LECTURE 20: THEORETICAL ASPECTS OF SINGLE MOLECULE FORCE SPECTROSCOPY 2 : EXTENSIBILITY AND THE WORM LIKE CHAIN (WLC)

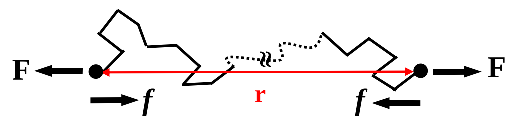
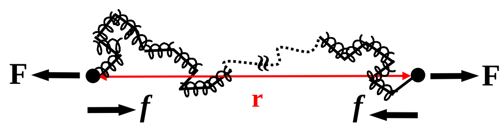
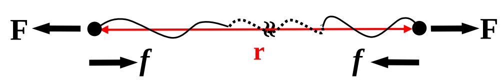
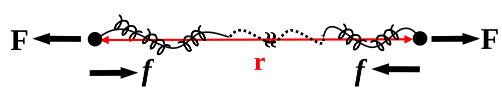
Outline :

Objectives: To understand how extensibility of chain segments affects the FJC elasticity model and to understand the differences between the FJC and WLC models

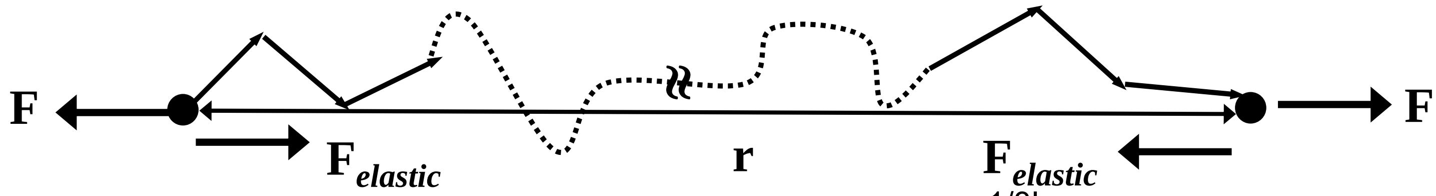
Readings: Course Reader Document 31, CR Documents 32-39 are the original theoretical papers for reference, English translations of CR 33 and 36 are available as handouts.

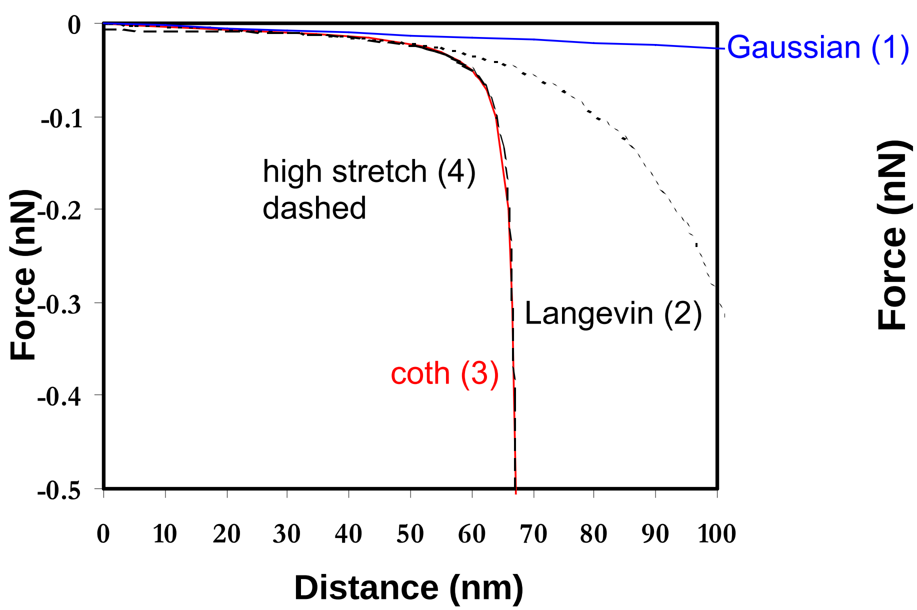
Multimedia : Podcast : Sacrificial Bonds in Biological Materials; Fantner, et al. *Biophys. J.* **2006** 90, 1411

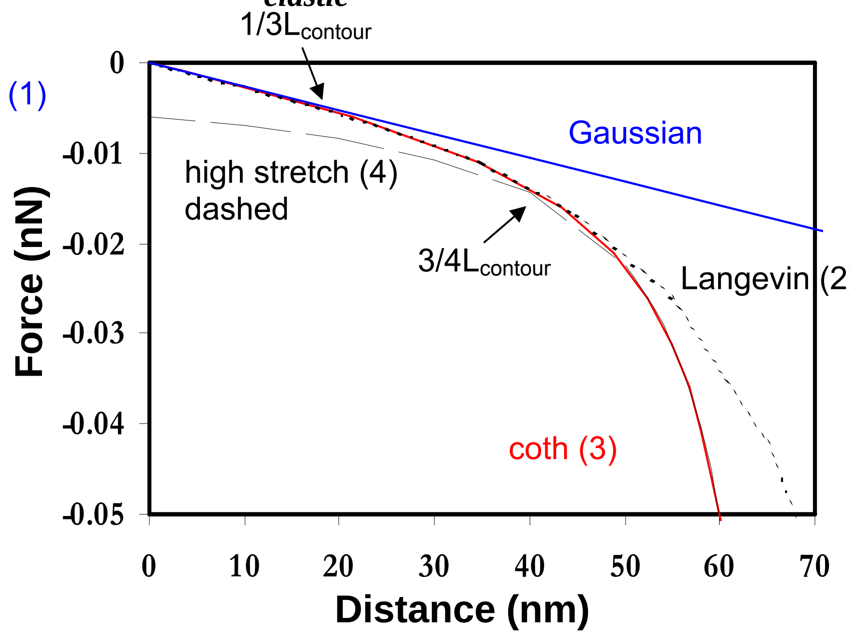
REVIEW LECTURE 19 : MODELS FOR SINGLE POLYMER CHAIN ELASTICITY

MODEL	SCHEMATIC	FORMULAS
Freely-Jointed Chain (FJC) (Kuhn, 1934 Guth and Mark, 1934)	 *(a, n)*	**Gaussian :** $f(r)=\left(\frac{3k_BT}{na^2}\right)r=\left(\frac{3k_BT}{aL_{contour}}\right)r$ (1) **Non - Gaussian :** Exact Formula : $r(f)=na\left(\coth(x)-\frac{1}{x}\right)$ where : $x=\left(\frac{fa}{k_BT}\right)$ (2) Langevin Expansion : $f(r)=\left(\frac{k_BT}{a}\right)\beta$ (3) $\beta=\mathscr{L}^{-1}\left(\frac{\mathbf{r}}{na}\right)$ = Inverse Langevin Function $=3\left(\frac{\mathbf{r}}{na}\right)+\left(\frac{9}{5}\left(\frac{\mathbf{r}}{na}\right)^3\right)+\left(\frac{297}{175}\left(\frac{\mathbf{r}}{na}\right)^5\right)+\left(\frac{1539}{875}\left(\frac{\mathbf{r}}{na}\right)^7+...\right)$ High Stretch Approximation : $f(r)=\left(\frac{k_BT}{a}\right)\left(1-\frac{r}{L_{contour}}\right)^{-1}$ (4)
Extensible Freely-Jointed Chain (Smith, et. al, 1996)	 *(a, n, $k_{segment}$)*	Non - Gaussian : $f(r)=\left(\frac{k_BT}{a}\right)\mathscr{L}^{-1}\left(\frac{\mathbf{r}}{L_{total}}\right)$; $L_{total}=L_{contour}+n\left(\frac{f}{k_{segment}}\right)$
Worm-Like Chain (WLC) (Kratky and Porod, 1943 Fixman and Kovac, 1973 Bouchiat, et al. 1999)	 *(p, n)*	Exact : Numerical Solution Interpolation Formula : $f(r)=\left(\frac{k_BT}{p}\right)\left[\frac{r}{L_{contour}}+\frac{1}{4\left(1-\frac{r}{L_{contour}}\right)^2}-\frac{1}{4}\right]$
Extensible Worm-Like Chain (Odijk, 1995 Wang, et al. 1997)	 *(p, n, $k_{segment}$)*	Interpolation Formula : $f(r)=\left(\frac{k_BT}{p}\right)\left[\frac{r}{L_{total}}+\frac{1}{4\left(1-\frac{r}{L_{total}}\right)^2}-\frac{1}{4}\right]$; $L_{total}=L_{contour}+n\left(\frac{f}{k_{segment}}\right)$

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)

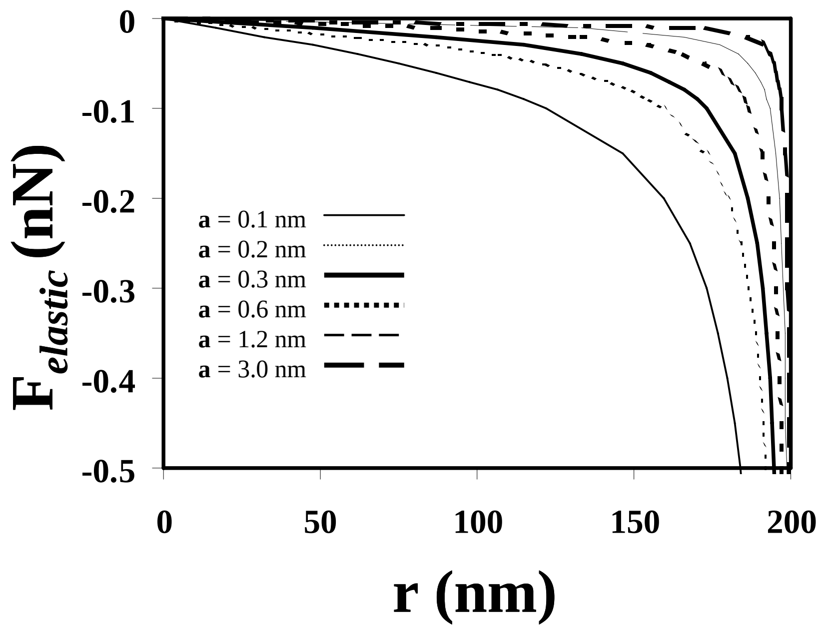
(1) Gaussian physically unrealistic; force continues to increase forever beyond $L_{contour}$, valid for r,D<1/3 $L_{contour}$

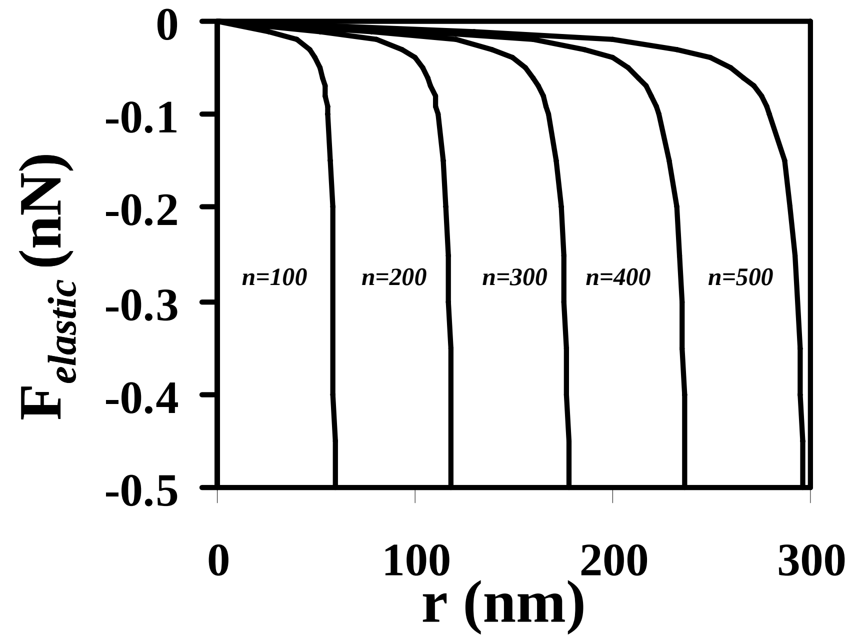
(3) Langevin Series Expansion; finite force beyond $L_{contour}$ (physically unrealistic); valid for r,D<3/4 $L_{contour}$

(4) High stretch approximation underestimates force for r,D<3/4$L_{contour}$, valid for r,D>3/4$L_{contour}$

EFFECT OF *a* and *n* on INEXTENSIBLE FJC

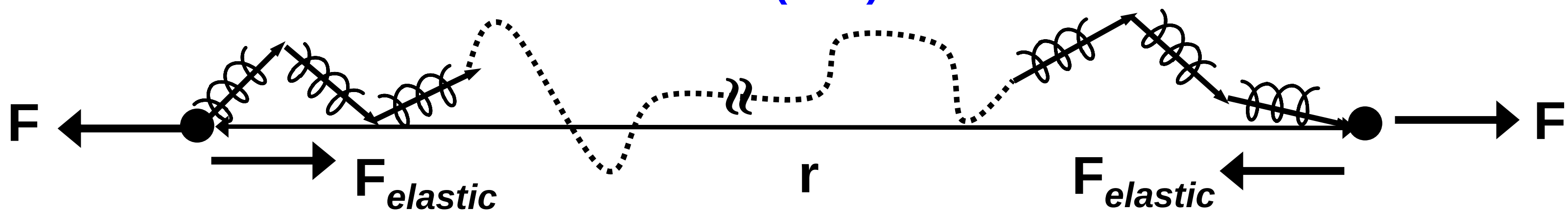
$$\textbf{Gaussian:}\ f(r) = \left(\frac{3k_BT}{na^2}\right) r$$





(*left*) Elastic force versus displacement as a function of the statistical segment length, a, for the non-Gaussian FJC model ($L_{contour}$ = 200 nm) and (*right*) elastic force versus displacement as a function of the number of chain segments, n, for the non-Gaussian FJC model (a = 0.6 nm)

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, $k_{segment}$ →springs is series, forces are equal, strain additive;

$k_{segment}$; $f_{segment} = k_{segment}\,\delta_{segment}$

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

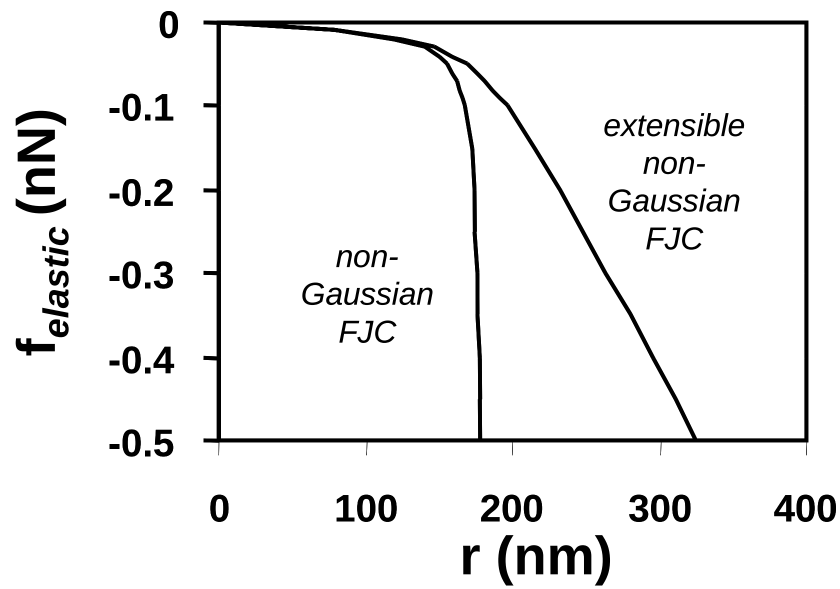
Add displacement term to $L_{contour}$:

$$L_{total} = \underbrace{L_{contour}}_{=na} + \underbrace{n\left(\frac{f}{k_{segment}}\right)}_{\text{extension beyond } L_{contour} \text{ due to enthalpic stretching of chain segments}}$$

n= number of statistical segments

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

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



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, $k_{segment}$ = 1 N/m) - note units

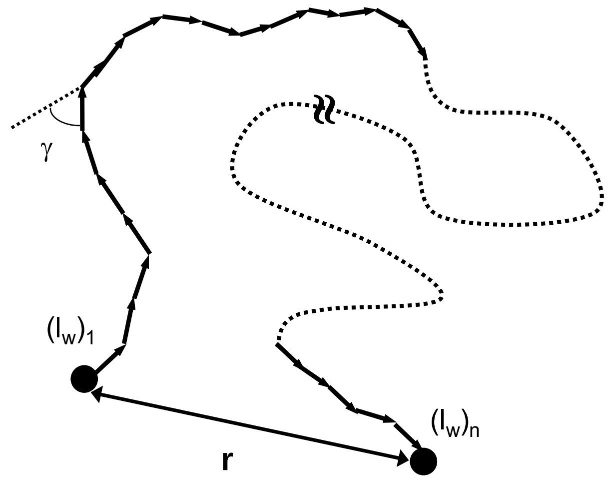
WORM LIKE CHAIN (WLC) MODEL

*(*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

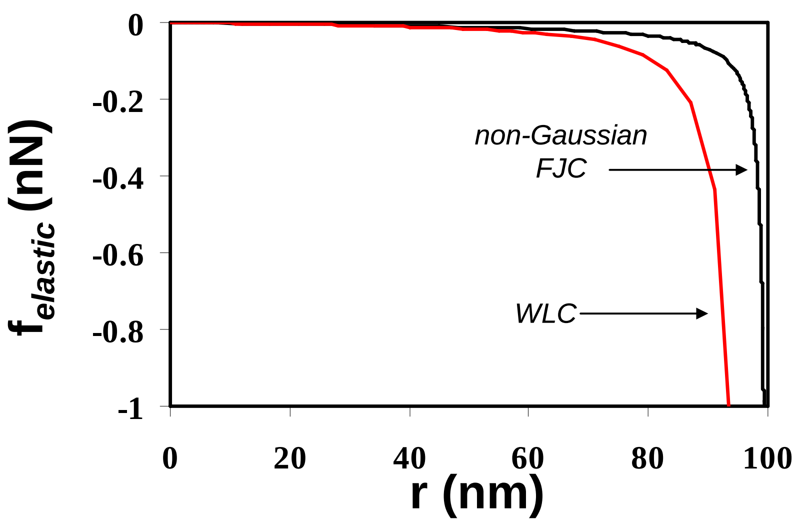
-chain is treated as an isotropic, homogeneous elastic rod whose trajectory varies continuously and smoothly through space as opposed to the jagged contours of the FJC



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

Exact : Numerical Solution

Interpolation Formula : $$f(r) = \left(\frac{k_B T}{p}\right)\left(\frac{r}{L_{contour}} + \frac{1}{4\left(1 - \frac{r}{L_{contour}}\right)^2} - \frac{1}{4}\right)$$



-WLC stiffer at higher extensions, force rises sooner than FJC since statistical segments are constrained, can also make an extensible form of WLC→ replace $L_{contour}$ by L_{total} as before for FJC

-In reality the FJC and WLC are very similar and just produce slightly different values of the local chain stiffness

FITS TO EXPERIMENTAL SINGLE MOLECULE FORCE SPECTROSCOPY DATA

AFM retract data on single polymer chain of polystyrene in toluene; comparison to Freely-Jointed Chain Model (a = 0.68 nm) - right plot aata normalized by $L_{contour}$ to create a master plot