IV.2. Random Walk and Brownian Motion

IV.2.1. Random Walk

In the absence of spatial asymmetries leading to drifts in time of the entire probability distribution, the probabilities for transitions are isotropic, not dependent on the direction of the transition. This is the so-called diffusion limit. If the process occurs on a discrete spatial grid or lattice, one speaks of a random walk in space. In Fig. IV.7, a one-dimensional grid in *x*-direction is shown with bins labeled according to the number *m* of steps from the origin (*x=0*) of the random walk. Each step of size Δx is chosen at random with an equal probability for a step to the left ($p_- = 1/2$) or to the right ($p_+ = 1/2$).

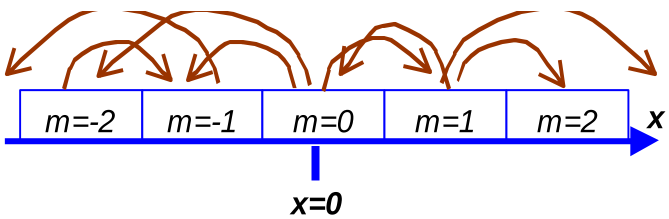

Figure IV-7: Random walk in one dimension

Obviously, since the probabilities are equal to go left or right, on average, the random walker will still be at $x = 0$ or $m = 0$. However, the probability $f_m(N)$ is not zero for reaching position *m* after a total number of *N* steps. For this to happen, the walker must have made *m* more steps in the positive *x* direction than in the opposite direction. Since the total number of steps is equal to *N*, the numbers of steps in negative (N_-) and positive (N_+) direction are

$$N_- = \frac{1}{2}(N - m) \qquad N_+ = \frac{1}{2}(N + m) \qquad \text{(IV.31)}$$

For example, if the total number of steps is $N=11$, the number $N_+ = 9$ implies that there have been *9* steps in positive and *2* steps in negative direction. Hence, on this (and any) $N_+ = 9$ trajectory, $m=7$ more steps have been made in positive direction than in the opposite direction. For positive *m*-values, the number N_+ can range from $N_+ = 0$ (no step to the ***right***) to $N_+ = 11$ (all steps to the ***right***). For negative values of *m*, the number N_+ can range from $N_+ = -1$ (one step to the ***left***) to $N_+ = -11$ (all steps to the ***left***).

However, whenever N_+ has been determined, the number $N_- = N - N_+$ of steps to the other side is determined by the normalization $N = N_+ + N_-$. Therefore, the ***entire range of possibilities is covered already by considering the range of*** $N_+ \geq 0$, i.e., $0 \leq m \leq N$. Varying N_+ over its total range covers, hence, all trajectories twice. This affects the calculation of higher moments from the distribution for all N_+. For example, the variance in N_+ calculated with the full N_+ distribution is twice the real variance and equal to that calculated for only the distribution for $N_+ \geq 0$. One further realizes that, because of the linear relationship between N_+ and *m* given by Equ. IV. 31, the *m*-distribution resembles the N_+-distribution but is shifted and stretched by a factor of (2).

Since the process is random, all pathways of length *N* are equally likely. Hence, to evaluate the probability for a given N_+, which is equal to that for a given *m*, is equivalent to asking, how many ways there are to distribute N_+ steps along a total of *N* steps. In other words, one has to answer the question as to how many ways there are to form an N_+-tuple of numbers out of *N* total numbers.

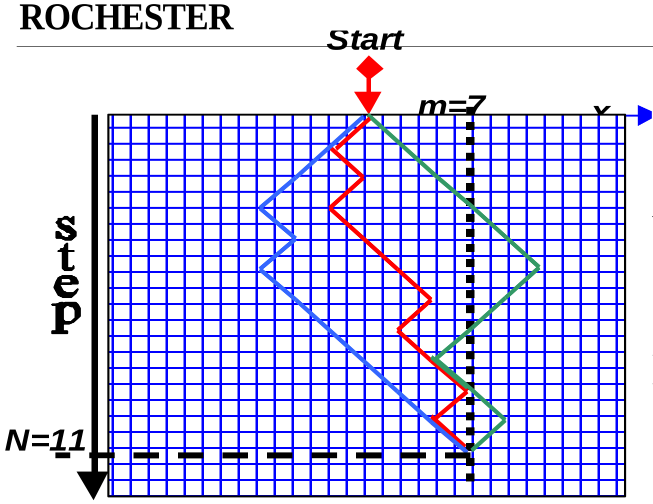

Figure IV-8: Some *N=11* trajectories ending in *m=7*.

An example is given in Fig. IV.8. The random degree of freedom is *x*, which is discretized by the vertical grid lines. In each step *x* changes by $\Delta x = \pm 2$. The horizontal grid lines indicate the number of steps. For example, *N=11* steps correspond to *22* lines (squares) vertically down. The figure shows of the many ($2^N = 2^{11} = 2048$) possible trajectories with *N = 11* steps only *3*. These three have been selected to end up in the same *x*-bin *m=7*. However, there are actually *55* trajectories ending up in bin *m=7*.

To calculate the number of trajectories ending in a given bin *m* is obviously just a combinatorial counting problem. It is solved by the binomial coefficient for the associated number N_+,

$$\binom{N}{N_+} = \frac{N!}{(N_+)! \cdot (N - N_+)!} = \frac{N!}{(N_+)! \cdot (N_-)!}$$
$$= \frac{N!}{\left(\frac{1}{2}(N-m)\right)! \cdot \left(\frac{1}{2}(N+m)\right)!} \qquad \text{(IV.32)}$$

This coefficient is equal to the number of ways that a given number of objects N_+ (*e.g.* N_+*= 9 particular steps*), or N_- (*e.g.* N_-*= 2 steps*) numbers can be selected out of a total of *N* (*e.g., N = 11 total steps*). Therefore, the ***probability*** for a random trajectory to land at position

$m = 2N_+ - N$ (e.g., $m=7$) after N total steps in random directions is given by the binomial distribution in N_+ (or N_-)

$$f_{N_+}(N) = \frac{N!}{(N_+)!\cdot(N-N_+)!}\cdot p_+^{N_+}\cdot p_-^{N-N_+} \qquad \text{(IV.33)}$$
$$= \frac{N!}{(N_-)!\cdot(N-N_-)!}\cdot p_-^{N_-}\cdot p_+^{N-N_-} = f_{N_-}(N)$$

All these probabilities contain the common factor $p^N = (1/2)^N$, which is important only as an overall scaling factor, when comparing trajectories with different numbers of steps N. Since here, interest is on the ***relative probabilities within a given group of trajectories of equal length N***, this factor could be dropped.

Average value and variance for a binomial distribution are readily calculated (see Tutorial Moments). In this particular case, because of the symmetry of f ($f_{N_+}(N) = f_{N_-}(N)$), the average number of steps in positive direction must be equal to one-half the total number of steps, and the average m-value must be zero

$$\langle N_+\rangle = N/2 \quad \leftrightarrow \quad \langle m\rangle = 0 \qquad \text{(IV.34)}$$

This can be demonstrated directly with the binomial distribution of Equ. IV.33, using the fact that averages over the trajectories with respect to this probability distribution are calculated as

$$\langle a\rangle = \sum_{N_+}^{N} a(N_+)\, f_{N_+}(N) \qquad \text{(IV.35)}$$

with the normalization

$$\sum_{N_+}^{N} f_{N_+}(N) = \sum_{N_+=0}^{N} \frac{N!}{(N_+)! \cdot (N-N_+)!} \cdot p_+^{N_+} \cdot p_-^{N-N_+} = (p_+ + p_-)^N = 1 \qquad \text{(IV.36)}$$

Therefore, one obtains from Equ. IV.35 for the average N_+:

$$\begin{aligned}
\langle N_+ \rangle &= \sum_{N_+=0}^{N} N_+ f_{N_+}(N) = \sum_{N_+=0}^{N} N_+ \frac{N!}{(N_+)! \cdot (N-N_+)!} \cdot p_+^{N_+} \cdot p_-^{N-N_+} \\
&= \sum_{N_+=1}^{N} \frac{N_+ \cdot N!}{(N_+)! \cdot (N-N_+)!} \cdot p_+^{N_+} \cdot p_-^{N-N_+} = \\
&= Np_+ \sum_{N_+=1}^{N} \frac{(N-1)!}{(N_+-1)! \cdot (N-N_+)!} \cdot p_+^{N_+-1} \cdot p_-^{N-N_+} = \\
&= Np_+ \sum_{N'=0}^{N-1} \frac{(N-1)!}{(N')! \cdot (N-1-N')!} \cdot p_+^{N'} \cdot p_-^{N-N'} = \\
&= Np_+ \sum_{N'=0}^{N-1} f_{N'}(N-1) = Np_+ = \frac{N}{2} \qquad \text{(IV.37)}
\end{aligned}$$

Here, a change in the start of the summation index from $N_+=0$ to $N_+=1$ is possible, because the $N_+=0$-term is zero. On line 4 in the above equation, the summation index has been transformed to $N'=N_+-1$. This allows one to transform the sum to a complete binomial sum over all possibilities to form groups of N' out of $(N-1)$ numbers, which is equal to unity (see Equ. IV.36 for $N-1$ total steps). Hence, the expectation of Equ. IV.34 has been proven.

The same scheme can be applied to calculate the ***mean-square N_+***, yielding

$$\langle N_+^2 \rangle = Np_+ + N(N-1)p_+^2 \qquad \text{(IV.38)}$$

With this information, one can calculate the ***variance in*** N_+:

$$\sigma^2_{N_+} = \langle N_+^2 \rangle - \langle N \rangle^2 = \{ Np_+ + N(N-1)p_+^2 \} - \{ Np_+ \}^2 = = Np_+(1-p_+) = Np_+ p_- \qquad \text{(IV.39)}$$

It is an important property of the random-walk process that both average and variance grow in proportion to the number of steps N. This implies a decrease with the number of steps of the relative deviation from the mean, defined by the ratio of standard deviation and mean,

$$\frac{\sigma_{N_+}}{\langle N_+ \rangle} \sim \frac{1}{\sqrt{N}} \qquad \text{(IV.40)}$$

From the definition of m in terms of the number of steps in positive x-direction, N_+, given in Equ. IV.31, one calculates for the variance in m,

$$\sigma_m^2 = \langle m^2 \rangle - \langle m \rangle^2 = \langle (2N_+ - N)^2 \rangle = \langle 4N_+^2 - 4N_+N + N^2 \rangle$$
$$= 4\langle N_+^2 \rangle - 4N\langle N_+ \rangle + N^2 = 4\langle N_+^2 \rangle - 2N^2 + N^2 =$$
$$= 4\langle N_+^2 \rangle - N^2 = 4\left(\langle N_+^2 \rangle - \langle N_+ \rangle^2 \right) = 4\sigma^2_{N_+} \qquad \text{(IV.41)}$$

Hence, the first two moments of the m-distribution are given by

$$\langle m \rangle = 0 \quad and \quad \sigma_m^2 = N \qquad \text{(IV.42)}$$

Correspondingly, the associated moments in coordinate representation are obtained just by scaling with the step size Δx

$$\langle x \rangle = \langle m \cdot \Delta x \rangle = 0 \qquad \sigma_x^2 = \sigma_m^2 \cdot (\Delta x)^2 = N \cdot (\Delta x)^2 \tag{IV.43}$$

As noted previously, although the average displacement after N steps is zero, a random walk has covered a net distance (displacement) corresponding to the square-root of the number of steps,

$$x_{rms} = \sqrt{\langle x^2 \rangle} = \sqrt{N} \cdot \Delta x \tag{IV.44}$$

It is shown elsewhere (see Tutorial Moments) that in the limit of a very large number N of transitions and a finite probability, the binomial distribution becomes a Gaussian

$$f_m(N) = \frac{1}{\sqrt{2\pi N}} \cdot \exp\left\{ -\frac{m^2}{2N} \right\} \tag{IV.45a}$$

and correspondingly,

$$f(x) = \frac{1}{\sqrt{2\pi N (\Delta x)^2}} \cdot \exp\left\{ -\frac{x^2}{2N(\Delta x)^2} \right\} \tag{IV.45b}$$

Thus, the ***diffusion limit*** is recovered for a ***quasi-continuous*** (many small steps) random walk. This follows also directly from Equ. IV.33 by employing Stirling's approximation to $N!$ for large values of N. In any case, the solution for the random-walk problem is equivalent to that for a diffusion process (see Equ. IV.21a), as it should! Comparing the respective solutions, Equs. IV.21a and 45b, one identifies the variances of the two Gaussians:

$$\sigma_x^2(t) = N \cdot (\Delta x)^2 = 2D_{xx}t \qquad \text{(IV.45c)}$$

This is expected, since the total mean-square displacement of an cumulative process of independent intermediate steps equals the sum of the individual mean square displacements (see Tutorial). Further, the equivalence of the two expressions for the probability leads to

$$\frac{m^2}{2N} = \frac{x^2}{4Dt} \qquad \text{(IV.46)}$$

Realizing that *x/m* = Δx, the step size, and *N/t* = *Z* the number of steps (transitions, interactions) per time *t*, one calculates

$$D_{xx} = \frac{x^2 N}{2tm^2} = \frac{(x/m)^2}{2(t/N)} = \frac{1}{2} \cdot Z \cdot (\Delta x)^2 \qquad \text{(IV.46)}$$

This result is equivalent to the expression of the diffusion coefficient derived in Equ. IV.27. The ***diffusion coefficient is equal to 1/2 the total quadratic displacement N*** $(\Delta x)^2$ ***per unit time***.

This result can be applied to the random walk (or flight) of the particles in a gas. Here, the *rms* distance between collisions is called the mean free path *l* and *Z* is the rate of collisions between the gas particles. Then, the diffusion coefficient can be expressed in a beautifully simple way:

$$D_{xx} = \frac{1}{2} \cdot Z \cdot \lambda^2 \qquad \text{(IV.47)}$$

For example, according to a homework problem, for air particles at normal conditions (*p = 1 atm, T = 300K*), the mean free path for collisions is $\lambda = 9.3 \cdot 10^{-8} m$. The collision rate is approximately equal to $Z = 5.35 \cdot 10^9 s^{-1}$. Then, Equ. IV.47 predicts a diffusion coefficient of $D_{xx} = 2.31 \cdot 10^{-5} m^2 s^{-1}$, which is in reasonable agreement with experimental data (cf. Table IV.1).

Since the random walk is an independent process, even step by step, it is simple to generalize this process to a three-dimensional random walk. The three-dimensional probability density is simply the product of the functions for the individual degrees of freedom:

$$f(\vec{r}) = f(x) f(y) f(z) = \frac{1}{\sqrt{4\pi Dt}^3} \cdot \exp\left\{-\frac{r^2}{4Dt}\right\} \quad \text{(IV.48)}$$

This derivation has made use of the fact that, since the random walk is isotropic, all diffusion coefficients are identical, i.e., $D_{xx}= D_{yy}= D_{zz}=D$. Therefore all variances are the same. Furthermore, it is $r^2 = x^2 + y^2 + z^2$. Since this distribution function is essentially a radial function, depending only on the distance r from the origin, it is useful to transform it to spherical (polar) coordinates and integrate over angles. Then, one obtains the radial probability function

$$f(r) = \frac{d\, f(r)}{dr} = \frac{4\pi}{\sqrt{4\pi Dt}^3} \cdot r^2 \cdot \exp\left\{-\frac{r^2}{4Dt}\right\} \quad \text{(IV.49)}$$

The distribution of Equ. IV.48 applies for a given direction ($\vec{r}/|\vec{r}|$), while Equ. IV.49 is angle-integrated. An actual probability is obtained from this latter distribution by multiplying with the radial bin width Δr:

$$\Delta f(r) = \frac{d\, f(r)}{dr} \Delta r = \frac{4\pi}{\sqrt{4\pi Dt}^3} \cdot r^2 \cdot \exp\left\{-\frac{r^2}{4Dt}\right\} \cdot \Delta r \quad \text{(IV.49a)}$$

Integrated over all distances, the distribution function of Equ. IV.49 gives unity (100%), it is properly normalized.

It is now straight forward to calculate the displacement achieved in a three-dimensional random walk within a given time *t*. One has just to calculate the mean-square distance $\langle r^2 \rangle$ with the distribution function of Equ. IV.49:

$$\langle r^2 \rangle = \frac{4\pi}{\sqrt{4\pi Dt}^3} \cdot \int_0^\infty dr\, r^4 \cdot \exp\left\{ -\frac{r^2}{4Dt} \right\} = 6Dt \qquad \text{(IV.50)}$$

This result was to be expected, since for one degree of freedom, say *x*, $\langle x^2 \rangle = N \cdot \lambda^2 = 2Dt$. Since no direction is preferred, one expects

$$\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle = 3N \cdot \lambda^2 = 6Dt \qquad \text{(IV.51)}$$

Hence, random walk on a grid with equal probabilities to either side ($p_+ = p_-$ for each degree of freedom) is just the discrete form of a diffusion process. The analogue of a quasi-random walk, where $p_+ \neq p_-$ leads to an overall drift of the probability distribution, exists also: It is the Fokker-Planck process.