FJC: freely jointed chain

**Thermodynamics**

- Free energy $A = U - TS$ (fixed $N, V, T$)
- Want to maximize $S$: purely entropic reasoning
  - $U = 0$ for all configurations (assumption)
  - No penalty for bending or crossing

**Single link point of view**

- $b_i$: orientation of link $i$
- $\mathbf{b}_i$: orientation vector of link $i$
- $r_{\mathbf{i}}$: end-to-end vector

**Sample configuration (microstate)**

- $R$: end-to-end vector
- Measure of coil size

**Statistics of a random walk**:

- Mean:
  \[
  \left\langle \mathbf{R} \right\rangle = \sum_{i=1}^{N} \mathbf{b}_i
  \]
- Variance:
  \[
  \left\langle \mathbf{R} \cdot \mathbf{R} \right\rangle = \sum_{i=1}^{N} \left\langle \mathbf{b}_i \cdot \mathbf{b}_i \right\rangle = N \left\langle b_i^2 \right\rangle
  \]

- Contour length of chain $= N b$

**Probability distribution for $R$**

- $p(x, y, z, N) = \left( \frac{3}{2\pi N b^2} \right)^{3/2} \exp \left( -\frac{3R^2}{2Nb^2} \right)$ Gaussian
  - Mean: $\left\langle \mathbf{R} \right\rangle = 0$
  - Variance: $\left\langle \mathbf{R} \cdot \mathbf{R} \right\rangle = \sum_{i=1}^{N} \left\langle b_i^2 \right\rangle = N \left\langle b_i^2 \right\rangle$

**Probability that chain end is in volume**

\[
\left\langle \alpha \right\rangle = \int dx_1 \cdots dx_N \int dy \int dz
\]

**Limit of validity**

- Calculate correction term
- $p(R, N) = \frac{1}{\sqrt{2\pi (r/2)^2}} \left[ 1 - \frac{3}{2\pi r^2} \right] \exp \left( -\frac{3R^2}{2Nb^2} \right)$ Gaussian
- $N \gg 1$, many links
- $R^2 \ll N b^2$, not valid for large extensions
- $R \to L = N b$

**Force-extension behavior of a single molecule**

- Let's constrain our system to fixed $R$:
  - Force $f$ allowed to vary
  - Extension $x$ fixed
The probability of random walk $p(R) = \frac{\Omega(R)}{\Omega_{total}}$ is the number of configurations with $R$ over the total number of configurations for molecule $R$.

For a thermodynamic system, $\Delta A = -\Delta H + T \Delta S = -TS$; hence $S = k \ln \Omega(R)$.

$S = k \ln \frac{\Omega_{total}}{p(R)} + k \ln p(R)$

\[
\langle f \rangle = -kT \frac{\partial}{\partial R} \ln p(R) = \frac{3kT}{N_b^2} R
\]

where $f$ is the internal force and $R$ is the distance between ends of a polymer. $N_b$ is the number of monomers in a segment.

\[
\langle f \rangle = \frac{3kT}{N_b^2} \frac{R}{L}
\]

Linear relationship between $f$ and $R$.

For $N_b \gg 1$, $R \ll L$ and $kT$ is not a function of $R$.

If $N_b \ll 1$, $R \gg L$.

$\frac{kT}{b}$ determines how difficult it is to extend a polymer. Smaller $b$ means easier to extend ($N = \frac{b}{kT}$ for polymer, see configurations).

The form of $\langle f \rangle$ allows for $R > L$ (unphysical).

For DNA, the double stranded DNA,

- Kuhn length $b \approx 100$ nm
- Recall $\frac{kT}{1 \text{nm}} = 4 \text{ pN}$
- $\langle f \rangle \approx \frac{kT}{100 \text{ nm}} = 0.04 \text{ pN}$
- $\langle f \rangle_{DNA} \approx 0.12 \text{ pN} \cdot \frac{R}{L}$

See overview for arbitrary force (you fix force rather than extension).

By getting $\Omega$, one can express $\langle f \rangle$ as a function of $f$.

\[
\langle f \rangle = N_b \left[ \text{coth} \left( \frac{f_b}{kT} \right) - \frac{kT}{f_b} \right] \frac{f}{f_b}
\]

- Good approximation if $f_b \ll kT$ back to Gaussian.

- Check on Current Opinion plot that approximates fairly well the force-extension behavior of DNA.
- but not as well as the real model... WLC.
WLC - worm-like chain

Continuous, thin, flexible rod, constant contour length

\[ s_{+L} = \text{arc length} \]

\[ \frac{d}{ds} = \text{tangent at } s \]

.. Bending energy (from continuum mechanics)

\[ E_{\text{bend}} = \frac{R_c}{2} \left( \frac{\partial \mathbf{t}}{\partial s} \right)^2 \]

- \( R_c \): radius of curvature
- \( \mathbf{t} \): tangent vector
- \( k_f \): flexural rigidity
- \( Y \): Young's modulus
- \( I \): second moment of inertia
- \( E_{\text{arc}} \): arc energy

\[ \text{continuous model: } E_{\text{arc}} = \frac{k_f}{2} \int_0^L \left( \frac{\partial \mathbf{t}}{\partial s} \right)^2 ds \]

Total internal energy:

\[ U = \frac{k_f}{2} \int_0^L \left( \frac{\partial \mathbf{t}}{\partial s} \right)^2 ds \]

Some properties of the worm-like chain model

- equilibrium (no force)

\[ \langle \mathbf{t}(s) \cdot \mathbf{t}(s + \Delta s) \rangle = \exp \left( \frac{-\Delta s k T}{k_f} \right) \]

- persistence length

\[ \frac{k_f}{k T} \]

- coil size

\[ \langle R^2 \rangle = 2 \ell_p \left[ \frac{L}{\ell_p} + \exp \left( \frac{-L}{\ell_p} \right) - 1 \right] \]

- two regimes

\[ \ell_p \gg L \]

\[ \text{rigid} \Rightarrow \langle R^2 \rangle \rightarrow L^2 \]

\[ \ell_p \ll L \]

- flexible

\[ \text{recall} \quad \langle R^2 \rangle_{\text{FJC}} = b L \]

\[ \ell_p = \frac{b}{2} \]

Conversion between WLC & FJC