1 Molecular Diffusion

- Notion of concentration
- Molecular diffusion, Fick's Law
- Mass balance
- Transport analogies; salt-gradient solar ponds
- Simple solutions
- Random walk analogy to diffusion
- Examples of sources and sinks

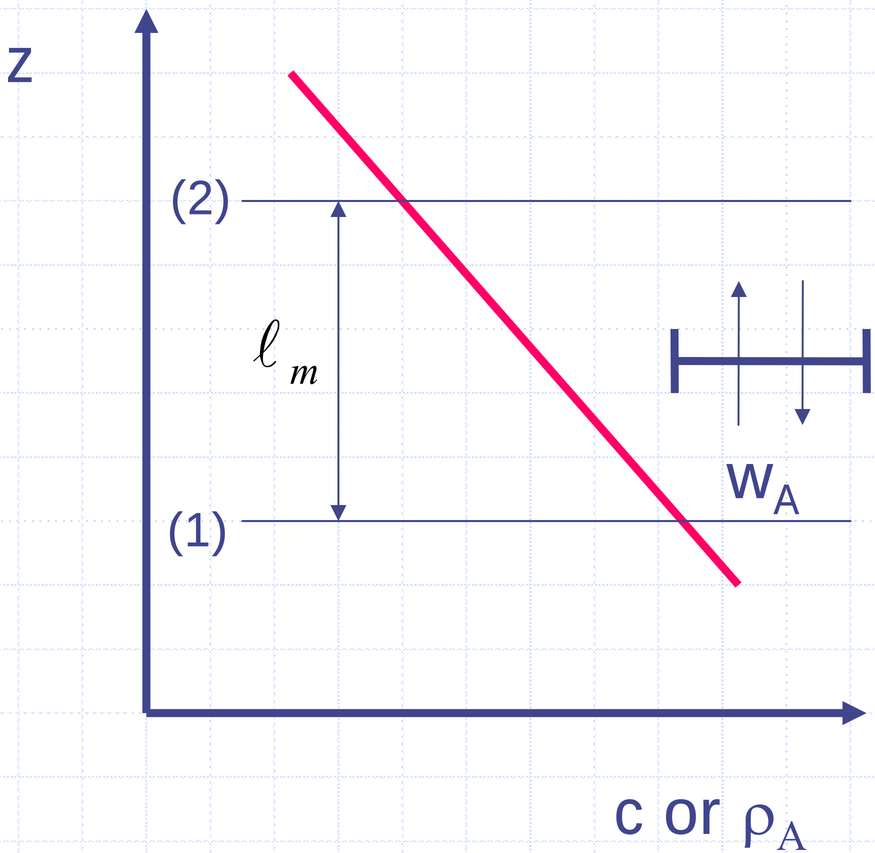
Motivation

- Molecular diffusion is often negligible in environmental problems
- Exceptions: near interfaces, boundaries
- Responsible for removing gradients at smallest scales
- Analytical framework for turbulent and dispersive transport

Concentration

- Contaminant => mixture
  - Carrier fluid (B) and contaminant/tracer (A)
  - If dissolved, then solvent and solute
  - If suspended, then continuous and dispersed phase
- Concentration (c or ρ_A) commonly based on mass/volume (e.g. mg/l); also
  - mol/vol (chemical reactions)
  - Mass fraction (salinity): ρ_A/ρ
- Note: 1 mg/l ~ 1 mg/kg (water) = 1ppm

Molecular Diffusion



One-way flux (M/L^2-T)

$$= \rho_A w_A$$

Net flux

$$= w_A(\rho_{A1} - \rho_{A2})$$

$$= -\underbrace{w_A \ell_m}_{D_{AB}} \partial \rho_A / \partial z$$

$$\vec{J}_A = -D_{AB} \nabla \rho_A$$

Ficks Law and Diffusivities

$$\vec{J}_A = -D_{AB} \nabla \rho_A$$

$$\nabla(\,) = \frac{\partial}{\partial x}(\,)\,\vec{i} + \frac{\partial}{\partial y}(\,)\,\vec{j} + \frac{\partial}{\partial z}(\,)\,\vec{k}$$

D_{AB} is isotropic and essentially uniform (temperature dependent), but depends on A, B

Table 1.1 summarizes some values of D_{AB}

Roughly: $D_{air} \sim 10^{-1}$ cm^2/s; $D_{water} \sim 10^{-5}$ cm^2/s

Diffusivities, cont'd

Diffusivities often expressed through Schmidt no.

$Sc = \nu / D$

Roughly: $\nu_{air} \sim 10^{-1}$ cm^2/s; $\nu_{water} \sim 10^{-2}$ cm^2/s

$Sc_{air} \sim 1$

$Sc_{water} \sim 10^3$

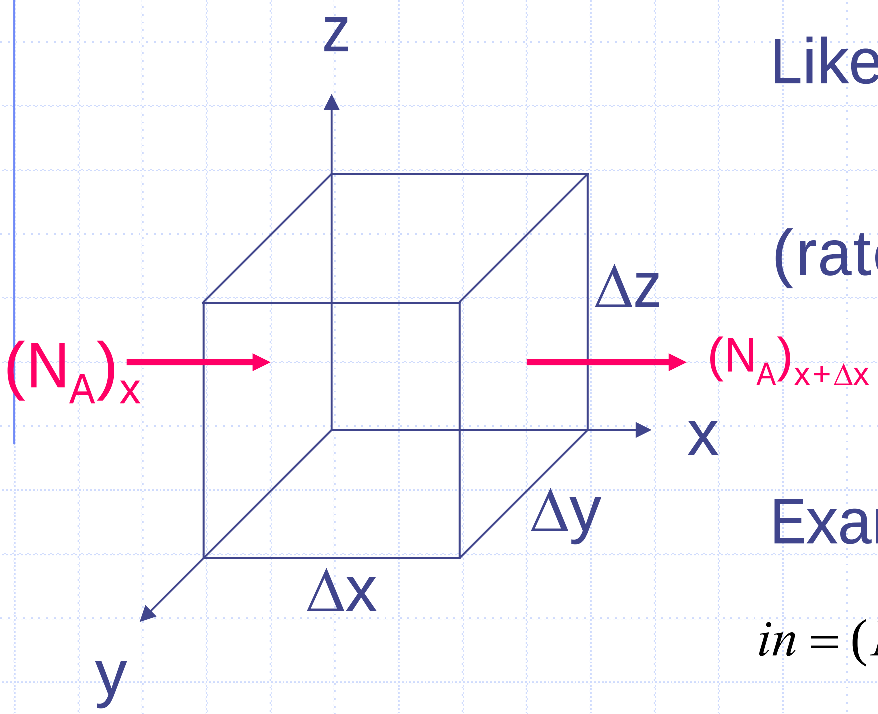
Also: Prandlt no. $Pr = \nu/\kappa$ (κ = thermal cond.)

Add advection; total flux of A is:

$$\vec{N}_A = \rho_A \vec{q} - D_{AB} \nabla \rho_A$$

macroscopic velocity vector

Conservation of Mass



Like a bank account except expressed as rates:

(rate of) change in account = (rate of) (inflow – out) +/- (rate of) prod/consumption

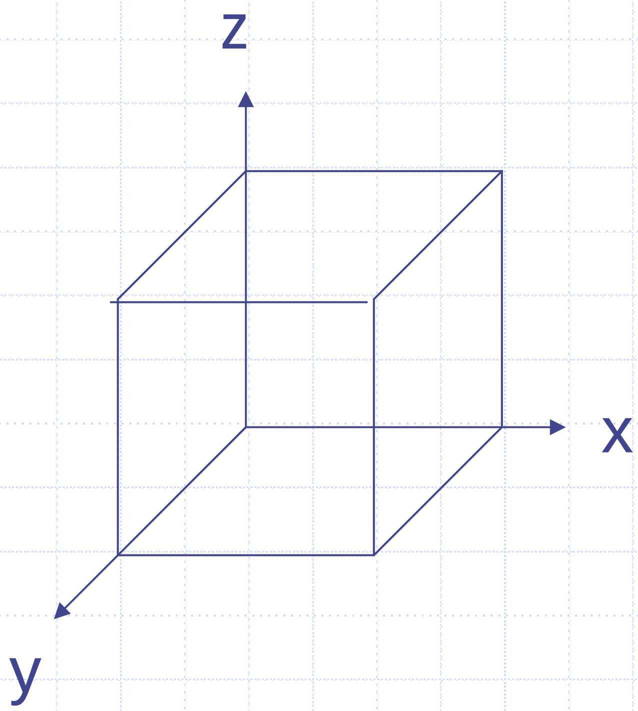
Example for x-direction

$$in = (N_A)_x \Delta y \Delta z$$

$$out = (N_A)_{x+\Delta x} \Delta y \Delta z = \left[(N_A)_x + \left(\frac{\partial N_A}{\partial x} \right) \Delta x \right] \Delta y \Delta z$$

$$net\ in = \left[-\left(\frac{\partial N_A}{\partial x} \right) \Delta x \right] \Delta y \Delta z$$

Conservation of Mass, cont'd



Account balance

$$= \rho_A \Delta x \Delta y \Delta z$$

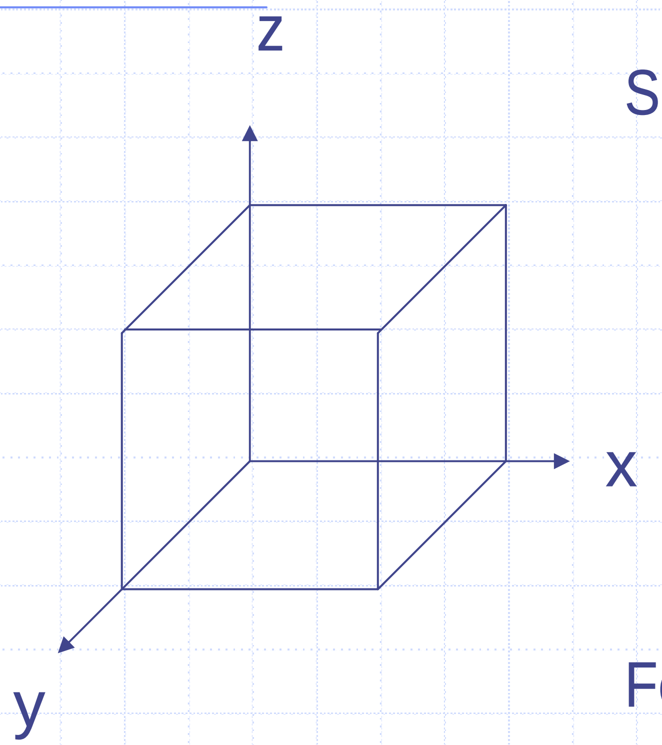
Rate of change of account balance

$$= \frac{\partial}{\partial t}(\rho_A)\Delta x \Delta y \Delta z$$

Rate of production

$$= r_A \Delta x \Delta y \Delta z$$

Conservation of Mass, cont'd



Sum all terms (incl. advection in 3D)

$$\frac{\partial \rho_A}{\partial t} + \frac{\partial}{\partial x}(N_A)_x + \frac{\partial}{\partial y}(N_A)_y + \frac{\partial}{\partial z}(N_A)_z$$

$$\frac{\partial \rho_A}{\partial t} + \nabla \cdot \vec{N}_A = r_A$$

Flux divergence (dot product of two vectors is scalar)

For carrier fluid B

$$\frac{\partial \rho_B}{\partial t} + \nabla \cdot \vec{N}_B = r_B$$

Conservation of Mass, mixture

$$r_A = -r_B$$

Conservation of total mass

$$\vec{N}_A + \vec{N}_B = \rho \vec{q}$$

$\rho_A + \rho_B = \rho$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{q}) = 0$$

$$\frac{\partial \rho}{\partial t} \cong \nabla \rho \cong 0$$

Liquids are nearly incompressible

$$\nabla \cdot \vec{q} = 0$$

Divergence = 0; Continuity

Conservation of Mass, contaminant

$$\rho_A = c$$ drop subscript A

$$\frac{\partial c}{\partial t} + \nabla \cdot (c\vec{q}) = \nabla \cdot (D \nabla c) + r$$ Conservative form of mass cons.

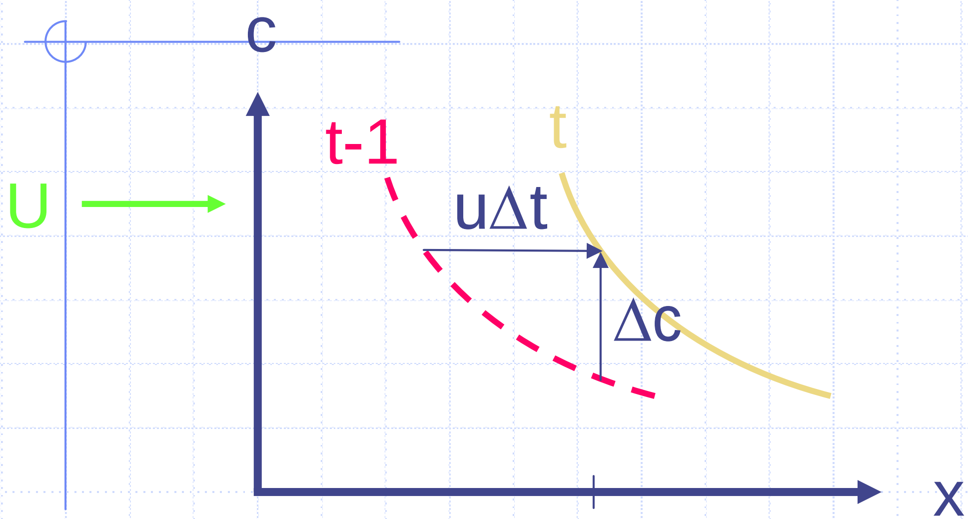
$$\frac{\partial c}{\partial t} + c\nabla \cdot \vec{q} + \vec{q} \cdot \nabla c = D\nabla^2 c + (\nabla D)(\nabla c) + r$$

0 0

$$\frac{\partial c}{\partial t} + \vec{q} \cdot \nabla c = D\nabla^2 c\nabla + r$$ N.C. form

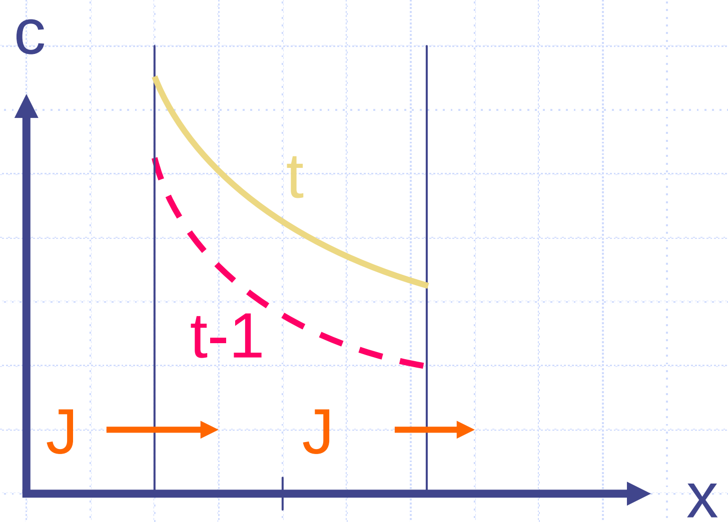
$$\frac{\partial c}{\partial t} = D\nabla^2 c\nabla$$ If $\vec{q} = r = 0$ => Ficks Law of Diffusion

Heuristic interpretation of Advection and diffusion



Advection

Flux ~ negative gradient



Diffusion

Difference in fluxes
(divergence) ~ curvature

Analogs

$$\frac{\partial c}{\partial t} = D\nabla^2 c$$ Ficks Law (mass transfer)

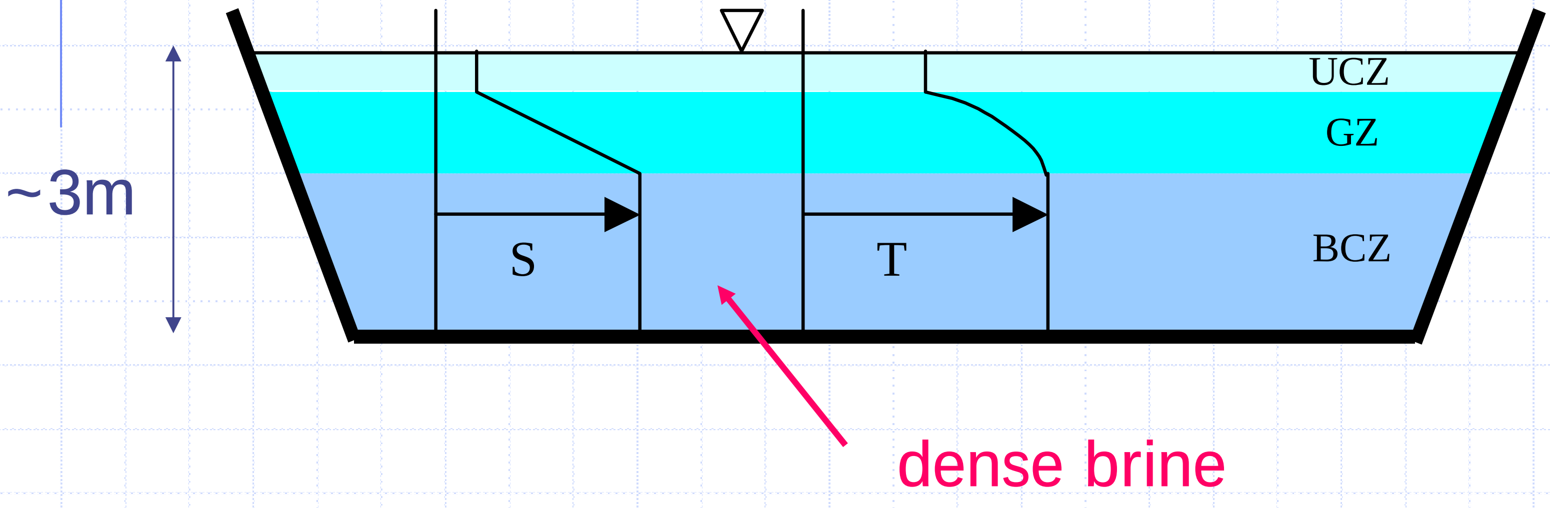
$$\frac{\partial T}{\partial t} = \kappa\nabla^2 T$$ Fourier's Law (heat transfer)

$$\frac{\partial \vec{q}}{\partial t} + (\vec{q}\cdot\nabla)\vec{q} = \upsilon\nabla^2 \vec{q} + \frac{\vec{r}_m}{\rho}$$ Newton's Law (mom. Transfer)

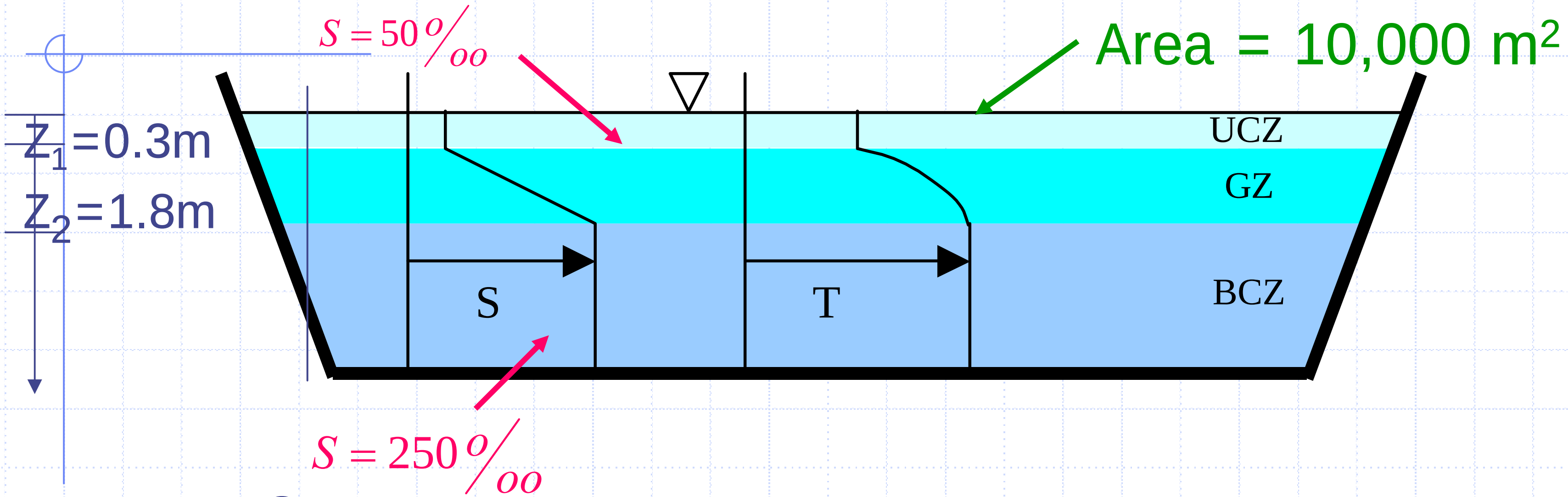
		Air	Water
ν/D	Sc	~1	~10^3
ν/κ	Pr	~0.7	~8
		D~κ~ν	D<<κ<ν

Example: Salt Gradient Solar Ponds (WE 1-1)

like El Paso Solar Pond



Solar Pond, diffusive salt flux to UCZ



$c = \rho S$

$c_{UCZ} = (1033\ \text{Kg/m}^3)(50\text{x}10^{-3}\ \text{Kg/Kg}) = 52\ \text{Kg/m}^3$

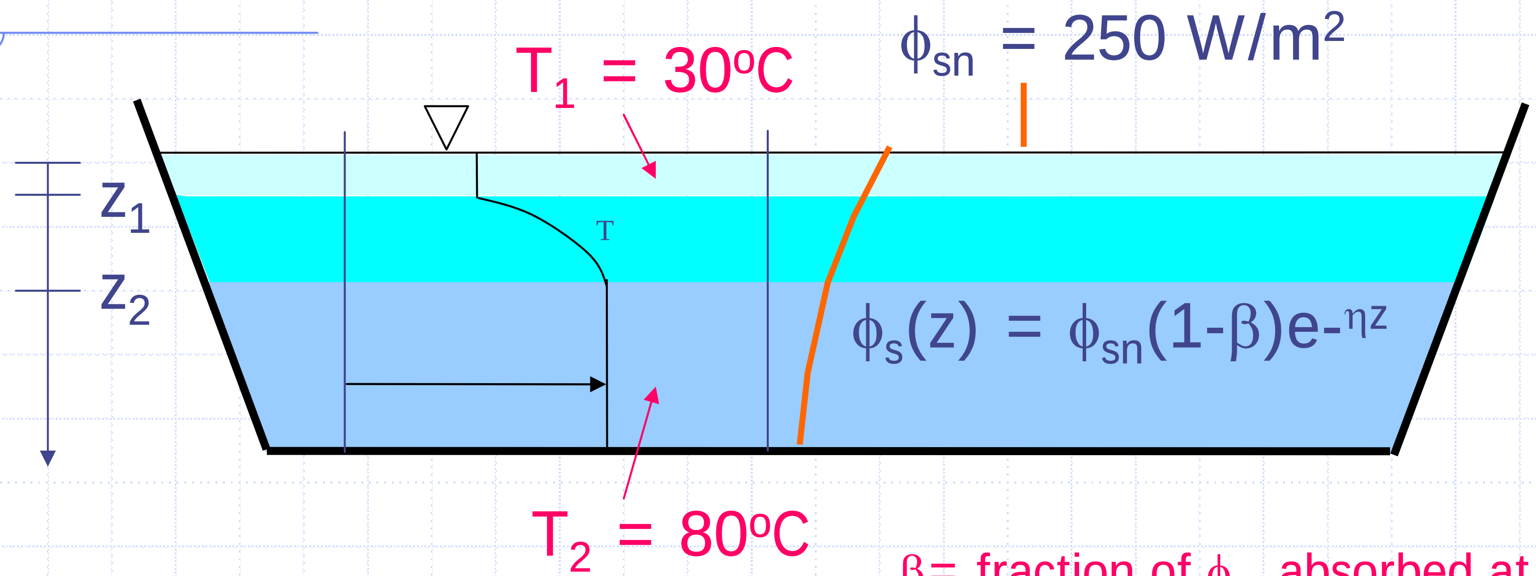
$c_{BCZ} = (1165\ \text{Kg/m}^3)(250\text{x}10^{-3}\ \text{Kg/Kg}) = 291\ \text{Kg/m}^3$

$$J_s = Ddc/dz$$

$=(2\text{x}10^{-9})(239\ \text{Kg/m}^3)/1.2\text{m} = 4.0\text{x}10^{-7}\ \text{Kg/m}^2\text{-s}$

$= 344$ Kg/day

Solar Pond: diffusive thermal flux to UCZ



$$0 = \rho C_p \kappa \frac{d^2T}{dz^2} + \eta(1-\beta)\phi_{sn}e^{-\eta z}$$

$$T = \frac{-\phi^*}{\eta^2}e^{-\eta z} + c_1 z + c_2$$

β = fraction of ϕ_{sn} absorbed at surface

η = extinction coefficient

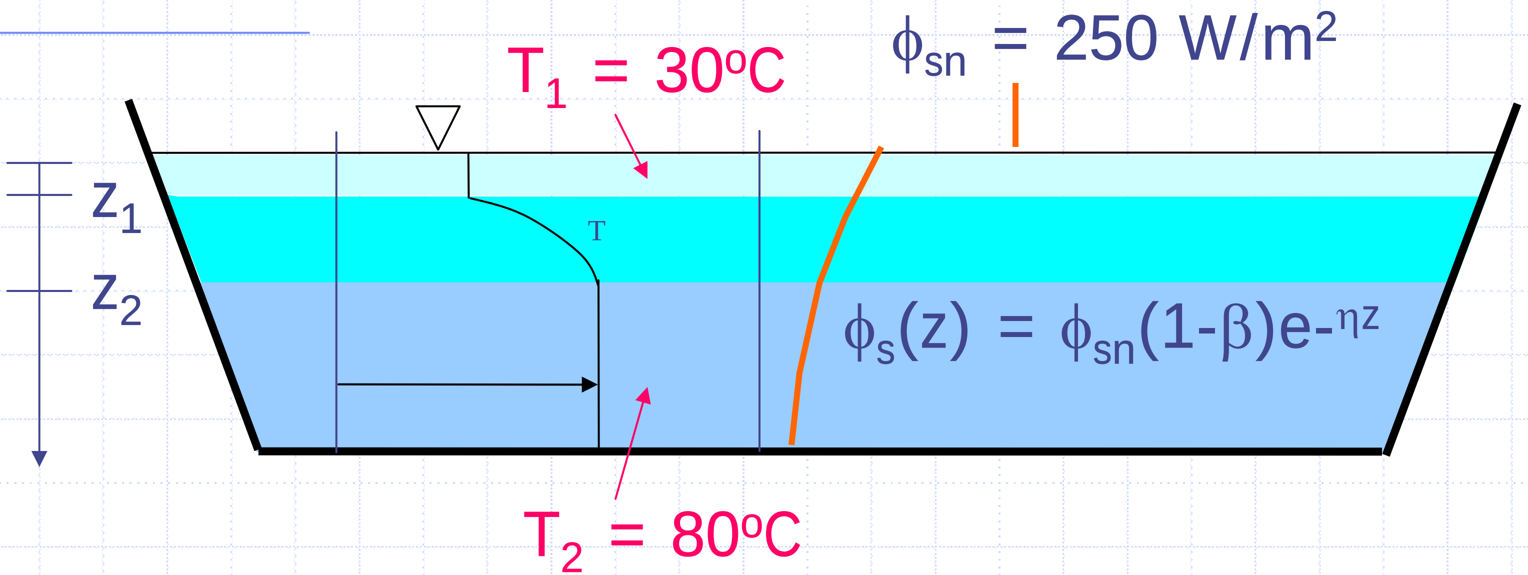
C_p = heat capacity (4180 J/Kg^{o}C);

κ = thermal diffusivity (1.5x10^{-7} m^2/s)

$$\phi^* = \eta(1-\beta)\phi_{sn} / \rho C_p \kappa$$

c_1, c_2 from $T=T_1$ at z_1, $T=T_2$ at z_2

Solar Pond: thermal flux



$$J_t = \rho C_p \kappa (dT/dz)_{z=z_2}$$

$$= \rho C_p \kappa \frac{T_2 - T_1}{z_2 - z_1} + (1-\beta)\phi_{sn}\left[e^{-\eta z_2} + \frac{(e^{-\eta z_2} - e^{-\eta z_1})}{\eta(z_2 - z_1)} \right]$$

$z_1 = 0.3\text{m}$; $z_2 = 1.5\text{m}$, $\beta=0.5$, $\eta = 0.6$ => $J_t = 7\ \text{W/m}^2$

Compare with (1-0.5)(250)exp(-0.6*1.5) = 51 W/m^2 reaching BCZ (~13% lost)

Rankine Cycle Heat Engine

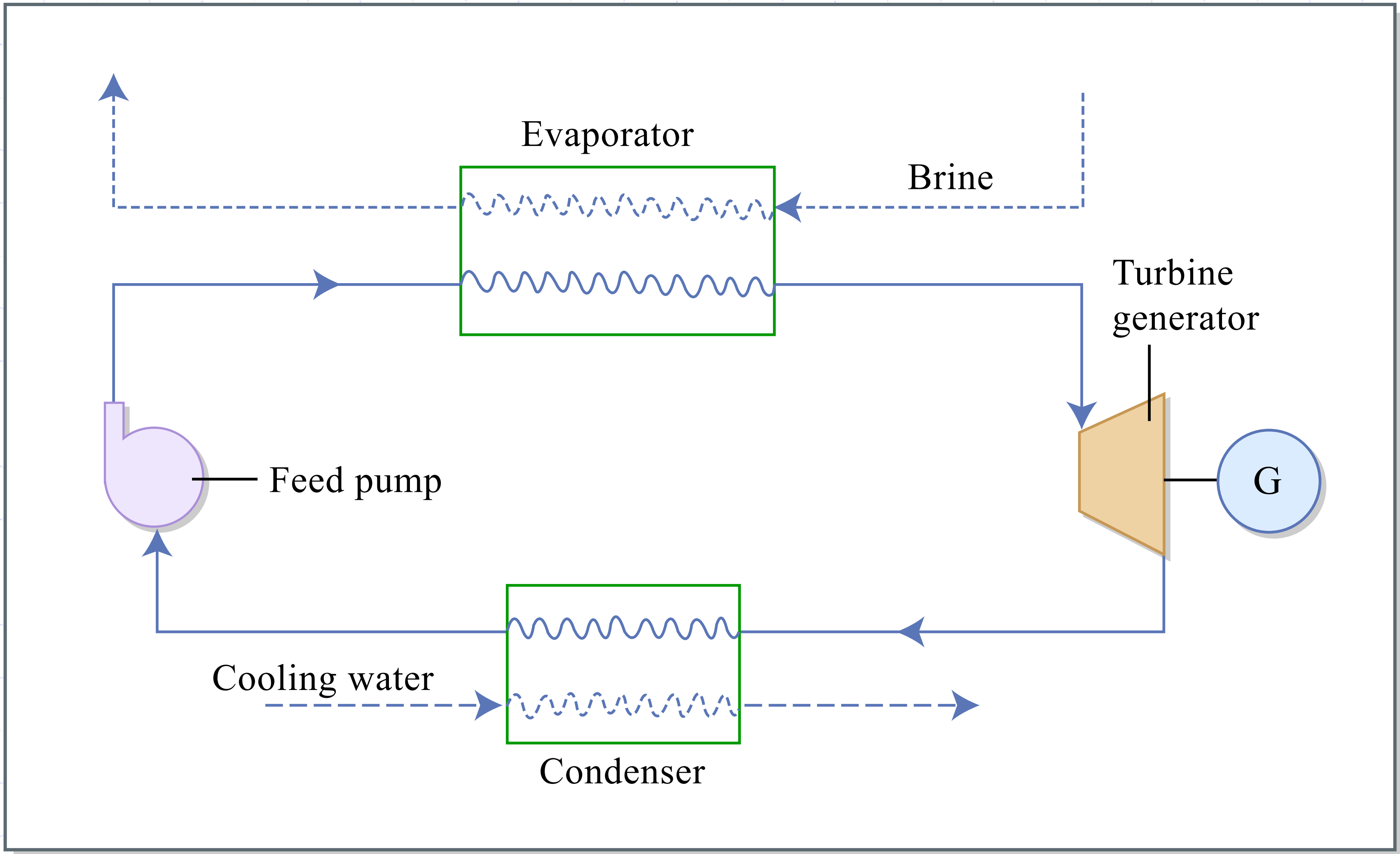
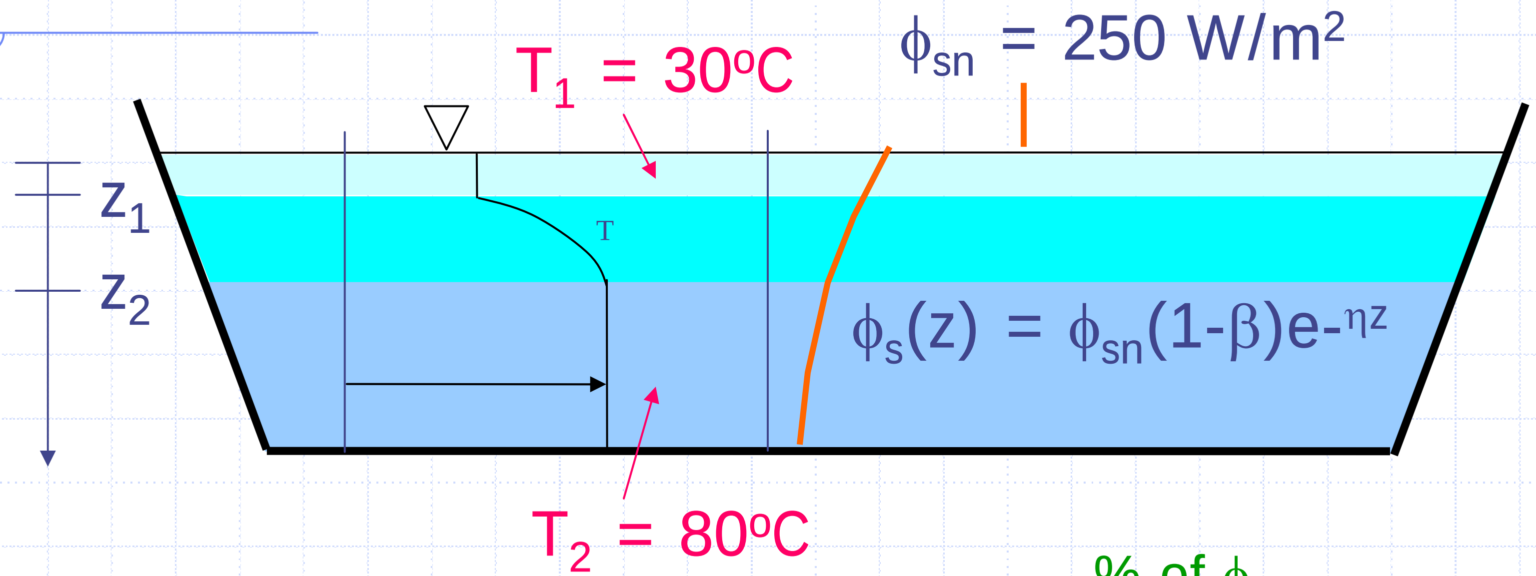


Figure by MIT OCW.

Solar Pond: total energy extraction



		% of ϕ_{sn}
Energy Flux at surface	250 W/m^2	100
Energy Flux reaching BCZ	51	20
Energy Flux extracted	34	14
Electricity extracted (theoretical)	4.8	2
Electricity extracted (net actual)	2.4	1

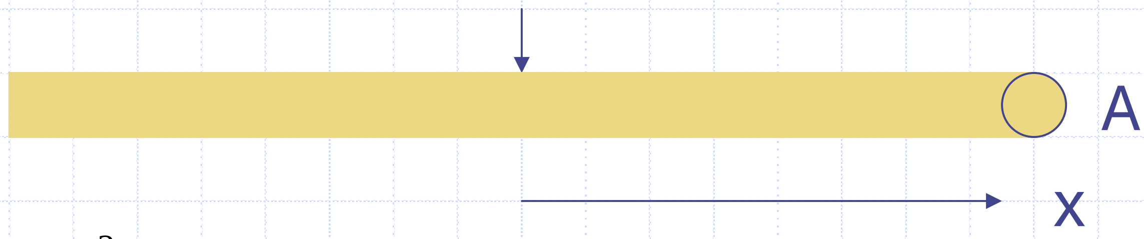
Carnot efficiency

$\eta_c = (T_2 - T_1)/(T_2 + 273)$

[24 KWe for 1 ha]

Simple Solutions

Inst. injection of mass M



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

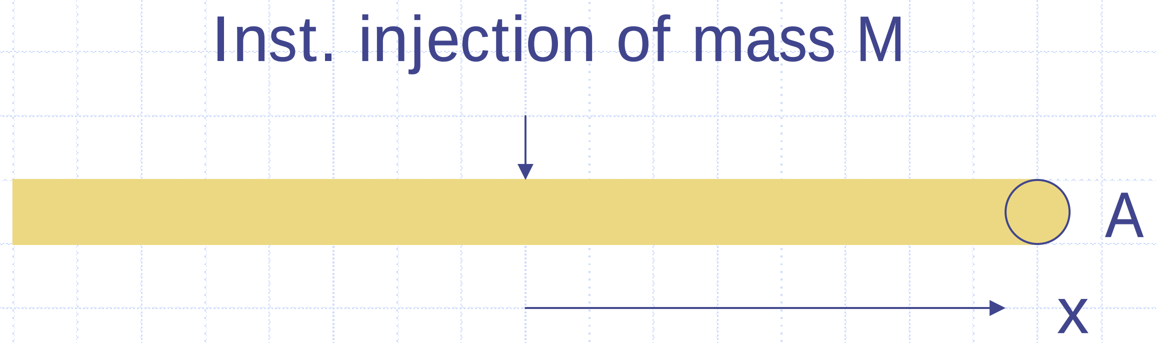
$$bc: \quad c = 0 \quad at \quad x = \pm\infty$$

$$ic: \quad c = \frac{M}{A}\delta(x) \quad at \quad t = 0_+$$

alternative

$$r = \frac{M}{A}\delta(x)\delta(t) \quad with \quad c = 0 \quad at \quad t = 0$$

Simple Solutions, cont'd



Solution by similarity transform (Crank, 1975) or inspection

$$c = \frac{B}{t^{1/2}} e^{-\frac{x^2}{4Dt}}$$

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

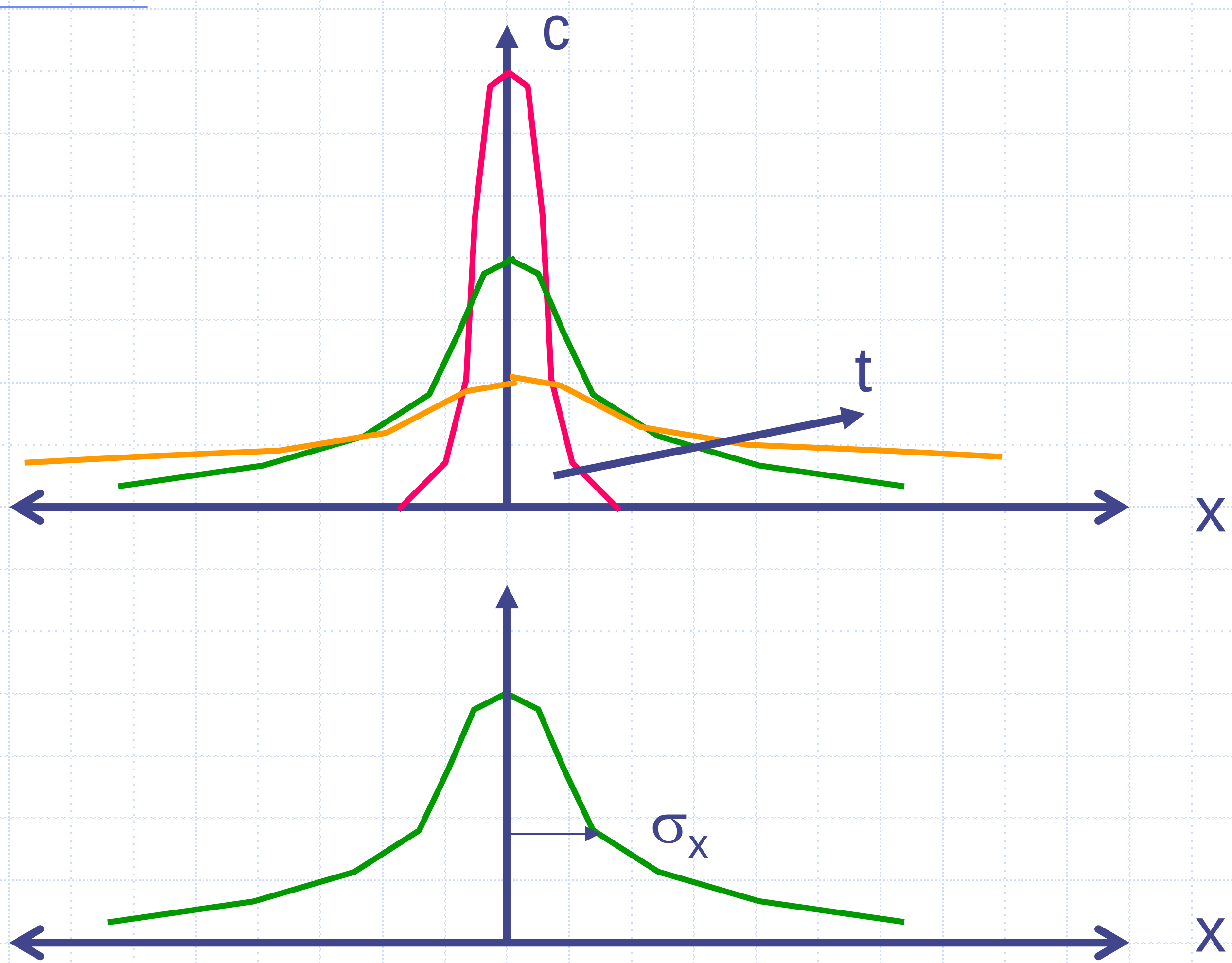
$$A\int_{-\infty}^{\infty} c\,dx = M$$

Add a current

$$M = 2AB\sqrt{\pi D}$$

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

Gaussian Solution



Spatial Moments

interpretation

$$m_o = \int_{-\infty}^{\infty} c(x,t)\,dx$$

$$M = m_o A$$

Mass; indep of t

$$m_1 = \int_{-\infty}^{\infty} cx\,dx$$

$$x_c = \frac{m_1}{m_o} = \underline{ut}$$

Center of mass

$$m_2 = \int_{-\infty}^{\infty} cx^2\,dx$$

$$\sigma_x^{\ 2} = \frac{m_2}{m_o} - \left(\frac{m_1}{m_2}\right)^2 = \underline{2Dt}$$

Plume variance

Spatial Moments, cont'd

Relationship of moments to equation parameters

$$m_2 = \int_{-\infty}^{\infty} \frac{M}{2A\sqrt{\pi D t}} e^{\frac{-x^2}{4Dt}} x^2 dt$$

$$= 2\frac{M}{A} Dt$$

$$\sigma_x{}^2 = \frac{m_2}{m_o} = \frac{2MDt / A}{M / A} = 2Dt$$

Without current, odd moments are 0

Spatial Moments, cont'd

Rewrite in terms of σ

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

$$= \frac{M}{A\sqrt{2\pi}\sigma_x} e^{-\frac{x^2}{2\sigma^2}}$$

or in 3-D (isotropic)

$$c(x,t) = \frac{M}{8(\pi D t)^{3/2}} e^{-\frac{(x^2+y^2+z^2)}{4Dt}}$$

$$= \frac{M}{(2\pi)^{3/2}\sigma^3} e^{-\frac{(x^2+y^2+z^2)}{2\sigma^2}}$$

Plume dilutes by spreading:

In 1-D, $c \sim t^{-1/2} \sim \sigma_x^{-1}$

In 3-D, $c \sim t^{-3/2} \sim \sigma^{-3}$

Moment generating equation

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

$$m_i = \int_{-\infty}^{\infty} x^i c\,dx$$

Approach 1: moments of c(x,t) => σ^2 = m^2/mo = 2Dt

Approach 2: moments of ge => moment generation eq.

$$\int_{-\infty}^{\infty} x^i (each\ term)\, dx$$

Moment generating eq., cont'd

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad m_i = \int_{-\infty}^{\infty} x^i c\,dx$$

0th moment

$$\int_{-\infty}^{\infty}\frac{\partial c}{\partial t}dx = \frac{\partial}{\partial t}\int_{-\infty}^{\infty} c\,dx = \frac{dm_o}{dt}$$

$$\int_{-\infty}^{\infty} D\frac{\partial^2 c}{\partial x^2}dx = D\left(\frac{\partial c}{\partial x}\right)_{-\infty}^{\infty} = 0$$

0

2nd moment

$$\int_{-\infty}^{\infty} x^2\frac{\partial c}{\partial t}dx = \frac{\partial}{\partial t}\int_{-\infty}^{\infty} x^2 c\,dx = \frac{dm_2}{dt}$$

$$\int_{-\infty}^{\infty} Dx^2\frac{\partial^2 c}{\partial x^2}dx = Dx^2\left(\frac{\partial c}{\partial x}\right)_{-\infty}^{\infty} - 2\int_{-\infty}^{\infty} xD\frac{\partial c}{\partial x}dx = -2xD(c)_{-\infty}^{\infty} + 2\int_{-\infty}^{\infty} Dc\,dx = 2Dm_o$$

0 0

Moment generating eq., cont'd

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad m_i = \int_{-\infty}^{\infty} x^i c\,dx$$

0^{th} moment

$$\frac{dm_o}{dt} = 0$$

=> m_o = const = M/A

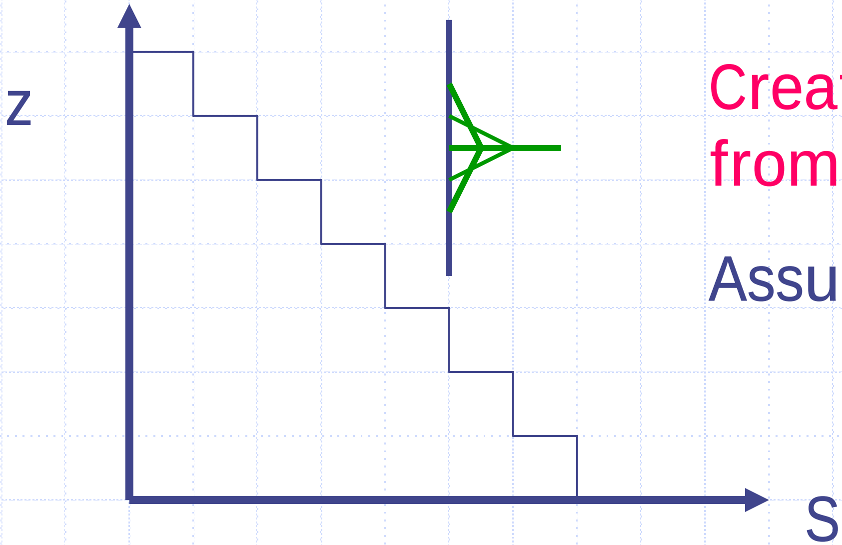
2nd moment

$$\frac{dm_2}{dt} = 2Dm_o$$

$$m_o \frac{d\sigma^2}{dt} = 2Dm_o$$

=> $d\sigma^2/dt = 2D$ or $\sigma^2 = 2Dt$

How fast is molecular diffusion?



Creating linear salinity distribution from initial step profile

Assume 80 cm tank; 40 2cm steps

Table 1-1

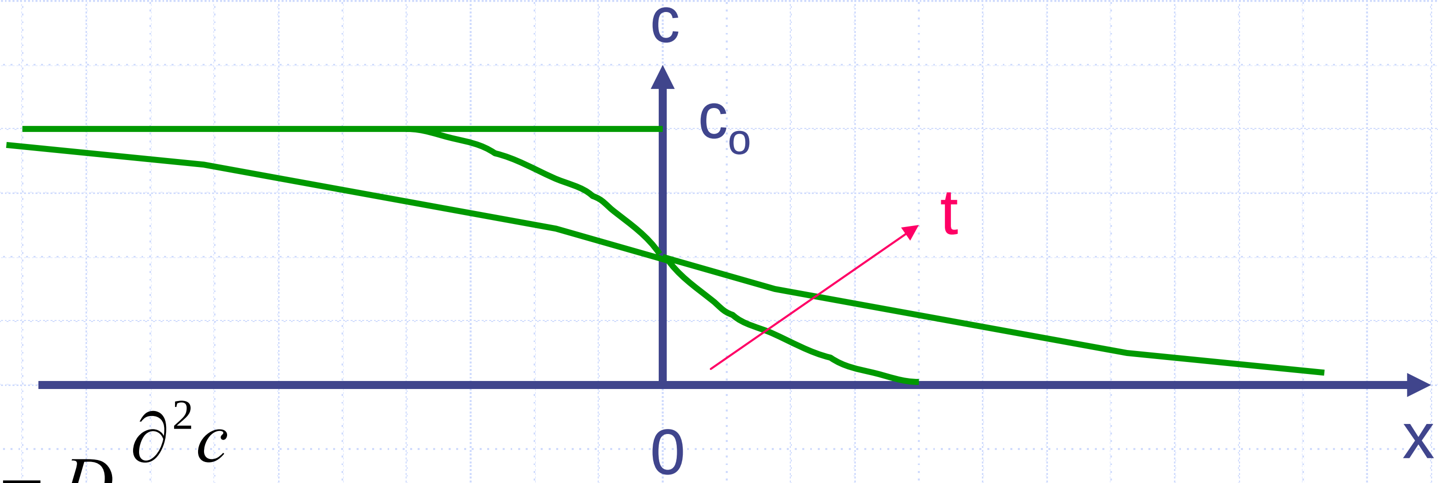
Time to diffuse: $\sigma^2 = 2Dt$

$t = \sigma^2/2D \sim (2cm)^2/(2)(1.3x10^{-5}\ cm^2/s)$

$= 1.5x10^5 s \sim 2$ days   slow!

If thermal diffusion (100 x faster), t < 1 hr

Spatially distributed sources



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

$$bc \quad c = 0 \quad at \quad x = \infty$$

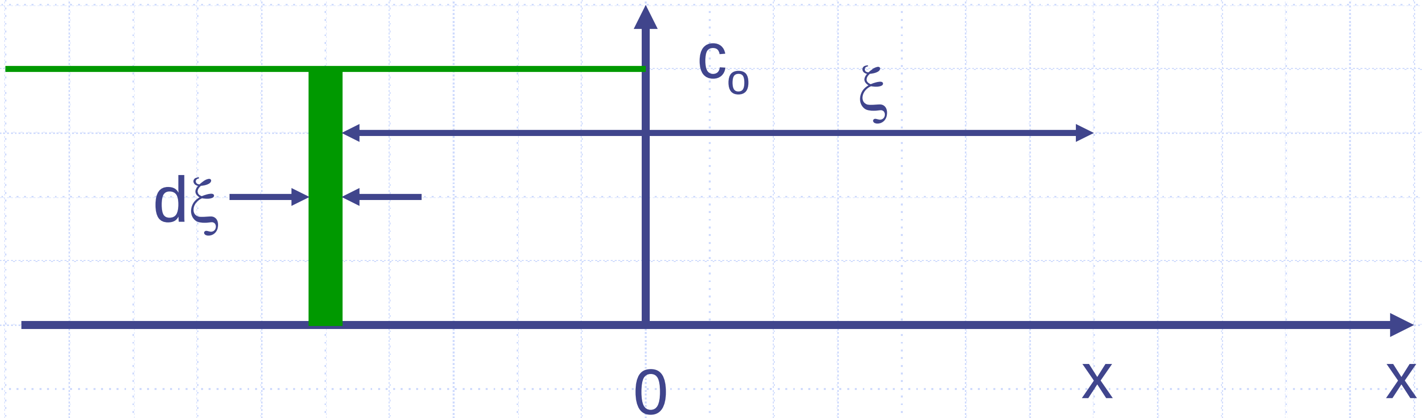
$$c = c_o \quad at \quad x = -\infty$$

or $c = c_o/2$ at $x = 0$

$$ic \quad c = c_o \quad for \quad x < 0 \quad at \quad t = 0$$

$$c = 0 \quad for \quad x > 0 \quad at \quad t = 0$$

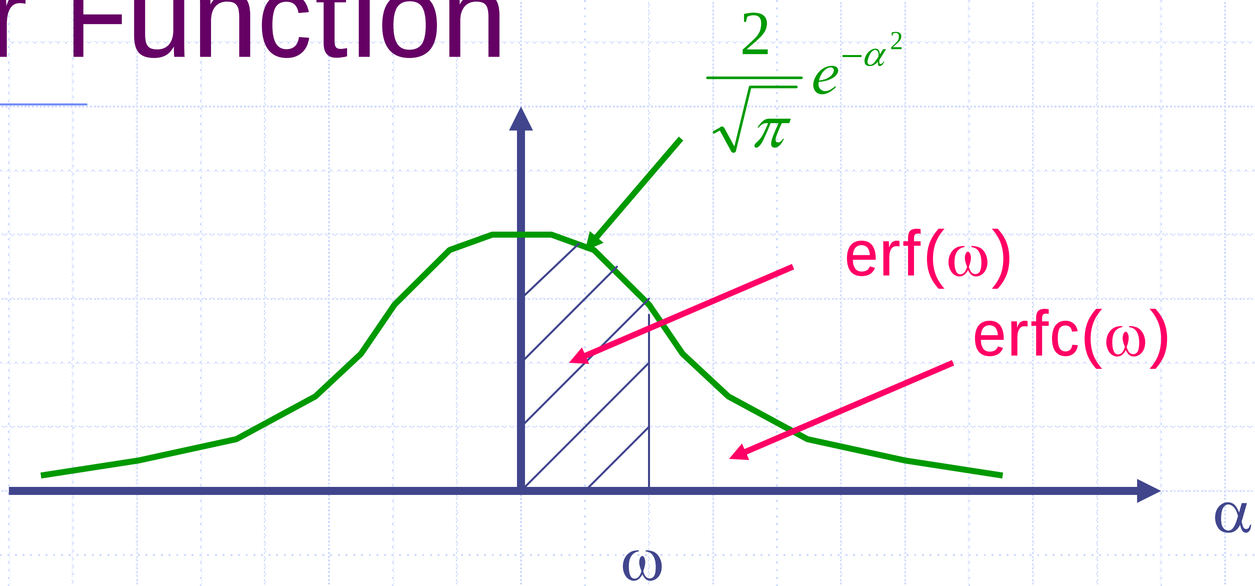
Spatially distributed sources



$$dc(\xi,t) = \frac{dM}{2A\sqrt{\pi Dt}} e^{-\frac{\xi^2}{4Dt}} = \frac{c_o d\xi}{2\sqrt{\pi Dt}} e^{-\frac{\xi^2}{4Dt}}$$

$$c(x,t) = \int_x^\infty \frac{c_o d\xi}{2\sqrt{\pi Dt}} e^{\frac{-\xi^2}{4Dt}} = \frac{c_o}{2}\left[1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)\right] = \frac{c_o}{2} erfc\left(\frac{x}{2\sqrt{Dt}}\right)$$

Error Function



$$erf(\omega) = \frac{2}{\sqrt{\pi}} \int_0^{\omega} e^{-\alpha^2} d\alpha$$

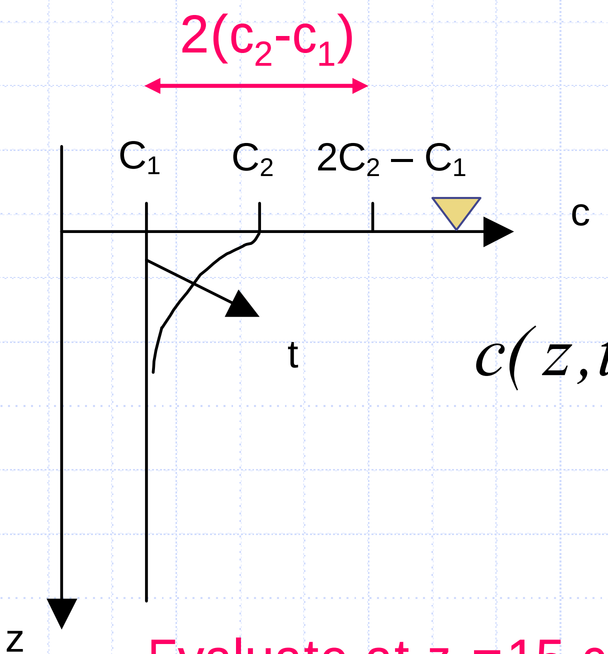
$$erfc(\omega) = \frac{2}{\sqrt{\pi}} \int_{\omega}^{\infty} e^{-\alpha^2} d\alpha$$

$$erf(0) = 0$$

$$erf(\infty) = 1$$

$$erfc(x) = 1 - erf(x)$$

Example: DO in Fish aquarium (WE 1-4)



t=0: $c=c_1=8$ mg/l (c_{sat} at 27°C)

t>0: $c(0)=c_2=10$ mg/l (c_{sat} at 16°C)

$$c(z,t) = c_1 + \frac{1}{2} 2(c_2 - c_1)\,\mathrm{erfc}\left(z / 2\sqrt{Dt}\right)$$

$$\frac{c - c_1}{c_2 - c_1} = \mathrm{erfc}\left(z / 2\sqrt{Dt}\right)$$

Evaluate at z =15 cm, D = 2×10^{-5} cm^2/s (Table 1-1)

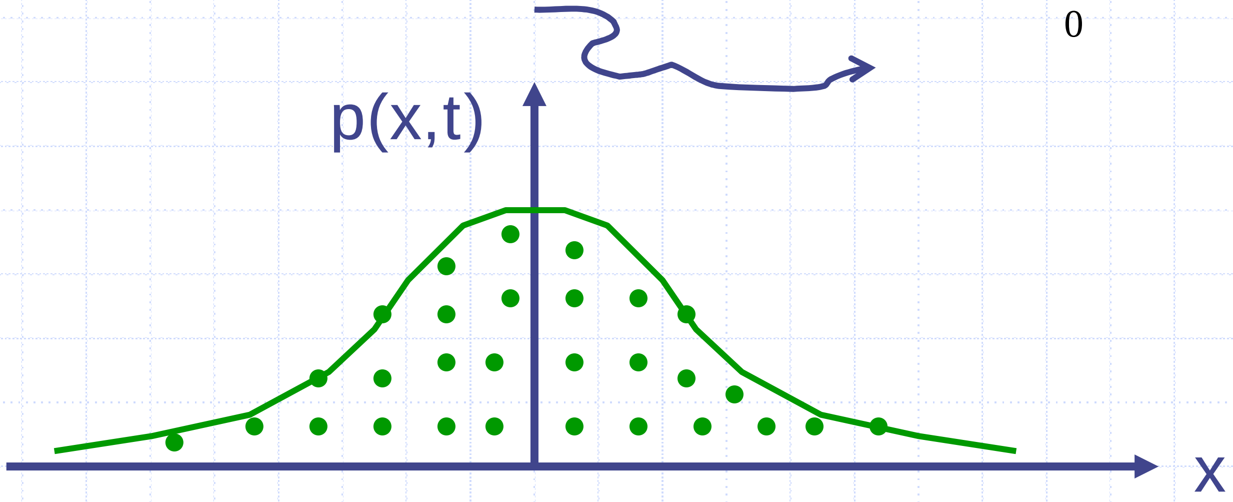
t	$z/(4Dt)^{0.5}$	$\mathrm{erfc}[(z/(4Dt)^{0.5}]$
1hr	28	0
1d	5.7	10^{-15}
1 mo	1.0	0.15

Again, very slow!

Diffusion as correlated movements

x=0 at t=0

$$x(t) = \int_0^t u(t')\,dt'$$



Analogy between p(x) and c(x); ergotic assumption

For many particles, both distributions become Normal (Gaussian) through Central Limit Theorem

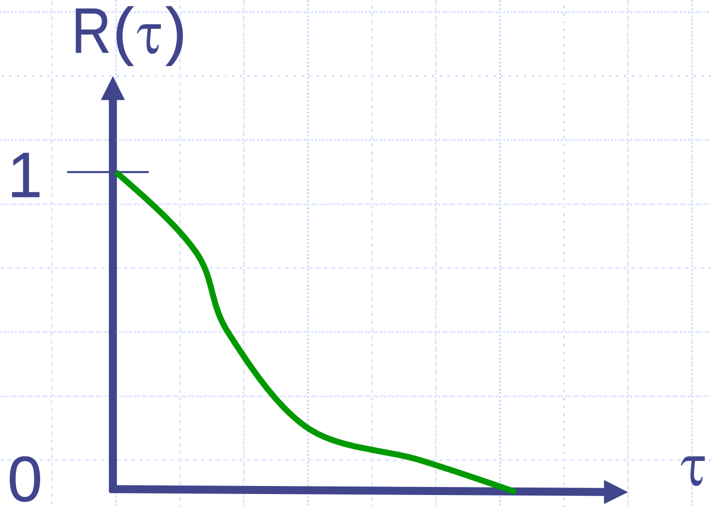
Statistics of velocity

$\overline{u} = 0$ mean velocity

$\overline{u^2} = const.$ variance

$\overline{u(t)u(t-\tau)} = \overline{u(0)u(\tau)} = \overline{u(-\tau)u(0)}$ auto co-variance

$\dfrac{\overline{u(t)u(t-\tau)}}{\overline{u(t)^2}} = R(\tau)$ auto correlation



Statistics of position

$$x(t) = \int_0^t u(t')dt'$$

$$\overline{x} = \overline{\int_0^t u(t')dt'} = \int_0^t \overline{u}(t)dt = 0$$

$\overline{x^2(t)}$ increases with time, as follows

$$\frac{dx^2(t)}{dt} = 2x(t)\frac{dx}{dt} = 2\left[\int_0^t u(t')dt'\right]u(t) = 2\int_0^t u(t)u(t')dt'$$

$$\frac{d\overline{x^2(t)}}{dt} = 2\overline{u^2(t)}\int_0^t R(t-t')dt' = 2\overline{u^2(t)}\int_0^t R(\tau)d\tau$$

$$D = \frac{d\overline{x^2}}{2dt} = \frac{d\sigma^2}{2dt} = \overline{u^2}\int_0^t R(\tau)d\tau$$ Taylor's Theorem (1921); classic

[D] = [V^{2}T]

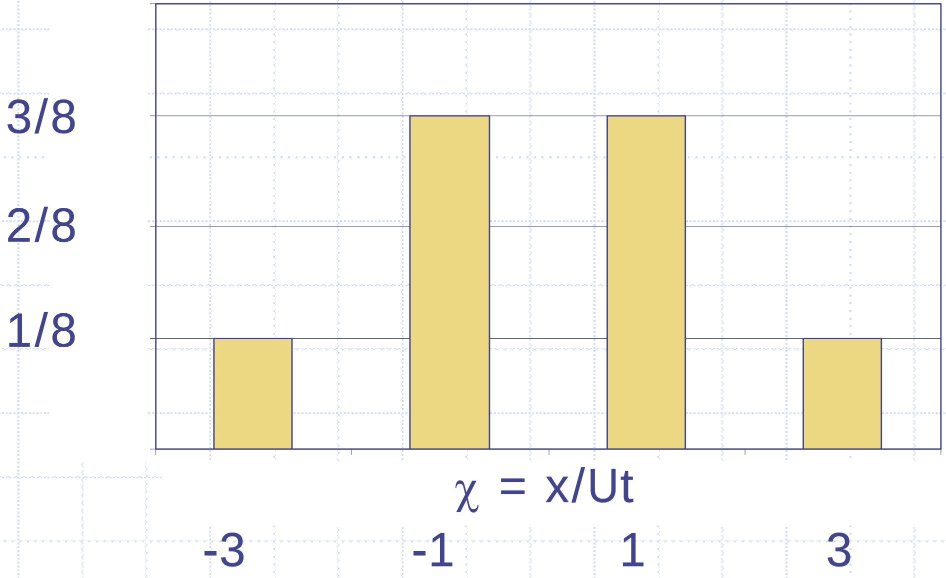
Earlier, $D = w_A \ell_m$ [VL] or $D = \dfrac{\sigma^2}{2t}$ [L^2/T]

Random Walk (WE 1-3)

Special case: $u(t) = U \ or \ -U$ direction changes randomly after Δt

Walker's position at time t=NΔt $x = \sum_{1}^{N} u \Delta t$

Probability distribution $p(\chi, N) = \frac{N!}{\left(\frac{N+\chi}{2}\right)! \left(\frac{N-\chi}{2}\right)!} \left(\frac{1}{2^N}\right)$



Bernoulli Distribution

Approaches Gaussian for large N

Example for N=3

Statistics of position

$$\bar{x}(t) = \sum_{i=1}^{N} \bar{u}(t) = 0$$

$$\sigma^2 = \overline{\left(\sum_{i=1}^{N} u \Delta t \right)^2} = \Delta t^2 \overline{\left[(u_1 + u_2 \ldots u_i + \ldots u_N)(u_1 + u_2 + \ldots u_N) \right]}$$

$$= N \Delta t^2 U^2 = t U^2 \Delta t = t \Delta x^2 / \Delta t$$

$$D = \frac{\sigma^2}{2t} = \frac{U^2 \Delta t}{2} = \frac{\Delta x^2}{2 \Delta t}$$ [L²/T]

Alternatively, derive D from Taylor's Theorem

Examples of Sources and Sinks (r terms)

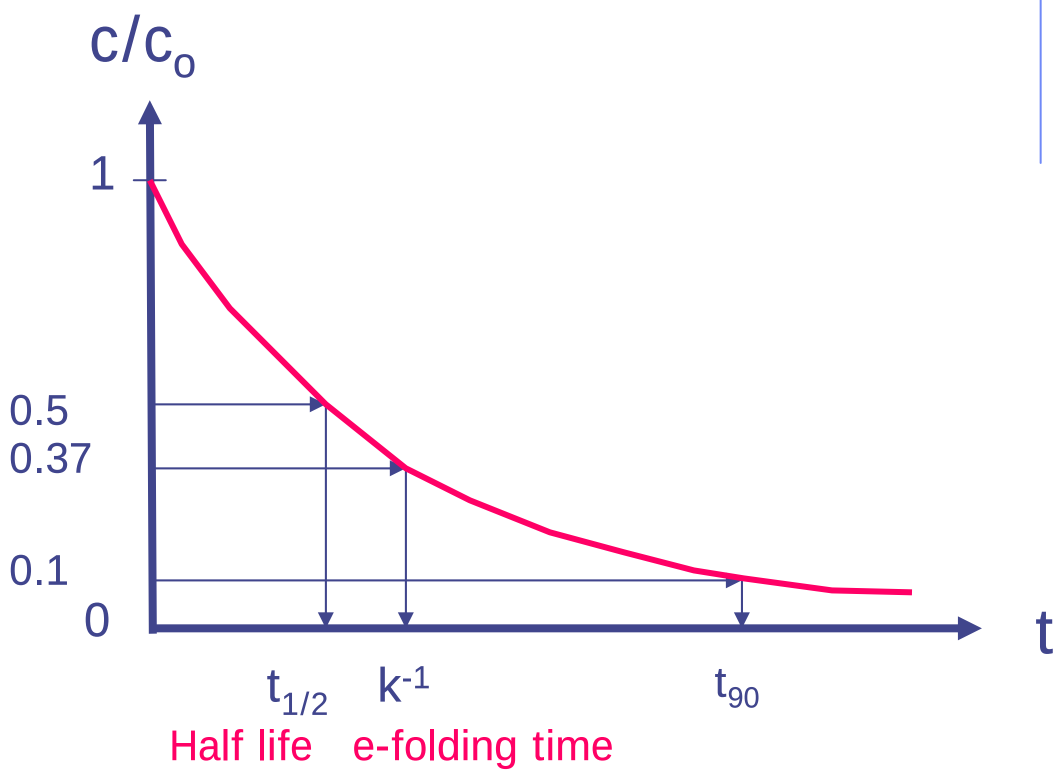
- 1st order
- 0th order
- 2nd order
- Coupled reactions
- Mixed order

1^{st} Order

Example:
radioactive decay

$$\frac{dc}{dt} = -kc$$

$$c / c_o = e^{-kt}$$



Linearity => 1^{st} O decay multiplies simple sol'n by e^{-kt}; e.g.

Also very convenient in particle tracking models

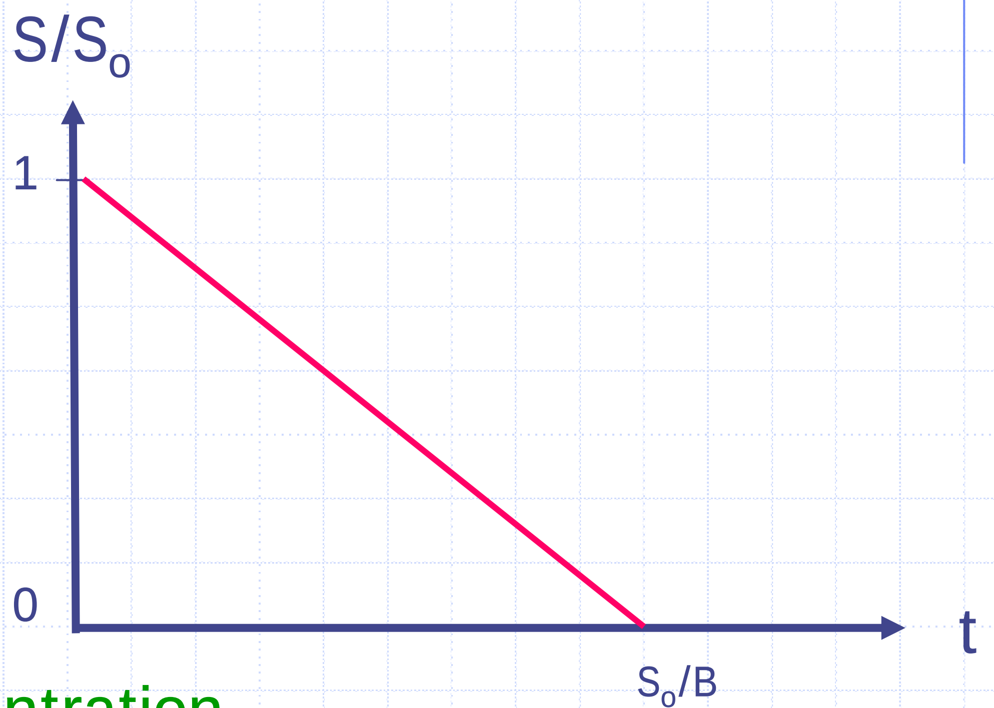
$$c = \frac{M}{2A\sqrt{\pi Dt}} e^{-kt}$$

0^{th} Order

Example: silica uptake by diatoms (high diatom conc)

$$\frac{dS}{dt} = -B$$

$$S = S_o - Bt$$



S=substrate (silica) concentration

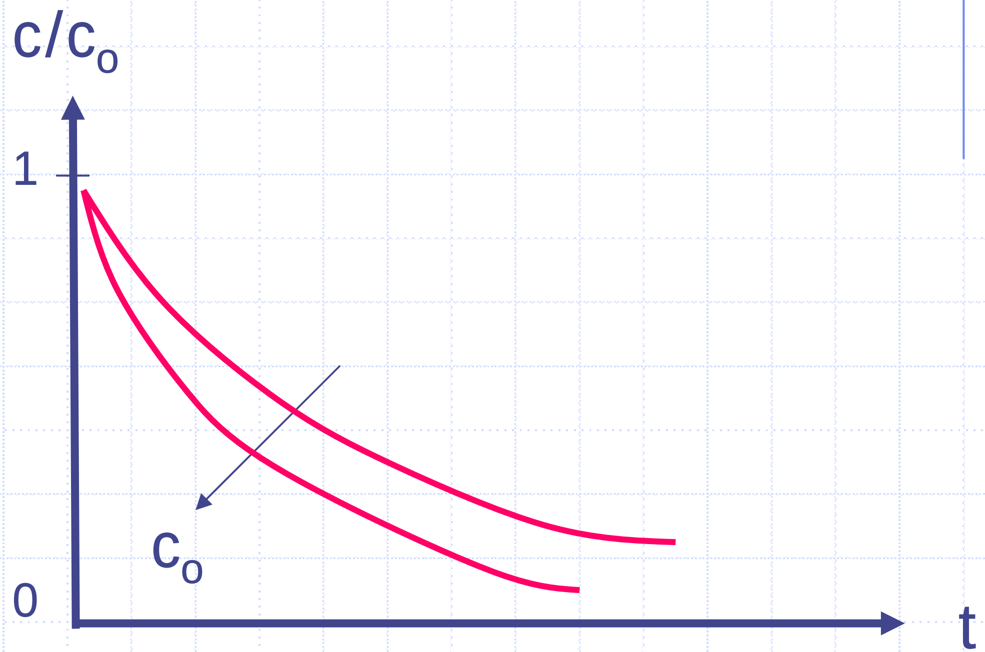
B=rate (depends on diatom population, but assume large)

2^{nd} Order

Example: particle-particle collisions/reactions; flocculant settling)

$$\frac{dc}{dt} = -Bc^2$$

$$\frac{c}{c_o} = \frac{1}{1 + Btc_o}$$



Behavior depends on c_o; slower than e^{-kt}.

Can be confused with multiple species undergoing 1^{st} order removal

Coupled Reactions

Example: Nitrogen oxidation

$$\frac{dN_1}{dt} = -K_{12}N_1$$ $N_1 = NH_3$-N

$$\frac{dN_2}{dt} = K_{12}N_1 - K_{23}N_2$$ $N_2 = NO_2$-N

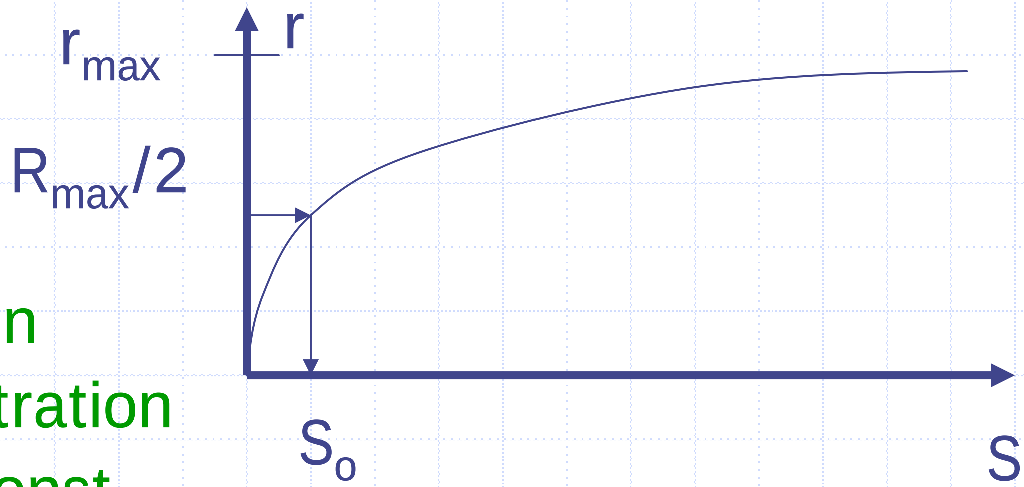
$$\frac{dN_3}{dt} = K_{23}N_2$$ $N_3 = NO_3$-N

If N's are measured as molar quantities, or atomic mass, then successive K's are equal and opposite

Mixed Order—Saturation Kinetics (Menod kinetics)

Example: algal uptake of nutrients—focus on algae

$$\frac{dc}{dt} = \frac{kS}{S + S_o}$$



c = algal concentration

S = substrate concentration

S_o = half-saturation const

S << S_o => $$\frac{dc}{dt} \cong \frac{kS}{S_o} = k'S$$ (1st Order)

S >> S_o => $$\frac{dc}{dt} \cong k$$ (0th Order)

1 Wrap-up

- Molecular diffusivities

$$D = w\ell_m$$ Molecular motion; Eulerian frame

$$D = \frac{d\sigma^2}{2dt^2}$$ Method of moments

$$D = \overline{u^2}\int_0^\infty R(\tau)d\tau$$ Molecular motion; Lagrangian frame

- D is “small” ~ 1×10^{-5} cm^2/s for water
- Inst. point source solutions are Gaussian; other solutions built from
  - Spatial and temporal integration, coordinate translation, linear source/sink terms