From nano to macro: Introduction to atomistic modeling techniques

IAP 2006

Size Effects in Deformation of Materials

Smaller can be stronger!

Lecture 4

Department of
Civil & Environmental Engineering
Massachusetts Institute of Technology

Markus J. Buehler

Room 1-272

Email: mbuehler@MIT.EDU

Behavior of different “kinds” of materials

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

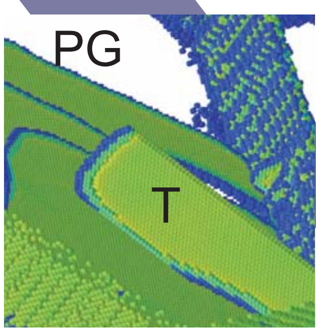
(Buehler *et al.*, *Nature*, 2003, Buehler and Gao, Nature 2006)

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

(Buehler *et al.*, *CMAME*, 2004)

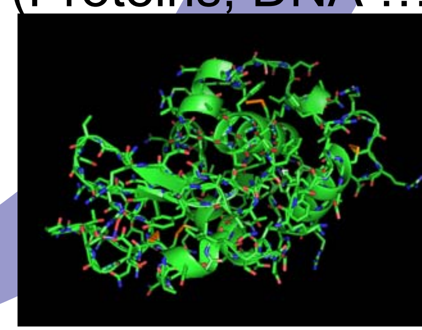
How to use large-scale computing in multi-scale modeling in order to develop fundamental understanding

“geometric confinement”
Nanostructured materials, carbon nanotubes



(Buehler *et al.*, *JMPS*, 2002)

“biological materials”
(Proteins, DNA …)



(Buehler *et al.*, *MRS Proceedings*, 2004)

Fracture and deformation at small scales

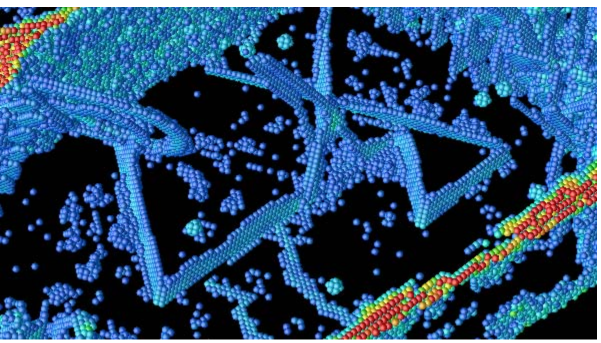
- In the past lectures, we discussed failure and deformation of brittle and ductile bulk materials
- The effect of material size was "neglected", as it was quietly assumed that materials are large and no boundary effects exist
- Here: Investigate the effect of size reduction on the material behavior
- Size effects typically appear due to different scaling behavior of properties
- **Examples:**
  - Strain energy scales ~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 (σ_Y~1/h) to parallel glide dislocations (σ_Y~const.) if the film thickness is reduced, along with a plateau in yield stress

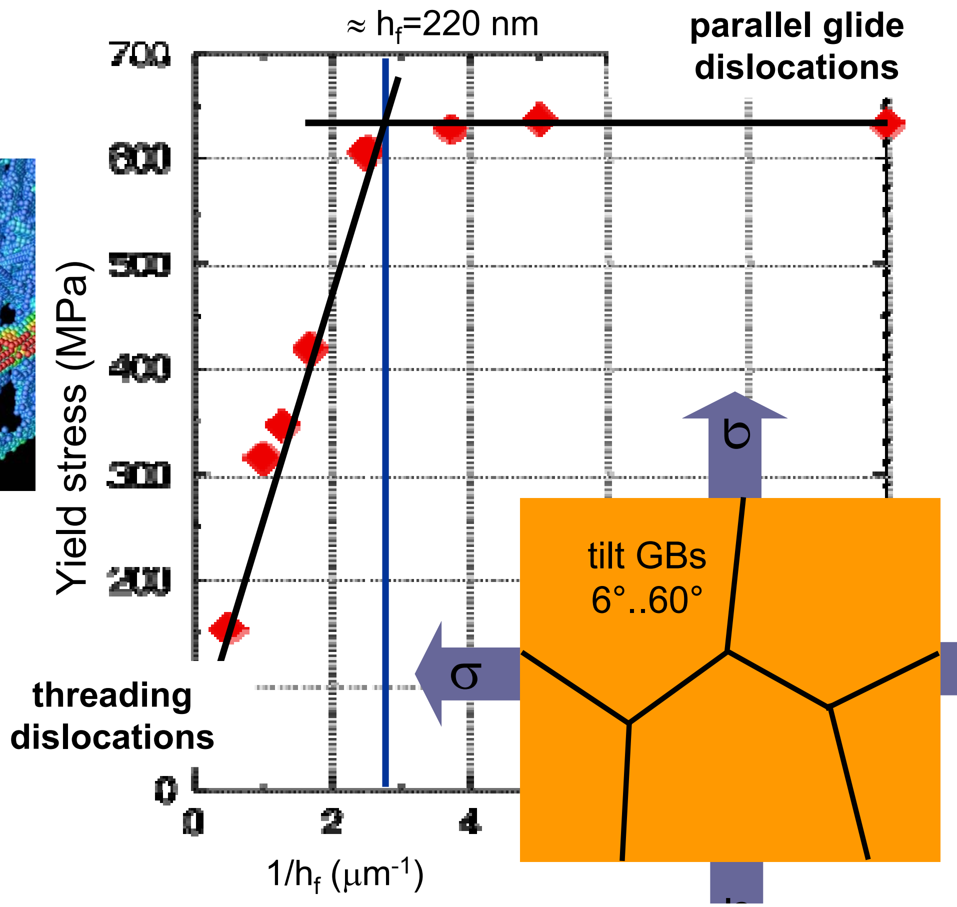
<u>Example</u>: Deformation of ultra thin copper films dislocations/diffusion

"Large"

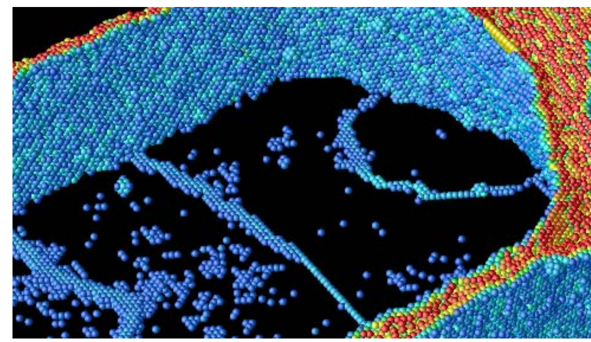


- Threading dislocations (glide)

Nix, Freund, Matthews



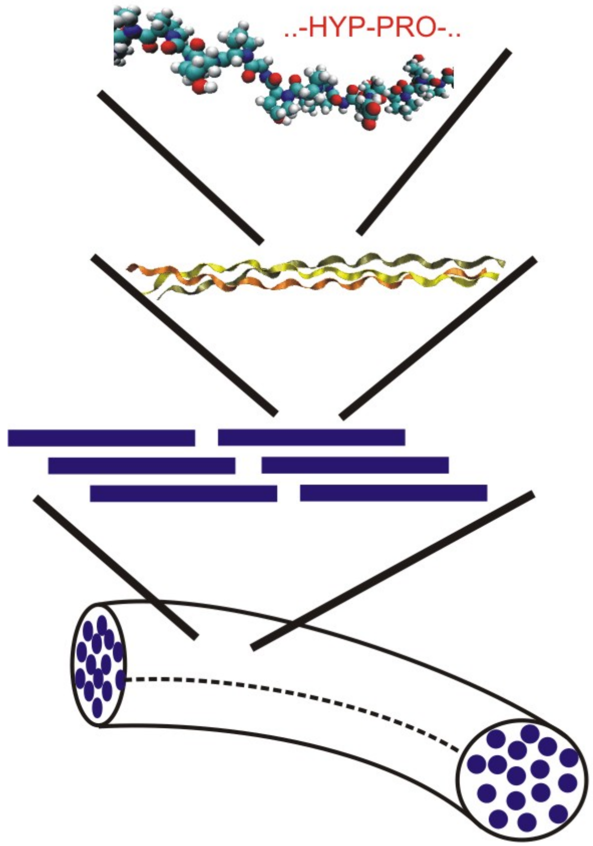
"Small"



- Diffusional creep
- Parallel glide dislocations

(Gao, 1999, Balk, Arzt, Dehm, 200, Buehler et al., 2003-2005)

Chemical complexity: Collagen, a hierarchical nanomaterial



amino acids
~1 nm

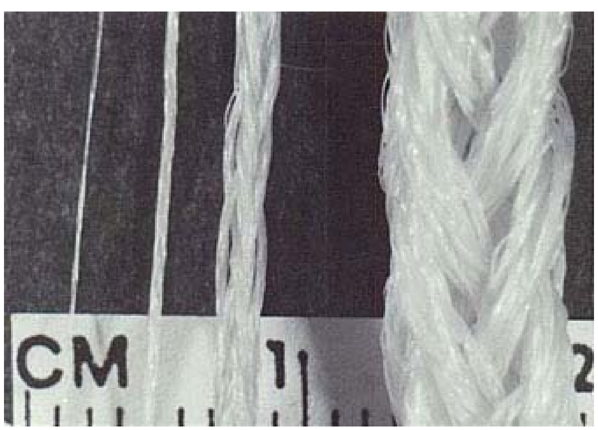
tropocollagen
~300 nm

fibrils
~1 μm

fibers
~10 μm

Collagen features a hierarchical design

Nanoscale features assemble into microscopic and large-scale features



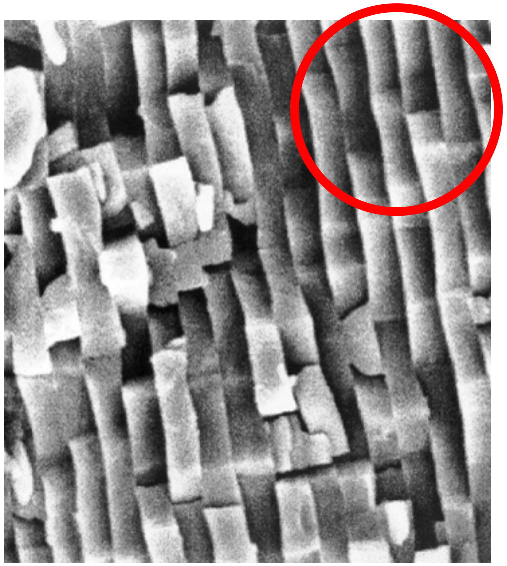
Braided collagen fibers

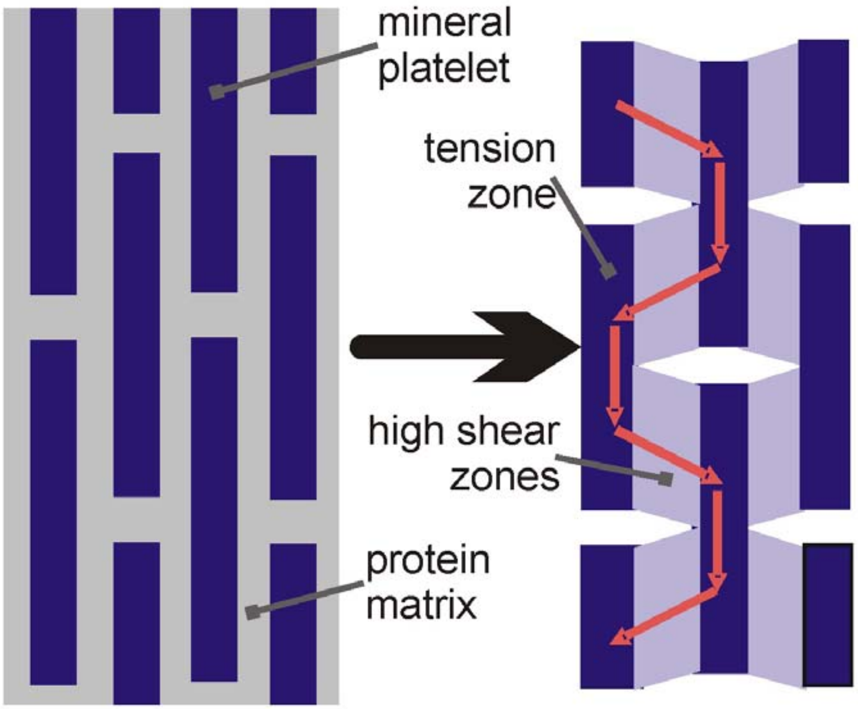
http://images.google.com/images?q=tbn:DmUAjp_nQN7S0M:www.atp.nist.gov/eao/sp950-2/tissue_1lo.jpg

Why nanoscale features?

Motivation: Biocomposites in bone with nanoscale features

Characteristic size: 10..100 nm





• What are the <u>engineering principles</u> of biological systems in producing <u>tough materials</u> out of <u>weak constituents</u>?

• Why is <u>nanometer scale</u> so important to biological composite materials?

(Gao *et al*., 2003, 2004)

A: Size effects in brittle materials

Objectives and hypothesis

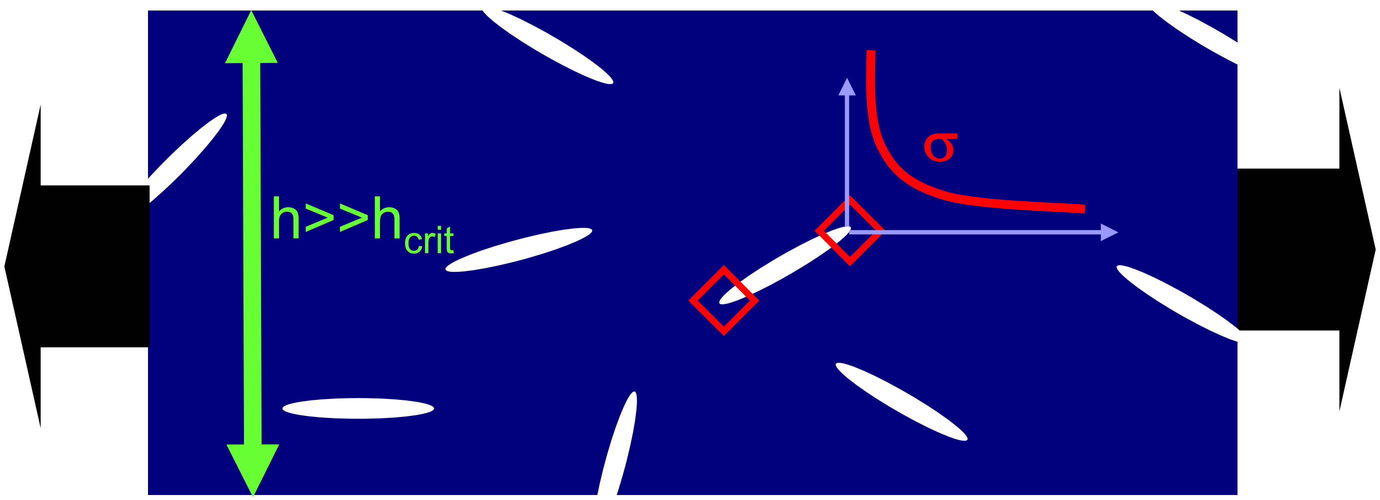
- Failure mechanism of ultra small brittle single crystals as a function of material size
- Properties of adhesion systems as a function of material size: How can optimal adhesion be achieved despite presence of defects (roughness)?

- Hypothesis:

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

(Gao et al., 2003)

"Macro"



Griffith

Objectives and hypothesis

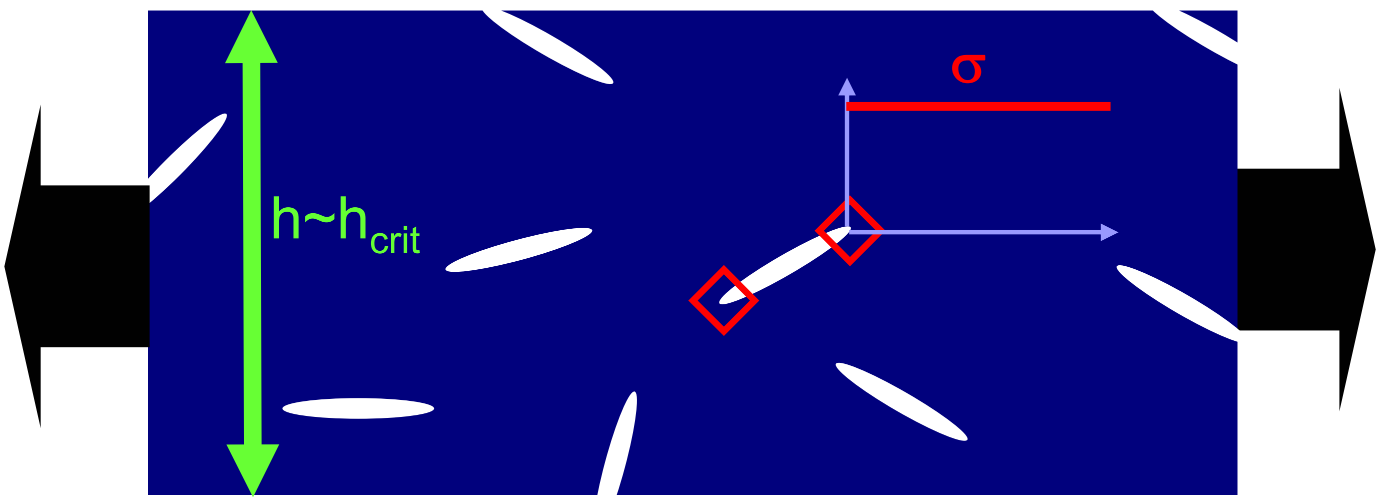
- Failure mechanism of ultra small brittle single crystals as a function of material size
- Properties of adhesion systems as a function of material size: How can optimal adhesion be achieved despite presence of defects (roughness)?

- Hypothesis:

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

(Gao et al., 2003)

"Nano"



Griffith

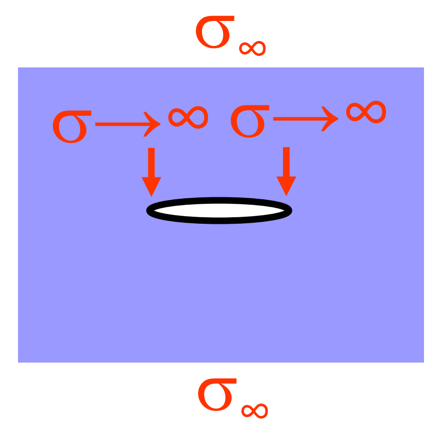
Two paradoxes of classical fracture theories

• 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

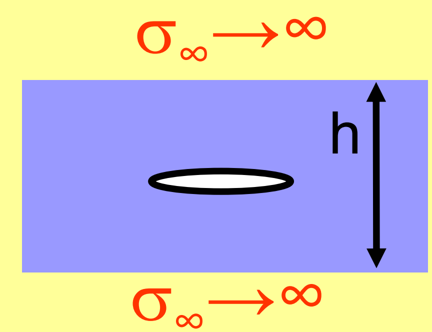
$$\boxed{G = 2\gamma}$$



Infinite peak stress

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

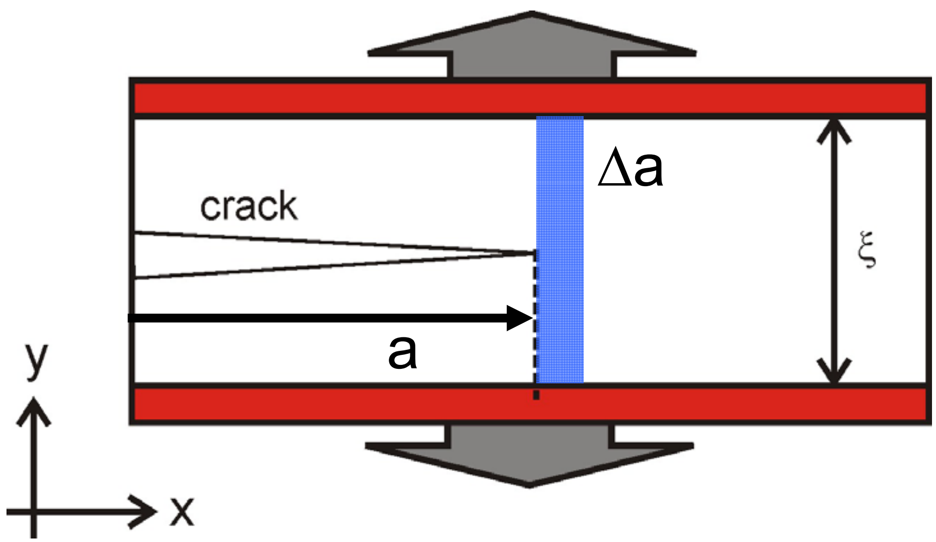
Topic of this lecture



Infinite bulk stress

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

How materials break: Theoretical considerations



Spontaneous crack nucleation occurs when the energy released due to crack propagation of Δa is larger than the energy necessary to create two new surfaces

(Griffith)

$2\gamma\Delta a$ Energy necessary to create two new surfaces

$$\frac{\sigma^2\xi(1-\nu^2)}{2E}\Delta a$$ Energy stored ahead of the crack, in strip Δa

How materials break **at small scales** Theoretical considerations

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

$2\gamma = G$ Griffith

E Young's modulus
ν Poisson ratio, and
σ Stress far ahead of the crack tip

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

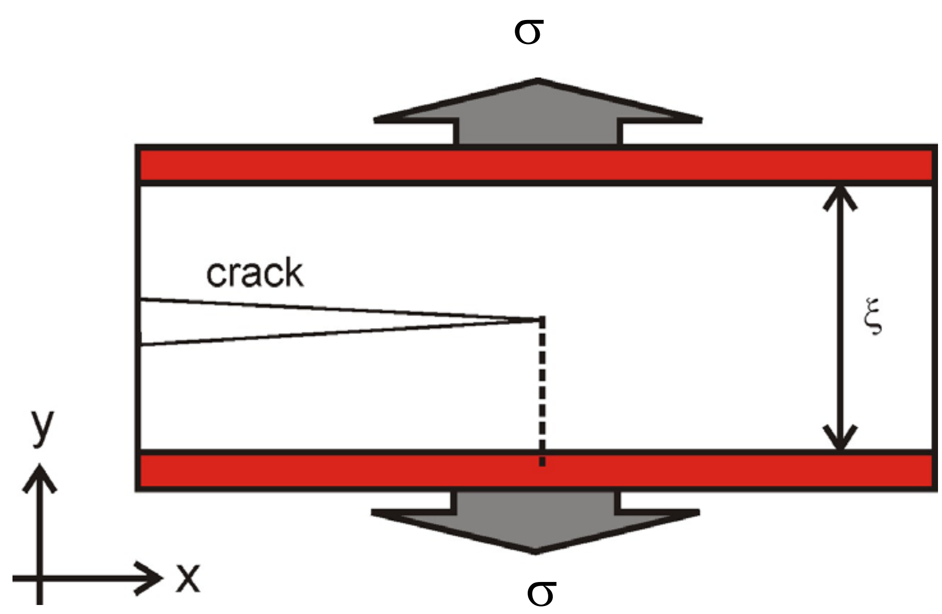
$\sigma \rightarrow \infty$ for $\xi \rightarrow 0$

Impossible: $\sigma_{max} = \sigma_{th}$

Stress for spontaneous crack propagation

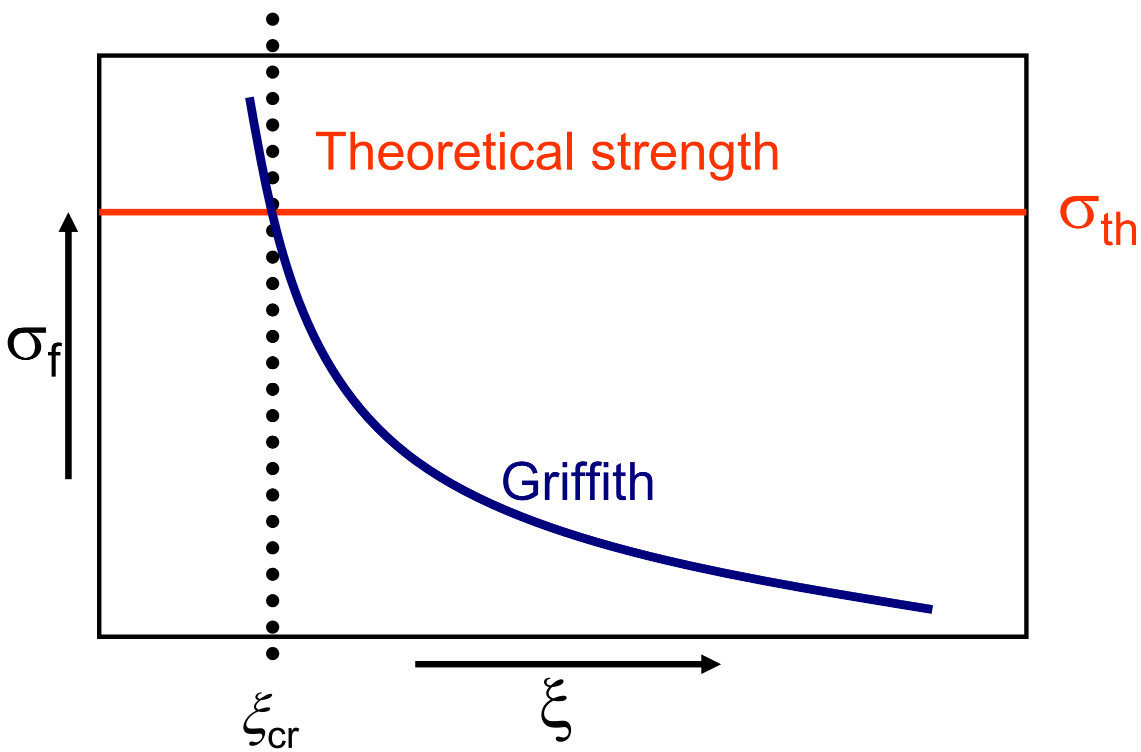
$$\xi_{cr} = \frac{4\gamma E}{\sigma_{th}^2 (1-\nu^2)}$$

Length scale ξ_{cr} at σ_{th} cross-over



ξ.. size of material

From macro to nano…



$$\xi_{cr} \sim \frac{\gamma E}{\sigma_{max}^2}$$

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

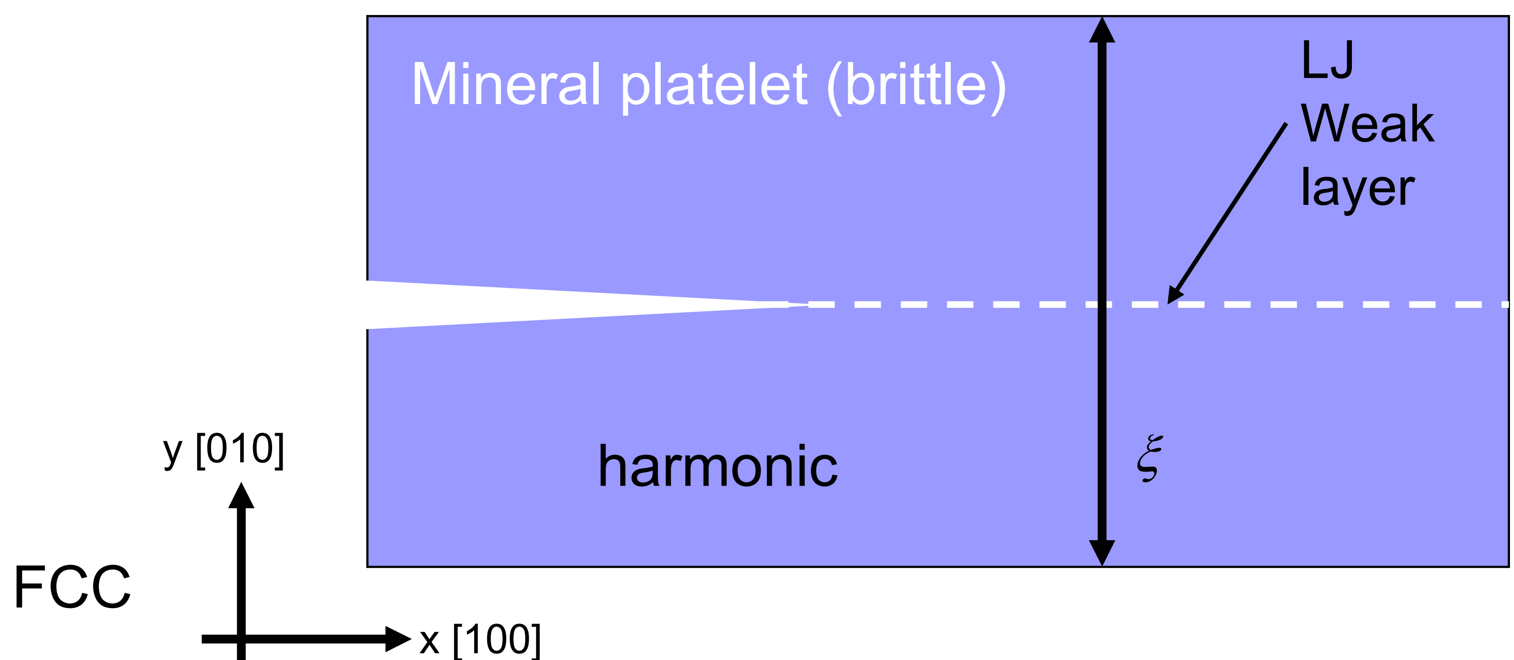
Atomistic model: Model material

- LJ potential across a weak fracture layer
- Harmonic potential with spring constant k_0 in the bulk (simple force field)
- Avoid complexity of accurate potentials: Focus on "model material" to demonstrate scaling laws (Buehler *et al*., Nature, 2003, Nature, 2006)

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

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

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

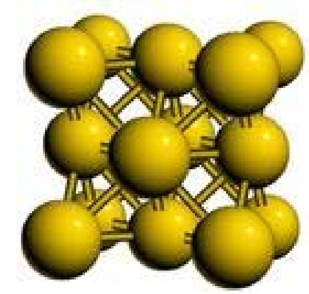


Atomistic model

Bulk (harmonic, FCC)

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

$$r_0 = 2^{1/6} \qquad a \approx 1.587 \qquad k_0 = 572.0$$



$$\mu = \frac{r_0^2}{2}k_0 \qquad E = 8/3\mu \qquad \nu = 1/3$$

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

Interface (LJ) “dispersive-glue interactions”

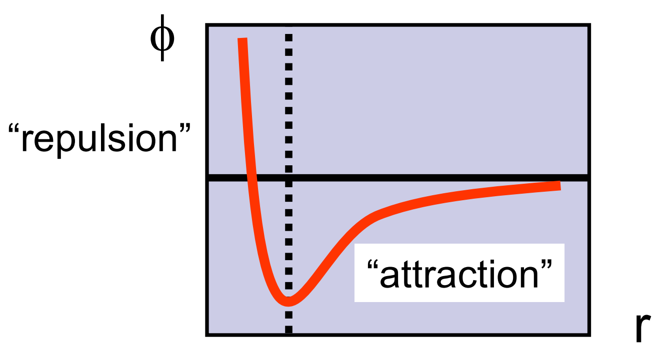
$$h_{cr} = \frac{4\gamma E}{\sigma_{th}^2(1-\nu^2)}$$

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

$$\gamma = N_b \rho_A \Delta\phi \qquad \sigma_{th} \approx 9.3$$

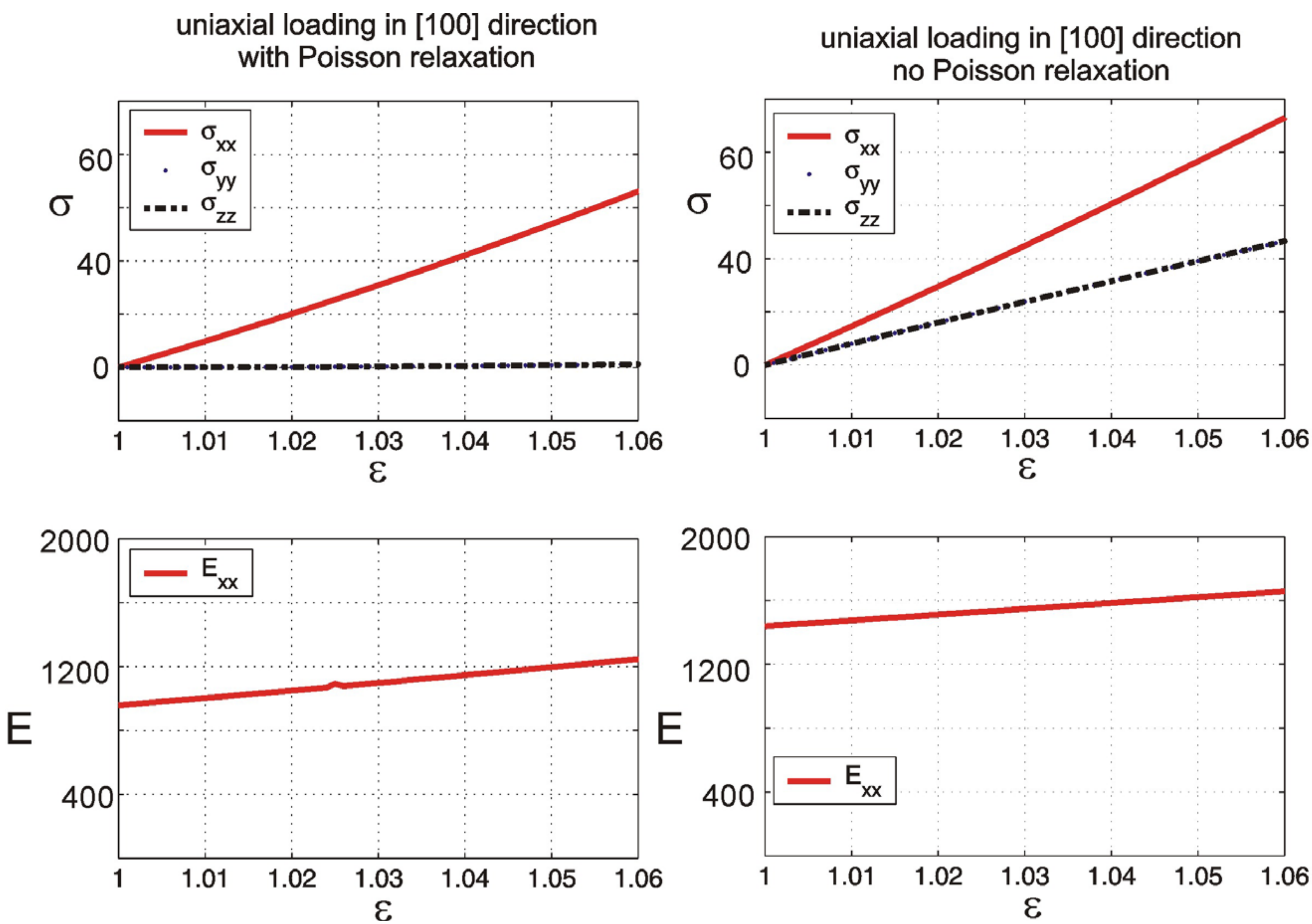
$$\rho_A = 1/r_0^2 \approx 0.794$$

$$N_b = 4 \qquad \Delta\phi \approx 1$$



Choose *E* and γ such that length scale is in a regime easily accessible to MD

Elasticity associated with harmonic potential



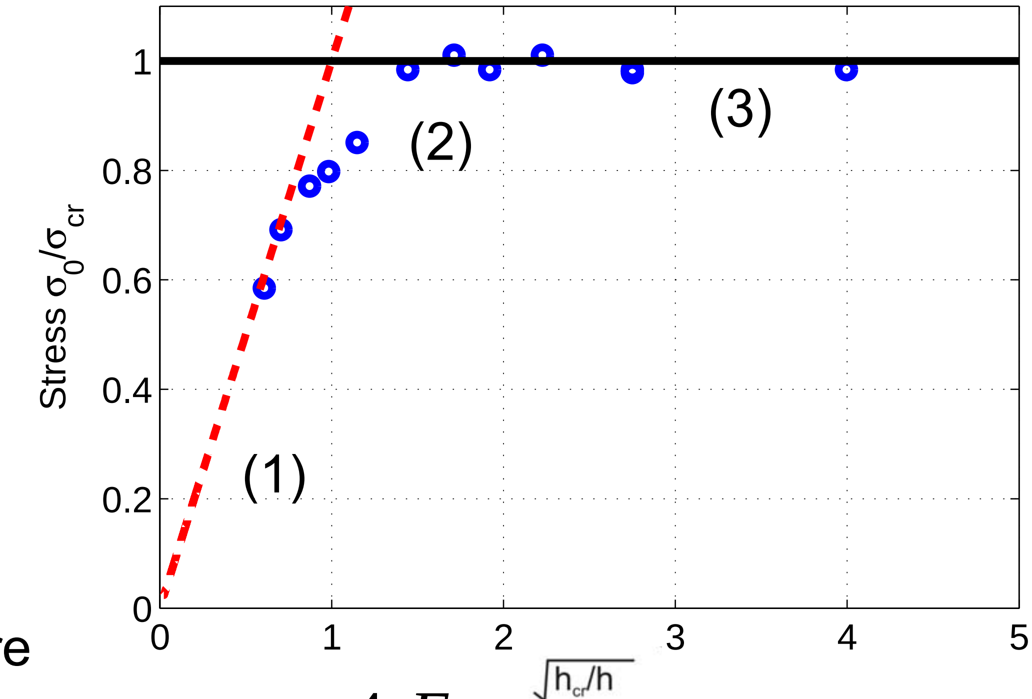
Elastic and fracture properties

Spring constant k_0	Young's modulus E	Poisson ratio ν	Surface energy γ (numerical result)
572	960	0.33	2.33

- 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

Size dependence of fracture strength

$\sigma_f = \sigma_{th}$ Failure at theor. strength



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

Griffith-governed failure

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

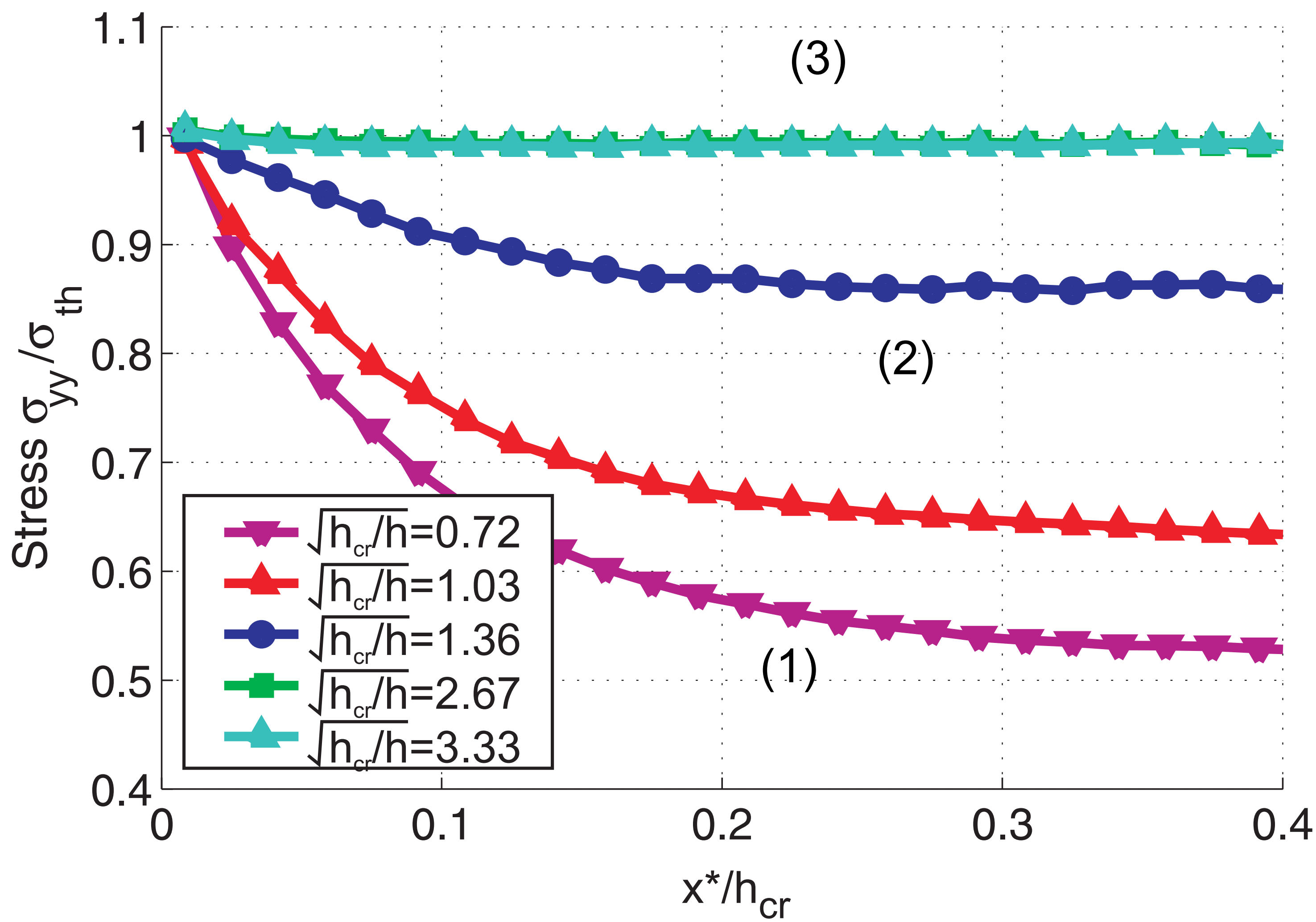
Atomistic simulation indicates:

➢ 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 ξ

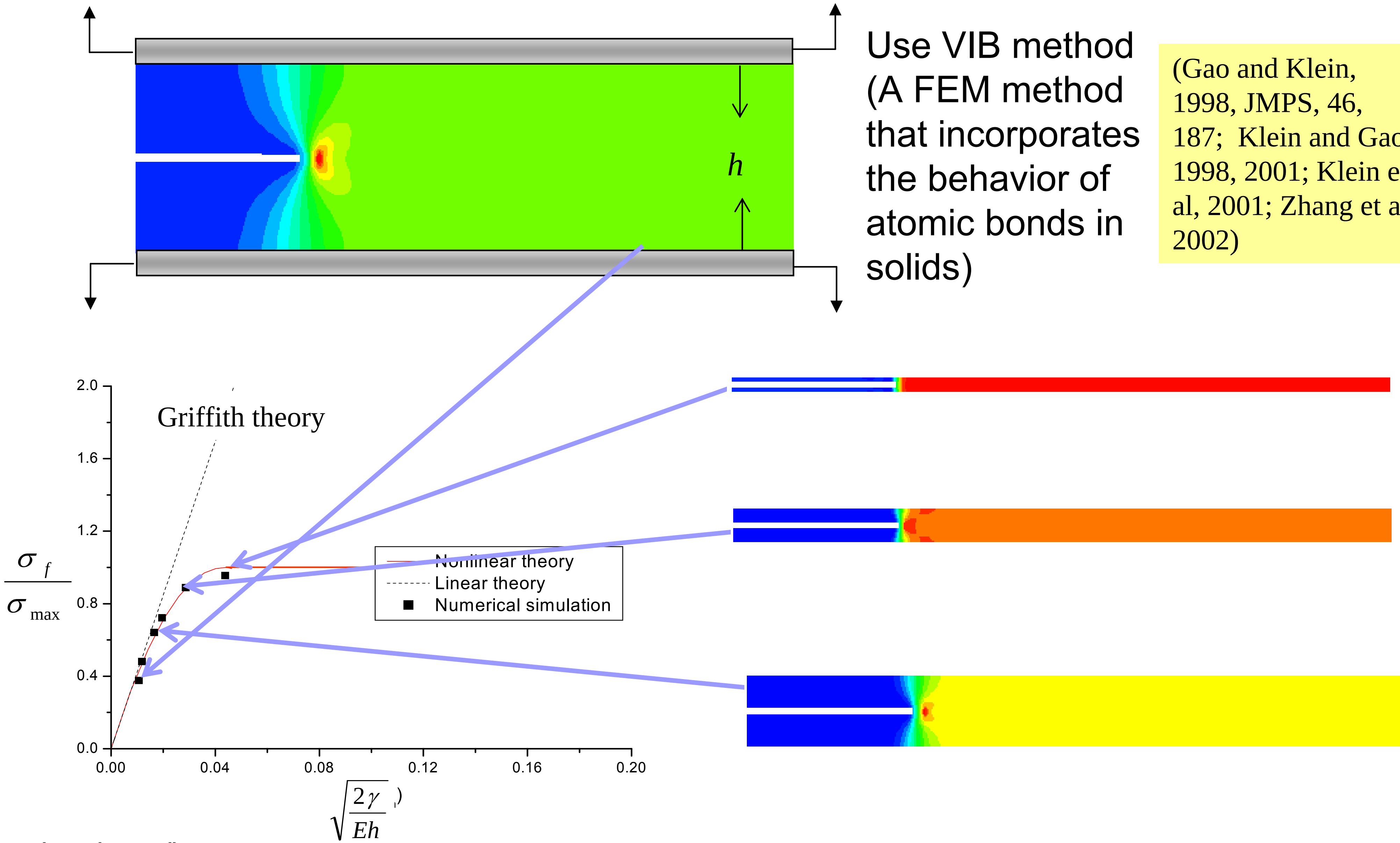


(1): Griffith (2): Transition (3): Flaw tolerance

Continuum mechanics simulations

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

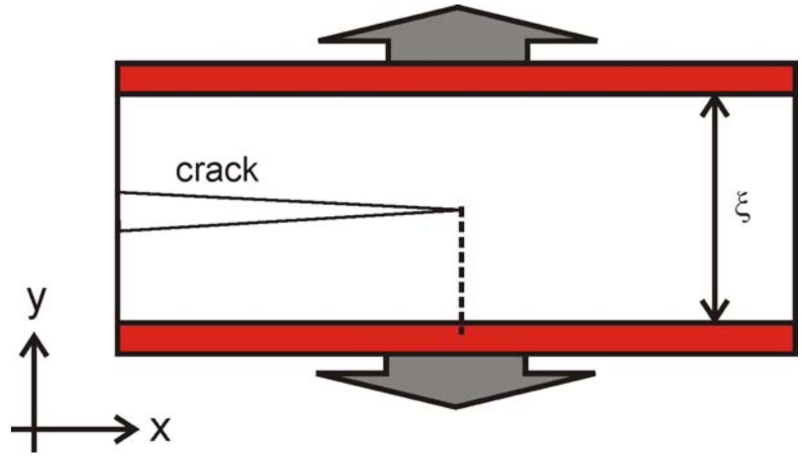
(Gao and Klein, 1998, JMPS, 46, 187; Klein and Gao, 1998, 2001; Klein et al, 2001; Zhang et al, 2002)



(Baohua Ji)

Summary: Small-scale structures for strength optimization & flaw tolerance

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

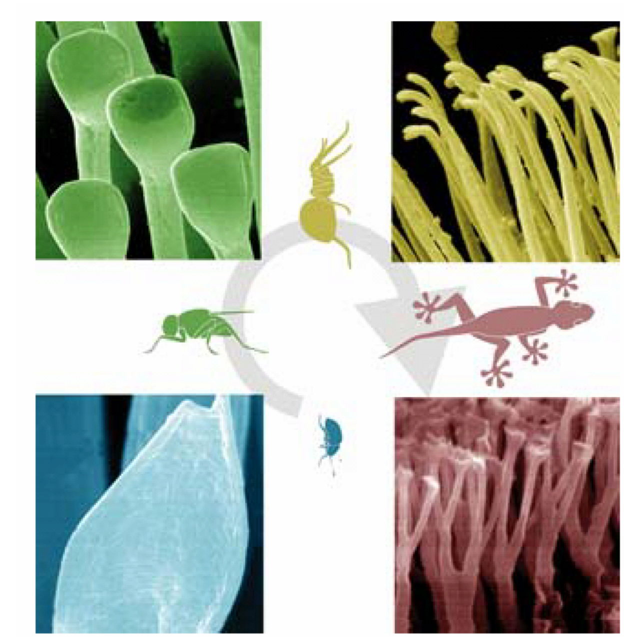


$h > h_{cr}$	$h < h_{cr}$
Material is sensitive to flaws.	Material becomes insensitive to flaws.
Material fails by stress concentration at flaws.	There is no stress concentration at flaws. Material fails at theoretical strength.
Fracture strength is sensitive to structural size.	Fracture strength is insensitive to structure size.

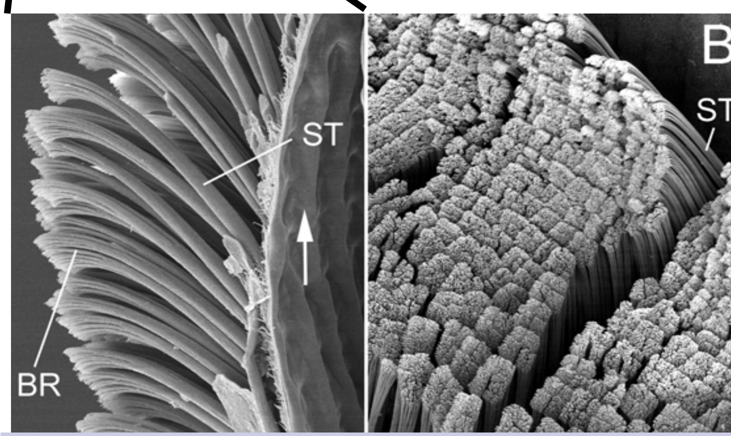
(Gao *et al*., 2003, 2004; Gao, Ji, Buehler, MCB, 2004)

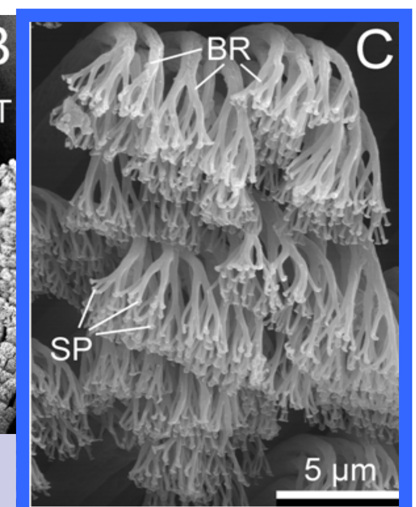
B: Size effects in adhesion systems

Hierarchical Adhesion Structures of Gecko



(Dr. Gorb, MPI-MF)

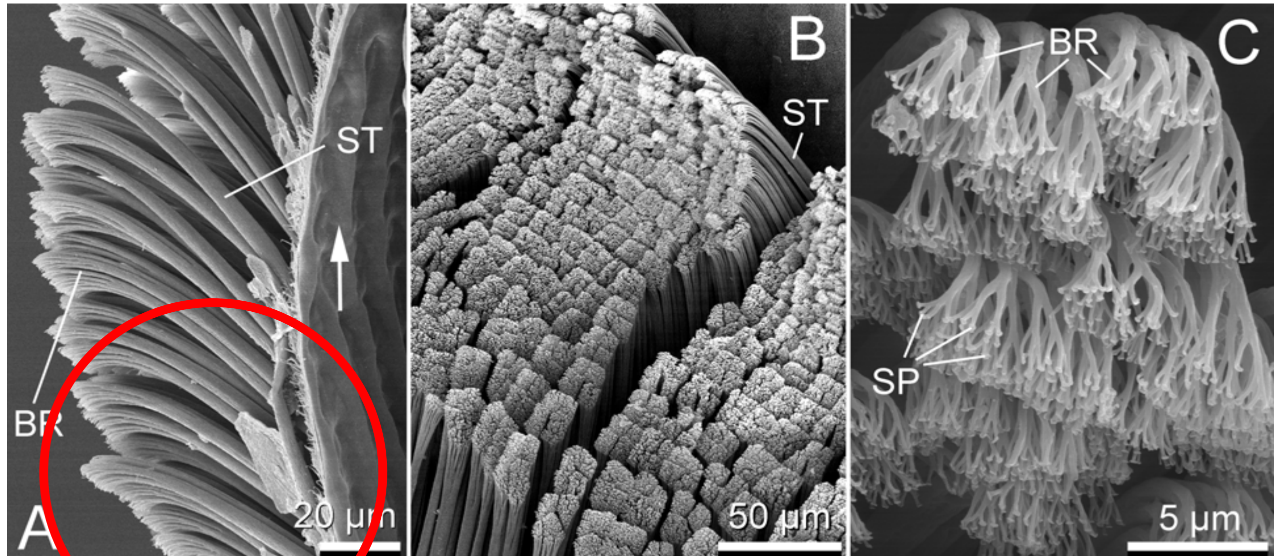




What are the secrets of (very strong) attachment devices in nature?

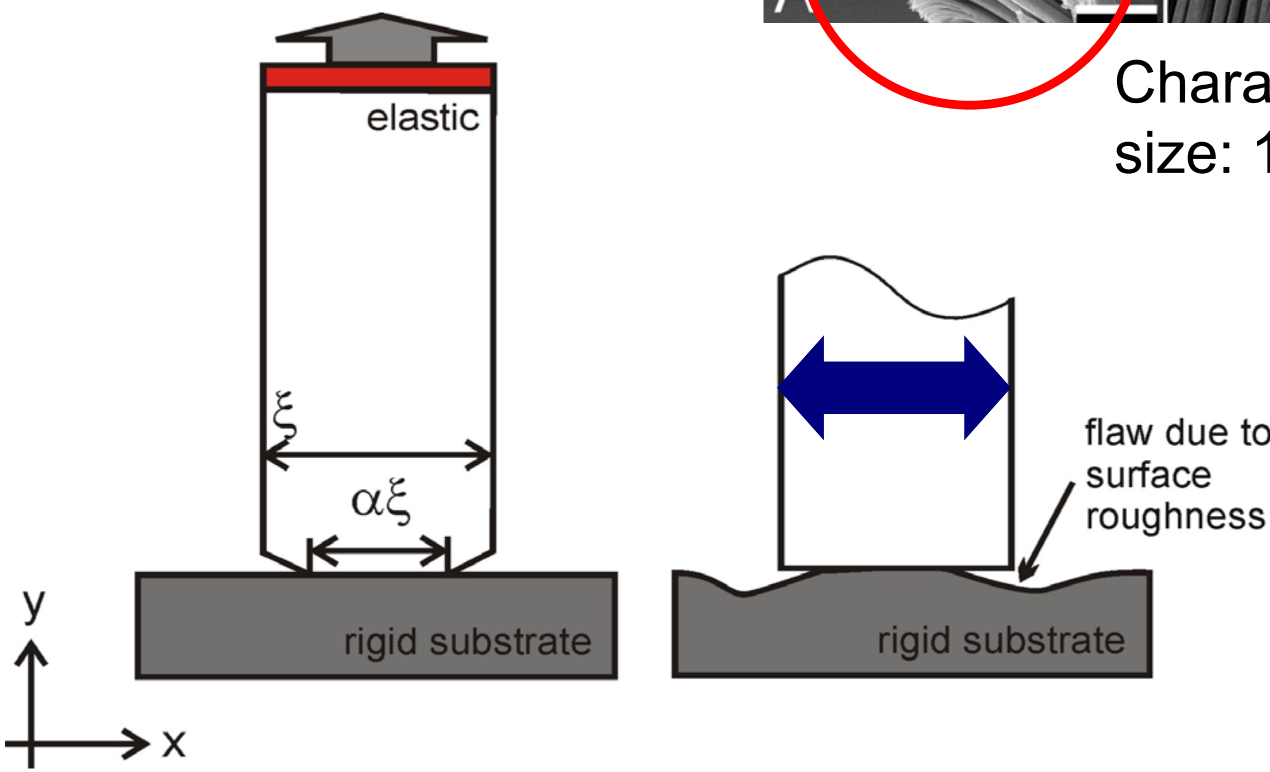
Observe 200..300 nm radius

Adhesion at small length scales



(S. Gorb)

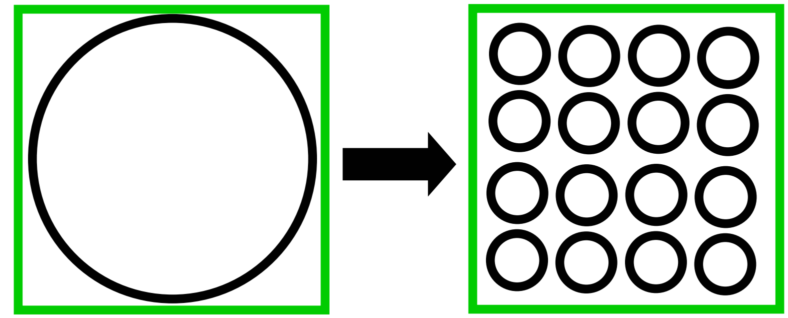
Characteristic size: 100..300 nm



Adhesion at small length scales

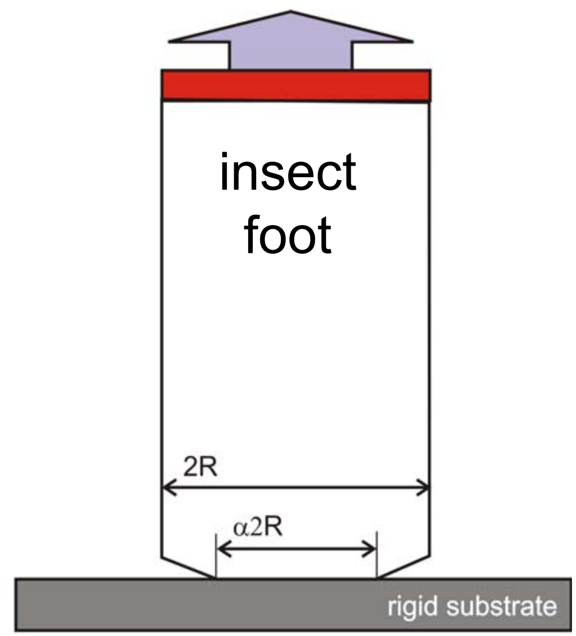
Experiment: Animals have fine, hierarchical structure at the ends of their feet!!

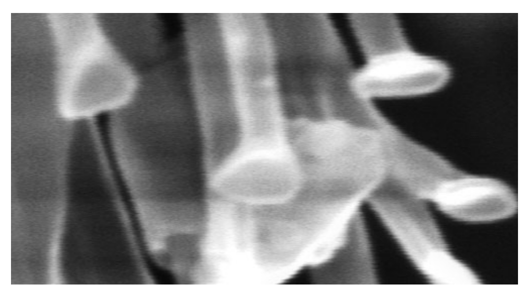
Possible reasons…:

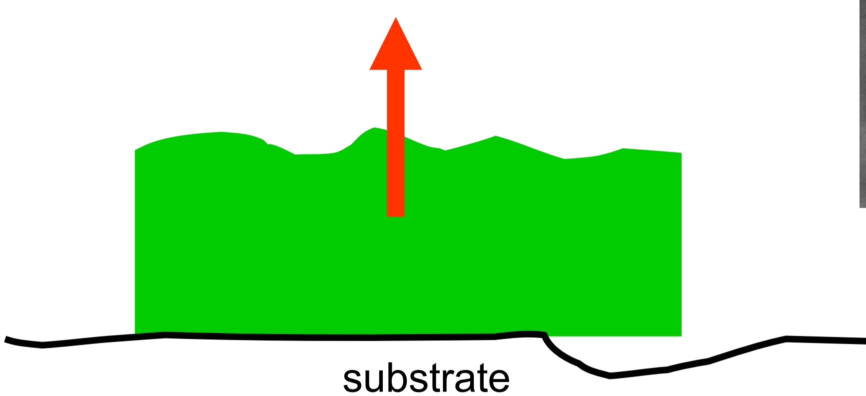


- Since F ~ γ R (JKR model), increase line length of surface by <u>contact splitting</u> (Arzt *et al*., PNAS, 2003)

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

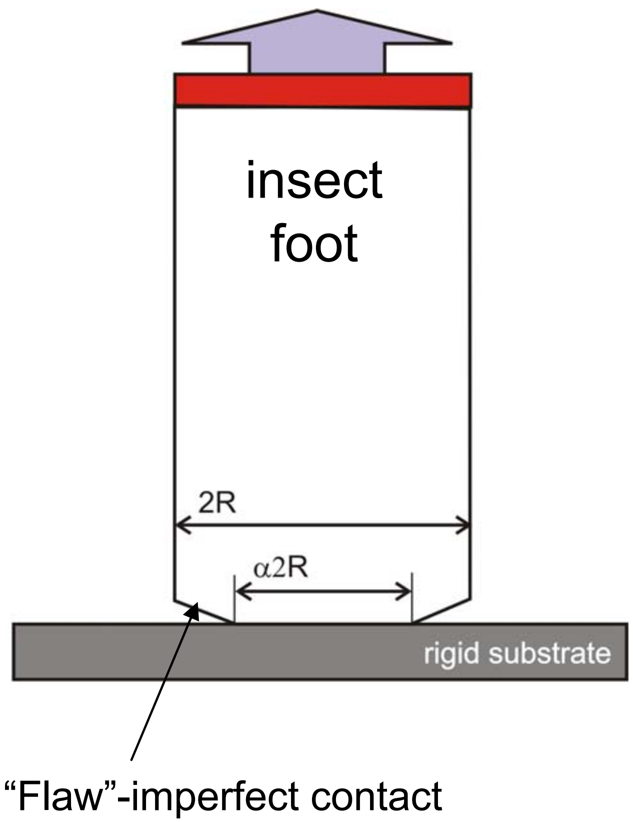






flaw
surface roughness

Theoretical considerations



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

$$\psi = \sqrt{\frac{\Delta\gamma E^*}{R\sigma_{th}^2}} \qquad \beta = \sqrt{2/\left(\pi\alpha F_1^2(\alpha)\right)}$$

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

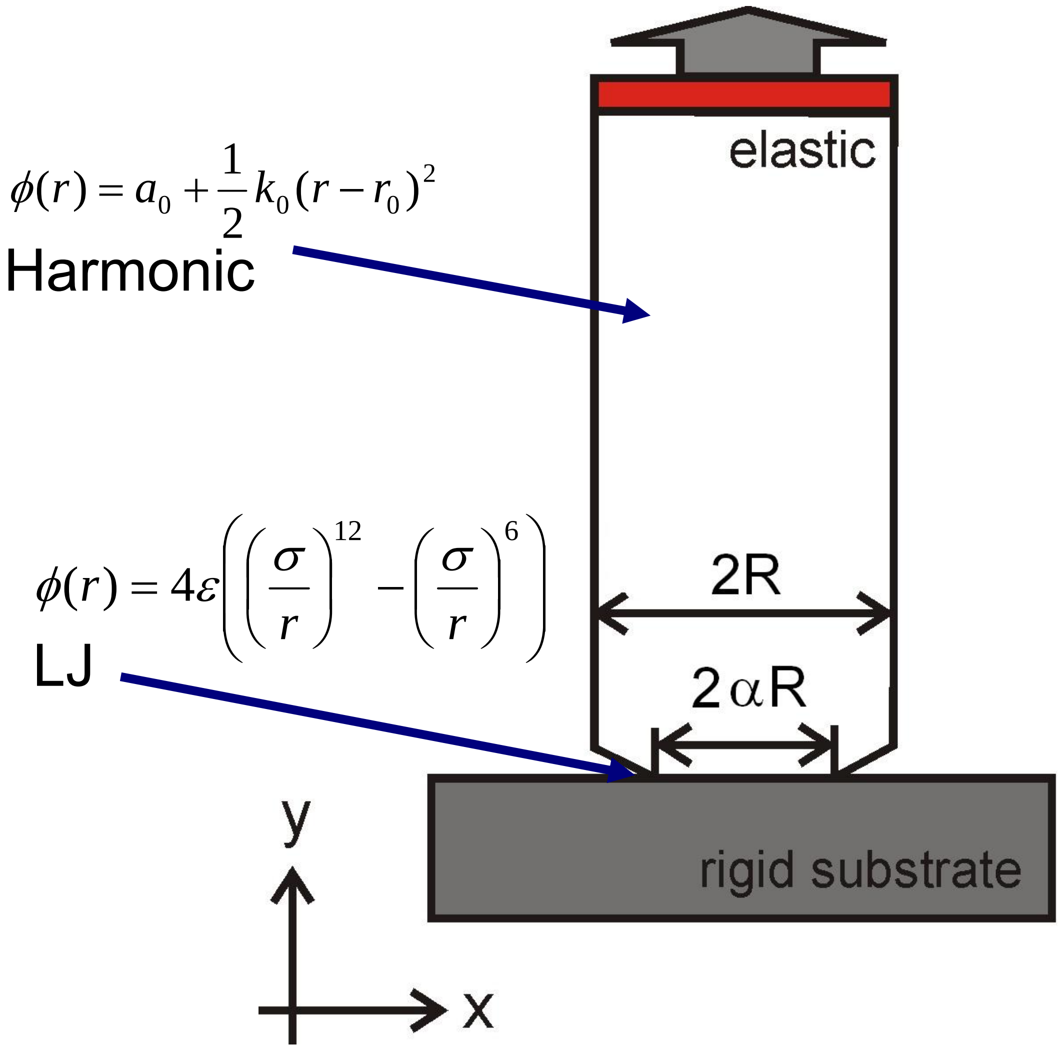
$$\boxed{R_{cr} = \beta^2\frac{\Delta\gamma E^*}{\sigma_{th}^2}}$$

$R_{cr} \sim 225nm$

Typical parameters

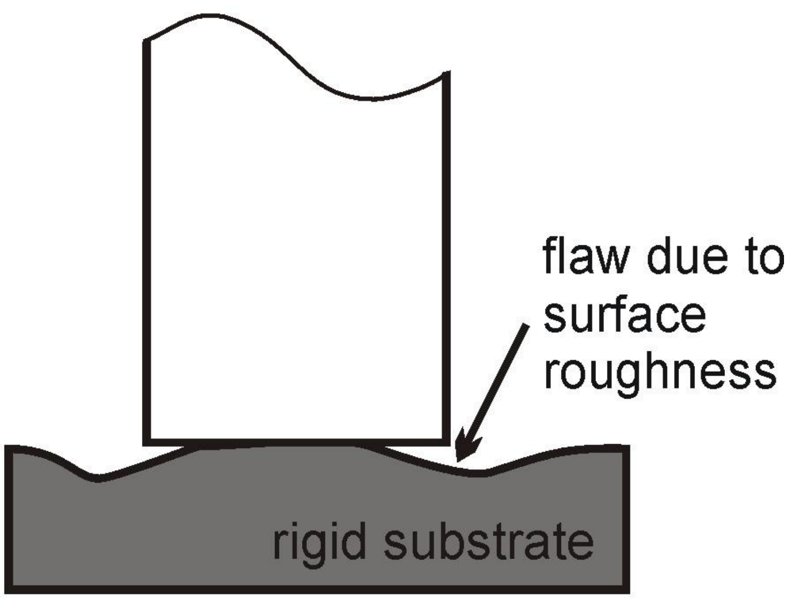
➢ At critical radius, spatula becomes <u>insensitive to flaws</u>: Transition from Griffith governed failure to <u>failure at theoretical strength</u>, independent of presence of flaws!!

Continuum and atomistic model



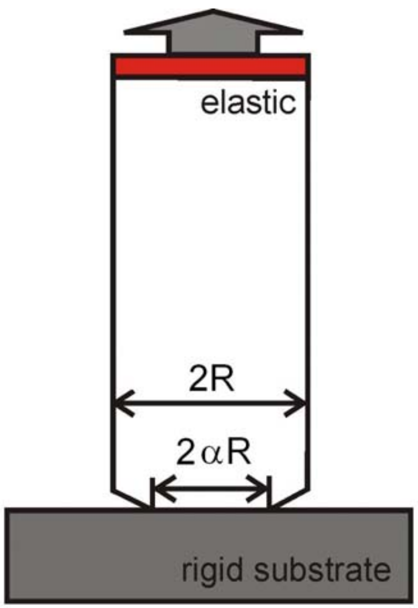
Three-dimensional model

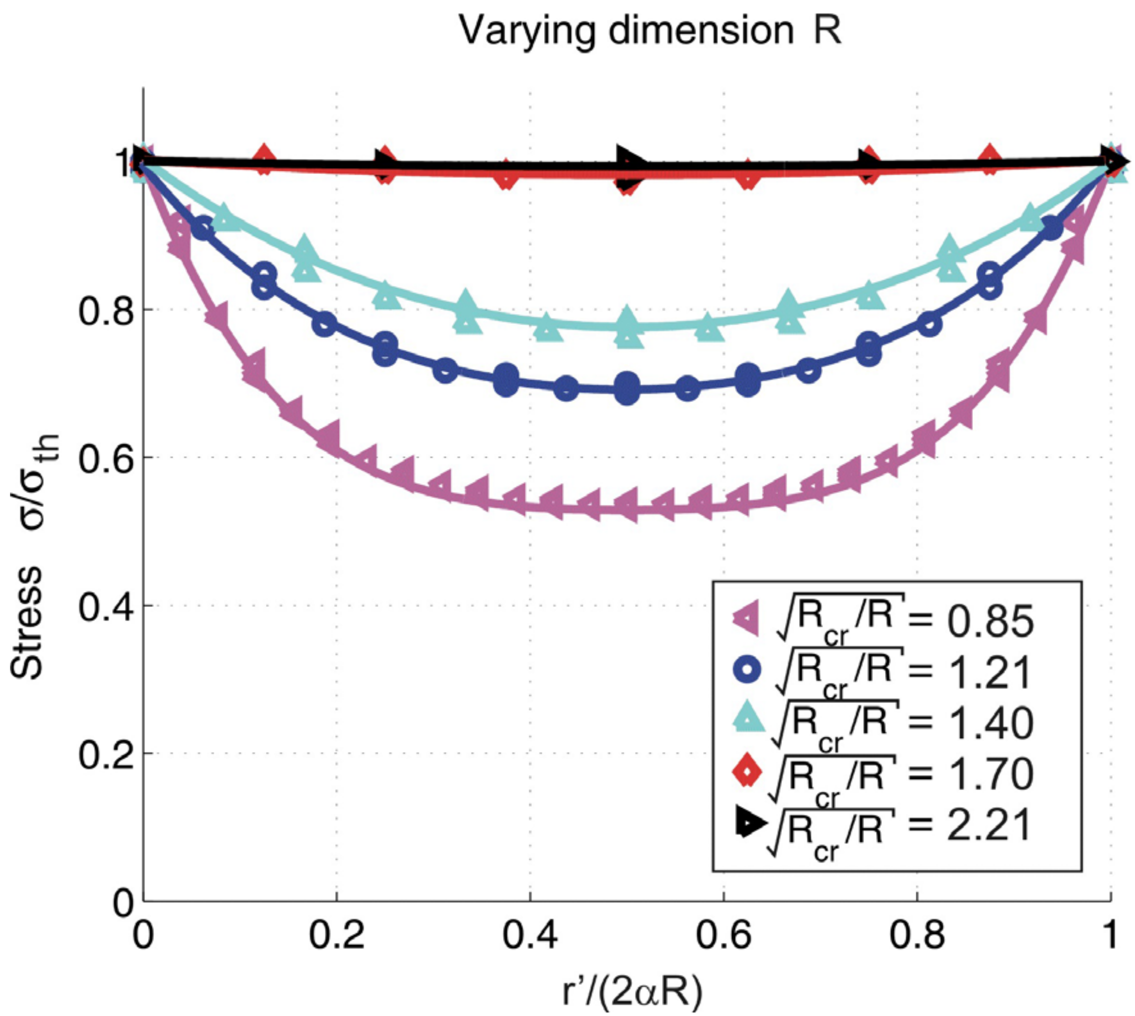
Cylindrical attachment device



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

Stress close to detachment as a function of adhesion punch size





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

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

Smaller size leads to homogeneous stress distribution

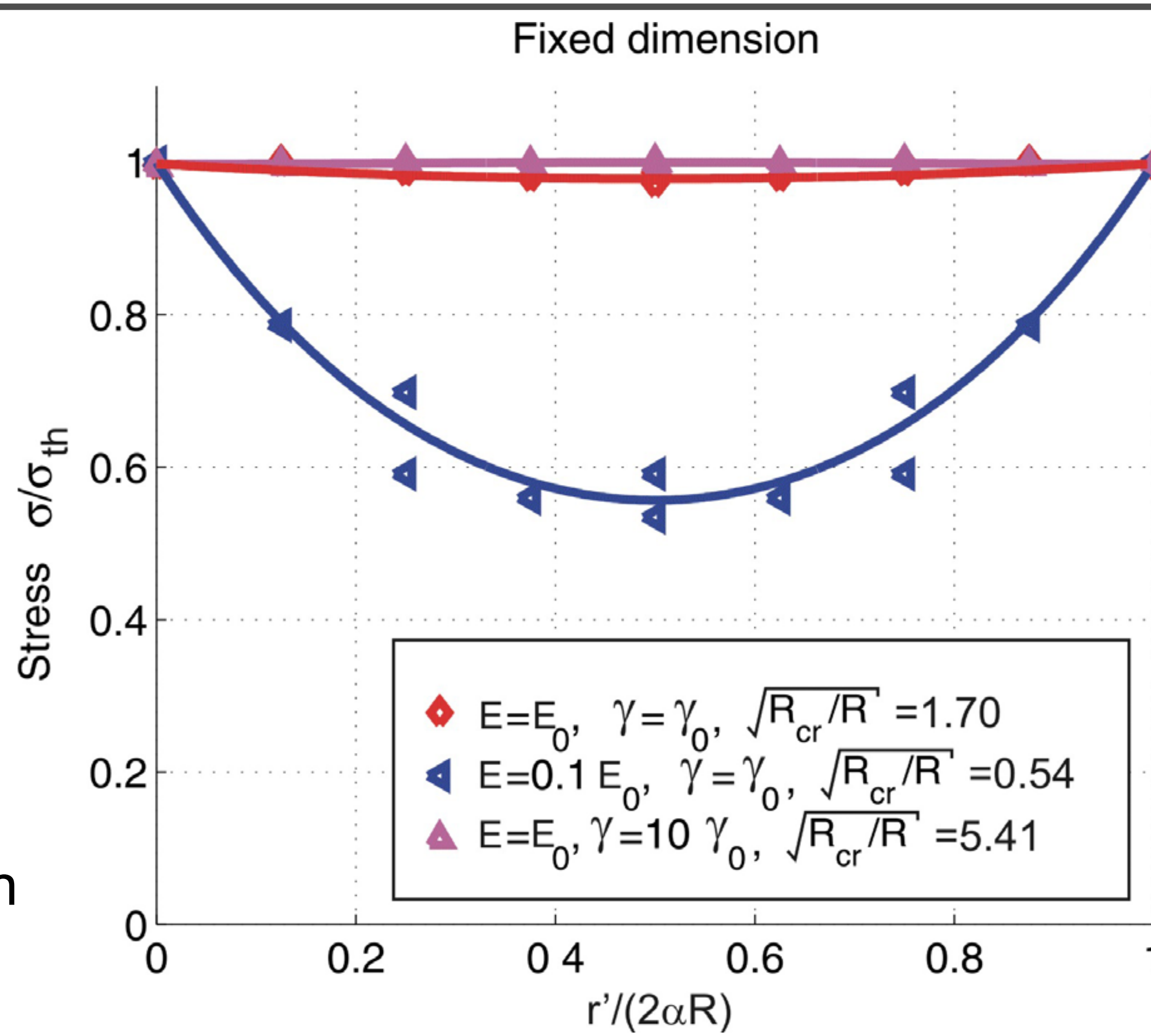
Vary E and γ in scaling law

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

The ratio

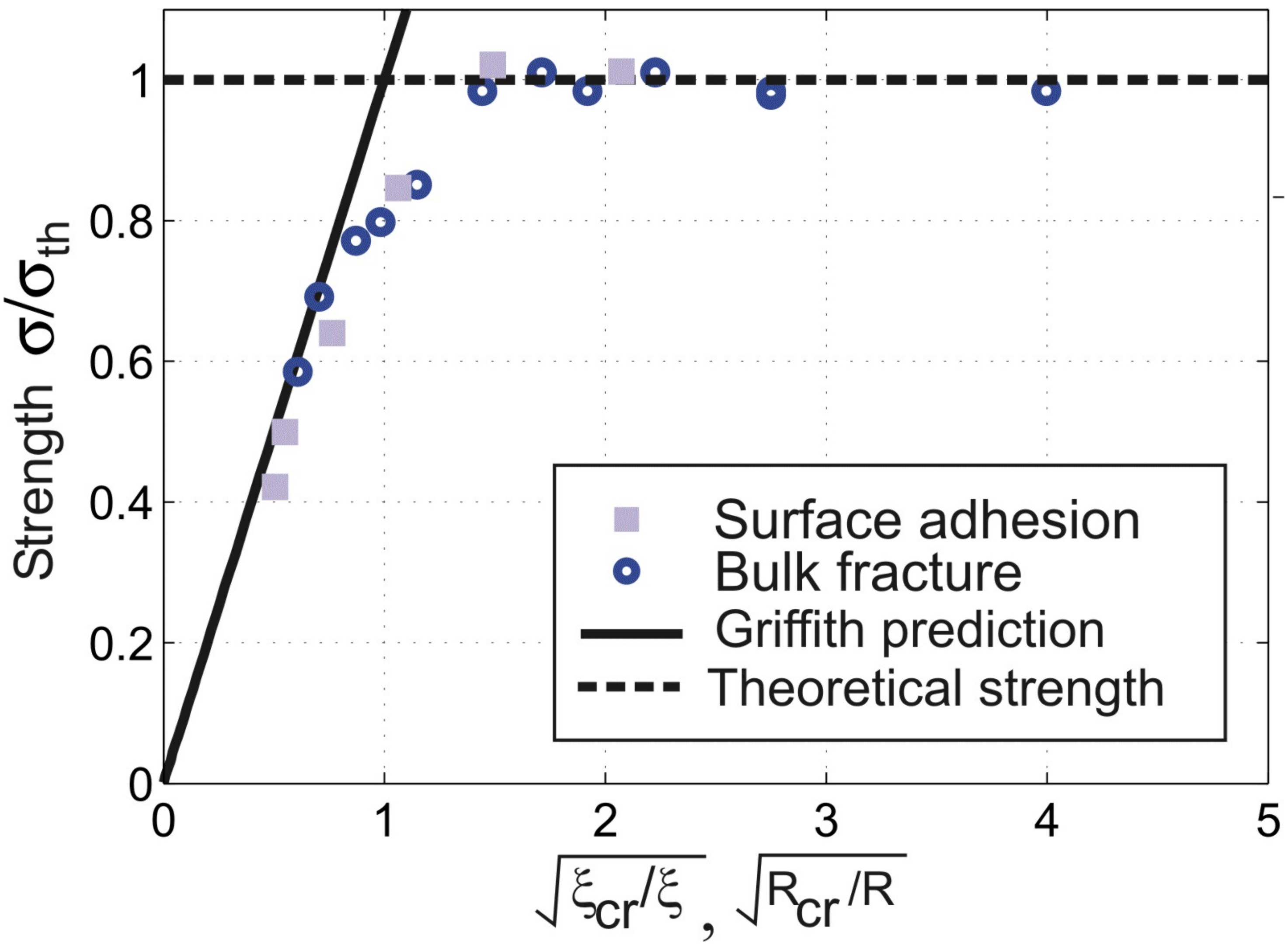
$$\sqrt{R_{cr} / R}$$

governs adhesion strength



- Results agree with predictions by scaling law
- Variations in Young's modulus or γ may also lead to optimal adhesion

Adhesion strength as a function of size

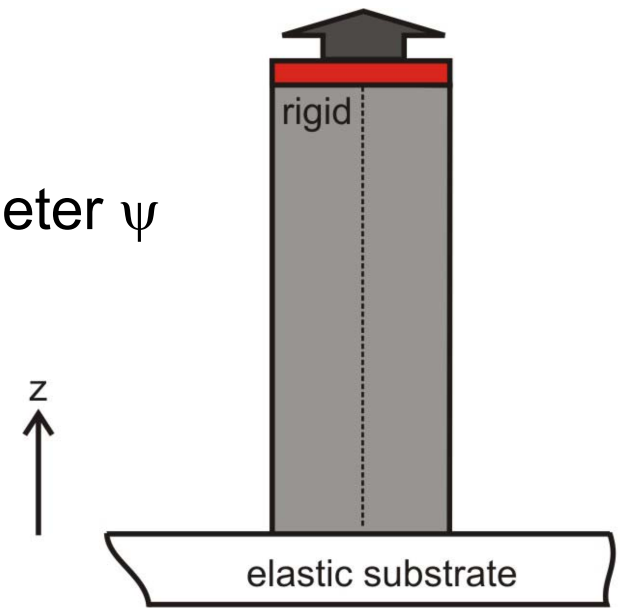


Optimal surface shape

Single punch

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

Concept:
Shape parameter ψ

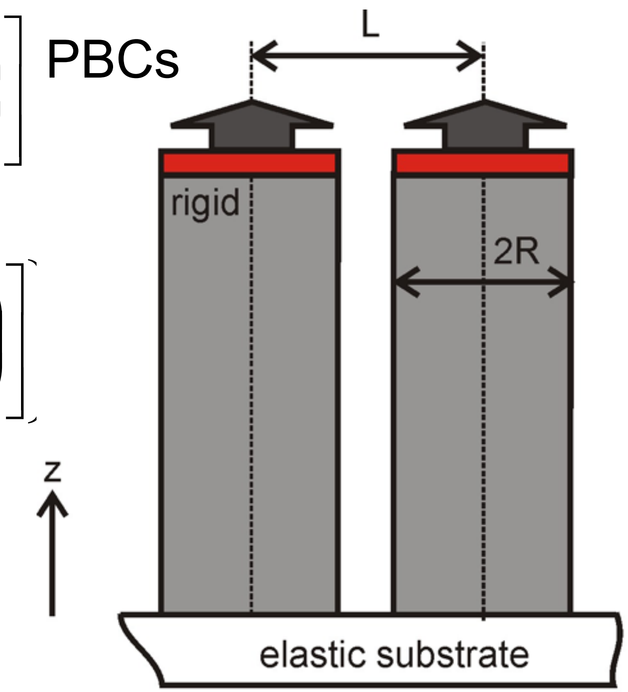


Periodic array of punches

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

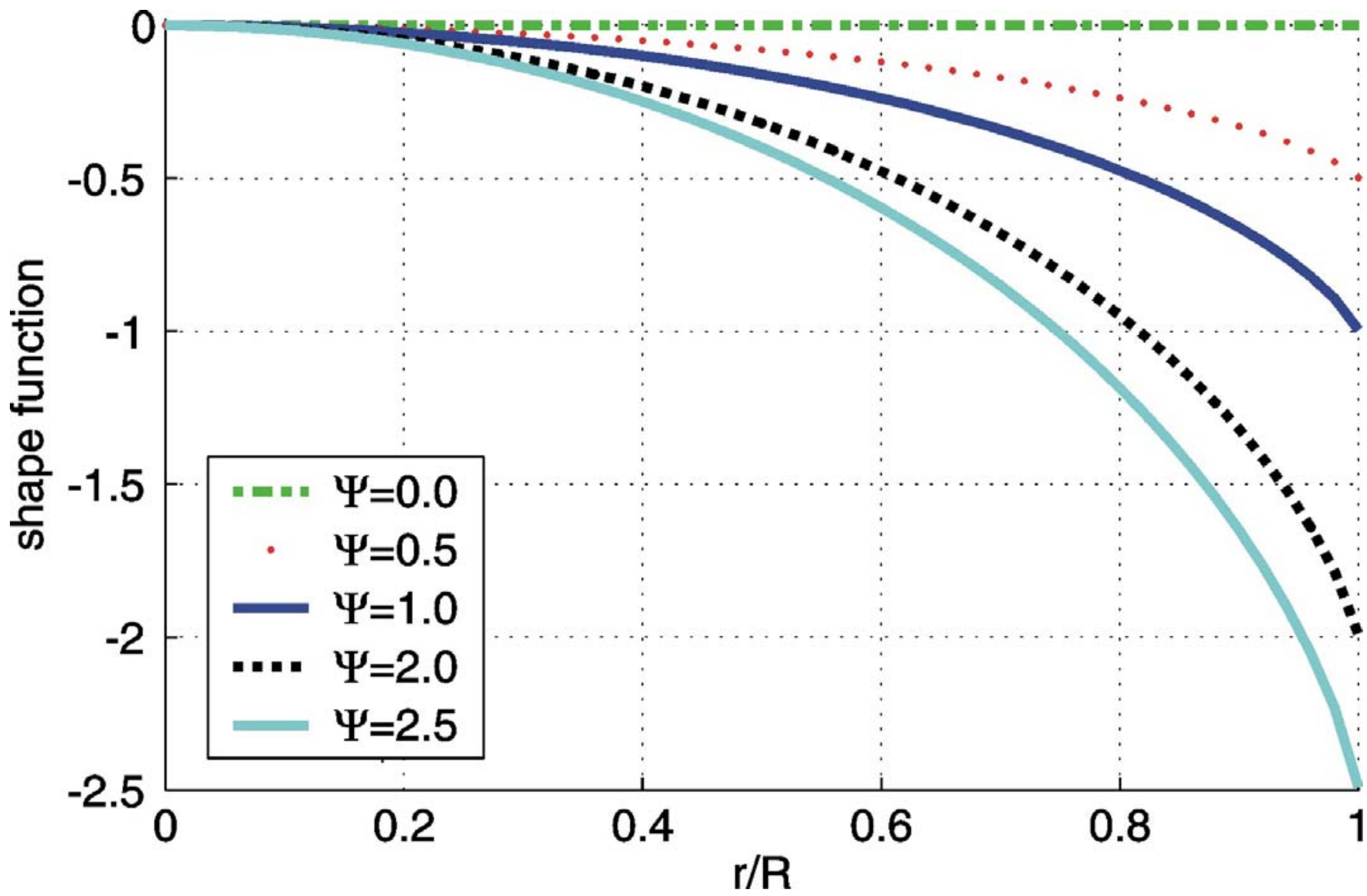
$$-\sum_{n=1}^{\infty}\left[\ln\left(\frac{(2n\lambda+\bar{r})^2-1}{(2n\lambda)^2-1}\right)+(2n\lambda+\bar{r})\ln\left(\frac{2n\lambda+\bar{r}+1}{2n\lambda+\bar{r}-1}\right)-2n\lambda\ln\left(\frac{2n\lambda+1}{2n\lambda-1}\right)\right]$$

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



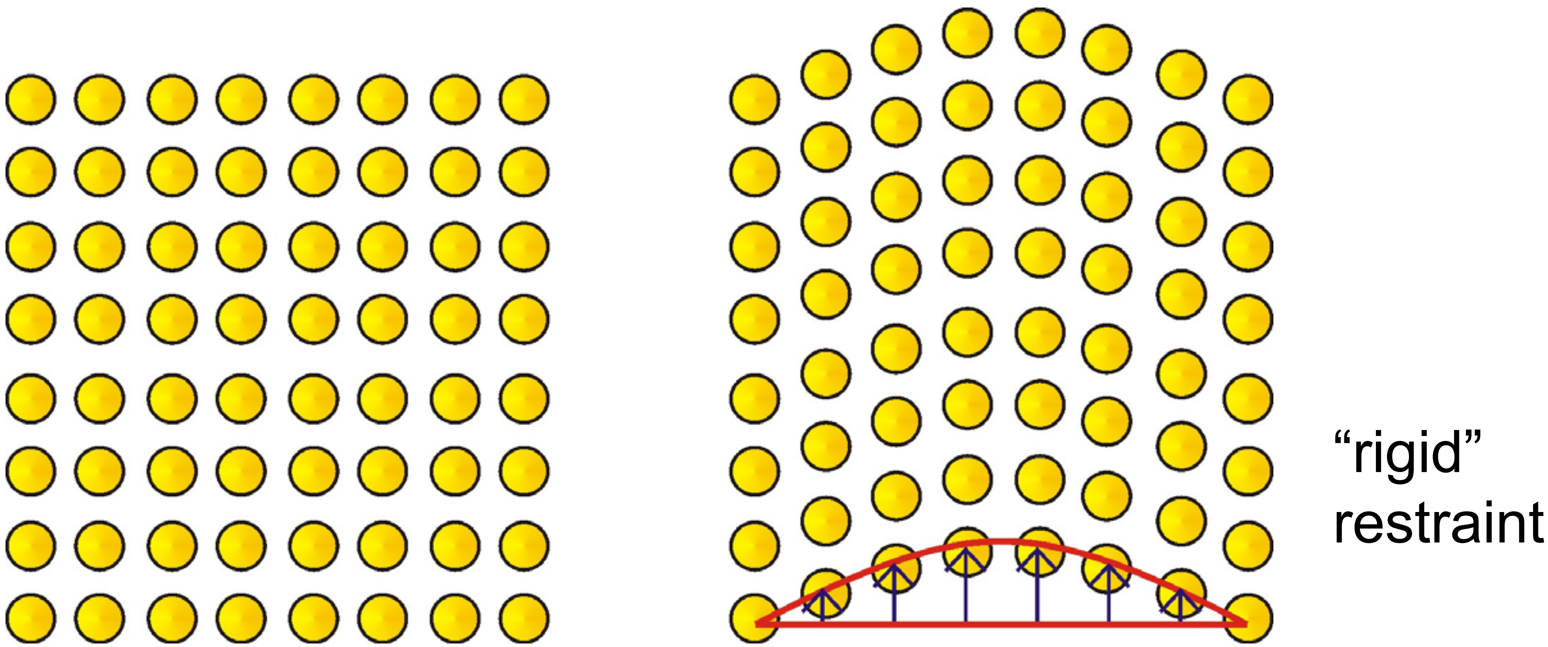
Derivation: Concept of superposition to negate the singular stress

Optimal shape predicted by continuum theory & shape parameter ψ



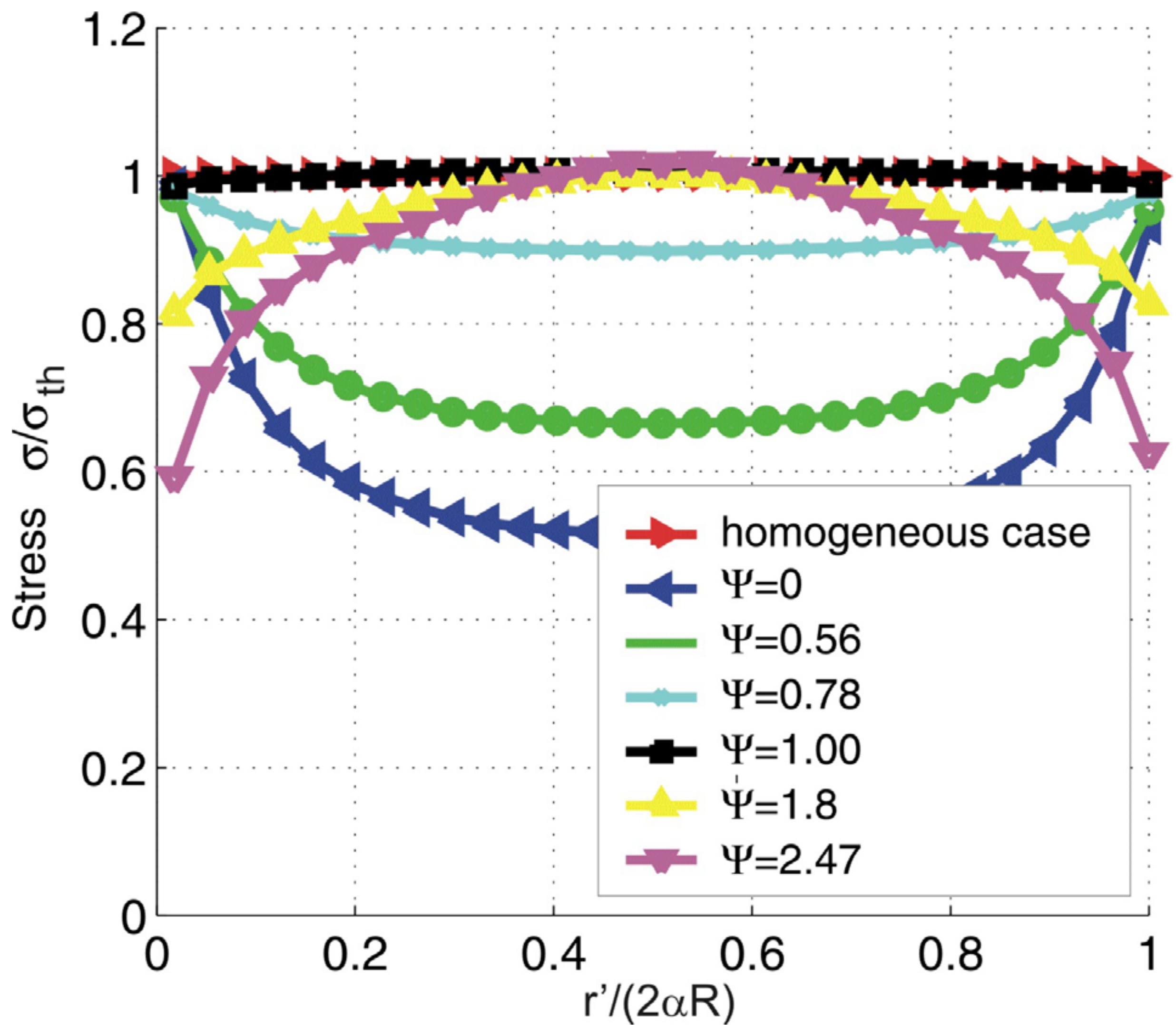
The shape function defining the surface shape change as a function of the shape parameter ψ. For $\psi=1$, the optimal shape is reached and stress concentrations are predicted to disappear.

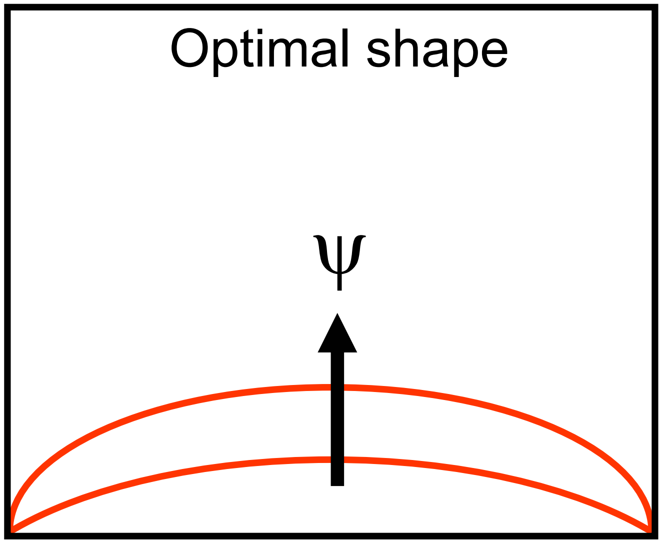
Creating optimal surface shape in atomistic simulation



Strategy: Displace atoms held rigid to achieve smooth surface shape

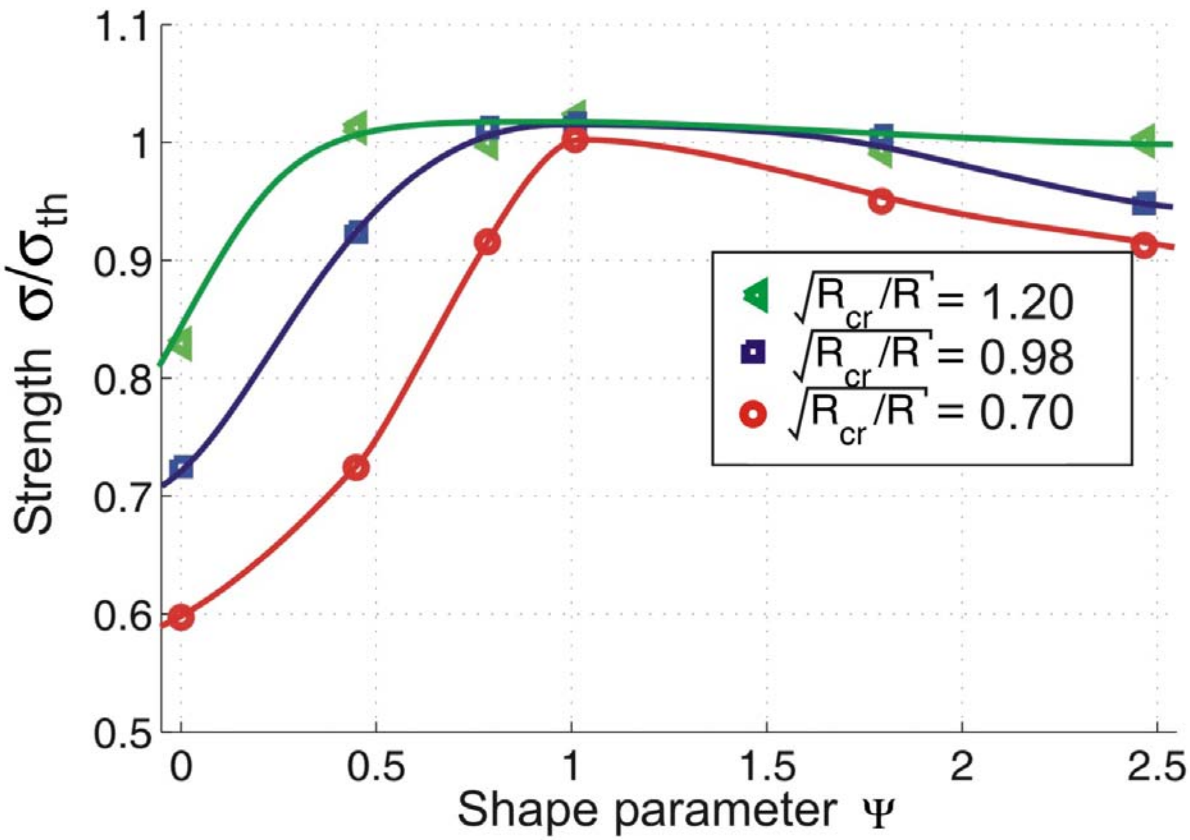
Stress distribution at varying shape





ψ=1: 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.

Discussion and conclusion

- 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

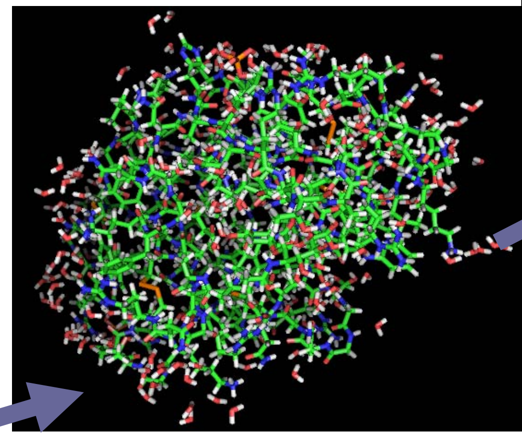
Structure-function relationship across hierarchies of scales

• Biological materials show enormous complexity

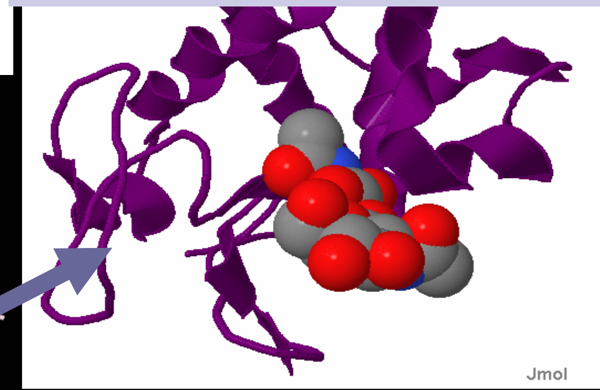
• Represents the frontier of research to sustain and evolve human life

Secondary, tertiary structure

1E-8..1E-7 m



Structure/ Function
(Elasticity
Fracture properties)

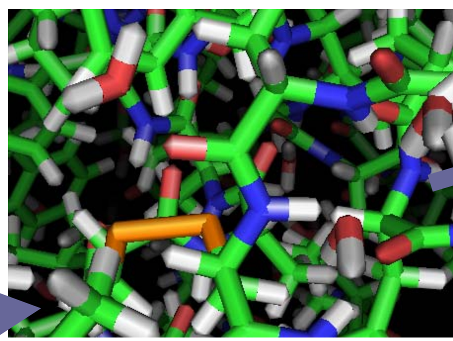


Quaternary structure

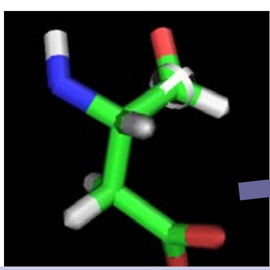
1E-7..1E-6 m

Primary structure

1E-9..1E-8 m



1E-10 m



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

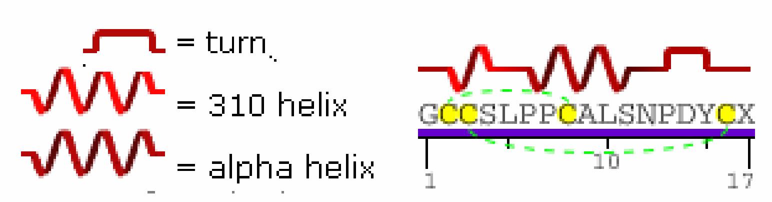
Example:
Mutations

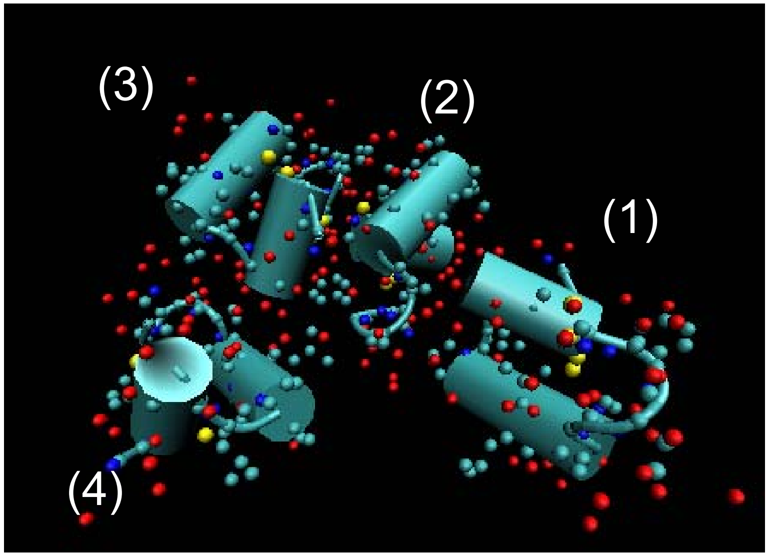
Scale-specific versus interaction properties

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 2_1 2_1 2_1 (orthorombic)
4 proteins per unit cell



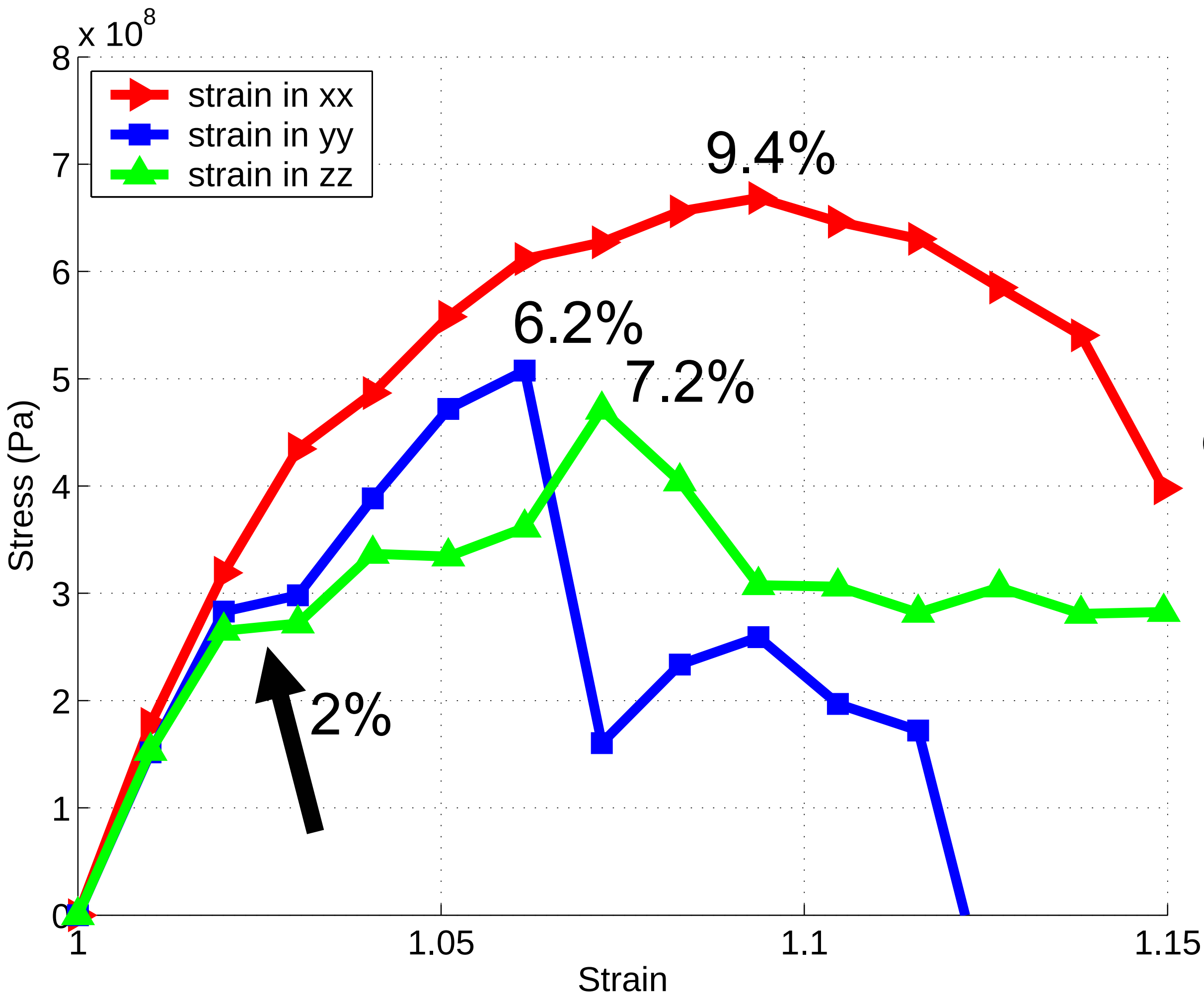


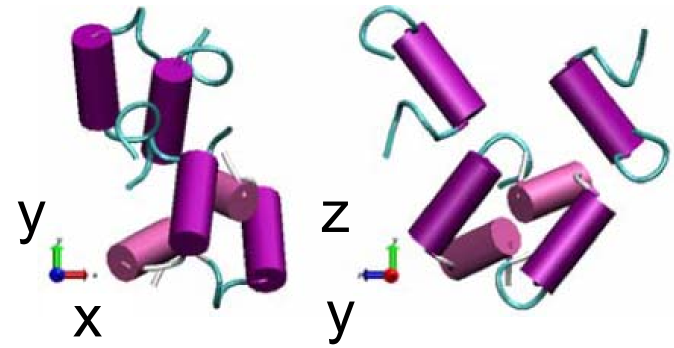
Goals

- 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



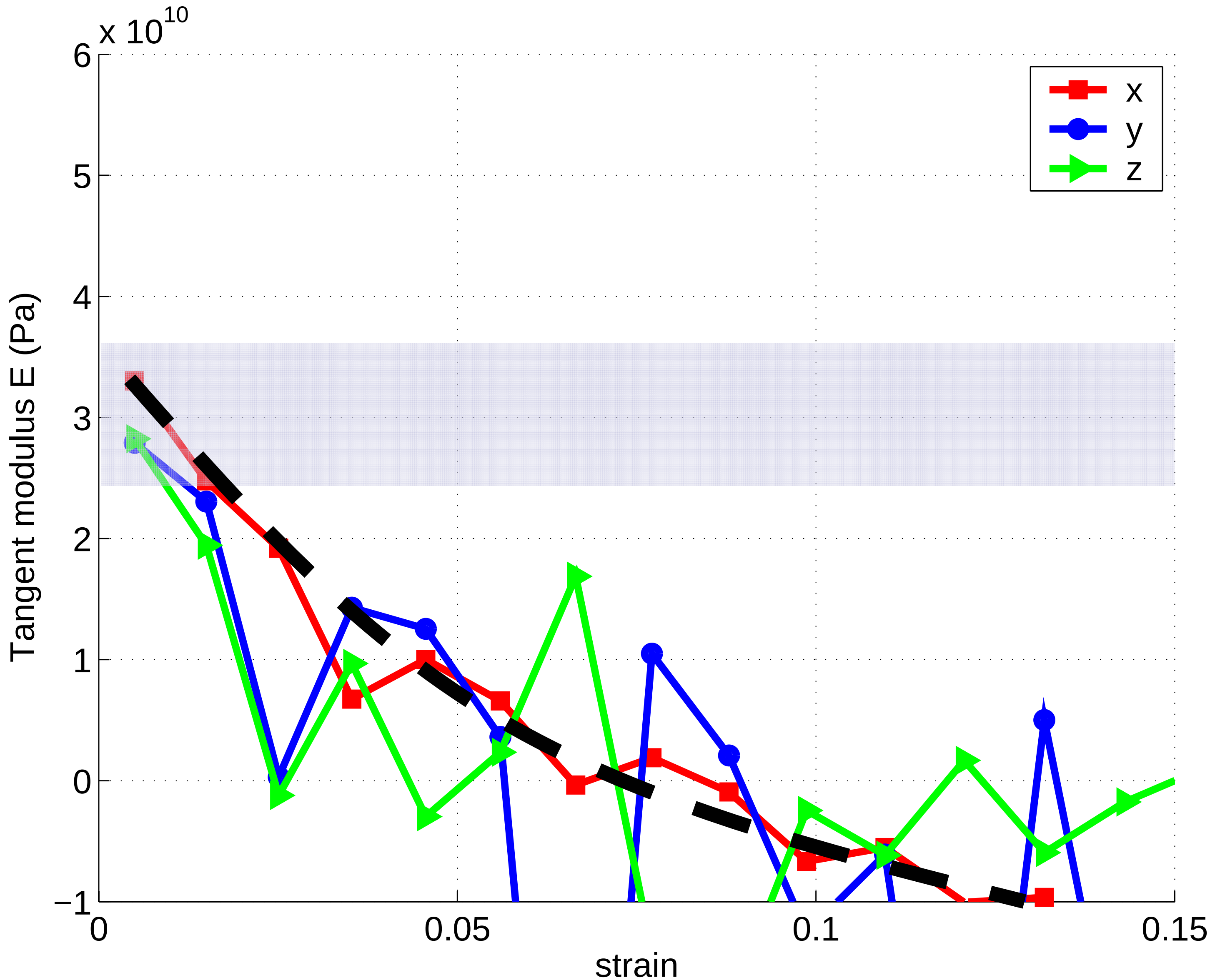


Fracture surface energy for different crystal planes

- (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_α during deformation

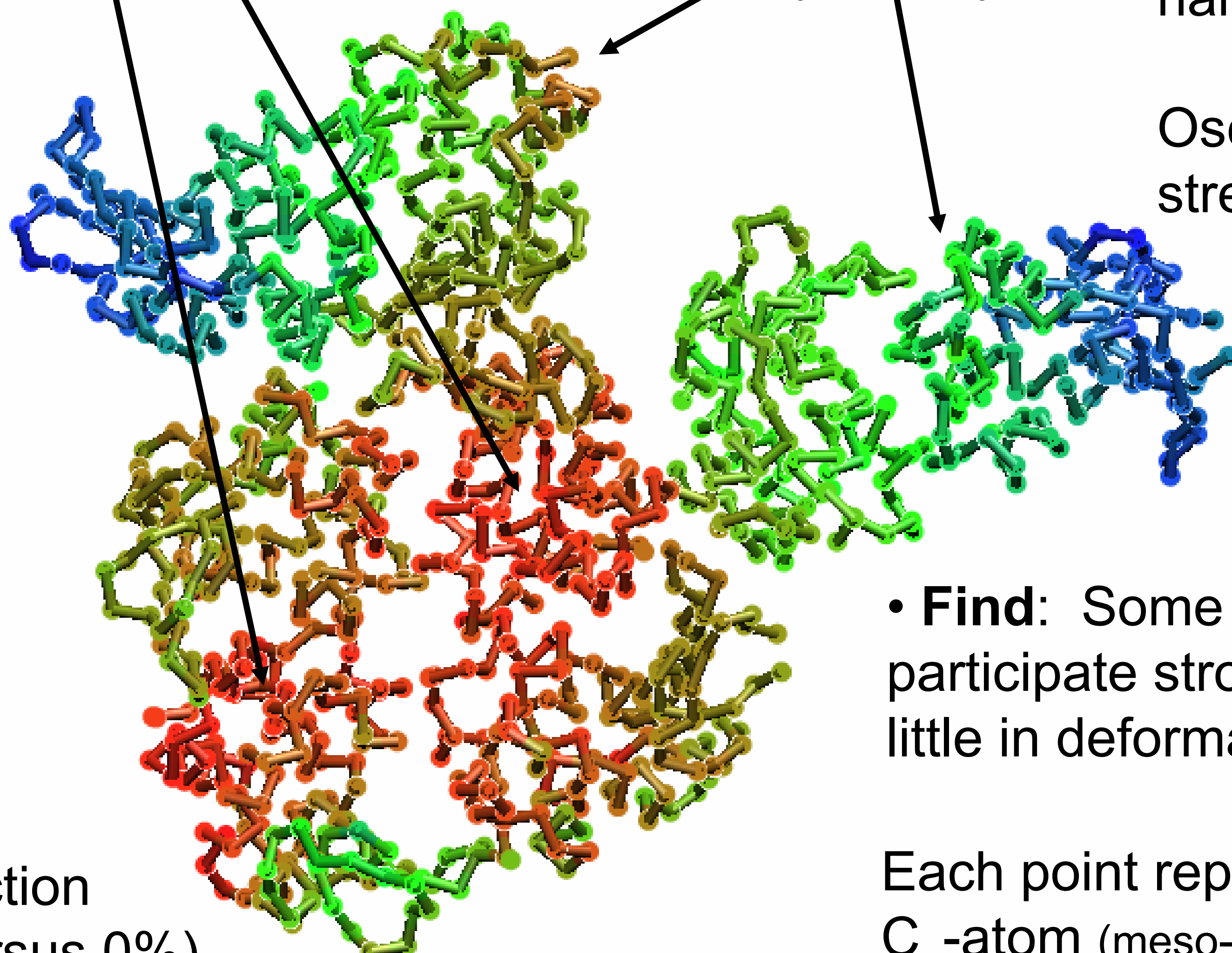
Hotspots of deformation (red)

8 proteins/unit cell

Symmetry

Length scale of a few nanometers

Oscillations of stress



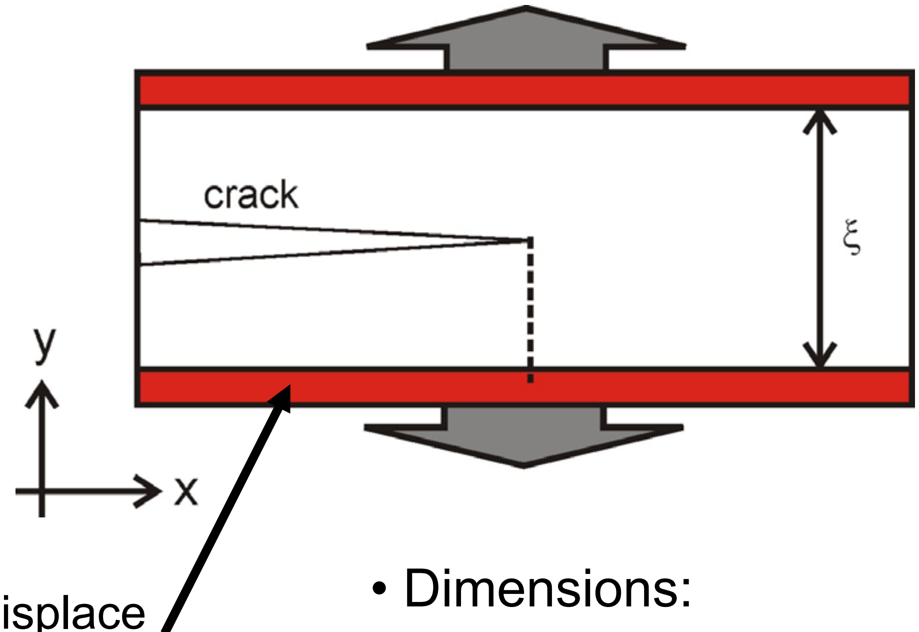
• **Find**: Some domains participate strongly, others little in deformation

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

Each point represents a C_α-atom (meso-view)

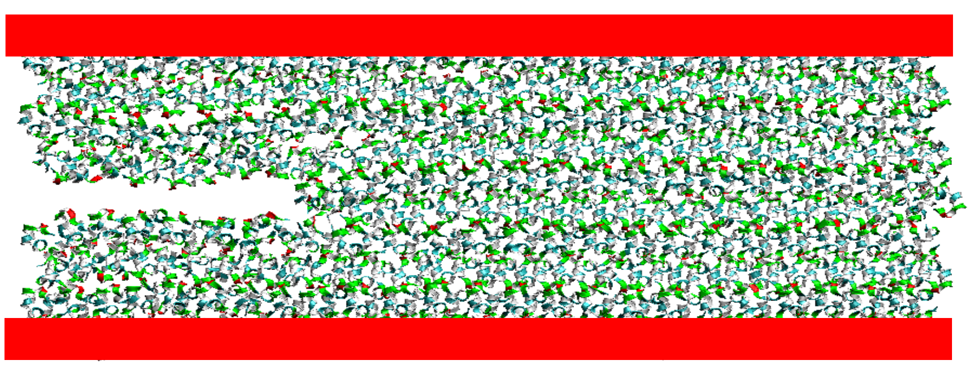
Cracking of protein crystals

- 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



Displace atoms in red region at each load increment

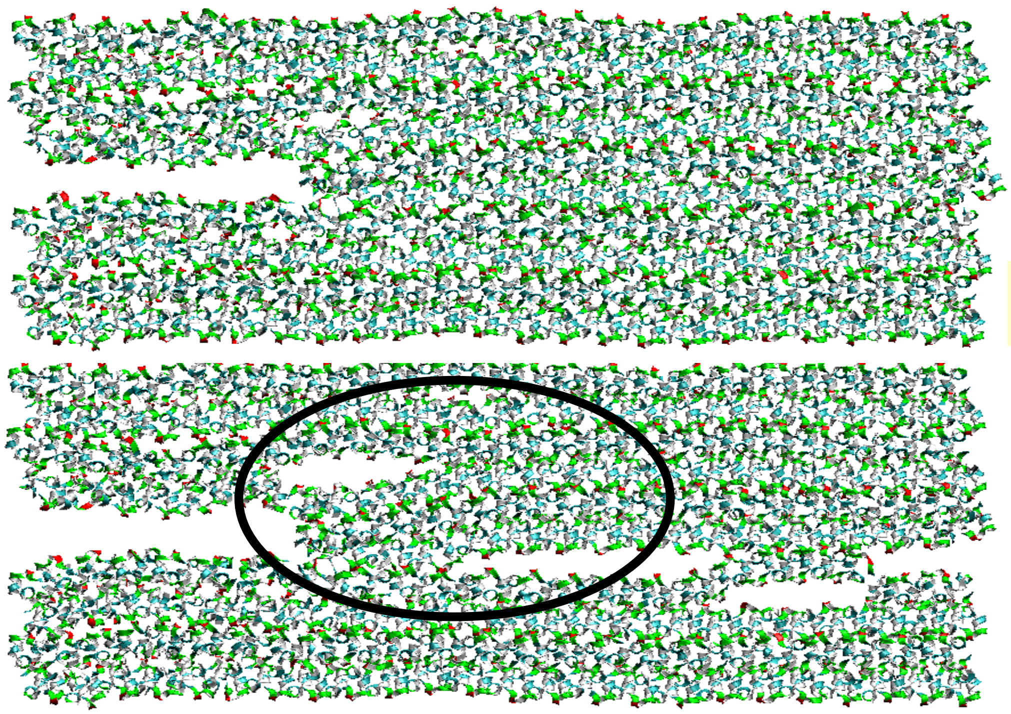
- Dimensions: 12 nm x 30 nm
- Ca. 130,000 atoms



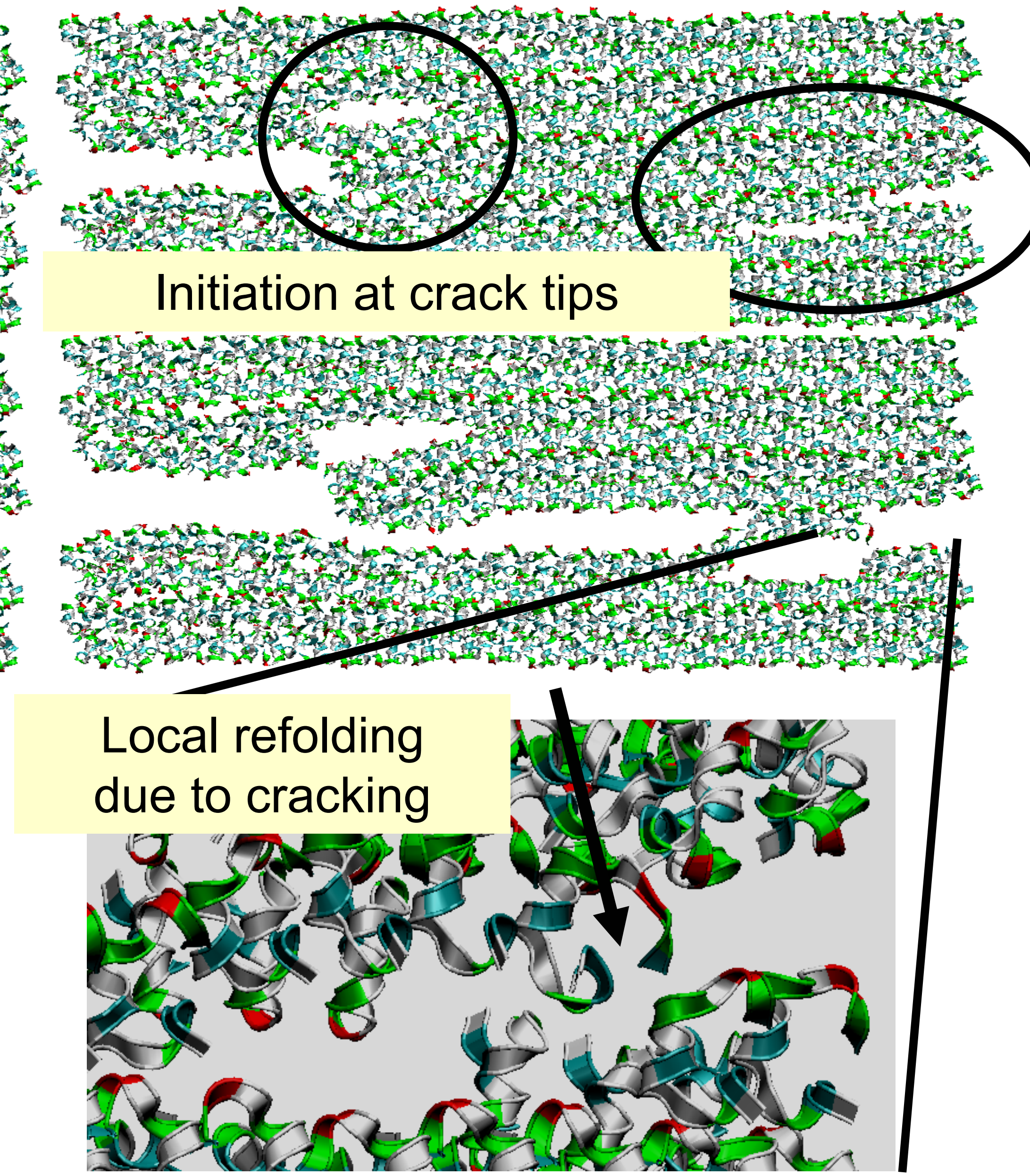
$$\varepsilon_f = \sqrt{\frac{4\gamma}{E\xi(1-\nu^2)}}$$

$$\varepsilon_f^{theory} \approx 5\%$$

Crack dynamics in protein crystals



Coalescence of cracks



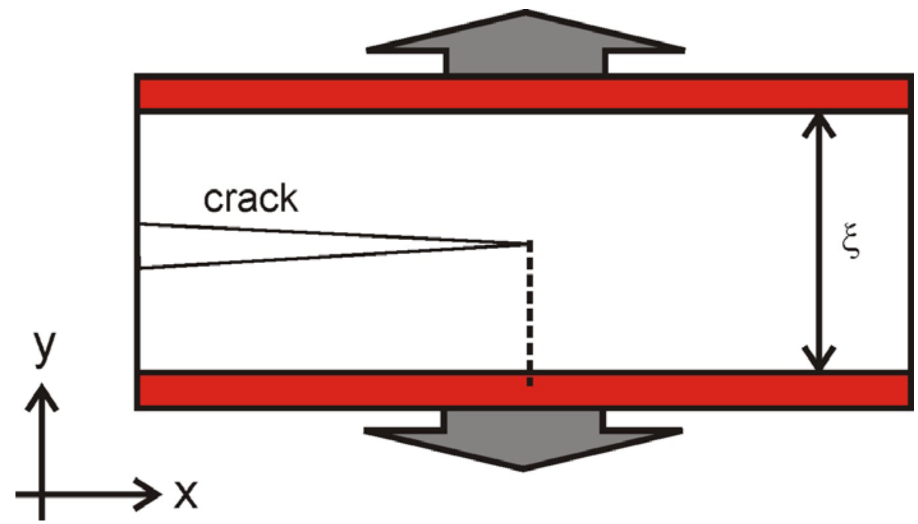
Comparison fracture initiation theory-MD simulation

$$\varepsilon_f^{MD} \approx 12\% \qquad \varepsilon_f^{theory} \approx 5\%$$

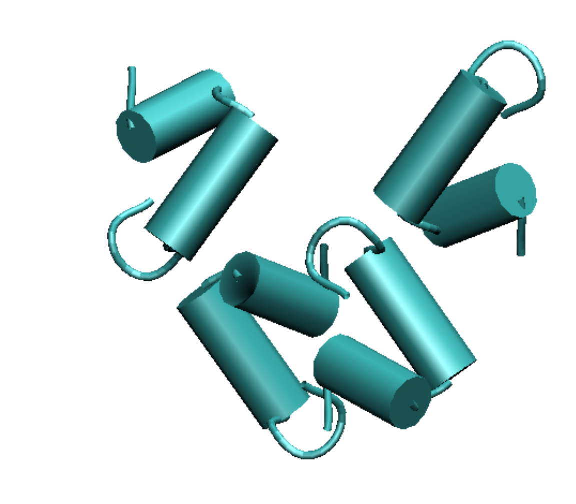
Nano-protein crystals can be flaw tolerant

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

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



1AKG



Cell size ≈ 2.9 nm
Thus: ~ 4 layers thickness

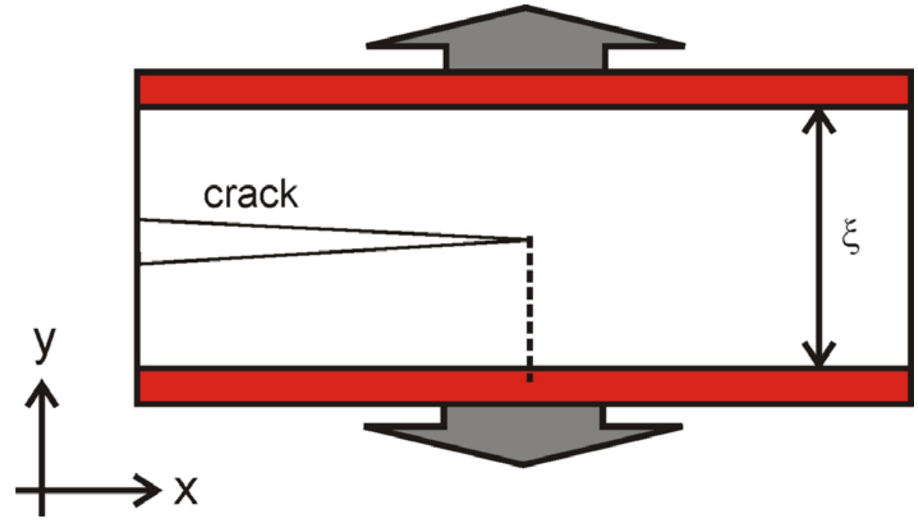
- Design a protein crystal such that the critical length scale is maximized
- Possible objectives:
  - Make $\sigma_{\max}$ small
  - Make γ and E large

- Possible approaches: AA mutations, structural change, chemistry…..

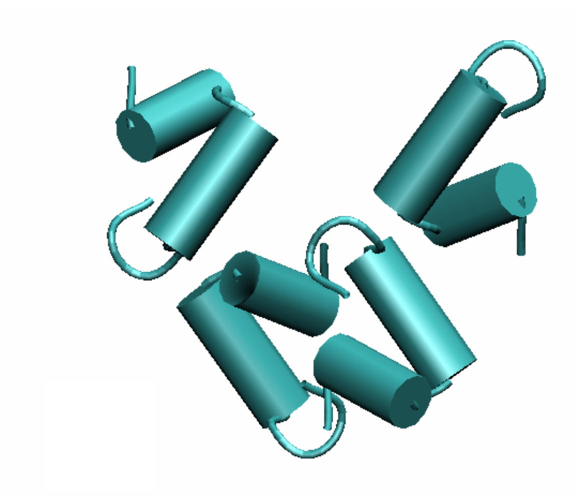
Nano-protein crystals can be flaw tolerant

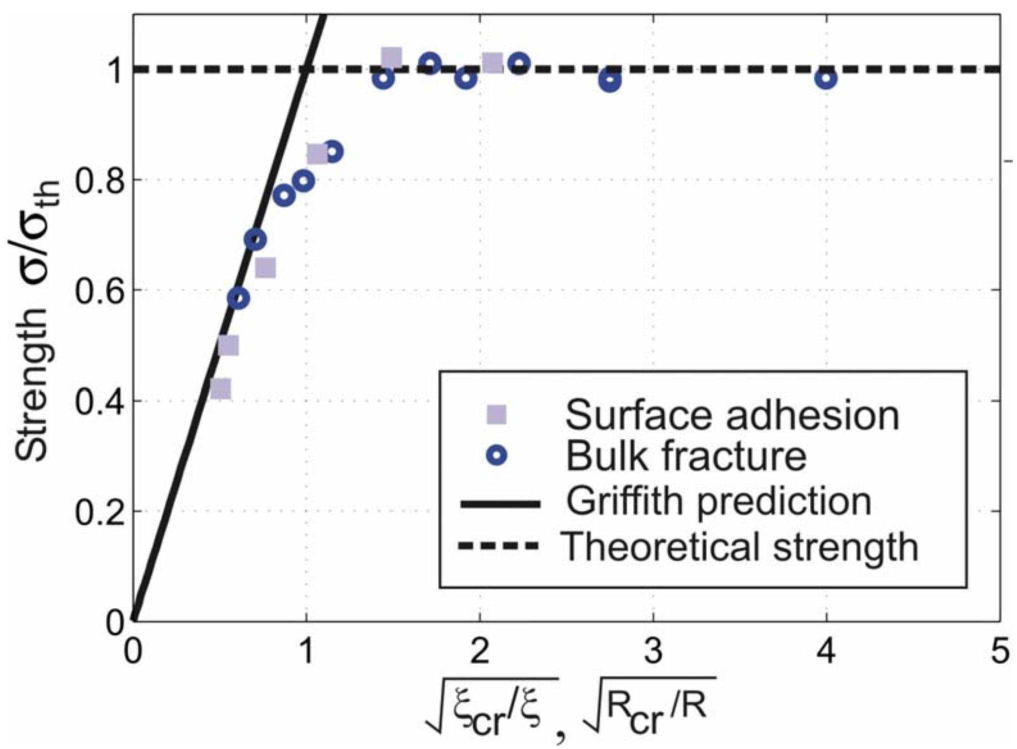
$$h_{cr} \propto \frac{\gamma E}{\sigma_{\max}^2} \approx 13\,\mathrm{nm}$$

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



1AKG

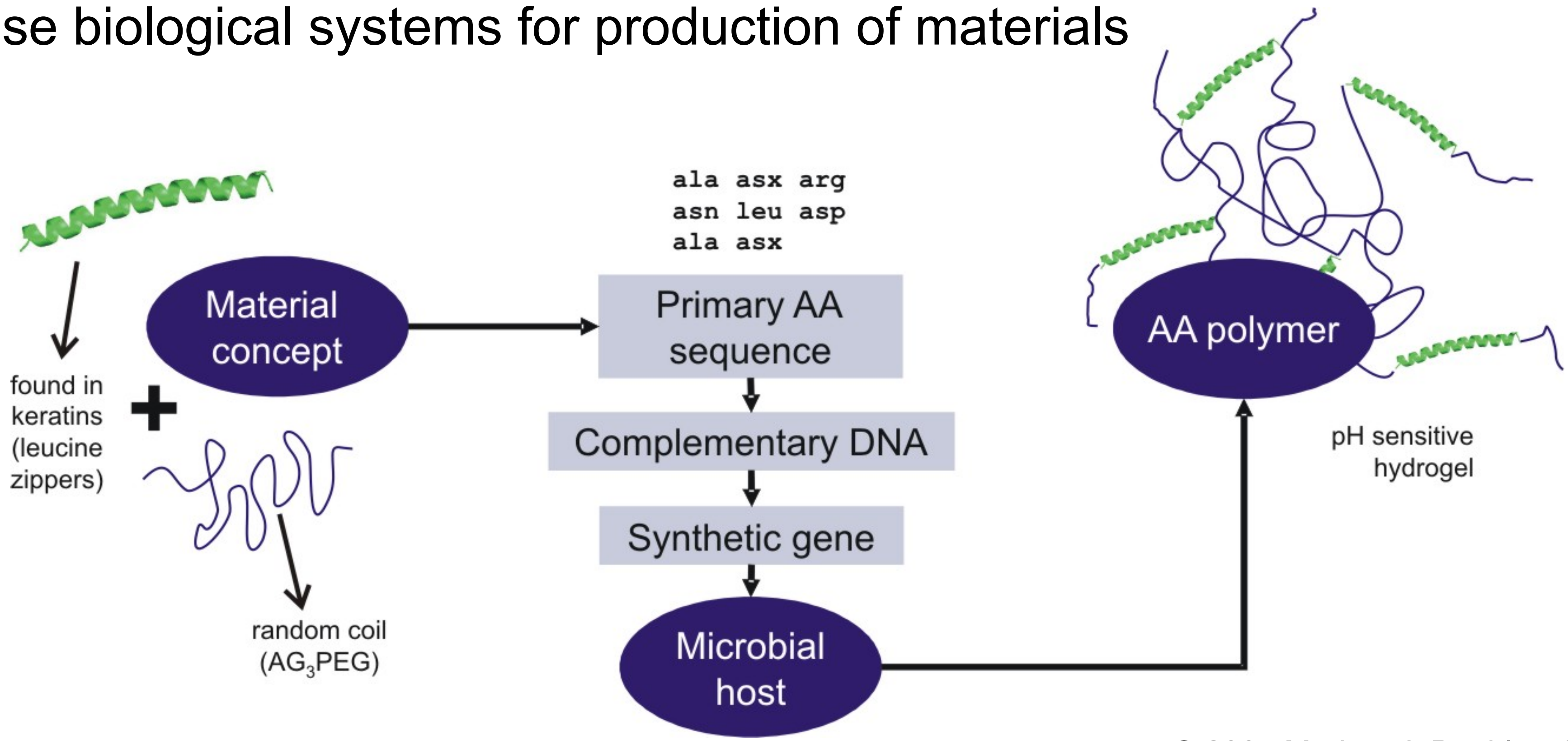




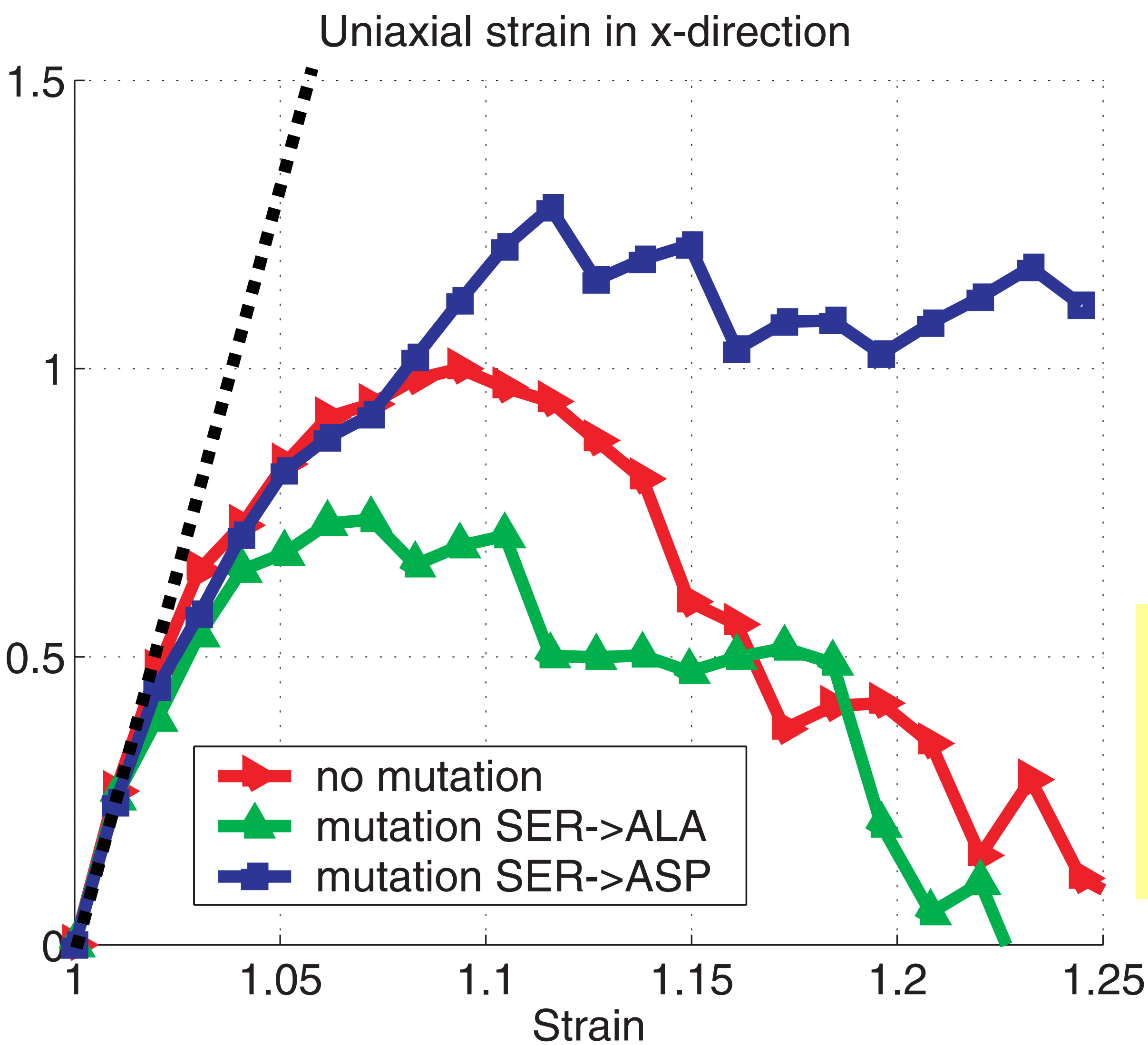
Cell size ≈ 2.9 nm
Thus: ~ 4 layers thickness

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

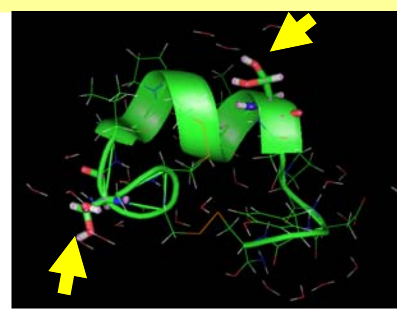


Effect of double point mutations on elasticity of protein crystals*



* α–Conotoxin PnIB From Conus Pennaceus

- 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

Protein engineering to design flaw-tolerant crystals

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

$$h_{cr} \sim \frac{\gamma E}{\sigma^2_{\max}}$$

this provides a possible strategy to design flaw-tolerant materials

- For example, for the mutation SER→ALA,

$$h_{cr} = \frac{\gamma E}{\sigma^2_{\max}} \approx 208 \text{ nm}$$

- This represents a flaw-tolerant μm crystal

Summary and conclusions

- Upon nucleation at a critical load, we observe rapid propagation of the crack with cleavage along the initial crack plane; protein crystal starts to fails 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

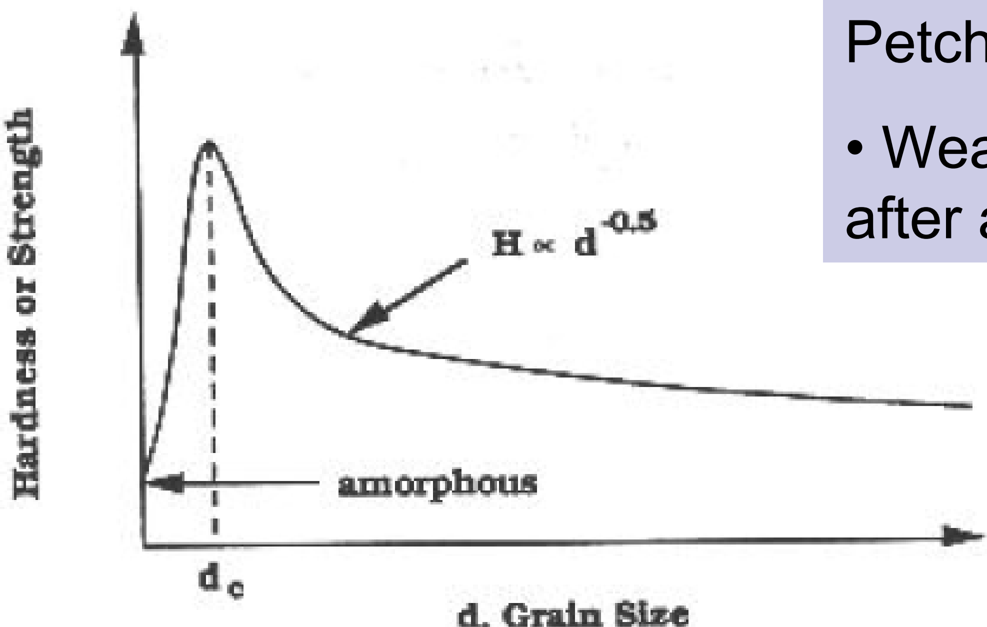
Fundamental length scales in nanocrystalline ductile materials

- Similar considerations as for brittle materials and adhesion systems apply also to ductile materials

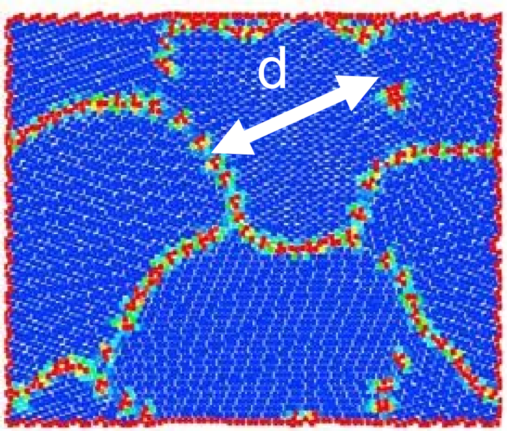
- In particular, the deformation mechanics of nanocrystalline materials has received significant attention over the past decade

• Strengthening at small grain size (Hall-Petch effect)

• Weakening at even smaller grain sizes after a peak



T.G. Nieh, J. Wadsworth, 1991



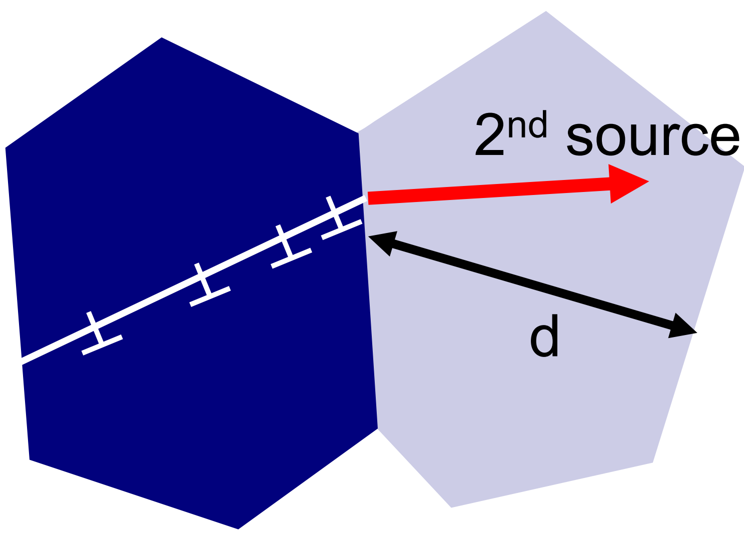
http://me.jhu.edu/~dwarner/index_files/image003.jpg

http://www.sc.doe.gov/bes/IWGN.Worldwide.Study/ch6.pdf

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:



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!*

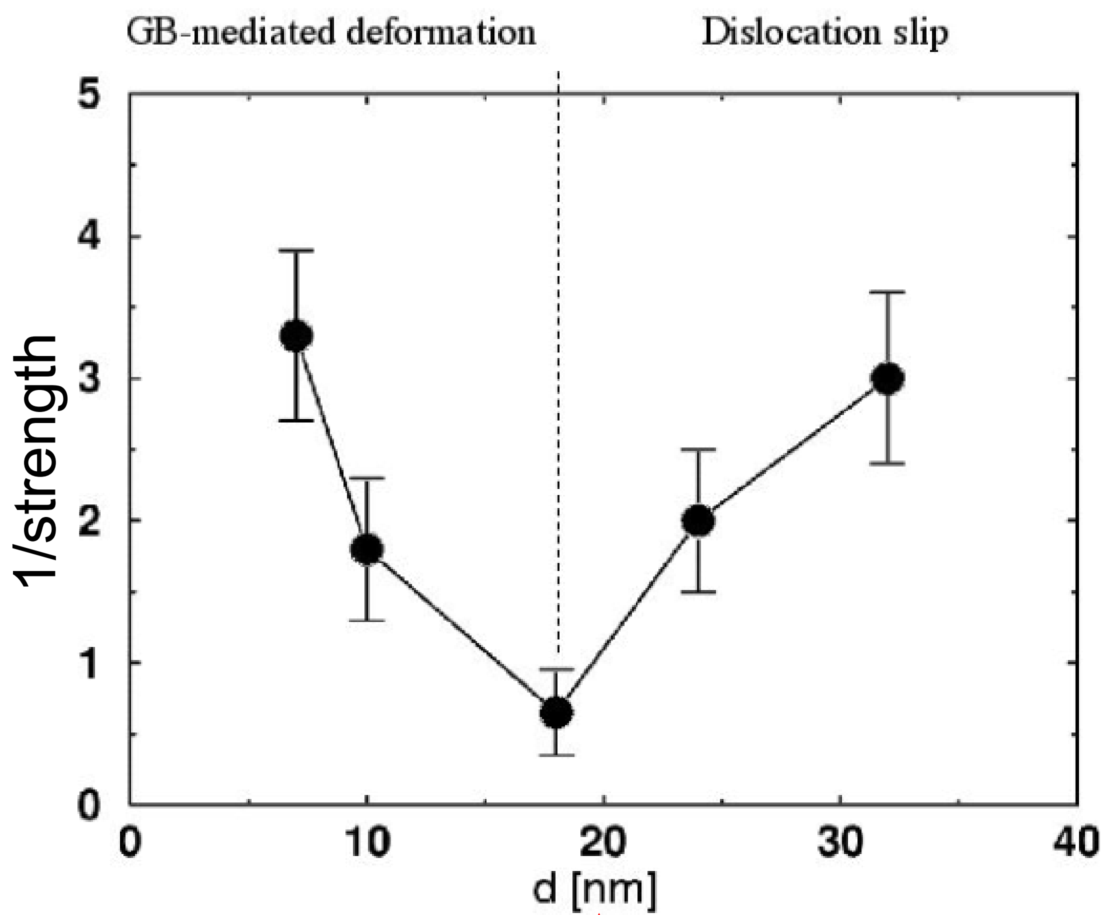
Al (MD model)

Different mechanisms have been proposed at nanoscale, including

• GB diffusion (even at low temperatures) – Wolf *et al*.

• GB sliding – Schiotz *et al*.

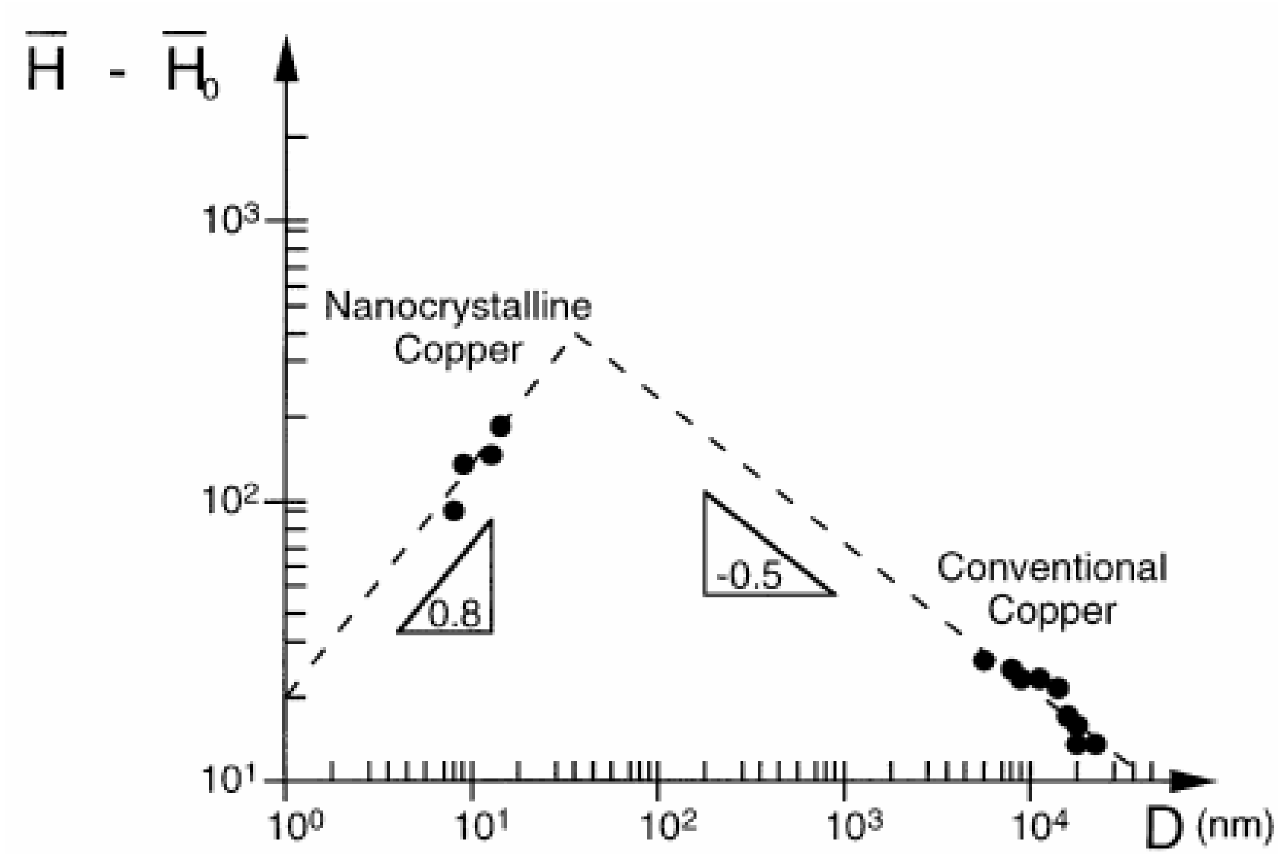
• GBs as sources for dislocations – van Swygenhoven, stable SF energy / unstable SF energy (shielding)



Strongest size depends on material

Yamakov *et al*., 2003, Schiotz et al., 2003
http://www.imprs-am.mpg.de/summerschool2003/wolf.pdf

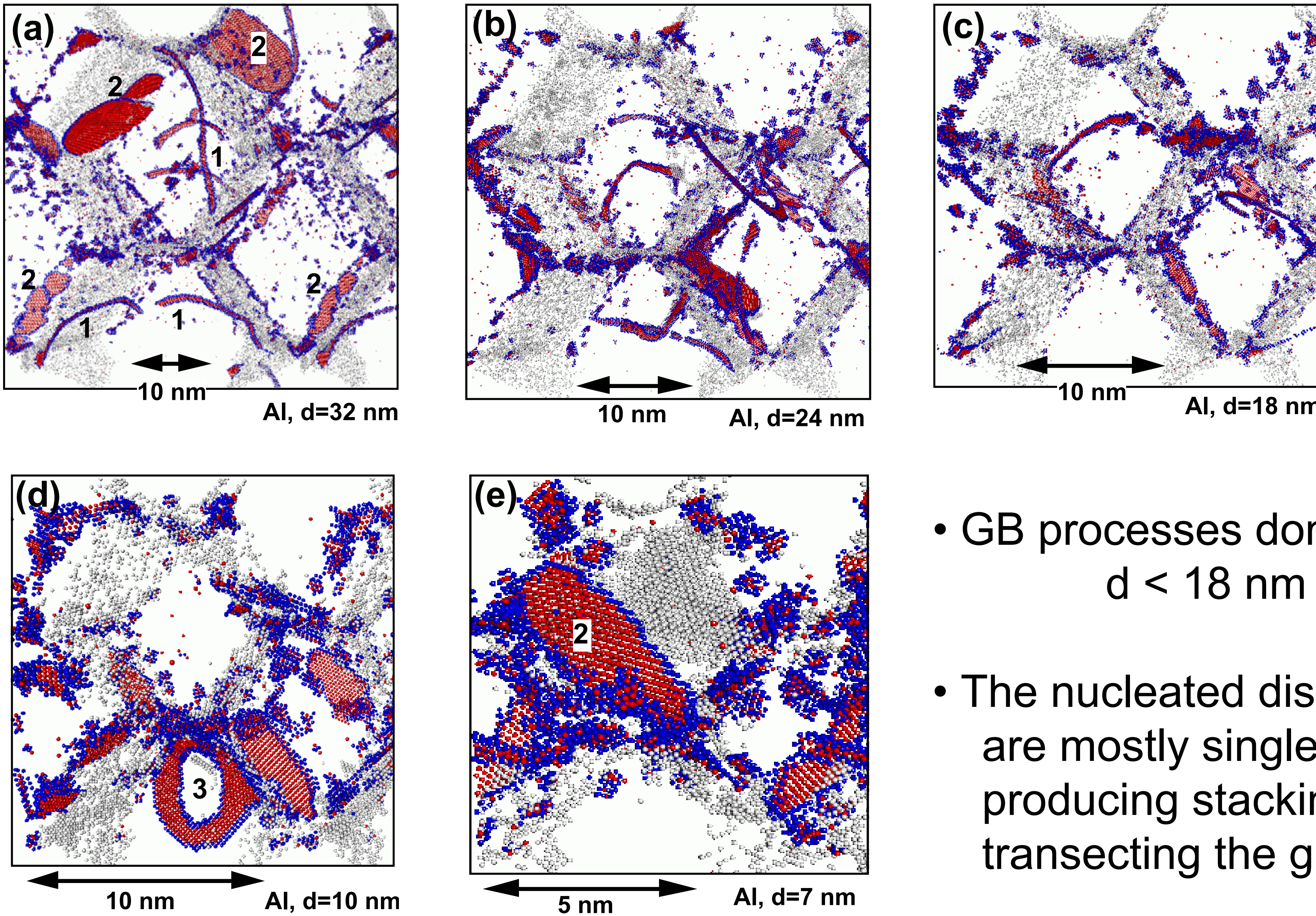
Fundamental length scales in nanocrystalline ductile materials



Chokshi *et al.*

From: E. Arzt

Suppression of dislocation activity with decreasing grain size



- GB processes dominate for d < 18 nm in Al
- The nucleated dislocations are mostly single partials producing stacking faults transecting the grains

D. Wolf *et al*., Nature Materials, 2004

The strongest size

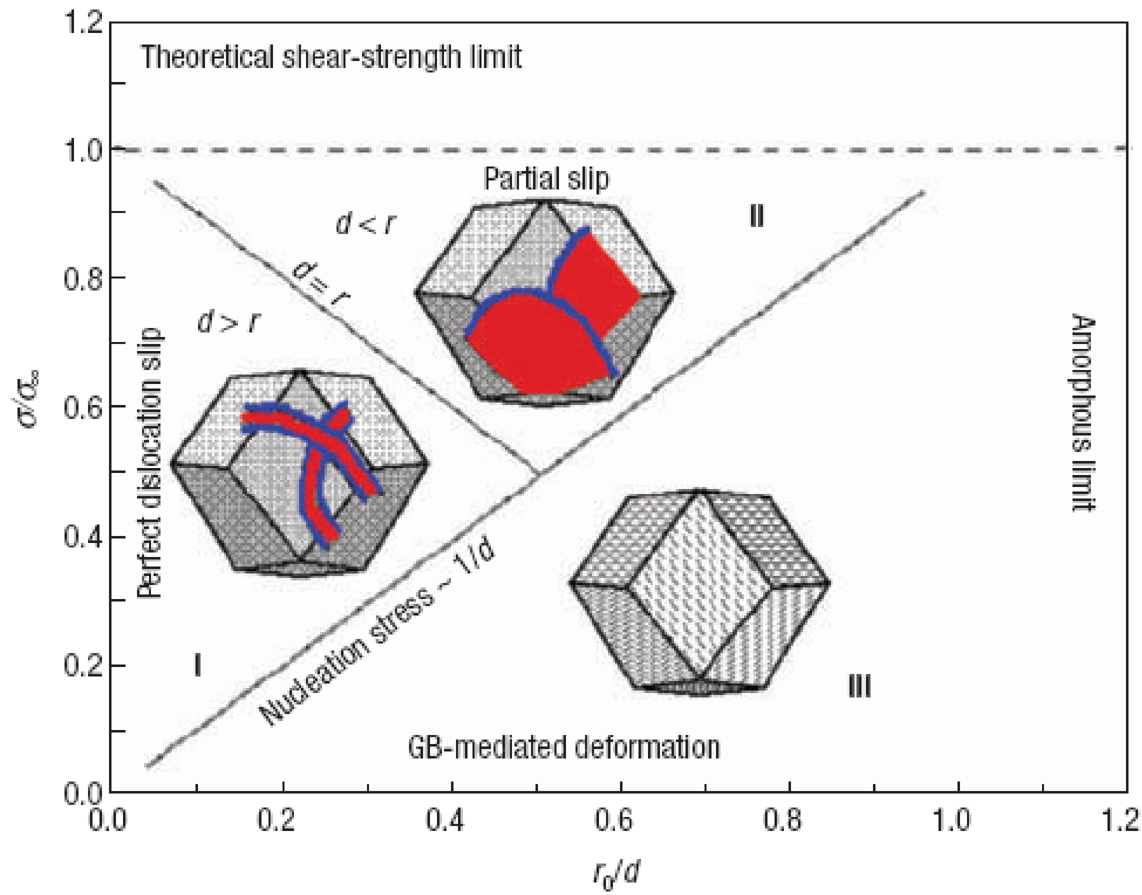
- Strongest size determined by grain size which becomes comparable to separation of two partial dislocations

$$r = \frac{r_0(\gamma)}{1-\sigma/\sigma_\infty(\gamma)}$$

(splitting distance of two partial dislocations)

D. Wolf *et al*., Nature Materials, 2004

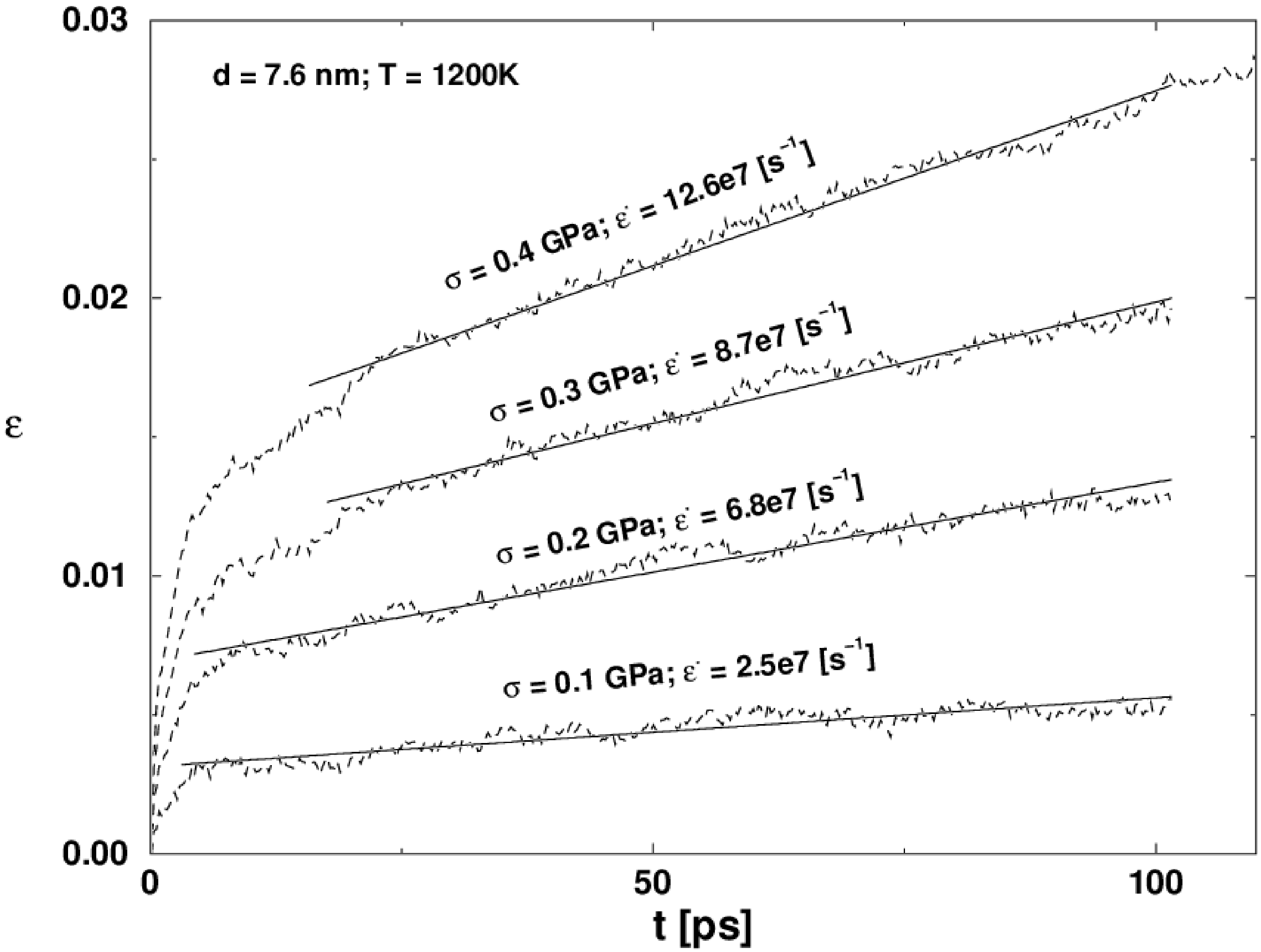
- This length scale *r* competes with *d* (grain size)



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

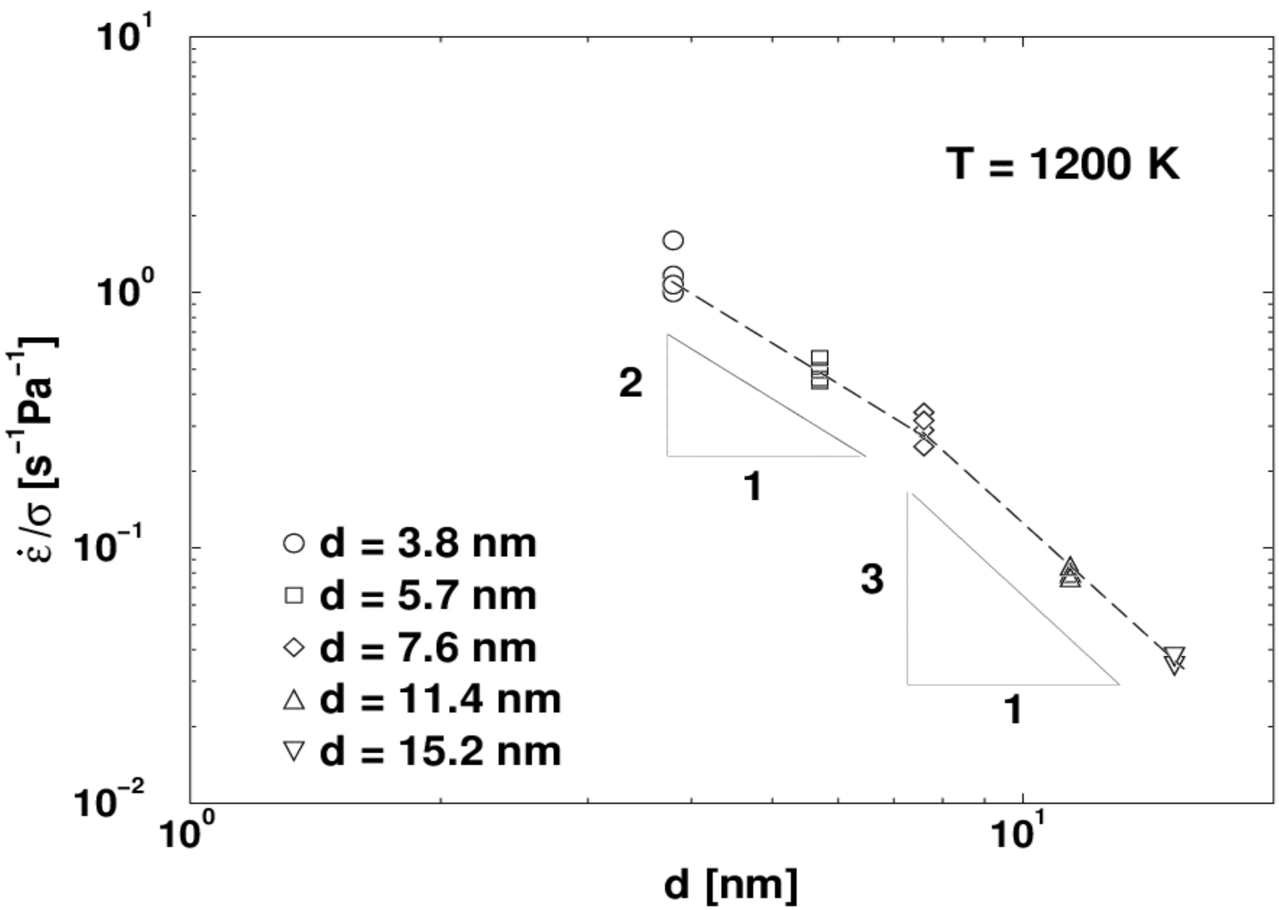
The map is expressed in reduced units of stress (σ/σ_∞) and inverse grain size (r_0/d).The parameters σ_∞ and r_0 are functions of the stacking-fault energy and the elastic properties of the material.

Steady-state creep under uniform tensile stress: Nanoscale



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

Grain size dependence



$$A\frac{\sigma\Omega_D}{k_B T}\frac{\delta_D D_{GB}}{d^3}$$

Large grain size (d >> d): creep rate ~ d^{-3} (Coble!)

Small grain size: (d ≈ d): creep rate ~ d^{-2} (Nabarro-Herring!)

Deformation in nanocrystalline materials

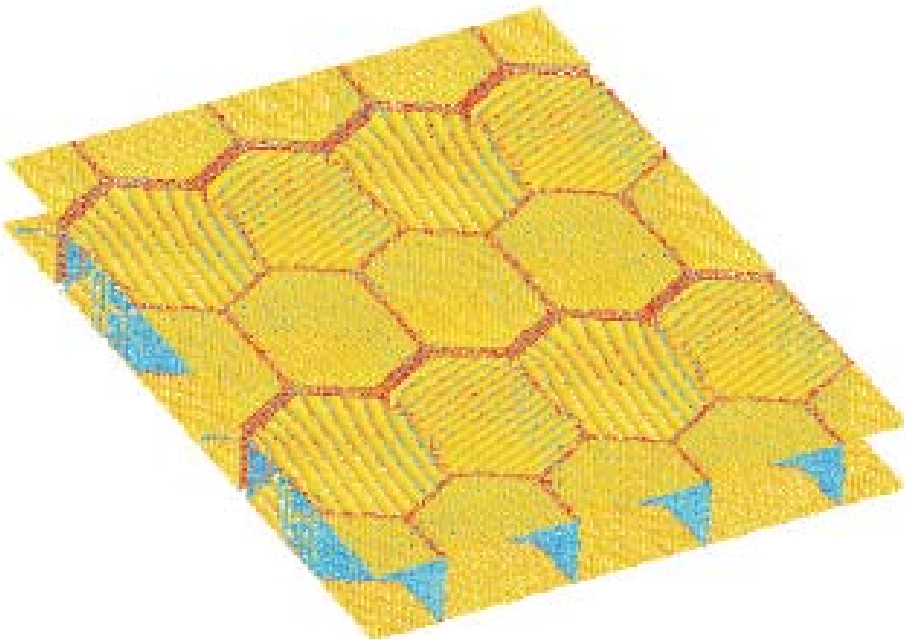
- **Review articles:**

  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

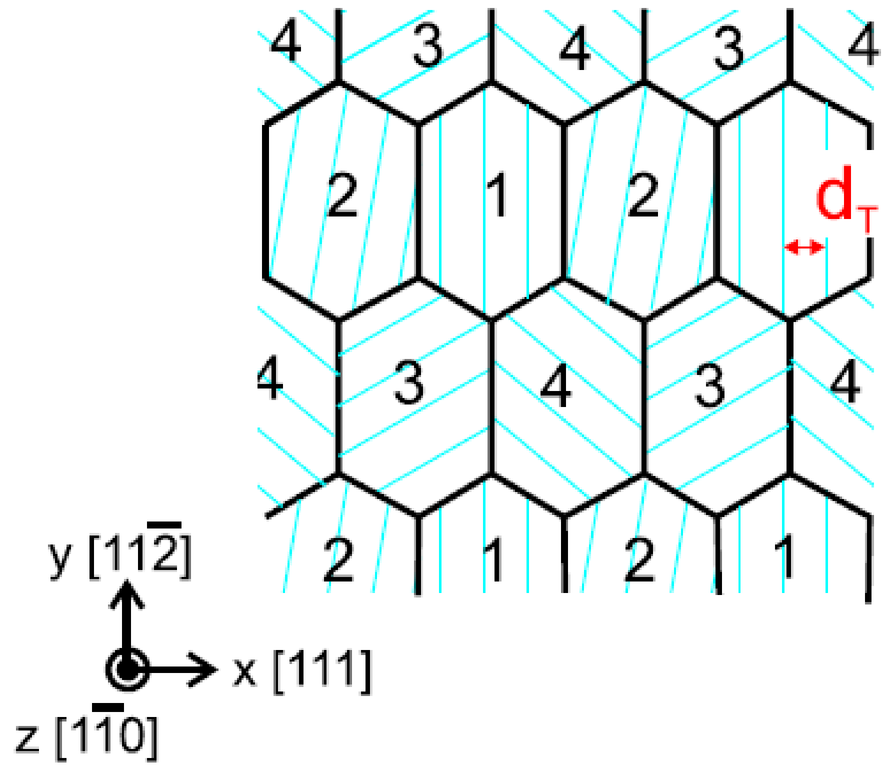
Nanocrystalline copper with twin lamella



3D view

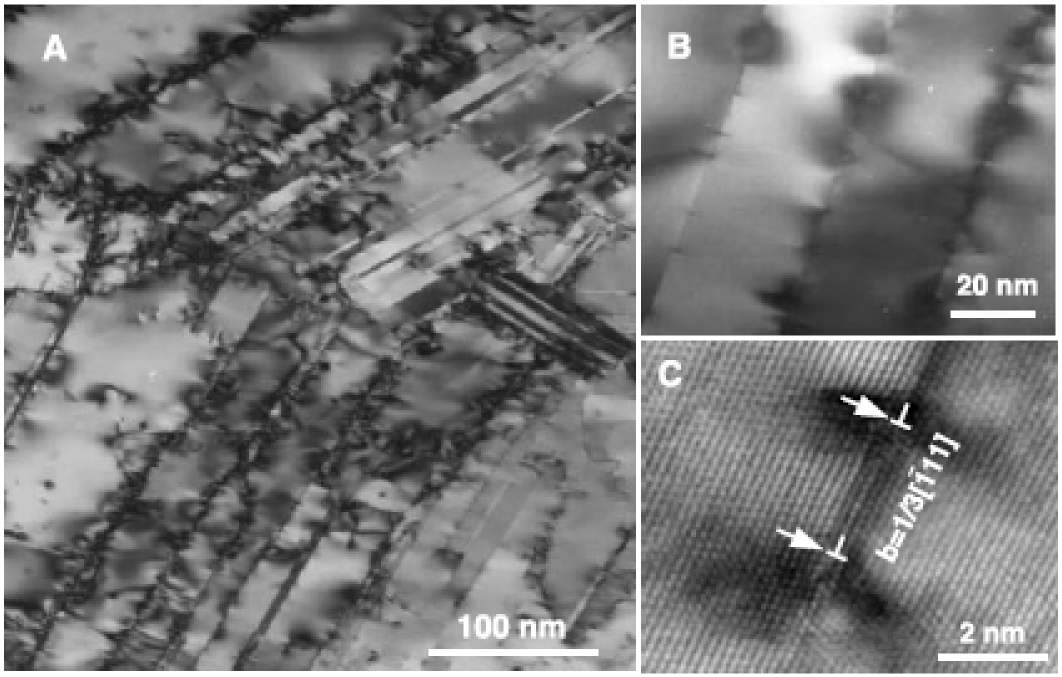
Copper nano-crystal with twin lamella grain boundary

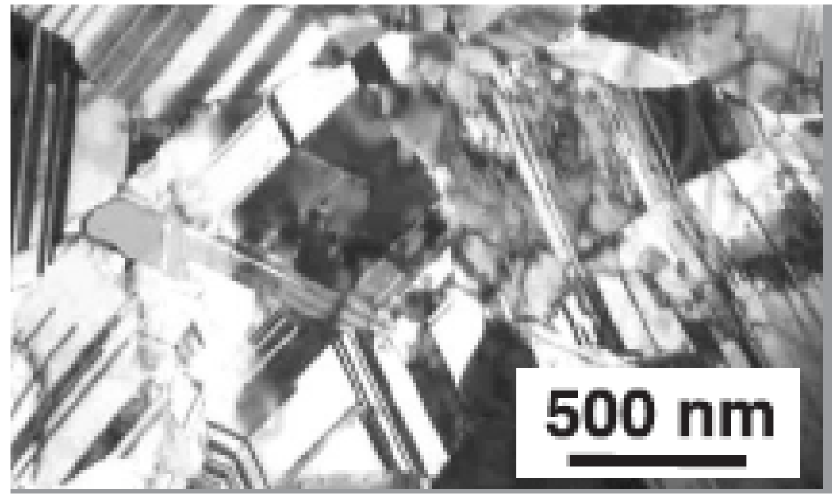
Synthesized in experiment by Lu *et al*., 2003 (Science)

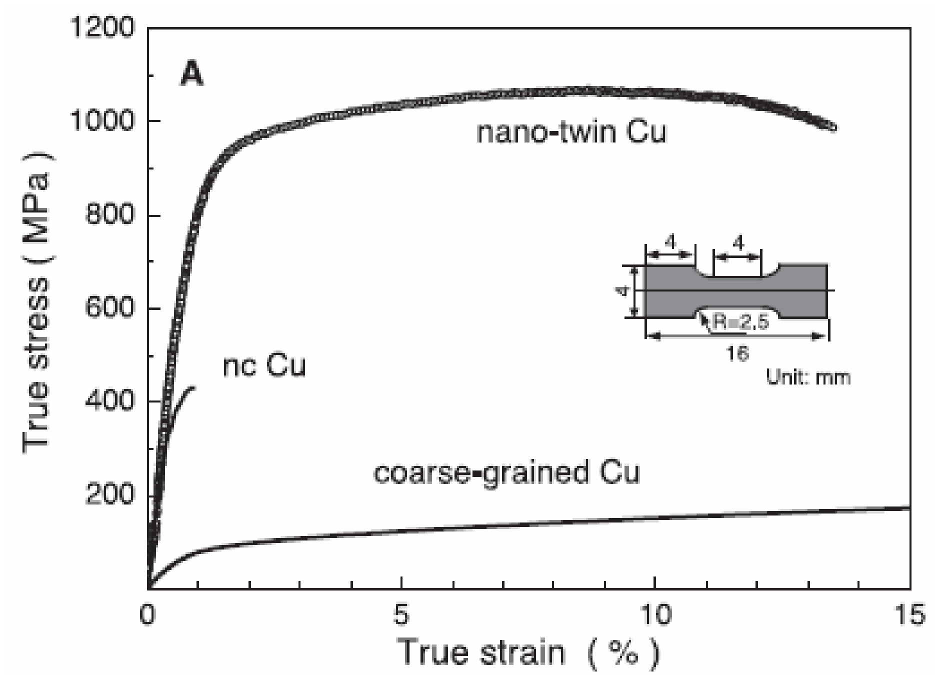


Nanocrystalline copper with twin lamella

Nanocrystalline copper with twin lamella



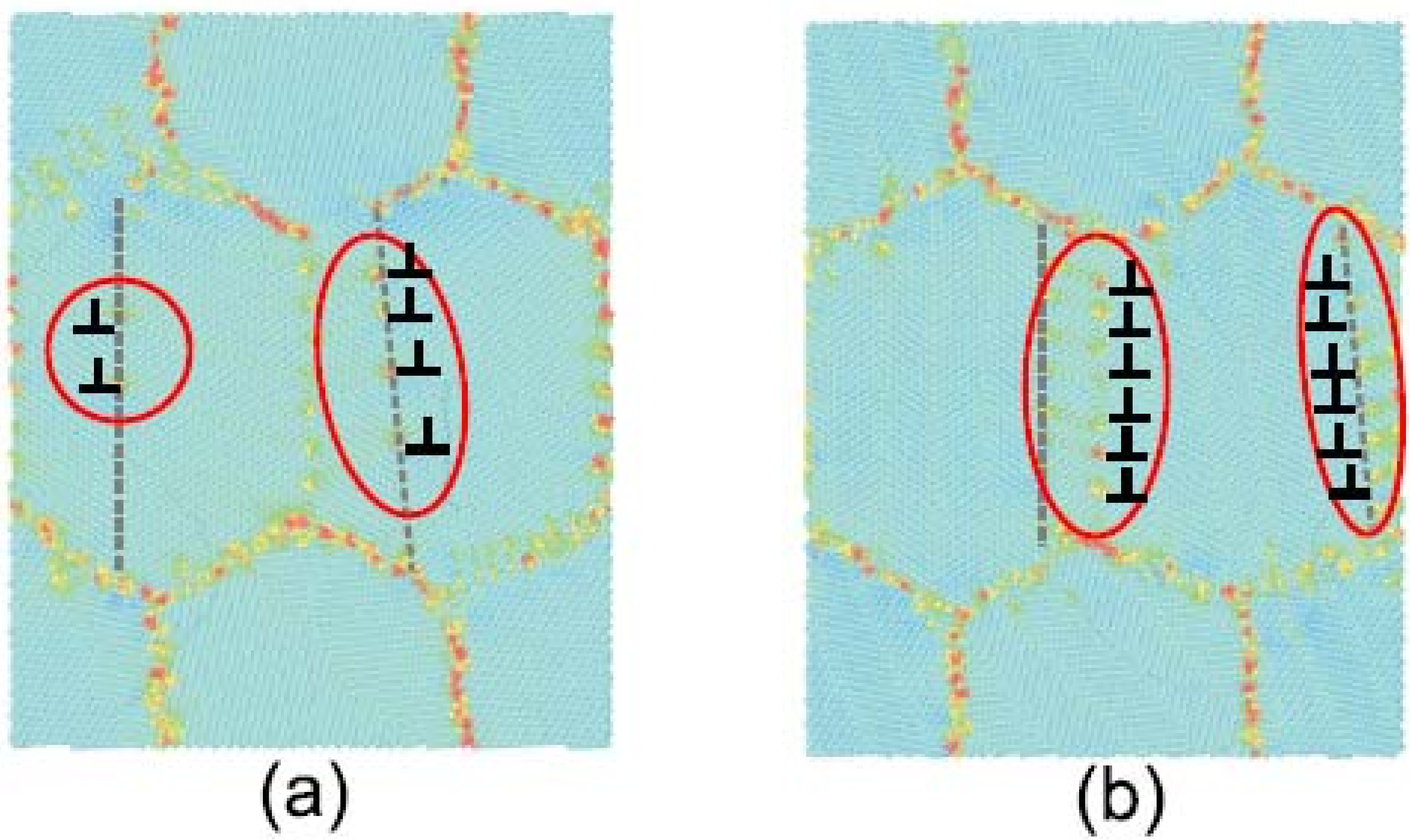




- Pileups of dislocations at grain boundaries and twin boundaries

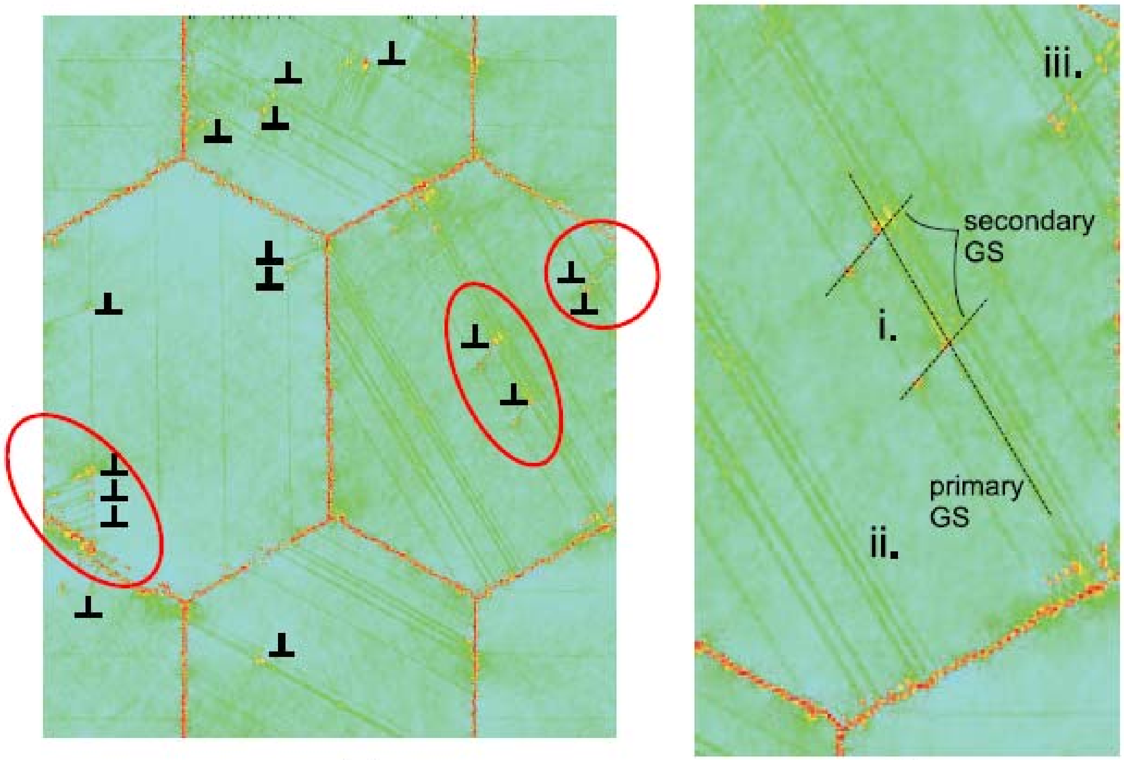
K. Lu *et al.*, Science, 2004

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~15 *nm* > *d*) and subplot (b) for thinner twin lamella (d_T~2.5 *nm* < *d*). Motion of dislocations is effectively hindered at twin grain boundaries in both cases

Nanocrystalline copper with twin lamella



(a) (b)

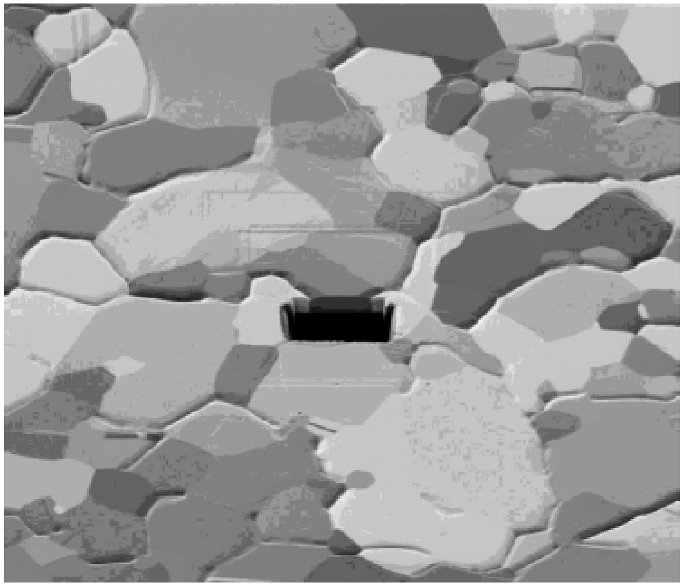
Simulation results of nanostructured material with twin lamella substructure under uniaxial loading for two different twin lamella thicknesses, all high-energy grain boundaries.

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

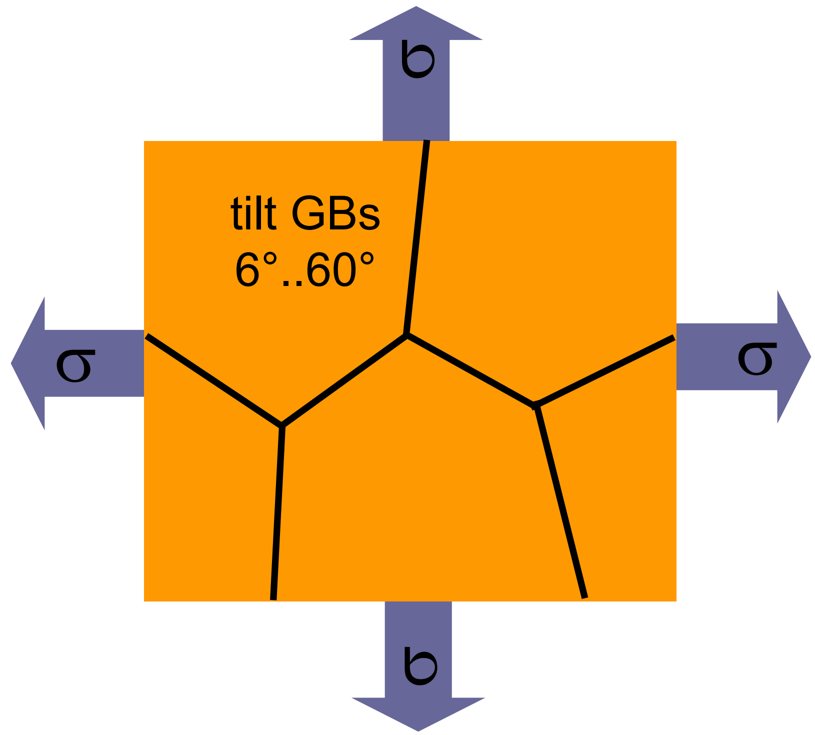
Example: Ultra thin copper films

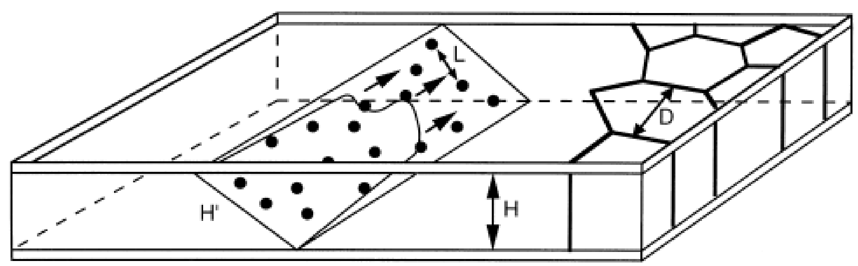


Courtesy Dirk Weiss, MIT

Polycrystalline thin metal film of copper grains (111) aligned

Schematic





• Biaxial loading by thermal mismatch of film substrate material: High stresses cause sev problems during operation of the device

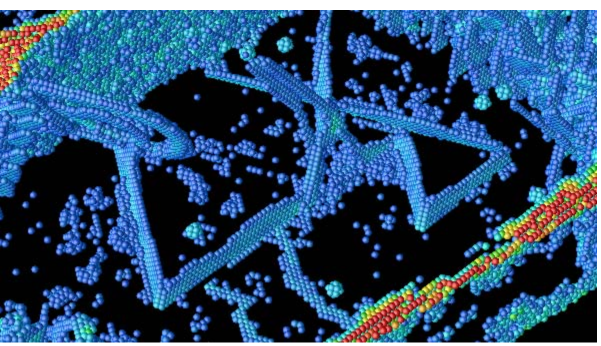
• Ultra thin, submicron copper films become critically important in next generation integrated circuits (see, e.g. *Scientific American*, April 2004), MEMS/NEMS

Introduction

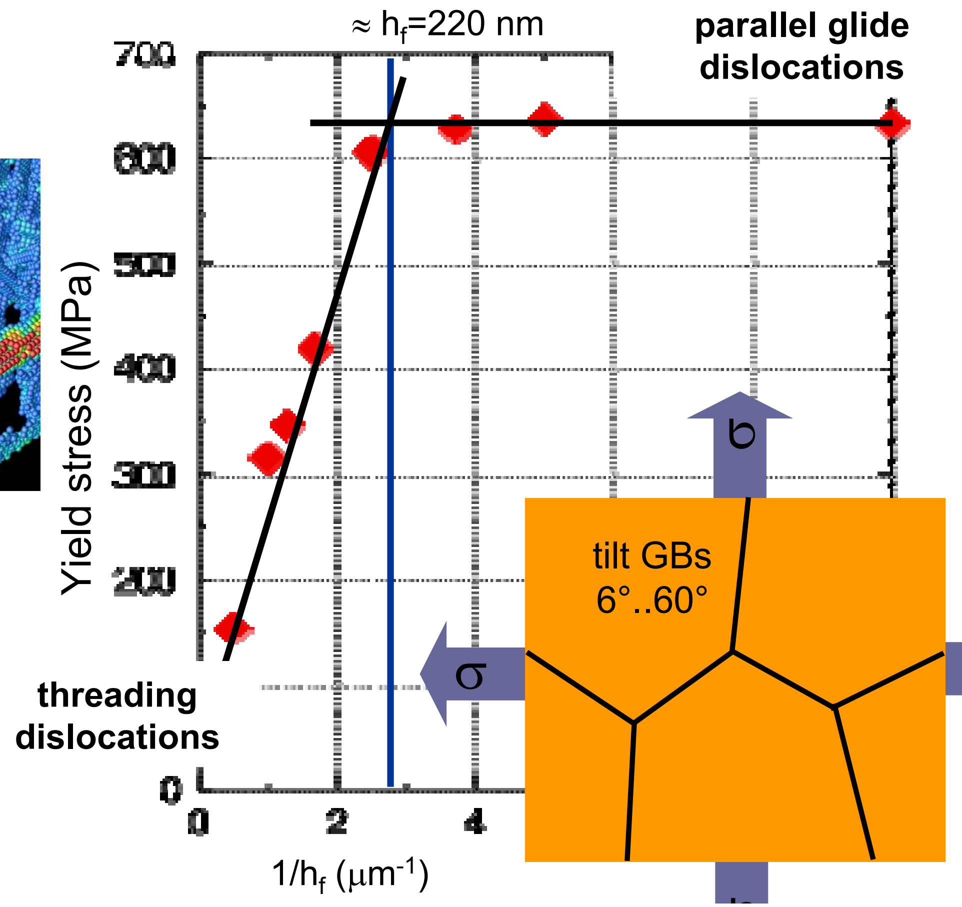
- Many materials show significant size effects re. their mechanical behavior
- For example, in thin films, dislocation behavior changes from threading dislocations (σ_Y~1/h) to parallel glide dislocations (σ_Y~const.) if the film thickness is reduced, along with a plateau in yield stress

Example: Deformation of ultra thin copper films dislocations/diffusion

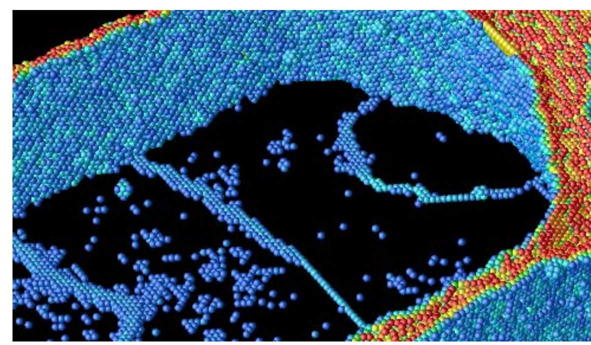
"Large"



- Threading dislocations (glide)



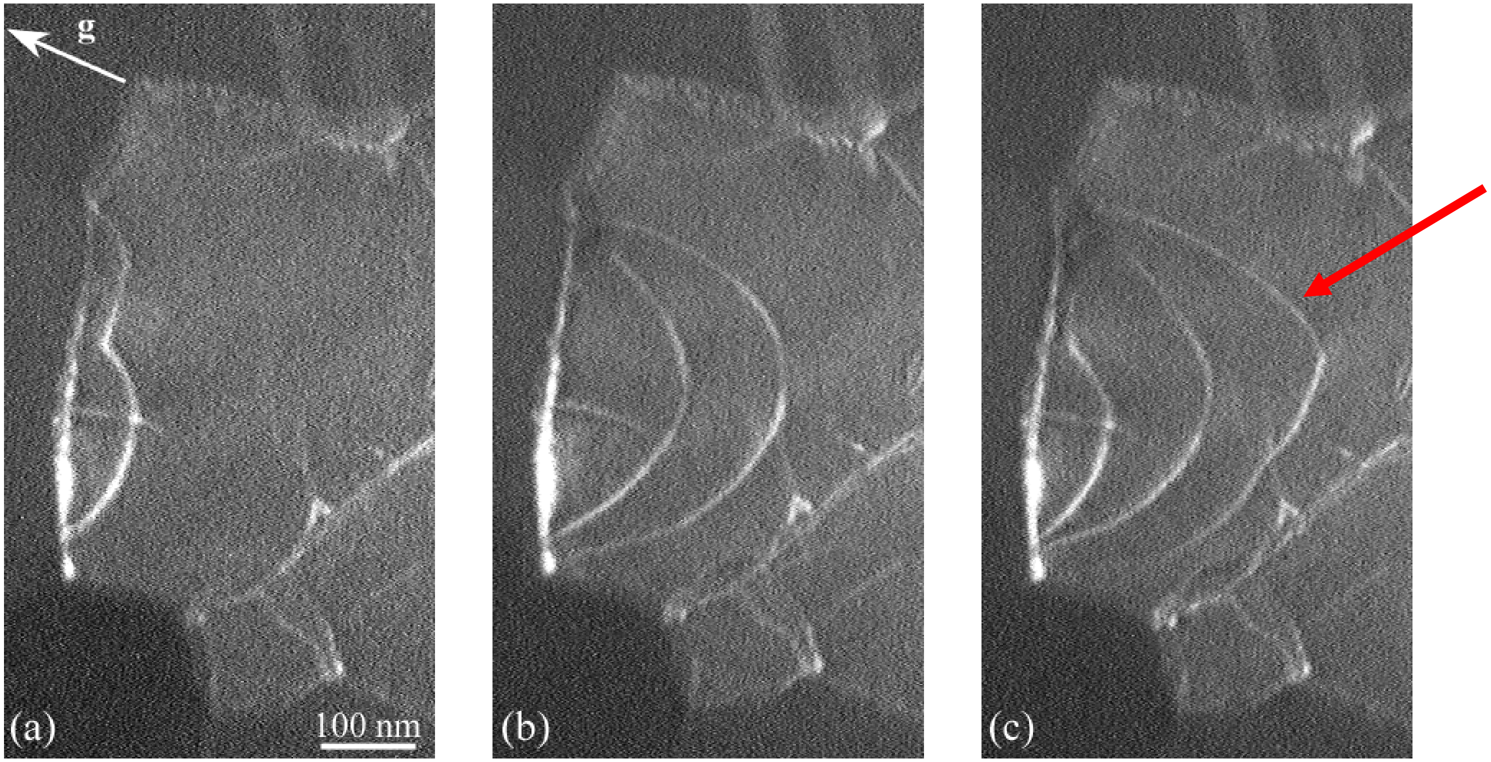
"Small"



- Diffusional creep
- Parallel glide dislocations

(Buehler et al., 2003-2005)

Experimental observation of parallel glide



(Dehm, Balk, von Blanckenhagen, Gumbsch, Arzt, 2002)

Plateau regime (suspected deformation mechanism)

- Surface and grain boundary diffusion with subsequent nucleation of dislocations on parallel slip planes (seen below h=400 nm)
- Sriving force: inhomogeneous stress through grain boundary diffusion (Gao, Zhang, Nix, Thompson, Arzt, 1999)

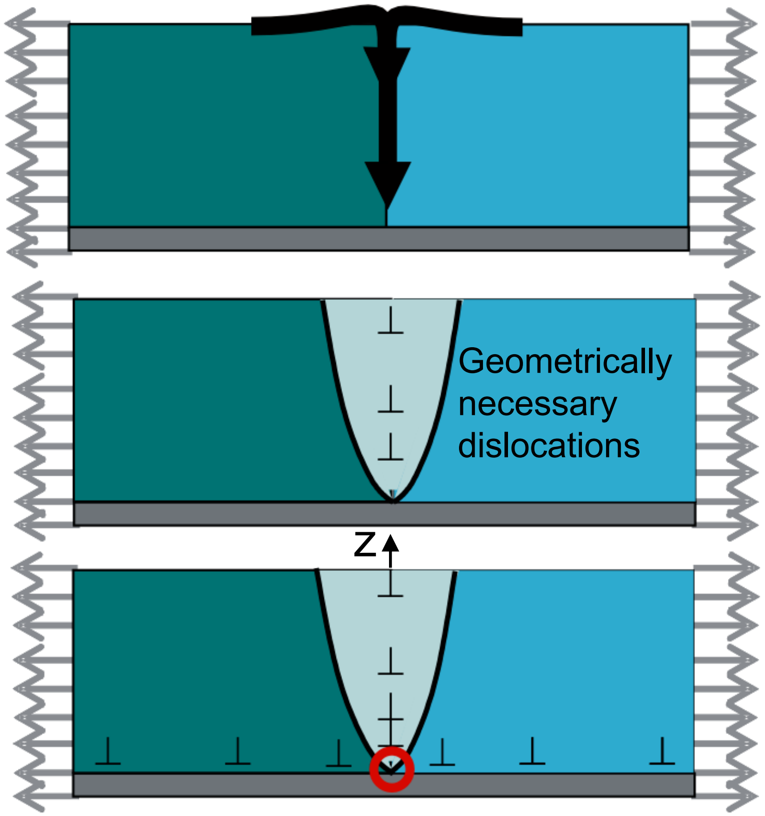
Continuum model: Constrained diffusional creep

Gao *et al.*, *Acta Mat.* (1999):

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 <u>parallel glide dislocations</u> at the root of the grain boundary



$$\frac{\partial \sigma_{gb}(z,t)}{\partial t} = \frac{E D_{gb} \delta_{gb} \Omega}{4\pi(1-\nu^2)\mathrm{k}T} \int_0^{h_f} S(z,\zeta) \frac{\partial^3 \sigma_{gb}(\zeta,t)}{\partial \zeta^3} \mathrm{d}\zeta$$

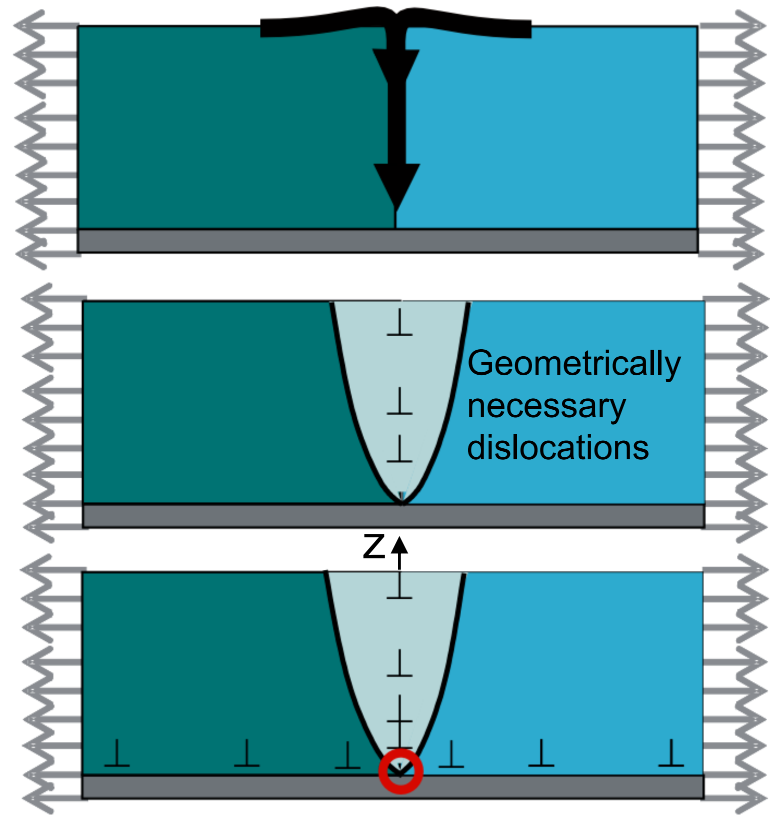
Continuum model: Constrained diffusional creep

Gao *et al.*, *Acta Mat.* (1999):

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

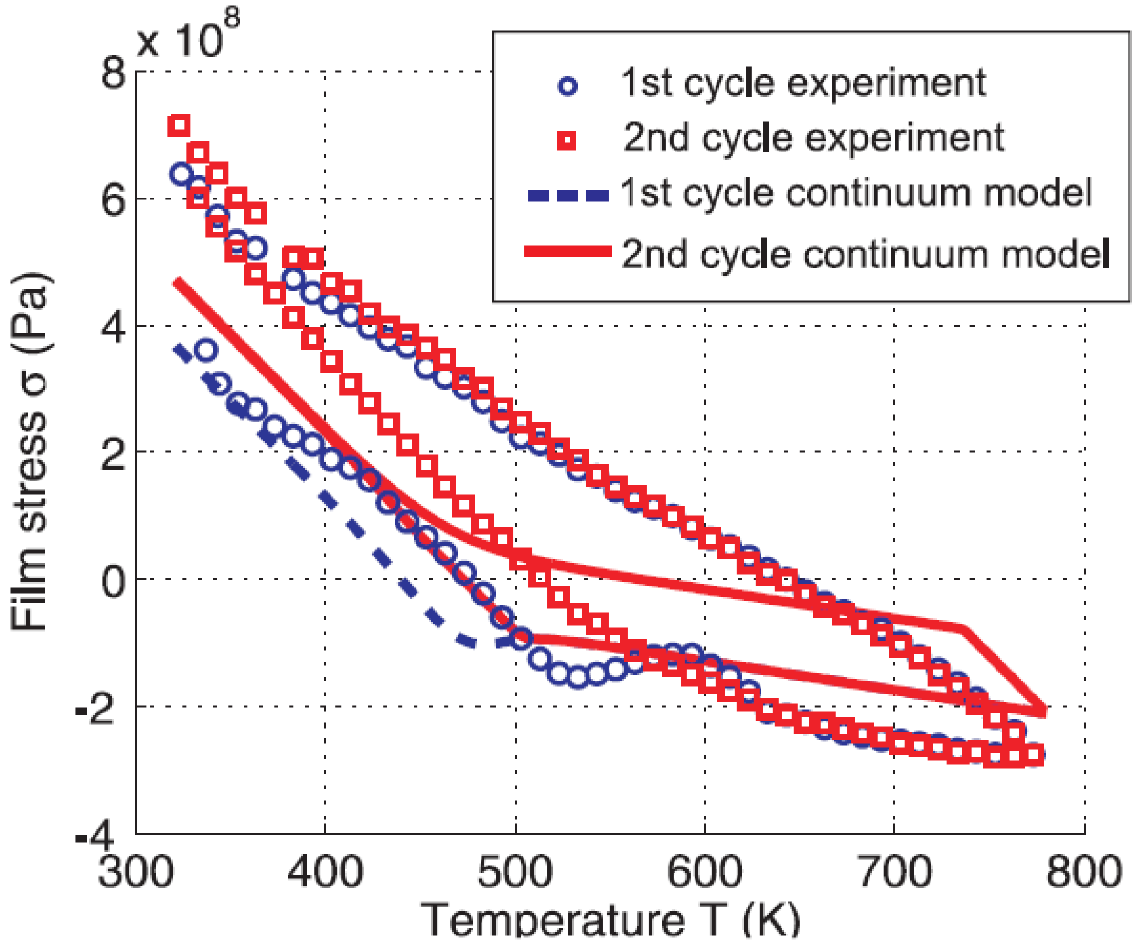
Step 2: Form a pileup of climb dislocations
Crack-like diffusion wedge

Step 3: Emission of <u>parallel glide dislocations</u> at the root of the grain boundary



Goal: Develop atomistic modeling of these mechanisms to gain further insight into mechanisms

Thermal cycling experiments



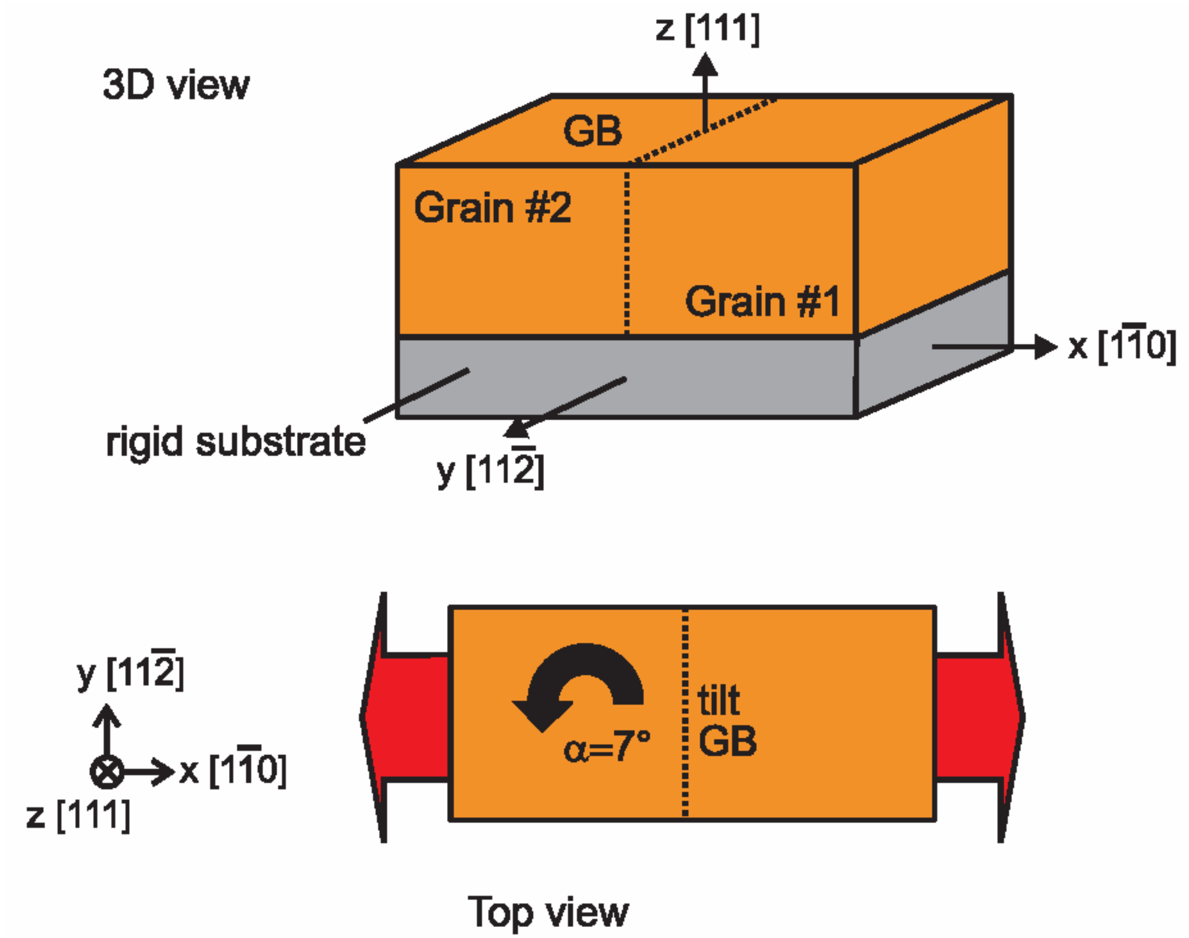
- ➢ Compare continuum model with threshold stress to the experimental data of thermal cycling
(Buehler *et al.*)

The film thickness is

h_f = 100 nm

- ➢ Measure stress in thin copper film during thermal cycling

Atomistic model

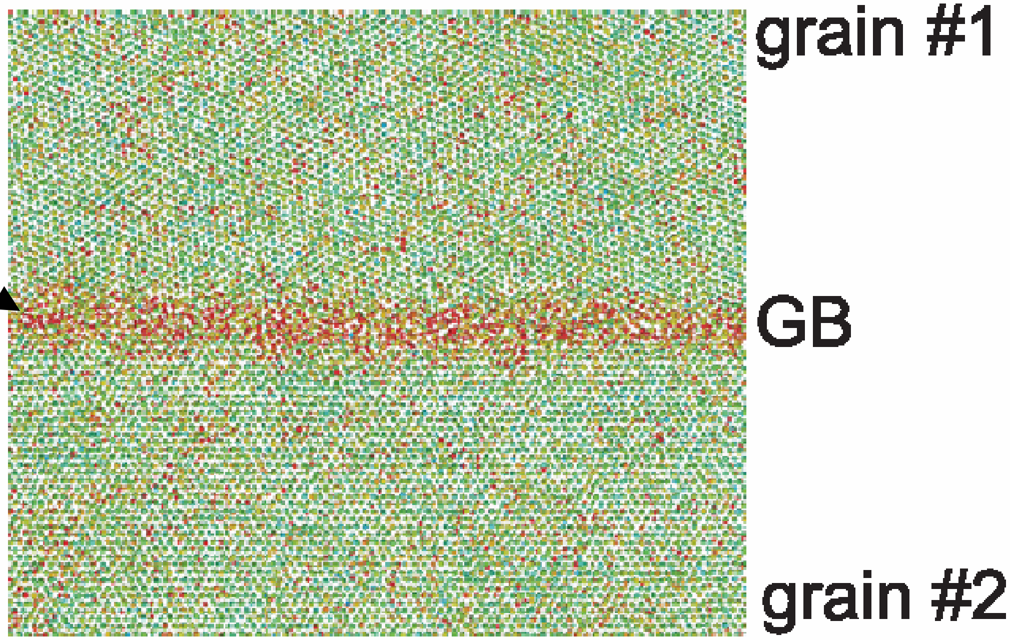


- Copper atoms deposited on a rigid substrate (atoms constrained)
- Use Mishin's EAM potential for copper
- 80%..90% of melting temperature to allow modeling of diffusion with MD at ns timescale (Wolf *et al*., 2001)+ construct high energy GB

Loading applied by displacing the outermost rows of atoms

(Buehler *et al*., MSMSE, 2004)

Liquid-like grain boundary



Liquid like
structure
fast diffusion

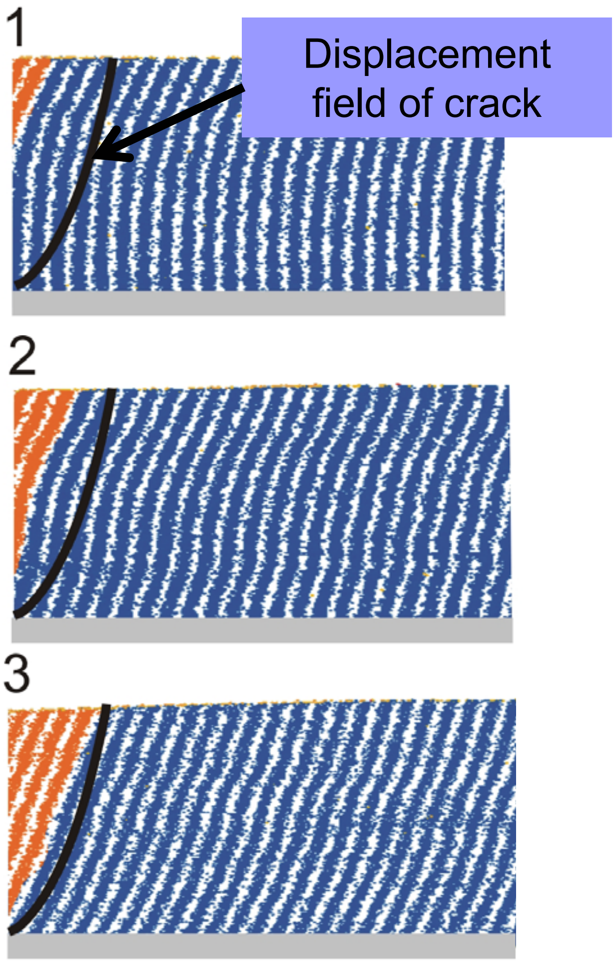
(T=85% of melting temperature)

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

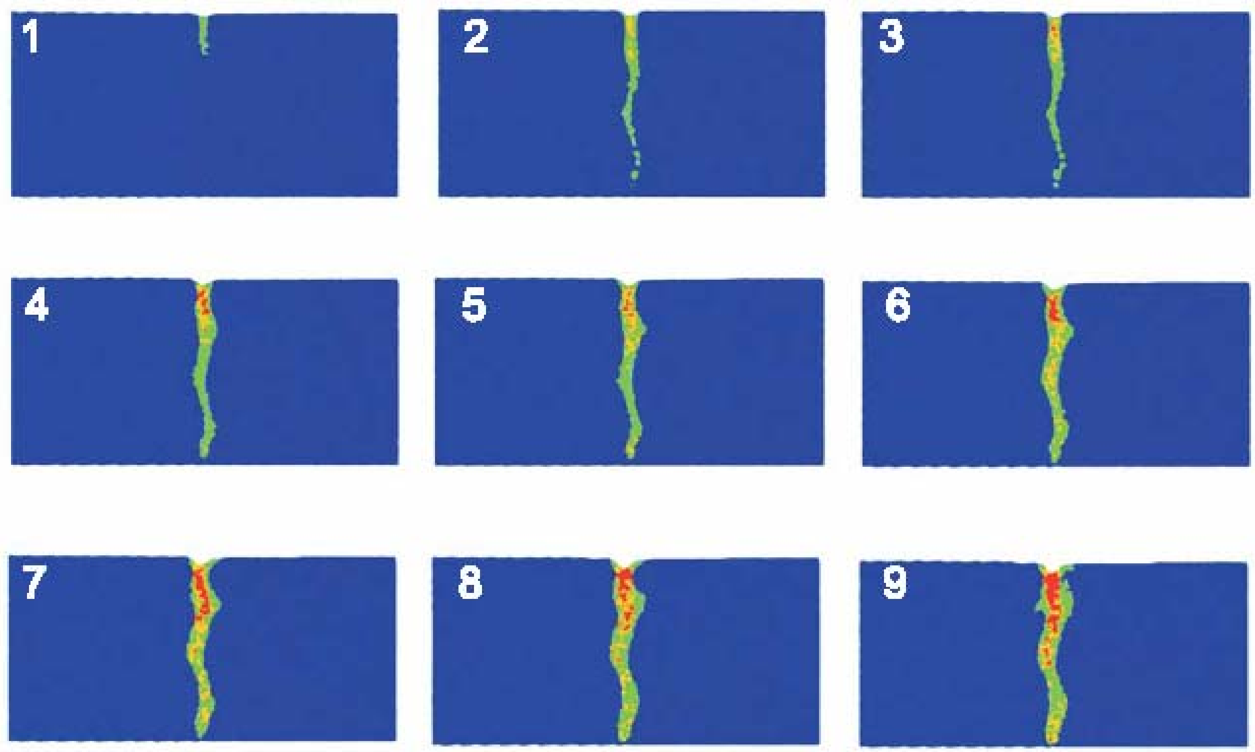
(Buehler, 2004)

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):

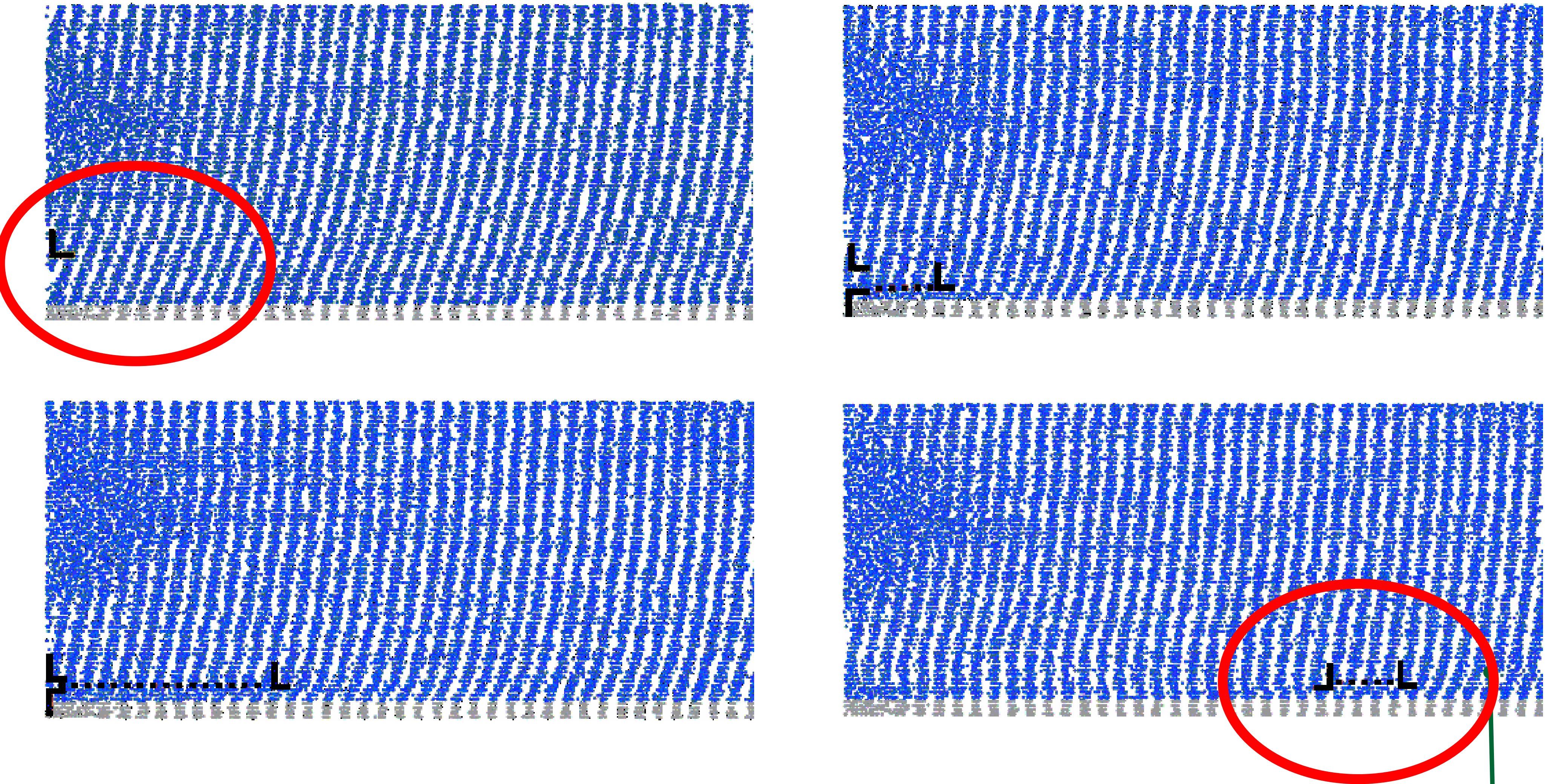


Diffusive displacement along GB toward the substrate

➢ 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

Lattice planes viewed along [211]

(Buehler *et al*., MSME, 2004)

Nucleation of PG dislocations: Diffusion wedge versus crack

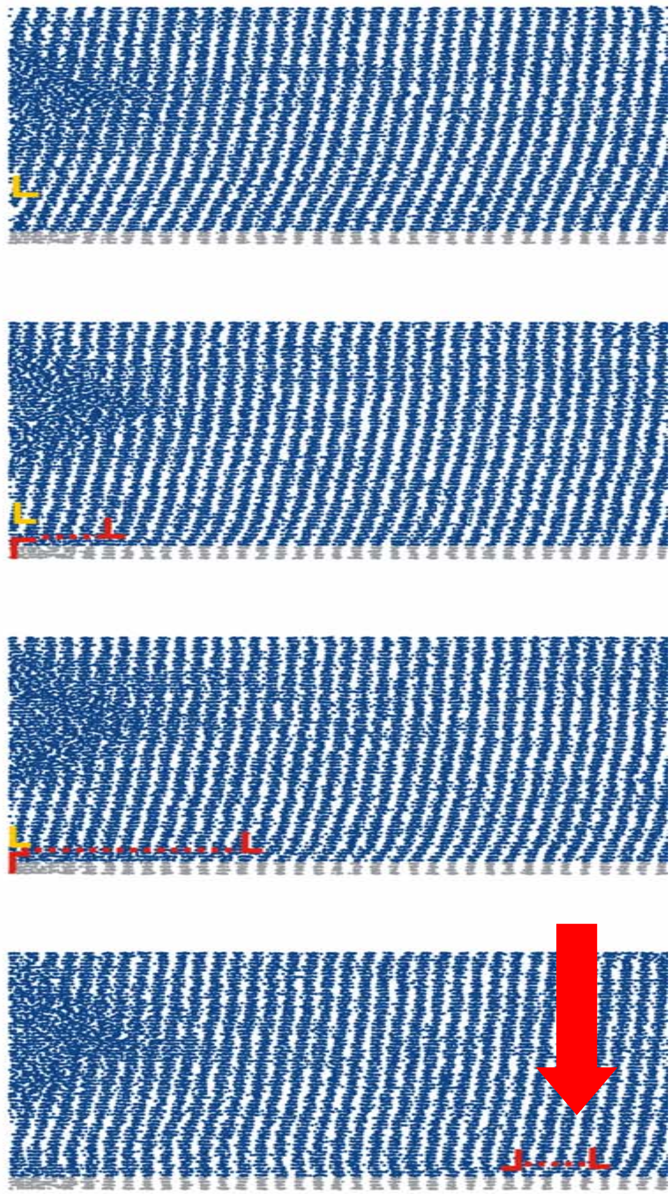
Diffusion wedge

Crack

Dislocation dipole

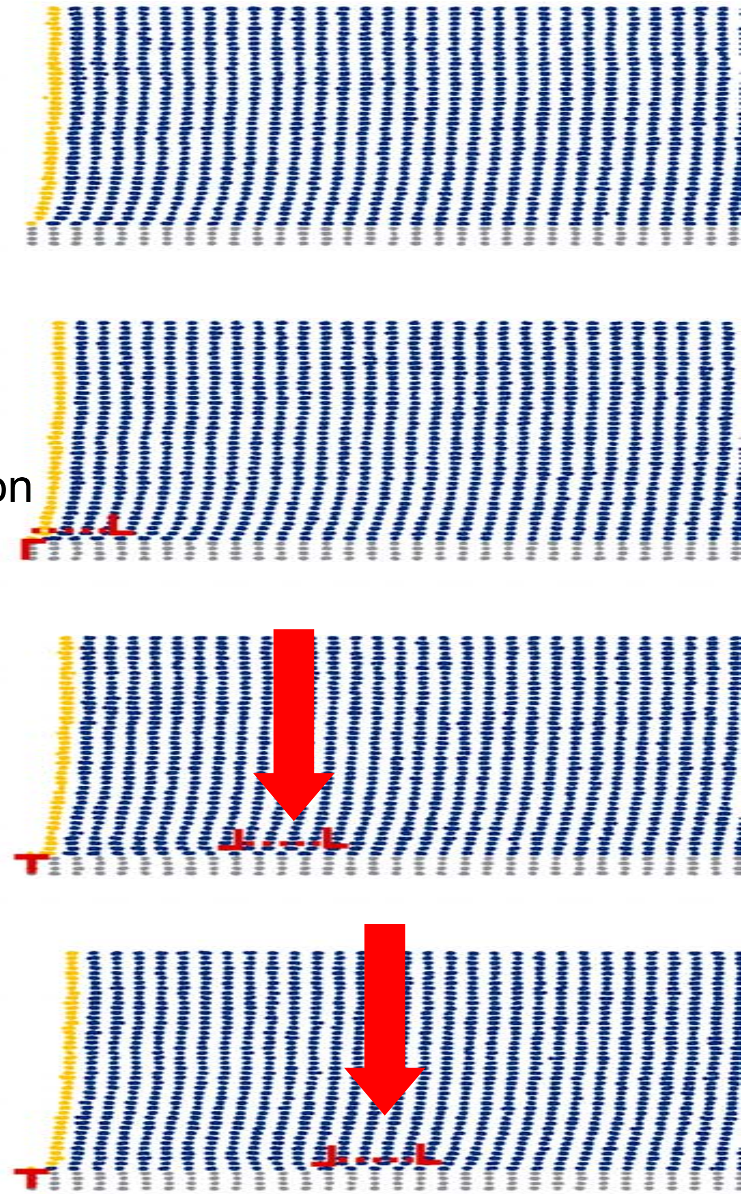
Annihilation

Repulsion
Nucleation



Incipient dislocation

Crack blunting



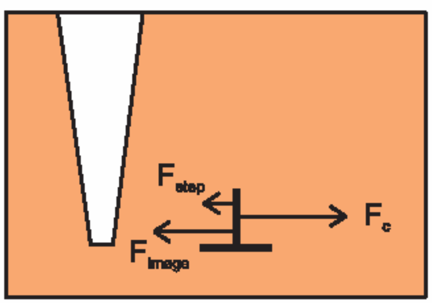
(Buehler *et al.*, JMPS, 2003)

Critical SIF cracks versus diffusion wedge

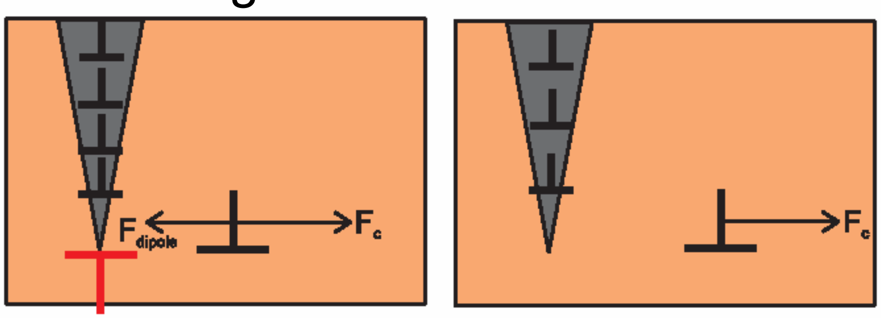
T (K)	h_f (nm)	K^{PG} (MPa $\times$ m^s)
Crack		
300	27.2	4.95
Diffusion wedge		
1150	27.2	11.91
1250	27.2	11.35
1250	34.2	11.23

- 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

Crack



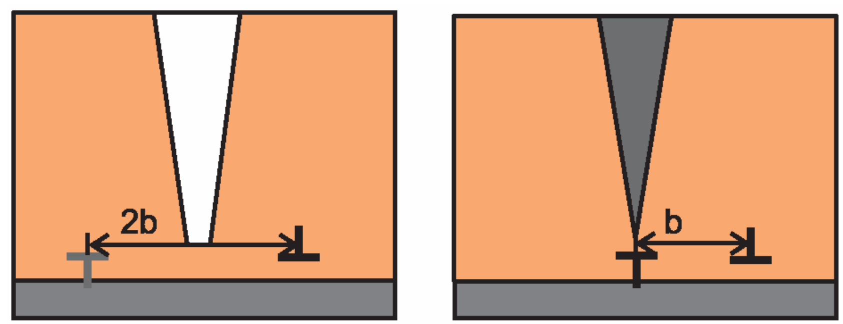
Diffusion wedge



Rice-Thomson model

Crack

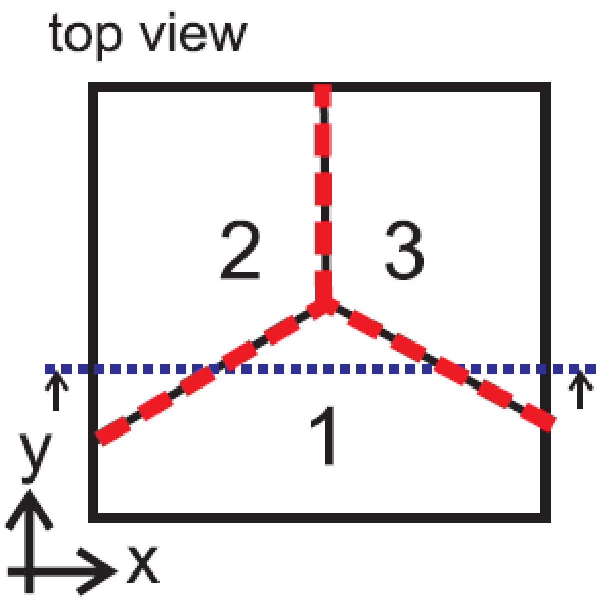
Diffusion wedge

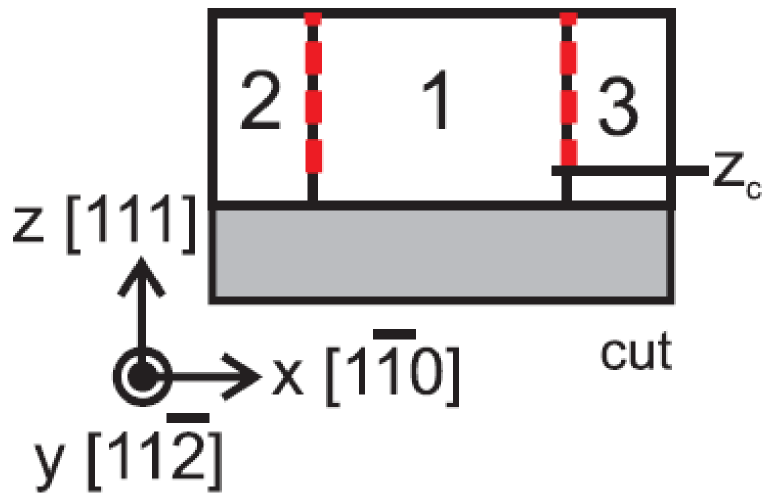


$$K_{cr}^{PG} = \frac{E(2\pi b_x)^s}{8\pi(1-\nu^2)} \qquad K_{dw}^{PG} = \frac{E(2\pi b_x)^s}{4\pi(1-\nu^2)}$$

Explains ratio of 2

Extension to triple junction model

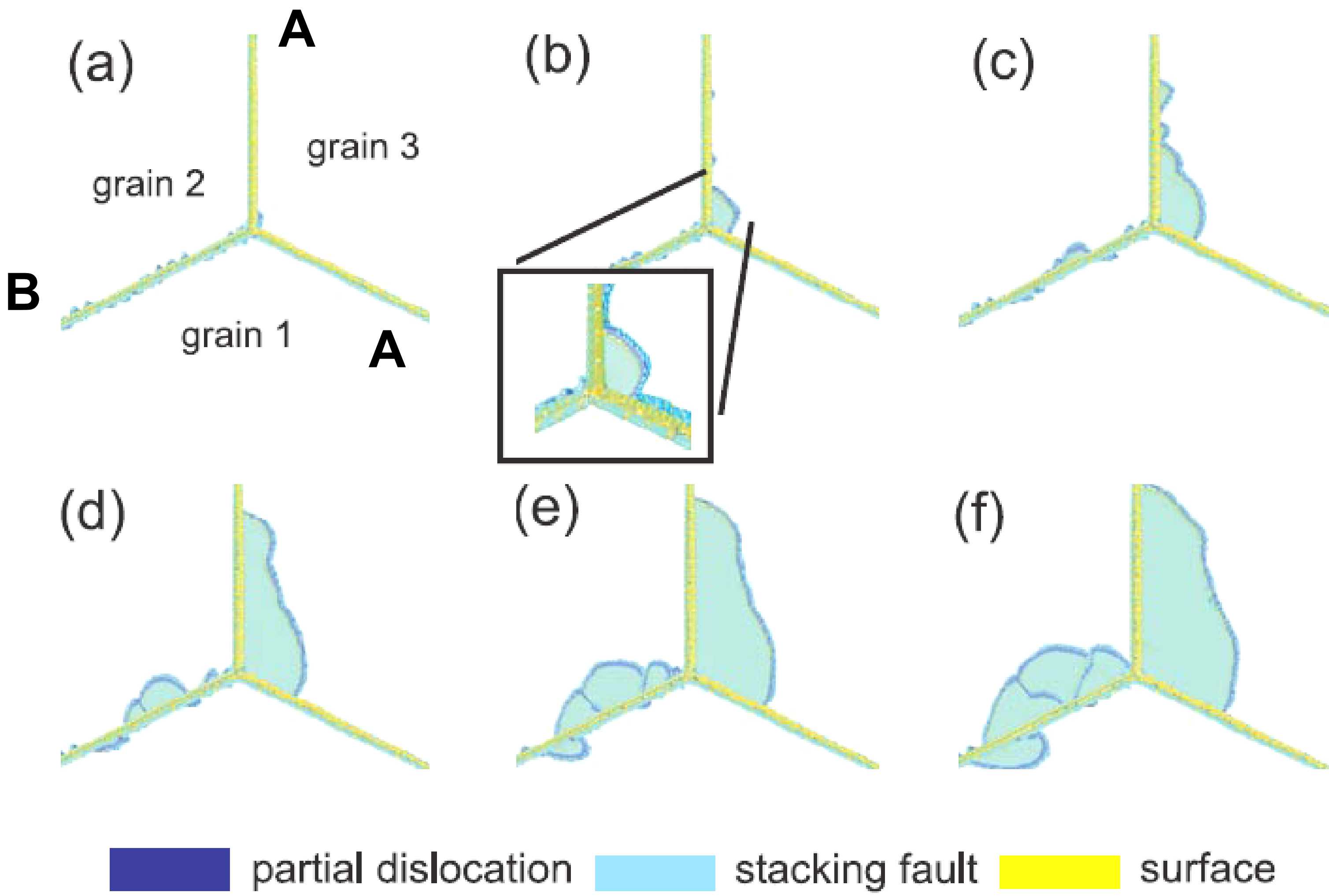




GB traction relaxed

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

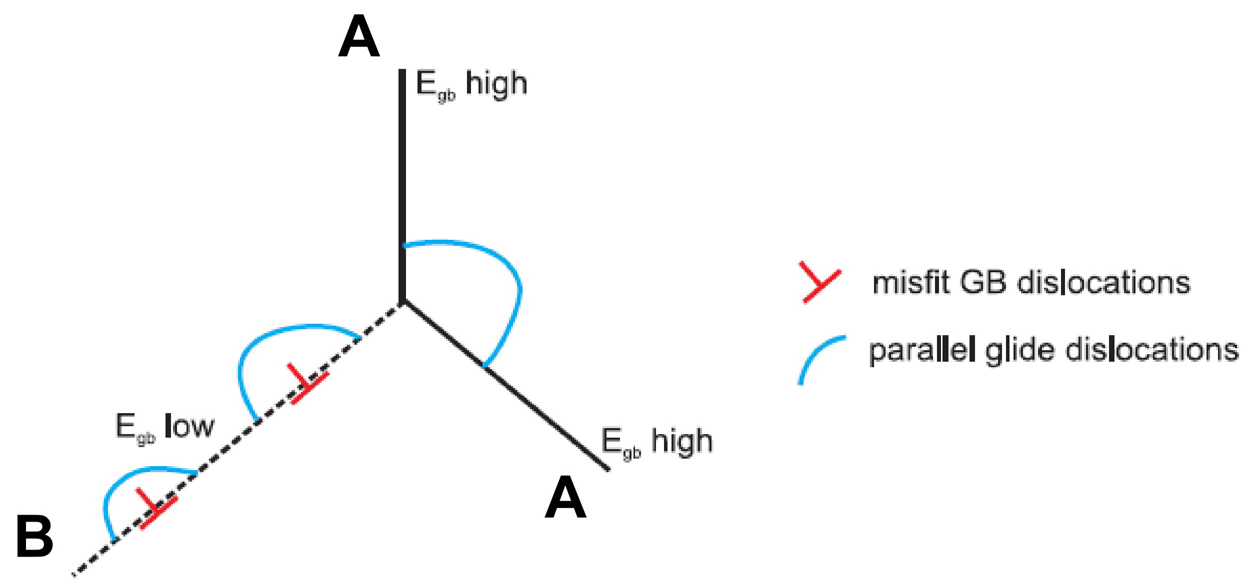
Extension to triple junction model

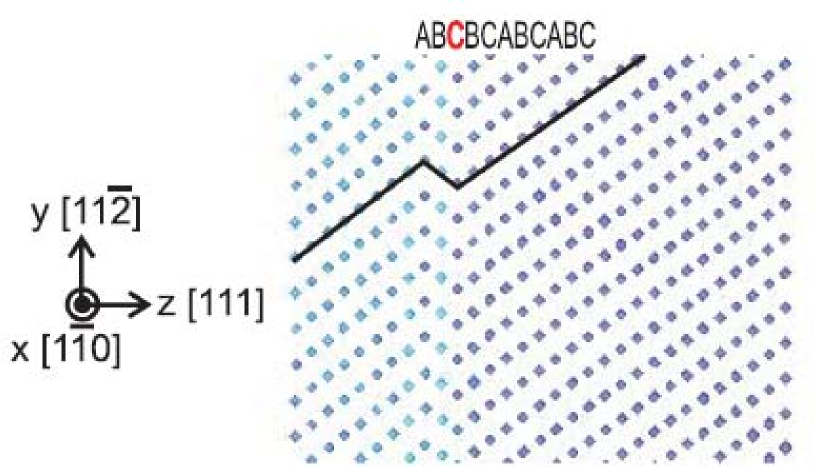


Upon application of biaxial tensile load, observe nucleation of PG dislocations

Misfit GB dislocations to serve as nucleation points for PG dislocations

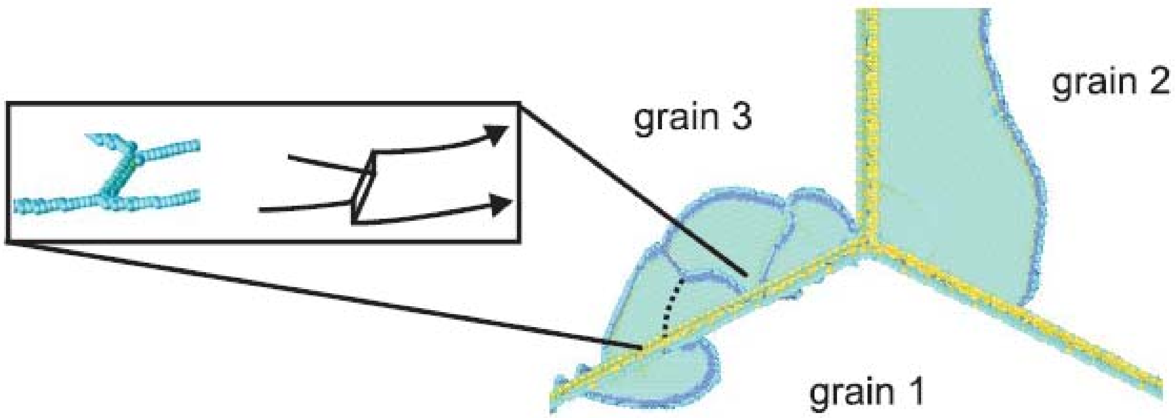
Schematic



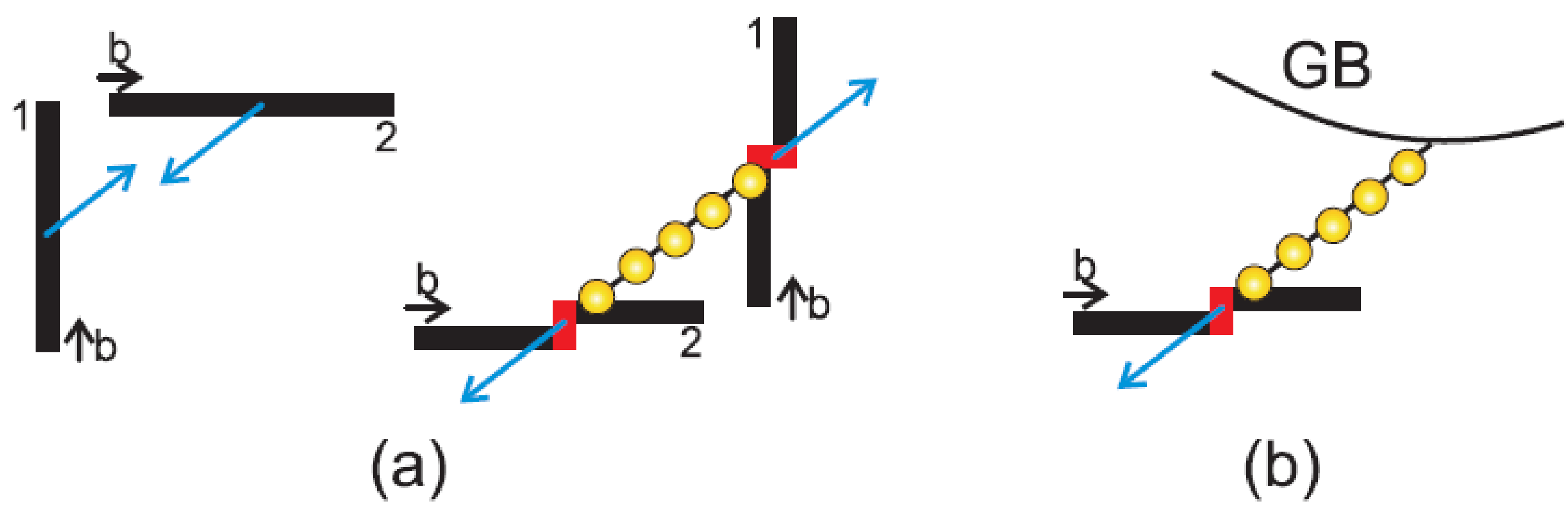


- Deformation twinning by repeated nucleation of partial dislocations.
- Repeated slip of partial dislocations leads to generation of a twin grain boundary.

Formation of jogs: Dislocation reactions

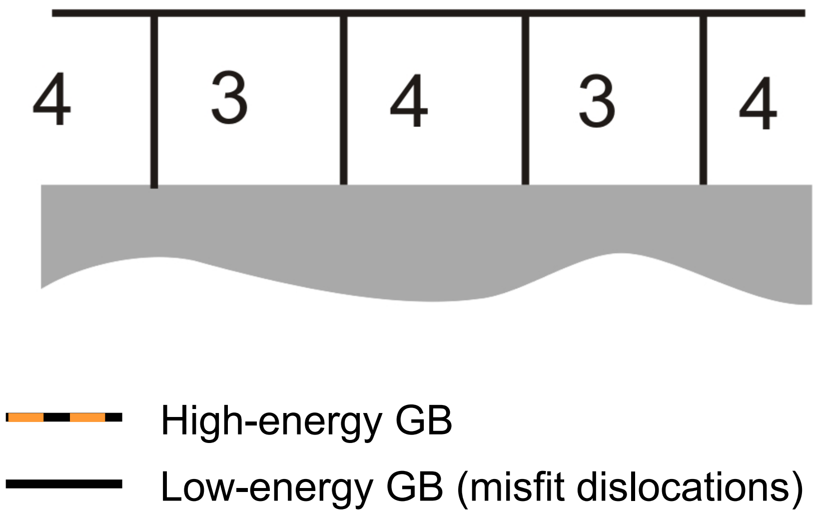


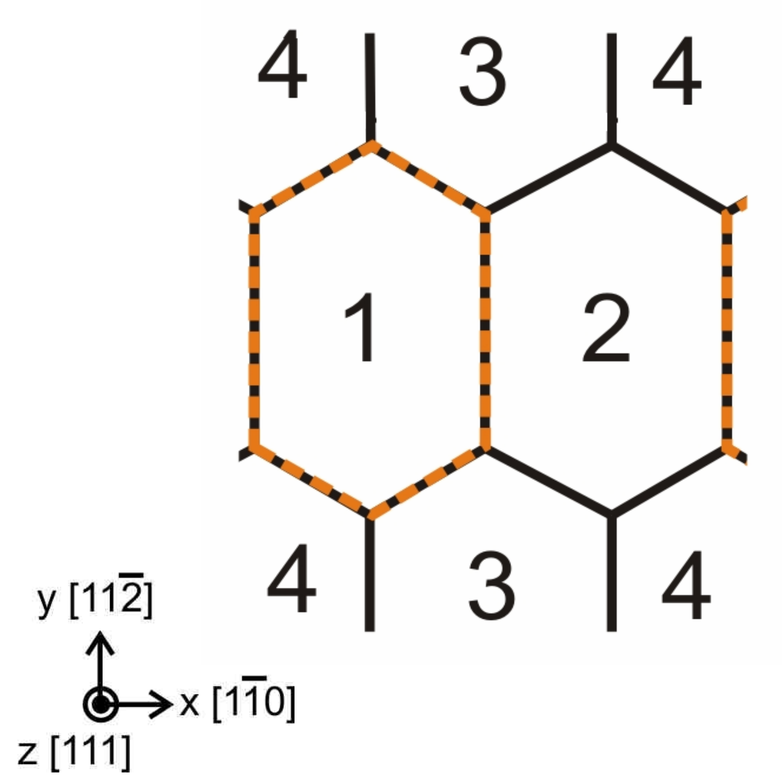
- Dislocation junction and bowing of dislocations by jog dragging.
- A trail of point defects is produced at the jog in the leading dislocation, which is then repaired by the following partial dislocation.



Constrained grain boundary diffusion in polycrystalline models: 3D model

Biaxial loading



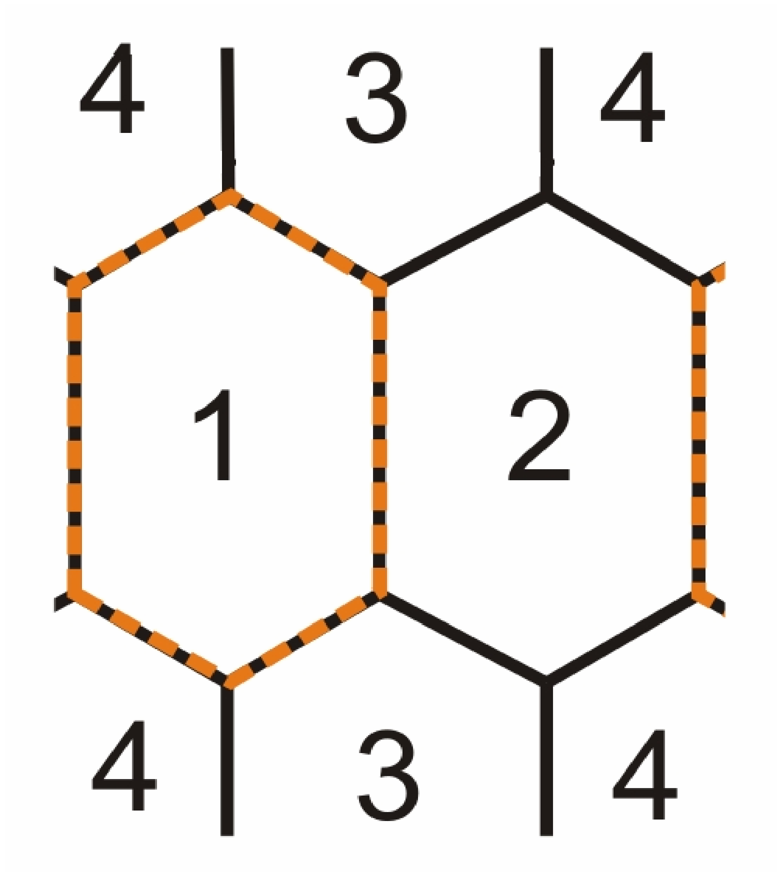


Model:

<u>Polycrystalline sample</u> 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)

• <u>Temperature</u>: About 90 % of melting temperature (similar as Yamakov *et al*.)

Constrained grain boundary diffusion in polycrystalline models



High-energy GB

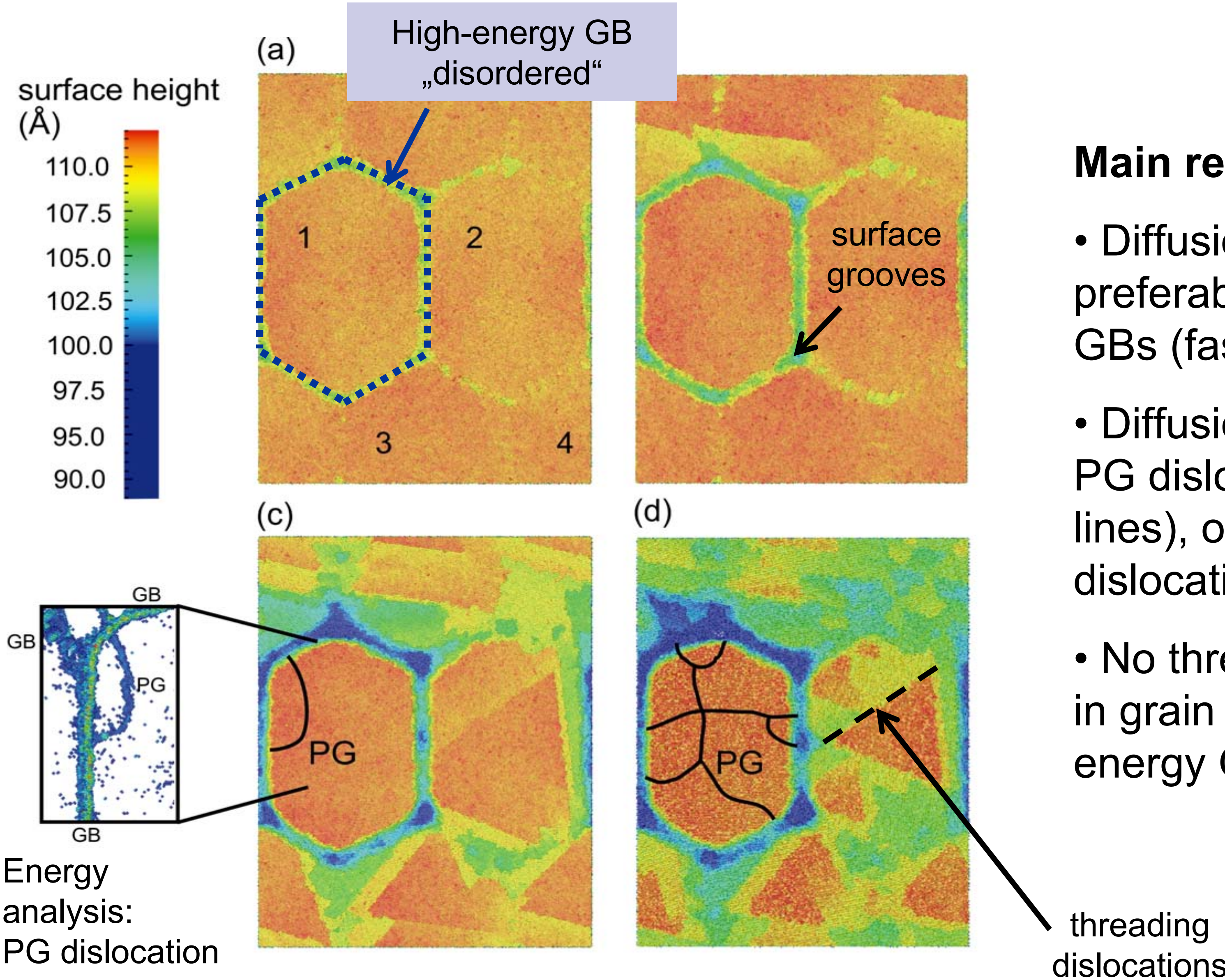
Low-energy GB (misfit dislocations)

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)

Polycrystalline atomistic model



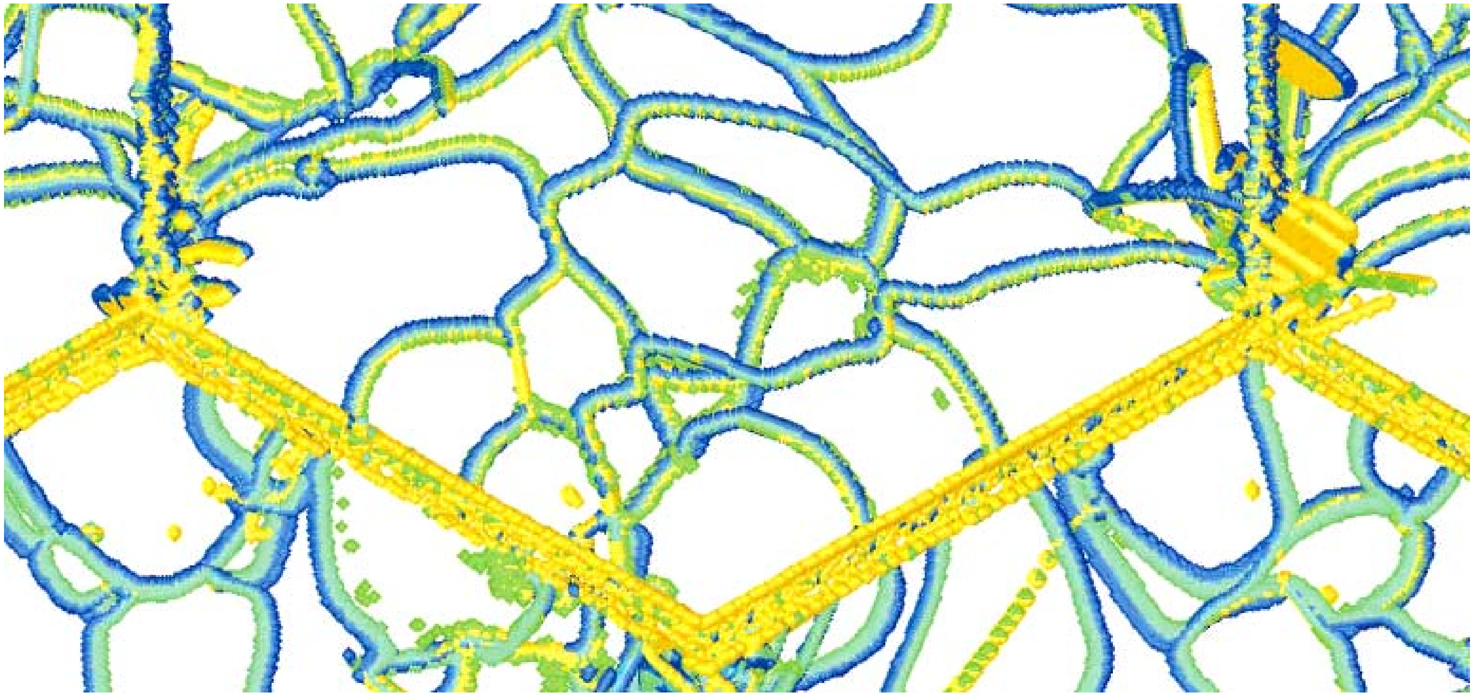
Energy analysis: PG dislocation

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

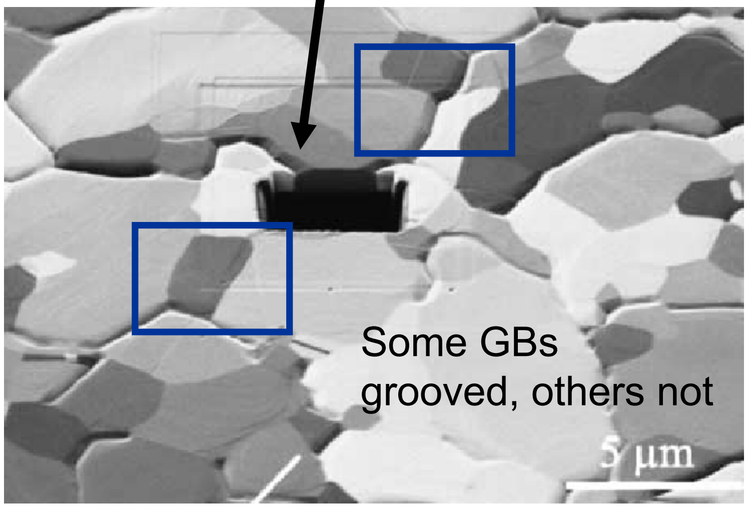


• The plot shows an analysis of the complex dislocation network of partial parallel glide dislocations that develops inside the grains.

• All defects besides stacking fault planes are shown in this plot.

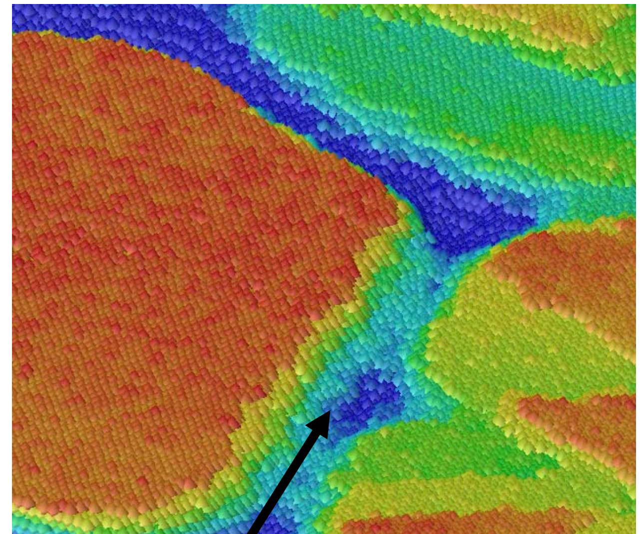
Qualitative comparison of MD results with experiment

Surface grooves

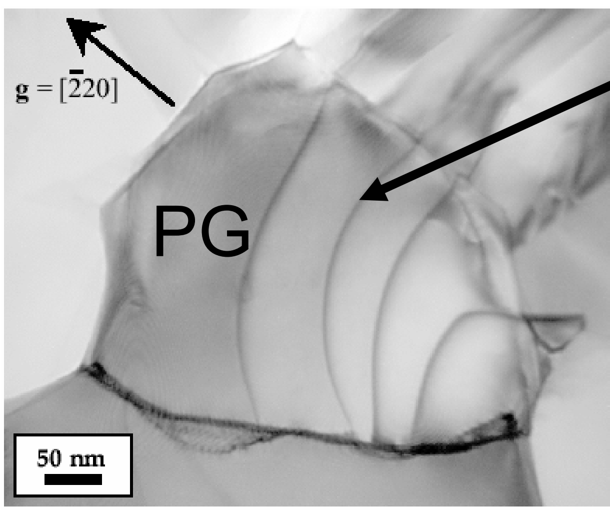


Experiment (Weiss *et al.*)

MD simulation

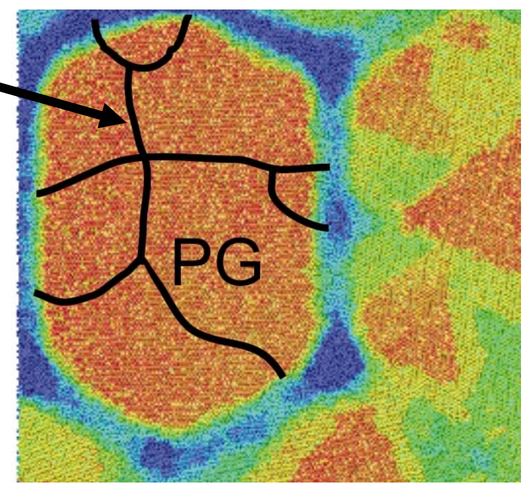


Surface grooves
at specific GBs



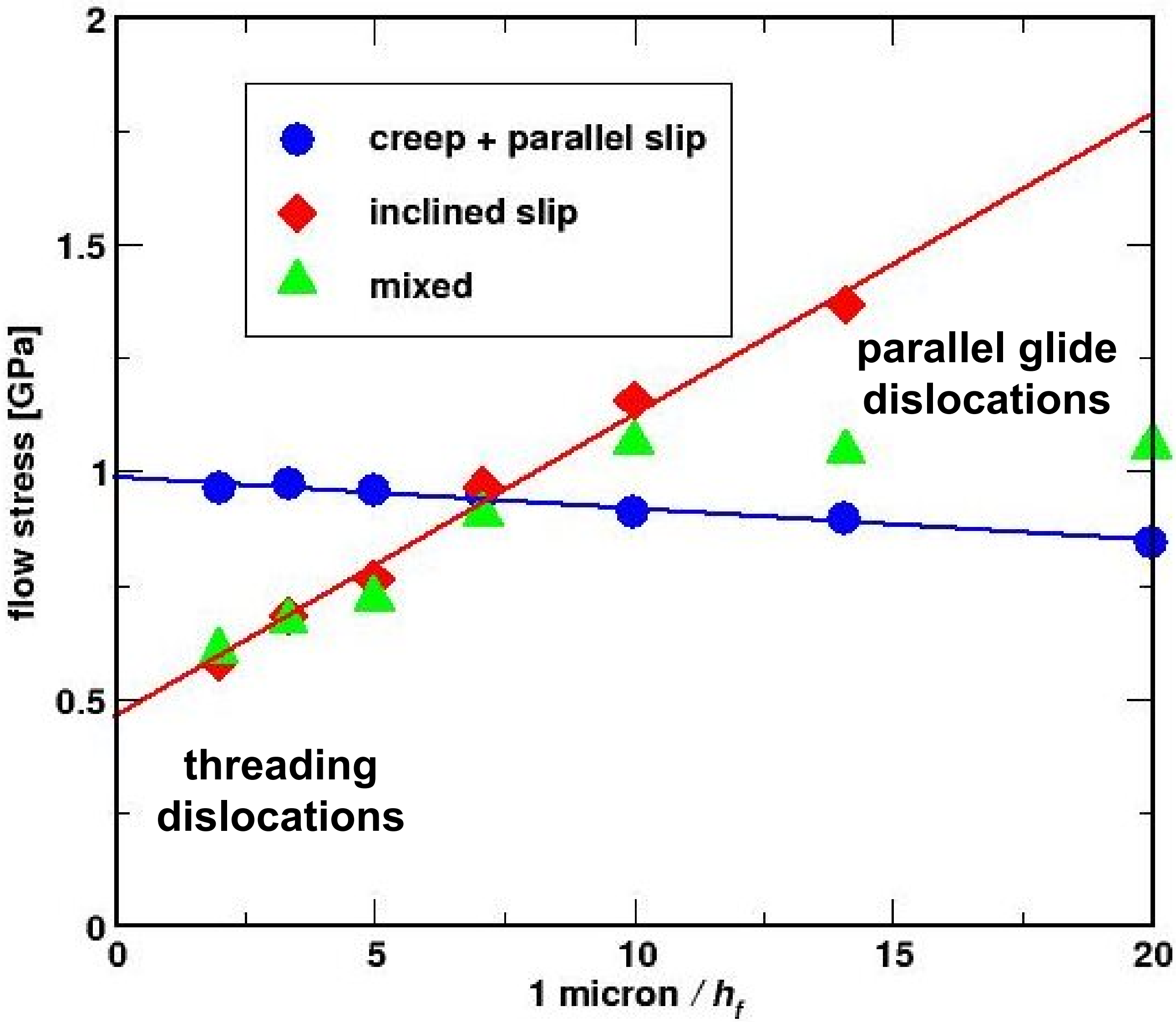
Experiment (Balk *et al.*)

PG
dislocations
in some grains



Competing mechanisms: Slip versus diffusion

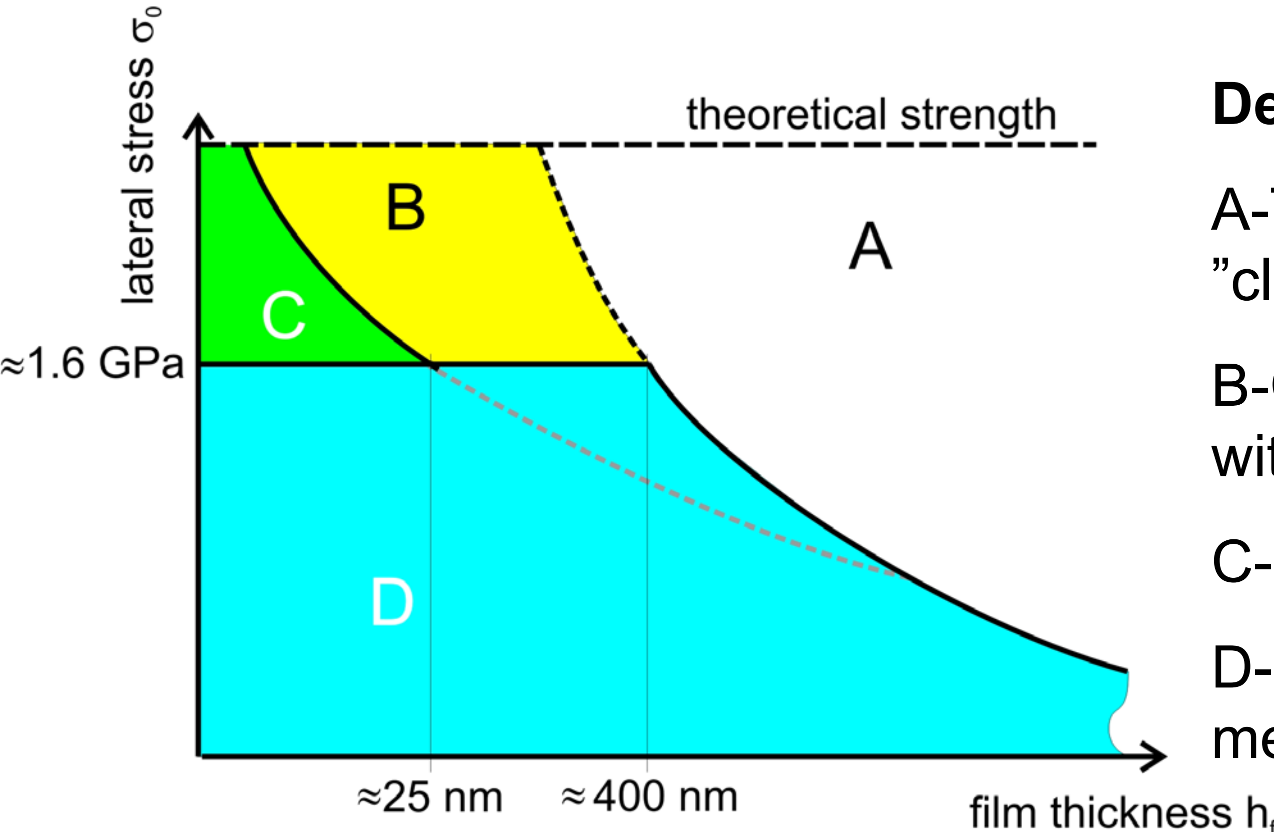
DDD modeling (mesoscale)



- ✓ 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)

(A. Hartmaier, Buehler, Gao, Advanced Engrg. Materials, 2005)

Deformation map of submicron copper films



Deformation mechanism map *

A-Threading dislocations (Nix)—”classical”

B-Constrained diffusional creep with parallel glide dislocations

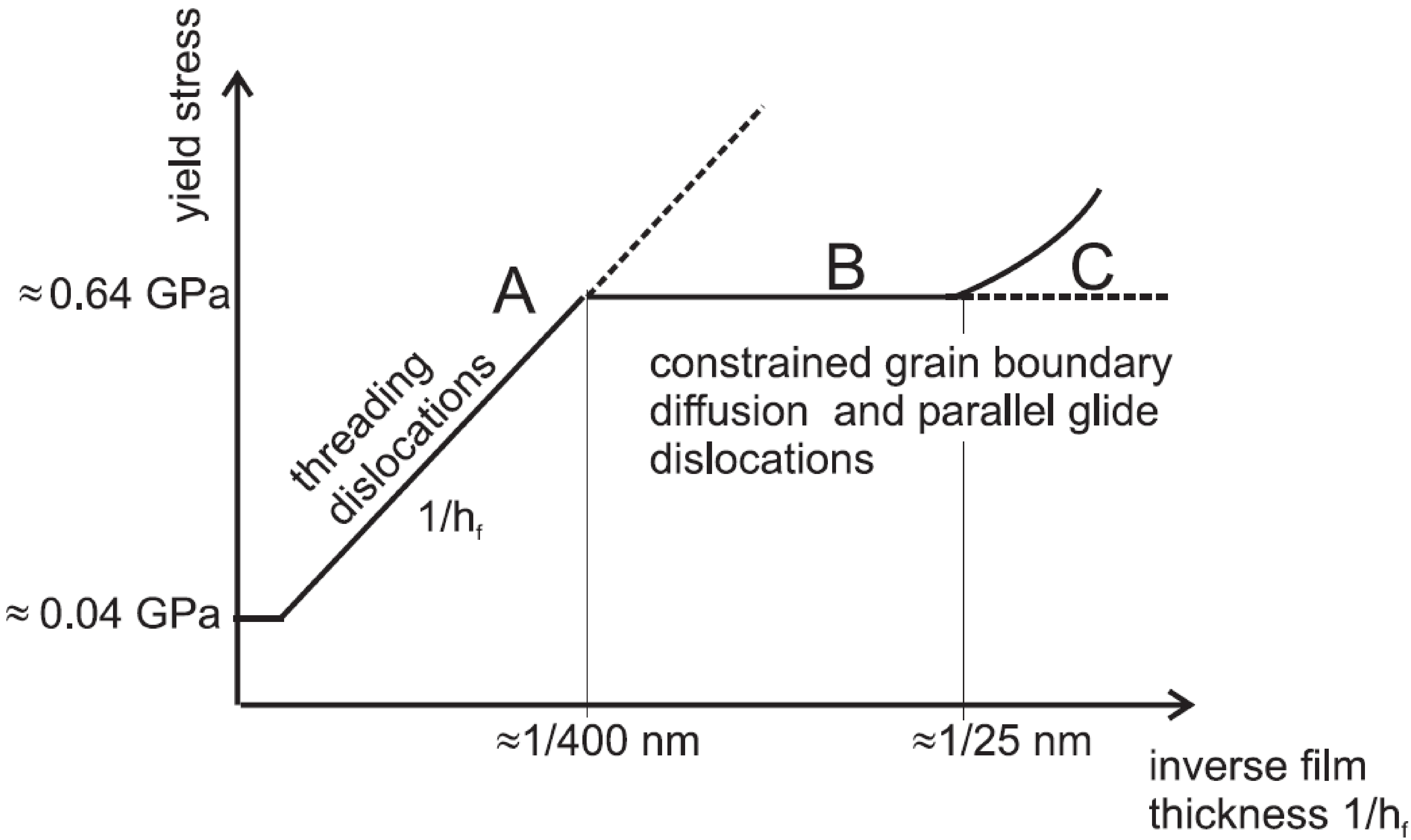
C-Diffusional creep

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



Conclusion

• 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

Additional references

Biological materials

- **Arzt E**, Enders S, Gorb S
  Towards a micromechanical understanding of biological surface devices
  ZEITSCHRIFT FUR METALLKUNDE 93 (5): 345-351 MAY 2002
- **Arzt E**, Gorb S, Spolenak R
  From micro to nano contacts in biological attachment devices
  PROCEEDINGS OF THE NATIONAL ACADEMY OF SCIENCES OF THE UNITED STATES OF AMERICA 100 (19): 10603-10606 SEP 16 2003
- Gao HJ, Wang X, Yao HM, et al.
  Mechanics of hierarchical adhesion structures of geckos
  MECHANICS OF MATERIALS 37 (2-3): 275-285 FEB-MAR 2005
- Spolenak R, Gorb S, Gao HJ, et al.
  Effects of contact shape on the scaling of biological attachments
  PROCEEDINGS OF THE ROYAL SOCIETY OF LONDON SERIES A-MATHEMATICAL PHYSICAL AND ENGINEERING SCIENCES 461 (2054): 305-319 FEB 8 2005
- **Gao HJ**, Chen SH
  Flaw tolerance in a thin strip under tension
  JOURNAL OF APPLIED MECHANICS-TRANSACTIONS OF THE ASME 72 (5): 732-737 SEP 2005
- Ji BH, **Gao HJ**
  Mechanical properties of nanostructure of biological materials
  JOURNAL OF THE MECHANICS AND PHYSICS OF SOLIDS 52 (9): 1963-1990 SEP 2004
- Gupta HS, Wagermaier W, Zickler GA, et al.
  Nanoscale deformation mechanisms in bone
  NANO LETTERS 5 (10): 2108-2111 OCT 2005
- Huber G, Gorb SN, Spolenak R, et al.
  Resolving the nanoscale adhesion of individual gecko spatulae by atomic force microscopy
  BIOLOGY LETTERS 1 (1): 2-4 MAR 2005

Size effects in general

- **Arzt E**
  Overview no. 130 - **Size** effects in materials due to microstructural and dimensional constraints: A comparative **review**
  ACTA MATERIALIA 46 (16): 5611-5626 OCT 9 1998