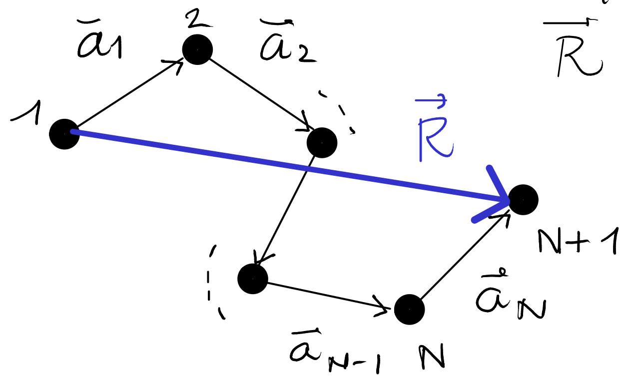
CATENA IDEALE

- N+1 monomeri
- lunghezza di legame $a = \text{cost}$
- orientazioni indipendenti

$\Big\}$ RW



$$\vec{a}_i = \vec{r}_{i+1} - \vec{r}_i$$
$$\vec{R} = \vec{r}_{N+1} - \vec{r}_1$$

$$\langle \vec{a}_i \cdot \vec{a}_j \rangle = \begin{cases} a^2 & i=j \\ 0 & i \neq j \end{cases} = a^2 \delta_{ij} \qquad \langle \vec{a}_i \rangle = \vec{0}$$

Vettore end-to-end

$$\langle \vec{R} \rangle = \langle \sum_{i=1}^{N} \vec{a}_i \rangle = \vec{0}$$

Distanza end-to-end

$$\boxed{\langle |\vec{R}|^2 \rangle} = \langle \Big(\sum_{i=1}^{N} \vec{a}_i \Big) \cdot \Big(\sum_{j=1}^{N} \vec{a}_j \Big) \rangle = \sum_{i=1}^{N} \underbrace{\langle \vec{a}_i \cdot \vec{a}_i \rangle}_{=a^2} + \sum_{i=1}^{N} \sum_{j \neq i} \underbrace{\langle \vec{a}_i \cdot \vec{a}_j \rangle}_{=0} = \boxed{a^2 N} \sim N$$

$$\langle \vec{a}_i \cdot \vec{a}_j \rangle = \underbrace{\langle \vec{a}_i \rangle}_{=0} \cdot \underbrace{\langle \vec{a}_j \rangle}_{=0}$$

Distribuzione di prob. per $\vec{R}$ (teor. limite centrale $\rightarrow$ Gaussiana)

$$\langle |\vec{R}|^2 \rangle = \langle R_x^2 \rangle + \langle R_y^2 \rangle + \langle R_z^2 \rangle = 3 \langle R_x^2 \rangle$$

$$p(\vec{R}) = p(R_x)\, p(R_y)\, p(R_z) \qquad \langle R_x \rangle = 0 \qquad \langle R_x^2 \rangle - \underbrace{\langle R_x \rangle^2}_{=0} = \frac{\langle |\vec{R}|^2 \rangle}{3} = \frac{a^2}{3} N$$

$$\simeq \left(\frac{3}{2\pi a^2 N} \right)^{3/2} \exp\left[- \frac{R_x^2 + R_y^2 + R_z^2}{2\, a^2/3\, N} \right]$$

se $N \gtrsim N_0 = 10$

$|\vec{R}| < aL$

$$p(\vec{R}) = \left(\frac{3}{2\pi a^2 N} \right)^{3/2} \exp\left[- \frac{3 |\vec{R}|^2}{2a^2 N} \right]$$

$\vec{R} \to$ macrostato

$\{ \vec{r}_1, \dots, \vec{r}_{N+1} \} \to$ microstato

Energia libera:

$$F(\vec{R}) = -K_B T \ln Z = -K_B T \ln[\Omega(\vec{R})]$$

$$= -K_B T \ln[p(\vec{R})] + \text{cost}$$

$$F(\vec{R}) = \frac{1}{2} \frac{3 K_B T}{a^2 N} |\vec{R}|^2 \to \text{elasticità entropica}$$

CATENA GAUSSIANA

- $M+1$ monomeri $\longrightarrow \vec{R}_1, \dots, \vec{R}_{M+1}$
- $\vec{b}_i$ segmenti indipendenti e distribuiti come Gaussiana

$$p(\vec{b}_i) = \left(\frac{3}{2\pi b^2}\right)^{3/2} \exp\left[-\frac{3|\vec{b}_i|^2}{2b^2}\right] \quad \rightarrow \quad \langle \vec{b}_i \rangle = 0 \qquad \langle |\vec{b}_i|^2 \rangle = b^2 = \text{cost}$$

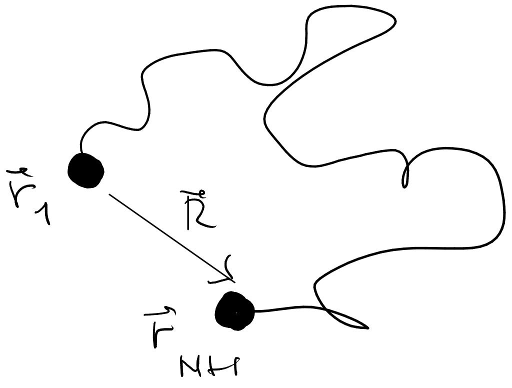
Prob. $\{\vec{R}_1, \dots, \vec{R}_{M+1}\}$

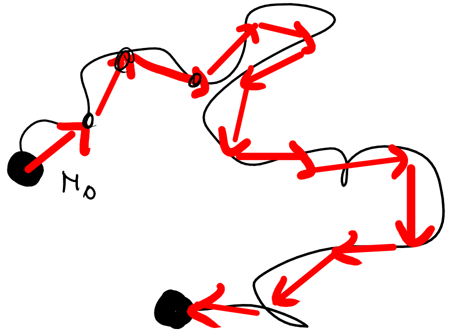
$$p(\vec{R}_1, \dots, \vec{R}_{M+1}) = \left(\frac{3}{2\pi b^2}\right)^{3M/2} \exp\left[-\frac{3\sum_{i=1}^{M} |\vec{b}_i|^2}{2b^2}\right] \quad \Rightarrow \quad \langle |\vec{R}|^2 \rangle = b^2 M$$

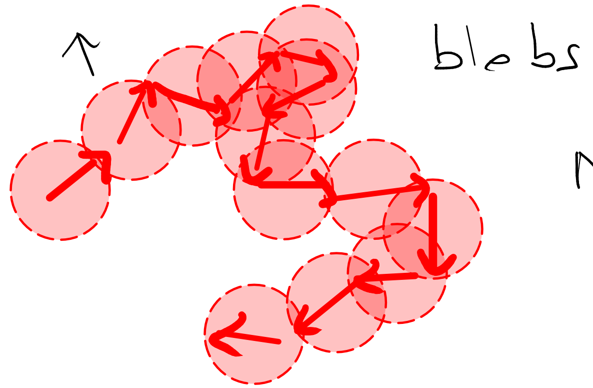
$$= \left(\frac{3}{2\pi b^2}\right)^{\frac{3M}{2}} \exp\left[-\frac{3}{2b^2}\sum_{i=1}^{M} |\vec{R}_{i+1} - \vec{R}_i|^2\right] \qquad \vec{R} = \sum_{i=1}^{M} \vec{b}_i$$

Giustificazione: catena ideale coarse-grained

$$\langle |\vec{b}_i|^2 \rangle = a^2 N_0 = b^2$$ segmenti di <u>Kuhn</u>







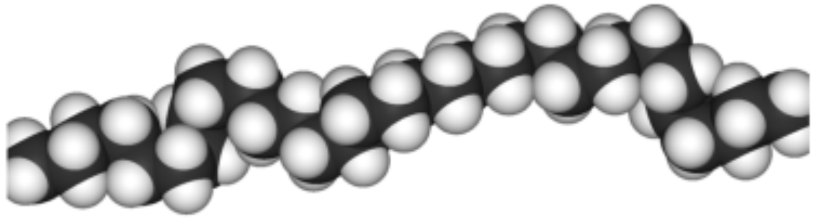
$$N \rightarrow N = M N_0$$

Interpretazione meccanica: equilibrio a T, $p(\{\bar{R}_i\}) = \frac{1}{Z} \exp\left[-\frac{H(\{\bar{R}_i\})}{k_B T}\right]$

$$H(\bar{R}_1, \dots, \bar{R}_{M+1}) = \frac{1}{2} \frac{3 k_B T}{b^2} \sum_{i=1}^{M} |\bar{R}_{i+1} - \bar{R}_i|^2$$

$\sim$ catena di oscillatori armonici accoppiati

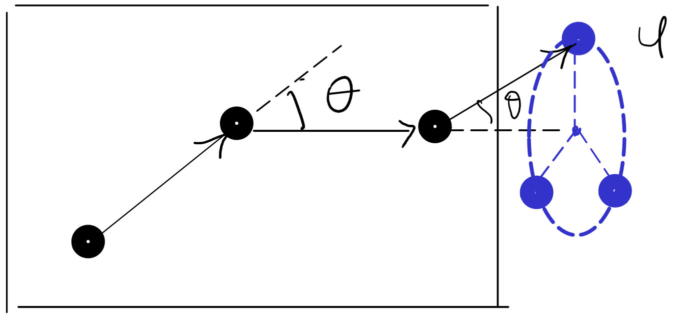
MODELLO DI KRATKY – POROD

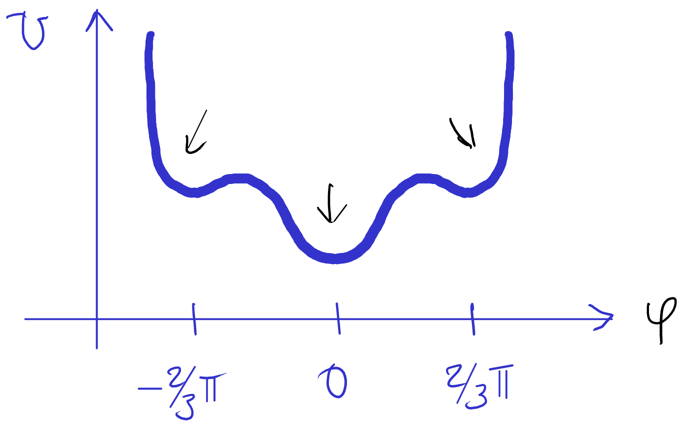


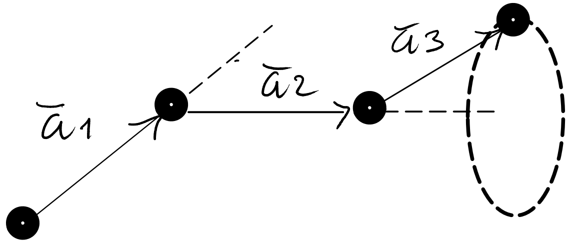
Polietilene $[CH_2]_N$

distanza di legame : $a \approx 1{,}5$ Å

angolo di legame : $\theta \approx 68°$







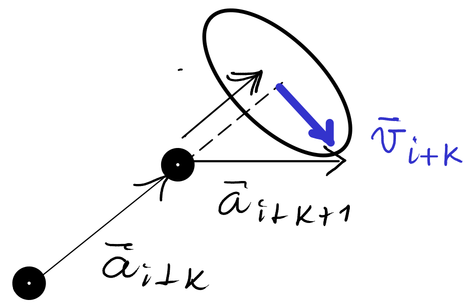
- N+1 monomeri
- distanza legame a = cost
- angolo legame θ = cost
- angolo torsione libero

Caso ideale: $\langle \bar{a}_i \cdot \bar{a}_{i+1} \rangle = 0 \quad \forall\, i$

Modello Kratky-Porod : $\langle \bar{a}_i \cdot \bar{a}_{i+1} \rangle = a^2 \cos\theta$

(freely rotating chain)

$$\langle \bar a_i \cdot \bar a_{i+k} \rangle = a^2 (\cos\theta)^k \qquad \cos\theta < 1$$



dim : induzione $k \Rightarrow k+1$

$$\langle \bar a_i \cdot \bar a_{i+k+1} \rangle = \langle \bar a_i \cdot (\bar a_{i+k} \cdot \cos\theta + \vec v_{i+k}) \rangle$$

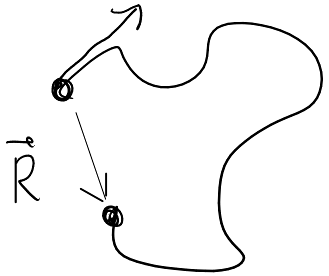
$$= \cos\theta \cdot a^2 (\cos\theta)^k + \underbrace{\langle \bar a_i \cdot \vec v_{i+k} \rangle}_{\langle \bar a_i \rangle \cdot \langle \vec v_{i+k} \rangle} = a^2 (\cos\theta)^{k+1}$$

$$\langle \bar a_i \rangle = \bar 0 \qquad \langle \vec v_{i+k} \rangle = \bar 0$$

$\square$

Lunghezza di persistenza

$$\left\langle \frac{\bar a_1}{a} \cdot \vec R \right\rangle = \frac{1}{a} \left\langle \bar a_1 \cdot \sum_{i=1}^{N} \bar a_i \right\rangle = \frac{1}{a} \sum_{i=1}^{N} \langle \bar a_1 \cdot \bar a_i \rangle = a \sum_{i=1}^{N} (\cos\theta)^{i-1} \qquad \cos\theta = r$$



$$= a \, \frac{1-(\cos\theta)^N}{1-\cos\theta} \qquad \sum_{i=1}^{N} r^{i-1} = \frac{1-r^N}{1-r}$$

$$N \to \infty \Rightarrow \left\langle \frac{\bar a_1}{a} \cdot \vec R \right\rangle \to \frac{a}{1-\cos\theta} \equiv l_p$$

Distanza end-to-end

$$\langle |\vec{R}|^2 \rangle = \sum_{i=1} \sum_{j=1} \langle \bar{a}_i \cdot \bar{a}_j \rangle = N a^2 + \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \langle \bar{a}_i \cdot \bar{a}_j \rangle = N a^2 + 2 a^2 \sum_{i=1}^{N} \sum_{j>i} (\cos\theta)^{j-i}$$

$j \neq i$

$$= a^2 N + 2a^2 \underbrace{\sum_{i=1}^{N} (\cos\theta)^{-i}}_{2} \underbrace{\sum_{j=i+1}^{N} (\cos\theta)^{j}}_{1} \underset{\text{(es.)}}{=} \ldots = a^2 N \left[\frac{1+\cos\theta}{1-\cos\theta} - \frac{2\cos\theta}{N} \frac{1-(\cos\theta)^{N+1}}{(1-\cos\theta)^2} \right]$$

$N \to \infty$:

$$\langle |\vec{R}|^2 \rangle \approx a^2 \frac{1+\cos\theta}{1-\cos\theta} N \sim N \qquad b^2 M$$

$$= \underbrace{a^2 \left(\frac{1+\cos\theta}{1-\cos\theta} \right)^2}_{b^2} \underbrace{\frac{1-\cos\theta}{1+\cos\theta} N}_{M} = b^2 M \qquad \text{(catena Gaussiana)}$$

segmento Kuhn

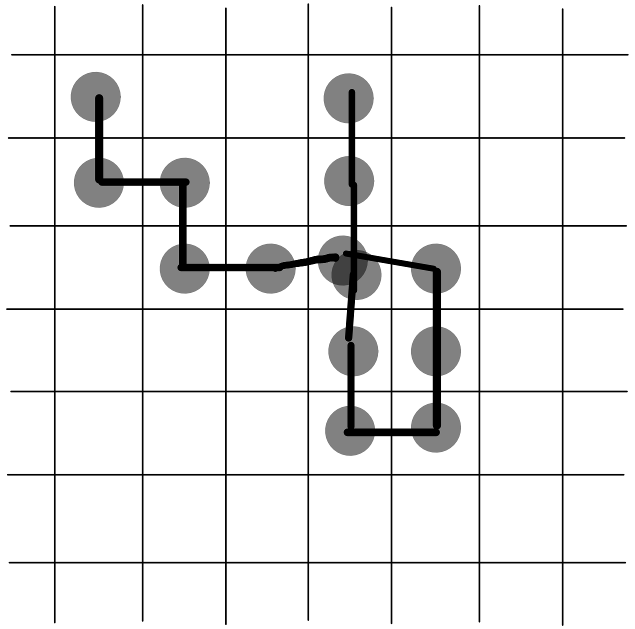
Forte persistenza : $\theta \ll 1$

$$\langle |\vec{R}|^2 \rangle \approx a^2 \frac{1+1+\theta^2/2}{\theta^2/2} N = a^2 \frac{2+\theta^2/2}{\theta^2/2} N \approx \frac{4a^2}{\theta^2} N = \underbrace{a^2 \left(\frac{4}{\theta^2}\right)^2}_{b^2} \underbrace{\frac{\theta^2}{4} N}_{M}$$

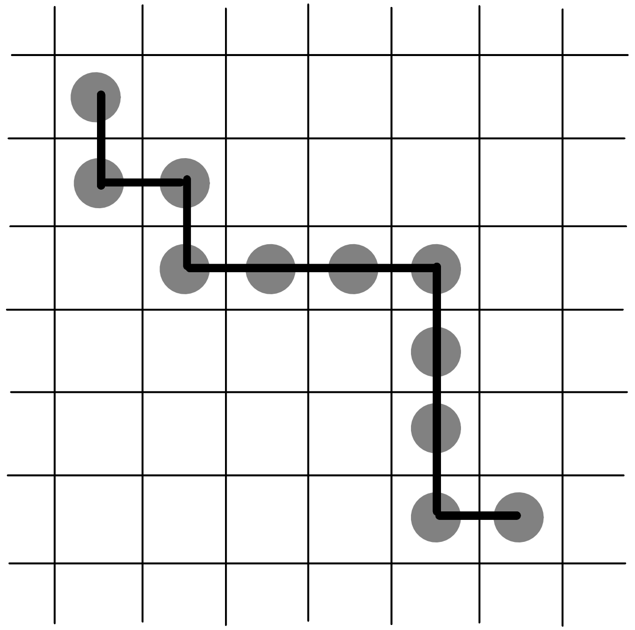
$$b = a \frac{4}{\theta^2} = 4 \frac{a}{\theta^2}$$

$$l_p \equiv \frac{a}{1-\cos\theta} \approx \frac{a}{\theta^2/2} = 2 \frac{a}{\theta^2} = \frac{b}{2}$$

MODELLI SU RETICOLO



RW
discreto



SAW
Self-avoiding
walk