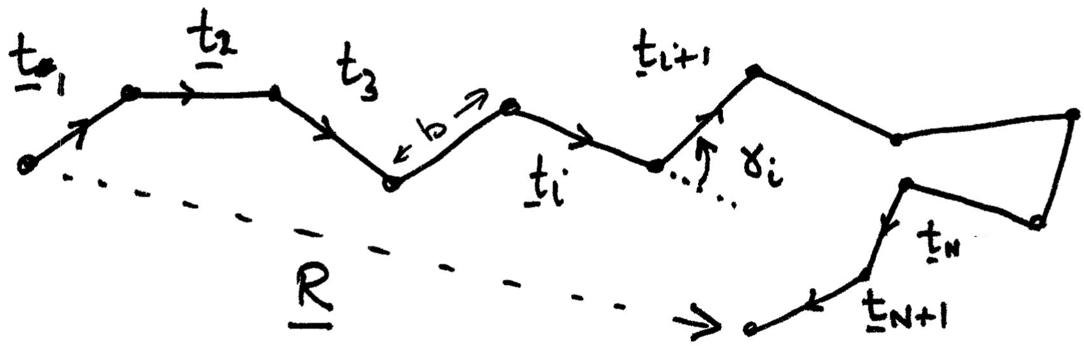
Worm Like Chain Models

Including the effects of bending stiffness

Discrete Model   Kratky-Porod (1949)



Internal Energy $E = -K \sum_{i=1}^{N} \underline{t}_i \cdot \underline{t}_{i+1} = -K \sum_{i=1}^{N} \cos\gamma_i$

Analogous to Freely Jointed Chain Model.

Partition Function

$$Z = \int d\Omega_1 \dots d\Omega_N \; e^{\frac{K}{k_bT} \sum_{i=1}^{N} \cos\gamma_i}$$

$$\overset{\text{as before}}{=} \left(\frac{4\pi \sinh\lambda}{\lambda} \right)^N \qquad \text{where } \lambda = \frac{K}{k_bT}$$

For stiff polymers $\lambda = \beta K \gg 1$

We can determine $\langle \underline{R} \cdot \underline{R} \rangle = \langle R^2 \rangle = b^2 \left\langle \left(\sum_i \underline{t}_i \right)^2 \right\rangle$

$$\therefore \langle R^2 \rangle = b^2 \sum_{i,j} \langle \underline{t}_i \cdot \underline{t}_j \rangle$$

$$\omega_1 := \langle \underline{t}_i \cdot \underline{t}_{i+1} \rangle = \langle \cos \gamma_i \rangle$$

$$= \frac{1}{Z} \int d\Omega_1 \ldots d\Omega_N \exp\left[\frac{K}{k_b T} \sum_{i=1}^{N} \cos \gamma_i\right] \cos \gamma_i$$

$$\swarrow \beta = \frac{1}{k_b T}$$

$$= \frac{\int d\gamma_i \sin\gamma_i \exp\left[\beta K \cos \gamma_i\right] \cos\gamma_i}{\int d\gamma_i \sin\gamma_i \exp\left[\beta K \cos\gamma_i\right]}$$

Langevin function

$$= \frac{\partial}{\partial(\beta K)} \ln\left[\int d\gamma \sin\gamma \, e^{\beta K \cos\gamma}\right] = \mathcal{L}(\beta K)$$

<u>Now</u> $\quad \omega_n := \langle \underline{t}_i \cdot \underline{t}_{i+n} \rangle$

$$\underline{t}_i \cdot \underline{t}_{i+n} = \cos\left(\gamma_i + \gamma_{i+1} + \ldots + \gamma_{i+n-1}\right)$$

$$= \cos\gamma_i \cos(\gamma_{i+1} + \ldots + \gamma_{i+n-1}) - \sin\gamma_i \sin(\gamma_{i+1} + \ldots + \gamma_{i+n-1})$$

But $\langle \sin\gamma_i \rangle$ dominated by $\langle \cos\gamma_i \rangle$ for $\beta K \gg 1$ as contribution from integrand localised to gamma ~ 0

$\therefore$

$$\omega_n = \langle \underline{t}_i \cdot \underline{t}_{i+n} \rangle = \langle \cos\gamma_i \rangle \langle \cos(\gamma_{i+1} + \ldots + \gamma_{i+n-1}) \rangle$$

$$= \omega_1 \, \omega_{|n|-1} \qquad \therefore \boxed{\omega_n = (\omega_1)^{|n|}}$$

$$\therefore \quad \omega_n = \omega_1^{|n|} = \left[\mathcal{L}(\lambda)\right]^{|n|} \quad \text{with } \lambda = \beta K = \frac{K}{k_b T}$$

Stiff polymer $\quad \lambda = \beta K \gg 1$

$$\langle \underline{t}_i \cdot \underline{t}_{i+n} \rangle \sim \left(1 - \frac{1}{\beta K}\right)^{|n|} = \exp\left[|n| \ln\left(1 - \frac{1}{\beta K}\right)\right]$$

$$\overset{\beta K \gg 1}{\simeq} \exp\left(-\frac{|n|}{\beta K}\right) = \exp\left(-\frac{|n| k_b T}{K}\right)$$

$$= \exp\left(-\frac{|n| b}{\xi_p}\right)$$

with $\xi_p := \dfrac{K b}{k_b T}$, the persistence length, the scale on which tangent-tangent correlations decay.

With L the polymer length

	$\xi_p \gg L$	Stiff chain
[DNA]	$\xi_p \ll L$	Flexible Chain... well captured by flexible joint model
[Microtubule]	$\xi_p \simeq L$	semi-flexible

for stiff polymers

Returning to mean square end to end distance

$$\langle \underline{R}^2 \rangle = b^2 \left\langle \sum_{i,j} \underline{t}_i \cdot \underline{t}_j \right\rangle = b^2 \sum_{i,j} w_1^{|i-j|}$$

$$= b^2 \sum_{i=1}^{N+1} \left[\left(\sum_{j=1}^{i-1} w_1^{i-j} \right) + 1 + \sum_{j=i+1}^{N+1} w_1^{j-i} \right]$$

as $\underline{t}_i \cdot \underline{t}_i = 1$

$\therefore \langle \underline{t}_i \cdot \underline{t}_i \rangle = 1$

Recall $W_1 < 1$ as Langevin function < 1

$$= b^2 \sum_{i=1}^{N+1} \left[\underbrace{\left(W_1 + W_1^2 + \dots + W_1^{i-1} \right)}_{\frac{W_1 (1 - W_1^{i-1})}{1 - W_1}} + \underbrace{\left(1 + W_1 + \dots + W_1^{N+1-i} \right)}_{\frac{1 - W_1^{N+2-i}}{1 - W_1}} \right]$$

$$= \frac{b^2}{1 - W_1} \left[\sum_{i=1}^{N+1} W_1 - \sum_{i=1}^{N+1} W_1^{i-1} + \sum_{i=1}^{N+1} 1 - \sum_{i=1}^{N+1} W_1^{N+2-i} \right]$$

$$= \frac{b^2 N (W_1 + 1)}{1 - W_1} + \text{h.o.t.s}$$

as $N \to \infty$

Continuous Filaments

We define a continuous filament, or rod, by its centreline, parametrised as $\underline{r}(S,T)$, where S is the arclength in the <u>stress-free</u> configuration, and a material parameter, and T is time.

In general, the arclength of the rod is given by

$$s = \int_0^S d\bar{S} \left| \frac{\partial \underline{r}(\bar{S},T)}{\partial \bar{S}} \right|$$

though for an unstretchable rod, $s = S$, which is normally assumed.

Continuous Limit

The unit tangent of a rod is given by $\underline{t} = \frac{d\underline{r}}{ds}$. The curvature, κ, satisfies $|\kappa| = \left|\frac{d\underline{t}}{ds}\right|$. The energy of the Worm-like chain can be seen to be equivalent to the bending energy of a rod

$$\mathcal{E}_{el} = \frac{EI}{2}\int_0^L ds\, \kappa^2(s)$$

where $E \equiv$ Young's modulus, I is the second moment of the cross section area.

Note for a circular cross section $I = \frac{\pi r^4}{4}$.

Also $M = EI\kappa := \underset{\substack{\uparrow \\ \text{Bending Stiffness}}}{B}\kappa$ is the moment required to bend the rod to curvature κ.

Consider

$$E = -K \sum_{i=1}^{N} (\underline{t}_i \cdot \underline{t}_{i+1})$$

but shift the energy of the ground state so that the minimum energy is zero (Changing E by an additive constant alters no results presented thus far).

$\therefore$ Consider

$$H = -K \sum_{i=1}^{N} (\underline{t}_i \cdot \underline{t}_{i+1} - 1)$$

$\boxed{\text{We want to take the limit } N \to \infty,\ b \to 0,\ Nb = L, \text{ fixed}}$

Note $\dfrac{(\underline{t}_{i+1} - \underline{t}_i)^2}{2} = \dfrac{1}{2}\left[2 - 2\,\underline{t}_{i+1} \cdot \underline{t}_i + 1\right] = 1 - \underline{t}_i \cdot \underline{t}_{i+1}$

$$\therefore\ H = \frac{K}{2} \sum_{i=1}^{N} (\underline{t}_{i+1} - \underline{t}_i)^2 = \left(\frac{Kb}{2}\right) \sum_{i=1}^{N} b \underbrace{\left(\frac{\underline{t}_{i+1} - \underline{t}_i}{b}\right)^2}_{\left(\frac{\partial \underline{t}}{\partial s}\right)^2\Big|_{\underline{r}_i} \text{ in the limit}}$$

$$= \frac{Kb}{2} \sum_{i=1}^{N} \delta s \left(\frac{\partial \underline{t}}{\partial s}\right)^2\Bigg|_{\underline{r}_i}$$

$$\xrightarrow[\substack{N \to \infty \\ b \to 0 \\ Nb = L, \\ \text{fixed.}}]{} \frac{Kb}{2} \int ds \left(\frac{\partial \underline{t}}{\partial s}\right)^2 = \frac{Kb}{2} \int_{s=0}^{s=Nb=L} ds\ \kappa^2(s)$$

in the limit, noting

$$|\kappa| = \left|\frac{\partial \underline{t}}{\partial s}\right|$$

Compare to the classical result

$$\mathcal{E}_{elastic} = \frac{EI}{2}\int_0^L \kappa^2 \, ds$$

$\therefore$ We identify

$K_b = EI = B$,

bending stiffness.

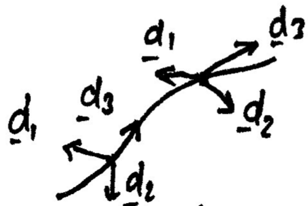
$\therefore$ ξ_p, persistance length satisfies

$$\xi_p = \frac{K_b}{k_b T} = \frac{B}{k_b T}$$

$\therefore$ We can define bending stiffness from persistance length (given the model assumptions)

Continuous Filaments - General Frames

A general frame is an orthonormal basis defined at each point along the curve.



Let $\underline{d}_1(S,T)$, $\underline{d}_2(S,T)$ be continuous, orthogonal unit vectors fixed in the material cross section $S = \text{const.}$

Let $\underline{d}_3 = \underline{d}_1 \wedge \underline{d}_2$. Then $\{\underline{d}_1, \underline{d}_2, \underline{d}_3\}$ is a general frame.

We can write a vector relative to the local basis, $\{\underline{d}_1\, \underline{d}_2 \underline{d}_3\}$ or a basis in an inertial frame $\{\underline{e}_1, \underline{e}_2, \underline{e}_3\}$

$$\underline{a} = \sum_{p=1}^{3} a_p \underline{e}_p = \sum_{i=1}^{3} a_i \underline{d}_i$$

$$\therefore \quad a_p = \sum_{i=1}^{3} \underline{e}_p \cdot \underline{d}_i \, a_i \qquad \text{i.e.} \quad \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} = \overbrace{\left(\underline{d}_1 \,\middle|\, \underline{d}_2 \,\middle|\, \underline{d}_3\right)}^{\underline{\underline{D}}} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}$$

Note $\quad D^T D = I \quad \therefore D, D^T$ inverses $\therefore DD^T = I.$

$$\therefore \quad \frac{\partial D}{\partial S} D^T + D \frac{\partial D^T}{\partial S} = 0$$

also $\dfrac{\partial \underline{d}_1}{\partial S} = \alpha \underline{d}_1 + \beta \underline{d}_2 + \gamma \underline{d}_3$ as $\{\underline{d}_1, \underline{d}_2, \underline{d}_3\}$ a basis

$$\therefore \quad \frac{\partial D}{\partial S} = \frac{\partial}{\partial S}\left(\underline{d}_1 \,\middle|\, \underline{d}_2 \,\middle|\, \underline{d}_3\right) = D\,\mathcal{U}$$

for some $\mathcal{U}$.

$$\therefore \quad 0 = DUD^T + D(DU)^T = DUD^T + DU^TD^T = D(U+U^T)D^T$$

D, D^T inverses of each other $\quad \therefore \quad D^T \cdot 0 \cdot D = 0 = U + U^T$

$\therefore$ $\underline{U \text{ anti-symmetric}}$

Similarly $\quad \dfrac{\partial D}{\partial T} = DW$, with W anti-symmetric $\left(\partial/\partial S \to \dfrac{\partial}{\partial T} \right)$.

<u>Compatability</u>

$$0 = \frac{\partial^2 D}{\partial T \partial S} - \frac{\partial^2 D}{\partial S \partial T} = \frac{\partial}{\partial T}(DU) - \frac{\partial}{\partial S}(DW) = \frac{\partial D}{\partial T} U + D \frac{\partial U}{\partial T} - \frac{\partial D}{\partial S} W - D \frac{\partial W}{\partial S}$$

$$= D\left[WU - UW\right] + D\left[\frac{\partial U}{\partial T} - \frac{\partial W}{\partial S}\right]$$

D invertible $\quad \therefore \quad \underline{\dfrac{\partial U}{\partial T} - \dfrac{\partial W}{\partial S} = [U, W]}$

<u>Note</u> $\quad U = \begin{pmatrix} 0 & -u_3 & u_2 \\ u_3 & 0 & -u_1 \\ -u_2 & u_1 & 0 \end{pmatrix} \qquad \underline{u} = (u_1 u_2 u_3)$

$$\therefore \quad \frac{\partial D}{\partial S} = \left(\underline{d}_1 \middle| \underline{d}_2 \middle| \underline{d}_3 \right) \begin{pmatrix} 0 & -u_3 & u_2 \\ u_3 & 0 & -u_1 \\ -u_2 & u_1 & 0 \end{pmatrix} = \left(+u_3 \underline{d}_2 - u_2 \underline{d}_3 \;\middle|\; -u_3 \underline{d}_1 + u_1 \underline{d}_3 \;\middle|\; u_2 \underline{d}_1 - u_1 \underline{d}_2 \right)$$

$$= \left(u_3 \underline{d}_3 \wedge \underline{d}_1 + u_2 \underline{d}_2 \wedge \underline{d}_1 + u_1 \underline{d}_1 \wedge \underline{d}_1 \;\middle|\; u_1 \underline{d}_1 \wedge d_2 + u_2 \underline{d}_2 \wedge \underline{d}_2 + u_3 \underline{d}_3 \wedge \underline{d}_2 \;\middle|\; \ldots \right.$$

$$= \left(\left[u_1 \underline{d}_1 + u_2 \underline{d}_2 + u_3 \underline{d}_3 \right] \wedge \underline{d}_1 \;\middle|\; \left[u_1 \underline{d}_1 + u_2 \underline{d}_2 + u_3 \underline{d}_3 \right] \wedge d_2 \;\middle|\; \ldots \right)$$

∴ We can rewrite as

$$\frac{\partial}{\partial S} \underline{d_i} = \underline{u} \wedge \underline{d_i} \qquad \frac{\partial}{\partial T} \underline{d_i} = \underline{w} \wedge \underline{d_i}$$

for some $\underline{u}, \underline{w}$.

Also we need $\frac{\partial \underline{r}}{\partial \mathcal{S}} = \underline{v}$ for a complete kinematic description.

We restrict ourselves to unstretchable, unshearable rods below.

Hence $$\boxed{\frac{\partial \underline{r}}{\partial \mathcal{S}} = \underline{d_3} = \underline{t} = \frac{\partial \underline{r}}{\partial s}}$$

$\mathcal{S} = s$ and the rod does not stretch.

Also we assume material cross sections remain perpendicular to $\underline{t}$, and thus there is no shear.

Reduction from the unstretchable, unshearable rod to the elastica/beam equation

We have the kinematics

- Centreline $r(s,T)$ with $s = \mathcal{S}$.
- Frame $\{\underline{d_1}, \underline{d_2}, \underline{d_3}\}$ with $\underline{d_3} = \frac{\partial r}{\partial s}$, $\frac{\partial D}{\partial S} = DU$, $\frac{\partial D}{\partial T} = DW$
- Let L be the rod length

$$\frac{\partial U}{\partial T} - \frac{\partial W}{\partial \mathcal{S}} = [U, W]$$

We need the momentum balances

Def^n. Let $n(s,T)$ be the resultant contact force exerted BY