

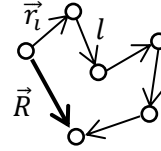
## Freely-Jointed-Chain (FJC) Model

Assumptions:  $N$  elements of fixed length  $l$  and random orientation, full length  $L = N l$ .

### End-to-end distance:

$$\langle \vec{R} \rangle = \left\langle \sum_{i=1}^N \vec{r}_i \right\rangle = \sum_{i=1}^N \underbrace{\langle \vec{r}_i \rangle}_0 = 0$$

with  $\langle \vec{r}_i \rangle = 0$  because random orientation



### Squared end-to-end distance:

$$\langle R^2 \rangle = \langle \vec{R} \cdot \vec{R} \rangle = \left\langle \sum_{i=1}^N \vec{r}_i \cdot \sum_{j=1}^N \vec{r}_j \right\rangle = \left\langle \sum_{i=1}^N \vec{r}_i \cdot \vec{r}_i \right\rangle$$

sort vectors of same and of different indices:  $\sum_{i=1}^N \vec{r}_i \cdot \vec{r}_j = \sum_{i=1}^N r_i^2 + \sum_{i \neq j}^N \vec{r}_i \cdot \vec{r}_j$

$$= \left\langle \sum_{i=1}^N r_i^2 \right\rangle + \left\langle \sum_{i \neq j}^N \vec{r}_i \cdot \vec{r}_j \right\rangle = \sum_{i=1}^N \underbrace{\langle r_i^2 \rangle}_{l^2} + \sum_{i \neq j}^N \underbrace{\langle \vec{r}_i \cdot \vec{r}_j \rangle}_0 = N l^2 = L l$$

with  $\underbrace{\langle \vec{r}_i \cdot \vec{r}_j \rangle}_0$  because random orientation

### Probability distributions:

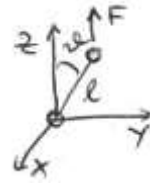
$$p_{1D}(x) \propto e^{-\frac{x^2}{2Nl^2}}$$

$$p_{3D}(R) \propto e^{-\frac{3R^2}{2Nl^2}} \quad \text{with} \quad R^2 = x^2 + y^2 + z^2$$

$$= e^{-\frac{3x^2}{2Nl^2}} \cdot e^{-\frac{3y^2}{2Nl^2}} \cdot e^{-\frac{3z^2}{2Nl^2}} \quad \text{since } x, y, z \text{ independent}$$

## Extension vs. Force:

First, consider just one element of length  $l$ , fixed at one end, and force  $F$  acting on free end. So position of free end  $z = l \cdot \cos \vartheta$ .



What is the average  $z$ -position  $\langle z \rangle$  of the free end?

- a) Without external force  $F = 0$  all configurations  $-l \leq z \leq +l$  equally probable, because  $p(\vartheta, \varphi) \propto e^0 = \text{const}$   
 $\rightarrow$  average  $z$ -position  $\langle z \rangle = \langle l \cdot \cos \vartheta \rangle = l \cdot \underbrace{\langle \cos \vartheta \rangle}_0 = 0$

$$\text{because } \langle \cos \vartheta \rangle = \int \cos \vartheta p(\vartheta, \varphi) d\Omega \propto 2\pi \int_0^\pi \cos \vartheta \sin \vartheta d\vartheta = 0$$

$\frac{1}{2} \sin^2 \vartheta \Big|_0^\pi = 0$

- b) With external force  $F = \text{const}$  in  $z$ -direction

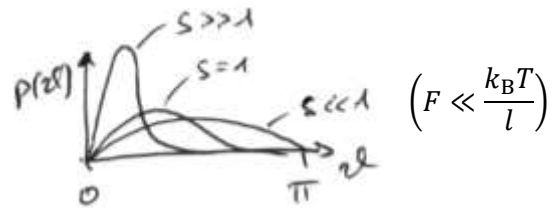
$\rightarrow$  corresponds to potential  $U(z) = -F \cdot z = -F l \cdot \cos \vartheta$

$\rightarrow$  Boltzmann factor  $p(\vartheta, \varphi) = \frac{1}{Z} e^{-\frac{U(z)}{k_B T}} = \frac{1}{Z} e^{+\frac{F l}{k_B T} \cos \vartheta} = \frac{1}{Z} e^{s \cos \vartheta}$  with  $s := \frac{F l}{k_B T}$   
 and with standardization  $Z = \frac{2\pi}{s} (e^{+s} - e^{-s}) = \frac{4\pi}{s} \sinh(s)$

Distribution of  $\vartheta$ :

$$p(\vartheta) = \int_0^\pi p(\vartheta, \varphi) \sin \vartheta d\varphi$$

$$= \frac{s}{2 \sinh(s)} e^{s \cos \vartheta} \sin \vartheta$$



Average  $z$ -position of free end:

$$\langle z \rangle = \langle l \cdot \cos \vartheta \rangle = l \cdot \langle \cos \vartheta \rangle = l \cdot \int \cos \vartheta p(\vartheta, \varphi) d\Omega$$

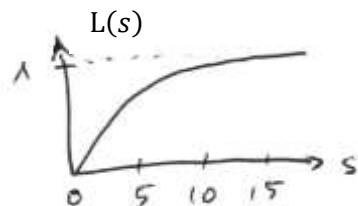
$$= \dots = l \cdot \left[ \frac{e^{+s} + e^{-s}}{e^{+s} - e^{-s}} - 1 \right] = l \cdot L(s)$$

$\frac{\cosh(s)}{\sinh(s)} = \coth(s)$

where  $L(s)$  is the "Langevin function":

$$\text{with } L(s) \cong s/3 \text{ for } s \ll 1$$

$$\cong 1 - 1/s \text{ for } s \gg 1$$



Now we consider the whole chain with  $N$  elements. Since force  $F$  acting on elements is identical for all, their  $z$ -positions add up to the total  $z$ -elongation of the whole chain:

$$\langle z \rangle_{\text{total}} = N \cdot \langle z \rangle = \underbrace{N l}_L \cdot L(s)$$