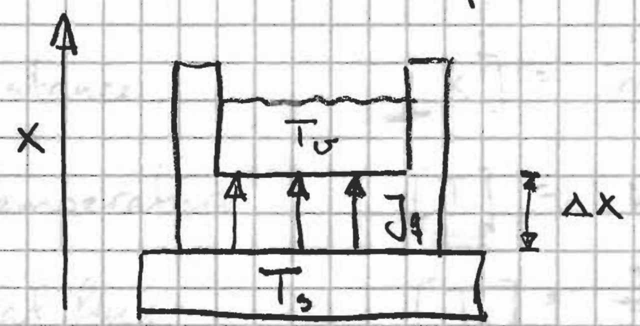
Diffusion of heat and mass

Empirical observation:

Put a pan with hot water on the stove. The hotter the stove, the faster the water heats up

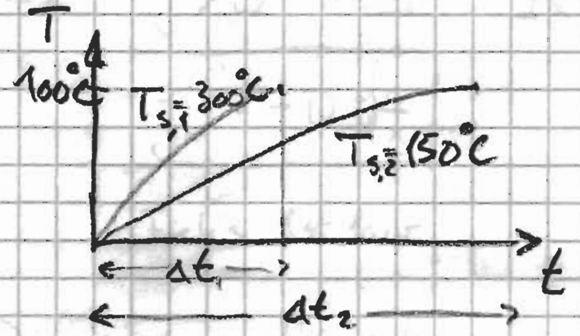


Heat flux (thermal energy flux) J_q

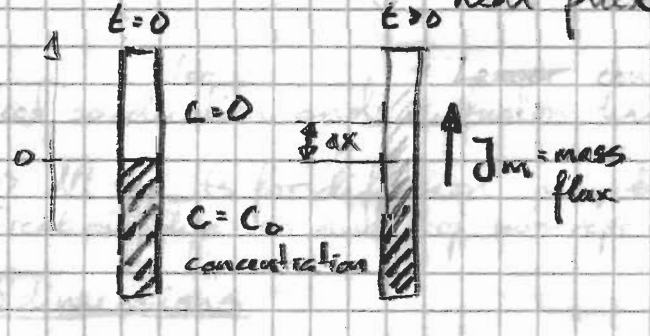
J_q = Amount of heat per time unit and per area

Δx = Transport distance

$\Delta T = T_s - T_v$ = temperature difference



=> Empirical law: « Larger temperature difference gives larger heat flux



Larger concentration difference gives larger mass flux

$$J_m \propto \frac{\Delta c}{\Delta x} \quad , \quad J_q \propto \frac{\Delta T}{\Delta x}$$

concentration $[c] = \frac{kg}{m^3}$

mass flux $[J_m] = \frac{kg}{m^2 s}$

distance $[x] = m$

temperature $[T] = K$

heat flux $[J_q] = \frac{J}{m^2 s}$

J is positive when flow in positive x-direction

J from high c / T to low c / T

$\Rightarrow$ $J > 0$ when $\frac{\Delta c}{\Delta x} < 0$ / $\frac{\Delta T}{\Delta x} < 0$

$$\boxed{J_m = -D \frac{dc}{dx}} \qquad \boxed{J_q = -\lambda \frac{dT}{dx}}$$

Fick's 1st law — Joule's law

Diffusion coefficient $[D] = \frac{kg}{m^2 s} \frac{m}{kg/m^3} = \frac{m^2}{s}$ > 0

Thermal conductivity $[\lambda] = \frac{J}{m^2 s} \frac{m}{K} = \frac{J}{msK}$ > 0

Heat conduction and diffusion have the same mathematical form

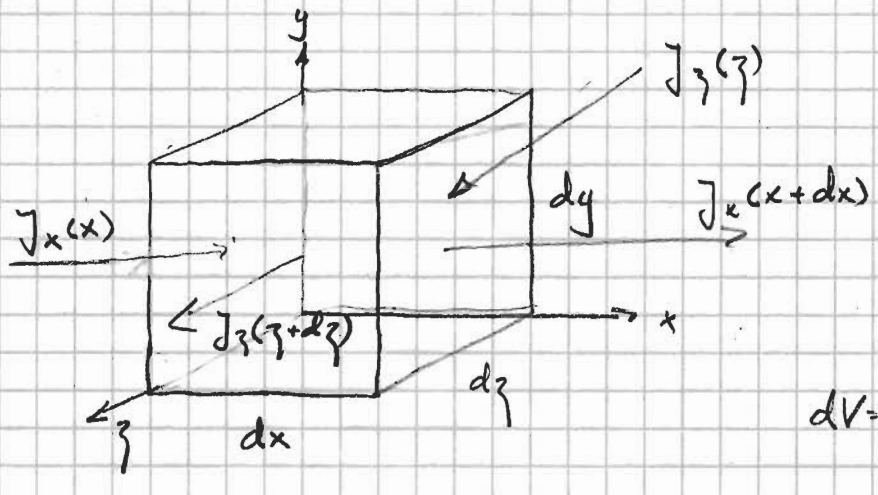
$\Rightarrow$ All results for diffusion may be transformed to heat conduction
(Treat only diffusion and drop subscript m)

<u>3 dimensions</u>

Heat flux is a vector (has a direction in space)

$$\vec{J} = -D \nabla c = -D \left(\mathbf{i} \frac{\partial c}{\partial x} + \mathbf{j} \frac{\partial c}{\partial y} + \mathbf{k} \frac{\partial c}{\partial z} \right)$$

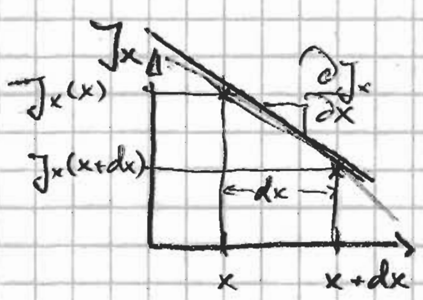
$$\Rightarrow \quad J_x = -D \frac{\partial c}{\partial x}, \quad J_y = -D \frac{\partial c}{\partial y}, \quad J_z = -D \frac{\partial c}{\partial z}$$



$dV = dx\,dy\,dz$

Mass conservation: Mass change inside volume = mass in − mass out

$$dV \cdot \frac{\partial c}{\partial t} = J_x(x)\,dy\,dz - J_x(x+dx)\,dy\,dz$$
$$+ \left(J_y(y) - J_y(y+dy)\right) dx\,dz$$
$$+ \left(J_z(z) - J_z(z+dz)\right) dx\,dy$$



$$J_x(x+dx) = J_x + \frac{\partial J_x}{\partial x} dx$$
$$\Rightarrow J_x(x) - J_x(x+dx) = -\frac{\partial J_x}{\partial x} dx$$

$$\Rightarrow \quad dV \frac{\partial c}{\partial t} = -\frac{\partial J_x}{\partial x} dx\,dy\,dz - \frac{\partial J_y}{\partial y} dx\,dy\,dz - \frac{\partial J_z}{\partial z} dx\,dy\,dz$$

$$\Rightarrow \quad \boxed{\frac{\partial c}{\partial t} = -\frac{\partial J_x}{\partial x} - \frac{\partial J_y}{\partial y} - \frac{\partial J_z}{\partial z} = -\nabla \vec{J}}$$ mass conservation

(one dimension : $\frac{\partial c}{\partial t} = -\frac{\partial J_x}{\partial x}$)

Ficks 1st law : $J_x = -D \frac{\partial c}{\partial x}$ $\qquad \vec{J} = -D \nabla c$

$$\Rightarrow \frac{\partial c}{\partial t} = -\frac{\partial}{\partial x}\left(-D \frac{\partial c}{\partial x}\right) \qquad \frac{\partial c}{\partial t} = D \nabla^2 c$$

Constant D $\qquad \boxed{\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}}$ $\qquad = \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}$

Fick's 2nd law

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

Partial differential equation. We need initial and boundary conditions to solve it!

$$c(x=0, t=0) = \infty$$
$$c(x \neq 0, t=0) = 0$$

delta function (size is undefined)

$$\boxed{c = \frac{A}{\sqrt{t}} e^{-\frac{x^2}{4Dt}}}$$

Oppgave: utfør differensiering på begge sider og sjekk at det er en løsn.

A is an undefined constant. We must define how ~~much~~ large the source is $M = \int_{-\infty}^{\infty} c\,dx$

Coordinate transformation:

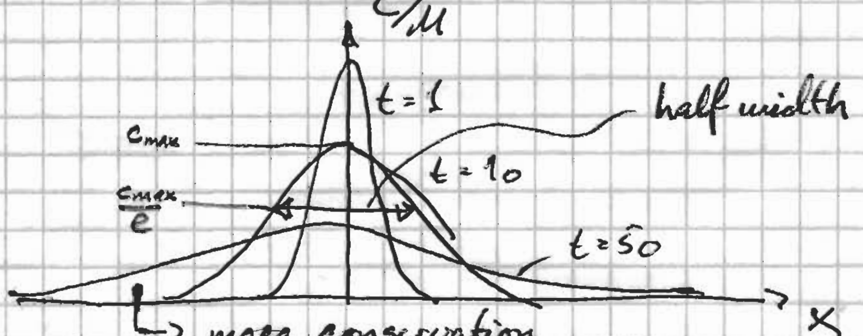
$$\eta = \frac{x}{2\sqrt{Dt}} \qquad \frac{d\eta}{dx} = \frac{1}{2\sqrt{Dt}} \Rightarrow dx = 2\sqrt{Dt}\,d\eta$$

$$M = \int_{-\infty}^{\infty} \frac{A}{\sqrt{t}} e^{-\eta^2} 2\sqrt{Dt}\,d\eta = \int_{-\infty}^{\infty} 2A\sqrt{D}\, e^{-\eta^2} d\eta$$

(49) i Rotm.
$$= 2A\sqrt{D}\sqrt{\pi} \Rightarrow A = \frac{M}{2\sqrt{\pi D}}$$

$$\Rightarrow \boxed{c = \frac{M}{2\sqrt{\pi D t}} e^{-\frac{x^2}{4Dt}}}$$

Maxwell / Gaussian distribution



$c_{max} \cdot 0{,}368$

→ mass conservation
⇒ same area under all curves

Exercise: calculate diffusion coefficient from curve

1-dimensional random walk

- Particles jump distance $\underline{d}$ in time $\underline{\tau}$
- Particles jump in random direction (left or right)

Find probability that particle is found at position $\underline{x}$ (relative to starting point) at time $\underline{t}$

Number of steps : $n = t/\tau$

—— " —— to left n_L and to right n_R

$$\Rightarrow n = n_L + n_R$$

$$x = d(n_R - n_L)$$

Total number of step combinations : 2^n

Number of ways to make n_R steps to right : $\frac{n!}{(n-n_R)!\cdot n_R!}$

ex:

-4	-2	0	2	4
LLLL	LLLR	LLRR	LRRR	RRRR
	LLRL	LRLR	RLRR	
	LRLL	LRRL	RRLR	
	RLLL	RLRL	RRRL	
		RRLL		
		RLLR		
$\frac{4!}{1!4!}$	$\frac{4!}{1!3!}$	$\frac{4!}{2!2!}$	$\frac{4!}{1!3!}$	$\frac{4!}{1!4!}$
Probability $\frac{1}{16}$	$\frac{4}{16}$	$\frac{6}{16}$	$\frac{4}{16}$	$\frac{1}{16}$

$\Sigma = \frac{16}{16}$

$$\Rightarrow \quad P(x) = \frac{n!}{n_R!\,(n-n_R)!\,2^n}$$

$n = n_R + n_L$, $s = \frac{x}{d} = n_R - n_L$

$$P(x) = \frac{n!}{\frac{n+s}{2}!\;\frac{n-s}{2}!\;2^n}$$

Stirlings approximation: $\ln N! \sim (N+\frac{1}{2})\ln N - N + \ln\sqrt{2\pi}$

$$\ln P = \ln n! - \ln \frac{n+s}{2}! - \ln \frac{n-s}{2}! - n\ln 2$$

exercise!

$$\Rightarrow \ln P \approx \ln\sqrt{\frac{2}{\pi n}} - \frac{1}{2}(n+s+1)\ln(1+\frac{s}{n}) - \frac{1}{2}(n-s+1)\ln(1-\frac{s}{n})$$

$\frac{s}{n} \ll 1$ use $\ln(1+\frac{s}{n}) \sim \frac{s}{n}$

$n = t/\tau$

$s = x/d$

$$\Rightarrow P \sim \sqrt{\frac{2}{\pi n}}\, e^{-\frac{s^2}{2n}}$$

$$= \sqrt{\frac{2\tau}{\pi t}}\, e^{-\frac{x^2\tau}{2td^2}}$$

$$\Rightarrow \boxed{D = \frac{d^2}{2\tau}}$$

Einstein - Smoluchowski - relation

Analytical:

$$\frac{c}{M} = \frac{1}{2\sqrt{\pi D t}}\, e^{-\frac{x^2}{4Dt}}$$

Matlab simulation

find distribution $A e^{-\left(\frac{x}{x_h}\right)^2}$

Half width (e^{-1}) $\quad 1 = \frac{x^2\tau}{2td^2} = \frac{1}{2}\left(\frac{x}{d}\right)^2 \frac{1}{\text{timesteps}}$

$d=1$ $\quad \Rightarrow x_h = \sqrt{2\cdot\text{timesteps}}$

$$\text{Area} = \#\text{particles} \cdot 2$$

$$= \int_{-\infty}^{\infty} A e^{-\left(\frac{x}{x_h}\right)^2} dx = A x_h \sqrt{\pi}$$

$$\Rightarrow A = \#\text{particles} \cdot 2 / x_h \cdot \sqrt{\pi}$$

Next: coordinate transformation and error function