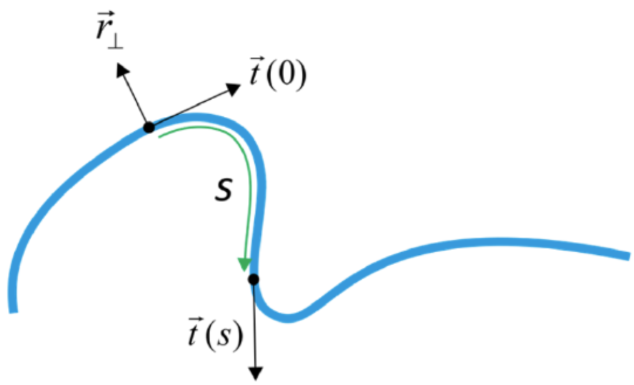
9.2: Worm-like Chain

The **worm-like chain** (WLC) is perhaps the most commonly encountered models of a polymer chain when describing the mechanics and the thermodynamics of macromolecules. This model describes the behavior of a thin flexible rod, and is particularly useful for describing stiff chains with weak curvature, such as double stranded DNA. Its behavior is only dependent on two parameters that describe the rod: κ_b its **bending stiffness**, and L_C, the **contour length**.



Let's define the variables in this WLC model:

- s The distance separating two points along the contour of the rod
- $\vec{r}_\perp$ Normal unit vector
- $\vec{t} = \dfrac{\partial \vec{r}_\perp}{\partial s}$ Tangent vector
- $\dfrac{\partial \vec{t}}{\partial s}$ Curvature of chain
- $= \dfrac{1}{R}$ is inverse of local radius of curvature

The worm-like chain is characterized by:

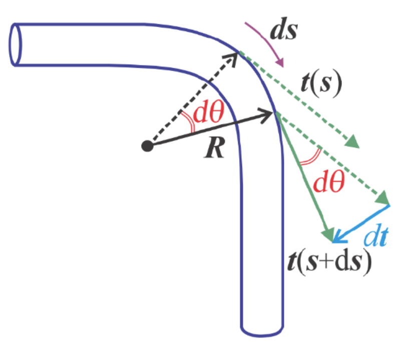
- **Persistence length**, which is defined in terms of tangent vector correlation function:

$$g(s) = \langle \vec{t}\,(0) \cdot \vec{t}\,(s) \rangle = \exp[-|s|/\ell_p] \tag{9.2.1}$$

- **Bending energy**: The energy it takes to bend the tangent vectors of a segment of length s can be expressed as

$$U_b = \frac{1}{2}\kappa_b \int_0^L ds \left(\frac{\partial \vec{t}}{\partial s}\right)^2 \tag{9.2.2}$$

Bending Energy



Let's evaluate the bending energy of the WLC, making some simplifying assumptions, useful for fairly rigid rods. If we consider short distances over which the curvature is small, then $\theta \approx s/R$ and

$$\frac{\partial \vec{t}}{\partial s} \approx \frac{d\theta}{ds} = \frac{1}{R} \tag{9.2.3}$$

Then we can express the bending energy in terms of an angle:

$$U_b \approx \frac{1}{2s}\kappa_b \theta^2 \tag{9.2.4}$$

Note the similarity of this expression to the energy needed to displace a particle bound in a harmonic potential with force constant k: U = ½kx^2. The bending energy can be used to obtain thermodynamic averages. For instance, we can calculate the variance for the tangent vector angles as a function of s (spherical coordinates):

$$\langle \theta^2(s) \rangle = \frac{1}{Q_{bend}} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \, \sin\theta \, \theta^2 \, e^{-U_b(\theta)/k_B T} \tag{9.2.5}$$

$$= \frac{2sk_B T}{\kappa_b} \tag{9.2.6}$$

Here we have used $sin\theta \approx \theta$. The partition function for the bending of the rod is:

$$Q_{bend} = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \, \sin\theta \, e^{-U_b(\theta)/k_B T}$$

Persistence Length

To describe the persistence length of the WLC, we recognize that Equation 9.2.1 can be written as $g(s) = \langle \cos\theta(s) \rangle$ and expand this for small θ:

$$\begin{aligned} g(s) &= \langle \cos\theta(s) \rangle \\ &= \langle 1 - \frac{\theta^2(s)}{2} + \ldots \rangle \\ &\approx 1 - \frac{1}{2}\langle \theta^2(s) \rangle \end{aligned}$$

and from Equation 9.2.3 we can write:

$$g(s) \approx 1 - \frac{sk_B T}{\kappa_b}$$

If we compare this to an expansion of the exponential in Equation 9.2.1

$$g(s) = e^{-|s|/\ell_p} \approx 1 - \frac{|s|}{\ell_p}$$

we obtain an expression for the persistence length of the worm-like chain

$$\ell_p = \frac{\kappa_b}{k_B T}$$

End-to-End Distance

The end-to-end distance for the WLC is obtained by integrating the tangent vector over one contour length:

$$\vec{R} = \int_0^{L_C} ds \, \vec{t}(s)$$

So the variance in the end-to-end distance is determined from the tangent vector autocorrelation function, which we take to have an exponential form:

$$\begin{aligned}\langle R^2\rangle &= \langle R\cdot R\rangle \\ &= \int_0^{L_C} ds \int_0^{L_C} ds' \langle t(s)t(s')\rangle \\ &= \int_0^{L_C} ds \int_0^{L_C} ds'\, e^{-(s-s')/\ell_p} \\ \langle R^2\rangle &= 2\ell_p L_C - 2\ell_p^2\left(1-e^{-L_C/\ell_p}\right)\end{aligned}$$

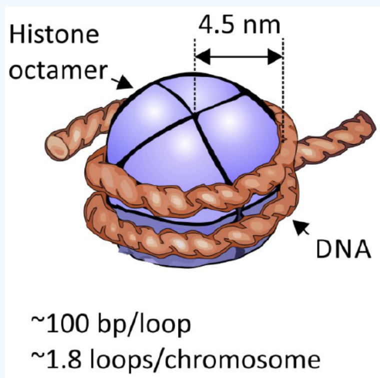
Let’s examine this expression in two limits:

rigid: $\ell_p \gg L_C$ $\langle R^2\rangle \approx L_C^2$

flexible: $\ell_p \ll L_C$ $\langle R^2\rangle \approx 2L_C\ell_p \rightarrow n_e\ell_e^2 \rightarrow \therefore 2\ell_p = \ell_e$

Example 9.2.1: DNA Bending in Nucleosomes

What energy is required to wrap DNA around the histone octamer in the nucleosome? Double stranded DNA is a stiff polymer with a persistence length of $\ell_p \approx 50$ nm, but the nucleosome has a radius of ~4.5 nm.



Solution

From ℓ_p and k_BT = 4.1 pN nm, we can determine the bending rigidity using:

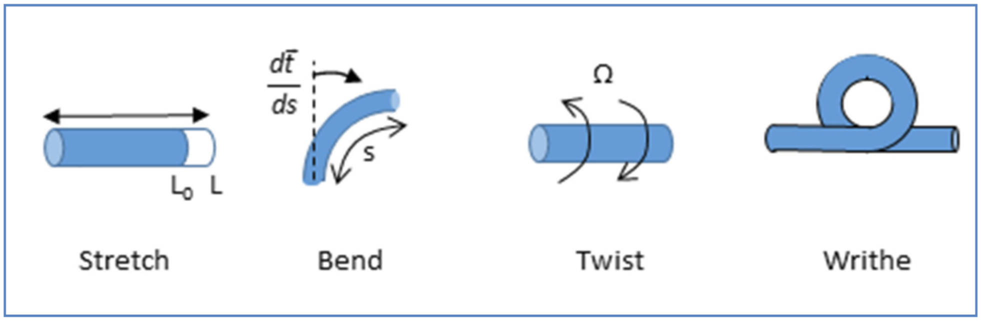
$$\kappa_b = \ell_p k_B T = (50 \text{ nm})(4.1 \text{ pN nm}) = 205 \text{ pN nm}^2$$

Then the energy required to bend dsDNA into one full loop is

$$\begin{aligned}U_b &\cong \frac{\kappa_b\theta^2}{2s} \approx \frac{\kappa_b(2\pi)^2}{2(2\pi R)} = \frac{\pi\kappa_b}{R} \\ &= \frac{\pi(205 \text{ pn nm}^2)}{4.5 \text{ nm}} = 143 \text{ pN nm} \\ &= 35k_BT = 15 \text{ kcal (mol loops)}^{-1} \\ &\quad \text{or } 0.15 \text{ kcal basepair}^{-1}\end{aligned}$$

Continuum Mechanics of a Thin Rod[1]

The worm-like chain is a model derived from the continuum mechanics of a thin rod. In addition to bending, a thin rod is subject to other distortions: stretch, twist, and write.



Let's summarize the energies required for these deformations:

Deformation variables:

- s: Position along contour of rod
- L_0: Unperturbed length of rod
- $\vec{t}$: Tangent vector.
- $d\vec{t}/ds$: curvature
- Ω: Local twist

The energy for distorting the rod is

$$U = U_{st} + U_b + U_{tw}$$

In the harmonic approximation for the restoring force, we can write these contributions as

$$U = \frac{1}{2}\int_{L_0}^{L} \kappa_{st}\, s ds + \frac{1}{2}\int_{L_0}^{L} \kappa_b \left(\frac{d\vec{t}}{ds}\right)^2 ds + \frac{1}{2}\int_{L_0}^{L} \kappa_{tw} \Omega^2 ds$$

The force constants, with representative values for dsDNA, are:

Stretching: $\kappa_{st} = \kappa_{st-entropic} + \kappa_{st-enthalpic}$

$\kappa_{st-entropic} \approx 3k_BT/\ell_p L_c$

Bending: κ_b

$\kappa_b \approx 205\ \text{pN nm}^2$

Twisting: κ_{tw}

$\kappa_{tw} \approx (86\ \text{nm})k_BT = 353\ \text{pN nm}^2$

Writhe

An additional distortion in thin rods is **writhe**, which refers to coupled twisting and coiling, and is an important factor in DNA supercoiling. Twisting of a rod can induce in-plane looping of the rod, for instance as encountered with trying to coil a garden hose. The writhe number W of a rod refers to the number of complete loops made by the rod. The writhe can be positive or negative depending on whether the rod crosses over itself from right-to-left or left-to-right. The twist number T is the number of Ω = 2π rotations of the rod, and can also be positive of negative.

The linking number L = T+W is conserved in B-form DNA, so that twist can be converted into writhe and vice-versa. Since DNA in cells is naturally negatively supercoiled in nucleosomes, topoisomerases are used to change of linking number by breaking and reforming the phosphodiester backbone after relaxing the twist. Negatively supercoiled DNA can be converted into circular DNA by local bubbling (unwinding into single strands).

1. D. H. Boal, Mechanics of the Cell, 2nd ed. (Cambridge University Press, Cambridge, UK, 2012).