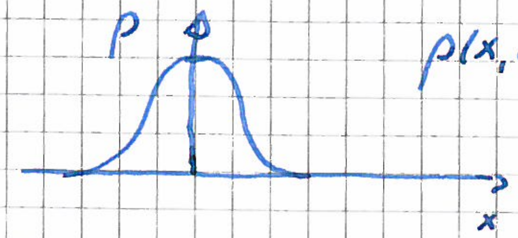
2. BROWNIAN MOTION

2.1 The diffusion eq.

Ex: Diffusion in one-dimension

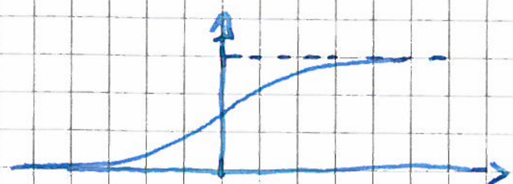
Density of particles: $\rho(x,t) = n(x,t)/V$

1)



$\rho(x,0) = \delta(x)$

2)



$\rho(x,0) = H(x)$

The process of diffusion tries to smear out density variations.

It is caused by random "kicks" from surrounding particles, i.e. the phenomenon is statistical.

Adolf Fick (German, 1829-1901) studies the diffusion phenomenon extensively.

He arrived at two <u>phenomenological</u> laws that today bear his name.

① Fick's 1st law (1855)

$$\vec{J} = -D\nabla\rho(\vec{x},t)$$

$\vec{J}$	:	particle current density	$m^{-2}s^{-1}$
ρ	:	particle density (concentration)	m^{-3}
D	:	diffusion constant	$m^2 s^{-1}$

- So the law says that the current density is proportional to the concentration gradient.
- The diffusion constant says something about the speed of diffusion

Q: Why is there a negative sign i FFL?

A: The current is in a direction so that concentration differences are smoothed out (opposite of the concentration grad.)

That is, in the direction of <u>high</u> <u>to</u> <u>low</u> concentration.

Typical values for the diffusion constant:

i) In gases $D \sim 10^{-6} - 10^{-5}$ $m^2 s^{-1}$

ii) In liquids $D \sim 10^{-10} - 10^{-9}$ $m^2 s^{-1}$

iii) Biological molecules $D \sim 10^{-11} - 10^{-10}$ $m^2 s^{-1}$

=> Diffusion is a SLOW process!

The driving force of diffusion is $\nabla \rho(x,t)$.

Fick's 1st law applies to idea systems.
(gases and mixtures).

Ex: Non-ideal system
In a chemical system

$$\vec{J}_i = - \frac{D \rho_i}{RT} \nabla \mu_i$$

chemical potential (J/mol)

— " —

Compare Fick's first law, with Fouriers law

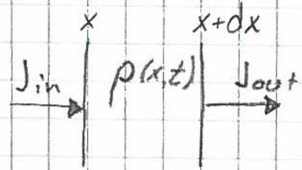
$$\vec{J} = - \kappa \nabla T(\vec{x},t)$$

Termal conductivity

② Fick's 2nd law

$$\boxed{\partial_t \rho(\vec{x},t) = D\, \nabla^2 \rho(\vec{x},t)} \quad \text{[Diffusion Eq.]}$$

This law can be derived from the 1st if one in addition assumes particle conservation:
The latter implies that



$$\partial_t \rho(\vec{x},t) + \nabla \vec{J} = 0$$

$J_{net} =$

which gives after combination with Fick's 1st law

$$\partial_t \rho(\vec{x},t) = \nabla \left[D\, \nabla \rho(\vec{x},t) \right]$$

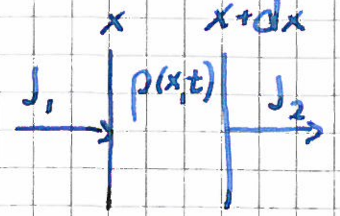
If D is constant, Fick's 2nd law follows.

Note:

- $D \equiv D(x)$ local diff. "constant"
- $D \equiv D(\rho, x)$ non-linear Diffusion eq.
- Steady state solution implies $\nabla^2 \rho = 0$.

Note:

The diffusion eq. is similar to the heat equation (that is derived from Fourier's law in a similar way).



Net current change :

$$J_{net} = J_2 - J_1 = -D\left(\partial_x \rho|_{x+dx} - \partial_x \rho|_x\right)$$

$$=$$

Application of the DE :

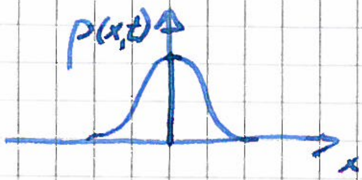
Transport processes in

- disorderd media
- porous – ″ –
- foods
- neurons
- population dynamics
- biophysical transport over membranes
- traffic
- fluid mechanics
- bio-medical application (tissue)

2.1.1 Solution of the diffusion eq

The solution will depend on the initial conditions (i.e. on the problem at hand).

We will consider the following system



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with initial condition:

$$\rho(x,0) = \delta(x)$$

The solution is:

$$\rho(x,t) = \frac{1}{\sqrt{4\pi D t}} \exp\left[\frac{x^2}{4Dt} \right]$$

i.e. a Gaussian with std $\sigma = \sqrt{2Dt}$.

Demonstrate that $\rho(x,t)$ given above is a solution!

2.1.2 The Fourier-Laplace transform method.

We will now use the Fourier-Laplace transf. method to demonstrate how to solve the diffusion eq.

However, before we do so, we will recap. the Fourier and Laplace transforms

Fourier transform :

$$\hat{f}(k) = \int_{-\infty}^{\infty} dx \; f(x)\, e^{-ikx} = \mathcal{F}\{f(x)\}(k)$$

$$f(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk \; \hat{f}(k)\, e^{+ikx} = \mathcal{F}^{-1}\{\hat{f}(k)\}(x)$$

Note : The factors of 2π can be differ from author to author, and so can the sign convention.
So, take care to check the conventions used !

$$\mathcal{F}\{f(x-x_0)\} = e^{-ikx_0}\,\mathcal{F}\{f(x)\}$$

$$\mathcal{F}\{f'(x)\} = -ik\,\mathcal{F}\{f(x)\}$$

Check tables for other pairs (or wikipedia ...)

The Laplace transform

The most common definition (one-sided)

$$\tilde{f}(s) = \int_{0^-}^{\infty} dt \; f(t)\, e^{st} = \mathcal{L}\{f(t)\}$$

including zero

The parameter s is in general <u>complex</u>

$$s = s_1 + i s_2$$

Inverse

$$f(t) = \frac{1}{2\pi i} \int_{\sigma - i\infty}^{\sigma + i\infty} ds \; \tilde{f}(s)\, e^{st} = \mathcal{L}^{-1}\{\tilde{f}(s)\}$$

parameter σ is <u>real</u> and $\sigma > \max\{Re(s_p)\}$ where s_p is potential singular points of $\tilde{f}(s)$. If all singulareties (if any) are in the left half-space, one may set $\sigma = 0$

Note: There is also a two-sided transform for which the lower limit in the forward transform is $-\infty$.

Normaly if one only say "the Laplace trans." the one given above is understood.

Properties (of the one-sided transform):

$$\mathcal{L}\{f'(t)\} = s\tilde{f}(s) - f(0)$$

(obtained by partial int.)

$$\mathcal{L}^{-1}\left\{\frac{1}{s+\alpha}\right\} = e^{-\alpha t} \underbrace{H(t)}_{1} \qquad t>0, \quad Re(s) > -\alpha$$

See tables or wikipedia for more transformation pairs.

Q: So which of the two transforms should one choose?

A: Laplace is the most general of the two, and Fourier is a special case of $\mathcal{L}$.

The quick answer is, choose

- Laplace for initial value problems
- Fourier for boundary value problems

Hence, for our diffusion eq. problem we combine the two, Fourier-Laplace transf, where we use Fourier for spacial, and Laplace for temporal variables.

We are now going to solve the diffusion eq. problem (in one-dimension)

$$\partial_t \rho(x,t) = D\partial_x^2 \rho(x,t)$$

$$\rho(x,0) = \delta(x-x_0)$$

by the use of the Fourier-Laplace transform technique.

We start by transforming the DE to the Laplace domain:

$$s\tilde{\rho}(x,s) - \underbrace{\rho(x,0)}_{\delta(x-x_0)} = D\partial_x^2 \tilde{\rho}(x,s)$$

Initial condition

Now we use the initial condition, and transform the resulting eq. to the Fourier domain:

$$s\hat{\tilde{\rho}}(k,s) - e^{-ikx_0} = -Dk^2\hat{\tilde{\rho}}(k,s)$$

Solving for $\hat{\tilde{\rho}}(k,s)$ gives:

$$\hat{\tilde{\rho}}(k,s) = \frac{e^{-ikx_0}}{s+Dk^2}$$

Details:

$$\hat{\tilde{p}}(k,s) = \frac{e^{-ikx_0}}{s + Dk^2}$$

$$p(x,t) = \mathcal{F}^{-1}\{\mathcal{L}^{-1}\{\hat{\tilde{p}}(k,s)\}\}$$

$$= \mathcal{F}^{-1}\left\{e^{-ikx_0}\,\mathcal{L}^{-1}\left\{\frac{1}{s+Dk^2}\right\}\right\}$$

$$= \mathcal{F}^{-1}\{e^{-ikx_0}\,e^{-Dk^2 t}\}$$

$$\rho(x,t) = \mathcal{F}^{-1}\Big\{ e^{-ikx_0} \underbrace{e^{-Dk^2t}}_{\mathcal{L}^{-1}\left\{\frac{1}{s+Dk^2}\right\}} \Big\}, \quad t>0$$

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty} dk\; e^{-ikx_0}\, e^{-Dtk^2}\, e^{ikx}$$

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty} dk\; e^{-Dtk^2}\, e^{ik(x-x_0)}$$

This is a Gaussian integral:

$$\int_{-\infty}^{\infty} dx\; e^{-\alpha^2x^2} e^{\pm\beta x} = \frac{\sqrt{\pi}}{\alpha}\, e^{\frac{\beta^2}{4\alpha^2}}, \quad \alpha>0$$

$$= \frac{1}{2\pi}\frac{\sqrt{\pi}}{\sqrt{Dt}} \exp\left\{\frac{-(x-x_0)^2}{4Dt}\right\}$$

$$= \frac{1}{\sqrt{4\pi Dt}} \exp\left\{-\frac{(x-x_0)^2}{4Dt}\right\}$$

This is elegant, is it not?

Note: In higher dimensions, a factor $1/\sqrt{4\pi Dt}$ comes from each dim.

So in 3D, one has a prefactor

$$\frac{1}{(4\pi Dt)^{3/2}}$$

and the exp. contains vectors.

How to calculate Gaussian integrals (a trick)

$$\int_0^\infty dx\, e^{-x^2} = \frac{1}{2}\int_{-\infty}^{\infty} dx\, e^{-x^2}$$

$$= \frac{1}{2}\left[\int_{-\infty}^{\infty} dx\, e^{-x^2} \int_{-\infty}^{\infty} dy\, e^{-y^2}\right]^{1/2}$$

$$= \frac{1}{2}\left[\int dx\,dy\, e^{-(x^2+y^2)}\right]^{1/2}$$

$$= \frac{1}{2}\left[\int_0^\infty dr \int_0^{2\pi} d\theta\; r\, e^{-r^2}\right]^{1/2}$$

$$= \frac{1}{2}\left[2\pi \int_0^\infty dr\, \underbrace{r\, e^{-r^2}}_{-\frac{1}{2}\frac{d}{dr}\left(e^{-r^2}\right)}\right]^{1/2}$$

$$= \frac{1}{2}\left[2\pi\left(-\frac{1}{2}\right)\left[e^{-r^2}\right]\Big|_0^\infty\right]^{1/2}$$

$$= \frac{1}{2}\sqrt{\pi}$$

More general

$$\int_0^a dx\, e^{-x^2} = \frac{\sqrt{\pi}}{2}\,\mathrm{erf}(a)$$

2.1.3 The propagator or Greens function

The solution (one-dimension)

$$\rho(x,t) = \frac{1}{\sqrt{4\pi D t}} \exp\left\{-\frac{(x-x_0)^2}{4Dt}\right\}$$

gives the particle concentration at <u>later</u> times for all given points in space, <u>given</u> that $\rho(x,0) = \delta(x-x_0)$.

When the initial condition is $\rho(x,0) = \delta(x-x_0)$ is a (localized) δ-function then $\rho(x,t)$ is known as the <u>propagator</u> or <u>Greens</u>-function.

If the initial condition instead had been

$$\bar{\rho}(x,0) = \bar{\rho}_0(x)$$

for som function $\rho_0(x)$, then since

$$\bar{\rho}_0(x) = \int dx_0\, \bar{\rho}_0(x_0)\, \delta(x-x_0)$$

the general solution is

$$\bar{\rho}(x,t) = \frac{1}{\sqrt{4\pi D t}} \int_{-\infty}^{\infty} dx_0\, \rho_0(x_0) \exp\left\{-\frac{(x-x_0)^2}{4D}\right\}$$

$$= \int_{-\infty}^{\infty} dx_0\, \bar{\rho}_0(x_0)\, \underbrace{\rho(x,t)}_{\text{propagator}}$$

Note : For the propagator, one also often use the notation :

$$p(x,t|x_0,t_0)$$

where

$$p(x,t_0|x_0,t_0) = \delta(x-x_0).$$

Summary

$$p(x,t|x_0,t_0) = \frac{1}{\sqrt{4\pi Dt}} \exp\left\{-\frac{(x-x_0)^2}{4Dt}\right\}$$

Alt :

$$p(x,t|x_0,t_0) = \frac{1}{\sqrt{2\pi\sigma^2(t)}} \exp\left\{-\frac{(x-x_0)^2}{2\sigma^2(t)}\right\}$$

$$\sigma(t) = \sqrt{2Dt}$$

A Gaussian with time-dependent std.

2.1.4 "Diffusion-like equations" or Related Equations

① Reaction - Diffusion equation

A mathematical model of a system where the spacial concentration of one (or-more) substances is controlled by both diffusion and local reactions

diffusion : spacial spreading
reactions : convertion into each other

Mathematically it is governed by the eq. (one-dimension)

$$\partial_t \rho(x,t) = \underbrace{D \nabla^2 \rho(x,t)}_{\text{diffusion}} + \underbrace{R(\rho)}_{\text{reactions}}$$

The reaction function $R(\rho)$ is often non-linear, causing often rather interesting dynamics. One can for instance have bistable and even chaotic behavior.

Note : In higher dimensions

$\rho, R \rightarrow$ vectors
$D \rightarrow$ matrix (diagonal)

The RDE describes a wide range of phenomena / behaviors:

- traveling waves
- wave-like phenomena (solitons)
- self-organized patterns (e.g. stripes, dots)

NB $\longrightarrow$ - pattern formation

In one-dimension the RDE is known as the KPP-equation (Kolmogorov-Petrovsky-Piscounov)

* $R(\rho) = \rho(1-\rho)$: Fischer's eq.

  spreading of biological populations

* $R(\rho) = \rho(1-\rho^2)$: Newell-Whitehead-Segel eq.

  describes Rayleigh-Benard convection

* $R(\rho) = \rho(1-\rho)(\rho-\alpha)$: general Zeldovich eq

  $0 < \alpha < 1$

  combustion theory

— ∽ —

Show some examples of pattern formation (e.g. Wikipedia) Reaction-Diffusion systems

Check out some of the videos on the homepage of Aric Hagberg (Los Alamos)
Section Movies

② Advection - Diffusion Equation

Also diffusion-advection eq is seen.

Q : What is advection?

A : Transport due to a vector field (shortan)

~~Advection eq~~.

Ex: Pollution in a river
Transport of heat in the river

[The vector-field here is the water current]

The advection eq. for the scalar ρ

$$\partial_t \rho + \nabla(\underbrace{\rho \vec{v}}_{\text{current}}) = 0 \quad \text{continuity eq.}$$

[if $\nabla \vec{v} = 0$ it is said to be solenoidal]

— ∽ —

The advection-diffusion (AD) equation combines the two transport mechanisms of advection and diffusion.

Ex: We pour salt water into a ~~riv~~ fresh water system consisting of rivers and calm lakes

The main transport mechanisms are

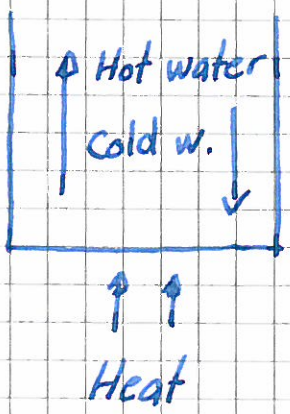
- in the rivers : advection
- in the lakes : diffusion

Convection

Convection = advection + diffusion

One of the major modes of heat and mass transfer

Ex : Pot of boiling water



Hence, the Advection - Diffusion equation becomes:

$\rho \equiv \rho(\vec{x},t)$

$$\partial_t \rho + \underbrace{\nabla(\rho\vec{v})}_{\text{advection term}} = \underbrace{\overbrace{D\nabla^2\rho}^{\nabla\cdot(D\nabla\rho)}}_{\text{diffusion term}}$$

also called convection term

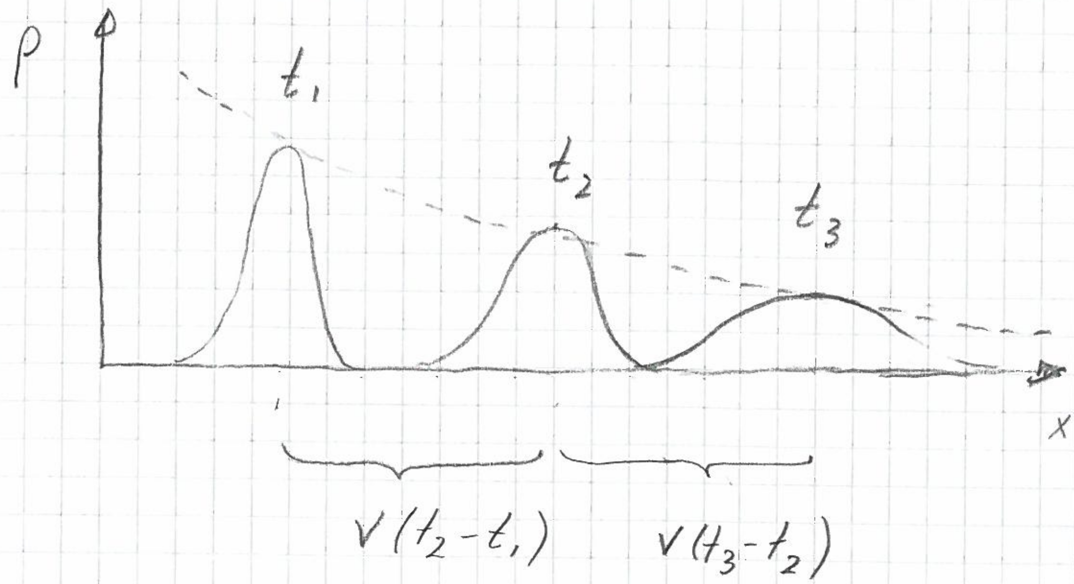
This is a hyperbolic diff. eq. and is difficult to solve numerically ("shock" solutions).

=> Use implicit schemes.

Analytically it is not too hard to solve. Try this in one-dimension.

Q : What do you expect from the solution? (if $\vec{v}$ is constant)

A : The advection term spacially translates the concentration



Hence one can transform the problem into a movable frame of reference by the change of variable

$$\bar{x} = x - (x_0 + vt) = x - x_0 - vt$$

$$\bar{t} = t$$

Exercise : if $\vec{v}$ is time-independent, show that the AD-eq. can be mapped onto the "standard" diffusion eq. with the coordinate transf. given above.

The Peclet number

In fluid mechanics, one tend to use the so-called Peclet number to measure the significance of advection vs. diffusion.

On physical grounds, one realizes that it depends on the physical quantities D, v and t.

The dimension-less Peclet number is defined

$$P_e = \frac{D}{v^2 t} \quad \begin{cases} \gg 1 & \text{Diffusion dominates} \\ \ll 1 & \text{Advection} \end{cases}$$

This form can be obtained from dimension analysis

$$Pe = D^{\alpha} V^{\beta} t^{\gamma}$$ (the only physical param that it depends on)

Units

$$[Pe] = 1^{0}$$
$$[D] = m^2/s$$
$$[V] = m/s$$
$$[t] = s$$

$$[Pe] = [D]^{\alpha} [V]^{\beta} [t]^{\gamma}$$
$$= \frac{m^{2\alpha}}{s^{\alpha}} \frac{m^{\beta}}{s^{\beta}} s^{\gamma}$$
$$= m^{2\alpha+\beta} s^{\gamma-\alpha-\beta}$$

$$\Rightarrow \quad 2\alpha + \beta = 0$$
$$\gamma - \alpha - \beta = 0$$

$$\beta = -2\alpha$$
$$\gamma = -\alpha$$

$$Pe = \left(\frac{D}{V^2 t}\right)^{\alpha}$$ ← conventionally $\alpha = 1$

③ The Advection-Diffusion Reaction Eq.

This eq. combines the two previous

$$\partial_t \rho + \nabla \cdot (\rho \vec{v}) = D \nabla^2 \rho + R(\rho)$$

We will not investigate it further.

$$\partial_t(x^2) = 2x\,\partial_t x$$

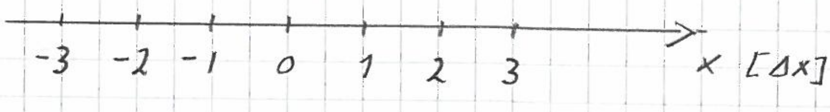
$$\begin{aligned}\partial_t^2(x^2) &= \partial_t\,(2x\,\partial_t x)\\ &= 2(\partial_t x)^2 + 2\,x\,\partial_t^2 x\end{aligned}$$

2.2 Relation between the Random Walk and Diffusion

Previously we discussed the random walk in discrete time and space; Δt and Δx

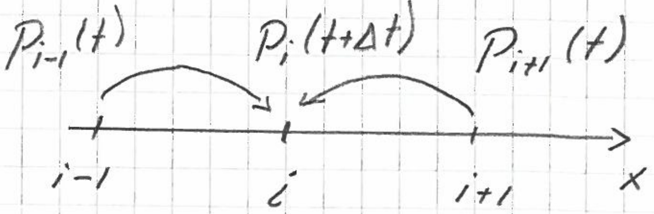
We introduced the probability $p(x,t)$ of being at x at time t, and since x is discrete

$$p_i(t) \equiv p(i\Delta x, t)$$



We most have (master eq.)

$$p_i(t+\Delta t) = \frac{1}{2} p_{i-1}(t) + \frac{1}{2} p_{i+1}(t)$$



Now we Taylor expand $p_i(t+\Delta t)$ around t

$$p_i(t+\Delta t) = p_i(t) + \Delta t\, \partial_t p_i(t) + O([\Delta t]^2)$$

In a similar way, we obtain

$$p_{i\pm1}(t) = p_i(t) \pm \Delta x\, \partial_x p_i(t) + \frac{(\Delta x)^2}{2} \partial_x^2 p_i(t) + O([\Delta x]^3)$$

Subsituting these two latter results into the master eq. gives:

$$\Delta t\, \partial_t p_i(t) + O([\Delta t]^2) = \frac{[\Delta x]^2}{2} \partial_x^2 p_i(t) + O([\Delta x]^3)$$

$$\partial_t p_i(t) = \frac{[\Delta x]^2}{2\Delta t} \partial_x^2 p_i(t) + O(\Delta t, [\Delta x]^3/\Delta t)$$

If we now want to draw the continuous limit, it has to be approach such that

$$D = \lim_{\substack{\Delta x \to 0 \\ \Delta t \to 0}} \frac{[\Delta x]^2}{2\Delta t}$$

is finite.

By doing so, we obtain our "old" friend — the diffusion eq.

NB
$$\left[\begin{aligned} \partial_t p(x,t) &= D\, \partial_x^2 p(x,t) \\ D &= \frac{\Delta x^2}{2\Delta t} \end{aligned}\right.$$

If the jump size distribution is not a sum of two delta-functions

$$\frac{1}{2}\left[\delta(x+\Delta x)+\delta(x-\Delta x)\right],$$

like here, what will then happen?

If the first two moments of the jump size dist. exist, and the first moment of the waiting time dist, then we can define

$$\boxed{D = \frac{\sigma_{\Delta x}^2}{2\langle \Delta t\rangle}}$$

$$\sigma_{\Delta x}^2 = \langle \Delta x^2\rangle - \langle \Delta x\rangle^2.$$

So, for the discrete random walk with steps $\pm\Delta x = \pm 1$ and timstep $\Delta t = 1$, one has

$$D = \frac{(\Delta x)^2}{2\Delta t} = \underline{\underline{\frac{1}{2}}}$$

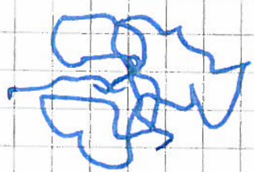
2.3 Brownian Motion

Named after Britisch botanist

Robert Brown (1773-1858)

who in 1827 studied pollen grains in liquid.

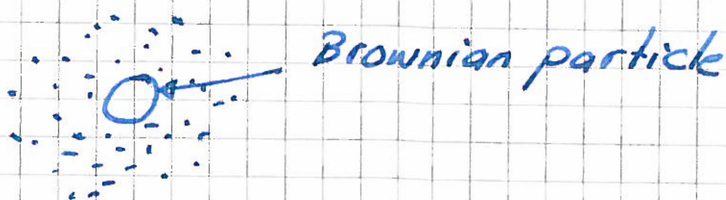
Today Brownian Motion denotes the erratic motion of a small particle in a surrounding media e.g. liquid or gas



Q : Was this motion due to life?

Note : Even if the particle is small, it is still larger then microscopic scaled molecules

Picture



The temporal movement of the "molecules" kick the (larger) Brownian particle around.

Note : BM is <u>not</u> by itself a molecular motion, but it is a result of it.

Illustration : Google for "Brownian Motion Java"

Some Java applets can be found.

2.4 Einsteins Contribution to BM

We have previously established the DE

$$\partial_t \rho = D \nabla^2 \rho \qquad (\vec{J} = - D \nabla \rho)$$

where D is the diffusion constant.
In this context it is a <u>macroscopic</u> quantity.

In 1905 Einstein studies the Brownian motion, and he this year published a seminal paper on the topic.

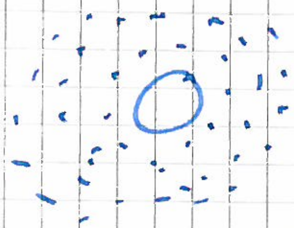
He showed that:

$$\langle [x(t) - x(0)]^2 \rangle = \langle \Delta x^2(t) \rangle = 2Dt$$

In this context D plays a <u>microscopic</u> role. Or, by study the microscopic behaviour of a Brownian particle, one can gain information on macroscopic properties of the system.

Ex: Position time records of a Brownian particle can be used to determine or estimate Avogadro's number. (see later)

Einsteins Picture



Assumptions:

1) The motion of the pollen particle is caused by exceedingly frequent impacts of the "liquid particles" (molecules)

2) The motion of the molecules is so complicated that its effect on the pollen grain can only be described probabilistically in terms of (exceedingly frequent) statistically <u>independent</u> impacts.

<u>NB</u> E. attempted a statistical explanation of BM.

<u>NB</u>. This was the beginning of stochastic modelling of natural phenomena.

Summary

* one-particle prop $\langle \Delta x^2(t) \rangle = 2Dt$
  (microscopic)

* many-particle prop $\vec{J} = -D\nabla\rho$
  (macroscopic) (or $\partial_t \rho = D\nabla^2\rho$)

— // —

That single particle properties can be related to ensamble of particles (many-part) is calle ergodicity in statistical physics.

— // —

What Einstein showed was that

$$\boxed{\text{Random Walk} = \text{Diffusion}}$$

They are essentially the same phenomena!

Moreover, Einstein proved that the diffusion constant D of a Brownian particle of mass m moving about in a surrounding medium is

$$D = \frac{k_B T}{\gamma m}$$

where k_B is Boltzmann constant, T is the temperature, and γ is the friction constant (of the surrounding medium).

2.4.1 Brownian Motion used to determine Avogadro's Number.

Let's assume that the Brownian particle can be modeled by a small sphere moving around in a liquid.

Then, according to Stokes, the friction coefficient (viscous drag) is

$$\gamma = \frac{6\pi \eta r}{m}$$

where r is the radius of the sphere, and η is the (dynamical) viscosity of the liquid.

By using that

$$k_B = \frac{R}{N_A}$$

Where R is the ideal gas constant, one arrives at

$$D = \frac{RT}{6\pi \eta r \, N_A}$$

Hence

$$\langle \Delta x^2(t) \rangle = 2Dt$$

$$\Rightarrow N_A = \frac{RT}{3\pi\eta r} \underbrace{\frac{t}{\langle \Delta x^2(t) \rangle}}$$

Determined from exp. data.

A Historical Note

It is true that Einstein was the one that propost a theoretical explanation of BM.

It is also true, that M. von Smoluchowski independent developed (at the same time period) a similar theory explaining BM.
He also was responsable for much of the later systematic development, but also experimental verification of BM.

In some sense, he has not been given the credit that he deserves.

Summary

Einstein showed in his 1905 paper that

$$D = \frac{k_B T}{\gamma m} \underset{\uparrow}{=} \frac{k_B T}{6\pi\eta r}$$

stokes law (Drag force $F = 6\pi\eta r \cdot v$)
$= m\gamma \cdot v$

This is the so-called <u>Stokes-Einstein relation</u>

— " —

More generally, it applies (as can be shown by kinetic theory) that

$$\boxed{D = \mu k_B T}$$

where the proposjonality constant μ is known as the <u>mobility</u> of the particles

This is known as the <u>Einstein-Smoluchowski</u> relation

— " —

Mobility is defined as the particle's drift velocity normalized with the applied force $\mu = v/F$.

Stoke's law

In 1851, George G. Stokes derived an expression for the friction force (or drag force) exerted on a ~~sm~~ spherical object (from the surronding liquid)

$$F = 6\pi \eta r \cdot v = m\gamma \cdot v$$

$$[\gamma] = s^{-1}$$

This relation is valid for very small Reynolds numbers, e.g. for for small particles.

Hence for small particles one has

$$\mu = \frac{1}{6\pi \eta r}$$

2.5 Langevin's Explanation of Brownian Motion

A year (or so) after Einstein's explanation of Brownian motion, Langevin gave an alternative derivation (1906)

This derivation was rather different in spirit and "infinitly simpler" according to L.

L's approach was based on a <u>stochastic equation of motion</u>.

Two forces are acting on the Brownian part.

1) Viscous drag : $-m\gamma\vec{v} = -m\gamma\dot{\vec{x}}$

$F = \frac{v}{\mu}$

2) Fluctuating force : due to the impact of the molecules

$$\vec{\aleph}(t) \propto \vec{\xi}(t)$$

Assumpions - No net fluctuating force on average.

$$\langle \aleph(t) \rangle = \langle \xi(t) \rangle = 0$$

- The random events are <u>uncorrelated</u>

$$\langle \xi(t)\, \xi(t') \rangle = \delta(t-t')$$

Newtons law applied to the Brownian particle:

$$m\,\partial_t^2 x(t) = \underbrace{-m\gamma\,\partial_t x(t) + \mathcal{H}(t)}_{f} \qquad (*)$$

multiply by x gives $(v = \partial_t x)$

$$\frac{m}{2}\partial_t^2(x^2) - mv^2 = -\frac{m\gamma}{2}\partial_t(x^2) + \mathcal{H}x$$

Average this eq. over an ensamble of particles and using the equipartition law result

$$\langle \tfrac{1}{2}mv^2\rangle = \tfrac{1}{2}k_BT$$

and

$$\langle \mathcal{H}(t)\,x(t)\rangle = 0 \quad \propto \quad \langle \xi(t)\,x(t)\rangle = 0$$

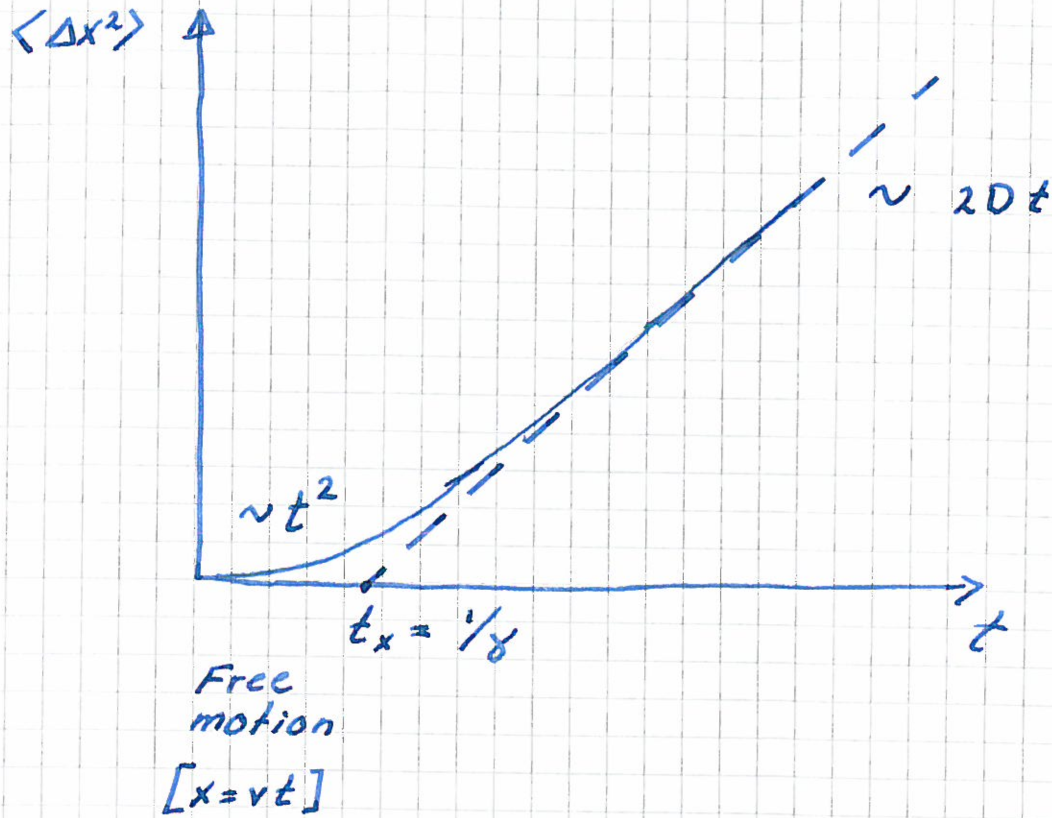
$$\frac{m}{2}\partial_t^2\langle x^2\rangle + \frac{m\gamma}{2}\partial_t\langle x^2\rangle = k_BT$$

Solution (see note for details) handed out

$$\langle \Delta x^2(t)\rangle = \begin{cases} 2Dt - \dfrac{2D}{\gamma} & t \gg 1/\gamma \\ \langle v^2\rangle t^2 & t \ll 1/\gamma \end{cases}$$

— " —

(*) is called Langevin's eq. and is an example of a stochastic differential eq.



Note : Since the Langevin eq. (*) is a stochastic diff. eq. the solution is stochastic in the sense that a different realization of the noise term corresponds to a different "solution".

Note : The mathematical fondation of L's approach was not available until 40 years later (just after 2 WW).

(Look up Ito and Stratonovich calculus)

What does it mean $\int d\xi(t)$

stoch. var (Wiener proc.)

Stochastic integrals

Ito :
$$\int_{t_0}^{t} F(t')\,d\xi(t') = \lim_{n\to\infty} \sum_{i=1}^{n} F(t_{i-1})\left[\xi(t_i)-\xi(t_{i-1})\right]$$

Stratonovich :
$$\int_{t_0}^{t} F(t')\,d\xi(t') = \lim_{n\to\infty} \sum_{i=1}^{n} \frac{F(t_i)+F(t_{i-1})}{2}\left[\xi(t_i)-\xi(t_{i-1})\right]$$

— // —

"Ito's formula" ($\xi(t)$ is a Wiener process)

$$dF[t,\xi(t)] = \left(\frac{\partial F}{\partial t} + \frac{1}{2}\frac{\partial^2 F}{\partial \xi^2}\right)dt + \frac{\partial F}{\partial \xi}\,d\xi(t)$$

(Note : $d\xi^2(t) = dt$)

— // —

Note : The Ito and Stratonovich interpretation of the stochastic integral are NOT equivalent.

Hence one must specify ~~as~~ which one use since the result depends on this choice.

2.6 The Fokker-Planck Approach to Brownian Motion

The FP eq. is an equation for the probability density $p(x,t)$ of finding a particle at x at time t.

This problem we have previously solved, since the FP eq. for BM is nothing else than the diffusion eq.:

$$\partial_t p(x,t) = D \nabla^2 p(x,t)$$

2.7 Diffusion Limited Aggregation

This pattern formation model was introduced by

T. A. Witten and L. M. Sander
Phys. Rev. Lett. 47, 1400 (1981)

The model gives rise to patterns observed in nature where diffusion is the main transport mechanism.

Check out wikipedia (e.g.) for some beautiful patterns:

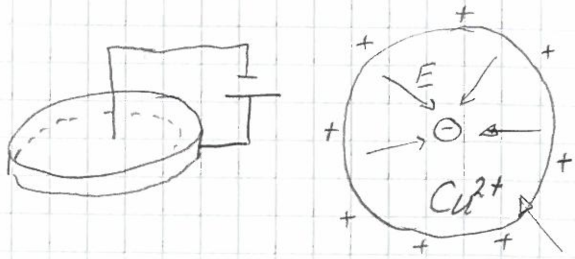
The model:

1) Start with a seed (randomly placed)
2) A particle starts far away from the initial seed and diffuses around.
3) Once it hits the seed it "sticks" to the seed to form an aggregate
4. Then "start" a new particle and let it diffuse around till it hits the aggregat and sticks.
5 Repeat #4 for a large number of particles.

The DLA patterns are examples of fractal patterns. For instance in 2D the fractal dimension is $D_F \simeq 1.71$

Such patterns can be observed, e.g., in

1) Electrodeposition
(also called electrochemical dep. (ECD))
"forkroming" → flat surface



$Cu^{2+} + 2e \rightarrow Cu$

Copper sulfate
Zink —"—

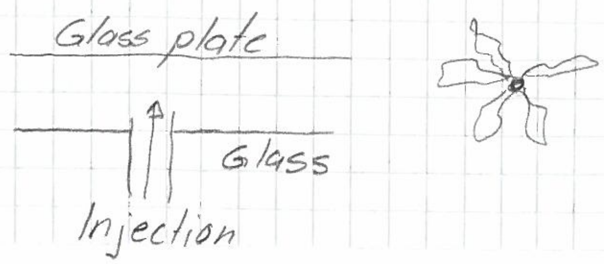
2) Viscous Fingering

Low viscosity liquid injected into a liquid of higher viscosity (e.g. water into oil)
⇒ viscous fingering

Patterns in Hele-Shaw cells look like DLA patterns

Side view   Top view

2D exp.



3] Dielectric Breakdown

Patterns known as Lichtenberg figures, named after the German physicist Georg Christoph Lichtenberg who studied them in 1777 (?).

Think of lightning!

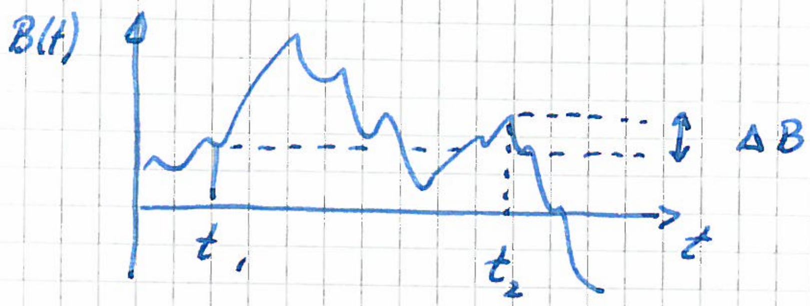
For short times after breakdown the patterns are DLA-like

For later times the DLA nature is changed (the electric field starts to play a role)

$\Rightarrow$ Dielectric breakdown model (DBM)

2.8 The scaling Property of BM

Let $B(t)$ denote a "Brownian function"



Then we know that

$$\sigma(t) = \sqrt{2Dt} \propto t^{1/2}$$

— " —

We will now study the quantity

$$\Delta B_{\Delta t}(t) = |B(t+\Delta t) - B(t)|$$

(i.e. the increment over a time-window Δt).

Since $\Delta B_{\Delta t}(t)$ essentially should behave like $\sigma(t)$ for $t = \Delta t$, one has that

$$\Delta B_{\Delta t}(t) \underset{\text{scales as}}{\sim} \Delta t^{1/2}$$

Let now $\Delta t \to \lambda \Delta t$ $(\lambda \in R^+)$; i.e. rescale Δt:

$$\begin{aligned}\Delta B_{\lambda\Delta t}(t) &= |B(t+\lambda\Delta t) - B(t)| \\ &\sim (\lambda \Delta t)^{1/2} \\ &= \lambda^{1/2} \Delta t^{1/2} \\ &\sim \lambda^{1/2} B_{\Delta t}(t)\end{aligned}$$

Hence, one has that

$$\boxed{\Delta B_{\lambda \Delta t}(t) \sim \lambda^{1/2} \Delta B_{\Delta t}(t)} \qquad (*)$$

This is an example of a scaling relation.

The power of such a scaling relation is that once we know the properties at <u>one</u> scale, we immediately know them at <u>all</u> scales.

This is a very powerful concept. !

The invariance shown in (*) is known as a self-affine scale invariance (insted of self-similar if the exponent of λ would have been one).

Alternatively one may express the same ting in terms of the probability, $p(\Delta B, \Delta t)$, of having an increment ΔB over a time-window Δt :

$$\boxed{p(\lambda^{1/2}\Delta B, \lambda \Delta t) = \lambda^{-1/2} p(\Delta B, \Delta t)}$$

ev. $\lambda^{-1/2} p(\lambda^{1/2}\Delta B, \lambda\Delta t) = p(\Delta B, \Delta t)$

[Mathematically, one says that p is a homogeneous function of degree $-1/2$]

You should be able to convince yourself of this by recalling our previously derived probability distribution for the BM

$$p(x,t) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-x^2/2\sigma^2}, \quad \sigma = \sqrt{2Dt}$$

with the initial condition $p(x, t=0) = \delta(x)$
Hence, $x = \Delta B$ and $t = \Delta t = t - 0$.

— // —

The exponent of λ appearing in the above equations are often called the Hurst exponent (or the roughess exp.)
Hence, the BM has a Hurst exponent of

$$H = 1/2.$$

If $H \neq 1/2$ (but $H \in [0,1]$) one has what is called fraction Brownian motion.

If $H \neq 1/2$ the increments are correlated. (long range correlations)