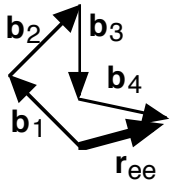
Lecture 30 – Random walks

What's important:
- random walks
- diffusion

Demonstrations: 4 sets of 12" plastic vectors

Random walks

The behaviour of a random walk underlies many physical phenomena, so it is worthwhile to derive its general form and then apply it to several situations of interest. We consider a walk with steps of equal length *b*, where the direction of successive steps is completely random:



We characterize a given walk by the end-to-end displacement vector $\mathbf{r}_{ee}$. To represent this mathematically, we use a set of bond vectors $\mathbf{b}_i$ with the same magnitude and direction as the monomers. Then we construct $\mathbf{r}_{ee}$ from all *N* vectors along the chain

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

Demo: do 8 configurations with the plastic vectors and compare $\langle \mathbf{r}_{ee}^2 \rangle$ with Nb^2.

The (squared) length of the walk is given by the dot product of $\mathbf{r}_{ee}$ with itself:

$$\mathbf{r}_{ee} \cdot \mathbf{r}_{ee} = (\Sigma_{i=1,N}\, \mathbf{b}_i) \cdot (\Sigma_{j=1,N}\, \mathbf{b}_j)$$

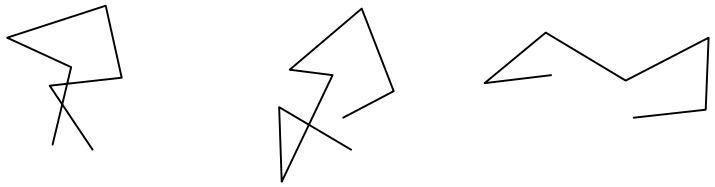
$$= (\mathbf{b}_1 + \mathbf{b}_2 + \mathbf{b}_3 + ...) \cdot (\mathbf{b}_1 + \mathbf{b}_2 + \mathbf{b}_3 + ...)$$

$$= \mathbf{b}_1^2 + \mathbf{b}_2^2 + \mathbf{b}_3^2 \ldots + 2\mathbf{b}_1 \cdot \mathbf{b}_2 + 2\mathbf{b}_1 \cdot \mathbf{b}_3 + 2\mathbf{b}_1 \cdot \mathbf{b}_4 + \ldots + 2\mathbf{b}_2 \cdot \mathbf{b}_3 ....$$

In this sum, there are *N* terms of the form $\mathbf{b}_i^2$, each of which is just b^2, since all steps have the same length. Thus, for a given walk

$$\mathbf{r}_{ee}^2 = Nb^2 + 2\mathbf{b}_1 \cdot \mathbf{b}_2 + 2\mathbf{b}_1 \cdot \mathbf{b}_3 + 2\mathbf{b}_1 \cdot \mathbf{b}_4 + \ldots + 2\mathbf{b}_2 \cdot \mathbf{b}_3 .... \qquad (2)$$

Now, we generate $\mathbf{r}_{ee}$ for a given chain with Eq. (2). But there are an infinite number of random walks of *N* steps starting from the same origin:



We can find the average value of $\langle \mathbf{r}_{ee}^2 \rangle$ by summing over all these paths. At first, this looks intimidating, but the mathematics is actually quite simple. From Eq. (2):

$$\langle \mathbf{r}_{ee}^2 \rangle = Nb^2 + 2(\mathbf{b}_1 \cdot \mathbf{b}_2)_{av} + 2(\mathbf{b}_1 \cdot \mathbf{b}_3)_{av} + 2(\mathbf{b}_1 \cdot \mathbf{b}_4)_{av} + \ldots + 2(\mathbf{b}_2 \cdot \mathbf{b}_3)_{av} \ldots . \qquad (3)$$

where < … > means "construct the average".

The average value of $\mathbf{b}_1 \cdot \mathbf{b}_2$ is the average of $\mathbf{b}_1$ with all other vectors $\mathbf{b}_2$, some of which point in the same direction as $\mathbf{b}_1$ and some of which point in the opposite direction:

$\mathbf{b}_1 \cdot \mathbf{b}_2 = b^2$ if $\mathbf{b}_1$ and $\mathbf{b}_2$ point in exactly the same direction

$\mathbf{b}_1 \cdot \mathbf{b}_2 = -b^2$ if $\mathbf{b}_1$ and $\mathbf{b}_2$ point in exactly the opposite direction

The bottom line is that for every configuration with $\mathbf{b}_1 \cdot \mathbf{b}_2 = b_{12}$, there is another configuration with $\mathbf{b}_1 \cdot \mathbf{b}_2 = -b_{12}$, because the configurations are completely random. Thus, averaged over all possible configurations

$(\mathbf{b}_1 \cdot \mathbf{b}_2)_{av} = 0$

The same goes for all other combinations, as long as the indices are different. So, we find the simple, elegant and **very important** result

$\langle \mathbf{r}_{ee}^2 \rangle = Nb^2$. (random walk)

Recognizing that the contour length L is equal to

$L = Nb$

then another way of writing $\langle \mathbf{r}_{ee}^2 \rangle$ is

$\langle \mathbf{r}_{ee}^2 \rangle = bL$. (random walk)

Example: proteins

A protein is a linear sequence of amino acids, of which 20 types are used for proteins in our bodies. Each contributes 0.36 nm to the string's contour length L (Creighton's *Proteins*)

AA — AA — AA — AA — AA

For example, the protein actin (major part of our muscles) is 375 AA long, giving an overall length of 135 nm. But the amino acid backbone of a protein does not behave like a stiff rod; rather, it wiggles and sticks to itself at various locations. The random walk gives an approximate value for its size (a better calculation would include self-

interactions along the protein chain):

$$\langle \mathbf{r}_{ee}^2 \rangle = Nb^2 = 375\ (0.36)^2$$

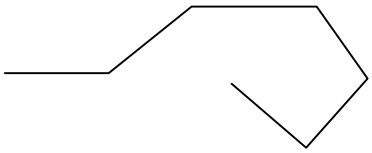
or

$$r_{ee,av} \sim \sqrt{375} \times 0.36 = 7.0 \text{ nm}$$

In other words, the radius of the ball (<10 nm) is *much* less than its length when fully stretched (135 nm). Attractive interactions among the AAs reduces the size further still.

Persistence length

The calculation above was for a freely-jointed chain – any angular orientation of the joint has the same energy. What happens if this is not true: suppose that a strong deformation requires more energy than a mild deformation? As an example, consider the configurations of a saturated alkane, $-CH_2-$ (repeated), where the polar angle between successive carbons is close to the tetrahedral value of 109.5°, but the chain is free to rotate in the azimuthal angle about the C-C bond.



One can show that the general behaviour of the ideal chain $\langle r_{ee}^2 \rangle \sim N$ still holds, but the prefactor in the scaling law is different. If the polar angle is fixed at α, then

$$\langle r_{ee}^2 \rangle = Nb^2\ (1 - \cos\alpha) / (1 + \cos\alpha)$$

where b is the bond length. Using $\alpha = 109.5^\circ$ ($\cos\alpha = -1/3$)

$$(1 - \cos\alpha) / (1 + \cos\alpha) = (4/3) / (2/3) = 2$$

Thus, in this case

$$\langle r_{ee}^2 \rangle = 2Nb^2 = (2b)\ (Nb) = (2b)\ L$$

where L is the total length of the chain, $L = Nb$.

First, this shows that the scaling is the same as a freely jointed chain, but $\langle r_{ee}^2 \rangle$ is larger, because the chain is effectively stiffer.

Second, this suggests a way of parametrizing the stiffness of the chain through the introduction of a persistence length ξ:

$$\langle r_{ee}^2 \rangle = 2\xi L$$

In the above examples:

Freely jointed chain	$\xi = b / 2$
Alkane model	$\xi = b$

Examples

Filament	ξ (nm)
Alkane	0.5
DNA	53
filamentous actin	10-20 x 10^3
microtubules	1-6 x 10^6

A simple calculation of $\langle r_{ee}^2 \rangle$ for DNA with a persistence length of 53 nm will show that bacterial DNA is balled up into a region roughly the size of a bactyerium, but human DNA is much too large to fit into a normal eucaryotic cell, let alone its nucleus.