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

Density of positive counterions

\[ n(y) = \bar{n}e^{-\phi(y)/k_B T} \]

Poisson-Boltzmann equation

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

\[ \phi(y) = \frac{2k_B T}{e_0} \ln \left[ 1 + \frac{|y|}{y_0} \right] \]

\[ y_0 = \frac{k_B T \varepsilon}{\pi e_0 |\sigma|} \]

\( y_0 \) - Guoy-Chapman length

Thickness of diffusive boundary layer that shields a charged membrane

electric field

\[ E(y) = -\frac{\partial \phi(y)}{\partial y} = -\frac{y}{|y|} \frac{2\pi |\sigma|}{\varepsilon} \frac{1}{(1 + |y|/y_0)} \]
Debye-Hückel approximation

Let’s assume that electrostatic energy due to the mean field electric potential is small compared to $k_B T$.

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

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

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

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

\[ \rho_{\text{mobile ions}}(\vec{r}) \approx -\frac{e_0^2 \phi(\vec{r})}{k_B T} \sum_{\alpha} z_{\alpha}^2 n_{\alpha} = -\ell_B \epsilon \phi(\vec{r}) \sum_{\alpha} z_{\alpha}^2 n_{\alpha} \]

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

\[ \lambda_D^{-2} = 4\pi \ell_B \sum_{\alpha} z_{\alpha}^2 n_{\alpha} \]

Electric potential for a point charge

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

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

Electrostatic interaction between macroions

\[ \rho_{\text{macroions}}(\vec{r}) = \sum_{m} z_m e_0 \delta(\vec{r} - \vec{r}_m) \]

\[ \phi(\vec{r}) = \sum_{m} \frac{z_m e_0}{\epsilon |\vec{r} - \vec{r}_m|} e^{-|\vec{r} - \vec{r}_m|/\lambda_D} \]

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

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

Change in distance between charges

\[ d_{mn}^0 = b|m - n| = R\theta \]

\[ \delta d_{mn} = 2R\sin(\theta/2) - d_{mn}^0 \]

\[ \delta d_{mn} \approx R\theta - R\theta^3/24 - d_{mn}^0 \]

\[ \delta d_{mn} \approx -\left(\frac{d_{mn}^0}{24R^2}\right)^3 \]

Change in electrostatic energy (assume Debye screening)

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

\[ \delta V(d_{mn}^0) = V'(d_{mn}^0)\delta d_{mn} = \frac{e^2 d_{mn}^0 (d_{mn}^0 + \lambda)}{24\epsilon\lambda R^2} e^{-d_{mn}^0/\lambda} \]
Bending of charged rod

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

Electrostatic energy

$$\delta V(d_{mn}^0) = \frac{e_0^2 d_{mn}^0 (d_{m+1n}^0 + \lambda)}{24 \epsilon \lambda R^2} e^{-d_{mn}^0/\lambda}$$

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

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

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

$$\delta V_{tot} \approx \frac{L e_0^2}{24 \epsilon R^2} f(b/\lambda)$$

$$\delta V_{tot} \approx \frac{L e_0^2}{24 \epsilon R^2} f(b/\lambda) = \frac{k_B T L \ell_B}{24} f(b/\lambda)$$

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

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

$L = N b$
Bending of charged rod

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

Electrostatic energy

$$\delta V_{\text{tot}} \approx \frac{L e_0^2}{24 \epsilon R^2} f(b/\lambda) = \frac{k_B T}{24} \frac{L \ell_B}{R^2} f(b/\lambda)$$

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

Mathematical trick

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

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

$$f(x) = \frac{e^{-x}(1 + x + xe^{-x} - e^{-x})}{(1 - e^{-x})^3}$$
Bending of charged rod

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

Electrostatic energy

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

Bending rigidity due to electrostatic energy

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

How this compares to measured bending rigidity for DNA?

$$\kappa \approx k_B T \ell_p$$

- $b \approx 0.17 \text{nm}$
- $\lambda \approx 1 \text{nm}$
- $\ell_B \approx 0.7 \text{nm}$
- $\ell_p \approx 50 \text{nm}$

$$\frac{\kappa_E}{\kappa} \approx \frac{\ell_B}{12 \ell_p} f\left(\frac{b}{\lambda}\right) \approx \frac{0.7}{12 \times 50} \times 104 \approx 0.12$$
DNA packaging in bacteriophage viruses

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: \( V_{\text{DNA}}/V_{\text{cap}} > 0.5 \)

![Typical bacteriophage](image1)

DNA is packaged by a motor

![Schematic of packaged DNA in bacteriophage φ29](image2)

<table>
<thead>
<tr>
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![Empty capsid](image3)

![Capsid with DNA](image4)

~ 50nm
Packaging of DNA in bacteriophage \( \Phi 29 \) requires \( \sim 10^5 \) \( k_B T \).

**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

\[
\Omega \sim g^{N_k} \quad N_k = \frac{L}{2\ell_p} \approx 70
\]

\[
T \Delta S \sim N_k k_B T \ln g \sim 10^2 k_B T
\]
DNA packaging in bacteriophage viruses

Debye-Hückel electrostatic energy between charges on DNA

\[ V(s) = \frac{k_B T \ell_B}{s} e^{-s/\lambda} \quad \ell_B \approx 0.7\text{nm} \quad \lambda \approx 1\text{nm} \]

Electrostatic energy between two neighboring charged loops

Number of charges per loop

\[ N = \frac{2\pi r}{b} \]

Distance between neighboring chains

\[ d \approx 2.3\text{nm} \]

DNA persistence length

\[ \ell_p \approx 50\text{nm} \]

DNA length

\[ L = 6.8\mu\text{m} \]

Distance between neighboring chains

\[ 2r = 42\text{nm} \]

Height

\[ h = 47\text{nm} \]
DNA packaging in bacteriophage viruses

Electrostatic energy between two neighboring charged loops

number of charges per loop

\[ N = \frac{2\pi r}{b} \]

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

\[
V_r \approx \frac{2\pi r^2 k_B T \ell_B}{b^2} \times \frac{2d}{r} \times \frac{e^{-d/\lambda}}{d}
\]

\[ V_r \approx \frac{4\pi r k_B T \ell_B}{b^2} e^{-d/\lambda} \]

\[ s(\theta) = \sqrt{d^2 + (2r \sin(\theta/2))^2} \]
DNA packaging in bacteriophage viruses

Electrostatic energy between two neighboring charged loops

number of charges per loop

\[ N = \frac{2\pi r}{b} \]

Electrostatic energy between all loops

\[ V \sim \frac{L}{2\pi r} \times V_r \quad \text{assuming only one level of loops} \]

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

(more accurate calculation would get even closer to \(10^5 k_B T\))

DNA length

\[ L = 6.8 \mu m \]

distance between neighboring chains

\[ d \approx 2.3 \text{nm} \]

DNA persistence length

\[ \ell_p \approx 50 \text{nm} \]
Deformations of macroscopic beams

undeformed beam

beam cross-section

beam made of material with Young’s modulus

$E_0$

stretching

$bending$

twisting

strain $\epsilon$

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

$k \propto E_0 t^2$

radius of curvature

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

$A \propto E_0 t^4$

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

$C \propto E_0 t^4$

Bending and twisting is much easier than stretching for long and narrow beams!
Bending and twisting represented as rotations of material frame

**Rotation Rate of Material Frame**

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

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

- **Bending around** \( \vec{e}_1 \)
- **Bending around** \( \vec{e}_2 \)
- **Twisting around** \( \vec{e}_3 \)

**Energy Cost of Deformations**

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

- \( R_1 = \Omega_1^{-1} \)
- \( R_2 = \Omega_2^{-1} \)
- \( p = 2\pi \Omega_3^{-1} \)
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

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

Energy density is positive definitive functional!

\[ A_{11}, A_{22}, A_{33}, k > 0 \]
\[ A_{ij}^2 < A_{ii} A_{jj} \]
\[ D_i^2 < k A_{ii} \]

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 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?

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

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

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

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

Twist is decoupled from bending and stretching!
Blades of propellers and turbines are chiral, therefore there is coupling between twist and bend deformations!