Physics 850: Soft Condensed Matter Physics, Fall04
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Lecture 6: the Worm-like Chain ('Kratky-Porod') Model

Another step beyond the ideal chain model –

"Worm-like chain model" a.k.a. Kratky Porod

- FJC assumes perfect rigidity in pieces shorter than a.
- (Some) real polymers can bend at all length scales
  e.g. DNA

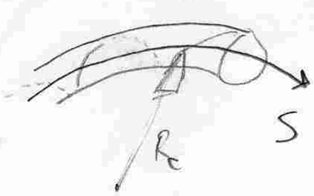
A model for DNA

not important if ends can spin — probably very stiff, ignore

$$\rightarrow \frac{F}{L} = \frac{1}{2}\tilde{A}(\text{curvature})^2 + \frac{1}{2}C(\text{twist})^2 + \frac{1}{2}\gamma(\text{stretch})^2 + \ldots$$

$$\text{curvature} = \frac{1}{R_{curvature}} = \frac{\partial^2 u(s)}{\partial s^2}$$ *(see next page for definition of u)*

can be pos. or neg. but F must ↑, so only (curvature)^2 can appear



S = backbone coordinate

- $\tilde{A}$ has units energy · length
- Dismiss terms $\propto$ (curvature)^4 etc. because coefficients must have more molecular-scale lengths in them, hence these terms are small

all of the molecular detail is in this one parameter

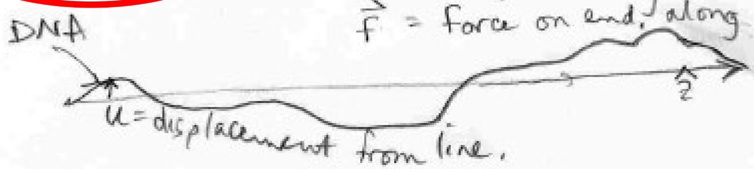
Hypothesis:

$$\frac{F}{L} = \frac{1}{2}\frac{k_B T \ell_p}{R_c^2}$$

$\tilde{A}$

ℓ_p = persistence length. (~50 nm for double-stranded DNA)

L_0 = contour length.
L = length along $\hat{z}$
$\vec{f}$ = force on end, along $\hat{z}$



$\theta(s)$ = local tangent vector (here local polar ∠ with respect to $\hat{z}$)

s = coordinate along chain,
u = displacement from $\hat{z}$ axis

$$\theta(s) = \frac{\partial u}{\partial s}$$

$$\frac{1}{R_c} = \frac{\partial^2 u}{\partial s^2} = \frac{\partial \theta}{\partial s}$$

so $$\frac{F}{L} = \frac{1}{2} k_B T \ell_p \left(\frac{\partial \theta}{\partial s}\right)^2 \quad \text{(free chain)}$$

What if we pull on the end? length along z

$$F = \underbrace{\int \frac{1}{2} k_B T \ell_p \left(\frac{\partial \theta}{\partial s}\right)^2 ds}_{F_{elastic}} - \underbrace{fL}_{\text{work term - same as in RNA exp of lecture 3}}$$

Working with WLC model...

Fourier transforms:

Define $\hat{\theta}(q) = \frac{1}{L_0}\int_0^{L_0} ds\, e^{iqs}\, \theta(s)$

$$\theta(s) = L_0 \int_{\frac{1}{L_0}}^{\infty} dq\, e^{-iqs}\, \hat{\theta}(q)$$

now, $\frac{\partial \theta(s)}{\partial s} = L_0 \int dq \frac{\partial}{\partial s} e^{-iqs} \hat{\theta}(q)$

$$= L_0 \int dq\, (-iq)\, e^{-iqs}\, \hat{\theta}(q)$$

$-i^2 = -1$

$$\int \left(\frac{\partial\theta}{\partial s}\right)^2 ds = -L_0^2 \int ds \int dq\, q\, e^{-iqs} \int dq'\, q'\, e^{-iq's}\, \hat{\theta}(q)\, \hat{\theta}(q')$$

$$\int ds\, e^{is(q+q')} = \delta(q+q')$$

(replace q' with $-q$)

$$= -L_0^2 \int dq (-q^2)\, |\hat{\theta}(q)|^2$$

$$F_{elastic} = \int \frac{1}{2} l_p kT\, ds \left(\frac{\partial\theta}{\partial s}\right)^2 = \frac{k_B T}{2} l_p L_0^2 \int dq\, q^2\, |\hat{\theta}(q)|^2$$

Note: $\int_{\frac{1}{L_0}}^{\infty} dq = \frac{1}{L_0} \sum_q$ (check units)

$$F_{elastic} = \sum_{q=\frac{1}{L_0}}^{\infty} \frac{k_B T}{2} l_p L_0\, q^2\, |\hat{\theta}(q)|^2$$

... WLC ...

Now the work term

some geometry:

$$dz = ds \cos\theta = ds\left(1-\frac{\theta^2}{2}\right) \text{ if } \theta \ll 1$$

$$L = \int_0^{L_0} dz = \int_0^{L_0} ds\left(1-\frac{\theta(s)^2}{2}\right) = L_0 - \int_0^{L_0} ds\, \frac{\theta(s)^2}{2}$$

this is a constant in the energy since L_0 = fixed. So disregard

$$\text{so } -fL = \frac{(-1)(-1)f}{2}\int ds\, \theta(s)^2 + \text{const} = \frac{-f}{2}\int ds\, L_0^2 \int dq\, dq'\, e^{-is(q+q')}\, \hat{\theta}(q)\, \hat{\theta}(q') + \text{const}$$

$\delta(q+q')$

$$= \frac{fL_0^2}{2}\int dq\, |\hat{\theta}(q)|^2$$

Again, replace $\int dq \rightarrow \frac{1}{L_0}\sum_q$

$$f\langle L\rangle = -\frac{fL_0}{2}\sum_q |\hat{\theta}(q)|^2$$

$$\text{so } F = \sum_q \left(\underbrace{\frac{k_BT}{2} l_p L_0 q^2}_{\text{elastic}} + \underbrace{\frac{fL_0}{2}}_{\text{work}}\right) |\hat{\theta}(q)|^2$$

... WLC ...

Equipartition theorem -
each quadratic degree of freedom (eg $|\hat{\theta}(q)|^2$)
contributes, on average, $\frac{1}{2}k_BT$ of energy

so $$\frac{1}{2}k_BT = \left(\frac{k_BT}{2}\ell_p L_0 q^2 + \frac{fL_0}{2}\right)\langle|\hat{\theta}(q)|^2\rangle$$ (ensemble) thermal avg

$$\rightarrow \boxed{\langle|\hat{\theta}(q)|^2\rangle = \frac{1}{L_0\left(\ell_p q^2 + \frac{f}{kT}\right)}}$$

Comments:

- large-q (small-λ) fluct. are small
- small-q (large-λ) fluct. are large

- But there are fluctuations at all lengths, unlike in FJC model.
- The longer the persistence length (ℓ_p) is, the smaller the fluctuations (indeed $F \propto \ell_p$)
- An applied force suppresses fluctuations

WLC & Force - extension curve

$$\frac{L}{L_0} = 1 - \frac{\int ds\,\theta^2}{2L_0}$$

note $\int ds\,\theta(s)^2 = \int ds\, L_0^2 \int dq \int dq'\, e^{-i(q+q')s}\,\hat\theta(q)\,\hat\theta(q')$

$\delta(q+q')$

$$= L_0^2 \int dq\, \underbrace{\langle |\hat\theta(q)|^2\rangle}_{= \frac{1}{L_0\left(l_p q^2 + \frac{f}{kT}\right)}}$$

so $\displaystyle \frac{L}{L_0} = 1 - \int_{\frac{1}{L_0}}^{\infty} dq\, \frac{1}{l_p q^2 + \frac{f}{kT}}$

let $y = q\sqrt{l_p} \rightarrow dq = \frac{dy}{\sqrt{l_p}}$

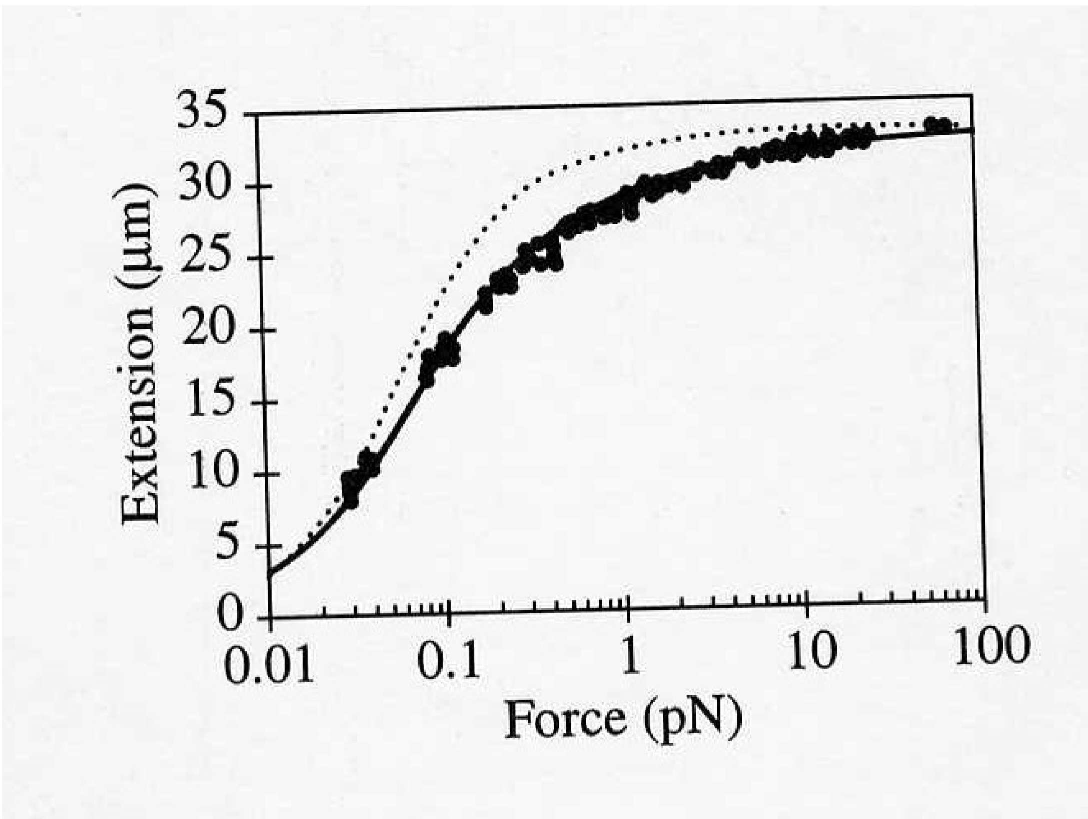
$$\frac{L}{L_0} = 1 - \frac{1}{2}\frac{1}{\sqrt{l_p}} \underbrace{\int_{\frac{\sqrt{l_p}}{L_0}}^{\infty} \frac{dy}{y^2 + \frac{f}{kT}}}_{= \sqrt{\frac{kT}{f}}\,\tan^{-1}\left(y\sqrt{\frac{kT}{f}}\right)\Big|_{\frac{\sqrt{l_p}}{L_0}}^{\infty}}$$

$$\frac{L}{L_0} = 1 + \pi\sqrt{\frac{kT}{f l_p}}$$

so $\rightarrow \left(\frac{L - L_0}{L_0}\right)^2 = \pi^2 \frac{kT}{f l_p} \rightarrow f \propto \frac{L_0^2}{(L-L_0)^2}\frac{kT}{l_p}$ //

Compares well to DNA data!

DNA experiment: 97,000-base DNA force-vs.-extension curve measured with laser trap and microscopy. (from R.H. Austin *et al*, Physics Today Feb., 1997 p32).



Solid curve: WLC model, l_p = 50 nm.
Dashed curve: FJC model.

Remarks

- *Model works for all extensions (for DNA, at least) until full extension ($L \sim L_0$), when bond stretching plays a role.*

- works even though it's in continuum limit

  ie molecule = elastic rod!

- A 1-parameter model based on simple symmetry arguments.

- "persistence length"

  correlation function

$$\langle \cos\theta(0) \cdot \cos\theta(s) \rangle = e^{-s/l_p}$$

ie direction becomes random over a length $\sim l_p$

(not proven here)