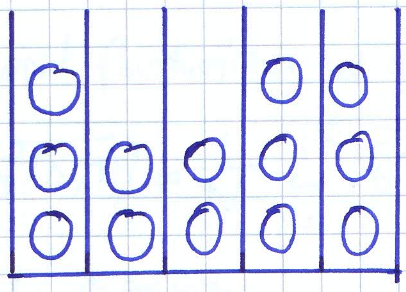
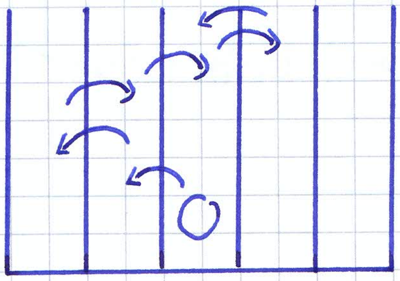
VI. Time versus ensemble averages, ergodicity, ageing.





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:

$$\overline{\delta^2(\Delta,T)} = \frac{1}{T-\Delta}\int_0^{T-\Delta}\left[x(t+\Delta)-x(t)\right]^2 dt$$

To avoid fluctuations we can average $\overline{\delta^2}$ over sufficiently many trajectories:

$$\left\langle\overline{\delta^2(\Delta,T)}\right\rangle = \frac{1}{N}\sum_{i=1}^{N}\overline{\delta_i^2(\Delta,T)}$$

In the expression

$$\left\langle\overline{\delta^2(\Delta,T)}\right\rangle = \frac{1}{T-\Delta}\int_0^{T-\Delta}\left\langle\left[x(t+\Delta)-x(t)\right]^2\right\rangle dt$$

we consider the integrand as a sequence of steps with average squared width $\langle\delta x^2\rangle$. The number of steps in the interval Δ is $n(t+\Delta)-n(t)$. On average:

$$\langle n(t+\Delta)-n(t)\rangle = \langle n(t+\Delta)\rangle - \langle n(t)\rangle = \frac{t+\Delta}{\tau}-\frac{t}{\tau}=\frac{\Delta}{\tau}$$

where τ is the typical time per step.

$$\Rightarrow \left\langle\overline{\delta^2(\Delta,T)}\right\rangle = \frac{1}{T-\Delta}\int_0^{T-\Delta}\frac{\langle\delta x^2\rangle}{\tau}\,\Delta\, dt = 2K_1\Delta \;;\quad K_1=\frac{\langle\delta x^2\rangle}{2\tau}.$$

$$\Rightarrow \left\langle\overline{\delta^2(\Delta,T)}\right\rangle = \langle x^2(\Delta)\rangle \text{ for any finite } T.$$

For long T the process is self-averaging, so that $\lim_{T\to\infty}\overline{\delta^2(\Delta,T)} = \langle x^2(\Delta)\rangle$ holds for a single trajectory.
We thus proved the ergodic behaviour of Brownian motion.

<u>Continuous time random walk process with $\psi(t)\simeq \tau^\alpha/t^{1+\alpha}$</u>

The number of jumps $\langle n(t)\rangle$:
We found for the probability to make i jumps up to time t: $Q_i(u)=\frac{1-\psi(u)}{u}\psi^i(u)$

$$\Rightarrow \underline{\underline{\langle n(u)\rangle}} = \sum_{i=0}^{\infty} i\,Q_i(u) = \frac{1-\psi(u)}{u}\,\frac{1/\psi(u)}{(1-1/\psi(u))^2} = \frac{1-\psi(u)}{u}\,\frac{\psi(u)}{(1-\psi(u))^2} = \underline{\underline{\frac{\psi(u)}{u(1-\psi(u))}}}$$

For $\psi(u)\sim 1-(u\tau)^\alpha \rightsquigarrow \langle n(u)\rangle \sim \frac{1-(u\tau)^\alpha}{u(u\tau)^\alpha} = \frac{1}{u(u\tau)^\alpha}-\frac{1}{u}\sim\frac{1}{u(u\tau)^\alpha}$

$$\Rightarrow \langle n(t)\rangle \approx \frac{(t/\tau)^\alpha}{\Gamma(1+\alpha)}$$

This must be proportional to the MSD: $\langle x^2(t)\rangle = \langle\delta x^2\rangle\langle n(t)\rangle = \dfrac{2K_\alpha t^\alpha}{\Gamma(1+\alpha)}$

where $K_\alpha = \dfrac{\langle\delta x^2\rangle}{2\tau^\alpha}$.

$$\left\langle\overline{\delta^2(\Delta,T)}\right\rangle = \frac{\langle\delta x^2\rangle}{(T-\Delta)\tau^\alpha}\int_0^{T-\Delta}\left(\frac{(t+\Delta)^\alpha - t^\alpha}{\Gamma(1+\alpha)}\right)dt = \frac{2K_\alpha}{T-\Delta}\,\frac{\Delta^\alpha\left(\frac{T^{\alpha+1}}{\Delta^\alpha}-\Delta\right)-(T-\Delta)^{1+\alpha}}{(1+\alpha)\,\Gamma(1+\alpha)}$$

$$\approx \frac{2K_\alpha}{\Gamma(1+\alpha)}\,\frac{T^{1+\alpha}-\Delta^{1+\alpha}-(T-\Delta)^{1+\alpha}}{(1+\alpha)(T-\Delta)} \sim \frac{2K_\alpha}{\Gamma(1+\alpha)}\,\frac{T^{1+\alpha}-\Delta^{1+\alpha}-T^{1+\alpha}\left(1-(1+\alpha)\frac{\Delta}{T}\right)}{(1+\alpha)(T-\Delta)}$$

$$\sim \frac{2K_\alpha}{\Gamma(1+\alpha)}\,T^{1+\alpha}\frac{(1+\alpha)\frac{\Delta}{T}-\left(\frac{\Delta}{T}\right)^{1+\alpha}}{\cancel{T^{1+\alpha}}(1+\alpha)T} \sim \frac{2K_\alpha}{\Gamma(1+\alpha)}\,\frac{\Delta}{T^{1-\alpha}}$$

$$\Rightarrow \left\langle\overline{\delta^2(\Delta,T)}\right\rangle \sim \frac{2K_\alpha}{\Gamma(1+\alpha)}\,\frac{\Delta}{T^{1-\alpha}} \neq \langle x^2(\Delta)\rangle$$

The TA MSD is different from the EA MSD: weak ergodicity breaking. Measuring the MSD of a subdiffusive CTRW would deceivingly suggest normal diffusion. Only the T-dependence shows the anomaly of the process. The longer T the less mobile appears the process.

For many realisations we see a scatter of the amplitudes of $\overline{\delta^2}$. To calculate the distribution we note that

$\overline{\delta^2} \sim \dfrac{Cn}{\cancel{\Delta}T}$ in terms of the number of steps, n (we count events of motion by n and we took $T-\Delta \approx T$; ~~C may still be time dependent~~).

Prob. to make n jumps in $(0,t)$: $Q_n(u) = \dfrac{1-\psi(u)}{u}\psi^n(u) = \dfrac{1-\psi(u)}{u}\exp\left(+n\ln\psi(u)\right)$

We use $\psi(u)\sim 1-(u\tau)^\alpha \Rightarrow Q_n(u)\sim \tau^\alpha u^{\alpha-1}\exp\left(-n(u\tau)^\alpha\right)$

$Q_n(t) \sim \dfrac{t/\tau}{\alpha n^{1+1/\alpha}}L_\alpha^+\left(\dfrac{t/\tau}{n^{1/\alpha}}\right) \quad :: \quad \mathcal{L}\{L_\alpha^+(t)\} = \exp(-u^\alpha)$

To determine C we note that $\langle \overline{\delta^2} \rangle = C \langle n \rangle / T$. With $\langle n \rangle \sim T^{\alpha} / (\tau^{\alpha} \Gamma(1+\alpha))$

and with $\langle \overline{\delta^2} \rangle = \frac{2K_\alpha}{\Gamma(1+\alpha)} \frac{\Delta}{T^{1-\alpha}}$ we have $C = 2K_\alpha \Delta / \tau^{\alpha}$

$\Rightarrow$ With the dimensionless variable $\xi = \frac{\overline{\delta^2}}{\langle \overline{\delta^2} \rangle}$

$$\underline{\underline{\lim_{T\to\infty} \phi_\alpha(\xi) = \frac{\Gamma^{1/\alpha}(1+\alpha)}{\alpha\, \xi^{1+1/\alpha}} L_\alpha^{+} \left(\frac{\Gamma^{1/\alpha}(1+\alpha)}{\xi^{1/\alpha}} \right)}}$$

$\phi_{1/2} = \frac{2}{\pi} \exp\left(-\frac{\xi^2}{\pi}\right)$ has a finite amount @ $\xi = 0$: some trajectories do not move

$\phi_1 = \delta(\xi - 1)$ ergodic limit

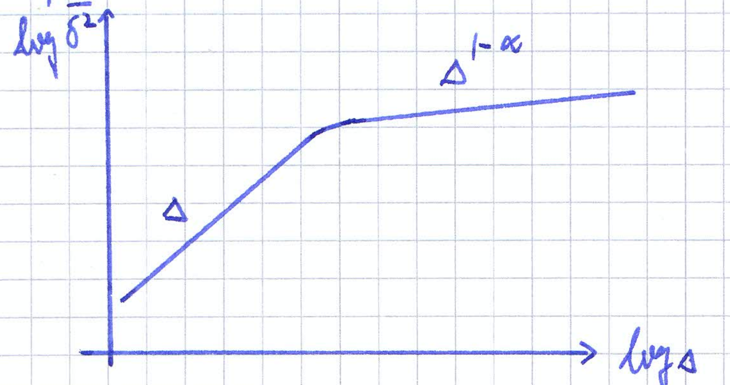
Ergodicity breaking parameter: $EB = \lim_{T\to\infty} \frac{\langle (\overline{\delta^2})^2 \rangle - \langle \overline{\delta^2} \rangle^2}{\langle \overline{\delta^2} \rangle^2} = \frac{2\Gamma(1+\alpha)^2}{\Gamma(1+2\alpha)} - 1$

$EB = 1,\ \alpha = 0 \ \wedge\ EB = 0,\ \alpha = 1$

<u>Confined motion:</u> $\langle x^2(t) \rangle$ reaches a plateau value

$$\langle \overline{\delta^2(\Delta, T)} \rangle \sim \left(\langle x^2 \rangle_B - \langle x \rangle_B^2 \right) \frac{2 \sin(\pi\alpha)}{(1-\alpha)\pi\alpha} \left(\frac{\Delta}{T} \right)^{1-\alpha}, \quad 1 \gg \frac{\Delta}{T} \wedge \Delta \gg \left(\frac{1}{K_\alpha \lambda_1} \right)^{1/\alpha}$$

where λ_1 is the lowest eigenvalue of the corresponding Fokker-Planck operator larger than zero.



Ageing phenomena:

Consider a process that was started @ $t=0$. Measurement starts @ $t_a > 0$, the ageing time. The MSD accumulated by the diffusing particle during the measurement time T is

$$\langle x^2(T)\rangle_a = \langle x^2(t_a+T)\rangle - \langle x^2(t_a)\rangle = \langle\delta x^2\rangle\left(\langle n(t_a+T)\rangle - \langle n(t_a)\rangle\right)$$

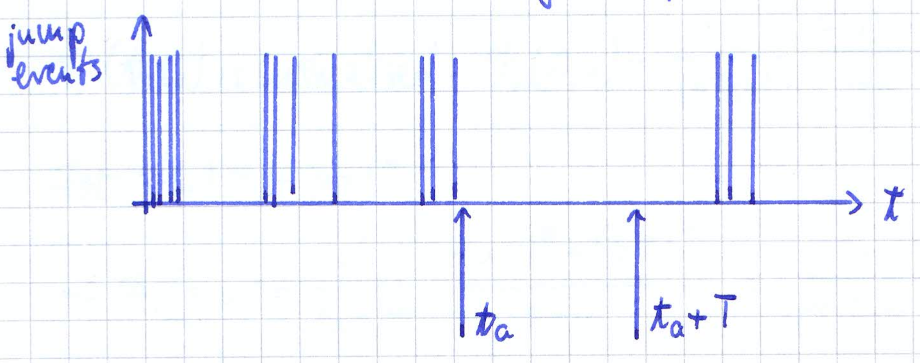
$$= \langle\delta x^2\rangle\left((t_a+T)^\alpha - t_a^\alpha\right)\frac{1}{\tau^\alpha\Gamma(1+\alpha)} = \frac{2K_\alpha}{\Gamma(1+\alpha)}\left((t_a+T)^\alpha - t_a^\alpha\right)$$

Brownian motion: $\langle x^2(T)\rangle_a = \frac{2K_1}{\Gamma(2)}T = \langle x^2(T)\rangle_a$ no ageing occurs

CTRW: $T \gg t_a$: $\langle x^2(T)\rangle_a \sim \frac{2K_\alpha}{\Gamma(1+\alpha)}T^\alpha = \langle x^2(T)\rangle$ asymptotically no ageing

$t_a \gg T$: $\langle x^2(T)\rangle_a \sim \frac{2K_\alpha\,\alpha}{\Gamma(1+\alpha)}\frac{T}{t_a^{1-\alpha}}$ ageing effect suggesting normal diffusion

What happens physically: after a long waiting period, there is a large probability that we have to wait a long time for the first jump to occur:



Let us calculate the PDF for the first jump to occur after the ageing period t_a: $\psi_1(t, t_a)$, the so-called forward waiting time PDF.

Until t_a the walker performs n steps $\Rightarrow$ t_a is in the interval between

$$t_n = \sum_{i=1}^{n} t_i \quad (\text{when } n^{\text{th}} \text{ step was made}) \quad \text{and} \quad t_{n+1}.$$

$\rightsquigarrow$ waiting time until next step is $t_a - t_n + t$.

$\rightsquigarrow$ conditional probability density of forward waiting time t given that exactly n steps occurred until time t_a:

$$\phi_n(t) = \int_0^{t_a} \psi_n(t')\, \psi(t_a - t' + t)\, dt'$$

$(n+1)^{st}$ step occurs between t' and $t_a + t$

occurrence of n^{th} step @ time t'

$$\Rightarrow \psi_1(t,t_a) = \sum_{n=0}^{\infty} \phi_n(t) = \int_0^{t_a} \underbrace{\left(\sum_{n=0}^{\infty} \psi_n(t')\right)}_{\xrightarrow{\mathcal{L}} \frac{1}{1-\psi(u)}} \psi(t_a - t' + t)\, dt'.$$

$$\rightsquigarrow \psi_1(t,u) = \mathcal{L}\{\psi_1(t,t_a);\, t_a \to u\} = \frac{1}{1-\psi(u)}\left(e^{ut}\psi(u) - \int_0^t \psi(\tau)\, e^{-u(\tau - t)}\, d\tau\right)$$

$$\underline{\underline{\psi_1(s,u)}} = \mathcal{L}\{\psi_1(t,u);\, t \to s\} = \underline{\underline{\frac{1}{1-\psi(u)}\, \frac{\psi(u)-\psi(s)}{s-u}}}$$

EX: Derive $\psi_1(s,u)$ from $\psi_1(t,t_a)$.

$\psi_1(t,t_a)$ is normalised: $\psi_1(0,u) = \frac{1}{1-\psi(u)}\, \frac{\psi(u)-1}{-u} = \frac{1}{u} = \mathcal{L}^{-1}\{1\}$.

For $\psi(u) \sim 1 - (u\tau)^\alpha$

$$\Rightarrow \psi_1(s,u) = \frac{1}{(u\tau)^\alpha}\, \frac{-(u\tau)^\alpha + (s\tau)^\alpha}{s-u} = \frac{s^\alpha - u^\alpha}{u^\alpha (s-u)}$$

$$\Rightarrow \underline{\underline{\psi_1(t,t_a)}} = \frac{t_a^{\alpha}}{t^\alpha (t+t_a)} \cdot \frac{1}{\Gamma(1-\alpha)\Gamma(\alpha)} = \underline{\underline{\frac{\sin(\pi\alpha)}{\pi}\, \frac{t_a^\alpha}{t^\alpha (t+t_a)}}}$$

t_a large $\rightsquigarrow$ value of ψ_1 small $\rightsquigarrow$ need to wait long for jump to occur

t_a small $\rightsquigarrow$ $\psi_1 \simeq t_a^\alpha\, t^{-(1+\alpha)}$ renormalised waiting time for non-aged process

$\alpha \to 1$: mass concentrated around $t=0$ $\rightsquigarrow$ regular Brownian process without aging