Size Effects in Deformation of Materials
Smaller can be stronger!

Lecture 4

Markus J. Buehler
Behavior of different “kinds” of materials

“brittle”: Materials that experience little, if any, plastic deformation before the onset of fracture

“ductile”: Materials that experience significant plastic deformation before the onset of fracture

How to use large-scale computing in multi-scale modeling in order to develop fundamental understanding

“geometric confinement” Nanostructured materials, carbon nanotubes

“biological materials” (Proteins, DNA …)

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In the past lectures, we discussed failure and deformation of brittle and ductile bulk materials.

The effect of material size was “neglected”, as it was quietly assumed that materials are large and no boundary effects exist.

Here: Investigate the effect of size reduction on the material behavior.

Size effects typically appear due to different scaling behavior of properties.

**Examples:**
- Strain energy scales $\sim h$ ($h$ is material size) whereas the fracture surface energy is a constant, independent of material size.
- Grain size effects; Hall-Petch/inverse Hall-Petch behavior.

This results in extreme cases for either very “large” or very “small” materials: Small-scale materials often have unusual properties.
Introduction

- Many materials show significant size effects re. their mechanical behavior
- For example, in thin films, dislocation behavior changes from threading dislocations ($\sigma_Y \sim 1/h$) to parallel glide dislocations ($\sigma_Y \sim \text{const.}$) if the film thickness is reduced, along with a plateau in yield stress

**Example:** Deformation of ultra thin copper films dislocations/diffusion

```
“Large”
- Threading dislocations (glide)
  Nix, Freund, Matthews

Yield stress (MPa) vs. $1/h_f (\mu m^{-1})$

≈ $h_f = 220 \text{ nm}$

parallel glide dislocations

≈ $h_f = 220 \text{ nm}$

“Small”
- Diffusional creep
- Parallel glide dislocations

(Gao, 1999, Balk, Arzt, Dehm, 200, Buehler et al., 2003-2005)
```
Chemical complexity: Collagen, a hierarchical nanomaterial

Collagen features a hierarchical design

Nanoscale features assemble into microscopic and large-scale features

Why nanoscale features?

- Amino acids
  - 1 nm

- Tropocollagen
  - 300 nm

- Fibrils
  - 1 μm

- Fibers
  - 10 μm

Braided collagen fibers
Motivation: Biocomposites in bone with nanoscale features

Characteristic size: 10..100 nm

- What are the engineering principles of biological systems in producing tough materials out of weak constituents?
- Why is nanometer scale so important to biological composite materials?

(Gao et al., 2003, 2004) © 2005 Markus J. Buehler, CEE/MIT
A: Size effects in brittle materials
Objectives and hypothesis

- Failure mechanism of ultra small brittle single crystals as a function of material size
- Properties of adhesion systems as a function of material size: How can optimal adhesion be achieved despite presence of defects (roughness)?

Hypothesis:

Once the dimensions of materials reaches nanoscale, flaws and defects play no role in determining the strength of materials

(Gao et al., 2003)
Objectives and hypothesis

- Failure mechanism of ultra small brittle single crystals as a function of material size
- Properties of adhesion systems as a function of material size: How can optimal adhesion be achieved despite presence of defects (roughness)?

Hypothesis:

Once the dimensions of materials reaches nanoscale, flaws and defects play no role in determining the strength of materials

(Gao et al., 2003)
Two paradoxes of classical fracture theories

• Inglis (~1910): Stress infinite close to a elliptical inclusion once shape is crack-like

"Inglis paradox": Why does crack not extend, despite infinitely large stress at even small applied load?

• Resolved by Griffith (~ 1950): Thermodynamic view of fracture

\[ G = 2\gamma \]

"Griffith paradox": Fracture at small length scales? Critical applied stress for fracture infinite in small (nano-)dimensions (h=O(nm))!

Topic of this lecture

Buehler et al., MRS Proceedings, 2004 & MSMSE, 2005; Gao, Ji, Buehler, MCB, 2004
Spontaneous crack nucleation occurs when the energy released due to crack propagation of $\Delta a$ is larger than the energy necessary to create two new surfaces (Griffith).

$2\gamma \Delta a$  \hspace{1cm} Energy necessary to create two new surfaces

$\frac{\sigma^2 \xi (1-v^2)}{2E} \Delta a$  \hspace{1cm} Energy stored ahead of the crack, in strip $\Delta a$
How materials break at small scales

Theoretical considerations

\[ G = \frac{\sigma^2 \xi (1 - \nu^2)}{2E} \]

\[ 2\gamma = G \quad \text{Griffith} \]

\[ \sigma_f = \sqrt{\frac{4\gamma E}{\xi (1 - \nu^2)}} \]

\[ \xi \to \infty \quad \text{for} \quad \xi \to 0 \]

Impossible: \( \sigma_{\text{max}} = \sigma_{\text{th}} \)

Stress for spontaneous crack propagation

\[ \xi_{\text{cr}} = \frac{4\gamma E}{\sigma_{\text{th}}^2 (1 - \nu^2)} \]

Length scale \( \xi_{\text{cr}} \) at \( \sigma_{\text{th}} \) cross-over

\( \xi \). size of material

\( E \) Young’s modulus

\( \nu \) Poisson ratio, and

\( \sigma \) Stress far ahead of the crack tip

Buehler et al., MRS Proceedings, 2004 & MSMSE, 2005; Gao, Ji, Buehler, MCB, 2004

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From macro to nano...

Transition from Griffith-governed failure to maximum strength of material

- Griffith theory breaks down below a critical length scale
- Replace Griffith concept of energy release by failure at homogeneous stress
Atomistic model: Model material

- LJ potential across a weak fracture layer
- Harmonic potential with spring constant $k_0$ in the bulk (simple force field)

➢ **Advantage**: Vary $E$ and $\gamma$ independently (check scaling of critical length scale)

\[
\phi(r) = 4\varepsilon \left( \frac{\sigma}{r} \right)^{12} \left( \frac{\sigma}{r} \right)^{6}
\]

\[
\phi(r) = a_0 + \frac{1}{2} k_0 (r - r_0)^2
\]

Mineral platelet (brittle)

LJ Weak layer

harmonic
Atomistic model

Bulk (harmonic, FCC)

\[ \phi(r) = a_0 + \frac{1}{2} k_0 (r - r_0)^2 \]
\[ r_0 = 2^{1/6} \quad k_0 = 572.0 \]
\[ a \approx 1.587 \]
\[ \mu = \frac{r_0^2}{2} k_0 \quad E = \frac{8}{3 \mu} \quad \nu = \frac{1}{3} \]

(See, e.g. paper by Baskes et al. (1984)

Interface (LJ) “dispersive-glue interactions”

\[ \phi(r) = 4 \varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right) \]
\[ \varepsilon = \sigma = 1 \]

\[ \gamma = N_b \rho_A \Delta \phi \quad \sigma_{th} \approx 9.3 \]
\[ \rho_A = \frac{1}{r_0^2} \approx 0.794 \]
\[ N_b = 4 \quad \Delta \phi \approx 1 \]

Choose \( E \) and \( \gamma \) such that length scale is in a regime easily accessible to MD
Elasticity associated with harmonic potential

uniaxial loading in [100] direction with Poisson relaxation

uniaxial loading in [100] direction no Poisson relaxation

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Elastic and fracture properties

- Elastic properties of the harmonic solid (analytical estimates), and surface energy (evaluated numerically for the chosen simulation parameters) across the LJ weak interface.

- The results agree reasonably well with the numerically calculated values of the elastic properties.

<table>
<thead>
<tr>
<th>Spring constant $k_0$</th>
<th>Young’s modulus $E$</th>
<th>Poisson ratio $\nu$</th>
<th>Surface energy $\gamma$ (numerical result)</th>
</tr>
</thead>
<tbody>
<tr>
<td>572</td>
<td>960</td>
<td>0.33</td>
<td>2.33</td>
</tr>
</tbody>
</table>

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Size dependence of fracture strength

\[ \sigma_f = \sigma_{th} \]

Failure at theor. strength

Griffith-governed failure

[Equation]

\[ \sigma_f = \sqrt{\frac{4\gamma E}{h(1-\nu^2)}} \]

Atomistic simulation indicates:

- At critical **nanometer-length scale**, structures become insensitive to flaws:
  - Transition from **Griffith governed failure** to failure at **theoretical strength**, independent of presence of crack!!

(Buehler et al., MRS Proceedings, 2004; Gao, Ji, Buehler, MCB, 2004)
Stress distribution ahead of crack

(3): Max. stress independent of $\zeta$

(1): Griffith  (2): Transition  (3): Flaw tolerance
Continuum mechanics simulations

Use VIB method (A FEM method that incorporates the behavior of atomic bonds in solids)


(Baohua Ji)
Summary: Small-scale structures for strength optimization & flaw tolerance

\[ h_{cr} \propto \frac{\gamma E}{\sigma_{\text{max}}^2} \]

<table>
<thead>
<tr>
<th>( h &gt; h_{cr} )</th>
<th>( h &lt; h_{cr} )</th>
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<tbody>
<tr>
<td>Material is sensitive to flaws.</td>
<td>Material becomes insensitive to flaws.</td>
</tr>
<tr>
<td>Material fails by stress concentration at flaws.</td>
<td>There is no stress concentration at flaws. Material fails at theoretical strength.</td>
</tr>
<tr>
<td>Fracture strength is sensitive to structural size.</td>
<td>Fracture strength is insensitive to structure size.</td>
</tr>
</tbody>
</table>

(Gao et al., 2003, 2004; Gao, Ji, Buehler, MCB, 2004)
B: Size effects in adhesion systems
Adhesion at small length scales

**Experiment:** Animals have fine, hierarchical structure at the ends of their feet!!

Possible reasons…:

- Since $F \sim \gamma R$ (JKR model), increase line length of surface by **contact splitting** (Arzt *et al.*, PNAS, 2003)

- At **very small length scales**, nanometer design results in optimal adhesion strength, independent of flaws and shape—design for robustness (Gao *et al.*, PNAS, 2004)
Theoretical considerations

\[ K_I = \frac{P}{\pi a^2} \sqrt{\pi a F_1(\alpha)} \quad \frac{K_I^2}{2E^*} = \Delta \gamma \]

\[ \psi = \sqrt{\frac{\Delta \gamma E^*}{R \sigma_{th}^2}} \quad \beta = \sqrt{2/(\pi \alpha F_1^2(\alpha))} \]

\[ E^* = E/(1 - \nu^2) \]

\[ R_{cr} = \beta^2 \frac{\Delta \gamma E^*}{\sigma_{th}^2} \quad R_{cr} \sim 225\text{nm} \]

- At critical radius, spatula becomes insensitive to flaws: Transition from Griffith governed failure to failure at theoretical strength, independent of presence of flaws!!

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Continuum and atomistic model

Harmonic

\[ \phi(r) = a_0 + \frac{1}{2} k_0 (r - r_0)^2 \]

LJ

\[ \phi(r) = 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right) \]

Three-dimensional model

Cylindrical attachment device

LJ: Autumn et al. have shown dispersive interactions govern adhesion of attachment in Gecko

\[ \sigma = 2\alpha R \]

flaw due to surface roughness

rigid substrate
Stress close to detachment as a function of adhesion punch size.

Varying dimension $R$

$\sqrt{R_{cr}/R}$ has major impact on adhesion strength:
- At small scale: no stress magnification
- Smaller size leads to homogeneous stress distribution

$\sigma/\sigma_{th}$ vs $r'/(2\alpha R)$

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Vary $E$ and $\gamma$ in scaling law

$$R_{cr} = \frac{8}{\pi} \frac{E^* \Delta \gamma}{\sigma^2_{th}}$$

The ratio

$$\sqrt{\frac{R_{cr}}{R}}$$

governs adhesion strength

• Results agree with predictions by scaling law
• Variations in Young’s modulus or $\gamma$ may also lead to optimal adhesion
Adhesion strength as a function of size

\[ \frac{\sigma}{\sigma_{th}} \text{ vs. } \sqrt{\frac{\xi_{cr}}{\xi}}, \sqrt{\frac{R_{cr}}{R}} \]

- Surface adhesion
- Bulk fracture
- Griffith prediction
- Theoretical strength

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Optimal surface shape

**Single punch**

\[ z = -\psi \frac{2\sigma_{th} R}{\pi E/(1-\nu^2)} \left[ \ln\left(1 - \frac{\bar{r}}{2}\right) + \bar{r} \ln\left(1 + \frac{\bar{r}}{1-\bar{r}}\right) \right] \]

**Concept:**
Shape parameter \( \psi \)

**Periodic array of punches**

\[ z = -\psi \frac{2\sigma_{th} R}{\pi E/(1-\nu^2)} \left\{ \ln\left(1 - \frac{\bar{r}}{2}\right) + \bar{r} \ln\left(1 + \frac{\bar{r}}{1-\bar{r}}\right) \right\} \]

\[ - \sum_{n=1}^{\infty} \left[ \ln\left(\frac{(2n\lambda + \bar{r})^2 - 1}{(2n\lambda)^2 - 1}\right) + (2n\lambda + \bar{r}) \ln\left(\frac{2n\lambda + \bar{r} + 1}{2n\lambda + \bar{r} - 1}\right) - 2n\lambda \ln\left(\frac{2n\lambda + 1}{2n\lambda - 1}\right) \right] \]

\[ - \sum_{n=1}^{\infty} \left[ \ln\left(\frac{(2n\lambda - \bar{r})^2 - 1}{(2n\lambda)^2 - 1}\right) + (2n\lambda - \bar{r}) \ln\left(\frac{2n\lambda - \bar{r} + 1}{2n\lambda - \bar{r} - 1}\right) - 2n\lambda \ln\left(\frac{2n\lambda + 1}{2n\lambda - 1}\right) \right] \]

**Derivation:** Concept of superposition to negate the singular stress

**PBCs**

Periodic array of punches
The shape function defining the surface shape change as a function of the shape parameter $\psi$. For $\psi=1$, the optimal shape is reached and stress concentrations are predicted to disappear.
Creating optimal surface shape in atomistic simulation

**Strategy:** Displace atoms held rigid to achieve smooth surface shape
Stress distribution at varying shape

\[ \psi = 1: \text{Optimal shape} \]
Robustness of adhesion

- By finding an optimal surface shape, the singular stress field vanishes.
- However, we find that this strategy does not lead to robust adhesion systems.
- For robustness, shape reduction is a more optimal way since it leads to (i) vanishing stress concentrations, and (ii) tolerance with respect to surface shape changes.
We used a systematic atomistic-continuum approach to investigate brittle fracture and adhesion at ultra small scales.

We find that Griffith’s theory breaks down below a critical length scale.

Nanoscale dimensions allow developing extremely strong materials and strong attachment systems: **Nano is robust**

**Small nano-substructures lead to robust, flaw-tolerant materials. In some cases, Nature may use this principle to build strong structural materials.**

Unlike purely continuum mechanics methods, MD simulations can intrinsically handle stress concentrations (singularities) well and provide accurate descriptions of bond breaking.

Atomistic based modeling will play a significant role in the future in the area of modeling nano-mechanical phenomena and linking to continuum mechanical theories as exemplified here.

Results currently under submission to MSMSE
C: Hierarchical protein-based materials
• Biological materials show enormous complexity

• Represents the frontier of research to sustain and evolve human life

Example: Mutations

Building blocks (e.g. amino acids, describe with QM)

Structure/Function
(Elasticity Fracture properties)

Primary structure

Quaternary structure

Secondary, tertiary structure

Scale-specific versus interaction properties

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Flaw-tolerant protein crystals

α-Conotoxin Pnib From Conus Pennaceus
Crystallized and deposited in PDB by Hu, S.-H. Martin, J.L.
Involved in pathogenesis (mechanism by which a certain etiological factor causes disease)

Space group P 2₁ 2₁ 2₁ (orthorombic)
4 proteins per unit cell

Goals
- Develop fundamental understanding of the elastic, plastic and fracture properties of protein-based materials
- Find analogies and differences to “classical” engineering materials like metals, semiconductors
Hyperelasticity of protein crystals
Model system 1AKG

• Perfect crystal shows strong nonlinear behavior: softening at large strains
• Crystals break at large strain (negative tangent slope), anisotropy

Fracture surface energy for different crystal planes
• (010) surface: ≈ 0.205 N/m
• (100) surface: ≈ 0.257 N/m
• (001) surface: ≈ 0.343 N/m

Griffith analysis
Elasticity of protein crystals: Model system 1AKG

- Tangent modulus about 30 GPa
Relative displacement of $C_\alpha$ during deformation

Hotspots of deformation (red)

8 proteins/unit cell

Symmetry

Length scale of a few nanometers

Oscillations of stress

• Find: Some domains participate strongly, others little in deformation

Strain in x-direction
Ca. 1.75 % (versus 0%)
(Protein shown: Lysozyme)

Each point represents a $C_\alpha$-atom (meso-view)
Involves large-scale studies of cracking of protein crystals (10E5..10E6 atoms); AMBER force field, use NAMD

Strain rate: 0.25% strain per 5,000 integration steps (energy minimization scheme)

Objectives:
- Mechanism of deformation in protein crystals
- Compare to Griffith theory

\[ \varepsilon_f = \sqrt{\frac{4\gamma}{E\xi(1-\nu^2)}} \]

\[ \varepsilon_{f\text{ theory}} \approx 5\% \]
Crack dynamics in protein crystals

Comparison fracture initiation theory-MD simulation

\[ \varepsilon_{f}^{MD} \approx 12\% \quad \varepsilon_{f}^{theory} \approx 5\% \]

Initiation at crack tips

Coalescence of cracks

Local refolding due to cracking

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Nano-protein crystals can be flaw tolerant

\[ h_{cr} \propto \frac{\gamma E}{\sigma_{\text{max}}^2} \approx 13 \text{ nm} \]

Length scale parameter for flaw tolerance (Gao et al., 2003)

Cell size \( \approx 2.9 \text{ nm} \)
Thus: \( \sim 4 \) layers thickness

- Design a protein crystal such that the critical length scale is maximized
- Possible objectives:
  - Make \( \sigma_{\text{max}} \) small
  - Make \( \gamma \) and \( E \) large
- Possible approaches: AA mutations, structural change, chemistry…..
Nano-protein crystals can be flaw tolerant

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Cell size \( \approx 2.9 \text{ nm} \)
Thus: \( \sim 4 \) layers thickness

\( 1\text{AKG} \)
Synthesis of protein-based materials: An alternative to conventional polymers

- Translating nature’s structural concepts into engineered materials requires high level of control of macromolecular architecture, beyond conventional polymerization process.

- Approach
  - Use protein engineering to genetically encode protein-based materials with desired features.
  - Use biological systems for production of materials.
Effect of double point mutations on elasticity of protein crystals*

- Change in maximum strain (ca. ±30%)
- Change in maximum stress (ca. ±25%)
- Change in shape of stress-strain behavior
- Impact primarily on hyperelasticity of protein crystal (preserve small-strain elasticity)

Possible explanation: Replacing polar groups by non-polar residues reduces electrostatic interaction: Thus “weaker” crystal

*α-Conotoxin PnIB From Conus Pennaceus

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Protein engineering to design flaw-tolerant crystals

- Find: Mutations can be used to decrease the theoretical strength
- Since

\[ h_{cr} \sim \frac{\gamma E}{\sigma_{\text{max}}^2} \]

this provides a possible strategy to design flaw-tolerant materials

- For example, for the mutation \( \text{SER} \rightarrow \text{ALA} \),

\[ h_{cr} = \frac{\gamma E}{\sigma_{\text{max}}^2} \approx 208 \, \text{nm} \]

- This represents a flaw-tolerant \( \mu \text{m} \) crystal
Upon nucleation at a critical load, we observe rapid propagation of the crack with cleavage along the initial crack plane; protein crystal starts to fail at the tip of the existing flaw.

Griffith theory under predicts critical load for nucleation: Possibly due to the fact that the crystal size is close to the critical length scale.

Demonstrated that we can model cracking of complex biological materials (chemical complexity and hierarchical design) using large-scale molecular dynamics simulations.

Exemplified coupling of materials science-biology using large-scale computing: Atomistic modeling can be a valuable “computational microscope” to understand the deformation of biopolymers such as protein crystals.

Future research: Model larger systems w/ crack, different crack orientations, effect of mutations on crack dynamics, complex systems.
D: Nanocrystalline materials
Fundamental length scales in nanocrystalline ductile materials

- Similar considerations as for brittle materials and adhesion systems apply also to ductile materials.
- In particular, the deformation mechanics of nanocrystalline materials has received significant attention over the past decade.

- Strengthening at small grain size (Hall-Petch effect).
- Weakening at even smaller grain sizes after a peak.

Figure by MIT OCW.
Hall-Petch Behavior

- It has been observed that the strength of polycrystalline materials increases if the grain size decreases.

- The Hall-Petch model explains this by considering a dislocation locking mechanism:

  ![Dislocation locking mechanism diagram](image)

  Nucleate second source in other grain (right)

  Physical picture: Higher external stress necessary to lead to large dislocation density in pileup

  \[ \sigma_Y \sim \frac{1}{\sqrt{d}} \]

See, e.g. Courtney, Mechanical Behavior of Materials
The strongest size: *Nano is strong!*

Different mechanisms have been proposed at nanoscale, including:

- GB diffusion (even at low temperatures) – Wolf *et al.*
- GB sliding – Schiotz *et al.*
- GBs as sources for dislocations – van Swygenhoven, stable SF energy / unstable SF energy (shielding)

Yamakov *et al.*, 2003, Schiotz *et al.*, 2003

Fundamental length scales in nanocrystalline ductile materials

From: E. Arzt

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The strongest size

- Strongest size determined by grain size which becomes comparable to separation of two partial dislocations
  \[ r = \frac{r_0(\gamma)}{1 - \sigma/\sigma_\infty(\gamma)} \]
  (splitting distance of two partial dislocations)

- This length scale \( r \) competes with \( d \) (grain size)

Complete extended dislocations (Region I)
Partial dislocations (Region II),
No dislocations at all (Region III)

The map is expressed in reduced units of stress \( (\sigma/\sigma_\infty) \) and inverse grain size \( (r_0/d) \). The parameters \( \sigma_\infty \) and \( r_0 \) are functions of the stacking-fault energy and the elastic properties of the material.

D. Wolf et al., Nature Materials, 2004

Figure by MIT OCW. © 2005 Markus J. Buehler, CEE/MIT
Steady-state creep under uniform tensile stress: Nanoscale

V. Yamakov et al., *Acta mater.* 50, 61, 2002

Figure by MIT OCW.

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Grain size dependence

Large grain size ($d >> d$): creep rate $\sim d^{-3}$ (Coble!)
Small grain size: ($d \approx d$): creep rate $\sim d^{-2}$ (Nabarro-Herring!)

$$\dot{\varepsilon} = A \frac{\sigma \Omega_D}{k_B T} \frac{\delta D_{GB}}{d^3}$$
Deformation in nanocrystalline materials

- Review articles:

  NATURE MATERIALS 3 (1): 43-47 JAN 2004

  Van Swygenhoven H, Derlet PM, Froseth AG
  Stacking fault energies and slip in nanocrystalline metals
  NATURE MATERIALS 3 (6): 399-403 JUN 2004

- Controversial debate about the mechanisms at ultra small scales
  - Wolf et al.: Coble creep as deformation mechanism
  - Van Swygenhoven and Schiotz suggest dislocation mechanisms to be active even to small grain sizes (even full dislocations) and grain boundary sliding or short range atomic rearrangements in the grain boundary
Nanocrystalline copper with twin lamella

3D view

Copper nano-crystal with twin lamella grain boundary

Synthesized in experiment by Lu et al., 2003 (Science)
Nanocrystalline copper with twin lamella

- Simulation results of nanostructured material with twin lamella substructure under uniaxial loading for two different twin lamella thicknesses.
- Subplot (a) shows the results for thick twin lamella ($d_T \sim 15 \text{ nm} > d$) and subplot (b) for thinner twin lamella ($d_T \sim 2.5 \text{ nm} < d$). Motion of dislocations is effectively hindered at twin grain boundaries in both cases.
Simulation results of nanostructured material with twin lamella substructure under uniaxial loading for two different twin lamella thicknesses, all high-energy grain boundaries.

Subplot (a) shows the potential energy field after uniaxial loading was applied. Interesting regions are highlighted by a circle.

Unlike before dislocations are now nucleated at all grain boundaries. The nucleation of dislocations is now governed by the resolved shear stress on different glide planes. Subplot (b) highlights an interesting region in the right half where i. cross-slip, ii. stacking fault planes generated by motion of partial dislocations and iii. intersection of stacking fault planes left by dislocations is observed.
E: The mechanics of ultra thin metal films
Example: Ultra thin copper films

- Biaxial loading by thermal mismatch of film and substrate material: High stresses cause severe problems during operation of the device

- Ultra thin, submicron copper films become critically important in next generation integrated circuits (see, e.g. *Scientific American*, April 2004), MEMS/NEMS

Polycrystalline thin metal film of copper grains (111) aligned

Courtesy Dirk Weiss, MIT
Introduction

- Many materials show significant size effects re. their mechanical behavior
- For example, in thin films, dislocation behavior changes from threading dislocations ($\sigma_Y \sim 1/h$) to parallel glide dislocations ($\sigma_Y \sim \text{const.}$) if the film thickness is reduced, along with a plateau in yield stress

**Example:** Deformation of ultra thin copper films dislocations/diffusion

"Large"

- Threading dislocations (glide)

"Small"

- Diffusional creep
- Parallel glide dislocations

($\sigma_Y \sim \text{const.}$) if the film thickness is reduced, along with a plateau in yield stress.

(Buehler et al., 2003-2005)
Continuum model: Constrained diffusional creep


Step 1: To relax stress, surface atoms diffuse into the grain boundary

Step 2: Form a pileup of climb dislocations

Crack-like diffusion wedge

Step 3: Emission of parallel glide dislocations at the root of the grain boundary

\[
\frac{\partial \sigma_{gb}(z, t)}{\partial t} = \frac{ED_{gb}\delta_{gb}\Omega}{4\pi(1 - \nu^2)kT} \int_0^{h_f} S(z, \zeta) \frac{\partial^3 \sigma_{gb}(\zeta, t)}{\partial \zeta^3} d\zeta
\]

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Continuum model: Constrained diffusional creep


**Step 1:** To relax stress, surface atoms diffuse into the grain boundary

**Step 2:** Form a pileup of climb dislocations

**Crack-like diffusion wedge**

**Step 3:** Emission of parallel glide dislocations at the root of the grain boundary

**Goal:** Develop atomistic modeling of these mechanisms to gain further insight into mechanisms
Thermal cycling experiments

- Compare continuum model with threshold stress to the experimental data of thermal cycling (Buehler et al.)

The film thickness is

\[ h_f = 100 \text{ nm} \]

- Measure stress in thin copper film during thermal cycling
Atomistic model

• Copper atoms deposited on a rigid substrate (atoms constrained)
  • Use Mishin’s EAM potential for copper
  • 80%..90% of melting temperature to allow modeling of diffusion with MD at ns timescale (Wolf et al., 2001)+ construct high energy GB

Loading applied by displacing the outermost rows of atoms

(Buehler et al., MSMSE, 2004)
- We find glassy, liquid-like GB structure at elevated temperatures
- This allows modeling of GB diffusion with molecular dynamics (limited to nanosecond time scale)

(Buehler, 2004)
Formation of the diffusion wedge

Climb of edge dislocations in the GB

Formation of crack-like field can be correlated with mass transport along GB (towards substrate):

As material is transported into the GB, the field becomes increasingly crack-like

(Buehler et al., JMPS, 2003)
Nucleation of PG dislocations

Atomistic simulation of grain boundary diffusion and nucleation of parallel glide dislocations

(Buehler et al., MSME, 2004)
Nucleation of PG dislocations: Diffusion wedge versus crack

Diffusion wedge

Crack

Dislocation dipole

Incipient dislocation

Annihilation

Crack blunting

Repulsion

Nucleation

(Buehler et al., JMPS, 2003)

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Critical SIF cracks versus diffusion wedge

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$h_f$ (nm)</th>
<th>$K^{PG}$ (MPa $\times$ m$^s$)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Crack</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>27.2</td>
<td>4.95</td>
</tr>
<tr>
<td></td>
<td>Diffusion wedge</td>
<td></td>
</tr>
<tr>
<td>1150</td>
<td>27.2</td>
<td>11.91</td>
</tr>
<tr>
<td>1250</td>
<td>27.2</td>
<td>11.35</td>
</tr>
<tr>
<td>1250</td>
<td>34.2</td>
<td>11.23</td>
</tr>
</tbody>
</table>

- Concept of SIF is a reasonable concept to link atomistic results to continuum description
- Observe: Critical SIF for diffusion wedge is about twice as large as in the case of a crack

Rice-Thomson model

\[
K_{cr}^{PG} = \frac{E(2\pi b_x)^s}{8\pi(1 - \nu^2)}
\]

\[
K_{dw}^{PG} = \frac{E(2\pi b_x)^s}{4\pi(1 - \nu^2)}
\]

Explains ratio of 2

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Build atomistic model of a triple junction with different types of GBs: High-energy (disordered)-**A** and low-energy (array of dislocations)-**B**
Extension to triple junction model

Upon application of biaxial tensile load, observe nucleation of PG dislocations
Misfit GB dislocations to serve as nucleation points for PG dislocations

Schematic

- Deformation twinning by repeated nucleation of partial dislocations.
- Repeated slip of partial dislocations leads to generation of a twin grain boundary.
Formation of jogs: Dislocation reactions

- Dislocation junction and bowing of dislocations by jog dragging.
- A trail of point defects is produced at the jog in the leading dislocation, which is then repaired by the following partial dislocation.
Constrained grain boundary diffusion in polycrystalline models: 3D model

Model:
Polycrystalline sample with low- and high energy grain boundaries (grains rotated around z axis, > 2,000,000 atoms, EAM potential for copper-Mishin et al., ITAP-IMD code)

• Temperature: About 90% of melting temperature (similar as Yamakov et al.)
Constrained grain boundary diffusion in polycrystalline models

Theoretical predictions

- Diffusional creep strong along high-energy GBs (Wolf et al.), should lead to stress relaxation and development of crack-like stress field, leading to PG dislocations according to Gao (1999)

- Along low-energy GBs, threading dislocations should prevail (since no GB traction relaxation possible by diffusion)
Main results

- Diffusion wedges develop preferably at high-energy GBs (fast diffusion paths)
- Diffusion wedges lead to PG dislocations (black lines), otherwise: Threading dislocations.
- No threading dislocations in grain surrounded by high-energy GBs

High-energy GBs: Liquid-like structure – fast diffusion paths
Formation of dislocation networks

- The plot shows an analysis of the complex dislocation network of partial parallel glide dislocations that develops inside the grains.
- All defects besides stacking fault planes are shown in this plot.
Competing mechanisms: Slip versus diffusion

DDD modeling (mesoscale)

- Creep mechanism yields constant (or slowly decreasing) flow stress
- Inclined slip yields linear strengthening with inverse film thickness
- Deformation mechanisms interact (inclined slip shuts down creep mechanism)

Figure by MIT OCW.

Deformation map of submicron copper films

Deformation mechanism map *

A-Threading dislocations (Nix)—”classical”

B-Constrained diffusional creep with parallel glide dislocations

C-Diffusional creep

D-No stress relaxation mechanism

➤ Conclusion: In ultra thin copper films without capping layer, constrained grain boundary diffusion and parallel glide dislocations play a governing role

* Results based on MD modeling, experiments, continuum theory and mesoscopic modeling (joint experiment-theory-simulation effort with Prof. Arzt group at MPI-MF)
Deformation map of submicron copper films

- Yield stress
  - ≈ 0.64 GPa
  - ≈ 0.04 GPa

- Inverse film thickness \(1/h_f\)
  - ≈ 1/400 nm
  - ≈ 1/25 nm

- Threading dislocations
- Constrained grain boundary diffusion and parallel glide dislocations
The preliminary study on nanostructured materials reported here showed that an intergranular nano-substructure constituted by twin lamellas could play an important role in effectively strengthening materials.

Since twin grain boundaries are relatively poor diffusion paths (since they are low-energy grain boundaries), such materials could potentially be successfully employed at elevated temperatures where “usual” materials with ultra-fine grains can not be utilized since creep becomes the dominant deformation mechanism.

The study supports the notion that geometric confinement has strong impact on the deformation, and could potentially be utilized to create materials with superior mechanical properties.
F: Conclusion
Overall conclusion

- Size effects are abundant in many important materials phenomena, in particular in modern new developments of nano- and bio-technologies.

- In particular, recent research suggests that size effects are abundant in many biological materials.

- Size effects have not been fully exploited for engineering applications, and thus constitute an area of huge scientific and technological possibilities for the coming years.
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