How a non-equilibrium system evolve over time

Theory of diffusion

2 assumptions

1. A substance will move down to its concentration gradient (Fick's first law)

$\underbrace{\vec{J}}_{\text{flux}} = -\underbrace{D}_{\text{diffusion constant}}\nabla \underbrace{C}_{\text{concentration}}$ 1D: $J = -D\frac{\partial C}{\partial x}$

2. conservation of matter

$\frac{\partial C}{\partial t} = -\underbrace{\vec{\nabla}\cdot}_{\text{divergence}}\vec{J}$ 1D: $\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x}$

All together, we get Diffusion equation

$\frac{\partial C}{\partial t} = D\underbrace{\nabla^2}_{\text{Laplacian operator}} C$ 1D: $\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$

Diffusion equation: a partial differential equation

how a spatial distribution of material changes over time

Define solution $\begin{cases}\text{initial conditions}\\ \text{boundary conditions}\end{cases}$

One-dimensional diffusion from a point

Initial conditions: $C = M\underbrace{\delta(x)}_{[L]^{-1}}$ @ $t=0$ which means $\int_{-\infty}^{\infty} C(x)dx = M$

boundary conditions: Length $= \infty$

Brown part: If not familiar with complex form of Fourier transformation

Periodic functions: expand to Fourier series

Non-periodic functions: functions of ∞ period → Fourier integrals

frequency: $0 \to \infty$

$F(x) = \int_0^{\infty} A(s)\sin(sx)ds + \int_0^{\infty} B(s)\cos(sx)ds$ where $\begin{cases} A(s) = \frac{1}{\pi}\int_{-\infty}^{\infty} F(x)\sin(sx)dx \\ B(s) = \frac{1}{\pi}\int_{-\infty}^{\infty} F(x)\cos(sx)dx\end{cases}$

$\begin{cases}\cos(sx) = \frac{1}{2}(e^{ixs} + e^{-ixs}) \\ \sin(sx) = \frac{1}{2i}(e^{ixs} - e^{-ixs})\end{cases}$

$F(x) = \int_0^{\infty}\frac{1}{2}[B(s) - iA(s)]e^{ixs}ds + \underbrace{\int_0^{\infty}\frac{1}{2}[B(s) + iA(s)]e^{-ixs}ds}_{\int_{-\infty}^{0}\frac{1}{2}[A(|w|) + iB(|w|)]e^{isx}ds}$

set $G(s) = \begin{cases}\frac{1}{2}[B(w) - iA(w)] & (s \geq 0)\\ \frac{1}{2}[B(|w|) + iA(|w|)] & (s < 0)\end{cases}$

$F(x) = \int_{-\infty}^{\infty} G(s)e^{ixs}ds$ transformation between two domains: (x, s)

Fourier integrals in complex form

$F(x) = \int_{-\infty}^{\infty} G(s)e^{ixs}ds$

For $s \geq 0$, $G(s) = \frac{1}{2\pi}\int_{-\infty}^{\infty} F(x)[\cos(sx) - i\sin(sx)]dx$

$= \frac{1}{2\pi}\int_{-\infty}^{\infty} F(x)e^{-ixs}dx$

For $s < 0$, $G(s) = \frac{1}{2\pi}\int_{-\infty}^{\infty} F(x)[\cos|s|x + i\sin(|s|w)]dx$

$= \frac{1}{2\pi}\int_{-\infty}^{\infty} F(x)e^{ix|s|}dx$

$= \frac{1}{2\pi}\int_{-\infty}^{\infty} F(x)e^{-ixs}dx$

$G(s) = \frac{1}{2\pi}\int_{-\infty}^{\infty} F(x)e^{-ixs}dx$

typo: P479

(A3.10) should be

$\int_{-\infty}^{\infty} F(x)e^{-ixs'}dx = 2\pi\int_{-\infty}^{\infty} G(s)\delta(s-s')ds$

$G(s) \xrightarrow{\Phi} F(x)$ denote $F(x) = \Phi(G) = \int_{-\infty}^{\infty} G(s)\, e^{ixs}\, ds$

P460 (A3.11) should be

$G(s') = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(x) e^{-ixs'} dx$

$$\Phi\left(\frac{dG}{ds}\right) = \int_{-\infty}^{\infty} \frac{dG}{ds} e^{ixs} ds$$

$$= \underbrace{G(s) e^{ixs} \Big|_{-\infty}^{\infty}}_{G(\pm\infty)=0} - ix \int_{-\infty}^{\infty} G(s) e^{ixs} ds$$

$$= -ix\,\Phi(G)$$

since we have $\frac{\partial^2 C}{\partial x^2}$ in diffusion equation

$\frac{\partial^2 C}{\partial x^2} \updownarrow \frac{d^2 G}{ds^2}$

similarly, $\Phi\left(\frac{d^2G}{ds^2}\right) = -x^2 \Phi(G)$

$\rightleftharpoons$

$F(x) = \int_{-\infty}^{\infty} G(s) e^{ixs} ds$ $\quad G(s) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(x) e^{-ixs} dx$

old	x	s	$F(x)$	$G(s)$
↓ new	f	x	$C_f(f,t)$	$C(x,t)$

$\overset{?}{\rightleftharpoons}$

$C_f(f,t) = \int_{-\infty}^{\infty} C(x,t) e^{ifx} dx$ $\quad C(x,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} C_f(f,t) e^{-ifx} df$

note that there is no "t" be intergrated

$\Rightarrow \Phi\left(\frac{\partial C}{\partial t}\right) = \frac{\partial}{\partial t}[\Phi(C)] = \frac{\partial}{\partial t} C_f$

$C_f = \Phi(C)$

$\Phi\left(\frac{\partial^2 C}{\partial x^2}\right) = -f^2 \Phi(C)$

$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$

$\Phi\left(\frac{\partial C}{\partial t}\right) = \Phi\left(D \frac{\partial^2 C}{\partial x^2}\right) = D\Phi\left(\frac{\partial^2 C}{\partial x^2}\right)$

$\qquad = -Df^2 \Phi(C)$

$\frac{\partial C_f}{\partial t} = -Df^2 C_f \Rightarrow C_f(f,t) = C_f(f,0)\, e^{-Df^2 t}$

typo: P145 $C(x,t) = \frac{M}{2\pi} \int_{-\infty}^{\infty} e^{-Df^2 t} e^{-ifx} df$

- - - -

$= \frac{M}{2\pi} e^{-\frac{x^2}{4Dt}} \int_{-\infty}^{\infty} e^{-\left(f\sqrt{Dt} + \frac{ix}{2\sqrt{Dt}}\right)^2} df$

$C_f(f,0) = \int_{-\infty}^{\infty} M\delta(x) e^{ifx} dx = M$ significance:

from delta function to a constant

get rid of x, solving PDE to ODE

$C_f(f,t) = M e^{-Df^2 t}$

$$C(x,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} M e^{-Df^2 t} e^{-ifx} df$$

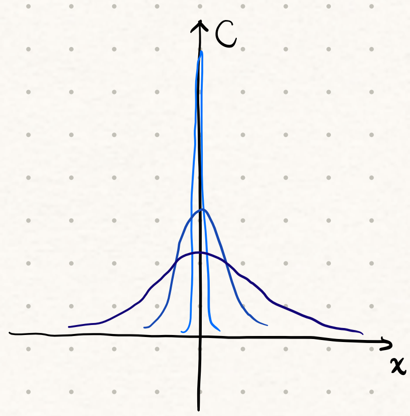
$$= \frac{M}{2\pi} \int_{-\infty}^{\infty} e^{-(f\sqrt{Dt})^2 - 2\cdot\frac{ix}{2\sqrt{Dt}} f\sqrt{Dt} - \left(\frac{ix}{2\sqrt{Dt}}\right)^2 - \frac{x^2}{4Dt}} df$$

$$= \frac{M}{2\pi} e^{-\frac{x^2}{4Dt}} \underbrace{\int_{-\infty}^{\infty} e^{-\left(f\sqrt{Dt} + \frac{ix}{2\sqrt{Dt}}\right)^2} df}_{\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}}$$

$$= \frac{M}{2\pi} e^{-\frac{x^2}{4Dt}} \sqrt{\frac{\pi}{Dt}}$$

$$= \frac{M}{\sqrt{4\pi Dt}} e^{-\frac{x^2}{4Dt}}$$

A Gaussian function



always: $\int_{-\infty}^{\infty} C(x)\, dx = M$ mass is conserved

$p(x,t) = \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{x^2}{4Dt}}$

Important hallmark of diffusion: rms displacement $\sqrt{\overline{x^2}}$

$$\overline{x^2} = \int_{-\infty}^{\infty} x^2 p(x,t)\,dx = 2Dt$$

$$\sqrt{\overline{x^2}} = \sqrt{2Dt}$$

ambiguous: P146

$\overline{x^2} = \int_{-\infty}^{\infty} x^2 p(x,t)\,dx = 2Dt$

not $C(x,t)$

Initial condition: $C(x) = M\delta(x)$

to estimate how long it will take a metabolite to diffuse through a cell when it is produced at one location

Three-dimensional diffusion from a point

homogeneous in direction → spherical coordinate

only care about the radial distance

$$\frac{\partial C}{\partial t} = D\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C}{\partial r}\right)$$

Derive by result from 1D situation

the probability one can find the particle at x_i axis:

$$P(x_i,t) = \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{x_i^2}{4Dt}}$$

ambiguous: P146 6.2.2 below (6.11)

we can't multiply Eq. (6.8) for $C(x,t)$, $C(y,t)$, $C(z,t)$

we should multiply $p(x,t)$, $p(y,t)$, $p(z,t)$

and $C(x,y,z,t) = M p(x,t)p(y,t)p(z,t)$

mass multiplied

x_i: x, y, z (independent)

$$p(x,y,z,t) = \frac{1}{(4\pi Dt)^{\frac{3}{2}}} e^{-\frac{x^2+y^2+z^2}{4Dt}} \qquad C(x,y,z,t) = k\,p(x,y,z,t)\ \&\ \int_x\int_y\int_z C(x,y,z,t)\,dx\,dy\,dz = M$$

$$C(x,y,z,t) = \frac{M}{(4\pi Dt)^{\frac{3}{2}}} e^{-\frac{x^2+y^2+z^2}{4Dt}} \qquad C'(r,\theta,\varphi,t) = C'(r,t) = \frac{M}{(4\pi Dt)^{\frac{3}{2}}} e^{-\frac{r^2}{4Dt}}$$

$$\int_x\int_y\int_z C(x,y,z,t)\,dx\,dy\,dz = \int_r\int_\theta\int_\varphi C_1(r,t)\,r^2\,dr\,d\theta\,d\varphi$$

$$= \int_r 4\pi r^2 C_1(r,t)\,dr$$

ambiguous: P146 6.2.2 below (6.11) line 4

for "$C(r,t)$", it is not a concentration with a dimension of $\frac{[M]}{[L]^3}$ anymore!

For a reall concentration, it should be like

but "$C(r,t)$" is actually

$$M = \int_r C_2(r,t)\,dr \Rightarrow C_2(r,t) = \frac{M\,4\pi r^2}{(4\pi Dt)^{\frac{3}{2}}} e^{-\frac{r^2}{4Dt}}$$

$$\overline{r^2} = \overline{x^2+y^2+z^2}$$

$$= \overline{x^2} + \overline{y^2} + \overline{z^2}$$

$$= 2Dt + 2Dt + 2Dt$$

$$= 6Dt$$

$$\sqrt{\overline{r^2}} = \sqrt{6Dt}$$