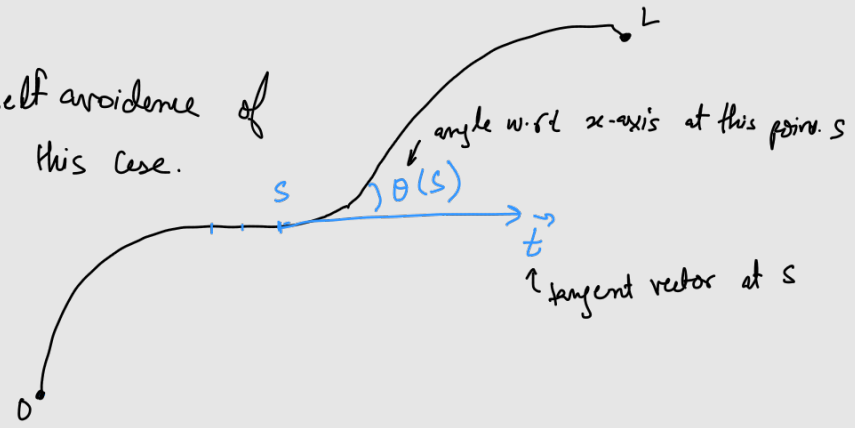
The Wormlike Chain

- polymers are rather rigid on short scales

- neglecting self avoidence of length in this case.



- $E_{WLC} = \frac{1}{2}\alpha \int_0^L ds \; k^2(s)$ (Hooke's law)

  α: bending stiffness; ds: arc length

- Persistence length: $l_p = \frac{\alpha}{k_B T} = \frac{l_K}{2}$ (l_K: Kuhn length)

- Curvature: $k(s) = \frac{d\theta}{ds}$

- quantifying probability of a certain config:

$$P[\theta] = \frac{e^{-E_{WLC}/k_B T}}{Z}$$

→ Boltzmann distribution because we have energy here

Z: normalization factor (integration over all the configs of the chain)

$$\therefore \quad P[\theta] = \frac{1}{Z} e^{-\frac{\alpha}{2k_BT}\int_0^L ds \left(\frac{d\theta}{ds}\right)^2}$$

* we'll use transfer matrix method to solve this integral.

→ if at s, angle is θ'
at $s+ds$, angle is θ

probability that the tangent vector makes an angle θ at chain length $(s+ds)$, given it makes an angle θ' at s.

$$P(\theta, s+ds) = \int W(\theta, \theta') \, P(\theta', s) \, d\theta'$$

$W(\theta, \theta')$: probability to go from θ' to θ

define $\Delta\theta = \theta - \theta'$

now, from the probability distribution:

$W(\theta, \theta') \propto$ energy required to bend the chain by $\Delta\theta$

$$\Rightarrow W(\theta, \theta') = \frac{e^{-\alpha/2k_BT \; \frac{(\Delta\theta)^2}{ds}}}{Z'}$$

$\left(\int d\theta \, W(\theta, \theta') = 1\right)$

taylor

$$P(\theta', s) = P(\theta, s) + \Delta\theta \frac{\partial}{\partial\theta} P(\theta, s) + \frac{1}{2}(\Delta\theta)^2 \frac{\partial^2}{\partial\theta^2} P(\theta, s)$$

plugging into $P(\theta, s+ds)$:

$$P(\theta, s+ds) = \int d\Delta\theta\, W(\Delta\theta) \Big\{ P(\theta,s) + \Delta\theta \frac{\partial}{\partial\theta} P(\theta,s) + \frac{1}{2}(\Delta\theta)^2 \frac{\partial^2}{\partial\theta^2} P(\theta,s) \Big\}$$

$$\Rightarrow P(\theta, s+ds) = P(\theta,s) + D_\theta \frac{\partial^2 P}{\partial\theta^2}$$

(D_θ: const.)

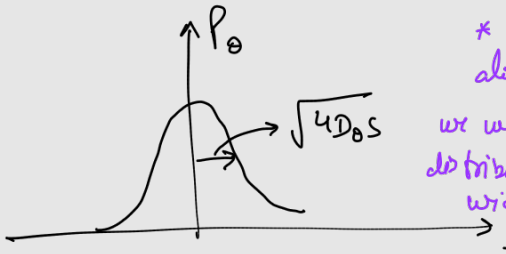
$$\Rightarrow \boxed{\frac{\partial P}{\partial s} = D_\theta \frac{\partial^2 P}{\partial\theta^2}}, \quad D_\theta = \frac{1}{2 l_p}$$

(D_θ: diffusion coeff. of the angle.)

diffusion eqn for θ

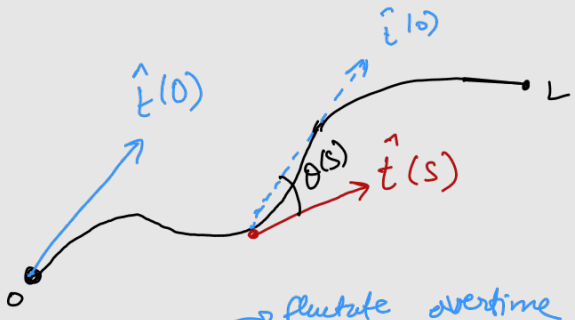
* WLC is very similar a chain,
  ↳ you take a step along the chain & the next segment length's direction is given by the diffusion eqn.

so, if $\theta(0) = 0$, $P(\theta, s) = \frac{1}{\sqrt{4\pi D_\theta s}} e^{-\theta^2/4D_\theta s}$



* the further along the chain we walk, probability distribution is more wider (less certain of the angle)

Tangent correlation



fluctuate overtime

$$\hat{t}(0) \cdot \hat{t}(s) = \cos\theta(s)$$

↓ thermal average.

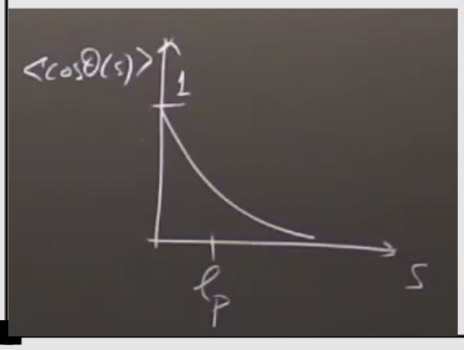
$$\langle \hat{t}(0) \cdot \hat{t}(s) \rangle = \langle \cos\theta(s) \rangle$$

tangent correlation fn

* similar to how $P(\theta, s) = \frac{1}{\sqrt{4\pi D_\theta s}}$ ( ) has only one length scale: persistence length ($\because D_\theta = \frac{1}{2\ell_p}$), the same way tangent correlation fn would also have only one length scale: ℓ_p

$$\therefore \boxed{\langle \hat{t}(0) \cdot \hat{t}(s) \rangle = \langle \cos\theta \rangle = e^{-s/2\ell_p}} \quad \text{(in 2-d)}$$

$$\boxed{= e^{-s/\ell_p}} \quad \text{(in 3-d)}$$

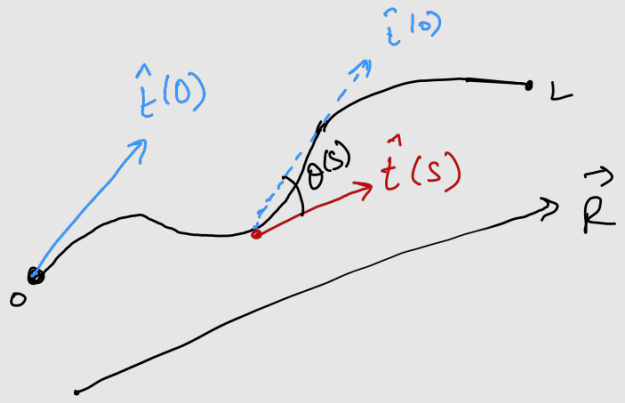


* persistence length is the dist. over which the memory of previous segment's orientation is lost.

* in language of $P(\theta, s)$, ℓ_p is the dist. after which $P(\theta, s)$ becomes wide enough that it covers 360° → could visualize this using Manim.

End-to-end distance

$$R = |\vec{R}|$$



now we want expression of R in terms of tangent correlation fn. One can show:

start with $\vec{R} = \int_0^L \hat{t}(s) \cdot d\vec{s}$

.
.
.
math.
Square and average.
.
.
.

$$\langle R^2 \rangle = \int_0^L ds_1 \int_0^L ds_2 \langle \hat{t}_1(s_1) \quad \hat{t}(s_2) \rangle$$

$$\Rightarrow \boxed{\langle R^2 \rangle = 2 l_p L \left[1 - \frac{l_p}{L} \left(1 - e^{-L/l_p} \right) \right]}$$

expanding.

$$\approx 1 - 1 + \frac{L}{l_p} + \frac{1}{2} \left(\frac{L}{l_p} \right)^2$$

Special cases:

If $L \ll l_p$ (rod doesn't bend a whole lot)

then, $e^{-L/l_p} \approx 1$

$$\rightarrow \boxed{\langle R^2 \rangle = L^2}$$

If $L \gg l_p$, $e^{-L/l_p} \approx 0$

$$\rightarrow \boxed{\langle R^2 \rangle = 2 l_p L}$$

↳ if we compare this with the earlier expression of $\langle R^2 \rangle$ in terms of Kuhn length:

$$\langle R^2 \rangle = l_K^2 N$$

$$= l_K^2 \left(\frac{L}{l_K}\right) \quad \left[N = \frac{L}{l_K} \text{ for WLC}\right]$$

$$\langle R^2 \rangle = l_K L$$

$$\langle R^2 \rangle = 2 l_p L$$

$$\Rightarrow \boxed{l_K = 2 l_p}$$

Wormlike chain with an external force

using the transfer matrix approach, this problem becomes a problem of biased diffusion in angle space.

The wormlike chain with an external force

$$\alpha = k_B T / \ell_p$$

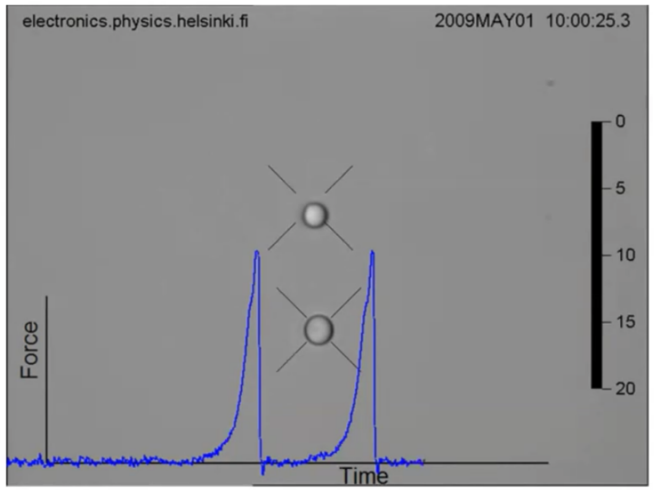
bending rigidity

energy of

$$E = \int_0^L \mathrm{d}s \left(\tfrac{1}{2}\alpha\kappa^2 - \vec{f}\cdot\hat{t}(s) \right)$$

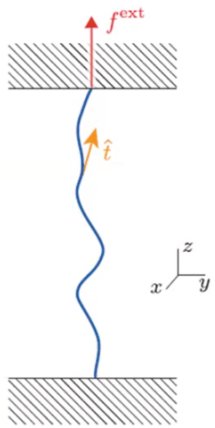
↳ work done by force at segment s (force × extension)

Pulling on DNA and measuring force-extension curve



https://www.youtube.com/watch?v=fZDQ1s79Mpc

48 kb long dsDNA-molecule stretched between optically trapped 2 μm diameter polystyrene beads



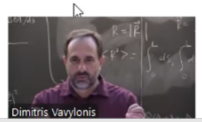
Consider $L/\ell_p \gg 1$

+ neglect excluded volume interactions

For small forces: ideal chain behavior

$$\vec{f} = -\frac{\mathrm{d}\Delta F(\vec{R})}{\mathrm{d}\vec{R}} = -\frac{3k_B T\,\vec{R}}{R_0^2}$$

$$R_0^2 = 2l_p L$$



* for long chains, this becomes a problem of a straight line undergoing transverse fluctuations.

⇒ fourier decomposition of modes ⇐

looking at $\vec{t}_\perp$ b/c the fluctuations are in transverse direction, so we need $\perp$ component of tension for fourier decomposition (I concluded this myself, need to make sure)

For large forces:

$$\vec{t}_\perp = t_x\hat{x} + t_y\hat{y} \qquad t_z = \sqrt{1-\vec{t}_\perp^{\,2}} \approx 1 - \frac{1}{2}\vec{t}_\perp^{\,2}$$

(behaviour in the limit of very strong stretching)

To lowest order: $E = \int_0^L \mathrm{d}s\, \frac{1}{2}\left(\alpha \left|\frac{\mathrm{d}\vec{t}_\perp}{\mathrm{d}s}\right|^2 + f\,\vec{t}_\perp^{\,2}\right) - fL$

$\vec{t}_\perp = \sum_q \vec{t}_\perp(q) e^{iqs}$; $q = \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \cdots$ (wave number, multiples of $\frac{\pi}{L}$; standing waves)

$\vec{t}_\perp$ ↓ fourier transform of $t_\perp$

$$E = \tfrac{1}{2}L\sum_q (\alpha q^2 + f)\,|\vec{t}_\perp(q)|^2$$

expression of energy as a sum of the bending modes.

$$\frac{1}{L}\int_0^L \mathrm{d}s\, g^2(s) = \sum_q |g(q)|^2$$

(Parseval's theorem integral to summation)

Decoupling of modes + Equipartit. $\langle |t_x(q)|^2\rangle = \langle |t_y(q)|^2\rangle = \dfrac{k_\mathrm{B}T}{L(\alpha q^2 + f)}$

b/c modes are quadratic (equipartition theorem)

this term tells which modes will be suppressed. Bigger 'f' would suppress modes of the smallest q (corresponding to the biggest wavelength)

integrating in perpendicular direction.

$$\frac{1}{2}\int_0^L \mathrm{d}s\, \langle |\vec{t}_\perp|^2\rangle = \sum_q \frac{k_\mathrm{B}T}{(\alpha q^2 + f)} = \frac{L}{2\pi}\int \mathrm{d}q\, \frac{k_\mathrm{B}T}{\alpha q^2 + f} = \frac{L}{2}\frac{k_\mathrm{B}T}{\sqrt{f\alpha}} = \frac{L}{2}\sqrt{\frac{k_\mathrm{B}T}{f\ell_\mathrm{p}}}$$

avg. extension in z-direction.

$$\langle R_z\rangle = L\langle t_z\rangle = L\left(1 - \frac{1}{2}\sqrt{\frac{k_\mathrm{B}T}{f\ell_\mathrm{p}}}\right)$$

this expression also tells us that in the absence of external force f, the mode corresponding to the longest wavelength has the biggest amplitude.

$$\Rightarrow \quad \frac{f\ell_\mathrm{p}}{k_\mathrm{B}T} = \frac{1}{4}\left(1 - \frac{\langle R_z\rangle}{L}\right)^{-2}$$

expression of force

$$\langle R_z \rangle = L \langle t_z \rangle$$

$$\approx L \left\langle 1 - \frac{1}{2} \vec{t}_\perp^{\,2} \right\rangle$$

$$\approx L \left[1 - \frac{1}{2} \langle \vec{t}_\perp^{\,2} \rangle \right]$$

$$\left(\because t_z = \sqrt{1 - \vec{t}^{\,2}} \approx 1 - \frac{1}{2} \vec{t}_\perp^{\,2} \right) \quad \text{(prev. page)}$$

$\langle R_z \rangle =$ (expression of R_z on prev. page)

- So far in WLC in an external force:

for small forces:

$$\vec{f} = -\frac{d \Delta F(\vec{R})}{d\vec{R}} = -\frac{3 k_B T \vec{R}}{R_0^2}$$

(ideal chain behavior)

with $R_0^2 = 2 l_p L$

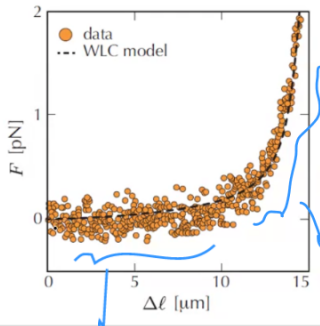
for high forces:

$$\frac{f l_p}{k_B T} = \frac{1}{4} \left(1 - \frac{\langle R_z \rangle}{L} \right)^{-2}$$

Combining the two expressions using empirical interpolation?

Empirical Interpolation

$$\frac{f\ell_p}{k_B T} = \frac{\langle R_z \rangle}{L} + \frac{1}{4(1-\langle R_z \rangle / L)^2} - \frac{1}{4}$$



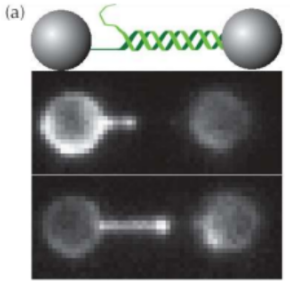
DNA pulling $\ell_p = 50$ nm, $L = 15.6$ μm

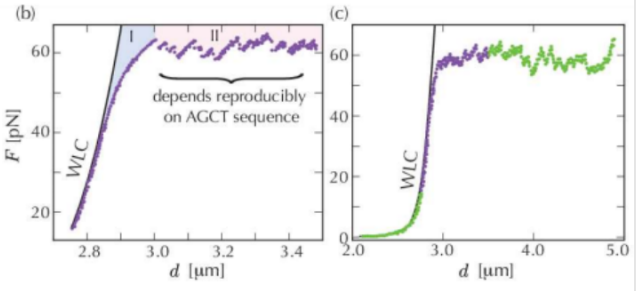
non-linear for large forces.

small force, linear regime

DNA overstretching

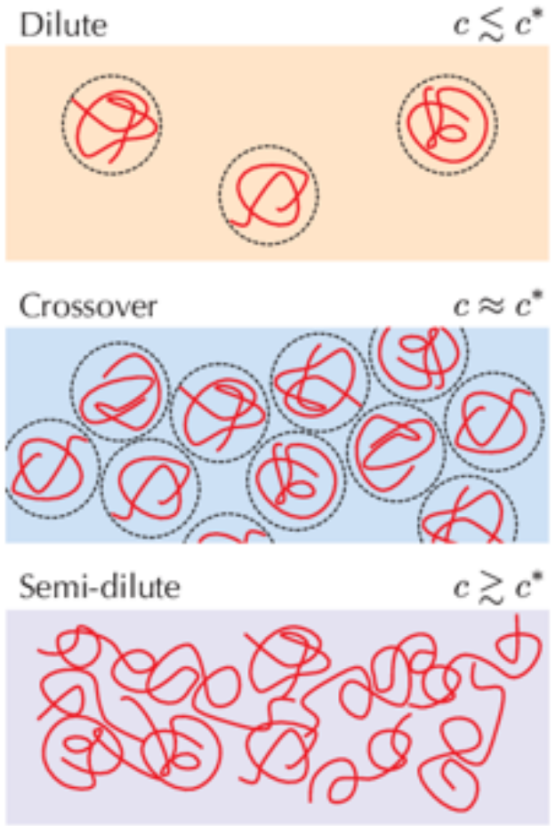
Fluorescent protein binds to single-stranded DNA





Polymer Solutions

$b = l_K$



Overlap threshold (athermal solvents) $c^* \simeq \frac{N}{R^3} \simeq \frac{N}{\ell_K^3 N^{3\nu_{Flory}}} \simeq \ell_K^{-3} N^{-4/5}$

Volume fraction (dimensionless) $\phi^* = N^{-4/5}$ Can be ~ 1%

$\frac{c}{l_K^3}$ ($\frac{\text{conc}^n}{\text{Vol}}$ & assuming that each monomer takes volume of a kuhn segment for simplicity)

van't Hoff formula for osmotic pressure in dilute regime $\Pi \approx \frac{c}{N} k_B T$

$\frac{\text{Conc}^n}{\text{Vol.}}$ degree of polymerization of every molecule

Expect this to be valid up to ϕ^*

$$\Pi(\phi^*) \approx k_B T \frac{\phi^*}{l_K^3 N} \approx k_B T \frac{1}{l_K^3 N^{9/5}} \approx \boxed{\frac{k_B T}{R^3}}$$

(ϕ^* : c)

When ϕ approaches 1, we have
a "concentrated solution", or polymer melt (ϕ=1)