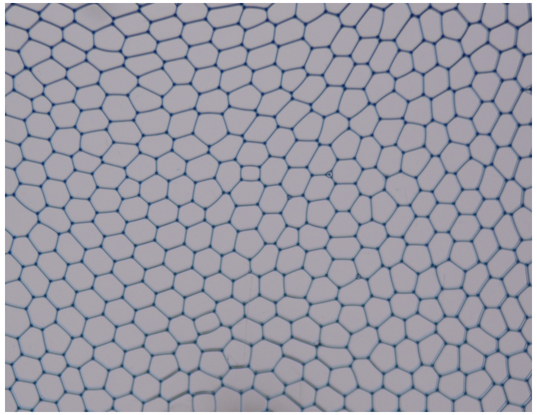
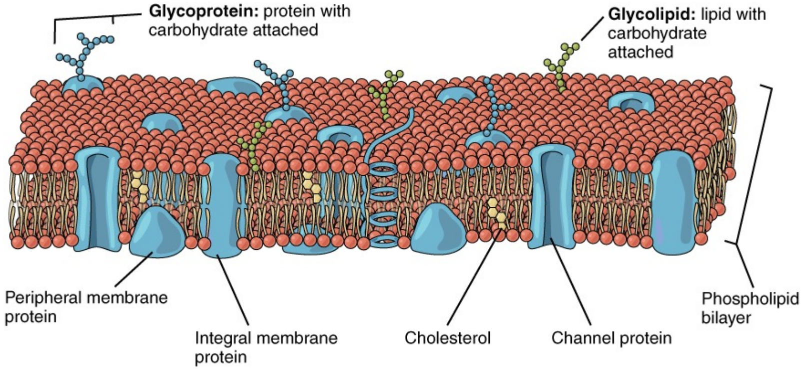
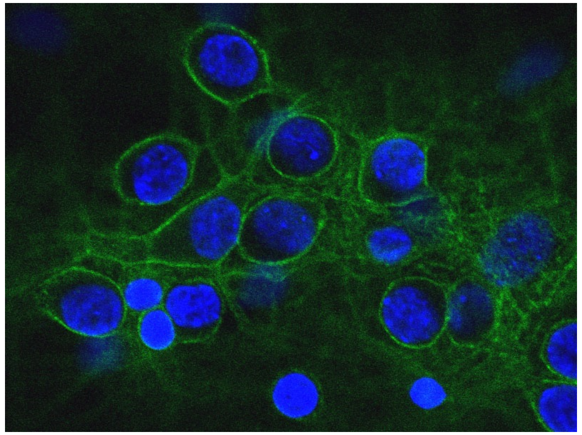
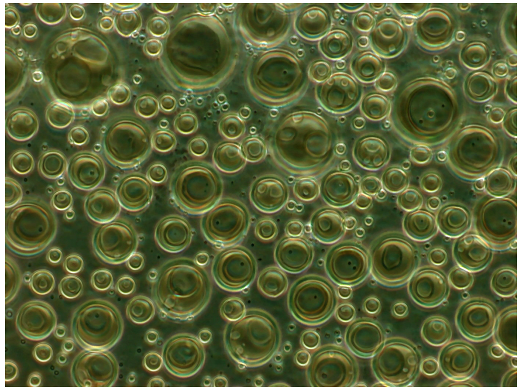
ME470: Mechanics of Soft and Biological Matter
Lecture5-1: Worm-like Chain, Bulk Entropic Materials









Red Blood Cells

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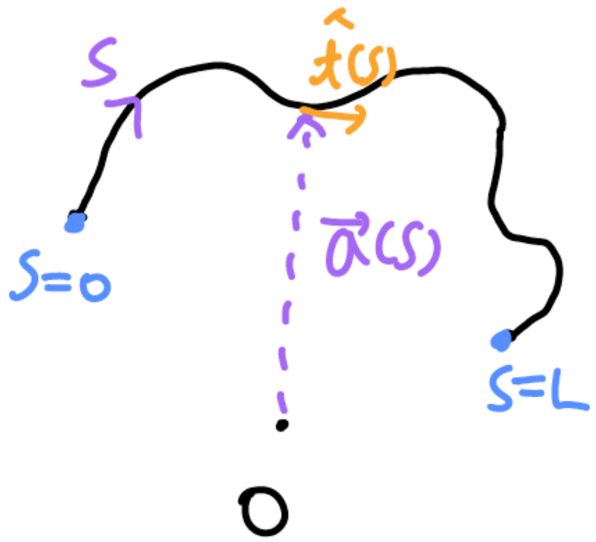
Worm-Like Chain (WLC)

Replace n links by a continuous, elastic curve in 3D



Enforce a fixed contour length

$$\left(\frac{\partial \vec{a}}{\partial s}\right)^2 = 1 \qquad \forall\, s \quad \Rightarrow \quad \int_0^L \sqrt{\left(\frac{\partial \vec{a}}{\partial s}\right)^2}\, ds = L$$

Unit tangent vector from differential geometry

$$\hat{t}(s) = \frac{\partial \vec{a}}{\partial s}$$

$$U_b = \frac{EI}{2}\int_0^L \kappa^2\, ds = \frac{1}{2} k_B T l_p \int_0^L \left(\frac{\partial^2 \vec{a}}{\partial s^2}\right)^2 ds$$

(curvature, $\kappa(s) = \frac{\partial^2 \vec{a}(s)}{\partial s^2}$)

Worm-Like Chain (WLC)

⇨ Canonical ensemble with $U = U_b - F_z R_z(\vec{a})$

(Note: $R_z(\vec{a}) = \int_0^L \frac{\partial \vec{a}(s)}{\partial s} \cdot \hat{e}_z ds$)

⇨ $$U = \int_0^L \left[\frac{k_B T l_p}{2} \left(\frac{\partial^2 \vec{a}}{\partial s^2} \right)^2 - F_z \left(\frac{\partial \vec{a}(s)}{\partial s} \cdot \hat{e}_z \right) \right] ds$$

Probability: $P(\vec{a}) = \frac{1}{Z} exp\left(-\frac{U(\vec{a})}{k_B T} \right)$

Partition function: $Z = \int_{All} exp\left(-\frac{U(\vec{a})}{k_B T} \right)$

Z: not analytically computable, but approximation by combining asymptotes exist

⇨ $$F_z = \frac{k_B T}{l_p} \left[\frac{1}{4} \left(1 - \frac{\langle R_z \rangle}{L} \right)^{-2} - \frac{1}{4} + \frac{\langle R_z \rangle}{L} \right]$$

Worm-Like Chain (WLC)

Check: $\frac{\langle R_z \rangle}{L} \ll 1$ ⇨ $F_z = \frac{k_B T}{l_p}\left[\frac{1}{4}\left(1 + 2\frac{\langle R_z \rangle}{L}\right) - \frac{1}{4} + \frac{\langle R_z \rangle}{L}\right] = \frac{3k_B T}{2 l_p L}\langle R_z \rangle$

Need to show that $b = 2l_p$, to apply chain models with freely rotating Kuhn links

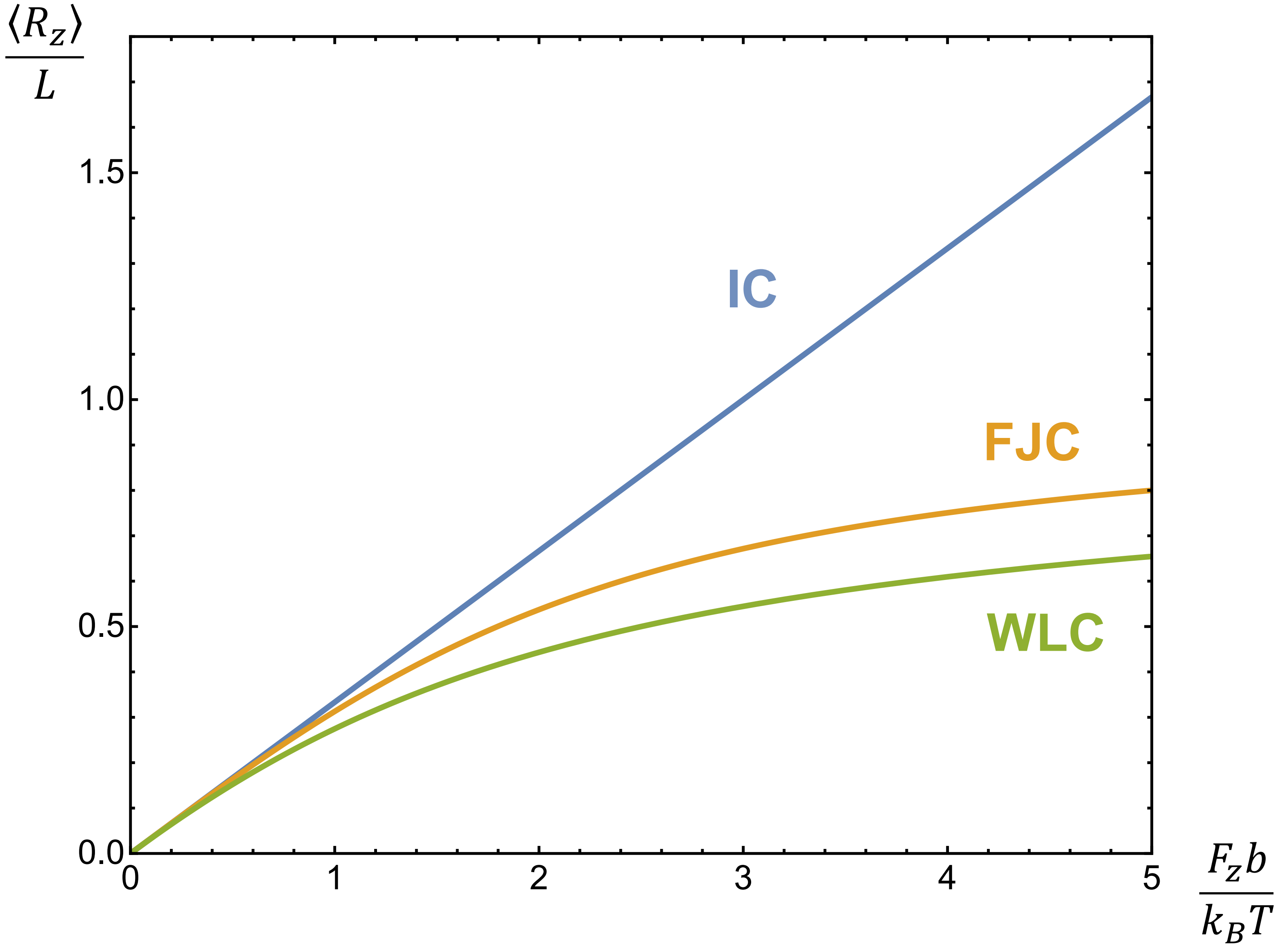
Q: Show $b = 2l_p$ (Exercise)

$$\langle R^2 \rangle = \int_0^L \frac{\partial \vec{a}(s)}{\partial s} ds \int_0^L \frac{\partial \vec{a}(u)}{\partial u} du$$

$$= \int_0^L \int_0^L exp\left[-\frac{|u-s|}{l_p}\right] dsdu = 2l_p^2\left[\frac{L}{l_p} - 1 + e^{-L/l_p}\right]$$

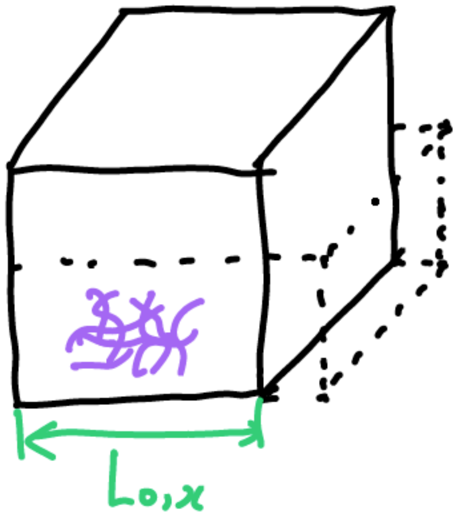
$L \ll l_p$ ⇨ $\langle R^2 \rangle \approx 2l_p L = nb^2 = bL$ ⇨ $b = 2l_p$

Comparison between IC, FJC, WLC



Bulk Entropic Materials

e.g) rubber, made of entangled entropic springs (disordered)



Assumption: affine deformation
(microscopic deformation=macroscopic deformation

⇨ Individual chain extent in x,y,z changes proportionally to that of the bulk

Under stretch: $\lambda_x, \lambda_y, \lambda_z$

End to end distance: $\vec{R}(X,Y,Z)$ ⇨ $\vec{r}(x,y,z)$

with

$$\langle x^2\rangle = \lambda_x^2\langle X^2\rangle$$

$$\langle y^2\rangle = \lambda_y^2\langle Y^2\rangle$$

$$\langle z^2\rangle = \lambda_z^2\langle Z^2\rangle$$

Bulk Entropic Materials

Recall entropy of IC: $S(\vec{R}) = -\frac{3k_BT}{2nb^2}R^2 + S_0$

$$\Rightarrow \langle \Delta\Psi \rangle = \left\langle -T\left(S(\vec{r}) - S(\vec{R})\right)\right\rangle = \frac{3k_BT}{2nb^2}\left(\lambda_x^2\langle X^2\rangle + \lambda_y^2\langle Y^2\rangle + \lambda_z^2\langle Z^2\rangle - nb^2\right)$$

(here, $\langle X^2\rangle = \langle Y^2\rangle = \langle Z^2\rangle = \frac{nb^2}{3}$)

$$\Rightarrow \langle \Delta\Psi \rangle = \frac{k_BT}{2}\left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\right)$$

For a single chain

For N chains: $\Delta\Psi_{bulk} = N\langle \Delta\Psi \rangle$

Bulk Entropic Materials

Rubber: ideally elastic, volume conserved $\lambda_x \lambda_y \lambda_z = 1$

e.g) uniaxial stretch, $\lambda_x = \lambda, \lambda_y = \lambda_z = 1/\sqrt{\lambda}$

$$\Rightarrow \quad \langle \Delta\Psi \rangle = \frac{k_B T}{2}\left(\lambda^2 + \frac{2}{\lambda^2} - 3\right)$$

$$F_x = \frac{\partial \Delta\Psi_{bulk}}{\partial L_x} = \frac{1}{L_{0,x}} \frac{\partial \Delta\Psi_{bulk}}{\partial \lambda} = \frac{N k_B T}{L_{0,x}}\left(\lambda - \frac{2}{\lambda^2}\right)$$

Given a cross-section perpendicular to x is A,

$$\sigma_{xx} = \frac{F_x}{A} = \frac{N}{A L_{0,x}} k_B T\left(\lambda - \frac{2}{\lambda^2}\right) = \rho_c k_B T\left(\lambda - \frac{2}{\lambda^2}\right)$$

Chain volume density

EPFL

Bulk Entropic Materials

A hyperelastic constitutive relation can be derived for small strain

$$\lambda = 1 + \varepsilon \quad \Rightarrow \quad \left(\lambda - \frac{2}{\lambda^2}\right) \approx 3\varepsilon$$

$$\Rightarrow \quad \boxed{E = 3\rho_c k_B T}$$

Notes:

- The stiffness scales linearly with the chain density
- The stiffness increase for higher temperature (different from most engineering materials)