Image-based stochastic modeling of the 3D morphology of energy materials on various length scales

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3D microstructure of uncompressed graphite electrodes

3D microstructure of compressed graphite electrodes

3D morphology of hybrid organic solar cells

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Overview

Microscopic scale
1. Stochastic modeling of 3D microstructure of graphite electrodes used in Li-ion batteries
   1.1 Uncompressed electrode
   1.2 Compressed electrode

Nanoscopic scale
2. Stochastic modeling of 3D morphologies in organic electronics
   2.1 Hybrid-organic solar cells (mesoscopic scale)
   2.2 Organic semiconductors (nanosopic scale)
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Synchrotron tomography image data

O. Stenzel et al., Modelling and Simulation in Materials Science and Engineering, to appear

- 3D image of uncompressed graphite electrode used in Li-ion batteries
- tomography: Helmholtz Center Berlin, material: ZSW Baden-Württemberg
- yellow: graphite phase
- transparent: pore phase, volume fraction ca. 56%
Goal: stochastic simulation model

- Modeling of the 3D morphology of graphite electrodes
- Size: $100 \times 100 \times 100$ voxels
Functionality

3D microstructure ⇔ functionality

Detect improved microstructures by virtual materials design
Simulated annealing for generation of microstructures

- Start with **random allocation** of voxels given volume fraction $\alpha$
- **Coarsening** of morphology by interchanging voxels.
  - $T$ temperature, $c(\cdot)$ cost function to be reduced (e.g. surface area)
  - Pick a pair of voxels at random
  - Swap voxels if cost function decreases, otherwise accept swap with probability $\exp \left( \frac{c(\text{no change}) - c(\text{change})}{T} \right)$
  - Decrease $T$ with time
- Stop if desired value of $c(\cdot)$ is reached.
Our approach: graph-based simulated annealing

- Simulated annealing: simple but computational expensive, limited control of microstructure
- Hybrid approach: combining spatial stochastic graph modeling with simulated annealing
  - simulate random geometric graph
  - start configuration of voxels by project voxels onto the graph
  - run simulated annealing on new start configurations
  - voxels of graph fixed
- spatial graph serves as backbone of microstructure
- fast, good control on microstructure
Stochastic graph model

- Extract spatial graph \((V, E)\) from experimental data by skeletonization
  - \(V\) set of vertices
  - \(E\) set of edges

- Stochastic modeling by
  - Point process model for the set of vertices
  - a stochastic model for setting edges
  - Fitting of model parameters to corresponding experimental data
Point process model: modulated hardcore point process

(1) Simulation of homogeneous Poisson process
(2) Simulation of Boolean Model
(3) Simulation of Poisson hardcore model inside the Boolean Model
Stochastic model for setting edges

- **Connecting nearest neighbors**
  - Connect each point $S_i$ with its $n$ nearest neighbors.
  - Start with nearest neighbor
  - Connection is rejected if angle to previous edges undercuts a threshold $\gamma_1$

- **Postprocessing** of edges
  - If angles undercut threshold $\gamma_2$: deletion with probability $p \in (0, 1)$.
  - Control of angles

Cut-out of experimental graph (left) and simulated graph (right)
Model validation

Cut-out of experimental (left) and simulated (right) microstructure

Spherical contact distribution from pore phase to graphite (left) and vice versa (right). Red curve displays experimental data and black curve simulated data.
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X-ray tomography image data

P.R. Shearing et al., Electrochemistry Communications, 12 (2010), 374–377.

- 3D image of compressed graphite electrode used in Li-ion batteries
- tomography: Imperial College
- yellow: pore phase, volume fraction ca. 16.6%
- transparent: graphite phase
Goal: stochastic simulation model

Modeling of the 3D morphology of graphite electrodes
Modeling idea: ‘smart’ system of spheres

- Modeling idea: representation of the pore phase as a complex system of spheres
- Spatial correlation of sphere centers
- Spatial correlation of radii
- Question: how to choose point process model for sphere centers?
Data preprocessing: morphological smoothing

\[
B' = \left( (B \ominus b(o, \sqrt{3})) \oplus b(o, \sqrt{3}) \right) \oplus b(o, 1)
\]

- Opening of pore phase \( B \) (elimination of small pores)
  - Eroding the pore phase \( B \)
  - Dilating the pore phase \( B^c \)
- Dilating the pore phase \( B \) (smoothing of boundary)
Multi-scale approach

- Splitting of complexity
- Separate modeling of both scales
Random placement of midpoints in pore phase (uniformly distributed)
Radius = minimal distance to boundary (from Euclidean distance transform)
Stop if 99% of pore phase are covered
Repeat these steps several times
Use kernel density estimation to find preferred midpoint locations
3D Representation of graphite electrode domains by unions of spheres

Results: enormous data reduction
mean number of voxel per sphere: 27.7
3D Representation of the macro-scale by unions of spheres

Macro-scale represented by marked point process
Transformation of battery data into mathematical language
Simulation of sphere centers: elliptical Matérn cluster process

Modeling in 2 steps:

1. 3D spheroid process
2. 3D homogeneous Poisson process in each spheroid
Fitting of model parameters

Model Parameters

- Axis length of the ellipsoids $l_1, l_2, l_3$
- Intensity $\lambda_p$ of parent point process
- Expected number of child points per cluster $c$

Minimum–contrast estimation

- Estimator for $\hat{\theta} = (\hat{\lambda}_p, \hat{l}_1, \hat{l}_2, \hat{l}_3)$:

$$
\hat{\theta} = \operatorname{argmin}_\theta \int_{r_1}^{r_2} (g_\theta(r) - \hat{g}(r))^2 dr,
$$

where $g(r)$ is the pair-correlation function

- $\hat{c} = \hat{\lambda}/\hat{\lambda}_p$

Estimated parameters

$\hat{\lambda}_p = 0.00015$, $\hat{c} = 33.33$, $\hat{l}_1 = \hat{l}_2 = 22.2$, and $\hat{l}_3 = 3$
Modeling of spheres

spherical distances with fitted gamma distribution

Fitted shifted gamma distribution

Rate $= 2.26$
Shape $= 2.85$
Shift $= \sqrt{3}$
Modeling of spheres

Dependence structure of sphere radii

**Convolution of marks** from 10 nearest neighbors, i.e., $Z_1, \ldots, Z_n \sim \Gamma(2.26, 2.85/11.0, 0)$:

$$Z_i + Z_{i_1} + \ldots + Z_{i_{10}} + \sqrt{3} \sim \Gamma(2.26, 2.85, \sqrt{3})$$
Modeling of spheres

example: influence of 3 nearest neighbors
Modeling of sphere

example: influence of 3 nearest neighbors
Modeling of spheres

example: influence of 3 nearest neighbors
Modeling of spheres

eexample: influence of 3 nearest neighbors
Inversion of morphological smoothing by stochastic modeling

original

macro-scale  micro-scale
Inversion of morphological smoothing by stochastic modeling

Integration of missing connections

- Inhomogeneous Poisson point process
Inversion of morphological smoothing

Closing of pore phase

- 'Inversion' of opening
Inversion of morphological smoothing

Erosion of pore phase

- 'Inversion' of dilation
Result: stochastic simulation model

- Excellent visual agreement
**Structural validation of simulation model**

<table>
<thead>
<tr>
<th></th>
<th>real data</th>
<th>simulated data</th>
</tr>
</thead>
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<tr>
<td></td>
<td>mean</td>
<td>mean</td>
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<tr>
<td>porosity</td>
<td>0.166</td>
<td>0.166</td>
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<td>connectivity</td>
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<td>0.967</td>
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<td>specific interior surface area</td>
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<td>spherical contact distribution</td>
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<td>geometric tortuosity</td>
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<td>coordination number</td>
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<tr>
<td>relative MST-length</td>
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<td>0.56</td>
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</tbody>
</table>
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Tomographic solar cell data

5000 rpm \( \sim \) 57 nm
1500 rpm \( \sim \) 100 nm
1000 rpm \( \sim \) 167 nm


- 3D TEM images of P3HT-ZnO solar cells with different thicknesses
- TEM: Technical University Eindhoven
- P3HT-phase: transparent
- ZnO-phase: yellow, volume fraction 13.3% – 21.1%
- Morphology is anisotropic
Goal: stochastic simulation model

- same model type for all layer thicknesses
- different model parameters for different layer thicknesses
Functionality

- Device architecture: bulk heterojunction
- Light activates the polymer phase of the solar cell
- **Excitons** are generated
- **Diffusion** of excitons in the polymer phase
- Excitons reaching the ZnO phase generate charges: quenching
- Transportation of charges to the electrodes
- 3D microstructure ⇔ functionality
- Detect improved microstructures by virtual materials design
Modeling idea: ‘smart’ system of spheres

- Representation of the ZnO phase as a complex system of spheres
- Contrast to compressed battery modeling: anisotropic point pattern
- Anisotropy by Markov chain of 2D point processes
Multi-scale approach

Original

Morphologically smoothed

"Misspecified" voxels

Macro-Scale

Micro-Scale
3D Representation of the macro-scale by unions of spheres

Macro-scale represented by marked point process

Transformation of solar cells into mathematical language
Modeling in 2 steps:
- 2D point patterns: elliptical Matérn cluster process
- 3D stack of 2D point patterns: spatial birth-and-death process
Inversion of morphological smoothing by stochastic modeling

Real data (unsmoothed)  ⇔  Real data (smoothed)

Real data (smoothed)  ⇔  Simulated data (smoothed)

Simulated data (smoothing inverted)  ⇔  Simulated data (smoothed)
Result: stochastic simulation model

- Good visual agreement
Important structural characteristics for the morphology

- **Spherical contact distribution function** (probability of a random polymer voxel to find the ZnO phase within a given distance)

Distribution functions; solid lines: simulations; dashed lines: lower & upper bounds from original data.
Important structural characteristics for the morphology

- Volume fraction
- Connectivity (existence of percolation pathways to electrodes)

<table>
<thead>
<tr>
<th>Model/Size</th>
<th>Volume fraction</th>
<th>Connectivity (monotonous)</th>
</tr>
</thead>
<tbody>
<tr>
<td>57 nm model</td>
<td>0.115</td>
<td>0.887</td>
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<tr>
<td>57 nm data</td>
<td>0.133</td>
<td>0.928</td>
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<tr>
<td>100 nm model</td>
<td>0.216</td>
<td>0.888</td>
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<td>100 nm data</td>
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<td>167 nm model</td>
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<tr>
<td>167 nm data</td>
<td>0.210</td>
<td>0.851</td>
</tr>
</tbody>
</table>
Physical characteristic for model validation

Quenching probability $\eta_Q$ (probability of a random exciton to reach the ZnO-phase)

- $\eta_Q$ obtained from the field $\{n(x), x \in B^c\}$ of local exciton densities in the polymer phase
- $\{n(x), x \in B^c\}$ computed by solving the steady-state diffusion equation

$$0 = \frac{dn(x)}{dt} = -\frac{n(x)}{\tau} + D\nabla^2 n(x) + g, \quad x \in B^c,$$

$D$: diffusion constant, $\tau$: exciton life time, $g$: rate of exciton generation

- boundary condition: $n(x) = 0$ for all $x \in \partial B^c \setminus \partial W$.
- $\eta_Q = 1 - \bar{n}/(\tau g)$
Physical characteristic for model validation

Real data

Simulated data

167 nm
100 nm
57 nm

Original 3D morphology: upper limit
Simulated 3D morphology
Original 3D morphology: lower limit
Model for morphology

![Image of 3D morphology model]

Validated by 3D real image data

Model for transport processes

![Image of 3D transport model]

Validated by physical experiments

Virtual Material Design
Virtual material design

\[
\vec{\lambda} = (\lambda_1, \ldots, \lambda_m)
\]

Stochastic simulation model

⇒ 3D morphology represented by parameter vector \( \vec{\lambda} \)
Spin coating speed determines morphology

- Regression of parameter vector $\vec{\lambda}$ allows prediction of morphologies which were not fabricated
- Manufacturing process can be realized virtually
Regression of model parameters

Spin coating speed determines morphology

- **Regression models** of type
  \[ \lambda_i(\omega) = a_i + b_i \exp(c_i \omega) + \varepsilon_i \] or
  \[ \lambda_i(\omega) = a_i + b_i \omega + \varepsilon_i \]

- \( \Rightarrow \) analytical formulae for \( \hat{\lambda} \) in dependence of \( \omega \).
- **Prediction** of morphologies which were not fabricated
Scenario analysis

Model for layer thickness

- layer thickness $= c \omega^\alpha$, $\alpha = -0.5$
- estimation of $c$ by least squares
- simulation of virtual morphologies with ‘correct’ layer thickness
Scenario analysis

- Simulation of virtual morphologies for $\omega = 500, 750, \ldots, 5250$
- Estimation of structural and physical characteristics
Scenario analysis - results

left: connectivity, right: mean spherical contact distance (in nm); experimental data added by filled symbols
Scenario analysis - results

left: quenching efficiency by bulk, right: quenched by electrodes; experimental data added by filled symbols

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Organic electronics

Efficiency influenced by charge mobility $\mu = \frac{\bar{v}^T \cdot \bar{F}}{||F||^2}$.

Charge dynamics (transport properties of holes and electrons) are of interest.

pictures: Fraunhofer ISE Freiburg, Samsung
Charge dynamics

- **Gaussian Disorder Model (GDM):** fast, large system sizes, relies on experimental input
- **Microscopic model:** link macroscopic observables to chemical structure or the morphology, restrictions to small system sizes
- **Marry the two approaches:**
  1. realistic, off-lattice morphologies
  2. Fit ingredients of model to (calculated) properties of microscopic systems

⇒ **Stochastic network model**
Reference model

- Max Planck Institute for Polymer Research, Mainz
- Simulation of amorphous morphology containing 4096 Alq3 molecules by atomistic molecular dynamics
- Center of masses $\rightarrow$ hopping sites
- Charge hopping rates using charge transfer theory by

$$\omega_{ij} = \frac{2\pi}{\hbar} \frac{J_{ij}^2}{\sqrt{4\pi\lambda_{ij} k_B T}} \exp \left[ - \frac{(\Delta E_{ij} - \lambda_{ij})^2}{4\lambda_{ij} k_B T} \right]$$

Stochastic network model
Stochastic model

(1) Stochastic model for the network of the molecules
   1. Stochastic model for the hopping sites
   2. Stochastic model for connecting hopping sites

(2) Stochastic model for the charge hopping rate
   1. Stochastic model for site energies $E_i$ and transfer integrals $J_{ij}^2$
Stochastic model for the vertices (hopping sites)

vertices by microscopic model; box-size: 13.55 nm

- vertices have a rather regular structure.
Stochastic model for the hopping sites

Iterative Matérn-Softcore point process model

- simulation of Matérn-Softcore point process (1-4)
- iteration for higher densities (5-8)
Stochastic model for the hopping sites - validation

- Pair correlation function
- Distribution function of nearest neighbor distances

▶ good agreement
Stochastic model for the edges

Black: Relative frequency of two vertices (hopping sites) being connected in dependence of their distance.
Red: Fitted curve $f()$.

Two vertices (hopping sites) with distance $d$ connected with probability $f(d)$. 
Stochastic model for the site energies

- $E_i \sim \mathcal{N}(a, \sigma^2)$, spatially correlated.
- Idea: convolution stability: $\sum_{i=1}^{k} X_i \sim \mathcal{N}(\sum_{i=1}^{k} m_i, \sum_{i=1}^{k} \sigma_i^2)$
- assign each hopping site $S_i$ a 'small' site energy $\tilde{E}_i \sim \mathcal{N}(\frac{a}{M}, \frac{\sigma^2}{M})$
- sum up 'small' site energies $\tilde{E}_j$ of $M$ neighboring vertices
Validation

▶ Putting everything into

\[ \omega_{ij} = \frac{2\pi}{\hbar} \frac{J_{ij}^2}{\sqrt{4\pi \lambda_{ij} k_B T}} \exp \left[ -\frac{(\Delta E_{ij} - \lambda_{ij})^2}{4\lambda_{ij} k_B T} \right] \]

▶ Charge hopping according to a time-continous Markov chain
▶ Markov chain Monte Carlo simulations to determine speed of electrons

Histogram of logarithm of hopping rates
Charge dynamics

Mobility for microscopic and stochastic model.

B. Baumeier et al., *Stochastic Modeling of Molecular Charge Transport Networks*, Physical Review B 86 (2012), 184202
Conclusions

- Large system sizes
- control on positional disorder
- control on correlation of site energies
- application to different (non-spherical) molecules
- realistic device geometries
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Motivation

- Stochastic models allow simulation of large-scale molecular networks
- Charge hopping according to continuous-time Markov chain
- Charge transport modeling by Markov chain Monte Carlo simulations
- Charge mobility $\mu = \frac{V}{F}$ of interest
- Problem: areas of low energies: difficult estimation of $\mu$
Problem

- Charge hopping rates follow \( \omega_{ij} = \frac{2\pi}{\hbar} \frac{J_{ij}^2}{\sqrt{4\pi \lambda_{ij} k_B T}} \exp \left[ -\frac{(\Delta E_{ij} - \lambda_{ij})^2}{4\lambda_{ij} k_B T} \right] \)

- roughly \( 10^9 \) steps for accurate estimation of \( \mu \)

- General: Markov chain nearly decomposable: \( P = \begin{pmatrix} A_1 \\ \cdot \cdot \\ A_n \end{pmatrix} + \epsilon \cdot C \)
Idea: Aggregate Monte Carlo

- Collapse problem regions into a single superstate
- Run embedded Markov chain on coarsened state space
- Calculate conditional sojourn times given the entrance into superstate
Coarsening of state space

- Idea: Identify regions of low energy
- Build energy landscape by Gaussian interpolation
- Segmentation of low energy regions by stochastic watershed
Results

- Reduction of computational time by factor $10^2$
Acknowledgements

- DFG: SPP 1355: ‘Elementary Processes of Organic Photovoltaic’
- DAAD: programme ‘Go8’
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