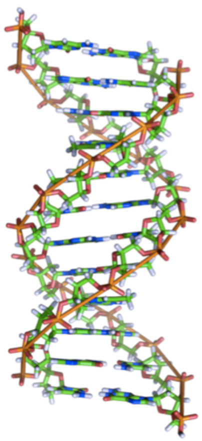
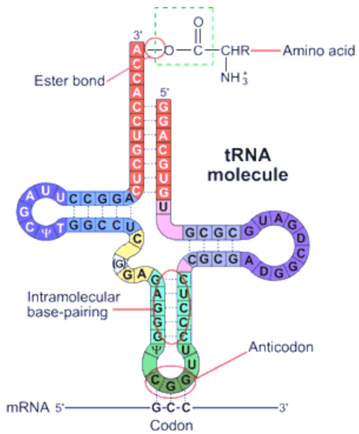
BioPolymer Statistics I

Basic Theory

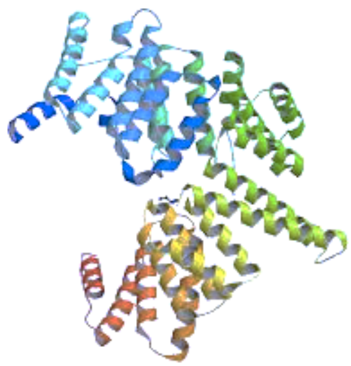
BioPolymers



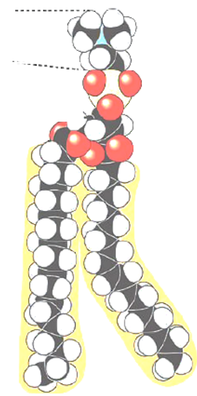
DNA



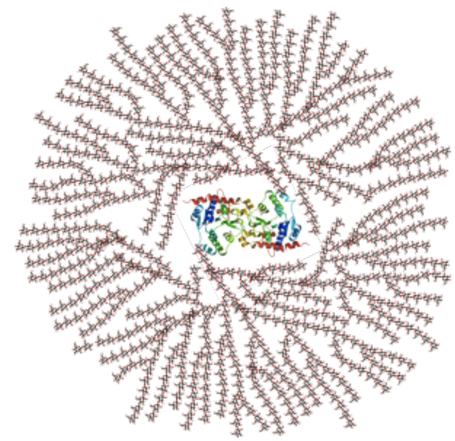
RNA



proteins



lipids



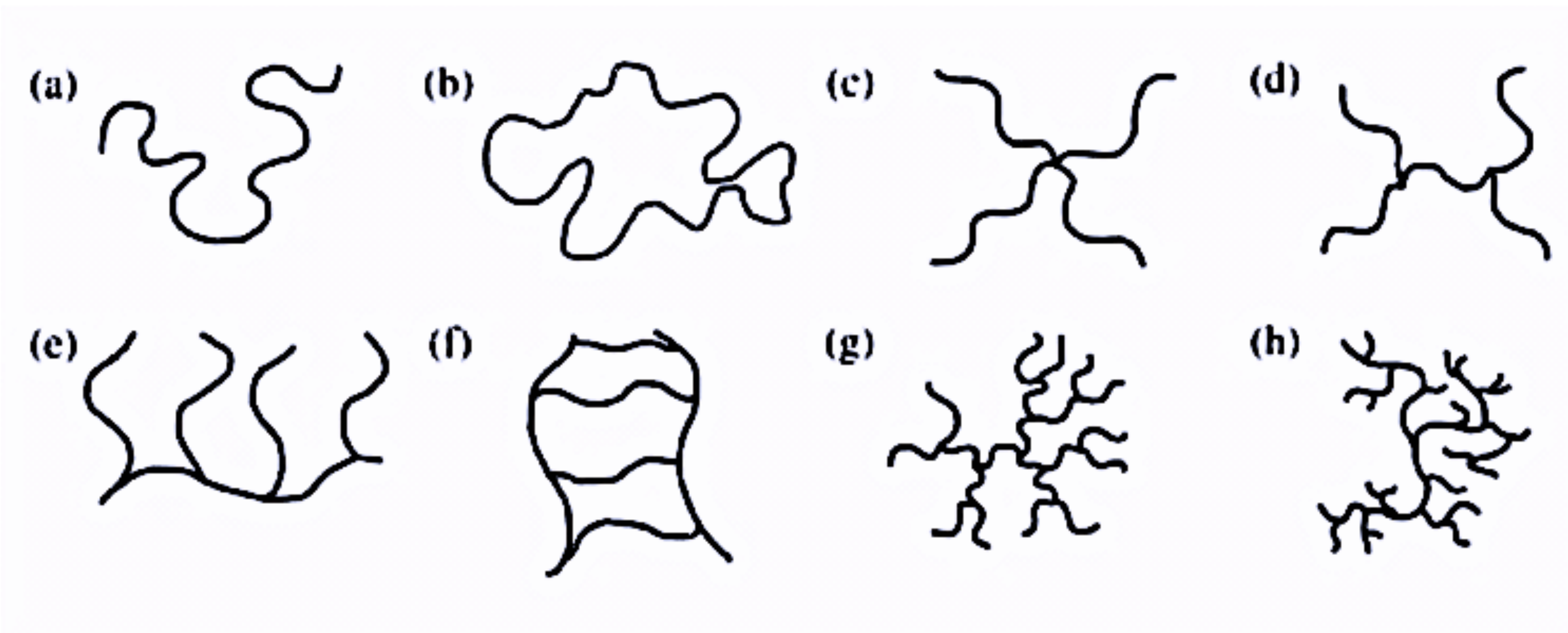
polysaccharides

BioPolymers

THE PROPERTIES OF BIOPOLYMERS DEPEND ON:

- CHEMICAL COMPOSITION OF THE MONOMER
- DEGREE OF POLYMERIZATION
- FLEXIBILITY
- ARCHITECTURE
- HOMO- VS. HETERO-POLYMER

ARCHITECTURE



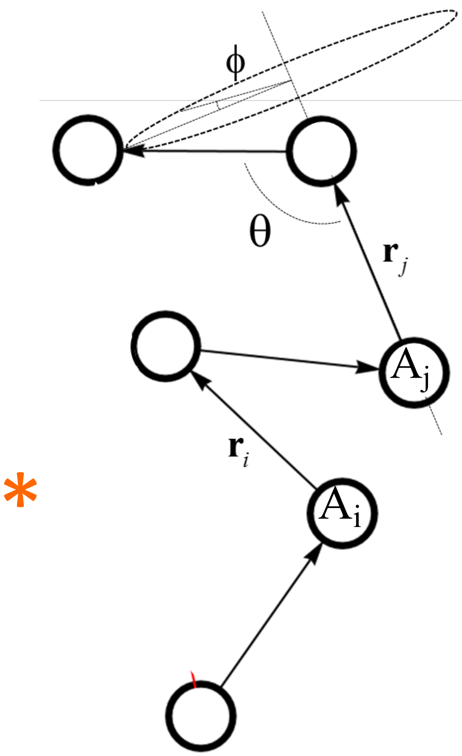
BioPolymers

a disordered/unfolded
protein or single-stranded
nucleic acid
is very dynamic and
explores many different
conformations.

ideal chain

AN IDEAL CHAIN HAS NO NET INTERACTIONS BETWEEN TWO ELEMENTS A_i AND A_j.

*



ideal chain

CONFORMATIONS

HOW CAN WE DESCRIBE THE CONFORMATIONS OF AN IDEAL CHAIN?

CONFORMATIONS

HOW CAN WE DESCRIBE THE CONFORMATIONS OF AN IDEAL CHAIN?

WE NEED TO INTRODUCE SOME USEFUL QUANTITIES:

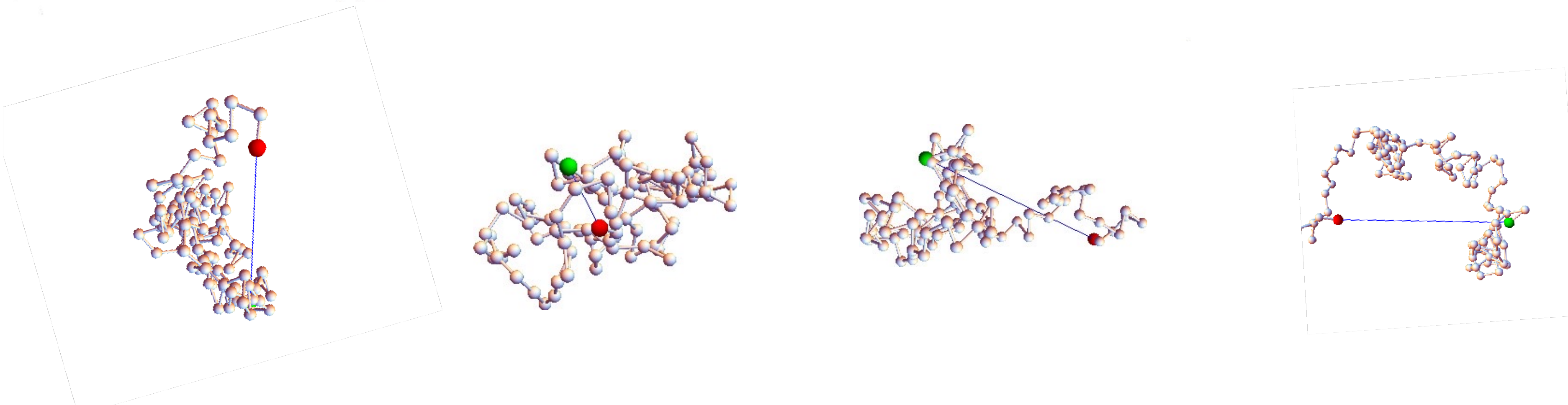
- END-TO-END VECTOR
- RADIUS OF GYRATION
- ASPHERICITY AND SHAPE FACTOR
- DISTANCE DISTRIBUTION

ideal chain

SINCE A POLYMER ADOPTS MANY CONFORMATIONS, WE ARE INTERESTED IN <u>AVERAGE PROPERTIES</u>!

$\Downarrow$

$\langle \dots \rangle$: WE ARE GOING TO CONSIDER AVERAGE OVER ALL CONFORMATIONS IN THE ENSEMBLE



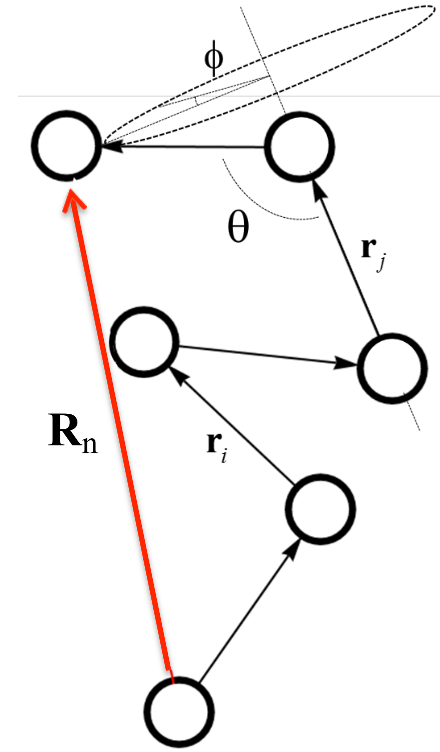
end-to-end vector

THE END-TO-END VECTOR IS THE SUM OF ALL m BOND VECTORS r_m IN THE CHAIN

$$\vec{R}_m = \sum_{i=1}^{m} \vec{r}_i$$

END TO END VECTOR

BOND VECTOR



end-to-end vector

SINCE THERE IS NO PREFERRED DIRECTION FOR AN IDEAL CHAIN, THE MEAN END TO END VECTOR IS EQUAL TO ZERO :

$$\boxed{\langle \vec{R}_M \rangle = 0 \quad \left(= \sum_{i=1}^{M} \langle r_i \rangle \right)} \; *$$

$-\vec{R}_M$ HAS THE SAME PROBABILITY OF $+\vec{R}_M$

end-to-end vector

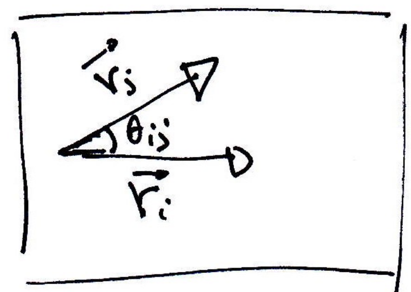
WHAT ABOUT THE "MEAN-SQUARE END-TO-END DISTANCE"?

$$\langle R^2 \rangle \equiv \langle \vec{R}_M^{\,2} \rangle = \langle \vec{R}_M \cdot \vec{R}_M \rangle =$$

ASSUMING THE VECTOR BOND HAS CONSTANT LENGTH

$$|\vec{r}_i| = b$$

$$= \boxed{M b^2 + b^2 \sum_{i=1}^{M} \sum_{j \neq i} \langle \cos \theta_{ij} \rangle}$$



demonstration

$$\langle R^2 \rangle \equiv \langle \vec{R}^2_m \rangle = \langle \vec{R}_m \cdot \vec{R}_m \rangle =$$

$$= \left\langle \left(\sum_{i=1}^{m} \vec{r}_i \right) \left(\sum_{j=1}^{m} \vec{r}_j \right) \right\rangle =$$

$$= \left\langle \sum_{i=1}^{m} \vec{r}_i \cdot \vec{r}_i + \sum_{i=1}^{m} \sum_{j \neq i} \vec{r}_i \cdot \vec{r}_j \right\rangle =$$

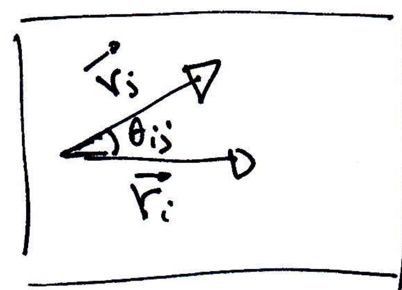
MEAN OF THE SUM IS THE SUM OF THE MEANS

$$= \left\langle \sum_{i=1}^{m} |\vec{r}_i|^2 \right\rangle + \left\langle \sum_{i=1}^{m} \sum_{j \neq i} \vec{r}_i \vec{r}_j \right\rangle =$$

ASSUMING THE VECTOR BOND HAS CONSTANT LENGTH

$$|\vec{r}_i| = b$$

$$= \left\langle \sum_{i=1}^{m} b^2 \right\rangle + \left\langle \sum_{i=1}^{m} \sum_{j \neq i} b^2 \cos\theta_{ij} \right\rangle =$$

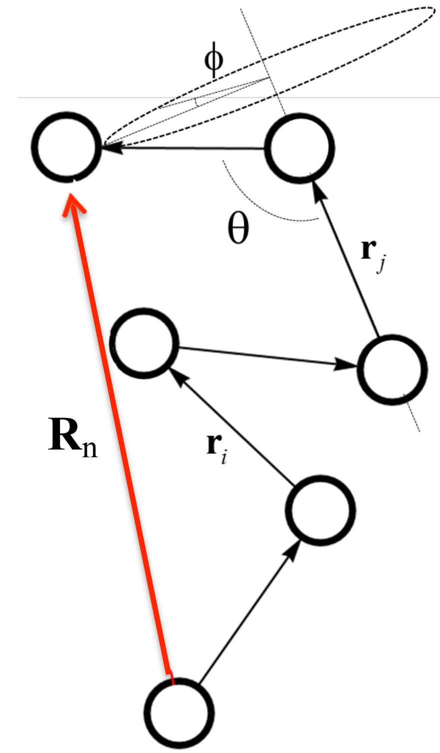


$$= \boxed{m b^2 + b^2 \sum_{i=1}^{m} \sum_{j \neq i} \langle \cos\theta_{ij} \rangle}$$

Freely jointed chain

$|\mathbf{r}_i| = b$ fixed

θ, ϕ free



Freely jointed chain

$|\mathbf{r}_i| = b$ fixed

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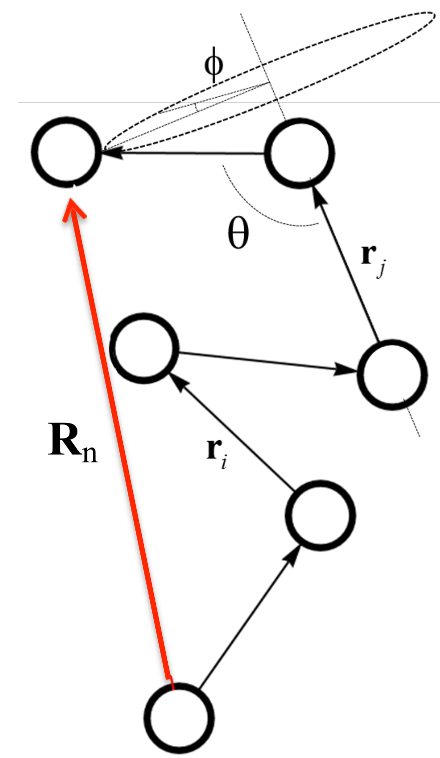


$$\langle R^2 \rangle = \boxed{n b^2 + b^2 \sum_{i=1}^{n} \sum_{j \neq i} \langle \cos \theta_{ij} \rangle}$$

FOR A "FREELY JOINTED CHAIN" THERE IS NO CORRELATION BETWEEN THE DIRECTION OF DIFFERENT BONDS, SO $\langle \cos \theta_{ij} \rangle = 0$ AND $\boxed{\langle R^2 \rangle = n b^2}$ *

Flory's characteristic ratio

IN A TYPICAL POLYMER $\langle \cos\theta_{ij} \rangle \neq 0$

AND ONLY WHEN $\lim_{|i-j| \to \infty} \langle \cos\theta_{ij} \rangle = 0$.

IN THIS CASE:

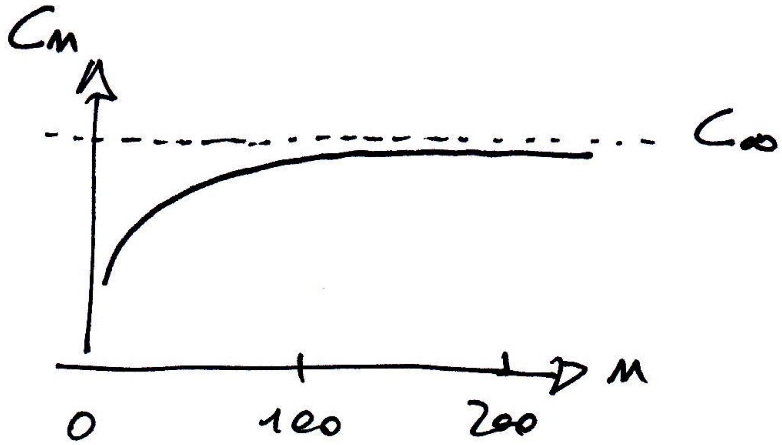
$$\langle R^2 \rangle = b^2 \sum_{i=1}^{n} \underbrace{\sum_{j=1}^{n} \langle \cos\theta_{ij} \rangle}_{C_i} = b^2 \sum_{i=1}^{n} C_i = C_n n b^2$$

$$\boxed{C_n = \frac{1}{n} \sum_{i=1}^{n} C_i}$$

FLORY'S CHARACTERISTIC RATIO

C_n

Flory's characteristic ratio



FLORY'S CHARACTERISTIC RATIO

FOR SUFFICIENTLY LONG CHAINS

$$\boxed{\langle R^2 \rangle \cong C_\infty n b^2}$$

Kuhn segment

- LET'S DEFINE A DIFFERENT SEGMENT:

$$N_K b_K = l_c$$

CONTOUR LENGHT

$\boxed{\text{THE KUHN SEGMENT}}$ *

NUMBER OF KUHN SEGMENTS (N_K)

LENGTH OF KUHN SEGMENTS (b_K)

$$\begin{cases} \langle R^2 \rangle = N_K b_K^2 = C_\infty n b^2 \\ N_K b_K = l_C = n b \end{cases}$$

THEREFORE:

$$N_K = \frac{n^2 b^2}{C_\infty n b^2} = \frac{l_c^2}{C_\infty n b^2}$$

$$b_K = \frac{C_\infty n b^2}{l_c}$$

Kuhn segment

• HOW TO USE KUHN SEGMENTS ?

FOR A GIVEN SYSTEM WE USUALLY KNOW THE CONTOUR LENGTH AND WE CAN ACCESS THE END-TO-END DISTANCE

$$\langle R^2 \rangle,\ l_c \ \text{KNOWN} \Rightarrow \begin{cases} l_c = N_K b_K \\ \langle R^2 \rangle = N_K b_K^2 \end{cases}$$

$$\Downarrow$$

$$\boxed{b_K = \frac{\langle R^2 \rangle}{l_c}} \ * \qquad \boxed{N_K = \frac{l_c}{b_K} = \frac{l_c^2}{\langle R^2 \rangle}} \ *$$

Kuhn segment

- HOW TO USE KUHN SEGMENTS ?

ANY SEGMENT OF AN IDEAL CHAIN R_{ij} FOR $|i-j| >> 0$ IS "IDEAL" AND FOLLOWS THE SAME STATISTICS

$\langle R_{ij}^2 \rangle$ UNKNOWN / $\langle R^2 \rangle$, l_c KNOWN

$$\frac{\langle R_{ij}^2 \rangle}{\langle R^2 \rangle} = \frac{N_K^{ij}\, \cancel{b_K^2}}{N_K\, \cancel{b_K^2}} = \frac{(i-j)\,\cancel{b}}{n\,\cancel{b}}$$

O-END DISTANCE SCALES WITH NUMBER OF

Kuhn segment

• HOW TO USE KUHN SEGMENTS ?

ANY SEGMENT OF AN IDEAL CHAIN R_{ij} FOR $|i-j| \gg 0$ IS "IDEAL" AND FOLLOWS THE SAME STATISTICS

$\langle R_{ij}^2 \rangle$ UNKNOWN / $\langle R^2 \rangle$, l_c KNOWN

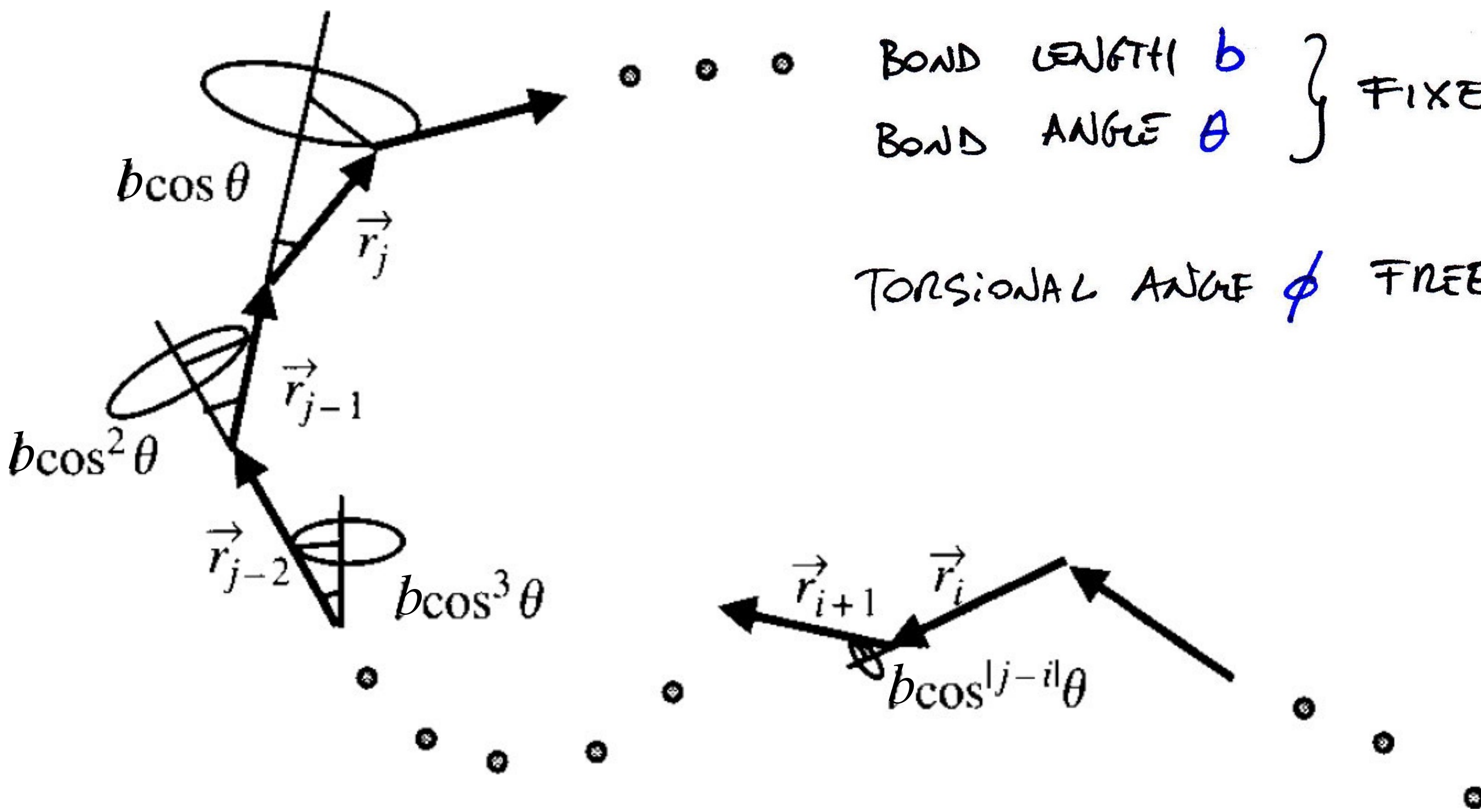
$$\frac{\langle R_{ij}^2 \rangle}{\langle R^2 \rangle} = \frac{N_K^{ij} \, \cancel{b_K^2}}{N_K \, \cancel{b_K^2}} = \frac{(i-j) \cancel{b}}{n \cancel{b}}$$

*

• THE MEAN-SQUARE END-TO-END DISTANCE SCALES WITH NUMBER OF BONDS

*

Freely rotating chain

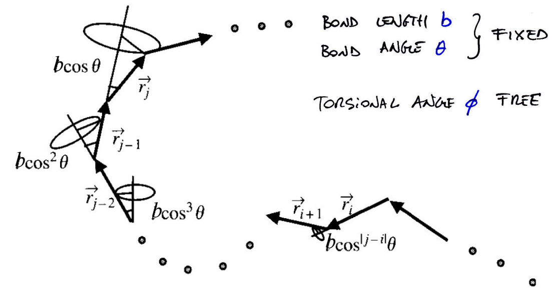


BOND LENGTH b
BOND ANGLE θ } FIXED

TORSIONAL ANGLE ϕ FREE

Freely rotating chain

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



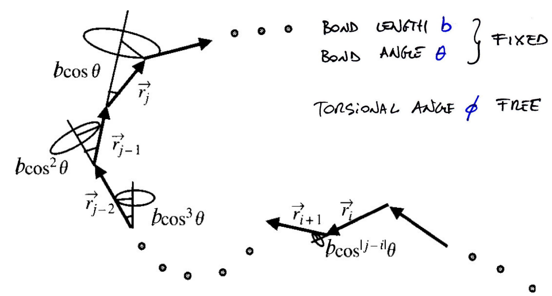
$$\langle \vec{r}_i \cdot \vec{r}_j \rangle = b^2 \underbrace{\cos\theta^{|i-j|}}_{=\, e^{|i-j| \log(\cos\theta)}}$$

$$e^{|i-j| \log(\cos\theta)} = e^{-\frac{|i-j|}{s_p}} = e^{-\frac{|i-j| b}{\underbrace{s_p b}_{l_p}}}$$

AFTER s_p SEGMENTS THE CHAIN STARTS TO LOSE MEMORY OF THE PREVIOUS CONFIGURATION!

$\boxed{s_p \cdot b}$ DEFINES THE "PERSISTENCE LENGTH" $\boxed{l_p}$

Freely rotating chain



$$\boxed{\langle R^2 \rangle = b^2 \sum_{i=1}^{M} \sum_{j=1}^{M} e^{-\frac{|i-j|\, b}{l_p}}}$$

$$\langle R^2 \rangle = 2 l_p l_c - 2 l_p^2 \left(1 - e^{-l_c/l_p}\right)$$

Freely rotating chain

$$\langle R^2 \rangle = 2 l_p l_c - 2 l_p^2 \left(1 - e^{-l_c/l_p}\right)$$

$\boxed{\text{TWO LIMITS}}$:

① $\boxed{l_c >> l_p}$

FLEXIBLE CHAIN

$$\langle R^2 \rangle = 2 l_p l_c = N_K b_K^2 = b_K N_K b_K$$

FROM KUHN SEGMENT WE CAN COMPUTE THE PERSISTENCE LENGTH AND VICEVERSA

$$\boxed{b_K = 2 l_p}$$

*

② $\boxed{l_p >> l_c}$

ROD - LIKE

TAYLOR SERIES OF e^{-l_c/l_p}

$$\left(e^{-x} = 1 - x + \frac{1}{2} x^2 - \frac{1}{6} x^3 \dots\right)$$

$$\langle R^2 \rangle = l_c^2 - \frac{l_c^3}{3 l_p} + \dots$$