# Ideal chains

# Probability distribution of end-end distances

## One dimension

Number of ways of arriving a distance x from the origin after N steps

$$W(N, x) = \frac{N!}{(n_+!)(n_-!)}$$

Probability

$$p(N, x) = \frac{1}{2^N} \frac{N!}{(n_+!)(n_-!)}$$

Using Stirling's approximation,

$$N! \cong \sqrt{2\pi N}\,(N/e)^N$$

# Probability distribution of end-end distances

Assuming that $x \ll N$

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

$$\left\langle x^2 \right\rangle = \int_{\infty}^{\infty} x^2 P(N,x) dx = N$$

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

**Three dimension**

$$P(N,R) = \left(\frac{3}{2\pi N b^2}\right)^{3/2} \exp\left(\frac{-3R^2}{2Nb^2}\right)$$

# Radius of gyration

**Radius of gyration** is the name of several related measures of the size of an object, a surface, or an ensemble of points.
It is calculated as the root mean square distance of the objects' parts from either its center of gravity or a given axis.

**In molecular**

the radius of gyration is used to describe the dimensions of a polymer chain

$$R_g^2 = \frac{1}{N}\sum_{k=1}^{N}(\boldsymbol{r}_k - \boldsymbol{r}_{mean})^2$$

$\boldsymbol{r}_{mean}$ is the mean position of the monomers

Proportional to the root mean square distance between the monomers

$$R_g^2 = \frac{1}{2N^2}\sum_{i,j}(\boldsymbol{r}_i - \boldsymbol{r}_j)^2$$

# Radius of gyration

the radius of gyration which is measured is an average over time or ensemble

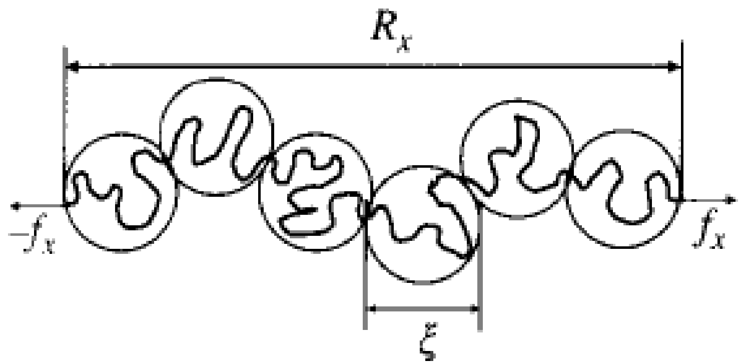
$$R_g^2 = \frac{1}{N}\left\langle \sum_{k=1}^{N} (\boldsymbol{r}_k - \boldsymbol{r}_{mean})^2 \right\rangle$$

An entropically governed polymer chain (i.e. in so called theta conditions) follows a random walk in three dimensions.
The radius of gyration for this case is given by

$$R_g = \frac{1}{\sqrt{6}}\sqrt{N}a$$

# Scaling argument for chain stretching

**Blobs : crossover length scales**




We divide the polymer chain into blobs of size $\xi$, with g monomers per blob.

The size of the blob is described by ideal chain statistics, so

$$\xi \approx gb^{1/2}$$

# Scaling argument for chain stretching

**Polymer chain in tension**

The number of blobs $N / g$

extension $R \approx \xi (N / g)$

The free energy of the chain is increased in tension due to the restriction of the degrees of freedom of the blobs
each blob in this case contributes kT and so,

$$F \approx kTN / g \approx kT \frac{R^2}{Nb^2}$$

Force required to stretch the polymer coil

$$f = \frac{\partial F}{\partial R} \approx kT \frac{R}{Nb^2} \approx kT / \xi$$

# Free energy of a polymer chain

The entropy as a function of the end to end distance R

Boltzmann's relation

$$S = k \ln \Omega(R)$$

$\Omega(R)$ is simply the number of ways (conformations) of arranging monomers such that the chain has an end-end distance R

**Free energy**

$$S(N,R) = \frac{-3}{2} k \frac{R^2}{Nb^2} + S_0$$

$$F(N,R) = \frac{-3}{2} kT \frac{R^2}{Nb^2} + F_0$$

# Free energy of an ideal chain

The force required to perturb the chain dimensions is just given by

$$f = \frac{\partial F}{\partial R} = \frac{3kT}{Nb^2} R$$

Worm-like chain model

$$f = \frac{kT}{b}\left[\frac{2\langle R\rangle}{R_{\max}} + \frac{1}{2}\left(\frac{R_{\max}}{R_{\max} - \langle R\rangle}\right)^2 - \frac{1}{2}\right]$$

# THANK YOU