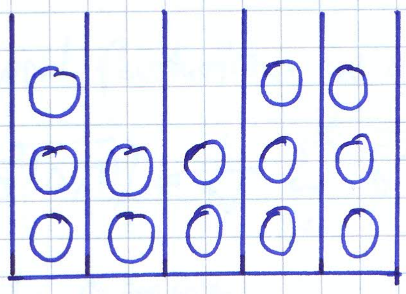
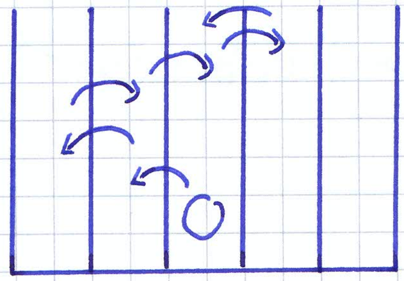
VI. Time versus ensemble averages, ergodicity, ageing.





Distribute $N \gg 1$ identical particles randomly into the boxes ⇝ probability to find a given particle in box i:

$$\langle p_i \rangle = \frac{N_i}{N}$$

Let a single particle hop randomly in between the boxes over a long time t ⇝ probability to find the particle in box i:

$$\overline{p_i} = \frac{t_i}{t}$$

Ergodicity in the Boltzmann sense postulates the equivalence of the ensemble average of a physical observable & its time average if only the ensemble is sufficiently large and the averaging time long enough. Here:

$$\langle p_i \rangle = \lim_{N\to\infty} \frac{N_i}{N} = \lim_{t\to\infty} \frac{t_i}{t} = \overline{p_i} .$$

In his experiments, Jean Perrin measured ensembles of particles to determine their diffusive properties. Ivar Nordlund came up with the idea to use long time averages over single particle trajectories. How can we show the equivalence of both approaches for a diffusion experiment? Consider the mean squared displacement

$$\langle x^2(t) \rangle = \int_{-\infty}^{\infty} x^2 P(x,t)\, dx = 2K_1 t .$$

Single particle tracking experiments provide the time series $x(t)$, $t \in (0,T)$ of individual particle trajectories. Typically these are evaluated by the time averaged MSD: