Lecture 10
Notes on the physical basis of muscle elasticity
Conformations of molecules under a stretching force

Polymers:
Polyethylene

\[
\text{CH}_2 - \text{CH}_2 \\
\text{CH}_2 - \text{CH}_2 - \text{CH}_2 \\
\text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2
\]

1... 4.5 Å... 1

Amylose

Polypeptide

[Chemical structures and bond lengths]
**Mathematical background for elasticity**

2. **The Freely Jointed Chain**

\[ \vec{r} = \sum_{i} \vec{r}_i \]

\[ \vec{r}^2 = \vec{r} \cdot \vec{r} = \sum_{i} \vec{r}_i \cdot \sum_{j} \vec{r}_j = \sum_{i,j} \vec{r}_i \cdot \vec{r}_j \]

but \( \vec{a} \cdot \vec{b} = |\vec{a}| |\vec{b}| \cos \theta \)

\[ \vec{r}^2 = \sum_{i,j} \vec{r}_i \cdot \vec{r}_j = \sum_{i=j} \vec{r}_i^2 + \sum_{i \neq j} \vec{r}_i \cdot \vec{r}_j \]

\[ \therefore \text{for a given distribution of } \vec{r}_1, \ldots, \vec{r}_N \]

if we observe over a long time, we ask what is the expected value (mean value)

\[ \langle \vec{r}^2 \rangle = N \vec{r}_1^2 + 2 \sum_{i \neq j} \langle \vec{r}_i \cdot \vec{r}_j \rangle + 2 \vec{r}_1^2 \sum \langle \cos \theta \rangle_{i \neq j} \]
\[
\langle r^2 \rangle = NL^2 = L_c \cdot l
\]

\[
\therefore \quad r = \langle r^2 \rangle^{1/2} = L_c^{1/2} \cdot l^{1/2}
\]

- Although this was a useful approximation, the assumption that \( \langle \cos \theta \rangle = 0 \) is not true because bonds are constrained and cannot freely adopt all configurations.

\[\text{Examples}\]

1. A polypeptide chain of 100 aa.
   
   \( L \approx 0.4 \text{ mm} \)
   
   \( L_c = 40 \text{ mm} \)

   \[
   \therefore \quad r = L_c^{1/2} \cdot l^{1/2} = 4 \text{ mm}
   \]

eg. \( \Theta \) is fixed and corresponds to a bond angle; hence, it can be shown that...
\[ r = \left( \langle r^2 \rangle \right)^{1/2} \approx L_c^{1/2} l^{1/2} \left[ \frac{1 - \cos \theta}{1 + \cos \theta} \right]^{1/2} \]

In the particular case of a tetrahedrally bonded chain

\[ \theta = 109.5^\circ \text{ and } \cos \theta = -\frac{1}{3} \]

\[ r \approx 0.2 \quad L_c^{1/2} l^{1/2} \]

for our example before \( l = 0.4 \text{ mm} \)

\( L_c = 40 \text{ mm} \) 

Suppose a carbon chain 

with 100 bonds 

Even here we have made a simplifying assumption. Rotation about steric constraints means that is more complex in real molecules: a bond is not free but hindered by 

Hence one finds a rotation tension energy

\[ E_\phi = \frac{U'}{2} \left( 1 \pm \cos m \phi \right) \]

where \( \phi \) is the rotation angle. 

\[ E_\phi \]

Notation: \( \phi \)
Radius of Gyration

The radius of gyration of a system of particles is defined as:

\[ R_{cm} = \sqrt{\frac{1}{M} \sum M_i r_i^2} \]

where \( M \) is the total mass of the system and \( r_i \) is the position of the \( i^{th} \) particle.

If the weight of each discrete value that follows follows
The radius of gyration is the expected value of the distance between an element of a chain and its center of mass. In the case of a FJC it can be shown that:

\[ R_0 = \frac{\langle R^2 \rangle^{1/2}}{U^0} \]

**Elasticity of a FJC**

1. **F** applies to all segments, \( l = \) Kuhn segment.
2. The orientational energy of each segment is given by

\[ W = E_0 = -\hat{\theta} \cdot \hat{F} = -lF \cos \theta = -FX_2 \]

\[ P_2 = C e^{\frac{FX_2}{kT}} \]
but \( \sum P_i = 1 = c \sum_{i=1}^{N} e^{\frac{FX_i}{kT}} \)

\[
c = \frac{1}{\sum_{i=1}^{N} e^{\frac{FX_i}{kT}}} \]

\( P_i = \frac{e^{\frac{FX_i}{kT}}}{\sum_{j=1}^{N} e^{\frac{FX_j}{kT}}} \)

Then \( \langle X_e \rangle = \frac{\sum_{i=1}^{N} x_i e^{\frac{FX_i}{kT}}}{\sum_{i=1}^{N} e^{\frac{FX_i}{kT}}} \)

\[
\approx \frac{e \int_{-e}^{e} x e^{\frac{FX}{kT}} dx}{\int_{-e}^{e} e^{\frac{FX}{kT}} dx} \]

\[
= \frac{e \int_{-e}^{e} \frac{e^{\frac{FX}{kT}}}{\left(\frac{FX}{kT}\right)^2} \left(\frac{FX}{kT} - 1\right) dx}{\int_{-e}^{e} \frac{e^{\frac{FX}{kT}}}{\left(\frac{FX}{kT}\right)} dx} \]
\[
\langle x \rangle = L \left[ \frac{e^{\frac{F \theta}{kT}} + e^{-\frac{F \theta}{kT}}}{e^{\frac{F \theta}{kT}} - e^{-\frac{F \theta}{kT}}} - \frac{kT}{F \theta} \right]
\]

\[
\langle x^2 \rangle = L \left[ \coth\left( \frac{F \theta}{kT} \right) - \frac{kT}{F \theta} \right]
\]

Now, the average of the sum of all the projections of each of \( m \) bonds is

\[
\langle x \rangle = \sum_{i=1}^{m} \langle x_i \rangle = \frac{mL}{L_c} \left[ \coth\left( \frac{F \theta}{kT} \right) - \frac{kT}{F \theta} \right]
\]

This is the FJC model for polymer elasticity.

Recently, investigators have added a component of elasticity where the individual segments are elastic.

\[
x = \left[ \coth\left( \frac{F \theta}{kT} \right) - \frac{kT}{F \theta} \right] \left[ L_c + \frac{mT}{S_{segment}} \right]
\]
Conformational transitions

\[ \alpha \rightarrow \]

\[ \Delta G_0 \]

\[ \Delta G_0 - F \Delta x \]

\[ \alpha = A e^\frac{-\Delta G_0}{kT} \]

\[ \alpha = \alpha_0 e^{\frac{F \Delta x}{kT}} \]

\[-\text{let's now examine the effect of force on a simple unfolding reaction}\]

\[ F \rightarrow U \]

\[ P_F(t) = e^{-\alpha t} \]

\( P_F \) is the probability of remaining folded for a time \( t \).
\[ P_F + P_U = 1 \]

\[ \frac{dP_F(t)}{dt} = - \frac{dP_U(t)}{dt} \]

\[ \frac{dP_F(t)}{dt} = -\alpha P_F(t) \quad \Rightarrow \quad \frac{dP_U(t)}{dt} = \alpha (1 - P_U(t)) \]

We can write this as:

\[ \frac{dP_U(t)}{1 - P_U(t)} = \alpha dt \]

If we integrate on both sides we get,

\[ \int \frac{dP_U(t)}{1 - P_U(t)} = \int \frac{-dx}{x} = -\ln x \]

Hence

\[ \int_0^T \alpha \, dt \]

but remember that \( x = 1 - P_U(t) \)
\[ \ln x = -\int_0^T x \, dt \]

so

\[ x = e^{-\int_0^T x \, dt} \]

on

\[ p_u(t) = 1 - e^{-\int_0^T x \, dt} \]

now

Let's imagine that we pull on the protein at a constant rate \( a \) (pN/s), then we develop force at a constant rate \( a \).

\[ F(t) = a \cdot t \]

Then

\[ \frac{dF(t)}{dt} = a \]

\[ dt = \frac{dF(t)}{a} \]

we can then write

\[ p_u(F) = 1 - e^{-\int_0^T \frac{dF(t)}{a}} \]

but remember that

\[ \alpha(F) = \alpha_0 e^{\frac{F\alpha x}{kT}} \]
\[ P_u(F) = 1 - e^{-\frac{\alpha_0}{a} \int_0^F e^{\frac{F \Delta x}{kT}} df} \]

but \[ \int_0^F e^{\frac{F \Delta x}{kT}} df = \frac{kT}{\Delta x} (e^{\frac{F \Delta x}{kT}} - 1) \]

so

\[ P_u(F) = 1 - e^{-\frac{\alpha_0 kT}{\Delta x a} \left[ e^{\frac{F \Delta x}{kT}} - 1 \right]} \]

The probability density is calculated as

\[ \frac{dP_u(F)}{dF} = \frac{\alpha_0}{a} e^{\frac{F \Delta x}{kT}} - \frac{\alpha_0 kT}{\Delta x a} \left( e^{\frac{F \Delta x}{kT}} - 1 \right) \]

and if we make \[ \frac{d^2P_u(F)}{dF^2} = 0 \]
we find that the most probable unfolding occurs at a force given by

\[ F = \frac{kT}{\Delta x} \ln \left[ \frac{\Delta x \cdot a}{\alpha_0 kT} \right] \]
Description of a force dependent first order protein unfolding reaction

for $F(t) = a \cdot t$

$P_u(F) = 1 - e^{-\frac{\alpha_o \cdot \int_0^F e^{\frac{F \cdot \Delta x}{kT}} \, df}{a}}$

$\frac{dP_u(F)}{dF} = \frac{\alpha_o}{a} \cdot e^{\frac{F \cdot \Delta x}{kT}} \cdot \left[ \frac{\alpha_o \cdot kT}{\Delta x \cdot a} \cdot e^{\frac{F \cdot \Delta x}{kT} - 1} \right]$

$F_{\text{max}} = \frac{kT}{\Delta x} \ln \left[ \frac{\Delta x \cdot a}{\alpha_o \cdot kT} \right]$
review two models of complex polymer elasticity:

1. the elasticity of a protein
   - entropic component
   - conformational transitions by unfolding.

2. the elasticity of polysaccharides
   - entropic component
   - conformations of the pyranose ring.