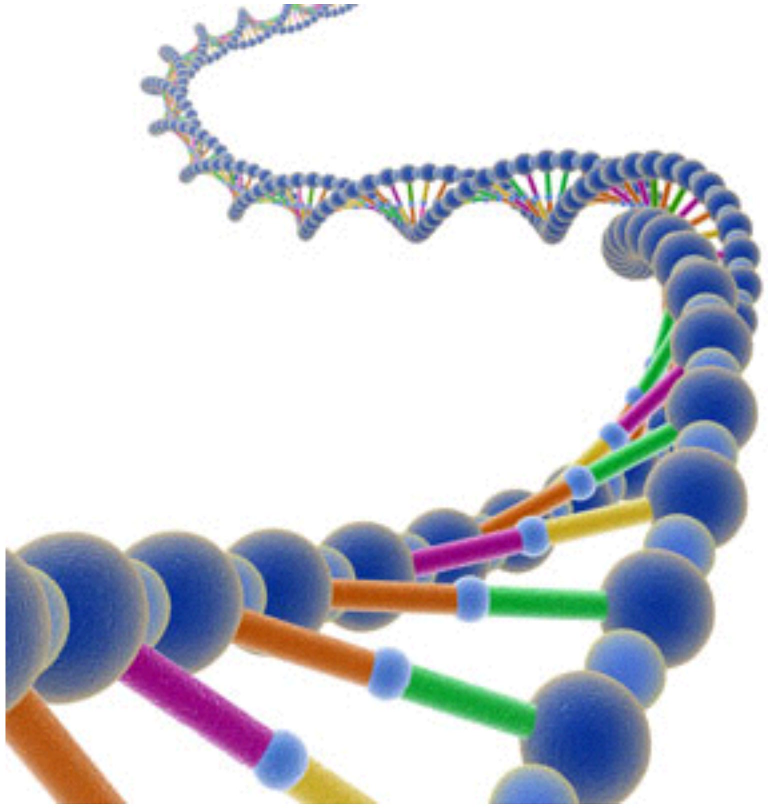
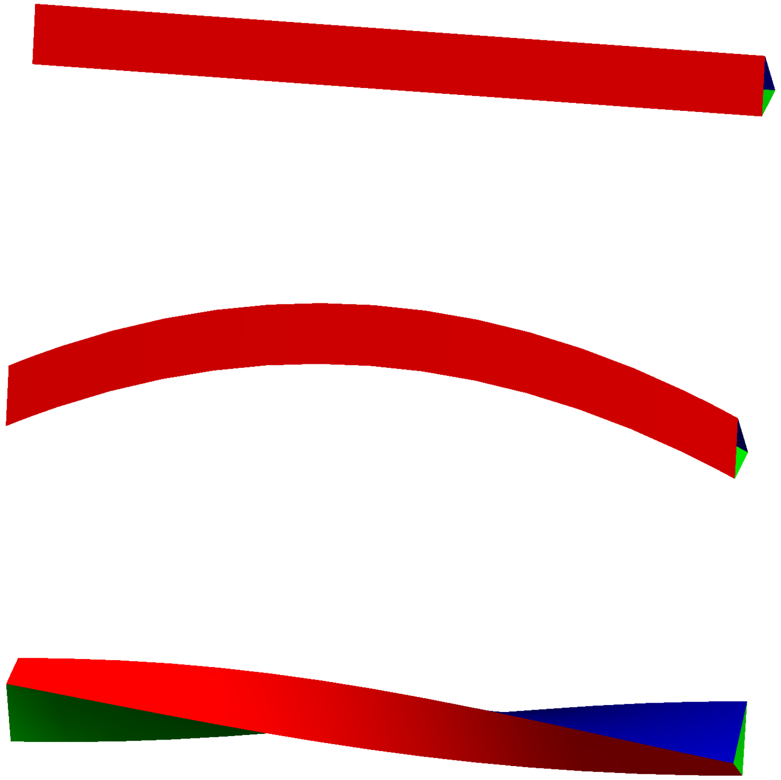
MAE 545: Lecture 12 (10/27)

Electrostatic energy for bending DNA

Elastic deformation energy for beams and thin filaments





Poisson-Boltzmann equation

Let's assume some mean-field electric potential $\phi(\vec{r})$ throughout the cell.

Local density of mobile ions carrying charge $z_\alpha e_0$.

$$n_\alpha(\vec{r}) = \overline{n}_\alpha e^{-z_\alpha e_0 \phi(\vec{r})/k_B T}$$

$$\int d^3\vec{r}\, \overline{n}_\alpha e^{-z_\alpha e_0 \phi(\vec{r})/k_B T} = N_\alpha$$

Charge density of mobile ions

$$\rho_{\text{mobile ions}}(\vec{r}) = \sum_\alpha z_\alpha e_0 \overline{n}_\alpha e^{-z_\alpha e_0 \phi(\vec{r})/k_B T}$$

Poisson equation

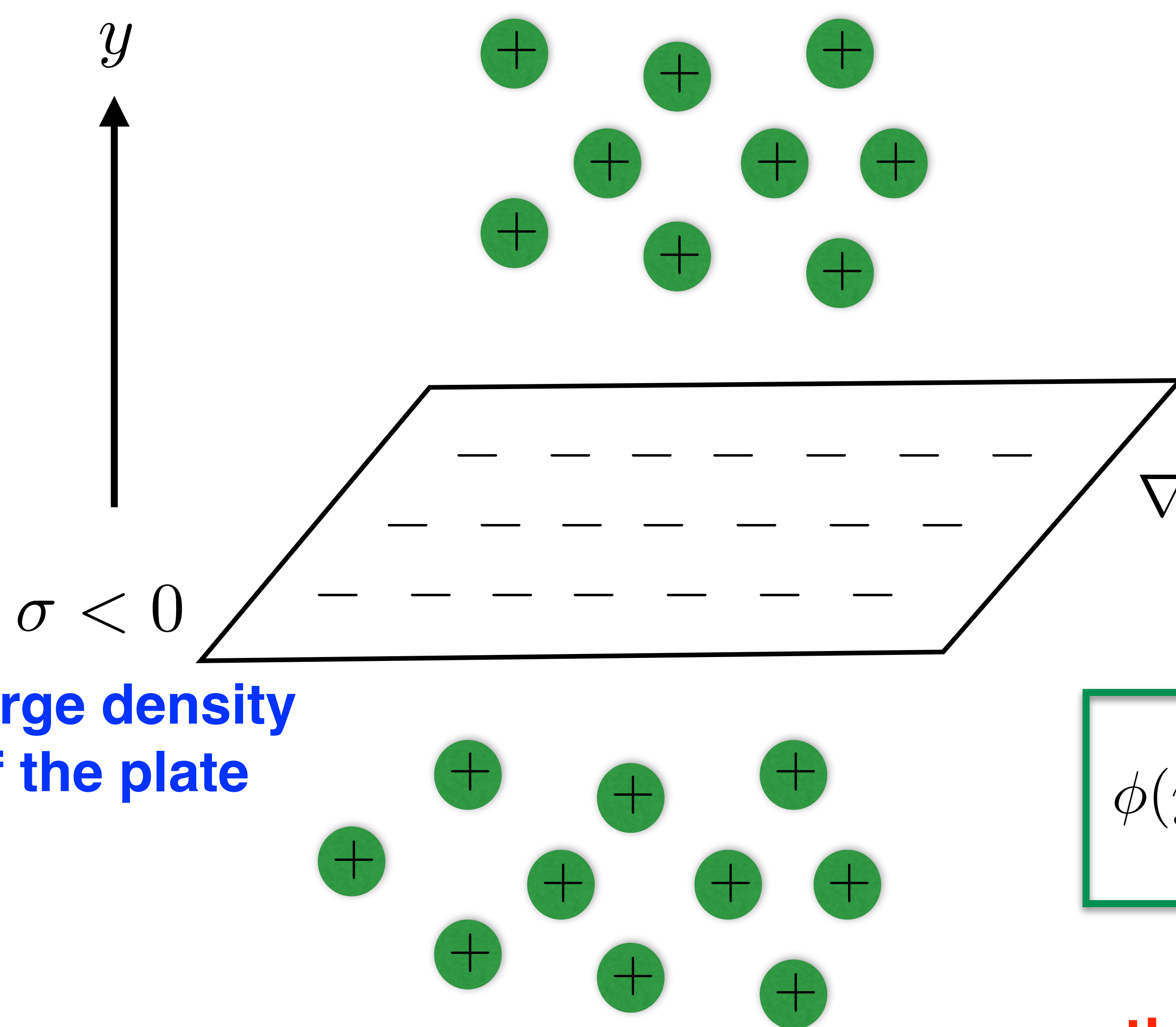
$$\nabla^2 \phi(\vec{r}) = -\frac{4\pi}{\epsilon} \rho(\vec{r})$$

Poisson-Boltzmann equation

$$\nabla^2 \phi(\vec{r}) = -\frac{4\pi}{\epsilon} \left[\rho_{\text{macroions}}(\vec{r}) + \sum_\alpha z_\alpha e_0 \overline{n}_\alpha e^{-z_\alpha e_0 \phi(\vec{r})/k_B T} \right]$$

For a given distribution of macroions Poisson-Boltzmann equation must be solved self-consistently for the electric potential $\phi(\vec{r})$.

Dissociation of charge from a plate



charge density of the plate

density of positive counterions

$$n(y) = \overline{n} e^{-e_0 \phi(y)/k_B T}$$

Poisson-Botzmann equation

$$\nabla^2 \phi(y) = -\frac{4\pi}{\epsilon}\left[\sigma \delta(y) + e_0 \overline{n} e^{-e_0 \phi(y)/k_B T}\right]$$

$$\boxed{\phi(y) = \frac{2 k_B T}{e_0} \ln\left[1 + \frac{|y|}{y_0}\right]} \qquad y_0 = \frac{k_B T \epsilon}{\pi e_0 |\sigma|}$$

***y_0* - Guoy-Chapman length**
thickness of diffusive boundary layer that shields a charged membrane

density of positive counterions

$$n(y) = \frac{\pi |\sigma|^2}{2 \epsilon k_B T} \frac{1}{(1 + |y|/y_0)^2}$$

$$\int dy \; n(y) = \sigma$$

electric field

$$E(y) = -\frac{\partial \phi(y)}{\partial y} = -\frac{y}{|y|} \frac{2\pi |\sigma|}{\epsilon} \frac{1}{(1 + |y|/y_0)}$$

Debye-Hückel approximation

Let's assume that electrostatic energy due to the mean field electric potential is small compared to k_BT.

Local density of mobile ions carrying charge $z_\alpha e_0$.

$$n_\alpha(\vec{r}) = \overline{n}_\alpha e^{-z_\alpha e_0 \phi(\vec{r})/k_B T}$$

$$n_\alpha(\vec{r}) \approx \overline{n}_\alpha \left(1 - \frac{z_\alpha e_0 \phi(\vec{r})}{k_B T}\right)$$

$$\int d^3\vec{r}\, \overline{n}_\alpha e^{-z_\alpha e_0 \phi(\vec{r})/k_B T} = N_\alpha$$

$$\overline{n}_\alpha \approx N_\alpha / V$$

Charge neutrality

$$\sum_\alpha z_\alpha \overline{n}_\alpha = 0$$

Charge density of mobile ions

$$\rho_{\text{mobile ions}}(\vec{r}) = \sum_\alpha z_\alpha e_0 \overline{n}_\alpha e^{-z_\alpha e_0 \phi(\vec{r})/k_B T}$$

$$\rho_{\text{mobile ions}}(\vec{r}) \approx -\frac{e_0^2 \phi(\vec{r})}{k_B T} \sum_\alpha z_\alpha^2 \overline{n}_\alpha = -\ell_B \epsilon \phi(\vec{r}) \sum_\alpha z_\alpha^2 \overline{n}_\alpha$$

Debye-Hückel approximation

Charge density of mobile ions

$$\rho_{\text{mobile ions}}(\vec{r}) \approx -\frac{e_0^2 \phi(\vec{r})}{k_B T} \sum_\alpha z_\alpha^2 \overline{n}_\alpha = -\ell_B \epsilon \phi(\vec{r}) \sum_\alpha z_\alpha^2 \overline{n}_\alpha$$

Poisson equation

$$\nabla^2 \phi(\vec{r}) = -\frac{4\pi}{\epsilon} \left[\rho_{\text{macroions}}(\vec{r}) + \rho_{\text{mobile ions}}(\vec{r})\right]$$

$$\nabla^2 \phi(\vec{r}) = -\frac{4\pi}{\epsilon} \rho_{\text{macroions}}(\vec{r}) + \frac{\phi(\vec{r})}{\lambda_D^2}$$

Debye screening length

$$\lambda_D^{-2} = 4\pi \ell_B \sum_\alpha z_\alpha^2 \overline{n}_\alpha$$

Electric potential for a point charge

$$\rho_{\text{macroions}}(\vec{r}) = z e_0 \delta(\vec{r})$$

$$\phi(\vec{r}) = \frac{z e_0}{\epsilon r} e^{-r/\lambda_D}$$

Electrostatic interaction between macroions

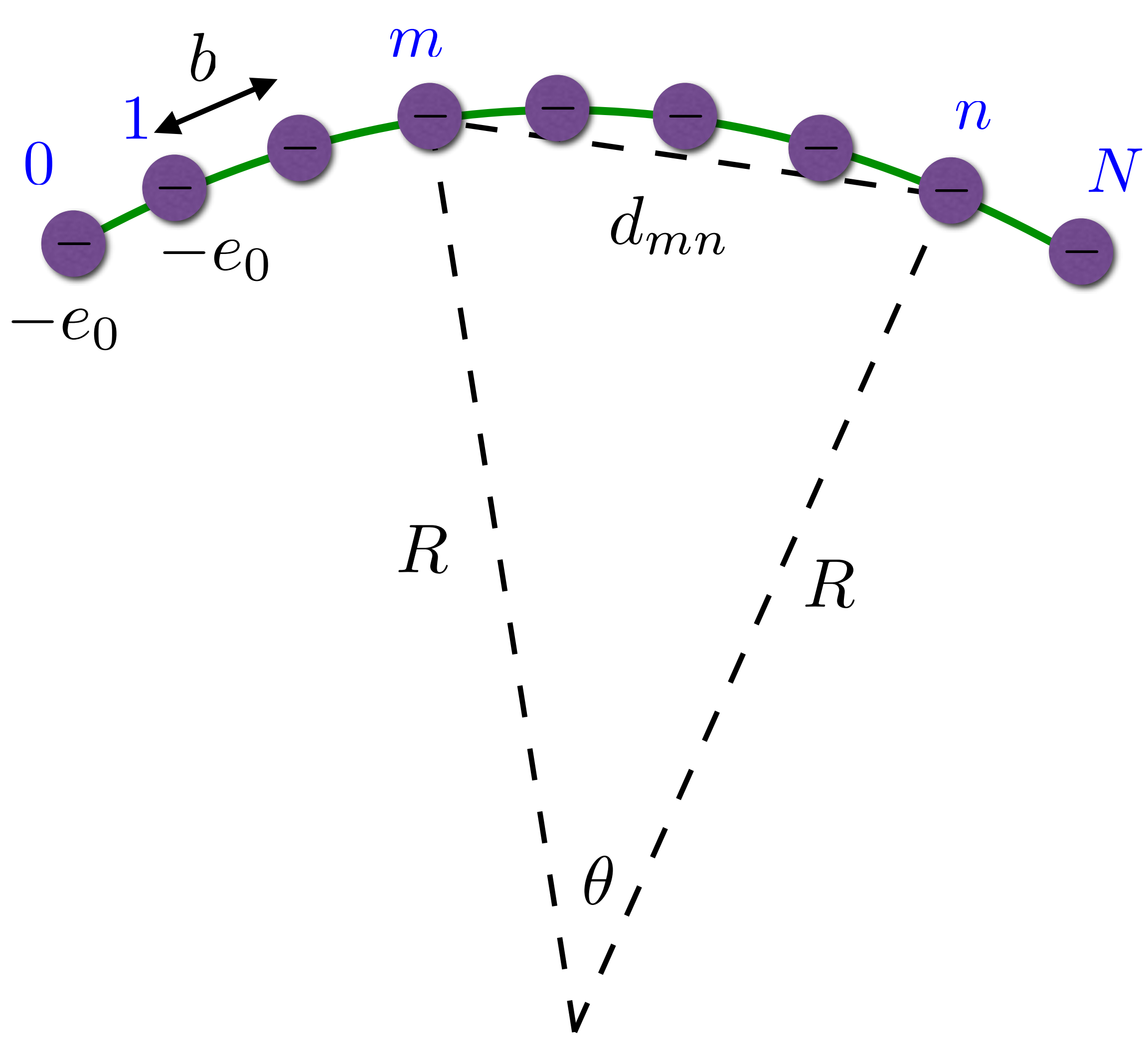
$$\rho_{\text{macroions}}(\vec{r}) = \sum_m z_m e_0 \delta(\vec{r} - \vec{r}_m)$$

$$\phi(\vec{r}) = \sum_m \frac{z_m e_0}{\epsilon |\vec{r} - \vec{r}_m|} e^{-|\vec{r} - \vec{r}_m|/\lambda_D}$$

$$\frac{E_{\text{interactions}}}{k_B T} = \sum_n \frac{1}{2} \frac{z_n e_0 \phi(\vec{r}_n)}{k_B T} = \sum_{m<n} \frac{z_m z_n \ell_B}{|\vec{r}_m - \vec{r}_n|} e^{-|\vec{r}_m - \vec{r}_n|/\lambda_D}$$

Bending of charged rod

Negative unit charges separated by distance *b* along the rod.



What is the energy cost associated with bending the charged rod due to electrostatic interactions?

Change in distance between charges

$$d^0_{mn} = b|m-n| = R\theta$$

$$\delta d_{mn} = 2R\sin(\theta/2) - d^0_{mn}$$

$$\delta d_{mn} \approx R\theta - R\theta^3/24 - d^0_{mn}$$

$$\delta d_{mn} \approx -\frac{\left(d^0_{mn}\right)^3}{24R^2}$$

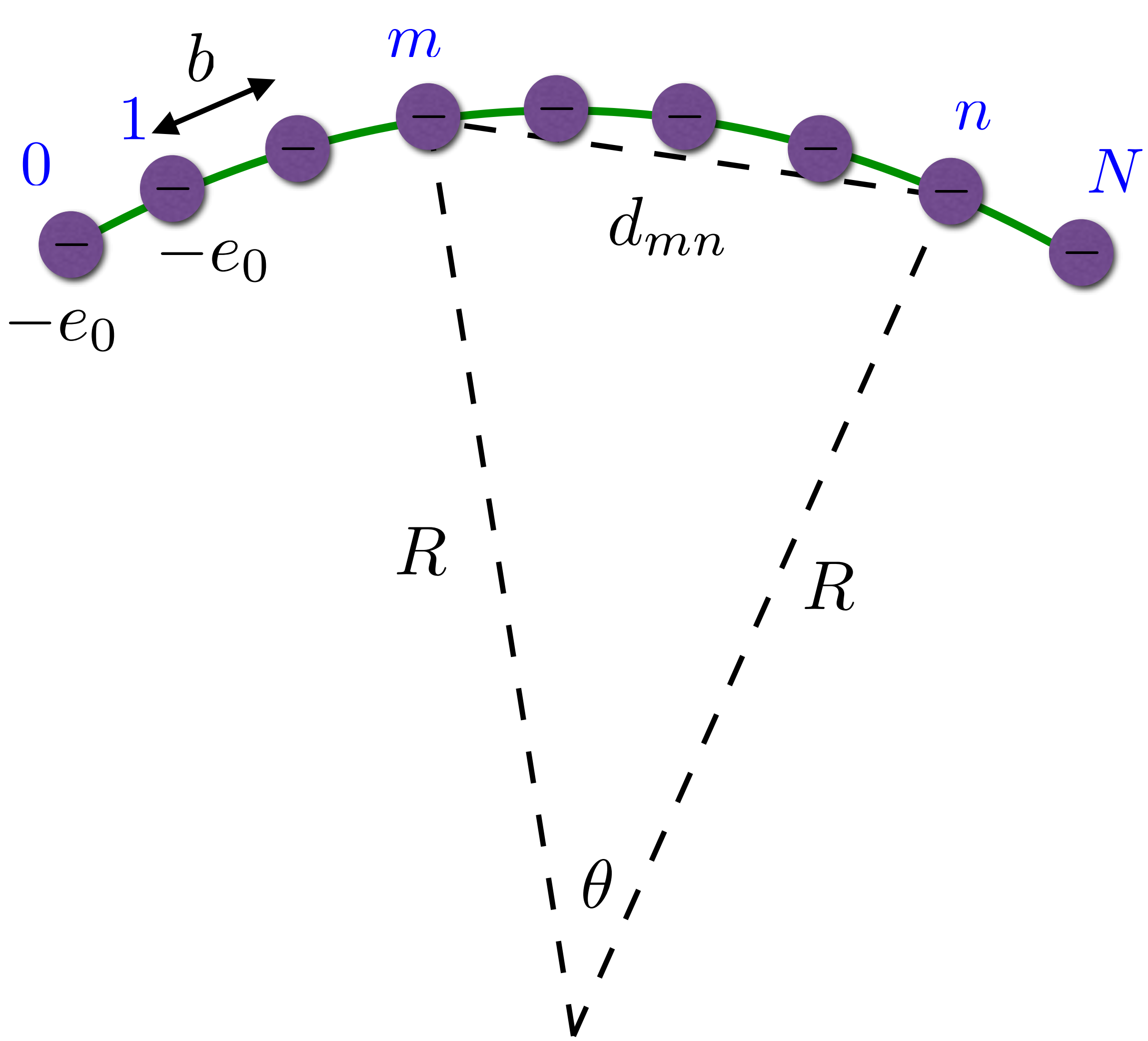
Change in electrostatic energy (assume Debye screening)

$$V(d) = \frac{e_0^2 e^{-d/\lambda}}{\epsilon d}$$

$$\delta V(d^0_{mn}) = V'(d^0_{mn})\delta d_{mn} = \frac{e_0^2 d^0_{mn}\left(d^0_{mn}+\lambda\right)}{24\epsilon\lambda R^2} e^{-d^0_{mn}/\lambda}$$

Bending of charged rod

Negative unit charges separated by distance *b* along the rod.



$$d^0_{mn} = b|m-n|$$
$$L = Nb$$

Electrostatic energy

$$\delta V(d^0_{mn}) = \frac{e_0^2 d^0_{mn}\left(d^0_{mn}+\lambda\right)}{24\epsilon\lambda R^2} e^{-d^0_{mn}/\lambda}$$

$$\delta V_{\mathrm{tot}} = \sum_{m<n} \delta V(d^0_{mn})$$

$$\delta V_{\mathrm{tot}} \approx N \sum_{n=1}^{\infty} \delta V(d^0_{0n})$$

$$\delta V_{\mathrm{tot}} \approx N \sum_{n=1}^{\infty} \frac{e_0^2 bn\,(bn+\lambda)}{24\epsilon\lambda R^2} e^{-bn/\lambda}$$

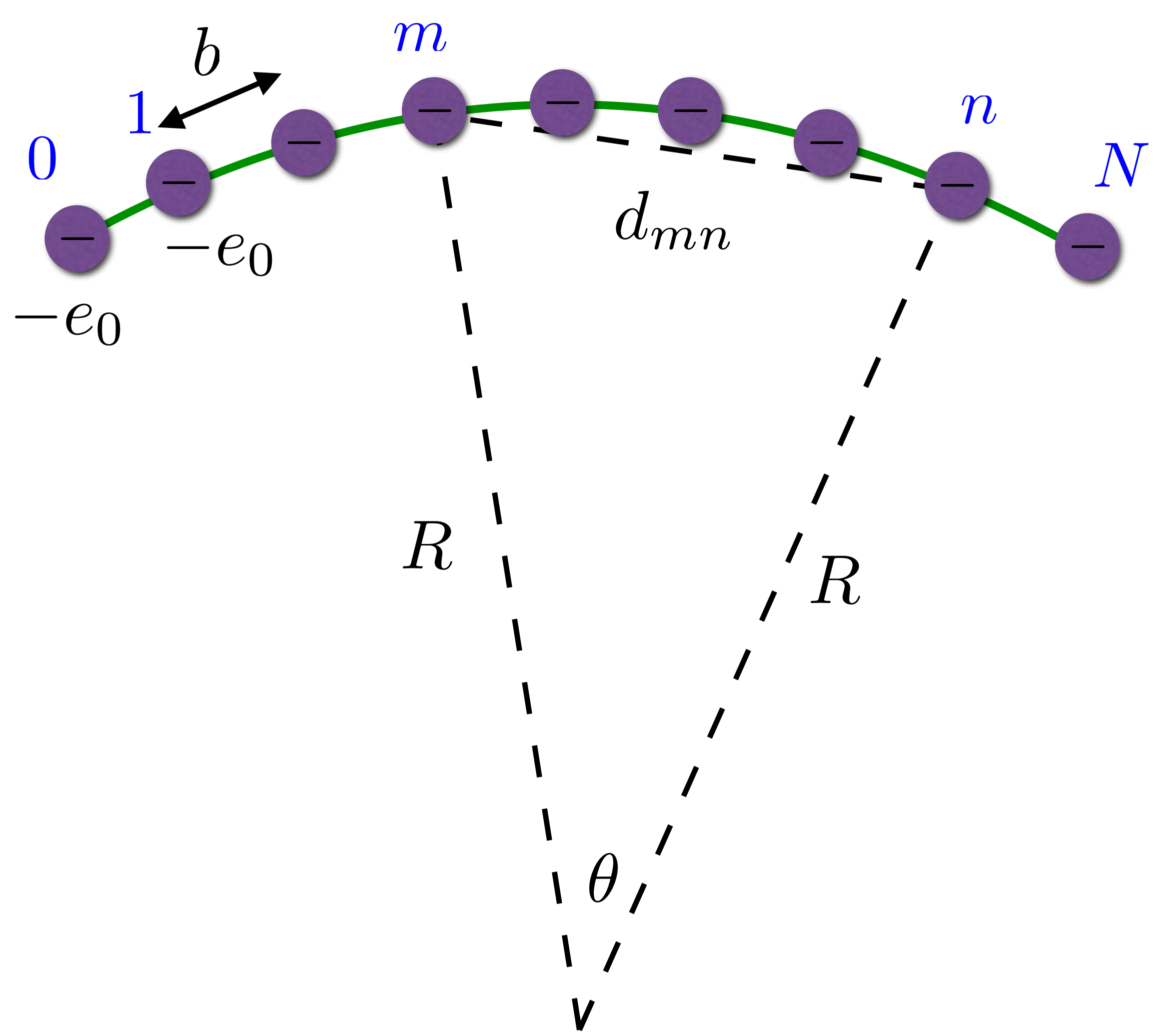
$$\delta V_{\mathrm{tot}} \approx \frac{Le_0^2}{24\epsilon R^2} f(b/\lambda)$$

$$\delta V_{\mathrm{tot}} \approx \frac{Le_0^2}{24\epsilon R^2} f(b/\lambda) = \frac{k_B T}{24}\frac{L\ell_B}{R^2} f(b/\lambda)$$

$$f(x) = \sum_{n=1}^{\infty} n(1+nx)e^{-nx}$$

Bending of charged rod

Negative unit charges separated by distance *b* along the rod.



$$d_{mn}^0 = b|m-n|$$

$$L = Nb$$

Electrostatic energy

$$\delta V_{\text{tot}} \approx \frac{Le_0^2}{24\epsilon R^2} f(b/\lambda) = \frac{k_B T}{24}\frac{L\ell_B}{R^2} f(b/\lambda)$$

$$f(x) = \sum_{n=1}^{\infty} n(1+nx)e^{-nx}$$

Mathematical trick

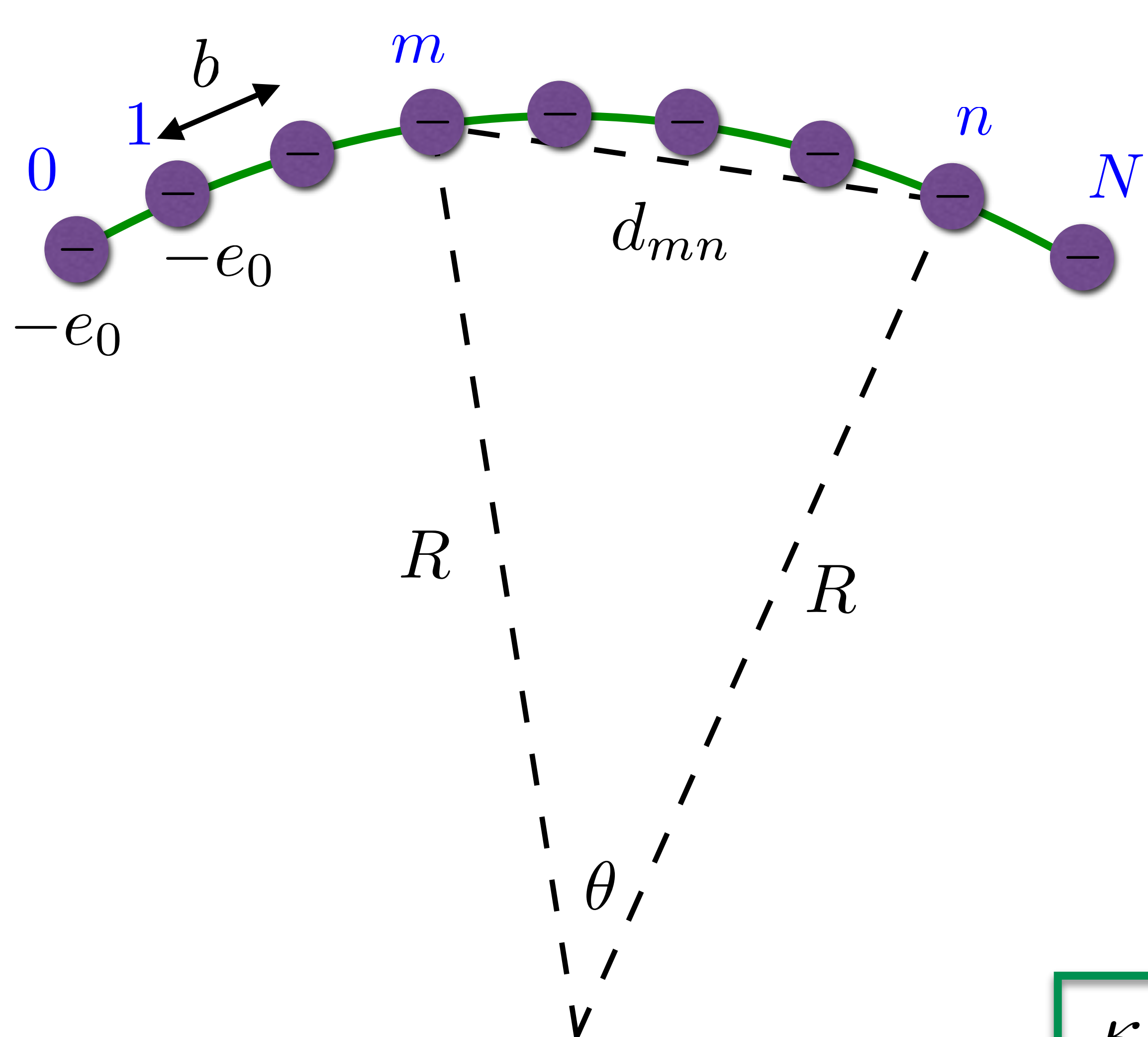
$$g(x) = \sum_{n=1}^{\infty} e^{-nx} = \frac{e^{-x}}{1-e^{-x}}$$

$$f(x) = -g'(x) + xg''(x)$$

$$f(x) = \frac{e^{-x}\left(1+x+xe^{-x}-e^{-x}\right)}{\left(1-e^{-x}\right)^3}$$

Bending of charged rod

Negative unit charges separated by distance *b* along the rod.



$$d^0_{mn} = b|m-n|$$

$$L = Nb$$

Electrostatic energy

$$\delta V_{\text{tot}} \approx \frac{k_B T}{24} \frac{L\ell_B}{R^2} f(b/\lambda) = \frac{1}{2}\frac{\kappa_e L}{R^2}$$

Bending rigidity due to electrostatic energy

$$\kappa_E \approx \frac{k_B T}{12} \ell_B f(b/\lambda)$$

How this compares to measured bending rigidity for DNA?

$$\kappa = k_B T \ell_p$$

$b \approx 0.17\text{nm}$ $\lambda \approx 1\text{nm}$

$\ell_B \approx 0.7\text{nm}$ $\ell_p \approx 50\text{nm}$

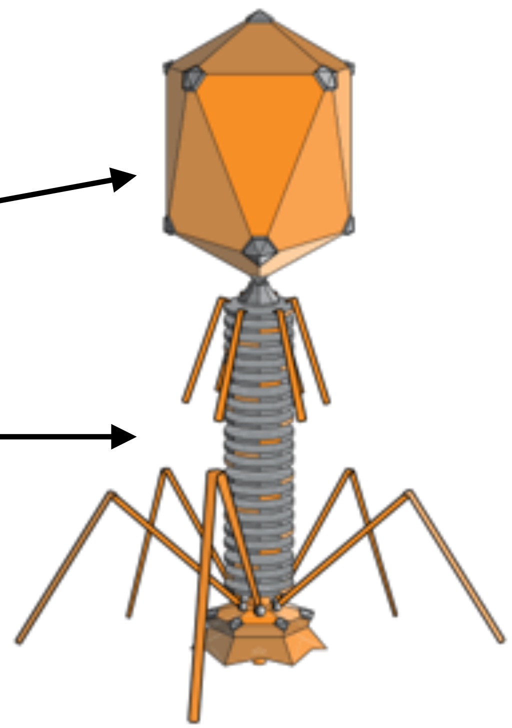
$$\frac{\kappa_E}{\kappa} \approx \frac{\ell_B}{12\ell_p} f(b/\lambda) \approx \frac{0.7}{12\times 50} \times 104 \approx 0.12$$

DNA packaging in bacteriophage viruses

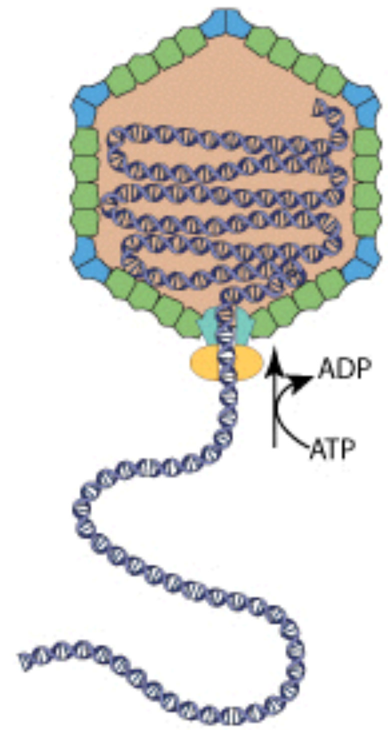
typical bacteriophage

capsid

tail



DNA is packaged by a motor



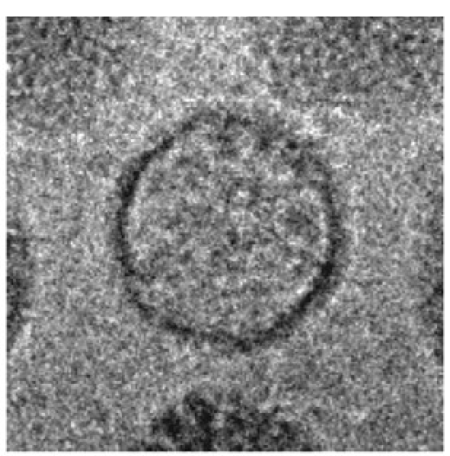
The whole DNA is packaged in 2-5 min.

Velocity of DNA packing is ~50-200 nm/s.

Packaging motors produce force ~60 pN.

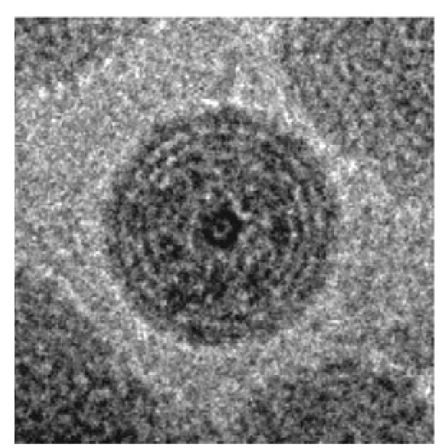
DNA is tightly packed inside the capsid:
$V_{DNA}/V_{cap} > 0.5$

empty capsid



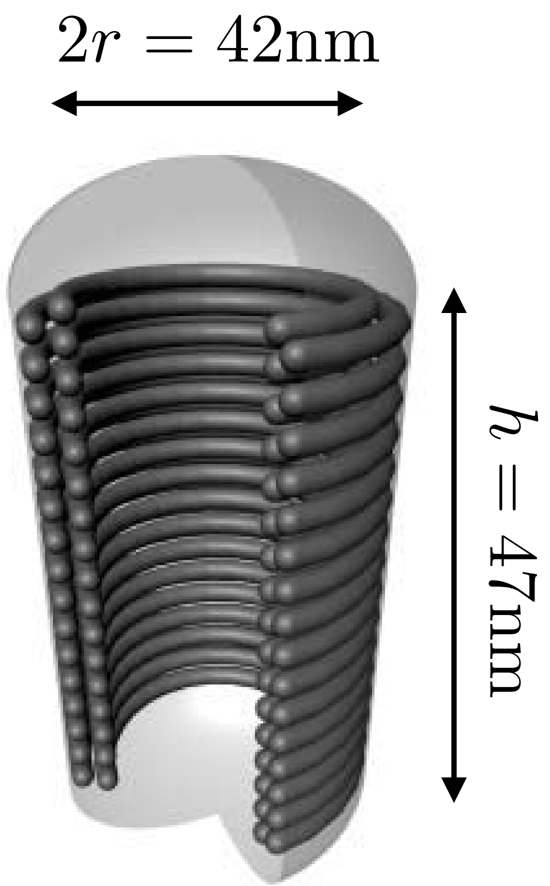
$\sim 50\mathrm{nm}$

capsid with DNA



schematic of packaged DNA in bacteriophage ϕ29

DNA packaging in bacteriophage viruses



DNA length

$L = 6.8\mu\text{m}$

distance between neighboring chains

$d \approx 2.3\text{nm}$

DNA persistence length

$\ell_p \approx 50\text{nm}$

Packaging of DNA in bacteriophage ϕ29 requires ~10^5 k_BT.

Bending energy

$$E_b \sim L\frac{\kappa}{2r^2} \sim L\frac{k_B T \ell_P}{2r^2} \sim 4 \times 10^2 k_B T$$

Loss of entropy

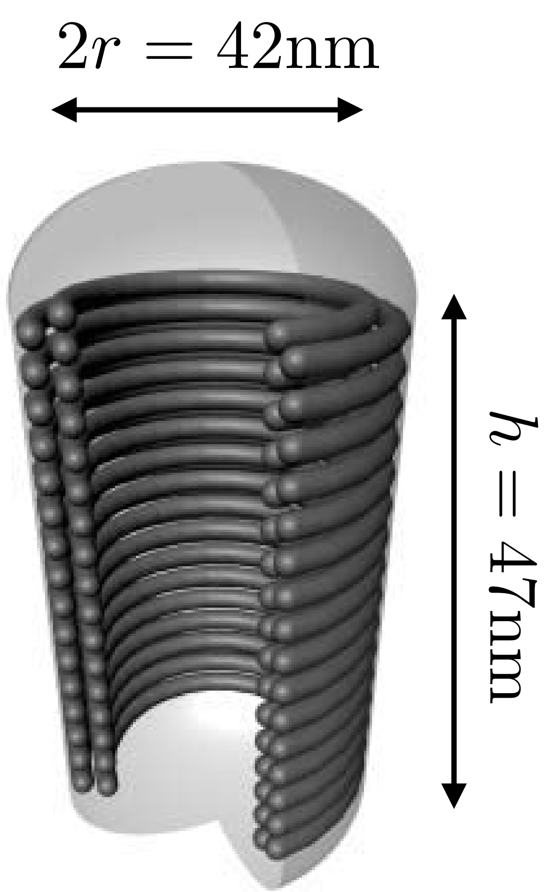
$$T\Delta S = k_B T \ln \Omega$$

Estimate the entropy outside capsid with ideal chain made of *N_k* Kuhn segments

$$\Omega \sim g^{N_k} \qquad N_k = L/2\ell_p \approx 70$$

$$T\Delta S \sim N_k k_B T \ln g \sim 10^2 k_B T$$

DNA packaging in bacteriophage viruses



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Debye-Hückel electrostatic energy between charges on DNA

$$V(s) = \frac{k_B T \ell_B}{s} e^{-s/\lambda}$$

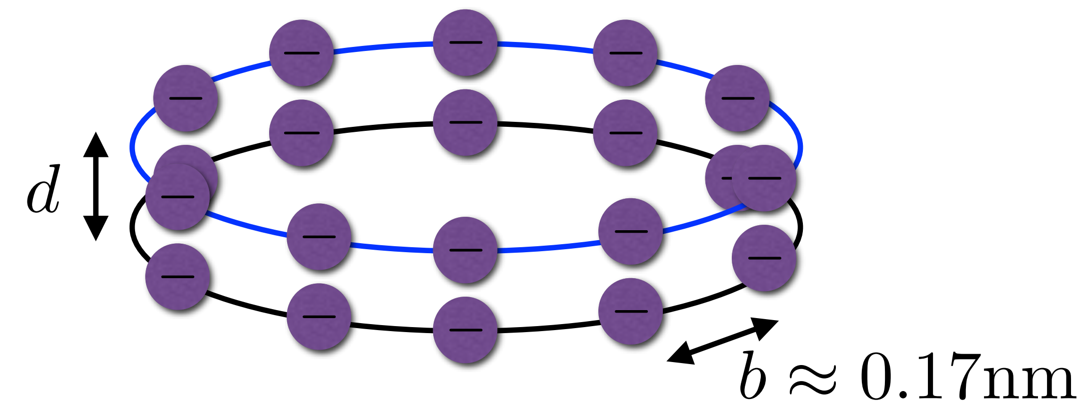
$\ell_B \approx 0.7\text{nm}$

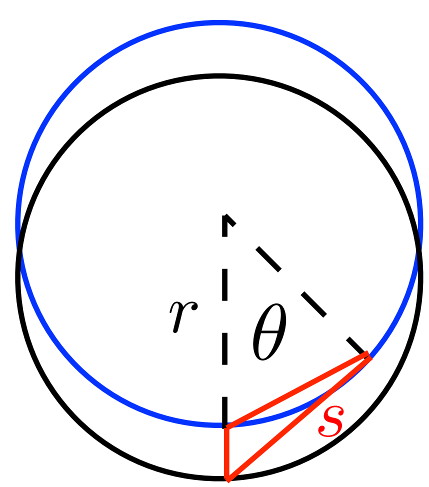
$\lambda \approx 1\text{nm}$

Electrostatic energy between two neighboring charged loops

number of charges per loop

$$N = \frac{2\pi r}{b}$$



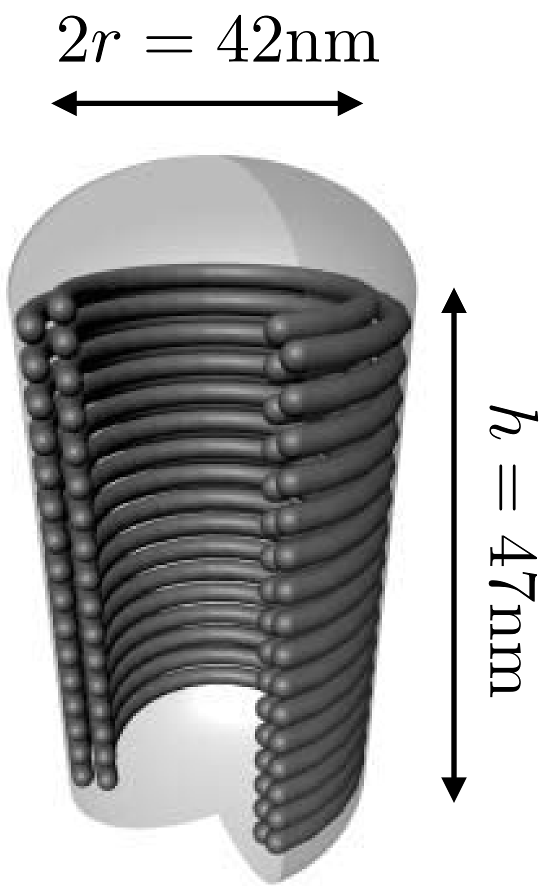


$$s(\theta) = \sqrt{d^2 + (2r\sin(\theta/2))^2}$$

$$V_r = \frac{2\pi r}{b} \int_{-\pi}^{\pi} \frac{r d\theta}{b} V(s(\theta))$$

$$V_r = \frac{2\pi r^2 k_B T \ell_B}{b^2} \int_{-\pi}^{\pi} d\theta \frac{e^{-\sqrt{d^2+(2r\sin(\theta/2))^2}/\lambda}}{\sqrt{d^2 + (2r\sin(\theta/2))^2}}$$

DNA packaging in bacteriophage viruses



DNA length

$L = 6.8\mu\text{m}$

distance between neighboring chains

$d \approx 2.3\text{nm}$

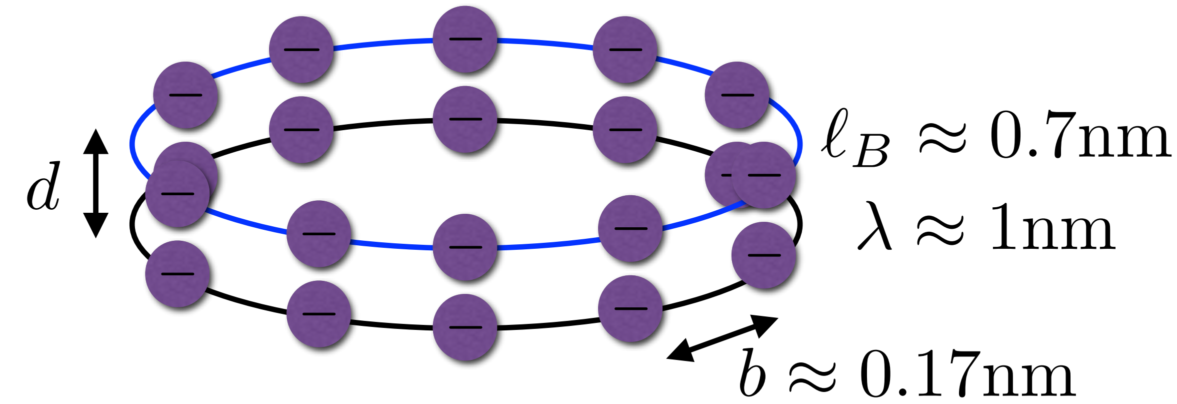
DNA persistence length

$\ell_p \approx 50\text{nm}$

Electrostatic energy between two neighboring charged loops

number of charges per loop

$$N = \frac{2\pi r}{b}$$

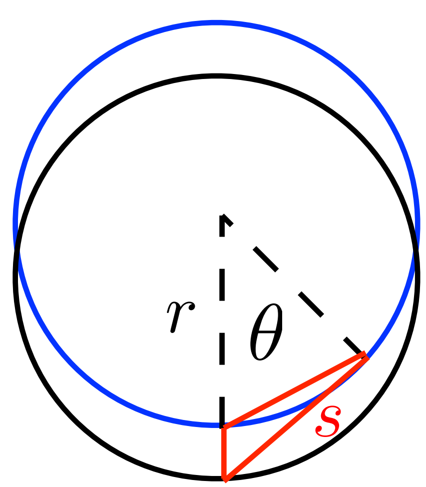


$$V_r = \frac{2\pi r^2 k_B T \ell_B}{b^2} \int_{-\pi}^{\pi} d\theta \frac{e^{-\sqrt{d^2+(2r\sin(\theta/2))^2}/\lambda}}{\sqrt{d^2+(2r\sin(\theta/2))^2}}$$

Electrostatic energy is exponentially small for charges that are far apart. Consider only charges in the range $|\theta| < d/r$**, such that** $s(\theta) \sim d$**.**

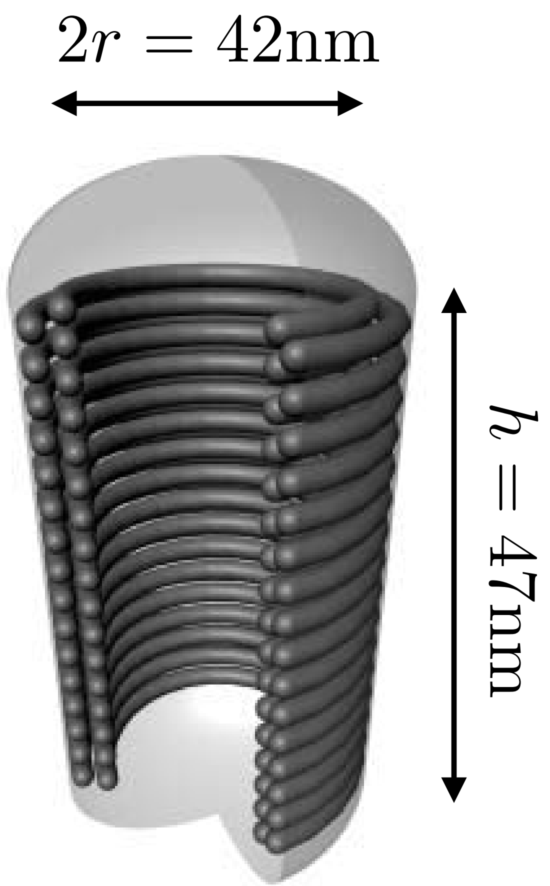
$$V_r \sim \frac{2\pi r^2 k_B T \ell_B}{b^2} \times \frac{2d}{r} \times \frac{e^{-d/\lambda}}{d}$$

$$V_r \sim \frac{4\pi r k_B T \ell_B}{b^2} e^{-d/\lambda}$$



$$s(\theta) = \sqrt{d^2 + (2r\sin(\theta/2))^2}$$

DNA packaging in bacteriophage viruses



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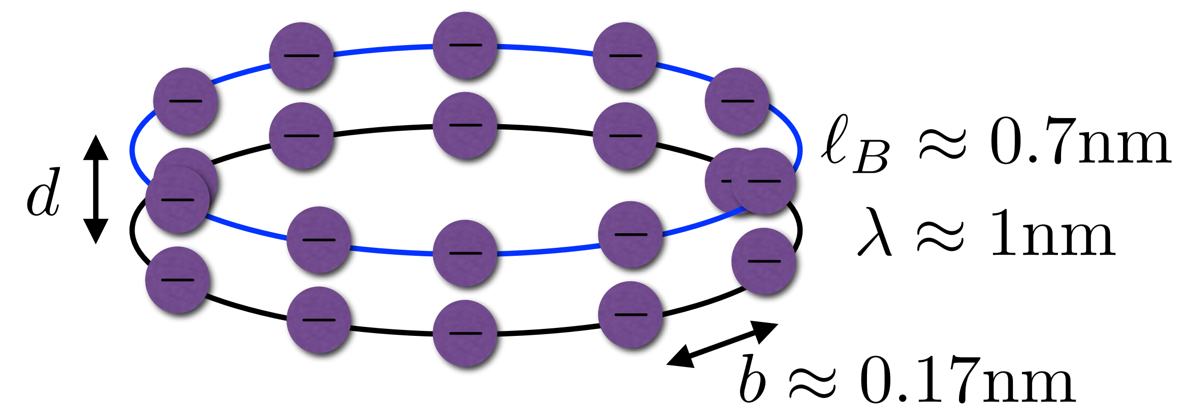
Electrostatic energy between two neighboring charged loops

number of charges per loop

$$N = \frac{2\pi r}{b}$$



$$V_r \sim k_B T \frac{4\pi r \ell_B}{b^2} e^{-d/\lambda}$$

Electrostatic energy between all loops

$$V \sim \frac{L}{2\pi r} \times V_r$$

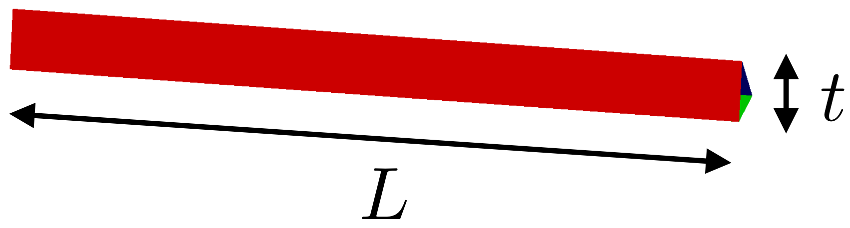
assuming only one level of loops

$$V \sim k_B T \frac{2L\ell_B}{b^2} e^{-d/\lambda} \sim 3 \times 10^4 k_B T$$

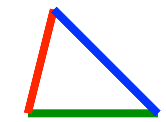
(more accurate calculation would get even closer to 10^5 k_BT)

Deformations of macroscopic beams

undeformed beam



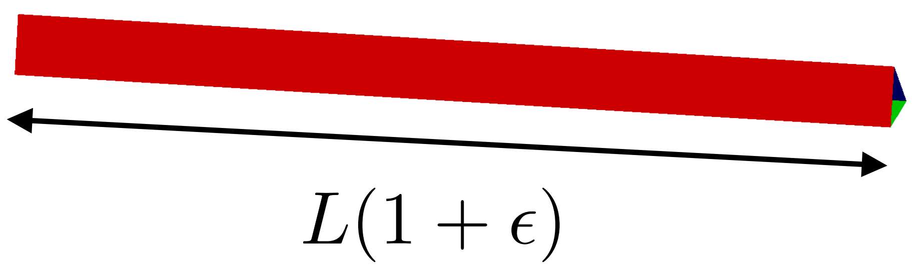
beam cross-section



beam made of material with Young's modulus

E_0

stretching

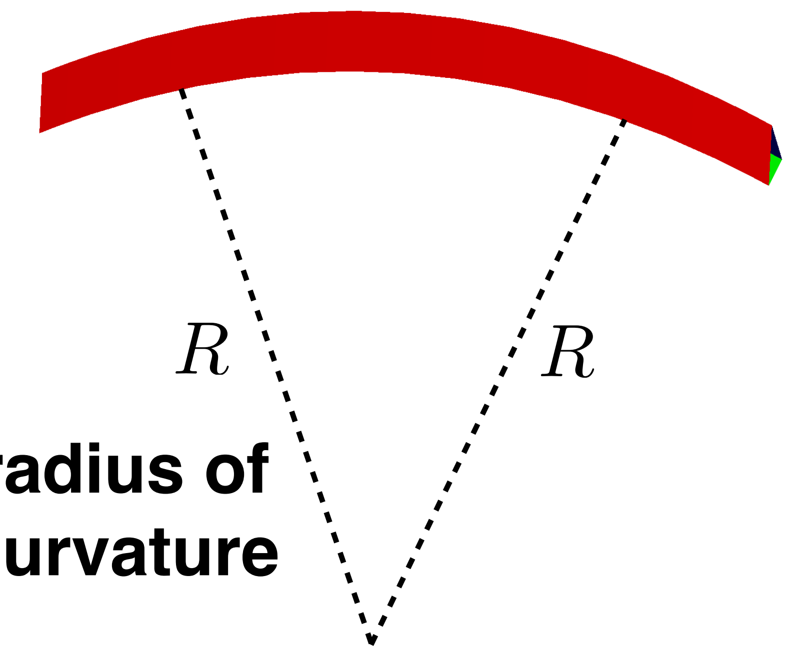


strain ϵ

$$\frac{E_s}{L} = \frac{k\epsilon^2}{2}$$

$$k \propto E_0 t^2$$

bending

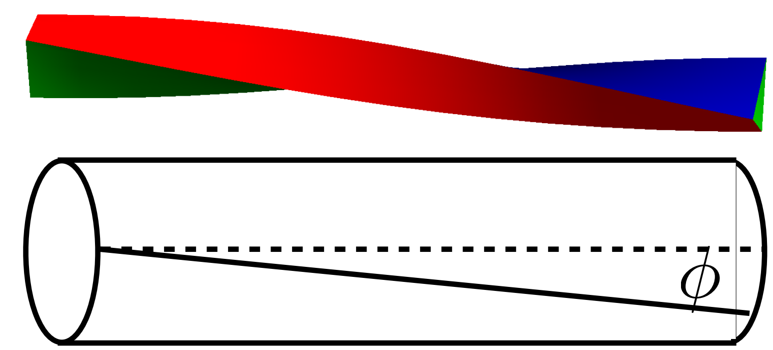


radius of curvature

$$\frac{E_b}{L} = \frac{A}{2R^2}$$

$$A \propto E_0 t^4$$

twisting



angle of twist $\phi = \Omega L$

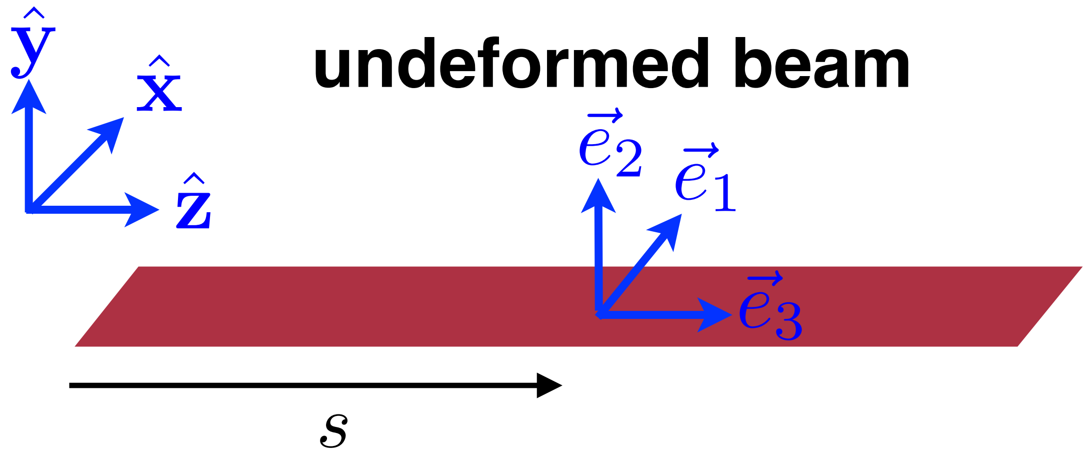
$$\frac{E_t}{L} = \frac{C\Omega^2}{2}$$

$$C \propto E_0 t^4$$

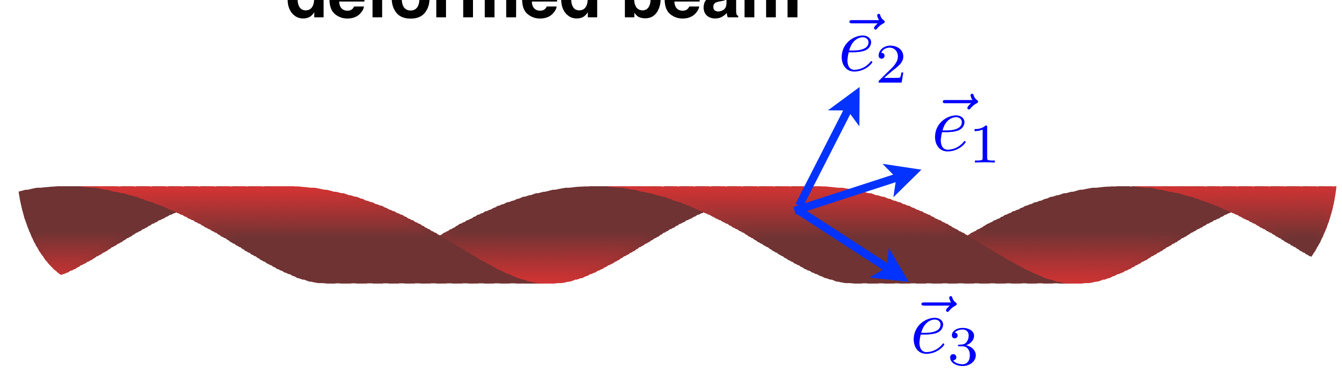
Bending and twisting is much easier than stretching for long and narrow beams!

Bending and twisting represented as rotations of material frame

undeformed beam



deformed beam



rotation rate of material frame

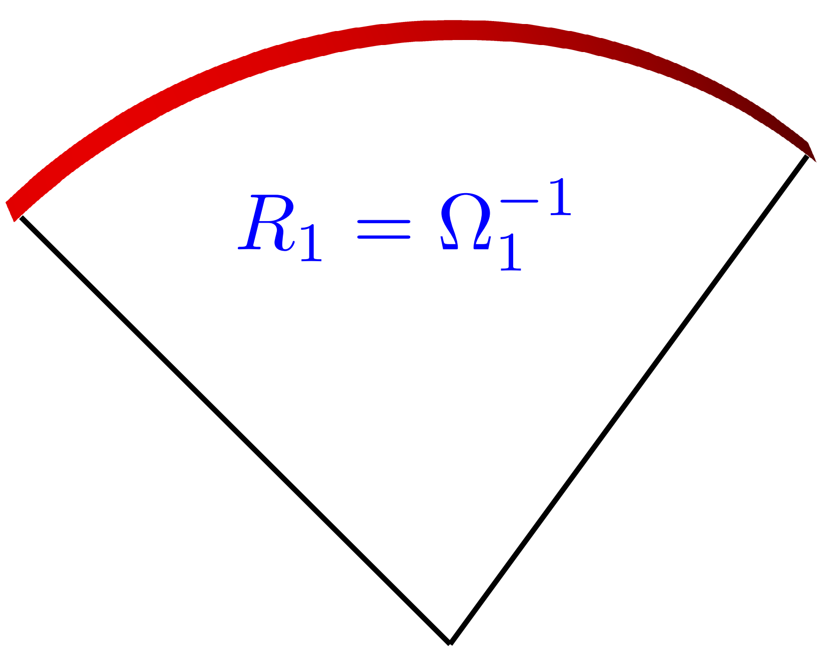
$$\frac{d\vec{e}_i}{ds} = \vec{\Omega} \times \vec{e}_i$$

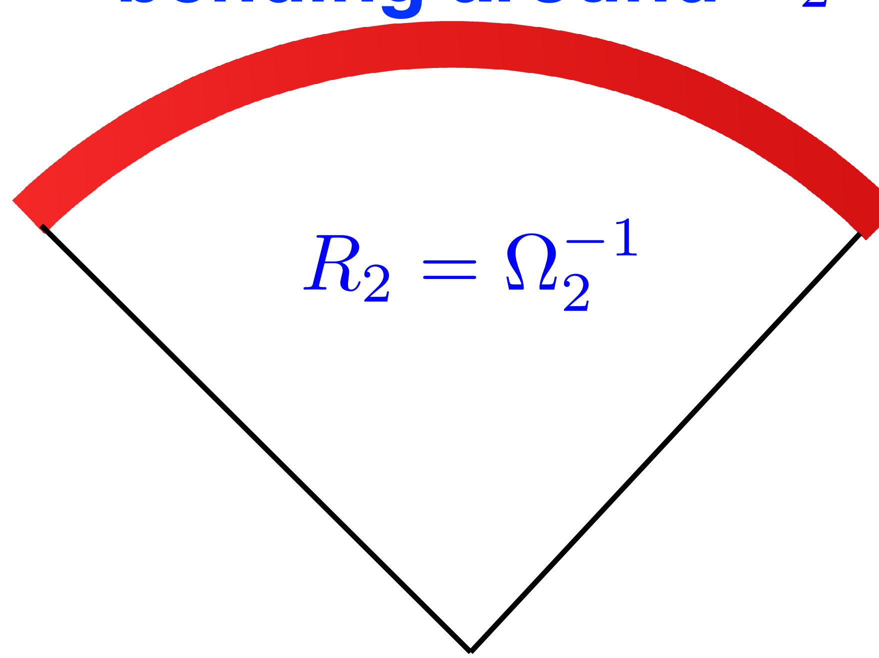
$$\vec{\Omega} = \Omega_1 \vec{e}_1 + \Omega_2 \vec{e}_2 + \Omega_3 \vec{e}_3$$

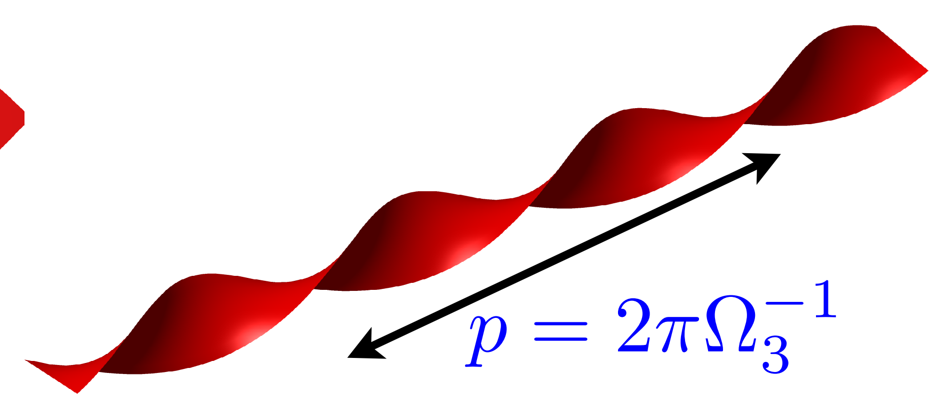
Energy cost of deformations

$$E = \int \frac{ds}{2} \left[A_1 \Omega_1^2 + A_2 \Omega_2^2 + C \Omega_3^2 \right]$$

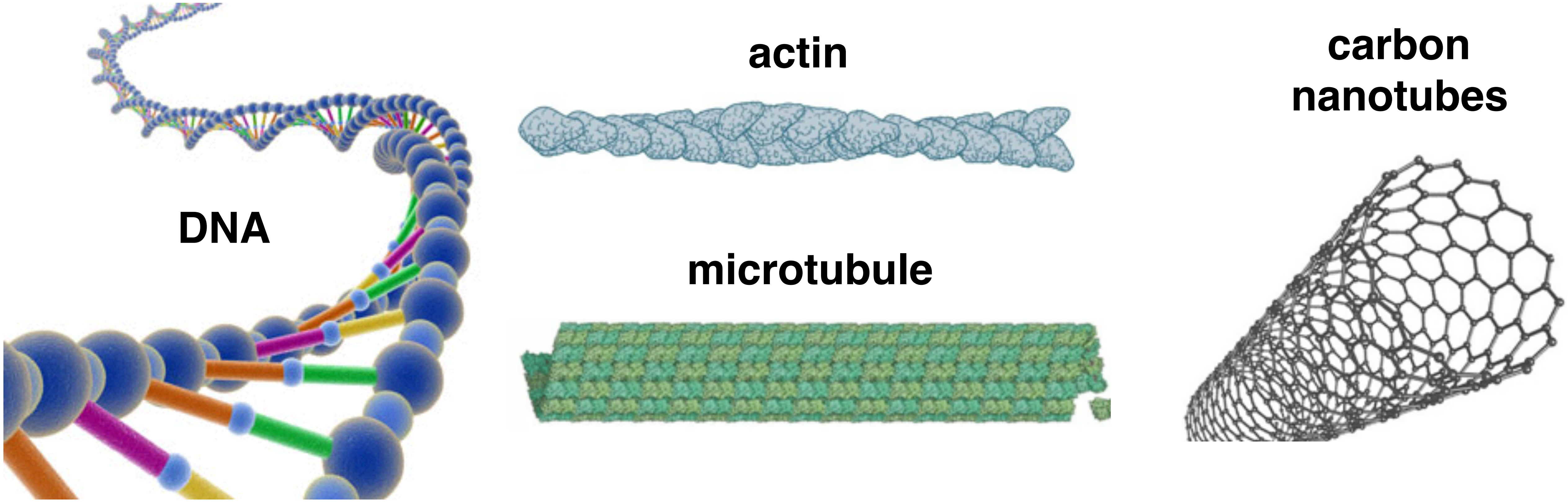
bending around $\mathbf{e}_1$ **bending around $\mathbf{e}_2$** **twisting around $\mathbf{e}_3$**







Deformations of microscopic filaments

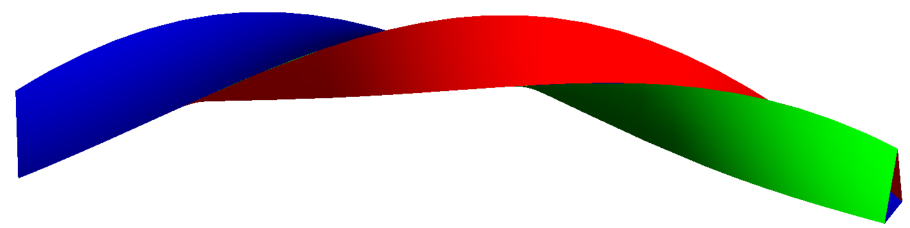


Deformations of microscopic filaments can still be described with stretching, bending and twisting.

Elastic constants (*k*, *A*, *C*) can be extracted from deformation energies of bonds and are in general not related to the microscopic thickness of filaments!

Couplings between stretching, bending and twisting deformations may also be allowed by symmetries of filament shapes.

Elastic energy of deformations in the general form



Energy density for a deformed filament can be Taylor expanded around the minimum energy ground state

$$E = \int_0^L \frac{ds}{2} \Big[A_{11}\Omega_1^2 + A_{22}\Omega_2^2 + C\Omega_3^2 + 2A_{12}\Omega_1\Omega_2 + 2A_{13}\Omega_1\Omega_3 + 2A_{23}\Omega_2\Omega_3$$

$$+ k\epsilon^2 + 2D_1\epsilon\Omega_1 + 2D_2\epsilon\Omega_2 + 2D_3\epsilon\Omega_3 \Big]$$

twist-bend coupling

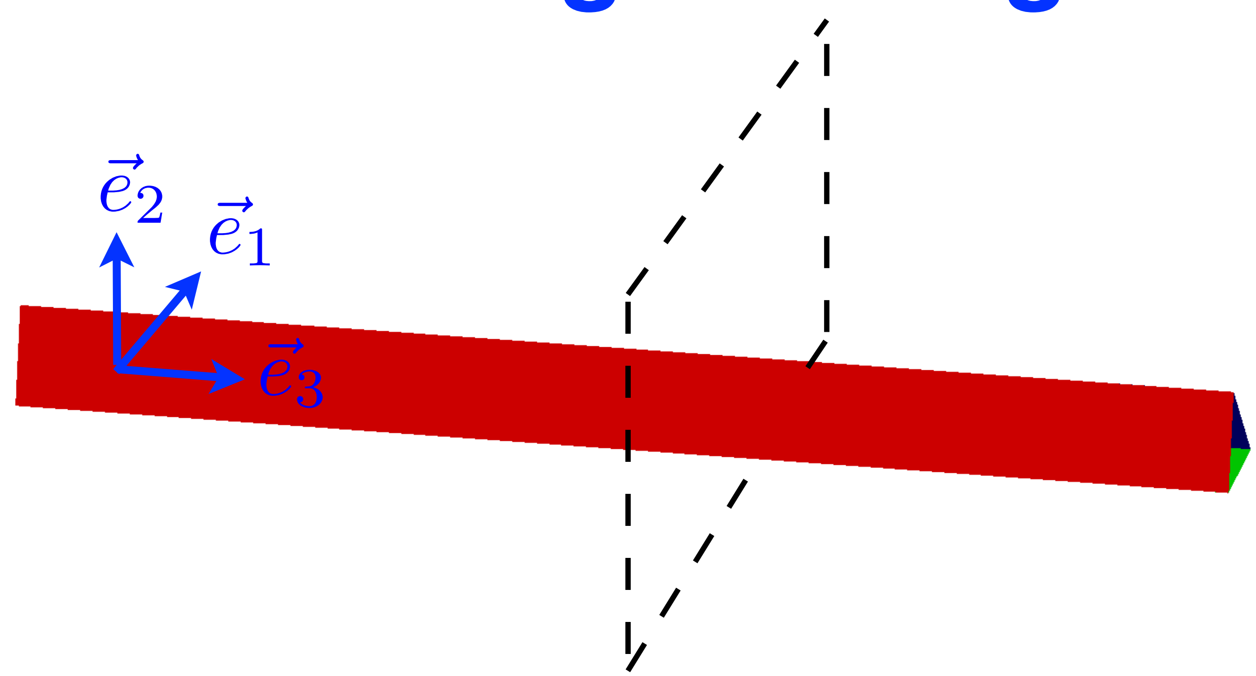
bend-stretch coupling **twist-stretch coupling**

Energy density is positive definitive functional!

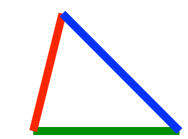
$$A_{11}, A_{22}, A_{33}, k > 0$$
$$A_{ij}^2 < A_{ii}A_{jj}$$
$$D_i^2 < kA_{ii}$$

In principle 10 elastic constants, but symmetries of filament shape determine how many independent elastic constants are allowed!

Beams with uniform cross-section along the long axis

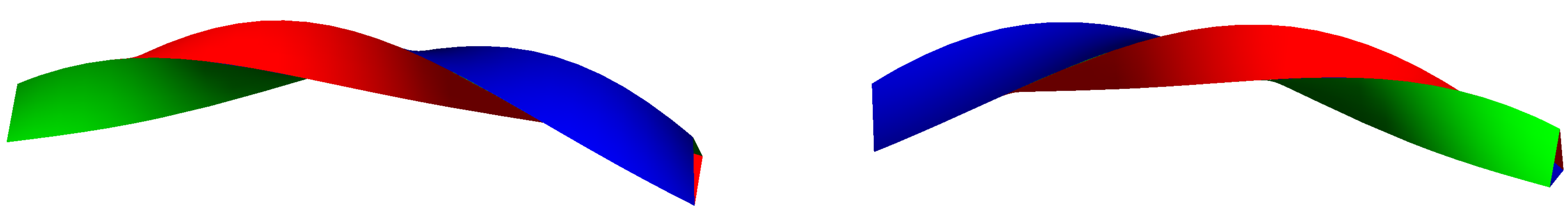


beam cross-section

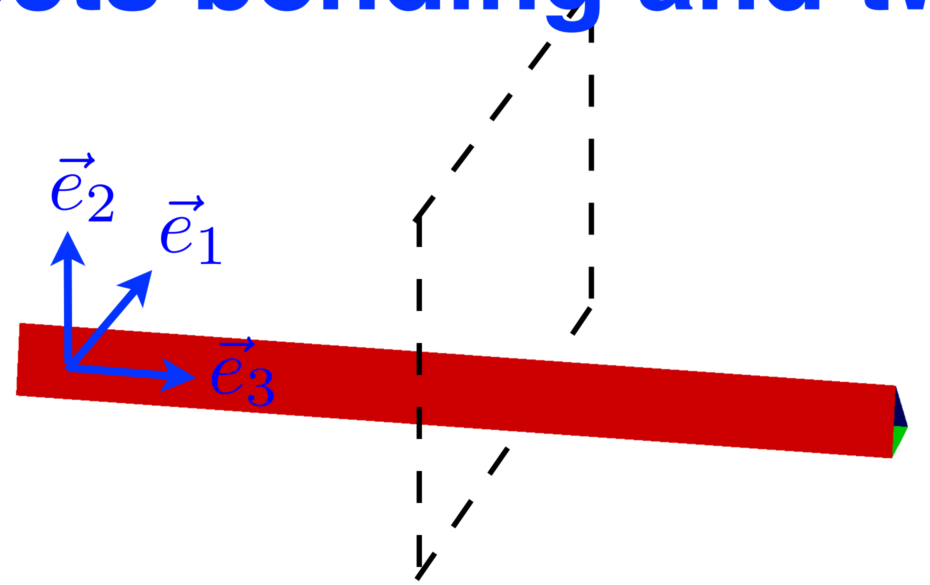


Beam has mirror symmetry through a plane perpendicular to $\vec{e}_3$.

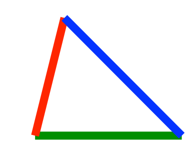
Two beam deformations that are mirror images of each other must have the same energy cost!



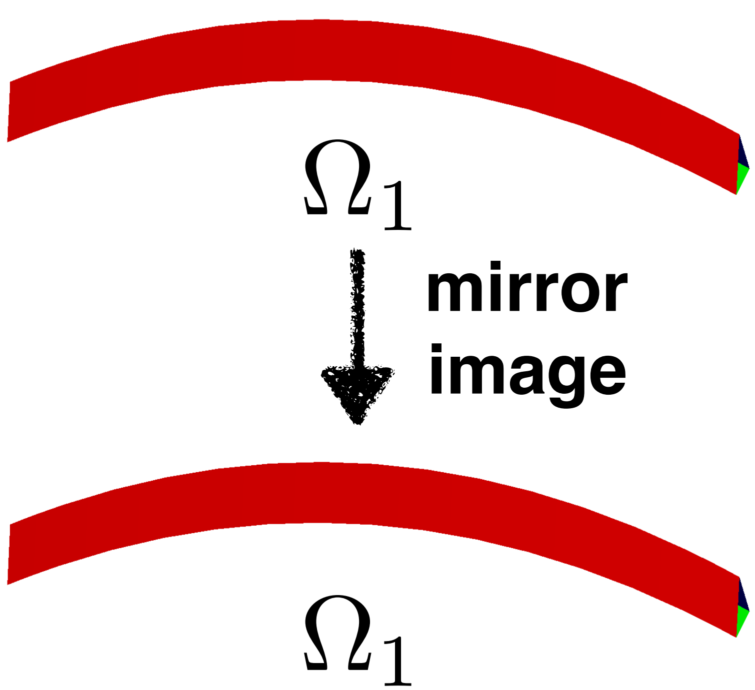
How mirroring around $\vec{e}_3$ affects bending and twisting?



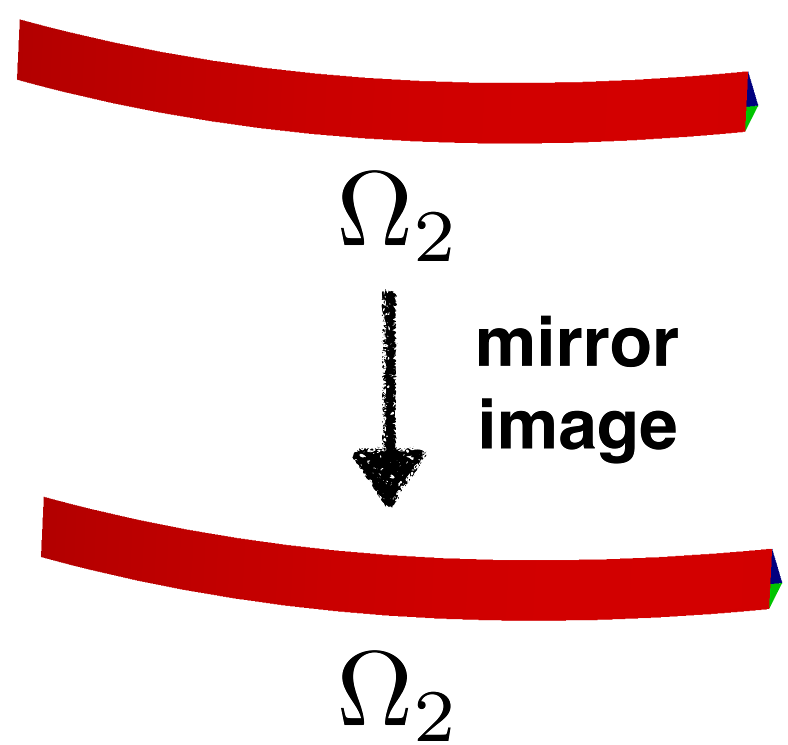
beam cross-section



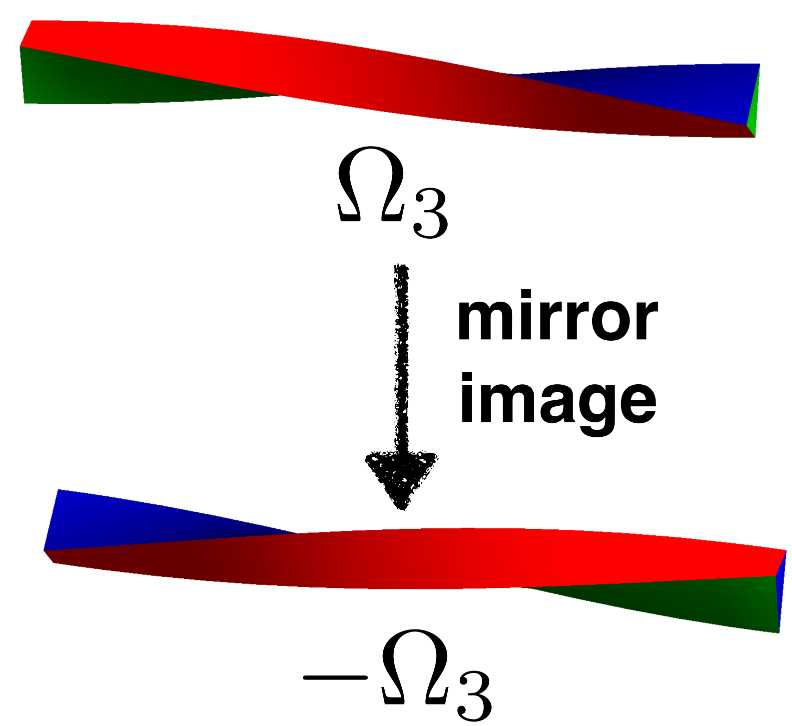
bending around $\vec{e}_1$



bending around $\vec{e}_2$

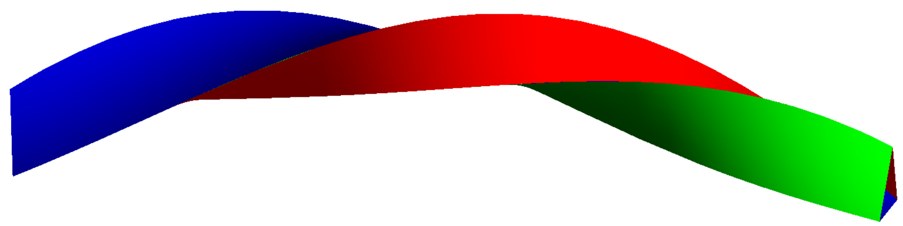


twisting around $\vec{e}_3$



Note: mirroring doesn't affect stretching

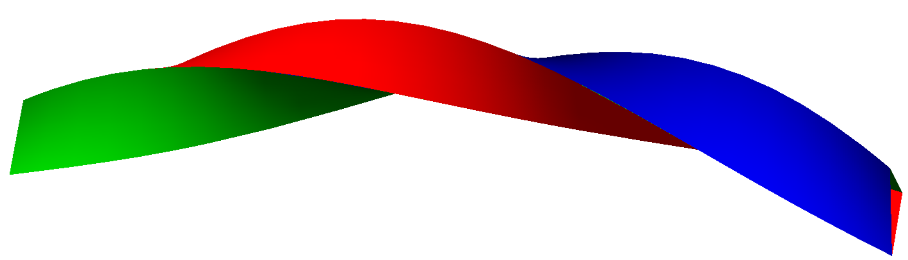
Beams with uniform cross-section along the long axis



$$E = \int_0^L \frac{ds}{2} \Big[A_{11}\Omega_1^2 + A_{22}\Omega_2^2 + C\Omega_3^2 + 2A_{12}\Omega_1\Omega_2 + 2A_{13}\Omega_1\Omega_3 + 2A_{23}\Omega_2\Omega_3 + k\epsilon^2 + 2D_1\epsilon\Omega_1 + 2D_2\epsilon\Omega_2 + 2D_3\epsilon\Omega_3 \Big]$$

mirror image ↓ $\Omega_3 \to -\Omega_3$

↓

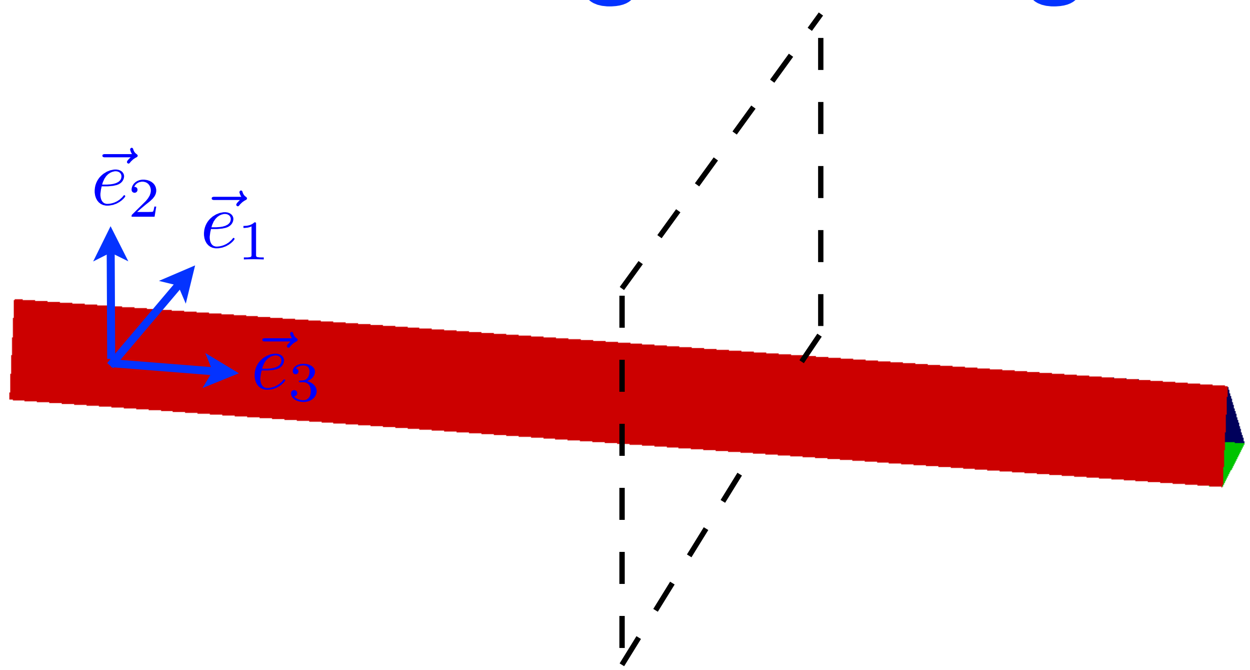


$$E = \int_0^L \frac{ds}{2} \Big[A_{11}\Omega_1^2 + A_{22}\Omega_2^2 + C\Omega_3^2 + 2A_{12}\Omega_1\Omega_2 - 2A_{13}\Omega_1\Omega_3 - 2A_{23}\Omega_2\Omega_3 + k\epsilon^2 + 2D_1\epsilon\Omega_1 + 2D_2\epsilon\Omega_2 - 2D_3\epsilon\Omega_3 \Big]$$

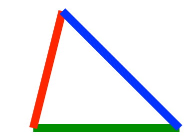
Two mirror configurations have the same energy cost:

$$A_{13} = A_{23} = D_3 = 0$$

Beams with uniform cross-section along the long axis



beam cross-section



Beam has mirror symmetry through a plane perpendicular to $\vec{e}_3$.

$$E = \int_0^L \frac{ds}{2} \Big[A_{11}\Omega_1^2 + A_{22}\Omega_2^2 + C\Omega_3^2 + 2A_{12}\Omega_1\Omega_2 + k\epsilon^2 + 2D_1\epsilon\Omega_1 + 2D_2\epsilon\Omega_2 \Big]$$

Twist is decoupled from bending and stretching!

Twist-bend coupling in propellers and turbines

wind turbine

airplane propeller

ship propeller

Blades of propellers and turbines are chiral, therefore there is coupling between twist and bend deformations!