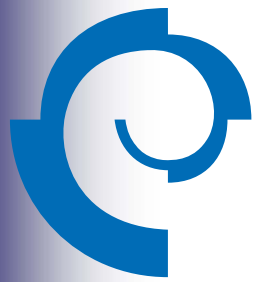
Nanomechanics of hierarchical biological materials (cont'd)

Lecture 7



Department of
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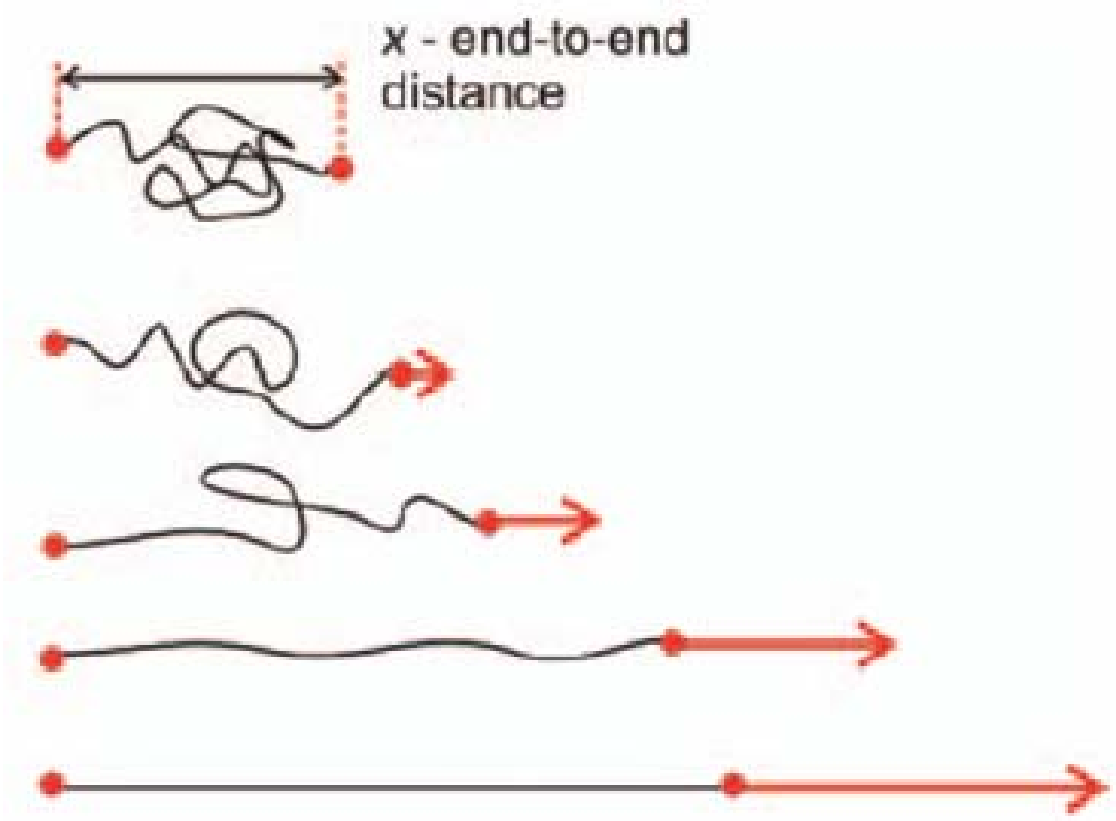
Outline

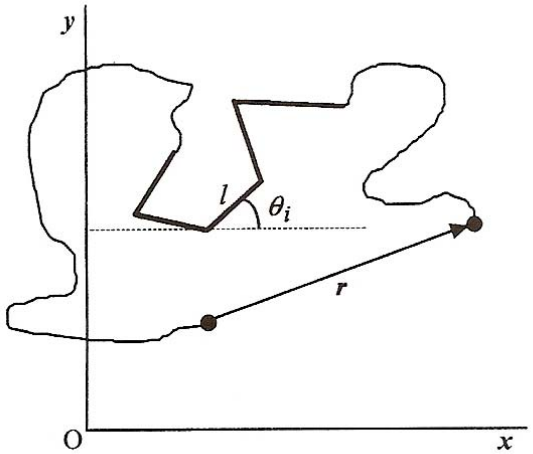
1. **Introduction to Mechanics of Materials**
   Basic concepts of mechanics, stress and strain, deformation, strength and fracture
   Monday Jan 8, 09-10:30am
2. **Introduction to Classical Molecular Dynamics**
   Introduction into the molecular dynamics simulation; numerical techniques
   Tuesday Jan 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

Entropic regime



Energetic regime



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

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

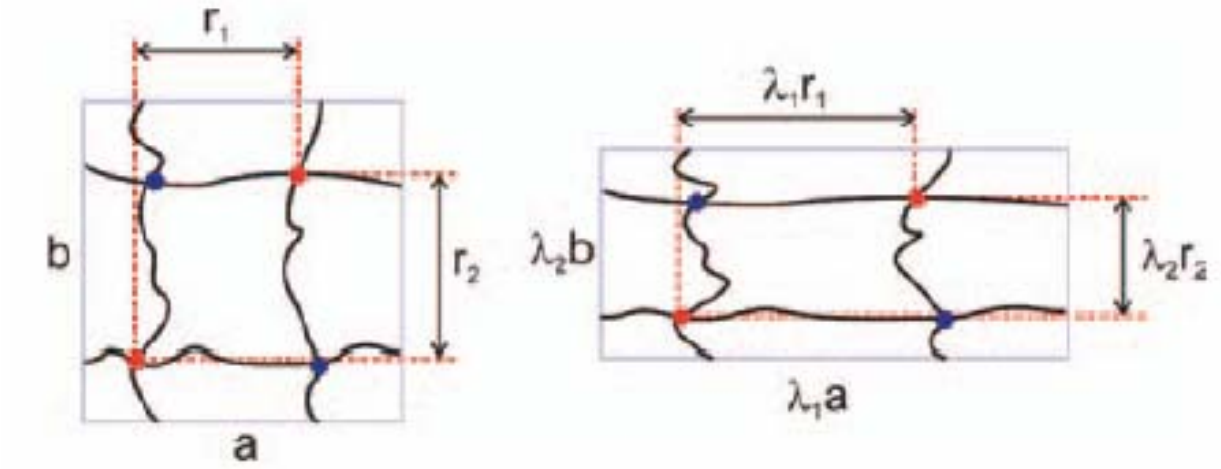
Entropic elasticity: Derivation

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

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



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

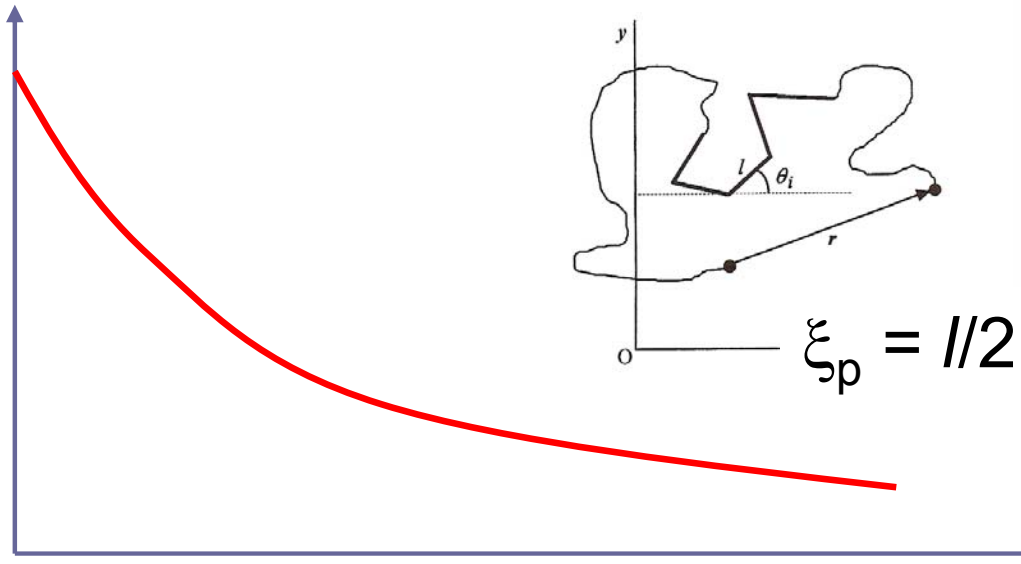
$$U = -T\Delta S = \tfrac{1}{2} N_b kT\left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3\right) \qquad C = E/6$$

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

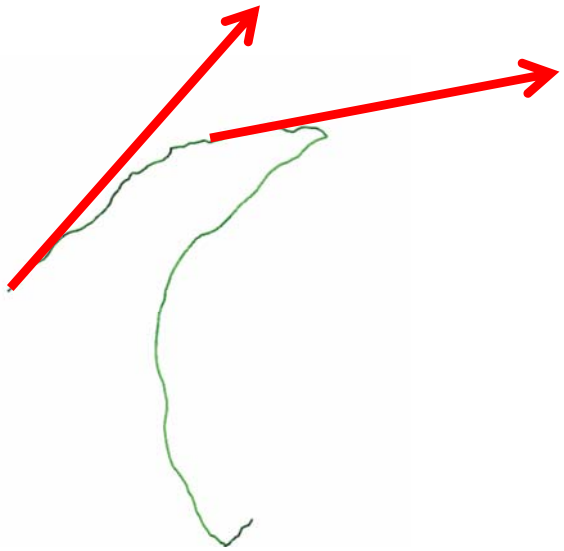
Persistence length

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

t(s) tangent slope



$\xi_p = l/2$

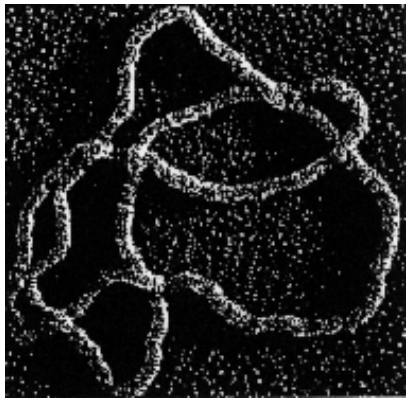


s

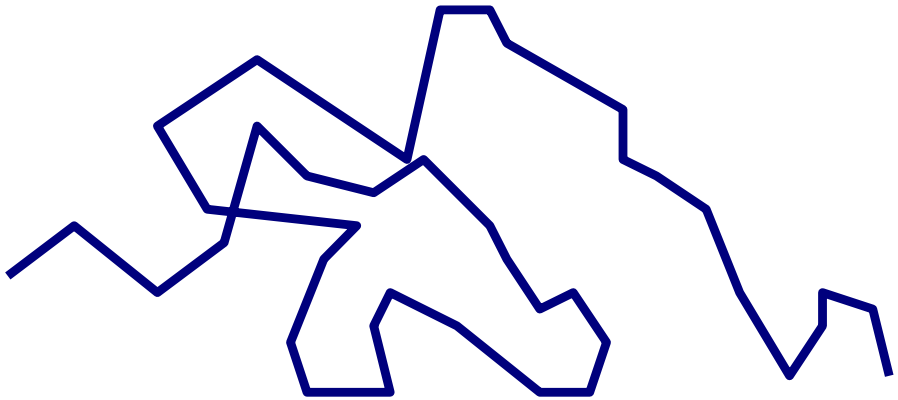
The length at which a filament is capable of bending significantly in independent directions, at a given temperature.
This is defined by a autocorrelation function which gives the characteristic distance along the contour over which the tangent vectors **t(s)** become uncorrelated

Worm-like chain model

Freely-jointed rigid rods

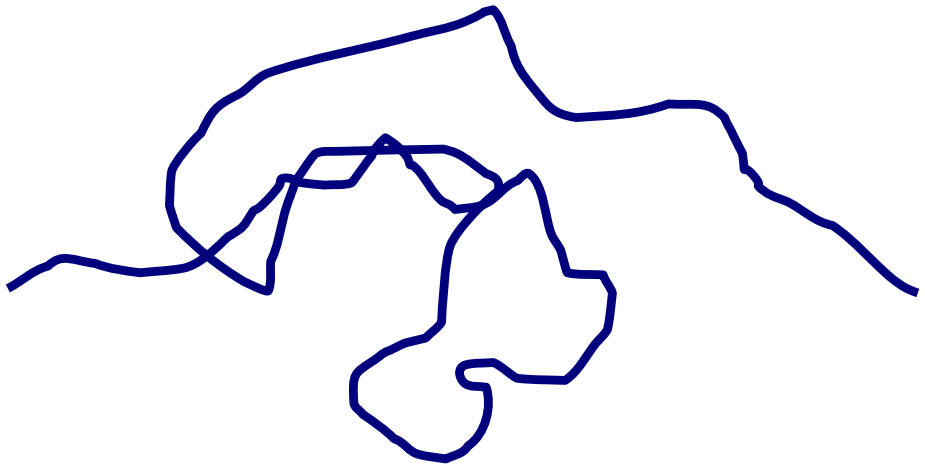


DNA 4-plat electron micrograph
(Cozzarelli, Berkeley)



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

Proteins

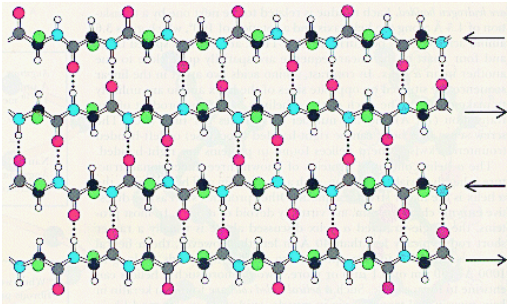
- An important building block in biological systems are proteins
- Proteins are made up of amino acids
- 20 amino acids carrying different side groups (R)
- Amino acids linked by the amide bond via condensation
- Proteins have four levels of structural organization: primary, secondary, tertiary and quaternary

Protein structure

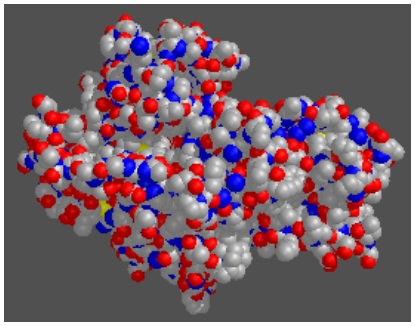
- **Primary structure:** Sequence of amino acids

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

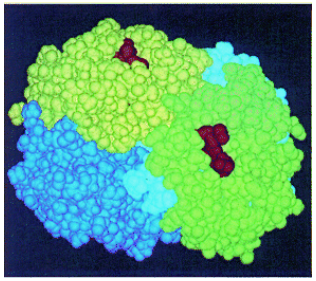
- **Secondary structure:** Protein secondary structure refers to certain common repeating structures found in proteins. There are two types of secondary structures: alpha-helix and beta-pleated sheet.



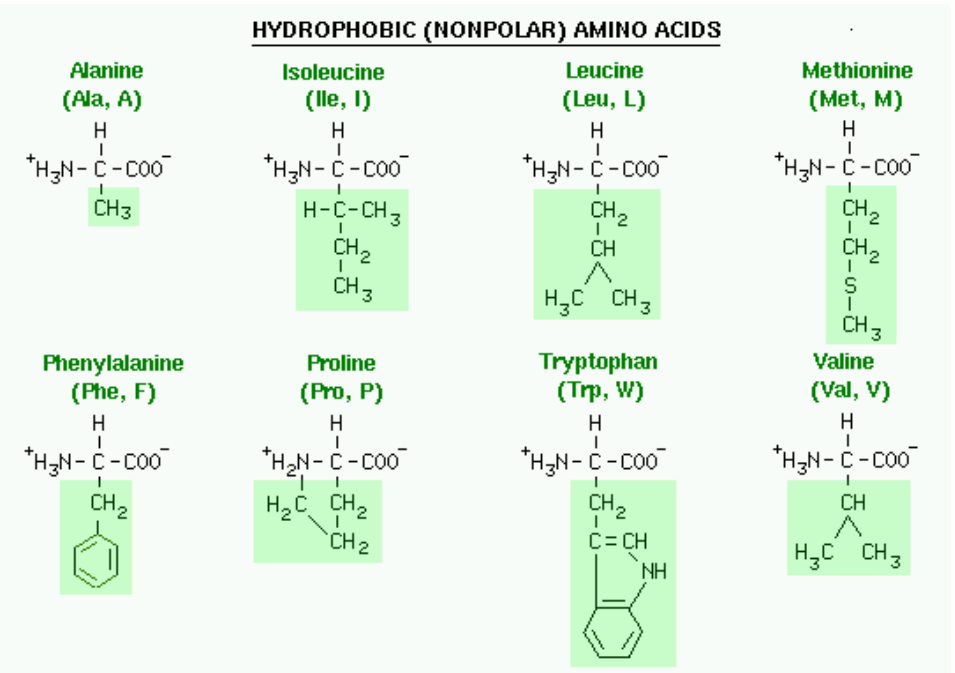
- **Tertiary structure:** Tertiary structure is the full 3-dimensional folded structure of the polypeptide chain.

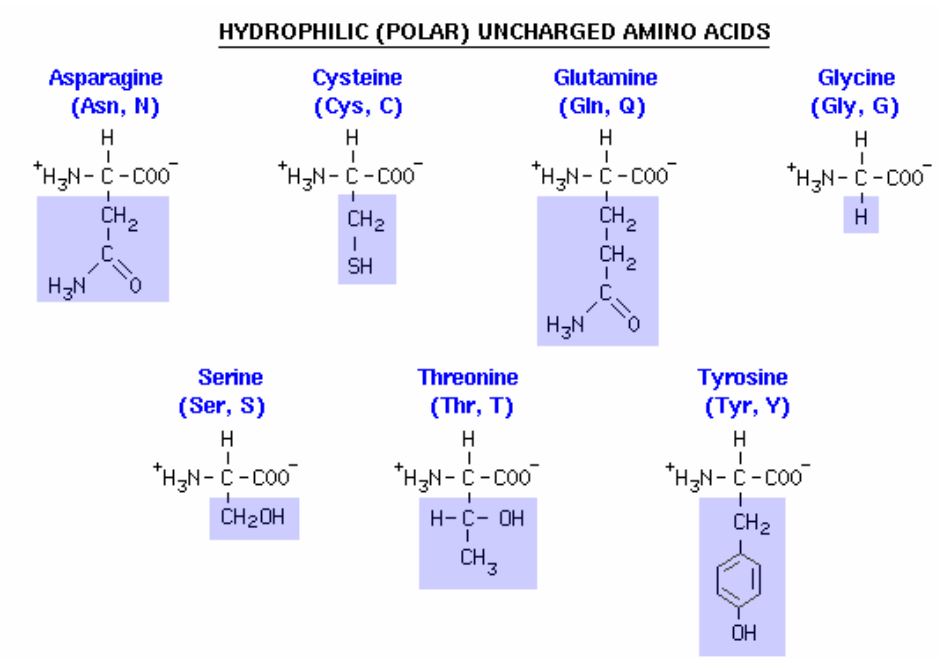


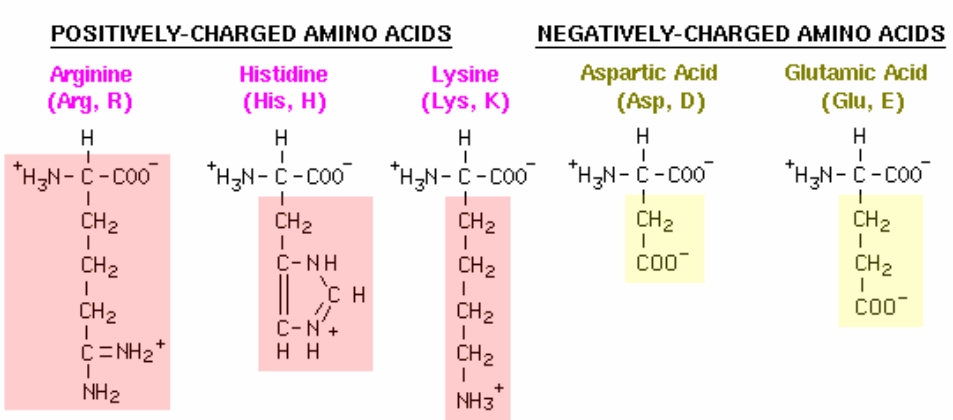
- **Quartenary Structure:** Quartenary structure is only present if there is more than one polypeptide chain. With multiple polypeptide chains, quartenary structure is their interconnections and organization.



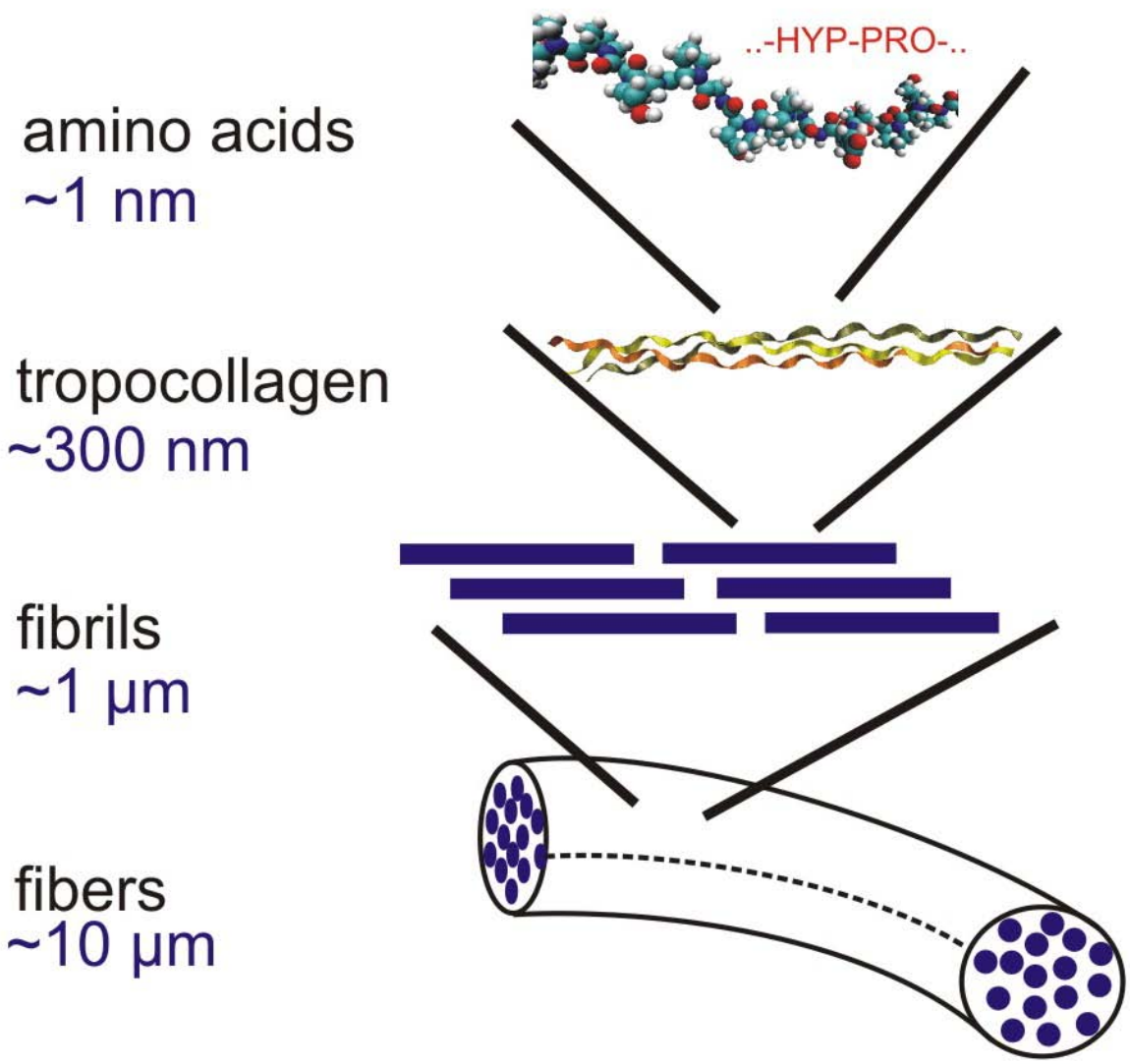
20 natural amino acids







Hierarchical structure of collagen



Collagen features hierarchical structure

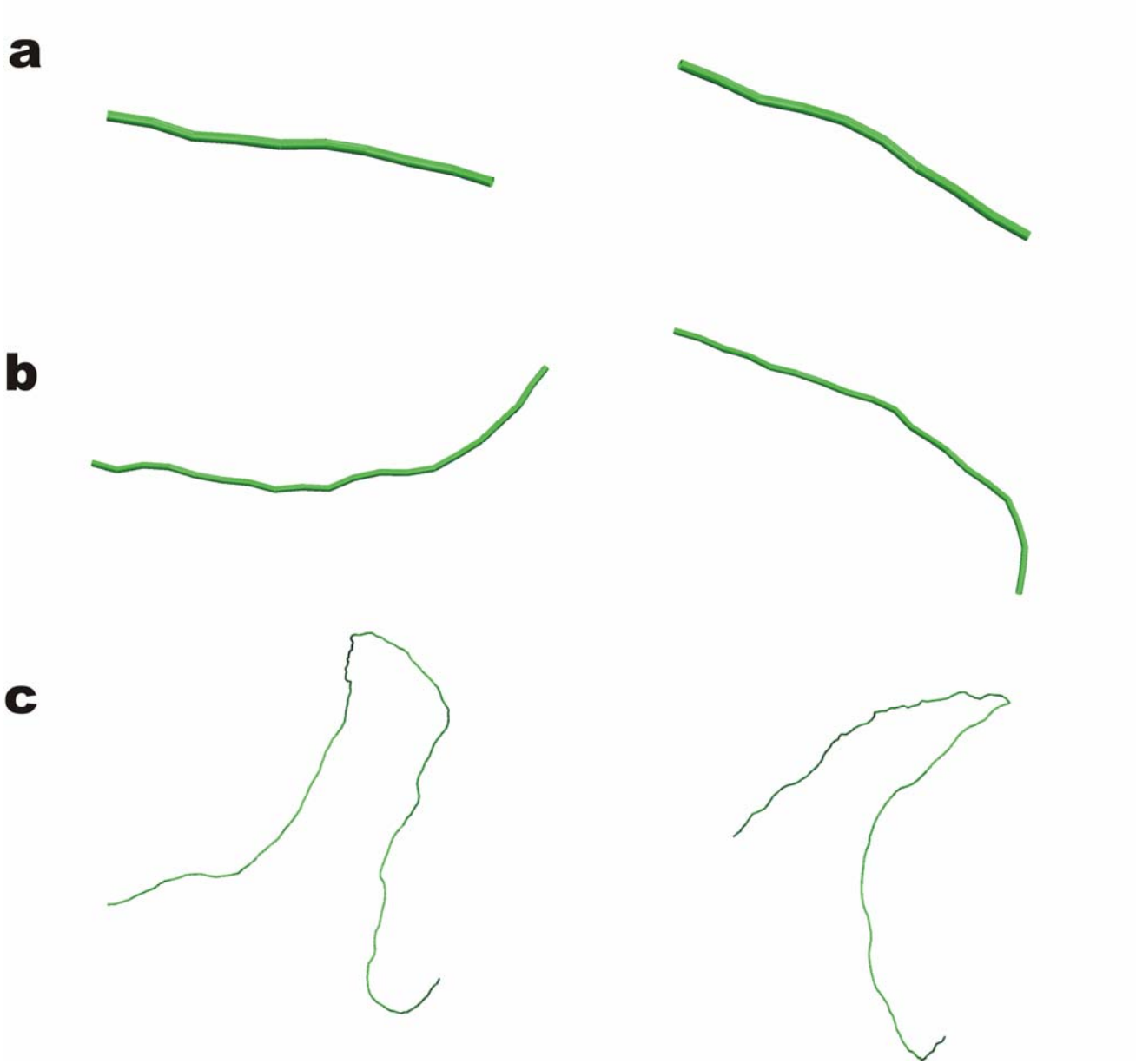
Goal: Understand the *scale-specific properties* and *cross-scale interactions*

Macroscopic properties of collagen depend on the finer scales

Material properties are scale-dependent

(Buehler, JMR, 2006)

Dynamics at different lengths



$L << \xi_p$

$L > \xi_p$

(Buehler, JMR, 2006)

Elasticity of tropocollagen molecules

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

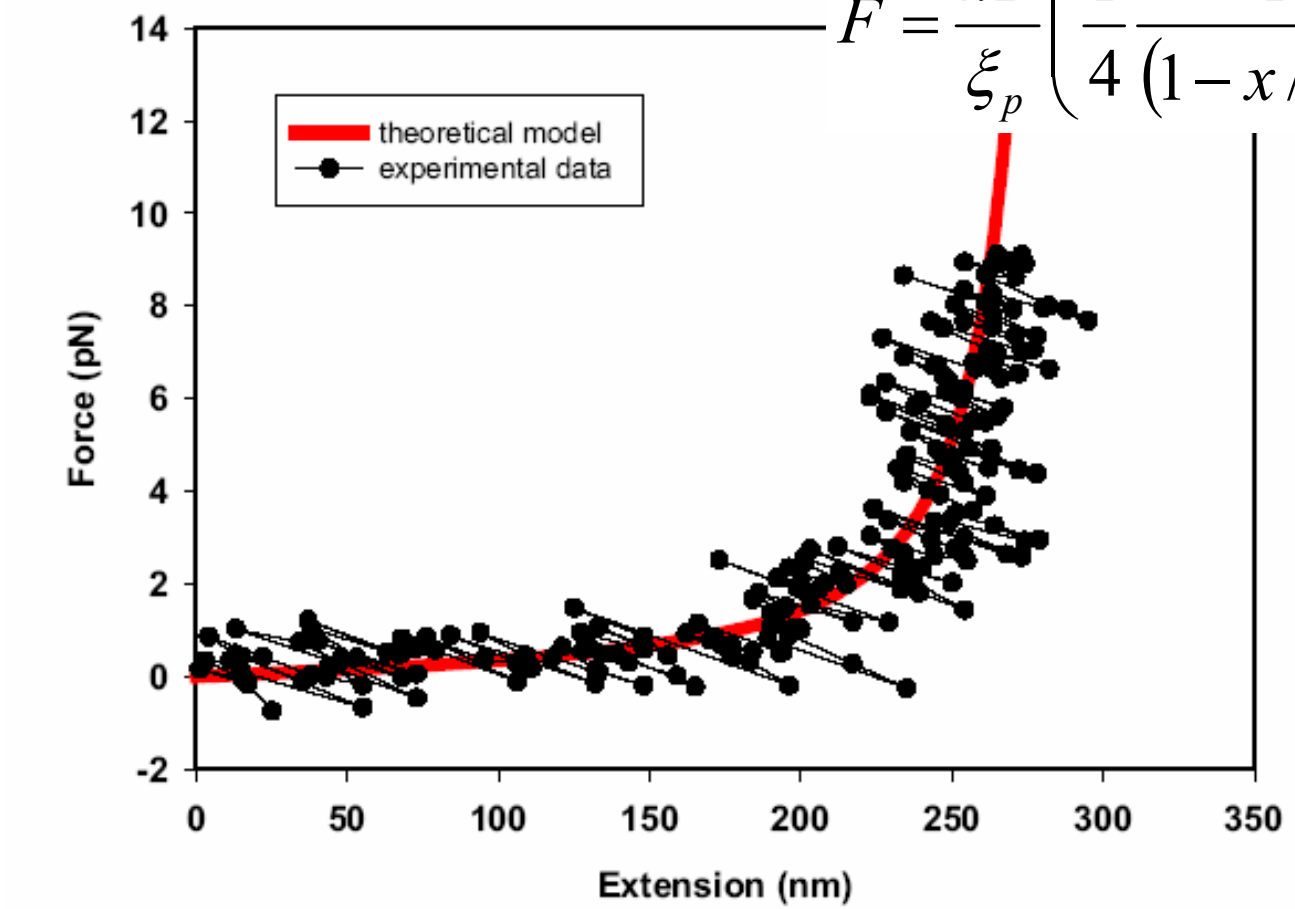
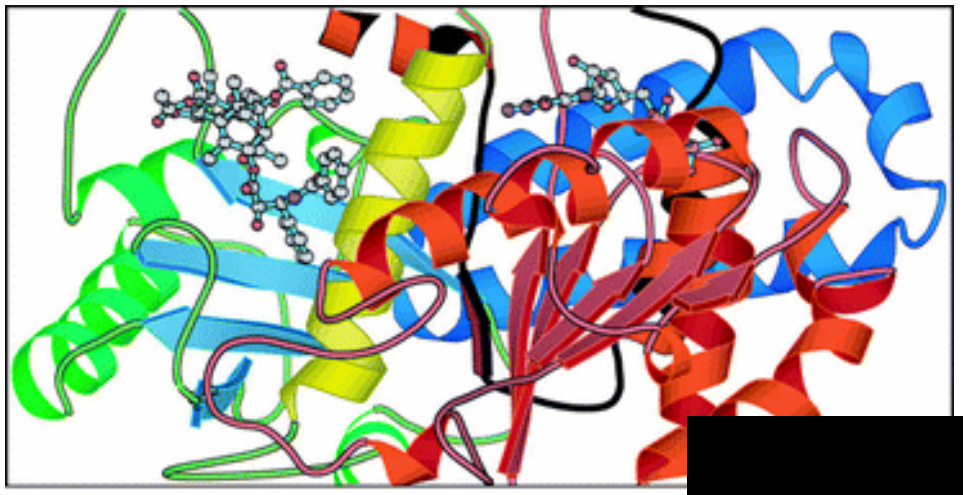


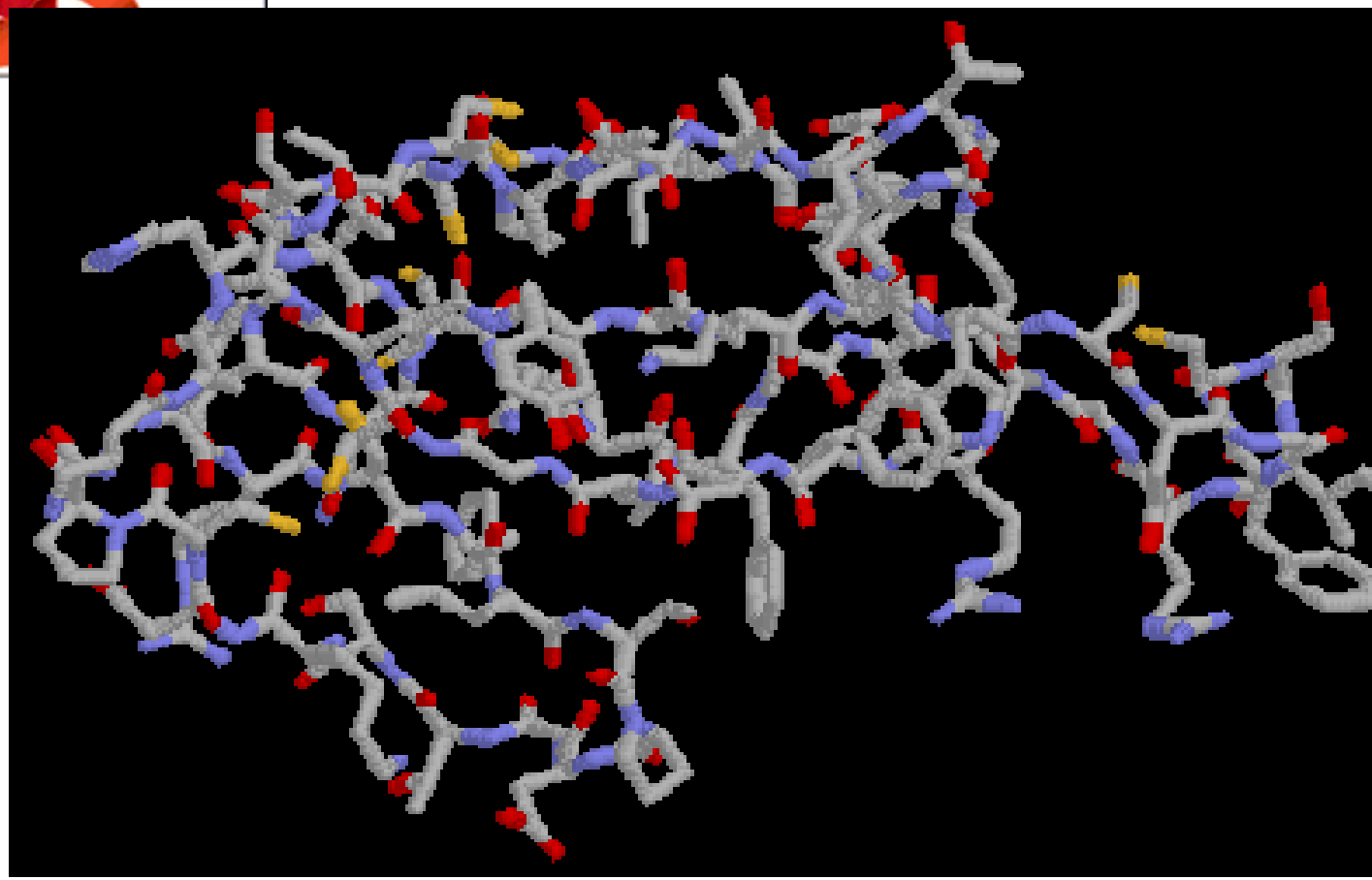
Fig. 2. The force-extension curve for stretching a single type II collagen molecule. The data were fitted to Marko–Siggia entropic elasticity model. The molecule length and persistence length of this sample is 300 and 7.6 nm, respectively.

Sun, 2004

Modeling organic chemistry



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

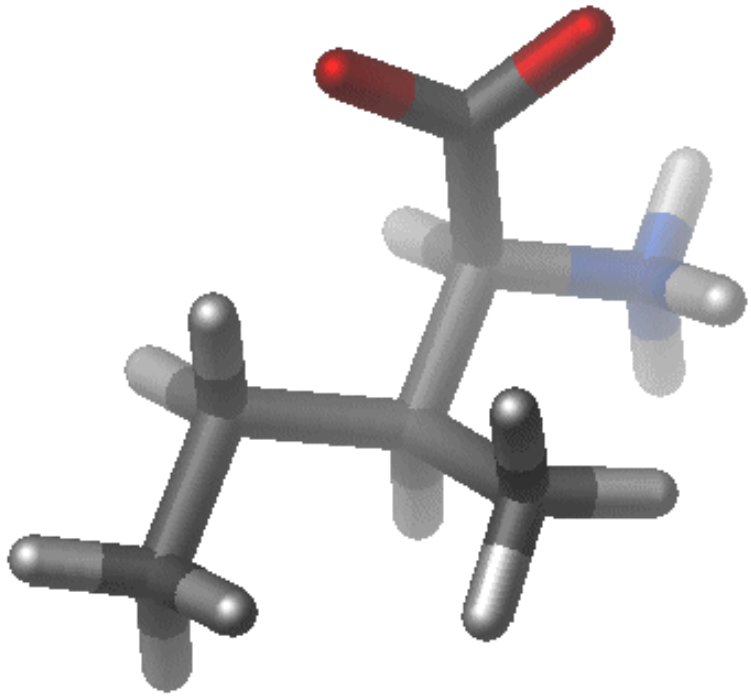


Model for covalent bonds

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

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

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



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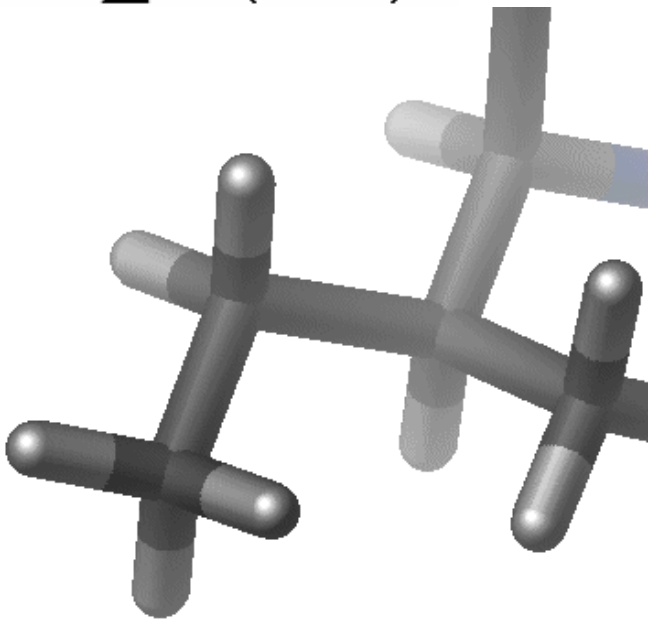
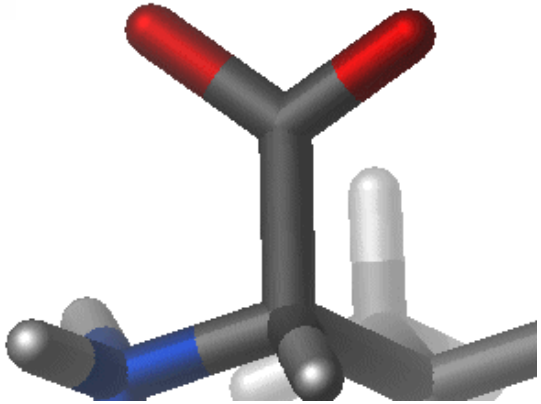
http://www.ch.embnet.org/MD_tutorial/pages/MD.Part2.html
http://www.pharmacy.umaryland.edu/faculty/amackere/force_fields.htm

Model for covalent bonds

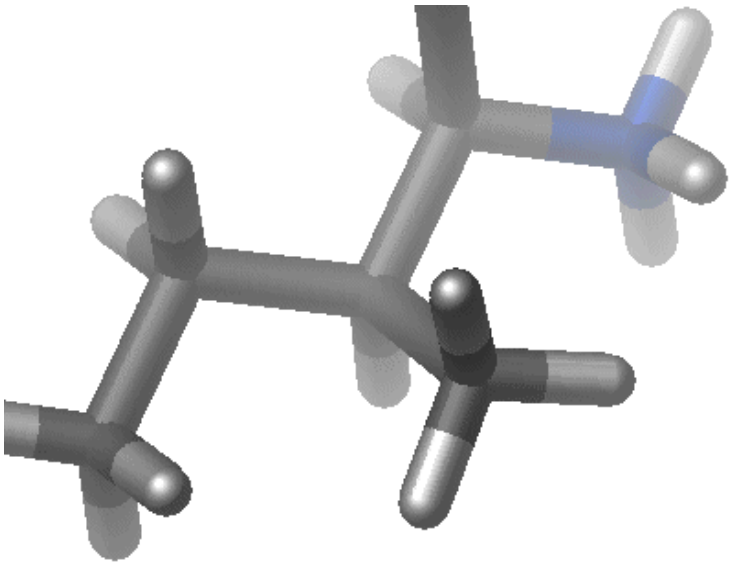
$$E_{bond-stretch} = \sum K_b (b - b_0)^2$$

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





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



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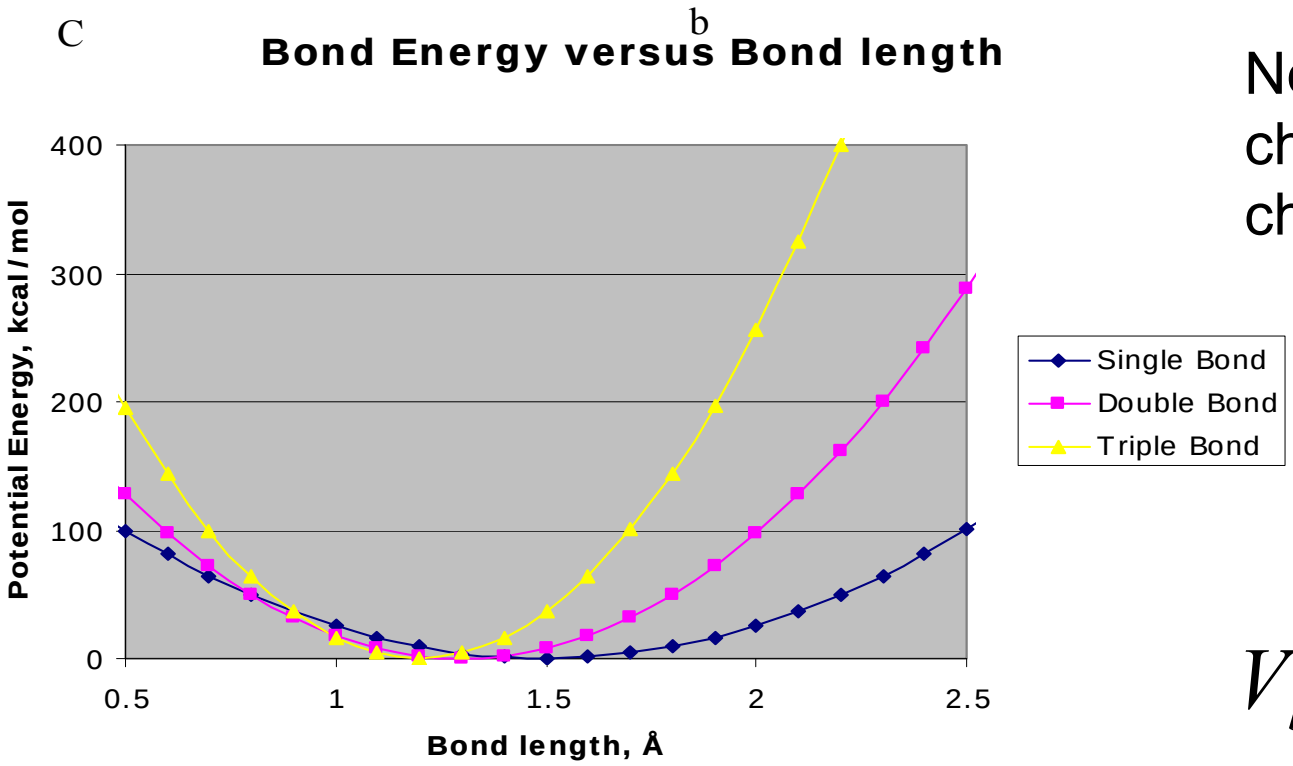
http://www.ch.embnet.org/MD_tutorial/pages/MD.Part2.html

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	400 kcal/mole/Å^2	1.2 Å



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

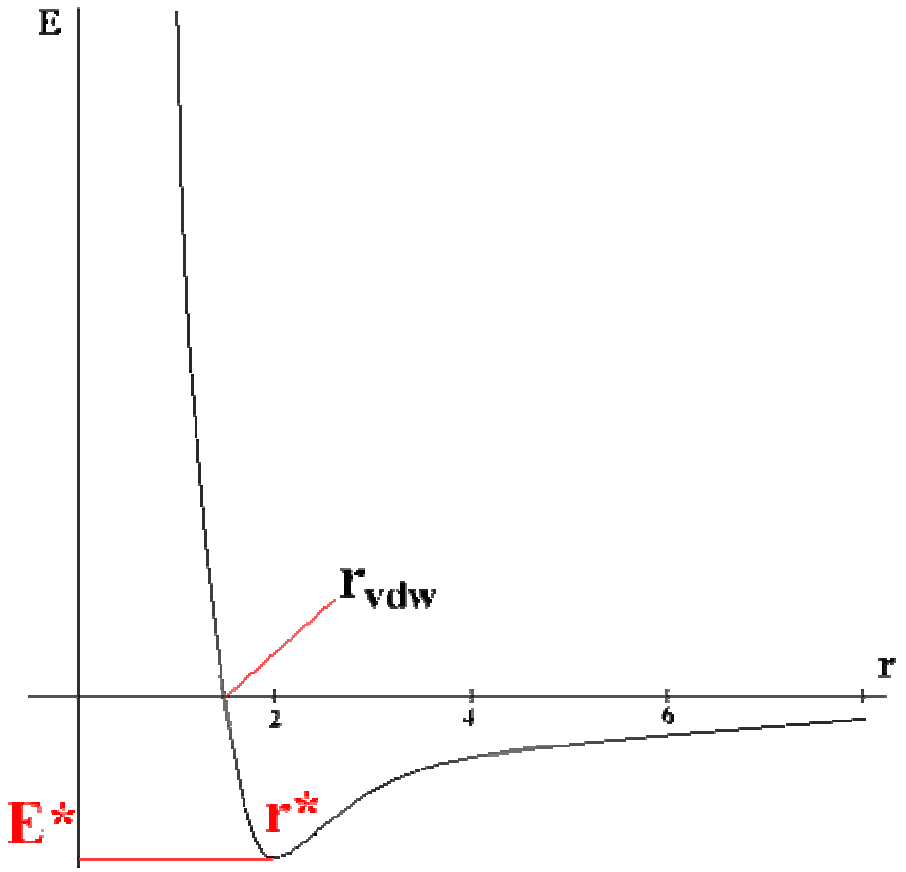
Need to retype when chemical environment changes

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

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

Review: CHARMM potential

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



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

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

Nonbonding interactions

vdW (dispersive)

Coulomb (electrostatic)

H-bonding

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

DREIDING potential

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

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

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

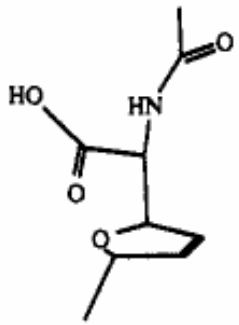
$$E = \tfrac{1}{2}k_e(R - R_e)^2$$

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

TABLE I: Geometric Valence Parameters for DREIDING

atom	bond radius R^0_I, Å	bond angle, deg	atom	bond radius R^0_I, 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
Al3	1.047	109.471			

$$K_{IJ}(1) = 700\ (\text{kcal/mol})/\text{Å}^2$$



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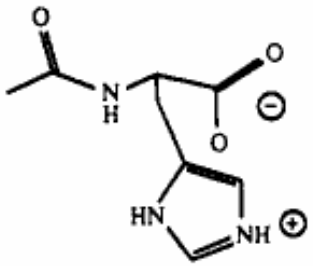

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TABLE III: Valence Force Constants for DREIDING

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	

UFF "Universal Force Field"

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

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

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

Features:

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

Pauling-type bond order correction

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

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

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

Rappé *et al.*

Common empirical force fields

Class I (experiment derived, simple form)

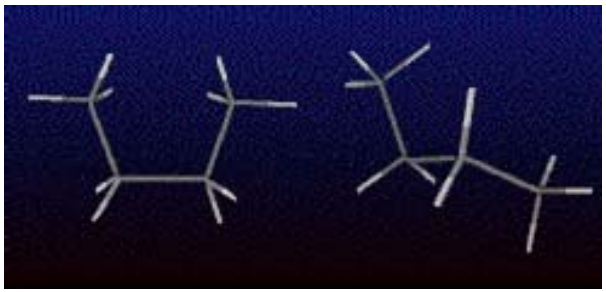
- CHARMM
- CHARMm (Accelrys)
- AMBER
- OPLS/AMBER/Schrödinger
- ECEPP (free energy force field)
- GROMOS

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



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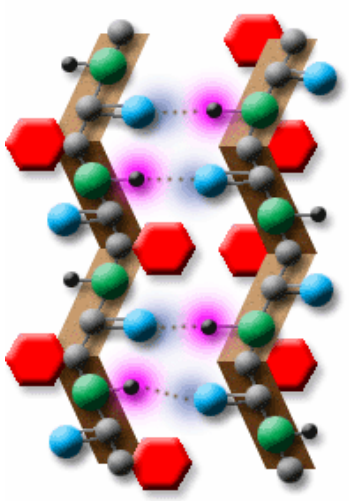
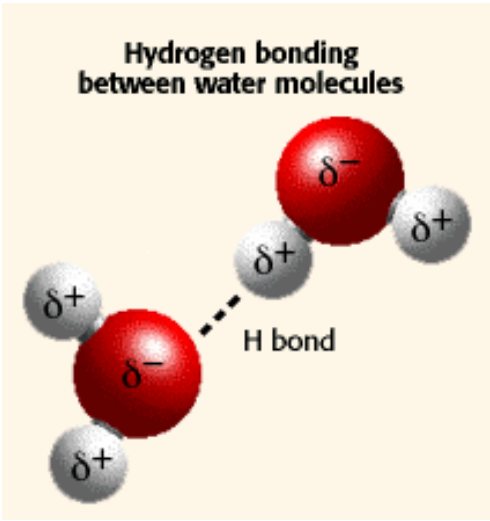
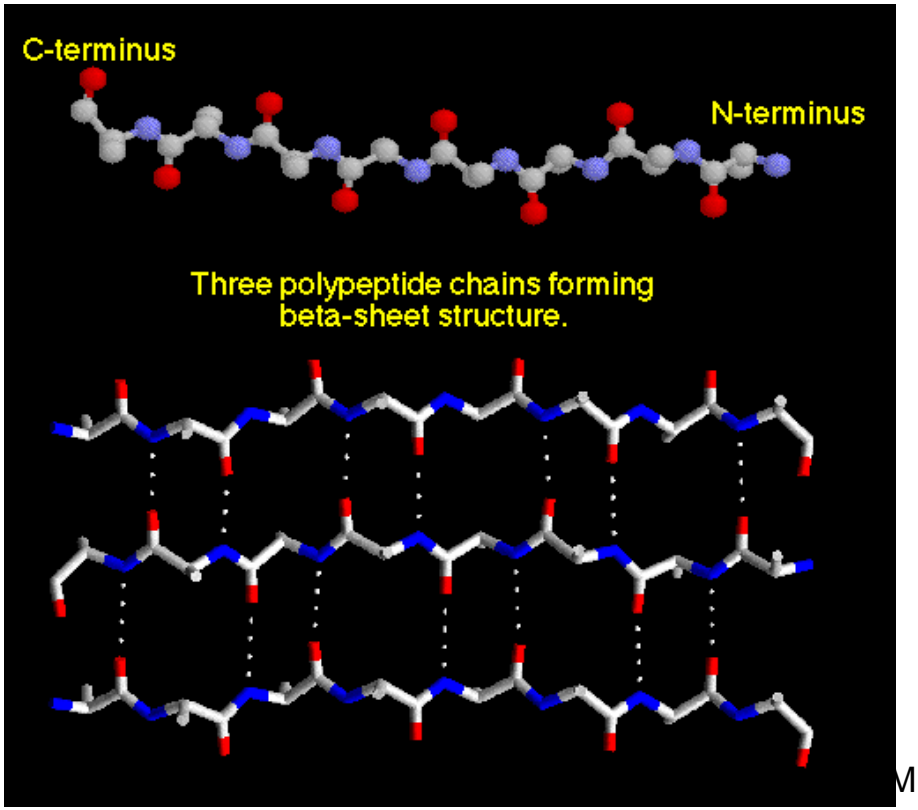
Alpha helix and beta sheets

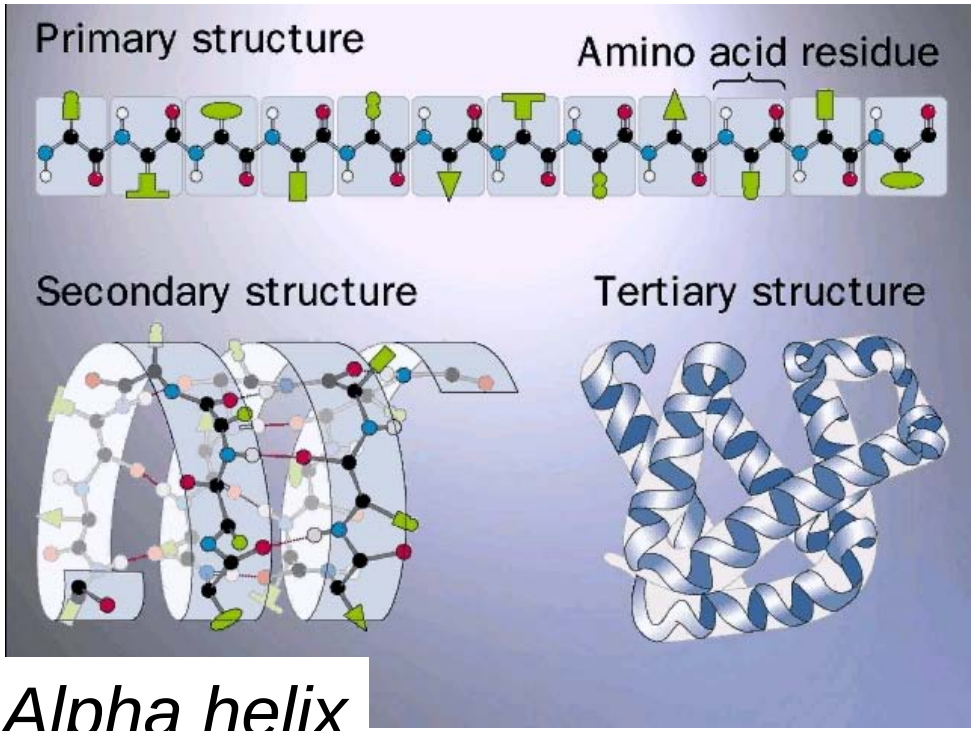


Hydrogen bonding
e.g. between O and H in H_2O
Between N and O in proteins…



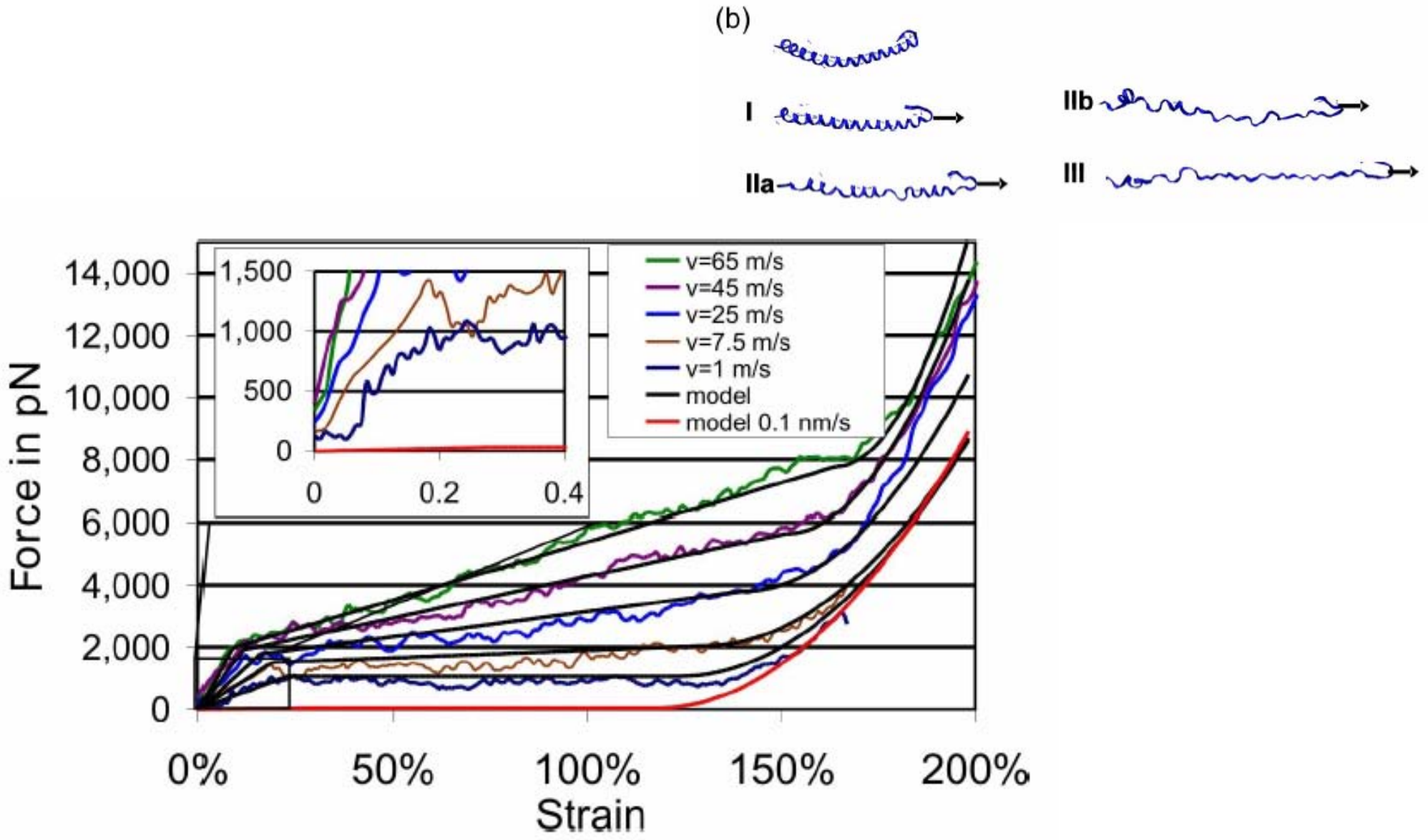
Beta sheet





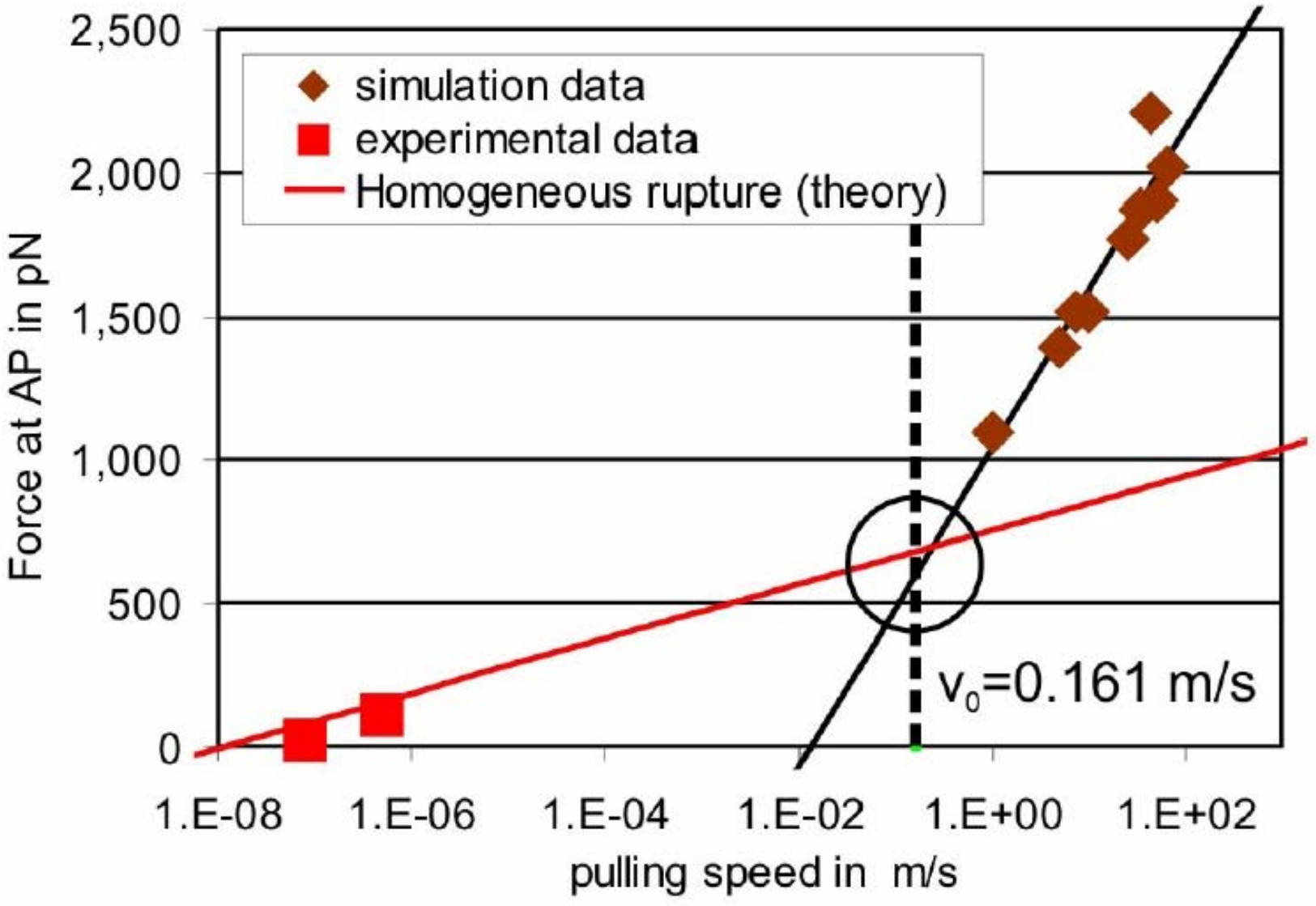
Alpha helix

Unfolding of alpha helix structure



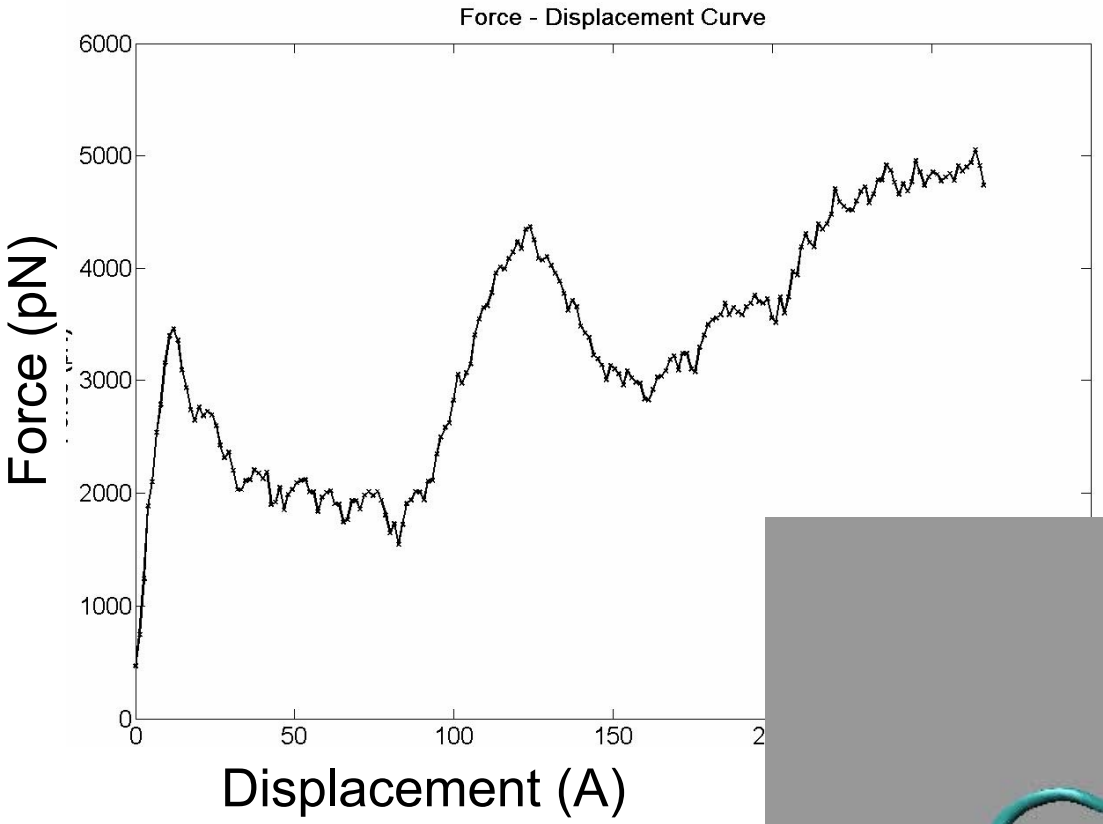
Ackbarow and Buehler, 2007

Unfolding of alpha helix structure

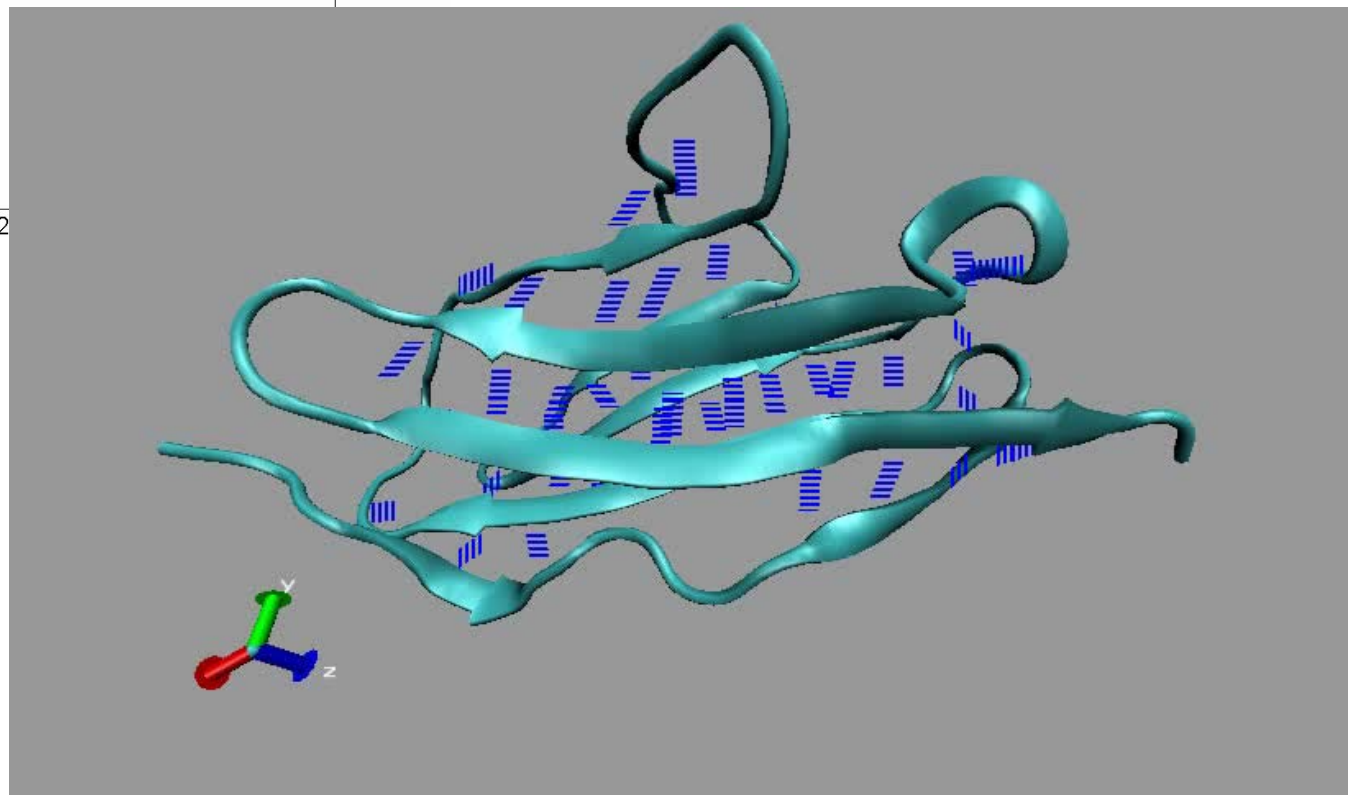


Ackbarow and Buehler, 2007

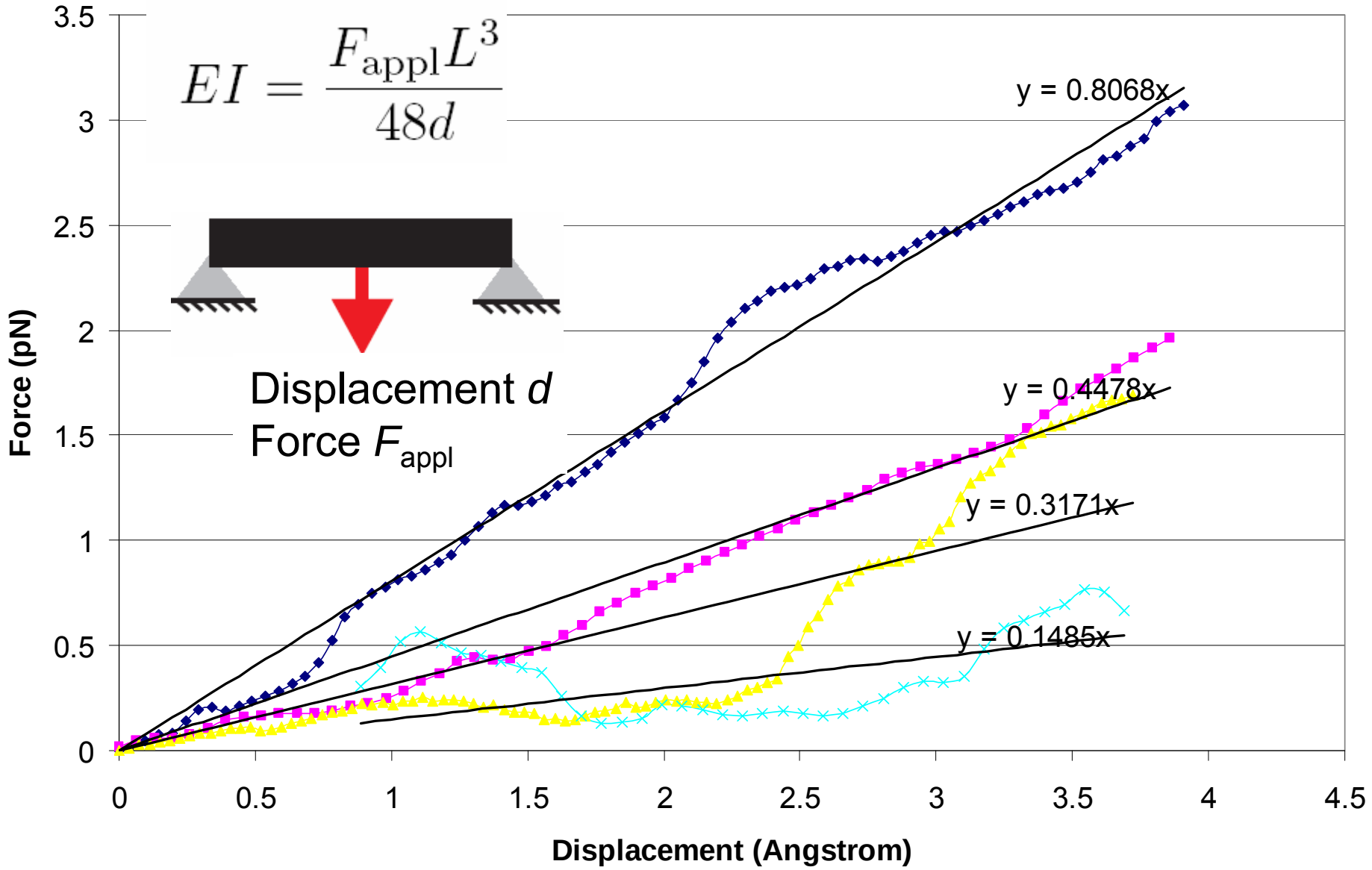
Unfolding of beta sheet



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

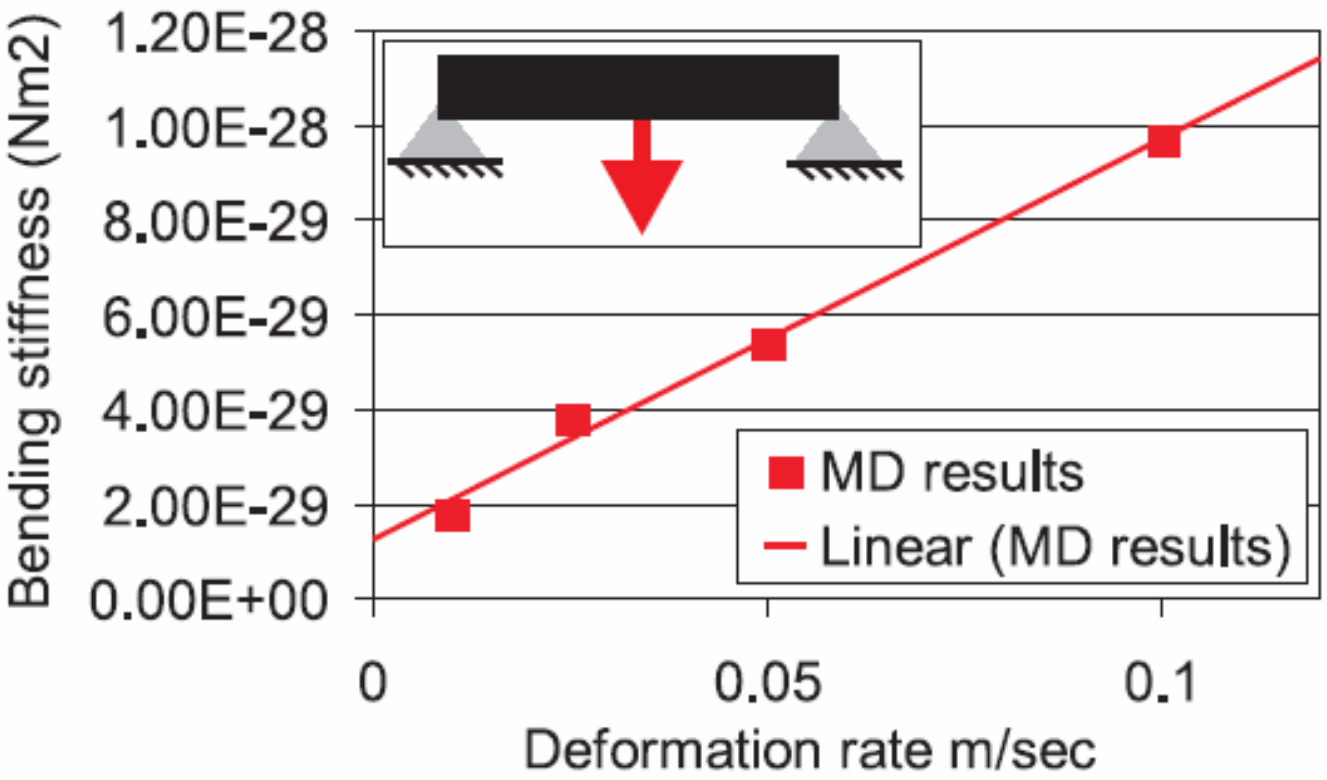


Three-point bending test: Tropocollagen molecule



Buehler and Wong, 2007

Three-point bending test: Tropocollagen molecule



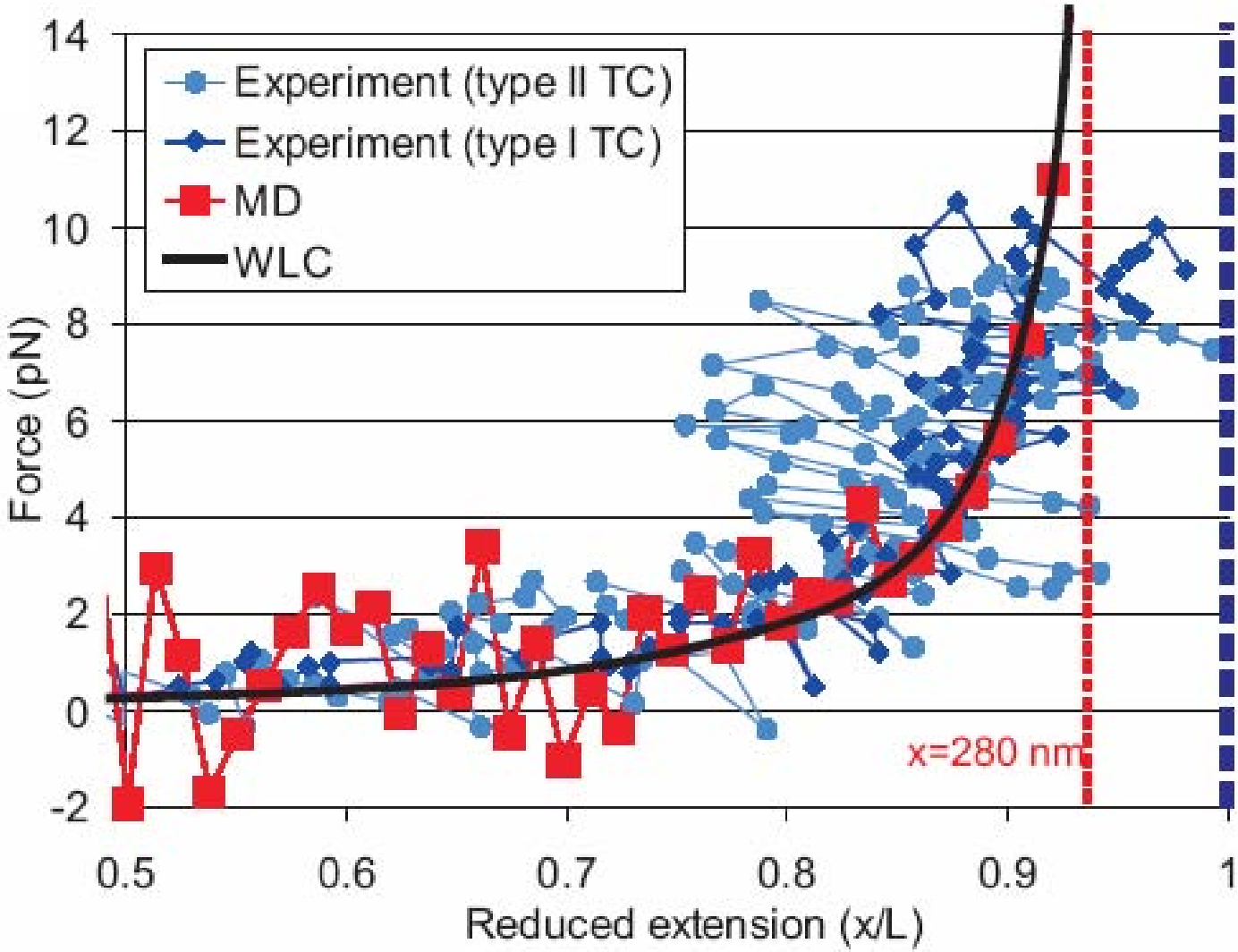
MD: Calculate bending stiffness; consider different deformation rates

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



Buehler and Wong, 2007, under submission

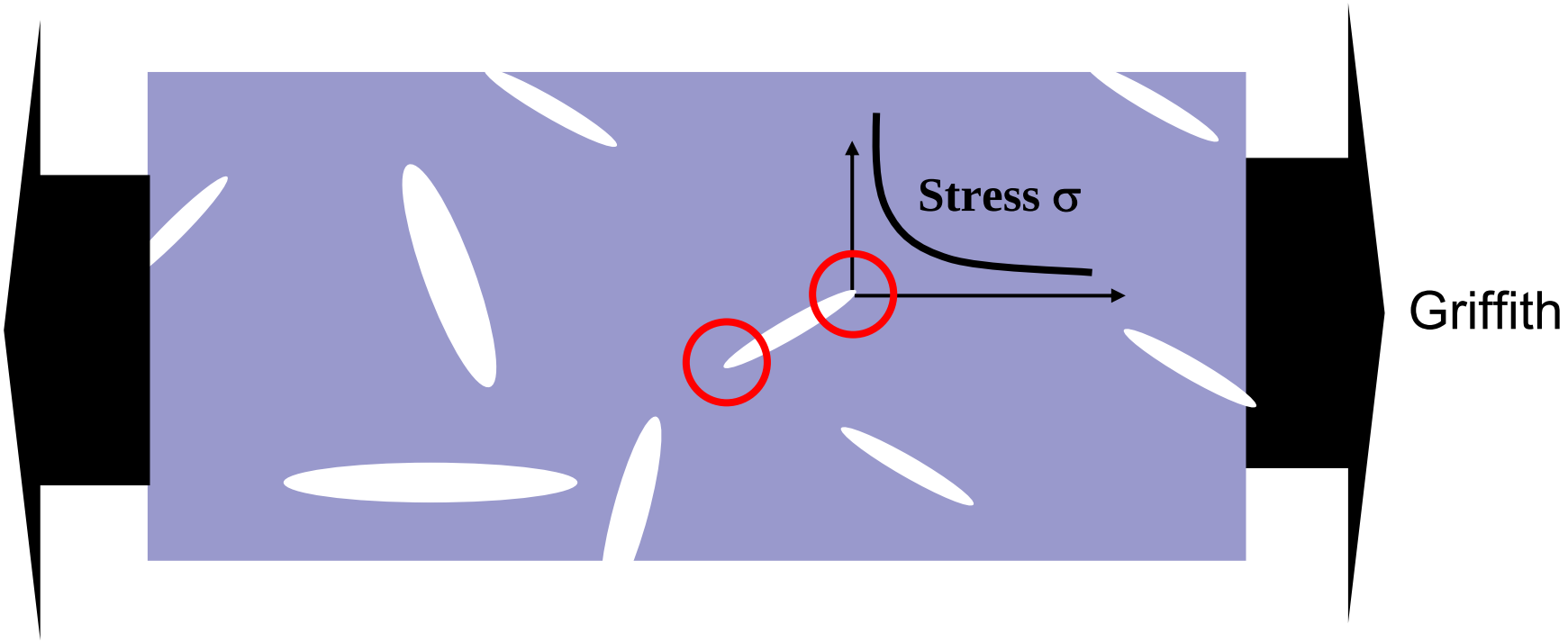
Fracture at ultra small scales

Size effects

Nano-scale fracture

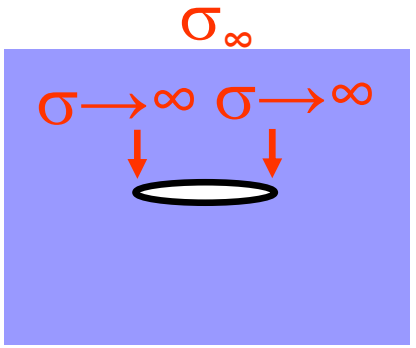
- Failure mechanism of ultra small brittle single crystals as a function of material size
- Properties of adhesion systems as a function of material size: Is Griffith's model for crack nucleation still valid at nanoscale?

"Nano"



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

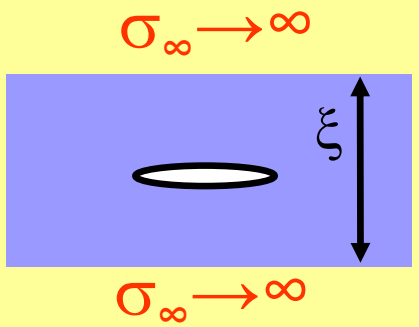
"Inglis paradox": Why does crack not extend, despite infinitely large stress at even small applied load?

- 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))!

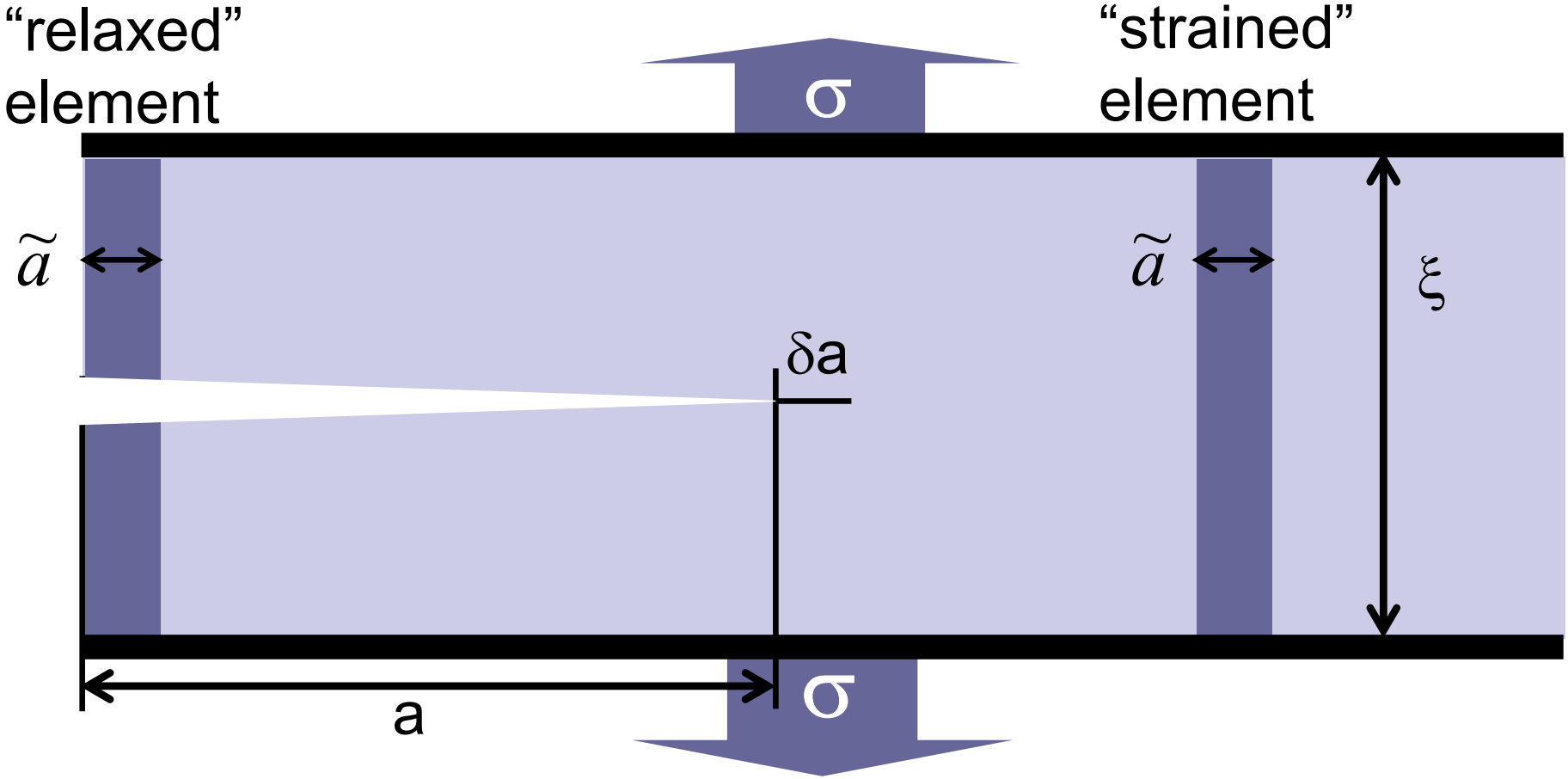
Considered here



Infinite bulk stress

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

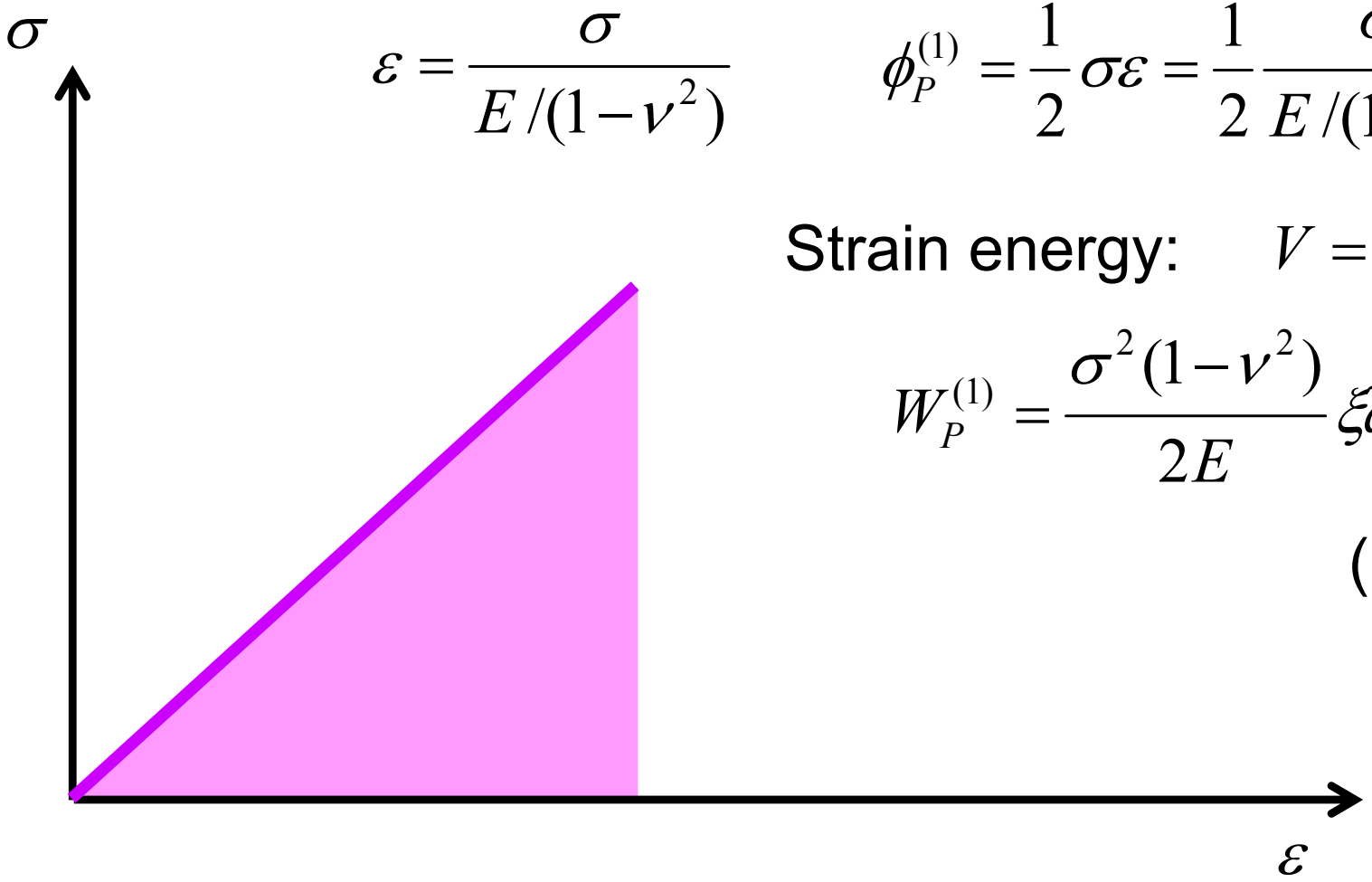
Thin strip geometry



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:

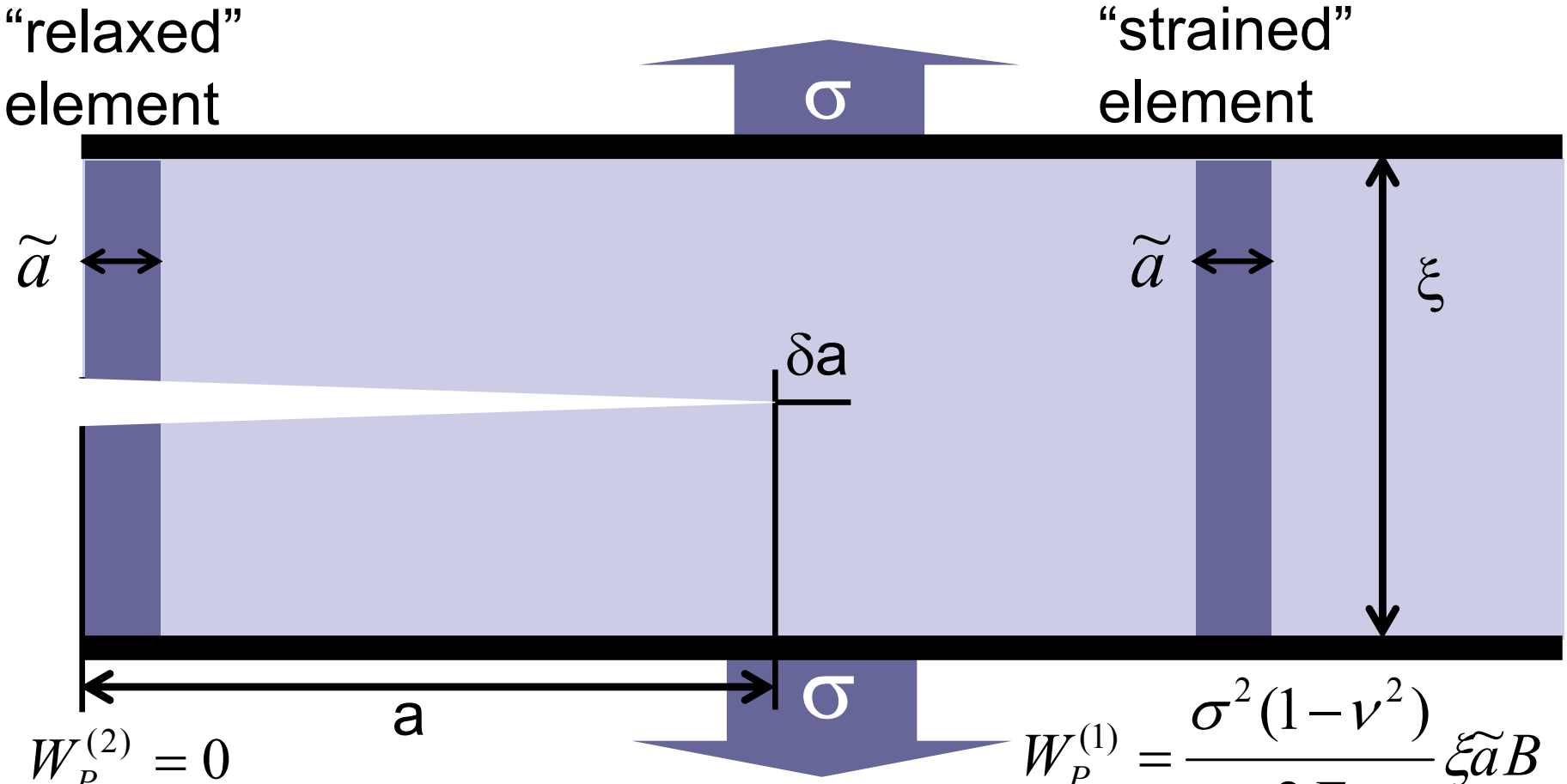
$$\phi_P^{(1)} = \frac{1}{2}\sigma\varepsilon = \frac{1}{2}\frac{\sigma^2}{E/(1-\nu^2)}$$

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



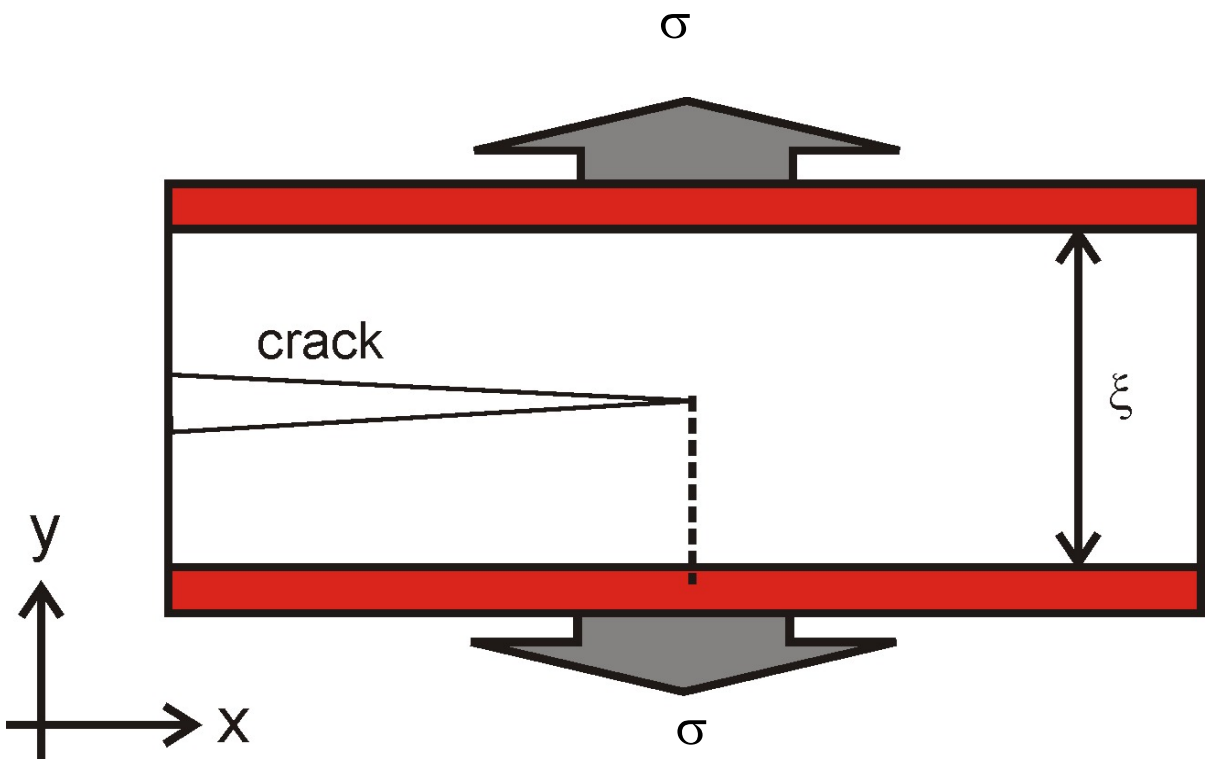
$$W_P = W_P^{(2)} - W_P^{(1)} = -\frac{\sigma^2(1-\nu^2)}{2E}\xi aB$$

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

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



ξ.. size of material

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

Fracture of thin strip geometry
Theoretical considerations

Stress for spontaneous crack propagation

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

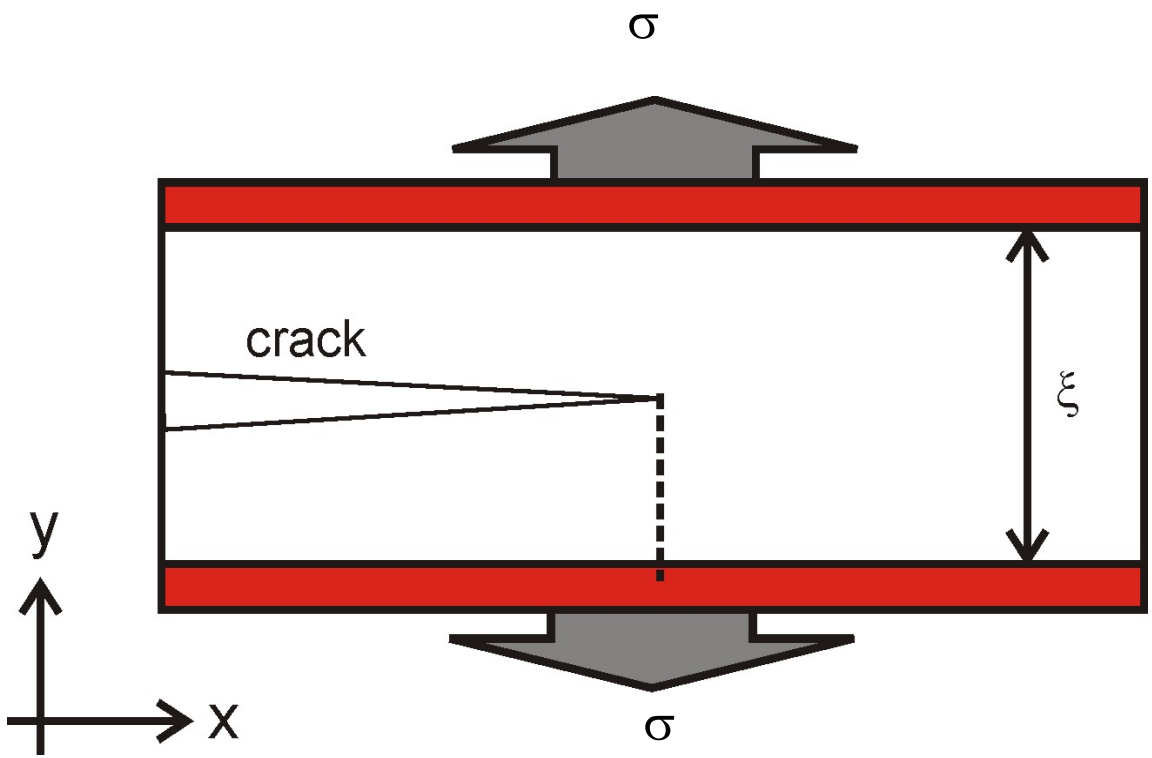
$\sigma \rightarrow \infty$ for $\xi \rightarrow 0$

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

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

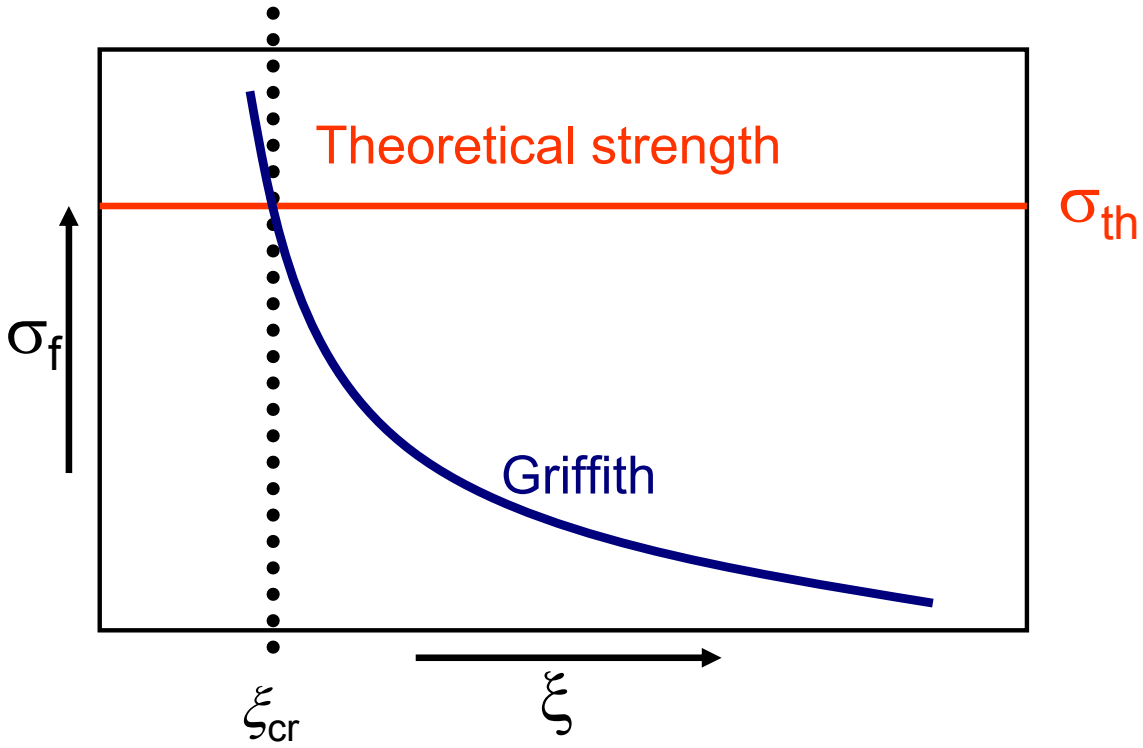
$$\xi_{cr} = \frac{4\gamma E}{\sigma_{th}^2(1-\nu^2)}$$

ξ.. size of material



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"

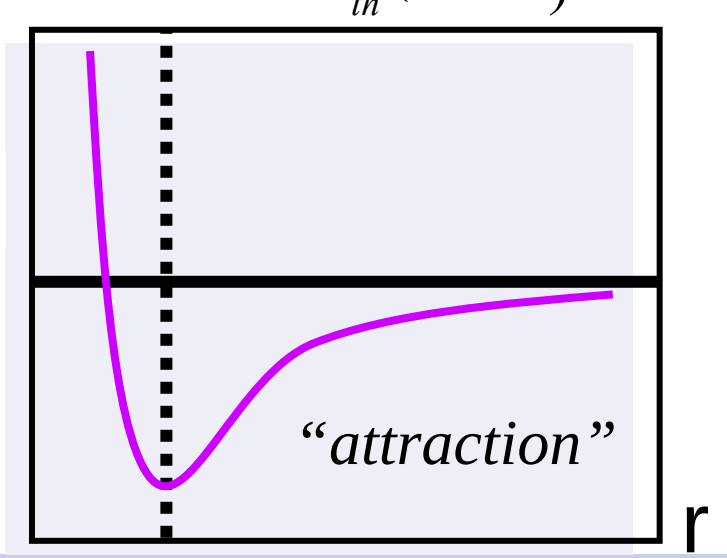
$$\phi(r) = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right) \qquad \varepsilon = \sigma = 1$$

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

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

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

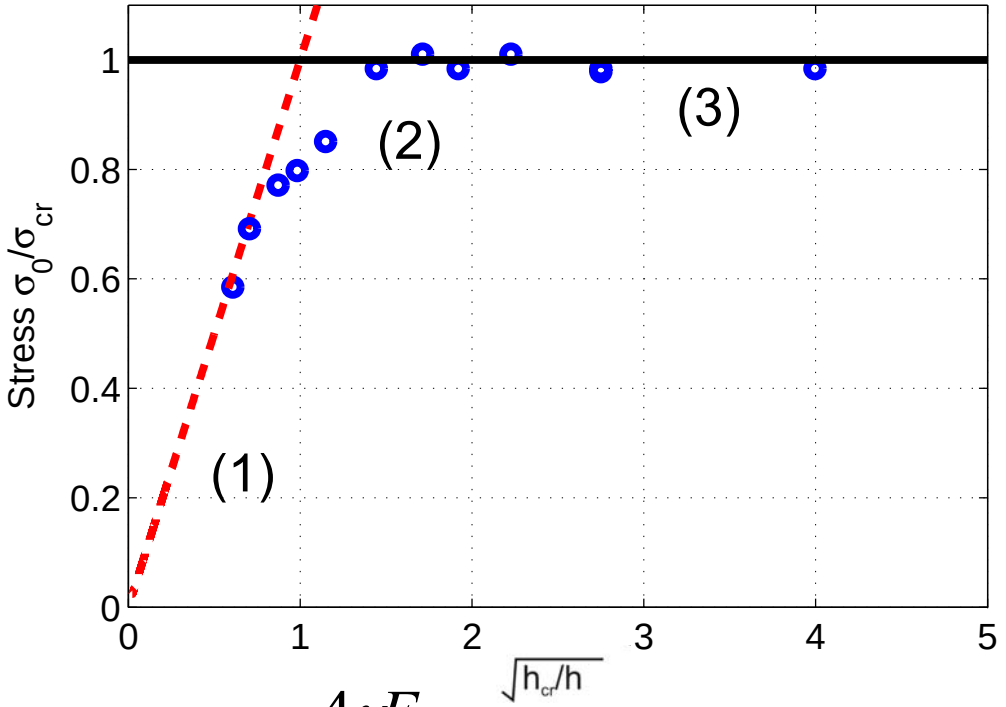
$$h_{cr} = \frac{4\gamma E}{\sigma_{th}^2 (1 - \nu^2)}$$



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

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

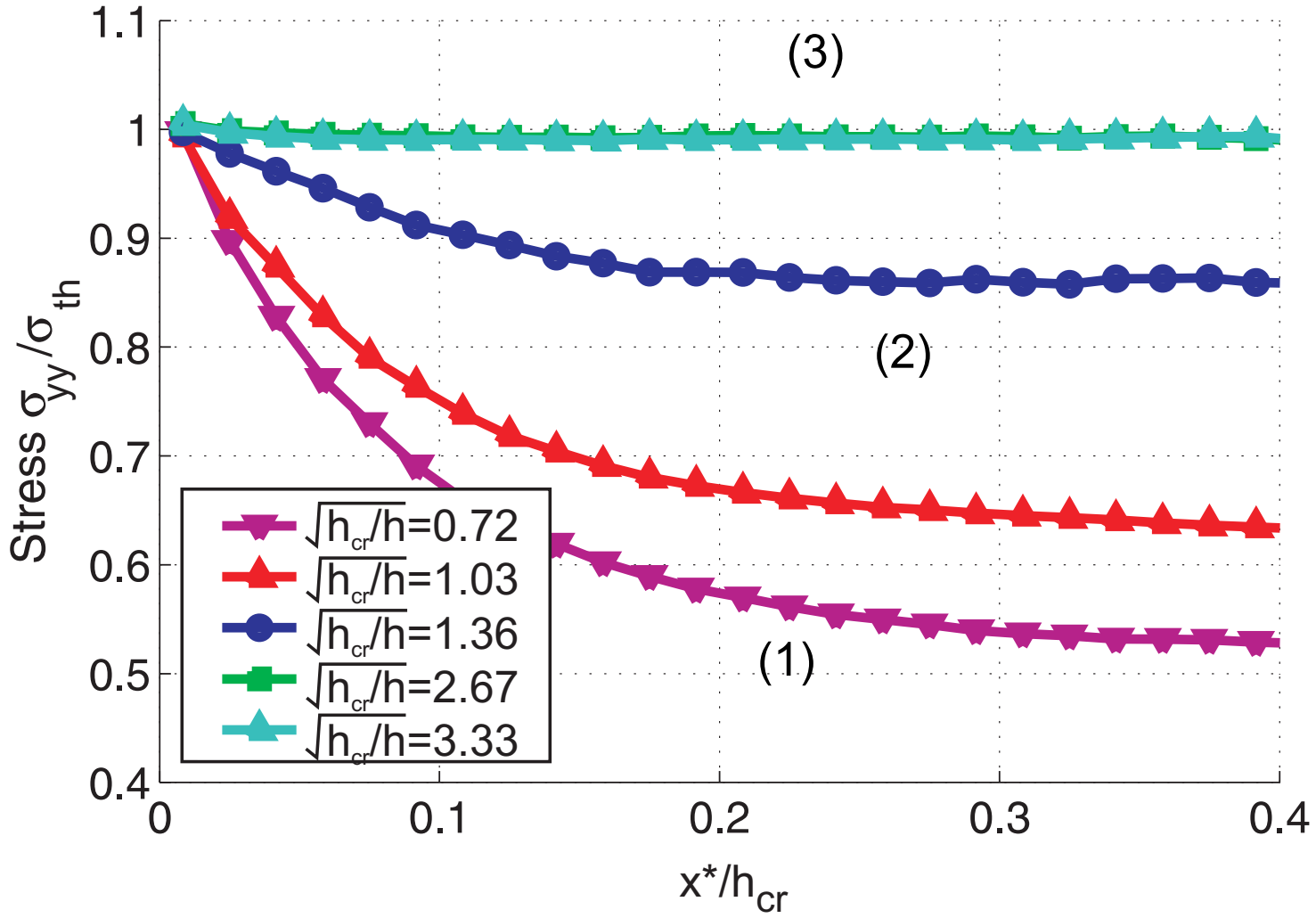
Atomistic simulation indicates:

➢ 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)

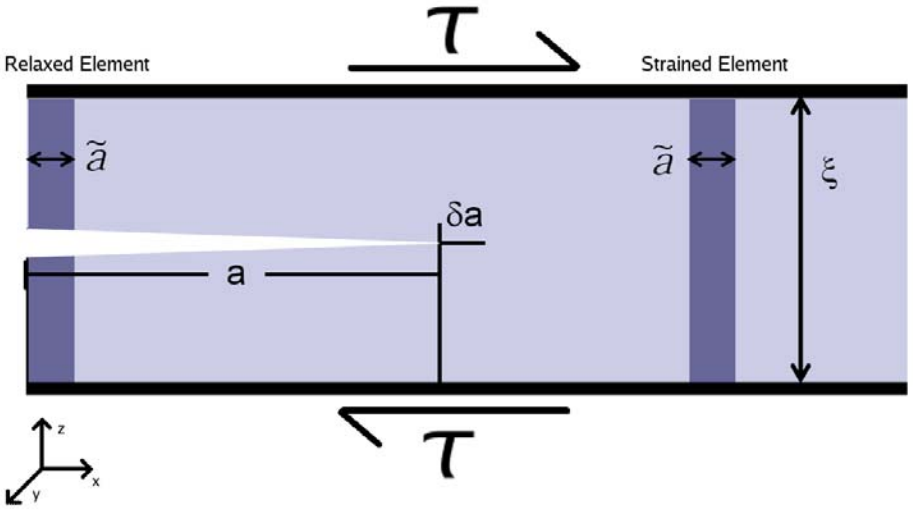
Stress distribution ahead of crack

(3): Max. stress independent of ξ



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

Shear loading



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

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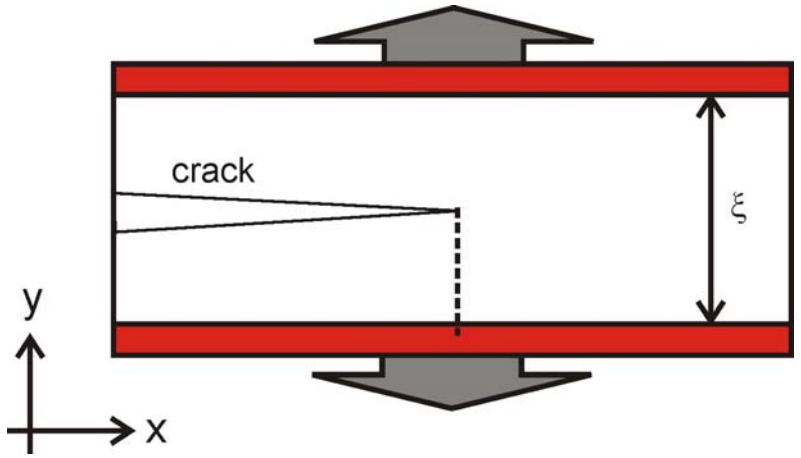
Keten and Buehler, 2007

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*., 2004; Gao, Ji, Buehler, MCB, 2004)

Can this concept explain the design of biocomposites in bone?

Characteristic size: 10..100 nm

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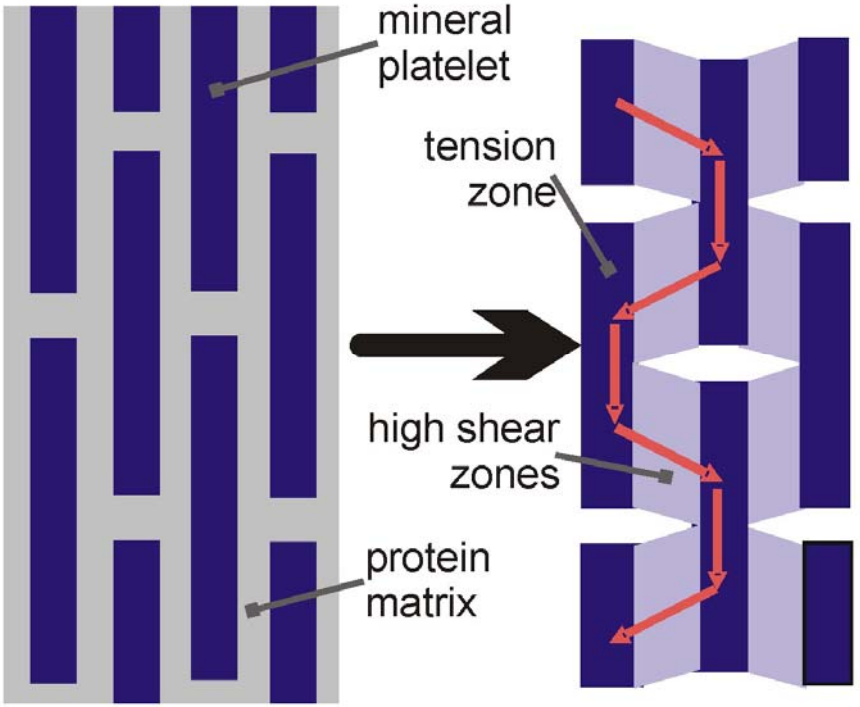


Estimate for biominerals:

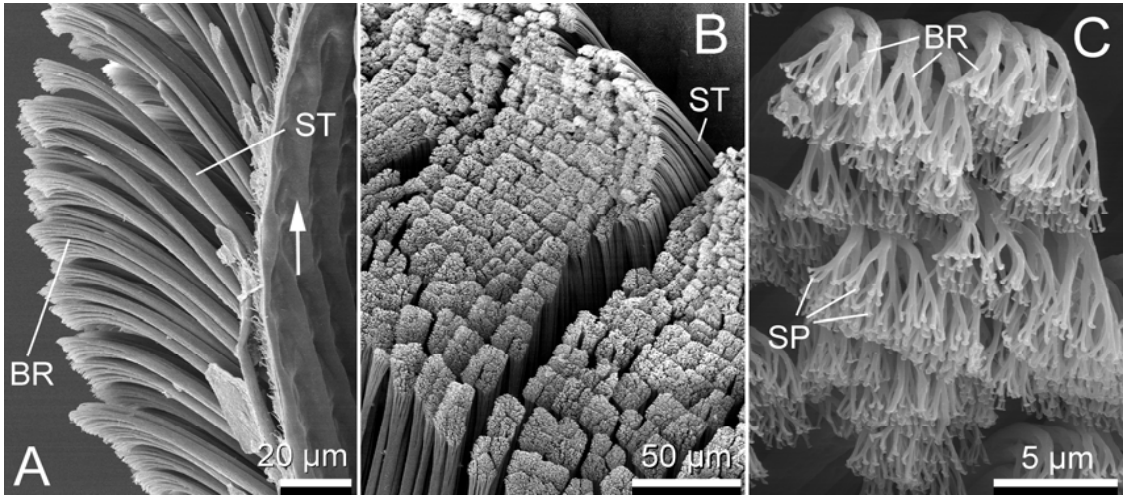
$$\sigma_{\max} \approx \frac{E}{30}, \; \nu \approx 0.25, \; E = 100 \text{ GPa}, \quad \gamma = 1 \text{J/m}^2$$

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

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

Adhesion of Geckos

Autumn et al., PNAS, 2002



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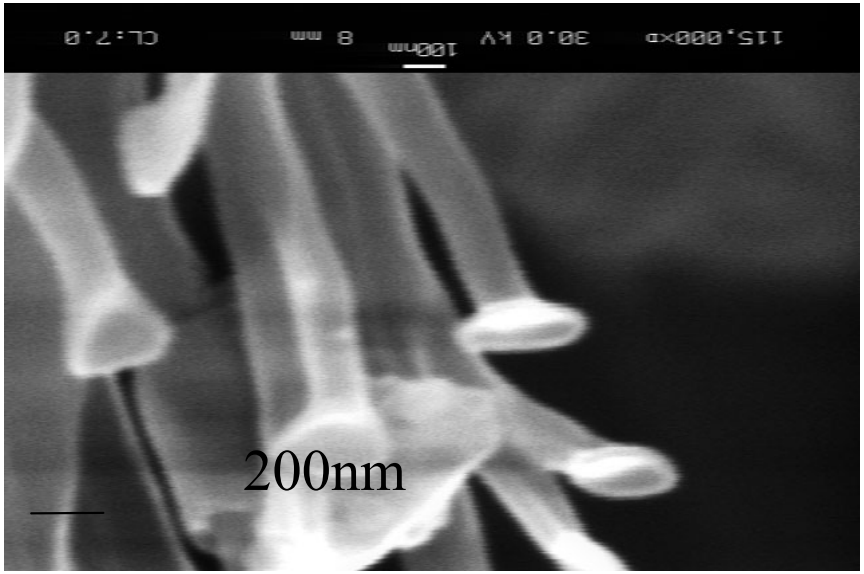
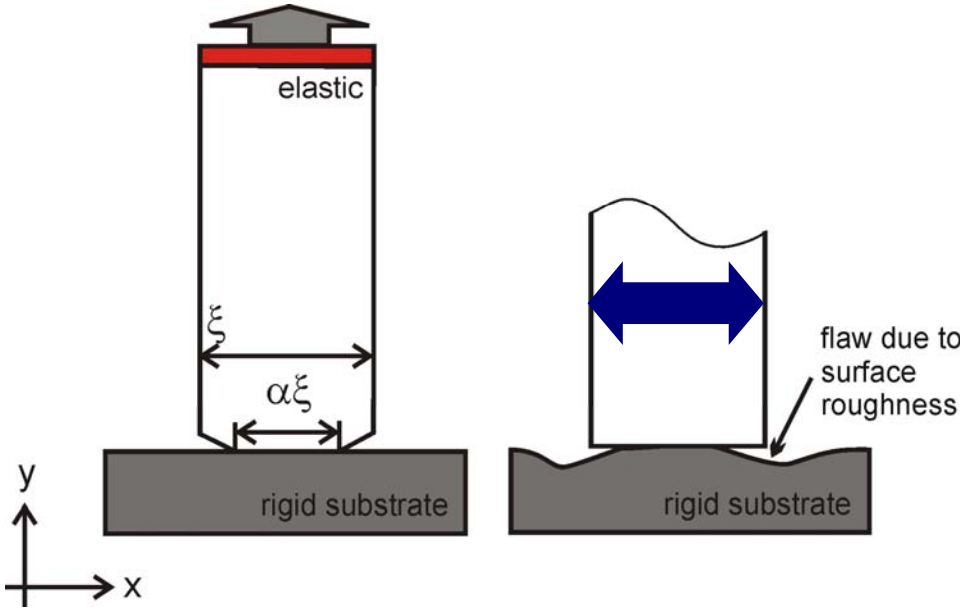


Adhesion at small length scales



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Characteristic
size: 100..300 nm

Strategies to increase adhesion strength

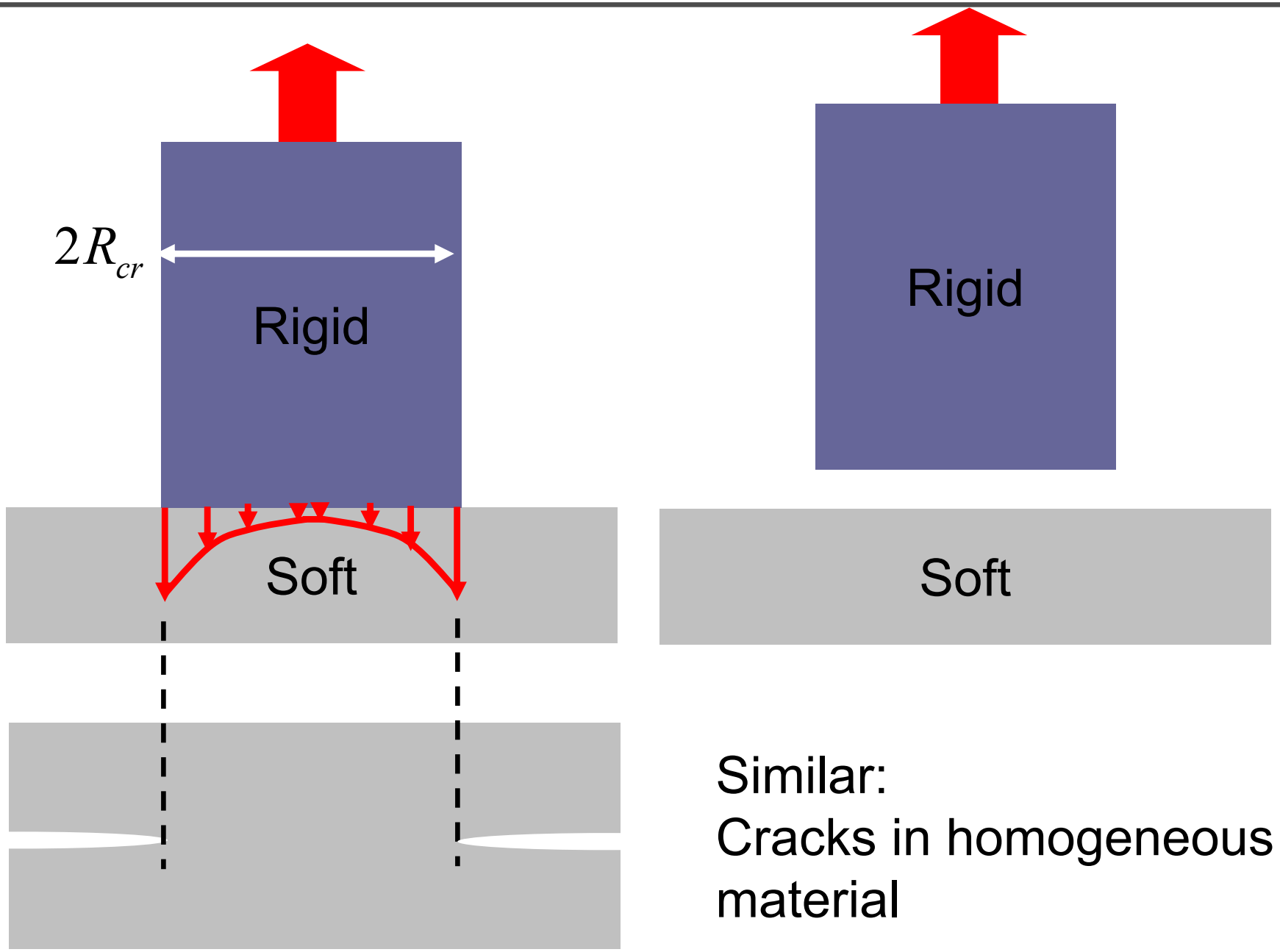
-Since F ~ gR (JKR model), increase line length of surface by contact splitting
(Arzt *et al*., 2003)

-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.

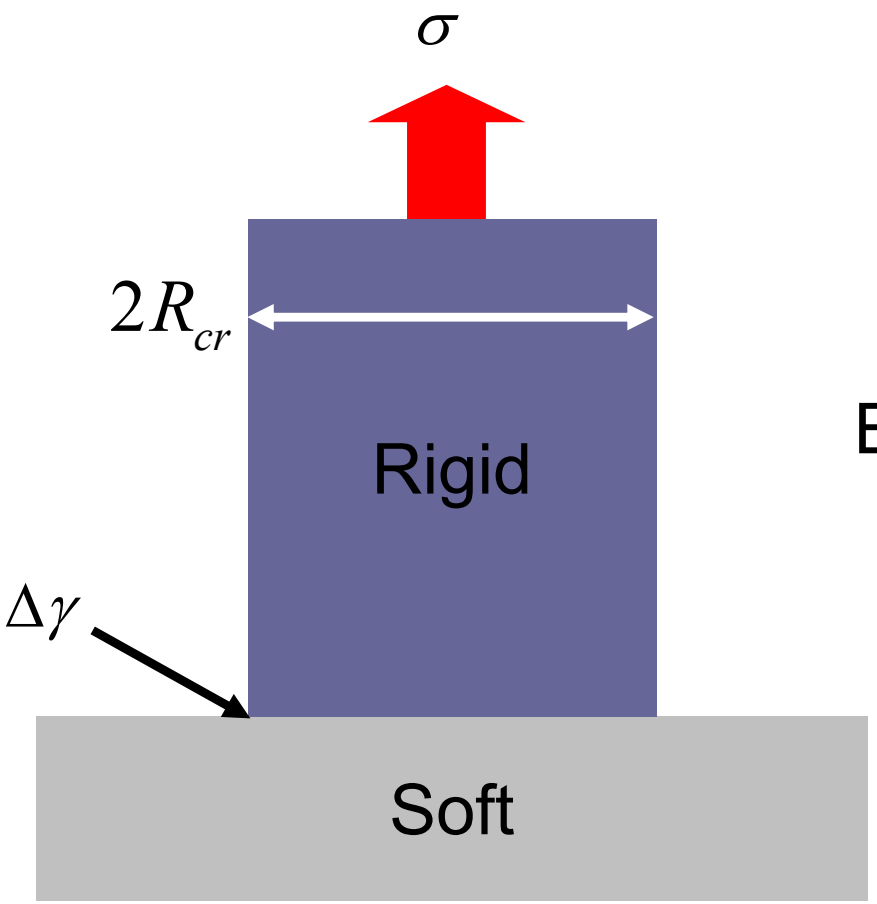
• A circumferential crack represents flaws for example resulting from surface roughness. The parameter denotes the dimension of the crack.

Equivalence of adhesion and fracture problem



Similar:
Cracks in homogeneous material

Equivalence of adhesion and fracture problem



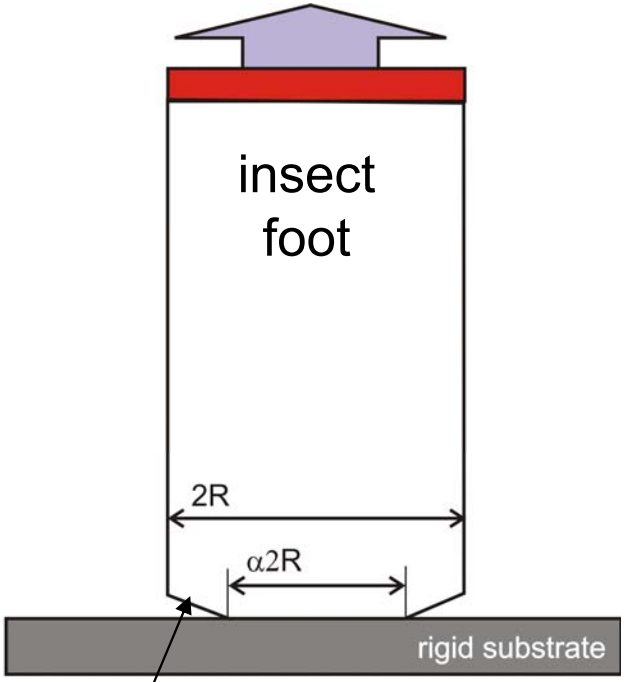
Energy release rate $K_I = \sqrt{\frac{\pi}{8} R_{cr} \sigma^2}$

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

$$G = 2\gamma = \Delta\gamma$$

Adhesion energy

Theoretical considerations
Adhesion problem as fracture problem



"Flaw"-imperfect contact

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

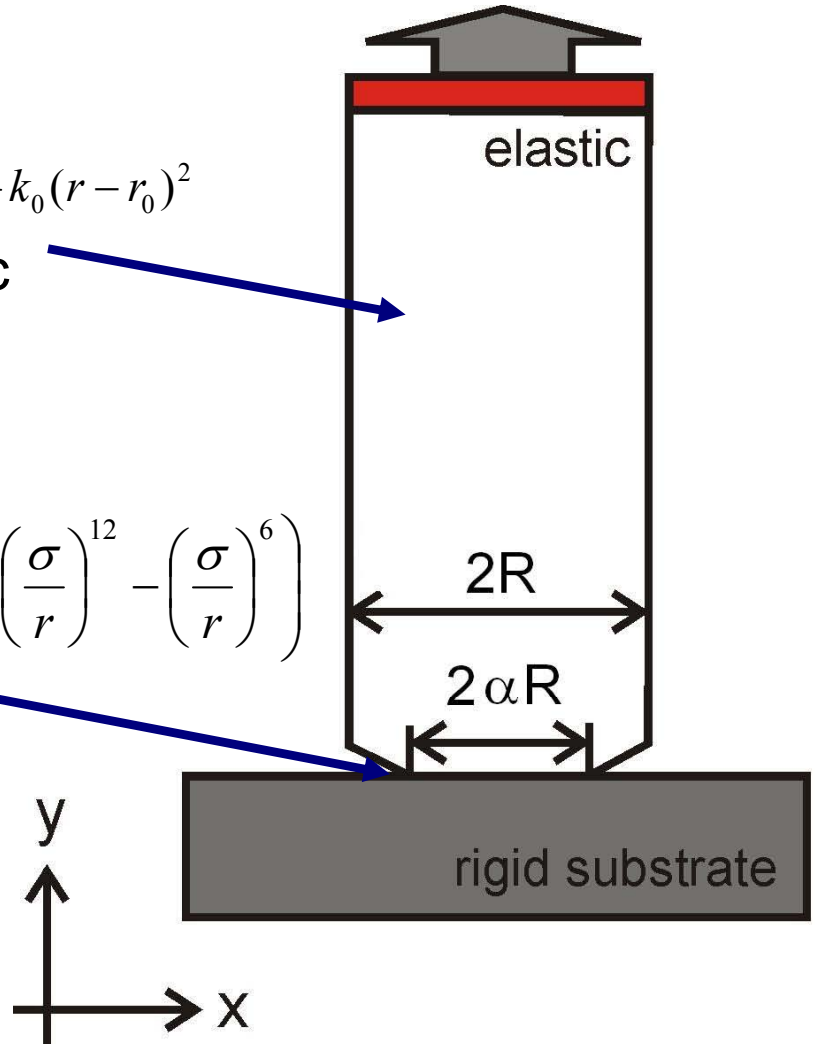
Continuum and atomistic model

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

Harmonic

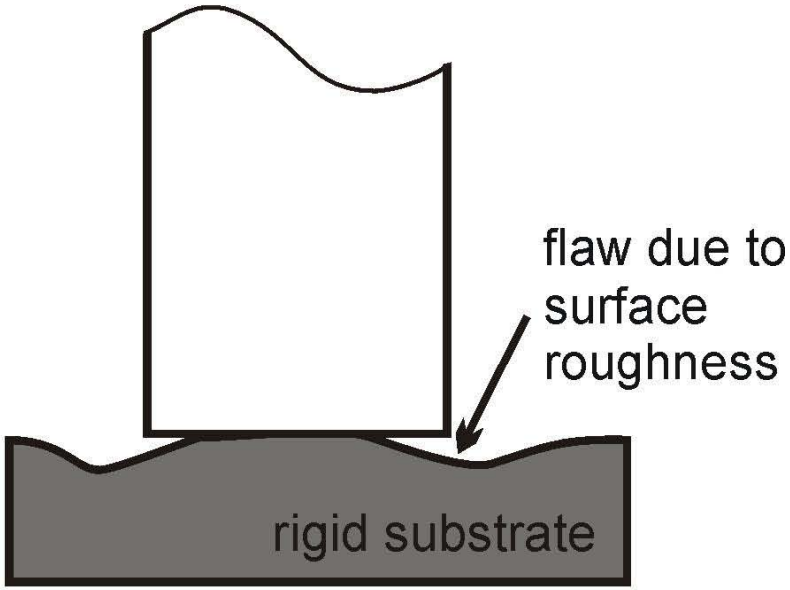
$$\phi(r) = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$$

LJ



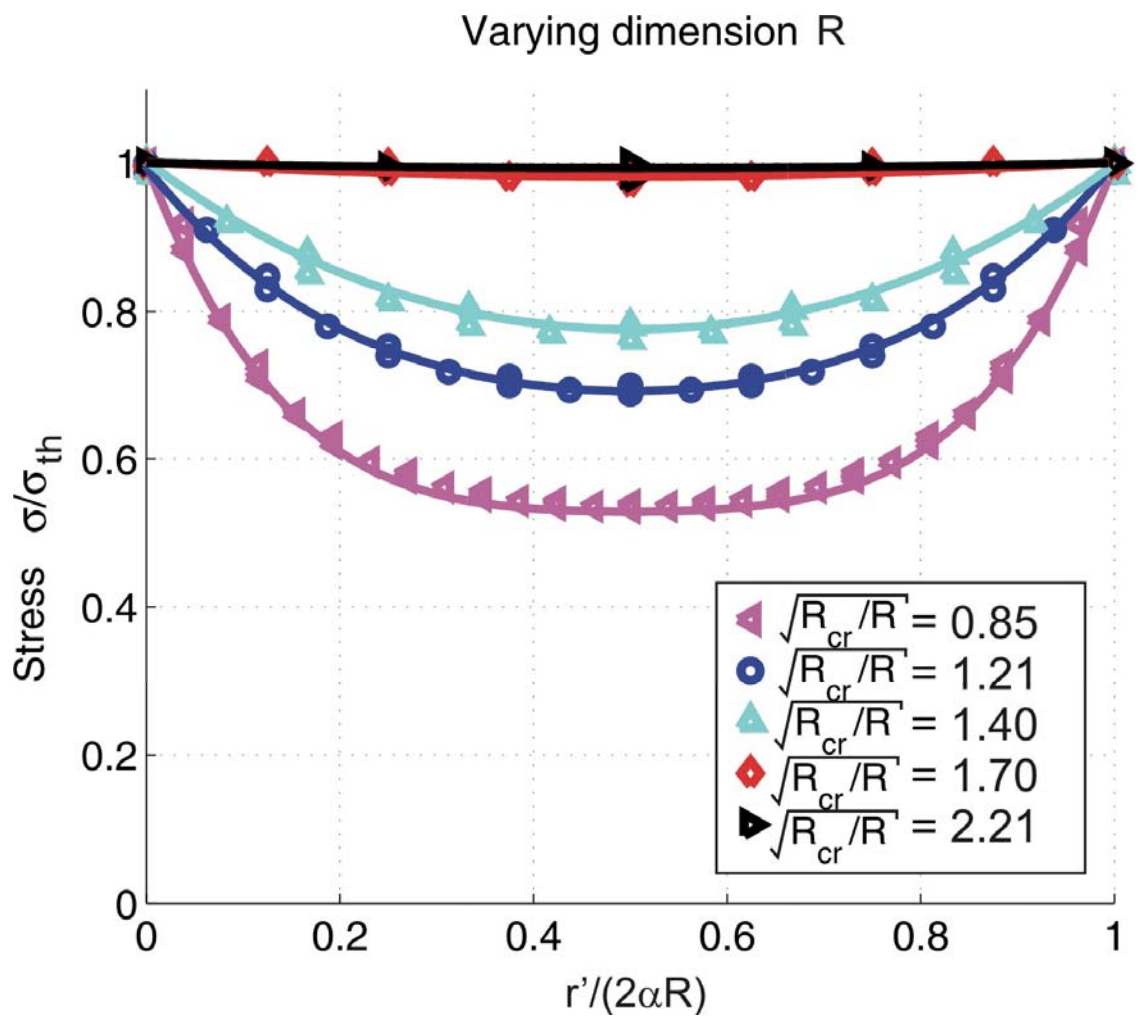
Three-dimensional model

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

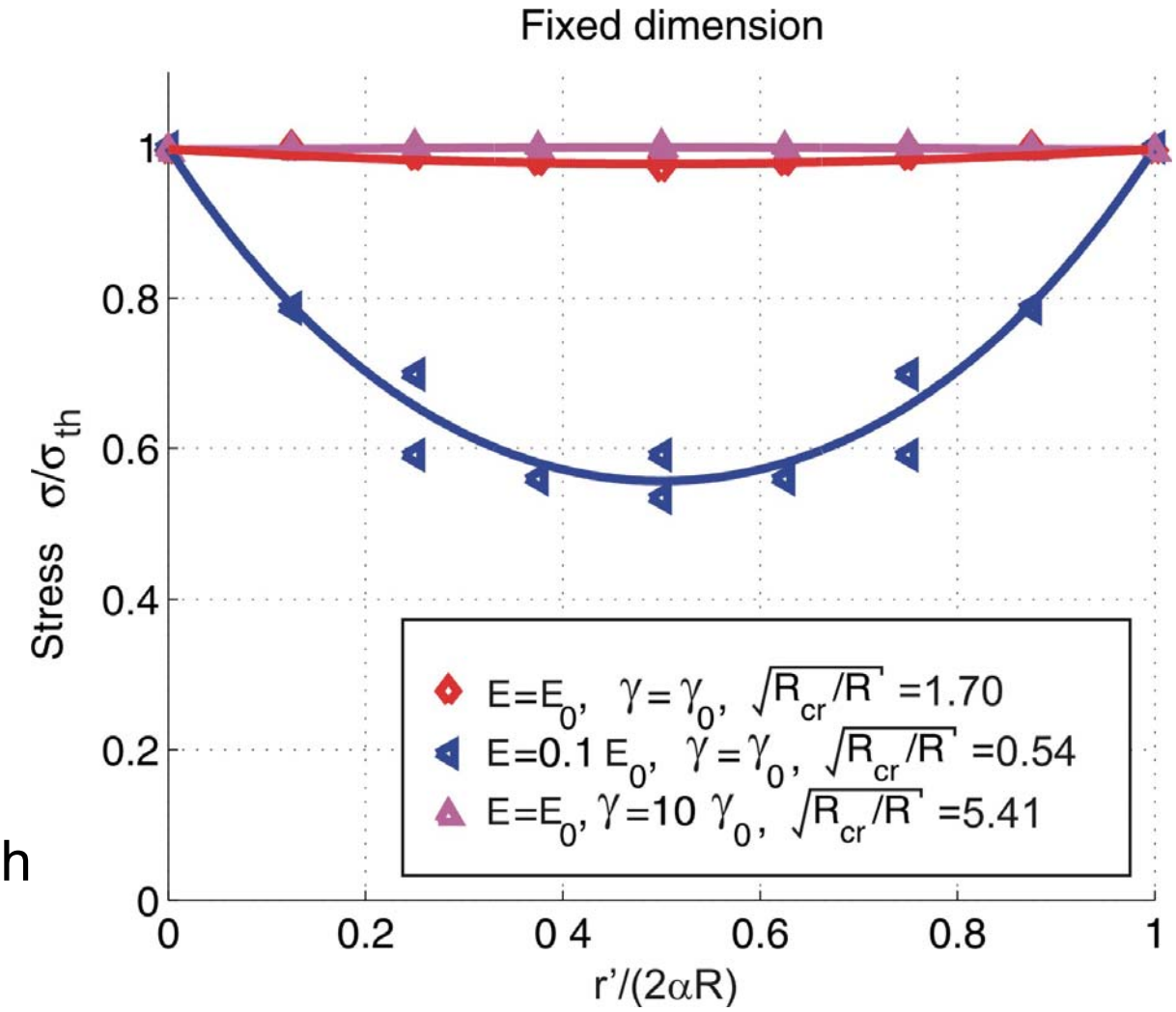
Vary E and γ in scaling law

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

The ratio

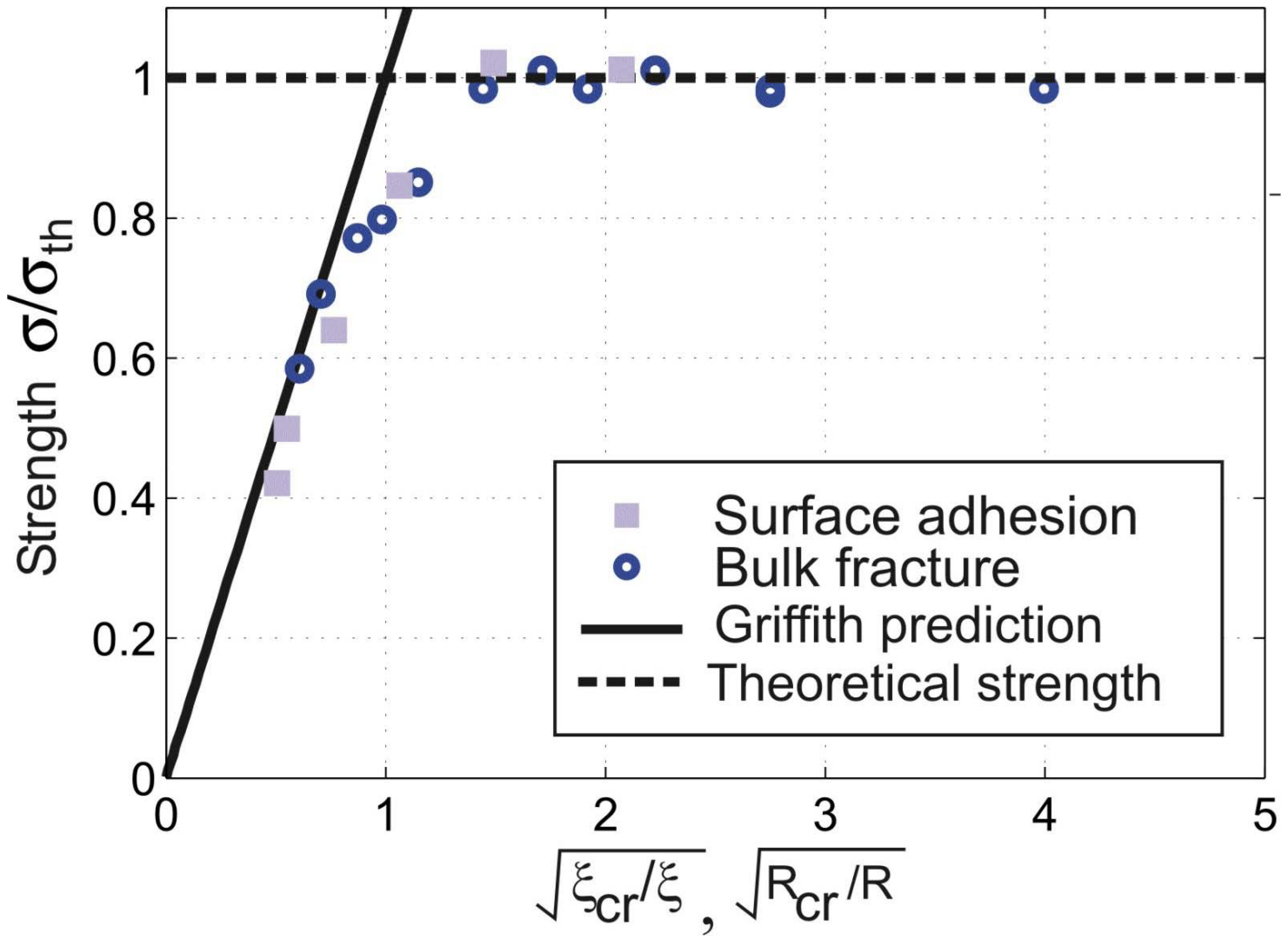
$$\sqrt{R_{cr} / R}$$

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

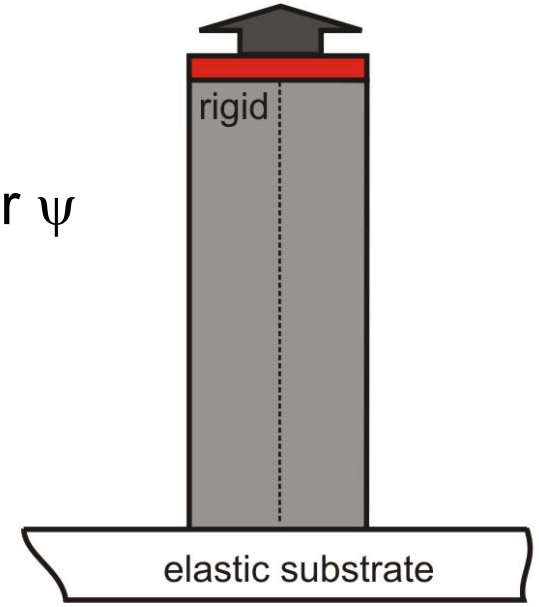


Optimal surface shape

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



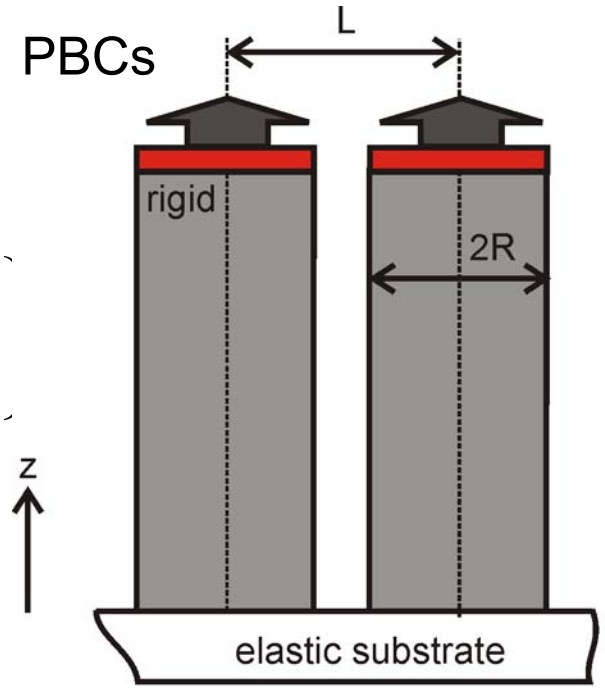
Periodic array of punches

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

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

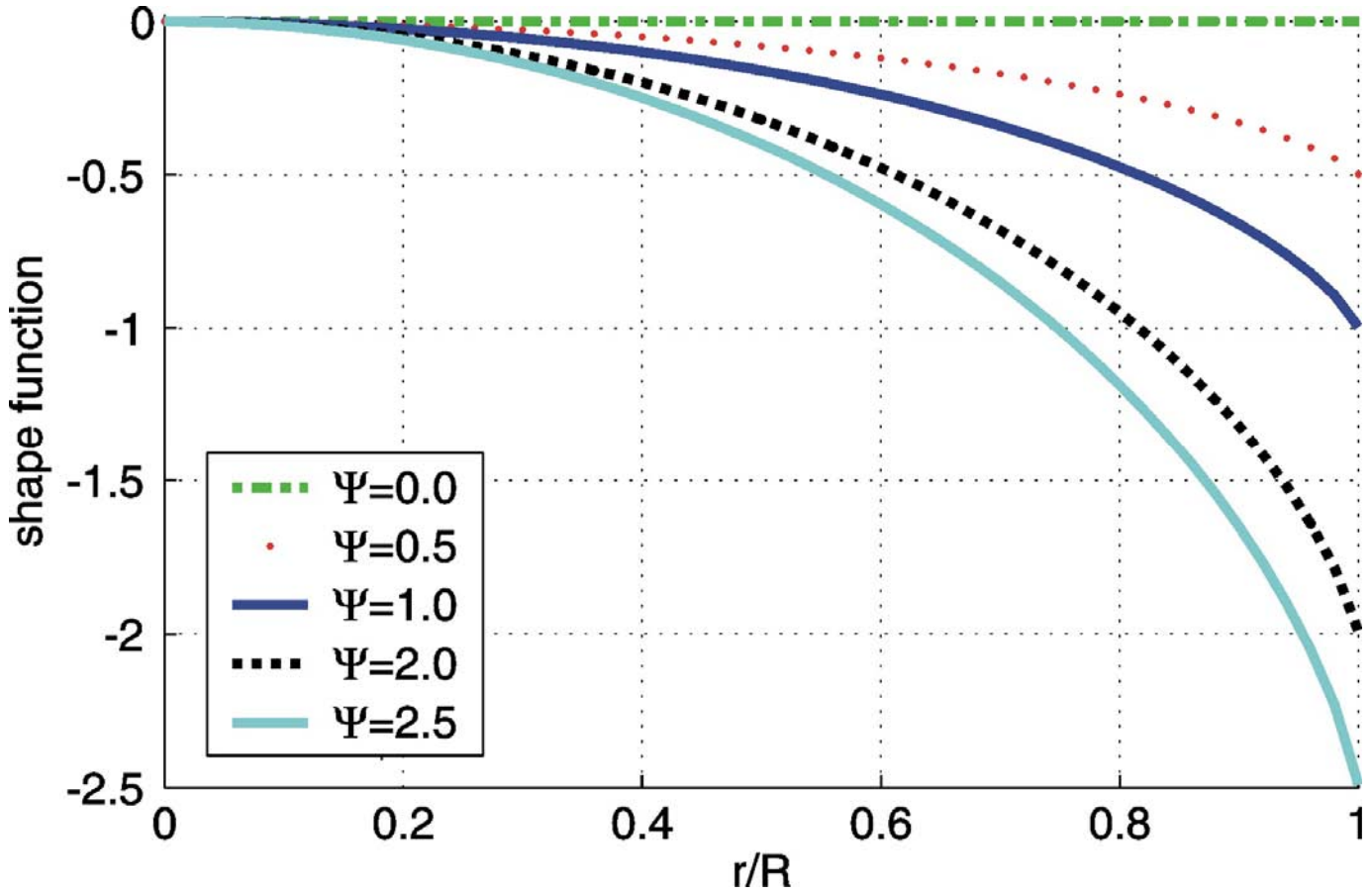
$$\left. - \sum_{n=1}^{\infty} \left[\ln\left(\frac{(2n\lambda-\bar{r})^2 - 1}{(2n\lambda)^2 - 1}\right) + (2n\lambda-\bar{r}) \ln\left(\frac{2n\lambda-\bar{r}+1}{2n\lambda-\bar{r}-1}\right) - 2n\lambda \ln\left(\frac{2n\lambda+1}{2n\lambda-1}\right) \right] \right\}$$

PBCs



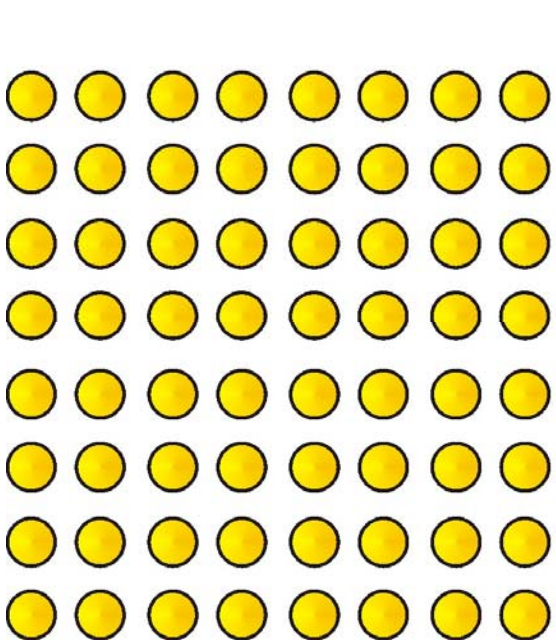
Derivation: Concept of superposition to negate the singular stress

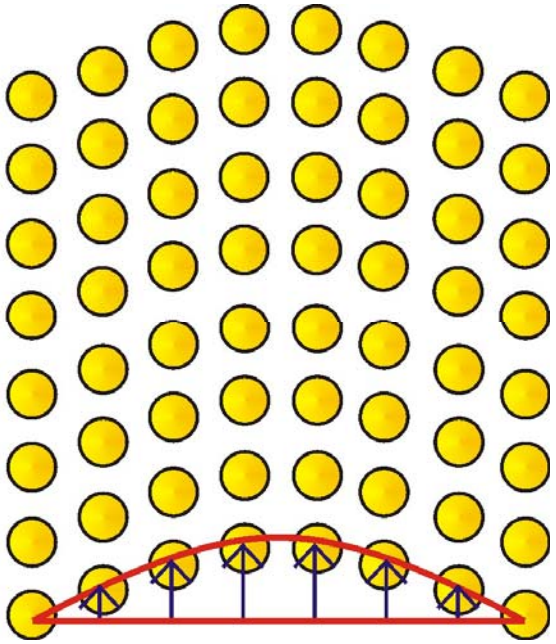
Optimal shape predicted by continuum theory & shape parameter ψ



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

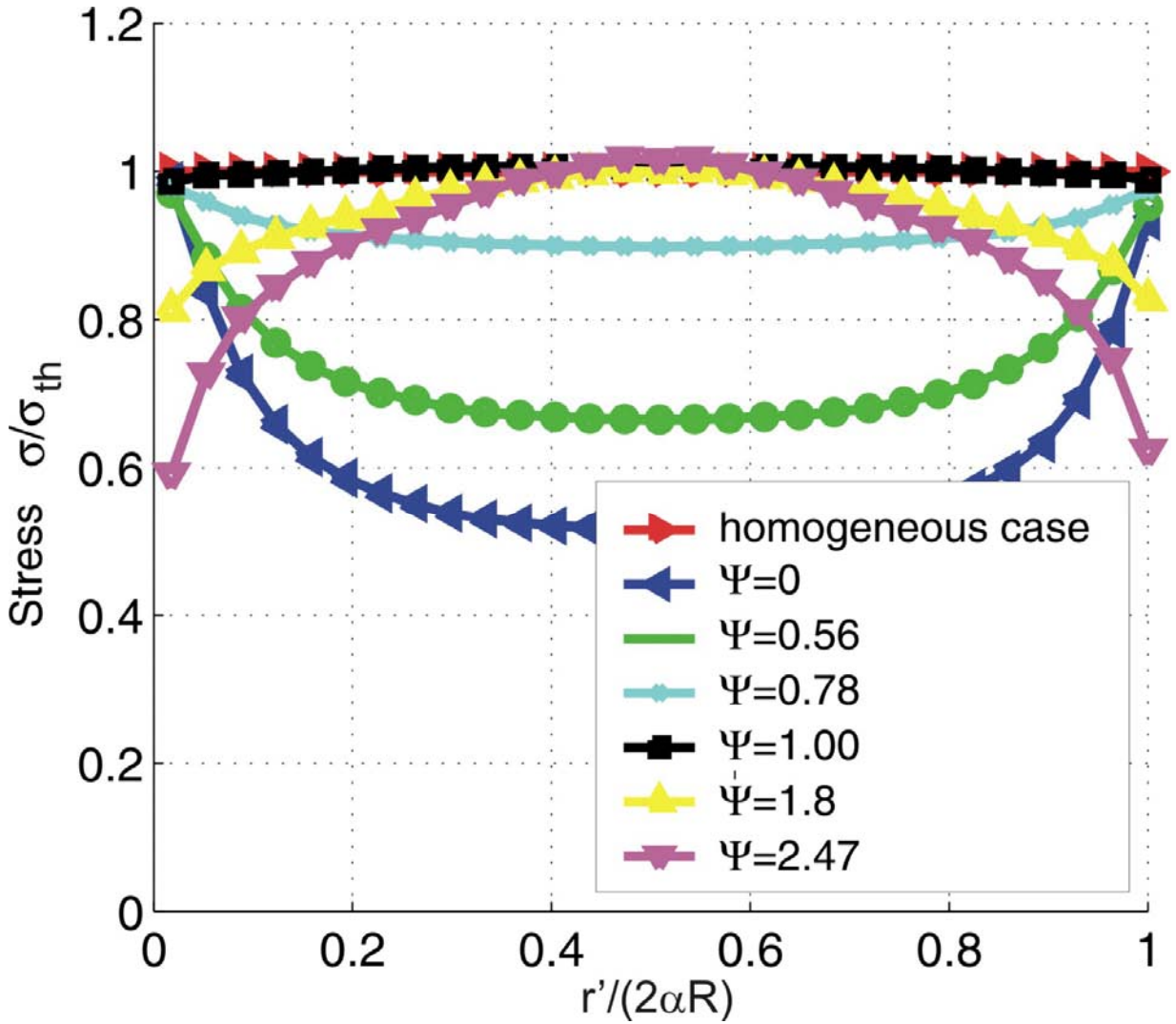


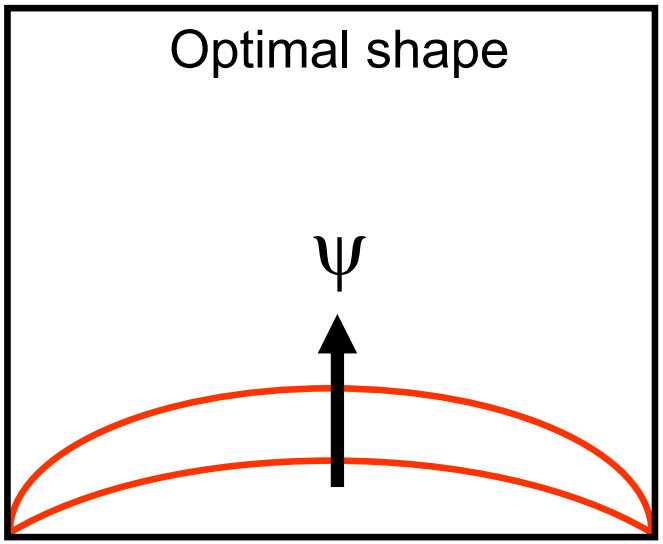


"rigid" restraint

Strategy: Displace atoms held rigid to achieve smooth surface shape

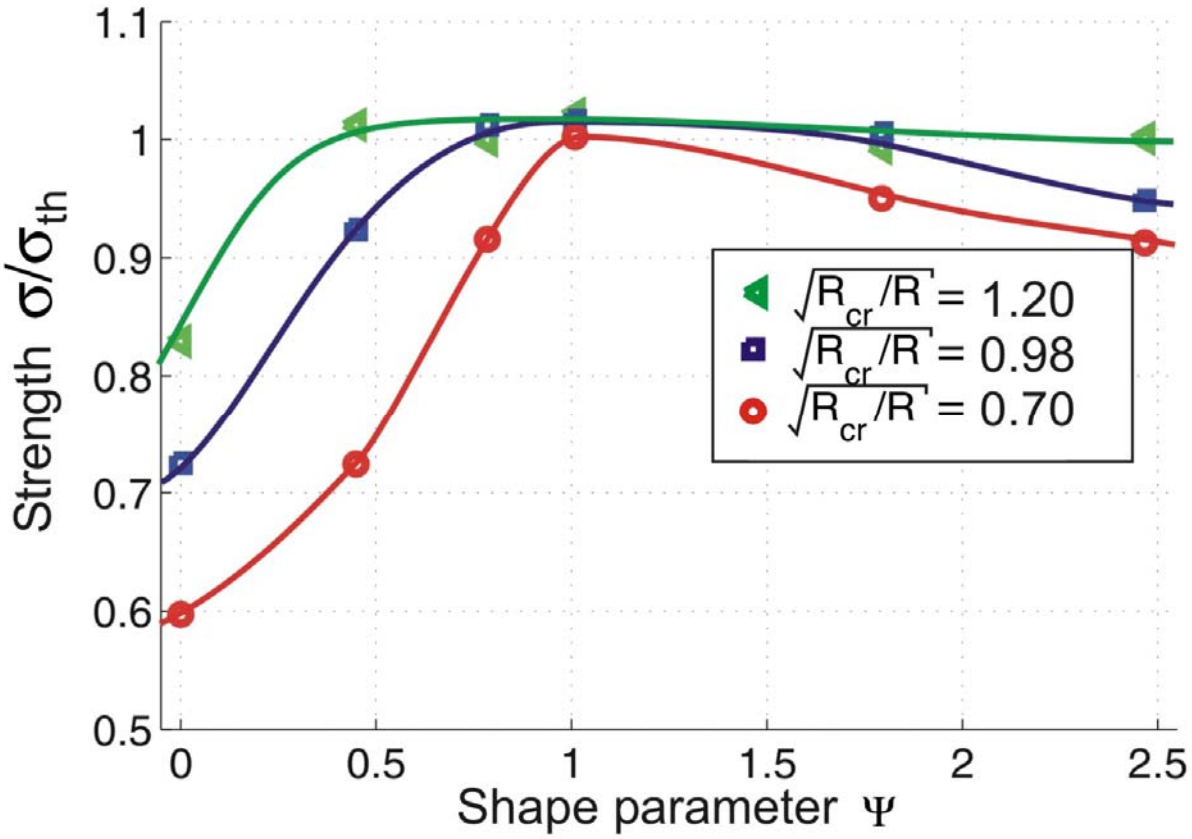
Stress distribution at varying shape





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

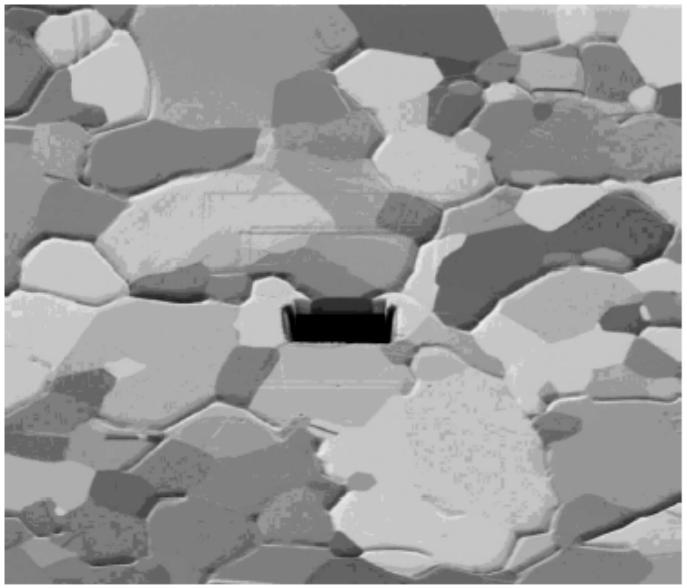
- Nanoscale dimensions allow developing extremely strong materials and strong attachment systems: **Nano is robust**

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.

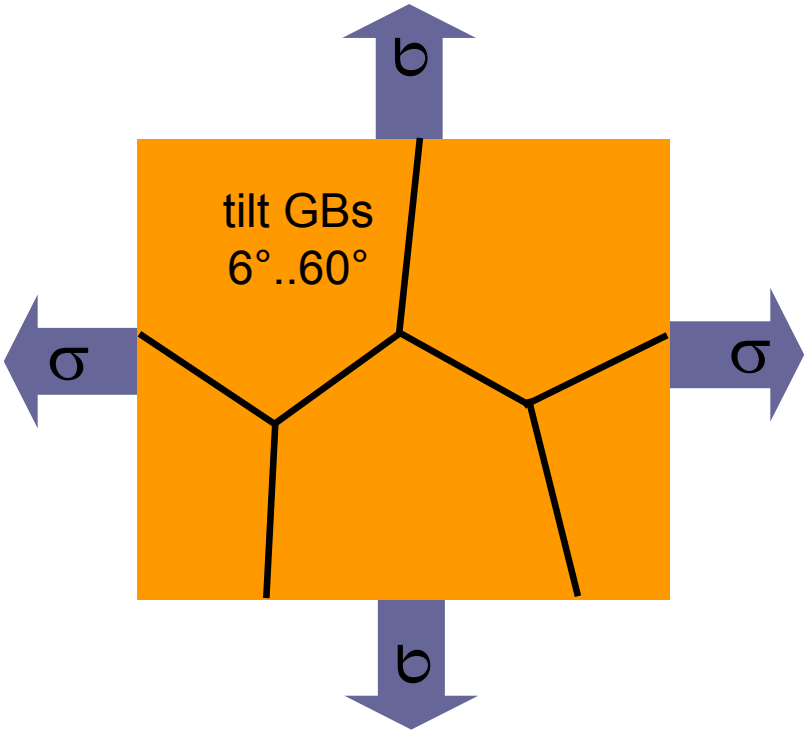
Example: Ultra thin copper films

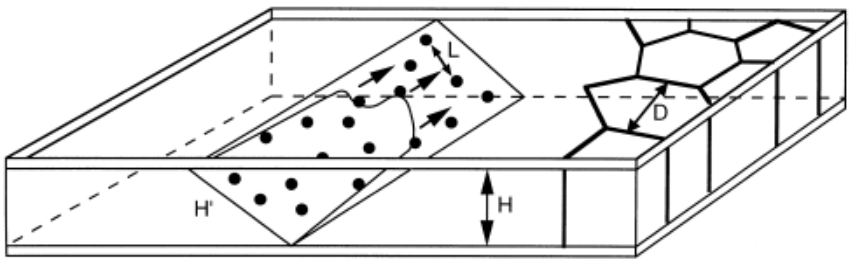


Courtesy Dirk Weiss, MIT

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

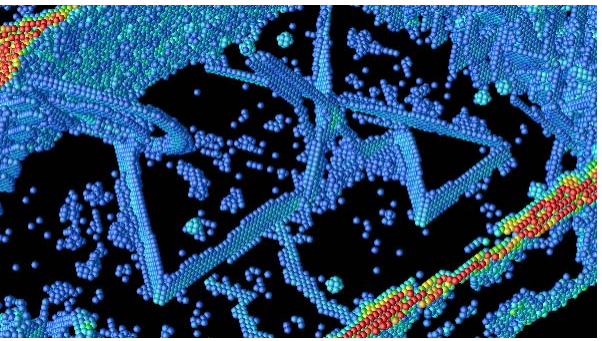
- Ultra thin, submicron copper films become critically important in next generation integrated circuits (see, e.g. *Scientific American*, April 2004), MEMS/NEMS

Thin copper films: Smaller is stronger

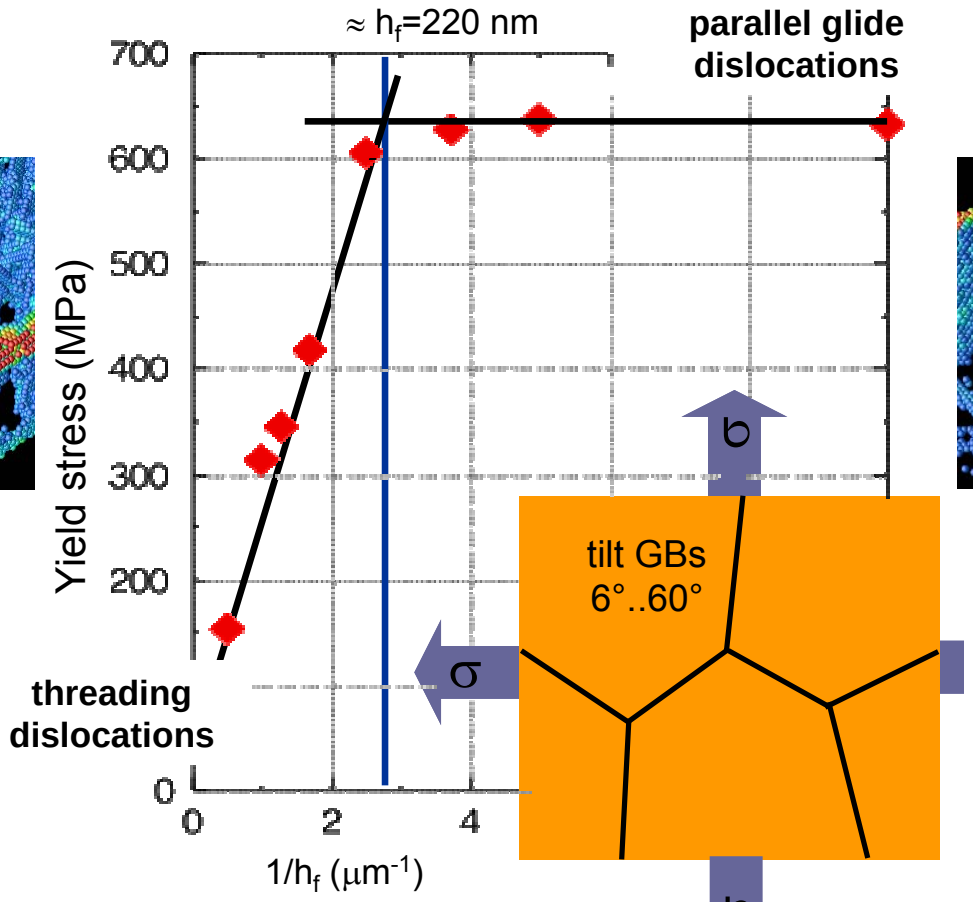
- Many materials show significant size effects re. their mechanical behavior
- For example, in thin films, dislocation behavior changes from threading dislocations (σ_Y~1/h) to parallel glide dislocations (σ_Y~const.) if the film thickness is reduced, along with a plateau in yield stress

Example: Deformation of ultra thin copper films dislocations/diffusion

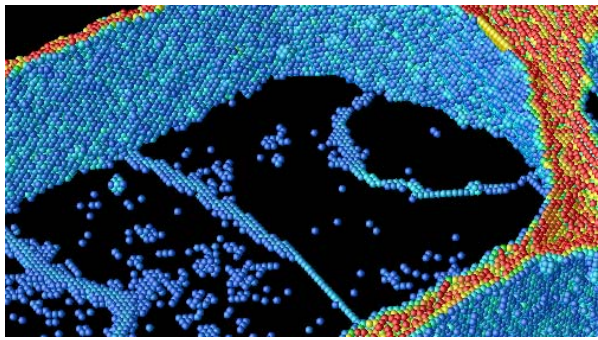
"Large"



- Threading dislocations (glide)



"Small"

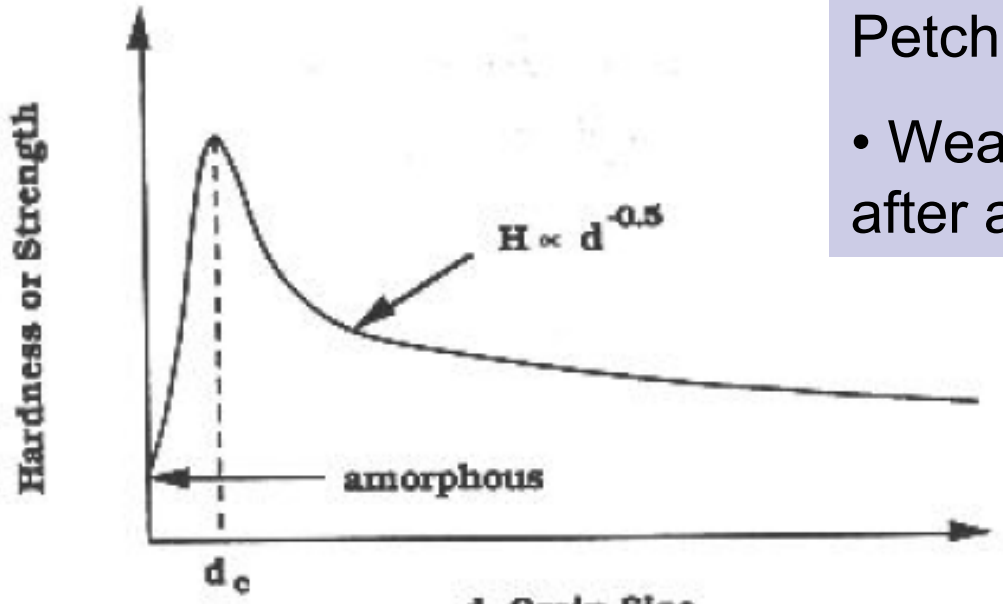


- Diffusional creep
- Parallel glide dislocations

(Buehler et al., 2003-2005)

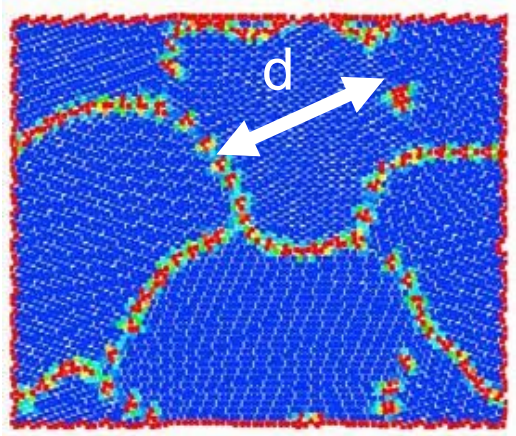
Fundamental length scales in nanocrystalline ductile materials

- 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



T.G. Nieh, J. Wadsworth, 1991

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



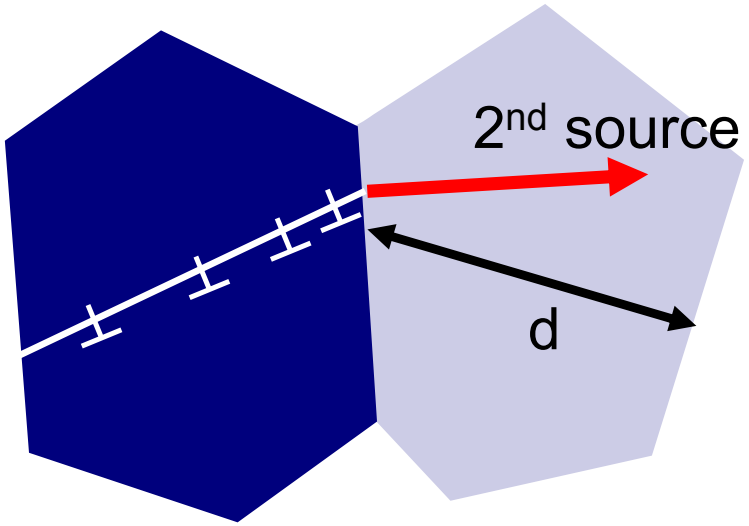
http://me.jhu.edu/~dwarner/index_files/image003.jpg

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

$$\sigma_Y \sim \frac{1}{\sqrt{d}}$$

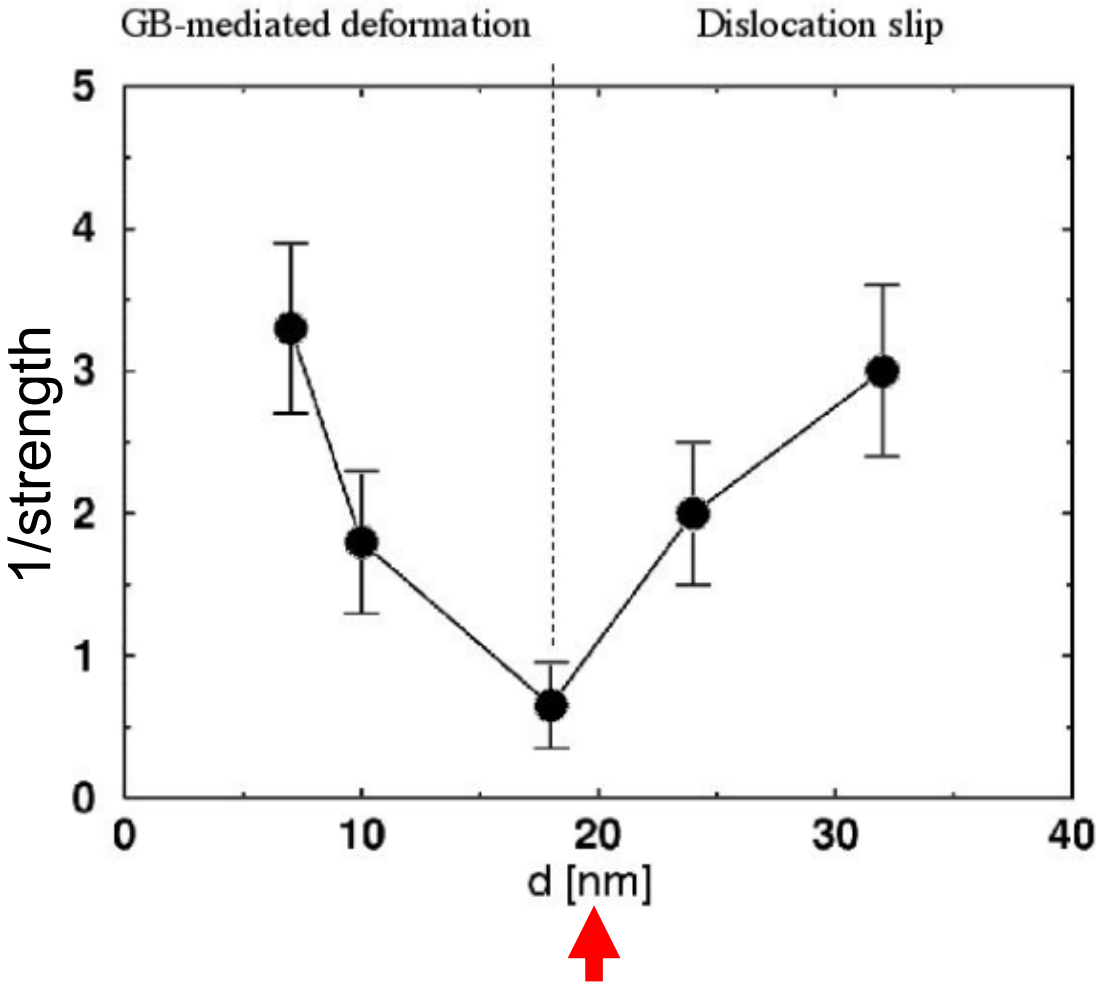
See, e.g. Courtney, Mechanical Behavior of Materials

The strongest size: *Nano is strong!*

Al (MD model)

Different mechanisms have been proposed at nanoscale, including

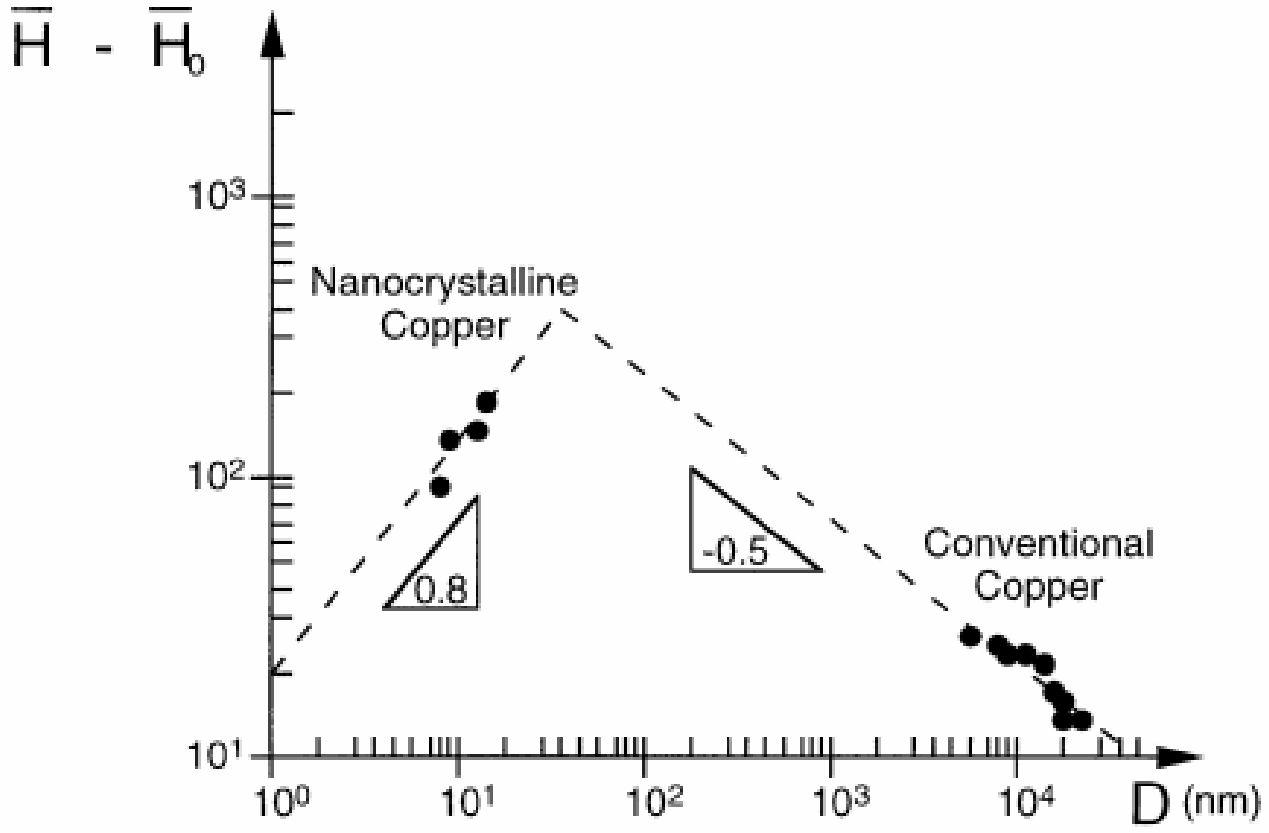
- GB diffusion (even at low temperatures) – Wolf *et al*.
- GB sliding – Schiotz *et al*.
- GBs as sources for dislocations – van Swygenhoven, stable SF energy / unstable SF energy (shielding)



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