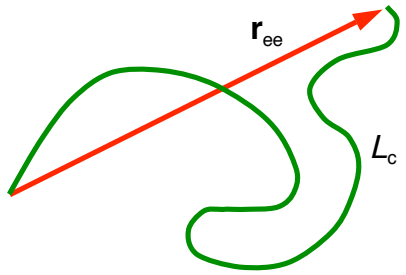
PHYS 4xx Poly 2 - Sizes of polymer chains

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.



- $\mathbf{r}(s)$ = position at arc length s, so that
  $\langle \mathbf{r}_{ee}^2 \rangle = \langle [\mathbf{r}(L_c) - \mathbf{r}(0)]^2 \rangle$ $\langle ... \rangle$ = ensemble average (1)

- cast (1) into an integral using the unit tangent vector $\mathbf{t}(s) = \partial \mathbf{r} / \partial s$
  $\mathbf{r}(s) = \mathbf{r}(0) + \int_0^s du\, \mathbf{t}(u)$, (2)
  then
  $\langle \mathbf{r}_{ee}^2 \rangle = \int_0^{Lc} du \int_0^{Lc} dv \langle \mathbf{t}(s) \cdot \mathbf{t}(0) \rangle$. (3)

- replace the correlation function $\langle \mathbf{t}(s) \cdot \mathbf{t}(0) \rangle$ by $\exp(-s/\xi_p)$
  $\langle \mathbf{r}_{ee}^2 \rangle = \int_0^{Lc} du \int_0^{Lc} dv \exp(-|u-v| /\xi_p)$. (4)

- the argument of the exponential must be negative: break the integral into two pieces where one integration variable is kept less than the other:
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  $\langle \mathbf{r}_{ee}^2 \rangle = 2 \int_0^{Lc} du \int_0^{u} dv \exp(-[u-v] /\xi_p)$, (5)

- solve this integral using a few changes of variables

$$2\int_0^{L_c} du\ \exp(-u/\xi_p) \int_0^{u} dv \exp(v/\xi_p) = 2\int_0^{L_c} du\ \exp(-u/\xi_p) \cdot \xi_p \cdot [\exp(u/\xi_p) - 1]$$
$$= 2\xi_p^2 \int_0^{L_c/\xi_p} dw\ [1 - \exp(-w)]. \quad (6)$$

- evaluating the last integral gives
  $\langle \mathbf{r}_{ee}^2 \rangle = 2\xi_p^2 \{ (L_c/\xi_p - 0) + [\exp(-L_c/\xi_p) - 1] \}$.

or

$\langle \mathbf{r}_{ee}^2 \rangle = 2\xi_p L_c - 2\xi_p^2 [1 - \exp(-L_c /\xi_p)]$. (7)

- rod-like limit $\xi_p >> L_c$:

$$\langle \mathbf{r}_{ee}^2 \rangle = 2\xi_p L_c - 2\xi_p^2 \left\{1 - [1 + (-L_c/\xi_p) + (-L_c/\xi_p)^2/2....] \right\}$$
$$= 2\xi_p L_c - 2\xi_p L_c + 2L_c^2/2$$

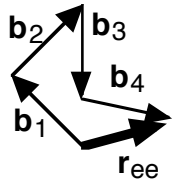
or $\langle \mathbf{r}_{ee}^2 \rangle^{1/2} = L_c$

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

$$\langle \mathbf{r}_{ee}^2 \rangle = 2\xi_p L_c - 2\xi_p^2 \cong 2\xi_p L_c \quad (8)$$

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

Discrete representation: polymer is a set of bond vectors $\mathbf{b}_i$ with the same magnitude and direction as the monomers



- construct $\mathbf{r}_{ee}$ from all N vectors along the chain

$$\mathbf{r}_{ee} = \Sigma_{i=1,N}\, \mathbf{b}_i, \quad (9)$$

- take the ensemble average over all chains with the same N

$$\langle \mathbf{r}_{ee}^2 \rangle = \Sigma_i \Sigma_j \langle \mathbf{b}_i \cdot \mathbf{b}_j \rangle. \quad (10)$$

- now assume that all $\mathbf{b}_i$ have the same length b. Break the sum up into 2 parts

$$\langle \mathbf{r}_{ee}^2 \rangle = \Sigma_{i=j} \langle \mathbf{b}_i \cdot \mathbf{b}_j \rangle + \Sigma_i \Sigma_{j \neq i} \langle \mathbf{b}_i \cdot \mathbf{b}_j \rangle \quad (11)$$

the first summation has N terms, all of the form $\mathbf{b}_i \cdot \mathbf{b}_i = b^2$.
the second term is a sum over randomly oriented vectors, with any $\mathbf{b}_i$ being uncorrelated with respect to any other $\mathbf{b}_j$. Thus
$\Sigma_i \Sigma_{j \neq i} \langle \mathbf{b}_i \cdot \mathbf{b}_j \rangle = 0$

- add two contributions in (11) to give

$$\langle \mathbf{r}_{ee}^2 \rangle = Nb^2 \quad \text{(random chain)} \quad (12)$$

or, since $L_c = Nb$

$$\langle \mathbf{r}_{ee}^2 \rangle = L_c b \quad (13)$$

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

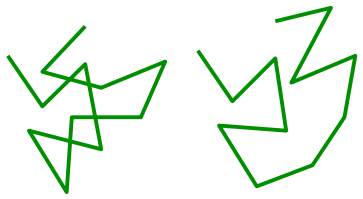
$$\xi_p = b/2 \quad \text{(random chain)} \quad (14)$$

- in Eqs. (8) and (13), the power law behavior

$\langle \mathbf{r}_{ee}^2 \rangle^{1/2} \sim N^{1/2}$ is called *ideal* scaling

Other chain geometries

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



random self-avoiding

- 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.* $\langle \mathbf{r}_{ee}^2 \rangle^{1/2} \sim L_c^{1/2}$ for all ideal chains)

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

$$r \sim N^{\nu} \quad \text{with} \quad \nu = 3 / (2+d) \qquad \text{(Flory)} \tag{15}$$

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 ℓ before it collides with some other component of the system, then the end-to-end displacement $\mathbf{r}_{ee}$ of the trajectory of a specific diffusing particle obeys

$$\langle \mathbf{r}_{ee}^2 \rangle = \ell^2 N, \tag{16}$$

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

$$\langle \mathbf{r}_{ee}^2 \rangle = \ell^2 t. \tag{17}$$

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}]•[*time*]. We accommodate this by writing the displacement as

$$\langle \mathbf{r}_{ee}^2 \rangle \equiv 6Dt \qquad \text{diffusion in three dimensions} \tag{18}$$

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

$$\langle \mathbf{r}_{ee}^2 \rangle = 2Dt \qquad \text{diffusion in one dimension} \qquad (19)$$

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

$$\langle \mathbf{r}_{ee}^2 \rangle = \langle \mathbf{r}_{ee,x}^2 \rangle + \langle \mathbf{r}_{ee,y}^2 \rangle$$
$$= 2Dt + 2Dt = 4Dt. \qquad \text{diffusion in two dimensions} \qquad (20)$$

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:

System	D (m^2/s)
Xenon	5760×10^{-9}
Water	2.1×10^{-9}
Sucrose in water	0.52×10^{-9}
Serum albumin in water	0.059×10^{-9}

(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 η is the viscosity of the fluid.

$$D = k_B T / 6\pi\eta R. \qquad \text{Einstein relation} \qquad (21)$$

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

$$\langle \theta^2 \rangle = 2D_r t, \qquad (22)$$

where D_r is the rotational diffusion coefficient.

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

$$D_r = k_B T / 8\pi\eta R^3. \qquad \text{rotational diffusion} \qquad (23)$$

Note, the units of D_r 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).