Dipl.-Ing. Steffen Kampmann
Chair of Materials Science and Nanotechnology, TU Dresden

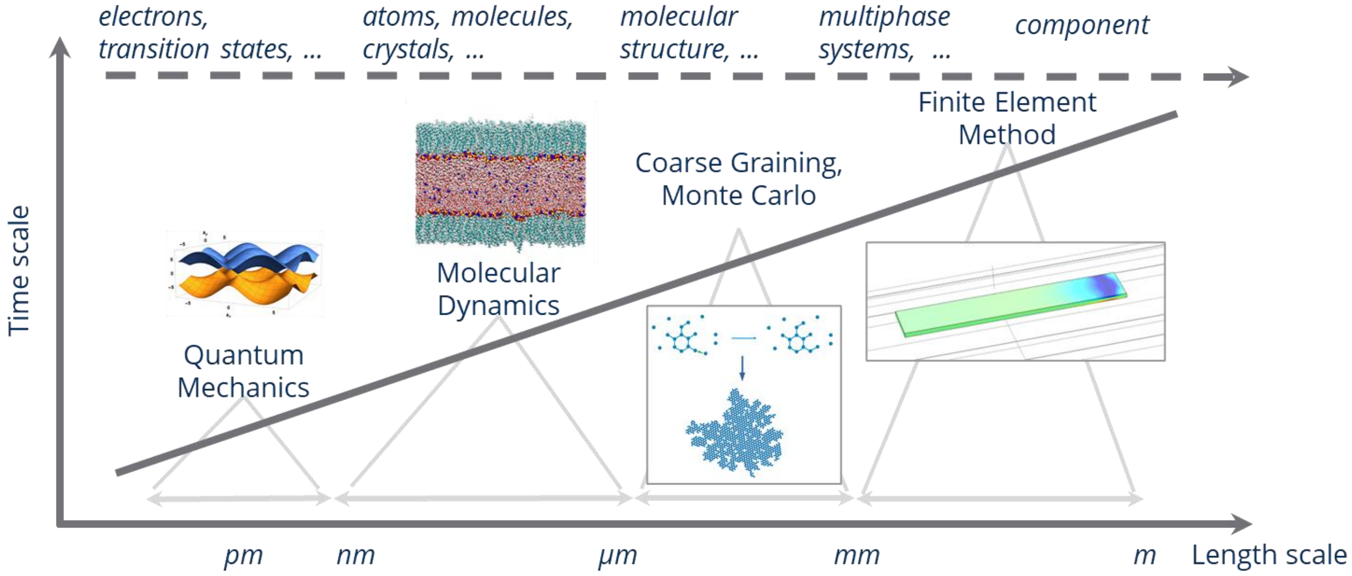
Multiscale Simulation Framework for Functional Polymers

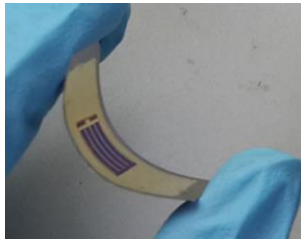
PhD Phase: Present and Future

Thesis Advisory Committee Meeting
TU Dresden, 14.02.2024

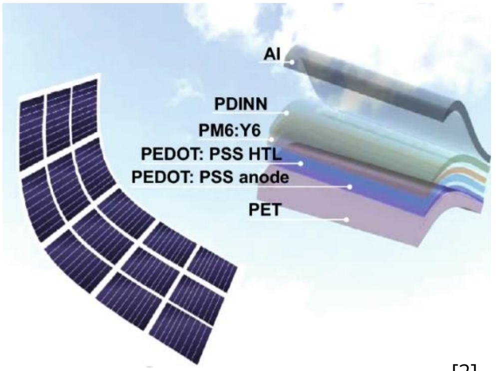
Motivation

- Combination of **electronic** and **mechanical** properties of polymers can play important role for energy solution technologies
  → Solar cells (Perovskite [1], organic [2], hybrid [3])
- **How can we predict electromechanical behavior?**
  → Consideration of different time and length scales





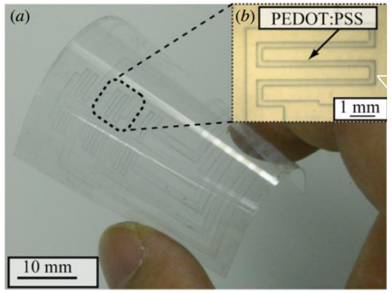
[3]



[2]

Example:
Strain gauge

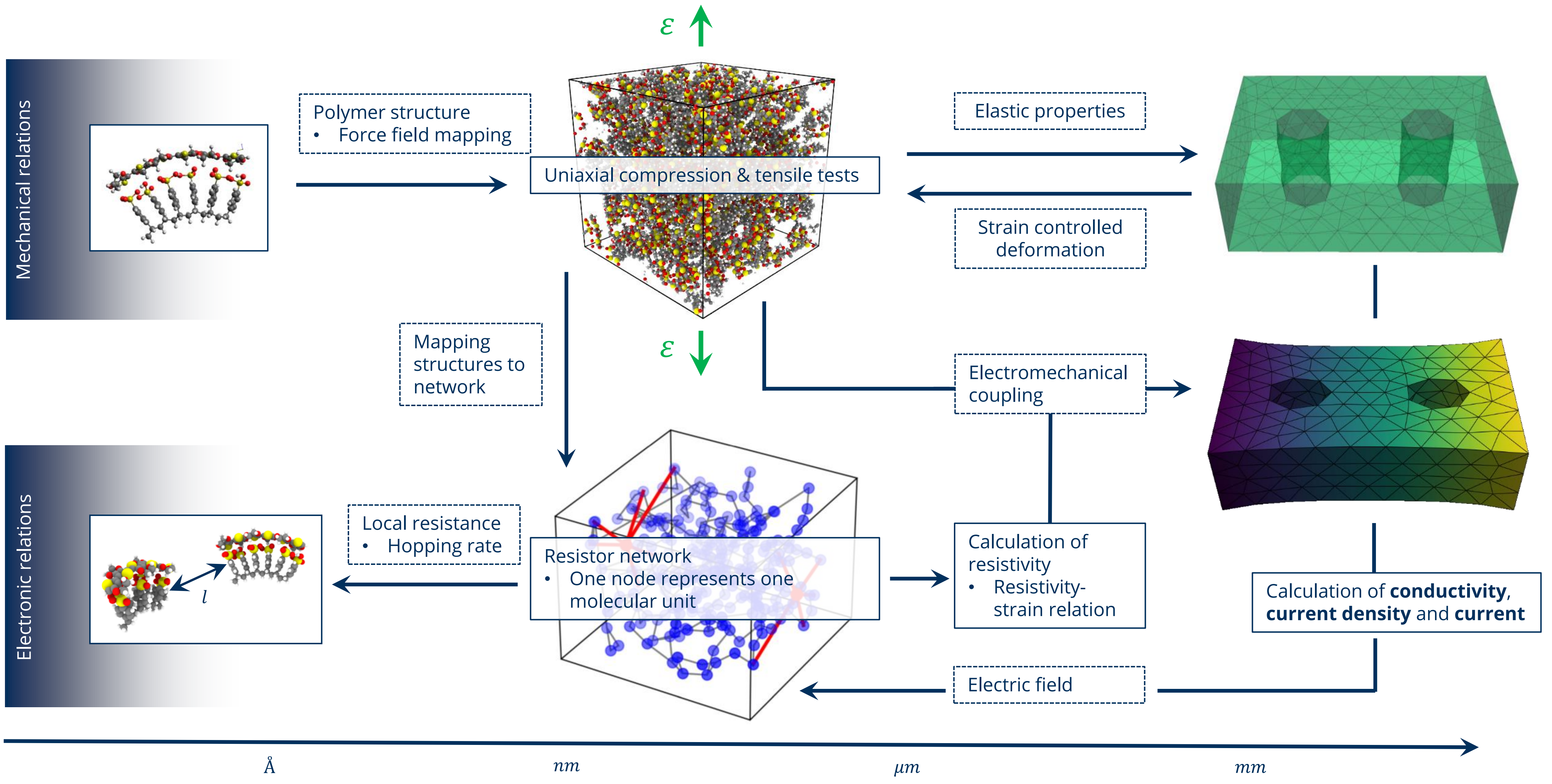
PEDOT:PSS
(poly(3,4-ethylenedioxythiophene polystyrene sulfonate)



[4]

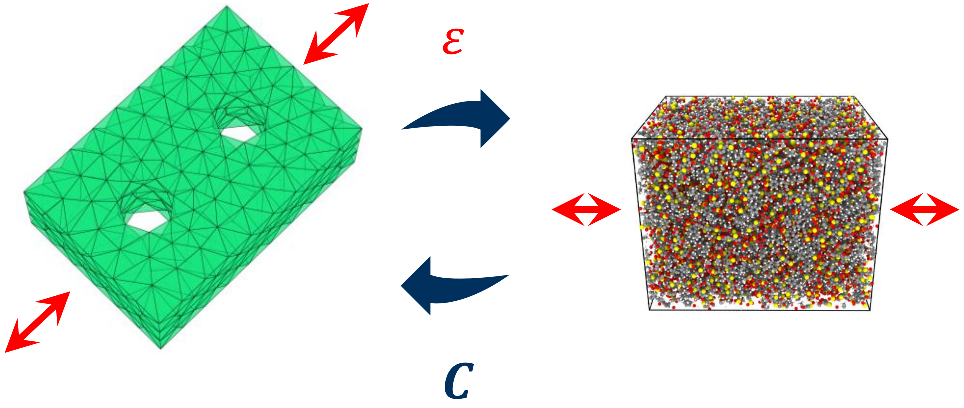
Hierarchical property relations → Different time and length scales → **Multiscale simulation framework**

Schematic Overview



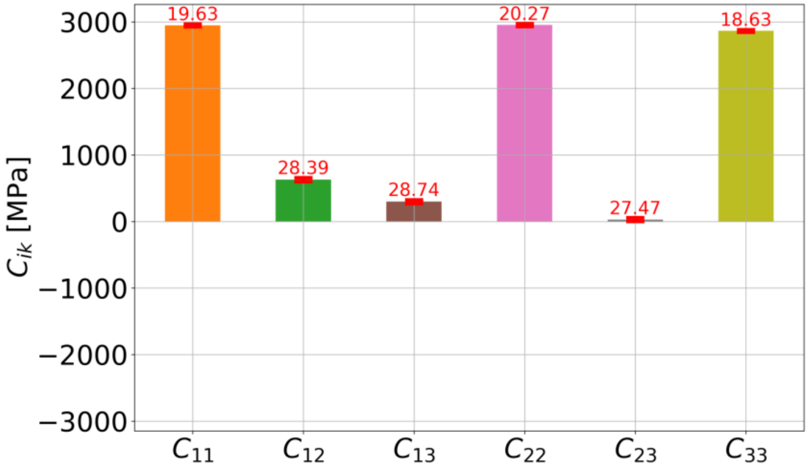
Mechanical Properties

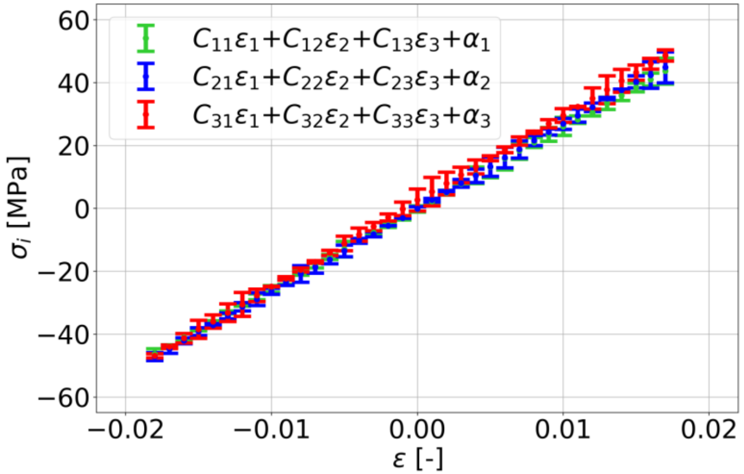
- Strain-controlled mechanical deformation of the polymer structures
  - Uniaxial compression and tensile test on **mesoscale** with Molecular Dynamics (MD)
  - Strain states result from the **microscale**
  - Capturing stress-strain relations of main and sub directions



- Multilinear regression of stress and strain states to determine components of the elasticity tensor $\boldsymbol{C}$

$$\sigma_{ij} = C_{ijkl}\varepsilon_{kl}$$





Elasticity tensor based on many different stress and strain states

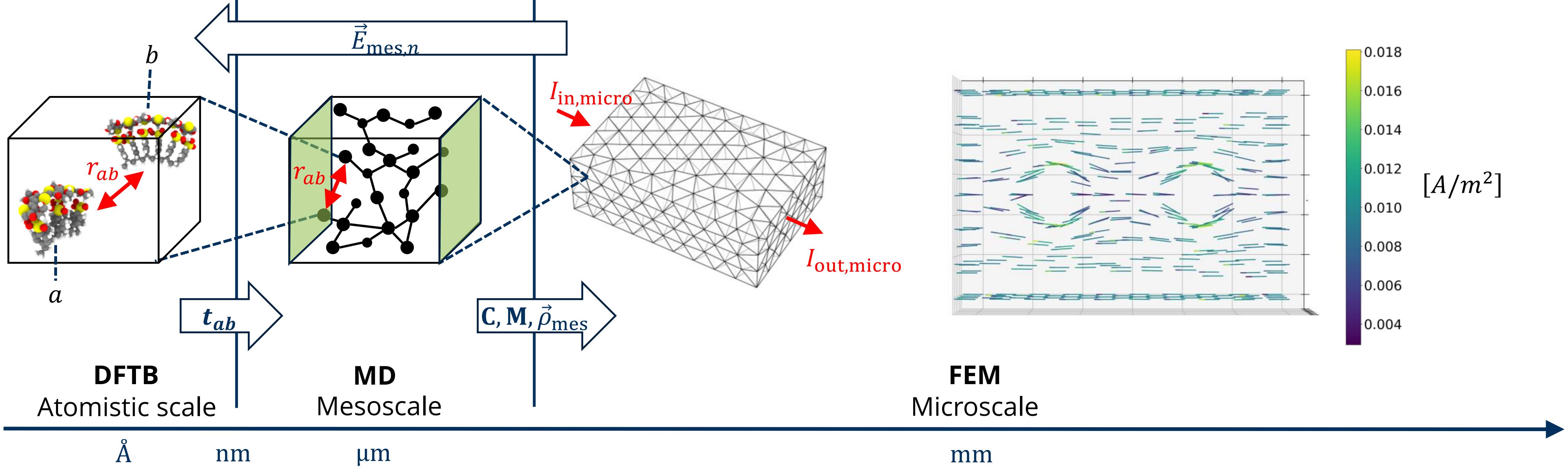
Electronic Properties

- Calculation of hopping rate t_{ab} with Marcus theory [5]

- Solving equation system of Kirchhoff's law

- Solving of Poisson equation

$$-\nabla \cdot (\boldsymbol{\kappa}_{\mathrm{mic}} \nabla \Phi) = 0 \quad \text{with} \quad \boldsymbol{\kappa}_{\mathrm{mic}} = \boldsymbol{\kappa}(\mathbf{M}, \vec{\varepsilon}) + \boldsymbol{\kappa}(\vec{E})$$

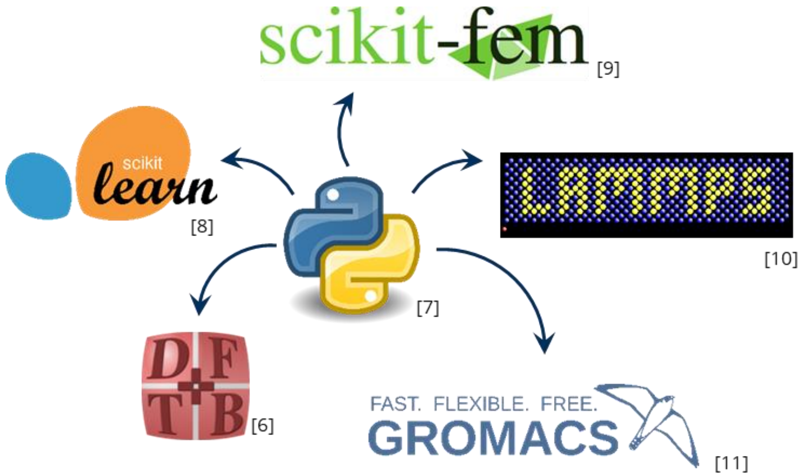


Calculation of electronic properties across three scales

[5] Marcus, R. Chemical and Electrochemical Electron-Transfer Theory. Annu. Rev. Phys. Chem. 1964, 15, 155–196.

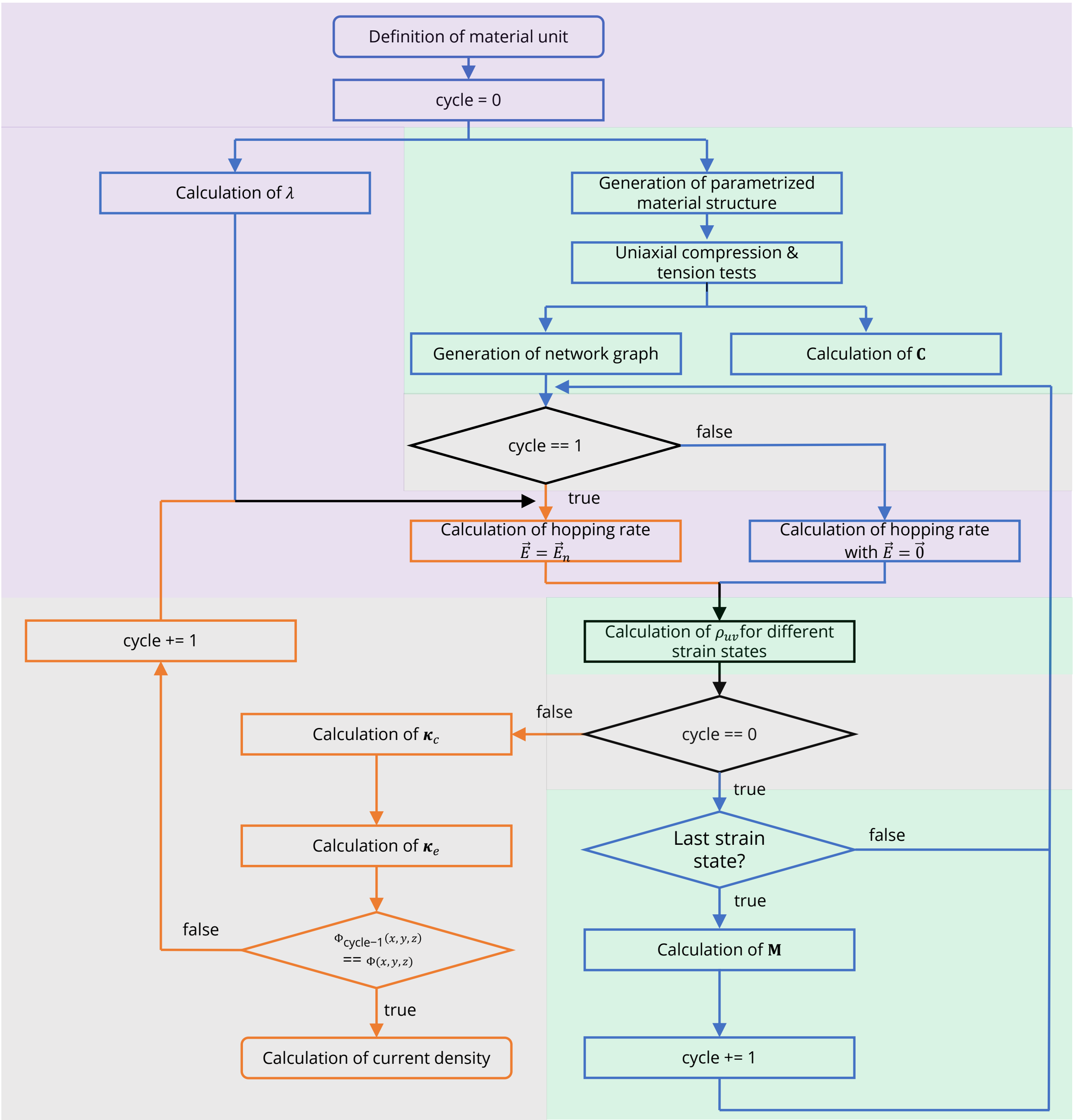
Github

M3F
***M**ultiscale **M**echatronic **M**aterial **F**ramework*



Initial cycle:
- Calculation of elasticity and elastoresistance tensor

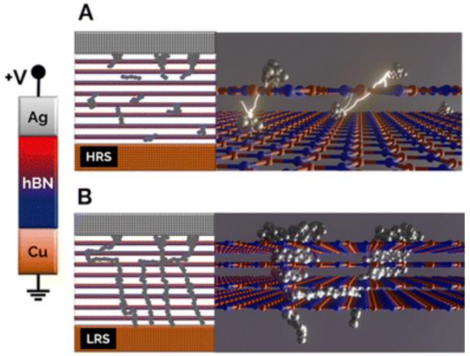
Further cycles:
- Calculation of current density on microscale level



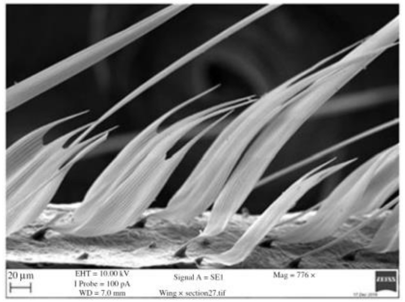
atomistic scale
mesoscale
microscale

Summary and Other Projects

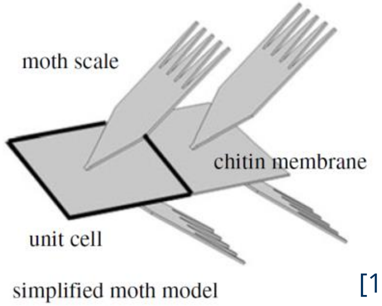
- Multiscale simulation framework for electro-mechanical coupling is ready for use
  - Publication in progress
- Collaboration with Vivek Dey finished
  - Calculation of neuromorphic network based on hexagonal Boron Nitride (hBN) layers with Ag-particles in between
  - Publication in progress
- Supervision of Master student Sina Seyedibavilolyaei
  - Bioinspired passive noise cancelling
  - Adaptation of the ultrasound absorption property of moth wings
  - Structure optimization for audible frequency range



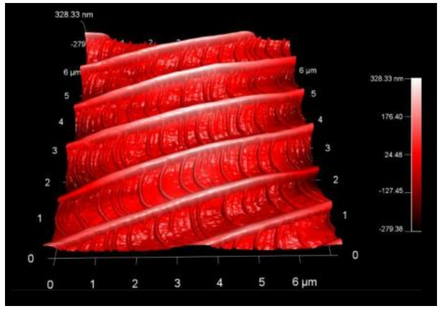
[12]



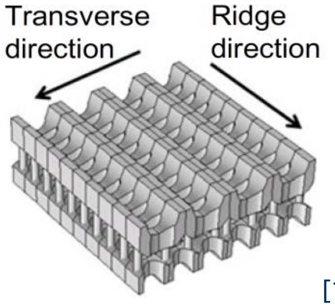
[13]



[13]



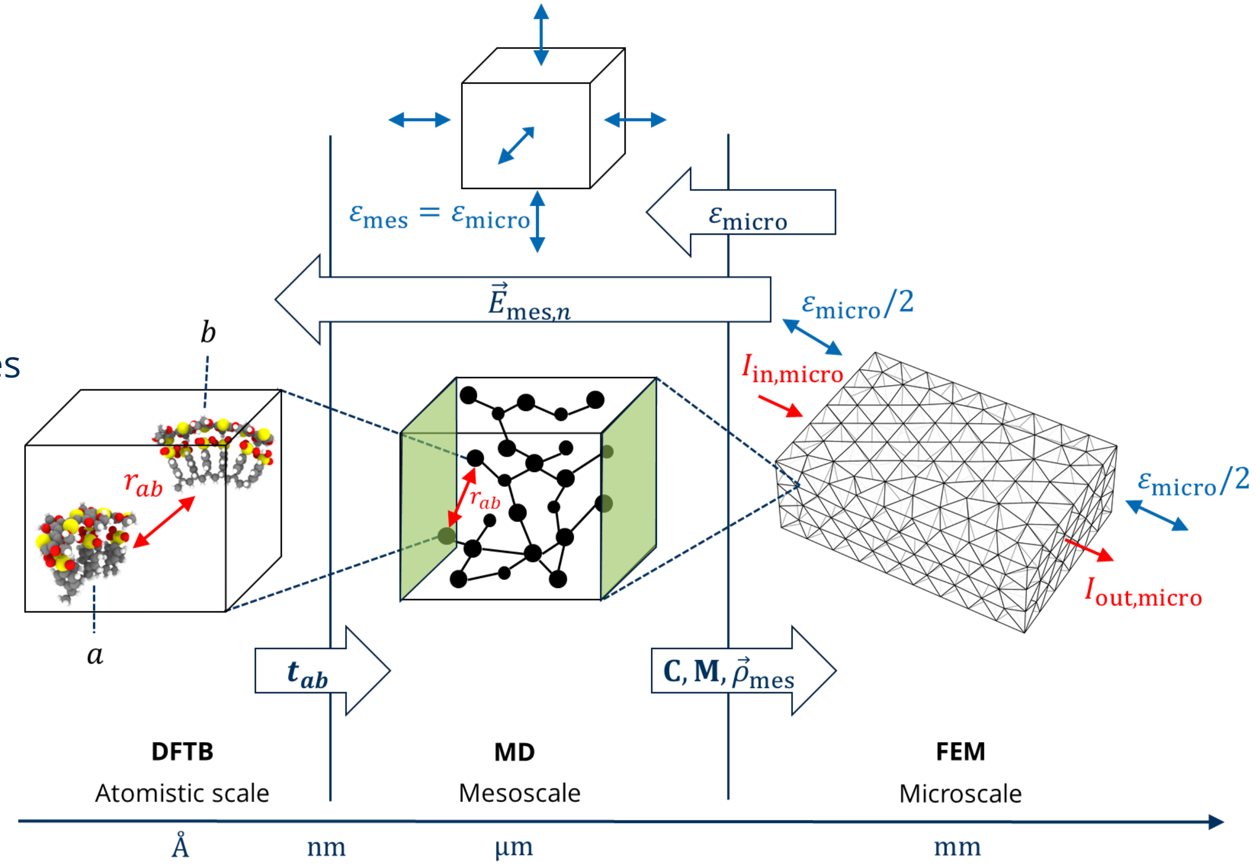
[14]



[13]

Outlook

- Extensions of multiscale framework
  - Implementation of different kind of local Resistances (contact, intrinsic) for CNT-composites materials
  - Prediction of stress states on microscale in combination with Molecular Dynamics
  - Testing framework for other applications, for example gas-sensing applications



Timeline:

Two publications for multiscale framework

Writing thesis

Thesis defense

DPG

MSE

February

June

Fourth quarter

Thank you for your attention!

References

[1] S. Ma, et al., Solar Energy Materials and Solar Cells, 208, 2020

[2] J. Wan, et al., Efficiency. Nano-Micro Lett. 13, 44,2021

[3] S. Li, et al., Nano Research, 8, 3141–3149, 2015

[4] S. Takamatsu et al., J. Micromech. Microeng., 20, 6, 2010

[5] Marcus, R. Chemical and Electrochemical Electron-Transfer Theory. Annu. Rev. Phys. Chem. 1964, 15, 155−196.

[6] https://dftbplus.org/

[7] https://python.org/

[8] https://scikit-learn.org/

[9] https://pypi.org/project/scikit-fem/2.2.0.dev0/

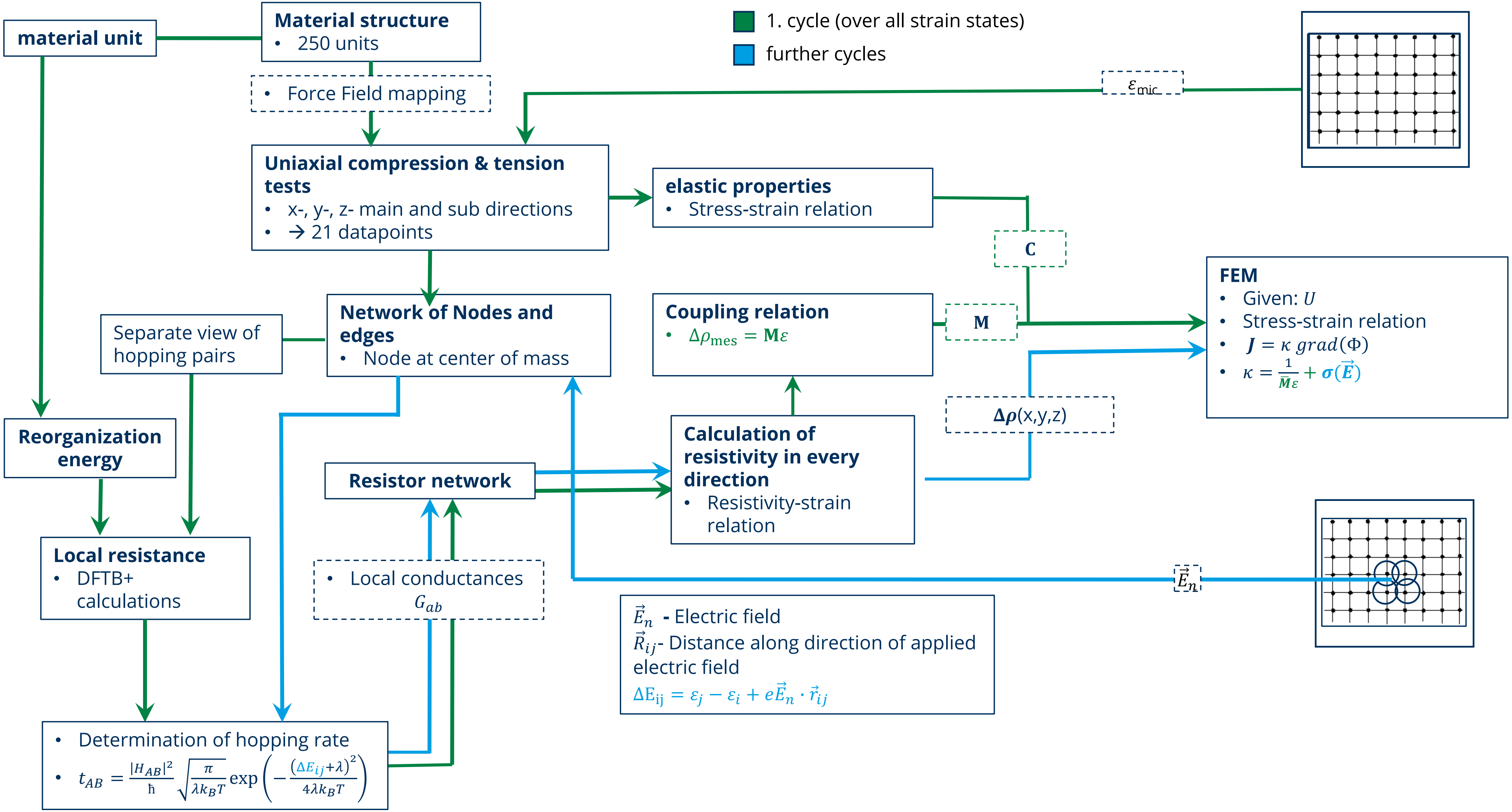
[10] https://lammps.org

[11] https://gromacs.org

[12] A. Rao et al., Materials Horizons, 11, 2023

[13] Shen et. al., Biophysics and computational Biology, 115 (48), 12200-12205, 2018

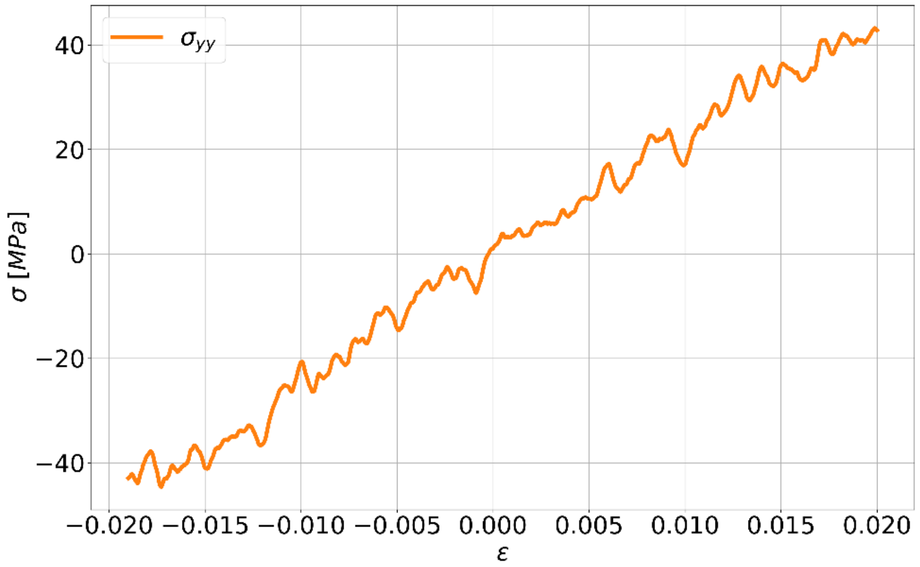
[14] https://www.uibk.ac.at/ionen-angewandte-physik/chemphys/afm.html

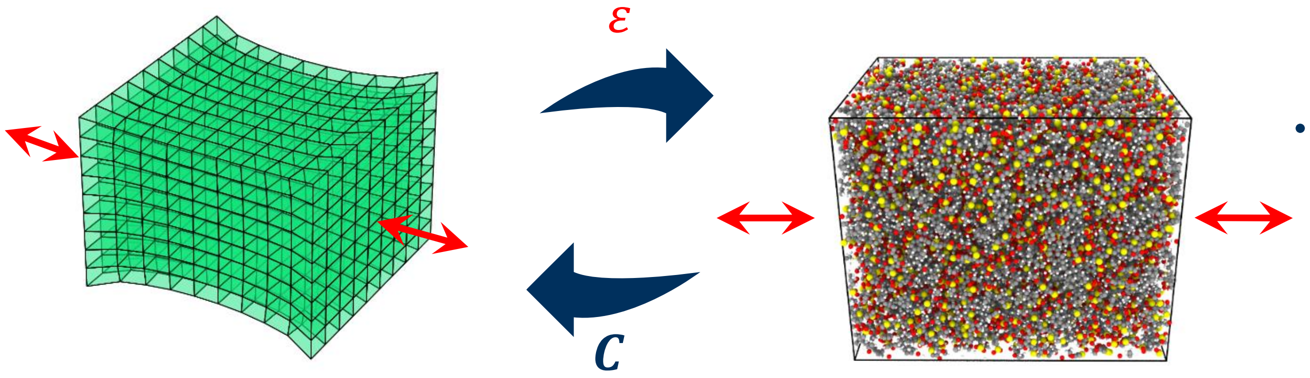

material unit
Material structure
• 250 units
• Force Field mapping
1. cycle (over all strain states)
further cycles
ε_{mic}
Uniaxial compression & tension tests
• x-, y-, z- main and sub directions
• → 21 datapoints
elastic properties
• Stress-strain relation
C
FEM
• Given: U
• Stress-strain relation
• $\boldsymbol{J} = \kappa\, grad(\Phi)$
• $\kappa = \frac{1}{\boldsymbol{M}\varepsilon} + \boldsymbol{\sigma}(\vec{\boldsymbol{E}})$
Separate view of hopping pairs
Network of Nodes and edges
• Node at center of mass
Coupling relation
• $\Delta\rho_{\text{mes}} = \mathbf{M}\varepsilon$
M
$\boldsymbol{\Delta\rho}$(x,y,z)
Reorganization energy
Resistor network
Calculation of resistivity in every direction
• Resistivity-strain relation
Local resistance
• DFTB+ calculations
• Local conductances G_{ab}
$\vec{E}_n$
$\vec{E}_n$ - Electric field
$\vec{R}_{ij}$- Distance along direction of applied electric field
$\Delta \mathrm{E_{ij}} = \varepsilon_j - \varepsilon_i + e\vec{E}_n \cdot \vec{r}_{ij}$
• Determination of hopping rate
• $t_{AB} = \frac{|H_{AB}|^2}{\hbar}\sqrt{\frac{\pi}{\lambda k_B T}}\exp\left(-\frac{(\Delta E_{ij}+\lambda)^2}{4\lambda k_B T}\right)$

Mechanical Properties

Molecular Dynamics (MD)

- **Input:** Polymer structures as Representative Volume Elements (RVE)
- Using LAMMPS and UFF force field
- Strain-controlled mechanical deformation of the polymer structures
  - Uniaxial compression and tensile tests
  - Strain states result from the microscale
  - Capturing stress-strain relations of main and sub directions





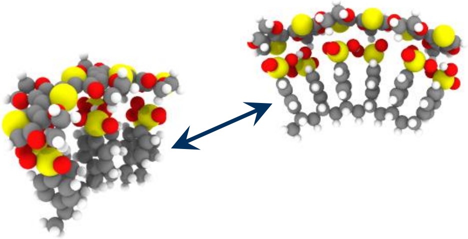
- Calculation of components of elasticity tensor $\boldsymbol{C}$

$$\sigma_{ij} = C_{ijkl}\varepsilon_{kl}$$

  - Multilinear regression of stress and strain states to determine C_{ijkl}

Elasticity tensor is input component for **Finite Element Method**

Electronic Properties

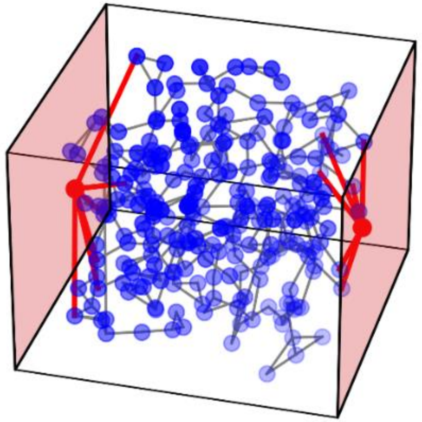


- **Input for Density Functional based Tight Binding :**
  Two PEDOT:PSS units from polymer structures deformed with molecular dynamics simulations
  - Distances and Orientations of the two PEDOT:PSS units are preserved

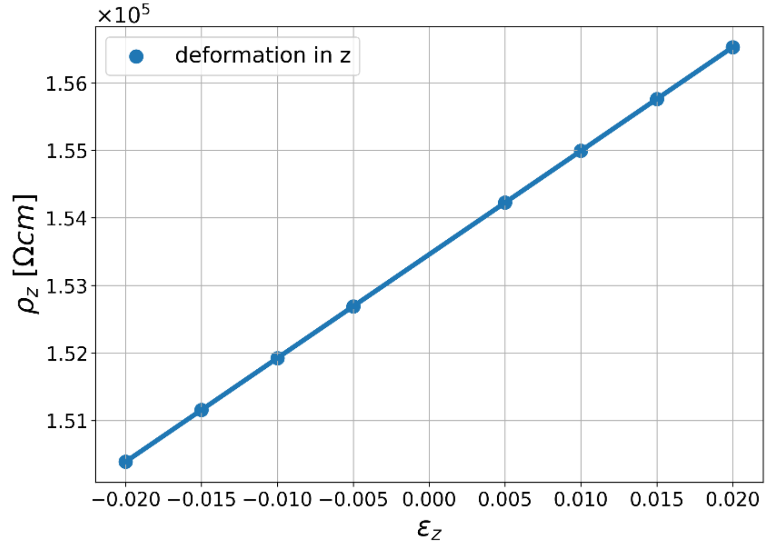
- Calculation of hopping rate with Marcus theory [5]:

$$t_{AB} = \frac{|H_{AB}|^2}{\hbar}\sqrt{\frac{\pi}{\lambda k_B T}}\, e^{-\frac{\left(\Delta E_{ij}+\lambda\right)^2}{4\lambda k_B T}} \quad \text{with } \Delta E_{ij}\left(\vec{E},\vec{R}_{ij}\right)$$

λ – reorganization energy, H_{AB} – transfer integral
$\vec{E}$ – Electrical field,
$\vec{R}_{ij}$ – Distance between unit i and atom j



- **Resistivity** ρ depends on:
  - **Hopping rate**
  - **Cross section** of RVE
  - **Length** of RVE
  - **Local distance** between two units

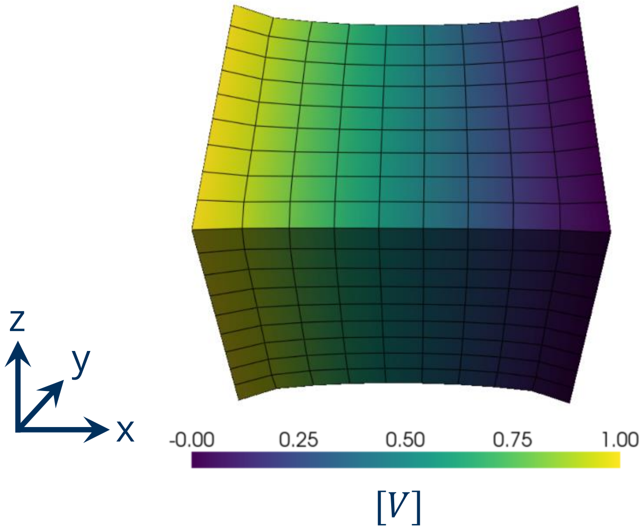


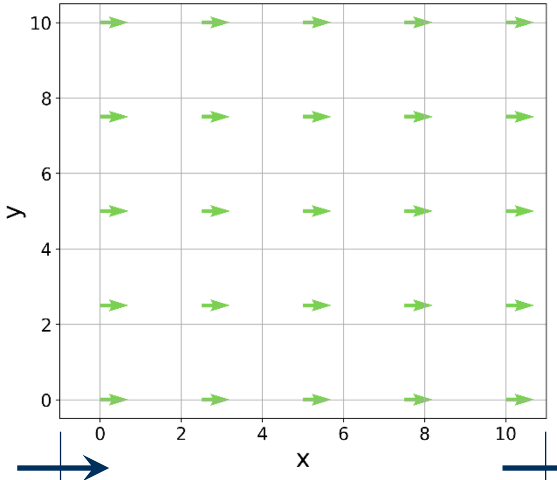
The resistivity of RVE increases almost linearly!

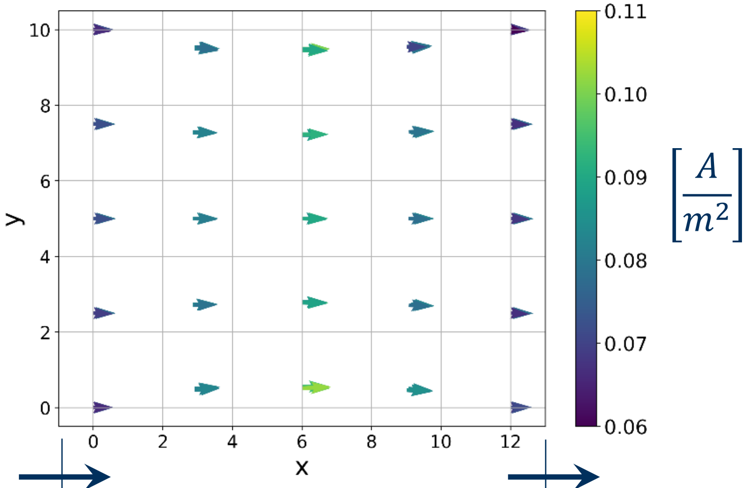
[5] Marcus, R. Chemical and Electrochemical Electron-Transfer Theory. Annu. Rev. Phys. Chem. 1964, 15, 155–196.

Mapping to Microscale

- **Input:** Elasticity Tensor $\boldsymbol{C}$ for elastic problem and elastoresistance tensor $\boldsymbol{M}$ for electromechanical problem
- Calculation of location dependent **conductivity:** $\boldsymbol{\sigma} = \boldsymbol{\sigma_0}(\boldsymbol{E}) + \boldsymbol{M}_{\boldsymbol{\varepsilon}}^{-1}$
- Solving Poisson equation $\nabla \cdot (\boldsymbol{\sigma}\, \nabla u) = 0$
- Calculation of current density: $\boldsymbol{J} = \boldsymbol{\sigma}\; grad(u)$
- Evaluate electric field at every node and recalculate hopping rate → update coupling tensor $\mathbf{M}$
- Integration of current density to get **electric current** I at boundaries







$I_{in} = 2.5\ A$ | $I_{out} = -2.5\ A$ | $I_{in} = 1.28\ A$ | $I_{out} = -1.28\ A$