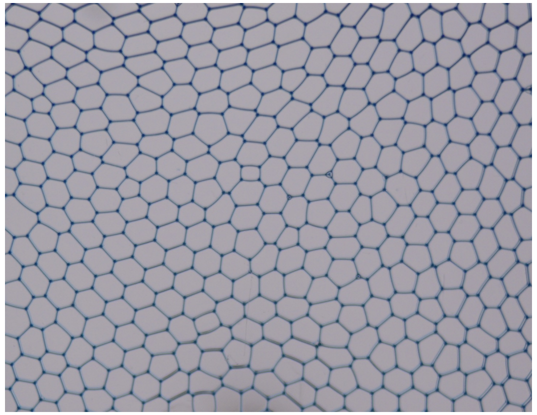
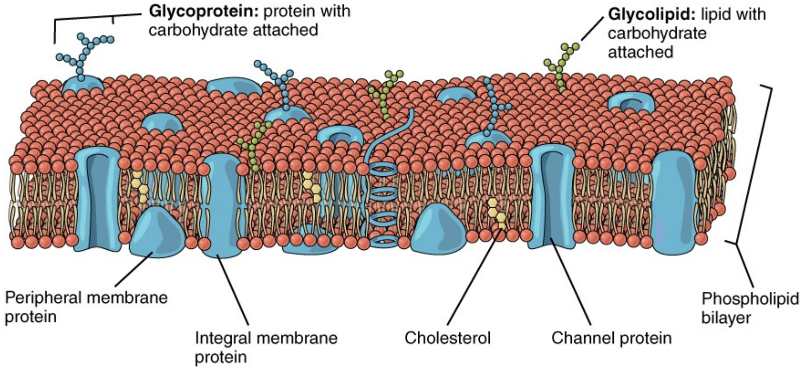
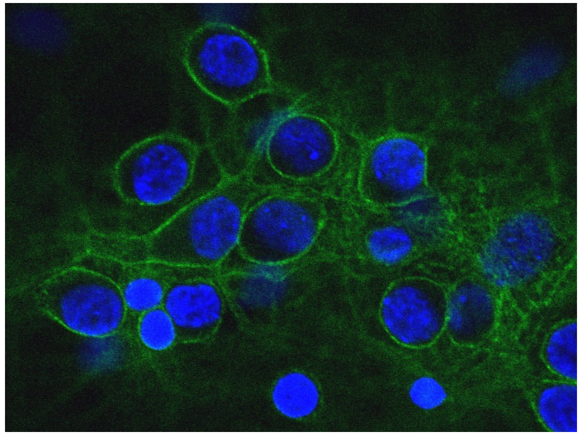
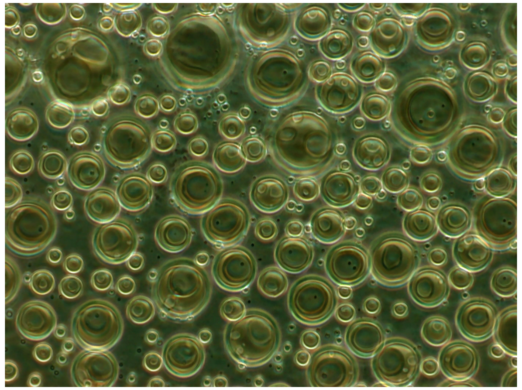
ME470: Mechanics of Soft and Biological Matter
Lecture4: Idea Chain & Freely Jointed Chain









Red Blood Cells

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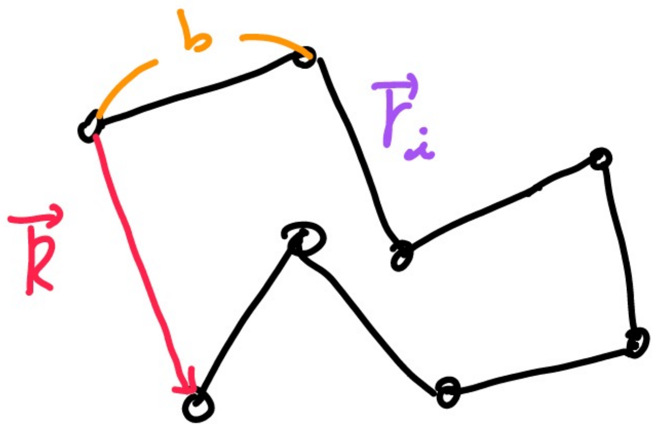
Ideal chain (IC)

Ideal chain: polymer model in the flexible limit



Assumptions
- n segments of length b (Kuhn length)
- Inextensible ($L_c = nb$)
- Freely rotation, no internal energy change ($dU = 0$)

$$\vec{R} = \sum_{i=1}^{n} \vec{r}_i$$ (end-to-end vector)

$$\langle \vec{R} \rangle = 0$$ (random orientation of $\vec{r}_i$)

$$\langle R^2 \rangle = \langle \vec{R} \cdot \vec{R} \rangle = nb^2 \Rightarrow \langle R^2 \rangle \sim n$$

Same as random walk

Ideal chain (IC)

Random walk ⟺ Probability of the chain having a specific length

⟺ Free energy & force-displacement relation

Probability of at distance r with n step for 1D random work

$$P_{1d}(n,r) = \frac{1}{2^n}\binom{n}{\frac{n+r/b}{2}} = \frac{1}{2^n}\frac{n!}{\left(\frac{n+r/b}{2}\right)!\left(\frac{n-r/b}{2}\right)!}$$

Binomial coefficient

In the limit of large n ⇒

$$P_{1d}(n,r) = \frac{1}{\sqrt{2\pi\langle r^2\rangle}} e^{-r^2/2\langle r^2\rangle}$$

Ideal chain (IC)

Here, $\vec{R} = R_x \hat{e}_x + R_y \hat{e}_y + R_z \hat{e}_z$

$$\langle R^2 \rangle = 3\langle r^2 \rangle \Rightarrow \langle r^2 \rangle = \frac{\langle R^2 \rangle}{3} = \frac{nb^2}{3}$$

$$\Rightarrow P_{1d}(n, R_i) = \sqrt{\frac{3}{2\pi\langle R^2 \rangle}} e^{-3R_i^2/2\langle R^2 \rangle} \qquad i = x, y, z$$

$$\Rightarrow P_{3d}(n, R) = \left(\frac{3}{2\pi\langle R^2 \rangle}\right)^{3/2} e^{-3R^2/2\langle R^2 \rangle}$$

Gaussian distribution!

Ideal chain (IC)

Now, translate probability distribution function to free energy

$$F = -TS$$

$$S = k_B \ln \Omega (n, R) = k_B \ln[P_{3d}(n, R)\Omega_{tot}]$$

$$S \sim -\frac{3k_B R^2}{2nb^2} + \frac{3}{2} k_B \ln\left(\frac{3}{2\pi n b^2}\right) + k_B \ln \Omega_{tot}$$

S_0: constant

$$\Rightarrow \quad F = -TS = k_B T \frac{3R^2}{2nb^2} - TS_0$$

Ideal chain (IC)

Under external force, $\vec{F}$, in the direction of $\vec{R}$

$$G = -TS - FR \qquad dG = 0$$

$$\Rightarrow \quad \frac{\partial G}{\partial R} = \frac{3k_BT}{nb^2}R - F = 0 \quad \Rightarrow \quad F = \left(\frac{3k_BT}{nb^2}\right)R$$

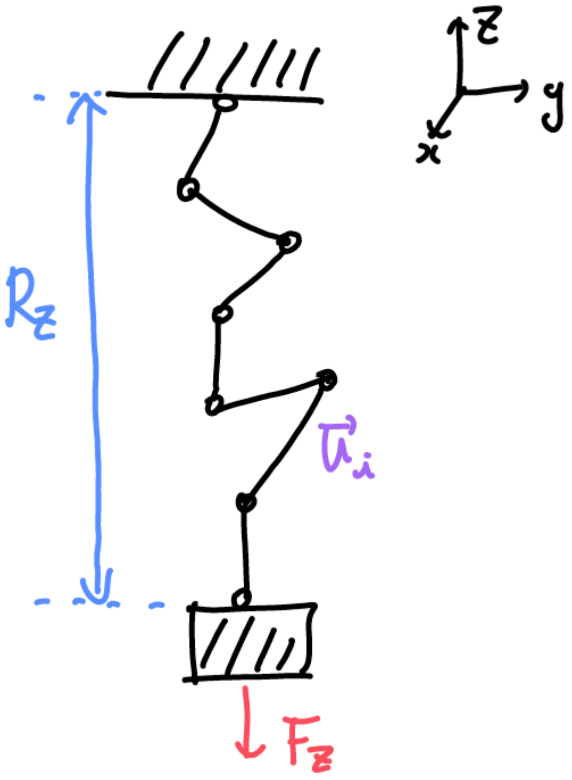
k_{sp}: spring constant

Note

- Non-zero force for non-zero R.
- Linear relation between force-displacement → ENTROPIC spring.
- As T increases, stiffness increases.
- Valid only for flexible polymer with small R.
- Kuhn length is related to the persistence length, $b = 2l_p$

Freely Jointed Chain (FJC)

IC limitation: linear response beyond $L = nb$ ⇨ FJC for realistic description at $R \sim L$



Assumptions

- Inextensible segments (same as IC)
    - End-to end vector

$$\vec{R} = b \sum_{i=1}^{n} \vec{u}_i$$

- Chain extended in direction only
- Describe microstates by directional angle, $(\phi_i, \theta_i) = \Theta$

$$u_{i,x} = \sin\theta_i \cos\phi_i$$
$$u_{i,y} = \sin\theta_i \sin\phi_i$$
$$u_{i,z} = \cos\theta_i$$

- Consider a system, chain and weight,

$$U = -F_Z R_Z$$

Freely Jointed Chain (FJC)

⇨ Use canonical ensemble (constant T, Boltzmann distribution)

Microscopic description: θ_i is an angle w.r.t z-axis

$$R_z = \vec{R} \cdot \hat{e}_z = b \sum_{i=1}^{n} \cos\theta_i \quad \Rightarrow \quad U = -F_z b \sum_{i=1}^{n} \cos\theta_i$$

Probability: $$P(\Theta) = \frac{1}{Z} e^{-U(\Theta)/k_B T}$$

$$Z = \int_{\Theta} exp\left(-\frac{U(\Theta)}{k_B T}\right) d\Theta$$

EPFL

Freely Jointed Chain (FJC)

$$\frac{U(\Theta)}{k_B T} = -\kappa \sum_{i=1}^{n} \cos\theta_i \qquad \kappa \equiv \frac{bF_z}{k_B T}$$

$$Z = \prod_{i=1}^{n} \int_0^{2\pi} \int_0^{\pi} exp(-\kappa\cos\theta_i)\sin\theta_i \, d\theta_i d\phi_i = z^n$$

$$z = 2\pi \int_0^{\pi} exp(-\kappa\cos\theta)\sin\theta \, d\theta = \frac{4\pi}{\kappa}\sinh\kappa$$

Freely Jointed Chain (FJC)

We seek $$\langle R_z \rangle = \int_\Theta P(\Theta)\, R_z d\Theta = \frac{1}{Z}\int_\Theta exp\left(\frac{\kappa R_z}{b}\right) R_z d\Theta$$

One can show $$\int_\Theta exp\left(\frac{\kappa R_z}{b}\right) R_z d\Theta = b\frac{\partial Z}{\partial \kappa}$$

$$\Rightarrow \quad \langle R_z \rangle = \frac{b}{Z}\frac{\partial Z}{\partial \kappa} = b\frac{\partial(\ln Z)}{\partial \kappa} = bn\frac{\partial(\ln z)}{\partial \kappa}$$

$$\langle R_z \rangle = nb\left[\coth\left(\frac{bF_z}{k_BT}\right) - \frac{k_BT}{bF_z}\right]$$

Freely Jointed Chain (FJC)

Note: this could be written as

$$\langle R_z \rangle = k_B T \frac{\partial(\ln Z)}{\partial F_z}$$

Which is generally true (for any spring)

Exercise: $F_z \ll 1$ (Taylor expansion around F_z), show

$$\Rightarrow \quad F = \left(\frac{3k_B T}{nb^2}\right) R_z + H.O.T$$

(IC recovered)

As $F_z \to \infty$, $\coth(*) \to 1$, and $\langle R_z \rangle \to nb = L$