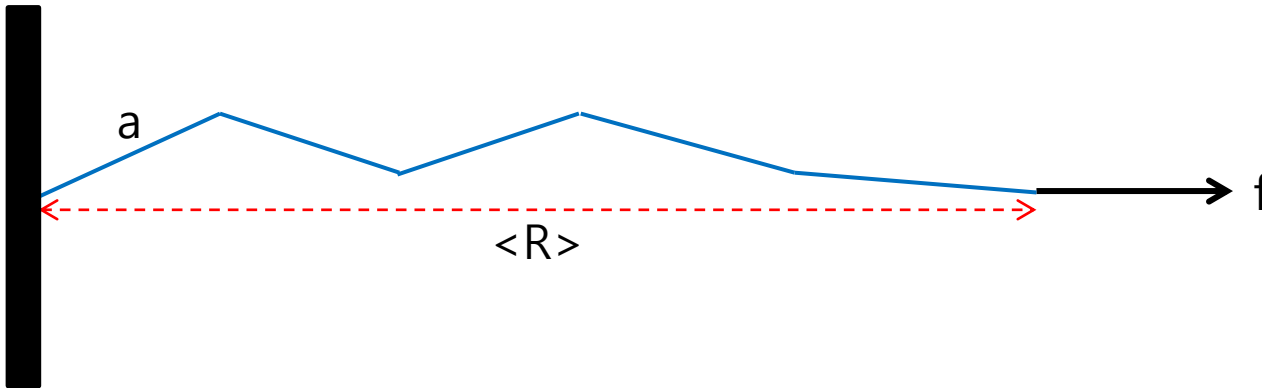


freely jointed chain for Force-extension curves

Why we study this subject?



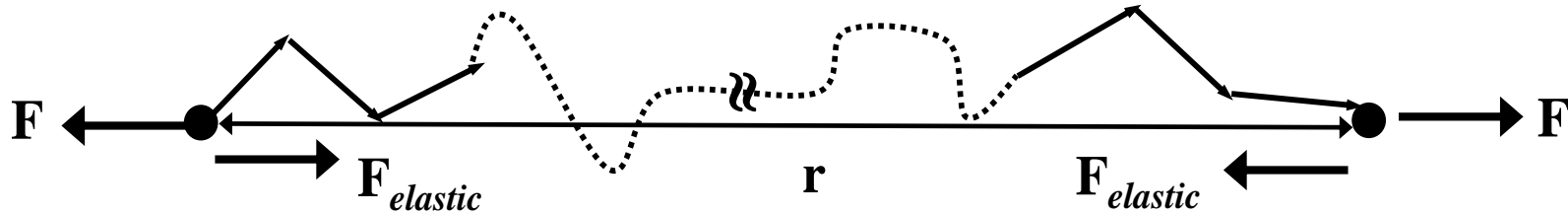
In the presence of a force, F , the segments tend to align in the direction of the force.

Opposing the stretching is the tendency of the chain to maximize its entropy.

Extension corresponds to the equilibrium.

We want know that relation of the external force and the entropic elastic force of the chain.

Freely jointed chain model (briefly)



Head in one direction for length a
then turn in any direction for length a

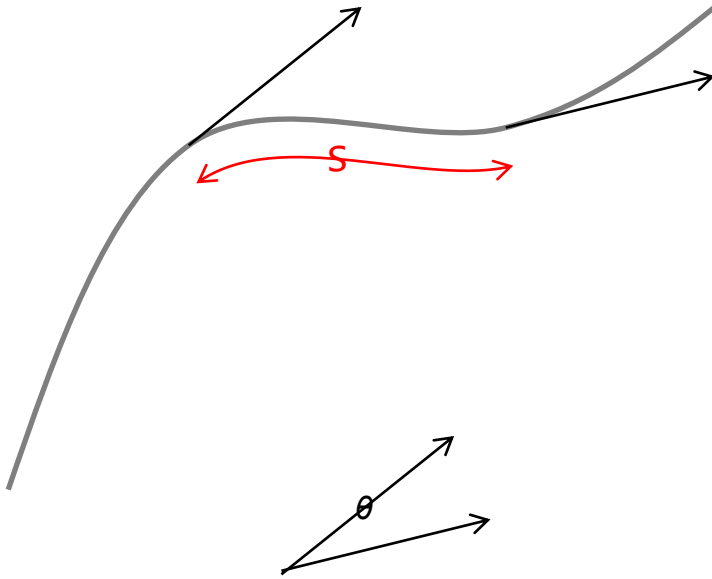
$a = \text{Kuhn length} = 0.5P$
where $P = \text{Persistence Length}$

Completely straight, unstretchable.

No thermal fluctuations away from straight line are allowed

The polymer can only disorder at the joints between segments

Worm-like chain model(briefly)



$$\langle \vec{t}(s) \cdot \vec{t}(0) \rangle = \langle \cos \theta(s) \rangle = e^{-s/P}$$

s is tangent vector at a distance

θ is between a vector that is tangent to the polymer

p = persistence length

length over which statistical segments remain directionally correlated in space

Directed random walk"- segments are correlated, polymer chains intermediate between a rigid rod and a flexible coil (e.g. DNA)

takes into account both local stiffness and long range flexibility

chain is treated as an isotropic, homogeneous elastic rod whose trajectory varies continuously and smoothly through space as opposed to the jagged contours of the FJC

Distribution of end to end vectors

be the number of different possible trajectories for a position x in N steps

$$W(N, x) = \frac{(N_+ + N_-)!}{N_+! N_-!} = \frac{N!}{[(N+x)/2]! [(N-x)/2]!} \quad N! = 1 \cdot 2 \cdot 3 \cdot 4 \cdots N$$

Each step has two possibilities, which are independent from step to step

$$\frac{W(N, x)}{2^N} = \frac{1}{2^N} \frac{N!}{[(N+x)/2]! [(N-x)/2]!}$$

probability distribution function

$$P_{1d}(N, x) = \frac{1}{\sqrt{2\pi N}} \exp\left(-\frac{x^2}{2N}\right)$$

	$N=1$	$N=2$	$N=3$	$N=4$
$x=-4$	0	0	0	1
$x=-3$	0	0	1	0
$x=-2$	0	1	0	4
$x=-1$	1	0	3	0
$x=0$	0	2	0	6
$x=1$	1	0	3	0
$x=2$	0	1	0	4
$x=3$	0	0	1	0
$x=4$	0	0	0	1

Rewrite probability distribution function in 1-D

$$P_{1d}(N, R_x) = \frac{1}{\sqrt{2\pi \langle R_x^2 \rangle}} \exp\left(-\frac{R_x^2}{2 \langle R_x^2 \rangle}\right) = \frac{1}{\sqrt{2\pi N a^2}} \exp\left(-\frac{R_x^2}{2 N a^2}\right)$$

Probability distribution function in 3-D

$$P_{3d}(N, \vec{R}) dR_x dR_y dR_z = P_{1d}(N, R_x) dR_x P_{1d}(N, R_y) dR_y P_{1d}(N, R_z) dR_z$$

$$P_{3d}(N, \vec{R}) = \left(\frac{3}{\sqrt{2\pi \langle R_x^2 \rangle}} \right)^{\frac{3}{2}} \exp\left(-\frac{3(R_x^2 + R_y^2 + R_z^2)}{2 \langle R_x^2 \rangle}\right) = \frac{1}{\sqrt{2\pi N a^2}} \exp\left(-\frac{3\vec{R}^2}{2 N a^2}\right)$$

Free energy of FJC model

1-D case

Entropy S is

$$S = k \ln \Omega$$

k : Boltzmann constant , Ω : number of states

$\Omega(N, \vec{R})$ as the number of conformations of a freely jointed chain of N monomers with end to end vector \mathbf{R}

Rewrite S is $S(N, \vec{R}) = k \ln \Omega(N, \vec{R})$

The probability distribution function is the fraction of all conformations that actually have an end to end vector \mathbf{R} between \mathbf{R} and $\mathbf{R}+d\mathbf{R}$


$$P_{1d}(N, \vec{R}) = \frac{\Omega(N, \vec{R})}{\int \Omega(N, \vec{R}) d\vec{R}}$$

Probability distribution is

$$P_{1d}(N, R_x) = \frac{1}{\sqrt{2\pi \langle R_x^2 \rangle}} \exp\left(-\frac{R_x^2}{2\langle R_x^2 \rangle}\right) = \frac{1}{\sqrt{2\pi Na^2}} \exp\left(-\frac{R_x^2}{2Na^2}\right)$$

We obtain entropy

$$S(N, \vec{R}) = -\frac{1}{2}k \frac{\vec{R}^2}{Na^2} + \frac{1}{2}k \ln\left(\frac{1}{2\pi Na^2}\right) + k \ln\left[\int \Omega(N, \vec{R}) d\vec{R}\right]$$


 Depend only on the number of monomers N $S(N, 0)$

Helmholtz free energy of the chain

$$F(N, \vec{R}) = U(N, \vec{R}) - TS(N, \vec{R})$$

We obtain free energy

$$F(N, \vec{R}) = \frac{1}{2}kT \frac{\vec{R}^2}{Na^2} + F(N, 0)$$

$$F(N, 0) = U(N, 0) - TS(N, 0)$$

Free energy of the chain
Both ends at the same point

Finally, we obtain the force-extension equation

$$f_x = \frac{\partial F(N, \vec{R})}{\partial R_x} = \frac{kT}{Na^2} R_x = \frac{kT}{a} \left(\frac{R_x}{R_{\max}} \right)$$

This is like a simple elastic spring

3-D case (using same method such as 1-D case)

$$\vec{f} = \frac{\partial F(N, \vec{R})}{\partial \vec{R}} = \frac{3kT}{Na^2} \vec{R}$$

This equation also like a simple elastic spring

Other calculate

Partition function is

$$Z = \sum_{states} \exp\left(-\frac{fR_z}{kT}\right)$$

The sum of the Boltzmann factors over all possible conformations of the chain

The sum over all possible conformations of a freely jointed chain corresponds to the integral over all possible orientations of all bond vectors of the chain

$$Z = \sum_{states} \exp\left(-\frac{fR_z}{kT}\right) = \int \exp\left(-\frac{fR_z}{kT}\right) \prod_{i=1}^N \sin \theta_i d\theta_i d\varphi_i$$

notation $\prod_{i=1}^N$ denotes the product of N terms

Z component of the end-to-end vector can be represented as the sum of the projections of all bond vectors onto the z axis

$$R_z = \sum_{i=1}^N a \cos \theta_i$$

Calculate partition function

$$\begin{aligned} Z(T, f, N) &= \int \exp\left(\frac{fa}{kT} \sum_{i=1}^N \cos \theta_i\right) \prod_{i=1}^N \sin \theta_i d\theta_i d\varphi_i \\ &= \left[\int_0^\pi 2\pi \sin \theta_i \exp\left(\frac{fa}{kT} \sum_{i=1}^N \cos \theta_i\right) d\theta_i \right]^N \\ &= \left[\frac{2\pi}{fa / (kT)} \left[\exp\left(\frac{fa}{kT}\right) - \exp\left(-\frac{fa}{kT}\right) \right] \right]^N \\ &= \left[\frac{4\pi \sinh(fa / (kT))}{fa / (kT)} \right]^N \end{aligned}$$

Gibbs free energy G can be directly calculated from partition function

$$G(T, f, N) = -kT \ln Z(T, f, N) = -kTN \left[\ln \left(4\pi \sinh \left(\frac{fa}{kT} \right) \right) - \ln \left(\frac{fa}{kT} \right) \right]$$

Average end to end distance

$$\langle R \rangle = -\frac{\partial G}{\partial f} = aN \left[\coth \left(\frac{fa}{kT} \right) - \frac{1}{fa / (kT)} \right]$$

Small force $\frac{fa}{kT} \ll 1$

Using power series $\coth x = x^{-1} - \frac{1}{3}x - \frac{1}{45}x^3 - \frac{2}{945}x^5 - \dots$

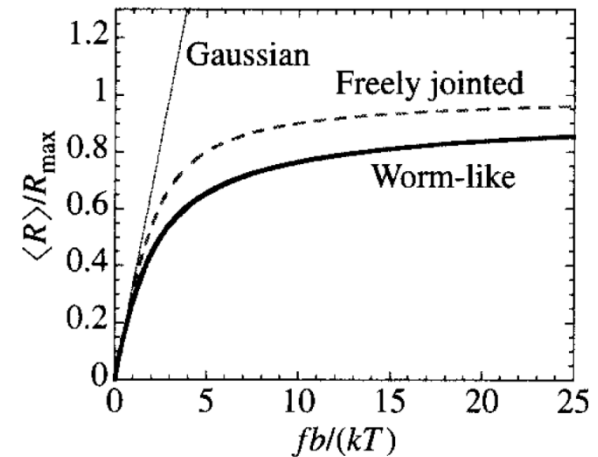
$$\langle R \rangle \cong \frac{fa}{3kT} (aN)$$

Extension is $\frac{\langle R \rangle}{R_{\max}} \cong \left(\frac{a}{kT} \right) f$

Large force $\frac{fa}{kT} \gg 1$

$$\langle R \rangle \cong aN \left[1 - \frac{kT}{fa} \right]$$

Extension is $\frac{\langle R \rangle}{R_{\max}} \cong \left[1 - \frac{kT}{fa} \right] \quad \frac{fa}{kT} \cong \frac{R_{\max}}{R_{\max} - \langle R \rangle}$



WLC force versus extension

$$\frac{fP}{k_B T} = \frac{z}{L} + \frac{1}{4(1 - z/L)^2} - \frac{1}{4}$$

This is asymptotically exact in the large and small force limits

