II. DIFFUSION.

Diffusion describes the spread of particles from regions of higher concentration to regions of lower concentration through random motion.
Originally, diffusion of particles was thought of in terms of concentrations while later the probabilistic picture of individual particles' independent motion emerged.

In around 50 BCE Titus Lucretius Carus describes the "battling" motion of dust particles in air.

1757 Dutch physician Jan Ingenhousz accounts experiments on the jittery motion of coal dust particles on an alcohol surface.

In 1827 Scottish botanist Robert Brown describes the zigzag motion of small particles enclosed in pollen grains found in amber.

Brown and Ingenhousz used control experiments to exclude active motion of "animalcules".

In 1855 Adolf Fick derived the diffusion equation

$$\frac{\partial P(x,t)}{\partial t} = D \frac{\partial^2 P(x,t)}{\partial x^2}$$

Here, D is the diffusion coefficient of physical dimension $[D] = \frac{cm^2}{sec}$.
P is the probability density function (PDF).

Solution:

(1) Laplace transform:

$$u P(x,u) - P(x,0) = D \frac{\partial^2 P(x,u)}{\partial x^2} \quad \text{with } P(x,0) \doteq \delta(x)$$

$$u P(x,u) - \delta(x) = D \frac{\partial^2 P(x,u)}{\partial x^2}$$ reduction to ODE of 2nd order.

Standard methods.

(2) Fourier-Laplace method:

Fourier transform: $g(k) \equiv \mathcal{F}\{g(x); x \to k\} = \int_{-\infty}^{\infty} g(x) e^{ikx} dx$

$$g(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} g(k) e^{ikx} dk$$

Differentiation theorem: $\int_{-\infty}^{\infty} \frac{dg(x)}{dx} e^{ikx} dx = \left[g(x) e^{ikx}\right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} ik\, g(x) e^{ikx} dx$

$$= -ik\, g(k)$$

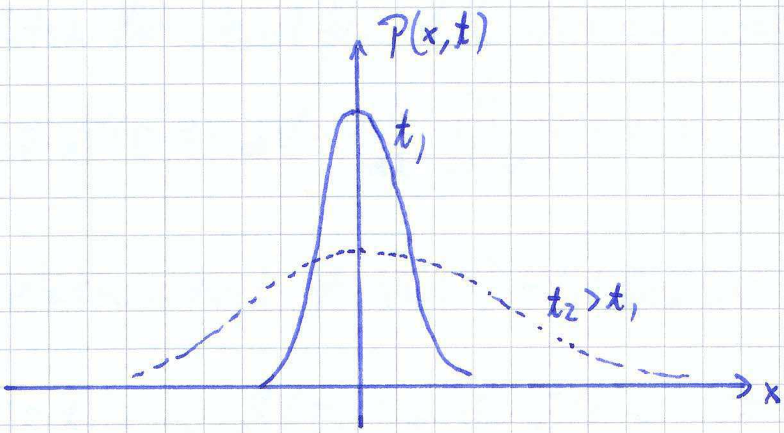
$$\int_{-\infty}^{\infty} \frac{d^2 g(x)}{dx^2} e^{ikx} dx = -k^2 g(k)$$

$\Rightarrow u P(k,u) - 1 = -Dk^2 P(k,u)$ algebraic equation!

$\Rightarrow P(k,u) = \dfrac{1}{u + Dk^2}$

Laplace inversion: $P(k,t) = e^{-Dk^2 t}$ Gaussian

Fourier inversion: $\underline{\underline{P(x,t) = \dfrac{1}{\sqrt{4\pi D t}} e^{-x^2/4Dt}}}$



Das 2. Moment:

$\underline{\underline{\langle x^2(t) \rangle}} = \int_{-\infty}^{\infty} x^2 P(x,t)\, dx \overset{\text{Tabelle}}{=\!=} \underline{\underline{2Dt}}$

Trick to calculate: start with diffusion equation

$$x^2 \frac{\partial P}{\partial t} = \frac{\partial}{\partial t} x^2 P = D x^2 \frac{\partial^2 P}{\partial x^2} \quad \Big| \int_{-\infty}^{\infty} dx \, .$$

$$\frac{d}{dt}\langle x^2\rangle = D\left\{ \left[x^2 P'\right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} 2x \frac{\partial P}{\partial x} dx \right\} = D\left\{ -\left[2xP\right]_{-\infty}^{\infty} + \int_{-\infty}^{\infty} 2P\, dx \right\} = 2D$$

$\Rightarrow \langle x^2\rangle = 2Dt.$

<u>Fick's derivation of the diffusion equation:</u>

(1) <u>Continuity equation:</u> Given a probability density $P(\underline{r}, t)$ with $\iiint_{-\infty}^{\infty} P(\underline{r}, t)\, dV = 1$, and the probability flux $\underline{S}(\underline{r}, t)$:

$$\oiint_{\delta V} \underline{S}(\underline{r}, t)\, d\underline{A} = -\frac{d}{dt} \iiint_V P(\underline{r}, t)\, dV = -\frac{d}{dt} \mathcal{S}(t)$$

where $\mathcal{S}(t)$ is the survival probability.
With the divergence theorem (Gauss' theorem):

$$\oiint_{\delta V} \underline{S}(\underline{r}, t)\, d\underline{A} = \iiint_V \nabla \cdot \underline{S}(\underline{r}, t)\, dV$$

we obtain the integral form of the continuity equation:

$$\iiint_V \nabla \cdot \underline{S}(\underline{r}, t)\, dV = -\frac{d}{dt} \iiint_V P(\underline{r}, t)\, dV = -\iiint_V \frac{\partial P(\underline{r}, t)}{\partial t}\, dV$$

This relation is valid $\forall\ (V, \delta V) \Rightarrow$ differential form:

$$\underline{\underline{\frac{\partial}{\partial t} P(\underline{r}, t) = -\nabla \cdot \underline{S}(\underline{r}, t) = -\operatorname{div} \underline{S}(\underline{r}, t).}} \quad \text{continuity equation}$$

(2) <u>Fick's first law:</u>

$$\underline{\underline{\underline{S} = -D \nabla P(\underline{r}, t)}}$$ the flux is proportional to the gradient of the probability density function P.

III. RANDOM WALKS.

1905 Karl Pearson poses the problem of the random walk, being interested in the dynamics how mosquito populations invade cleared jungle regions:
"Can any of your readers refer me to a work wherein I should find the solution to the following problem [...]:
A man starts from a point O and walks l yards in a straight line; he then turns through any angle whatever and walks l yards in a second straight line. He repeats this process n times. I require the probability that after these n stretches he is at a distance between r and $r+dr$ from his starting point, O."

Lord Rayleigh pointed out one week later that in the limit of large n the solution is a Gaussian.

Consider a jump process on a one-dimensional lattice with spacing a. At each step the probability to jump left or right is equal.
$\rightsquigarrow$ Probability to reach site m after N steps ($N \pm m$ are always even!)

$$g(m,N) = \left(\frac{1}{2}\right)^N \frac{N!}{\underbrace{\left[\frac{1}{2}(N-m)\right]!}_{\frac{N-m}{2}\text{ jumps to left}}\underbrace{\left[\frac{1}{2}(N+m)\right]!}_{\frac{N+m}{2}\text{ jumps to right}}}$$

Stirling's formula: $\log N! = \left(N+\frac{1}{2}\right)\log N - N + \frac{1}{2}\log 2\pi + \mathcal{O}\left(N^{-1}\right)$

Expansion of log: $\log(1+z) \sim z - \frac{z^2}{2}$, $z \ll 1$.

$$\Rightarrow \log g(m,N) \approx -\frac{1}{2}\log N + \log 2 - \frac{1}{2}\log 2\pi - \frac{m^2}{2N}$$

$$g(m,N) \simeq \sqrt{\frac{2}{\pi N}}\,\exp\left(-\frac{m^2}{2N}\right)$$

m is either always even (N even) or always odd (N odd)

$\Rightarrow$ probability to meet the walker at site m:

$$P(m,N) = \frac{1+(-1)^{N-m}}{2}\, g(m,N) \approx \frac{1+(-1)^{N-m}}{\sqrt{2\pi N}} \exp\left(-\frac{m^2}{2N}\right). \quad (*)$$

Note that $P(m,N)=0$ for $|m|>N$ for exact expression, but not for approximation. This result is one form of the <u>centrale limit theorem (CLT)</u>: the (normalised) sum of independent random variables with finite variance is well approximated by a random variable with a Gaussian distribution in the limit of large numbers.

Even for $N=10$ the approximation $(*)$ containing the Gaussian is almost exact (normalisation is 0.999594).

The factor $\frac{1+(-1)^{N-m}}{2}$ is essential for the normalisation.

<u>Continuum limit:</u>

Position of the walker is $x = ma$:

$$P(x,N) \approx \sqrt{\frac{1}{2\pi N a^2}} \exp\left(-\frac{x^2}{2Na^2}\right)$$

from Jacobian

Time $t = N\Delta t$ and diffusion constant $K = \frac{a^2}{2\Delta t}$

$$\Rightarrow P(x,t) \approx \sqrt{\frac{1}{4\pi K t}} \exp\left(-\frac{x^2}{4Kt}\right).$$

IV. THE FOKKER-PLANCK EQUATION.

Let us start from a random walk, but now the probability to jump left or right depends on the walker's position: we start from the discrete master equation

$$W_j(t+\Delta t) = A_{j-1}\, W_{j-1}(t) + B_{j+1}\, W_{j+1}(t)$$

Pr to find walker at j at $t+\Delta t$

$$\begin{tikzcd} j-1 \arrow[r, bend left, "A_{j-1}"] & j & j+1 \arrow[l, bend right, "B_{j+1}"'] \end{tikzcd}$$

$A_j + B_j = 1$ jump w/ Pr $= 1$.

Taylor expansions: $W_j(t+\Delta t) \approx W_j(t) + \Delta t \frac{\partial}{\partial t} W_j(t)$

$$A_{j-1} W_{j-1} \approx A(x)W(x) - \Delta x \frac{\partial}{\partial x} A(x)W(x) + \frac{(\Delta x)^2}{2} \frac{\partial^2}{\partial x^2} A(x)\, W(x)$$

$$B_{j+1} W_{j+1} \approx B(x)\, W(x) - \Delta x \frac{\partial}{\partial x} B(x)W(x) + \frac{(\Delta x)^2}{2} \frac{\partial^2}{\partial x^2} B(x)\, W(x)$$

$$\Rightarrow W(x,t) + \Delta t \frac{\partial W}{\partial t} = \underbrace{\left[A(x) + B(x)\right]}_{\equiv 1} W(x,t) + \Delta x \frac{\partial}{\partial x}\left(B(x) - A(x)\right) W(x,t)$$
$$+ \frac{(\Delta x)^2}{2} \frac{\partial^2}{\partial x^2}\left[A(x) + B(x)\right] W(x,t)$$

$$\frac{\partial}{\partial t} W(x,t) = \frac{\Delta x}{\Delta t} \frac{\partial}{\partial x}\left[B(x) - A(x)\right] W(x,t) + \frac{(\Delta x)^2}{2\Delta t} \frac{\partial^2}{\partial x^2} W(x,t)$$

Continuum limit $\Delta x \to 0$, $\Delta t \to 0$:

$$\frac{\partial}{\partial t} P(x,t) = \frac{\partial}{\partial x} \frac{V'(x)}{m\eta} P(x,t) + K \frac{\partial^2}{\partial x^2} P(x,t)$$

Fokker-Planck equation

$$\lim_{\Delta x \to 0, \Delta t \to 0} \frac{\Delta x}{\Delta t}\left[B(x) - A(x)\right] = \frac{V'(x)}{m\eta}$$

$$\lim_{\Delta x \to 0, \Delta t \to 0} \frac{(\Delta x)^2}{2\Delta t} = K$$

for proper limit we must have that $B(x) - A(x) \approx \Delta x$

$F(x) = -V'(x)$ is the external force. η is the friction coefficient.

In a confining potential the long-time limit of $P(x,t)$ reaches the equilibrium distribution:

$$P_{eq}(x) = \mathcal{N} \exp\left(-\frac{V(x)}{k_B T}\right).$$

$$\frac{\partial}{\partial t} P(x,t) = 0 \Rightarrow 0 = \left(\frac{\partial}{\partial x} \frac{V'(x)}{m\eta} + K \frac{\partial^2}{\partial x^2}\right) P(x,t)$$

$$\rightsquigarrow \quad 0 = \left(\frac{V'(x)}{m\eta} + K \frac{\partial}{\partial x}\right) P_{eq}(x)$$

$$\Rightarrow \quad P_{eq}(x) = \mathcal{N} \exp\left(-\frac{V'(x)}{K m\eta}\right)$$

$$\Rightarrow \quad \underline{\underline{K = \frac{k_B T}{m\eta}}}$$ Einstein-Stokes-Smoluchowski relation (fluctuation-dissipation relation).

<u>Constant external force F_0:</u>

$$\frac{\partial}{\partial t} P(x,t) = -\frac{F_0}{m\eta} \frac{\partial}{\partial x} P(x,t) + K \frac{\partial^2}{\partial x^2} P(x,t)$$ sometimes called diffusion-advection eq.

(i.) <u>Similarity solution</u> with Galilei (wave) variable $\xi = x - \frac{F_0}{m\eta} t$

$$P(x,t) = G\left(x - \frac{F_0}{m\eta} t, t\right) \therefore G(x,t) = \frac{1}{\sqrt{4\pi K t}} \exp\left(-\frac{x^2}{4Kt}\right).$$

(ii.) <u>Second Einstein relation (linear response):</u>

$$\frac{d}{dt}\langle x(t)\rangle = \frac{F_0}{m\eta} \quad \Rightarrow \langle x(t)\rangle = \frac{F_0}{m\eta} t = \frac{F_0 K}{k_B T} t$$

w/o force we know that: $\langle x^2(t)\rangle_0 = 2Kt$

$$\Rightarrow \langle x(t)\rangle_{F_0} = \frac{F_0}{2 k_B T} \langle x^2(t)\rangle_0 .$$