

## Why are we looking at polymer theory?

- 1) There are some polymers in biology where this is important.
- 2) The theoretical ideas and terminology in polymer theory are important.
- 3) We want to avoid falling into habit of forgetting the flexible nature of proteins (this was actually a common “mistake” before). The idea of “lock and key”, as important as it is, leads to the interpretation that the macromolecular structures are as solid as rocks.
- 4) The idea of a polymer is very important – theoretically and practically - for biotechnology and bioengineering.
- 5) Protein folding <-> unfolding proceeds through “loose” states – this is sometimes referred to as the “molten globule”. We can learn some important things about these states by looking at the behavior of dense, globular, polymers.
- 6) To understand protein structures better, it is good to know the additional effects that can happen when proteins “fold” into their specific structures. We get an appreciation for the forces necessary to counteract the entropic tendencies of a polymer chain.
- 7) The idea of “entropic forces” is important, and is easy to understand with polymers.

## Some polymer statistics

### Freely jointed chain

The end-to-end distance is:

$$\vec{L} = \sum_{i=1}^N \vec{l}_i \quad ; \quad \text{and the mean square end-to-end distance is}$$

$$\langle \vec{L}^2 \rangle = \langle \vec{L} \cdot \vec{L} \rangle = \left\langle \left( \sum_{i=1}^N \vec{l}_i \right) \cdot \left( \sum_{i=1}^N \vec{l}_i \right) \right\rangle = \left( \sum_{i=1}^N l_i^2 \right) + 2 \sum_{1 < i < j < N} \langle \vec{l}_i \cdot \vec{l}_j \rangle$$

If there is **no correlation** between the orientation of segments  $i$  and  $j$  ( $i$  and  $j$  different), and  $l_i = l$  for all  $i$ , then

$$\langle \vec{L}^2 \rangle = Nl^2 \quad ; \quad \text{or, if the chain segments are a little different,}$$

$$\langle \vec{L}^2 \rangle = Nl_{av}^2$$

The distribution function of the end-to-end distance,  $L$ , for a freely jointed chain with  $N$  segments of length  $l$  can be shown to be Gaussian:

$$W(L, N)dL = 4\pi \left( \frac{3}{2\pi Nl^2} \right)^{3/2} \exp\left( -\frac{3L^2}{2Nl^2} \right) L^2 dL$$

This gives:

$$\langle L^2 \rangle = \int_0^{\infty} W(L, N) L^2 dL = 4\pi \left( \frac{3}{2\pi Nl^2} \right)^{3/2} \int_0^{\infty} \exp\left( -\frac{3L^2}{2Nl^2} \right) L^4 dL = Nl^2$$

You can easily show that the **mean square radius** (average of the square distance from the center of mass) of the chain is given by

$$\langle R^2 \rangle = \frac{1}{6} l^2 N = \frac{1}{6} \langle L^2 \rangle \quad ; \quad \text{we will not derive this, but note that it is}$$

easier to **calculate**  $\langle L^2 \rangle$  and easier to **measure**  $\langle R^2 \rangle$ .

### Chain with bond angles held constant

If we have a chain that is not freely jointed, but the direction of every chain segment is on a cone at an angle of  $\theta$  to the previous segment then:

$$\langle \vec{L}^2 \rangle = \vec{L} \cdot \vec{L} = \left( \sum_{i=1}^N l_i^2 \right) + 2 \sum_{1 < i < j < N} \langle \vec{l}_i \cdot \vec{l}_j \rangle = Nl^2 + 2l^2 \sum_{j=2}^N \sum_{i=1}^N \langle \cos \theta_{ij} \rangle$$

can show that  $\langle \cos \theta_{ij} \rangle = (\cos \theta)^{|i-j|}$ , so that

$$\langle L^2 \rangle = Nl^2 \frac{1 + \cos \theta}{1 - \cos \theta} - 2l^2 \cos \theta \frac{1 - \cos^N \theta}{(1 - \cos \theta)^2}$$

usually  $N(1 - \cos \theta) \gg 1$ , so that for this chain with bond angles held constant, and segment lengths identical, with lengths  $l$

$$\langle L^2 \rangle = Nl^2 \frac{1 + \cos \theta}{1 - \cos \theta} = Nl^2 \sigma; \text{ compare to the equation for the fully freely}$$

jointed chain above. The mean square of the end-to-end distance  $\langle L^2 \rangle$  is still proportional to  $N$ , but the “effective” bond length is increased by  $[(1 + \cos \theta)/(1 - \cos \theta)]^{1/2}$ .

If not only the bond angles are constant, but the internal rotation about the bonds,  $\phi$ , is hindered, where the angle of rotation about the bond is measured from  $\phi=0$  at the *trans* position, it can be shown that:

$$\langle L^2 \rangle = Nl^2 \frac{1 + \cos \theta}{1 - \cos \theta} \cdot \frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle}$$

Note that all the equations above for the mean square end-to-end distance can be written simply as

$$\langle L^2 \rangle = Nl^2 \sigma, \text{ where the } \sigma \text{ is a factor that depends on the underlying model, or molecular details.}$$

This suggests that we can replace the real chain by a **fictitious chain** with fewer **chain segments**,  $N_e$ , and longer **effective bond lengths**,  $l_e$ , and these new effective segments are **statistically independent**, and the effective chain behaves like a freely jointed chain with the characteristics  $N_e$ , and  $l_e$ . This simplifies all the calculations if we can do this.

## **“Kuhn” statistical segment length of a polymer**

Define  $l_e$  such that we have  $\langle L^2 \rangle = Nl^2\sigma = l_e^2 N_e$

The **contour length**  $\Lambda$  is the same for all representations,  $\Lambda = Nl = N_e l_e$

**and this means that**  $\langle L^2 \rangle = l \cdot (Nl\sigma) = l \cdot (\Lambda\sigma) = l_e \cdot (l_e N_e) = l_e \Lambda$ ,

so

$$l\sigma = l_e$$

and

$$\sigma = \frac{l_e}{l} = \frac{N}{N_e}$$

$l_e$  is called the *statistical segment length (Kuhn length)*, and  $l_e$  is clearly equal to the *mean square end-to-end length of the bonds in a statistical segment*,

$$l_e = \langle L_\sigma^2 \rangle^{1/2} . \text{ This is an important length quantity to remember for polymers.}$$

The real molecule is treated as a freely jointed chain of  $N_e = \Lambda/l_e$  Kuhn segments

## Wormlike polymer chains

This analysis is a little more involved than the above models, so we will not go through the details. But there are a few important relationships. DNA behaves as this model.

1) **Persistence length,  $l_p$** . The **statistical segment length,  $l_e$** , is related to the persistence length by,  $l_e = 2 l_p$ .

2) The directional correlation of two segments of a macromolecule diminishes exponentially with the length of the chain length separating the two segments.

Look at the above equation: if  $\langle \vec{l}_i \cdot \vec{l}_j \rangle \propto \langle \cos(\theta_{ij}) \rangle \neq 0$ , then

$$\sum_{1 < i < j < N} \langle \vec{l}_i \cdot \vec{l}_j \rangle \neq 0.$$

This means that the segments of the chain are correlated, and this correlation can be expressed qualitatively as the mean cosine of the angle between segments of the polymer.

Call  $\langle \cos \theta(s) \rangle$  the mean cosine of the angle between two segments of the polymer separated by a distance along the polymer of “s”. Then this function has the property called multiplicativity

$$\langle \cos \theta(s + s') \rangle = \langle \cos \theta(s) \rangle \langle \cos \theta(s') \rangle$$

and this is an exponential relationship. So,

$$\langle \cos \theta(s) \rangle = \exp\left(-\frac{s}{l_p}\right) = \exp\left(-\frac{s}{(l_e/2)}\right); \text{ the pre-exponential factor is}$$

unity because  $\cos(0) = 1$ , and  $l_p$  is a constant for the polymer. This equation defines  $l_p$ , and is the definition (one of them) for the **persistence length** of the polymer. So, when you have traveled a length of  $s = l_p$  along the polymer, the average cosine of the angle between the segments separated by the distance  $s = l_p$  is  $e^{-1}$ . This relation is exact if the polymer has isotropic rotational symmetry around its axis. Otherwise the relationship is not exact, but if the chain is long enough the notion can still be applied to the polymer.

3) In the literature the persistence length can roughly be considered as a *maximum chain section that remains straight*; at greater lengths, bending fluctuations destroy the memory of the chain direction. This is not really correct (see 5, below), but is a useful conception.

4) Double helical DNA has  $l_{p, \text{DNA}} = 50 \text{ nm}$  (i.e. approximately 150 base pairs). A synthetic polymer of polystyrene has a persistence length of about =1.0-1.4 nm, which corresponds to about 4-5 longitudinal chain bonds.  $l_p$  is somewhat sequence dependent.

5) How can we correlate the bending modulus of the polymer chain with  $l_p$ ? Consider that the valence angle,  $\gamma$ , between two neighboring segments (separated by  $l$  – the *real* segment length) is fixed, but rotation of the next segment about the axis defined by the previous segment is free (isotropic bends). Using the above multiplicativity property above, we have

$\langle \cos \theta_{i,i+k} \rangle = (\cos \gamma)^k$ ; setting  $k=1$ , so that the distance along the polymer  $s=l$  and comparing this equation to  $\langle \cos \theta(s) \rangle = \exp\left(-\frac{s}{l_p}\right)$  from above, you find,

$l_p = \frac{l_e}{2} = l/|\ln(\cos \gamma)|$ , or more generally  $\ln(\cos(\theta)) = -s/l_p$ , where we can graph to find  $l_p$ ; of course the smaller the valence angle, the longer  $l_p$ .

Now we can derive a relationship between the modulus of “bending elasticity” and the persistence length as follows. For a very short length of polymer

$$\langle \cos \theta(s) \rangle = 1 - \frac{s}{l_p}, \text{ since } \theta \text{ is small, and } \cos \theta(s) \cong 1 - \theta^2(s)/2$$

so that  $\langle \theta^2(s) \rangle \cong 2s/l_p$ . So we can relate the average angular variation over a short distance  $s$  to the persistence length. The bending fluctuations of an elastic rod (isotropic) produce a bending energy proportional to the square of deformation.

$$\Delta E = \left(\frac{1}{2}\right)s\alpha(\theta/s)^2 = \alpha\theta^2/2s, \text{ where } \frac{1}{R_{\text{curvature}}} = \frac{(s/R)}{s} = (\theta/s) \text{ is}$$

**the curvature**, and  $\alpha$  is the effective modulus of bending elasticity for a unit length of the molecule. So the mean square of the bending angle is:

$$\langle \theta^2(s) \rangle = 2 \int \theta^2 \exp(-\Delta E/kT) d\theta / \int \exp(-\Delta E/kT) d\theta = 2skT/\alpha$$

The factor of 2 is because the bending takes place in two planes independently.

Comparing this to the above equation for  $\langle \theta^2(s) \rangle$ , we have:

$$l_p = \frac{l_e}{2} = \alpha/kT. \text{ If we can measure } l_p \text{ we can determine } \alpha, \text{ or the inverse.}$$

A very general equation for the end-to-end distance of a polymer chain is:

$\vec{R} = \int_0^L \vec{u}(s) ds$  (Note we gave the discrete form for a freely jointed chain at the beginning of the lecture),  $\mathbf{u}(\mathbf{s})$  is a unit vector at the position “ $\mathbf{s}$ ”.

We can calculate the mean square:

$$\langle \vec{R}^2 \rangle = \int_0^L ds \int_0^{L-s} ds' \langle \vec{u}(s) \cdot \vec{u}(s') \rangle = 2 \int_0^L ds \int_0^{L-s} dt \langle \cos \theta(t) \rangle$$

where  $t = s' - s$ .

Using the definition of the persistence length:  $\langle \cos \theta(s) \rangle = \exp\left(-s/l_p\right)$

We have:

$$\langle \vec{R}^2 \rangle = 2l_p^2 \left[ \left( \frac{L}{l_p} \right) - 1 + \exp\left(-L/l_p\right) \right].$$

This is a general equation, and the two interesting limiting cases are:

1)  $\langle \vec{R}^2 \rangle \approx L^2$ , for  $L \ll l_p$  Hardly bending, and very stiff for the length.

and

2)  $\langle \vec{R}^2 \rangle \approx 2Ll_p = Ll_e$ , for  $L \gg l_p, l_e$  This is for the long polymer, where the statistical theories hold. This is a very important relationship.

Note for the long polymer, this derivation also shows that the persistence length is  $1/2$  the Kuhn length: remember the contour length discussion above,  $\Lambda = Nl = N_e l_e$

**Relation between the Kuhn length and the persistence length:**

That is:  $l_e = 2l_p$ . The factor of two, signifies that the segment orientation spreads in two opposing direction on the chain.