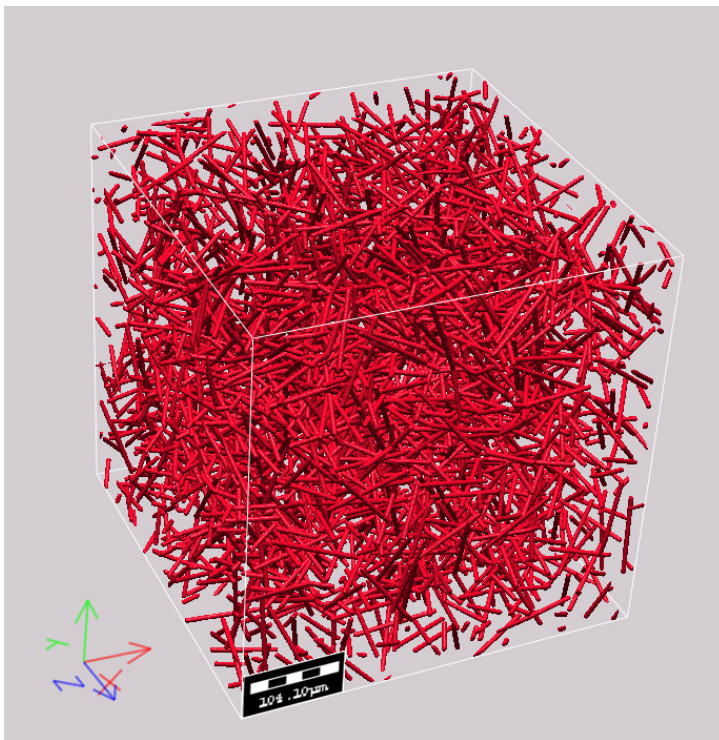

Modelling and prediction of percolation and conductivity properties of CNT-polymer compounds



Andreas Wiegmann



Oleg Iliev



W3D,
Fontainebleau
21.4. 2010

Acknowledgement:

We thank Dr. Michael Bierdel of Bayer Technology Services for introducing us to the needs and challenges of the simulation of Carbon Nano Tubes many discussions on the subject, simulations using CO-Graph and providing feedback about experimental results in the area.



Bayer Technology Services

What, how and why?

- Carbon nano tubes (CNT) can be added to polymers to create conducting plastics
- The specific electrical conductivity of CNT can be up to 20 orders of magnitude (**we consider here $1e8$**) larger than that of the matrix material.
- The specific thermal conductivity of CNT can be 4 orders of magnitude (**we consider here $1e4$**) larger than that of the matrix material.
- A relatively low CNT concentration can dramatically change the polymer's electrical conductivity by orders of magnitude, from an insulator to a conductor.
- CNT are expensive: Want to use as few CNT as possible, yet create conductors.

What we consider here (and what not)



- Manufacturing of polymers with CNT
 - Non-Newtonian flows, complex rheologies



- 3d images of real polymers with CNT
 - CT-images and processing thereof

- 3d fibrous composite material model
 - Analytic and as 3d image



- Percolation and effective (thermal, electric) conductivity
 - On analytic data and on 3d images



- Optimization of geometric configurations
 - Volume fractions
 - Directional Anisotropy
 - Length / Diameter Ratio



Geometric fiber model

Carbon Nano Tubes are cylinders

- of finite length,
- that are straight,
- that may (not) overlap
- with circular cross section
- with hemispherical caps

Design parameters are

- fiber volume fraction,
- *fiber anisotropy*,
- fiber length to fiber diameter ratio

Algorithm for CNTs

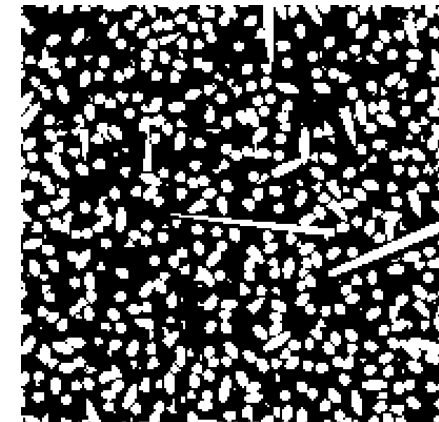
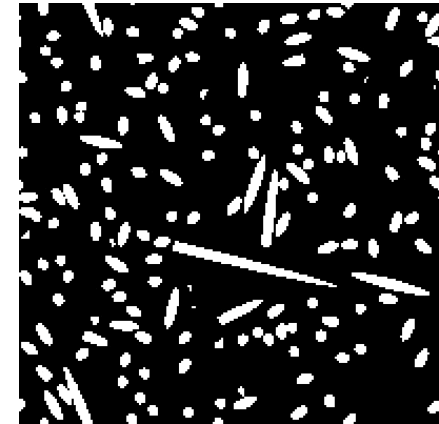
1. Fix image domain: n_x, n_y, n_z, h
2. Choose fiber direction according to desired statistic
3. Place center of gravity
4. Discretize into 3d image. If overlap is detected, go back to 3.
5. If solid volume fraction is below desired svf, go back to 2.

Guarantees fiber orientation distribution

Avoid preference of faces / edges / corners of image by creating periodic fibers

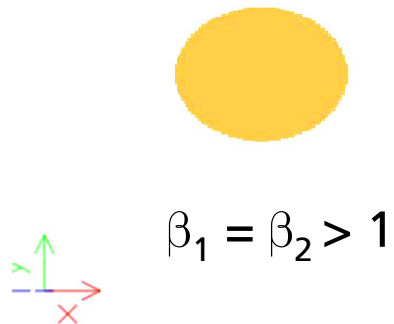
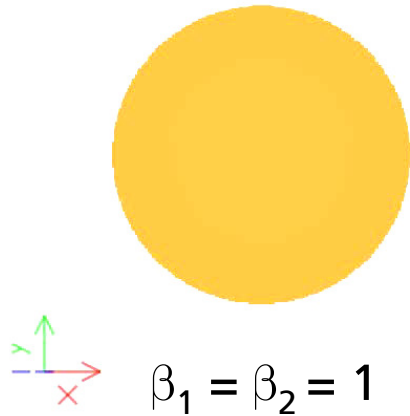
Probably create too few contacts

 current work on adding "tunnel connecting fibers"



Fiber anisotropy:

orientation parameter β



$\xi \in [-1, 1]$, uniformly distributed,

$\Phi \in [0, 2\pi)$, uniformly distributed,

$$u = \frac{\beta_1 \cos \Phi \sqrt{1 - \xi^2}}{\sqrt{\xi^2 + (1 - \xi^2) \{ \beta_1^2 \cos \Phi + \beta_2^2 \sin \Phi \}}},$$

$$v = \frac{\beta_2 \sin \Phi \sqrt{1 - \xi^2}}{\sqrt{\xi^2 + (1 - \xi^2) \{ \beta_1^2 \cos \Phi + \beta_2^2 \sin \Phi \}}},$$

$$w = \frac{\xi}{\sqrt{\xi^2 + (1 - \xi^2) \{ \beta_1^2 \cos \Phi + \beta_2^2 \sin \Phi \}}}.$$

Uniform distribution of directions gets mapped to non-uniform one by picking point with uniform ξ and ϕ on $(\beta_1, \beta_2, 1)$ ellipsoid and pulling it back to the unit sphere.

3. Schladitz, S. Peters, D. Reinel-Bitzer, A. Wiegmann and J. Ohser, *Design of acoustic trim based on geometric modelling and flow simulation for non-woven*, Computational Materials Science, Volume 38, Issue 1, 2006, pp 56-66.

Variation of fiber volume fraction

Consider

0.05, 0.06, 0.07, 0.08 and 0.09

as fiber volume fractions

Isotropic orientation,

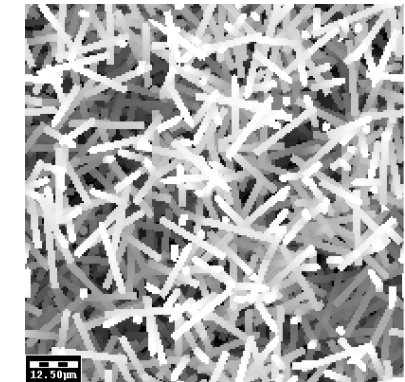
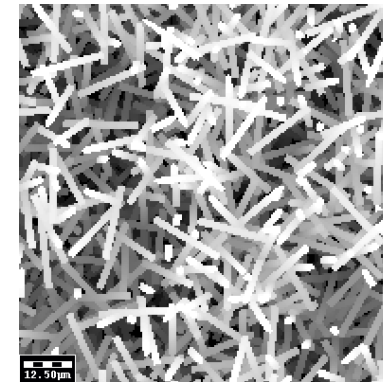
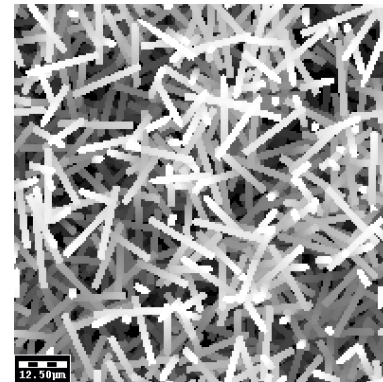
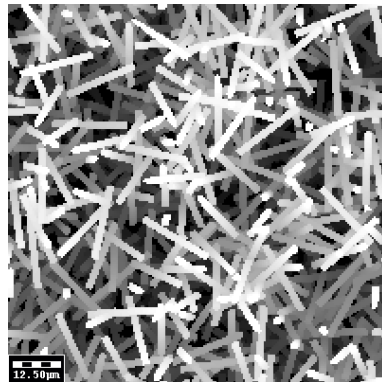
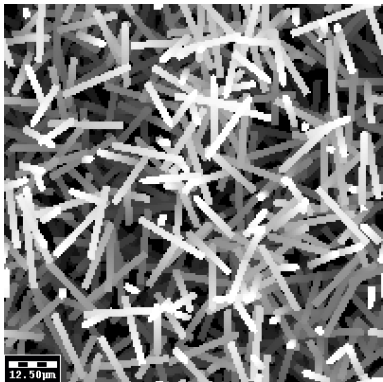
Length to Diameter ratio is

Image size

$\beta = 1$

10

200³



Variation of fiber anisotropy

Consider

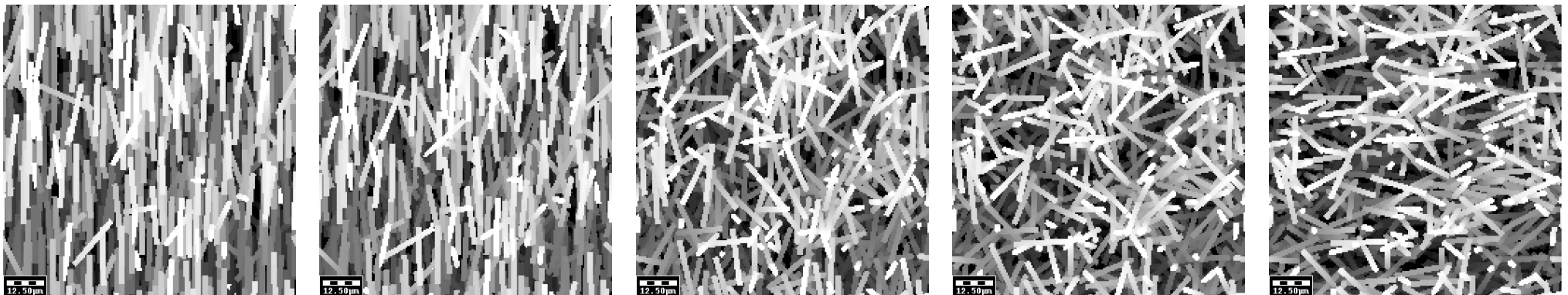
0.05, 0.1, 0.5, 1 and 2

as anisotropy values (for β)

Fiber volume fraction is 0.065

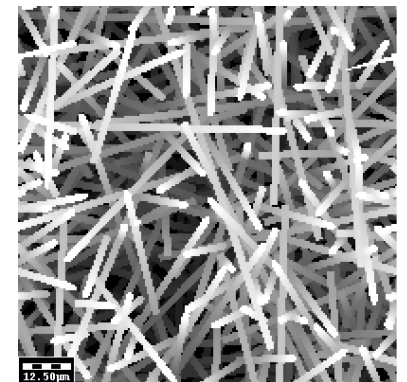
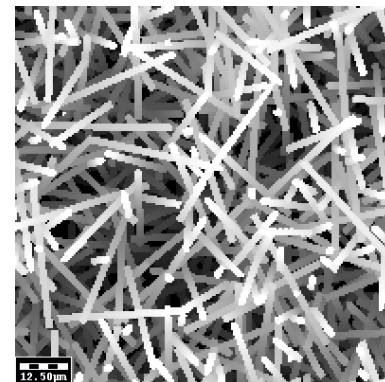
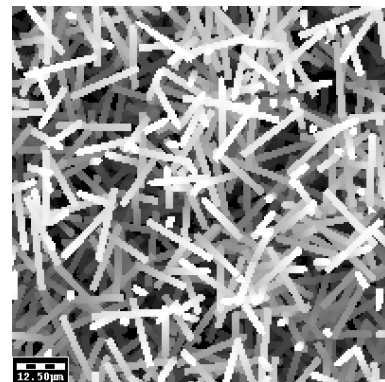
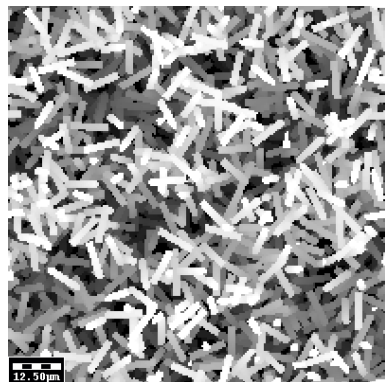
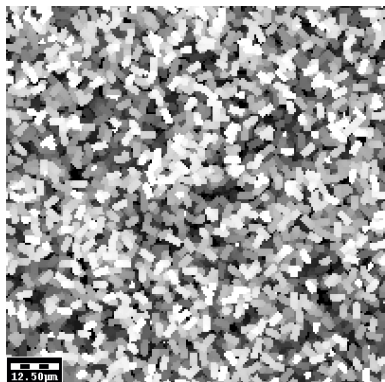
Length to Diameter ratio is 10

Image size 200³



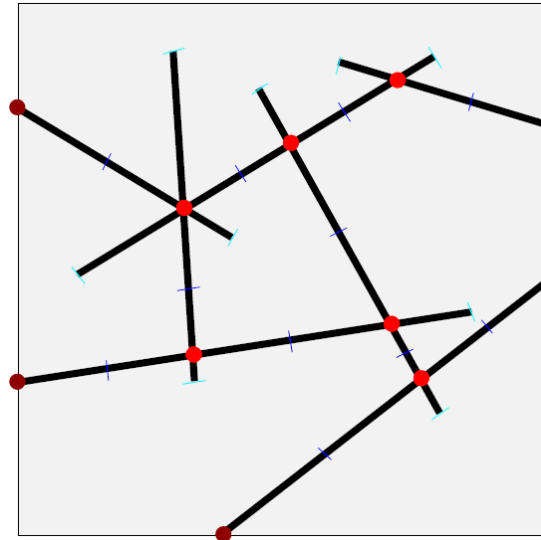
Variation of fiber length to fiber diameter (L / D ratio)

Consider	Fiber volume fraction is	0.065
2, 5, 10, 20 ,50	Isotropic orientation,	$\beta = 1$
as length to diameter ratios	Image size	200 ³



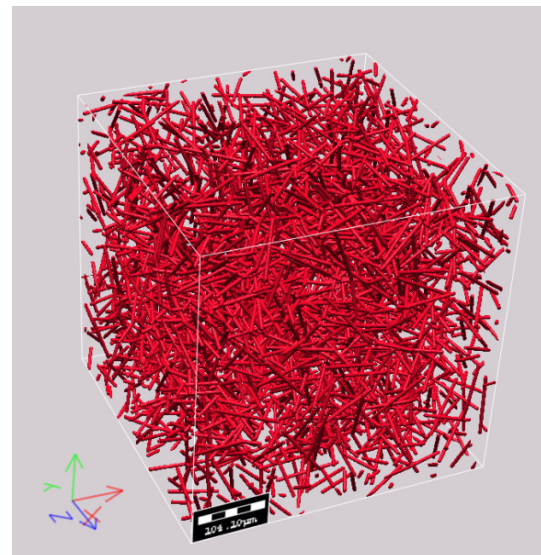
Representation as analytic positions, graph and 3d image

```
<Object1>  
  Color 1  
  Point1 0.0007,0.0003,0.0007  
  Point2 0.0021,-0.0006,0.0018  
  Radius1 6e-05  
  Radius2 6e-05  
  RoundedEnd1 0  
  RoundedEnd2 0  
  Type CircularFiberSegment  
</Object1>
```



Nodes where
CNTs **intersect**
each other or
intersect the
boundary.
Edges follow
CNTs between
nodes

```
<Object2>  
  Color 1  
  Point1 0.0012,0.0007,0.0011  
  Point2 4.99e-05,0.001,-0.00013  
  Radius1 6e-05  
  Radius2 6e-05  
  RoundedEnd1 0  
  RoundedEnd2 0  
  Type CircularFiberSegment  
</Object2>
```

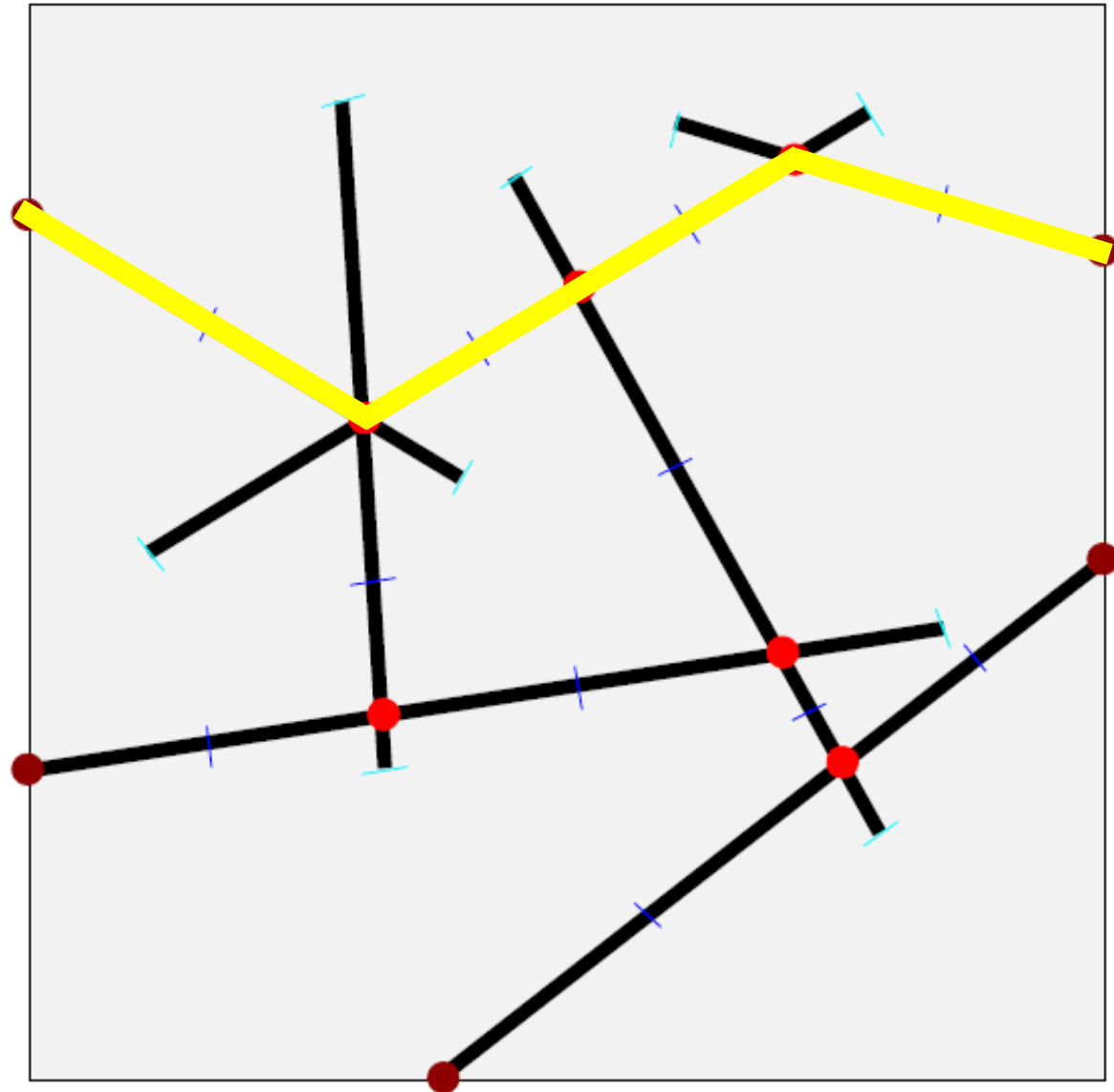


Voxels "on" if
center inside a
CNT,
otherwise
"off"

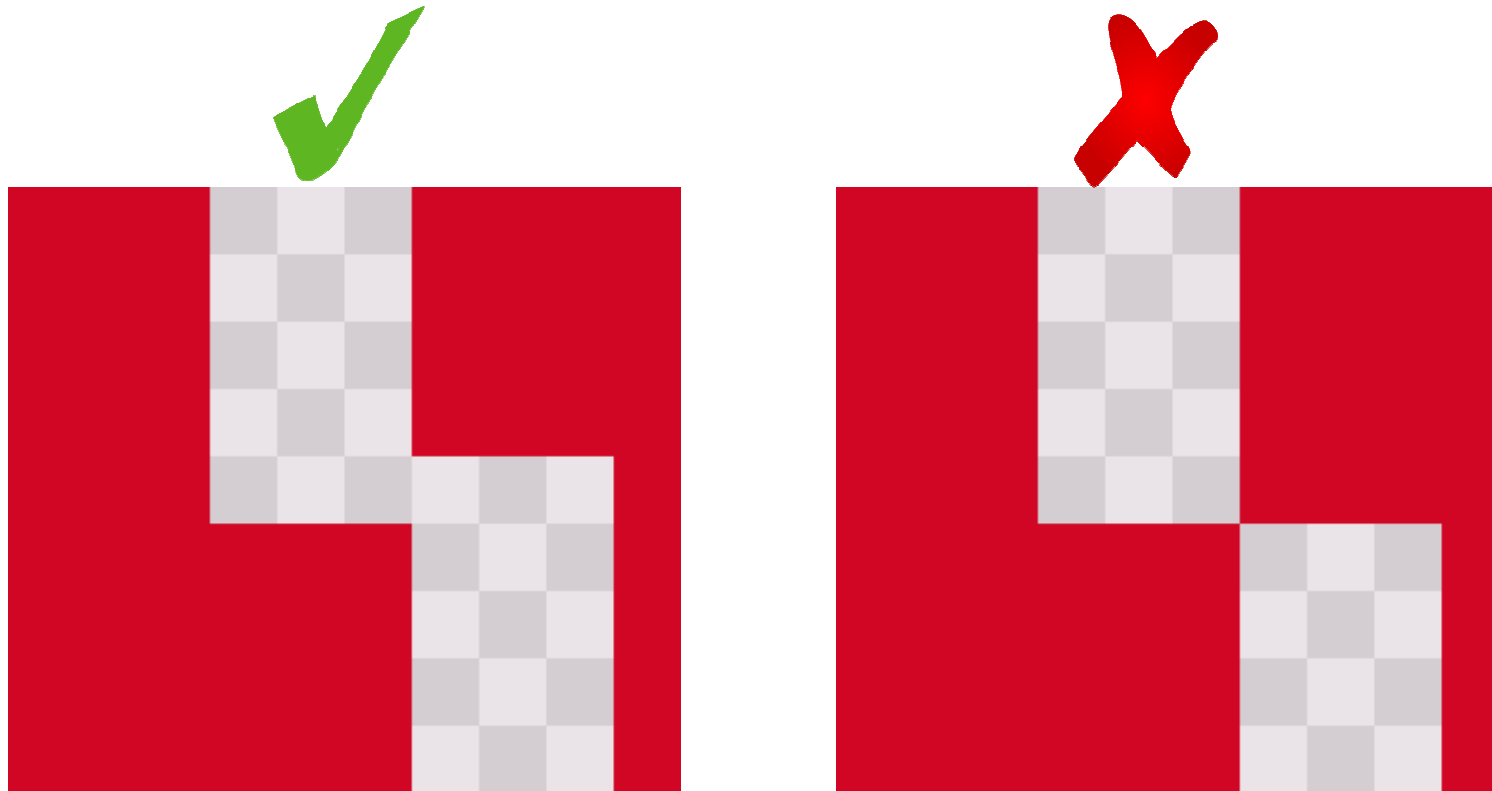
...

Percolation in a fiber graph

A path through the graph connecting the opposite faces of the volume.



Percolation in a 3d image



Percolation in 3d images through cube faces ✓

Cube edges and cube corners do not count ✗

Solving the Poisson equation on a 3d image

$$\operatorname{div}(\beta(\vec{x})\nabla\bar{U}_3) = \operatorname{div}(\beta(\vec{x}))\cdot\nabla\bar{U}_3 + \beta(\vec{x})\operatorname{div}(\nabla\bar{U}_3) = 0, \quad \vec{x} \in \Omega = (0, d_1) \times (0, d_2) \times (0, d_3),$$

with boundary conditions

$$\bar{U}_3(x_1, x_2, 0) = \bar{U}_3(x_1, x_2, d_3) - d_3,$$

$$\bar{U}_3(x_1, 0, x_3) = \bar{U}_3(x_1, d_2, x_3),$$

$$\bar{U}_3(0, x_2, x_3) = \bar{U}_3(d_1, x_2, x_3),$$

$$\beta(x_1, x_2, 0) \frac{\partial \bar{U}_3(x_1, x_2, 0)}{\partial x_3} = \beta(x_1, x_2, d_3) \frac{\partial \bar{U}_3(x_1, x_2, d_3)}{\partial x_3},$$

$$\beta(x_1, 0, x_3) \frac{\partial \bar{U}_3(x_1, 0, x_3)}{\partial x_2} = \beta(x_1, d_2, x_3) \frac{\partial \bar{U}_3(x_1, d_2, x_3)}{\partial x_2},$$

$$\beta(0, x_2, x_3) \frac{\partial \bar{U}_3(0, x_2, x_3)}{\partial x_1} = \beta(d_1, x_2, x_3) \frac{\partial \bar{U}_3(d_1, x_2, x_3)}{\partial x_1}.$$

Wiegmann and A. Zemitis, *EJ-HEAT: A Fast Explicit Jump Harmonic Averaging Solver for the Effective Heat Conductivity of Composite Materials*, Bericht des Fraunhofer ITWM, Nr. 94, 2006.

Discretization by harmonic averaging

$$\begin{aligned}
& \frac{1}{h} \left(\left(\frac{\beta_{i+1,j,k} + \beta_{i,j,k}}{2\beta_{i+1,j,k}\beta_{i,j,k}} \right)^{-1} \frac{u_{i+1,j,k} - u_{i,j,k}}{h} - \left(\frac{\beta_{i,j,k} + \beta_{i-1,j,k}}{2\beta_{i,j,k}\beta_{i-1,j,k}} \right)^{-1} \frac{u_{i,j,k} - u_{i-1,j,k}}{h} \right. \\
& + \left(\frac{\beta_{i,j+1,k} + \beta_{i,j,k}}{2\beta_{i,j+1,k}\beta_{i,j,k}} \right)^{-1} \frac{u_{i,j+1,k} - u_{i,j,k}}{h} - \left(\frac{\beta_{i,j,k} + \beta_{i,j-1,k}}{2\beta_{i,j,k}\beta_{i,j-1,k}} \right)^{-1} \frac{u_{i,j,k} - u_{i,j-1,k}}{h} \\
& \left. + \left(\frac{\beta_{i,j,k+1} + \beta_{i,j,k}}{2\beta_{i,j,k+1}\beta_{i,j,k}} \right)^{-1} \frac{u_{i,j,k+1} - u_{i,j,k}}{h} - \left(\frac{\beta_{i,j,k} + \beta_{i,j,k-1}}{2\beta_{i,j,k}\beta_{i,j,k-1}} \right)^{-1} \frac{u_{i,j,k} - u_{i,j,k-1}}{h} \right) = 0
\end{aligned}$$

Wiegmann and A. Zemitis, *EJ-HEAT: A Fast Explicit Jump Harmonic Averaging Solver for the Effective Heat Conductivity of Composite Materials*, Bericht des Fraunhofer ITWM, Nr. 94, 2006.

Effective conductivity via homogenization

$$\begin{aligned}\nabla \cdot (\beta(\vec{x})(\nabla U_l + \vec{e}_l)) &= 0, \quad \vec{x} \in \Omega, \\ U_l(\vec{x} + id_1\vec{e}_1 + jd_2\vec{e}_2 + kd_3\vec{e}_3) &= U_l(\vec{x}), \quad i, j, k \in \mathbb{Z}, l = 1, 2, 3\end{aligned}$$

$$\beta_{ml}^* = \frac{1}{d_1 d_2 d_3} \int_{\Omega} \langle \vec{e}_m, \beta(\vec{x})(\nabla U_l + \vec{e}_l) \rangle d\vec{x}, \quad l = 1, 2, 3; \quad m = 1, 2, 3,$$

Wiegmann and A. Zemitis, *EJ-HEAT: A Fast Explicit Jump Harmonic Averaging Solver for the Effective Heat Conductivity of Composite Materials*, Bericht des Fraunhofer ITWM, Nr. 94, 2006.

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$$\beta_{ml}^* = \frac{1}{d_1 d_2 d_3} \int_{\Omega} \langle \vec{e}_m, \beta(\vec{x})(\nabla U_l + \vec{e}_l) \rangle d\vec{x}, \quad l = 1, 2, 3; \quad m = 1, 2, 3,$$

U_l has kinks where β is discontinuous – must be careful evaluating ∇U_l .

Wiegmann and A. Zemitis, *EJ-HEAT: A Fast Explicit Jump Harmonic Averaging Solver for the Effective Heat Conductivity of Composite Materials*, Bericht des Fraunhofer ITWM, Nr. 94, 2006.

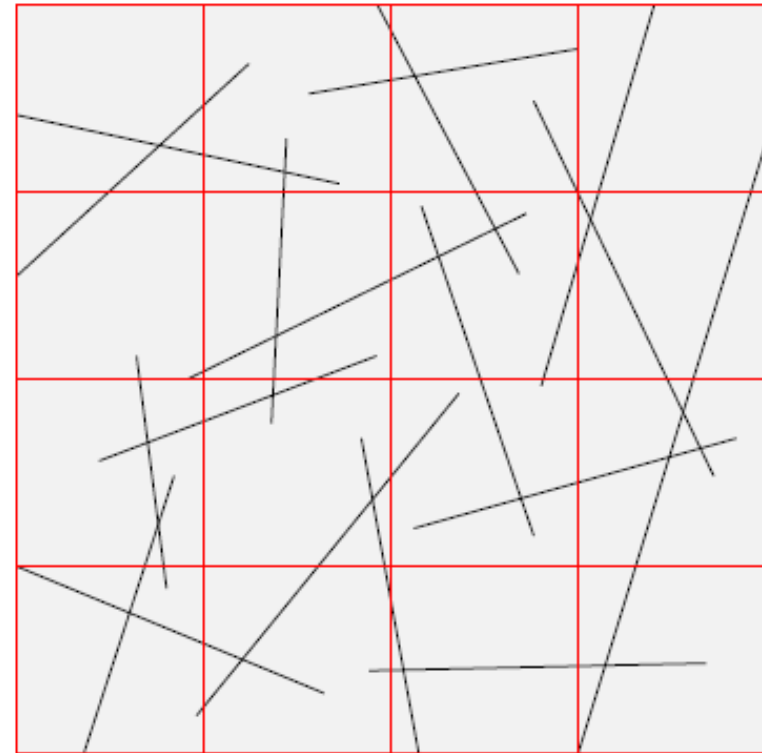
Effective conductivity from graph representation

1. Find intersections of fibers and set up graph
 - Nodes where fibers intersect each other and where fibers intersect boundary
 - Edges are straight segments between fibers
2. Set up and solve matrix for the Graph Laplacian
 - Boundary nodes in through direction have value equal to coordinate
 - Boundary nodes in tangential directions “ignored” by embedding in larger domain
3. Post-process solution to find effective conductivity

Iliev, R. Lazarov and J. Willems, *Fast Numerical Upscaling of Heat Equation for Fibrous Materials*, J. Computing and Visualization in Science, to appear.

Rapid Graph Creation by Domain Decomposition

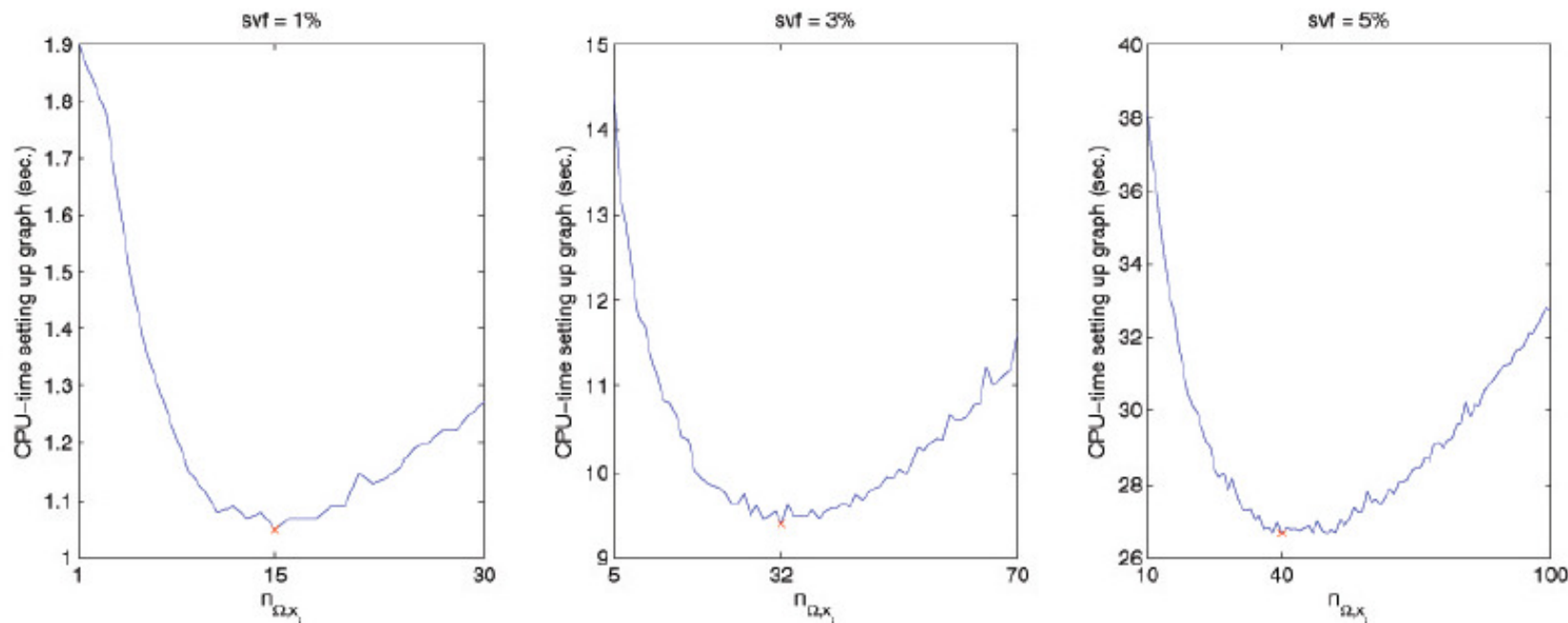
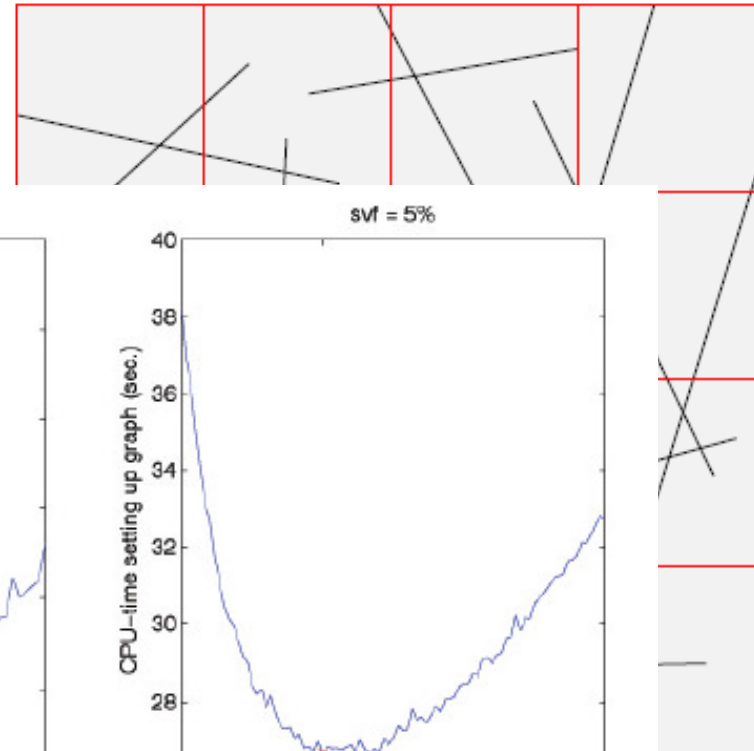
Partition domain and check only for intersections with fibers that lie in "own cells".



- Brandt, O. Iliev, and J. Willems, *A Domain Decomposition Approach for Calculating the Graph Corresponding to a Fibrous Geometry*, Proceedings of DD18 Conference on Domain Decomposition, 2008.

Rapid Graph Creation by Domain Decomposition

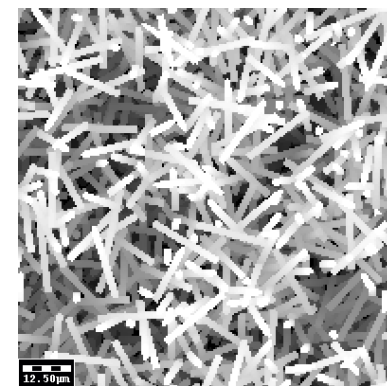
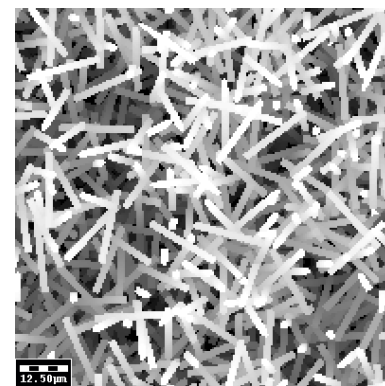
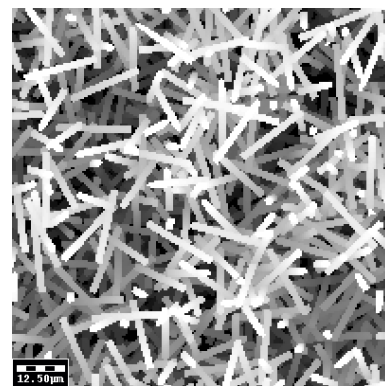
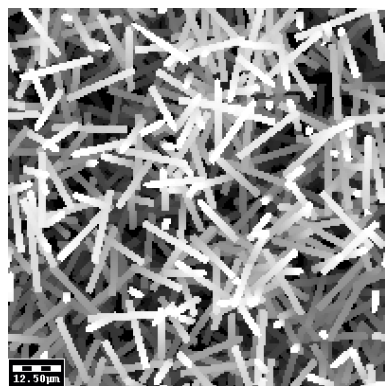
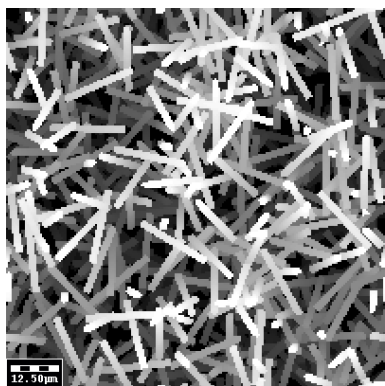
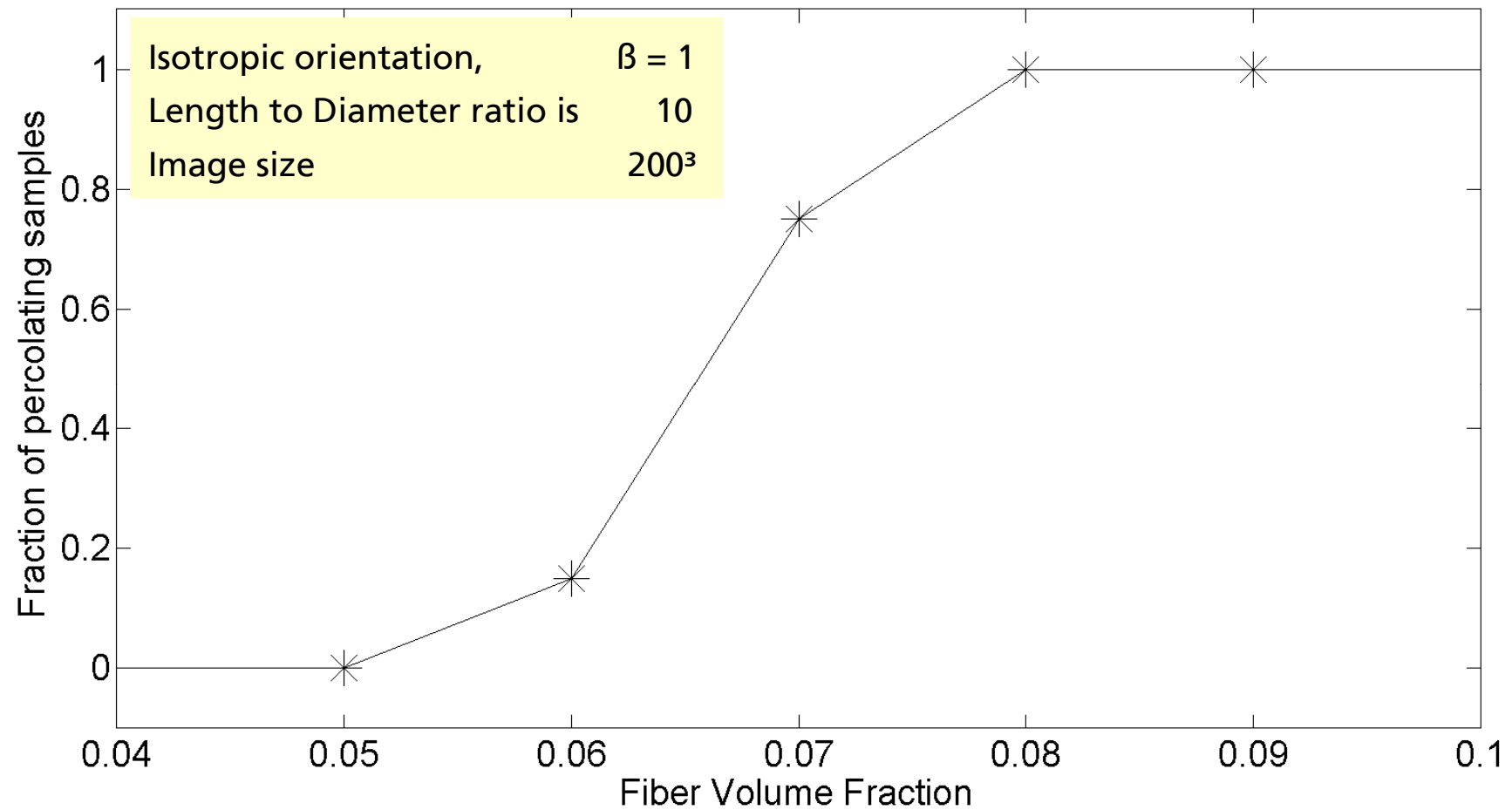
Partition domain and check only for intersections with fibers that lie in "own cells".



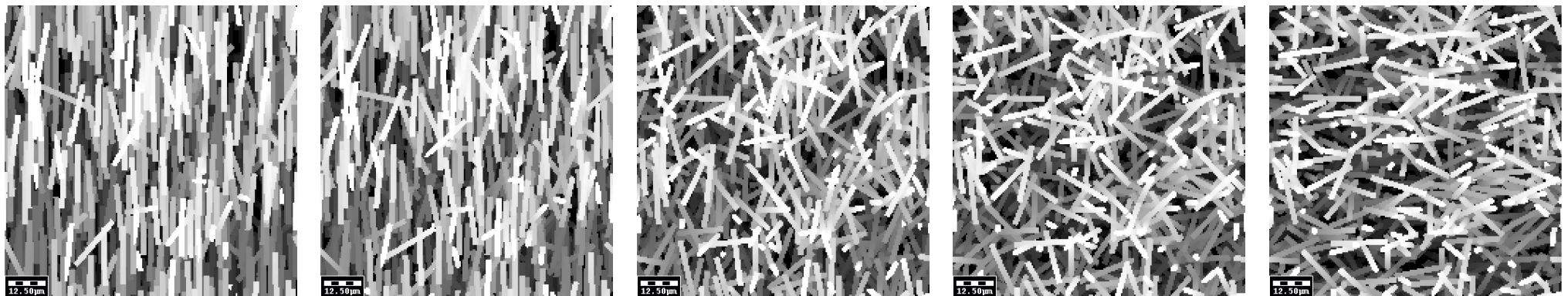
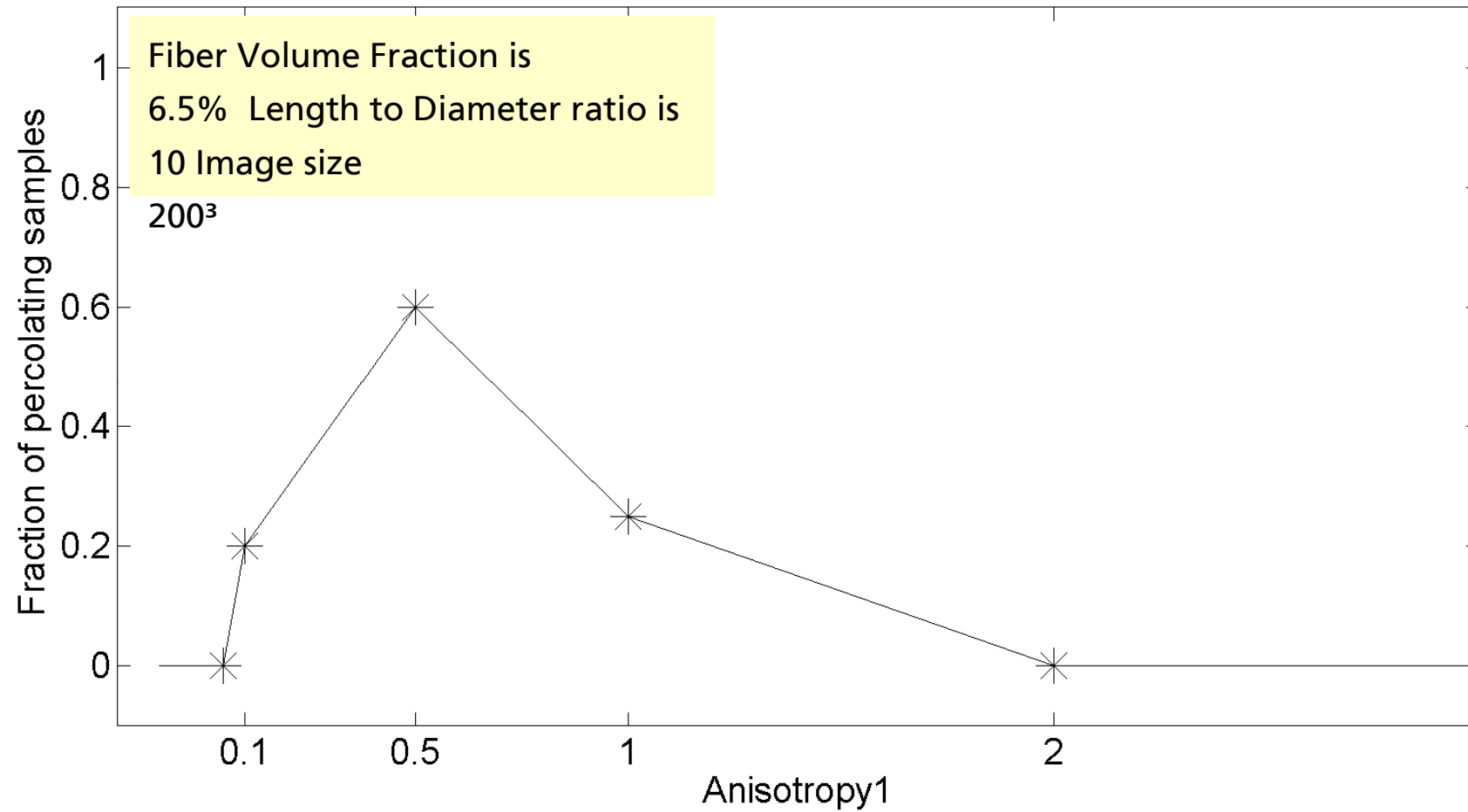
CPU-times needed for setting up the graph for different choices of $n_{\Omega, x_1} = n_{\Omega, x_2} = n_{\Omega, x_3}$.

- Brandt, O. Iliev, and J. Willems, *A Domain Decomposition Approach for Calculating the Graph Corresponding to a Fibrous Geometry*, Proceedings of DD18 Conference on Domain Decomposition, 2008.

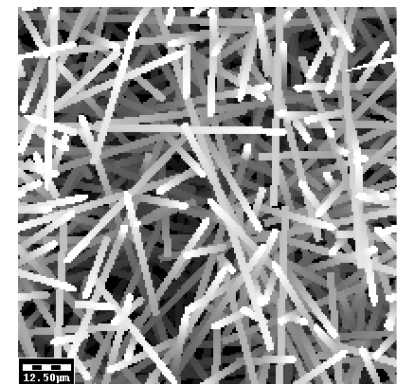
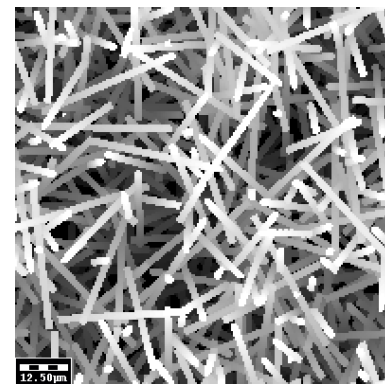
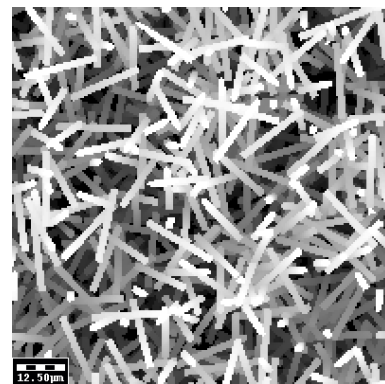
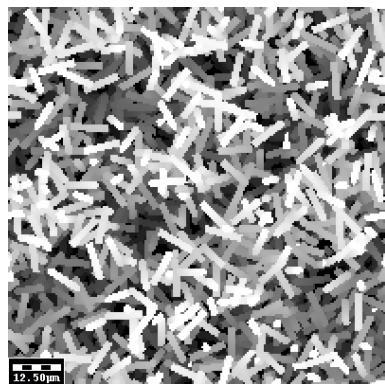
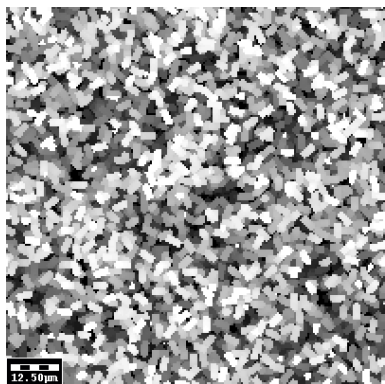
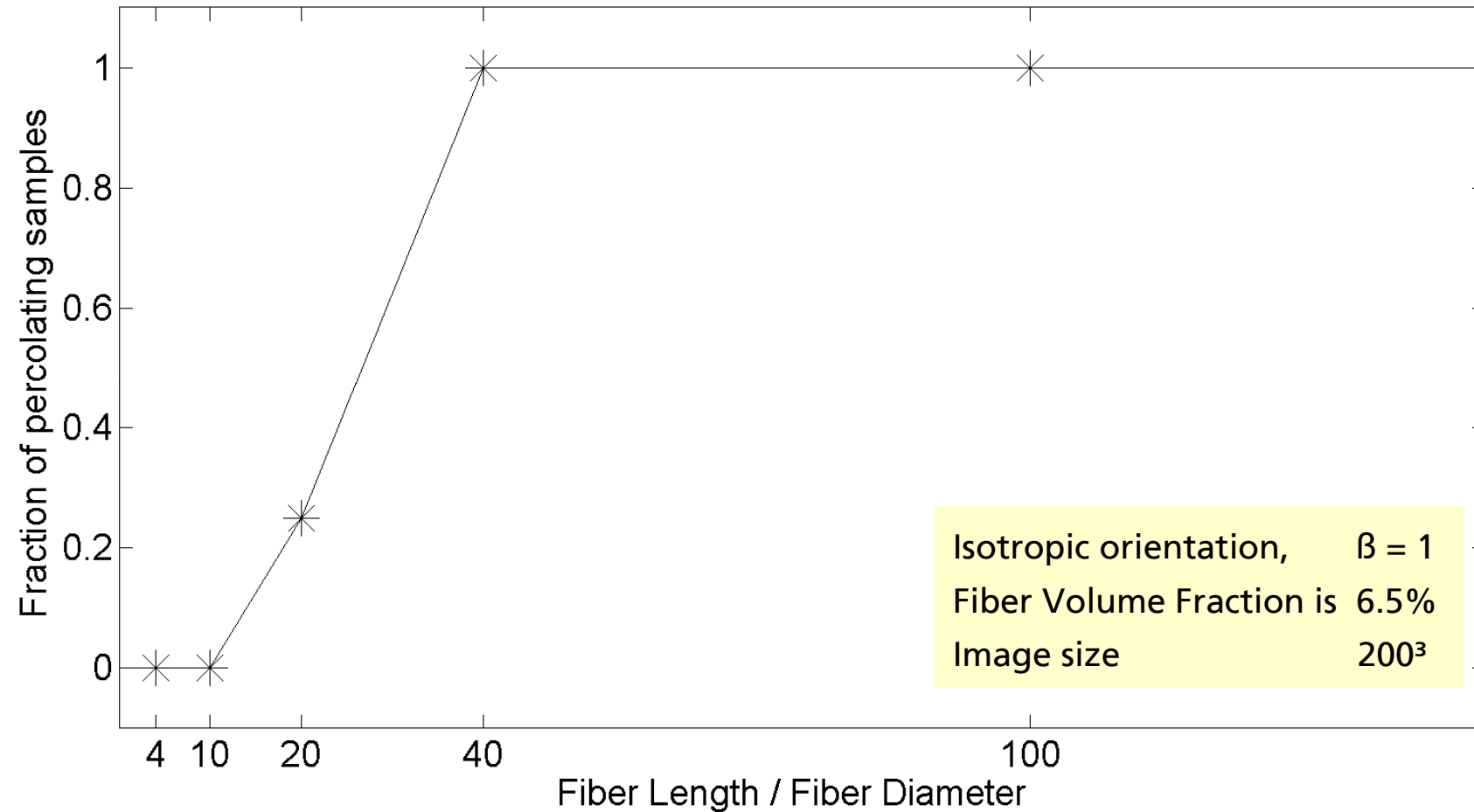
Influence of Fiber Volume Fraction on percolation



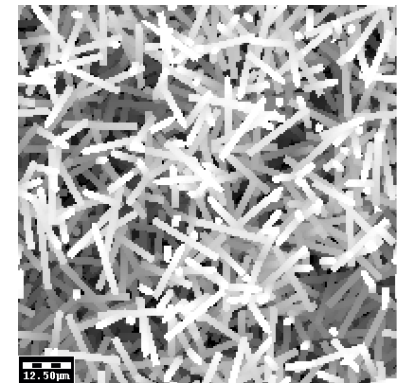
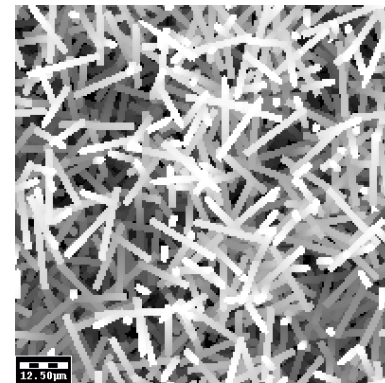
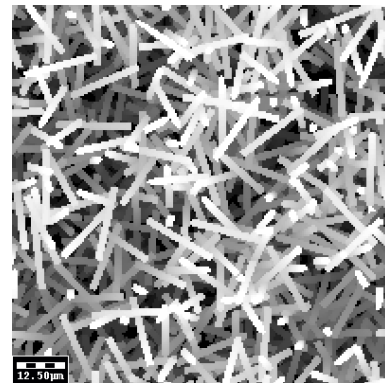
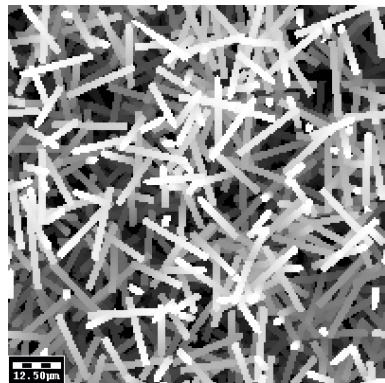
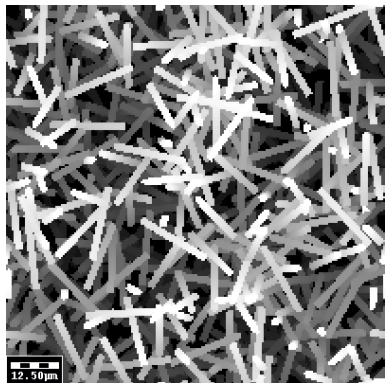
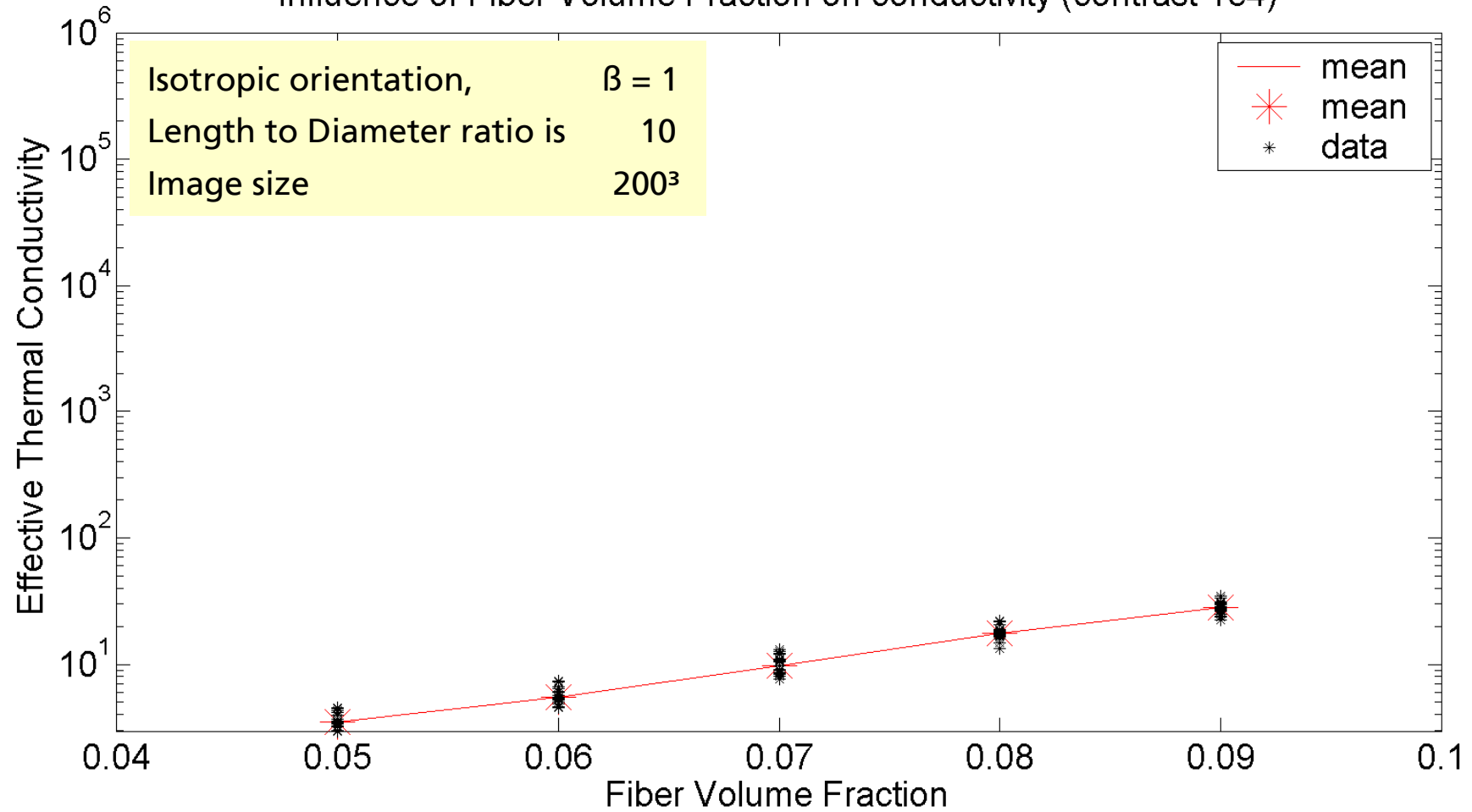
Influence of Anisotropy on percolation



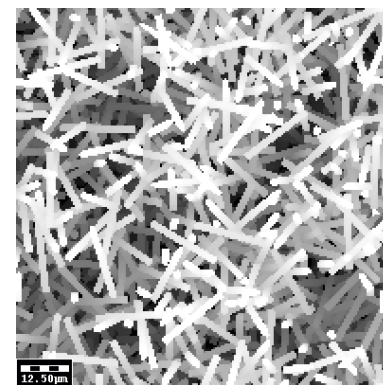
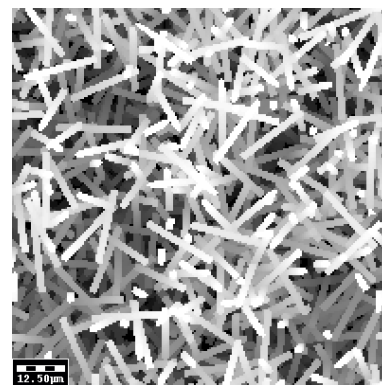
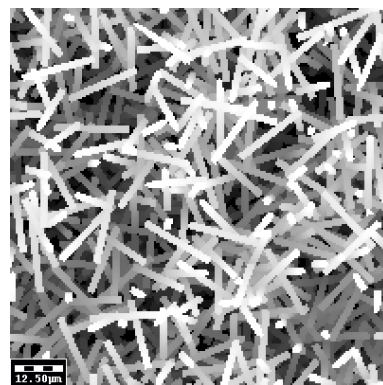
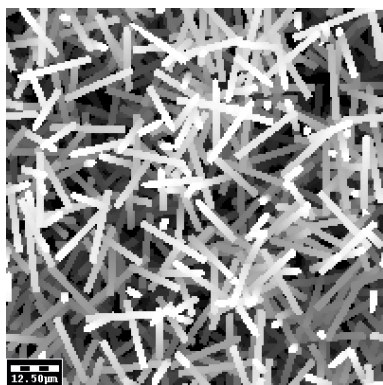
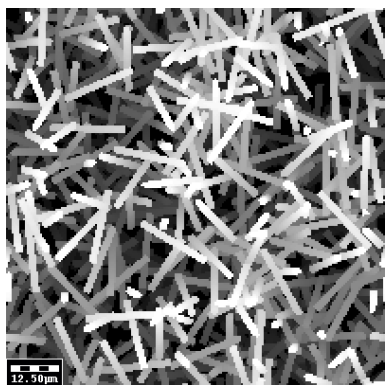
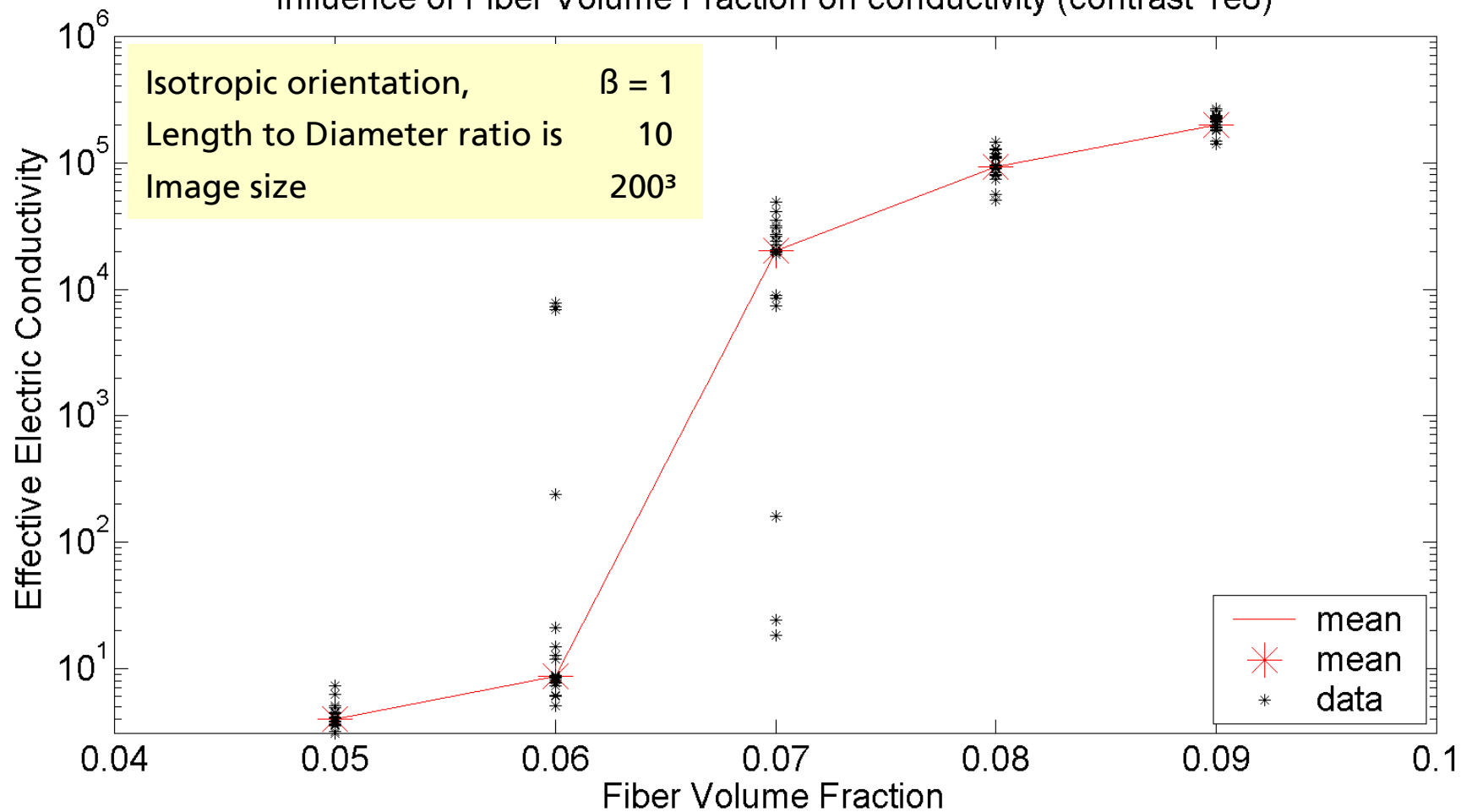
Influence of Fiber Length / Fiber Diameter on percolation



Influence of Fiber Volume Fraction on conductivity (contrast 1e4)



Influence of Fiber Volume Fraction on conductivity (contrast 1e8)



GeoDict vs CO-Graph: Performance

Image: 500 x 500 x 500

Fiber volume fraction: 0.05

Contrast: 50

Isotropic

Bi-modal fiber diameter distribution

	GeoDict			COGraph		
$\tilde{K} =$	1.653	-	-	1.672	-	-
	-	1.637	-	-	1.643	-
	-	-	1.614	-	-	1.624
# unknowns	1.25e8			3859		
runtime	> 5500sec.			< 1sec.		
memory	3169MB			13MB		

GeoDict vs CO-Graph: Performance

Image: 500 x 500 x 500

Fiber volume fraction: 0.15

Contrast: 50

Isotropic

Bi-modal fiber diameter distribution

	GeoDict			COGraph		
$\tilde{K} =$	3.244	-	-	3.158	-	-
	-	3.190	-	-	3.094	-
	-	-	3.274	-	-	3.205
# unknowns	1.25e8			26549		
runtime	> 6000sec.			< 5sec.		
memory	4876MB			84MB		

Conclusions and Outlook

- For 3d image, any cell can have its own conductivity
- For 3d image, large contrast deteriorates performance
- For graph, only straight fibers can be handled
- For graph, only large contrast can be handled
- “Real” computations at Bayer Technology Services done with CO-Graph on 200.000 fibers via 2000^3 images with L/D ratios of 500:1
- “Real” CNTs occur in bundles
- Electrical Conductivity jump found e.g. in measurements by Bayer Material Science in BMBF-project CarboNet
- Accelerate CNT generation via analytic collisions from CO-Graph
- Introduce connections in graph for nearby fibers

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