Multiscale Models of Metallic and Biological Crystals

• Foundation: 1917

• Basic corporate budget financed equally by Max-Planck-Society (50%) and European, US, and Asian industry (Fe, Ti, Ni, Mg) through VDEH

• Budget (2009): 16,4 Mio. € (70% basic corporate budget, 30% third party funds)

• Personnel (2009): 260

• Structural materials (mainly metals)
Shareholder:
Max-Planck-Society, German Steel Institute

MPIE

Scientific Board

Trustees Board

Strategy Board

MPIE Departments

Microstructure Physics and Metal Forming

Interface Chemistry and Surface Engineering

Computational Materials Design

Administration

Dierk Raabe

Martin Stratmann

Jörg Neugebauer

Herbert Wilk
Overview

- Multiscale Crystal Plasticity FEM
- Examples at different scales
  - Indentation
  - Grain boundaries in CPFEM
  - Grain-scale deformation
- Homogenization and large scale forming
- Ab initio crystal mechanics
  - Steel
  - Titanium-Niobium
  - Magnesium-Lithium
  - Chinese food
Multiscale crystal plasticity FEM

- External boundary conditions
- Elastic tensor
- Phase fractions
- Defect dynamics
- Crystal kinematics
- Orientation
- Homogenization

\[ \dot{\gamma} = \frac{d\gamma}{dt} = \rho_m b v \]

\[ L_p = \sum_{\alpha=1}^{12} \dot{\gamma}_\alpha \tilde{b}_\alpha \otimes \tilde{n}_\alpha \]
▪ Multiscale Crystal Plasticity FEM

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3D EBSD: automated sequence of serial sectioning and 2D EBSD


Nanoinindentation (smaller is stronger): 3D EBSD and CPFEM

Cu, 60° conical, tip radius 1μm, loading rate 1.82mN/s, loads: 4000μN, 6000μN, 8000μN, 10000μN

Hardness and GND* in one experiment

Higher GND density at smaller scales responsible?

* GND: geometrically necessary dislocations (accomodate curvature)
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Comparison, crystal rotations about [11-2] axis

viscoplastic CPFEM

experiment 3D EBSD

dislocation-based CPFEM


From local misorientations to GNDs

\[ \Delta \phi = \phi(2) \phi(1)^{-1} \]

misorientation

\[ |\Delta \phi| = \min \{ \cos^{-1} \{ \text{tr} \left[ (O_i^{\text{cry}} \phi(1)) \phi(2)^T O_j^{\text{cry}} \right] \} \} \]

\( i = 1 \ldots 24, \ j = 1 \ldots 24 \)

orientation difference

\[ \phi(2) - \phi(1) = (\Delta \phi - I) \phi(1) \]

orientation gradient

\[ g_{ij,k} = \frac{\phi(2)_{ij} - \phi(1)_{ij}}{d_k} \]

(spacing d from EBSD scan)
From local misorientations to GNDs

\[ \beta_{ij} = \frac{\delta u_i}{\delta x_j} = \beta_{ij}^{el} + \beta_{ij}^{pl} \]

distortion
(sym, a-sym)

\[ \alpha = \nabla \times \beta^{el} \]

\[ \alpha_{pi} = e_{pkj} \left( \epsilon_{ij,k}^{el} + g_{ij,k} \right) \]

\[ \alpha_{pi} = e_{pkj} \ g_{ij,k} \]

dislocation tensor (GND)

From local misorientations to GNDs

Slip and line directions of dislocations for GNDs in a FCC crystal

$\sqrt{2} \, \hat{b} : \begin{array}{ccccccccccccc} 110 & 10\bar{1} & 0\bar{1}1 & \bar{1}10 & 101 & 01\bar{1} & 110 & \bar{1}01 & 0\bar{1}1 & 110 & \bar{1}01 & 011 & \bar{1}10 & 10\bar{1} & 0\bar{1}1 \end{array}$

$\sqrt{6} \, \hat{t} : \begin{array}{ccccccccccccc} 1\bar{1}2 & 12\bar{1} & 2\bar{1}1 & \bar{1}21 & 211 & 1\bar{1}2 & 121 & 2\bar{1}1 & 112 & 1\bar{2}1 & 2\bar{1}1 & 110 & 101 & 011 & \bar{1}10 & 10\bar{1} & 0\bar{1}1 \end{array}$

$B = b(\hat{t} \cdot r) = (b \otimes \hat{t})r$

Frank loop

$\alpha_{ij} = \sum_{a=1}^{18} \rho_{gnd}^a b_i^a t_j^a$

DDT in terms of 18

$\alpha_{ij} = \sum_{a=1}^{9} \rho_{gnd}^a b_i^a t_j^a$

DDT in terms of 9 $t$
Extract geometrically necessary dislocations

Indentation depths (μm)

Position (μm)

Hardness (GPa)

GND density (1/m^2)

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Size effect as a mean-field break down phenomenon

- Correlation length $\xi$
  - $(1/\sqrt{p};$ cell size)

Critical bow-out length (half probe size) $L$ [a.u. · b]

- Mean-field breakdown regime
- Mean-field regime

Probed volume $<$ correlation length $\xi$
- Fluctuations important
- Low probability that probe contains a source
- Most probable source $=$ softest source $=$ half sample size

Probed volume $>$ correlation length $\xi$
- Statistical distribution of sources
- High probability that probe contains a source
- Most probable source $<$ half sample size
Al Bicrystals, low angle g.b. [112] 7.4°, von Mises strain

CPFEM: viscoplastic phenomen. model

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CPFEM: dislocation-based model; g.b. model

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Homogeneity and boundary conditions at grain scale

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8%

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Crystal plasticity FEM, grain scale mechanics (3D Al)

- Multiscale Crystal Plasticity FEM

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  - Grain-scale deformation

- Homogenization and large scale forming

- Ab initio crystal mechanics
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  - Chinese food
Crystal plasticity FEM for large scale forming predictions

too many grains
Multiscale crystal plasticity FEM for large scale forming

- External boundary conditions
- Elastic stiffness tensor
- Mesh
- Integration point
- Kinematics of plastic flow; here: multiple deformation mechanisms (dislocations, twinning)
- Dynamics of plastic flow; here: multiple deformation mechanisms (dislocations, twinning)
- Constituents; here: single orientation, single phase
- Input on orientation, phase, interfaces, homogenization, etc.
Multiscale crystal plasticity FEM for large scale forming

FFT

TC-CPFEM

Clustermodels

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Texture component crystal plasticity FEM for large scale forming

Zhao, Mao, Roters, Raabe: Acta Mater. 52 (2004) 1003
Texture component crystal plasticity FEM for large scale forming

Multiscale crystal plasticity FEM for large scale forming

Numerical Laboratory: From CPFEM to yield surface (engineering)

DC04 study with Mercedes, Volkswagen, Audi, Inpro

Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany
- **Multiscale Crystal Plasticity FEM**
- **Examples at different scales**
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- **Ab initio crystal mechanics**
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Ab initio and crystal modeling

- Combine to atomic scale experiments
- Obtain data not accessible otherwise
- Use in continuum theory
- Electronic rules for alloy design
Develop new materials via ab-initio methods

BCC-Titanium

TWIP-Steel

Magnesium

Food
Stress shielding

Elastic Mismatch:
Bone degeneration, abrasion, infection
BCC Ti biomaterials design

Design-task: reduce elastic stiffness

Bio-compatible elements

BCC structure: Ti-Nb, ...

Free energy $F(x,c,T) = U - T \cdot S$

U: Density functional theory (DFT)
S: configuration entropy
elastic tensor
Polycrystal stiffness (homogenization)
From ab-initio to polycrystal stiffness

- plane wave pseudopotential (VASP)
- cutoff energy: 170 eV
- 8×8×8 Monkhorst supercells of 2×2×2 cubic unit cells
- total of 16 atoms
- 48 bcc and 28 hcp configurations

Hershey homogenization
- discrete FFT
- crystal elasticity FEM
Ab initio alloy design: Elastic properties: Ti-Nb system

Young's modulus surface plots

\[ A_z = \frac{2 C_{44}}{C_{11} - C_{12}} \]

- Ti: 115 GPa
- Ti – 35 Nb - 7 Zr - 5 Ta: 59.9 GPa (elastic isotropic)

[Diagram showing Young's modulus surface plots for different compositions of Ti-Nb alloy systems, with modulus values for each composition.]
Every year more than one million hips are implanted

The development of elastically soft Ti alloys reduces the number of surgeries
Develop new materials via ab-initio methods

BCC-Titanium

TWIP-Steel

Magnesium

Food
Ab-initio methods for the design of high strength steels

The diagram illustrates the stress-strain curves for TRIP steel and TWIP steel. The stress is plotted on the vertical axis in MPa, while the strain is plotted on the horizontal axis in %. The curves show the mechanical behavior of these steels under stress. TRIP steel exhibits a more ductile behavior, while TWIP steel displays a higher strength. The graphs also include molecular models to represent the atomic structure of these steels.
Ab-initio methods for the design of high strength steels

Stacking fault

Series expansion of formation energy

\[ F_{ISF} - F_0 \approx F[AB] + 2F[ABC]B - 3F[ABC] \]

\((1^{st} \text{ order})\)

\[ F_{ISF} - F_0 \approx F[AB] + 2F[ABC]B - 3F[ABC] \]

\((2^{nd} \text{ order})\)

BCC-Titanium

TWIP-Steel

Magnesium

Food
Ultralight weight materials derived by DFT

\[ \frac{Y}{\rho} \text{ (MPa m}^3/\text{kg)} \]

\[ \frac{Y}{\rho} \text{ (MPa m}^3/\text{kg)} \]

Weak against normal load

Weak against shear load

\[ Y: \text{Young's modulus} \]
\[ \rho: \text{mass density} \]
\[ B: \text{compressive modulus} \]
\[ G: \text{shear modulus} \]
Develop new materials via ab-initio methods

BCC-Titanium

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Food
Structure hierarchy of chitin-compounds

The materials science of chitin composites
Exocuticle and endocuticle have different stacking density of twisted plywood layers.

Cuticle hardened by mineralization with CaCO$_3$
$180^\circ$ rotation of fiber planes
Endocuticle

Exocuticle

Hardness Universal, MPa

Cut Depth, µm

Hardness (mesoscopic)
Mechanical properties (microscopic, nanoindentation)

- Endocuticle A
  - Reduced elastic modulus $E_{\text{red}}$ (blue)
  - Hardness $H$ (red)
  - Sinodial fit (black)

- Exocuticle A
  - Reduced elastic modulus $E_{\text{red}}$ (blue)
  - Hardness $H$ (red)
  - Sinodial fit (black)

Position of row [µm]

Reduced elastic modulus [GPa]

Hardness [MPa]
What is α-chitin?

The crystal structure of α-chitin

Carlstrom, D.


<table>
<thead>
<tr>
<th>Polymer</th>
<th>Unit cell dimensions (Bohhradius)</th>
<th>Space group</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Chitin</td>
<td>8.96 35.64 19.50 90°</td>
<td>P21</td>
</tr>
</tbody>
</table>
108 atoms / 52 unknown H-positions

What is $\alpha$-chitin?

Hierarchy of theoretical methods

**Empirical Potentials**
Geometry optimization
Molecular Dynamics
(universal force field)

**Tight Binding**
(SCC-DFTB)
Geometry optimization
(SPHIngX)

**DFT**
(PWs, PBE-GGA)
Geometry Optimization
(SPHIngX)

<table>
<thead>
<tr>
<th>Method</th>
<th>CPU time</th>
<th>Accuracy</th>
<th>Resulting structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Potentials</td>
<td>~10 min</td>
<td>Low</td>
<td>~$10^3$</td>
</tr>
</tbody>
</table>

Image of a molecular structure showing C, C, N, H atoms.
Ab initio prediction of α-chitin elastic properties

\[
\begin{bmatrix}
119 & 0.1 & 1.1 & 0 & 0 & 0 \\
0.1 & 28 & 2 & 0 & 0 & 0 \\
1.1 & 2 & 24 & 0 & 0 & 0 \\
0 & 0 & 0 & 5 & 0 & 0 \\
0 & 0 & 0 & 0 & 8 & 0 \\
0 & 0 & 0 & 0 & 0 & 2 \\
\end{bmatrix}
\]

\(C_{CH}\) [GPa]

C, C, N, H

Energy \(E - E_0\) [kcal/mol]

Lattice elongation [%]
## Hierarchical modeling of stiffness starting from ab initio

<table>
<thead>
<tr>
<th>Scale</th>
<th>0.1 nm – 10 nm</th>
<th>10 nm – 100 nm</th>
<th>100 nm – 10 µm</th>
<th>10 µm – 1 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hierarchical structure unit</strong></td>
<td>α-chitin (H-bonded anti-parallel N-acetyl-glucosamine molecular chains)</td>
<td>Mineralized chitin-protein nanofibrils in a planar array</td>
<td>Twisted plywood stack of mineralized chitin-protein planes without pore canals</td>
<td>Twisted plywood stack of mineralized chitin-protein planes with pore canals</td>
</tr>
<tr>
<td><strong>Experimental method</strong></td>
<td>Transmission electron microscope</td>
<td>Field emission scanning electron microscope</td>
<td>Field emission scanning electron microscope</td>
<td>Field emission scanning electron microscope</td>
</tr>
<tr>
<td><strong>Microstructure</strong></td>
<td><img src="image1.png" alt="Image 50 nm" /></td>
<td><img src="image2.png" alt="Image 200 nm" /></td>
<td><img src="image3.png" alt="Image 10 µm" /></td>
<td><img src="image4.png" alt="Image 10 µm" /></td>
</tr>
<tr>
<td><strong>Schematic</strong></td>
<td><img src="image5.png" alt="Schematic 10 Å" /></td>
<td><img src="image6.png" alt="Schematic 10 nm" /></td>
<td><img src="image7.png" alt="Schematic 10 µm" /></td>
<td><img src="image8.png" alt="Schematic 10 µm" /></td>
</tr>
<tr>
<td><strong>Simulation method</strong></td>
<td>Ab initio; density functional theory</td>
<td>Mori-Tanaka scheme (chitin-protein fiber); Torquato 3-point scheme (mineral-protein matrix)</td>
<td>Voigt estimate, tensor rotation</td>
<td>Torquato 3-point homogenization</td>
</tr>
<tr>
<td><strong>Elastic behavior, 3D map of Young’s modulus [GPa]</strong></td>
<td><img src="image9.png" alt="3D map a, b-axis" /></td>
<td><img src="image10.png" alt="3D map 100 Å" /></td>
<td><img src="image11.png" alt="3D map 10 nm" /></td>
<td><img src="image12.png" alt="3D map 10 µm" /></td>
</tr>
<tr>
<td>a, b-axis: basal directions of chitin cell</td>
<td>c-axis: longitudinal axis of molecule</td>
<td></td>
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</tbody>
</table>
Best-case (red, upper curve) and worst-case (green, lower curve) scenarios obtained with accumulative changes that maximize (red) / minimize (green) the elastic overall moduli.