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

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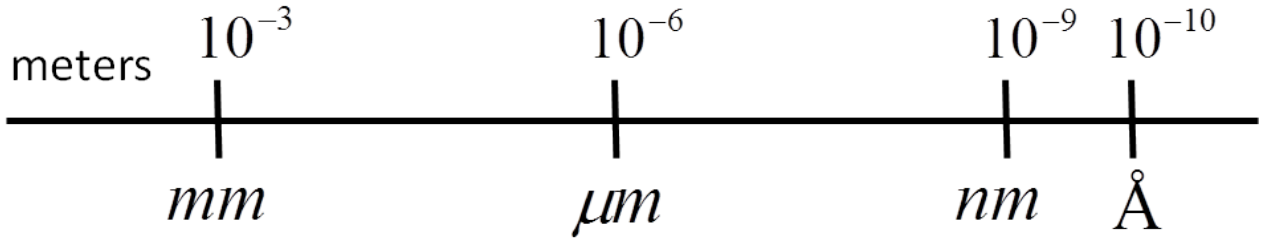
Ulm University, Institute of Stochastics

Grenoble, April 4, 2013

Contents

Contents

Overview



Microscopic scale

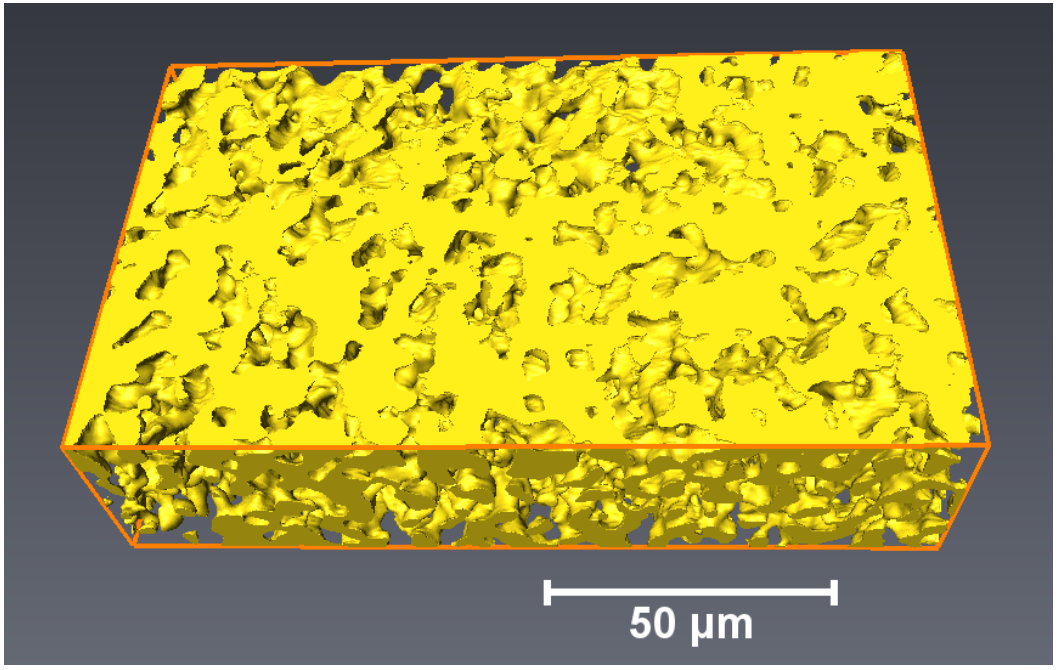
1. Stochastic modeling of 3D microstructure of graphite electrodes used in Li-ion batteries
   - 1.1 Uncompressed electrode
   - 1.2 Compressed electrode

Nanoscopic scale

2. Stochastic modeling of 3D morphologies in organic electronics
   - 2.1 Hybrid-organic solar cells (mesoscopic scale)
   - 2.2 Organic semiconducturs (nanosopic scale)

Contents

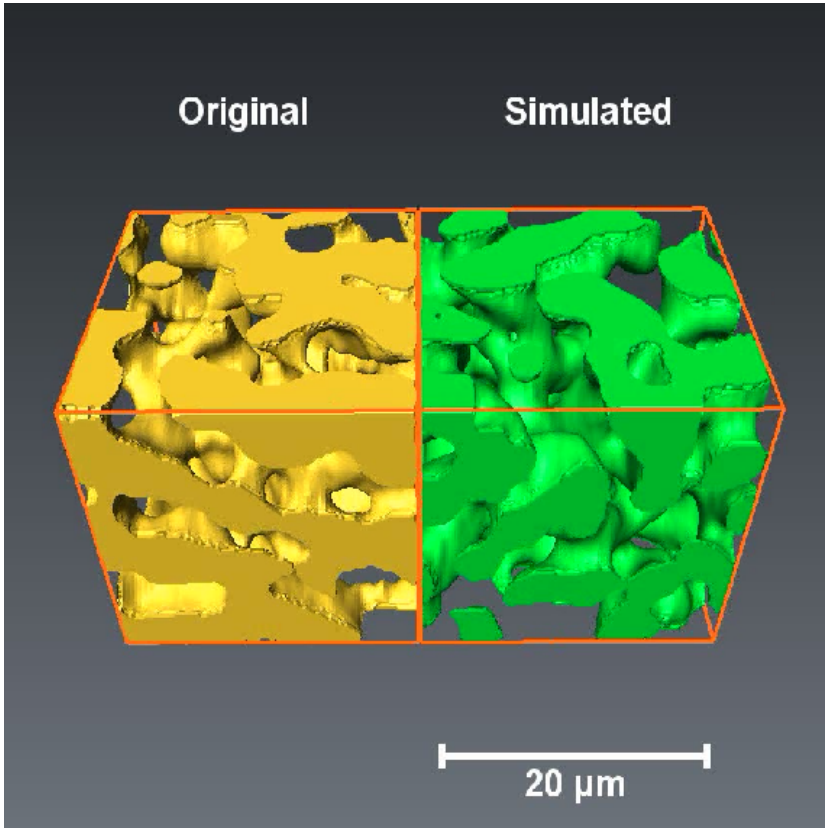
Synchrotron tomography image data



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

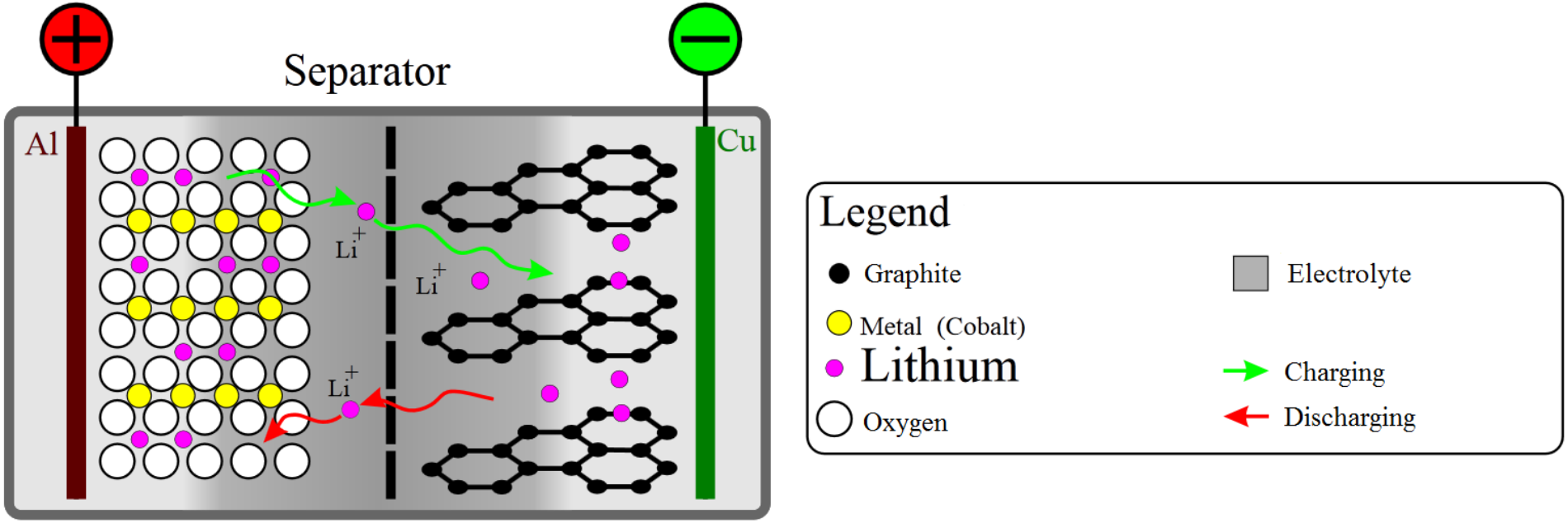
- 3D image of uncompressed graphite electrode used in Li-ion batteries
- tomography: Helmholtz Center Berlin, material: ZSW Baden-Württemberg
- yellow: graphite phase
- transparent: pore phase, volume fraction ca. 56%

Goal: stochastic simulation model



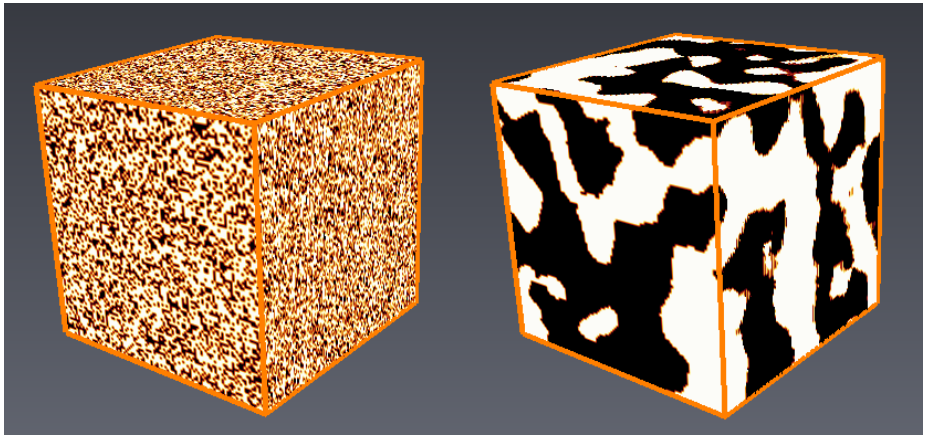
- Modeling of the 3D morphology of graphite electrodes
- Size: $100 \times 100 \times 100$ voxels

Functionality



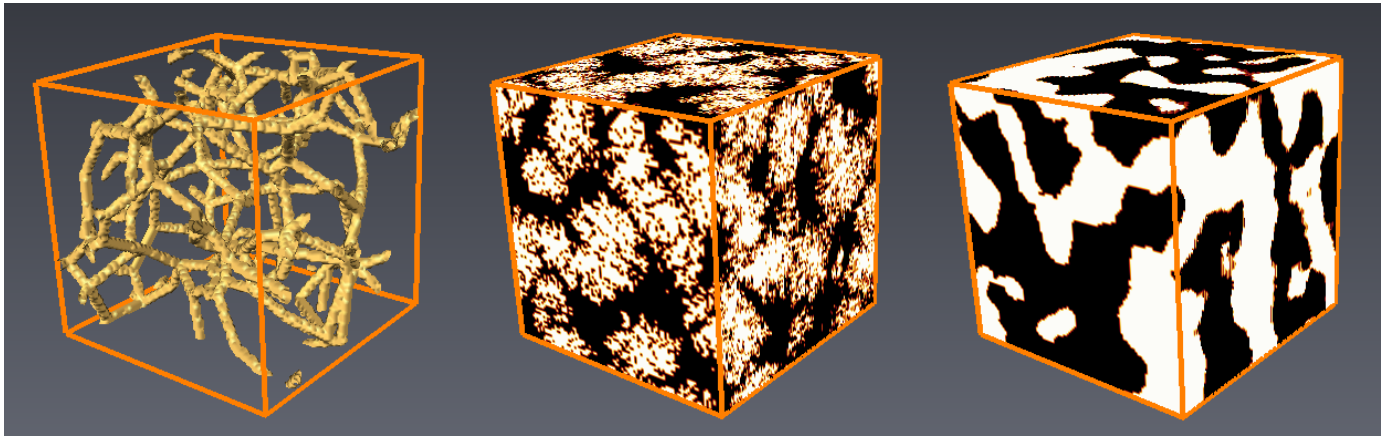
- 3D microstructure $\Leftrightarrow$ functionality
- Detect improved microstructures by virtual materials design

Simulated annealing for generation of microstructures



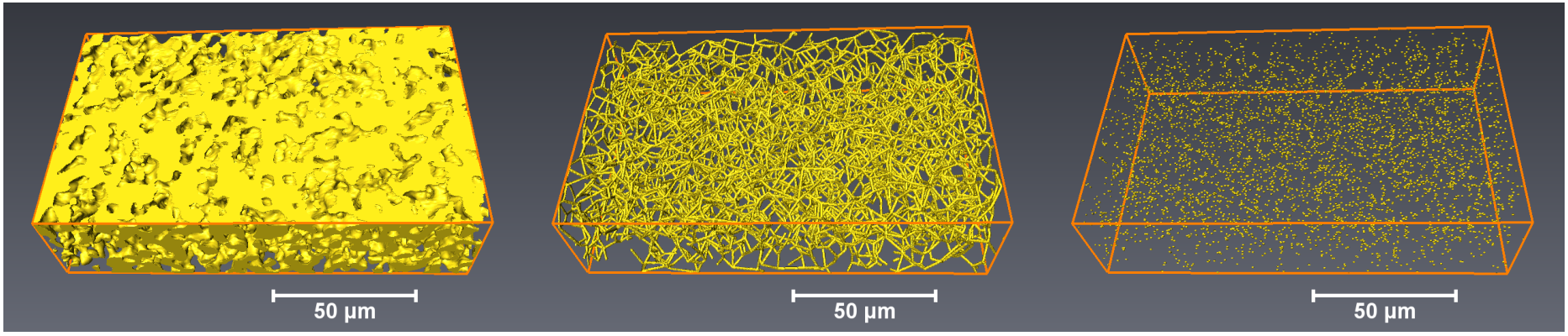
- Start with random allocation of voxels given volume fraction α
- Coarsening of morphology by interchanging voxels.
  - T temperature, $c(\cdot)$ cost function to be reduced (e.g. surface area)
  - Pick a pair of voxels at random
  - Swap voxels if cost function decreases, otherwise accept swap with 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



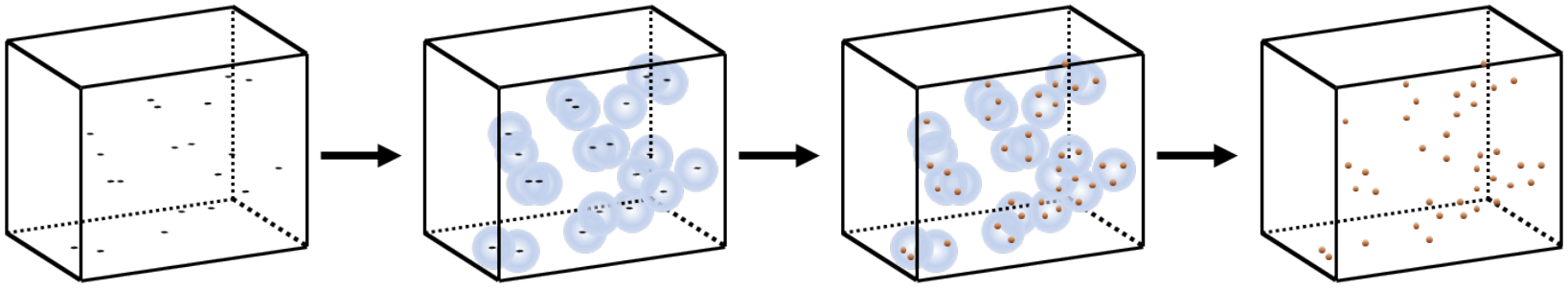
- Simulated annealing: simple but computational expensive, limited control of microstructure
- Hybrid approach: combining spatial stochastic graph modeling with simulated annealing
  - simulate random geometric graph
  - start configuration of voxels by project voxels onto the graph
  - run simulated 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

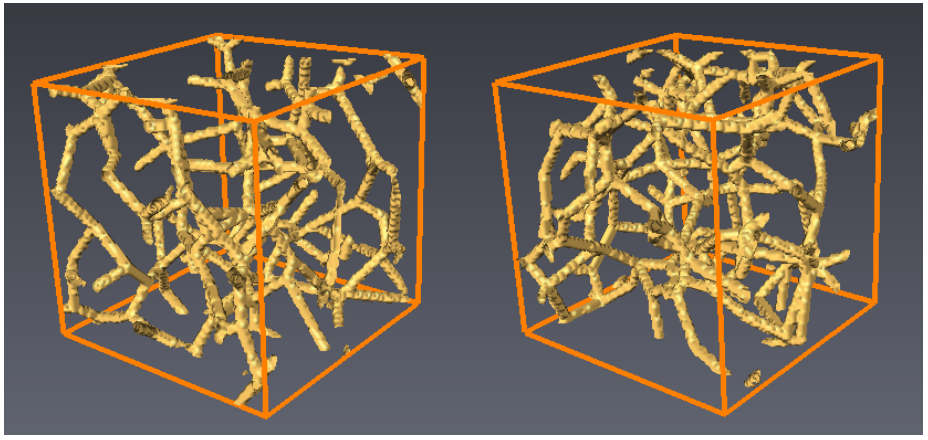


(1) Simulation of homogeneous Poisson process

(2) Simulation of Boolean Model

(3) Simulation of Poisson hardcore model inside the Boolean Model

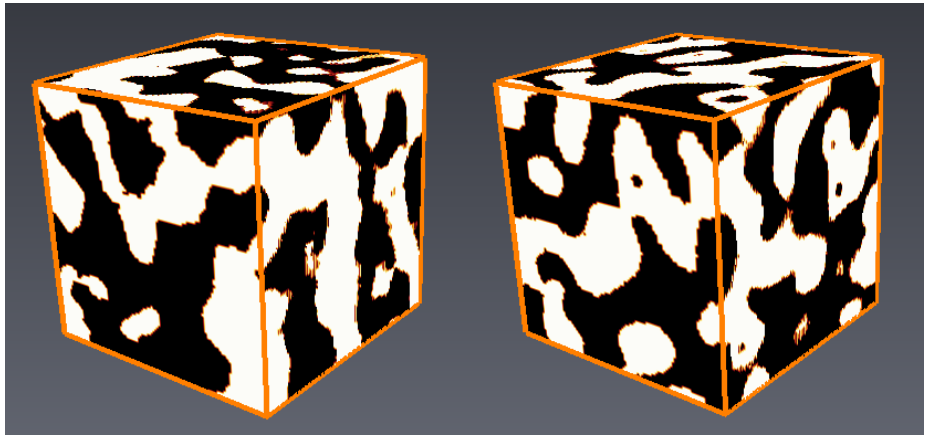
Stochastic model for setting edges



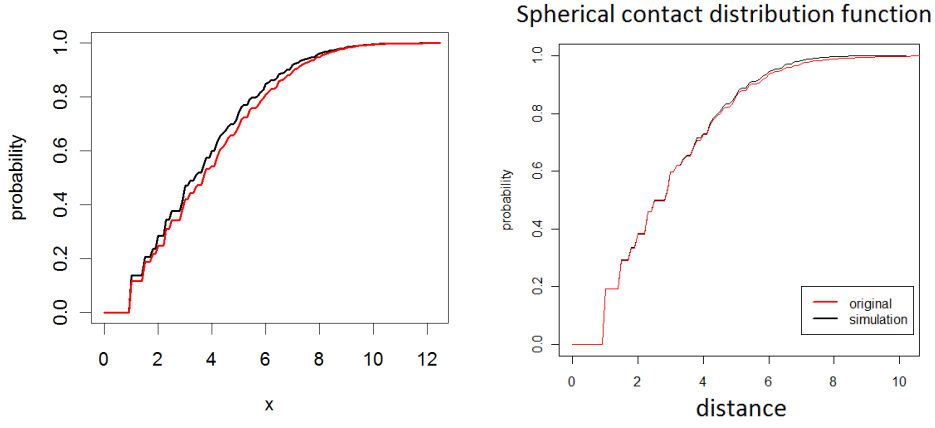
Cut-out of experimental graph (left) and simulated graph (right)

- 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 γ_1
- Postprocessing of edges
  - If angles undercut threshold γ_2: deletion with probability $p \in (0, 1)$.
  - Control of angles

Model validation



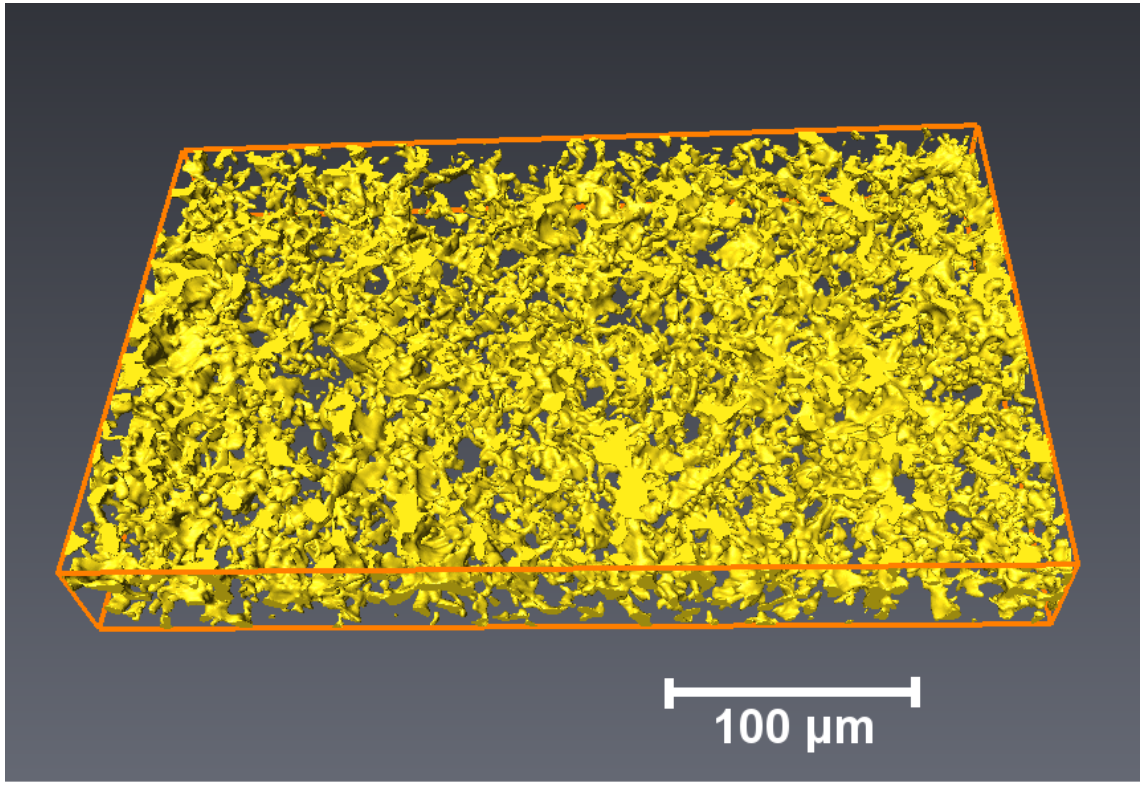
Cut-out of experimental (left) and simulated (right) microstructure



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

Contents

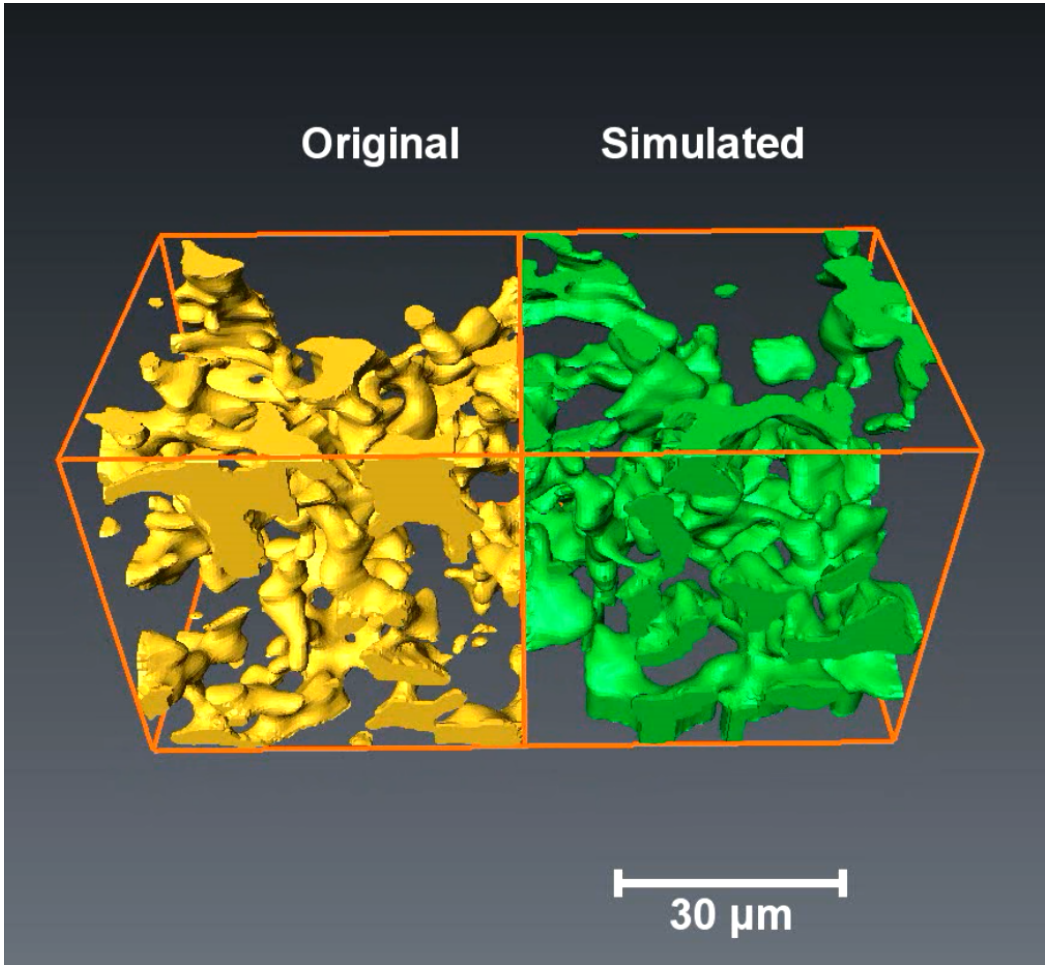
X-ray tomography image data



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

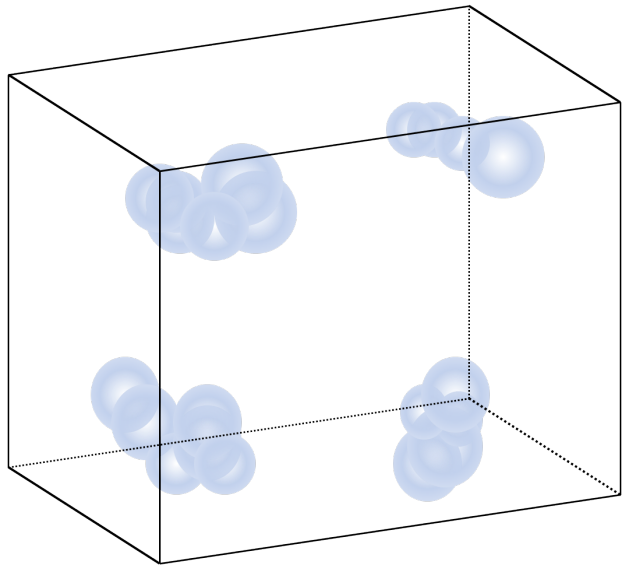
- 3D image of compressed graphite electrode used in Li-ion batteries
- tomography: Imperial College
- yellow: pore phase, volume fraction ca. $16,6\%$
- transparent: graphite phase

Goal: stochastic simulation model



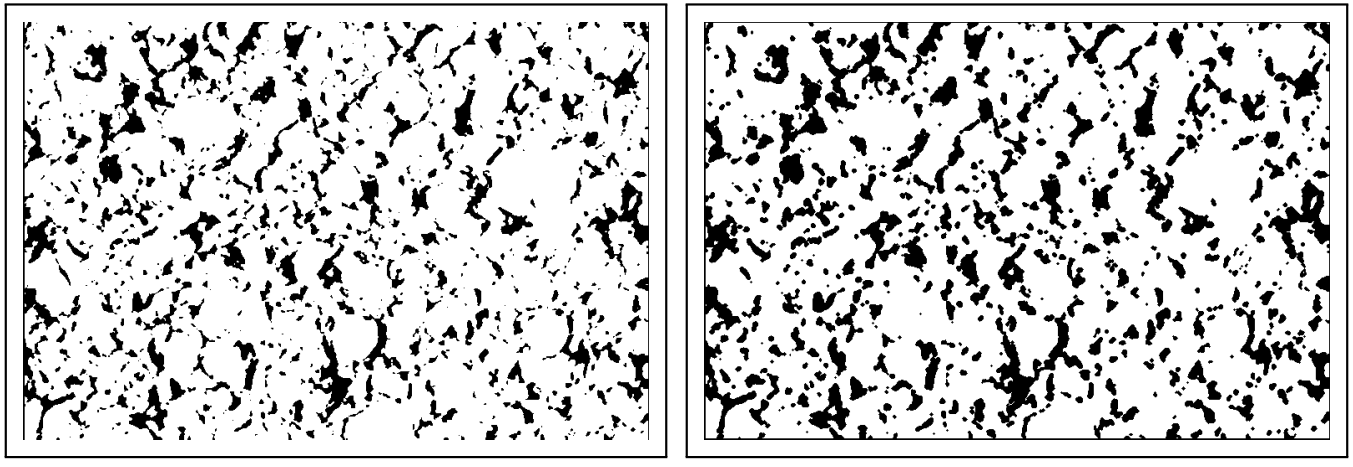
- Modeling of the 3D morphology of graphite electrodes

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?

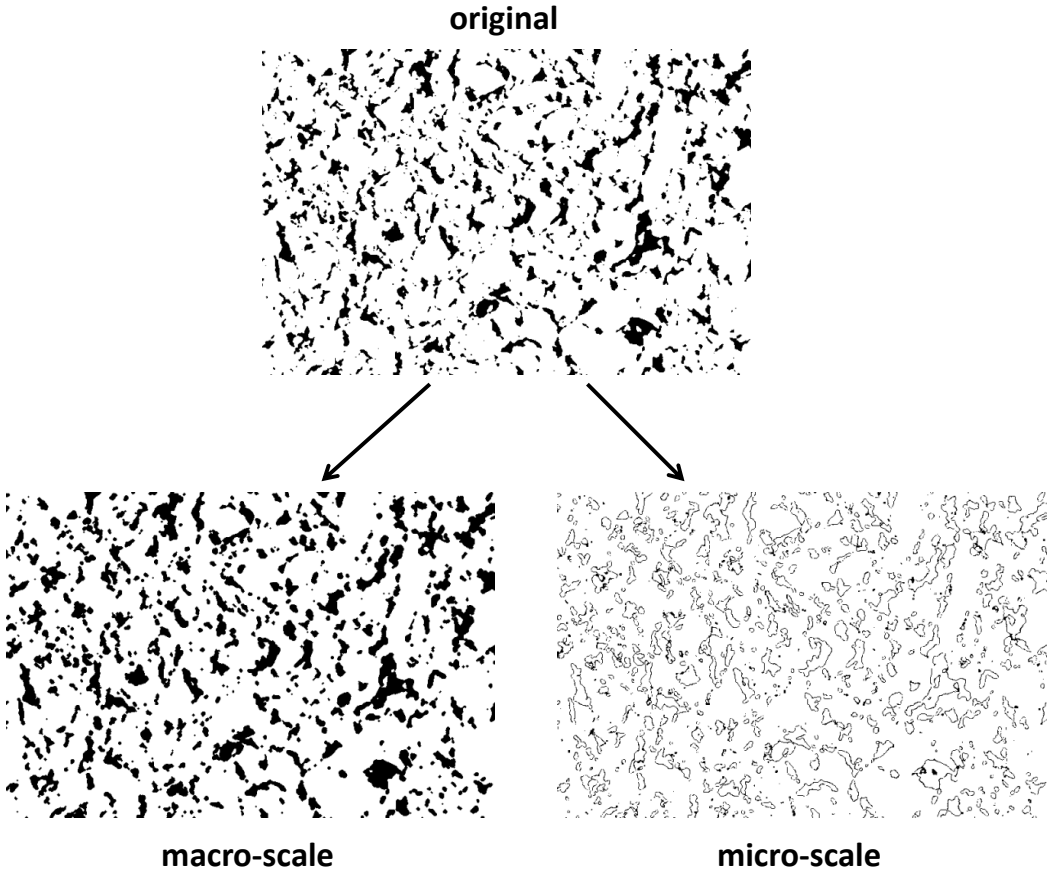
Data preprocessing: morphological smoothing



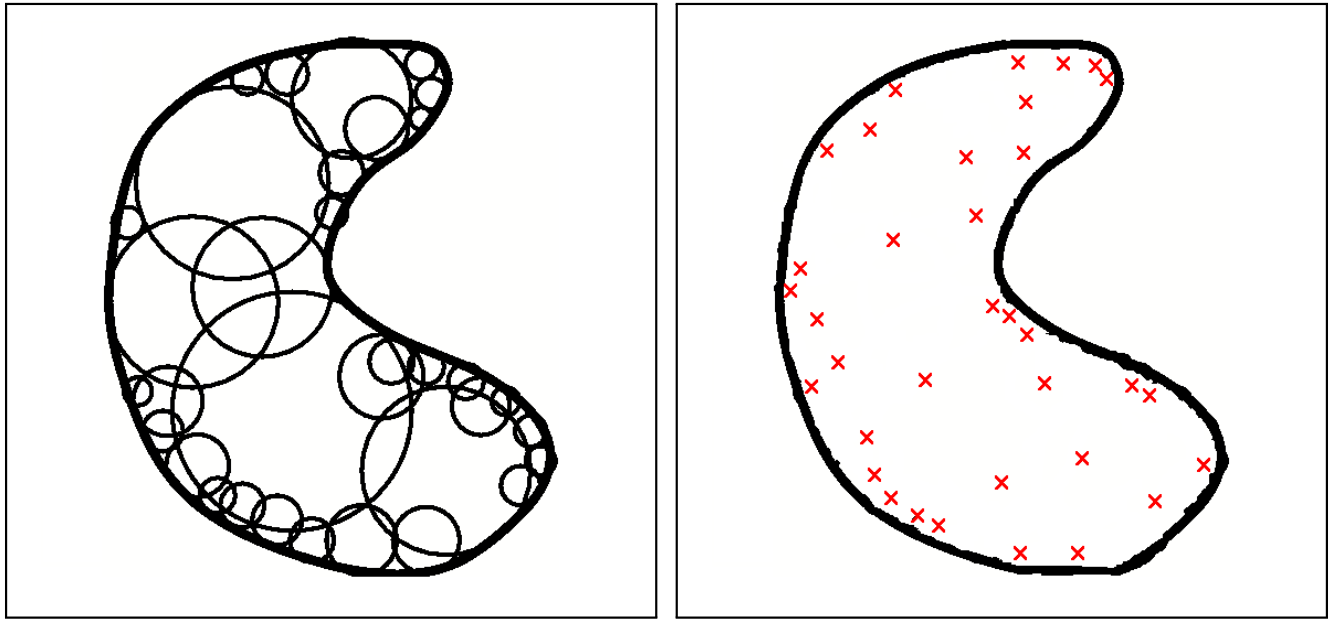
$$B' = \Big(\big(B \ominus b(o, \sqrt{3}) \big) \oplus b(o, \sqrt{3}) \Big) \oplus b(o, 1)$$

- 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

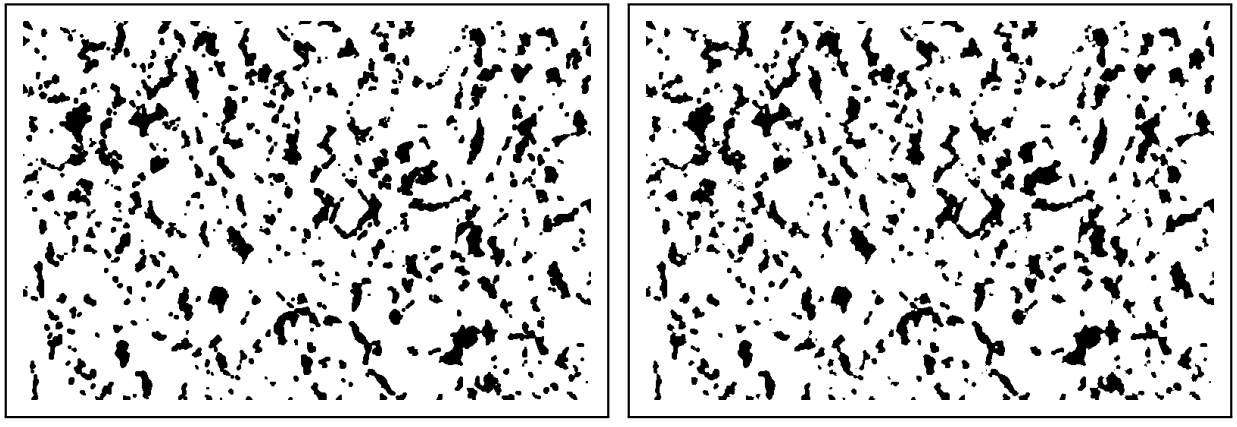


- Splitting of complexity
- Separate modeling of both scales



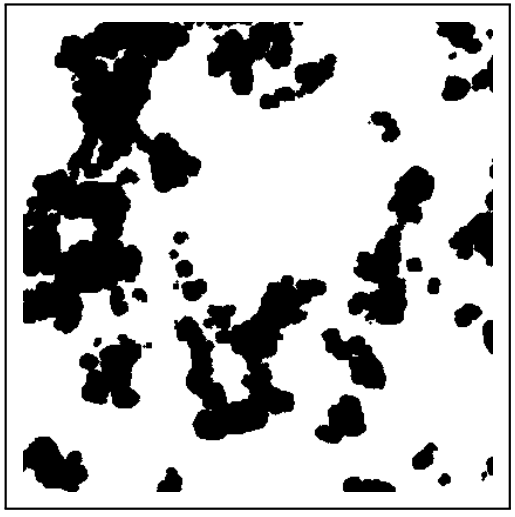
- Random placement of midpoints in pore phase (uniformly distributed)
- Radius = minimal distance to boundary (from Euclidean distance transform)
- Stop if 99% of pore phase are covered
- Repeat these steps several times
- Use kernel density estimation to find preferred midpoint locations

3D Representation of graphite electrode domains by unions of spheres

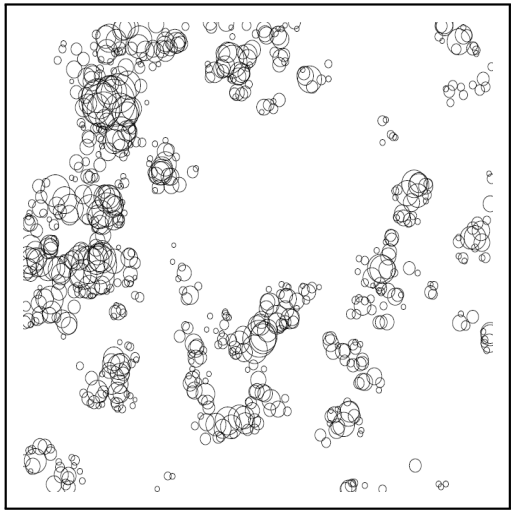


Results: enormous data reduction
mean number of voxel per sphere: 27.7

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



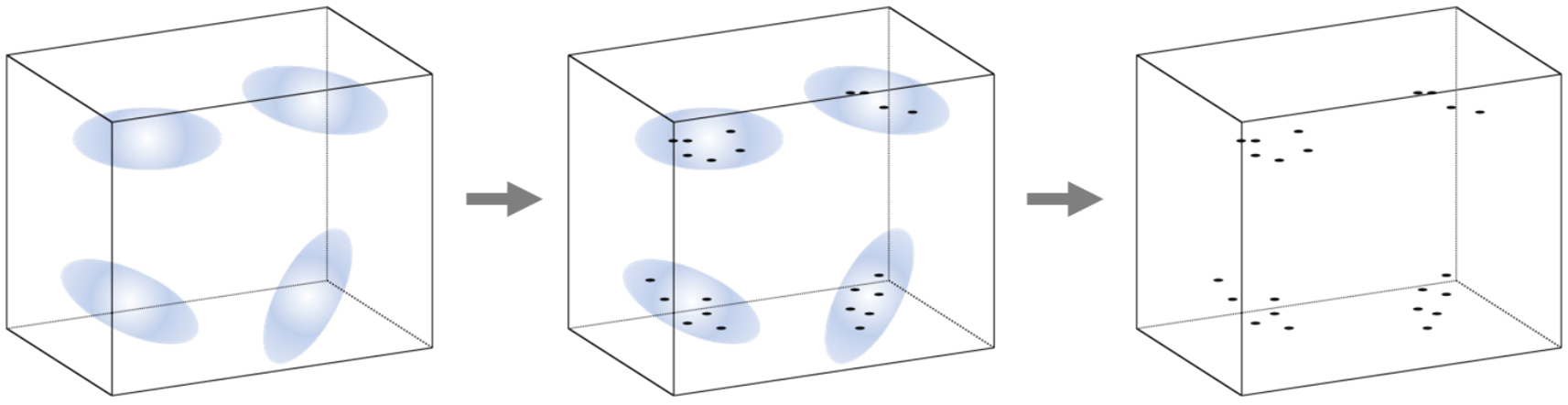
$\Longrightarrow$



$$= \bigcup_{i=1}^{n} b(s_i, r_i)$$

- Macro-scale represented by marked point process
- Transformation of battery data into mathematical language
- R. Thiedmann *et al.*, A multiscale approach to the representation of 3D images, with applications to polymer solar cells, Image Analysis and Stereology **30** (2011), 19–30.

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 λ_p of parent point process
- Expected number of child points per cluster c

Minimum–contrast estimation

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

$$\widehat{\theta} = \text{argmin}_\theta \int_{r_1}^{r_2} (g_\theta(r) - \widehat{g}(r))^2 \mathrm{d}r\,,$$

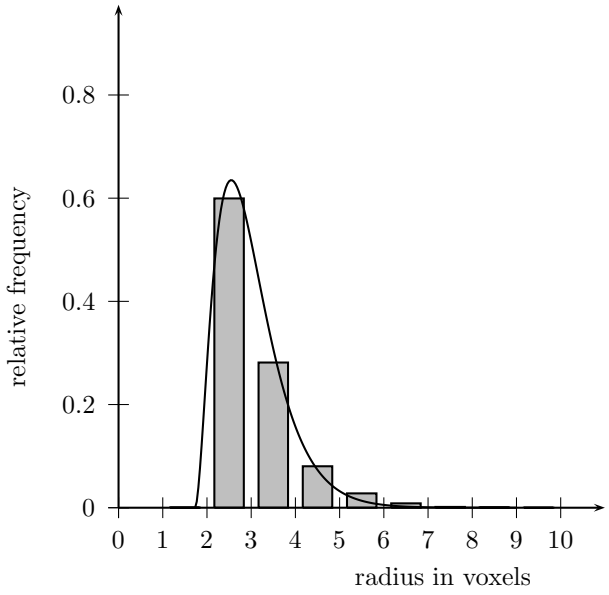
  where $g(r)$ is the pair-correlation function

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

Estimated parameters

$\widehat{\lambda}_p = 0.00015$, $\widehat{c} = 33.33$, $\widehat{l}_1 = \widehat{l}_2 = 22.2$, and $\widehat{l}_3 = 3$

Modeling of spheres

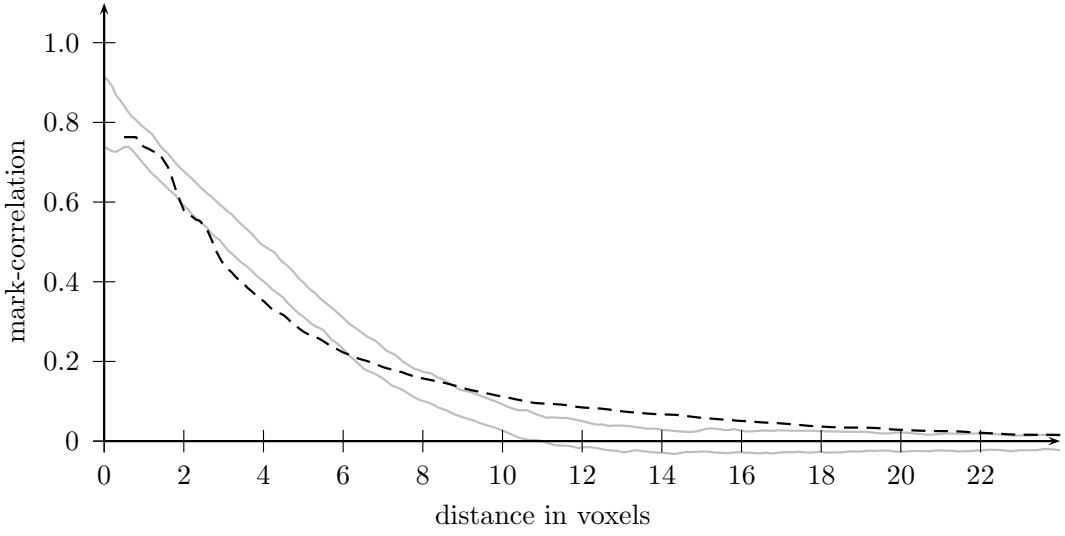


spherical distances with fitted gamma distribution

Fitted shifted gamma distribution

$$\begin{aligned} \text{Rate} &= 2.26 \\ \text{Shape} &= 2.85 \\ \text{Shift} &= \sqrt{3} \end{aligned}$$

Modeling of spheres



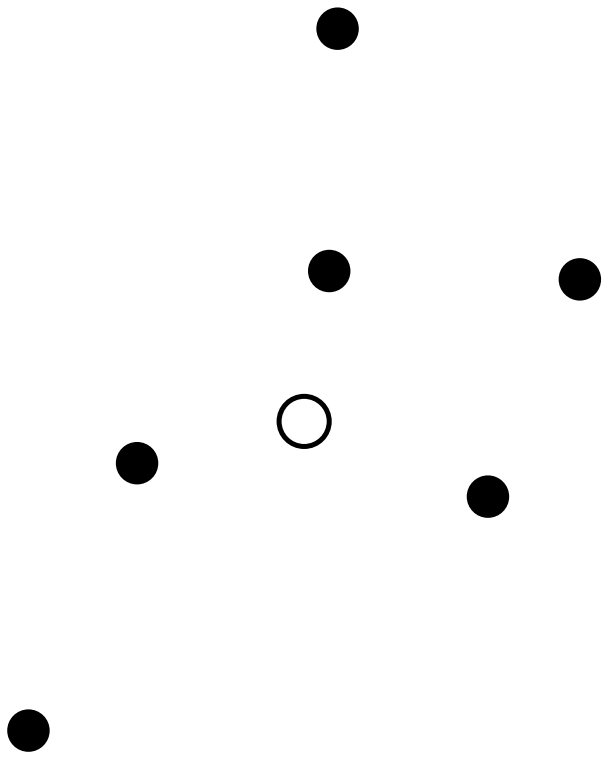
correlation structure

Dependence structure of sphere radii

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

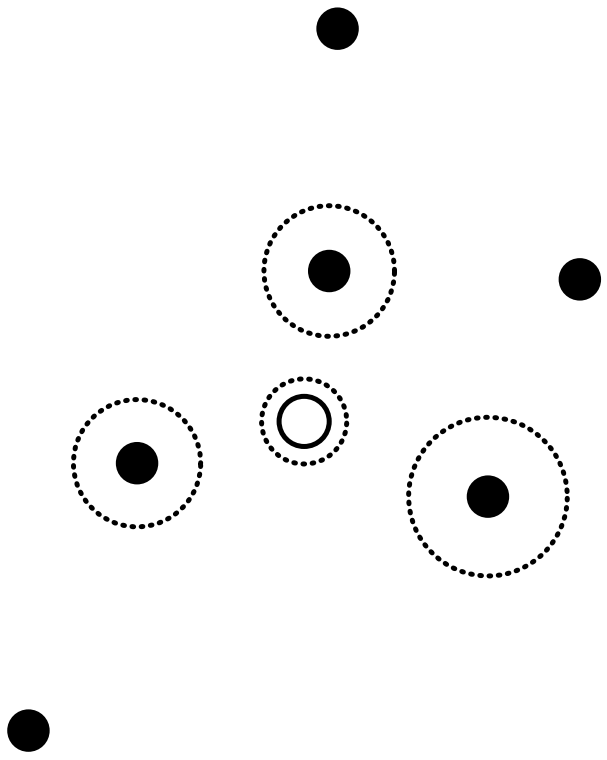
$$Z_i + Z_{i_1} + \ldots + Z_{i_{10}} + \sqrt{3} \sim \Gamma(2.26, 2.85, \sqrt{3})$$

Modeling of spheres



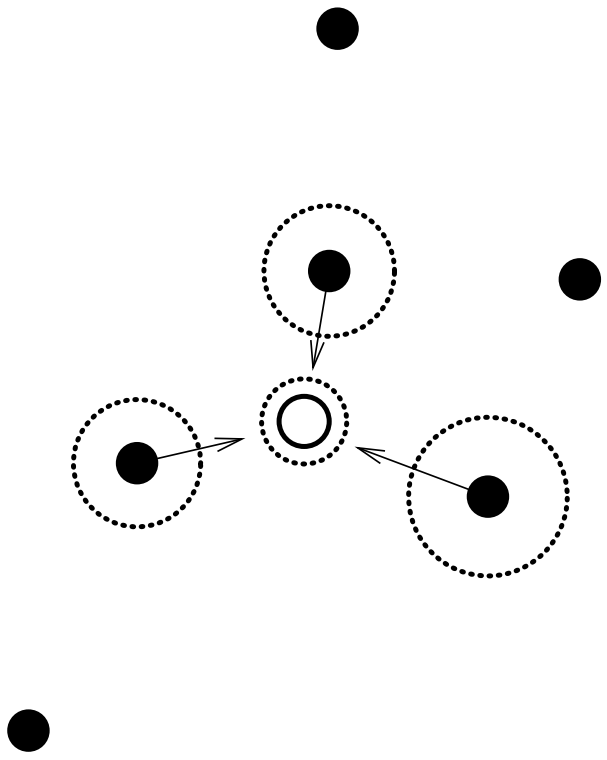
example: influence of 3 nearest neighbors

Modeling of sphere



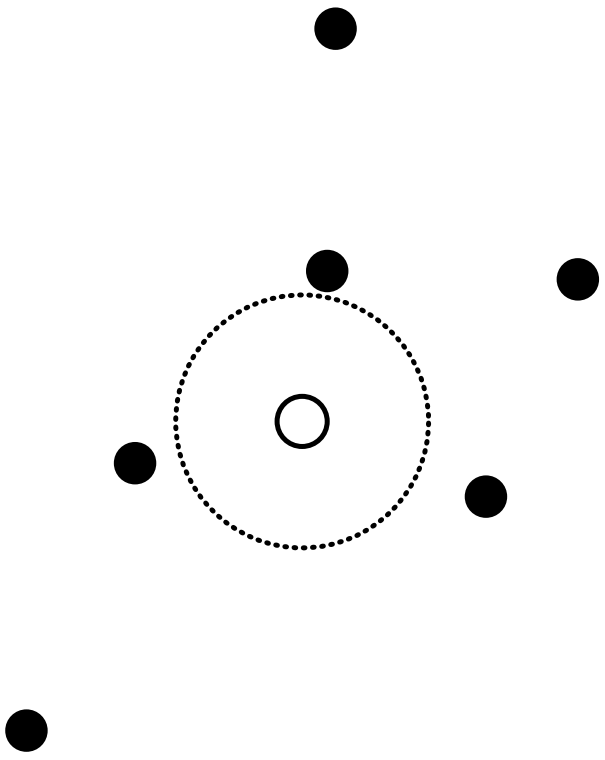
example: influence of 3 nearest neighbors

Modeling of spheres



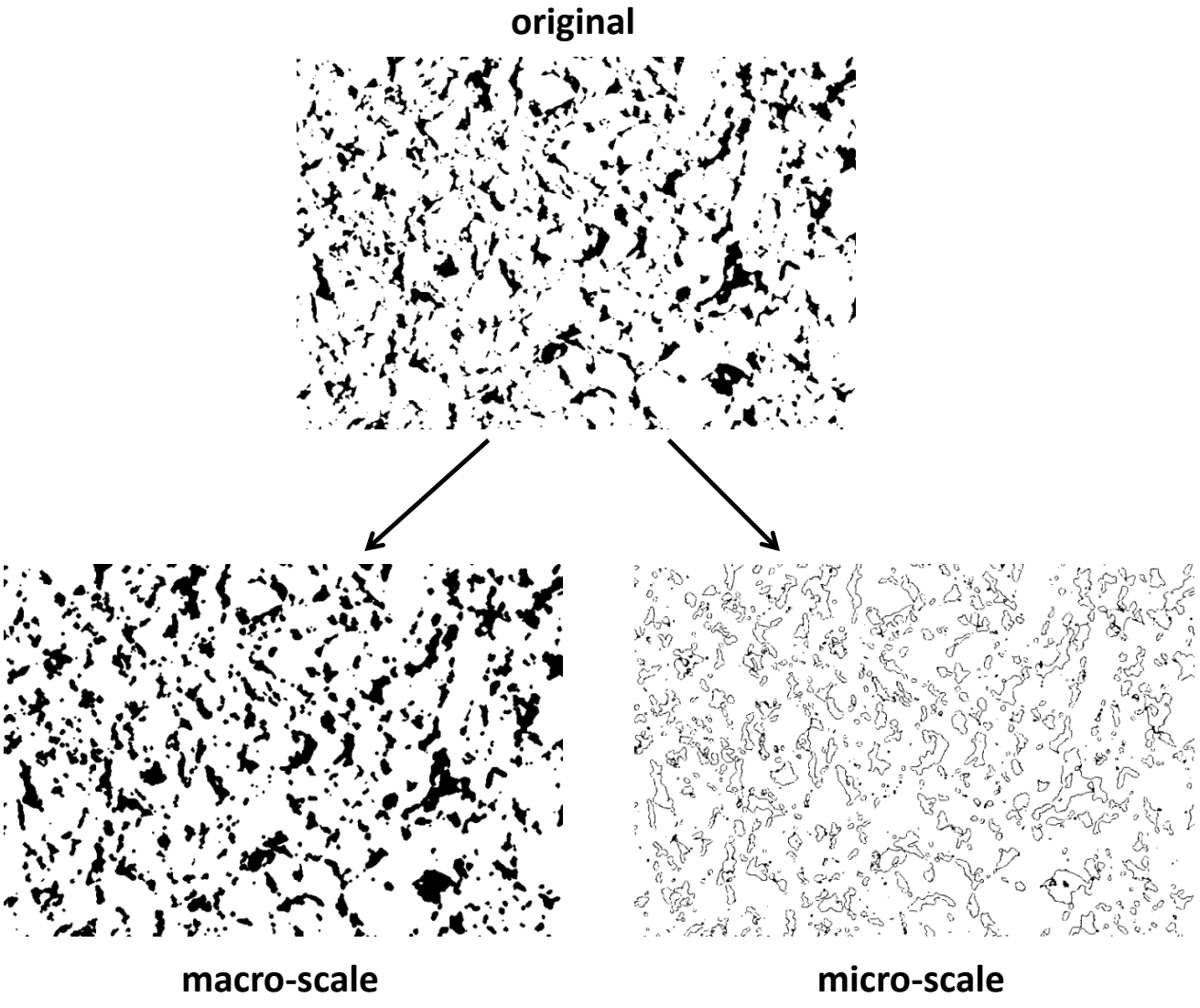
example: influence of 3 nearest neighbors

Modeling of spheres

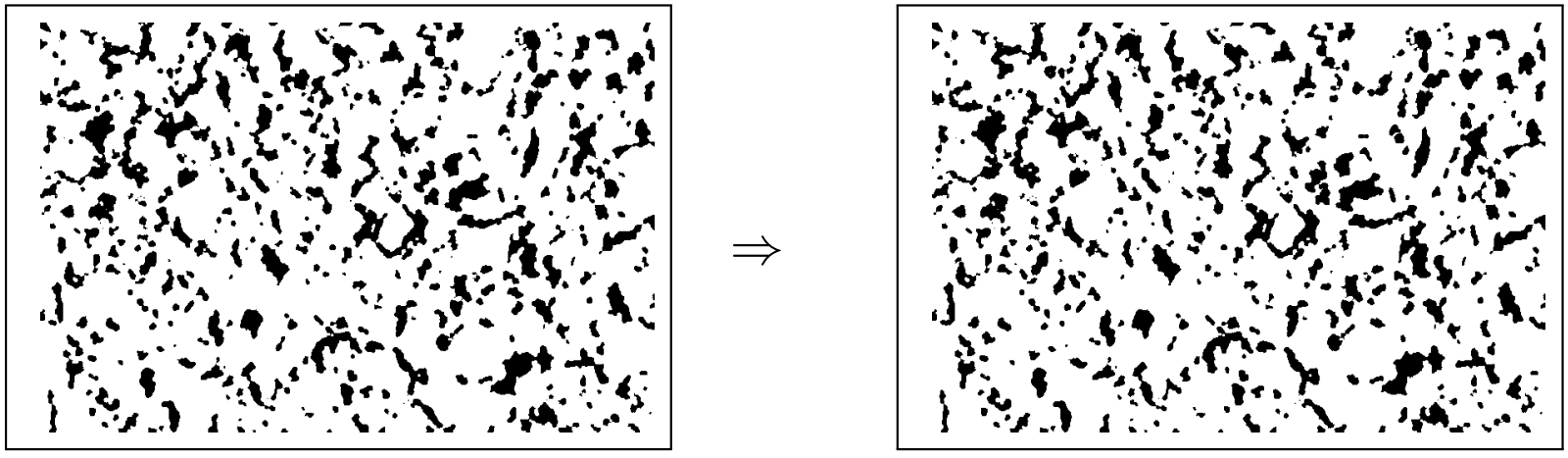


example: influence of 3 nearest neighbors

Inversion of morphological smoothing by stochastic modeling



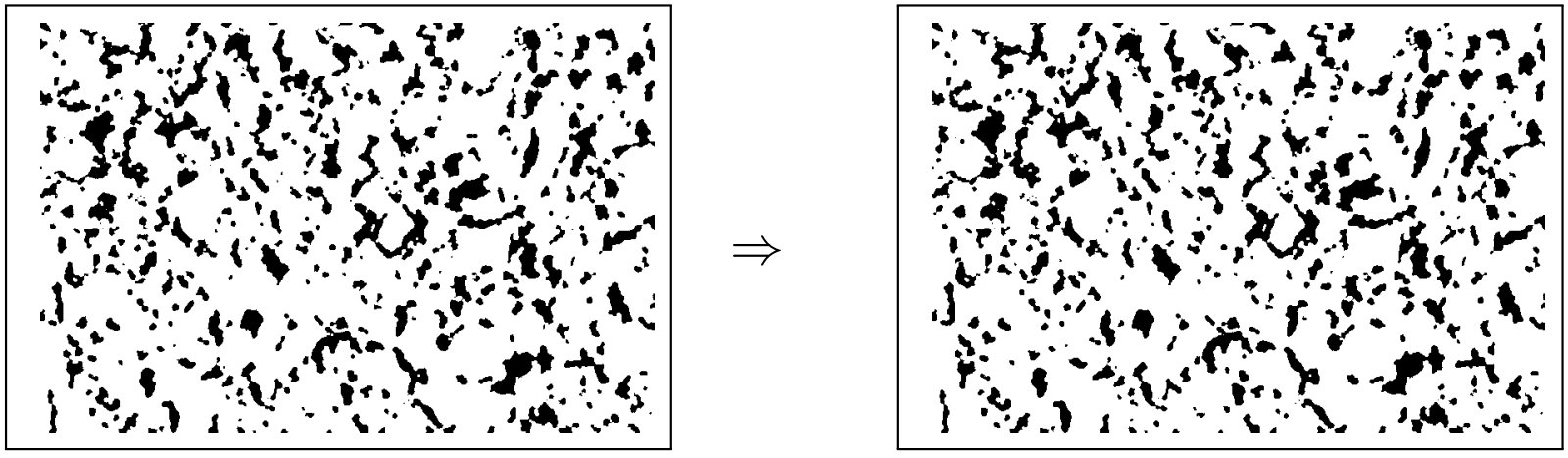
Inversion of morphological smoothing by stochastic modeling



Integration of missing connections

- Inhomogeneous Poisson point process

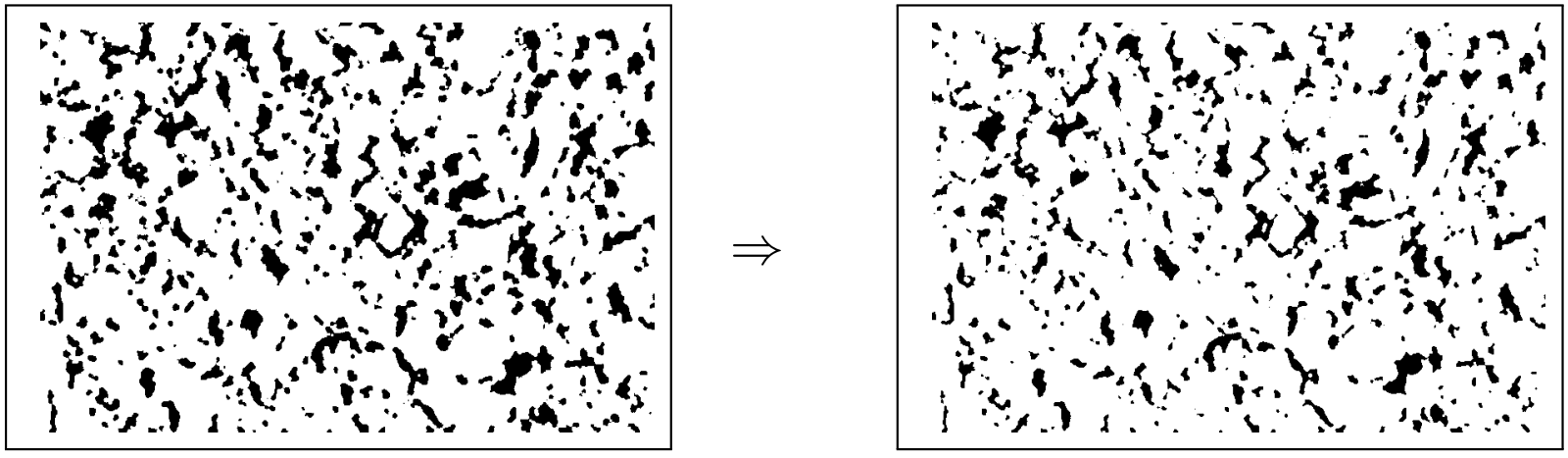
Inversion of morphological smoothing



Closing of pore phase

- 'Inversion' of opening

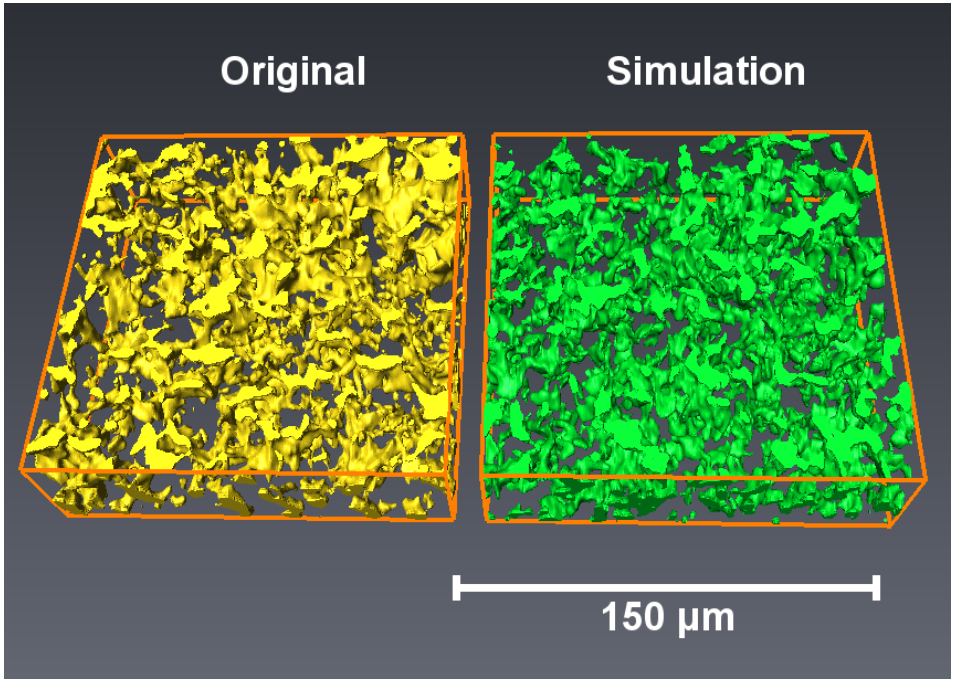
Inversion of morphological smoothing



Erosion of pore phase

- 'Inversion' of dilation

Result: stochastic simulation model



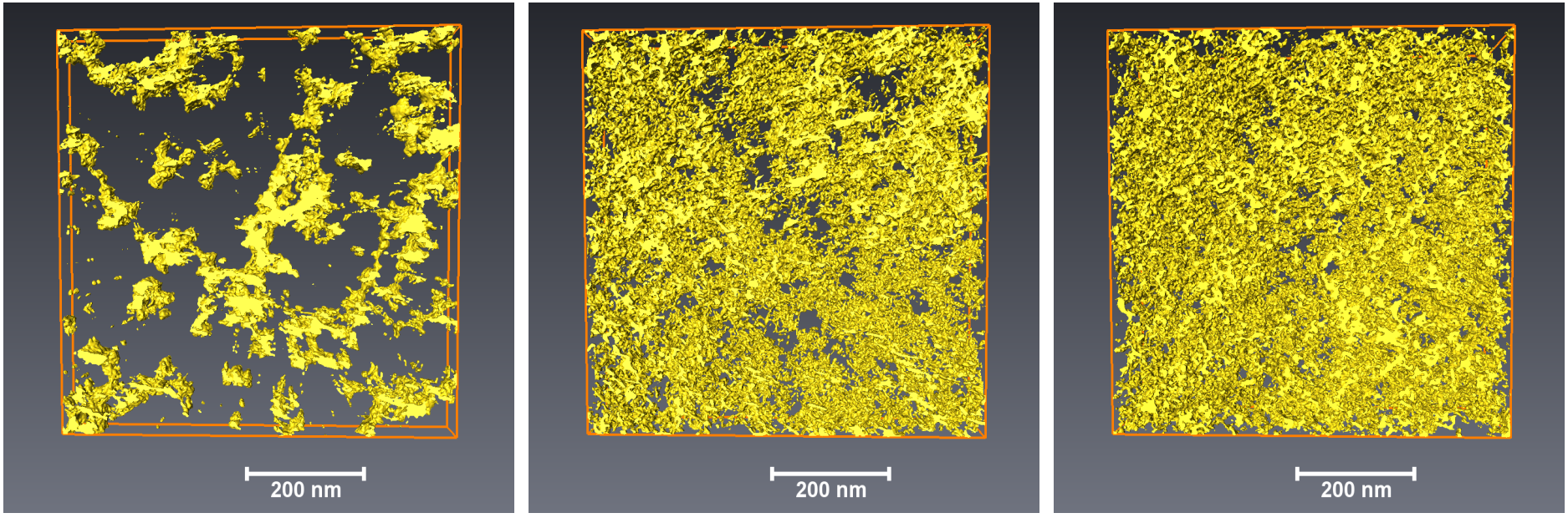
- Excellent visual agreement
- R. Thiedmann *et al.*, Stochastic Simulation Model for the 3D Morphology of Composite Materials in Li-Ion Batteries, Computational Materials Science **50** (2011), 3365–3376.

Structural validation of simulation model

	real data mean	simulated data mean
porosity	0.166	0.166
connectivity	0.967	0.967
specific interior surface area	0.079	0.085
spherical contact distribution	1.83	1.70
geometric tortuosity	1.59	1.82
object based pore size	3.12	3.09
coordination number	2.73	2.71
relative MST-length	0.56	0.56

Contents

Tomographic solar cell data

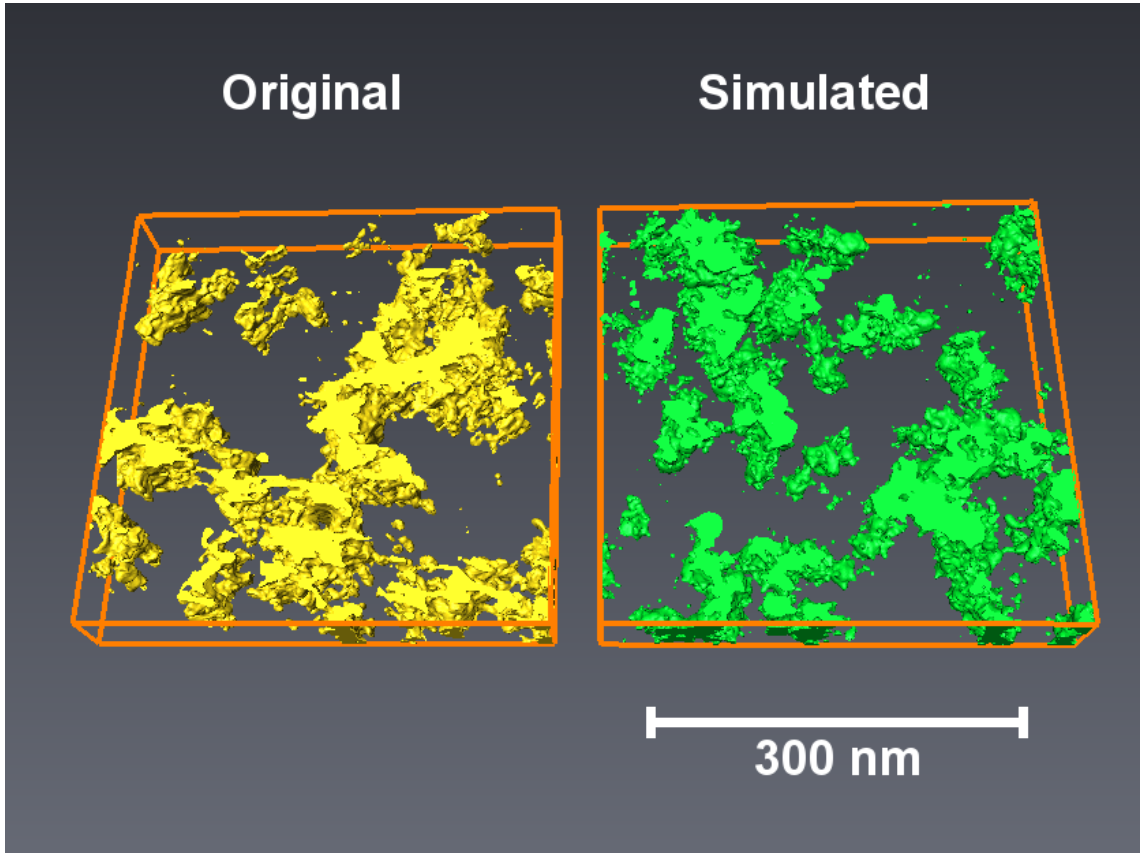


5000 rpm $\sim$ 57 nm 1500 rpm $\sim$ 100 nm 1000 rpm $\sim$ 167 nm

S.D. Oosterhout *et al.*, Nature Materials **8** (2009), 818–824.

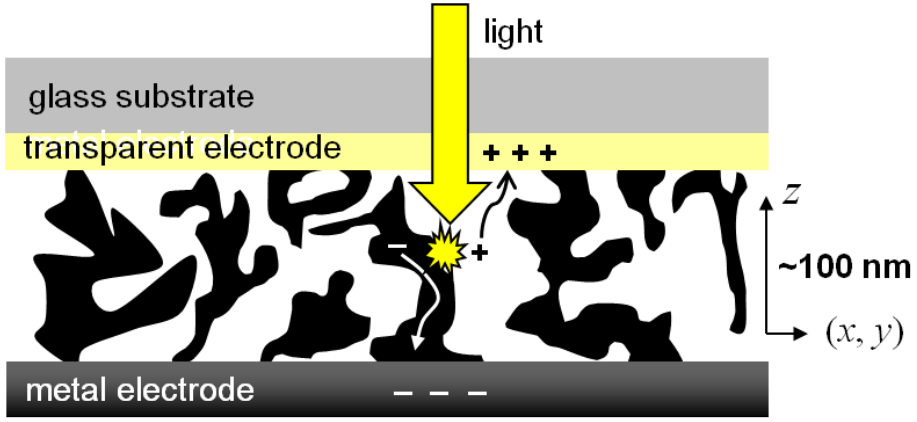
- 3D TEM images of P3HT-ZnO solar cells with different thicknesses
- TEM: Technical University Eindhoven
- P3HT-phase: transparent
- ZnO-phase: yellow, volume fraction 13.3% – 21.1%
- Morphology is anisotropic

Goal: stochastic simulation model



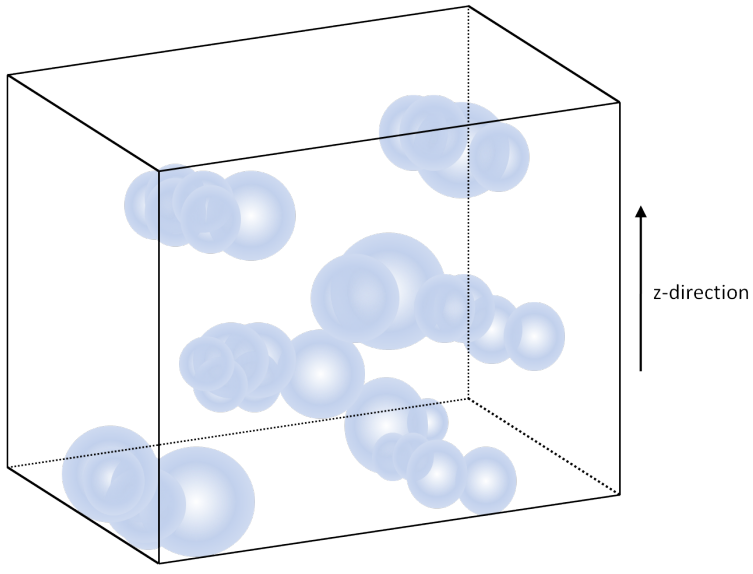
- same model type for all layer thicknesses
- different model parameters for different layer thicknesses

Functionality



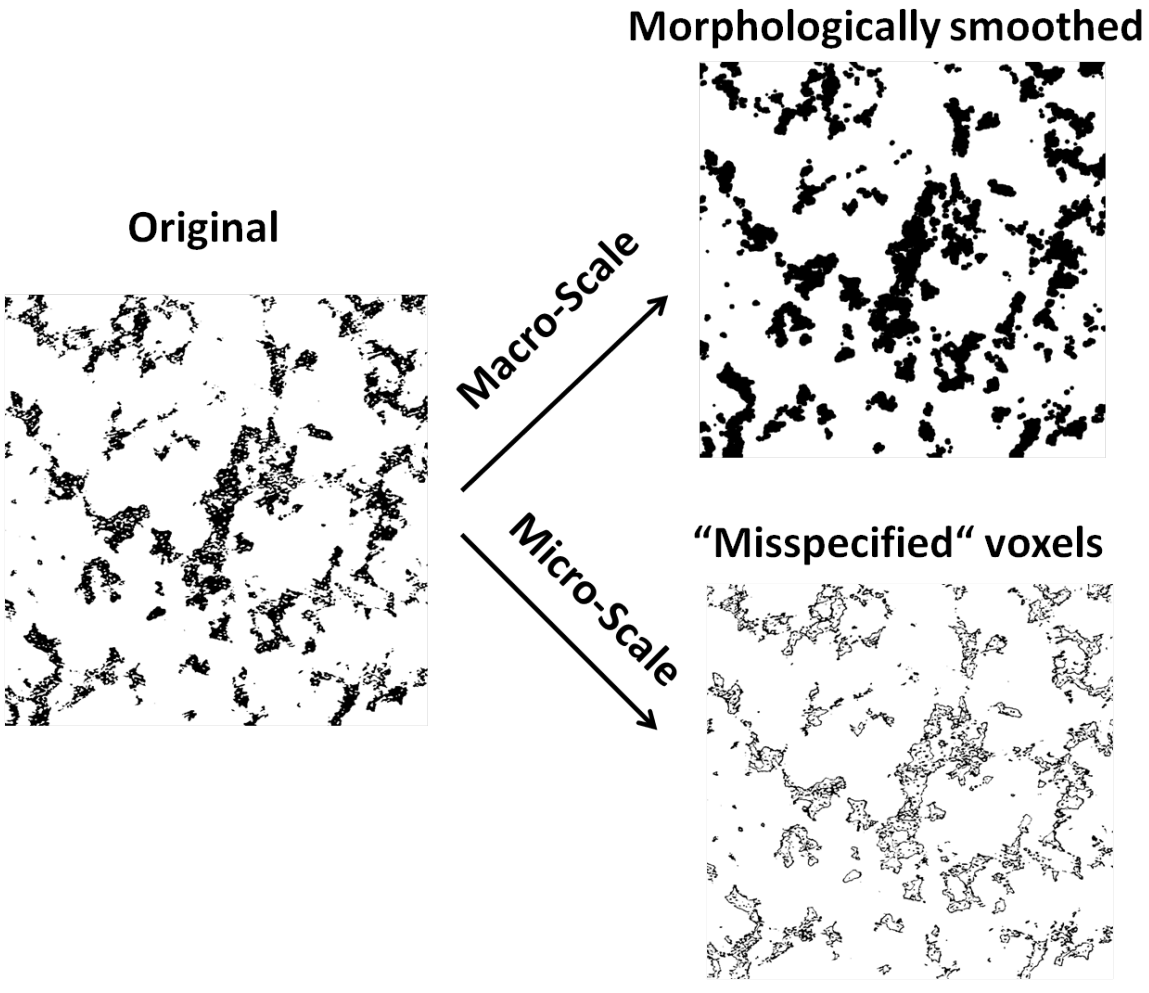
- Device architecture: bulk heterojunction
- Light acitivates the polymer phase of the solar cell
- Excitons are generated
- Diffusion of excitons in the polymer phase
- Excitons reaching the ZnO phase generate charges: quenching
- Transportation of charges to the electrodes
- 3D microstructure $\Leftrightarrow$ functionality
- Detect improved microstructures by virtual materials design

Modeling idea: 'smart' system of spheres

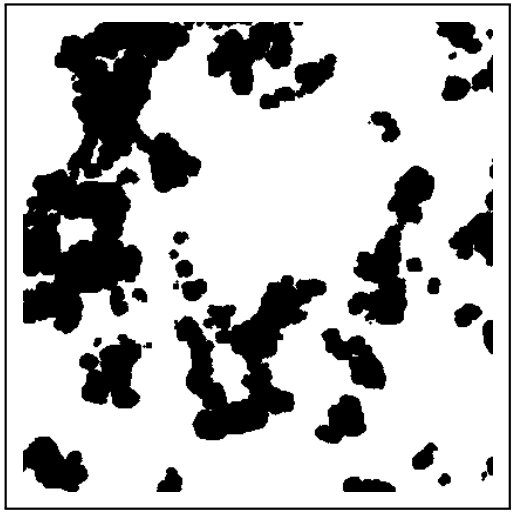


- Representation of the ZnO phase as a complex system of spheres
- Contrast to compressed battery modeling: anisotropic point pattern
- Anisotropy by Markov chain of 2D point processes

Multi-scale approach



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



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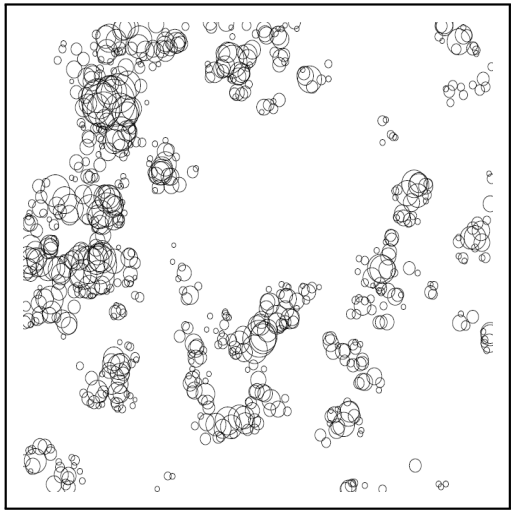
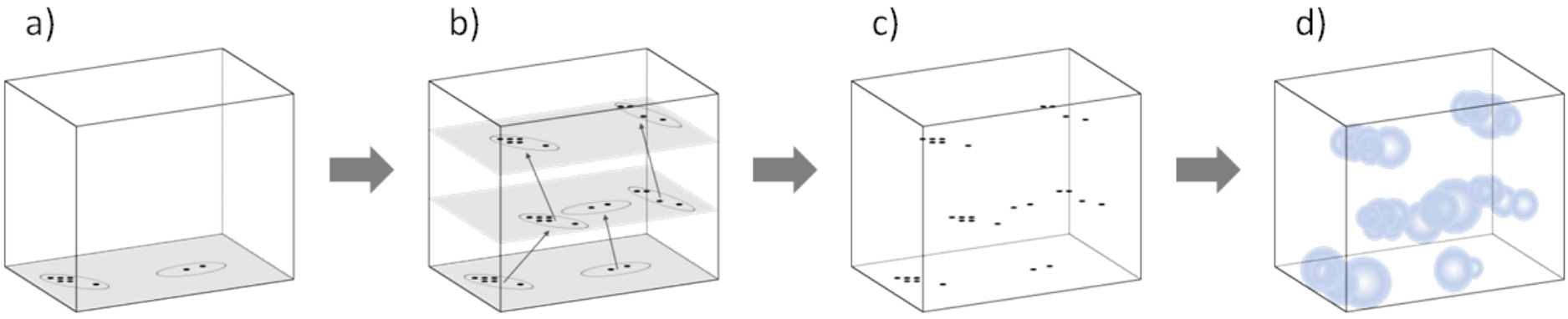


$$= \bigcup_{i=1}^{n} b(s_i, r_i)$$

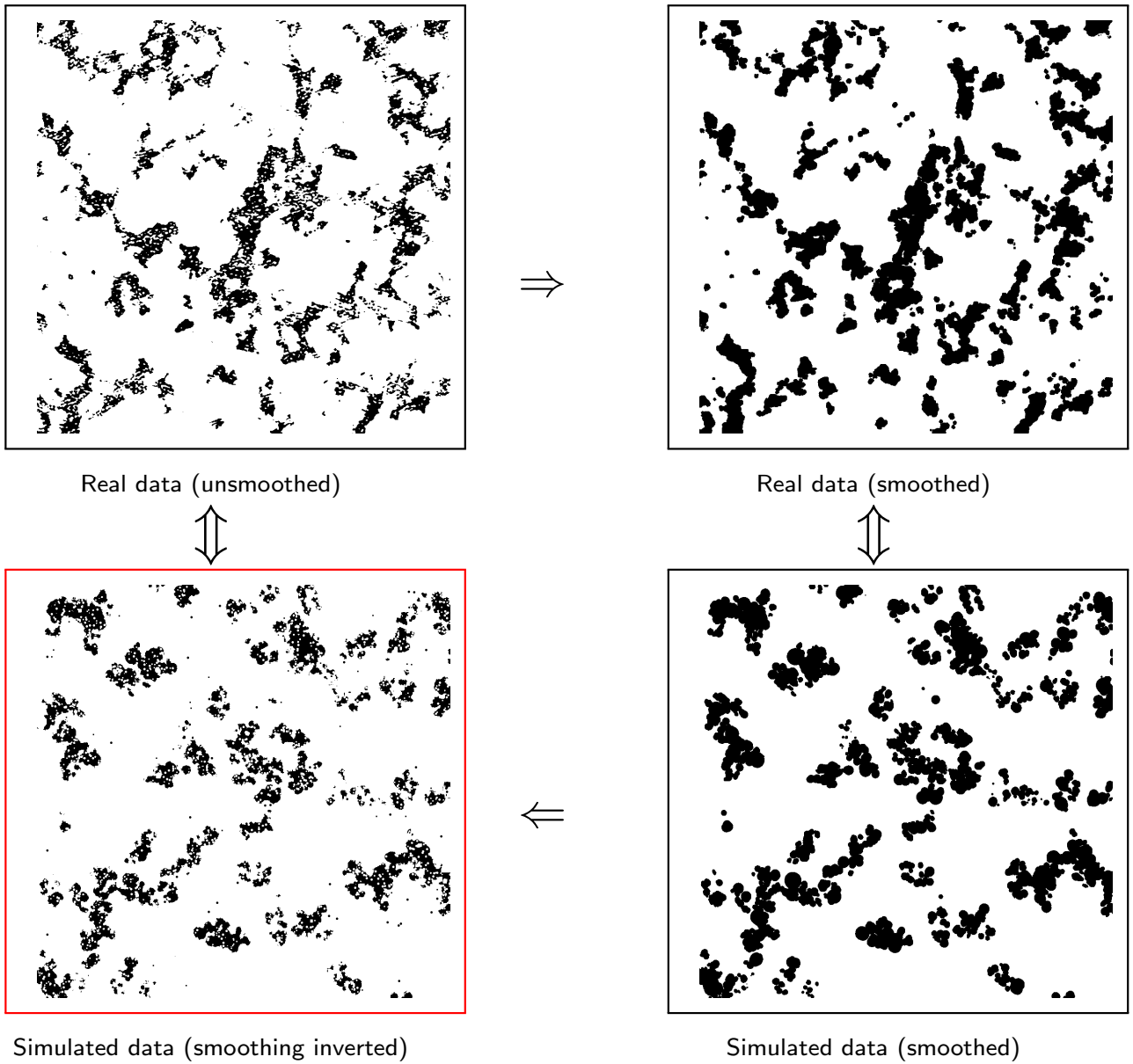
- Macro-scale represented by marked point process
- Transformation of solar cells into mathematical language

Modeling in 2 steps:

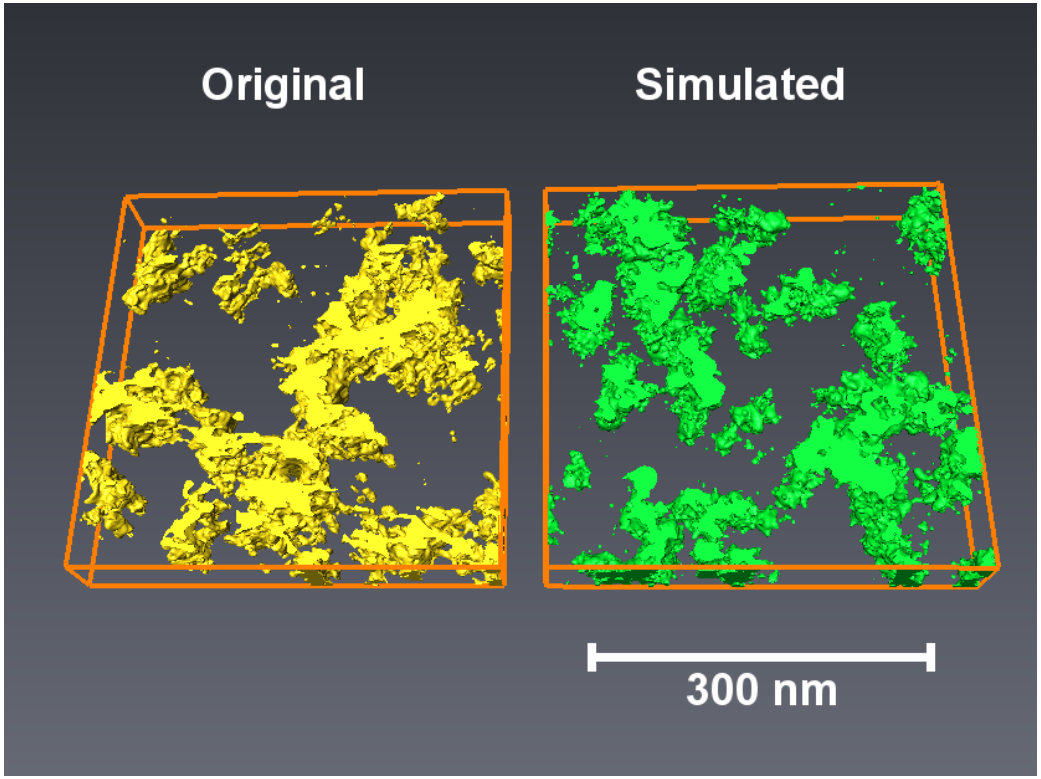
- 2D point patterns: elliptical Matérn cluster process
- 3D stack of 2D point patterns: spatial birth-and-death process



Inversion of morphological smoothing by stochastic modeling



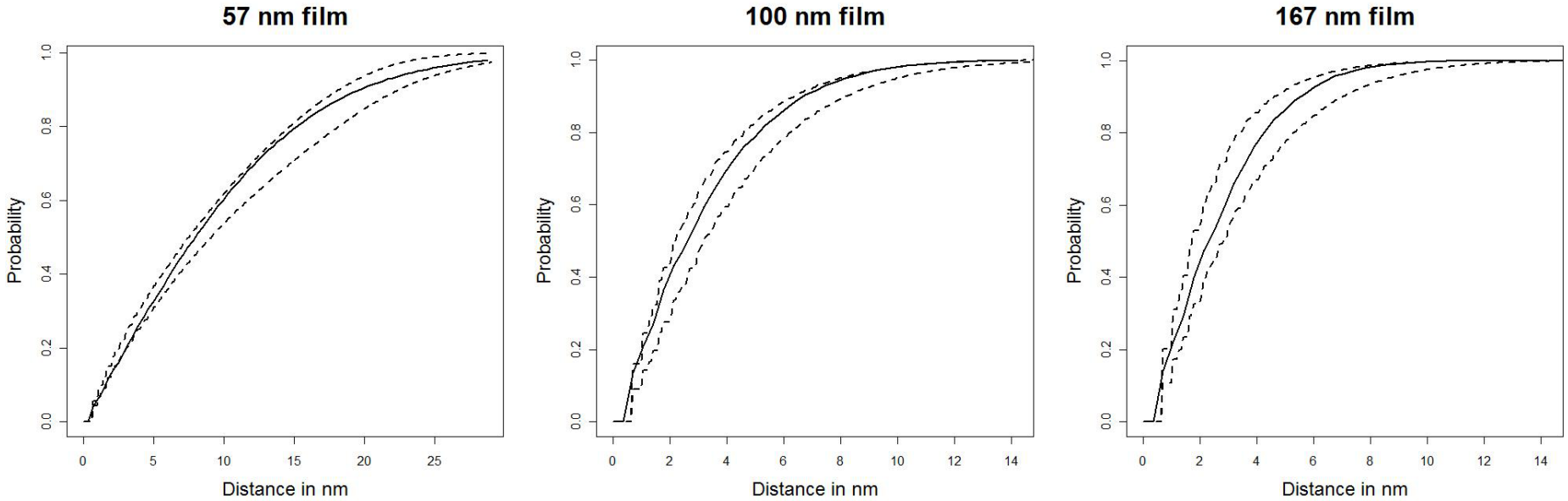
Result: stochastic simulation model



- Good visual agreement
- O. Stenzel *et al.*, Spatial Modelling of the 3D Morphology of Hybrid Polymer-ZnO Solar Cells, based on Tomographic Image Data, Annals of Applied Statistics **5** (2011), 1920–1947.

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)

		Volume fraction	Connectivity (monotonous)
57 nm	model	0.115	0.887
	data	0.133	0.928
100 nm	model	0.216	0.888
	data	0.211	0.910
167 nm	model	0.210	0.809
	data	0.210	0.851

Physical characteristic for model validation

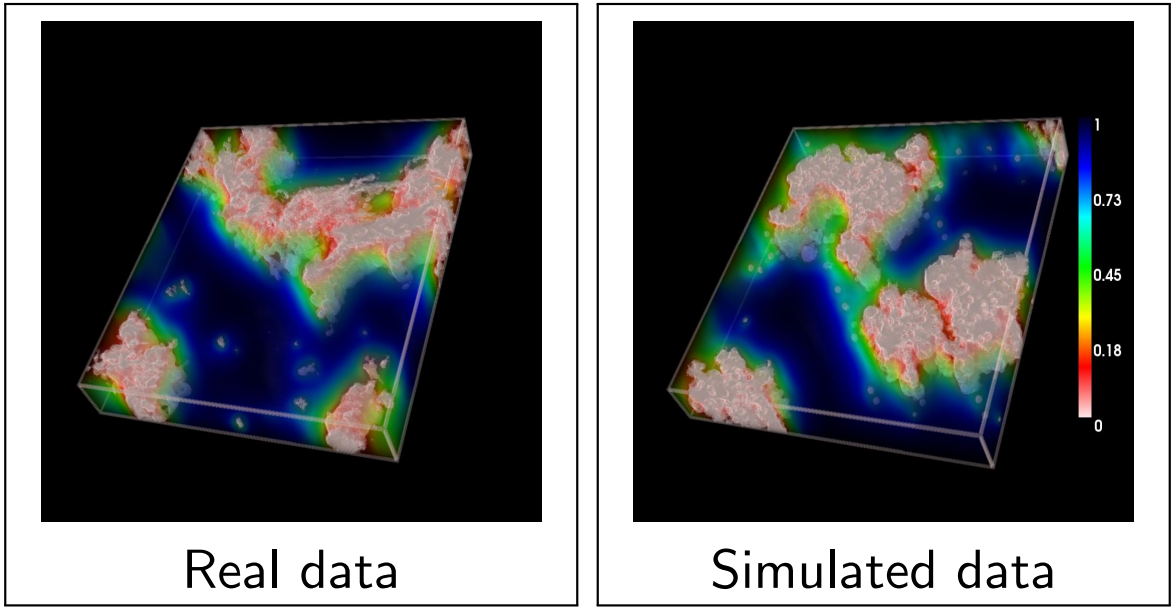
Quenching probability η_Q (probability of a random exciton to reach the ZnO-phase)

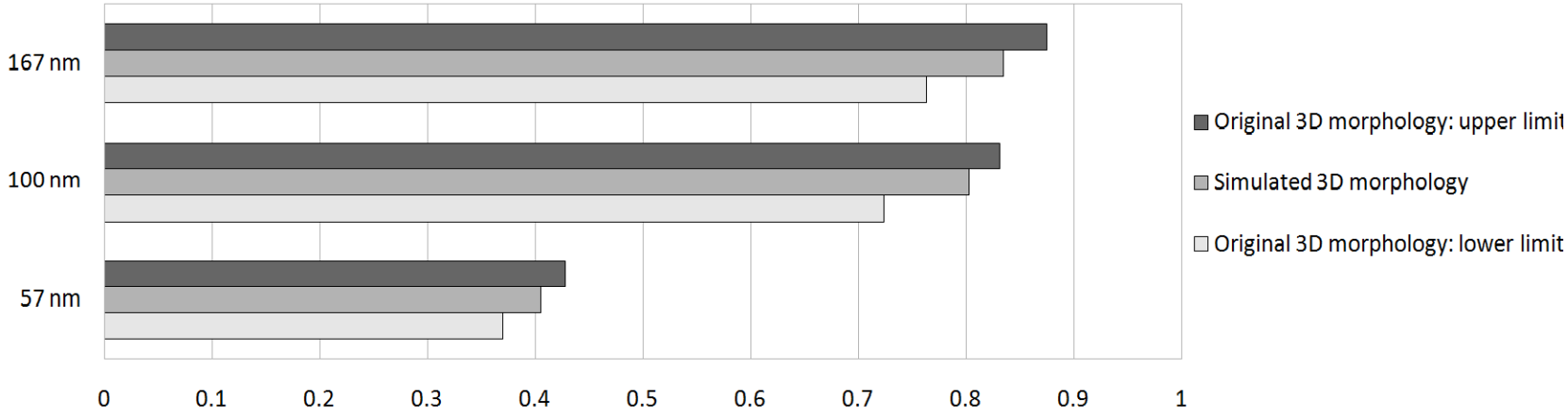
- η_Q obtained from the field $\{n(x), x \in B^c\}$ of local exciton densities in the polymer phase
- $\{n(x), x \in B^c\}$ computed by solving the steady-state diffusion equation

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

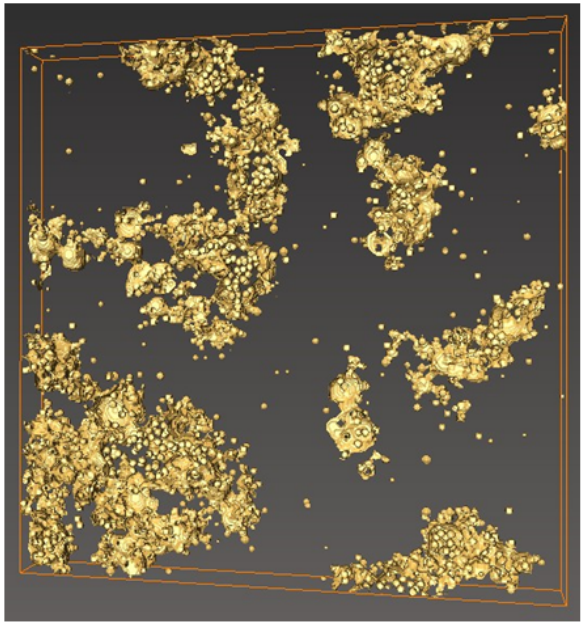
  D: diffusion constant, τ: exciton life time, g: rate of exciton generation
- boundary condition: $n(x) = 0$ for all $x \in \partial B^c \setminus \partial W$.
- $\eta_Q = 1 - \bar{n}/(\tau g)$

Physical characteristic for model validation

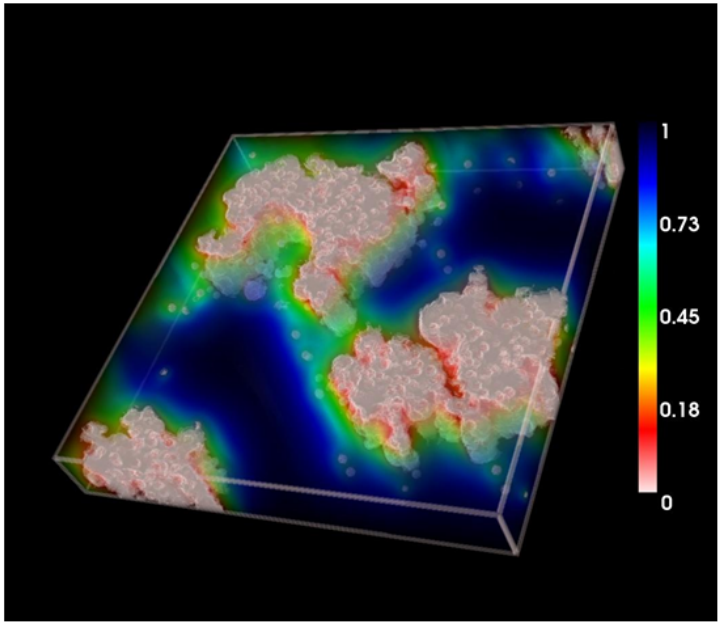




Model for morphology



Model for transport processes

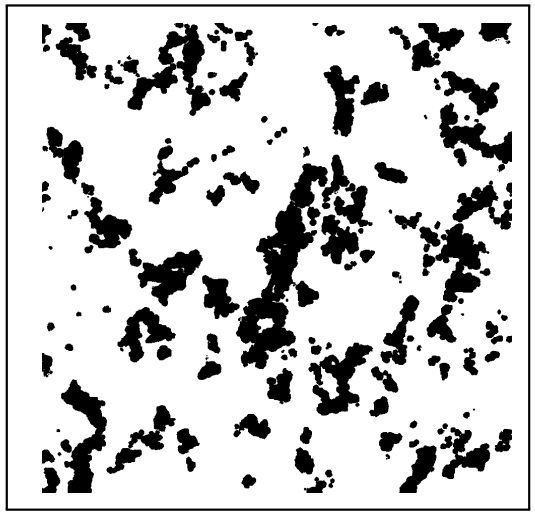


validated by
3D real image data

validated by
physical experiments

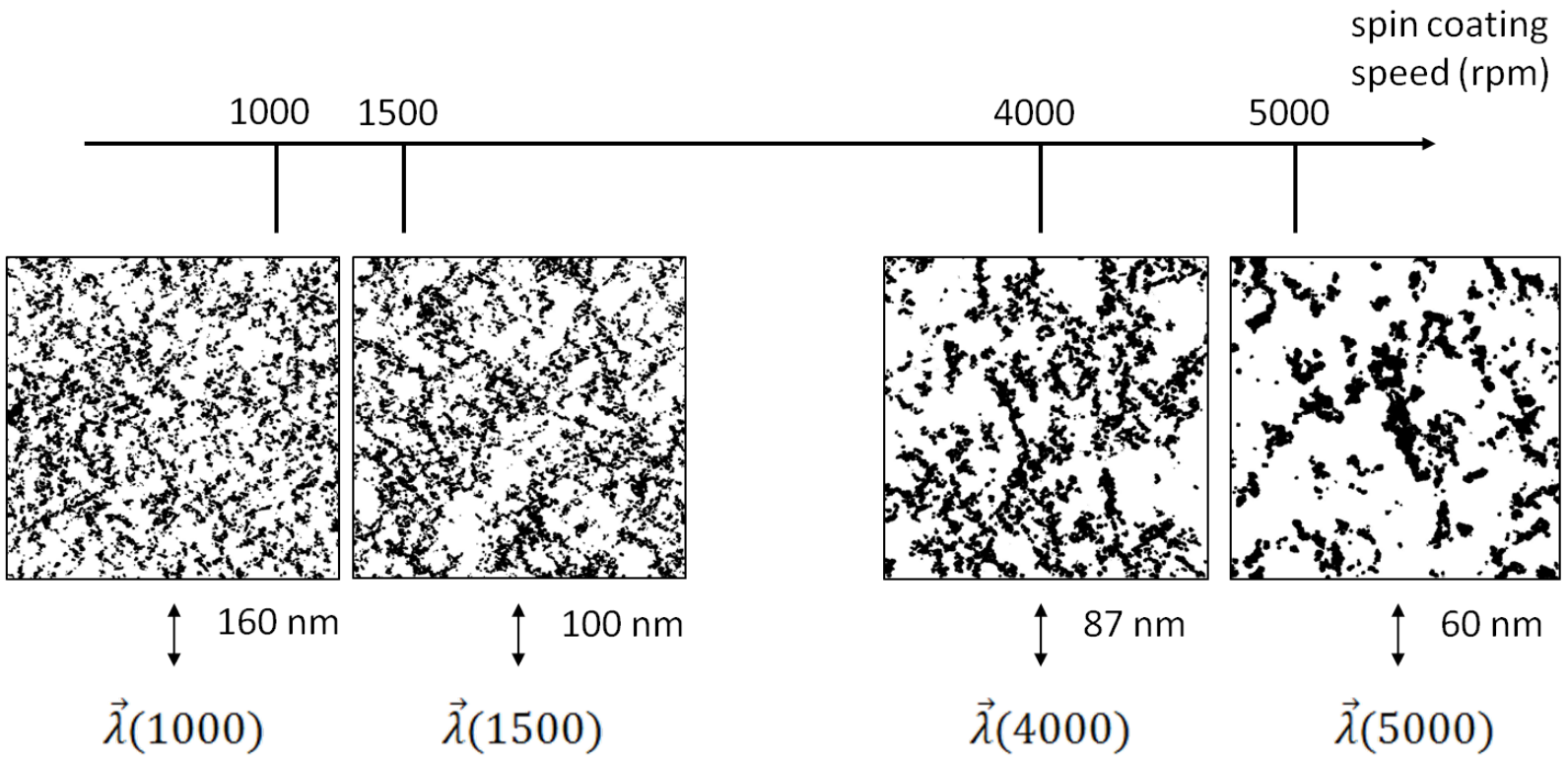
Virtual Material Design

Virtual material design



$\overset{\text{Model}}{\Longleftrightarrow}$ $\vec{\lambda} = (\lambda_1, \ldots, \lambda_m)$

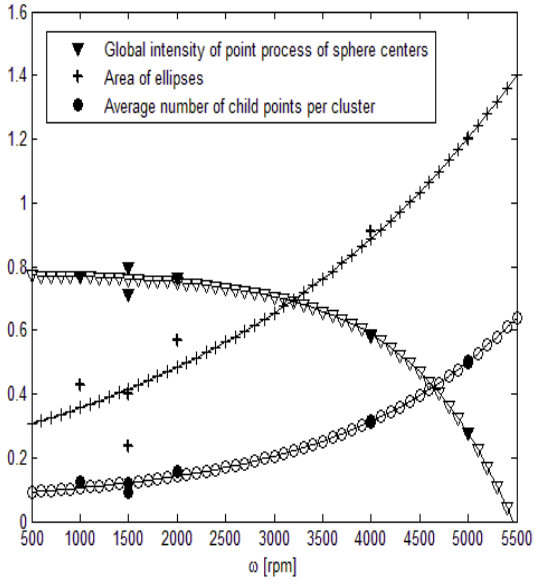
Stochastic simulation model
$\Rightarrow$ 3D morphology represented by parameter vector $\vec{\lambda}$

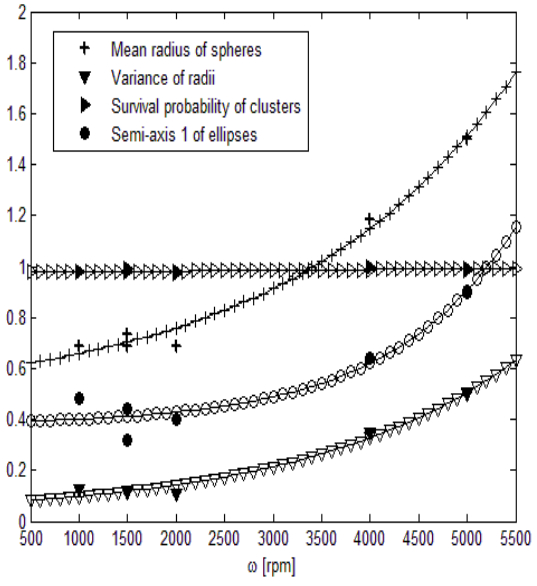


Spin coating speed determines morphology

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

Regression of model parameters





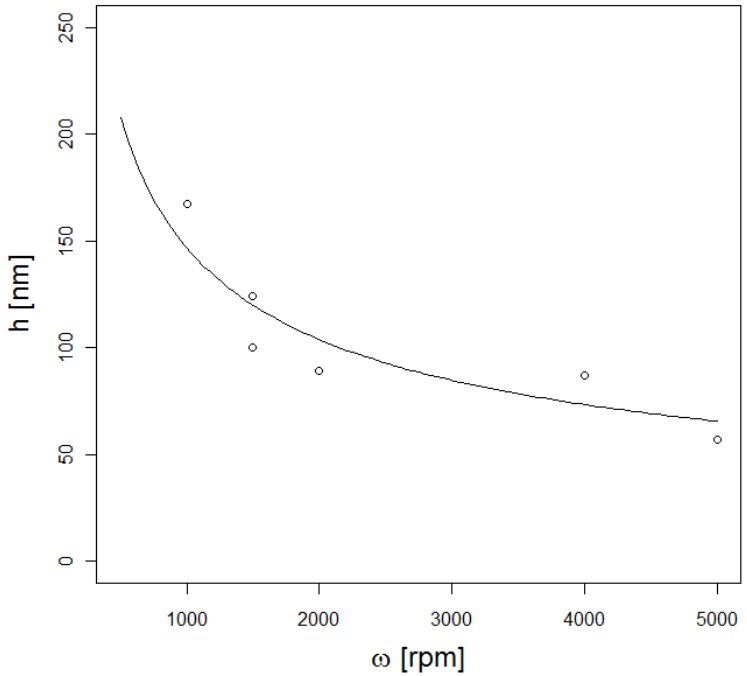
Spin coating speed determines morphology

- 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 $\vec{\lambda}$ in dependence of ω.
- Prediction of morphologies which were not fabricated

Scenario analysis

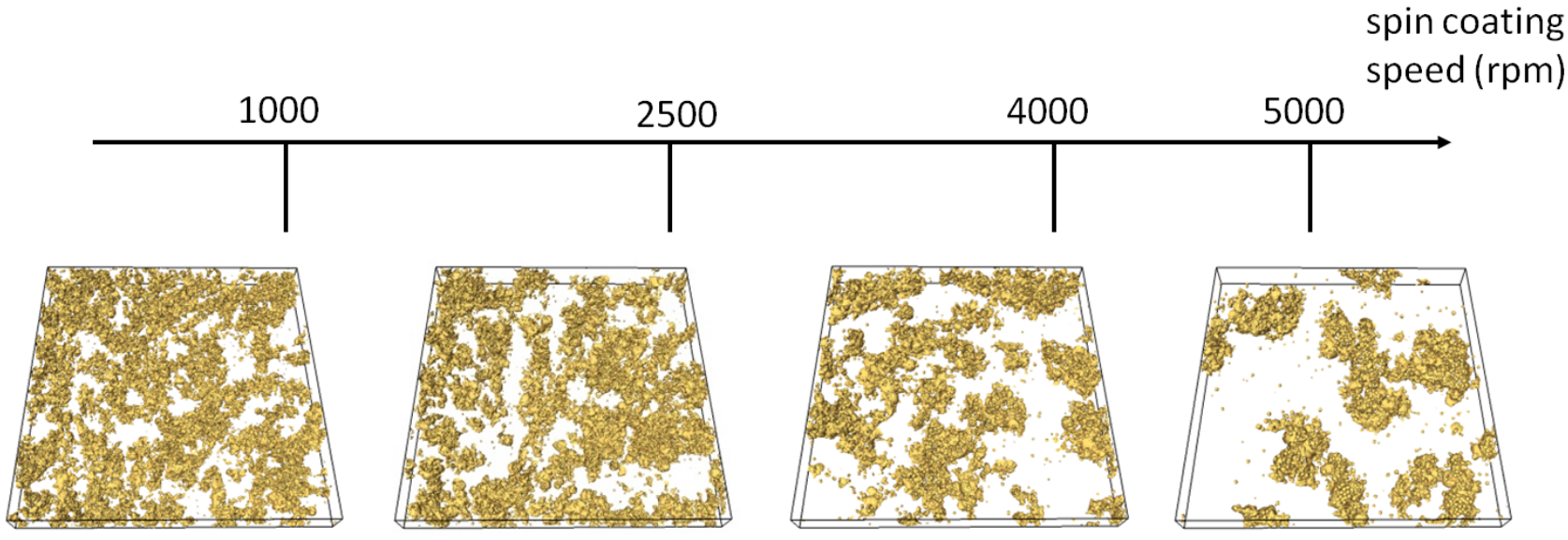
Model for layer thickness

- layer thickness $= c\omega^{\alpha}$, $\alpha = -0.5$
- estimation of c by least squares
- simulation of virtual morphologies with 'correct' layer thickness

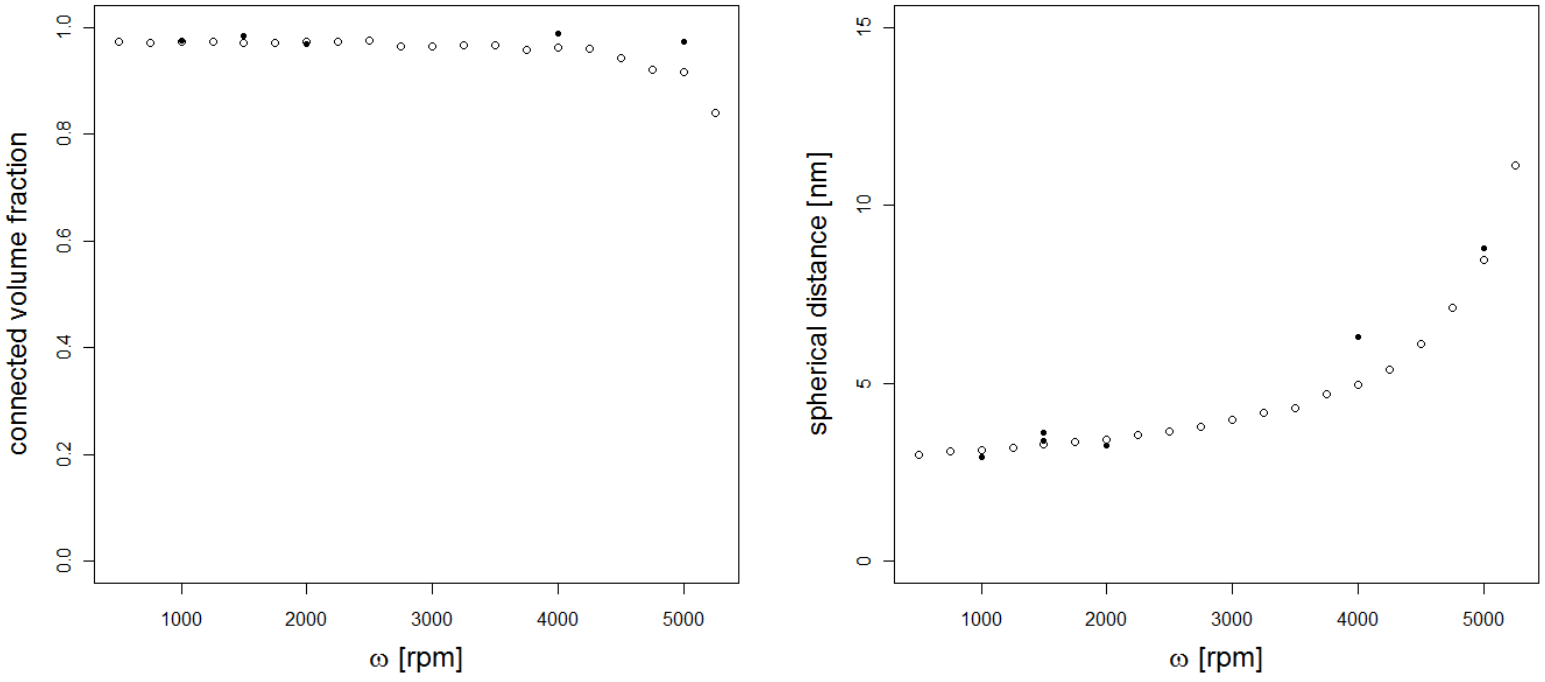


Scenario analysis

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

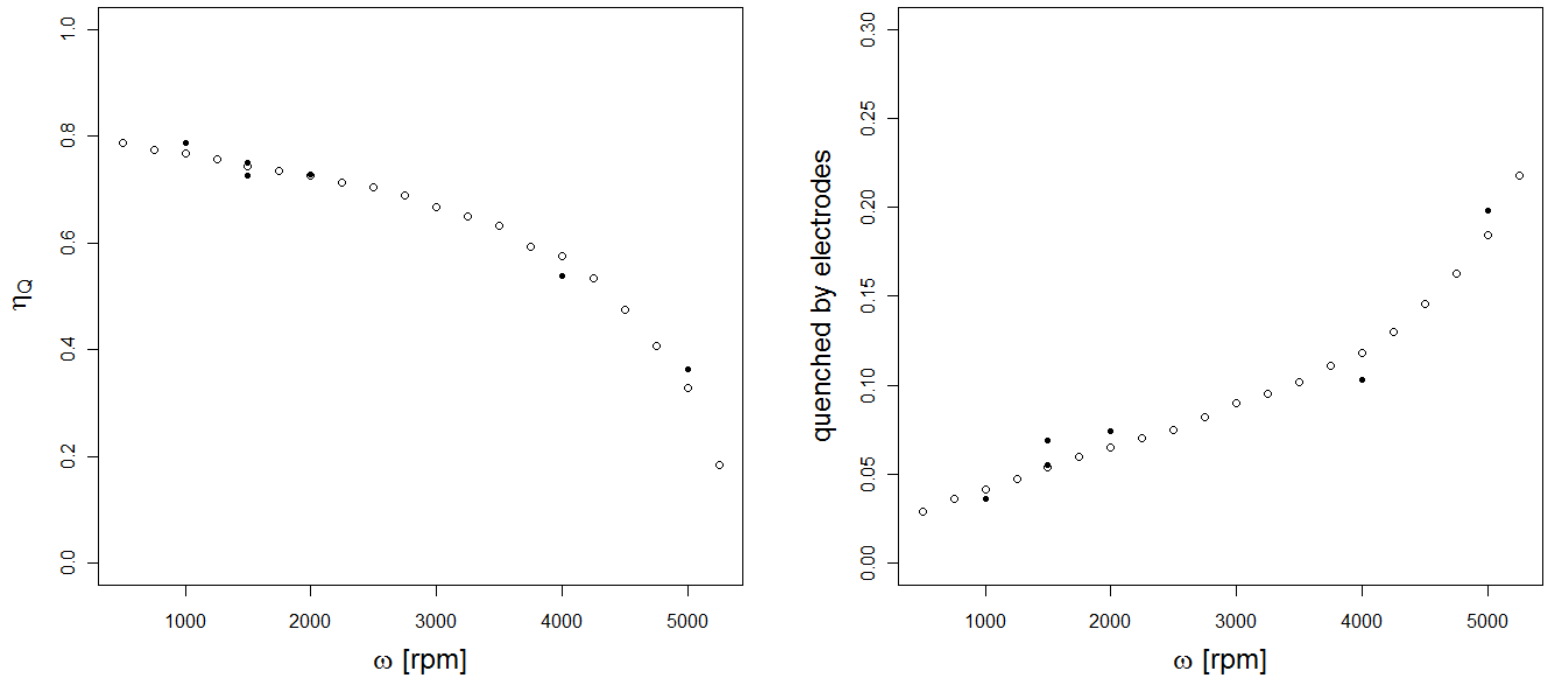


Scenario analysis - results



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

Scenario analysis - results

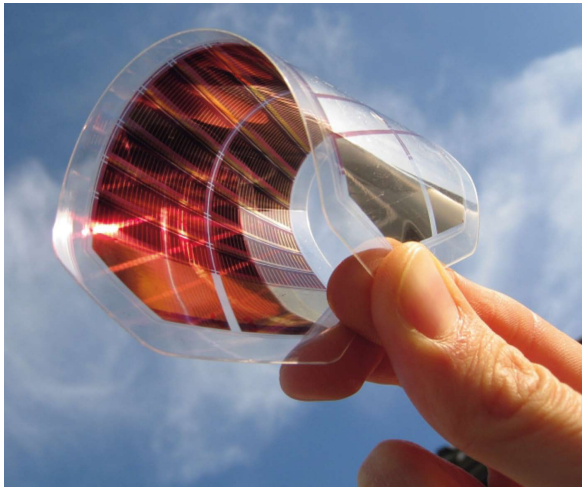


left: quenching efficiency by bulk, right: quenched by electrodes; experimental data added by filled symbols

O. Stenzel *et al.*, A New Approach to Model-Based Simulation of Disordered Polymer Blend Solar Cells, Advanced Functional Materials **22** (2012), 1236–1244.

Contents

Organic electronics

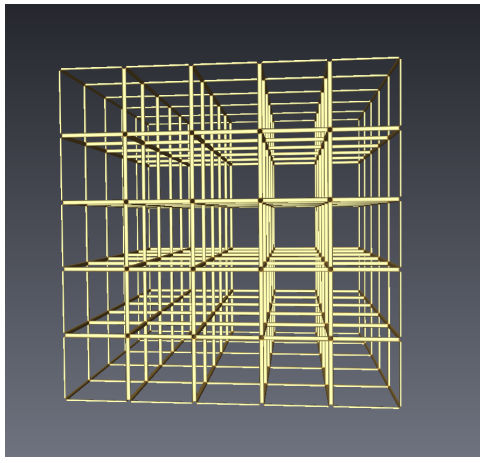


Left: organic solar cell; right: OLED display.

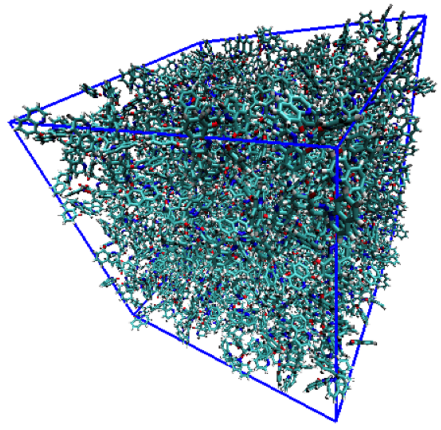
- Efficiency influenced by charge mobility $\mu = \frac{\vec{v}^T \cdot \vec{F}}{\|F\|^2}$.
- Charge dynamics (transport properties of holes and electrons) are of interest.

pictures: Fraunhofer ISE Freiburg, Samsung

Charge dynamics



Gaussian Disorder Model (GDM)



Microscopic simulation

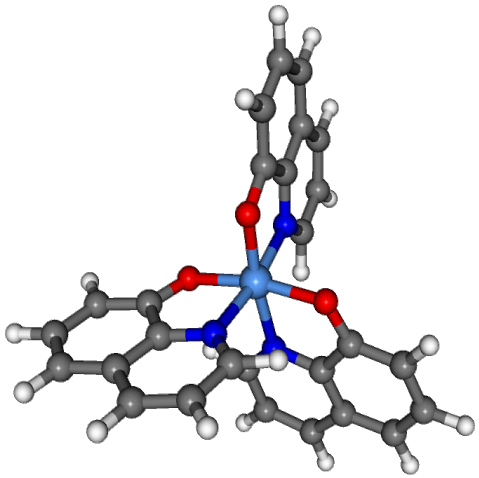
- Gaussian Disorder Model: fast, large system sizes, relies on experimental input
- Microscopic model: link macroscopic observables to chemical structure or the morphology, restrictions to small system sizes
- Marry the two approaches:
  (1) realistic, off-lattice morphologies
  (2) Fit ingredients of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

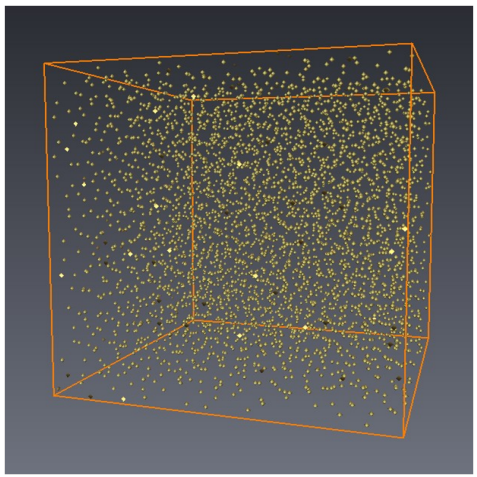
Reference model

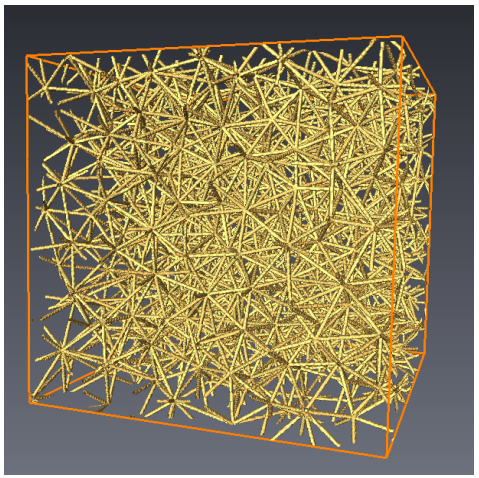
- Max Planck Institute for Polymer Research, Mainz
- Simulation of amorphous morphology containing 4096 Alq3 molecules by atomistic molecular dynamics
- Center of masses $\Longrightarrow$ hopping sites
- Charge hopping rates using charge transfer theory by

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

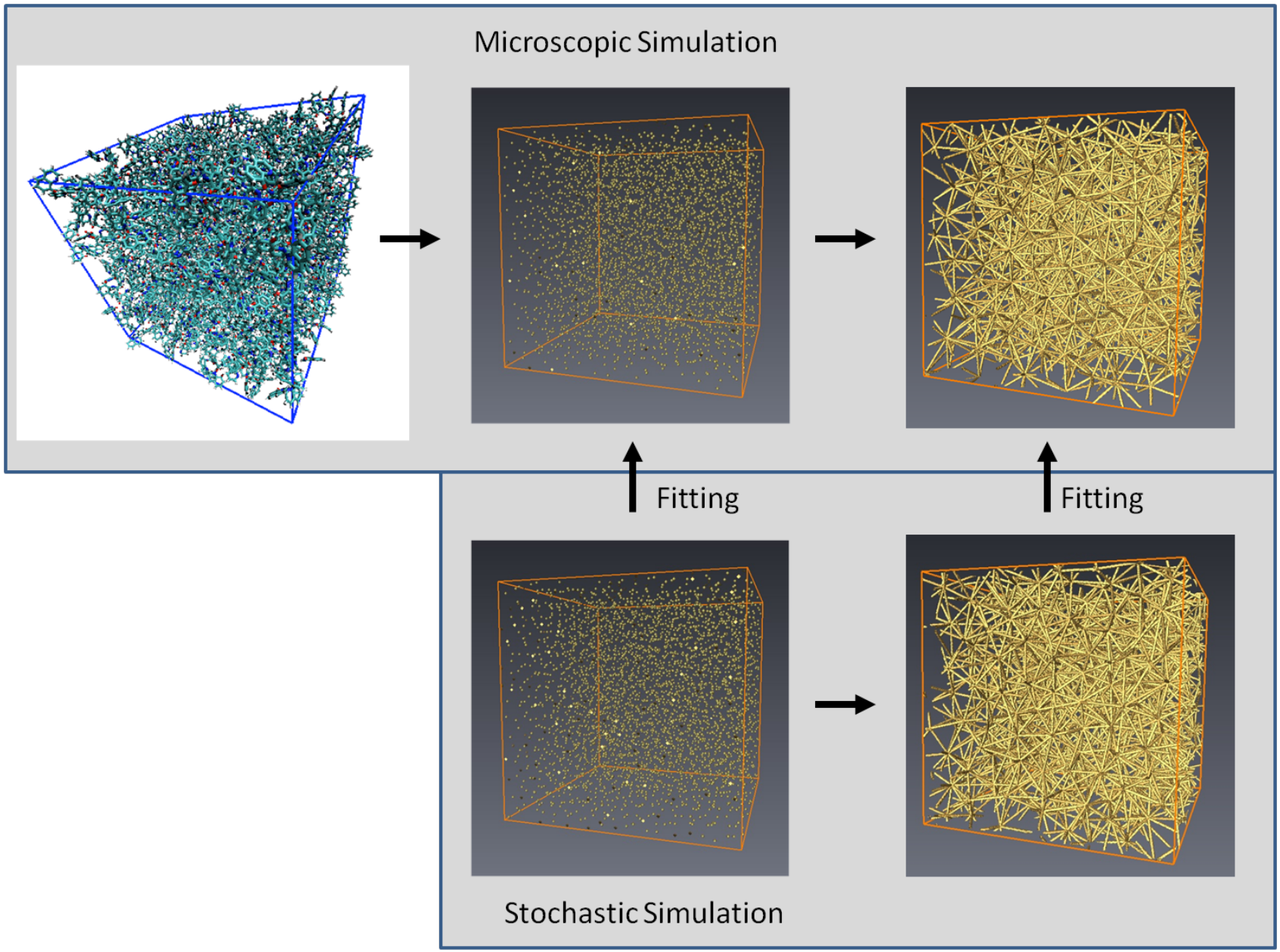
- V. Rühle *et al.*, Journal of Chemical Theory and Computation, **7** (2011), 3335.







Stochastic network model

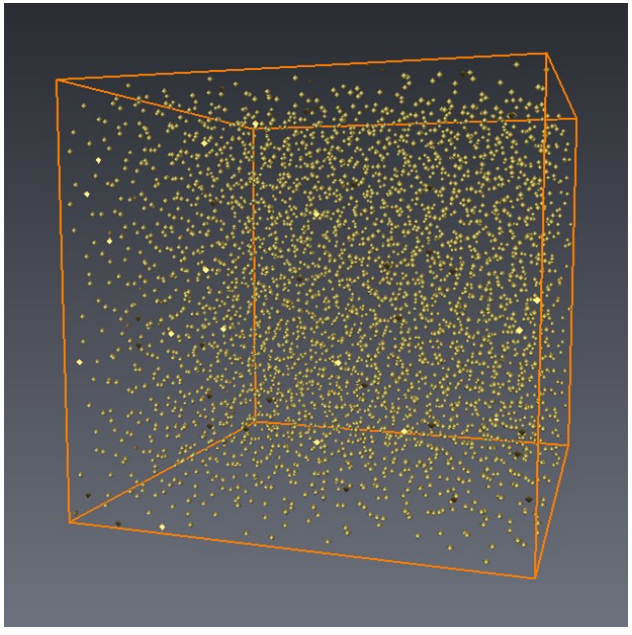


Stochastic model

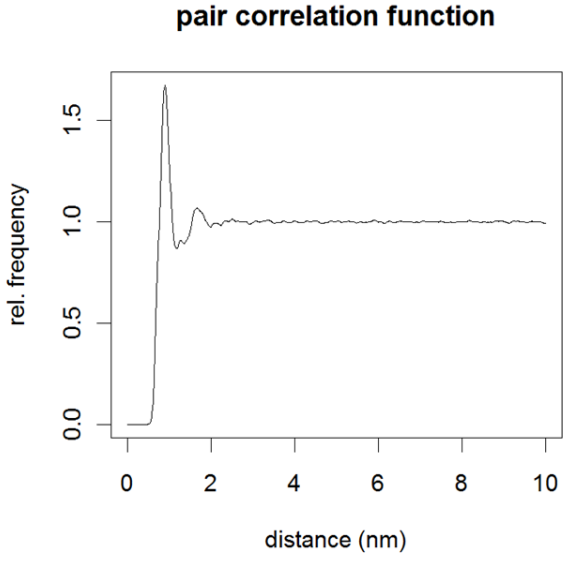
(1) Stochastic model for the network of the molecules
   1. Stochastic model for the hopping sites
   2. Stochastic model for connecting hopping sites

(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)

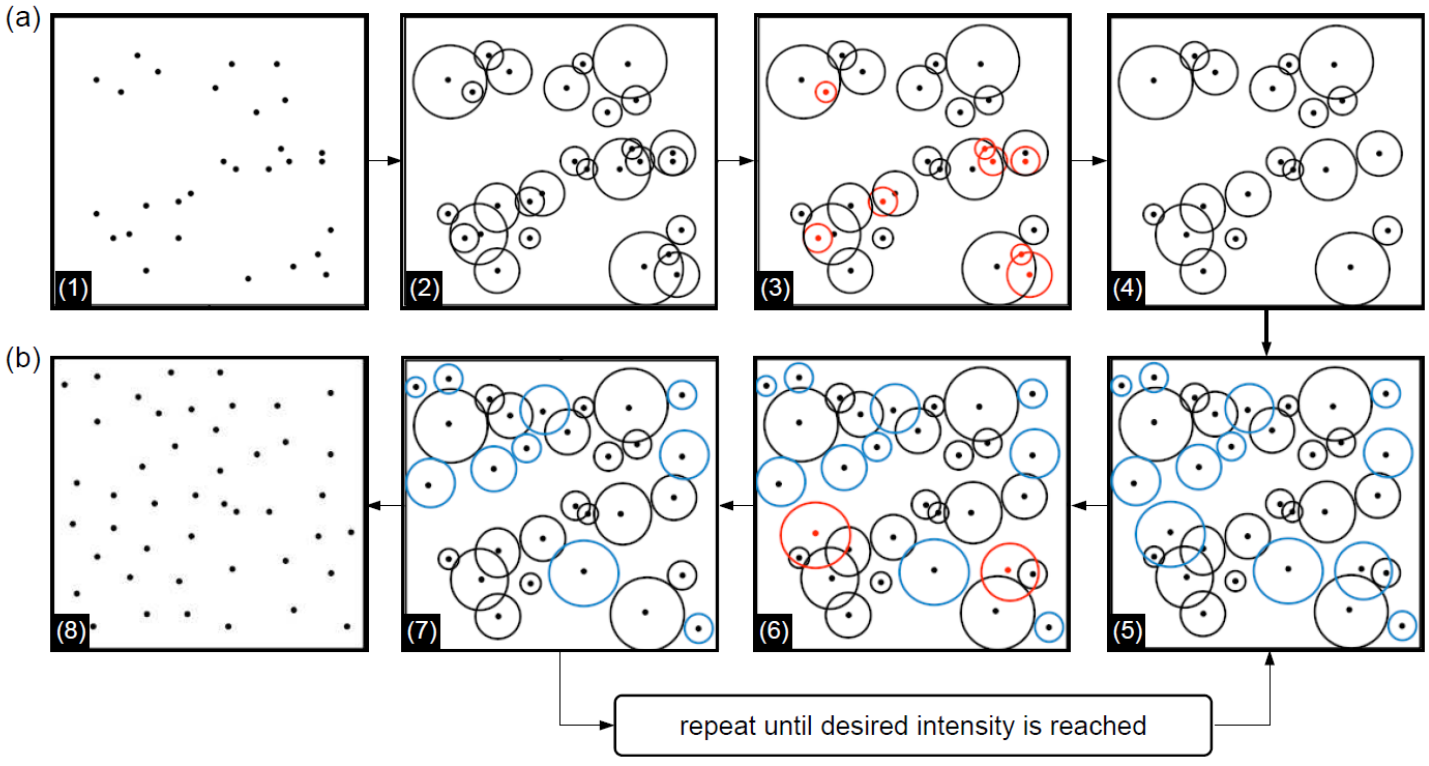


vertices by microscopic model;
box-size: 13.55 nm



- vertices have a rather regular structure.

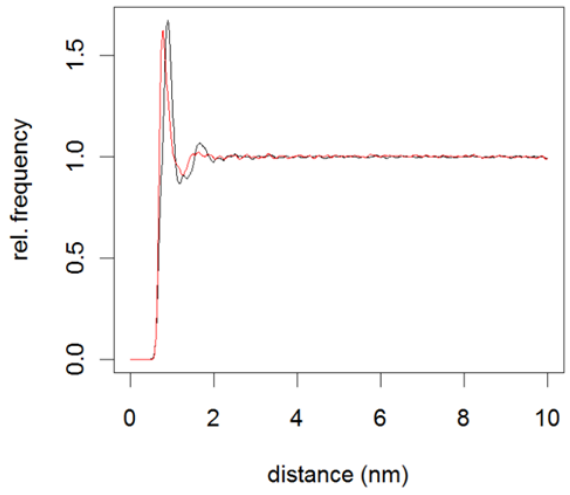
Stochastic model for the hopping sites



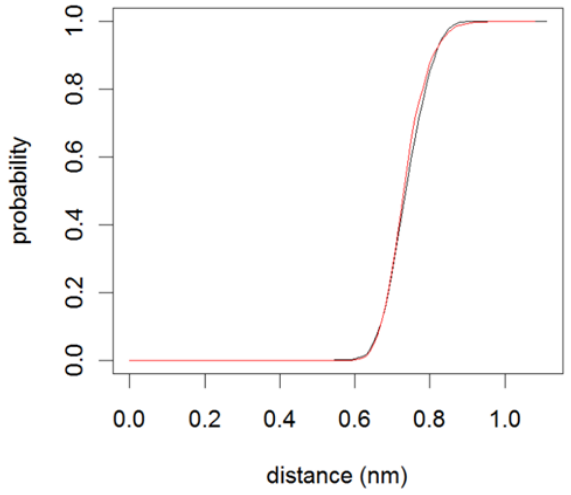
Iterative Matérn-Softcore point process model

- simulation of Matérn-Softcore point process (1-4)
- iteration for higher densities (5-8)

Stochastic model for the hopping sites - validation



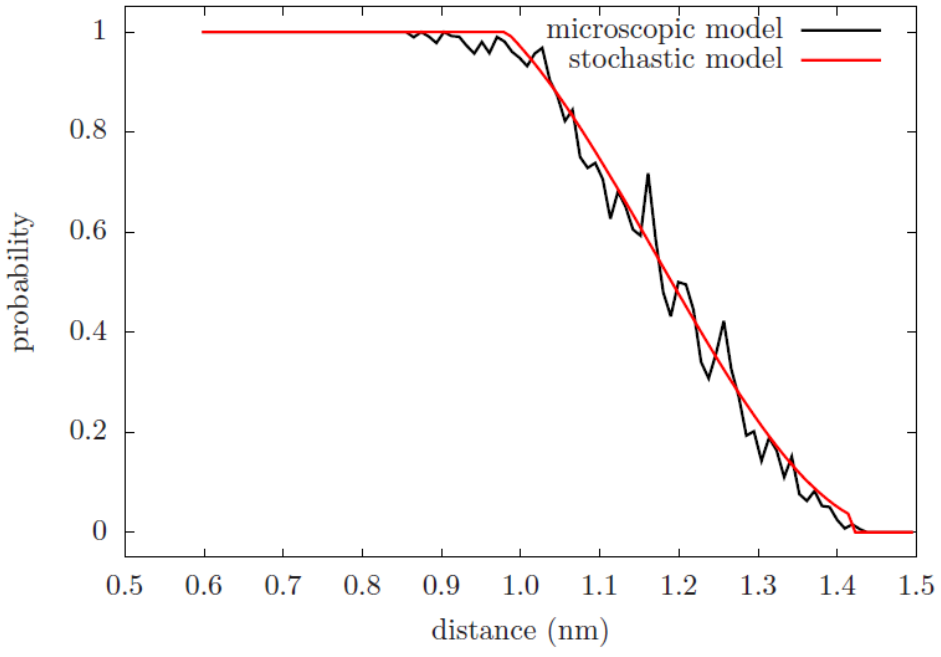
pair correlation function



distribution function of nearest neighbor distances

- good agreement

Stochastic model for the edges

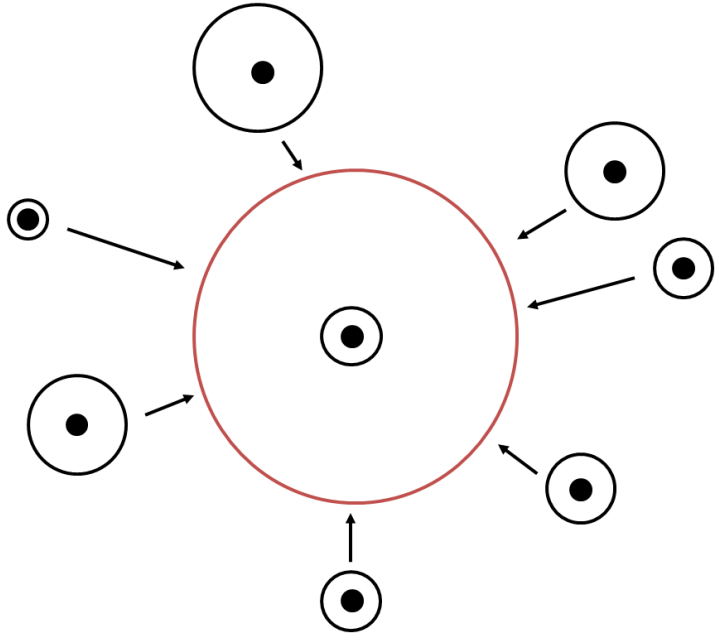


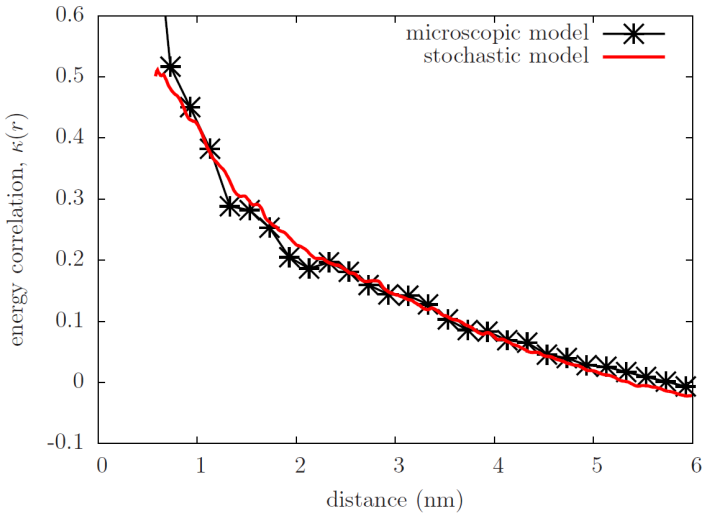
Black: Relative frequency of two vertices (hopping sites) being connected in dependence of their distance.
Red: Fitted curve $f()$.

- 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 $\widetilde{E}_i \sim \mathcal{N}(\frac{a}{M}, \frac{\sigma^2}{M})$
- sum up 'small' site energies $\widetilde{E}_j$ of M neighboring vertices



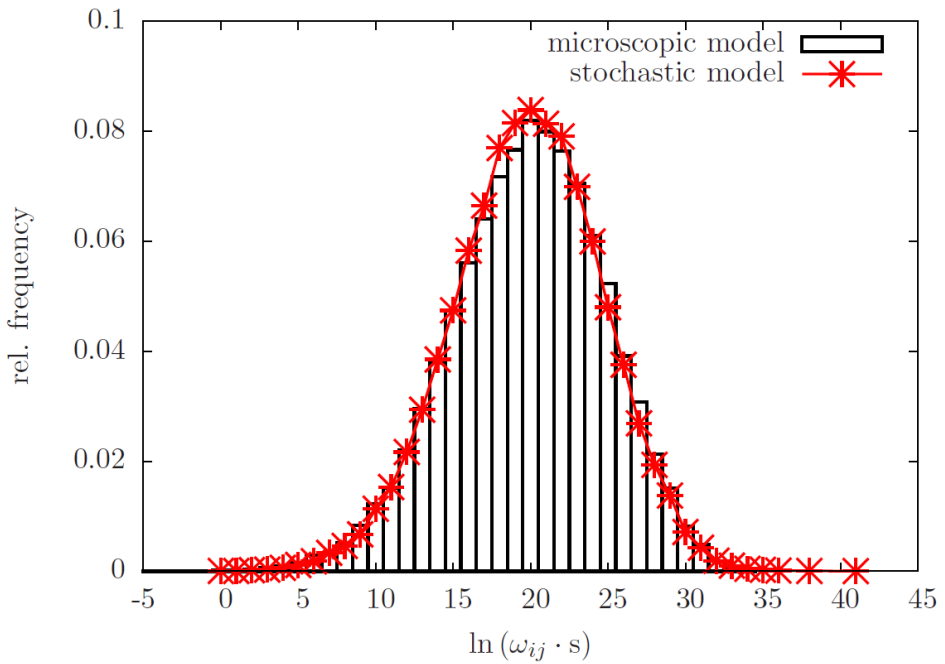


Validation

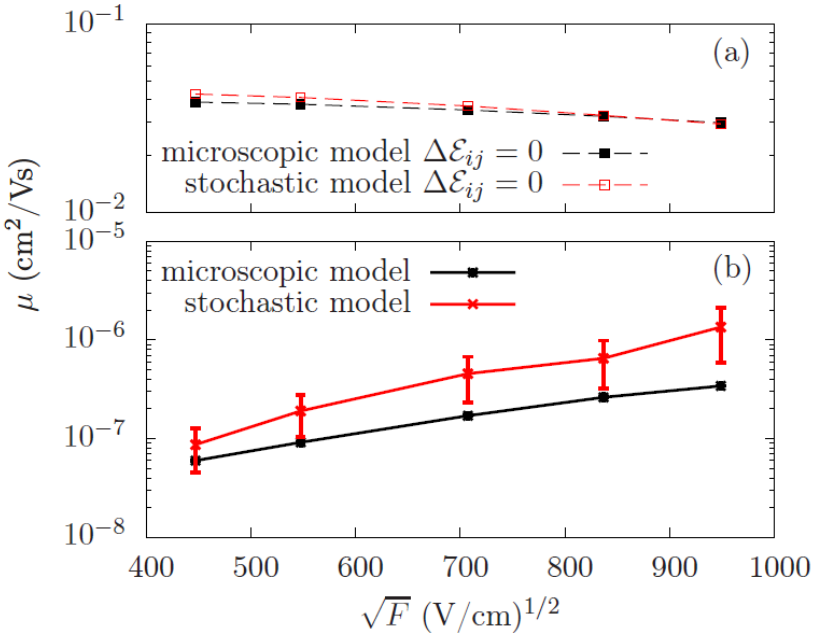
- Putting everything into

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

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



Charge dynamics

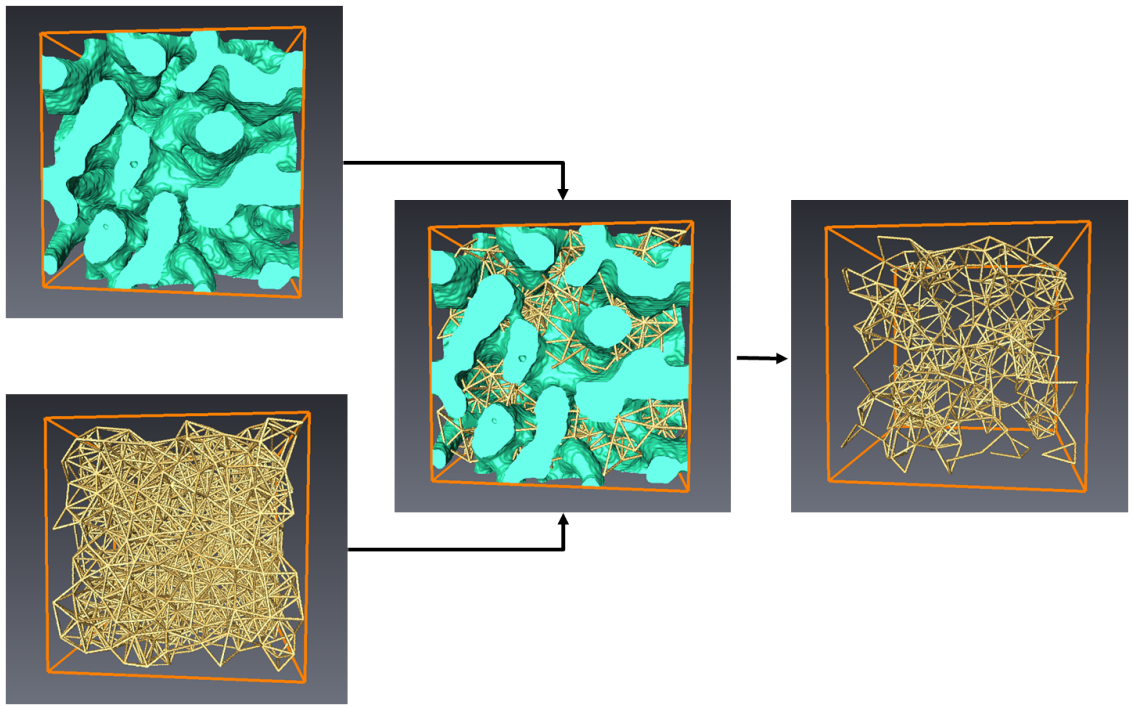


Mobility for microscopic and stochastic model.

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

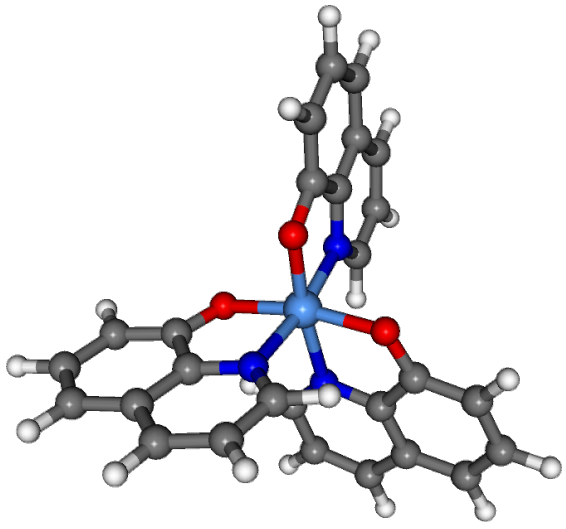
Conclusions

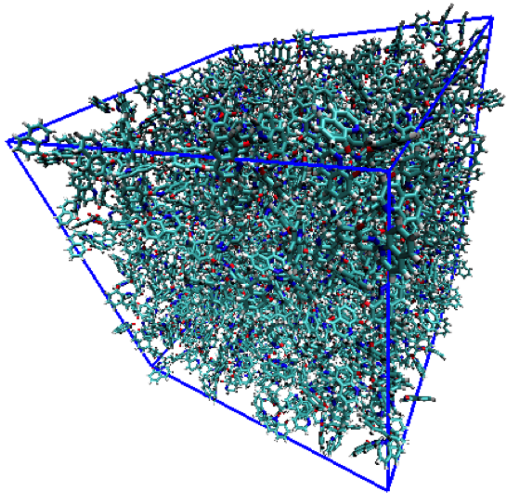
- Large system sizes
- control on positional disorder
- control on correlation of site energies
- application to different (non-spherical) molecules
- realistic device geometries

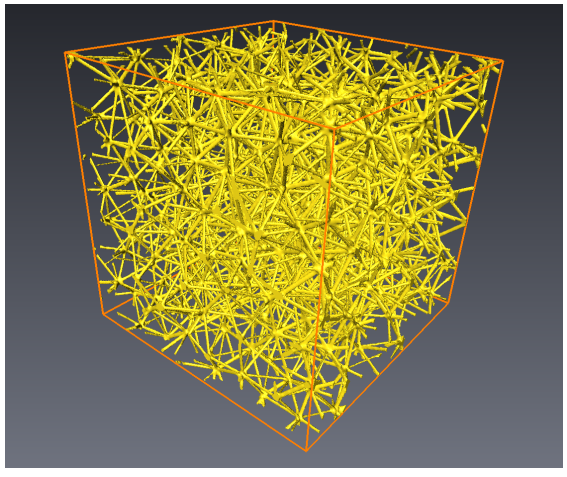


Contents

Motivation

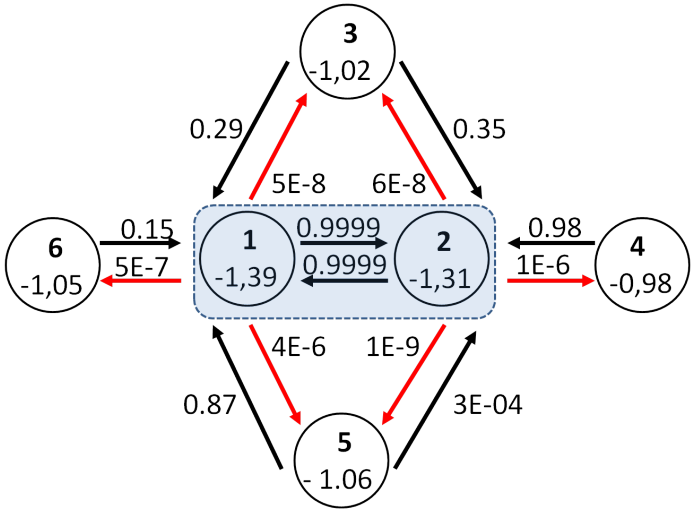






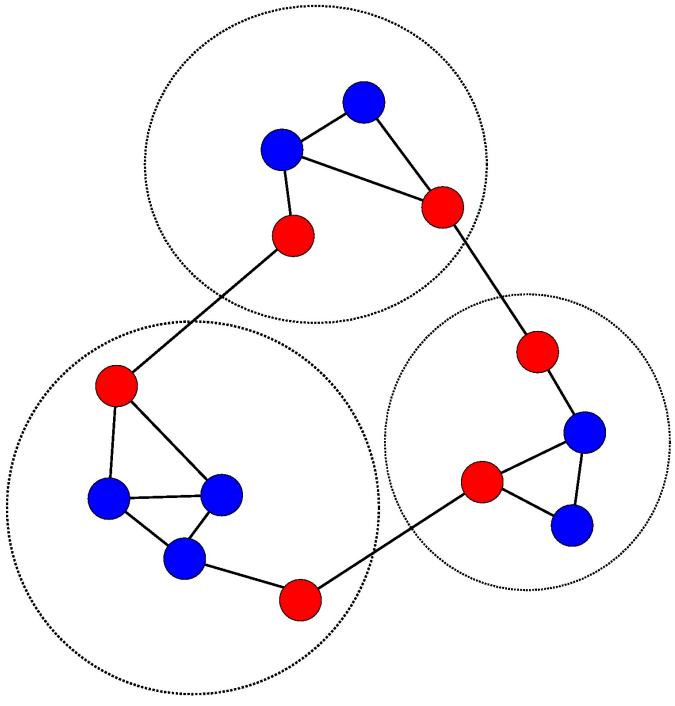
- Stochastic models allow simulation of large-scale molecular networks
- Charge hopping according to continous-time Markov chain
- Charge transport modeling by Markov chain Monte Carlo simulations
- Charge mobility $\mu = \frac{v}{F}$ of interest
- Problem: areas of low energies: difficult estimation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

Problem



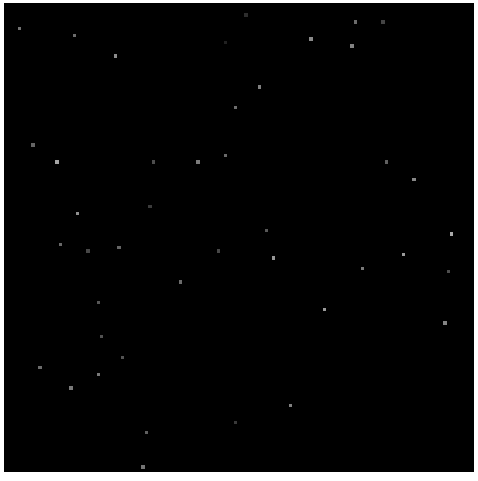
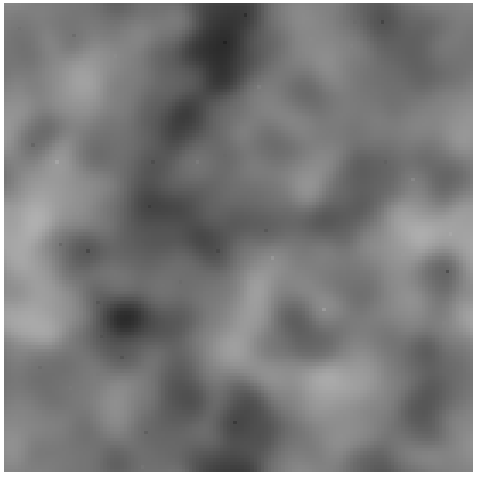
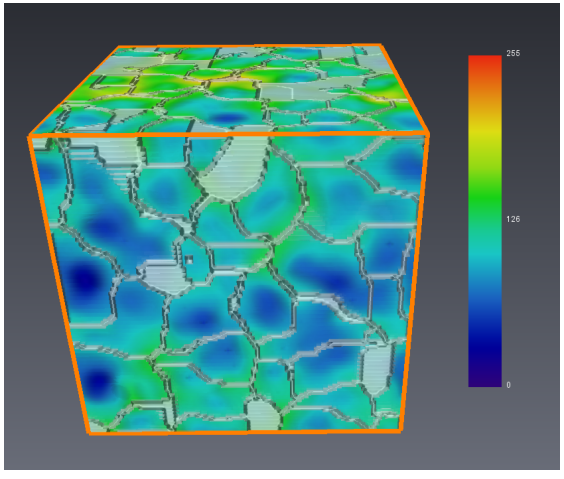
- Charge hopping rates follow $\omega_{ij} = \frac{2\pi}{\hbar} \frac{J_{ij}^2}{\sqrt{4\pi\lambda_{ij} k_B T}} \exp\left[-\frac{(\Delta E_{ij} - \lambda_{ij})^2}{4\lambda_{ij} k_B T}\right]$
- roughly 10^9 steps for accurate estimation of μ
- General: Markov chain nearly decomposable: $P = \begin{pmatrix} A_1 & & \\ & \ddots & \\ & & A_n \end{pmatrix} + \varepsilon \cdot C$

Idea: Aggregate Monte Carlo



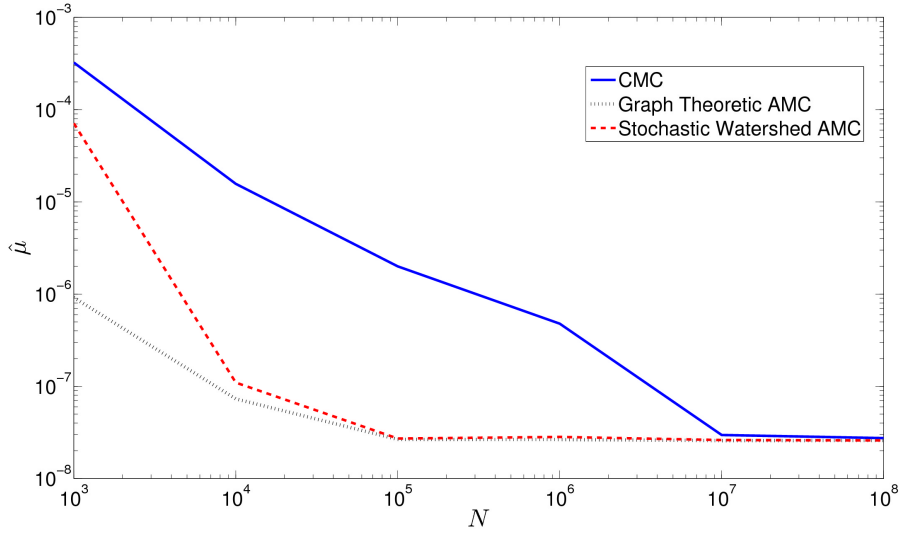
- Collapse problem regions into a single superstate
- Run embedded Markov chain on coarsened state space
- Calculate conditional sojourn times given the entrance into superstate

Coarsening of state space

- Idea Identify regions of low energy
- Build energy landscape by Gaussian interpolation
- Segmentation of low energy regions by stochastic wateshed

Results



- Reduction of computational time by factor 10^2
- T. J. Brereton *et al.*, Efficient Simulation of Markov Chains using Segmentation, Methodology and Computing in Applied Probability, to appear.

Acknowledgements

Deutsche Forschungsgemeinschaft DFG

DAAD Deutscher Akademischer Austauschdienst German Academic Exchange Service

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

Contents


O. Stenzel, D. Westhoff, I. Manke, M. Kasper, D. P. Kroese and V. Schmidt, Graph-Based Simulated Annealing: A Hybrid Approach to Stochastic Modeling of Complex Microstructures. Modelling and Simulation in Materials Science and Engineering, 2013, to appear.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