Diffusion

1/. Mixing of two fluids in contact, due to the migratory movement of molecules.

2/. Motion of molecules is random.

3/. Diffusion is rapid in gases, slow in liquids. (Longer mean free path for gases).

4/. Diffusion depends on the rate of change of density at spatial positions.

5/. Can continue in opposition to gravity.

6/. Diffusive movement is not due to any bulk motion of the material.

Graham's Experiment

Rate of diffusion of aqueous solutions depends on:

1/. Type of solute (salt).

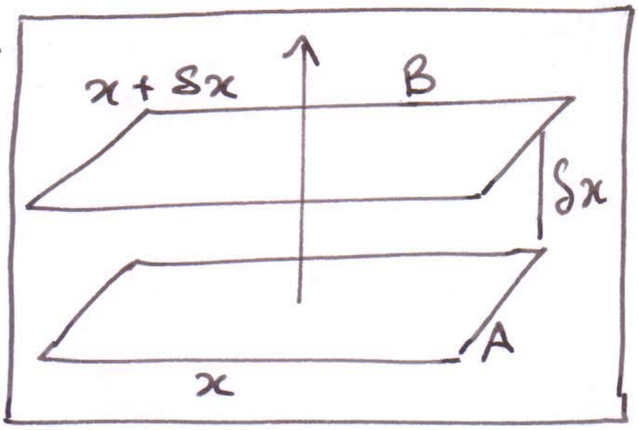
2/. Increases with greater concentration.

3/. Increases with temperature.

(All the observations are gathered in Fick's law)

(ADOLF FICK)

Fick's Law



i.) A and B are two planes of constant density of a liquid.

ii.) The planes have unit area.

iii.) Concentration of fluid at a position x and at time t is $\boxed{c(x,t)}$.

iv.) The gradient of the concentration is $\boxed{\frac{\partial c}{\partial x}}$.

> Fick's Law: Mass of the dissolved substance crossing unit area of the plane in unit time is in proportion to $\boxed{\frac{\partial c}{\partial x}}$, or equal to $\boxed{D \frac{\partial c}{\partial x}}$, where D is the COEFFICIENT OF DIFFUSION. (The proportional constant)

The Diffusion Equation

Let the concentration on the plane A be $c(x,t)$. Hence, on plane B the concentration is $\boxed{c - \frac{\partial c}{\partial x} \delta x}$. The negative sign implies that the concentration decreases with the height. In time δt,

(P.T.O.)

by Fick's law, the inflow of dissolved substance on the plane A is $\boxed{D\frac{\partial c}{\partial x}\delta t}$

($\because$ the concentration gradient at A is $\frac{\partial c}{\partial x}$).

On plane B the concentration gradient is $\frac{\partial}{\partial x}\left(c - \frac{\partial c}{\partial x}\delta x\right)$

$\boxed{= \frac{\partial c}{\partial x} - \frac{\partial^2 c}{\partial x^2}\delta x}$. Therefore, by Fick's law,

the outflow of the dissolved substance on plane B is $\boxed{D\frac{\partial c}{\partial x}\delta t - D\frac{\partial^2 c}{\partial x^2}\delta x\,\delta t}$ in a time interval δt. The net gain in the space between A and B is

$$\boxed{\cancel{D\frac{\partial c}{\partial x}\delta t} - \cancel{D\frac{\partial c}{\partial x}\delta t} + D\frac{\partial^2 c}{\partial x^2}\delta x\,\delta t = D\frac{\partial^2 c}{\partial x^2}\delta x\,\delta t}.$$

Volume enclosed between A and B is $1 \times \delta x$.

$\therefore$ Change in concentration between A and B in unit time is $D\frac{\partial^2 c}{\partial x^2}\frac{\cancel{\delta x}\,\cancel{\delta t}}{1\times\cancel{\delta x}\times\cancel{\delta t}}$.

But (time) ~~rate~~ rate of change in concentration is $\frac{\partial c}{\partial t}$ as well.

Hence $\boxed{\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}} \rightarrow$ The Diffusion Equation.

$C \equiv C(x,t)$. The above equation is the one-dimensional diffusion equation — second order in space and first order in time. $[D] = L^2T^{-1}$.

A Solution of the Diffusion Equation

$$\boxed{\frac{\partial \psi}{\partial t} = D\,\frac{\partial^2 \psi}{\partial x^2}} \quad \text{with} \quad \boxed{\psi \equiv \psi(x,t)}.$$

The Diffusion Equation requires:

i.) One initial condition (at $t=0$).

ii.) Two boundary conditions.

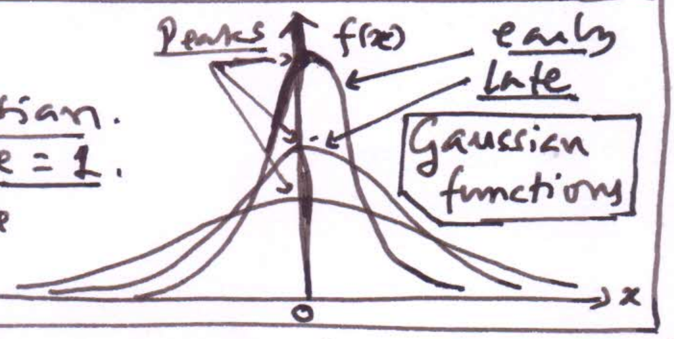
At $t=0$ for all x

We use the initial condition $\boxed{\psi(x,0) = \delta(x)}$.

in which $\underbrace{\delta(x-x')}_{\text{DIRAC DELTA FUNCTION}} = \begin{cases} 0 & \text{when } x-x' \neq 0 \\ \infty & \text{when } x-x' = 0. \end{cases}$

$\delta(x) = \delta(x-0) \Rightarrow$ "spike" at $x=0$.

Dirac Delta Function as a limiting case of the Gaussian. The area under the curve $= 1$. When the width $\to 0$, the height $\to \infty$ at $x=0$.



The Point-Source Solution (for $\psi(x,0) = \delta(x)$)

Initial condition

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

Apply this solution to the diffusion equation.

Time derivative

$$\frac{\partial \psi}{\partial t} = \frac{1}{\sqrt{4\pi D}}\,\exp\left(-\frac{x^2}{4Dt}\right) \times -\frac{1}{2}\,\frac{t^{-1/2}}{t}$$

$$+ \frac{1}{\sqrt{4\pi D}}\,t^{-1/2}\,\exp\left(-\frac{x^2}{4Dt}\right) \cdot \frac{-x^2}{4D} \times -t^{-2}$$

(P.T.O.)

$$\Rightarrow \boxed{\frac{\partial \psi}{\partial t} = \psi\left(-\frac{1}{2t} + \frac{x^2}{4Dt^2}\right)} \longrightarrow$$ The left-hand side.

Space derivatives:

First derivative $\longrightarrow$ $$\frac{\partial \psi}{\partial x} = \frac{1}{\sqrt{4\pi D t}} \exp\left(\frac{-x^2}{4Dt}\right) \times -\frac{2x}{4Dt}.$$

$$\Rightarrow \boxed{\frac{\partial \psi}{\partial x} = -\frac{2x}{4Dt}\psi}$$

Second Derivative $\rightarrow$ $$\frac{\partial^2 \psi}{\partial x^2} = -\frac{2x}{4Dt}\frac{\partial \psi}{\partial x} - \frac{2\psi}{4Dt}$$

$$\Rightarrow \frac{\partial^2 \psi}{\partial x^2} = \left(-\frac{2x}{4Dt}\right)\left(-\frac{2x}{4Dt}\right)\psi - \frac{\psi}{2Dt}$$

$$\Rightarrow \boxed{\frac{\partial^2 \psi}{\partial x^2} = \psi\left(\frac{x^2}{4D^2t^2} - \frac{1}{2Dt}\right)}$$

$$\therefore \boxed{D\frac{\partial^2 \psi}{\partial x^2} = \psi\left(-\frac{1}{2t} + \frac{x^2}{4Dt^2}\right)} \longrightarrow$$ The right-hand side.

Compare: L.H.S. = R.H.S. $\Rightarrow \boxed{\frac{\partial \psi}{\partial t} = D\frac{\partial^2 \psi}{\partial x^2}}$

COMPARISON

Gaussian function: $$\boxed{P(x) = \frac{1}{\sqrt{2\pi}\,\sigma}\exp\left[-\frac{(x-\mu)^2}{2\sigma^2}\right]}$$

Point-Source Solution: $$\boxed{\psi(x,t) = \frac{1}{\sqrt{2\pi}\sqrt{2Dt}}\exp\left[-\frac{x^2}{2(2Dt)}\right]}$$

$\boxed{\mu \rightarrow 0}$ (Mean) and $\boxed{\sigma^2 \rightarrow 2Dt}$ (variance) $\boxed{\sigma = \sqrt{2D}\,t^{1/2}}$. (Standard Deviation)

Spatio-Temporal Features of the Point-Source Solution

1/. At $\boxed{t=0, \quad x\neq 0}$. $\boxed{\psi(x,t)=\frac{1}{\sqrt{4\pi D t}}\exp\left[-\frac{x^2}{4Dt}\right]}$

$$\boxed{\psi=\frac{1}{\sqrt{4\pi D}}\frac{1}{t^{1/2}}\cdot\frac{1}{\exp\left(\frac{x^2}{4Dt}\right)}}$$ Expand $\boxed{e^{z}=1+z+\frac{z^2}{2!}+\cdots}$

$$\Rightarrow \psi=\frac{1}{\sqrt{4\pi D}}\cdot\frac{1}{t^{1/2}}\frac{1}{\left(1+\frac{x^2}{4Dt}+\frac{x^4}{2!(4D)^2}\cdot\frac{1}{t^2}+\frac{x^8}{3!(4D)^3}\cdot\frac{1}{t^3}+\cdots\right)}.$$

$$\Rightarrow \psi=\frac{1}{\sqrt{4\pi D}}\cdot\left[\frac{1}{t^{1/2}+\frac{x^2}{4D}\times\frac{1}{t^{1/2}}+\frac{x^4}{2!(4D)^2}\cdot\frac{1}{t^{3/2}}+\frac{x^8}{3!(4D)^3}\frac{1}{t^{5/2}}+\cdots}\right]$$

$\Rightarrow$ When $t\to 0$ $\psi\to\frac{1}{\infty}\to 0 \Rightarrow \boxed{\psi(x,0)=0}$

2/. At $\boxed{t=0, x=0}$. When $x\to 0, t\to 0$, x with a higher power converges faster.
The series will converge to zero at $x=0$.
$\Rightarrow \psi\longrightarrow\frac{1}{0}\to\infty$ i.e., the $\delta(x-0)$ Dirac Delta function
$\therefore \psi(0,0)\to\infty \to$ An infinite initial spike.

3/. At $\boxed{x=0, \text{ for } t>0}$. $\boxed{\exp\left(-\frac{x^2}{4Dt}\right)=1}$. $\frac{(x=0)}{\boxed{e^0=1}}$.

$\therefore$ $\boxed{\psi(0,t)=\frac{1}{\sqrt{4\pi D}}\frac{1}{t^{1/2}}}$ As t increases the central peak subsides.

$\Rightarrow$ As $t\to\infty$, $\psi(0,t)\to 0$ (complete diffusion through all space, and nothing is left at the source)

4/. At $\boxed{x\neq 0, \text{ for } t>0}$ As $t\to\infty$ $\boxed{\psi(x,t)\longrightarrow 0}$.

Also $\boxed{\frac{\partial\psi}{\partial t}=\psi\left(-\frac{1}{2t}+\frac{x^2}{4Dt^2}\right)\to 0}$. Similarly $\boxed{\frac{\partial\psi}{\partial x}=-\frac{2x\psi}{4Dt}\to 0}$

Nothing is left. There is no growth in space and time.