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

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Outline and content (Lecture 5)

- **Topic:** Elasticity in biological materials: Entropic versus energetic contributions

- **Examples:** Deformation of collagen, vimentin, …: Protein mechanics

- **Material covered:** Covalent bonding and models, chemical complexity, reactivity, molecular potentials: CHARMM

- **Important lesson:** Models for bonding in proteins, entropic vs. energetic elasticity

- **Historical perspective:** AFM, single molecule mechanics

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Very brief review:

Material covered in last 2-3 lectures
Dislocation nucleation from a crack tip

Ductile vs. brittle
Depends on atomic behavior at crack tip

Figure by MIT OCW.

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Ductile materials are governed by the motion of dislocations: Introduction

Dislocations are the discrete entities that carry plastic (permanent) deformation; measured by “Burgers vector”

http://www.people.virginia.edu/~lz2n/mse209/Chapter7.pdf

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Brittle or ductile?

Critical conditions for dislocation nucleation / beginning of fracture

\[
\begin{align*}
\begin{bmatrix}
\sigma_{rr} \\
\sigma_{\theta\theta} \\
\sigma_{r\theta}
\end{bmatrix} &= \frac{K_1}{\sqrt{2\pi}} \begin{bmatrix}
\cos \frac{\theta}{2} \\
\cos^2 \frac{\theta}{2} \\
\sin \frac{\theta}{2} \cos \frac{\theta}{2}
\end{bmatrix} \left(1 + \sin^2 \frac{\theta}{2}\right)
\end{align*}
\]

Rice-Thomson model

\[
\sigma_\infty = \sqrt{\frac{2b}{a}} \frac{1}{f(\theta)} \frac{\mu}{4\pi (1 - \nu)}
\]

\[
\sigma_\infty \sim \sqrt{\frac{b}{a} \mu}.
\]

Rice-Peirls model

\[
\tau_{\infty,\text{dist}} = \sqrt{\frac{2\gamma_{us} h}{H}}.
\]

\[
\tau_{\infty,\text{surf}} = \sqrt{\frac{4\gamma_s h}{H}}.
\]

\[
\alpha = \frac{\gamma_{us}}{2\gamma_s}
\]

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Strengthening mechanisms

Figure by MIT OCW.
Image removed due to copyright restrictions.

See:

Energy approach to elasticity

\[ F = k_s \Delta u \]
Energy approach to elasticity

**1\textsuperscript{st} law of TD**

\[
\frac{dU}{dt} = \delta W + \delta Q.
\]

**External work rate**

\[
\delta W = \dot{x} F_e
\]

**Applied force**

**2\textsuperscript{nd} law**

Change in entropy is always greater or equal than the entropy supplied in form of heat; difference is due to internal dissipation

\[
\frac{dS}{dt} \geq \frac{\delta Q}{T}
\]

\[
\frac{dD}{dt} = T \frac{dS}{dt} - \delta Q \geq 0
\]

**Dissipation rate**

\[
\delta Q = \frac{dU}{dt} - \delta W
\]

**Dissipation rate after consider 1\textsuperscript{st} law of TD:**

\[
\frac{dD}{dt} = \delta W - \frac{d}{dt} (U - TS)
\]

Dissipation rate = External work rate

-change in usable energy \(U - TS\)

\[
F = U - TS \text{ is defined as free energy or Helmholtz energy,}
\]

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Energy approach to elasticity

Elastic deformation (no dissipation by definition):

\[ \frac{dD}{dt} = 0 \quad \delta W - \frac{dF}{dt} = 0 \quad \text{Assume only internal energy change} \]

\[ \delta W = \dot{x}F_e \]

\[ \dot{x} \left( F_e - \frac{dF}{dx} \right) = 0. \quad \text{Expand equation} \]

\[ \dot{x}F_e - \frac{dF}{dx} \frac{dx}{dt} = 0 \]

Therefore: If applied force equals change in free energy of the system, have elastic deformation.

\[ F_e = \frac{dF}{dx} \quad F_e = \frac{dU}{dx} \]

With strain energy density:

\[ \Psi = \frac{F}{V} \quad \Psi = \frac{U}{V} \]

\[ \sigma_{ij} = \frac{d\Psi}{d\varepsilon_{ij}} \quad C_{ijkl} = \frac{d^2\Psi}{d\varepsilon_{ij} d\varepsilon_{kl}} \]

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Idea: Use thermodynamic approach to develop expression of elasticity of a atomic microstructure, provided a specific interatomic potential.

Assuming locally homogeneous deformation, take a unit cell representation (typically PBCs) and express free energy density as a function of strain tensor.

This provides direct link between interatomic potential and constitutive behavior.

For example: FCC crystal and EAM potential – can calculate elastic properties directly.
Cauchy-Born rule

- Idea: Express elastic energy (strain energy density) for a atomistic representative volume element as a function of macroscopic applied strain

\[ \Phi = \frac{1}{\Omega_0} \int_{\Omega_0} U(l) D_{\Omega} d\Omega \]

- \( U(l) \) a function of deformation gradient

- \( D_{\Omega} \): Mapping function, e.g.

\[ D(l_0, \theta, \phi) = \delta_D(l_0 - l_0^*) D_{\theta\phi}(\theta, \phi) \]

- Impose macroscopic deformation gradient on atomistic volume element, then calculate atomic stress – this corresponds to the macroscopic stress

- Strictly valid only far away from defects in periodic lattice (homogeneous deformation, perfect lattice, amorphous solid-average)

- Allows direct link of potential to macroscopic continuum elasticity
1D example: Cauchy-Born rule

- Impose homogeneous strain field on 1D string of atoms
- Then get \( \sigma_{ij} = c_{ijkl} \varepsilon_{kl} \) from that

\[
\Phi(\varepsilon) = \frac{1}{r_0 \cdot D} \phi(r) = \frac{1}{r_0 \cdot D} \phi((1 + \varepsilon) \cdot r_0) \\

r_0 \cdot D \quad \text{Atomic volume}
\]

Strain energy density function
Detailed write-up on 1D / 2D Cauchy-Born rule is included on line
Review

Continuum mechanics
\[ \text{div } \sigma = -\rho g \]

Atomistic modeling
\[ F = ma \]

Fracture mechanics (stress field)
Beam bending
Dislocation mechanics

Energy approach
Cauchy-Born-rule

Equations of motion
Virial stress
Numerical issues (parallelization, integration...)
Interatomic potential LJ, EAM

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Mechanics of biological materials

(a) Brittle

(b) Ductile

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Example: Stretching of proteins

Images removed due to copyright restrictions.

Physical origin?
Soft matter
Nonlinear
Viscoelastic (time dependent)

...
Additional Reading

**Book Chapters**

T. Courtney, Mechanical Behavior of Materials  
Chapter 2

D.I. Bower  
An Introduction to Polymer Physics (Chapter 6 [+7 and 3])

D. Boal  
Mechanics of the Cell (Chapters 1+2)

D. Whitford  
Proteins – Structures and Function (Chapters 1-4)
Interactions between atoms, molecules and/or particles govern the elastic response of materials.

For a fundamental understanding of elasticity, need to consider atomic bonding (chemistry or quantum mechanics).

Elastic response is governed by change of free energy as a function of deformation (yields stress versus strain); second derivative of free energy with respect to strain yields Young’s modulus.

\[ F(T, V) = U - TS \]

- Polymers
- Biological structures and materials (proteins, DNA, …)
Extension ratios: Large-strain deformation

\[ \varepsilon_{ii} = \frac{\partial u_i}{\partial x_i} \]

\[ \lambda_i = 1 + \Delta_i \]

\[ \varepsilon_{ii} = \varepsilon_i = \Delta_i \]

In small-strain elasticity

\[ \lambda_i^2 = 1 + 2\Delta_i + \Delta_i^2 \]

\[ \Delta_i \to 0 \quad \text{Leads to} \]

(small strains)

\[ \lambda_i^2 = 1 + 2\Delta_i \]

\[ \lambda_i \quad \text{Extension ratios in three directions; pure tensile stress state (directions of principal stress)} \]
Strain energy functions

- Phenomenological theory that uses the concept of strain-energy functions

\[ U = f(\lambda_i) \]

- Shear strains are assumed to be zero (coordinate system of principal stresses)

- \( U \) is (physically) **not** equivalent to the thermodynamic internal energy function; instead it is a function that maps changes in entropy and internal energy into a mathematical function (phenomenological model) – **free energy density**!

- **Examples**: Rivlin, Neo-Hook, …
Example: Neo-Hookean Solid

\[ U = C \left( \lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 \right) \]

Express “strain energy density” as a function of extension ratios \( \lambda_i \).

\( C \) is a constant (parameter) that is related to the Young’s modulus (will be derived later).

The SED function is used to calculate the stress for a given deformation state (note: 2\(^{nd}\) derivatives=modulus=not constant!!)
Uniaxial deformation

Incompressible (retain volume during deformation)

\[ U = C \left( \lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 \right) \]

\[ \sigma_1 = \sigma_2 = 0 \quad \sigma_3 = \sigma \]

Orthogonal to pulling direction:

\[ \lambda_1 \lambda_2 \lambda_3 = 1 \]

\[ \lambda_1 = \lambda_2 \quad \lambda_3 = \lambda \]

\[ \lambda_3 = \lambda_2 = 1 / \sqrt{\lambda} \]

\[ U = C \left( \lambda^2 + 2 / \lambda - 3 \right) \text{ for uniaxial tension} \]

\[ dU / d\lambda = 2C(\lambda - 1 / \lambda^2) = \sigma \]
Reduction to small-strain elasticity

Then, the relation between extension ratio and stress can be written as

\[
\sigma = 2C(\lambda^2 - 1/\lambda)
\]

Consider the nominal stress force/unit area of the undeformed medium:

\[
\sigma = 2C(\lambda - 1/\lambda^2)
\]

For small strains: \(\lambda_i = 1 + \varepsilon_i\)

\[
\sigma = 2C((1 + \varepsilon)^2 - 1/(1 + \varepsilon)) \approx 2C[1 + 2\varepsilon - (1 - \varepsilon) + O(0)]
\]

\[
\sigma = 6C\varepsilon = E\varepsilon
\]

Hooke’s law (linear elasticity)

\[C = E / 6\]
Entropic change as a function of stretch

High entropy

Low entropy
Entropic change as a function of stretch

Entropic Regime

Energetic Regime

x-end-to-end distance

Figure by MIT OCW.
Based on the assumption that the rubber entropy $S$ can be calculated in terms of $\lambda = l / l_0$

For example, it can be shown that

$$U = C(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3)$$

$$C = E / 6$$

$$\sigma_n = C(\lambda - 1 / \lambda^2)$$

This is the result for a neo-Hookean solid

(see Courtney, p. 64)
Note: No change in elastic energy of molecules

Needed to understand elasticity: Expression of free energy as a function of the applied strain!

Here: Entropic elasticity – therefore change in entropy
Single freely jointed chain

\[ S = c - kb^2 r^2 \]

\[ b^2 = \frac{3}{2nl^2} \]

Total length: \( nl = L \)

\[ r^2 = \langle r_b^2 \rangle = n \cdot l^2 \] RMS length of the chain (no force applied)

\[ \sqrt{n \cdot l} \rightarrow nl \] Maximum extension due to force

Physical meaning of \( l \): Length at which molecular bending is uncorrelated
Entropic elasticity: Derivation

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

\[
S = c - kb^2 r^2 \quad \text{where} \quad b^2 = \frac{3}{2nl^2} \quad r \quad \text{end-to-end distance of chain}
\]

\[
\Delta S = -kb^2 \sum_{N_b} \left( \lambda_1^2 - 1 \right)x^2 + \left( \lambda_2^2 - 1 \right)y^2 + \left( \lambda_3^2 - 1 \right)z^2
\]
Entropic elasticity: Derivation

\[ \Delta S = -k b^2 \sum_{N_b} \left( \lambda_1^2 - 1 \right) x^2 + \left( \lambda_2^2 - 1 \right) y^2 + \left( \lambda_3^2 - 1 \right) z^2 \]

\[ \Delta S = -k b^2 N_b \left[ \left( \lambda_1^2 - 1 \right) \langle x^2 \rangle + \left( \lambda_2^2 - 1 \right) \langle y^2 \rangle + \left( \lambda_3^2 - 1 \right) \langle z^2 \rangle \right] \]

\(< .. > \) Average values over all \( N_b \) chains
- need multiply by \( N_b \) to get total energy

Isotropic solid: End-to-end distances of the Nb chains are
directed equally in all directions; therefore

\[ \langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \frac{1}{3} \langle r_b^2 \rangle \]
The length $< r^2_b >$ in the unstressed state is equal to the mean square length of totally free chains.

It can be shown that

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

$$< r^2_b > = n \cdot l^2$$

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

$$\Delta S = -kN_b / 2\left[\left(\lambda^2_1 - 1\right) + \left(\lambda^2_2 - 1\right) + \left(\lambda^2_3 - 1\right)\right]$$

No explicit dep. on $b$ any more

$$U = -T\Delta S = \frac{1}{2} N_b kT \left(\lambda^2_1 + \lambda^2_2 + \lambda^2_3 - 3\right)$$

$$U = C \left(\lambda^2_1 + \lambda^2_2 + \lambda^2_3 - 3\right) \quad C = \frac{E}{6}$$

$$\sigma = \left(\frac{E}{3}\right) \left(\lambda^2 - 1 / \lambda\right)$$
Entropic elasticity

For SED: *Free energy density*
Young's modulus
\[ U = -T \Delta S = \frac{1}{2} N_b kT \left( \lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 \right) \]

Predictions:
\[ C = E / 6 \]
\[ E = 3 N^* kT \quad N^* = N_b / V \]

Stiffness is proportional to temperature
\[ E \sim T \]

Stiffness is proportional to degree of cross-linking (for ideal network, \( N^* \) equals twice the cross-link density)
\[ E \sim N^* \]
Summary

- Developed rigorous link extension ratio and elastic properties of rubber-like materials.

- Based on statistical theory and by considering changes in entropy due to deformation, arrived at an expression for the Neo-Hookean solid.

- This enables to link cross-linking density and temperature with Young’s modulus.
Persistence length

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

\( t(s) \) tangent slope

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

\[ \xi_p = l/2 \]

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Persistence length: Illustration

- Bending deformation (R=radius, EI=flexural rigidity of the rod)
  - energy
  \[ E_{\text{bend}} = EI \frac{L}{2R^2} \]

- Thermal (kinetic) energy per molecule (kinetic theory of gases)
  - energy
  \[ E_{\text{kin, mol}} = \frac{3}{2} kT \]

- Example: \( kT \approx 4 \times 10^{-21} \text{ J} \) at room temperature

- Persistence length is defined as
  \[ \xi_p = \frac{EI}{kT} \]
  (unit: length)
The contour length of a molecule is the total length in the stretched configuration, denoted as $L$.

When $L \ll \xi_p$, a filament appears relatively straight.

When $L \gg \xi_p$, a filament adopts more convoluted shapes.

To pull a highly convoluted molecule apart ($L \gg \xi_p$), a force is necessary; define effective spring constant

$$k_{sp} = \frac{3kT}{2L\xi_p} \quad F \sim k_{sp}x \quad x \ll L$$

No energetic interactions!
Worm-like chain model

Freely-jointed rigid rods

Continuously flexible ropes

Worm like chain model

Image removed due to copyright restrictions.
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

\[ x \ll L \]

- 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:

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

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

- **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

Images removed due to copyright restrictions.
Table of amino acid chemical structures.
See similar image:
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)
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.
Modeling organic chemistry

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

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Model for covalent bonds

\[ V(R) = E_{\text{bonded}} + E_{\text{non-bonded}} \]

\[ E_{\text{bonded}} = E_{\text{bond-stretch}} + E_{\text{angle-bend}} + E_{\text{rotate-along-bond}} \]

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

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

\[ E_{\text{bond-stretch}} = \sum K_b \left( b - b_0 \right)^2 \]

\[ E_{\text{bond-bend}} = \sum_{\text{angles}} K_\theta \left( \theta - \theta_0 \right)^2 \]

\[ E_{\text{rotate-along-bond}} = \sum_{1,4\text{pairs}} K_\phi \left( 1 - \cos(n\phi) \right) \]
Review: CHARMM potential

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

Need to retype when chemical environment changes

$$V_{\text{bond}} = K_b (b - b_0)^2$$

http://www.ch.embnet.org/LMD_tutorial/pages/LMD.Prt2.html
http://www.pharmacy.umaryland.edu/faculty/amackere/force_fields.htm

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Review: CHARMM potential

\[ E_{\text{non-bonded}} = E_{\text{van-der-Waals}} + E_{\text{electrostatic}} \]

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

\[ E_{\text{electrostatic}} = \sum_{\text{nonbonded pairs}} \frac{q_i q_k}{D r_{ik}} \]

Nonbonding interactions

vdW (dispersive)

Coulomb (electrostatic)

H-bonding
UFF “Universal Force Field”

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

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

Pauling-type bond order correction

\[ E_R = \frac{1}{2} k_{ij} (r - r_{ij})^2 \]

\[ r_{ij} = r_i + r_j + r_{BO} + r_{EN} \]

\[ r_{BO} = -\lambda (r_i + r_j) \ln (n) \]

\[ r_{EN} = r_i r_j (\sqrt{x_i} - \sqrt{x_j})^2 / (x_i r_i + x_j r_j) \]

\[ k_{ij} = \left( \frac{\partial^2 E_t}{\partial R^2} \right)_0 = 2G \frac{Z_i^* Z_j^*}{R^3} = 664.12 \frac{Z_i^* Z_j^*}{r_{ij}^3} \]

Rappé et al.

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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 H₂O
 Between N and O in proteins…

Images removed due to copyright restrictions.

See:
Unfolding of alpha helix structure

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

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

Keten and Buehler, 2007
Three-point bending test: Tropocollagen molecule

\[ EI = \frac{F_{\text{appl}} L^3}{48d} \]

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)

Stretching experiment: Tropocollagen molecule