Lecture 4 - Chains

What's Important:

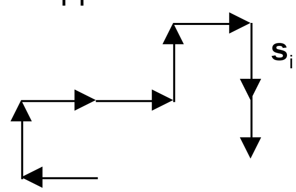
- random walk in higher dimensions
- self-avoiding walk
- central limit theorem

Text: Reif

Further reading: Secs. 1.7 to 1.11 of Reif

Random walk in higher dimensions

The one-dimensional random walk can be generalized to higher dimensions without difficulty. Consider a *d*-dimensional vector $\mathbf{s}_i$ describing the i[th] step of a walk. On a lattice, the walk would have the appearance



In terms of its elementary steps, the tail-to-tip vector **m** is

$$\mathbf{m} = \mathbf{s}_1 + \mathbf{s}_2 + \mathbf{s}_3 \ldots = \Sigma_i \, \mathbf{s}_i.$$

As in one dimension, let's assume that all elementary steps have the same length ℓ. Then the squared length of the walk is

$$\mathbf{m}^2 = m^2 = \Sigma_i \, \mathbf{s}_i \bullet \Sigma_j \, \mathbf{s}_j$$
$$= \Sigma_i \, \mathbf{s}_i^2 + \Sigma_i \Sigma_{j\neq i} \, \mathbf{s}_i \bullet \mathbf{s}_j$$
$$= N \ell^2 + \Sigma_i \Sigma_{j\neq i} \, \mathbf{s}_i \bullet \mathbf{s}_j.$$

This gives the length of a specific walk. The mean square length for a given *N* for all walks is

$$\langle \mathbf{m}^2 \rangle = N \ell^2 + \langle \Sigma_i \Sigma_{j\neq i} \, \mathbf{s}_i \bullet \mathbf{s}_j \rangle.$$

Now, if steps *i* and *j* are statistically independent (*i.e.*, the walks are truly random) then the expectations of the sums separate

$$\langle \Sigma_i \Sigma_{j\neq i} \, \mathbf{s}_i \bullet \mathbf{s}_j \rangle = \Sigma_i \Sigma_{j\neq i} \langle \mathbf{s}_i \rangle \bullet \langle \mathbf{s}_j \rangle.$$

If there is no preferred direction to the walk (in one dimension, this would be $p = q$) then

$$\langle \mathbf{s}_j \rangle = 0$$

and we are left with

$$\langle \mathbf{m}^2 \rangle = N \ell^2 \qquad \text{(random)}$$

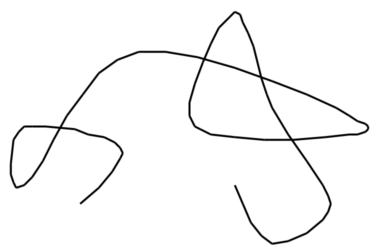
or

$$<\mathbf{m}^2>^{1/2} = N^{1/2}\,\ell. \qquad (4.1)$$

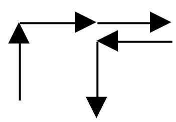
Note that this result is independent of the embedding dimension *d*.

Polymers and random walks

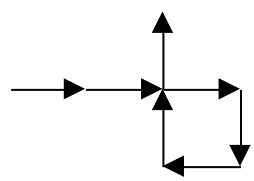
A polymer is a long (chain) molecule composed of many repeat units called monomers. An isolated chain (with no branches) in a good solvent looks like



Such configurations are similar to those of the random walk, **except** that the steric interactions between monomers forbids reversals or intersections. On a lattice, this means that the following configurations are forbidden:



reversal



intersection

Thus, a single polymer chain behaves like a self-avoiding random walk (SARW), for which

$$< m^2 >^{1/2} \sim N^{\frac{3}{d+2}} \qquad \text{(from Flory)} \qquad (4.2)$$

In one to four dimensions

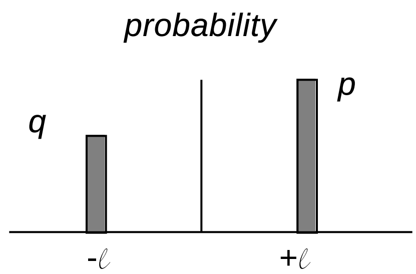
$d = 1$	$d = 2$	$d = 3$	$d = 4$
$< m^2 >^{1/2} \sim N^1$	$< m^2 >^{1/2} \sim N^{3/4}$	$< m^2 >^{1/2} \sim N^{3/5}$	$< m^2 >^{1/2} \sim N^{1/2}$
straight line	walk is larger than $N^{1/2}$		walk is same as $N^{1/2}$ SA is unimportant

In fact, in many cases the ideal random walk is still an accurate description of a polymer's properties.

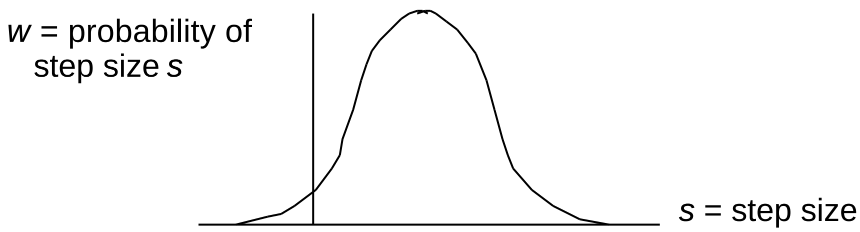
Continuous step sizes in one dimension

Note: Reif presents a longer description of continuous step sizes than what is provided here.

In one dimension, we considered only two steps - to the left or right with the same length, but possibly different probabilities:



Suppose instead that the step size is continuously distributed in either direction



Then, if

$$\bar{s} = \int w(s)\, s\, ds \qquad \text{for a single step}$$

we find

$$\bar{x} = \overline{\sum_i s_i} = \sum_{i=1}^{N} \overline{s_i} = N\bar{s} \qquad (4.3)$$

because each single step has the same mean value.

Dispersions can be evaluated in a similar way. The mean square difference in displacement is

$$\overline{\Delta x^2} = \overline{(x - \bar{x})^2}$$

where, *for a single configuration*

$$\Delta x = \left(\sum_{i=1,N} s_i \right) - N\bar{s}$$

$$= \sum_{i=1,N} (s_i - \bar{s})$$

$$= \sum_{i=1,N} \Delta s_i$$

Thus, *for a single configuration*

$$(\Delta x)^2 = \left(\sum_i \Delta s_i\right)\left(\sum_j \Delta s_j\right)$$
$$= \sum_i (\Delta s_i)^2 + \sum_i \sum_{j \neq i} \Delta s_i \cdot \Delta s_j$$

Now take the expectation, moving the average into the summation

$$\overline{(\Delta x)^2} = \sum_i \overline{(\Delta s_i)^2} + \sum_i \sum_{j \neq i} \overline{\Delta s_i \cdot \Delta s_j}$$

For a random walk, the steps inside the double summation are uncorrelated and may be factored into

$$\sum_i \sum_{j \neq i} \overline{\Delta s_i \cdot \Delta s_j} = \sum_i \sum_j \overline{\Delta s_i} \cdot \overline{\Delta s_j} = 0$$

where the second equality follows from

$\overline{\Delta s_i} = 0$ (from the definition of the mean $\overline{\Delta s_i} = \overline{(s_i - \bar{s})} = (\bar{s} - \bar{s}) = 0$)

Thus,

$$\overline{(\Delta x)^2} = N\overline{(\Delta s)^2} \tag{4.4}$$

where

$$\overline{\Delta s^2} = \int w(s)(\Delta s)^2 ds \tag{4.5}$$

Central limit theorem

In the large-N limit, the distribution in tail-to-tip displacements has the same general form as the *p - q* distribution

$$P(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right) \tag{4.6}$$

with

$$\sigma^2 = N\overline{(\Delta s)^2} \qquad \mu = N\bar{s}\ . \tag{4.7}$$

This result is very general. No matter what the form of $W(s)$ is, the distribution has the same Gaussian form in terms of $\bar{s}$ and $\overline{(\Delta s)^2}$. This is the **central limit theorem** for random distributions at large N.