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MODELS TO MEASURE MOBILITIES
BY TIME-OF-FLIGHT

DISSERTATION

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

By

Xiaoming Zou, M.S, MAS

*****

The Ohio State University
2002

Dissertation Committee:
Prof. Arthur J. Epstein, Advisor
Prof. Fernand A. Hayot
Prof. Linn Van Woerkom
Prof. Richard J. Furnstahl

Approved by

[Signature]
ABSTRACT

In this thesis I have developed two models to interpret Time-Of-Flight photocurrent in dispersive semiconducting materials. The two models are based on a dynamic equation derived based on electrodynamic principles.

Our first model says that the differential current displays singularity at the transit time. This model is based on the solution of the dynamic equation for a trap-free system. Although the hole transporting material TPD gives a good example of this model, our studies of other materials show that the singularity is smoothed out in dispersive transport.

Our second model is to solve the dynamic equation directly. The solution requires an expression for the average drift current in the sample. I have established a diffusion equation for the drift charges based on random walk model, and found that the velocity distribution can be well approximated by a Gaussian.

Simulations show that the second model can replicate all types of photocurrent observed in TOF experiments. And our results of TPD and a hole transporting polymer PVK agree very well with the second model. It is promising in studying the transporting properties of other dispersive semiconducting materials.
To my parent
Acknowledgement

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Xiaoming Zou, 7/24/02.
VITA

June 12, 1970 ..................................................Born – ChongQing, China

1992 ..............................................................B.S Chemistry, Beijing University, China

1995 ..............................................................M.S Chemistry, Beijing University, China

1996 – present ................................................Graduate Teaching and Research
Associate, The Ohio State University

2001 ..............................................................MAS Applied Statistics, The Ohio State
University

PUBLICATIONS

1. “New methods to measure carrier drifting mobility in dispersive organic and
polymer semiconductors”, X.M. Zou and A.J. Epstein, (Bulletin of The American
Physical Society, Vol.46, No.1, p861, S9-5, 2001)

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oligomers”, X.M. Zou, D.K. Wang, and A.J. Epstein, (Bulletin of The American

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FIELDS OF STUDY

Major Field: Physics
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Symbols and Nomenclature

For consistency with the literature, we have used the chemical names, symbols, and units most commonly used in research community and textbooks. A partial description of the more frequently used symbols is given below.

\[ \begin{align*} 
\alpha & \quad \text{Disorder parameter} \\
A & \quad \text{Sample area} \\
C & \quad \text{Capacitance, in F} \\
D & \quad \text{Diffusion coefficient, in cm}^2/\text{s} \\
E & \quad \text{Electric field, in V/cm} \\
\varepsilon & \quad \text{Dielectric constant} \\
\varepsilon_0 & \quad \text{Permittivity of free space, } 8.85 \times 10^{-14} \, \text{F/cm} \\
\varepsilon_r & \quad \text{Permittivity of sample} \\
f(x,t) & \quad \text{Distribution function} \\
J & \quad \text{Current Density, in amp/cm}^2 \\
& \quad \text{Probability flux} \\
k_B & \quad \text{Boltzmann's constant, } 1.38 \times 10^{-23} \, \text{J/K} \\
\delta & \quad \text{Photo absorption depth} \\
T & \quad \text{Temperature, in K or } \, ^\circ \text{C} \\
t_T & \quad \text{Transit time} \\
t_e & \quad \text{Light pulse duration} \\
\tau & \quad \text{Circuit reaction time} \\
\tau_0 & \quad \text{Dielectric relaxation time} \\
d & \quad \text{Sample thickness} \\
R & \quad \text{Resistance of resistor} \\
V(t) & \quad \text{Potential as a function of time} 
\end{align*} \]
$\mu$ Mobility, in $\text{cm}^2/\text{Vs}$

$q_0$ Amount of charge, in pC

$\rho$ Dark resistivity

$i(t)$ Photocurrent, $\mu$A

$i(t)'$ Differential current, in $\mu$A/$\mu$s

$\rho(x,t)$ Line charge density, in pC/m

$v$ Velocity, in m/s

$\sigma$ Standard deviation

$p$ Probability
CHAPTER 1

INTRODUCTION

1.1 Mobility, its Properties and Measurement

1.1.1 Mobility

Carrier motion properties are important in the applications of many organic and polymer semiconducting materials. For example, in xerography, electrostatic charges are applied to a surface of the photoreceptor film (polymer such as polyvinyl carbazole (PVK) doped with trinitrofluorenone (TNF), or inorganic such as amorphous Se). Charge pairs are then photo created in the photoreceptor film. A fundamental requirement for the photoreceptor is that charges can transit the medium in a time that is short compared to the time between the exposure and image development steps. Also, in organic light emitting diode (OLED), light is produced after charges transport through some organic materials and combine with other charges with opposite signs. The voltage for operation depends on the speed of response. More, in field effect transistors (FET), the reaction time also depends on the speed the charges transport to the gate. Finally, in photovoltaics, the maximum power of the photocell is directly proportional to the photocurrent, which is in turn proportional to the charge drifting speed. For these reasons, charge transport phenomena in these technologies are of considerable importance. I will give more examples of the materials applied in these fields at the end of this chapter.
A quantity called mobility, \( \mu \), of a carrier, as being the ratio of the drift velocity it achieves in a field \( E : v = \mu E \), is used to describe the carrier motion in semiconducting solids. There are two extreme types of carrier motion in solids: In one, the carriers move as a highly delocalized plane wave in a broad carrier band with a relatively large mean free path. Semiconducting crystalline inorganic materials, such as Si, Se and Ge, belong to this category, and they usually have high mobility (\( \mu >> 1 \text{ cm}^2/\text{V} \text{s} \)). At the other extreme, the carrier is highly localized and moves by hopping from site to site, being trapped or scattered at virtually every step. Semiconducting organic and polymer materials such as poly (p-phenylenevinylene) (PPV) usually belong to this category, and are characterized by their low mobility (\( \mu << 1 \text{ cm}^2/\text{V} \text{s} \)). Of course, there are a lot of materials falling in an intermediate category in which \( \mu \approx 10^{-3} \sim 1 \text{ cm}^2/\text{V} \text{s} \) and hopping motion is involved. This work is particularly interested in those organic and polymer semiconducting materials because of their potential applications in xerography, LEDs, FET and photovoltaics.

1.1.2 Properties of Mobility

In a crystal, defects formed by vacancies, dislocations and grain boundaries can scatter charge motions. In disordered organic and polymer semiconducting solids, charges are “trapped” at lower energy sites, and moves through hopping: either phonon-assisted or tunneling. The phonon-carrier interaction is highly field and temperature sensitive. In this part I will discuss several simple models relating mobility with field and temperature.
First, the effective mobility changes in the presence of traps. An example of a simple trap distribution is shown in Fig. 1.1. Let $\mu_0$ and $n_0$ be the mobility and carrier density in the conduction band. $N$, carriers are trapped, with trap depth $E_t$. Then the situation can be divided into two cases: shallow traps and deep traps.

First let us consider shallow traps[1], which are characterized by the condition $t_r << t_r$, with $t_r$ the lifetime of a carrier in a trap. During the transit, the average mobility $\mu$ is related to the trap-free value $\mu_0$ by,

$$n_0\mu_0 = (n_0 + n_t)\mu$$

with $n_t$, the density of trapped charge. At thermal equilibrium, we have,

$$\frac{n_t}{n_c} = \frac{N_t}{N_c} \exp\left(\frac{E_t}{kT}\right)$$

Fig 1.1 Effects of deep and shallow traps (redraw from [1]).
with \( N_t \) and \( N_c \) the total trap density (at \( E_t \)) and density of conduction states (at the band edge), respectively. Equations (1.1) and (1.2) lead to the effective mobility,

\[
\mu = \mu_0 \left[ 1 + \frac{N_t}{N_c} \exp\left( \frac{E_t}{kT} \right) \right]^{-1}
\]  

(1.3)

At sufficiently high temperature, \( \mu = \mu_0 \). At low temperatures, the exponential term in (1.3) dominates and,

\[
\mu = \mu_0 \exp\left( - \frac{E_t}{kT} \right)
\]  

(1.4)

The transition between the two types of transport has been observed in experiment [2].

The second group of traps is “deep” trap defined by the condition: \( t_r \gg t_T \). With the existence of deep traps, some of the carriers will be delayed and we would expect a more complicated dependence of mobility on temperature. If the shallow and deep traps dominate, all the carriers are trapped at least once or even the carriers are transported from trap to trap directly, we encounter the so-called dispersive transport which has been studied for several decades[3-5].

A simple model for field dependence is the so-called Poole-Frenkel[6] effect, which describes the reduction in ionization energy of a carrier in a Coulomb potential by an applied field. The effect of the field is through lowering of the potential barrier as illustrated in Fig.1.2 for a one-dimensional case. The electron potential in a field \( E \) is,

\[
eEx - \frac{e^2}{4\pi\varepsilon_0|\varepsilon|}
\]  

(1.5)
By maximizing the potential with $x > 0$, one can obtain that the barrier is lowered by $\beta E^{1/2}$ with \( \beta = 2e^{3/2} / (4\pi \varepsilon_0 \varepsilon_r)^{1/2} \). And so the effect of filed and temperature on conductivity is of the form,

$$\mu(E, T) = \mu_0 \exp(\beta E^{1/2} / k_B T)$$

(1.6)

This is sometimes referred as the Poole-Frenkel law[7-9]. While field dependencies predicted by this relation are frequently observed, experimental values of $\beta$ are very different from theoretical values.

![Potential energy of an electron in a Coulomb center under the influence of an electric field $E$](image)

Fig. 1.2 Potential energy of an electron in a Coulomb center under the influence of an electric field $E$ (from [6]).

A third model is formalized by Bässler[10]. It considers the distributions of hopping site energies and intersite distances. A fundamental assumption of the Bässler formalism is that upon abandoning long-range order, the transport is through the localized states with energy and intersite distance in Gaussian distribution. It has been shown[10] that a
carrier created within a Gaussian density-of-states manifold will relax to mean energy
\[ <\varepsilon>_{\infty} = -\frac{\sigma^2}{k_B T}, \]
with \( <\varepsilon>_{\infty} \) the average energy as \( t \to \infty \), and \( \sigma \) the standard
deviation of the Gaussian distribution. The temperature dependence associated with
\( <\varepsilon>_{\infty} \) then suggests that the activation energy of low-field mobility must decrease with
temperature as,
\[ \mu(T) = \mu_0 \exp \left[-\left(\frac{T_0}{T}\right)^2\right] \tag{1.7} \]
where \( T_0 \) the characteristic temperature proportional to the width of the distribution. The
field dependence of the mobility arises from the fact that a carrier can reach more
acceptor or donor sites without thermal activation in the presence of a field than it can in
the absence of a field. A first order analysis[11] gives,
\[ \mu(T, E) = \mu_0 \exp \left[-\left(\frac{T_0}{T}\right)^2\right] \exp \left(\frac{E}{E_0}\right) \tag{1.8} \]
The important predictions of this model are the field and temperature dependencies of the
mobility. The formalism also provides an explanation for a mobility that decreases with
increasing field[12]. Results by Schein et al. [13] and Hirao et al. [14] support Bssler
formalism, but studies by Emin[15] and Dunlap[16] have seriously challenged Bssler
model.

1.1.3 Mobility Measurement

For high mobility materials, the Hall effect provides a good method to measure the
mobilities. But the measurement and interpretation of the Hall effect in low mobility
materials become very difficult[17]. Several methods are used to measure the charge

\[ M(T) = \int_{0}^{1} i_0 \exp \left[-\left(\frac{T_0}{T}\right)^2\right] \exp \left(\frac{E}{E_0}\right) \]
motion in low mobility materials. They include methods based on space-charge-limited current (SCLC) measurement, field effect transistor (FET) measurement, and Time-Of-Flight (TOF) measurement.

The theory of space-charge-limited current is based on the fact that any current flow through an insulator under the action of an applied field will be analogous to that of a vacuum diode. If electrons are injected into an insulator, they will travel from the injecting electrode into the conduction band of the insulator and form a space-charge similar to a vacuum diode[18]. After neglecting the contribution of diffusion to current, one can derive the following relation for a trap-free insulator,

\[ J = \frac{9}{8} \epsilon_0 \epsilon \mu \frac{V^2}{d^2} \]  

(1.9)

with \( J \) the current density, \( \epsilon_0 \) the permittivity of the vacuum, \( \epsilon \) the permittivity of the sample, \( \mu \) the mobility, \( V \) the applied voltage and \( d \) the sample thickness. (1.9) is derived for one type of carrier injected from one electrode. For injection of both carriers, the current is a more complicated function of voltage and the hole and electron mobilities[18]. By measuring current dependence on voltage, one can obtain mobility by using relation (1.9). But if traps exist, an unknown factor reflecting the trapping effect has to be added to the right side of equation (1.9)[18]. This has largely limited the application of SCLC to study the transport properties of organic and polymer semiconducting materials.

Both FET and TOF are based on the same idea, i.e., to measure the transit time directly. If the measured transit time is \( t_r \), then the average velocity \( v = d / t_r \). And using \( E = V / d \), one can derive the following relation,
The charges in FET are produced by the field effect at the gate electrode. Thus using FET to measure charge mobility is only limited to those materials that have pure field effect.

The drifting charges in TOF are produced using some external sources, among which laser excitation is the most widely used. But before laser was introduced, electric pulse was the main excitation source. In principle, TOF can be used to study any material that is of interest, and its interpretation is pretty straightforward. TOF has become the standard method to measure transport phenomena in semiconducting solids.

In addition to the above techniques, other methods have been described to study charge transport properties. Thermally stimulated current methods have been described by Bässler[10], Hoshino[19], Glowacki[20] and other studies. Isothermal current decay techniques have been reported by Bässler et al.[21] and Samoc et al.[22]. These methods are generally more complex than conventional TOF, and have not been widely used for mobility measurements.

### 1.2 Time-Of-Flight

TOF was first described by Haynes and Shockley[23] and Lawrence and Gibson[24], Kepler[25] and LeBlanc[26] first applied TOF to study organic solids, and Vannikov[27] was the first to measure mobilities of polymers by this method. TOF was mainly used to study transport properties of high mobility inorganic solids at early times. As interest grew in the applications of polymers to xerography in 1970s and of organic and polymers in OLED and FET devices in 1990s, TOF are more often employed to measure the mobilities of semiconducting organic and polymers[28-30]. During the past several
decades, TOF measurements have become the conventional method for studies of transport phenomena in organic and polymers.

The schematic diagram of TOF is illustrated in Fig 1.3 [31]. A sample with thickness $d$ is sandwiched between two planar metal electrodes. The top electrode is semitransparent and should be a non-injecting or blocking electrode for the carrier transported across the sample. The two electrodes are connected to an external circuit via a resistor with resistance $R$ and a battery with potential $V$. The carriers are then generated with a short flash of laser pulse absorbed in a thickness $\delta$, with $\delta \ll d$. The light pulse duration $t_r$ should be short, i.e., $t_r \ll t_T$, with $t_T$ the transit time. The light exposure creates bound electron-hole pairs near one of the electrodes. Under the influence of the

![Diagram of TOF setup](image)

Fig 1.3 A typical experiment setup for measuring mobility using TOF (Redrawn after [31]).
applied electric field, a fraction of the pairs separate and then drift in a sheet across the sample, inducing a time dependent photocurrent in the external circuit. The transient photocurrent is recorded with a high-resolution digital oscilloscope. By switching the polarity of the battery, one can measure either hole or electron photocurrent.

The first condition for TOF is that the amount of charge generated should be small enough so that space-charge effects do not change the internal field strength significantly. This will be true as long as the injected charge \( q_0 \) satisfies,

\[
q_0 \ll CV
\]

with \( C \) the sample capacitance. The shape of the leading edge of the drifting current can broaden as a result of the mutual repulsion of the carriers within the generation volume. It has been shown[32] that the error in transit time due to this mutual repulsion is \( \Delta t / t_T = q_0 / CV \). But on the other hand, \( q_0 \) should be large enough to give unequivocal signals.

The second condition for conventional TOF is that the circuit reaction time \( \tau = RC \) is much smaller compared with the average drifting time of the charges. A small value of \( \tau \) can be realized by choosing small \( R \) or \( C \). But \( R \) has some lower bound so that the oscilloscope has enough precision. As capacitance is proportional to sample area and inversely proportional to sample thickness, small \( C \) can be realized with higher thickness and smaller cross section.

A third condition requires that the dielectric relaxation time \( \tau_0 = \rho \varepsilon \varepsilon_0 \) be long compared to the transit time, with \( \rho \) the dark resistivity. This is the time required for the insulator to restore itself to the state of neutrality after a small change in the carrier
population. The intrinsic concentration of carriers is very small for materials with small
dielectric relaxation time[32]. Organic and polymeric solids have dark resistivities such
that this condition for TOF is readily satisfied in most materials of potential interest for
xerography, field effect transistor and LEDs.

In TOF measurements, charge injection can be accomplished by direct
photoexcitation or by a photoemitting electrode. While direct photoexcitation is a simpler
technique, it has two fundamental limitations. First, the technique is limited to
photoconductors. Second, the TOF technique is usually based on the assumption that the
charge is injected at one surface. This requires that the light for exposures be very
strongly absorbed near an electrode. For these reasons, charge injection from a
photoemitting electrode has become a standard technique. The more common electrodes
are α-Se, α-As₂Se₃, or the phthalocyanines. In our experiments we evaporate a thin layer
of α-Se between the semitransparent electrode and sample as a photoemitting electrode.
A characteristic of this type of photocurrent is that it does not show a plateau region but
increases continuously with time and then decreases sharply. It has been claimed[33] that
this phenomena is due to delayed charge injection, i.e. all charges are trapped before they
started to drift. But we will show in chapter 4 that this is actually due to large circuit
reaction time.

During the past several decades, Time-Of-Flight photocurrent measurements have
become the conventional method for studies of transport phenomena in doped polymers.
The fundamental limitation is that it is difficult to measure mobilities in the presence of
trapping.
1.3 Experiments

1.3.1 Material Preparation

The semitransparent electrode in our experiment is ITO (Indium-Tin-Oxide), a layer pre-deposited on a glass substrate. The sample with thickness from several hundred nanometers to several microns is then deposited by heat evaporation (for materials with small organic molecules) or coated by spin coating (for polymers). A thin layer (10–30nm) of α-Se is deposited by vacuum deposition before or after sample deposition, depending on the desired configuration. Finally, a metal (usually Al) is deposited as the second electrode by vacuum evaporation. The device has a configuration as ITO/Se/Sample/Al or ITO/Sample/Se/Al. The thickness of the sample is measured with an Alpha-Step 500 Surface Profiler. Fig. 1.4 is an example using Alpha-step to measure sample thickness.

![Profiler thickness measurement of TPD](image)

Fig. 1.4. Profiler thickness measurement of TPD. Upper level is the surface of sample, and lower level corresponds to substrate surface. The difference (~2.56μm) is the thickness of the sample.
Sample evaporation is accomplished in a chamber with low vacuum \((<10^{-5}\text{torr}, \text{by diffusion pump})\). The roughness and thickness of the sample can be controlled by evaporation rate and time. The thickness of the sample can be read on a crystal monitor calibrated with the Alpha-step profiler.

For spin coating, one first dissolves the material into some organic solvent, and then spin coats the solution on the ITO glass, a film is then formed after the solvent is evaporated, and finally the film is dried in a vacuum oven at temperature 50-80 °C for 2-3 hours. The thickness of the sample film is controlled by choosing the spinning speed (usually several thousand rpm) and the solution concentration (several tens mg/ml). One disadvantage of spin coating is that the film is not uniform, because it’s difficult to totally remove the solvent from the film. Another disadvantage is that it’s very difficult to make films thicker than a micron, and the quality of film becomes worse as it gets thicker. Because polymer solids are not possible to be evaporated, spin coating is usually the best choice.

1.3.2 TOF Measurement

The sample is connected through the configuration as described in Fig.1.3. Then a pulsed laser is turned on to produce charges in the thin Se layer. Under the field supplied by the battery, one sign of charges drifts to the other electrode, and the other sign of charges moves through the circuit. A digital oscilloscope is used to measure the voltage change of the resistor in the circuit.

In our experiment, we use a Continuum Surelite I pulsed laser. We use the wavelength 532 nm so that absorption is occurred only in Se layer. The materials

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investigated in this study (see the end of this chapter) do not have substantial photo absorption at this wavelength[65-67], but α-Se does[93]. The pulse duration is about 10ns, much shorter than the charge drifting times (µs). And the pulse frequency is 15 Hz such that the second pulse will not disturb the charges produced by the first pulse. The power of the laser is several milliwatts. But for some strong absorption materials we use glass filters to decrease the power to microwatts to control the amount of charges produced by the laser.

The electric field is adjusted through the battery in Fig.1.3. We have used HP 6218A power supply to replace the battery, with range from zero to 50 volts. If higher voltage is needed, we use several power supplies in series. Because there's uncertainty of the work function difference between the two electrodes (for ITO and Al, it's about 0.3-0.5V), we don't use battery voltage lower than 10V.

The resistance of the resistor has to be in the proper range. Small resistance will decease the signal-noise ratio of the oscilloscope, whereas large resistance will share the voltage with the sample. The resistance in our experiment is chosen to be 10-20kΩ. The voltage of the resistor produced by the photocurrent is measured with a Tektronix TDS 430A Digital Oscilloscope with frequency 400MHz.

Finally, the signal recorded by the oscilloscope is analyzed using softwares (for example, the programs in appendix A or B) to obtain information about the charge transport in the sample.

1.3.3 Temperature Control
As the behavior of charge transport changes as temperature changes, TOF temperature measurement is a good method to study the transport mechanism. The sample is placed in the center of a metal chamber, which is then connected to four subsystems: a pump, a self-circulating cooling system, a heating system and the TOF photocurrent measurement system.

The chamber has a transparent glass window so that the TOF experiment can be performed in the chamber. We use a pumping system with a primary pump connected to a diffusion pump. The vacuum is below $10^{-5}$ torr.

The cooling system is a self-circulating helium refrigerator. The model is CTI-Cryogenics Model 22, which can cool down as low as 10 degree Kelvin. The heating system is a heater and a temperature sensor in the chamber connected to an outside temperature controller. The temperature sensor is silicon diode, and the controller is Palm Beach Model 4025 Cryogenic Thermometer/Controller. The cooling system works independent from the heating system. When the cooling system is stabilized, the temperature controller measures temperature and uses the heater to control temperature to some desired value. Usually it takes the temperature controller about ten minutes to get stabilized. But in the experiment we still wait for about one hour for the sample to get thermal equilibrium. We note that the temperature of the sample may differ from that of the sensor.

1.3.4 Experimental Errors

The experimental errors in TOF are from the four major measurements: sample thickness, electric field (or power supply voltage), photocurrent and temperature.
The profilometer used for the sample thickness measurement in our study can be so accurate to several angstroms. For a sample with thickness of more than one micron, the error from thickness measurement is negligible.

The voltages have been measured with a high performance Keithley 195A Digital Multimeter, which can measure to 0.01V. So the error from the voltage measurement is also negligible, but the difference of the electrode work functions may contribute to the voltage with an error up to 0.5V.

The error of photocurrent measurement is from the accuracy of the digital oscilloscope. The accuracy for TDS 430A provided by factory is 1.5%. But from my experience, when there’s strong E-M wave in the environment, the noise can be much larger than the instrument basic noise and are sometimes comparable to the signal.

The error of the temperature measurement is less than 0.5K. But the sensor measures the temperature in the chamber, but not that of the sample. Although we usually wait for one hour for the sample to reach the balance temperature, a deviation may still exist. A second sensor can be attached to the sample directly to measure this deviation.

The resulting errors can be seen as the scatter in the data. The extracted mobility errors indicated the statistical errors associated with the fitting procedure.

1.4 Models for TOF photocurrent

In an ideal case when all the charges propagate in a plane wave, the photocurrent pulse should display a rectangle-like shape when the circuit reaction time is negligible, as illustrated in Fig.1.5.
Fig. 1.5. Ideal case when charges drift in a plane (a), the measured photocurrent has a rectangle-like shape (b). The tail in (b) is due to circuit reaction delay.

For ideal case, there's a sharp decrease at the time when the carriers exit the sample. The time corresponding to this decrease is usually defined as the transit time. A small tail decaying exponentially should exist if the circuit reaction time is not zero.

Fig. 1.6 is the measured photocurrent of a real material. In addition to the plateau, the photocurrent in Fig. 1.6 displays a sharp decrease near the origin, and fatter tail than the ideal case. Although the sharp decrease near the origin has been observed in many experiments[28-30], a reasonable explanation has not been proposed yet. One of my models in this thesis will give a proposed explanation for that sharp decrease near the origin. The fact that the measured tail is longer than an exponential decay can be explained by the existence of traps. Traps are some localized states for electrons or holes. When the trap density is not high, the majority of the charges will drift in a thin plane.
But some of the charges will be trapped during their drift and the arriving time will be delayed. Thus we should be able to observe a wider tail.

An explanation in terms of density-of states is illustrated in Fig. 1.7. In a perfect crystal, the free electron states form bands separated by gaps with sharply defined edges, as shown in Fig. 1.7(a)[34]. In the presence of a single localized imperfection, the band edges will not be disturbed if there’s no interaction between the impurity state and the crystal. Then a carrier will move essentially as if it were in a perfect crystal. The impurity level will be sharp, as shown in Fig. 1.7(b). But if the impurity or defect level does interact with the lattice, then the energy levels of the impurity and the crystal will be changed. As shown in Fig. 1.7(c), the interaction between the impurity level and valence or conduction bands forms a band of localized states. A carrier moving in the crystal can
be trapped or scattered by these localized states, exhibiting a transient photocurrent shape as shown in Fig. 1.8 [35].

In the presence of translational or compositional disorders, the localized states in the gap can trail off in a continuous tail from the valence and conduction bands. The states are so numerous that transport is possible from one defect site to another. Since the motion of the carrier is wavelike in the extended states forming the conduction band, and is that of phonon-assisted hopping in the localized states, the mobility displays a gap[1].

![Diagram of density of electronic states](image)

Fig 1.7 Density of electronic states $n(E)$ as a function of energy $E$ for (a) a perfect crystal, (b) a crystal containing only one localized imperfection, (c) a crystal containing a low concentration of localized imperfection (from [34]).

In the case of amorphous materials or of materials with an almost continuous distribution of trapping centers extending deep into the forbidden gap, the shape of the
Transient photocurrent will resemble that shown in Fig. 1.8. There is a sharp spike followed by a rapid decay to a plateau that tails off gradually so that it is difficult, sometimes impossible to determine the transit time. The type of transport is referred as dispersive transport, which is characteristic of most amorphous inorganic solids and organic and polymeric solids.

In 1975, Scher and Montroll[36] developed a statistical theory to study the mobility in dispersive transport with disorder. The Scher-Montroll model has been widely used to describe dispersive phenomena in amorphous solids and doped polymer systems.

Their model system consists of a random array of hopping sites within a regular lattice of cells made up of these sites (Fig.1.9). The waiting time for a particle on a given
site follows a Continuous Time Random Walk (CTRW) Model. In the absence of disorder, the transition rate between hopping sites is a constant, and thus both the dwell time and hopping time obey an exponential distribution. But the presence of disorder changes the transition rate into a random variable, and as an effect the TOF photocurrent displays a long tail. Scher and Montroll proposed a power distribution for waiting time to describe the effect of disorder.

Fig 1.9 Schematic diagram for random walk model (from [36]). The carriers are injected as from left side and propagate toward an absorbing barrier on the right side.
\[ \psi(t) \sim t^{-(1+\alpha)} \] (1.12)

with \( \alpha \) a disorder parameter that has values between zero and unity. The more disordered the material, the smaller the value of \( \alpha \) and the more dispersive the transport. One way to look at this distribution function is that in \( \psi(t) \) decreases with increasing time. Thus, at shorter times there is a greater fractional change than at longer times.

A key prediction by Scher-Montroll model is that the transient photocurrent will decay as,

\[ i(t) \sim \begin{cases} 
 t^{-(1-\alpha)}, & \text{if } t < t_r \\
 t^{-(1+\alpha)}, & \text{if } t > t_r 
\end{cases} \] (1.13)

This relation is sometimes called “power law”, in which the tail current obeys the power relation. Following this relation, one can easily obtain the transit time by plotting the current and time in double-log scale. The point of intersection of the two branches in (1.13) defines the transit time. According to this model, the transit time is,

\[ t_r \sim \frac{C}{W_0} \left| \frac{L}{l(E)} \right|^{1/\alpha} \exp \left( \frac{\Delta_0}{kT} \right) \] (1.14)

where \( C \) is a constant of order unit, \( W_0 \) a scaling factor, \( \Delta_0 \) a zero field activation energy, and \( l(E) \) the mean displacement in the field direction per hop. At low field, it may be assumed that \( l(E) \approx E \) [37], thus the transit time varies with thickness and field as \( (L/E)^{1/\alpha} \).

Fig. 1.10 shows a successful application of Scher-Montroll model to study the mobility in dispersive transport[38].
The most important assumption in Scher-Montroll model is the power waiting time distribution (1.12), which is the reason for its success in amorphous inorganic solids, but which is also the cause of its failure in a lot of materials especially dispersive organic and polymeric solids. Bässler[39] has argued that the waiting time distribution \( \psi(t) \sim t^{-(1+\alpha)} \) in Scher and Montroll's model is realized in materials in which multiple trapping within an exponential distribution prevails, but organic glasses and molecularly doped polymers do not fall into this category. In most cases, the charge distribution can be well approximated by a Gaussian, which is not consistent with Scher-Montroll model. Furthermore, Godson and Hirsch[40] early observed that in 1:1 TNF-PVK, the tail of the
photocurrent was closer to an exponential than a power law, and we have observed the same phenomena in our studying organic and polymeric semiconducting solids.

Even for those materials that satisfy the assumptions in Scher-Montroll model, we may still encounter practical difficulty. In order to apply Scher-Montroll's power relation, one requires that the circuit reaction time $\tau = RC$ be much smaller than the transit time $t_T$ so that the measured photocurrent is the same as the drifting current in the sample. Another requirement is that the quantity of charge produced by the laser is much less than the product of the sample capacitance and battery voltage (relation (1.11)), in order that the drifting charges perturb the external electric field as less as possible. But at the same time the quantity of charge should be large enough to give unequivocal signals. However, in many low mobility organic and polymeric materials, these conditions are sometimes difficult to be satisfied simultaneously, a case which has limited the applicability of Scher-Montroll's method in these materials. A lot of efforts have been applied to solve this problem, but so far, it has not been successfully solved [41].

As we have discussed, the effect of traps is that the charges do not drift uniformly, not even the majority of charges do. Scher-Montroll model[36] and other studies[41] give results that the transit time for dispersive transport is a function of sample thickness. As a result, an interpretation in terms of charge carrier mobility is not meaningful.

Scott et al.[42] have described a method to obtain the mean carrier mobility defined by a carrier velocity distribution. In the framework of Scher-Montroll model, they found that the velocity distribution can be described by a Gaussian function. Then the mean mobility is the average of the mobilities of all the carriers. They applied this model to diethylaminobenzaldehyde-methylphenyl hydrazone (DEMPH) doped into polycarbonate.
(PC) at a concentration of 50% obtaining a good fit and a mobility in the order of $10^{-5}\, cm^2/Vs$.

In this thesis work, I have developed two models attempting to overcome the difficulty in studying mobility of dispersive materials. Both models are based on the same dynamic equation describing a TOF system. The second model is also based on the concept of average mobility.

1.5 Materials of Interest

TOF was originally designed to study the transport in crystalline materials. But great achievement was made after people began to employ it to study amorphous materials. Chalcogenide glasses such as $\alpha$-Se and As$_2$Se$_3$ are among the earliest interested material, because of their application in xerography at earlier times. There materials usually have high mobility ($>1cm^2/Vs$)[43-44], but their photocurrents are dispersive. The need for interpretation of these experimental measurements inspired the dispersion model developed by Scher and Montroll.

Trinitrofluorenone (TNF) with polyvinyl carbazole (PVK) is among the earliest interested organic/polymer solids studied by TOF technique, also because of its applications in xerography. The mobilities of organic and polymer solids are much smaller than those of inorganic solids. At a field near $=10^3\, V/cm$, the mobility varies from $10^{-9}$ to $10^{-6}\, cm^2/Vs$ with varying TNF:PVK molar ratio[45]. It has been shown[46] that films containing PVK and TNF are comprised of three components: (1) TNF:PVK charge-transfer complexes, (2) free TNF, and (3) free PVK. In TNF and the charge-transfer complexes, electron transport dominates, while in PVK only hole
transport is observed. The hole mobility of pure PVK varies from $10^{-6}$ to $10^{-3} \text{ cm}^2/\text{Vs}$ by different authors[47-50].

PPV/C$_{60}$ system has been observed to display photovoltaic effect [51-53]. Photoinduced charge transfer occurs above 2.3eV for C$_{60}$. TOF measured mobility[54] was reported as $\mu_e = \mu_h = 1.1 \pm 0.1 \text{ cm}^2/\text{Vs}$ at room temperature. The oligomer sexithiophene (6T) is another material showing photovoltaic effect[55].

Poly(3-methylthiophene) (P3MeT) has attracted a lot of attentions[56-58] because of its potential applications in FET. Its hole mobility is as high as in the order of $10^{-4} \sim 10^{-3} \text{ cm}^2/\text{Vs}$. 6T has also been studied for its FET effect[59-60]. Its mobility hole mobility has been determined to be in the order of $10^{-2} \text{ cm}^2/\text{Vs}$ [61].

LED is another field that organic and polymer semiconducting materials have broad applications. Tris (8-hydroxyquinolino) aluminum (Alq) has been widely studied [62-64], with TOF electron mobility in the order of $10^{-5} \text{ cm}^2/\text{Vs}$. And N,N'-diphenyl-N,N'-bis(3-methylphenyl)-benzidine (TPD) also has been widely used as a hole transport layer in LED, with hole mobility in the order of $10^{-4} \sim 10^{-3} \text{ cm}^2/\text{Vs}$ [65-66].

The purpose of this thesis is to build models, so only several widely studied materials such PVK, TPD and Alq will be carefully measured in this thesis. Their chemical structures and that of TNF are shown in Fig.1.11. The three materials do not have absorption at the laser wavelength at 532nm[67-69].
Fig. 1.11 Chemical structures of (a) TPD, (b) Alq, (c) TNF and (d) PVK.
CHAPTER 2

MASTER EQUATION AND MODEL-1:
DIFFERENTIATION OF PHOTOCURRENT

2.1 Introduction

In this chapter, on the basis of macroscopic assumptions we have derived a differential equation describing the dynamic behavior of photocurrent in Time-Of-Flight. From the equation we have developed two new models to measure the carrier drift mobility of dispersive organic semiconducting materials. The first model is based on the singularity of differential current when the effect of “dispersion” is not too strong. The second model deals with the case of strong “dispersive” effect. We have assumed a velocity distribution for the drifting carriers in the second model and then obtained the average mobility. Our models are free of any micro carrier transport mechanism, so they can in principle be applied to measure the mobility of any type of materials.

2.2 The Master Equation

In this part, we deduce a dynamic equation for the measured TOF photocurrent based on a simple assumption that the sample can be well approximated as a capacitor. The capacitor is symmetric and uniform so that we can treat it as one dimension in our derivation. Based on the dynamic equation we have developed two models to interpret and simulate the TOF photocurrent.
A schematic diagram of our deduction is shown in Fig. 2.1. Suppose that a single short laser pulse (the width of pulse is negligible) produces many electron-hole pairs or excitons in the Selenium layer, and then the external electric field by the battery successfully separates a total amount of positive charge $q_0$ and an equal amount of negative charge. The negative charge then drifts across the sample to the other side, while the positive charge flows to the other side through the external circuit. The charges inside the sample follow a random walk with different hopping probabilities in forward and backward directions[70].

Fig. 2.1 Schematic for TOF. The part in the circle is the sample, which has been magnified.
We can look at this phenomenon in a macroscopic picture and use the charge density to describe this process. When there is no trap in the sample, macroscopically all the negative charges will drift to the other side in a plane and the charge density is a delta function. If traps exist, the charges will be trapped and repeatedly released many times during their drift. Then we can use a function $\rho(x,t)$ to describe the line charge density for those charges drifting in the sample at position $x$ and time $t$. In our derivation we assume this function is continuous and differentiable.

The charge density inside the sample induces an electric field $E(x,t)$ other than the field by the battery, and this field in turn produces a potential difference between the two electrodes of the capacitor. The potential difference induced by the charge density is the driving force for the external photocurrent. Suppose the thickness of the sample is $d$.

Using Maxwell equation for the capacitor, we have,

$$\frac{\partial}{\partial x} E(x,t) = \frac{\rho(x,t)}{\varepsilon_0 \varepsilon_r A}, \quad 0 < x < d$$

(2.1)

$\varepsilon_0$ the permittivity of the vacuum, $\varepsilon_r$ the permittivity of the sample and $A$ the area of the electrodes.

However, the charge density is a delta function at the position of zero, due to the positive charges left on this electrode. Let that quantity of charge be $q_1(t)$, and denote the external photocurrent as $i(t)$. Obviously the external photocurrent is due to the change of this quantity of charge.

$$i(t) = -\frac{d}{dt} q_1(t)$$

(2.2)

Then the induced field $E(x,t)$ at position $x$ and time $t$ can be expressed as,
\[ E(x,t) = \frac{q(t)}{\varepsilon_0 \varepsilon_r A} + \frac{1}{\varepsilon_0 \varepsilon_r A} \int_0^x \rho(z,t)dz \]  
(2.3)

and then the induced potential difference is,

\[ \Delta V(t) = \int_0^d E(x,t)dx \]  
(2.4)

and because this potential difference is the driving force for the external current, by Ohm’s Law, we have,

\[ \Delta V(t) = i(t)R \]  
(2.5)

After combining equations (2.2), (2.3), (2.4), and (2.5), and defining the capacitance

\[ C = \frac{\varepsilon_0 \varepsilon_r A}{d} \]  
and the circuit characteristic constant \( \tau = RC \), we have derived the following relation,

\[ \tau \frac{d}{dt} i(t) = -i(t) + \bar{i}_n(t) \]  
(2.6)

with,

\[ \bar{i}_n(t) = \frac{1}{d} \int_0^d i_n(x,t)dx \]  
(2.7)

\[ i_n(x,t) = \frac{\partial}{\partial t} \int_0^x \rho(z,t)dz \]  
(2.8)

with \( \bar{i}_n(t) \) the average drifting current and \( i_n(x,t) \) the drifting current at position \( x \) and time \( t \) inside the sample. From the dynamic equation (2.6), the external photocurrent decays through the RC effect, but is powered by the drifting current inside the sample.

The average drifting current has appeared in literature[36], but as far as I know, it is the first time to appear as a power source in our dynamic equation.

The differential equation (2.6) has a general solution,
The solution depends on the average drifting current, which in turn depends on the charge density function.

2.3 Model-1: Differentiation of Photocurrent

Before proposing our model, we will first apply our differential equation to the ideal case of a trap-free system in which the charge distribution function is zero. The charge density function is a delta function that drifts with a constant velocity $v_0$. The charge density function is,

$$\rho(x,t) = \frac{q_0}{A} \delta(x - v_0 t)$$

From which we can solve for $\tilde{i}_m(t)$,

$$\tilde{i}_m(t) = \left\{ \begin{array}{ll}
q_0 / t_T, & t < t_T \\
0, & t > t_T
\end{array} \right. \quad (2.11)$$

With $q_0$ the total charge, and $t_T = d / v_0$ the transit time. Then the solution for the differential equation in this case can be expressed analytically as,

$$i(t) = \frac{q_0}{t_T} (1 - e^{-t/T}), \ldots, t < t_T$$

$$i(t) = \frac{q_0}{t_T} (e^{tr/T} - 1) - t > t_T$$

and its first order differentiation is,
The plots $i(t) \sim t$ and $i(t) \sim t$ for a trap-free system are shown in Fig.2.2. A remarkable feature is that the photocurrent displays cusp at the transit time, which is characterized by the discontinuity of differential current at the transit time.

\[
\begin{align*}
  i(t) &= \frac{q_0}{t \tau} e^{-t/\tau}, \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad t < t_\tau \\
  i(t) &= -\frac{q_0}{t \tau} (e^{t/\tau} - 1)e^{-t/\tau}, \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad t > t_\tau
\end{align*}
\]

(2.13)

After observing the cusp of photocurrent in a trap-free system, we extend our argument to the general case. As we have no information about the charge distribution function, we don’t attempt to solve the differential equation in our first model, but instead use the mathematical properties to deduce our argument.

Fig.2.2 Photocurrent (...) and its differential current (DOP) (—) for a trap-free system with $q_0=1$, $\tau=4.35\mu s$, and $t_\tau=3.75\mu s$.

After observing the cusp of photocurrent in a trap-free system, we extend our argument to the general case. As we have no information about the charge distribution function, we don’t attempt to solve the differential equation in our first model, but instead use the mathematical properties to deduce our argument.
In our first model, we assume that there exists a charge frontier, and then the photocurrent or differential current should display singularity. Without traps and in ideal case we have discussed above, the charges inside the sample drift in a very thin plane, and this is the basic assumption for the application of Time-of-Flight to measure mobility in semiconducting materials in early times. With traps, the charges are trapped and released randomly, but we still assume that there still exists a propagating charge plane and we call it charge frontier. When the position $x$ is smaller than the frontier, there is a smooth charge density function $\rho(x,t)$, but for positions further beyond the frontier, the charge density disappears. It is possible there are charges at the frontier. The assumption of frontier is equivalent to that the charge density function is piecewise smooth but displays singularity at the point of frontier.

For simplicity, we may assume that the charge frontier moves with a constant velocity $v_0$, then the time it spends in the sample is defined as the transit time, $t_T = d / v_0$, and we can calculate the mobility using formula (1.2). The frontier and the singularity of charge density disappear after the frontier arrives at the other side of the sample. Then for time smaller and larger than the transit time, we can write the average drifting current in equation (2.7) into two different forms:

$$\bar{i}_n(t) = \frac{1}{d} \int_0^{t_T} i_n(x,t)dx, \ldots, t < t_T$$

$$\bar{i}_n(t) = \frac{1}{d} \int_0^{t_T} i_n(x,t)dx, \ldots, t > t_T$$

The drifting current $i_n(x,t)$ is a smooth function of time at all positions behind the frontier, due to the assumption of continuity and differentiability of the charge density.
function. But from (2.14) and (2.15), we would not expect the average drifting current to be a smooth function of time at the transit time, since the upper limit of the integral in (2.14) is time dependent, but that in (2.15) is a constant. Therefore, we conclude that the average drifting current is two different functions with boundary at the transit time.

Furthermore, we can also conclude that the photocurrent $i(t)$ may not be a smooth function of time at the transit time, and this is the actual principle to find the transit time in a classic TOF photocurrent. This is the case for a "non-dispersive" transport, in which most of the charges are at the frontier. But for dispersive transport, because most charges are left behind the frontier, the non-smooth effect of the charge frontier is weak or even has been smoothened out by the integration effect in equation (2.9). However, the differential current, the first or some higher order of differentiation of photocurrent may display this nonsmoothness phenomenon at the transit time. This is the principle of our first approach to find transit time for dispersive TOF photocurrent — differentiation of photocurrent. In this study we have only used the first order differentiation, and we will call that first order differentiation differential current.

Actually, we even prove the condition under which the photocurrent itself should display cusp at the transit time. First, we establish a relation,

$$
\frac{d}{dt} \left. \int_{\tilde{t}}^{\infty} \left[ \int_{0}^{\infty} \rho(z,t)dz \right] dy \right|_{t_{m_t}} = \frac{d}{dt} \left. \int_{\tilde{t}}^{\infty} \left[ \int_{0}^{\infty} \rho(z,t)dz \right] dy \right|_{t_{m_t}} + v_{o} \int_{0}^{d} \rho(z,t_{r})dz
$$

(2.16)

Using the above relation, we have then obtained,

$$
i(t_{r} + 0^{-}) \rightarrow i(t_{r} + 0^{+}) + \frac{1}{\pi_{r}} \left[ q_{o} + \int_{0}^{d} \rho(z,t_{r})dz \right]
$$

(2.17)
Where \( i(t_r + 0^-) \) and \( i(t_r + 0^+) \) are the limits of \( i(t) \) at \( t = t_r \) from left hand side and right hand side of the transit time \( t_r \), respectively. As \( q_0 \) and \( \rho(z, t) \) have opposite sign, the term \(-[q_0 + \int_0^{t_r} \rho(z, t_r) dz] \) is the amount of charge at the frontier at the transit time. Therefore, it's obvious from (2.17) that if the amount of charge at the frontier at the transit time is nonzero, the differential current \( i(t) \) will be discontinuous at \( t = t_r \), and then the photocurrent should display singularity at transit time.

However, if the amount of charge is very small or even equal to zero at the frontier, the effect of cusp of photocurrent is indistinguishable or even does not exist at all. In these cases, we encounter the so-called dispersive transport[71,72]. In principle, the first order or higher order differentiation of photocurrent should display distinguishable cusps for dispersive transport. Our analysis is only focused on the first order differentiation, because it's almost impossible to calculate higher order differentiation numerically, due to the instrument noise in TOF experiment. Actually, we have even developed some mathematical tools to mitigate the effect of noise in doing numerical differentiation, and I have described that part of work in chapter 5.

## 2.4 Experimental Evidence for Model-1

### 2.4.1 Experimental Results for TPD

The TOF experiment was done as described in chapter 1.4. The configuration is ITO/Se/TPD/Al, with ITO (Indium-Tin-Oxide) semitransparent. Fig.2.3 is a plot of TPD photocurrent at electric field \( 1.0 \times 10^5 V/cm \). TPD is a widely used hole transport organic semiconducting material in OLEDs[73,74]. Its photocurrent is nondispersive, but does
not display the platform shape when using photoexciting electrode. We have also plotted in Fig. 2.3 the differential current. It's obvious that the differential current displays a cusp at time $t = 3.75 \mu s$. Under the classical sense, this time is the transit time, and we can use formula (1.2) to calculate the mobility, which is $5.33 \times 10^{-4} \text{cm}^2/\text{V}s$. This value is a little smaller than that measured in a nondispersive photocurrent[75], but of the same magnitude.

Fig. 2.3 Photocurrent (○) and differential current (▲) for TPD with $d=2.0\mu m$, $E=1.0\times10^5 \text{V/cm}$, $T=298 \text{K}$.
2.4.2 Experimental Results for PVK and Alq

The configuration for PVK is ITO/PVK(0.5µm)/Se(10nm)/Al(130nm). Fig.2.4 and 2.5 plots the hole photocurrent and its differential current at an electric field $8 \times 10^3 \, \text{V/cm}$. The photocurrent and differential current displays similar shapes to those for TPD. Although the photocurrent also displays dramatic change at the minimum, it's hard to conclude the existence of cusp.

Fig.2.4 Photocurrent (○) and differential current (▲) for PVK with configuration ITO/PVK(0.5µm)/Se(10nm)/Al(130nm) and parameters $E = 8 \times 10^3 \, \text{V/cm}$, $T=298\,\text{K}$. 

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Fig. 2.5. PVK photocurrent and differential current of Fig. 2.4 plotted in a time scale similar to Fig. 2.3 for TPD.

Fig. 2.6 and 2.7 are the electron photocurrent and its differential current of Alq with configuration ITO/Se(20nm)/Alq(0.45µm)/Al(100nm) at room temperature and electric field $E = 1.0 \times 10^6 \text{V/cm}$. It’s more obvious that there does not exist a singularity point on the differential current.
Fig. 2.6 Electron photocurrent (○) and differential current (▲) for Alq with configuration ITO/Se(20nm)/Alq(0.45μm)/Al(100nm) and parameters $E = 1.0 \times 10^6 V/cm$, $T=298K$.

Fig. 2.7 Alq photocurrent and differential current of Fig. 2.6 plotted in the same time scale as Fig. 2.3 for TPD and Fig. 2.5 for PVK.
Therefore, we cannot use the method of differential current to measure the mobilities for the two dispersive materials Alq and PVK. It means that the assumption of charge frontier is not valid in these two materials. Actually I have tested a lot of other so-called dispersive organic and polymer semiconducting materials. TPD is the only one that shows singularity in the differential current. It could be true that the frontier assumption holds well in non-dispersive transporting, but unfortunately we don’t have chance to study other non-dispersive materials.

2.4.3 Log-log Plots

As the last part of chapter 2, I also want to show the log-log plots for the photocurrents measured for the three materials in this chapter. They are shown in Fig. 2.8, 2.9 and 2.10. It’s very obvious that the Scher-Montroll model does not apply to this materials.

Fig. 2.8. Log-log plot of the TPD photocurrent of Fig. 2.3.
Fig. 2.9. Log-log plot of the PVK photocurrent of Fig. 2.4.

Fig. 2.10. Log-log plot of the Alq photocurrent of Fig. 2.6.
2.5 Summary

After assuming a charge distribution in the sample, I have derived a dynamic equation for the photocurrent in TOF experiment. The dynamic equation shows that the photocurrent decays through RC effect, but is powered by the average drifting current in the sample. Based on the dynamic equation and an assumption of charge frontier, I have proposed our first model to measure carrier drift mobility. This model says that the differential current should display singularity at the transit time. Experimental results of TPD agree well with this model, but measurements of PVK, Alq and some other materials contradict it. We have also shown that the log-log plots imply that the Scher-Montroll model does apply to the photocurrents of these materials.
CHAPTER 3

MODEL-2: A STOCHASTIC MODEL

3.1 Introduction

In chapter 2, I have derived a differential dynamic equation for TOF photocurrent and have also proposed a method to extract the transit time by differentiating the photocurrent. That method is based on the assumption that there exists a charge frontier for the drifting charges, and then the differential current display a significant curvature change or cusp at the transit time. We have shown that prediction holds true for the “non dispersive” glass material TPD, however, we have also seen that this is not true for the dispersive material PVK and Alq, which probably implies that the charge frontier cannot persist in dispersive materials due to strong scattering and trapping effects.

In this chapter, by assuming a macroscopic velocity distribution for the drifting charges, I have found a stochastic solution for the dynamic differential equation. The solution involves several parameters, which can be fitted by the experimentally measured photocurrent. Then we can use these best-fitted parameters to simulate the photocurrent. In the next chapter I will show that the results based on this model are surprisingly good. Furthermore, we have been able to obtain the average mobility for dispersive transport from the simulation. To emphasize the importance of this new model, I have placed this part of work in a separate chapter.
3.2 A Stochastic Solution

Based on electrodynamic principles, in chapter 2 I have derived a dynamic equation to describe the behavior of the drifting charges inside the sample. The time dynamics of external current $i(t)$ obeys the differential equation (copied from chapter 2):

$$
\tau \frac{d}{dt} i(t) = -i(t) + \bar{i}_m(t), \ldots, t > 0
$$

(3.1)

with,

$$
\bar{i}_m(t) = \frac{1}{d} \int_0^d i_m(x, t) dx
$$

(3.1a)

$$
i_m(x, t) = \frac{\partial}{\partial t} q(x, t)
$$

(3.1b)

$\tau$ a characteristic time constant of the circuit, $d$ the sample thickness, and $q(x, t)$ the total charges between 0 and $x$ at time $t$. $i_m(x, t)$ is the current at position $x$ at time $t$, which is due to the drifting charges inside the sample. The differential equation (3.1) has a general solution,

$$
i(t) = e^{-\tau t} \left[ \int_0^t \bar{i}_m(t') e^{\tau t'} dt' / \tau \right]
$$

(3.2)

From the dynamic equation (3.1), the external current $i(t)$ decays through the RC effect but is powered by the average drifting current $\bar{i}_m(t)$ in the sample. In a microscopic picture, the average current $\bar{i}_m(t)$ originates from the process of charge waiting and hopping, and this process is stochastic in nature. The charges inside the sample move through a mechanism called hopping[76]. Generally speaking, not all the places are friendly to the charges. The charges can only stay in a lot of separated sites for some random time, and then randomly hop to other neighboring friendly sites. The
process of charge movement is basically a Wiener process and the distributions of charge
waiting time and hopping positions characterize this stochastic process. But
macroscopically, we can use the distribution of drifting velocity to describe this random
process, which is equivalent to map the micro random process to a real random variable
(velocity). This transformation makes it possible to derive an expression for the drifting
current.

Now we assume a velocity distribution function \( f_v(v, t) \), \(-\infty < v < +\infty \), with
mean \( v_0 \), and variance \( \sigma^2 \). If we can calculate the total charge between position 0 and \( x \),
then the time derivative of the total charge is the current \( i_x(x, t) \) at position \( x \). But at
time \( t \), all the charges between positions 0 and \( x \) are those with velocities falling within
the range \([0, x/t] \). Assume the total initial charge \( q_0 \), we then have (see Fig.2.1),

At position \( x \in [0, d] \), at \( t \):
\[
q(x, t) = q_0 \int_0^{x/t} f_v(v, t)dv
\]
(3.3a)

At time \( t + dt \):
\[
q(x, t + dt) = q_0 \int_0^{x/(t+dt)} f_v(v, t + dt)dv
\]
\[
= q_0 \int_0^{x/(t+dt)} f_v(v, t)dv
\]
(3.3b)

So,
\[
dq(x, t) = q(x, t + dt) - q(x, t)
\]
\[
= -q_0 \int_{x/(t+dt)}^{x/t} f_v(v)dv + q_0 \int_0^{x/t} \frac{\partial f_v(v)}{\partial v}dv
\]
\[
= -q_0 \frac{x}{t^2} f_v(x/t)dt + q_0 \int_0^{x/t} \frac{\partial f_v(v)}{\partial v}dvdt
\]
(3.4)

And we have the current at position \( x \) at time \( t \),
\[
i_x(x, t) = -\frac{dq(x, t)}{dt}
\]
If we neglect the contribution of the second term in (3.5) to the average drifting current, then after plugging back into (3.1a), we also obtain the average current inside the sample,

\[
\tilde{i}_n(t) = \frac{q_0}{d} \int_0^d v f_s(v,t) dv
\]  

(3.6)

And finally, we have obtained an expression for external photocurrent using the velocity distribution,

\[
i(t) = \frac{q_0}{d} e^{-\frac{t}{\tau}} \left[ \int_0^t e^{\frac{t'}{\tau}} \left[ \int_0^d v f_s(v,t') dv \right] dt' \right] \frac{1}{\tau}
\]  

(3.7)

In next part I will develop a model for velocity distribution based on random walk and diffusion. We will see that Gaussian is good approximation for velocity distribution.

3.3 A Model for Velocity Distribution

3.3.1 From Random Walk to Diffusion

The charges inside the sample move through hopping, which can be described by the classical random walk model. Consider a simple 1-d random walk model (Fig.3.1). Suppose there are many traps evenly distributed between position 0 and d, with step width \(a\). We also assume that positions 0 and d are attractive. After being trapped for an average time \(\tau\) at any trap, each charge has a probability \(p\) to jump forward, and probability \(1-p\) to jump backward. We would expect \(p\) to be larger than 0.5. This is the so-called asymmetric hopping [77].
At time zero, the object starts to move at position $x$. Let $x_i$ be the displacement of $i$-th jump. Then $x_i$ is a Bernulli random variable with distribution,

$$x_i = \begin{cases} -a, & \text{w.p.} (1-p) \\ a, & \text{w.p.} (p) \end{cases}$$

(3.8)

After $n$ steps the displacement $x$ is the summation of all steps,

$$x = x_1 + x_2 + \cdots + x_n$$

(3.9)

$x$ is a random variable with Binomial distribution. Now let's analyze the probability it will come back to $x$ at time $t$,

$$t = 2n \tau, \quad n > 0$$

(3.10)

with $n$ positive integer. The probability $P(x,t)$ can be calculated by the binomial distribution as,

$$P(x,t) = \binom{2n}{n} p^n (1-p)^n$$

(3.11)

Next let's consider the probability changes as position and time change. For a small position or time change,

$$\Delta x = 2a$$
$$\Delta t = 2\tau$$

(3.12)

Then,
\[ P(x + \Delta x, t) = \left( \frac{2n}{n+1} \right) p^{n+1}(1-p)^{n-1} \]  

(3.13)

\[ P(x, t + \Delta t) = \left( \frac{2n+2}{n+1} \right) p^{n+1}(1-p)^{n+1} \]  

(3.14)

Then we can define,

\[
\frac{\Delta P(x, t)}{\Delta x} = \frac{1}{2a} (P(x + \Delta x, t) - P(x, t))
\]

\[
= \frac{1}{2a} P(x, t) \left\{ \frac{p}{1 - p} \frac{n}{n+1} - 1 \right\}
\]

(3.15)

and probability flux,

\[
\frac{\Delta P(x, t)}{\Delta t} = \frac{1}{2a} (P(x, t + \Delta t) - P(x, t))
\]

\[
= \frac{1}{2a} P(x, t) \left\{ 1 - 2p(1-p) \frac{(2n+1)}{n+1} \right\}
\]

(3.16)

After some algebra, (3.15) can be written as,

\[
\frac{2a}{P(x, t)} \frac{\Delta P(x, t)}{\Delta x} = \frac{2p - 1}{1 - p} \frac{p}{(1-p)(n+1)}
\]

(3.17)

and (3.16) as,

\[
\frac{2\tau}{P(x, t)} j(x, t) = (2p - 1)^2 + \frac{2p(1-p)}{n+1}
\]

(3.18)

Under the continuous limit, we have the following relations,

\[
\frac{\Delta P(x, t)}{\Delta x} \rightarrow \frac{\partial P(x, t)}{\partial x}
\]

(3.19.1)

and in the continuous limit, we also want to replace the probability by probability density \( f(x, t) \) times stepwise \( a \),
\[ P(x, t) \rightarrow a f(x, t) \quad \text{(3.19.2)} \]

Then combining (3.17) and (3.18), we have,

\[ j(x, t) = -\frac{(1-p)^2 a^2}{\tau} \frac{\partial f(x, t)}{\partial x} \frac{\partial f(x, t)}{\partial x} + \frac{2p-1}{2\tau} f(x, t) \quad \text{(3.20)} \]

The probability flux is composed of diffusion and drift effects. The diffusion is a result of random walk, but the drift effect originates from the asymmetry of jump probability.

### 3.3.2 Diffusion Equation and its Solution

After having obtained the expression for probability flux, we can use the following continuity equation to obtain the dynamics for probability density,

\[ \frac{\partial f}{\partial t} = -\frac{\partial j}{\partial x} \quad \text{(3.21)} \]

The dynamical equation is a diffusion equation,

\[ \frac{\partial f}{\partial t} = \frac{(1-p)^2 a^2}{\tau} \frac{\partial^2 f}{\partial x^2} + \frac{(2p-1)a}{2\tau} \frac{\partial f}{\partial x} \quad \text{(3.22)} \]

The first term at the right hand side is due to diffusion, and the second term due to drift.

Now we want to apply the diffusion model to study the charge movement in a TOF sample. The charges are produced near one of the electrodes, however, the electrodes also act as charge attractors. For the diffusion equation to have solution, we have to assume there's a small distance \( x_0 \) between the electrode and the place where charges are produced. Further, if the sample is thick, we can treat the boundary as semi-infinite, i.e., the charge is either attracted to the nearest electrode, or diffuses and drifts to infinite. So the initial condition is,

\[ f(x = 0, t = 0) = \delta(x) \quad \text{(3.23)} \]

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and the boundary condition is,

\[ f(x = -x_0, t) = f(x = \infty, t) = 0 \quad (3.24) \]

Then the solution for density function \( f(x, t) \) is the solution for the following Green function under boundary condition (3.24),

\[
\frac{\partial f}{\partial t} - \frac{(1 - p)^2 \alpha^2}{\tau} \frac{\partial^2 f}{\partial x^2} + \frac{(2p - 1)a \partial f}{2\tau} \frac{\partial f}{\partial x} = \delta(x)\delta(t) \quad (3.25)
\]

For convenience, let

\[
\alpha = \frac{(1 - p)^2 \alpha^2}{\tau} \quad (3.26)
\]

Then we can use standard method to solve for the Green function. We first make the following transformation to eliminate the drift term,

\[ b(x, t) = e^{-\alpha t} f(x, t) \quad (3.27) \]

Then equation (3.25) becomes,

\[
\frac{1}{\alpha} \frac{\partial b}{\partial t} - \frac{\partial^2 b}{\partial x^2} + \kappa^2 b = \delta(x)\delta(t) \quad (3.28)
\]

Then we can solve the partial differential equation by making a Laplace transformation,

\[ \tilde{b}(x, q) = \int_0^\infty b(x, t)e^{-qt} dt \quad (3.29) \]

then (3.28) becomes,

\[ \frac{q}{\alpha} \tilde{b} - \frac{\partial^2 \tilde{b}}{\partial x^2} + \kappa^2 \tilde{b} = \delta(x) \quad (3.30) \]

with boundary,
\[ \bar{b}(x = -x_0, q) = \bar{b}(x = \infty, q) = 0 \] (3.31)

It can be shown \( \bar{b}(x, q) \) has solution,

\[ \bar{b}(x, q) = \begin{cases} 
\frac{e^{-\lambda x} - e^{-\lambda(x+2x_0)}}{2\lambda}, & x > 0 \\
\frac{e^{\lambda x} - e^{-\lambda(x+2x_0)}}{2\lambda}, & 0 > x > -x_0 
\end{cases} \] (3.32)

with

\[ \lambda = \sqrt{\kappa^2 + q/\alpha} \] (3.33)

Then we need to use inverse Laplace transformation to transform variable \( q \) back to \( t \),

\[ b(x, t) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} \bar{b}(x, q)e^{qt} dq \] (3.34)

Although the branch point in (3.33) has complicated the inverse transformation, we can look for similar transformation from standard tables. From the Tables of Integral Transformation[78], we find,

\[ \frac{e^{-y\sqrt{q}}}{\sqrt{q}} \sim \frac{e^{\frac{y^2}{4t}}}{\sqrt{\pi t}}, \quad (t > 0, y > 0) \] (3.35)

Then,

\[ b(x, t) = \frac{e^{-x\sqrt{t}}(e^{\frac{(x-2x_0)^2}{4\alpha}} - e^{\frac{(x+2x_0-2x_0)^2}{4\alpha}})}{2\sqrt{\pi \alpha}}, \quad -x_0 < x < \infty \] (3.36)

Finally, from (3.27) we have,

\[ f(x, t) = \frac{1}{2\sqrt{\pi \alpha}} \left( e^{\frac{(x-2x_0)^2}{4\alpha}} - e^{-2x_0}e^{\frac{(x+2x_0-2x_0)^2}{4\alpha}} \right), \quad -x_0 < x < \infty \] (3.37)
The probability density is composed of two Gaussians. When $x \gg x_0$, it can be well approximated as one Gaussian,

$$f(x,t) = \frac{1}{2\sqrt{\pi \alpha t}} e^{\frac{(x-x_0)^2}{4\alpha t}} (1 - e^{-2\alpha t}), \quad x_0 << x < \infty \quad (3.38)$$

Far away from the origin, the probability propagates as a Gaussian, with center and variance linearly increasing,

$$x_c = 2\alpha x = \frac{(2p-1)\alpha t}{2\tau}$$

$$\sigma_x^2 = 2\alpha = \frac{4\alpha^2(1-p)^2}{\tau} \quad (3.39)$$

Fig 3.2 is a comparison with (3.37) and (3.38),

![Comparison of (3.37) and (3.38)](image)

Fig.3.2 Comparison of (3.37) and (3.38), Dashed line (—) two Gaussians by (3.37), Dotted line (...) one Gaussian by (3.38), with $t=0.9$, $\kappa=5$, $\alpha=1$, and $x_0=0.1$
If the position is Gaussian by (3.38), then the distribution of velocity is also a Gaussian, with center and variance,

\[ v_c = 2\alpha \kappa = \frac{(2p-1)a}{2\tau} \]
\[ \sigma_v^2 = 2\alpha / t = \frac{4a^2(1-p)^2}{\pi} \] (3.40)

The coefficient in (3.38) means that only part of the Gaussian density can propagate to the far right side, and the other part is absorbed at the electrode at \( x = -x_0 \). When we plug the density back to (3.7), that coefficient can be absorbed into the total charge \( q_0 \). In our next part derivation, we use the following expression for velocity distribution,

\[ f_v(v,t) = \frac{1}{\sqrt{2\pi \sigma^2 / t}} e^{-\frac{(v-v_0)^2}{2\sigma^2 / t}}, \quad t > 0 \] (3.41)

with \( \sigma^2 = t\sigma_v^2 \) and \( v_0 \) some constants calculated by (3.40) or fitted by experimental data. The Gaussian distribution for drifting velocity in TOF has also been observed and used in other studies[79-81].

The electric field can change the jumping probability \( p \) and the average lifetime \( \tau \). As the field increases, we would expect the forward jumping probability to increase and lifetime to decrease. Then from relations (3.40), it’s obvious that the center of the velocity distribution will increase, but the change of the variance is not necessarily monotonic.

The actual movement of the drifting charges is a 3-d instead of 1-d random walk. Nevertheless, we can still map the 3-d movement into a 1-d movement, which is a random walk. But we also have to be aware that we have neglected the effect of the other
electrode and treated the boundary as semi-infinite. As long as the sample is thick enough, this should be a good approximation.

Finally, we're only interested in those charges moving through the sample, so we can define an average velocity for those charges,

$$< v > = \frac{\int_0^\infty \int_0^\infty v f_v(v, t) dv}{\int_0^\infty \int_0^\infty f_v(v, t) dv} \quad (3.42)$$

And a related concept is the average mobility,

$$< \mu > = < v > / E \quad (3.43)$$

As mentioned in chapter 1, the concept of mobility in dispersive transport is not that meaningful anymore, which should be replaced by average mobility. Average mobility more appropriately describes the transport property than actual mobility.

### 3.4 Convergence and Transformation

Because the upper limit $d/d'$ of variable $v$ goes to infinite when variable $t'$ goes to zero, the double integral in equation (3.7) converges very slowly in numerical computation. Therefore, it is necessary to look for some transformation to simplify that integral. Before starting to do that, we will first rewrite equation (3.7) in a convenient compact form with Gaussian velocity distribution (3.41),

$$i(t) = \frac{q_0}{d'} e^{-t'/\tau} g(t) \quad (3.44)$$

with,

$$g(t) = \int_0^\infty dt' \int_0^\infty h(v, t') dv \quad (3.44a)$$
\[ h(v,t') = e^{jv't}vf(v,t) \]

\[ = \frac{1}{\sqrt{2\pi\sigma'^2 / t'}} e^{jv'(v-\theta)^2 / 2\sigma'^2 t'} \quad (3.44b) \]

Now we can make a transformation by introducing two new variables \( r \) and \( s \),

\[
\begin{aligned}
    r &= t' \\
    s &= vt'
\end{aligned}
\quad (3.45)
\]

With the inverse transformation,

\[
\begin{aligned}
    t' &= r \\
    v &= s / r
\end{aligned}
\quad (3.46)
\]

The Jacobian of this transformation is,

\[
\frac{\partial(t', v)}{\partial(r, s)} = \begin{vmatrix} 1 & 0 \\ -s/r^2 & 1/r \end{vmatrix} = 1/r
\quad (3.47)
\]

The upper and lower limits for the old variables are,

\[
\begin{aligned}
    t' : 0 &\rightarrow t \\
    v : 0 &\rightarrow d / t'
\end{aligned}
\quad (3.48)
\]

and for new variables,

\[
\begin{aligned}
    r : 0 &\rightarrow t \\
    s : 0 &\rightarrow d
\end{aligned}
\quad (3.49)
\]

The limits of these two new variables do not depend on one another anymore, and the integral for function \( g(t) \) can be expressed with the two new variables,

\[
g(t) = \int_0^t dr \int_0^d H(r, s) ds
\quad (3.50a)
\]

with,

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But the price for the transformation is the strange function \( H(r,s) \).

First, the function \( H(r,s) \) has a nice property that it goes to zero when one of \( r \) and \( s \) goes to zero. It's obvious for variable \( s \). For variable \( r \), when \( r \to 0 \),

\[
\lim_{r \to 0} H(r,s) \propto \frac{s}{r^{3/2}} e^{-\frac{(s^2 r - v_0)^2}{2a^2}}
\]  
(3.51)

So,

\[
\lim_{r \to 0} \frac{s}{r^{3/2}} e^{-\frac{s^2 r}{2a^2}} = \lim_{s \to 0} s^{1/2} e^{-\frac{s^2}{2a^2}}
\]  
(3.52)

However, the function does not always behave so nicely if \( r \) and \( s \) go to zero through some special paths. For example, when \( s = 2 \nu_0 r \to 0 \), \( H(r,s) \to \infty \). Thus we have to evaluate the convergence of integral (3.50a) at the vicinity of zero, but its convergence is guaranteed by the convergence of (3.7). Fig. 3.3 is a 3-D graph of function \( H(r,s) \) at the vicinity of zero.

\[
H(r,s) \equiv \frac{1}{\sqrt{2 \pi \sigma^2}} \frac{s e r}{r^{3/2}} e^{-\frac{(s/r - v_0)^2}{2a^2}}
\]  
(3.50b)
Despite the strange behavior of function $H(r,s)$, we will still use it in doing the theoretical computation in the following equation, because (3.44) converges too slowly.

$$i(t) = \frac{q_0}{d^2} e^{-r/t} \left[ \int_0^\infty \int_0^\infty H(r,s) ds \right]$$ \hspace{1cm} (3.53)

But whether (3.53) converges faster than (3.44) is still an unanswered question.

### 3.5 Principle of Comparison with Experiments

In the next chapter, I will provide experimental evidences to support the stochastic model developed in this chapter. Based on standard statistical methodology, I have derived the formulae needed to compare experimental measurement with theoretical computation. This part of work is based on equation (3.53).

The principle of data fitting is to choose parameters that can best fit the calculated values to experimental measurements. In TOF experiments, the sample thickness $d$ and
the external current $i(t)$ can be measured through different methods. Now the task is to find values for initial charge $q_0$, characteristic time $\tau$, average velocity $v_0$, and variance $\sigma^2$ that can best fit the measured external current by the calculated values through equation (3.53), and then we can calculate the desired average velocity by equation (3.42) and average mobility by (3.43). The data fitting can be accomplished by the method of minimizing the squared error (MSE).

If we denote the measured current as $i^*(t)$, then the method of MSE is to,

$$\min_{\{q_0, \tau, v_0, \sigma^2\}} \sum_{k=1}^{n} (i(t_k) - i^*(t_k))^2$$  \hspace{1cm} (3.54)

The first order conditions are four non-linear equations,

$$\sum_{k=1}^{n} (i(t_k) - i^*(t_k)) \frac{\partial i(t_k)}{\partial \xi} = 0, \ldots, \xi = q_0, \tau, \sigma, v_0 \hspace{1cm} (3.55)$$

with $n$ the number of time points, which is 250 in our experiments and simulations. The equation for $q_0$ can be further simplified as,

$$q_0 = \frac{\sum_{k=1}^{n} i(t_k \mid q = 1) i^*(t_k)}{\sum_{k=1}^{n} i(t_k \mid q = 1)^2} \hspace{1cm} (3.56)$$

with $i(t_k \mid q = 1)$ the current by (3.53) but charge equal to one.

In principle, we can solve for $q_0, \tau, \sigma$ and $v_0$ from the four equations in (3.55) and (3.56). However, the non-linearity of these equations has complicated this problem. In my computation I have made a program (Appendix A) to directly search the minimum value for (3.54) instead of solving equations (3.55) and (3.56). But the direct searching...
method may have only found some local instead of global minimum. Analogous to linear regression[82], we can define a quantity $R^2$ which shows the fitness of regression,

$$R^2 = \frac{\sum (i(t_i) - \bar{i}^*)^2}{\sum (i^*(t_i) - \bar{i}^*)^2}$$  \hspace{1cm} (3.57)

with $\bar{i}^* = \frac{1}{n} \sum i^*(t_i)$ the average of all current points. We would expect $R^2$ to be close to 1.0 for a good data fitting.

Another issue is how to estimate the standard deviations and thus the confidence intervals of these four estimated parameters. We have developed some technique based on the so-called $\delta$-method[83] to estimate the standard deviation of the parameters. If we denote the minimum value of the squared error in (3.54) $SSE$, then the standard deviation for our curve fitting is,  

$$Sd = \sqrt{\frac{SSE}{(n - 4)}}$$  \hspace{1cm} (3.58)

If we assume a random noise model,

$$i^*(t) = i(t \mid q_0, \tau, \sigma, v_0) + \varepsilon$$  \hspace{1cm} (3.59)

with $\varepsilon$ the random noise, $i^*(t)$ the measured photocurrent, and $i(t \mid q_0, \tau, \sigma, v_0)$ the calculated photocurrent by (3.53). The estimated standard deviation for $i^*(t)$ is given by (3.58).

To calculate the variance for any of the estimated parameters, we first use Taylor expansion to expand the photocurrent with respect to that parameter near the estimated values, keeping the other parameters constant,
with \( \zeta \), the parameter needed to estimate its variance, and \( \zeta_{10}, \zeta_{20}, \ldots \) the estimated values by (3.55). Then from (3.60) we have,

\[
Sd^2 = \left( \frac{\partial i(t)}{\partial \zeta_j} \right)^2 Var(\zeta_j) \tag{3.61}
\]

We may want to take the summation over all the time to get a more accurate value, then,

\[
Var(\zeta_j) = \frac{n}{n-4} \frac{\sum_{t=1}^{n} \left( \frac{\partial i(t)}{\partial \zeta_j} \right)^2}{\sum_{t=1}^{n} \left( \frac{\partial i(t)}{\partial \zeta_j} \right)} \tag{3.62}
\]

To calculate the covariance, we need to keep the second order in the Taylor series,

\[
i(t) = i(t \mid \zeta_{10}, \zeta_{20}, \ldots) + \sum_{j=1}^{2} (\zeta_j - \zeta_{j0}) \frac{\partial i(t)}{\partial \zeta_j} \bigg|_{\zeta_j=\zeta_{j0}} + \sum_{j=1}^{2} \frac{(\zeta_j - \zeta_{j0})^2}{2} \frac{\partial^2 i(t)}{\partial \zeta_j^2} \bigg|_{\zeta_j=\zeta_{j0}} + \ldots \tag{3.63}
\]

Throw away orders higher than two, take an expectation on the two estimated parameters \( \zeta_1 \) and \( \zeta_2 \), and sum over all the time. We have,

\[
\sum_{j=1}^{2} Var(\zeta_j) \frac{\partial^2 i(t)}{\partial \zeta_j^2} \bigg|_{\zeta_j=\zeta_{j0}} + 2Cov(\zeta_1, \zeta_2) \frac{\partial^2 i(t)}{\partial \zeta_1 \partial \zeta_2} \bigg|_{\zeta_1=\zeta_{10}, \zeta_2=\zeta_{20}} + \ldots = 0 \tag{3.64}
\]

Using the variances calculated by (3.62), we can find the covariance of \( \zeta_1 \) and \( \zeta_2 \) from (3.64).

A 95% confidence interval for parameter \( \zeta \), can also be obtained by,

\[
\zeta_{i0} \pm 1.96 \sqrt{Var(\zeta_i)} \tag{3.65}
\]

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In using (3.65), we have assumed a Normal distribution for the estimated value of parameter $\xi_\nu$ [83]. Finally by the same analysis as above, we can obtain the variance for the estimated average velocity from (3.42),

$$\text{Var}(\langle v \rangle) = \langle v \rangle^2 \text{Var}(\nu_0) + \langle v \rangle^2 \text{Var}(\sigma) + 2 \langle v \rangle \nu_0 \langle v \rangle \sigma \text{Cov}(\nu_0, \sigma) \quad (3.66)$$

with $\langle v \rangle_{\nu_0} = \frac{\partial \langle v \rangle}{\partial \nu_0}$, $\langle v \rangle_{\sigma} = \frac{\partial \langle v \rangle}{\partial \sigma}$. And for average mobility from (3.43),

$$\text{Var}(\langle \mu \rangle) = \text{Var}(\langle v \rangle) / E^2 \quad (3.67)$$

3.6 Summary

After assuming a velocity distribution for the drifting charges, I have found a stochastic solution for the differential equation describing the dynamics of TOF photocurrent. I have also developed a random walk and diffusion model for the drifting charges. The model gives a Gaussian velocity distribution under semi-infinite boundary conditions. However, the stochastic model with Gaussian velocity gives us a slowly converged solution. Finally I have also prepared the statistical foundation for comparing the stochastic model with experimental measurement in next chapter.
CHAPTER 4

DATA FITTINGS AND APPLICATIONS OF MODEL-2

4.1 Introduction

After having established the stochastic model in chapter 3, we are left in this chapter to compare the model with experimental measurements. The task is to choose best-fitted values for parameters \( \tau, \sigma_0, v_0 \) and \( q_0 \) using a program (appendix A), and then compute the photocurrent. We can then qualitatively compare the shape of the computed curve with that of the measured, or quantitatively we can calculate the indicator \( R^2 \) to test how the model fits the data.

In this chapter I will first do a simulation choosing simple values for the parameters, then fit the data for TPD and PVK by our stochastic model, and finally I will apply this model to study the mobilities of TPD under different electric fields and temperatures and of PVK under different fields.

4.2 Evidences for Model-2

4.2.1 Simulations

Fig. 4.1 is the calculated current with parameters \( \tau = 2, \sigma_0 = 0.4, v_0 = 1, q_0 = 1 \) and \( d = 1 \). The shape of the calculated current is very similar to our measurements (see Fig 2.3). In the simulation of Fig. 4.2, I have decreased the characteristic time \( \tau \) to 0.01, the
Fig 4.1 Simulated current with parameters

\( q_0 = 1, d = 1, v_0 = 1, \sigma_0 = 0.4, \tau = 2.0 \)

Fig 4.2 Simulated current with parameters

\( q_0 = 1, d = 1, v_0 = 1, \sigma_0 = 0.4, \tau = 0.01 \)
calculated current displays a configuration that decreases very fast at first, but then forms a plateau before it finally decreases steadily, exactly as the classical TOF model predicts and the photocurrent of the non-dispersive materials behaves[84-85]. Our simulation should have cleared the ambiguity that even the non-dispersive materials show a photocurrent similar to Fig.4.1. Fig.4.4 simulates the transition from Fig.4.1 to Fig.4.2 by choosing $\tau=0.05$. As $\tau$ becomes smaller, the calculated photocurrent increases more rapidly near the origin, and a plateau begins to form after the original peak.
But we are more interested to the distinction between dispersive and non-dispersive transports. I have made a third simulation in Fig 4.4 keeping $\tau$ to be 0.01, but increasing $\sigma_0$ to 0.7. The simulated photocurrent is very similar to the results of the so-called dispersive materials[86-87]. Although the characteristic time is still very small, the plateau of the photocurrent disappears after I have increased of the width of the Gaussian.

![Graph showing simulated current with parameters](image)

**Fig 4.4 Simulated current with parameters**

$q_0 = 1, d = 1, v_0 = 1, \sigma_0 = 0.7, \tau = 0.01$

My simulations show that the disappearance of the plateau is a continuous process, which means there does not exist a clear-cut boundary between dispersive and non-dispersive transport.
4.2.2 Data Fitting for TPD

The circles in Fig. 4.5 is the measured photocurrent for devices ITO/Se(30nm)/TPD(2.0µm)/Al(100nm) at temperature 300K and field $1.0 \times 10^5 \text{V/cm}$. By using the data fitting method described in chapter 3.5 and program 3.1, I have obtained the following best-fitted values for the parameters,

$$\tau = 4.38 \mu s, \sigma_0 = 0.22 m/s, v_0 = 0.722 m/s, q_0 = 877.6 pC$$  \hspace{1cm} (4.1)

Fig 4.5 Measured (○) and simulated (—) photocurrents for TPD at 300K and field $1.0 \times 10^5 \text{V/cm}$. 

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and \( SSE = 725.8 \). The solid line in Fig.4.3 is the calculated current using formula (3.53) and the above parameters. The shape of the calculated current fits very well to that of the measured. The calculated \( R^2 \) equals to 1.021, which further proves the effectiveness of our model in fitting TPD photocurrent.

By using the method in chapter 3.5, I have also found the standard deviations and some of the covariances,

\[
\begin{align*}
std(\tau) &= 0.226, \quad std(\sigma_0) = 0.14, \quad std(v_0) = 0.044, \quad std(q_0) = 28.6 \\
\text{cov}(v_0, \sigma_0) &= -0.00046 \quad \text{or} \quad \rho(v_0, \sigma_0) = -0.24
\end{align*}
\]

Then the 95% confidence intervals for these parameters are (using relation (3.65)),

\[
\begin{align*}
\tau &= 4.38 \pm 0.44 \mu s \\
\sigma_0 &= 0.22 \pm 0.27 \, m/s \\
v_0 &= 0.72 \pm 0.09 \, m/s \\
q_0 &= 877.6 \pm 56.1 \, \mu C
\end{align*}
\]

And finally using the fitted values for parameters \( \sigma_0 \) and \( v_0 \), I have calculated the average velocity and average mobility as,

\[
\begin{align*}
< v > &= 0.72 \pm 0.09 \, m/s \\
< \mu > &= (7.2 \pm 0.9) \times 10^{-4} \, cm^2/\text{Vs}
\end{align*}
\]

The mobility is similar to the study by Pai et al [88]. It should be noticed that the approximation method developed in chapter 3 to calculate covariances has some problem (see discussion in Epilogue).

### 4.2.3 Data Fitting for PVK
The device configuration is ITO/PVK(0.5μm)/Se(10nm)/Al(130nm). The TOF photocurrent measured at room temperature and field $7.0 \times 10^5 \text{V/cm}$ is plotted in Fig.4.6. The calculated photocurrent based on best-fitted parameters is also plotted in Fig.4.6. The calculation fits the measurement very well, and the $R^2$ value is 1.036.

The best-fitted parameters are,

$$\tau = 16.0 \mu s, \sigma_0 = 0.112 m/s, v_0 = 0.114 m/s, q_0 = 528.3 \text{pC}$$

(4.5)

And the standard deviations are,

$$std(\tau) = 1.8, \text{ std}(\sigma_0) = 0.081, \text{ std}(v_0) = 0.032, \text{ std}(q_0) = 40.0$$

$$\text{cov}(\sigma_0, v_0) = 0.000786, \text{ or } \rho(\sigma_0, v_0) = 0.303$$

(4.6)

Again, the covariance is questionable.

Fig.4.6 Measured (○) and simulated (—) photocurrent by model-2 for PVK at room temperature and field $7.0 \times 10^5 \text{V/cm}$. 
The 95% confidence intervals for the parameters are,

\[ \tau = 16.0 \pm 3.5 \mu s \]
\[ \sigma_0 = 0.112 \pm 0.159 \text{m/s} \]
\[ \nu_0 = 0.114 \pm 0.063 \text{m/s} \]
\[ q_0 = 528.3 \pm 78.4 \text{pC} \]  

(4.7)

And finally the average velocity and average mobility are calculated as,

\[ < \nu > = 0.115 \pm 0.063 \text{m/s} \]  

(4.8a)

\[ < \mu > = (1.64 \pm 0.9) \times 10^{-5} \text{cm}^2/\text{Vs} \]  

(4.8b)

Again, the mobility is in agree with early study[89,90].

The fittings of many other data for TPD and PVK show that the stochastic model developed in chapter 3 is appropriate to describe the TOF photocurrent for these two materials. Another interesting conclusion is that it's not necessary to distinguish between dispersive and non-dispersive transport. TPD is usually classified as non-dispersive material, whereas PVK is described as dispersive. But our data fittings show that the transport in both materials can be well described by a Gaussian velocity distribution, except that the center is much larger than the width for TPD. This point has also been supported by our simulation. Of course the uniqueness of velocity distribution does not testify the uniqueness of the fundamental transport mechanism.

4.3 Applications of Model-2 to TPD

4.3.1 Parameters as a Function of Field and Temperature

There are four parameters in the stochastic model: \( \tau, \sigma_0, \nu_0, \) and \( q_0. \) \( \tau = RC \) the circuit characteristic time should be a constant as long as the sample and resistor are
chosen. $\sigma_0$ and $v_0$ describe the deviation and center of the velocity distribution. We should expect them to change as a function field and temperature, for the jumping probability and waiting should depend on field and temperature. The amount of charge separated by the external electric field, $q_0$, is related to the strength of laser, electric field, temperature and the properties of materials used to produce exitons.

As $q_0$ equals the time integral of photocurrent, the fitted value can be used as an indicator by comparing it with the integral. For the TPD photocurrent studied in 4.2.2, the integral is 874.4 $\mu$C, very close to the fitted value 877.6 $\mu$C. For the PVK example in 4.2.3, the integral equals to 521.3 $\mu$C, again very close to the fitted value 528.3 $\mu$C.

Fig.4.7 is of characteristic time $\tau$ as a function of field and temperature. The values

![Graph showing characteristic time $\tau$ as a function of electric field and temperature.](image)

Fig.4.7 The characteristic time $\tau$ as a function of field and temperature.
Fig 4.8 $\sigma_0$ as a function of (a) electric field and (b) temperature
of τ is almost a constant around 4.2μs. This is another evidence that the stochastic model is appropriate to describe the TOF measurements.

Fig.4.8 (a) and (b) are plots for fitted σ₀ vs. electric field and temperature, respectively. σ₀ is in the range [0.1, 0.3], and does not change much as field or temperature changes. An exception is at T=320K, σ₀ all tend to be small. Whether such phenomenon is common at high temperature needs further investigation.

Unlike σ₀, v₀ is much more sensitive to both electric field and temperature. Fig.4.9 and 4.10 shows v₀ change as a function of field and temperature. At high temperature

Fig.4.9 v₀ as a function of field at high temperatures
(Fig. 4.8), $v_0$ increases as field or temperature increases, but at low temperature (Fig. 4.9), it seems that $v_0$ increases as field increases, but is independent of the change of temperature. The last point is especially interesting. We will come back to this later when we discuss mobility.

Fig. 4.10 $v_0$ as a function of field at low temperatures
4.3.2 Field and Temperature Dependent Mobility

The dependence of mobility on electric field is most described by the Poole-Frenkel relation (1.1). Fig 4.11 and 4.12 is the plot of field dependence mobility for TPD under several temperatures. The mobilities calculated by our method have well replicated early measurements[88]. In the short range of field, the Poole-Frenkel relation holds well.

Fig.4.11. Field dependence of hole mobility in TPD at various temperatures plotted in linear scale.
Fig 4.12 Field dependence of hole mobility in TPD at various temperatures plotted in $E^{1/2} \sim \ln \mu$ relation.

Fig 4.13 is the temperature dependence of mobility for TPD at electric field $2.0 \times 10^5$ V/cm. At low temperatures ($<200$K), the mobility is independent of temperature, but at high temperature the mobility increases as temperature increases. We note that there may exist a derivation between the measured temperature and the actual temperature of the sample. The phenomenon of independence of mobility on temperature at low temperatures has been reported in other studies[91,92] of AlGaN/GaN and sexithiophene(6T). A possible explanation is that, at low temperatures the interaction of electron-phonon is negligible, and quantum tunneling becomes the dominant mechanism for electron hopping. Another phenomenon in our study is that, the mobility is less sensitive to temperature at high temperatures when compared to an early study[88]. The
reason that is our method measures the average mobility, including those originating from temperature-independent quantum tunneling.

![Graph showing temperature-dependent hole mobility](image)

**Fig 4.13 Temperature dependent of TPD hole mobility**

### 4.4 Applications of Model-2 to PVK

Fig 4.14 plots the 95% confidence intervals for the best-fitted values of characteristic time $\tau$. Unlike the constant value for TPD, those for PVK have much larger variations. But from the 95% confidence intervals, we can still claim that $\tau$ is a constant (about 13 $\mu$s) for all the electric fields. From Fig 4.13, it seems that the variation of $\tau$ tends to be larger at low field, smaller at higher field, this is because at low field, the small values for $\sigma_0$ and $v_0$ make the calculated photocurrent less sensitive to the values of $\tau$. 

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Fig 4.14 95% CI of characteristic time $\tau$ as a function of field for PVK

Fig 4.15 is the field dependence of $\sigma_0$ and $\nu_0$. Similar to the case of TPD, it seems that the values of $\nu_0$ tends to increase linearly as field increases. But unlike those for TPD, the fitted values for $\sigma_0$ also tend to increase. Another significant difference is that the fitted values for $\sigma_0$ and $\nu_0$ are very close, whereas in TPD $\nu_0$ is much larger than $\sigma_0$. This means the Gaussian wave packet is much narrower for TPD than for PVK. This could be due to the higher disorder in PVK. I didn’t show the error bars for both $\sigma_0$ and $\nu_0$, as I mentioned earlier in this chapter that the approximation method to find variance and covariance matrix needs to be improved.
Finally, the field-dependent mobility is plotted in Fig 4.16. The average mobility of PVK is almost independent of electric field. This is different from other studies[89,90]. In our early studies, we have found that the mobility of PVK is closely related to the quality (e.g., purity and molecular weight) of PVK. The magnitude, however, is consistent with other studies.
Fig 4.16 Field dependent mobility for PVK at room temperature.

4.5 Summary

Simulations show that our stochastic model can replicate all types of photocurrent observed in TOF experiments. The results show that it may not be necessary to distinguish dispersive and non-dispersive transports. The model has also successfully fitted the experimental data for the so-called non-dispersive organic TPD and dispersive polymer PVK. The fitted parameters display some interesting features. Finally, we have applied the model to study the field and temperature dependent mobility for TPD and
field dependent mobility for PVK. The results agree with early studies. Our stochastic model should be a valid and powerful method to study the mobilities for organic and polymer semiconducting materials.
CHAPTER 5

NOISE ANALYSIS IN DIFFERENTIATION

5.1 Introduction

In chapter 2, I have developed a new technique to obtain the transit time from the photocurrent (Fig 5.1) measured by the Time-Of-Flight experiment. By this technique,
we need to calculate the first order differentiation of the photo current with respect to time. But because of the effect of noise, the accuracy of the numerical differentiation is limited. In this chapter, I have developed some numerical techniques to reduce the effect of noise. Although this part of work may be accomplished by any amateur mathematician, I put it here as an independent chapter because it's useful for calculating the differential current in chapter 2 and it's too long for an appendix.

Some notations used in this chapter:

\( i(t) \): photocurrent, the function needed to calculate first order differentiation numerically;

\( i(t)' \): actual first order derivative of \( i(t) \);

\( \hat{i}(t)' \) or \( \hat{i}' \): approximation of \( i(t)' \).

Other notations will be explained in the text.

5.2 Approximation by Taylor Expansion

The classical approach to compute the differentiation of a function numerically is to use Taylor expansion. Suppose that the current values are evenly spaced with a time interval \( \delta \) determined by the precision of instrument, and also assume that Taylor expansion is valid, then

\[
i(t + \delta) = i(t) + i(t)' \delta + \frac{i(t)'' \delta^2}{2!} + \frac{i(t)''' \delta^3}{3!} + ... \tag{5.1}
\]

where \( i(t)'\) is the m\(^{th}\) order of derivative of \( i(t) \). The so-called forward difference approximation of the first order derivative is,

\[
\hat{i}(t) = \frac{i(t + \delta) - i(t)}{\delta} \tag{5.2}
\]
From (4.1) we know the leading error of this approximation is in the order of $\delta$. The first order derivative of $i(t)$ calculated by this forward difference approximation is plotted in Fig 5.2, in which the noise dominates. Therefore we have to look for other ways to reduce the influence of noise.

![Differential current approximated by forward difference approximation (formula 2) from a software KaleidaGraph 3.0. (Inset: full scale for $i(t)$).](image)

Fig. 5.2: Differential current approximated by forward difference approximation (formula 2) from a software KaleidaGraph 3.0. (Inset: full scale for $i(t)$).
A better approximation of \( i(t)' \) is to subtract \( i(t - \delta) \) from \( i(t + \delta) \) to eliminate the \( \delta \) term, so that the error is in the order of \( \delta^2 \). The formula is,

\[
    i(t)' = \frac{i(t + \delta) - i(t - \delta)}{2\delta} - \frac{i(t)^{(3)}\delta^2}{6} + ... \tag{5.3}
\]

or we can use \( i(t + 2\delta) \) and \( i(t - 2\delta) \) to approximate \( i(t)' \),

\[
    i(t)' = \frac{i(t + 2\delta) - i(t - 2\delta)}{4\delta} - \frac{4i(t)^{(3)}\delta^2}{6} + ... \tag{5.4}
\]

Approximation by equation (5.3) or (5.4) gives an error in the order of \( \delta^2 \) and is usually called central difference approximation. Actually, any linear combination of equation (5.3) and (5.4) also gives an approximation for \( i(t)' \) and an error in the order of \( \delta^2 \). Let \( (3) + a \times (4) \), with \( a \) some constant, then

\[
    i(t)' = \frac{2i_1 + ai_2 - 2i_{-1} - ai_{-2}}{4(1 + a)\delta} - \frac{1 + 4a}{6(1 + a)}i(t)^{(3)}\delta^2 + ... \tag{5.5}
\]

where \( i_1 \) is \( i(t + \delta) \), \( i_{-1} \) is \( i(t - \delta) \), \( i_2 \) is \( i(t + 2\delta) \), and \( i_{-2} \) is \( i(t - 2\delta) \). If we neglect the error term \( 0(\delta^2) \), we have an approximation for \( i(t)' \),

\[
    i(t)' = \frac{2i_1 + ai_2 - 2i_{-1} - ai_{-2}}{4(1 + a)\delta} \tag{5.6}
\]

Because the approximation by equation (5.6) involves 4 neighboring points of \( i(t) \), we call it 5-point-difference approximation. In next part we will use statistical methods to determine a value for \( a \) which minimizes the effect of noise.
5.3 Random noise model and its application to 5-point-difference differentiation

Suppose at any time $t$, the current $i(t)$ is composed of two parts: the real current from the circuit, and the random noise:

$$i(t) = i_0(t) + \varepsilon$$

(5.7)

where $i_0(t)$ is the real current, and $\varepsilon$ is the noise which is a random variable. In our model, the random noise is independent of time. The noise usually originates from the electromagnetic waves in the environment and obeys statistical rules. We assume that the noises for all different photocurrent points are independent of each other and identically distributed, and that the mean of the noise is zero and the standard deviation is $\sigma$. $\sigma$ is some unknown constant determined by the measurement instrument. By statistical theory, $i(t)$ itself is a random variable with standard deviation $\sigma$ and mean $i_0(t)$. If we want to use formula (5.6) to approximate the first order derivative of $i(t)$, the standard method to reduce the error is to minimize the so-called Mean Squared Error (MSE). From statistical theory,

$$MSE(i') = \text{variance}(i') + \text{bias}^2$$

(5.8)

where $\text{bias} = \hat{i}(t)' - i(t)'$, is the difference between the actual value and the approximation of the first order derivative of $i(t)$. As it is difficult to estimate the bias term, in this chapter we have developed some numerical theory dealing with the case when the square of bias is much smaller than the variance in (5.8). Then we will minimize the variance instead of the MSE.

The variance of $\hat{i}(t)'$ in (5.6) is,
\[
\text{var}(\hat{i}(t)) = \frac{4 + a^2}{8(1 + a)^2} \frac{\sigma^2}{\delta^2}
\] (5.9)

It’s easy to show that when \( a = 4 \) var(\( \hat{i}(t) \)) is minimum,

\[
\min(\text{var}(\hat{i}(t))) = \frac{1}{10} \frac{\sigma^2}{\delta^2}
\] (5.10)

Otherwise, if \( i(t) \) is approximated by (5.2), \( \text{var}(\hat{i}(t)) = 2\sigma^2/\delta^2 \); or if \( i(t) \) is approximated by the first term in (5.3), \( \text{var}(\hat{i}(t)) = \sigma^2/(2\delta^2) \); or by the first term in (5.4), \( \text{var}(\hat{i}(t)) = \sigma^2/(8\delta^2) \). It’s obvious that different approximations not only have different errors, but the variance is also significantly different.

### 5.4 Generalization with \((2n + 1)\) Points

In part 2, we have obtained an optimized approximation for \( i(t) \) by using 4 neighboring points of \( i(t) \) with a method of minimizing the variance. In this part, we are going to derive some general formulae by extending to the \((2n)\) symmetric neighboring points of \( i(t) \). The idea is the same as that in part 2. We will use \( n \) pairs of difference to approximate \( i(t) \), combine them linearly and find the optimized combination by minimizing the variance of the linear combination.

Suppose now we want to use the \( 2n \) neighboring points to calculate \( i(t) \) by central difference approximation (assume that \( n\delta \) is still a small quantity). A graphic demonstration of the \( 2n \) points is shown in Fig 5.3. For convenience, we denote \( i(t + \delta) \) as \( i_1 \), \( i(t - \delta) \) as \( i_{-1} \), \( i(t + 2\delta) \) as \( i_2 \),... and so on.
Then by Taylor expansion we have \( n \) pairs of approximations for \( i(t) \) with the errors in the order of \( \delta^2 \),

\[
i(t) = \frac{d_1}{2\delta} - \frac{i(t)^{(3)} \delta^2}{6} + \ldots \\
i(t) = \frac{d_2}{4\delta} - \frac{4i(t)^{(3)} \delta^2}{6} + \ldots \\
\ldots
\]

\[
i(t) = \frac{d_n}{2n\delta} - \frac{n^2i(t)^{(3)} \delta^2}{6} + \ldots
\]  

(5.11.n)

with \( d_1 = i_1 - i_{-1}, \ d_2 = i_2 - i_{-2}, \ldots \ d_n = i_n - i_{-n} \).
By the random noise model, all the \( i_k \)'s are each composed of a time dependent term and a random noise term. The noise terms are independent of each other and identically distributed, as the case in part 2. We use a linear combination of the \( n \) \( i(t) \) in equation (5.11). Multiply (5.11.1) by 1, (5.11.2) by \( a_2 \), ..., (5.11.n) by \( a_n \), with \( a_2,a_3,...,a_n \) some parameters to be determined, then add together,

\[
i(t)' = \frac{1}{1 + a_2 + ... + a_n} \left\{ \frac{d_1}{2\delta} + a_2 \frac{d_2}{4\delta} + ... + a_n \frac{d_n}{2n\delta} \right\} - \frac{i(t)^{3\delta^2}}{6(1 + a_2 + ... + a_n)} \left\{ 1 + 4a_2 + ... + n^2a_n \right\} + ...
\]

(5.12)

If we ignore the terms \( 0(\delta^2) \), then \( i(t)' \) is approximated by

\[
i(t) = \frac{1}{1 + a_2 + ... + a_n} \left\{ \frac{d_1}{2\delta} + a_2 \frac{d_2}{4\delta} + ... + a_n \frac{d_n}{2n\delta} \right\}
\]

(5.13)

with truncation error

\[
Error = \frac{i(t)^{3\delta^2}}{6(1 + a_2 + ... + a_n)} \left\{ 1 + 4a_2 + ... + n^2a_n \right\} + ...
\]

(5.14)

The variance of \( i(t)' \) in equation (5.12) is

\[
\text{var}(i(t)') = \frac{\sigma^2}{(1 + a_2 + ... + a_n)^2} \left\{ \frac{2}{4\delta^2} + \frac{2a_2^2}{16\delta^2} + ... + \frac{2a_n^2}{4n^2\delta^2} \right\}
\]

\[
+ \frac{\sigma^2/\delta^2}{2(1 + a_2 + ... + a_n)^2} \left\{ 1 + \frac{a_2^2}{2^2} + ... + \frac{a_n^2}{n^2} \right\}
\]

(5.15)

To minimize \( \text{var}(i(t)') \), we take the first order derivatives of \( \text{var}(i(t)') \) with respect to the parameters \( a_2,a_3,...,a_n \) and set the derivatives equal to zero. Generally,

\[
\frac{\partial}{\partial a_k} \text{var}(i(t)') = \frac{\sigma^2/\delta^2}{2(1 + a_2 + ... + a_n)^2} \left\{ \frac{2a_k}{k^2} \right\} - \frac{(1 + \frac{a_2^2}{2^2} + ... + \frac{a_n^2}{n^2}) \sigma^2}{(1 + a_2 + ... + a_n)^3 \delta^2} = 0
\]

(5.16)
where $k$ equals to $2, 3, \ldots, n$. Equation (5.16) is actually $(n-1)$ equations with $(n-1)$ variables $a_2, a_3, \ldots, a_n$. It's obvious that all the terms $a_k/k^2$, $(k = 2, \ldots, n)$ in equation (5.16) are equal to each other. Let $a_k/k^2 = c$, $k = 2, \ldots, n$, then it's easy to show that the $(n-1)$ variables in equation (5.16) have unique solution,

\begin{align*}
 a_2 &= 2^2 \\
 a_3 &= 3^2 \\
 \vdots \\
 a_n &= n^2
\end{align*}

(5.17)

By taking the second order derivatives of $\text{var}(\hat{i}(t))$, one can show that when the $a_k$'s take the above values, the variance of $\hat{i}(t)$ is minimum, which is

\[
\text{min}(\text{var}(\hat{i}(t))) = \frac{1}{2(1+2^2+\ldots+n^2)} \frac{\sigma^2}{\delta^2} = \frac{3}{n(n+1)(2n+1)} \frac{\sigma^2}{\delta^2}
\]

(5.18)

then $i(t)$ is approximated by

\[
\hat{i}(t) = \frac{d_1 + 2d_2 + \ldots + nd_n}{2\delta(1+2^2+\ldots+n^2)}
\]

(5.19)

and the leading error $\delta^2$ term,

\[
\text{Error}_{(i)} = \frac{-i(t)^{(3)} \delta^2}{6} \frac{1+2^4+\ldots+n^4}{1+2^2+\ldots+n^2}
\]

(5.20)

From equation (5.18) and (5.20) we find that if we want to reduce the variance we would use larger $n$, however, as $n$ gets larger, the leading error will also tend to be larger. In practice, we have to compromise and try out some value for $n$ to satisfy our goal best.
Table 5.1 lists some values for $n$ and the variances and leading errors as well. Fig 5.4 is the $i(t)'\sim t$ plot with different values of $n$ and Fig 5.5 shows the difference between $n=3$ and $n=9$.

<table>
<thead>
<tr>
<th>$n$</th>
<th>Variance $\sigma^2 / \delta^2$</th>
<th>Error $(-i(t)^{(3)} \delta^2 / 6)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\frac{1}{2}$</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>$\frac{1}{10}$</td>
<td>$\frac{17}{5}$</td>
</tr>
<tr>
<td>3</td>
<td>$\frac{1}{28}$</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>$\frac{1}{60}$</td>
<td>$\frac{59}{5}$</td>
</tr>
<tr>
<td>5</td>
<td>$\frac{1}{110}$</td>
<td>$\frac{89}{5}$</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>9</td>
<td>$\frac{1}{570}$</td>
<td>$\frac{269}{5}$</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>
Fig 5.5 Differential current for $n = 3, 9$ and their difference (Inset: full scale).

5.5 An Alternative Derivation

Actually, we can derive the above formulae in a more general method. In this part we are going to show that by linearly combining $i(t)$ and its $(2n)$ neighboring points instead of the $n$ pair differences in part 3, we can still obtain the same optimized linear combination as that in part 3.

Suppose that again we want to use the $(2n+1)$ points $i(t-n\delta), i(t-(n-1)\delta), ..., i(t+n\delta)$ to approximate $i(t)$. Taylor expansions for $i_k = i(t + k\delta), \ k = -n, -n+1, ..., n \ (k \neq 0)$ are,

$$i_k = i(t) + k\delta i + \frac{k^2\delta^2 i^{(2)}}{2} + \frac{k^3\delta^3 i^{(3)}}{6} + ...$$ (5.21)
A linear combination of the \( 2n \) equations is,

\[
\sum_{k=0}^{n} b_k i_k = i(t) \sum_{k=0}^{n} b_k + \delta i \sum_{k=0}^{n} k b_k + \frac{\delta^2 i^{(2)}}{2} \sum_{k=0}^{n} k^2 b_k + \frac{\delta^3 i^{(3)}}{6} \sum_{k=0}^{n} k^3 b_k + \ldots \tag{5.22}
\]

or

\[
i = \frac{1}{\delta} \left( \sum_{k=0}^{n} b_k i_k - i(t) \sum_{k=0}^{n} b_k - \frac{\delta i^{(2)}}{2} \sum_{k=0}^{n} k^2 b_k - \frac{\delta^2 i^{(3)}}{6} \sum_{k=0}^{n} k^3 b_k + \ldots \right) \sum_{k=0}^{n} k b_k \tag{5.23}
\]

where \( b_{-n}, b_{-n+1}, \ldots, b_n \) are \( 2n \) parameters to be determined.

We want the coefficient of the leading error term (\( \delta \)) in (5.23) to be zero, that is

\[
\sum_{k=0}^{n} k^2 b_k = 0 \tag{5.24}
\]

Then \( i(t) \) is approximated by,

\[
\hat{i} = \frac{\sum_{k=0}^{n} b_k i_k - i(t) \sum_{k=0}^{n} b_k}{\delta \sum_{k=0}^{n} k b_k} \tag{5.25}
\]

with the leading error term,

\[
Error(t) = -\frac{\delta^2 i^{(3)}}{6} \sum_{k=0}^{n} k^3 b_k \tag{5.26}
\]

The variance of \( i(t) \) in equation (5.25) is,

\[
\text{var}(\hat{i}) = \frac{\sigma^2 \sum_{k=0}^{n} b_k^2 + (\sum_{k=0}^{n} b_k)^2}{\delta^2 \left( \sum_{k=0}^{n} k b_k \right)^2} \tag{5.27}
\]

To minimize \( \text{var}(\hat{i}) \), take the first order derivatives with respect to all the \( b_k \)'s and then set to zero, then
\[
\frac{\partial}{\partial b_i} \text{var} (\hat{i}) = \frac{2b_i + 2\sum_{k=0}^{l} b_k \sigma^2}{(\sum_{k=0}^{l} k b_k)^2} - 2l \frac{\left[ \sum_{k=0}^{l} b_k^2 + (\sum_{k=0}^{l} b_k)^2 \right] \sigma^2}{(\sum_{k=0}^{l} k b_k)^2} = 0 \tag{5.28}
\]

with \( l = -n, -n + 1, \ldots, n \ (l \neq 0) \).

or

\[
\frac{b_i + \sum_{k=0}^{l} b_k}{l} = \frac{\left[ \sum_{k=0}^{l} b_k^2 + (\sum_{k=0}^{l} b_k)^2 \right]}{\sum_{k=0}^{l} k b_k} \tag{5.29}
\]

By letting \( c = \frac{b_i + \sum_{k=0}^{l} b_k}{l} \), with \( c \) some constant, we can show that \( b_k = c k \). Then condition (5.24) is satisfied automatically. All the parameters \( b_k \)'s have a common proportion constant \( c \). If we let \( c = 1 \), then,

\[
b_k = k \tag{5.30}
\]

with \( k = -n, -n + 1, \ldots, n \ (k \neq 0) \). Then it's straightforward to show that the coefficients of \( \hat{i} \), error, and \( \text{var} (\hat{i}) \) are the same as those in part 3.

A note here is that we have used the \( (2n) \) symmetrical neighboring points of \( i(t) \), that is, \( n \) points in the left, and the other \( n \) points in the right side. Otherwise, we can't obtain those simple formulae.

### 5.6 The Role of \( \delta \)

From equations (5.18) and (5.20) we find that the value of the smallest time interval \( \delta \) plays an essential role in both calculating the variance of the differential current and evaluating the error of the approximation. The smaller \( \delta \), the smaller the absolute value...
of the error but the larger the variance; on the other hand, the larger \( \delta \) the smaller the variance but the larger the absolute value of the error. So we would naturally tend to choose some medium value for \( \delta \). But we will show that if we fix the time interval to calculate the differentiation of each point, it turns out that the smaller \( \delta \), the better (i.e. the smaller both the variance and the absolute value of the error).

Suppose that we fix the time interval \( 2n\delta \) to calculate the differentiation, say, let

\[
\Delta t = 2n\delta \tag{5.31}
\]

where \( \Delta t \) is some constant. We would expect small value of \( \Delta t \) for the validity of Taylor expansion. Plugging equation (5.31) into (5.18) and (5.20), we have the variance,

\[
\min(\text{var}(\hat{r}(t))) = \frac{3 \sigma^2}{n(n+1)(2n+1)^2 \delta^2} = \frac{12 \sigma^2}{\Delta t^2 \left( \frac{n}{2n^2 + 3n + 1} \right)} \tag{5.32}
\]

and the leading error,

\[
\text{Error}_{(t)} = -\frac{-i(t)^{(3)} \delta^2}{6} \frac{3n(n+1)-1}{5} = -\frac{-i(t)^{(3)} \Delta t^2}{120} \left( 3 + \frac{3}{n} - \frac{1}{n^2} \right) \tag{5.33}
\]

To evaluate equation (5.32) and (5.33), we define two functions,

\[
f_1(x) = \frac{x}{2x^2 + 3x + 1} \quad \text{where} \quad x \in \mathbb{R}^+ \tag{5.34}
\]

\[
f_2(x) = 3 + \frac{3}{x} - \frac{1}{x^2}
\]

\( f_1(x) \) and \( f_2(x) \) are graphed in Fig 5.6, from which we find that \( f_1(x) \) is maximized at \( x = \sqrt{2}/2 \) and goes to zero monotonously as \( x \) approaches zero and infinite, and \( f_2(x) \) is maximized at \( x = 1/3 \), and tends to be \( -\infty \) as \( x \) approaches zero and decreases to 3.
monotonously as \( x \) approaches infinity. If we replace the continuous variable \( x \) by the integer variable \( n \), then it's obvious that the larger \( n \), the smaller the variance and the absolute value of the error. From equation (5.31), larger \( n \) implies smaller \( \delta \). Therefore, we obtain our conclusion that if the time interval to calculate the differentiation of each point is fixed, the smaller value of the smallest time interval will lead to smaller values for the variance and the absolute value of the leading error. This is just the common sense that higher resolution of the instrument will give us better approximation for the differential current.

Another advantage of choosing smaller \( \delta \) is that we can choose smaller time interval \( \Delta t \) to evaluate the differentiation, without increasing the variance and error. We
want small interval $\Delta t$ to evaluate the differentiation because the differentiation is determined by the "locality" and the error is proportional to this time interval. Table 5.2 lists some of the values of $\delta$, $n$, and the corresponding values of $\Delta t$, variance and error.

<table>
<thead>
<tr>
<th></th>
<th>$\delta$</th>
<th>$n$</th>
<th>$\Delta t = 2$</th>
<th>min(var)</th>
<th>$\text{Error}_{(t)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.4</td>
<td>5</td>
<td>4.0</td>
<td>0.0568$\sigma^2$</td>
<td>$-0.475i(t)^3$</td>
</tr>
<tr>
<td>2</td>
<td>0.4</td>
<td>3</td>
<td>2.4</td>
<td>0.223$\sigma^2$</td>
<td>$-0.187i(t)^3$</td>
</tr>
<tr>
<td>3</td>
<td>0.04</td>
<td>25</td>
<td>2.0</td>
<td>0.0566$\sigma^2$</td>
<td>$-0.104i(t)^3$</td>
</tr>
<tr>
<td>4</td>
<td>0.04</td>
<td>20</td>
<td>1.6</td>
<td>0.109$\sigma^2$</td>
<td>$-0.067i(t)^3$</td>
</tr>
<tr>
<td>5</td>
<td>0.04</td>
<td>15</td>
<td>1.2</td>
<td>0.252$\sigma^2$</td>
<td>$-0.0383i(t)^3$</td>
</tr>
</tbody>
</table>

As the last part of the analysis of the role of $\delta$, we will find a relationship between $\delta$ and the higher orders of the error in equation (5.14) we had neglected when computing the leading error. All the error terms in equation (5.14) can be expressed as,

$$\text{Error}_{(m)} = \frac{-i(t)^{2m+1} \delta^{2m}}{(2m+1)!} \frac{1 + 2^{2m+2} + \ldots + n^{2m+2}}{1 + 2^2 + \ldots + n^2} \quad (5.35)$$

with $m = 1, 2, 3, \ldots$. $\text{Error}_{(m)}$ is the error term with order $\delta^{2m}$ and we call it the $m$th error term. For large $n$,

$$\frac{1 + 2^{2m+2} + \ldots + n^{2m+2}}{1 + 2^2 + \ldots + n^2} = c_m \frac{n^{2m+3}}{n^3} = c_m n^{2m} \quad (5.36)$$

where $c_m$ is a function of $m$ and can be calculated. Then, combined with equation (5.31),
The $m$th error term $\text{Error}_m$ is proportional to $\Delta t^m$.

From the results in this part it seems that the smaller $\delta$ the better. But the smallest value of $\delta$ we can use is determined by the resolution of the instrument, and a problem is that if $\delta$ is too small, the independent random noise assumption we have made in part 2 may not hold anymore.

5.7 The relationship to polynomial curve fit

The standard method to calculate the numerical differentiation is to fit (or smooth) the curve by polynomial approximation, then the differentiation can be obtained from the coefficients of the polynomial approximation. In this chapter we will analyze the relationship of our variance minimization method and polynomial curve fit. We have found that the variance minimization method is actually equivalent to the linear polynomial approximation.

By polynomial approximation, the photocurrent $i(t)$ at the vicinity of $t_0$ can be approximated by the polynomial,

$$i(t) = a_0 + a_1(t - t_0) + a_2(t - t_0)^2 + ... + a_k(t - t_0)^k$$  \hspace{1cm} (5.38)

with $a_0, a_1, ... a_k$ some parameters to be determined. Equation (5.38) is a $k$th order polynomial approximation. Then the coefficient $a_1$ is the approximation of the first order
derivative of \( i(t) \) at \( t = t_0 \), and higher order differentiations can also be approximated by higher order coefficients.

Suppose again that we want to use the symmetric \((2n)\) points of \( i(t) \) to approximate the numerical differentiation. A standard way to determine the coefficients in equation (5.38) is to minimize the MSE,

\[
MSE = \sum_{i=-n}^{n} (i_i - i)^2
\]

To minimize \( MSE \), take the first order derivative with respect to the parameters and set to zero, then

\[
\frac{\partial}{\partial a_m} MSE = \sum_{i=-n}^{n} 2[a_0 + a_1(l\delta) + \ldots + a_k(l\delta)^k - i_i](l\delta)^m = 0 \tag{5.40}
\]

Equation (5.40) is composed of \( k \) linear equations with \( k \) unknowns. A lot of textbooks have solution for these linear equations. We will only focus on the cases of \( k = 1 \) and 2. First, if \( k = 1 \), from equation (5.38) the polynomial approximation is linear, we have solution for \( a_1 \), which is,

\[
a_1 = (d_1 + 2d_2 + \ldots + nd_n)/(2\sum_{i=1}^{n} m^2) \tag{5.41}
\]

As \( a_1 \) is the approximation for the first order differentiation, we got the same answer here as our variance minimization method.
If \( k = 2 \), we have a more complicated expression for \( a_i \),

\[
a_i = \frac{\sum_{m=1}^{n} m^2 \sum_{m=1}^{n} m d_m - \sum_{m=1}^{n} m^4 \sum_{m=1}^{n} m^3 d_m}{2\delta [\sum_{m=1}^{n} m^2 \sum_{m=1}^{n} m^6 - (\sum_{m=1}^{n} m^4)^2]} \tag{5.42}
\]

If the first order differentiation is approximated by equation (5.42), the variance of the approximation is,

\[
\text{var}(a_i) = \frac{\sigma^2 \sum_{m=1}^{n} m^6}{\delta^2 [\sum_{m=1}^{n} m^2 \sum_{m=1}^{n} m^6 - (\sum_{m=1}^{n} m^4)^2]} \tag{5.43}
\]

The advantage of approximation by equation (5.42) is that the leading error is in the order of \( \delta^4 \), but with the price of a much larger variance. Table 5.3 compares the variances of \( n \) between the linear approximation by equation (5.41) and the quadratic approximation by equation (5.42) for the first order differentiation.

<table>
<thead>
<tr>
<th>( n )</th>
<th>Variance of Linear Approx. ((\sigma^2 / \delta^2))</th>
<th>Variance of Quadratic Approx. ((\sigma^2 / \delta^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>( \infty )</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>0.903</td>
</tr>
<tr>
<td>3</td>
<td>0.0357</td>
<td>0.465</td>
</tr>
<tr>
<td>4</td>
<td>0.0167</td>
<td>0.221</td>
</tr>
<tr>
<td>5</td>
<td>0.0091</td>
<td>0.119</td>
</tr>
</tbody>
</table>

Table 5.3 variances of linear and quadratic approximation

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5.8 Summary

In doing the first order numerical differentiation for TOF photocurrent, the noise plays an important role. Using more points and linearly combing them in an optimized way can dramatically decrease the effect of noise. The resolution of instrument is also key to our analysis, which shows that the better the resolution, the less the influence of the noise. Finally, we have proved that our analysis is equivalent to classic polynomial curve fitting, but our method can provide some insight to the variance.
CHAPTER 6

CONCLUSION AND SUMMARY

Time-Of-Flight is a classical method in condensed matter physics to measure carrier drift mobility in semiconducting materials. The principle is simple. By injecting a sheet of charges into a sample and measuring the induced photocurrent, one can easily find the time the charges drift through the sample, and thus calculate its mobility. The photocurrent of a crystal material displays a plateau and then decreases at the transit time. However, in the presence of strong trapping effects, the interpretation of experimental results becomes difficult. Sccher-Montroll's theory provided only limited success in these measurements. This thesis attempts to solve this problem.

First, we have derived a dynamic equation for TOF photocurrent after giving up the requirement of small characteristic time in traditional TOF. The dynamic equation shows that the measured photocurrent in TOF decays through the RC effect, but is powered by the average drift current in the sample.

The solution of the dynamic equation for a trap-free system has not only replicated the result of classical TOF, but also illuminated a special property of the differential current: a cusp at the transit time. On the basis of this result, we have proposed in our first model that the differential current display singularity at the transit time. Although experimental result of TPD agrees well with this model, results from other dispersive materials do not agree with it.
Our second model attempts to solve the dynamic equation even for the cases of strong trapping effects. First, based on the Random Walk model, I have shown that the drift charge can be described by a diffusion equation with a drift term. The drift term originates from the asymmetric jump probability. The solution of the diffusion equation can be well approximated by a Gaussian function. Finally, the photocurrent can be expressed by a double integral involving the Gaussian distribution function.

Simulations using the second model can replicate all types of photocurrent observed in TOF experiments. Our results show that the so-called non-dispersive photocurrent corresponds to a narrow Gaussian function and a small circuit characteristic time. Otherwise we should observe the dispersive photocurrent if the Gaussian is wide or a bell-shape photocurrent if the characteristic time is large.

Finally, we have shown that the second model fitted the experimental data for TPD and a semiconducting polymer PVK very well. We have also studied the field or temperature dependence of the parameters in the model. The mobilities calculated by the second model agree very well with other studies. We believe the second model is promising in studying the transporting properties of other semiconducting organics and polymers.
APPENDIX A: Fortran Program for Searching MSE

This program optimizes the four parameters in the stochastic model. The method is described in chapter 3.5. The copyright of the program is reserved by Xiaoming Zou at Physics Department of The Ohio State University in 2002.

```fortran
dimension t(400),ct(400),dct(400),ssl(400)
dimension si(-1:1,-1:1,-1:1)

d the thickness, ntot the total number of points.
ntot=246
open(07,name='t224i-2.txt')
do 15 i=1,ntot
*read time t(i) and photocurrent ct(i) from file 't224i-2.txt'.
read(07,*)t(i),ct(i)
15 continue

close(07)

*initial values: sig = i0/ssig, v0 = j0/sv0, tau = k0/stau.
write(06,*)'sig*1000, v0*1000, tau*100'
read(05,*)i0,j0,k0
write(06,*)'divisor of sig, v0, tau'
read(05,*)ssig,sv0,tau

ii=0
jj=4
kk=4

5 continue
do 55 i=-1,1
  do 55 j=-1,1
    do 55 k=-1,1
      sig=(i0+i)/ssig
      v0=(j0+j)/sv0
      tau=(k0+k)/stau
      ii=i+ii
      jj=j+jj
      kk=k+kk
      if(abs(ii).le.1.and.abs(jj).le.1.and.abs(kk).le.1)then
        si(i,j,k)=si(ii,jj,kk)
      else
        call calse(si(i,j,k),tau,d,q0,v0,sig,t,ct,iii)
      endif
    55 continue
  call findm(si,ii,jj,kk,si)
i0=i0+ii
```

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j0=j0+jj
k0=k0+kk
nn=nn+1
write(06,*)'nn ',nn
write(06,*)'i0,j0,k0 ',i0,j0,k0
write(06,*)'sij=',sij,' q0=',q0
ijk=abs(ii)+abs(jj)+abs(kk)
if(ijk.eq.0)goto 10
goto 5
continue

sig=i0/ssig
v0=j0/sv0
tau=k0/stau

ii=1
jj=1
kk=1
do 10 i=-1,1
  do 10 j=-1,1
    do 10 k=-1,1
      if (sij(i,j,k).lt.sij) then
        sij=sij(i,j,k)
        ii=i
        jj=j
        kk=k
      endif
    10 continue
return
end

* Subroutine findm is to find the minimum of the 27 elements
* in si(-1:1,-1:1,-1:1).
subroutine findm(si,ii,jj,kk,sij)
dimension si(-1:1,-1:1,-1:1)
ii=0
jj=0
kk=0

 10 continue
  return
end

* subroutine calse calculates the squared error.
subroutine calse(se,tau,d,q0,v0,sig,t,ct,iii)
dimension t(400),ct(400),ssl(400)
ntot=246
ccc=0.0
ddd=0.0

  do 10 m=1,ntot
    tt=t(m)
    if (tt.eq.0.0) then
      st1=0.0
    else
      call calcurr(st1,tt,tau,d,v0,sig)
    endif
    ssl(m)=st1
    ccc=ccc+ssl(m)*ct(m)
    ddd=ddd+ssl(m)**2

  10 continue
10 continue
   q0=ccc/ddd
   se=0.0
   do 20 m=1,ntot
      se=se+(q0*ssl(m)-ct(m))**2
20 continue
   if(iii.eq.1) then
      cta=0.0
      do 35 m=1,ntot
         cta=cta+ct(m)
   35 continue
   cta=cta/ntot
   ssr=0.0
   sst=0.0
   do 40 m=1,ntot
      sst=sst+(ct(m)-cta)**2
      ssr=ssr+(q0*ssl(m)-cta)**2
40 continue
   write(06,*)'R-square: ',ssr/sst
   open(14,name='t224i-2c.txt')
   do 30 m=1,ntot
      write(14,'(2f14.7)')t(m),q0*ssl(m)
   30 continue
endif
return
end

* Subroutine calcurr is to calculate the current based on formula (3.53),
* while tdintegral does the 2-d integral, and ssvalue calculate the
* values for H(r,s).
subroutine calcurr(curr,t,tau,d,v0,sig)
   dimension h(300,300)
   mpt=300
   pi=3.1415926
   c0=0.0
   dr=t/mpt
   ds=d/mpt
   call ssvalue(h,dr,ds,v0,sig,tau,mpt)
   call tdintegral(h,dr,ds,ss,mpt)
   curr=exp(-t/tau)*ss/(d*tau*sqrt(2*pi)*sig)
return
end

subroutine tdintegral(h,dr,ds,ss,mpt)
   dimension h(mpt,mpt)
   ss=0.0
   avr=0.0
   do 10 i=2,mpt
      do 10 j=2,mpt
         ave=(h(i,j)+h(i-1,j)+h(i,j-1)+h(i-1,j-1))/4
         ss=ss+ave*dr*ds
10 continue
return
end

subroutine ssvalue(h,dr,ds,v0,sig,tau,mpt)
   dimension h(mpt,mpt)
   do 20 i=1,mpt
      do 20 j=1,mpt

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\[ r = i \cdot dr \]
\[ s = j \cdot ds \]
\[ cc = s \cdot \exp(r/\tau)/\left(r \cdot \sqrt{r}\right) \]
\[ dd = -r \cdot (s/r-v0)^2/(2 \cdot \sigma^2) \]
\[ h(i,j) = cc \cdot \exp(dd) \]

20 continue
return
end
dimension t(500), t1(500), v(500), curr(500), curr1(500), di(500)
dimension t2(300), curr2(300), di2(300), d(15)
character*14 infil, outfile
character*9 waste(4)
parameter (amilln=1000000.0)
do 1 i=0, 300
  curr2(i)=0.0
  di2(i)=0.0
1 continue
open (11, name= 'names ')
* R is the resistance of the resistor, and m the pairs of points
* involved in calculating the numerical differentiation.
write(6, '*)'resistance in Ohms'
read(5,*)R
write(6, '*)'# of pairs involved in doing differentiation'
read(5,*)m
write(6, '*)'number of files'
read(6,*)n
* nn is the number of zero shift, i.e., when t is zero, how far
* is the point where i is zero. nn positive when zero i before t,
* otherwise negative.
write(6, '*)'number of zero shift'
read(5,*)nn
write(6, '*)'output file name'
read(5, '(a14)') outfile
* Do file by file.
do 100 k=1,n
read(11, '(a14)') infil
write(6, '(a18, i4, a10)')'input file number ', k, infil
open(07, name=infil)
do 10 i=1, 500
  read(07, *)t(i), v(i)
* Convert time to micro second, current to micro ampers.
t(i)=t(i)*amilln
curr(i)=v(i)*amilln/R
  if(t(i).eq.0.0)ii=i
10 continue
close(07)
do 20 i=ii, 500
  t1(i-ii)=t(i)
curr1(i-ii)=curr(i-nn)
20 continue
dt=t1(2)-t1(1)
nv=500-ii
* Starting to do numerical differentiation. This part is based on
* the numerical theory developed by X.M. Zou in 2000, at the Physics
* Department of The Ohio State University.

do 30 i=0,nv
   if(i.lt.m.or.i.gt.(nv-m))then
     if(i.eq.0)then
       di(i)=(curr1(i+1)-curr1(i))/dt
     else if(i.eq.nv)then
       di(i)=(curr1(i)-curr1(i-1))/dt
     else
       di(i)=0.0
     if(i.gt.(nv-m))kk=nv-i
     if(i.lt.m)kk=i
     kl=0
     do 40 j=1,kk
       kl=kl+2*j*j
       d(j)=(curr1(i+j)-curr1(i-j))/dt
       di(i)=di(i)+j*d(j)
     40 continue
     di(i)=di(i)/kl
   endif
   else
     kl=0
     di(i)=0.0
     do 70 j=1,m
       kl=kl+2*j*j
       d(j)=(curr1(i+j)-curr1(i-j))/dt
       di(i)=di(i)+j*d(j)
     70 continue
     di(i)=di(i)/kl
   endif
   curr2(i)=curr2(i)+curr1(i)
   di2(i)=di2(i)+di(i)
30 continue
100 continue

* Save the average to output file.

open(08,name=outfil)
write(6,'(a20,a20,a20,1x,3f15.7)')'Time Current Differential Current'
do 110 i=0,nv
   curr2(i)=curr2(i)/n
   di2(i)=di2(i)/n
   write(08,15)t1(i),curr2(i),di2(i)
15 format(1x,3f15.7)
110 continue
write(6,'a20,a20,a20')'calculation accomplished successfully!'
stop
end
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Partenkirch, 1974, p1015.


Epilogue

In this thesis, I have proposed two models to analyze Time-Of-Flight photocurrent. Both models are based on the same dynamic equation. As time is limited to finish this thesis, many problems still need to be solved.

In model-1, we have assumed a frontier for the drifting charges, then the differential current should display a cusp. However, the only successful example we have studied is the nondispersive material TPD. The model is not very successful for the dispersive materials. As in nondispersive materials the charges drift in a thin plane, the assumption of a charge frontier should be valid. More nondispersive materials should be tested for the final conclusion.

In model-2, after assuming a velocity distribution for the drifting charges, I was able to come up a solution for the dynamic equation. Many opportunities (or unsolved problems) exist for this model. First of all, I have used a Gaussian function for the velocity distribution. We have discussed that the Gaussian is the solution at semi-infinite boundary for the diffusion equation. This should be a good approximation for thick sample. But how thick is thick is an unanswered question. For thin sample, one may want to solve the diffusion equation numerically. Second, I have used four parameters $\tau$, $q_0$, $v_0$ and $\sigma$ in model-2. The values of these parameters are best fitted from the experimental measurement. The amount of computation is huge, taking from two hours to
a half day for every curve fitting. We notice that two of the parameters the circuit reaction time \( \tau \) and the total charge \( q_0 \) can be obtained by direct measurements. We can measure \( \tau \) by measuring the sample capacitance, and measure \( q_0 \) by integrating the photocurrent. Then the computation time should be greatly decreased, and it's even possible to solve for \( v_0 \) and \( \sigma \) directly (see chapter 3). Third, at the time when this thesis was almost finished, I found out that the approximation method developed in chapter 3 to estimate parameter covariances does not work well, because the higher order differentiation for \( \sigma \) is not negligible so that the Taylor expansion is not valid. A better method is to use Monte Carlo simulation to estimate the variance and covariance matrix. This is an urgent problem needing to be solved if one wants to use model-2 to study TOF. Finally, one might ask why I didn’t use a position distribution instead of the velocity distribution. The answer is that the solution is a triple integral if one uses the position distribution. Then the current computing power cannot handle the integral. But if one can find much better computing power or just uses Monte Carlo method to do the triple integration, it may be a good task to try position distribution.

Of course, more opportunities exist if one uses the methods in this thesis to study more new materials. In chapter 4, we discussed that model-2 can simulate different types of photocurrent under different conditions. It must be very interesting if one can use some material to justify these conditions. Another issue is that we also discussed that the mobility for TPD at very low temperature is temperature independent. I have proposed an explanation that at very low temperature all the charges hop through temperature-independent quantum tunneling. Obviously more experiments should be done to clear this issue. Finally, I would say that the phenomenon of negative dependence of mobility on
electric field is very interesting. Bässler et al. have done a lot of theoretical studies for this issue. It would be very interesting if one can design some special materials that show negative effect of field on mobility. Of course, more opportunities should exist if the studies about mobility go deeper, but that's beyond what I can predict.