PHYS 4xx Poly 2 - Sizes of polymer chains

Ideal chains and filaments

A flexible filament or polymer has an end-to-end displacement vector \( \mathbf{r}_{ee} \) that is less than the contour length \( L_c \) of the polymer.

\[ \mathbf{r}(s) = \text{position at arc length } s, \text{ so that} \]
\[ \langle r_{ee}^2 \rangle = \langle [\mathbf{r}(L_c) - \mathbf{r}(0)]^2 \rangle \]
\[ \langle .... > = \text{ensemble average} \]  

(1)

• cast (1) into an integral using the unit tangent vector \( \mathbf{t}(s) = \frac{\partial \mathbf{r}}{\partial s} \),

\[ \mathbf{r}(s) = \mathbf{r}(0) + \int_0^s du \mathbf{t}(u), \]
then

\[ \langle r_{ee}^2 \rangle = \int_0^{L_c} du \int_0^{L_c} dv \langle \mathbf{t}(s) \cdot \mathbf{t}(0) \rangle. \]

(2)

• replace the correlation function \( \langle \mathbf{t}(s) \cdot \mathbf{t}(0) \rangle \) by \( \exp(-s/\xi_p) \)

\[ \langle r_{ee}^2 \rangle = \int_0^{L_c} du \int_0^{L_c} dv \exp(-|u-v|/\xi_p). \]

(3)

• the argument of the exponential must be negative: break the integral into two pieces where one integration variable is kept less than the other:

\[ \langle r_{ee}^2 \rangle = 2 \int_0^{L_c} du \int_0^u dv \exp(-|u-v|/\xi_p), \]

(4)

• solve this integral using a few changes of variables

\[ 2 \int_0^{L_c} du \exp(-u/\xi_p) \int_0^{L_c} dv \exp(v/\xi_p) = 2 \int_0^{L_c} du \exp(-u/\xi_p) \cdot \xi_p \cdot [ \exp(u/\xi_p) - 1 ] \]

\[ = 2 \xi_p^2 \int_0^{L_c/\xi_p} dw \ [1 - \exp(-w)]. \]

(5)

• evaluating the last integral gives

\[ \langle r_{ee}^2 \rangle = 2 \xi_p^2 \{ (L_c/\xi_p - 0) + [ \exp(-L_c/\xi_p) - 1 ] \}. \]

or

\[ \langle r_{ee}^2 \rangle = 2 \xi_p L_c - 2 \xi_p^2 [1 - \exp(-L_c/\xi_p)]. \]

(6)
• rod-like limit $\xi_p >> L_c$:

$$<r_{ee}^2> = 2\xi_p L_c - 2\xi_p^2 \left\{ 1 - \left[ 1 + (-L_c/\xi_p) + (-L_c/\xi_p)^2/2 \right] \right\}$$

$$= 2\xi_p L_c - 2\xi_p^2 L_c + 2L_c^2/2$$

or $<r_{ee}^2>^{1/2} = L_c$

• spaghetti-like limit $\xi_p << L_c$: the exponential in (7) vanishes and

$$<r_{ee}^2> = 2\xi_p L_c - 2\xi_p^2 \approx 2\xi_p L_c$$

(8)

CONCLUSION: the size of the polymer grows like $L_c^{1/2}$.

Discrete representation: polymer is a set of bond vectors $b_i$ with the same magnitude and direction as the monomers

```
  \begin{align*}
    b_2 & \quad b_3 \\
    b_1 & \quad b_4 \\
    \text{ree} & \\
  \end{align*}
```

• construct $r_{ee}$ from all $N$ vectors along the chain

$$r_{ee} = \sum_{i=1,N} b_i,$$

(9)

• take the ensemble average over all chains with the same $N$

$$<r_{ee}^2> = \sum_i \sum_j <b_i \cdot b_j>.$$

(10)

• now assume that all $b_i$ have the same length $b$. Break the sum up into 2 parts

$$<r_{ee}^2> = \sum_{i,j} <b_i \cdot b_j> + \sum_i \sum_{j \neq i} <b_i \cdot b_j>$$

(11)

the first summation has $N$ terms, all of the form $b_i \cdot b_i = b^2$.

the second term is a sum over randomly oriented vectors, with any $b_i$ being uncorrelated with respect to any other $b_j$. Thus

$$\sum_i \sum_{j \neq i} <b_i \cdot b_j> = 0$$

• add two contributions in (11) to give

$$<r_{ee}^2> = Nb^2$$

(random chain)

(12)

or, since $L_c = Nb$

$$<r_{ee}^2> = L_c b$$

(13)

• the form of Eq. (13) is the same as Eq. (8), and we can identify

$$\xi_p = b/2$$

(random chain)

(14)

• in Eqs. (8) and (13), the power law behavior
Other chain geometries

- physical systems have an excluded volume that enforces self-avoidance of the chain

- example: a self-avoiding chain in one dimension cannot reverse on itself from one step to the next, so that $r_{ee} \sim L_c^1$ (vs. $<r_{ee}^2>^{1/2} \sim L_c^{1/2}$ for all ideal chains)

- Flory developed a model for self-avoiding chains which gave the scaling behavior

$$<r_{ee}^2>^{1/2} \sim N^{1/2}$$

Diffusion

The trajectory of an individual molecule diffusing through a medium has the form of a random walk. If the diffusing molecule travels a distance $\ell$ before it collides with some other component of the system, then the end-to-end displacement $r_{ee}$ of the trajectory of a specific diffusing particle obeys

$$<r_{ee}^2> = \ell^2 N,$$  \hspace{1cm} (16)

where $N$ is the number of steps. If there is one step per unit time, then $N = t$ and

$$<r_{ee}^2> = \ell^2 t.$$  \hspace{1cm} (17)

Now, the units of Eq. (17) aren't quite correct, in that the left-hand-side has units of [length$^2$] while the right hand side has [length$^2$]$\cdot$[time]. We accommodate this by writing the displacement as

$$<r_{ee}^2> = 6Dt,$$  \hspace{1cm} diffusion in three dimensions

where $D$ is the diffusion coefficient.

The factor of 6 in Eq. (18) is dimension-dependent: for each Cartesian axis, the mean squared displacement is equal to $2Dt$. That is, if an object diffuses in one dimension
only (for example, a molecule moves randomly along a track) then

\[ \langle r_{ee}^2 \rangle = 2Dt \]  \hspace{1cm} \text{diffusion in one dimension} \hspace{1cm} (19)

and if it is confined to a plane, such as a protein moving in the lipid bilayer of the cell's plasma membrane, then

\[ \langle r_{ee}^2 \rangle = \langle r_{ee,x}^2 \rangle + \langle r_{ee,y}^2 \rangle = 2Dt + 2Dt = 4Dt. \]  \hspace{1cm} \text{diffusion in two dimensions} \hspace{1cm} (20)

A molecule diffusing in a liquid of like objects has a diffusion coefficient \( D \) in the range \( 10^{-14} \) to \( 10^{-10} \) m\(^2\)/s, depending on the size of the molecule. Some examples:

<table>
<thead>
<tr>
<th>System</th>
<th>( D ) (m(^2)/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xenon</td>
<td>( 5760 \times 10^{-9} )</td>
</tr>
<tr>
<td>Water</td>
<td>( 2.1 \times 10^{-9} )</td>
</tr>
<tr>
<td>Sucrose in water</td>
<td>( 0.52 \times 10^{-9} )</td>
</tr>
<tr>
<td>Serum albumin in water</td>
<td>( 0.059 \times 10^{-9} )</td>
</tr>
</tbody>
</table>

(All measurements are at 25 °C, except xenon gas at 20 °C)

The diffusion coefficient can be determined analytically for a few specific situations. One case is the random motion of a sphere of radius \( R \) subject to Stokes' Law for drag: \( F = 6\pi \eta R v \) where \( v \) is the speed of the sphere and \( \eta \) is the viscosity of the fluid.

\[ D = \frac{k_B T}{6\pi \eta R}. \]  \hspace{1cm} \text{Einstein relation} \hspace{1cm} (21)

A molecule like a protein can rotate around its axis at the same time as it travels. A random "walk" in angle \( \theta \) as an object rotates around its axis can be written as

\[ \langle \theta^2 \rangle = 2D_t t, \]  \hspace{1cm} (22)

where \( D_t \) is the rotational diffusion coefficient.

For a sphere rotating in a viscous medium, there is an expression for \( D_t \) just like the translational diffusion of Eq. (21), namely

\[ D_t = \frac{k_B T}{8\pi \eta R^3}. \]  \hspace{1cm} \text{rotational diffusion} \hspace{1cm} (23)

Note, the units of \( D_t \) are [time\(^{-1}\)], whereas \( D \) is [length\(^2\)/time]; hence, there is an extra factor of \( R^2 \) in the denominator of Eq. (23) compared to Eq. (21).