Nanomechanics of hierarchical biological materials (cont’d)

Size Effects in Deformation of Materials

Lecture 8

Markus J. Buehler
Outline

1. **Introduction to Mechanics of Materials**
   Basic concepts of mechanics, stress and strain, deformation, strength and fracture
   Monday Jan 8, 09-10:30am

2. **Introduction to Classical Molecular Dynamics**
   Introduction into the molecular dynamics simulation; numerical techniques
   Tuesday Jan 9, 09-10:30am

3. **Mechanics of Ductile Materials**
   Dislocations; crystal structures; deformation of metals
   Tuesday Jan 16, 09-10:30am

4. **The Cauchy-Born rule**
   Calculation of elastic properties of atomic lattices
   Friday Jan 19, 09-10:30am

5. **Dynamic Fracture of Brittle Materials**
   Nonlinear elasticity in dynamic fracture, geometric confinement, interfaces
   Wednesday Jan 17, 09-10:30am

6. **Mechanics of biological materials**
   Monday Jan. 22, 09-10:30am

7. **Introduction to The Problem Set**
   Atomistic modeling of fracture of a nanocrystal of copper.
   Wednesday Jan 22, 09-10:30am

8. **Size Effects in Deformation of Materials**
   Size effects in deformation of materials: Is smaller stronger?
   Friday Jan 26, 09-10:30am
Typical simulation procedure

1. Pre-processing  
   (define geometry, build crystal etc.)
2. Energy relaxation  
   (minimization)
3. Annealing (equilibration at specific temperature)
4. “Actual” calculation; e.g. apply loading to crack
5. Analysis

Real challenge: Questions to ask and what to learn

\[ F = ma \]
Common empirical force fields

**Class I (experiment derived, simple form)**
- CHARMM
- CHARMm (Accelrys)
- AMBER
- OPLS/AMBER/Schrödinger
- ECEPP (free energy force field)
- GROMOS

Harmonic terms; Derived from vibrational spectroscopy, gas-phase molecular structures
Very system-specific

**Class II (more complex, derived from QM)**
- CFF95 (Biosym/Accelrys)
- MM3
- MMFF94 (CHARMM, Macromodel…)
- UFF, DREIDING

Include anharmonic terms
Derived from QM, more general

http://www.ch.embnet.org/MD_tutorial/pages/MD.Part2.html
http://www.pharmacy.umaryland.edu/faculty/amackere/force_fields.htm
http://amber.scripps.edu/

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Hydrogen bonding

e.g. between O and H in H₂O
Between N and O in proteins…
Unfolding of alpha helix structure

Figure by MIT OCW. After Ackbarow and Buehler, 2007.
Unfolding of beta sheet

Titin I27 domain: Very resistant to unfolding due to parallel H-bonded strands

Figure by MIT OCW.

Keten and Buehler, 2007
Stretching experiment: Tropocollagen molecule

Figure by MIT OCW. After Buehler and Wong.
Fracture at ultra small scales
Size effects
Nano-scale fracture

- Failure mechanism of ultra small brittle single crystals as a function of material size
- Properties of adhesion systems as a function of material size: Is Griffith’s model for crack nucleation still valid at nanoscale?

"Nano"

Griffith

\[ \sigma_{\text{Griffith}} \]

\[ h \geq h_{\text{crit}} \]

\[ \sigma_{\text{Griffith}} \]

\[ h \approx h_{\text{crit}} \]

Stress
Review: Two paradoxons 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

  \[ G = 2\gamma \]

  \[ \sigma_{yy} = \sigma_0^* \left(1 + 2\sqrt{\frac{a}{\rho}}\right) \]

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

“Considered here”

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

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Thin strip geometry

Change in potential energy: Create a “relaxed” element from a “strained” element, per unit crack advance

\[ W_P = W_P(\sigma, a, \ldots) \]

Figure by MIT OCW.
Thin strip geometry

Strain energy density:

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

\[ \phi_p^{(1)} = \frac{1}{2} \sigma \varepsilon = \frac{1}{2} \frac{\sigma^2}{E / (1 - \nu^2)} \]

Strain energy:

\[ V = \xi \tilde{a} B \]

\[ W_p^{(1)} = \frac{\sigma^2 (1 - \nu^2)}{2E} \xi \tilde{a} B \]

(plane strain)
Thin strip geometry

\[ W_P^{(2)} = 0 \]

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

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

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

Figure by MIT OCW.
Fracture of thin strip geometry
Theoretical considerations

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

\[ 2\gamma = G \] Griffith

- \( E \) Young’s modulus
- \( \nu \) Poisson ratio, and
- \( \sigma \) Stress far ahead of the crack tip

\( \xi \) size of material

Figure by MIT OCW.


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Fracture of thin strip geometry
Theoretical considerations

Stress for spontaneous crack propagation

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

\( \sigma \to \infty \) for \( \xi \to 0 \)  Impossible: \( \sigma_{\text{max}}=\sigma_{\text{th}} \)

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

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

\( \xi \). size of material

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

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Breakdown of Griffith at ultra small scales

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

**Bulk (harmonic, FCC)**

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

\[ r_0 = 2^{1/6} \quad k_0 = 572.0 \]

\[ a \approx 1.587 \]

\[ \mu = \frac{r_0^2}{2} k_0 \quad E = 8 / 3 \mu \quad \nu = 1 / 3 \]

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

**Interface (LJ) “dispersive-glue interactions”**

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

\[ \varepsilon = \sigma = 1 \]

\[ \gamma = N_b \rho_A \Delta \phi \]

\[ \sigma_{th} \approx 9.3 \quad \text{“repulsion”} \]

\[ \rho_A = 1 / r_0^2 \approx 0.794 \]

\[ N_b = 4 \quad \Delta \phi \approx 1 \]

Forces by \( d\phi/dr \)

Choose \( E \) and \( \gamma \) such that length scale is in a regime easily accessible to MD
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): Maximum Stress Independent of $\xi$

(1): Griffith  (2): Transition  (3): Flaw tolerance

Figure by MIT OCW.
Summary: Small-scale structures for strength optimization & flaw tolerance

Fracture strength is insensitive to structure size. Fracture strength is sensitive to structural size. There is no stress concentration at flaws. Material fails at theoretical strength. Material becomes insensitive to flaws. Fracture strength is insensitive to structural size.

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

<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 structural size.</td>
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(Gao et al., 2004; Gao, Ji, Buehler, MCB, 2004)
Can this concept explain the design of biocomposites in bone?

Characteristic size: 10..100 nm

Estimate for biominerals:

\[ \sigma_{\text{max}} \approx \frac{E}{30}, \quad \nu \approx 0.25, \quad E = 100 \text{ GPa}, \quad \gamma = 1 \text{J/m}^2 \]

\[ \Psi^* \approx 0.022 \quad h_{cr} \approx 30 \text{ nm} \]

(Gao et al., 2003, 2004)
Adhesion of Geckos

Autumn et al., PNAS, 2002

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Adhesion at small length scales

- Schematic of the model used for studies of adhesion: The model represents a cylindrical Gecko spatula with radius attached to a rigid substrate.

- A circumferential crack represents flaws for example resulting from surface roughness. The parameter denotes the dimension of the crack.

Strategies to increase adhesion strength

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

- At very small length scales, nanometer design results in optimal adhesion strength, independent of flaws and shape (Gao et al., 2004)

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(S. Gorb)
Equivalence of adhesion and fracture problem

Similar:
Cracks in homogeneous material
Equivalence of adhesion and fracture problem

\[ \sigma = \pi \frac{R_{cr}}{2E'} \]

Energy release rate

\[ K_I = \sqrt{\frac{\pi}{8}} R_{cr} \sigma^2 \]

\[ G = \frac{K_I^2}{E'} = \frac{\pi}{8} \frac{R_{cr}}{E'} \sigma^2 \]

\[ G = 2\gamma = \Delta\gamma \]

Adhesion energy

Figure by MIT OCW.

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Theoretical considerations
Adhesion problem as fracture problem

Function (tabulated)

\[ K_I = \frac{P}{\pi a^2} \sqrt{\pi a F_1(\alpha)} \]
\[ \frac{K_I^2}{2E^*} = \Delta \gamma \]
\[ \beta = \sqrt{2/(\pi a F_1^2(\alpha))} \]
\[ E^* = \frac{E}{1 - v^2} \]

\[ R_{cr} = \beta^2 \frac{\Delta \gamma E^*}{\sigma_{th}^2} \]

\[ R_{cr} \sim 225nm \]

Typical parameters for Gecko spatula

Figure by MIT OCW.
Continuum and atomistic model

Three-dimensional model

Cylindrical attachment device

Harmonic

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

LJ

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

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

Figure by MIT OCW.
Stress close to detachment as a function of adhesion punch size

Smaller size leads to homogeneous stress distribution

\[ \sqrt{\frac{R_{cr}}{R}} \]

Has major impact on adhesion strength:
At small scale no stress magnification

Figure removed due to copyright restrictions.
Vary $E$ and $\gamma$ in scaling law

\[ R_{cr} = \frac{8 E^* \Delta \gamma}{\pi \sigma_{th}^2} \]

The ratio

\[ \sqrt{R_{cr} / R} \]

governs adhesion strength

- Results agree with predictions by scaling law
- Variations in Young’s modulus or $\gamma$ may also lead to optimal adhesion

Figure removed due to copyright restrictions.
Adhesion strength as a function of size
Optimal surface shape

Single punch

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

Concept: Shape parameter \( \psi \)

Periodic array of punches

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

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

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

Derivation: Concept of superposition to negate the singular stress

PBCs

Images removed due to copyright restrictions.
Optimal shape predicted by continuum theory & shape parameter $\psi$

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.

Figure removed due to copyright restrictions.
Creating optimal surface shape in atomistic simulation

**Strategy:** Displace atoms held rigid to achieve smooth surface shape

Figure by MIT OCW.

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Stress distribution at varying shape

ψ=1: Optimal shape

Figure removed due to copyright restrictions.
• 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.

Figure removed due to copyright restrictions.
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.
Chemical complexity: Modeling chemical reactions
Conventional molecular models

- **Empirical potentials**: Treatment of large molecular systems to capture inhomogeneities at nanoscale; >>10,000 atoms

**Dilemma**: Many empirical potentials can not describe chemistry accurately (bond breaking, formation, …)

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Illustration of reaction: ethane to ethylene.

**Nonreactive models**: Require *a priori* knowledge of chemical state of atoms + connectivity: **Severely limits solution space**
Reactive force field: Concept

**Nonreactive FF:**

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

"Harmonic spring"

- \( r_0 \): EQ distance between atoms
- \( k \): Spring constant

Constant valency (available bonds)

**Reactive FF:**

\[ \phi = \frac{1}{2} k (BO)(r - r_0 (BO))^2 \]

\[ BO = f(r) \]

Bond properties (bond stiffness \( k \), EQ distance \( r_0 \)) are made dependent on bond order (BO)

BO is function of bond distance (Pauling): Theoretical link to quantum chemistry
Reactive versus non-reactive potential

**Difference between reactive and nonreactive model:** Reactive model capable of describing energetics of small and large deviation from equilibrium (key during instabilities, chemical reactions..)
ReaxFF: Formulation

\[ E_{\text{system}} = E_{\text{bond}} + E_{\text{vdWaals}} + E_{\text{Coulomb}} + E_{\text{val,angle}} + E_{\text{tors}} + E_{\text{over}} + E_{\text{under}} \]

- A bond length/bond order relationship is used to obtain smooth transition (Pauling) from non-bonded to single, double, and triple bonded systems.
- All connectivity-dependent interactions (i.e. valence and torsion angles) are made bond-order dependent: Ensures that their energy contributions disappear upon bond dissociation.
- Feature non-bonded interactions (van der Waals, Coulomb): Shielded
- ReaxFF uses a geometry-dependent charge calculation scheme (similar to QEq) that accounts for polarization effects.
- Many parameters in the formulation have physical meaning.
Charge equilibration

Charges in ReaxFF are not fixed, but can flow, depending on local environment:
- Assign one electronegativity and hardness to each element; optimize these parameters against QM-charge distributions
- Use system geometry in solving electronegativity equilibration equations in every iteration

Images removed due to copyright restrictions.
Molecular models with each atom's charge labeled, comparing ReaxFF-calculated charges with actual.
ReaxFF is highly transferable model

Published ReaxFF force fields for:
- Nitramines/RDX/TATP (Strachan, van Duin, Chakraborty, Dasupta and Goddard, PRL 2003, 91, 09301; Strachan, van Duin, Kober and Goddard, JCP 2005,122,054502; Han, Strachan, van Duin and Goddard, in preparation; van Duin, Dubnikova, Zeiri, Kosloff and Goddard, JACS 2005, 127, 11053)
- Al/Al2O3 (Zhang, Cagin, van Duin, Goddard, Qi and Hector, PRB 2004, 69,045423)
- Ni/Cu/Co/C (Nielson, van Duin, Oxgaard, Deng and Goddard, JPC-A 2005, 109, 493)
- Pt/PtH (Ludwig, Vlachos, van Duin and Goddard, JPC-B 2006)
- Mg/MgH (Cheung, Deng, van Duin and Goddard, JPC-A 2005, 109, 851)
- BN-nanotubes (Han, Kang, Lee, van Duin and Goddard, JCP 2005, 123,114703; Han, Kang, Lee, van Duin and Goddard, JCP 2005, 123,114704)
- Li/LiC (Han, van Duin and Goddard, JPC-A 2005, 109, 4575)
How is the ReaxFF model developed?

**Idea:** Use concept of handshaking or overlap: Calculate set of properties with QM and ensure that ReaxFF reproduces these properties.
Computational expense

Image removed due to copyright restrictions.
Graph showing that ReaxFF is 1,000,000 times faster than QM (DFT).
Concurrent multi-scale simulations

Concurrent integration of various scales and paradigms

- Concurrent FE-atomistic-ReaxFF scheme in a crack problem (crack tip treated by ReaxFF) and an interface problem (interface treated by ReaxFF).
- Highlighted transition regions as handshake domains between different scale and methods.

M.J. Buehler, 2006, unpublished
Example for potential coupling:
Concept of mixed Hamiltonian ("handshake")

- Developed scheme to couple different codes with each other based on weights describing the amount of force and energy contribution of different force engines: Works well for certain force fields

\[ \sum_{i=0 \ldots N} w_i = 1 \]

\[ \vec{F}_j = \sum_{i=0 \ldots N} \vec{F}_{j,i} w_i \]

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Oxidation of a metal (Al) surface

ReaxFF
EAM

Reactive region expands during simulation
Based on determination of reaction front

M.J. Buehler, 2006, unpublished
Oxidation of a metal (Al) surface

• Examples demonstrates the concept of the moving boundary between different computational engines

• Boundary location determined by position of oxygen atoms: Automatic update

M.J. Buehler, 2006, unpublished
Metal/metal oxide systems

Al/Al-O system

Ni/Ni-O system

M.J. Buehler, 2006, unpublished
Dynamic fracture of silicon: Hybrid multi-paradigm modeling of crack initiation, propagation and fracture instabilities
Handshaking: Application to fracture

- We consider a crack in a single silicon crystal under remote mode I loading.
- We use periodic boundary conditions in the z direction corresponding to a plane strain case.

- The smallest system contains 13,000 atoms and the largest system over 110,000 atoms.
- In the largest system, $L_x \approx 550 \, \text{Å}$ and $L_y \approx 910 \, \text{Å}$.
- The number of reactive atoms varies between 500 and 3,000.
- Calculation of forces and energies in the reactive region is the most expensive part.


Reactive versus non-reactive potential

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(110 crack surface)

• Crack propagation with a pure Tersoff potential (left) and the hybrid ReaxFF-Tersoff scheme (right) along the [110] direction (energy minimization scheme).
• The snapshots are both taken with the same loading applied and after the same number of minimization steps. The systems contain 28,000 atoms and $L_x \approx 270$ Å and $L_y \approx 460$ Å.

To model cracking in Silicon more efficiently, we developed a multi-paradigm scheme that combines the Tersoff potential and ReaxFF.

The ReaxFF region is moving with the crack tip (region determined based on local atomic strain).

**New hybrid scheme within CMDF**

Reactive region is moving with crack tip

(110) crack surface, 10 % strain

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*CMDF reproduces experimental results (e.g. Cramer, Wanner, Gumbsch, 2000)*
Crack orientation dependence

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Crack Speed as a function of Loading

Image removed due to copyright restrictions.
Graph illustrating jump in crack speed at critical strain.
Comparison: Experimental results

Image removed due to copyright restrictions.


SW/EDIP can not reproduce this phenomenon

Direct comparison with experiment

SW/EDIP can not reproduce this phenomenon, CMDF can!

Crack Speed vs. Loading (111)

- ReaxFF and Tersoff potentials
- Hauch et al. (experimental)
- Stillinger Weber
- EDIP force field

Figure by MIT OCW.

Tang, Buehler et al., 2006
Atomistic mechanisms at onset of fracture

Initial crack structure

Breaking of first 6-membered ring

bond that breaks first
Atomistic mechanisms at onset of fracture: Formation of 5-7 rings

Formation of 7-5-ring combination

Also observed in TB calculations by Gabor Csanyi (Cambridge Univ.)

Rupture occurs ahead of 7-membered ring ("micro-crack")
Atomistic mechanisms at onset of fracture

Crack propagation (creates smooth surface)

While crack propagates, formation of another 7-5 ring combination
Atomistic mechanisms at onset of fracture

5-7 ring combination leads to change in crack direction, creating a slight surface step

Instability sets in at ~66% of Rayleigh wave speed (assume $c_R \approx 4.5$ km/sec)

Close to experimental observation

Onset of instability

Time (seconds)
Atomistic mechanisms at onset of fracture
Oxidation versus brittle fracture

- Crack dynamics in silicon without (subplots (a) and (c)) and with oxygen molecules present (subplots (b) and (d))

- Subplots (a) and (b) show the results for 5 percent applied strain, whereas subplots (c) and (d) show the results for 10 percent applied strain.

- The systems contain 13,000 atoms and $L_x \approx 160 \text{ Å}$ and $L_y \approx 310 \text{ Å}$.


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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

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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:

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
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
Deformation in nanocrystalline materials

- **Review articles:**
  
  Yamakov V, **Wolf D**, Phillpot SR, et al.  
  Deformation-mechanism map for nanocrystalline metals by molecular-dynamics simulation  
  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