From nano to macro: Introduction to atomistic modeling techniques

IAP 2007

Nanomechanics of hierarchical biological materials (*cont'd*)

Lecture 7

Department of
Civil & Environmental Engineering
Massachusetts Institute of Technology

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

Entropic change as a function of stretch

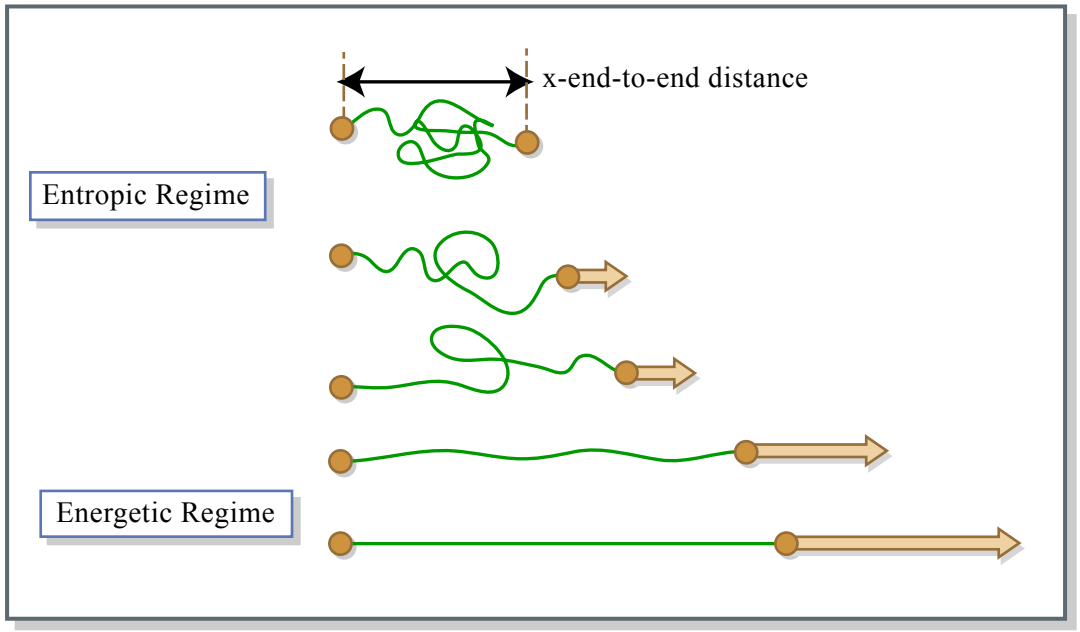
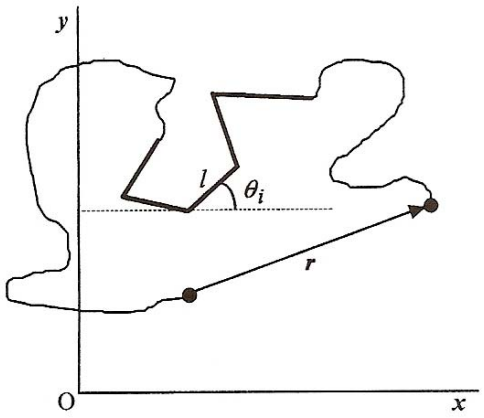


Figure by MIT OCW.



$$S = c - kb^2 r^2$$

$$b^2 = \frac{3}{2nl^2}$$

Entropic elasticity: Derivation

Freely jointed Gaussian chain with *n* links and length *l* each (same for all chains in rubber)

$$S = c - kb^2 r^2 \qquad \text{where} \quad b^2 = \frac{3}{2nl^2}$$

r end-to-end distance of chain

$$\Delta S = -kb^2 \sum_{N_b} \left(\lambda_1^2 - 1\right)x^2 + \left(\lambda_2^2 - 1\right)y^2 + \left(\lambda_3^2 - 1\right)z^2$$

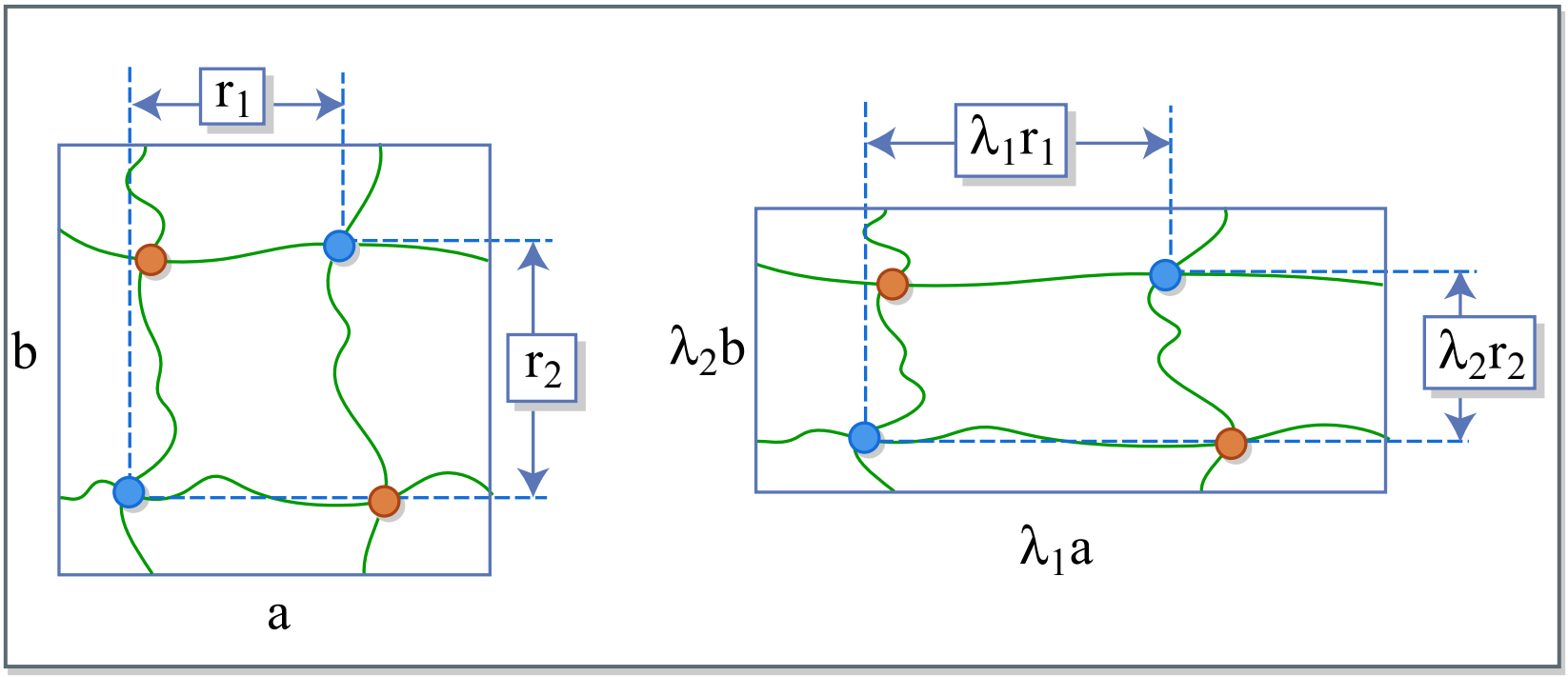


Figure by MIT OCW.

Entropic elasticity: Derivation

The length $< r_b^2 >$ in the unstressed state is equal to the mean square length of totally free chains.

It can be shown that

$$r_{RMS} = \sqrt{n} \cdot l =< \sqrt{< r_b^2 >}$$

$$< r_b^2 >= n \cdot l^2$$

$$< x^2 >=< y^2 >=< z^2 >= \tfrac{1}{3} n \cdot l^2 = \frac{1}{2b^2}$$

$$\Delta S = -kN_b / 2\left[\left(\lambda_1^2 - 1\right) + \left(\lambda_2^2 - 1\right) + \left(\lambda_3^2 - 1\right)\right]$$

No explicit dep. on *b* any more

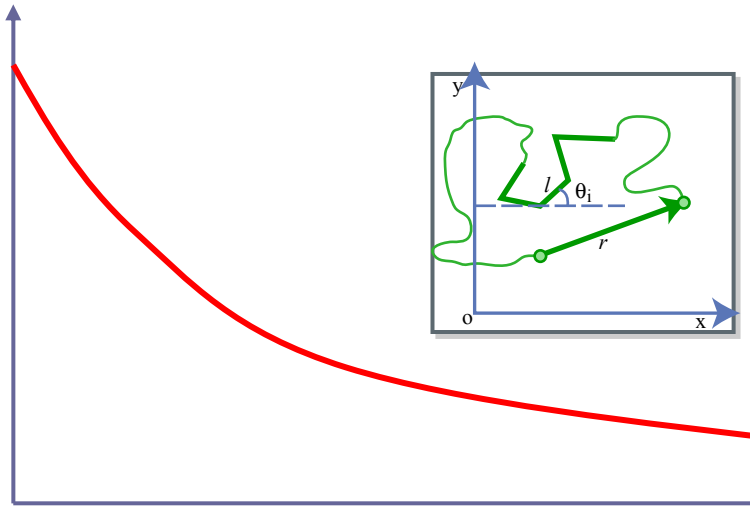
$$U = -T\Delta S = \tfrac{1}{2} N_b kT\left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3\right) \qquad C = E/6$$

$$U = C\left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3\right) \qquad \sigma = (E/3)(\lambda^2 - 1/\lambda)$$

Persistence length

$$\langle \boldsymbol{t}(s) \cdot \boldsymbol{t}(s') \rangle = e^{-|s-s'|/\ \xi_p}$$

t(s) tangent slope



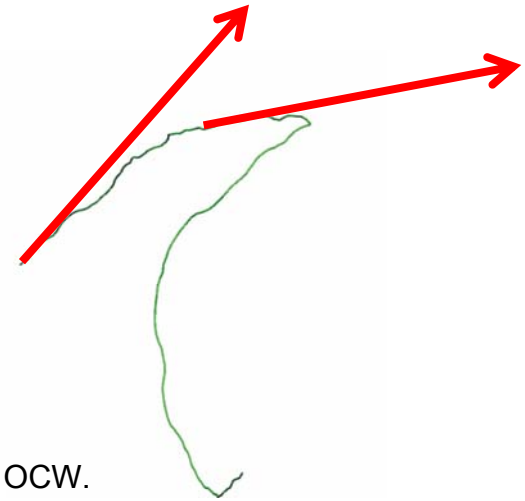


Figure by MIT OCW.

$\xi_p = l/2$

The length at which a filament is capable of bending significantly in independent directions, at a given temperature.
This is defined by a autocorrelation function which gives the characteristic distance along the contour over which the tangent vectors **t(s)** become uncorrelated

Worm-like chain model

Freely-jointed rigid rods

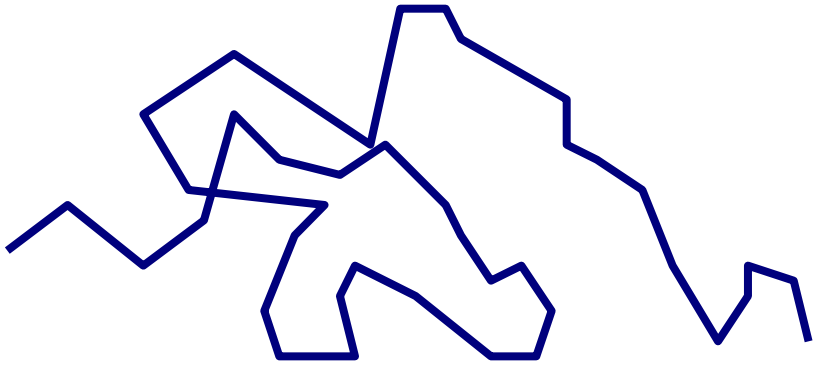
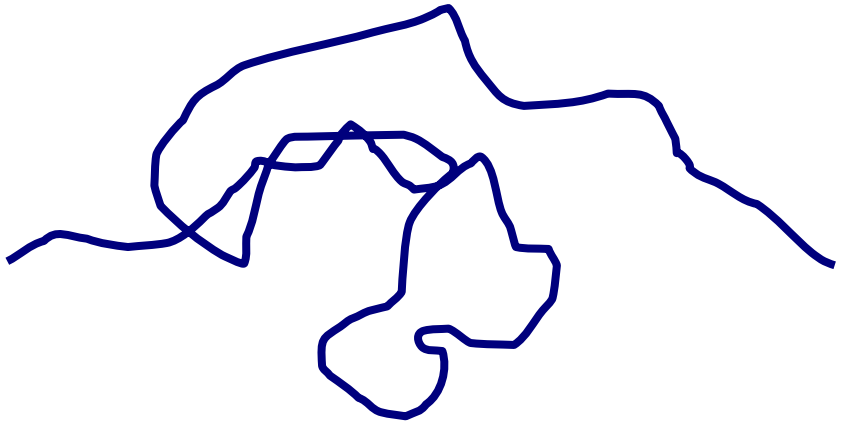


Image removed due to copyright restrictions.

DNA 4-plat electron micrograph
(Cozzarelli, Berkeley)

Continuously flexible ropes

Worm like chain model



Worm-like chain model

- This spring constant is only valid for small deformations from a highly convoluted molecule, with length far from its contour length

$$x << L$$

- A more accurate model (without derivation) is the Worm-like chain model (WLC) that can be derived from the Kratky-Porod energy expression (see D. Boal, Ch. 2)

- A numerical, approximate solution of the WLC model:

$$F = \frac{kT}{\xi_p}\left(\frac{1}{4}\frac{1}{\left(1-x/L\right)^2} - \frac{1}{4} + x/L\right)$$

Marko and Siggia, 1995

Outline and content (Lecture 7)

- **Topic:** Nanostructure of biological materials (proteins, molecules, composites of organic-inorganic components..); deformation mechanisms; size effects – fracture at nanoscale, adhesion
- **Examples:** Deformation of collagen, vimentin, …: Protein mechanics
- **Material covered:** Covalent bonding and models, chemical complexity, molecular potentials: CHARMM and DREIDING
- **Important lesson:** Models for bonding in proteins, entropic vs. energetic elasticity; complexity of biological materials (multi-functional, nanostructured, precise arrangement, ..); small-scale fracture/adhesion: smaller is stronger
- **Historical perspective:** AFM, single molecule mechanics; Griffith concept and adhesion strength, size effects

Proteins

- An important building block in biological systems are proteins
- Proteins are made up of amino acids
- 20 amino acids carrying different side groups (R)
- Amino acids linked by the amide bond via condensation
- Proteins have four levels of structural organization: primary, secondary, tertiary and quaternary

Protein structure

- **Primary structure:** Sequence of amino acids

A A S X D X S L V E
V H X X

- **Secondary structure:** Protein secondary structure refers to certain common repeating structures found in proteins. There are two types of secondary structures: alpha-helix and beta-pleated sheet.

Images removed due to copyright restrictions.

- **Tertiary structure:** Tertiary structure is the full 3-dimensional folded structure of the polypeptide chain.

- **Quartenary Structure:** Quartenary structure is only present if there is more than one polypeptide chain. With multiple polypeptide chains, quartenary structure is their interconnections and organization.

20 natural amino acids

Images removed due to copyright restrictions.
Table of amino acid chemical structures.
See similar image: http://web.mit.edu/esgbio/www/lm/proteins/aa/aminoacids.gif.

Hierarchical structure of collagen

Images removed due to copyright restrictions.

Collagen features hierarchical structure

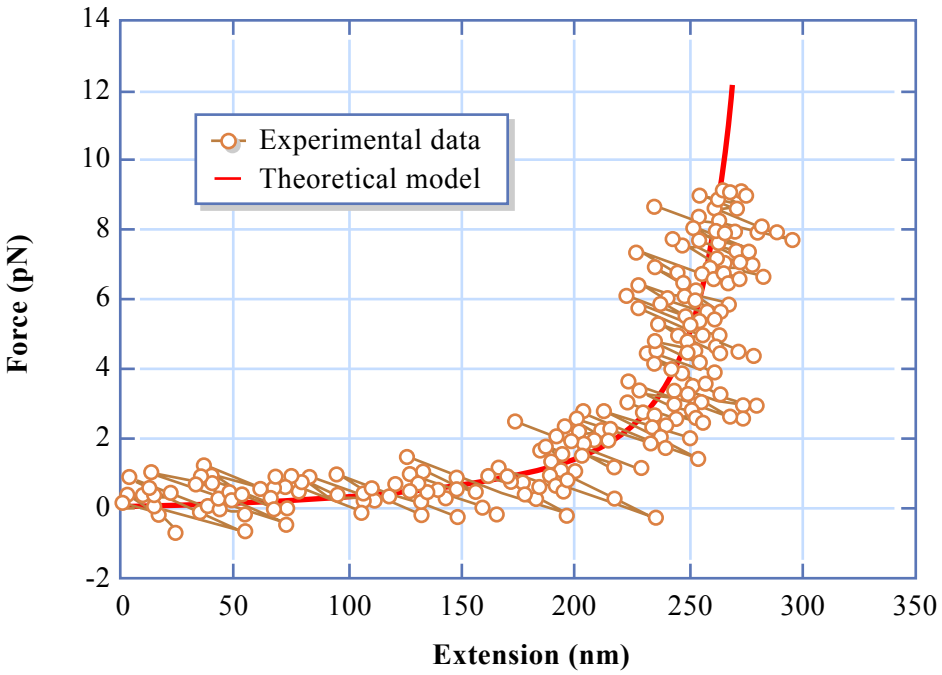
Goal: Understand the *scale-specific properties* and *cross-scale interactions*

Macroscopic properties of collagen depend on the finer scales

Material properties are scale-dependent

(Buehler, JMR, 2006)

Elasticity of tropocollagen molecules



The force-extension curve for stretching a single type II collagen molecule. The data were fitted to Marko-Siggia entropic elasticity model. The molecule length and persistence length of this sample is 300 and 7.6 nm, respectively.

$$F = \frac{kT}{\xi_p}\left(\frac{1}{4}\frac{1}{(1-x/L)^2} - \frac{1}{4} + x/L\right)$$

Figure by MIT OCW.

Sun, 2004

Modeling organic chemistry

Images removed due to copyright restrictions.

Covalent bonds (directional)
Electrostatic interactions
H-bonds
vdW interactions

Model for covalent bonds

$$V(R) = E_{bonded} + E_{non-bonded}$$

$$E_{bonded} = E_{bond-stretch} + E_{angle-bend} + E_{rotate-along-bond}$$

Bonding between atoms described as combination of various terms, describing the angular, stretching etc. contributions

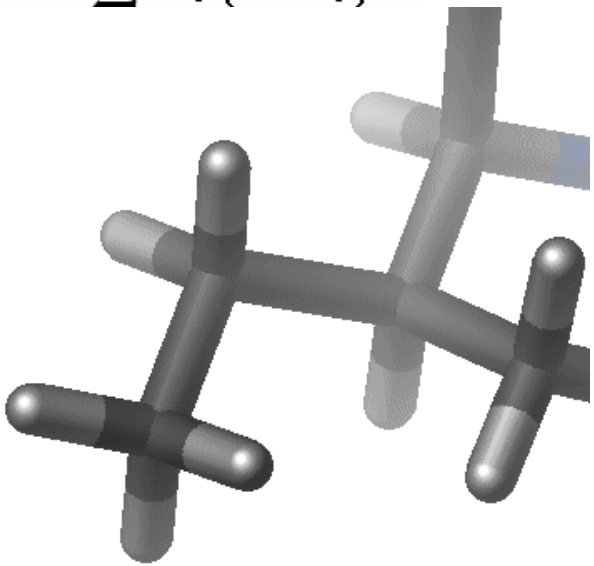
Image removed due to copyright restrictions.

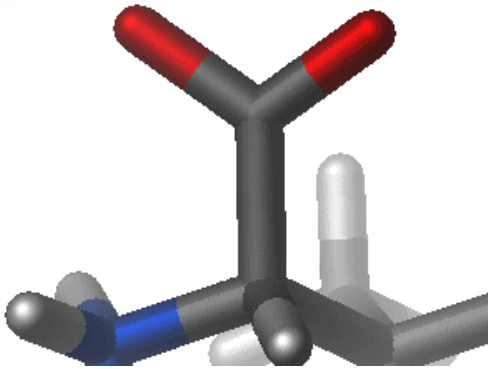
http://www.ch.embnet.org/MD_tutorial/pages/MD.Part2.html
http://www.pharmacy.umaryland.edu/faculty/amackere/force_fields.htm

Model for covalent bonds

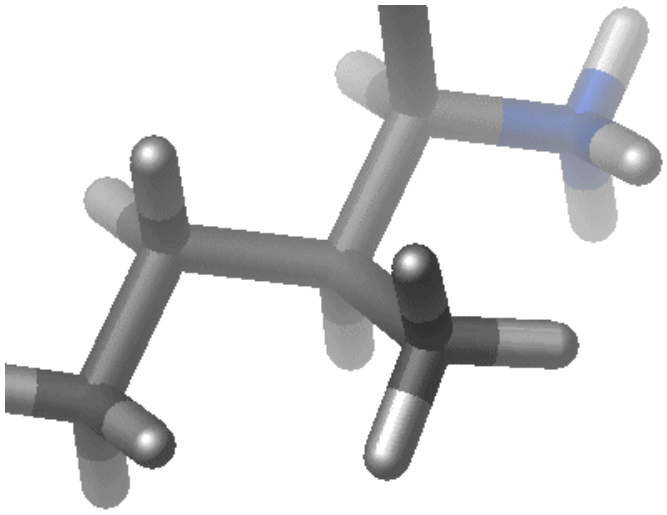
$$E_{bond-stretch} = \sum K_b (b - b_0)^2$$

$$E_{bond-bend} = \sum_{angles} K_\theta (\theta - \theta_0)^2$$





$$E_{rotate-along-bond} = \sum_{1,4\,pairs} K_\phi (1 - \cos(n\phi))$$

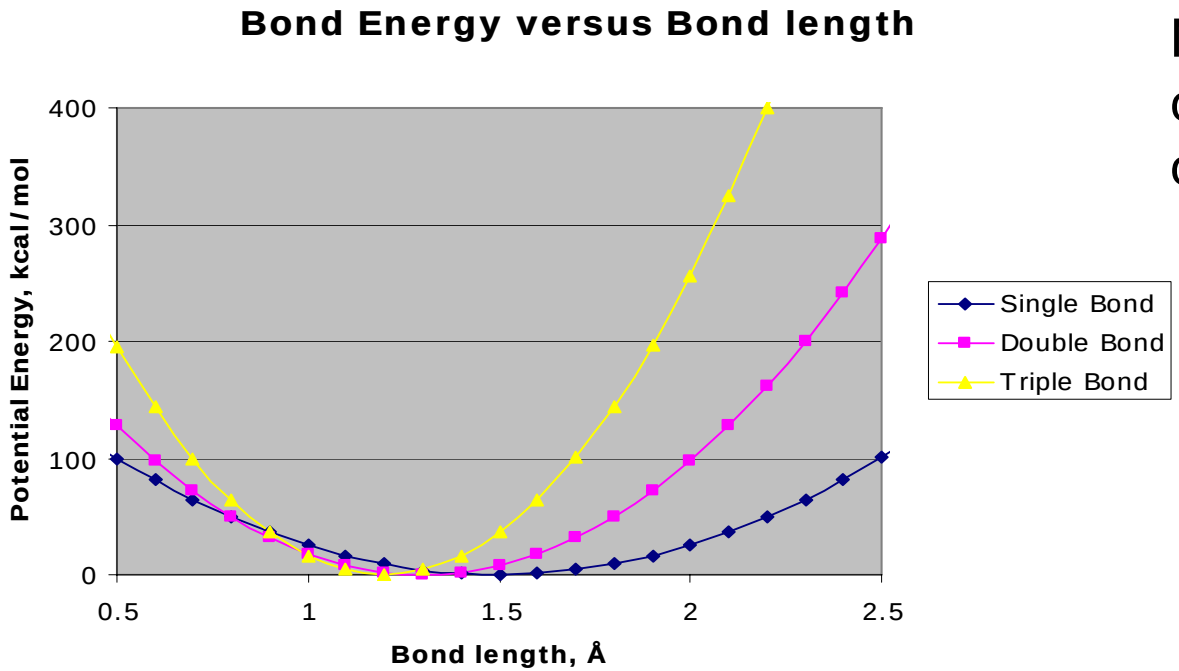


Courtesy of the EMBnetEducation & Training Committee.
Used with permission. Images created for the CHARMM
tutorial by Dr. Dmitry Kuznetsov(Swiss Institute of Bioinformatics)
for the EMBnetEducation & Training committee (http://www.embnet.org)

http://www.ch.embnet.org/MD_tutorial/pages/MD.Part2.html

Review: CHARMM potential

Chemical type	K_{bond}	b_o
C−C	100 kcal/mole/Å^2	1.5 Å
C=C	200 kcal/mole/Å^2	1.3 Å
C≡C	400 kcal/mole/Å^2	1.2 Å



Different types of C-C bonding represented by different choices of b_0 and k_b;

Need to retype when chemical environment changes

$$V_{bond} = K_b\left(b - b_o\right)^2$$

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

Review: CHARMM potential

$$E_{non-bonded} = E_{van-der-Waals} + E_{electrostatic}$$

$$E_{van-der-Waals} = \sum_{\substack{nonbonded \\ pairs}} \left(\frac{A_{ik}}{r_{ik}^{12}} - \frac{C_{ik}}{r_{ik}^{6}} \right)$$

Image removed for copyright restrictions.

See the graph on this page:
http://www.ch.embnet.org/MD_tutorial/pages/MD.Part2.html

$$E_{electrostatic} = \sum_{\substack{nonbonded \\ pairs}} \frac{q_i q_k}{D r_{ik}}$$

Nonbonding interactions

vdW (dispersive)

Coulomb (electrostatic)

H-bonding

DREIDING potential

$$E = E_{val} + E_{nb}$$

$$E_{val} = E_B + E_A + E_T + E_I$$

$$E_{nb} = E_{vdw} + E_Q + E_{hb}$$

$$E = \tfrac{1}{2}k_e(R - R_e)^2$$

$$E_{IJK} = \tfrac{1}{2}C_{IJK}[\cos\theta_{IJK} - \cos\theta_J^0]^2$$

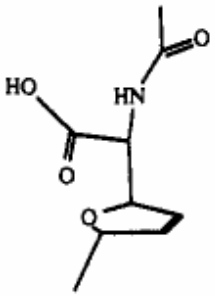
Geometric Valence Parameters for DREIDING

Atom	Bond radius R_I^0, Å	Bond angle, deg	Atom	Bond radius R_I^0, Å	Bond angle, deg
H_	0.330	180.0	Si3	0.937	109.471
H__HB	0.330	180.0	P_3	0.890	93.3
H_b	0.510	90.0	S_3	1.040	92.1
B_3	0.880	109.471	Cl	0.997	180.0
B_2	0.790	120.0	Ga3	1.210	109.471
C_3	0.770	109.471	Ge3	1.210	109.471
C_R	0.700	120.0	As3	1.210	92.1
C_2	0.670	120.0	Se3	1.210	90.6
C_1	0.602	180.0	Br	1.167	180.0
N_3	0.702	106.7	In3	1.390	109.471
N_R	0.650	120.0	Sn3	1.373	109.471
N_2	0.615	120.0	Sb3	1.432	91.6
N_1	0.556	180.0	Te3	1.280	90.3
O_3	0.660	104.51	I_	1.360	180.0
O_R	0.660	120.0	Na	1.860	90.0
O_2	0.560	120.0	Ca	1.940	90.0
O_1	0.528	180.0	Fe	1.285	90.0
F_	0.611	180.0	Zn	1.330	109.471
A13	1.047	109.471			

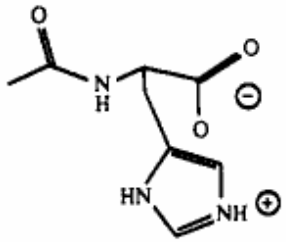
$K_{IJ}(1) = 700$ (kcal/mol)/Å^2

Valence Force Constants for DREIDING

Bonds		
$n = 1$	$K = 700$ (kcal/mol)/Å^2	$D = 70$ kcal/mol
$n = 2$	$K = 1400$ (kcal/mol)/Å^2	$D = 140$ kcal/mol
$n = 3$	$K = 2100$ (kcal/mol)/Å^2	$D = 210$ kcal/mol
Angles	$K = 100$ (kcal/mol)/rad^2	



ACFUCN



ACHIST20

Figure by MIT OCW.

UFF "Universal Force Field"

- Can handle complete periodic table
- Force constants derived using general rules of element, hybridization and connectivity

$$E_R = \tfrac{1}{2} k_{IJ} (r - r_{IJ})^2$$

$$r_{IJ} = r_I + r_J + r_{BO} + r_{EN}$$

Pauling-type bond order correction

$$r_{BO} = -\lambda (r_I + r_J) \ln (n)$$

$$r_{EN} = r_I r_J (\sqrt{\chi_I} - \sqrt{\chi_J})^2 / (\chi_I r_I + \chi_J r_J)$$

$$k_{IJ} = \left(\frac{\partial^2 E_r}{\partial R^2} \right)_0 = 2G \frac{Z_I^* Z_J^*}{R^3} = 664.12 \frac{Z_I^* Z_J^*}{r_{IJ}^3}$$

Features:

- Atom types=elements
- Chemistry based rules for determination of force constants

Rappé *et al.*

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

Image removed due to copyright restrictions.

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/

Alpha helix and beta sheets

Hydrogen bonding

e.g. between O and H in H_2O

Between N and O in proteins…

Images removed due to copyright restrictions.

Image removed due to copyright restrictions.

Image removed due to copyright restrictions.
See: http://www.columbia.edu/cu/biology/courses/c2005/images/3levelpro.4.p.jpg

Unfolding of alpha helix structure

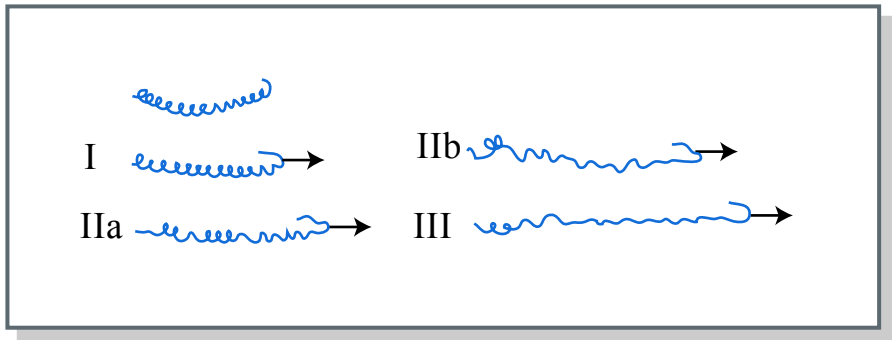


Figure by MIT OCW.

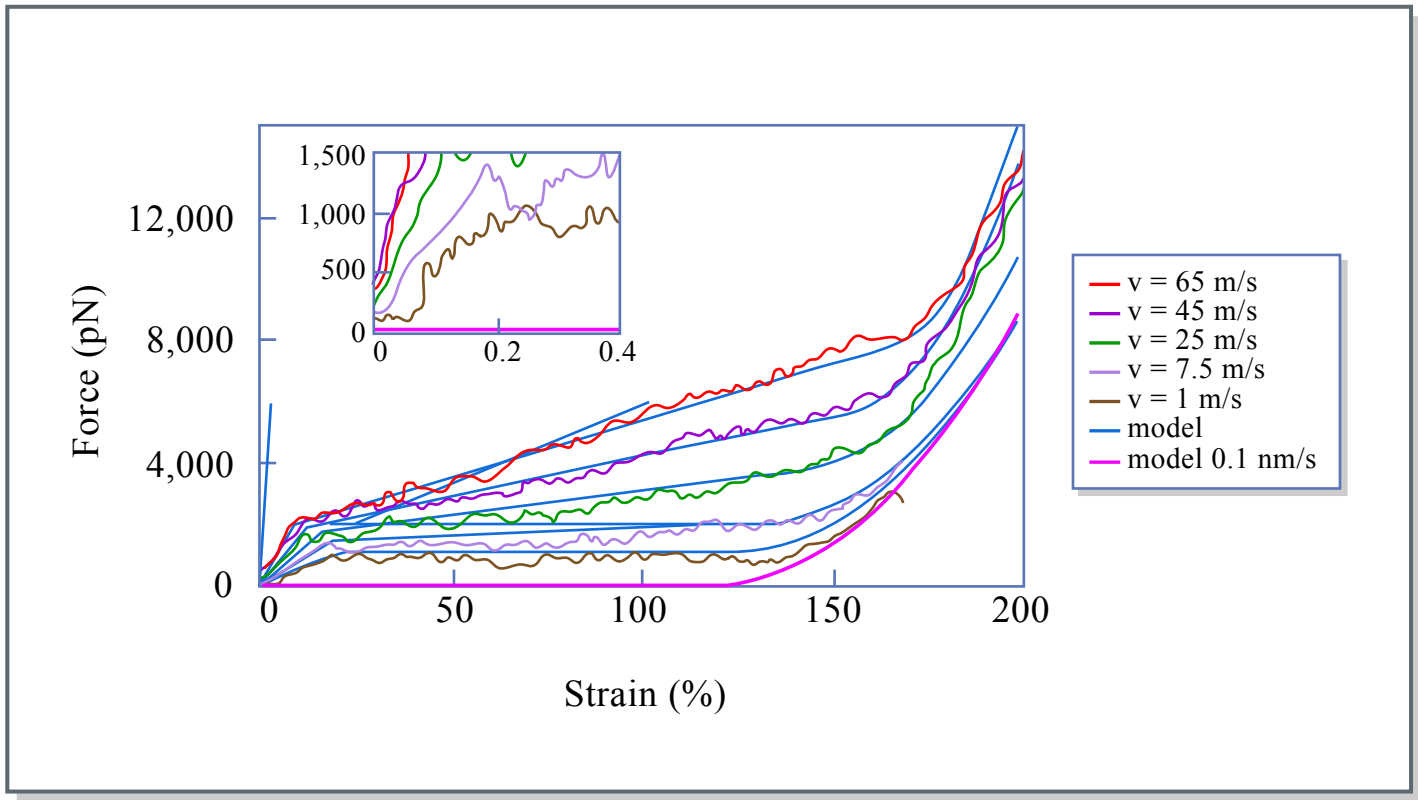


Figure by MIT OCW.

Source: Ackbarow, T., and M. J. Buehler. "Superelasticity, Energy Dissipation and Strain Hardening of Vimentin Coiled-coil Intermediate Filaments." Accepted for publication in: *J Materials Science* (in press), DOI 10.1007/s10853-007-1719-2 (2007).

Unfolding of alpha helix structure

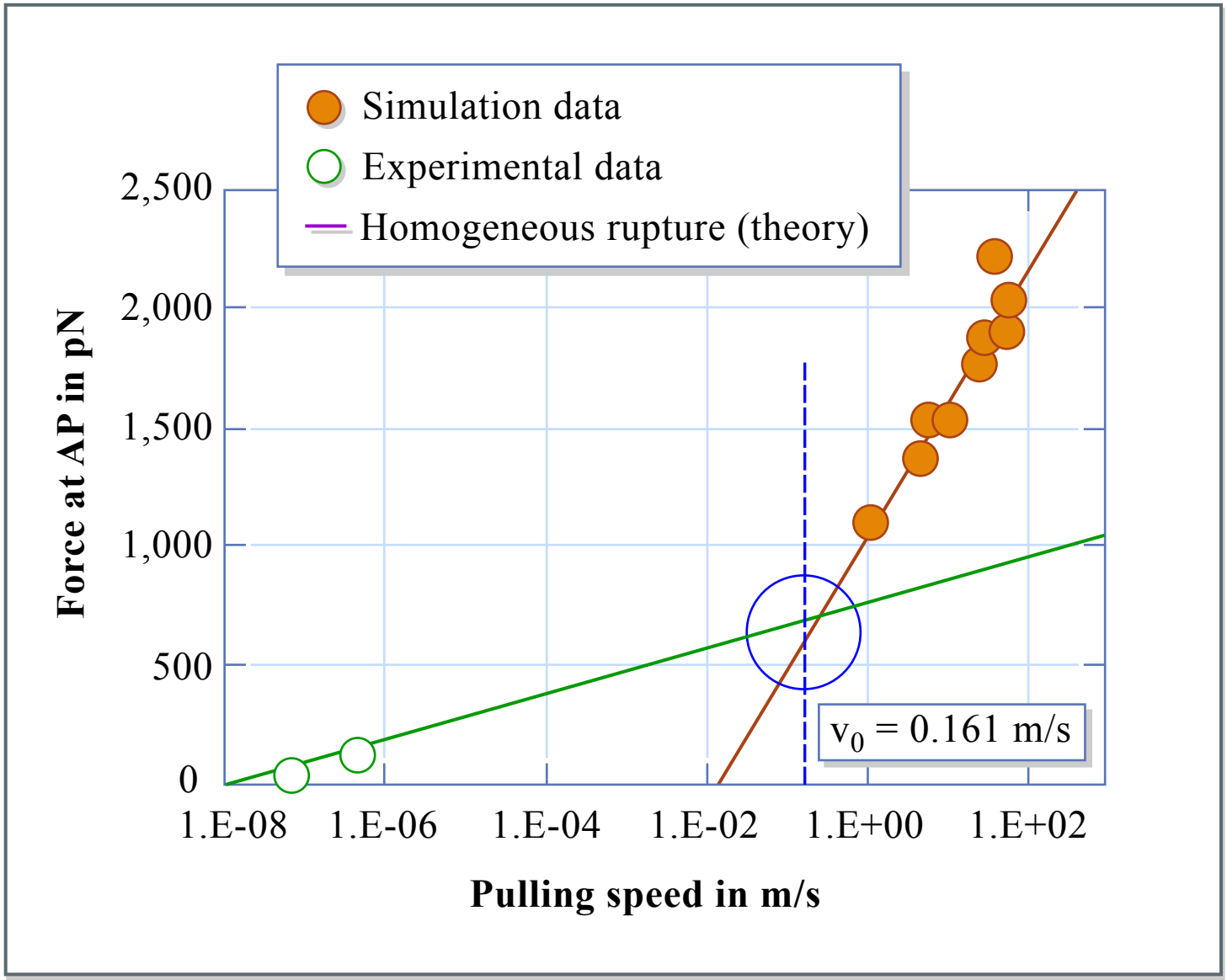


Figure by MIT OCW.

Source: Ackbarow, T., and M. J. Buehler. "Superelasticity, Energy Dissipation and Strain Hardening of Vimentin Coiled-coil Intermediate Filaments." Accepted for publication in: *J Materials Science* (in press), DOI 10.1007/s10853-007-1719-2 (2007).

Spider Silk

- Composed almost solely of protein, such as Spidroin (MaSp) I & II
- Semi-crystalline polymer
- Amorphous phase: Rubber-like chains, Gly-rich matrix
- Crystals: H-bonded β-sheets of poly-Ala sequences

Images removed due to copyright restrictions.

Keten and Buehler, 2007

Unfolding of beta sheet

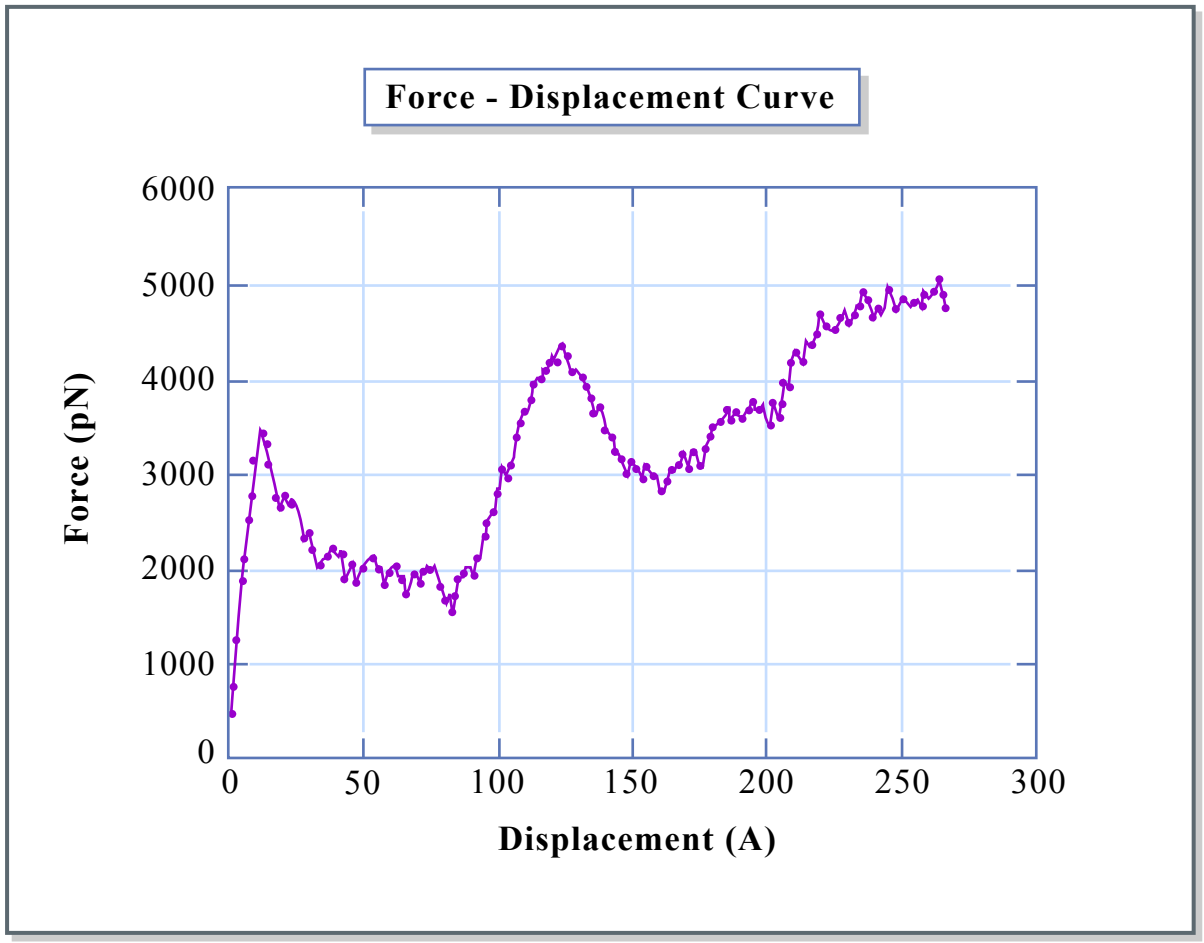


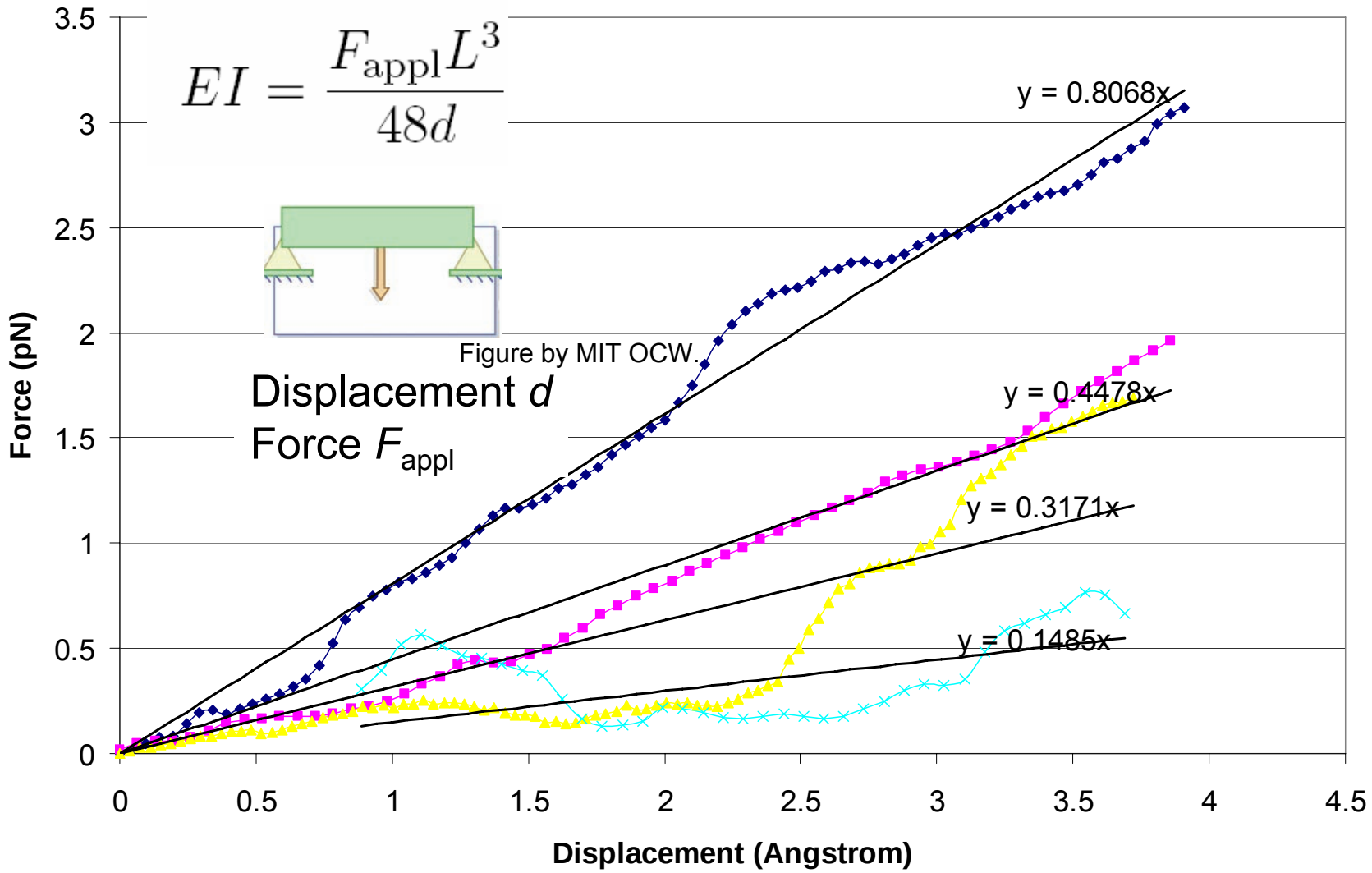
Figure by MIT OCW.

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

Image removed due to copyright restrictions.

Keten and Buehler, 2007

Three-point bending test: Tropocollagen molecule



Buehler and Wong, 2007

Three-point bending test: Tropocollagen molecule

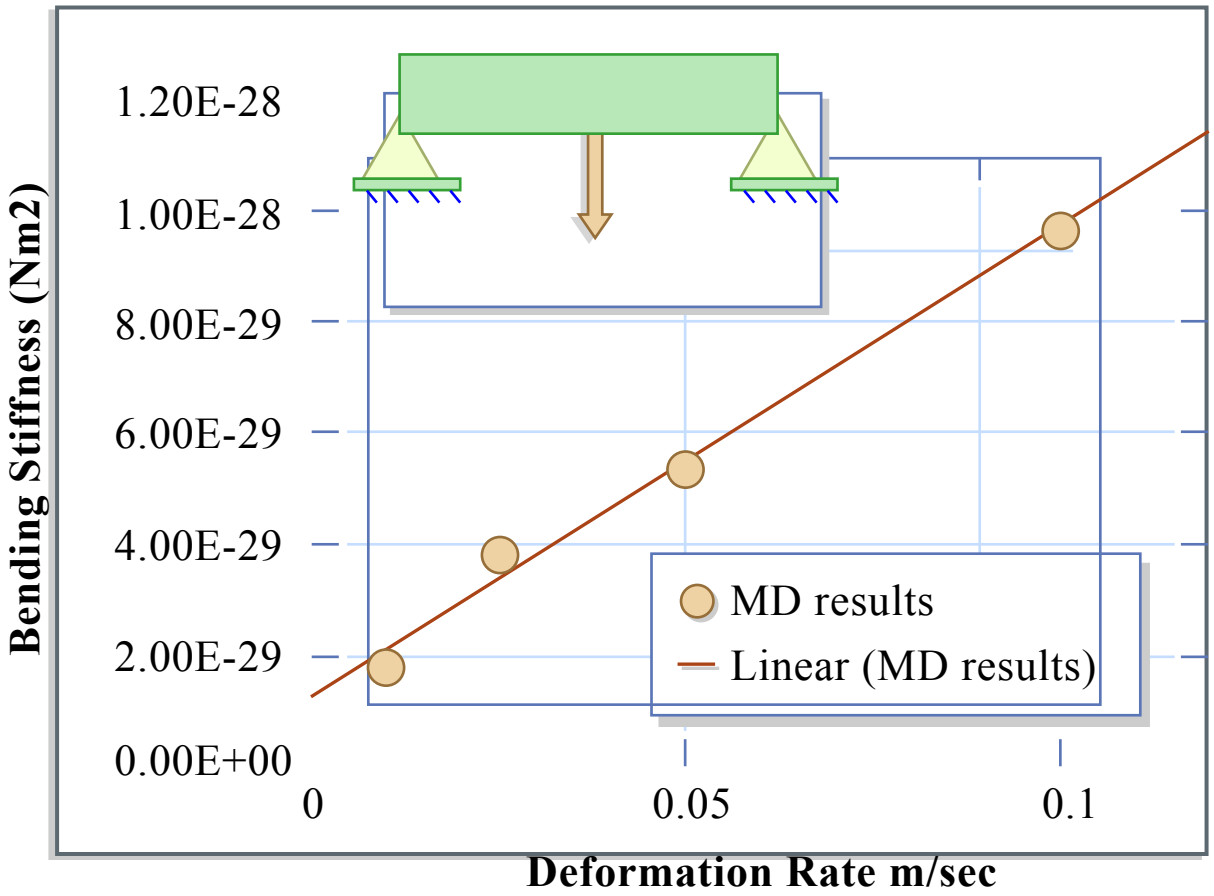


Figure by MIT OCW.

MD: Calculate bending stiffness; consider different deformation rates

Result: Bending stiffness at zero deformation rate (extrapolation)

Yields: Persistence length – between **3 nm** and **25 nm** (experiment: **7 nm**)

Buehler and Wong, 2007

Stretching experiment: Tropocollagen molecule

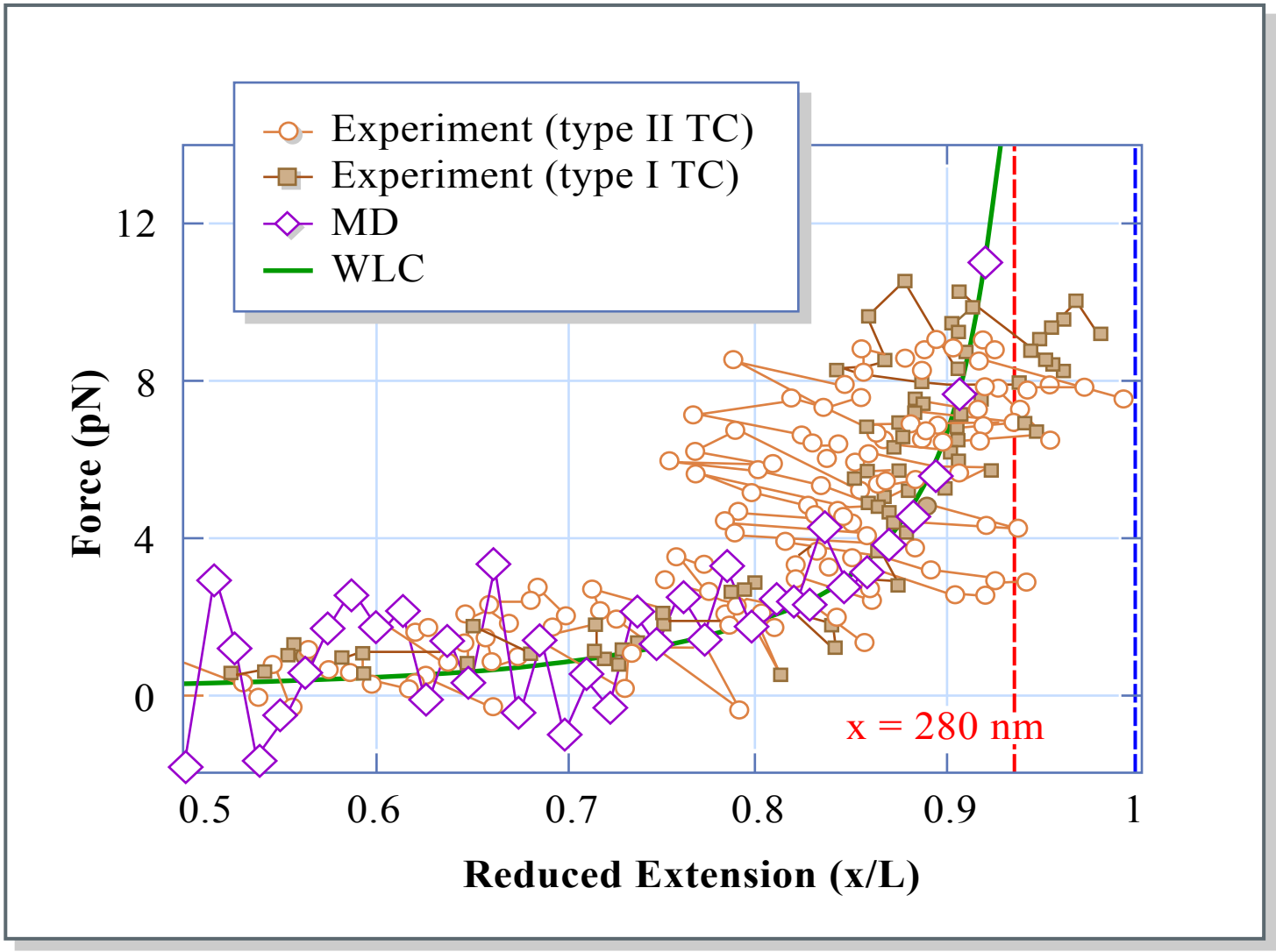


Figure by MIT OCW. After Buehler and Wong.

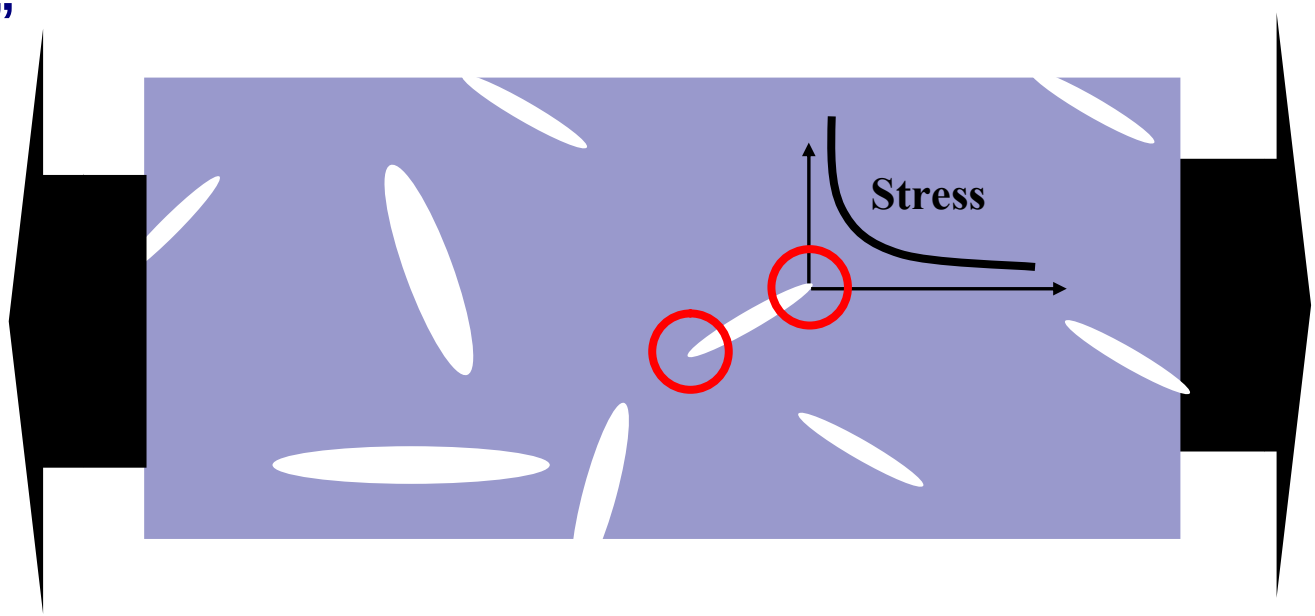
Fracture at ultra small scales

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?

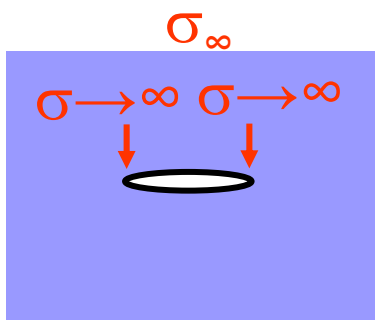
"Nano"



Griffith

Review: Two paradoxons of classical fracture theories

Infinite peak stress



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

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

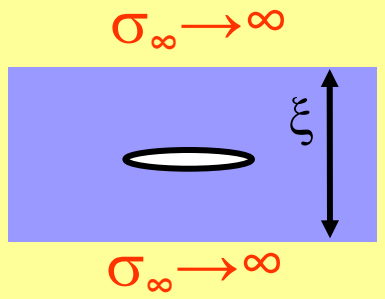
"Inglis paradox": Why does crack not extend, despite infinitely large stress at even small applied load?

- 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 (ξ=O(nm))!

Considered here



Infinite bulk stress

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

Thin strip geometry

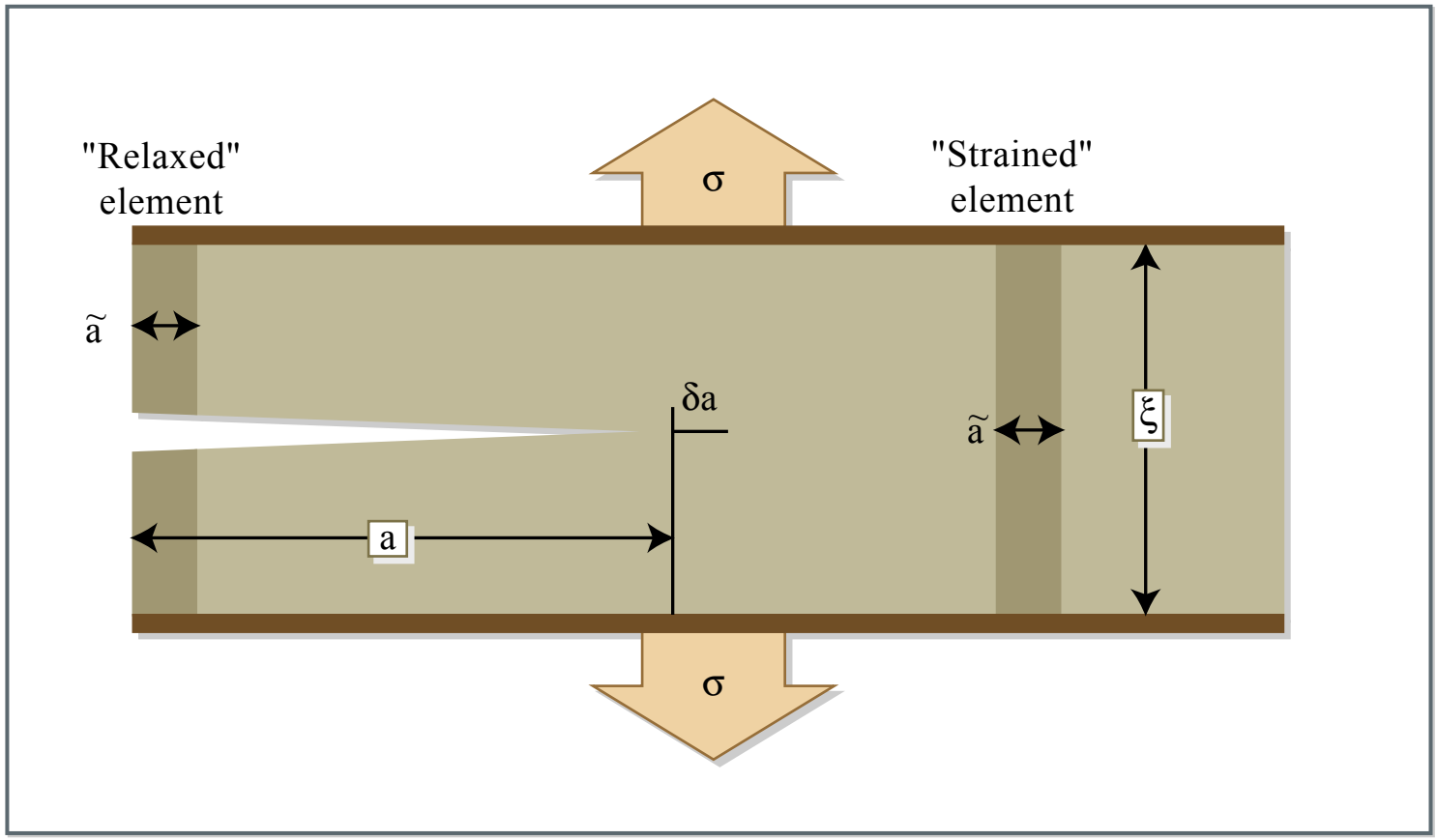
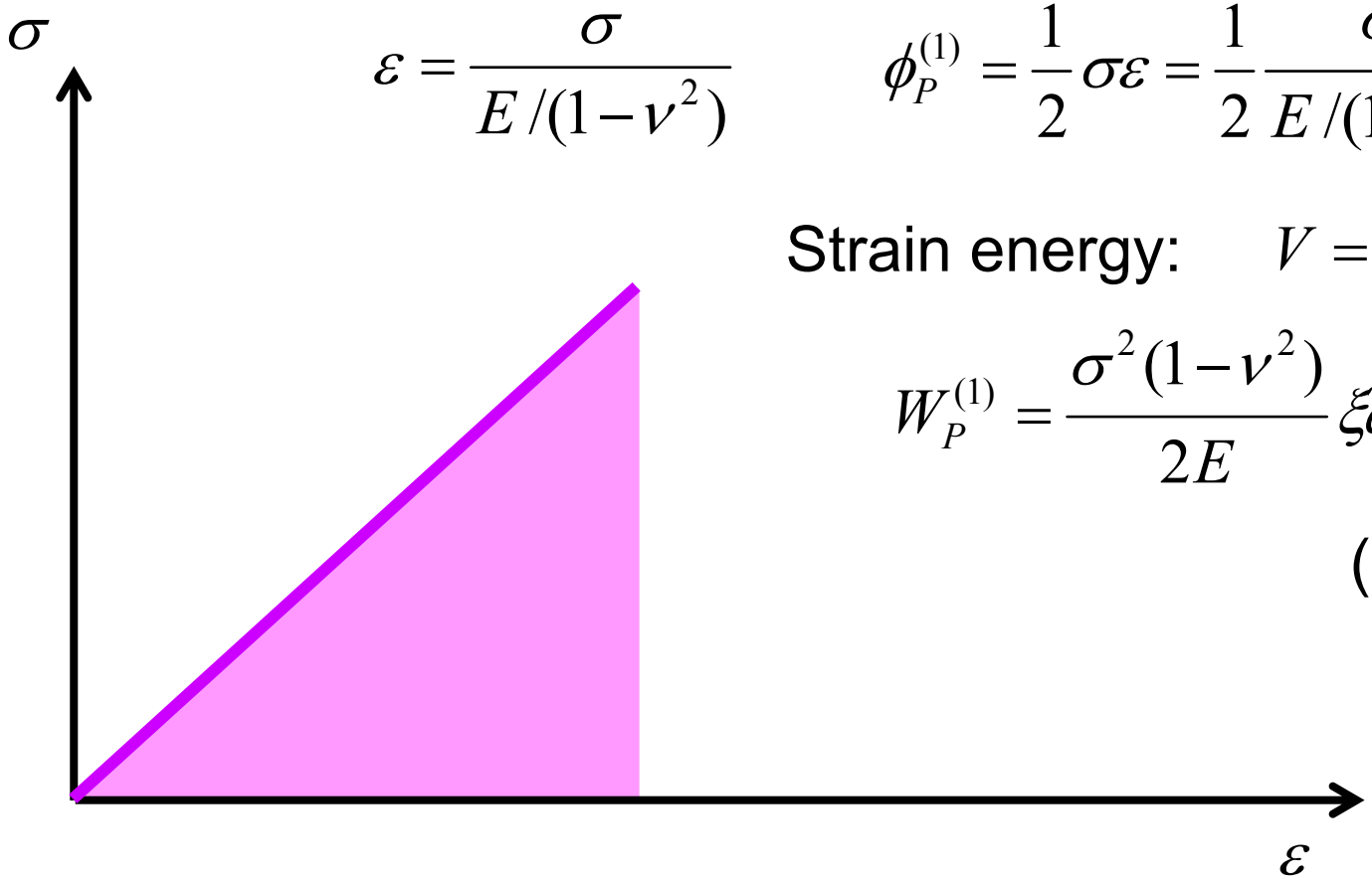


Figure by MIT OCW.

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

$$W_P = W_P(\sigma, a, \ldots)$$

Thin strip geometry



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

Strain energy density:

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

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

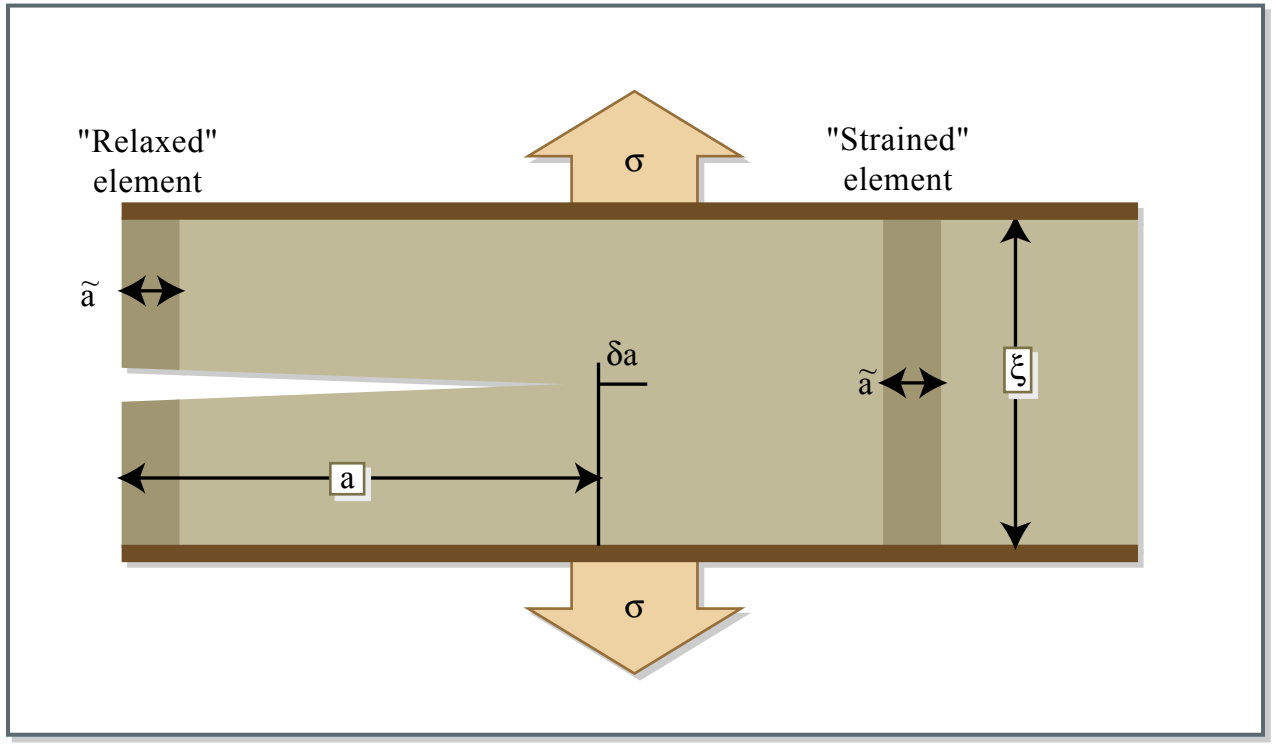


Figure by MIT OCW.

$$W_P^{(2)} = 0$$

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

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

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

Fracture of thin strip geometry
Theoretical considerations

$$G = \frac{\sigma^2 \xi (1-\nu^2)}{2E} \qquad 2\gamma = G \quad \text{Griffith}$$

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

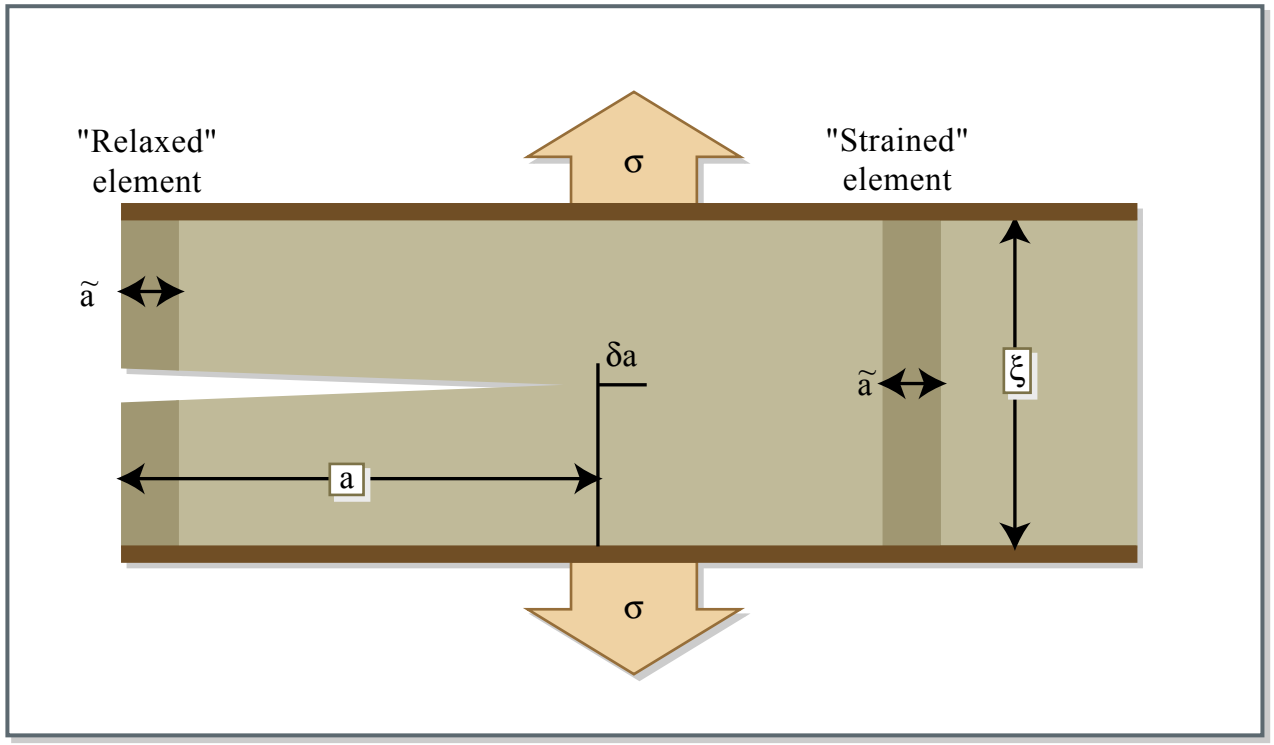


Figure by MIT OCW.

ξ.. size of material

Fracture of thin strip geometry
Theoretical considerations

Stress for spontaneous crack propagation

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

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

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

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

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

ξ.. size of material

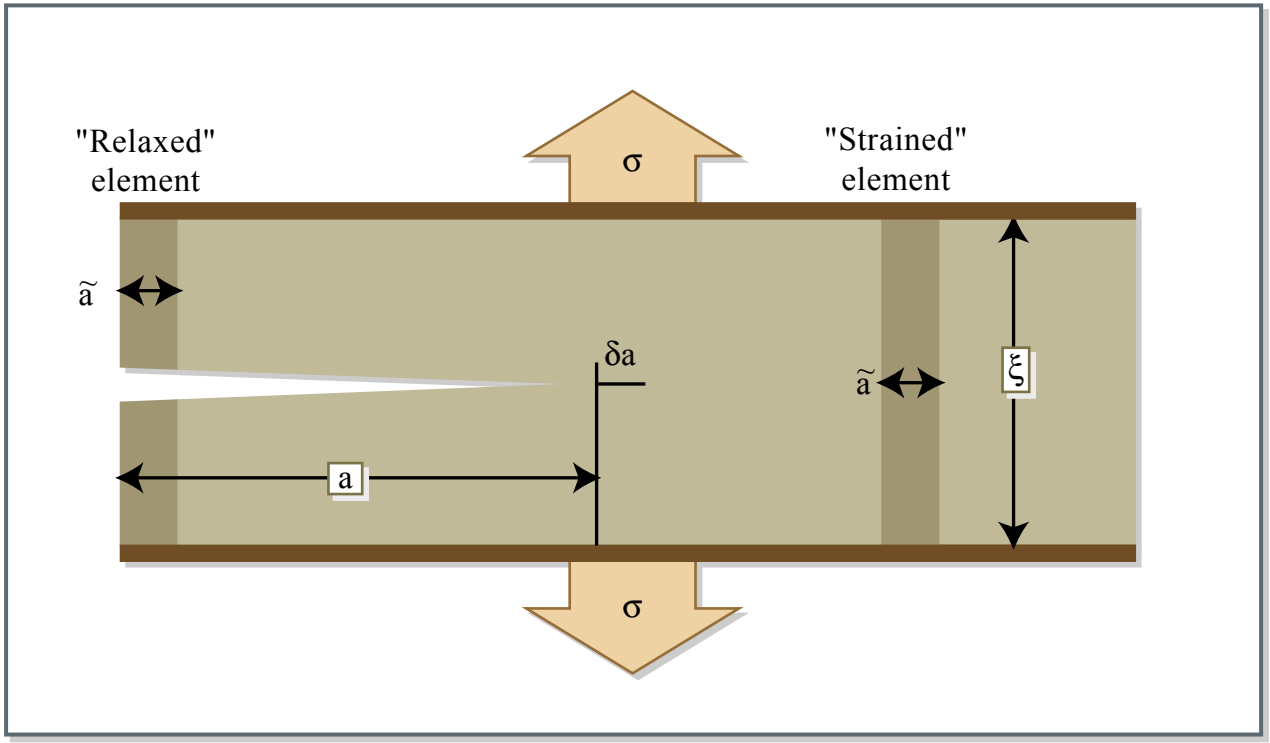
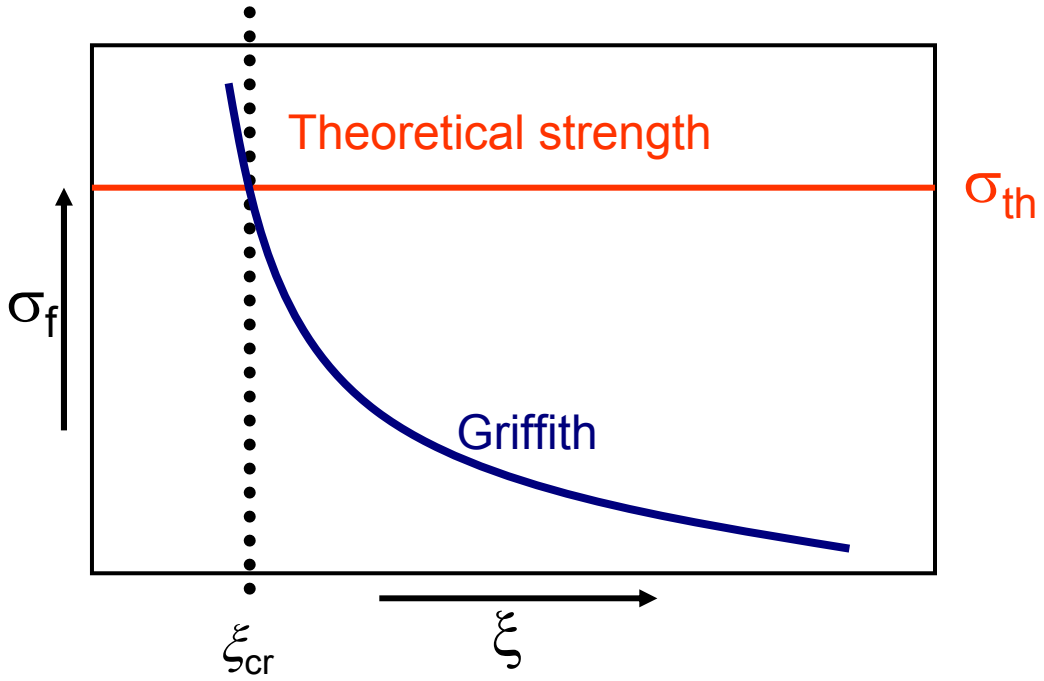


Figure by MIT OCW.

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

Breakdown of Griffith at ultra small scales



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

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

Bulk (harmonic, FCC)

$$\phi(r) = a_0 + \frac{1}{2} k_0 (r - r_0)^2 \qquad r_0 = 2^{1/6} \qquad k_0 = 572.0$$

$$a \approx 1.587$$

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

Interface (LJ) "dispersive-glue interactions"

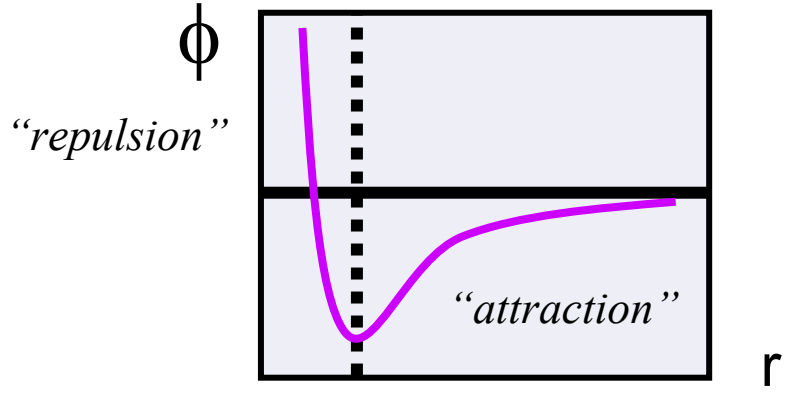
$$\phi(r) = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right) \qquad \varepsilon = \sigma = 1$$

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

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

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

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



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

Atomistic simulation results

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

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

Griffith-governed failure

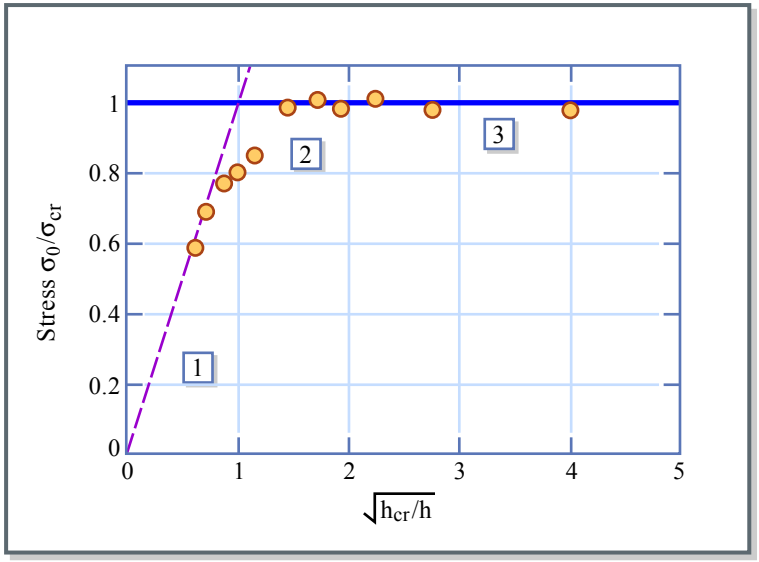


Figure by MIT OCW.

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

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

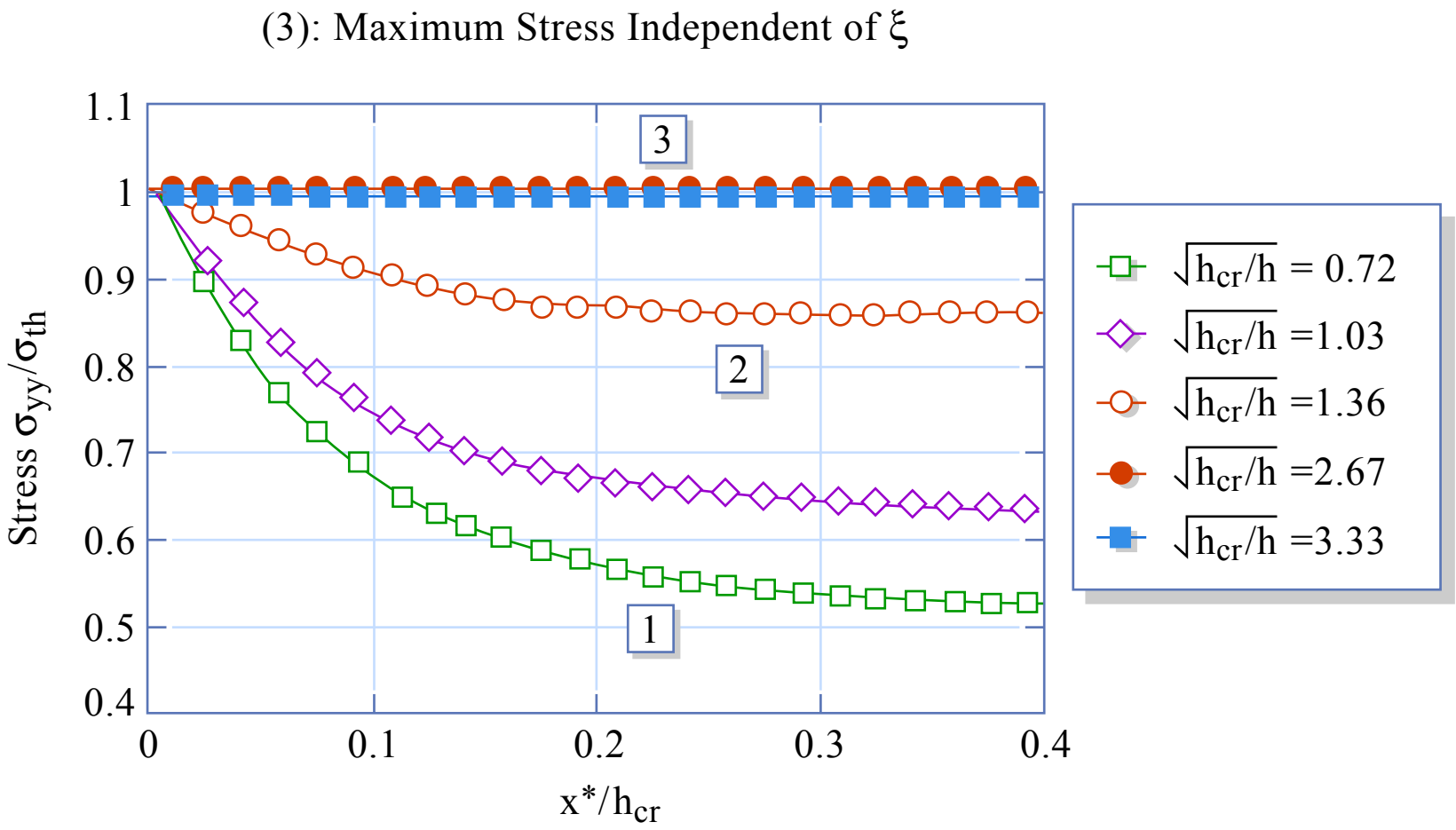
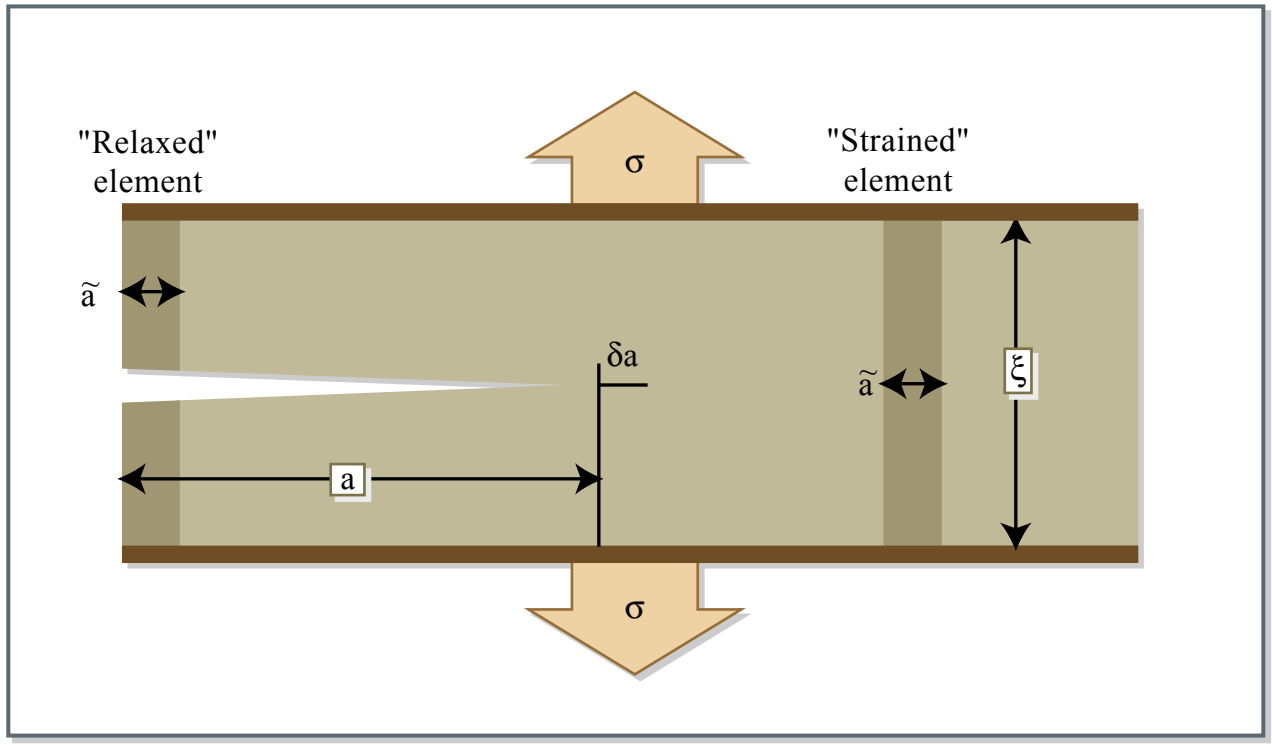


Figure by MIT OCW.

Shear loading



$$\xi_{cr} = \frac{4\gamma_s \mu \nu}{(1+\nu)(1-2\nu)\tau_{th}^2}$$

Image removed due to copyright restrictions.

Figure by MIT OCW.

Keten and Buehler, 2007

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

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

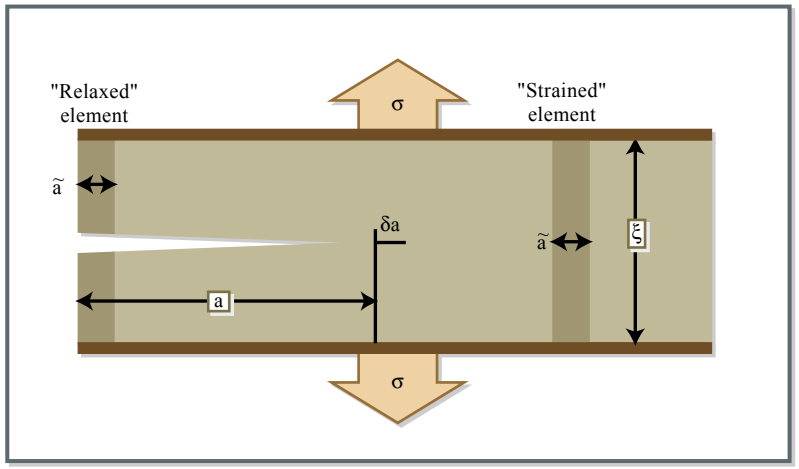


Figure by MIT OCW.

$h > h_{cr}$	$h < h_{cr}$
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*., 2004; Gao, Ji, Buehler, MCB, 2004)

Can this concept explain the design of biocomposites in bone?

Characteristic size: 10..100 nm

Image removed due to copyright restrictions.

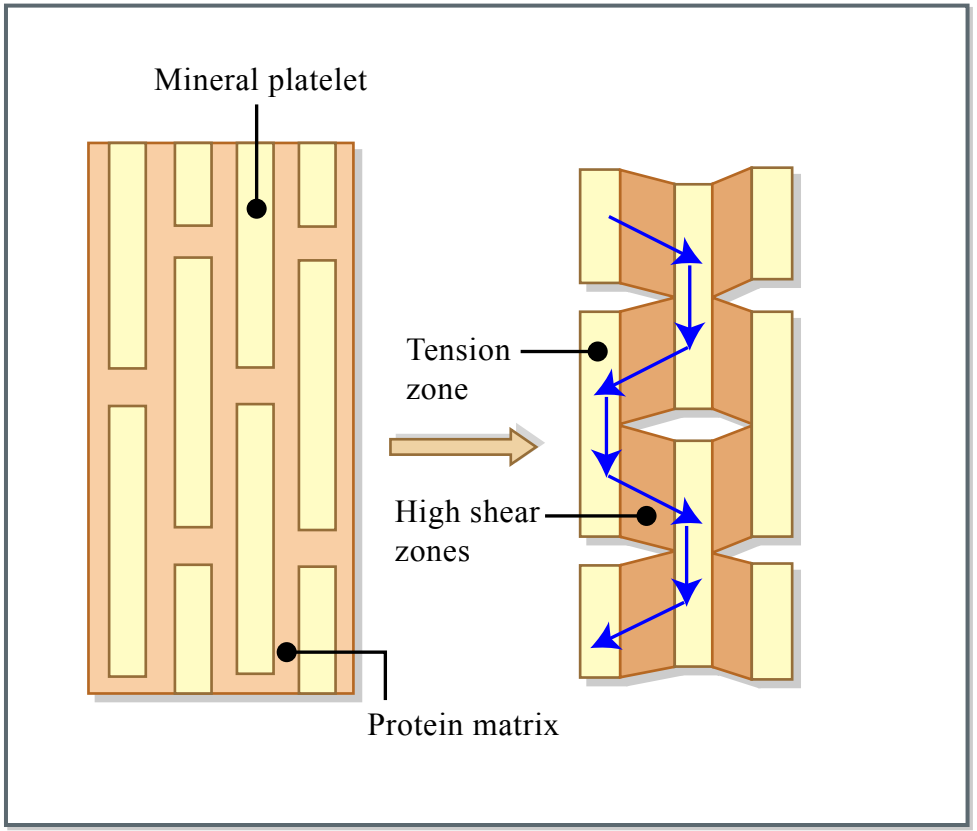


Figure by MIT OCW.

Estimate for biominerals:

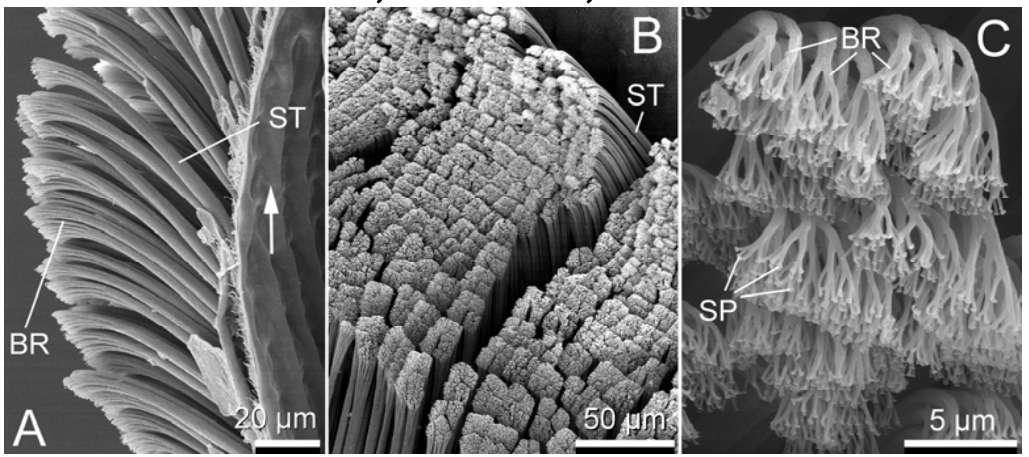
$$\sigma_{\max} \approx \frac{E}{30}, \ \nu \approx 0.25, \ E = 100 \text{ GPa}, \ \gamma = 1 \text{J/m}^2$$

$$\Psi^* \approx 0.022 \qquad h_{cr} \approx 30 \text{ nm}$$

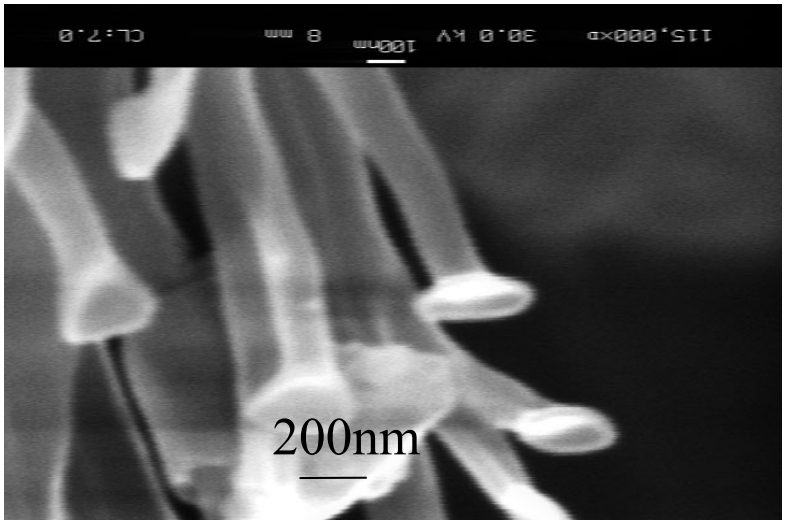
(Gao *et al.*, 2003, 2004)

Adhesion of Geckos

Autumn et al., PNAS, 2002



Courtesy of National Academy of Sciences, U.S.A. Used with permission.
Source: Autumn, Kellar, Metin Sitti, Yiching A. Liang, Anne M. Peattie, Wendy R. Hansen, Simon Sponberg, Thomas W. Kenny, Ronald Fearing, Jacob N. Israelachvili, and Robert J. Full. "Evidence for van der Waals adhesion in gecko setae." *PNAS* 99 (2002): 12252-12256.
(c) National Academy of Sciences, U.S.A.



Images remove due to copyright restrictions.

Adhesion at small length scales

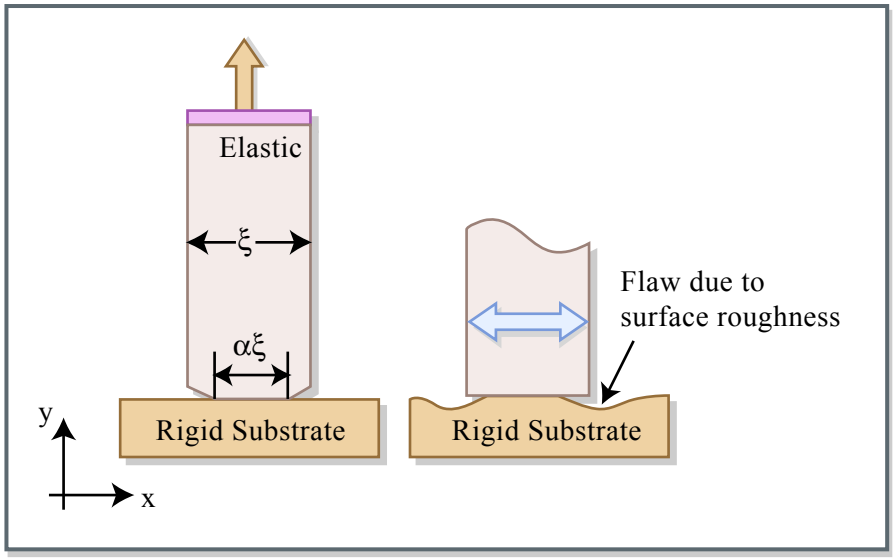


Image removed due to copyright restrictions.

Figure by MIT OCW.

Strategies to increase adhesion strength

-Since F ~ 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)

• 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.

Equivalence of adhesion and fracture problem

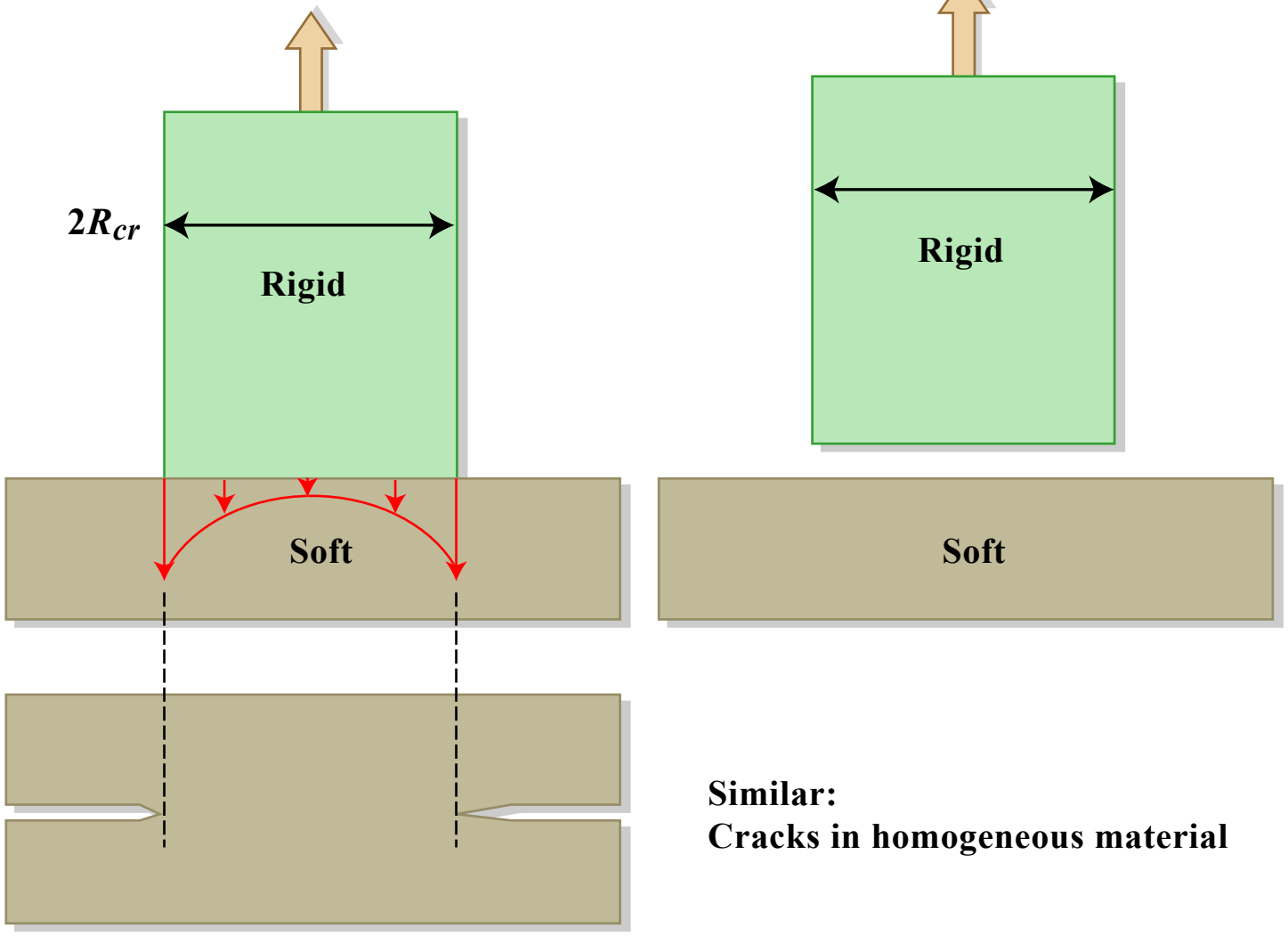


Figure by MIT OCW.

Equivalence of adhesion and fracture problem

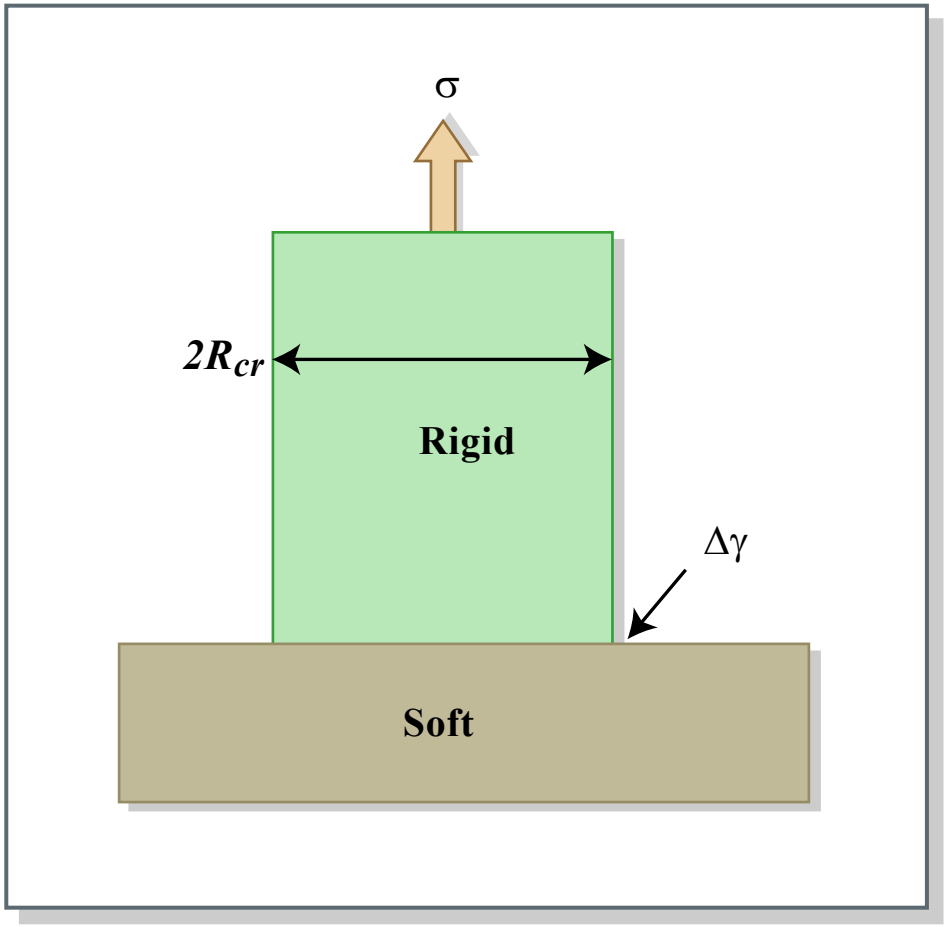


Figure by MIT OCW.

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

Theoretical considerations
Adhesion problem as fracture problem

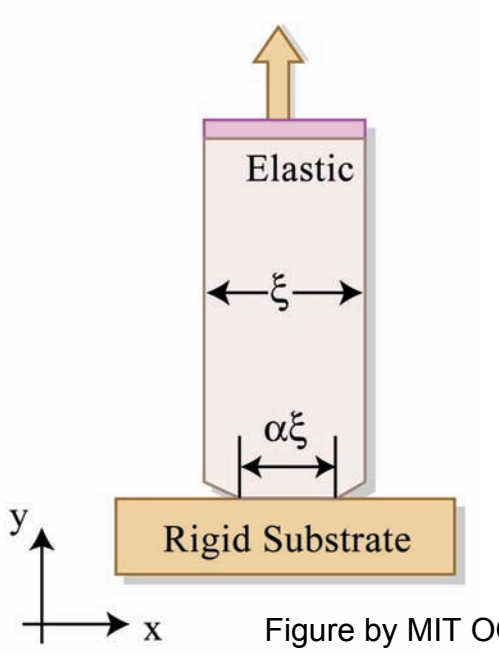


Figure by MIT OCW.

Function (tabulated)

$$K_I = \frac{P}{\pi a^2}\sqrt{\pi a}\,F_1(\alpha)$$

$$\frac{K_I^2}{2E^*} = \Delta\gamma$$

$$\psi = \sqrt{\frac{\Delta\gamma E^*}{R\sigma_{th}^2}}$$

$$\beta = \sqrt{2/\left(\pi\alpha F_1^2(\alpha)\right)}$$

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

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

$$R_{cr} \sim 225nm$$

Typical parameters for Gecko spatula

Continuum and atomistic model

Three-dimensional model

Cylindrical attachment device

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

Harmonic

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

LJ

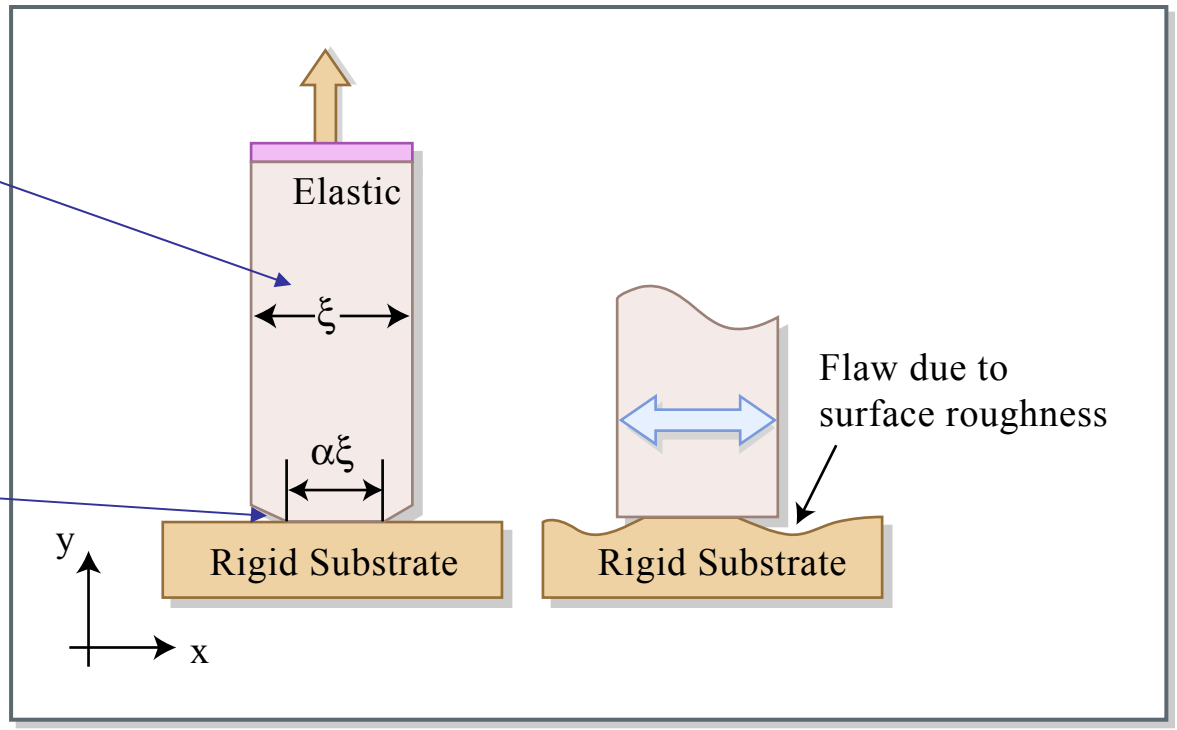


Figure by MIT OCW.

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

Figure removed due to copyright restrictions.

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

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

Figure removed due to copyright restrictions.

- 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

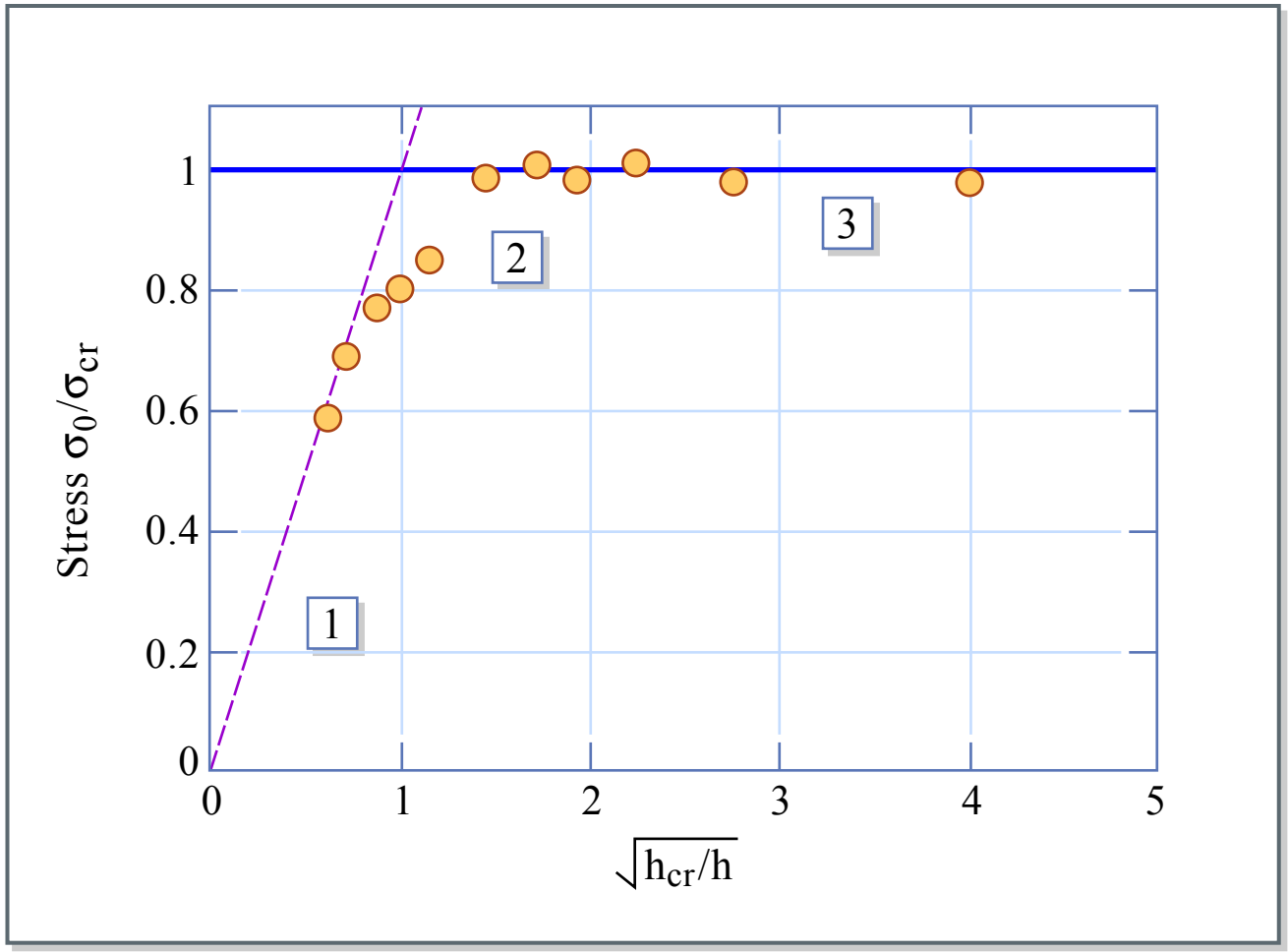


Figure by MIT OCW.

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

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

Images removed due to copyright restrictions.

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

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

Derivation: Concept of superposition to negate the singular stress

Optimal shape predicted by continuum theory & shape parameter ψ

Figure removed due to copyright restrictions.

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

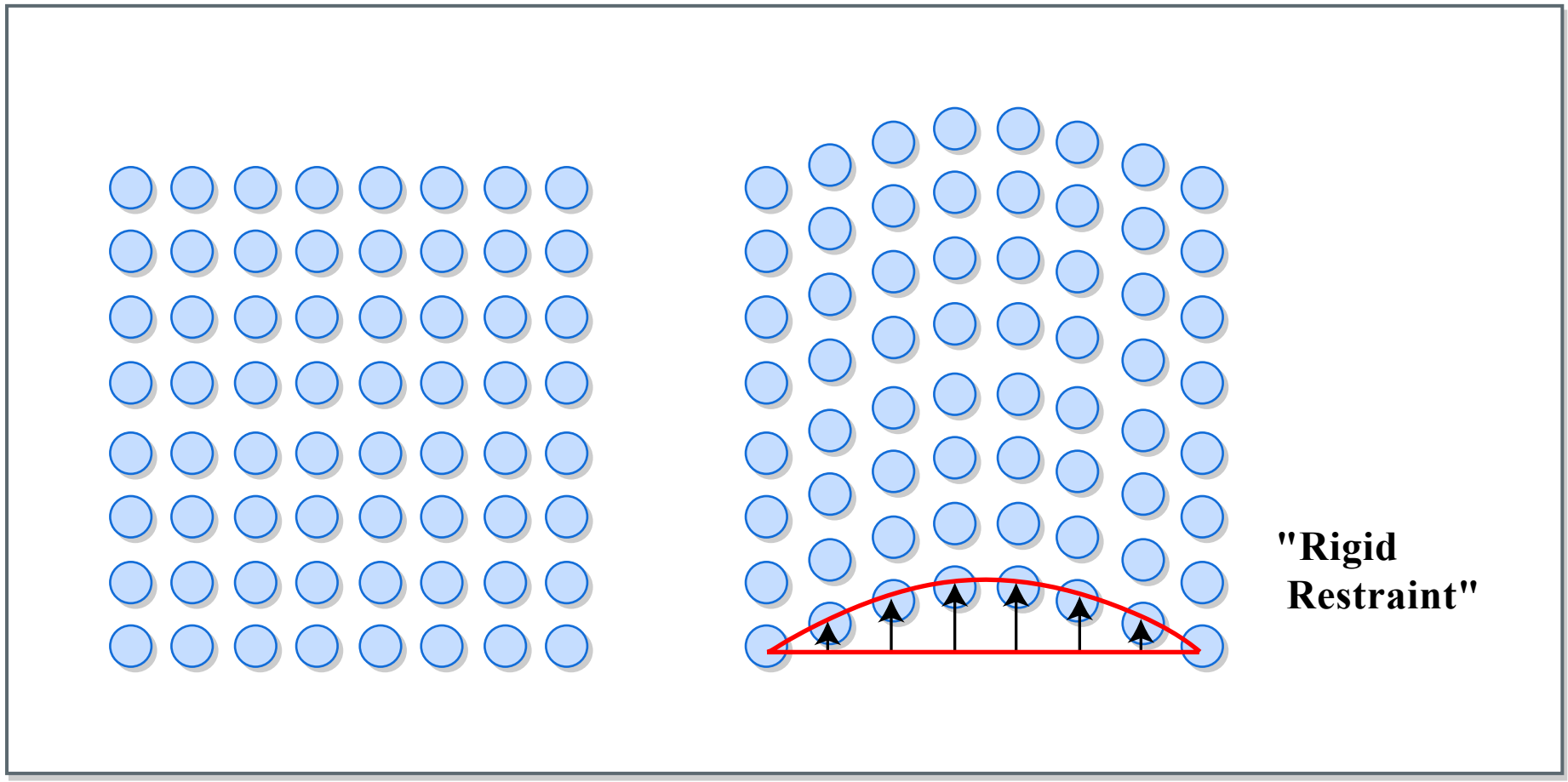
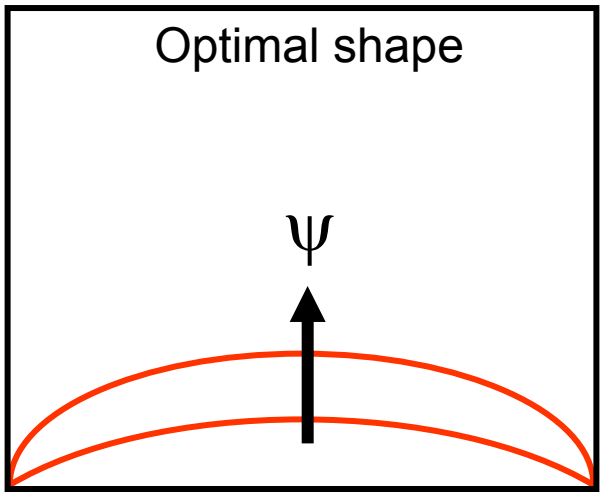


Figure by MIT OCW.

Strategy: Displace atoms held rigid to achieve smooth surface shape

Stress distribution at varying shape

Figure removed due to copyright restrictions.



ψ=1: Optimal shape

Robustness of adhesion

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.

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.

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

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

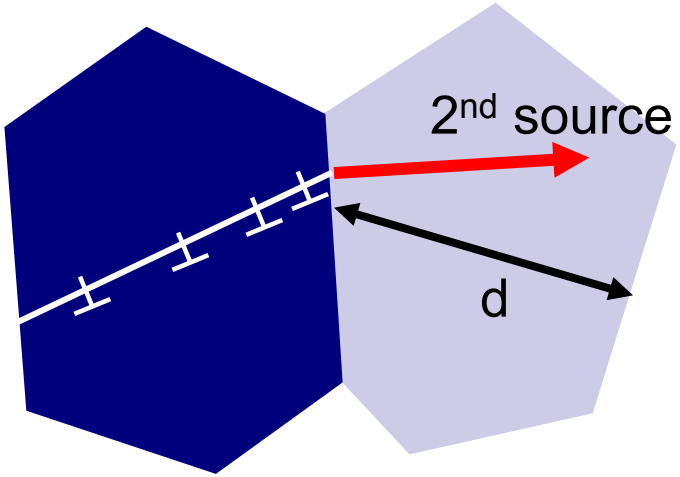
Images removed due to copyright restrictions.

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!*

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)

Figure removed due to copyright restrictions.
See p. 15 of http://www.imprs-am.mpg.de/summerschool2003/wolf.pdf

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

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

F=ma

Image removed due to copyright restrictions.

Real challenge:
Questions to ask and what to learn