Optimum Experimental Design for EGDM Modeled Organic Semiconductor Devices

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We apply optimum experimental design (OED) to organic semiconductors modeled by the extended Gaussian disorder model (EGDM) which was developed by Pasveer et al.\textsuperscript{2} We present an extended Gummel method to decouple the corresponding system of equations and use automatic differentiation to get derivatives with the required accuracy for OED. We show in two examples, whose parameters are taken from Pasveer et al.\textsuperscript{2} and Mensfoort and Coehoorn\textsuperscript{3} that the linearized confidence regions of the parameters can be reduced significantly by applying OED resulting in new experiments with a different setup.

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I. INTRODUCTION

Simulation of organic semiconductor devices, e.g. organic light emitting diodes (OLED), organic solar cells, etc., has gained great interest in the past decade. Accurate models often lack in precise parameters and their identification is time-consuming or expensive. One major problem is the uncertainty in the measurement data which leads to uncertain parameters. Carrying out more experiments would minimize this uncertainty in an expensive way. An alternative is to use OED in order to minimize the parameter uncertainty by planning new (optimal) experiments. New measurement data are received for which the parameter estimation yields parameters with minimal confidence intervals. We apply the concept of OED to the EGDM, a special model for the mobility of electron transport in organic polymeric material. The chapters are arranged as follows: We give a brief overview of the model equations in Sec. II and point out what the relevant quantities are. In Sec. III we explain the methodology of the optimum experimental design problem in more detail. After describing the equation solver methods we used, Sec. IV, numerical results of the optimization are presented in Sec. V.

II. EGDM EQUATIONS

A basic description of charge transport in semiconducting materials in the steady-state case is given by the coupled van Roosbroeck system\textsuperscript{4} consisting of the continuity equation, also called drift-diffusion equation, and the Poisson equation. Given a domain $\Omega := (0, L) \subset \mathbb{R}$, the state variables, i.e. the space dependent functions, are the electric charge density $n$ in $[m^{-3}]$ and the electric potential $\phi$ in $[eV]$ which are scalar real valued functions defined on $\Omega$. We assume that $n$ and $\phi$ are twice differentiable on $\Omega$. Pasveer et al.\textsuperscript{2} proposed the EGDM to conjugated semi-conducting polymers, where the diffusion and the mobility depend on the state variables and hence on the space variable $x$. Furthermore they introduced another state $E_F$, called Quasi-Fermi-Energy, and a corresponding equation which couples $E_F$ and $n$ at every space point. We omit the $x$-dependence in the following equations, only $n$, $\phi$ and $E_F$ are space dependent. The model equations are:

\begin{align}
0 &= \partial_x J(n, \phi, E_F), \\
-\partial_x^2 \phi &= \frac{e}{\varepsilon} n, \\
n &= \frac{N_i}{\sqrt{2\pi \sigma^2}} \int_{-\infty}^{\infty} e^{-\frac{(x-\bar{\phi})^2}{2\sigma}} \frac{1}{1 + \exp\left(\frac{E-E_F}{k_BT}\right)} dE,
\end{align}

where

\begin{align}
J(n, \phi, E_F) &= \mu_0 g_0 g_1(n) g_2(\phi) \Big( n \partial_x \phi - k_BT g_3(n, E_F) \partial_x n \Big), \\
g_0 &= \exp \left\{ -0.42 \left( \frac{\sigma}{k_BT} \right)^2 \right\}, \\
g_1(n) &= \exp \left\{ \frac{1}{2} (\sigma^2 - \hat{\sigma}) \left( \min \left\{ \frac{2n}{N_i}, 0.2 \right\} \right)^{\delta(x)} \right\}, \\
g_2(\phi) &= \exp \left( 0.44(\sigma^2 - 2.2) \right), \\
g_3(n, E_F) &= \frac{n}{k_BT \varepsilon} \frac{\partial \phi}{\partial x}.
\end{align}

In these equations $J$ is the electric current density in $[A/m^2]$, $k_B$ is the Boltzmann constant in $[J/K]$, $\varepsilon$ the permittivity in $[C/m]$, $e$ the elementary charge in $[As]$, $\hat{\sigma} := \frac{\sigma}{k_BT}$

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and \( \delta(\sigma) := \frac{2\log(\sigma - \sigma^2) - \log \log \sigma}{2} \). In the anorganic case, the \( g_i \)-factors, \( i = 1, 2, 3 \), would be constant. Their organic model is yield by comparison with the solution of the master equations. On the boundary \( \partial \Omega = \{0, L\} \) the following conditions are imposed:

\[
\begin{align*}
    n(0) &= \frac{N_t}{\sqrt{2\pi \sigma^2}} \int_{-\infty}^{\infty} e^{-\frac{x^2}{2\sigma^2}} \left( 1 + \exp \left( \frac{E + \varphi_1 - \sqrt{-\frac{1}{2\pi \sigma^2} \partial_x \phi(0)} - 0 \right) \right)^{-1} dE, \\
    n(L) &= \frac{N_t}{\sqrt{2\pi \sigma^2}} \int_{-\infty}^{\infty} e^{-\frac{x^2}{2\sigma^2}} \frac{1}{1 + \exp \left( \frac{E + \varphi_1}{k_B T} \right)} dE, \\
    \phi(0) &= 0, \\
    \phi(L) &= eV - (\varphi_2 - \varphi_1),
\end{align*}
\]

where \( V \) is the voltage in [V] and \( \varphi_{1,2} \) are given energy barriers in [eV]. On the entrance, \( x = 0 \), the energy barrier \( \varphi_1 \) is lowered according to the theory of Entage and O’Dwyer and Scott and Malliaras. For our computations we take the dimensionless form of the equations proposed by Bonham and Jarvis. For the later use we define

\[
p := (\mu_0, \sigma, N_t) \in \mathbb{R}^3, \\
q := (L, T) \in \mathbb{R}^2, \tag{11}
\]

where \( p \) are parameters of unknown numerical value given by nature. They have to be identified by comparing a model response to experimental data. \( \mu_0 \) is the zero temperature mobility in \( \mu_0 \), \( \sigma \) is the width of the Gaussian distribution of the density of states in \( eV \) and \( N_t \) is the site density in \([m^{-3}]\). We assemble quantities which are adjustable by an experimenter, the device length \( L \) in \([m]\) and the temperature \( T \) in \([K] \), in the vector \( q^T \).

III. SOLUTION METHODS FOR THE EGDM EQUATIONS

There are two established ways for solving the system \( (1)-(3) \):

1. Apply Newton’s method to the fully coupled system of equations

2. Use Gummel’s method\(^2\) i.e. a fixed point iteration which decouples the three EGDM equations

With Newton’s method, one can achieve quadratic convergence. However, finding good starting values is not simple. In the work of Knapp et al.\(^2\) a strategy motivated by physical considerations is described. Another aspect is that the Jacobian, i.e. derivatives of the functions w.r.t. the states, is required. To compute the Jacobian, the main two options are to use difference formulas or compute the exact derivatives. The latter can be done by hand or by using automatic differentiation (AD). Either way, the additional effort for computing the derivative in \( n \) directions is at least \( 2n \) times the effort of each function evaluation in every Newton step. Another possibility is to solve \( (1)-(3) \) with Gummel’s method. TABLE I shows the modified algorithm consisting of the classical system of equations \( (1)-(3) \) and the Quasi-Fermi energy \( E_F \) defining equation \( (3) \). We solve the equations sequentially and insert the interim results into the next equations. With the special linearization, used in the third equation of TABLE I, we do not need any derivatives and the effort of function evaluations is limited. We discretize the infinite dimensional problem \( (1)-(3) \) to a finite one. The domain \( \mathbb{T} \) is divided in \( N \) subintervals \( I_i := [x_i, x_i + h], x_i \in \{x_0 = 0, \ldots, x_N = L\} \) with a constant mesh size \( h := \frac{L}{N} \). Finite differences are applied to the spatial derivatives, i.e. with respect to \( x \). The so-called Scharfetter-Gummel scheme\(^11\) forces the function \( J \), defined in Eq. (5), to be constant on each interval \( I_i \), denoted by \( J_{i+\frac{1}{2}} \), and provides an upwind stabilization, so that computation on coarse meshes is possible.

On the interval \( I_i \), the scheme looks like

\[
J_{i+\frac{1}{2}} = \mu_0 g_0 \tilde{g}_i \tilde{g}_2 \frac{\phi_{i+1} - \phi_i}{h} n_{i+1} \exp \left( \frac{-\phi_{i+1} - \phi_i}{k_B T g_3} \right) - n_i \exp \left( \frac{\phi_{i+1} - \phi_i}{k_B T g_3} \right) - 1
\]

The terms \( \tilde{g}_j, j = 1, 2, 3 \) stand for average values of the non-constant functions \( g_j, j = 1, 2, 3 \). It is important that the averages are taken in an upwind conform way to prevent numerical oscillations.

\[
\begin{align*}
\text{TABLE I. Algorithm for the fixed point iteration of Gummel expanded by the EGDM-Quasi-Fermi-Equation and a derivative-free linearization.}
\end{align*}
\]

Let \( u^0 := (n^0, \phi_0, E_F^0) \) be given and choose \( ||\Delta u^0|| \gg TOL \) with given error tolerance \( TOL \).

Set \( i = 0 \).

while \( ||\Delta u^i|| > TOL \)

1. Solve

\[
n^i = \frac{N_t}{\sqrt{2\pi \sigma^2}} \int_{-\infty}^{\infty} e^{-\frac{x^2}{2\sigma^2}} \frac{1}{1 + \exp \left( \frac{E + \varphi_1}{k_B T} \right)} dE
\]

for \( E_F^{i+1} \) with Newton’s method started with \( E_F^i \).

2. Solve

\[
-\partial^2 \phi^{i+1} = \lambda n^i
\]

with corresponding boundary conditions for \( \phi^{i+1} \).

With \( n^i, \phi^{i+1} \) and \( E_F^{i+1} \) solve

\[
0 = \partial^n \left\{ g_1(n^i) g_2(\phi^{i+1}) \right\}
\]

\[
\left( n^{i+1} \partial_n \phi^{i+1} + k_B T g_3(n^i, E_F^{i+1}) \partial_n n^{i+1} \right) \right\}
\]

with corresponding boundary conditions for \( n^{i+1} \).

Set \( u^{i+1} := (n^{i+1}, \phi^{i+1}, E_F^{i+1}) \) and \( \Delta u^{i+1} := u^{i+1} - u^i \).

\[
i \leftarrow i + 1
\]

\[
I_{i+\frac{1}{2}} = \mu_0 g_0 \tilde{g}_i \tilde{g}_2 \frac{\phi_{i+1} - \phi_i}{h} n_{i+1} \exp \left( \frac{-\phi_{i+1} - \phi_i}{k_B T g_3} \right) - n_i \exp \left( \frac{\phi_{i+1} - \phi_i}{k_B T g_3} \right) - 1
\]

The terms \( \tilde{g}_j, j = 1, 2, 3 \) stand for average values of the non-constant functions \( g_j, j = 1, 2, 3 \). It is important that the averages are taken in an upwind conform way to prevent numerical oscillations.
IV. OPTIMUM EXPERIMENTAL DESIGN FOR MODEL VALIDATION

In this part, we follow the approaches of Lohmann\textsuperscript{12} and Körlkel et al.\textsuperscript{13} With different choices of the controls \( q \) and the voltage \( V \), defined in Sec. III, we set up multiple experiments in which the current density \( J \) is measured. Let \( M \) be the number of measurements we yield. In a parameter estimation, the parameters are identified by fitting a model response, here \( J \), to experimental data, i.e. measurements. We assume the measurement error to be normally distributed with mean zero and covariance matrix \( \Sigma^2 = \text{diag}(\sigma_i^2; i = 1, \ldots, M) \in \mathbb{R}^{M \times M} \). With the same experimental settings, i.e. equal controls \( q \), a fit from a different realization of the measurement errors may result in very different parameter values. The covariance matrix of the parameters allows to analyze the quality of a parameter estimation. The assumed model for the standard deviations of the measurement errors is:

\[
\sigma_i = 0.1 \cdot J_i + 0.1 \left[ \frac{A}{m^2} \right],
\]

where \( J_i \in \mathbb{R} \) is the function value of \( J \) corresponding to the \( i \)-th measurement. For further notation, we assemble the values \( J_i \) in the vector \( J \in \mathbb{R}^M \). If the confidence region of the parameters is approximated by assuming a linear propagation of the measurement errors, it can be parameterized by the covariance matrix defined by:

\[
\text{Cov}_p := \mathbb{E}[(p - \mathbb{E}[p])(p - \mathbb{E}[p])^T] \in \mathbb{R}^{N_p \times N_p},
\]

where \( N_p \) is the number of parameters. From now on, we denote by \( n \), \( \phi \) and \( E_F \) the discrete counterparts of the state variables which are \((N - 1)\)-dimensional vectors, without boundary values. They assemble the function values at the mesh points \( x_i \), \( i = 1, \ldots, N - 1 \), cf. Sec. III. We abbreviate the discrete solution of the system (1)-(3) dependent on parameters \( p \) and controls \( q \) by:

\[
u(p, q) := (n(p, q), \phi(p, q), E_F(p, q)) \in \mathbb{R}^N,
\]

cf. TABLE II. We used the notation \( N_u := 3(N - 1) \) for the overall state dimension. In the following we denote the derivative of a function \( f \) w.r.t. \( x \) in the direction \( \Delta x \) by:

\[
d_x f(\Delta x) := \lim_{\varepsilon \to 0} \frac{f(x + \varepsilon \Delta x)}{\varepsilon}
\]

and write accordingly the second derivatives of \( f \) w.r.t. \( x \) and \( y \) in the directions \( \Delta x \) and \( \Delta y \) as \( d_{yx}^2 f(\Delta x, \Delta y) \). We combine several directions \( \Delta x_i \) into a so-called seed matrix \( S = (\Delta x_1, \ldots, \Delta x_n) \) and define \( d_x f(S) \) by:

\[
(d_x f(S))_{ij} = d_x f_i(\Delta x_j)
\]

and accordingly \( d_{yx}^2 f(S_1, S_2) \) by:

\[
(d_{yx}^2 f(S_1, S_2))_{ijk} = d_{yx}^2 f_i(\Delta x_j, \Delta y_k)
\]

with \( S_1 = (\Delta x_j)_j \) and \( S_2 = (\Delta y_k)_k \). We define the \( M \times N_p \) Matrix:

\[
\text{Jac}(u(p, q), p, q) := -\Sigma^{-1} d_q \mathcal{J}(u(p, q), p, q)\{I_p\}
\]

\[
= -\Sigma^{-1} \left[ \partial_u \mathcal{J}(\partial_p u(I_p)) + \partial_p \mathcal{J}(I_p) \right],
\]

with the derivative of \( \mathcal{J} \) w.r.t. to the parameters \( p \) with the \( N_p \)-dimensional identity matrix \( I_p \) as seed matrix. Computing \( \partial_u \mathcal{J}(\partial_p u(I_p)) \) is much less expensive than computing the matrix product \( \partial_u \mathcal{J}(I_u) \cdot \partial_p u(I_p) \) with the identity matrix \( I_u \in \mathbb{R}^{N_u \times N_u} \). The covariance matrix in the unconstrained case can be computed by:

\[
\text{Cov}_p = (\text{Jac}(u(p, q), p, q))^T \text{Jac}(u(p, q), p, q)^{-1}.
\]

For given probability \( \alpha \in [0, 1] \) the linearized \( (100 \cdot \alpha)\%-\)confidence region is described by:

\[
G(\alpha, p) = \{ v \in \mathbb{R}^{N_p} : v = p + \delta p, \delta p^T \text{ Cov}_p^{-1} \delta p \leq \gamma(\alpha)^2 \},
\]

with the \((1 - \alpha)\)-quantile of the \( \chi^2 \)-distribution \( \gamma(\alpha)^2 \). As an approximation of the confidence intervals of the parameters we use:

\[
[p_i - \theta_i, p_i + \theta_i) \quad \text{with} \quad \theta_i = \gamma(\alpha) \sqrt{\text{Cov}_p}_{ii}, \quad i = 1, \ldots, N_p.
\]

We point out that for computing \( \text{Cov}_p \) (and the confidence intervals) no measurement data is necessary. We consider the reduced nonlinear optimization problem:

\[
\min_q \frac{1}{N_p} \text{trace} \left( \text{Cov}_p \right)
\]

which is called “optimum experimental design problem”. Efficient optimization algorithms require derivative information. For higher order difference formulas, the number of function evaluations increases which can be very costly like in our case. Additionally, low order schemes reduce the number of exact digits, in particular in combination with derivatives of higher order. To avoid such approximation errors, we use automatic differentiation where the derivatives are evaluated up to machine precision. For derivative based optimization, we need the derivative of the gradient of Jac with the seed matrix \( I_q \in \mathbb{R}^{N_q \times N_q} \), where \( N_q \) is the number of the controls. \( N_p \) and \( N_q \) are relatively small, so we use the forward mode, where we have to compute:

\[
d_q \text{Jac}(u(p, q), p, q)\{I_q\}
\]

\[
= -\Sigma^{-1} \left[ d_q \left( \partial_u \mathcal{J}(\partial_p u(I_p)) + \partial_p \mathcal{J}(I_p) \right) \right] \{I_q\}
\]

\[
= -\Sigma^{-1} \left[ \partial_u \mathcal{J}(\partial_p u(I_p)) \cdot \partial_q u(I_p) + \partial_p \mathcal{J}(I_p) \cdot \partial_q u(I_p) \right]
\]

\[
+ \partial_u \mathcal{J}(\partial_q u(I_p)) \cdot \partial_p u(I_p) \cdot \partial_q u(I_p)
\]

\[
+ \partial_p \mathcal{J}(I_p, I_q),
\]
see e.g. Griewank. We need derivatives of \( u \) w.r.t. the parameters \( p \), controls \( q \) and mixed second derivatives w.r.t. \( p \) and \( q \). One way would be to differentiate the fixed point iteration, TABLE I, and iterate over the derivatives as well. However, we are only interested in the derivatives of the solution of Gummel’s method \( u(p,q) \). In the solution it holds

\[
F(u(p,q), p, q) = 0 \quad \forall p, q,
\]

with \( F \) the discrete counterpart of the system of equations \( \text{(1)} \). To compute the required derivatives \( \partial_p u(I_p), \partial_q u(I_q) \) and \( \partial_{pq}^2 u(I_p, I_q) \), we use the sensitivity method, see e.g. Hinze et al. Using adjoint method is not recommended here, because the number of measurements \( M \) is much higher than the number of parameters \( N_p \). Differentiating \( \text{(16)} \) leads to

\[
\begin{align*}
\partial_p F(u(p,q), p, q)\{I_p\} &= 0, \\
\partial_q F(u(p,q), p, q)\{I_q\} &= 0, \\
\partial_{pq}^2 F(u(p,q), p, q)\{I_p, I_q\} &= 0.
\end{align*}
\]

Hence the required derivatives are given in form of

\[
\begin{align*}
\partial_p u\{I_p\} &= -\left(\partial_u F\{I_u\}\right)^{-1} \partial_q F\{I_p\}, \\
\partial_q u\{I_q\} &= -\left(\partial_u F\{I_u\}\right)^{-1} \partial_q F\{I_q\}, \\
\partial_{pq}^2 F\{I_p, I_q\} &= - \left(\partial_{pq} F\{I_p, I_q\}\right)^{-1} \left(\partial_{pp} F\{I_p, I_q\}\right) + \partial_{pq}^2 F\{I_p, I_q\} \partial_{pp} u\{I_p\}, I_q \\
&\quad + \partial_{pq}^2 F\{I_p, I_q\} \partial_{qq} u\{I_p\}, I_q) \\
&\quad + \partial_{pq}^2 F\{I_p, I_q\} \partial_{pp} u\{I_p\}, I_q) \right).
\end{align*}
\]

We can save the decomposition of the matrix \( \partial_u F\{I_u\} \) and use it for all three equations to reduce complexity.

V. NUMERICAL RESULTS

Experimenters proceed in the following way. Devices of different lengths \( L \) are produced by evaporating. At different temperatures \( T \), they apply voltage series \( V \), a vector consisting of various voltages \( V \), and measure the corresponding current values, combined in the vector \( J \). One choice of \( L, T \) and voltage series \( V \) we call one experiment subsequently. We will show in two examples how the confidence regions can be reduced by OED. In each example we consider three different lengths

\[
\mathcal{L} := (L_1, L_2, L_3)
\]

and three different temperatures

\[
\mathcal{T} := (T_1, T_2, T_3).
\]

The combination of each element of the vector \( \mathcal{L} \) with each element of the vector \( \mathcal{T} \) lead to nine experiments. We assemble all control variables, which are the optimization variables for the OED problem, in a vector

\[
\mathcal{Q} := (L_1, T_1, L_1, T_2, L_1, T_3, L_2, T_2, \ldots, L_3, T_3) \in \mathbb{R}^{18}.
\]

The result of the OED should be three lengths and three temperatures combined in nine experiments. To enforce that, we apply additional constraints to \( \mathcal{Q} \) for the lengths

\[
\begin{align*}
\mathcal{Q}_1 &= \mathcal{Q}_3 = \mathcal{Q}_5, \\
\mathcal{Q}_7 &= \mathcal{Q}_9 = \mathcal{Q}_{11}, \\
\mathcal{Q}_{13} &= \mathcal{Q}_{15} = \mathcal{Q}_{17},
\end{align*}
\]

and for the temperatures

\[
\begin{align*}
\mathcal{Q}_2 &= \mathcal{Q}_8 = \mathcal{Q}_{14}, \\
\mathcal{Q}_4 &= \mathcal{Q}_{10} = \mathcal{Q}_{16}, \\
\mathcal{Q}_6 &= \mathcal{Q}_{12} = \mathcal{Q}_{18}.
\end{align*}
\]

We solve problem (15) with the software package VPLAN where the optimization problem is solved with an inexact SQP method provided by SNOPT 7.2-9 (Jun 2008). In each iteration, the objective, i.e. the covariance matrix, is computed by solving the underlying system of equations. We implemented the extended Gummel method TABLE I in VPLAN to solve this system. For the optimization, the derivatives of the model functions are calculated with the AD tool ADIFOR 2.0. We implemented a routine in VPLAN, which solves the system of equations (17). In a first example we take configurations \( p, V, L \) and \( T \) from Pasveer et al., who used

\[
\begin{align*}
p &= (1.15 \cdot 10^{-5}, 0.14, 2.44 \cdot 10^{26}), \\
V &= (0.1, \ldots, 0.9, 1, 2, \ldots, 10), \\
L &= (275, 350, 475), \\
T &= (235, 270, 305).
\end{align*}
\]

Here and in the following example we set \( \varphi_1 = \varphi_2 = 0 \) for the energy barriers in \([eV]\) and \( \varepsilon = 2.66 \cdot 10^{-11} \) for the permittivity in \([\text{F}\text{m}^{-1}]\). We choose boundaries to the lengths and temperatures according to the practicability of experiments and the validity of the model:

\[
\begin{align*}
L_i \in [50, 500], \quad T_i \in [200, 350] \quad i = 1, 2, 3.
\end{align*}
\]

The optimization results in the vectors

\[
\begin{align*}
\mathcal{L}^* &= (50, 339.1, 471.6), \\
\mathcal{T}^* &= (277.2, 281.8, 350).
\end{align*}
\]

Where the lengths do not change much, a tendency to higher temperatures is observed. The algorithm gives back the exact numbers of the optimum. Dependent on the equipment of the laboratory these values can not be realized in practice. Nevertheless they can be taken as a guideline. All the values in the neighborhood of \( \mathcal{L}^* \) and \( \mathcal{T}^* \) are leading to similar results. In Fig. I we visualize the three dimensional ellipsoid and the projections corresponding to the set \( G_1(0.95, 0) \) before and after the optimization. TABLE II shows a comparison of the confidence intervals of the parameters. The average of the squared semi-axes of the optimized ellipsoid, i.e. the objective in (15), is 0.07 times the average of the squared
FIG. 1. Projections and three dimensional ellipsoid with shadows of the linearized 95%-confidence regions before (light part) and after (dark part) the optimization. Computed with Pasveer parameters (18).

TABLE II. Radii of the confidence intervals before and after the optimization computed by (14) with Pasveer parameters (18).

|      | \(\theta_{\text{start}}\) | \(\theta_{\text{optimal}}\) |
|------|-----------------------------|-----------------------------|
| \(p_1\) | 79.90%                      | 19.85%                      |
| \(p_2\) | 5.21%                       | 1.27%                       |
| \(p_3\) | 21.62%                      | 7.21%                       |

FIG. 2. Comparison of current-voltage characteristics before and after the optimization for Pasveer parameters (18). The continuous lines correspond to experiments with configuration \(L\) and \(T\) and the dashed lines correspond to experiments with optimal configuration \(L^*\) and \(T^*\).

Again we take boundaries like in (19) and the resulting vectors are

\[
\begin{align*}
\mathcal{L}^* &= (50, 187.8, 296.8), \\
\mathcal{T}^* &= (200, 274.7, 350).
\end{align*}
\]

Unlike the first example, the optimal lengths differ much more from the starting values and not all temperatures were raised, the lowest temperature was even reduced. In Fig. 3, we illustrate the confidence ellipsoid and the projections and TABLE III shows a comparison of the confidence intervals in this case. The average of the squared semi-axes of the optimized ellipsoid here is 0.16 times the average of the squared semi-axes of the ellipsoid not optimized, too. The results of the simulations before and after the optimization procedure are shown in Fig. 4. The optimized configuration leads to a wider range of current densities gaining more information.

VI. CONCLUSION AND OUTLOOK

We have applied optimum experimental design to organic semiconductors modeled by the EGDM in order
TABLE III. Radii of the confidence intervals before and after the optimization computed by (14) with Coehoorn parameters [20].

|         | $\theta_{\text{start}}$ | $\theta_{\text{optimal}}$ |
|---------|--------------------------|----------------------------|
| $p_1$   | 44.76%                   | 15.98%                     |
| $p_2$   | 7.20%                    | 3.42%                      |
| $p_3$   | 35.42%                   | 16.51%                     |

FIG. 4. Comparison of current-voltage characteristics before and after the optimization for Pasveer parameters [20]. The continuous lines correspond to experiments with configuration $L$ and $T$ and the dashed lines correspond to experiments with optimal configuration $L^*$ and $T^*$.

to reduce the parameter uncertainty caused by measurement errors. The variances of the parameters, i.e. the average of the squared semi-axes of the confidence ellipsoid, were 0.07 and 0.16 times the average of the squared semi-axes of the not optimized confidence ellipsoid respectively. The proposed experiments, followed by a parameter estimation lead to a model, which is approximately 10 times more exact with respect to the assumed measurement error than the previous one. The classical methods for solving semiconductor models were extended to fit with the EGDM. The derivatives required for the optimization were computed via automatic differentiation, leaving the error on machine precision level, even for higher derivatives. We used unipolar layer devices for simplicity, but the presented methods can also be applied to multi-layer devices, trap generation models and exciton rate equations or, more far-reaching, all other models which are based on the van Roosbroeck system.

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