Introduction to Polymer dynamics B

References:

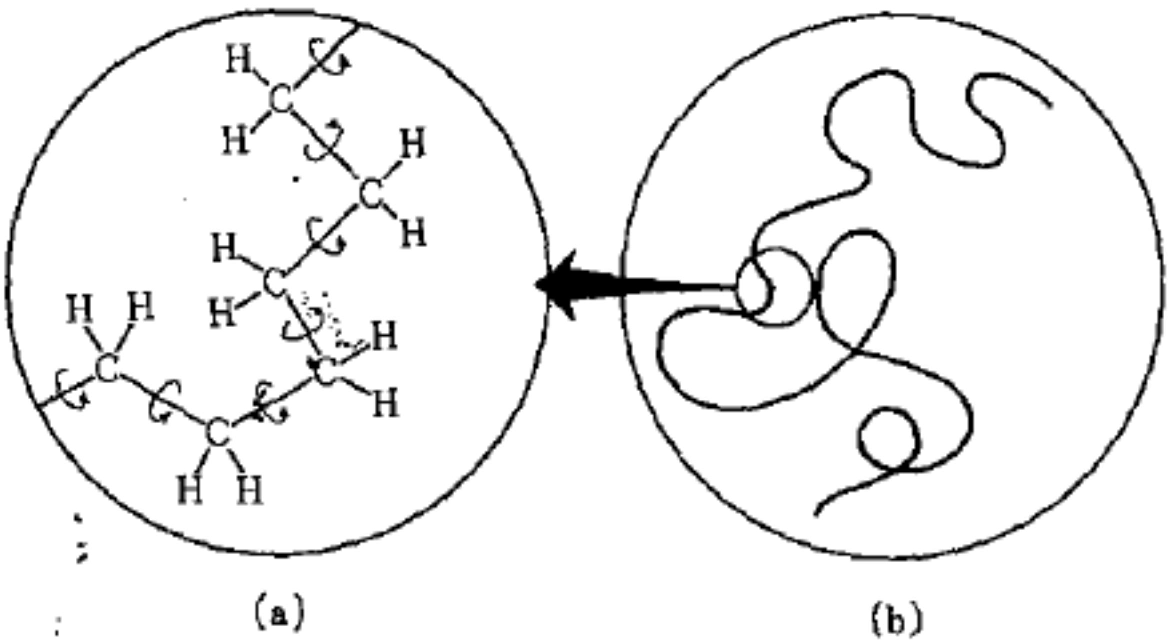
Philip Nelson, “Biological Physics” (2004, Ch. 9)

Masao Doi, “Introduction to polymer physics” (1996)

P.G. de Gennes, “Introduction to polymer dynamics” (1990)

Chia-Fu Chou@2010

The ideal chain
The random walk model



(a) The atomic structure of the polyethylene molecule.

(b) An overall view of the molecule. There is rotational freedom about each C-C bond, so the molecule as a whole resembles a long, flexible piece of string.

Deformations of a thin elastic rod

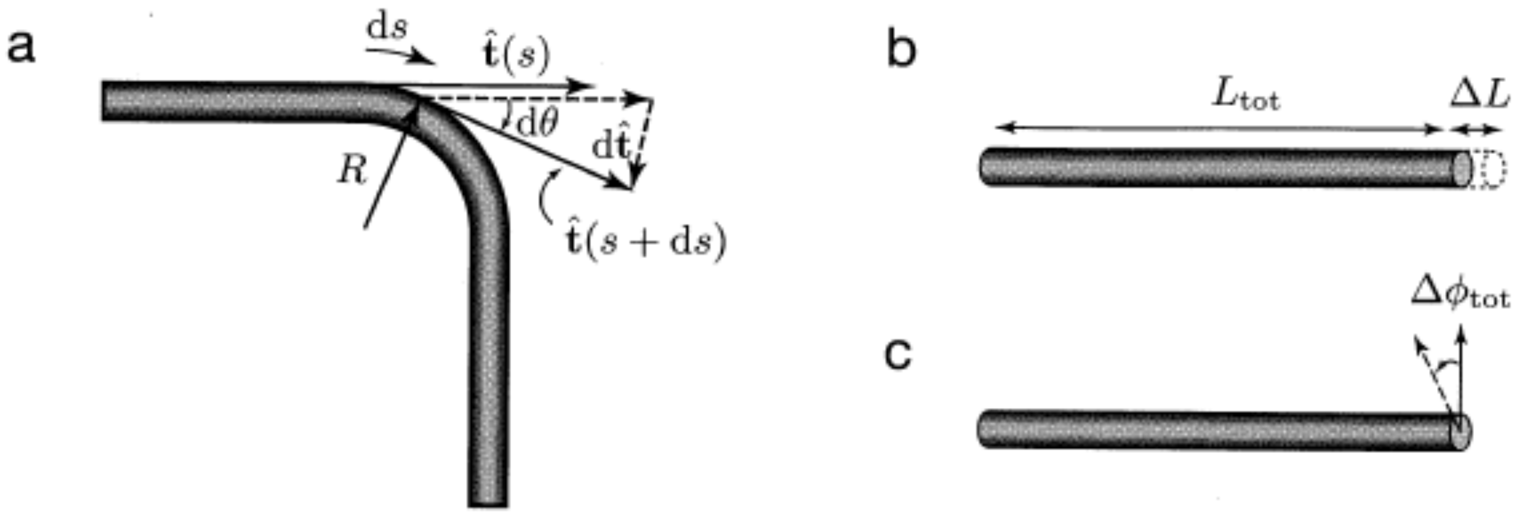


Figure 9.1: (Schematic.) Deformations of a thin elastic rod. (a) Definition of the bend vector, $\boldsymbol{\beta} = \mathrm{d}\hat{\mathbf{t}}/\mathrm{d}s$, illustrated for a circular segment of a thin rod. The parameter s is the contour length (also called arc length) along the rod. The tangent vector $\hat{\mathbf{t}}(s)$ at one point of the rod has been moved to a nearby point a distance $\mathrm{d}s$ away (*dashed arrow*), then compared with the tangent vector there, or $\hat{\mathbf{t}}(s+\mathrm{d}s)$. The difference of these vectors, $\mathrm{d}\hat{\mathbf{t}}$, points radially inward and has magnitude equal to $\mathrm{d}\theta$, or $\mathrm{d}s/R$. (b) Definition of stretch. For a uniformly stretched rod, $u = \Delta L/L_{\mathrm{tot}}$. (c) Definition of twist density. For a uniformly twisted rod, $\omega = \Delta\phi_{\mathrm{tot}}/L_{\mathrm{tot}}$.

Long elastic thin rod

Elastic energy change:

$$dE = \frac{1}{2}k_B T\left[A\boldsymbol{\beta}^2 + Bu^2 + C\omega^2 + 2Du\omega\right] ds.$$

bend stretch twist

A: bend persistence length

C: twist persistence length

Ak_BT: bend stiffness

Ck_BT: twist stiffness

Bk_BT: stretch stiffness

Dk_BT: twist-stretch coupling

Inextensible thin rod (Kratky-Porod or wormlike chain model)

$$E = \frac{1}{2}k_B T\int_0^{L_{tot}} ds\, A\boldsymbol{\beta}^2.$$

$$\text{elastic energy cost of a } 90^\circ \text{ bend } = \left(\frac{1}{2}k_B TA\right)\times\left(\frac{1}{4}2\pi R\right)\times R^{-2} = \frac{\pi A}{4R}k_B T.$$

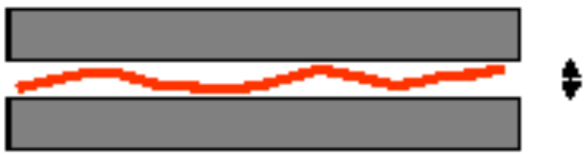
Polymer dynamics in confinement

DNA is stretched in small channels because the energy to form a loop is greater than kT

360° or 2π

$$W_{loop} = \pi k_B T \frac{L_p}{R}$$

$2R = 2\mu m$ $\quad W_{loop} \approx 0.15 k_B T < k_B T$

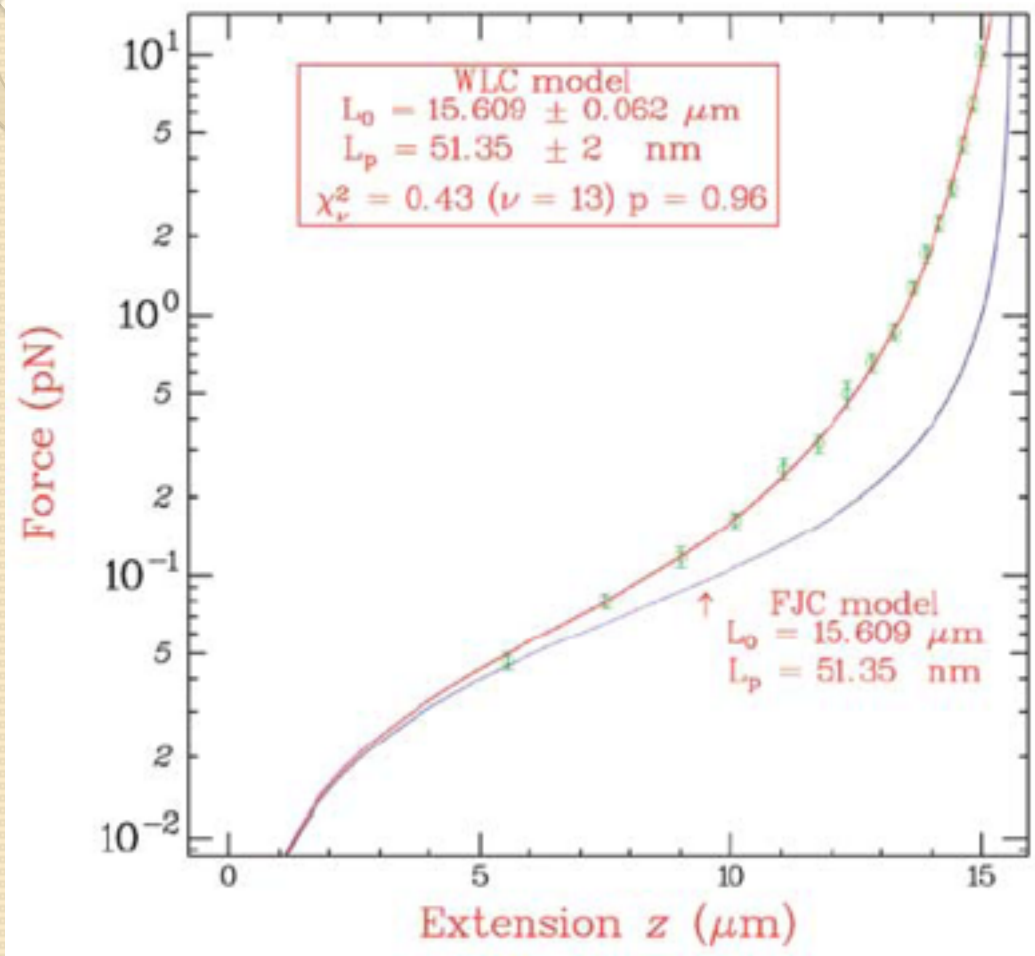


$2R = 0.1\mu m$ $\quad W_{loop} \approx 3 k_B T > k_B T$

For DNA the persistence length L_p=50nm

J. Tegenfeldt

Force-extension curve of λ -DNA



Worm-Like Chain Model:

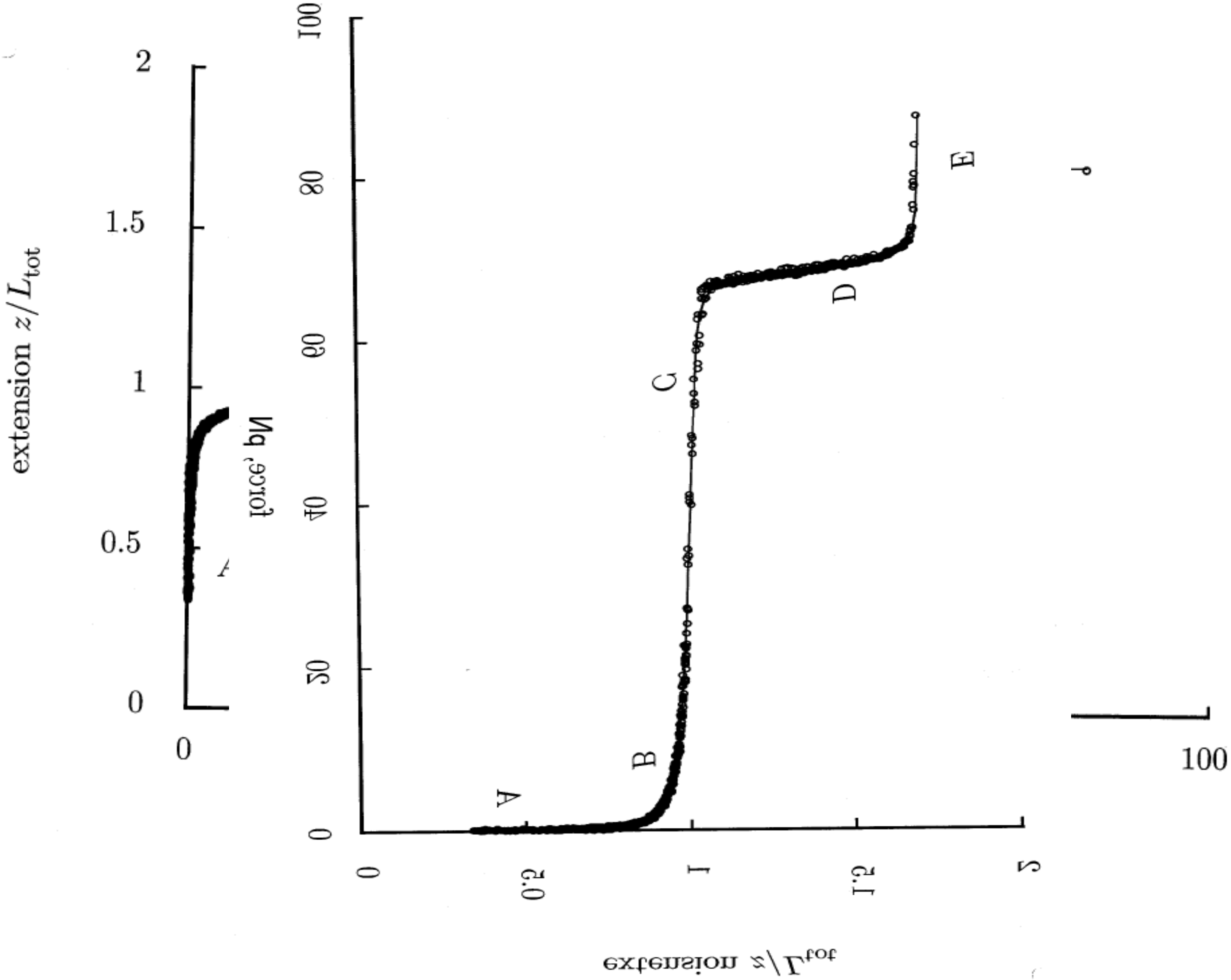
$$\frac{fA}{k_B T} = \frac{z}{L} + \frac{1}{4(1 - z/L)^2} - \frac{1}{4}$$

A: persistence length

L: contour length

T.R. Strick et al., C. R. Physique 3 (2002) 595–618

Wormlike chain model



Goals

Develop theory and simulations to help exploit the balances of forces in strong confinement in order to manipulate DNA molecules and proteins for nanopore detection

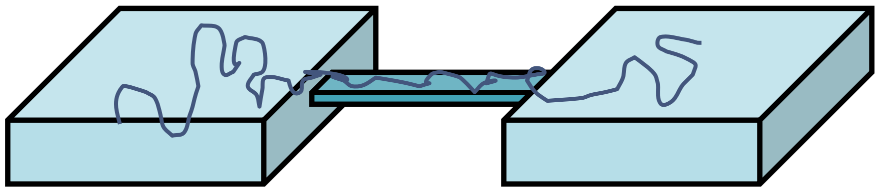
Macromolecule conformation and dynamics in micro- and nano-channels are controlled by

Thermal/Entropic forces

Electrostatic forces

Steric (Excluded volume) forces

Fluid / Hydrodynamic forces



Micro → Nano :

Polymer conformational freedom is restricted : Entropy ↓

Debye length / channel height ↑ : Electrostatics ↑

Diffusion length / channel height ↓ : Hydrodynamics screened

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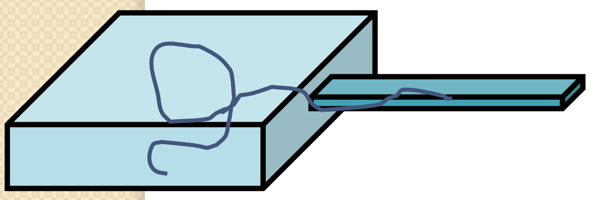
Problems

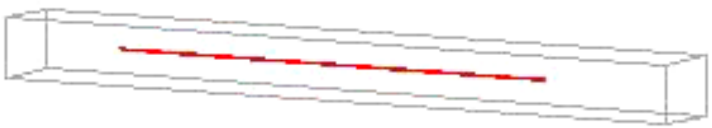
Chain dynamics in < 100nm channels is not well understood

Hybrid lattice-Boltzmann/Brownian dynamics simulations to capture DNA dynamics and interactions with the fluid

- **Translocation micro- to nano-channel**



- **Inside the nanochannel**

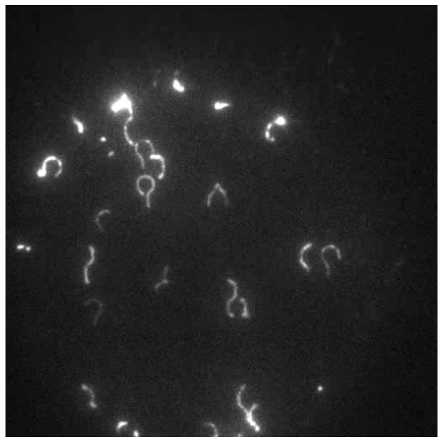


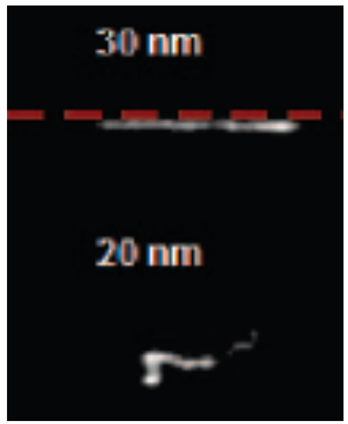
- **Collision with microposts and stretching**

Electrostatic interactions in strong confinement

As the nano-channel size approach the Debye length (5-20 nm), electrostatic interactions are *comparable or stronger* than the entropic and fluid forces

Develop coarse-grained simulations that fully captures DNA/Protein/Ion interactions in nanochannels





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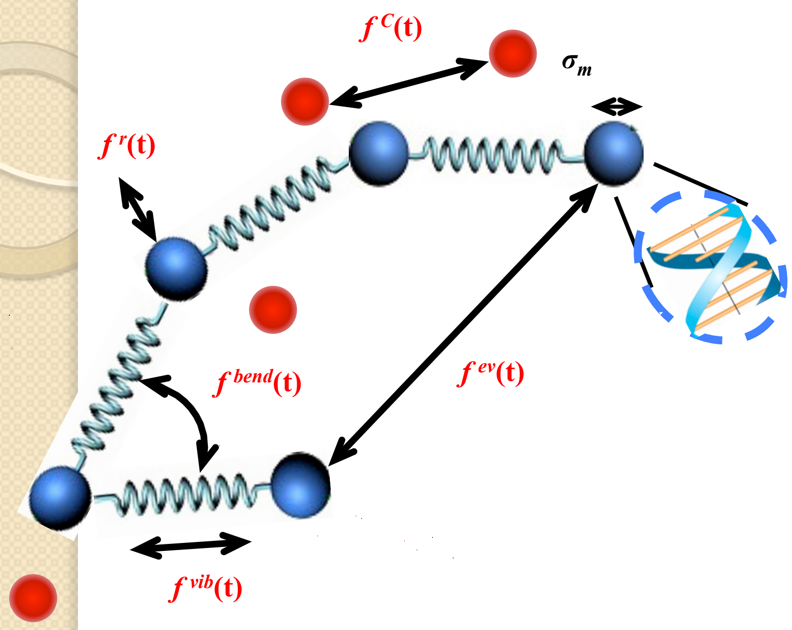
Method



Bending modulus is chosen to match DNA persistence length

$$U_{bend} = k_{bend} k_B T \sum \left(1 - \frac{(\vec{r}_{i-1} - \vec{r}_i)(\vec{r}_i - \vec{r}_{i+1})}{|\vec{r}_{i-1} - \vec{r}_i||\vec{r}_i - \vec{r}_{i+1}|} \right)$$

Electrostatic Coulomb interactions

$$U_C = k_B T \sum \frac{q_i q_j}{4\pi r_{ij}}$$

With HI – Lattice Boltzmann hydrodynamics

$$\vec{U}(t+\delta t) = \vec{U}(t)(1 - \delta t \zeta / m) + \Delta \vec{U}(t)$$

Without HI –free draining

$$\vec{r}(t+\delta t) = \vec{r}(t) + \delta t \, \vec{f}(t) / m\zeta + \delta \vec{r}^{\,G}$$

Electrostatic and hydrodynamic interactions both contribute significantly to DNA dynamics in nanochannels

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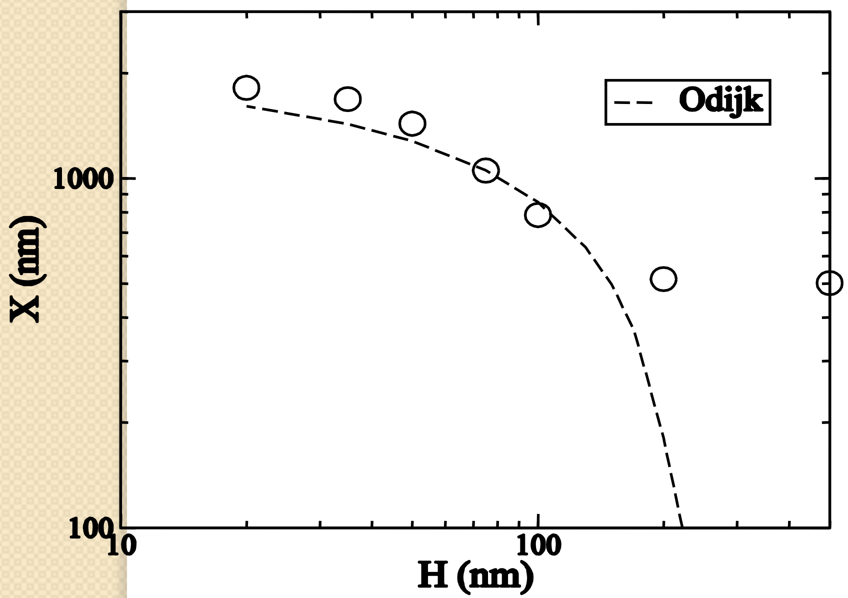
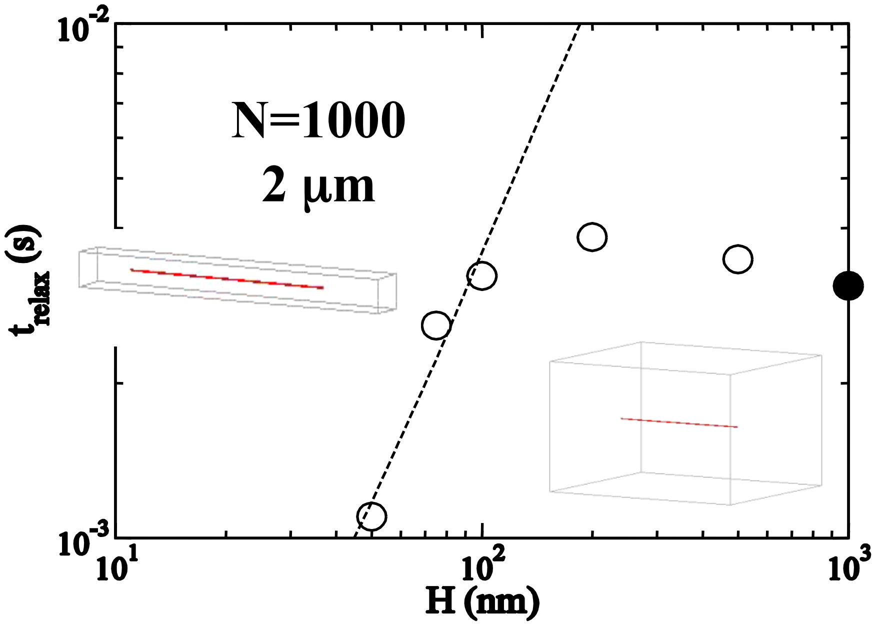
Outlook

• Model entropic and elastic forces on DNA in the nanochannel -- Collaborate with experiments to guide DNA manipulation in nanochannels.

• Model ions and nanochannel surface charge to determine DNA conformation with strong electrostatic interactions in nanochannels – Collaborate with experiments to study electric field driven flow in nanopores.

Predictions of DNA conformation and dynamics in nanochannels





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