicht bevinden gedragen zich anders dan wanneer ze in evenwicht zijn. Een belangrijk voorbeeld hiervan is de tweede hoofdwet van de thermodynamica. De interpretatie van die wet komt er op neer dat het onmogelijk is om energie te ontrekken van systemen die zich in thermodynamisch evenwicht bevinden. Eén van de (teleurstellende) gevolgen hiervan is dat perpetuum mobiles niet mogelijk zijn en dat we toch nog hard moeten werken om onze energievoorziening in de toekomst veilig te stellen. Toen deze wet geformuleerd werd in de negentiende eeuw was het moeilijk om deze wet experimenteel te controleren. Om de wet uitgebreider te kunnen testen werden er gedachtenexperimenten bedacht, die werden gebruikt om te kijken of de wet echt houdbaar was. Eén van die gedachtenexperimenten was de Brownse ratchet van Marian von Smoluchowski, gepubliceerd in 1912.1

Een plaatje van de Brownse ratchet van von Smoluchowski is te zien in Figuur 1. Het apparaat heeft aan de ene kant een wiel met een pal, lijkend op een ratel, dat ervoor zorgt dat het apparaat maar één kant op kan draaien. Het Engelse woord voor ratel is ratchet, daar komt dus de tweede helft van de naam van deze apparaten vandaan. Aan de andere kant heeft het apparaat een schoepenrad. Tegen deze schoepen zullen luchtmoleculen botsen. De luchtmoleculen zijn continu in beweging door de temperatuur die ze hebben. Bij een hogere temperatuur zal deze beweging sterker zijn. Er gaan alleen evenveel moleculen de ene als de andere kant op, en netto gaat de lucht dus nergens heen. Deze beweging heet Brownse beweging, wat de eerste helft van de naam van deze apparaten verklaart. Het idee van dit apparaat is dat de ratel aan de linkerkant er voor zorgt dat de botsingen
tussen de schoepen en de moleculen het wiel wel de ene kant op laten draaien, maar niet de andere. Op die manier halen we uit de ongerichte moleculaire bewegingen toch een netto draaiing van het wiel. Als we dan ook nog een touwtje met een gewicht aan de as hangen, kunnen we het gewicht optillen en toch energie halen uit een systeem dat in thermodynamisch evenwicht is.

Aangezien de Brownse ratchet al honderd jaar geleden bedacht is en fysici nog steeds volhouden dat de tweede wet van de thermodynamica toch echt geldig is, zal het niet als een verassing komen dat er hier iets niet klopt. De fout zit er in dat het apparaat heel klein zou moeten zijn om het daadwerkelijk te laten draaien door botsingen met moleculen. In een dergelijk klein apparaat zal het palletje van de ratel zelf ook trillen, door zijn eigen Brownse beweging. En als het palletje dan ver genoeg omhoog komt, draait het wiel weer terug.

Ruim vijftig jaar na de publicatie van von Smoluchowski bedacht Richard Feynman hoe je deze Brownse ratchet, nu ook bekend als de Feynman-Smoluchowski ratchet, toch zou kunnen laten werken.\(^3\) Als je het schoepenrad in een omgeving zou brengen die een hogere temperatuur heeft dan de omgeving van het ratelwiel heb je wel veel botsingen met het schoepenrad terwijl het palletje nauwelijks trilt. Zo kan toch een netto draaiing in een welbepaalde richting ontstaan. Een temperatuursverschil betekent ook dat het systeem zich niet in thermodynamisch evenwicht bevindt, en er dus geen problemen zijn met de tweede hoofd wet van de thermodynamica.

De laatste twee decennia zijn Brownse ratchets niet meer alleen iets dat in theorie bestaat, maar zijn er heel wat varianten ook daadwerkelijk experimenteel
gerealiseerd. De eigenschap die je altijd terug vindt in Brownse ratchets is dat het systeem uit evenwicht gebracht wordt, en dat er zich ergens in het systeem een asymmetrie bevindt, zoals het ratelwiel, die er voor zorgt dat een beweging makkelijker de ene kant op kan dan de andere.

In dit proefschrift is een Brownse ratchet onderzocht waarmee een netto beweging gerealiseerd wordt van polystyreen deeltjes van 300 en 500 nanometer, gebruikmakend van hun ongerichte Brownse beweging. Het type Brownse ratchet dat hier gebruikt is wordt ook wel het aan/uit ratchet genoemd en is schematisch weergegeven in Figuur 2. Figuur 2(b) laat het bijbehorende ‘asymmetrische potentiaallandschap’ zien. Dit kun je visualiseren als een periodieke rij heuveltjes waarin we in één van de dalen een stel knikkers opgesloten zien zitten. In het onderzochte systeem zijn de knikkers polystyreen nanodeeltjes met een geioniseerde mantel, die zich in een elektrisch potentiaallandschap bevinden dat gemaakt wordt met behulp van de elektroden in Figuur 2(a). Als we deze heuvels nu tijdelijk plat kunnen maken door de spanning op de elektroden uit te schakelen, zullen de deeltjes zich in alle richtingen verspreiden. Als we na verloop van tijd de spanning weer aanzetten, zorgt de asymmetrie van onze dalen ervoor dat er meer deeltjes rechts gevangen worden dan links, en hebben we dus netto beweging gerealiseerd. Omdat deeltjes van verschillende grootte een verschillende Brownse beweging hebben, zal de netto verplaatsing per deeltjessoort verschillen. Op die manier zou de Brownse ratchet kunnen werken als een scheidingsapparaat voor verschillende deeltjes. Hoe zoiets eruit zou zien is schematisch weergegeven in Figuur 2(c). Een mix van twee deeltjes van verschillende grootte wordt links in een kanaal geïnjecteerd. De verspreiding van de deeltjes wordt voor de ene grootte met een zwarte lijn weergegeven, en voor de andere grootte met de grijze lijn. Terwijl de spanning op de elektroden aan en uit gaat bewegen de deeltjes zich gemiddeld naar rechts en zullen ze zich ook wat meer verspreiden. Na genoeg oscillaties zijn de twee soorten deeltjes gescheiden en kunnen ze afzonderlijk uit het kanaal getrokken worden.

Het soort nanodeeltje dat hier gebruikt wordt kan in de toekomst toepassing krijgen in biomedische sensoren, waarbij artsen hopelijk nog sneller problemen kunnen diagnosticeren. Wellicht dat de Brownse ratchets in dat veld een nuttige toepassing vinden.

In hoofdstuk 2 hebben we beschreven dat bij het opnieuw invangen van de deeltjes in de asymmetrische vallen niet de lading van de geioniseerde mantel het belangrijkste is, maar het verschil in polarisatie tussen het polystyreen en het water. Watermoleculen reageren heel sterk op elektrische velden. Eén kant van het watermolecuul is een beetje positief geladen, en de andere kant negatief. Als alle moleculen door het elektrische veld op dezelfde manier georiënteerd worden, vormt er aan de ene kant van het polystyreen deeltje een laagje positieve lading, en aan de andere kant een laagje negatieve lading. Dit heeft invloed op hoe het
Figuur 2: (a) Tekening van de Brownse ratchet beschreven in dit proefschrift. De bovenste laag is transparant waarin zich een microkanaal bevindt met de oplossing met polystyreen deeltjes. De vingerelektroden worden gebruikt om de potentiaal te creëren in het microkanaal. (b) Weergave van de potentiaal tegen positie op drie opeenvolgende momenten in de tijd en hoe dit zorgt voor een gemiddelde verplaatsing van deeltjes naar rechts. (c) De Brownse ratchet als een manier om deeltjes van verschillende grootte te scheiden. Een mix van twee soorten deeltjes wordt links in een microkanaal geïnjecteerd. De twee lijnen reprenteren de verdeling van de deeltjes. Rechts worden de twee verdelingen gescheiden aan het kanaal onttrokken.
deeltje reageert op het elektrische veld. Door dit effect kan dit type Brownse ratchet nog beter werken als er een extra potentiaal-offset gebruikt wordt voor de elektroden, waardoor de negatieve elektrode nog iets negatiever wordt en de positieve elektrode iets minder positief. Dit is ook terug te zien in de meetresultaten, waarbij het rendement van de Brownse ratchet gelijk werd aan wat maximaal verwacht zou mogen worden op basis van de geometrie van de Brownse ratchet. Een belangrijke implicatie van deze ontdekking is dat deze ratchets niet alleen werken voor geladen deeltjes, maar ook voor ongeladen deeltjes waardoor deze ratchets meer toepassingen kunnen krijgen.

In hoofdstuk 3 hebben we laten zien dat de verbreding van de verdeling van de deeltjes sterker is dan verwacht zou worden op basis van de diffusieconstante. Dat er dus sprake is van een versterking van de effectieve diffusie komt doordat gedurende het opnieuw invangen van de deeltjes de totale deeltjesdistributie extra verbreedt. Deze versterking kan goed beschreven worden door een simpel Master equation model. Vanuit berekeningen met het Master equation model ontdekten we dat de vorm van de effectieve diffusiecurve alleen afhankelijk is van de asymmetrie van de ratchet. Het feit dat de curves van verschillende experimenten met dezelfde asymmetrie zo met elkaar te schalen zijn is te verklaren met behulp van een analytische vergelijking voor de diffusie die met name geldig is voor heel korte uittijden.

Als laatste hebben we het Master equation model gebruikt om de optimale parameters te bepalen voor het scheiden van twee groepen deeltjes van verschillende groottes. In het geval van een groot verschil in deeltjesgrootte valt er een goede resolutie te halen. De Brownse ratchet die wij gebruikten in de experimenten is erg langzaam wanneer je een scheiding probeert te bereiken die vergelijkbaar is met de nauwkeurigheid in de grootte van commercieel verkrijgbare deeltjes. Het is met het model uit te rekenen dat een verkleining van de ratchet met een factor 10, de scheidingstijd verkleint tot nochtans een half uur. Deze verbetering is voornamelijk toe te schrijven aan de kortere tijd die nodig is om de deeltjes in te vangen.

Thermo-elektrische Eigenschappen van Wanordelijke Halfgeleiders
Het thermo-elektrisch effect is een ander effect waarbij energie onttrokken kan worden uit een systeem dat uit evenwicht is. Als je een temperatuursverschil aanbrengt over een thermo-elektrische module kun je thermische energie omzetten naar elektrische energie. De verhouding tussen de gegenereerde elektrische spanning $\Delta V$ en het temperatuursverschil $\Delta T$ heet de Seebeck-coëfficiënt ($S = \Delta V / \Delta T$). Dat deze spanning ontstaat heeft te maken met hoe de ladingsschagers (elektronen of gaten) zich verspreiden over toestanden van verschillende energie. Aan de warme kant van een materiaal is meer thermische energie waardoor ladingsschagers makkelijker toegang krijgen tot toestanden met hoge energie dan aan de koude kant. Afhankelijk van de verdeling van
beschikbare toestanden, de zogenaamde toestandsdichtheid, kan daardoor ook de chemische potentiële variëren met temperatuur. Een verschil in chemische potentiaal tussen de koude en de warme kant kun je meten als een spanningsverschil.

De grootte van de Seebeck-coëfficiënt hangt af van de hoeveelheid warmte die wordt verplaatst door de mobiele ladingstragers die ook voor de elektrische geleiding zorgen. Hierdoor is de Seebeck-coëfficiënt ook goed te gebruiken als een manier om het ladingstransport in een materiaal te onderzoeken. In hoofdstukken 4 tot en met 6 is dit thermo-elektrische effect gebruikt om onderscheid te maken tussen verschillende ladingstransportmodellen die er bestaan voor wanordelijke materialen. Met behulp van de Seebeck-coëfficiënt is te bepalen welk model er van toepassing is op de onderzochte materialen.

Twee belangrijke modellen die vaak gebruikt worden voor wanordelijke halfgeleiders zijn het mobility edge model en het variable range hopping model. In een kristallijn materiaal, zoals kristallijn silicium, zijn de mobiele ladingstragers niet gelokaliseerd op één atoom, maar ze zijn gedelokaliseerd. Als een gelokaliseerde lading (of ‘toestand’) voor te stellen is als een punt dan is een gedelokaliseerde lading een veel grotere grijze wolk: de lading zit overal tegelijk een beetje! Je kunt uiteenkleden dat wanneer je wanorde in een materiaal aanbrengt door enige variatie aan te brengen in de beschikbare energiepieken er in de eerder genoemde toestandsdichtheid een staart van gelokaliseerde toestanden ontstaat met een lagere energie dan de gedelokaliseerde toestanden. Deze gedelokaliseerde toestanden kunnen werken als een val voor de ladingstragers waar ze alleen nog uitkomen door een grote hoeveelheid thermische energie te absorberen. Het mobility edge model beschrijft deze situatie. Een significant deel van de ladingstragers zit gevangen in gelokaliseerde toestanden, en alleen de ladingstragers in de gedelokaliseerde toestanden dragen bij aan het totale ladingstransport. Het ladingstransport is dan temperatuur afhankelijk omdat bij een hoge temperatuur het waarschijnlijker wordt dat een gevangen ladingstrager genoeg thermische energie kan absorberen om in een gedelokaliseerde toestand te komen.

Echter, het is ook mogelijk dat een ladingstrager zich verplaatst van de ene gelokaliseerde toestand naar een volgende gelokaliseerde toestand. Dit gebeurt dan via thermisch geactiveerd tunnelen, wat ook wel hoppen genoemd. Hoppen is de basis van het variable range hopping model. Hiervoor geldt ook dat er thermische energie nodig is om naar een toestand te gaan die hoger in energie ligt en dus is de temperatuur weer een belangrijke parameter. Ook de toestandsdichtheid is weer een erg belangrijke parameter. Als er veel gelokaliseerde toestanden zijn is de kans groter dat er een toestand in de buurt is die niet zo veel in energie verschilt. Daarnaast neemt de waarschijnlijkheid van hoppen sterk (exponentieel) af met afstand.
In hoofdstuk 4 zijn metingen van de veldeffectmobiliteit en de Seebeck-coëfficiënt in een polytriarylamine (PTAA) veldeffecttransistor gepresenteerd. Zowel een mobility edge model als een Mott-Martens model op basis van variable range hopping geven geen goede beschrijving van de temperatuursafhankelijkheid die experimenteel wordt waargenomen. Verdere analyse suggereert dat het gebruikte variable range hopping model de hoeveelheid warmte die de ladingsdragers verplaatsen overschat. Voor het mobility edge model lijkt het verschil niet anders uit te leggen dan dat het ladingstransport niet met dit model te beschrijven is. Uit een analyse van de temperatuursafhankelijkheid van de Seebeck-coëfficiënt voor de twee modellen is aangetoond dat een afname in de Seebeck-coëfficiënt met een afname van de temperatuur, zoals we dat in PTAA waargenomen hebben, in het algemeen een sterke indicatie is van variable range hopping.

In hoofdstuk 5 wordt een meting van een ongebruikelijke toename in de Seebeck-coëfficiënt in een pentaceen dunnefilmtransistor gepresenteerd. Voor zowel het mobility edge model als het variable range hopping model zou een afname van de Seebeck-coëfficiënt verwacht worden wanneer de ladingsdichtheid vergroot wordt. Bij lage temperaturen, 250 K en 200 K, zien we echter een toename van de Seebeck-coëfficiënt met een toename van de ladingsdichtheid. De toename wordt verklaard door een overgang van hopping gedomineerd transport, naar transport zoals beschreven in het mobility edge model. Omdat bij dit laatste transport meer warmte verplaatst wordt dan bij het hoppen gaan de ladingsdragers met de overgang relatief meer warmte verplaatsen en neemt daarom de Seebeck-coëfficiënt toe. Deze overgang kan verwacht worden voor organische halfgeleiders waar zowel statische energetische wanorde als dynamische wanorde belangrijk zijn. Dynamische wanorde wordt veroorzaakt door molecuulvibraties en is sterk temperatuursafhankelijk. Deze transitie konden we heel duidelijk waarnemen als een ongebruikelijke toename in de Seebeck-coëfficiënt, maar viel niet op in de metingen van de ladingsdragermobiliteit.

In hoofdstuk 6 is het ladingstransport in amorf indium-gallium-zink oxide (a-IGZO), een metaaloxide halfgeleider, onderzocht. Behalve de veldeffectmobiliteit en de Seebeck-coëfficiënt hebben we ook een scanning Kelvin probe techniek gebruikt om de toestandsdichtheid van a-IGZO te bepalen. Deze toestandsdichtheid is gebruikt bij het modelleren van het ladingstransport. Om het transport in a-IGZO te beschrijven is in de literatuur vaak een zgn. bandpercolatie-model gebruikt dat aannemt dat ladingen overwegend in gedelokaliseerde toestanden zitten. Daarnaast wordt ook het mobility edge model regelmatig gebruikt. Omdat het niet wenselijk is dat er twee modellen gebruikt worden die duidelijk verschillen in fysische interpretatie van het ladingstransport zijn wij beide modellen gaan vergelijken. Echter, beide modellen zijn niet in staat om alle experimentele resultaten te beschrijven. Door het mobility edge model uit te breiden met hopping transport in de gelokaliseerde toestanden konden de drie
experimenten wel beschreven worden. De resultaten geven aan dat het ladingstransport in a-IGZO wordt gedomineerd door hopping in plaats van bandtransport dat tot nu toe in de literatuur gebruikt werd.

De Seebeck-coëfficiënt is een bruikbare parameter gebleken in het onderzoek naar het ladingstransport in wanordelijke halfgeleiders en kan in combinatie met andere experimenten gebruikt worden om onderscheid te maken tussen verschillende ladingstransportmodellen. Hierbij is vooral de temperatuursafhankelijkheid van de Seebeck-coëfficiënt erg nuttig, aangezien de ladingsdichtheidsafhankelijkheid vaak hetzelfde is voor de verschillende modellen.

*Tijdsafhankelijke Effecten in Ladingstransport*  
Admittantiespectroscopie is een andere techniek waarmee ladingstransport in wanordelijke halfgeleiders bestudeerd kan worden. Bij admittantiespectroscopie spelen de tijdsafhankelijke effecten in het ladingstransport een rol. Bovenop een constante spanning wordt een kleine oscillatie toegevoegd waardoor er ook een kleine oscillatie in de stroom ontstaat. De admittance is gedefinieerd als de verhouding tussen de oscillatie in de stroomdichtheid en de oscillatie in de spanning. Het imaginaire deel van de admittance is gelijk aan het product van de hoekfrequentie en de differentiële capaciteit, het reële gedeelte is gelijk aan de differentiële geleiding. Admittantiespectroscopie wordt hier toegepast op een organische licht-emitterende diode (OLED). De waarde van de admittance hangt niet alleen af van de mobiliteit van de ladingsdragers, maar ook van waar de ladingsdragers zich in de OLED bevinden. Hierdoor is het een zeer geschikt experiment om ladingstransportmodellen te verifiëren, maar kan het ook heel moeilijk zijn om onverwachte resultaten te verklaren.

In de literatuur is beschreven hoe de injectiebarrières bij de elektroden van een OLED en de ingebouwde spanning in OLEDs bepaald kunnen worden vanuit de differentiële capaciteit bij lage frequenties. Wanneer de differentiële capaciteit uitgezet wordt tegen de spanning is er een piek te zien. Vanuit de positie en de hoogte van deze piek zijn de injectiebarrières en de ingebouwde spanning te berekenen. In hoofdstuk 7 wordt het effect van Gaussisch-verdeelde energetische wanorde op deze analyse bestudeerd, voor zowel OLEDs met één type ladingsdrager als OLEDs met elektronen en gaten. We laten zien dat de wanorde zowel de piekpositie als de piekhoogte beïnvloeden en hoe je met een combinatie van metingen en modelleren de injectiebarrières en de ingebouwde spanning bepaalt. Als voorbeeld nemen we blauw-emitterende polyfluoreen-triarylamine lagen die tussen twee elektroden liggen, welke ook wel sandwich-type devices genoemd worden. Door het elektrodemateriaal te variëren zijn devices met alleen gatentransport en devices met zowel elektronen- als gatentransport gemaakt en onderzocht.

In materialen met een hoge mate van wanorde kan de tijdsafhankelijkheid van het ladingstransport erg sterk zijn. Wanneer ladingsdragers in een materiaal
geïnjecteerd worden met een hoge energie duurt het daarom lang voordat de ladingen met de energie hebben zoals die verwacht wordt in thermisch evenwicht. Dit proces wordt energierelaxatie genoemd. Het *multiple trapping and release* model kan de relaxatie goed beschrijven. Bij dit model, vergelijkbaar met het *mobility edge* model, zijn alleen de ladingen op een zeker transport-niveau mobiel en werken de overige gelokaliseerde toestanden als vallen voor de ladingen. Waar dit transportniveau precies ligt en met welke frequentie de ladingen naar het transport niveau kunnen hoppen is voor een willekeurig materiaal niet *a priori* bekend. In hoofdstuk 8 worden voor een Gaussische toestandsdichtheid beide parameters afgeleid door gebruik te maken van parameters die gelijkstroomexperimenten beschrijven in het raamwerk van het *extended Gaussian disorder* model. Deze aanpak is gevalideerd met *Monte Carlo* modellering. Het model laat zien dat we succesvol de lage-frequentie differentiële capaciteit kunnen voorspellen van *sandwich-type devices* van polyfluoreen-triarylamine copolymeren.

**Conclusie**

We hebben verschillende experimenten beschreven waarbij transport plaatsvindt van geladen deeltjes in fluctuerende en wanordelijke energielandschappen. We hebben de werking van een aan/uit ratchet voor deeltjes in oplossing opgehelderd, we hebben de mogelijkheden bestudeerd om het te gebruiken om nanodeeltjes op grootte te scheiden en bekeken hoe de ratchet verder geoptimaliseerd kan worden. We hebben het thermo-elektrisch effect gebruikt om het type ladingstransport in wanordelijk halfgeleiders te bepalen, en onderzocht hoe de temperatuurafhankelijkheid gerelateerd is aan de verschillende ladingstransportmodellen. We zijn geëindigd met admittantiespectroscopie om het effect van wanorde op de differentiële capaciteit te onderzoeken en de energierelaxatie van ladingen te bestuderen en te beschrijven.

**Referenties**

Appendix A: Additional Measurements to Check Ratchet Behavior

Along the finger electrodes large average movements will be prevented by the presence of the micro channel. In fact Figs. A1(a) and (b) show the absence of even small traces of switching-related lateral motion for both forward and reverse drive.

A second check for true ratchet behavior is demonstrating zero net motion by employment of a symmetric drive. The most obvious realization of such a scheme is by setting equal but anti-phased amplitudes on both electrodes which indeed yielded zero particle current (not shown) since there is no time given for diffusion. A more complex symmetric driving scheme is reached by alternating between forward and reverse driving. This leads to the average movement depicted in Fig. 2.2(a) followed by that of Fig. 2.2(b), also resulting in a negligible average movement over one complete cycle.

Figure A1: Average position during one driving cycle determined from approximately 200 particles (500 nm), (a) and (b) show the movement parallel to the finger electrodes of forward and reverse drive respectively.
Appendix B: Electric Field Calculations

Calculations of the electric field and potential are performed using the COMSOL Multiphysics 3.4 Package. We used the Electrostatics Application Mode of the AC/DC module. This software performs a finite element analyses and thus solves the problem numerically.

We calculated the field for one asymmetric ratchet unit and put periodic boundary conditions to the left- and right-hand sides. Below the substrate the boundary value was set to 0 V (grounded) and at 15 \mu m height the boundary was set as well at 0 V (grounded), which represents the boundary value at infinity.

As explained in the main text, we calculate the fields in steady state and can therefore assume local equilibrium. The charge density was set according to the Boltzmann equation

\[
\rho = e N_A 10^3 \sum_i z_i M_i \exp \left( -\frac{z_i e V}{k_B T} \right),
\]

with \( N_A \) being Avogadro’s number, \( z_i \) the valency of the ion species and \( M_i \) its molarity in mol dm\(^{-3}\).

For the 1.5 \times 10^{-5} M PBS solution this resulted in a charge density of

\[
\rho = e N_A 10^3 \left( 1.62 \times 10^{-5} \exp \left( -\frac{e V}{k_B T} \right) - 1.44 \times 10^{-5} \exp \left( \frac{2e V}{k_B T} \right) - 2 \times 7.2 \times 10^{-7} \exp \left( \frac{2e V}{k_B T} \right) \right).
\]

The surface charge on the SiO\(_2\) surface can be determined using the Grahame equation, which for a monovalent solution has the form\(^1\)

\[
\sigma_{\text{surface}} = \sqrt{8\varepsilon_0 \varepsilon_r n_0 k_B T \sinh \left( \frac{e V_0}{2k_B T} \right)},
\]

with \( n_0 \) the ion concentration and \( V_0 \) the surface potential. This equation is derived by assuming that the surface charge is equal to, but opposite in sign of the total charge in the double layer.
Not assuming a monovalent solution gives a generalized Grahame equation equal to

\[
\sigma_{\text{surface}} = \sqrt{4\varepsilon_0 \varepsilon_r k_B T \sum_i n_{0i} \exp\left(\frac{-e z_i V_0}{k_B T}\right) - 1},
\]  

which results in a surface charge density equal to \(-5.4 \times 10^{-5} \text{ C m}^{-2}\) for SiO\(_2\), that is used for the calculations in Fig. 2.4.

References

Appendix C: Sphere-Surface Distance

The height at which the particles float is important if the exact asymmetry of the ratchet is to be determined. Figs. 2.4 (c) and (d) show that the field minima change position with the distance to the device surface.

The distribution of particles as a function of distance to the SiO₂ surface can be determined from Derjaguin-Landau-Verwey-Overbeek (DLVO) theory.²³ First we calculate the interaction energy of the Van der Waals force, the electrostatic and double layer forces and gravitational energy. The total interaction energy is given by the sum of these energies. In Fig. C1 we show the total interaction energy as a function of the distance to the SiO₂ surface. The most likely position for particles is at the energy minimum. By using units $k_B T$ on the energy axis, one can instantly make an estimate of the typical spread of particles.

A relatively short and clearly written explanation of the theory can be found in Ref. 3.

The Van der Waals interaction energy for a sphere close to a surface can be written as

$$ E_{\text{VDW}} = -AR / 6x, \quad (C1) $$

with $R$ being the radius of the sphere, $x$ the distance to the surface and $A$ the Hamaker constant. The typical range for the Hamaker constant in a liquid medium is $0.5–1.5 \times 10^{-20}$ J (Ref. 3), we therefore estimated it at $10^{-20}$ J.

The electrostatic and double layer interactions for a sphere close to a surface can be described as³

$$ E_{\text{DL}} = RZ \exp(-\kappa x), \quad (C2) $$

with

$$ \kappa^{-1} = \sqrt{\frac{\varepsilon_0 \varepsilon_r k_B T}{2e^2 n_0}} \quad (C3) $$

the Debye length for a monovalent solution and $n_0$ the ion concentration at 0 V. The interaction coefficient $Z$ is equal to
\[ Z = 64\pi \varepsilon_0 \varepsilon_r (k_B T / e)^2 \tanh \left( \frac{eV_{\text{surf}}}{4k_B T} \right) \tanh \left( \frac{eV_{\text{sphere}}}{4k_B T} \right), \]  

(C4)

with \( V_{\text{surf}} \) and \( V_{\text{sphere}} \) being the SiO\(_2\) surface potential and the sphere surface potential, respectively.

The surface potential of the sphere, determined by the supplier, is equal to approximately \(-50\) mV at \( p_H \) 7.4. The SiO\(_2\) surface potential we estimate at \(-55 \pm 10\) mV (Fig. 9 in Ref. 4).

Figure C1: Interaction energy vs. distance to a SiO\(_2\) surface for a 500 nm polystyrene particle functionalized with carboxylic acid calculated using DLVO-theory. Energy minimum is found at 800 nm from the surface. The horizontal dashed line is 1\( k_B T \) above the energy minimum.

Fig. C1 shows an energy minimum around 800 nm. The region within one \( k_B T \) of the energy minimum ranges from 600 nm to 6.5 \( \mu m \). The slope in the interaction energy above 1 \( \mu m \) is mainly due to the gravitation force. The uncertainty in the SiO\(_2\) surface potential of 10 mV does not have a significant influence on these values. A \( 0.5 \times 10^{-20} \) J increase (decrease) in the Hamaker constant only shifts the outer 1 \( k_B T \) boundary 0.5 \( \mu m \) inward (outward).

Comparing this width to the electric field calculations of Figs. 2.4(c) and (d), one can see that it is very difficult to computationally determine the asymmetry \( \alpha \), as the particles float in a region of differing asymmetry.

References

Appendix D: Average Displacement Calculation

The average displacement calculation in Fig. 2.3(b) is performed numerically. The diffusion constant of the polystyrene spheres is calculated using the Einstein-Stokes relation

\[ D = \frac{k_B T}{6\pi \eta r}, \quad (D1) \]

in which \( \eta \) is the viscosity and \( r \) is the particle radius. For a 500 nm sphere in water at room temperature the diffusion constant is \( \approx 9.8 \times 10^{-13} \text{ m}^2 \text{ s}^{-1} \) and for a 300 nm sphere it is \( \approx 1.6 \times 10^{-12} \text{ m}^2 \text{ s}^{-1} \). Without loss of generality, the displacement upon switching the ratchet potential on is calculated for particles originating from a single trap that spread over four ratchet trap units, as displayed in Fig. D1 –taking more traps into account did not significantly alter the results due to the limited diffusion distances in the off times considered. Even for an off time of 10 s still 98.6% of all particles are taken into account. For each time \( t \), the width \( \sigma = \sqrt{2 D t} \) of the (Gaussian) distribution is calculated. When switching the potential on the particles are trapped in the energetically nearest trap, which is not necessarily the spatially nearest trap. With the Gaussian distribution \( f(x, t_{\text{off}}) \) being a function of position, the average displacement in one cycle is calculated by integrating over space the product of the particle probability distribution and the resulting net displacement \( X(x) = x - x_0 \) upon switching the potential on again,

\[ \int f(x, t_{\text{off}}) X(x) \, dx. \quad (D2) \]

Figure D1: Ratchet potential \( V \) as a function of position \( x \) displayed by the lower line. The upper line represents a Gaussian distribution of particles at time \( t \) originating from the trap at position \( x_0 \).
Appendix E: Supporting Figures on the Unusual Seebeck Behavior Indicating a Hopping to Bandlike Transport Transition in Pentacene

In this appendix the supporting material for Chapter 5 is shown. For the hybrid model the full figures of both the Seebeck coefficients associated with transport at the mobility edge, and the Seebeck coefficients associated with the transport at the transport level $E^*$ are presented. In the second section the mobility and Seebeck coefficient calculations are shown from both the band-only (i.e., ME) model analysis and the hopping-only (i.e., VRH) model analysis. Finally, some calculated curves of the effective band mobility in the hybrid model are discussed in relation to literature on single crystal organic semiconductors.

$S_{ME}$ and $S_{VRH}$ in the Hybrid Model

Figs. 5.2 and 5.3 show the calculation of the mobility and the corresponding Seebeck coefficients for the hybrid model. In addition, in Fig. 5.4(b) the values of $S_{ME}$ and $S_{VRH}$ are shown separately for $T = 200$ K.

Figs. E1 and E2 show $S_{ME}$ and $S_{VRH}$ for all four temperatures using the same fitting parameters as used in Chapter 5. Due to the temperature dependence of the transport level $E^*$, the $S_{VRH}$ hardly shows temperature dependence. In general this model may either show a decreasing, a constant or an increasing Seebeck coefficient with temperature, depending on the parameters used. However, within the ME model, a strong inverse temperature dependence is generally present due to the temperature independence of the mobility edge, $E_C$. For a complete analysis within the framework of either the ME or VRH model alone, other fitting parameters than in the hybrid model should be used. This is shown in the next section.
Band-only or Hopping-only Analysis

It has been explained in Chapter 5 that a band-only (i.e., ME) or a hopping only (i.e., VRH) analysis cannot explain the increasing Seebeck coefficient with increasing gate bias at $T = 200$ K and $250$ K. Such analyses are shown in Figs. E3 and E4 for the ME model and in Figs. E5 and E6 for the VRH model. The calculations do match quite well at high temperatures, but for low temperatures...
the calculations showing the common decrease in the Seebeck coefficient with increasing gate bias.

Figure E3: Mobility vs. gate bias measurements (symbols) and calculations (lines) for an ME analysis.

Figure E4: Seebeck coefficient measurements (symbols) and calculations (lines) for the ME analysis in Fig. E3.
**Effective Band Mobility**

The effective mobility $\mu_{\text{eff}}$ in a mobility edge model is determined by the product of the mobility and the fraction of charge carriers above the mobility edge. It is
expected that this part of the charge transport in the hybrid model is similar to the transport in single crystal organic field effect transistors (OFETs), albeit with a more pronounced tail of localized states. To compare the bandlike transport used in the hybrid model with single crystal results we plotted $\mu_{\text{free}} \times n_{\text{free}}$ vs. temperature for different gate bias in Fig. E7.

At high gate bias the temperature dependence curve of the effective mobility shows indeed very similar behavior as seen by Minder et al.\textsuperscript{1} in PDIF-CN\textsubscript{2} single crystal OFETs and by Podzorov et al.\textsuperscript{2} in rubrene single crystal OFETs. This behavior was explained by the presence of traps. The increase (with increasing temperature) at low temperature is explained by the increase in thermal activation over the mobility edge, the subsequent decrease at higher temperature by the temperature dependence of the mobility $\mu_{\text{free}}$. In the hypothetical situation that VRH would not be present in this system, one would measure a temperature dependence $\mu_{\text{eff}} \sim T^{-2.5}$ at room temperature for a gate bias of -50 V. The presence of trap states results in a much weaker temperature dependence of $\mu_{\text{eff}}$ than that of $\mu_{\text{free}}$. At somewhat lower gate voltage the decrease with increasing temperature reduces and at some point disappears. For the $\mu_{\text{free}} \times n_{\text{free}}$ vs. gate bias curves plotted in Fig. E8 this results in curves of different temperature curves crossing each other above $-20$ V. Due to the contribution of VRH we do not measure this in our pentacene OFETs, but similar behavior was measured by Podzorov et al.\textsuperscript{2} in rubrene and by Xie et al. in TMTSF.\textsuperscript{3}

Figure E7: Calculations of the product $\mu_{\text{free}} \times n_{\text{free}}$ vs. temperature for different gate bias using the fitting parameters of the hybrid model described in Chapter 5.
Figure E8: Calculations of the product $\mu_{\text{free}} \times n_{\text{free}}$ vs. gate bias for different temperatures using the fitting parameters of the hybrid model described in Chapter 5.

References

List of Publications


Submitted Manuscript

About the author

Wijnand Germs was born on November 2nd 1981 in Groningen, The Netherlands. With three brothers and one sister he was the youngest in a family of five children. He grew up in one of the outskirts of Groningen and spent a lot of his free time at the boy scouts and playing soccer with his friends.

In 2000 he obtained his pre-university secondary education diploma at the Wessel Gansfort College in Groningen, after which he started a study in psychology at the University of Groningen. Although psychology intrigued him, it could not keep his attention as a fulltime study and Wijnand decided to make a drastic switch to physics. However, first he would follow his dream to travel to Australia and New Zealand.

After returning home in 2002, he started his bachelor’s study in “Physics and Astronomy” at Utrecht University. Here he met Dorien, a fellow student, who became the love of his life. Satisfying his desire for another foreign adventure, he followed classes for one semester at the Universidad Complutense in Madrid as an Erasmus exchange student in 2004. In 2005 he was appointed as student member in the board of the newly formed Faculty of Science in Utrecht. After six departments were united in one faculty, he succeeded in creating cohesion between students involved in the co-determination and setting up of the organizational structure required to represent all students of the faculty.

After obtaining his bachelor’s degree in 2006, he started in the master’s program “Nanomaterials: Chemistry and Physics” at Utrecht University. He graduated with a master thesis on transient charge transport in organic light emitting diodes, written during an internship at Philips Research in Eindhoven, under supervision of prof. dr. R. Coehoorn.

In August 2008 he started a PhD project at the Eindhoven University of Technology in the group “Molecular Materials and Nanosystems” of prof. dr. ir. R. A. J. Janssen, under the daily supervision of his co-promotor dr. ir. M. Kemerink. In his PhD project electrical on/off ratchets for suspended particles and charge transport in disordered semiconductors were studied, the results of which are presented in this dissertation. During this time the work on transient charge transport in organic light emitting diodes was also continued and is presented in this dissertation as well. The results have been published in peer-reviewed journals and have been presented at international conferences.

Wijnand and Dorien have two sons, Bas and Erik. At present they live in a 19th century farm in Rhee, in the north of the Netherlands.
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