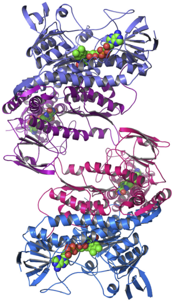
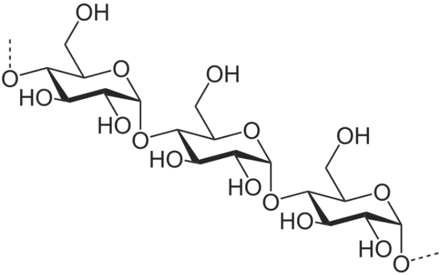
Statistical Theory of Polymers

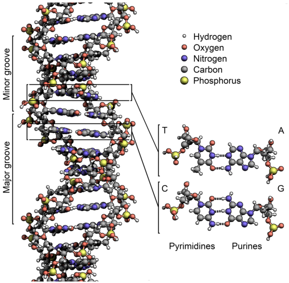
MSE 421 - Ceriotti

Common features of polymers

- Polymers are ubiquitous in biology, as well as in materials science
- Monomer as repeat units, typically joined by stiff covalent bond, but with relatively flexible chain conformation

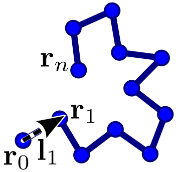


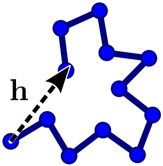


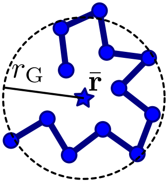


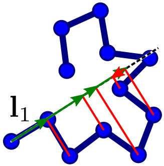
Characterizing polymer configurations

- **Coarse-grained** representation: each monomer is a single bead with position $\mathbf{r}_i$, with $i = 0 \ldots n$
- Vectors joining pairs of beads are labelled as $\mathbf{l}_i = \mathbf{r}_i - \mathbf{r}_{i-1}$, with $l = \sqrt{\langle \mathbf{l} \cdot \mathbf{l} \rangle}$
- Knowledge of the position of each bead matter relatively little - we can use average properties such as the **end-to-end** vector $\mathbf{h} = \mathbf{r}_n - \mathbf{r}_0$
- A more global picture of the size of the polymer is given by its **gyration radius** $\mathbf{r}_G^2 = \frac{1}{n+1} \sum_i \left(\mathbf{r}_i - \bar{\mathbf{r}}\right)^2$
- **Persistence length** $\xi = \frac{1}{l} \sum_{j=0}^{\infty} \mathbf{l}_i \cdot \mathbf{l}_{i+j}$ characterize the polymer rigidity









General relations

- The end-to *vector* is not very interesting: $\langle \mathbf{h} \rangle = \sum_i \langle \mathbf{l}_i \rangle = 0$ due to symmetry. The end-to-end *distance* however contains information about the extent of the polymer

$$h^2 = \sum_{ij} \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle = nl^2 + 2 \sum_i \sum_{j>i} \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle$$

- The gyration radius is closer to experimental observables, but harder to compute - can be shown to be related to the same ingredients as h^2

$$r_G^2 = \frac{(n+2)}{6(n+1)} nl^2 + \sum_{i=1}^{n} \sum_{j>i} \frac{i(n+1-j)}{(n+1)^2} \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle \approx \frac{h^2}{6}$$

- The persistence length can also be related to h

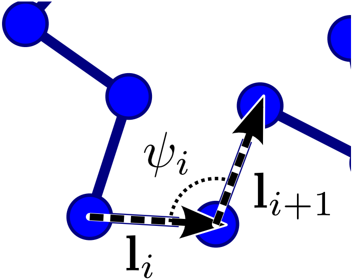
$$\xi = \frac{1}{l} \sum_{j=i}^{\infty} \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle \approx \frac{1}{2nl} \sum_i \left[\sum_{j=i}^{n} \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle + \sum_{j=1}^{i} \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle \right] = \frac{h^2}{2nl} + \frac{l}{2}$$

The derivation of the link between r_G and h is cumbersome, and is left as an optional exercise.

Freely jointed chain

- Simplest possible model: the chain is a random walk in 3D, with steps of equal length l
- The orientation of each segment is independent from that of the others, so $\langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle = l^2 \delta_{ij}$
  - Persistence length is just one bond $\xi = \frac{1}{l} \sum_{j=i}^{\infty} \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle = l$
  - End-to-end distance obeys simple scaling law $h^2 = nl^2 \rightarrow h = l\sqrt{n}$
  - Gyration radius

$$\frac{1}{(n+1)^2} \sum_{i,j>i} (j-i)\, l^2 = \frac{(n+2)}{6\,(n+1)} nl^2$$

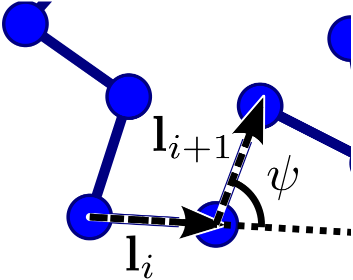


Freely rotating chain

- Often the joint angles are rather rigid, and can be taken to be constant ψ, so $\langle \mathbf{l}_i \cdot \mathbf{l}_{i+1} \rangle = l^2 \cos\psi$
- General correlation can be found iteratively, by considering a sum over orthogonal unit vectors, one of which is parallel to intermediate bonds
[integrals over projections $\perp$ bond average to zero by symmetry]

$$\langle \mathbf{l}_i \cdot \mathbf{l}_{i+2} \rangle = l^2 \cos^2\psi + 0 + 0$$

- In general, $\langle \mathbf{l}_i \cdot \mathbf{l}_{i+k} \rangle = l^2 \cos^k\psi$
  - Persistence length: $\xi = l \sum_{k=0}^{n} \cos^k\psi \sim l / (1 - \cos\psi)$
  - End-to-end distance: $h^2 \approx nl^2 (1 + \cos\psi) / (1 - \cos\psi)$
  - Polymer *stiffness* defined as $C_\infty = (1 + \cos\psi) / (1 - \cos\psi)$



Atomic force spectroscopy of a FJC

- Consider an experiment in which a constant force is applied to the end-points of a polymer (e.g. optical tweezers, AFM, . . .)
- Constant force f, so the work done to extend the polymer to an extension x is fx (equivalent to the pV term!)

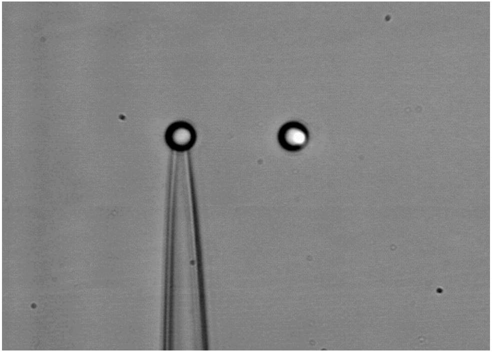
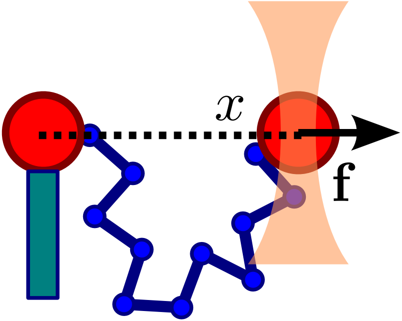


Image from Williams Laboratory @ NEU



Partition function at constant f/1

- The equivalent of the NpT ensemble here is nfT; partition function reads ($E_\nu = 0$!)

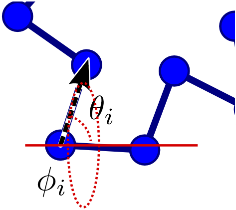
$$\Delta\left(n,f,T\right) = \sum_\nu e^{-\beta E_\nu + \beta f x_\nu} = \sum_\nu e^{\beta f x_\nu}$$

  - The microstates of the polymer can be described by the polar θ_i and ϕ_i bond

$$\sum_\nu \square \equiv \int \mathrm{d}\phi_1 \ldots \int \mathrm{d}\phi_n \int \mathrm{d}\theta_1 \sin\theta_1 \ldots \int \mathrm{d}\theta_n \sin\theta_n \square$$

  - The extension of the polymer along x can be computed as $x_\nu \equiv \sum_i l \cos\theta_i$

- All the polymer bonds are independent. The expression for Δ factors out



$$\Delta\left(n,f,T\right) = \prod_i \int \mathrm{d}\phi_i \mathrm{d}\theta_i \sin\theta_i e^{\beta f l \cos\theta_i} = \left[\frac{4\pi}{\beta f l} \sinh \beta f l\right]^n$$

Polymer extension

- We can obtain the mean extension of the polymer along x from Δ

$$\langle x\rangle = \frac{\partial \ln \Delta}{\partial \beta f} = nl\left(\coth \beta f l - \frac{1}{\beta f l}\right)$$

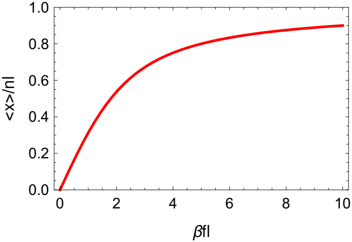
- For small f, harmonic restraint: an **entropic oscillator**!

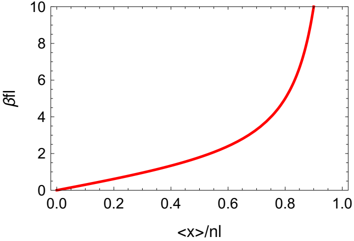
$[\coth x = \frac{1}{x} + \frac{x}{3} + \mathcal{O}\left(x^3\right)]$

$$\langle x\rangle \approx \frac{nl^2\beta}{3} f \rightarrow f \approx \frac{3}{nl^2\beta}\langle x\rangle$$

- For large f, $\coth x \rightarrow 1$. The force diverges when the polymer is fully extended

$$\langle x\rangle \approx nl\left(1 - \frac{1}{\beta f l}\right) \rightarrow f \approx \frac{n}{\beta}\frac{1}{nl - \langle x\rangle}$$





Limits of the statistical treatment

- Rigid bonds - pretty good approximation
- No excluded volume (beads can overlap with each other) - small effect!
- No interaction between the beads - good model when the polymer-solvent interactions match the polymer-polymer interactions (θ solvent)
- More accurate models? Explicit atomistic or coarse-grained simulations!