LECTURE 19: ELASTICITY OF SINGLE POLYMER CHAINS : THEORETICAL FORMULATIONS

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Objectives: To understand the theoretical formulations of single macromolecule elasticity

Readings: Course Reader Document 31, CR Documents 32-39 are the original theoretical papers for reference, English translations of CR 33 and 36 are handouts.

REVIEW : LECTURE 18 NANOMECHANICS AND BIOCOMPATIBILITY : PROTEIN-BIOMATERIAL INTERACTIONS 2

-Two examples of biomaterials: vascular graft and endotracheal tube (materials, design issues, relation to nanomechanics)

-Kinetics of protein adsorption; contributions to diffusion; ideal and activated (Szleifer model-CR 29,30); initial and secondary stage of protein adsorption

-Modes of protein adsorption : (I.) adsorption of proteins to the top boundary of the polymer brush (II.) local compression of the polymer brush by a strongly adsorbed protein (III.) protein interpenetration into the brush followed by the non-covalent complexation of the protein and polymer chain (IV.) adsorption of proteins to the underlying biomaterial surface via interpenetration with little disturbance of the polymer brush

-Use of steric repulsion (conformational entropy) to inhibit protein adsorption (Halperin model for polymer brushes-
Polimer brush is a layer of polymers attached with one end to a surface whereby the distance between neighboring chains, \( s < R_g \) where \( R_g \) is the radius of gyration of an isolated chain; this condition causes extension of the chains away from the surface)

(Halperin, *Langmuir* 1999) For a protein interacting with a planar surface: 

\[
U_{\text{eff}}(z) = U_{\text{bare}}(z) + U_{\text{brush}}(z)
\]

\( U^* \) = activation barrier determining rate of primary adsorption

\( k_{\text{ads}} \) = adsorption rate constant

Kramers rate theory: 

\[
k_{\text{ads}} \approx \exp \left( \frac{-U^*}{kT} \right) \frac{D}{aL_0} \]

\( D \) = diffusion constant

\( \alpha \) = width of barrier at \( U^* - kT \)

\( L_0 \) = uncompressed height of polymer brush

-Polyethylene oxide (PEO, PEG) - hydrophilic and water-soluble at RT, forms an extensive H-bonding network; intramolecular H-bond bridges between -O- groups and HOH → large excluded volume, locally \((7/2)\) helical supramolecular structure (tgt axial repeat = 0.278 nm), high flexibility, molecular mobility, low van der Waals attraction, neutral. However: poor mechanical stability, protein adhesion reported under certain conditions (long implant times), maintains some hydrophobic character.
# SUMMARY: THEORETICAL MODELS FOR SINGLE POLYMER CHAIN ELASTICITY

<table>
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| **Freely-Jointed Chain (FJC)**  
(Kuhn and Grün, 1942  
James and Guth, 1943) | ![FJC Diagram](image) | Gaussian:  
\( f(r) = \left( \frac{3k_BT}{na^2} \right)^r \times \left( \frac{3k_BT}{aL_{contour}} \right)^r \)  
Non-Gaussian:  
Exact Formula:  
\( r f(r) = na \left( \coth \left( \frac{r}{na} \right) - \frac{1}{x} \right) \) where:  
\( x = \left( \frac{fa}{k_BT} \right) \)  
Langevin Expansion:  
\( f(r) = \left( \frac{k_BT}{a} \right)^\beta \)  
\( \beta = \exp \left( \frac{r}{na} \right) \) = Inverse Langevin Function  
High Stretch Approximation:  
\( f(r) = \left( \frac{k_BT}{a} \right)^{\beta} \left( 1 - \frac{r}{L_{total}} \right)^{\beta} \) |
| **Extensible Freely-Jointed Chain**  
(Smith, et. al, 1996) | ![Extensible FJC Diagram](image) | Non-Gaussian:  
\( f(r) = \frac{k_BT}{a} \exp \left( \frac{r}{L_{total}} \right) \cdot L_{total} = L_{contour} + n \left( \frac{f}{k_{segment}} \right) \) |
| **Worm-Like Chain (WLC)**  
(Kratky and Porod, 1943  
Fixman and Kovac, 1973  
Bustamante, et. al 1994) | ![WLC Diagram](image) | Exact: Numerical Solution  
Interpolation Formula:  
\( f(r) = \left( \frac{k_BT}{p} \right) \left( \frac{r}{L_{contour}} + \frac{1}{4} \left( 1 - \frac{r}{L_{contour}} \right)^2 \right) \) |
| **Extensible Worm-Like Chain**  
(Odijk, 1995) | ![Extensible WLC Diagram](image) | Interpolation Formula:  
\( f(r) = \left( \frac{k_BT}{p} \right) \left( \frac{r}{L_{total}} + \frac{1}{4} \left( 1 - \frac{r}{L_{total}} \right)^2 \right) \)  
\( L_{total} = L_{contour} + n \left( \frac{f}{k_{segment}} \right) \) |
VARIOUS MATHEMATICAL FORMS FOR THE (INEXTENSIBLE) FREELY JOINTED CHAIN (FJC) MODEL

Gaussian : \( f(r) = \left( \frac{3k_B T}{na^2} \right) r = \left( \frac{3k_B T}{aL_{\text{contour}}} \right) r \) (1)

Non-Gaussian:

Analytical Formula : \( r(f) = na \left( \coth(x) - \frac{1}{x} \right) \) where : \( x = \left( \frac{fa}{k_B T} \right) \) (2)

Langevin Expansion : \( f(r) = \left( \frac{k_B T}{a} \right) \beta \) (3)

\[ \beta = \mathcal{L}^{-1}\left( \frac{r}{na} \right) \text{ = Inverse Langevin Function} \]

\[ = 3 \left( \frac{r}{na} \right) + \frac{9}{5} \left( \frac{r}{na} \right)^3 + \frac{297}{175} \left( \frac{r}{na} \right)^5 + \frac{1539}{875} \left( \frac{r}{na} \right)^7 + \ldots \]

High Stretch Approximation :

\[ f(r) = \left( \frac{k_B T}{a} \right) \left( \frac{1 - \frac{r}{L_{\text{contour}}} \right)^{-1} \) (4)

- entropic elasticity; chain wants to maximum # of conformations (random coil), when stretched; links rotate to uncoil, align, extend, polymer chain along stretching axis
# available conformations ↓ disorder and entropy ↓ restoring force driving back to random coil ↑ assume no enthalpy change (no stretching of backbone bonds)

Two molecular level parameters (can be used as fitting parameters) :
\( a \) = statistical segment length (local chain stiffness)
\( n \) = number of statistical segments
\( L_{\text{contour}} = na \) = fully extended length of polymer chain
COMPARISON OF VARIOUS MATHEMATICAL FORMS FOR THE INEXTENSIBLE FREELY JOINTED CHAIN (FJC) MODEL

Surface separation distance, $D = r$, chain end-to-end distance; sign convention (-) for attractive back force, however some scientists plot as (+); e.g. Zauscher (podcast)

1. Gaussian physically unrealistic; force continues to increase forever beyond $L_{\text{contour}}$, valid for $r < 1/3 L_{\text{contour}}$
2. Langevin Series Expansion; finite force beyond $L_{\text{contour}}$ (physically unrealistic); valid for $r < 3/4 L_{\text{contour}}$
3. High stretch approximation underestimates force for $r < 3/4 L_{\text{contour}}$, valid for $r > 3/4 L_{\text{contour}}$
EXTENSIBLE FREELY JOINTED CHAIN (FJC) MODEL

- Take into account a small amount of longitudinal (along chain axis) enthalpic deformability (monomer/bond stretching) of each statistical segment, approximate each statistical segment as a linear elastic entropic spring (valid for small deformations) with stiffness, $k_{\text{segment}}$ → springs is series, forces are equal, strain additive; $k_{\text{segment}} \cdot f_{\text{segment}} = k_{\text{segment}} \cdot \delta_{\text{segment}}$

solve for: $\delta_{\text{segment}} = f_{\text{segment}} / k_{\text{segment}}$

Add displacement term to $L_{\text{contour}}$:

$L_{\text{total}} = L_{\text{contour}} + n \left( f / k_{\text{segment}} \right)_{\text{extension beyond } L_{\text{contour}}}$

$n = $ number of statistical segments

$f(r) = \left( \frac{k_B T}{a} \right) e^{-1} \left( \frac{r}{L_{\text{total}}} \right)$

Now we have three physical (fitting) parameters; $a$, $n$, $k_{\text{segment}}$

Schematic of the stretching of an extensible freely jointed chain and (b) the elastic force versus displacement for the extensible compared to non-extensible non-Gaussian FJC ($a = 0.6$ nm, $n = 100$, $k_{\text{segment}} = 1$ N/m)
**WORM LIKE CHAIN (WLC) MODEL**

(*Kratky-Porod Model*)

"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

**p= persistence length**, length over which statistical segments remain directionally correlated in space

Exact : Numerical Solution

Interpolation Formula : 

\[
f(r) = \left( \frac{k_B T}{p} \right) \left( \frac{r}{L_{\text{contour}}} + \frac{1}{4 \left( 1 - \frac{r}{L_{\text{contour}}} \right)^2} - \frac{1}{4} \right)
\]

-WLC stiffer at higher extensions, force rises sooner than FJC since statistical segments are constrained, can also make an extensible form of WLC → replace \( L_{\text{contour}} \) by \( L_{\text{total}} \) as before for FJC
APPENDIX : THEORETICAL MODELS FOR THE ELASTICITY OF SINGLE POLYMER CHAINS : FULL CITATIONS OF ORIGINAL REFERENCES

FJC

Extensible FJC

WLC

Extensible WLC