Lecture 9 – Fick's Laws and Transport with External Forces

- Sections 5.3 and 5.4 in the textbook

- Fick's 1st and 2nd Laws
- Sedimentation
- Electrophoresis
- Convection and Chromatography

Review: Diffusion equation

- From calculating the probability of a molecule being a certain distance away from its starting point after a random walk, we derived the Einstein diffusion equation:

$$\langle r^2 \rangle^{1/2} = \sqrt{6Dt}$$

D has units $\frac{m^2}{s}$

rms $\propto \sqrt{t}$

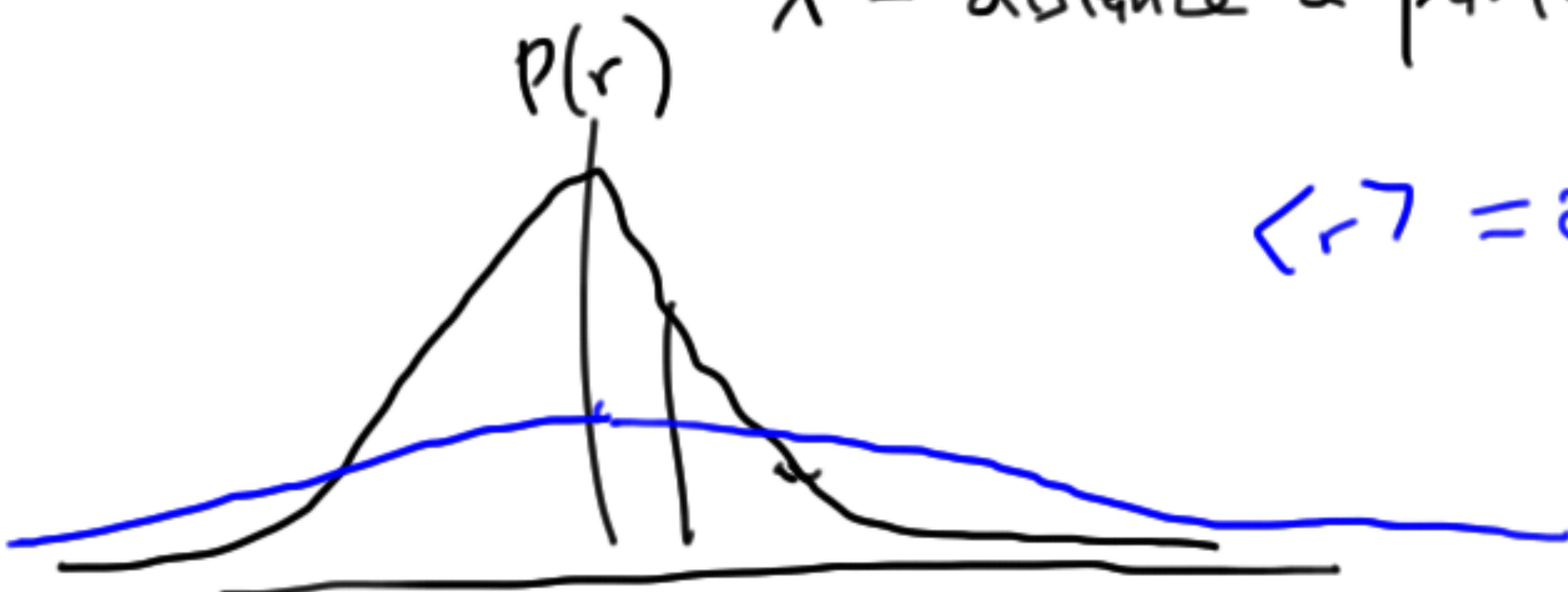
α (thermal diffusivity) $\frac{m^2}{s}$

μ (electron or hole mobility) $\frac{m^2}{V s}$

$$D = \frac{\gamma \lambda^2}{2}$$

γ = rate of collisions

λ = distance a particle travels between collisions



$\langle r \rangle = 0$

rms $= \sigma$ $\langle r^2 \rangle^{1/2}$

Fick's Laws of Diffusion

- Fick's laws of diffusion describe how concentration gradients affect diffusion rates

- Fick's first law describes how the flux of molecules, J, depends on the concentration gradient and diffusion coefficient under steady-state conditions:

not changing with time

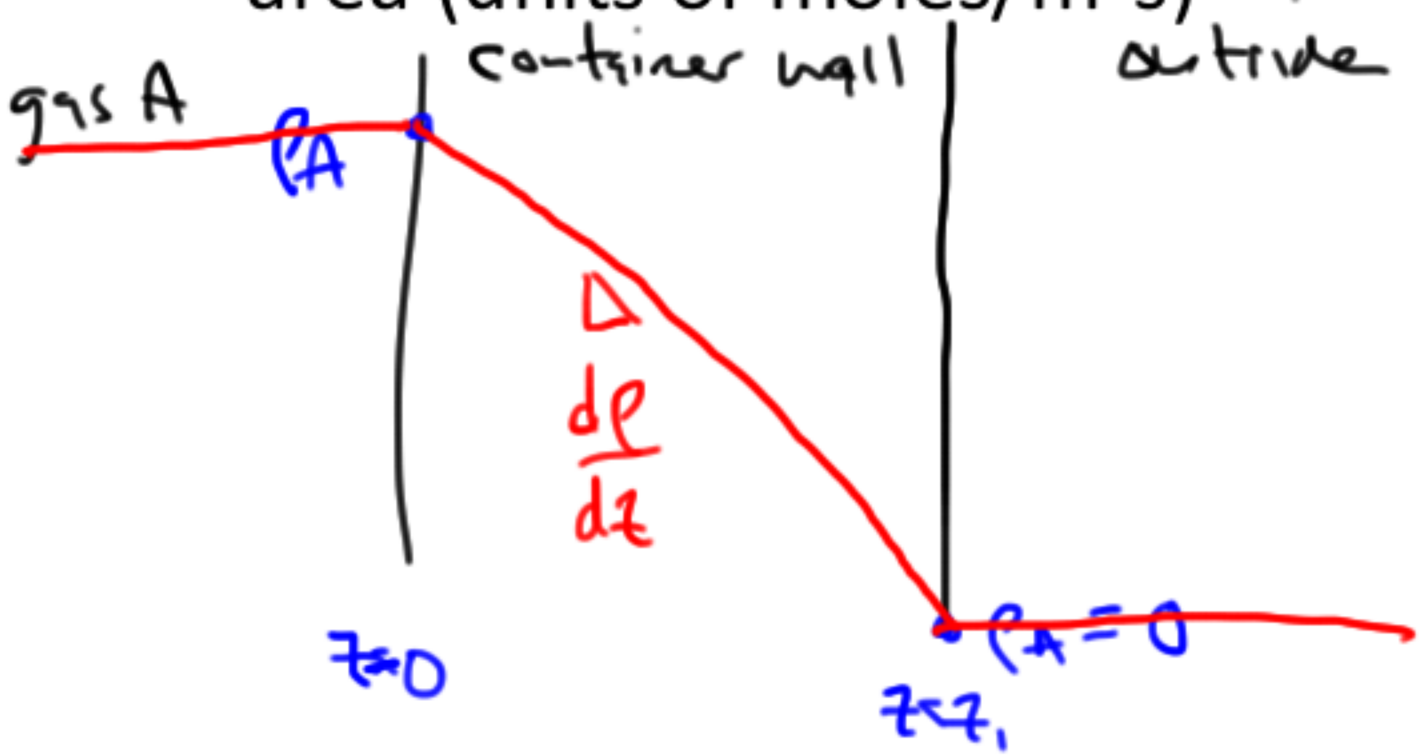
$$J = -D \underbrace{\frac{d\rho}{dz}}$$

ρ = density

z = distance

driving force → larger gradient = higher flux

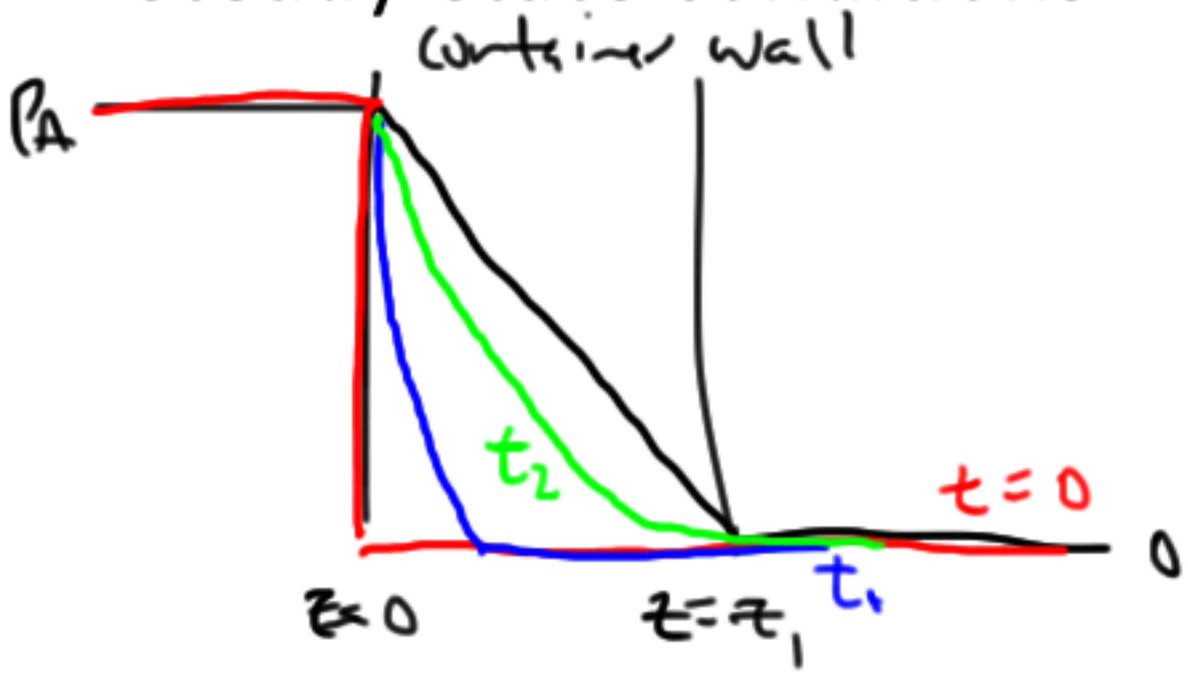
  - J is the number of molecules that pass a location per second per unit area (units of moles/m^{2}s)



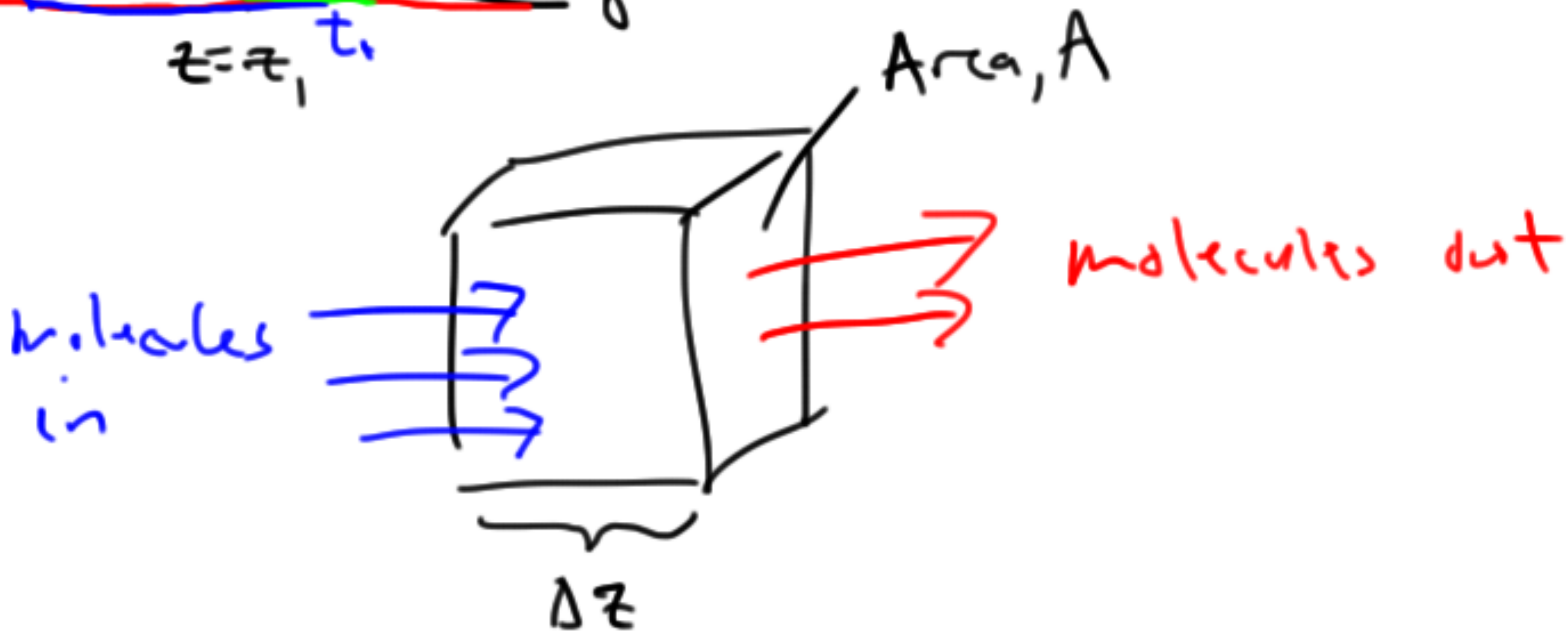
$$J = -D\left(\frac{\rho_A(z_1) - \rho_A(z_0)}{z_1 - z_0}\right)$$

Fick's Second Law

- Fick's 2nd Law can be used to derive concentration profiles for non-steady-state conditions



$t=0$, t_1, t_2 $\Rightarrow$ transient concentration profiles



$$\frac{mol}{m^3 s} \rightarrow \frac{d\rho}{dt} = \frac{J(z+\Delta z)\cdot \cancel{A} - J(z)\cdot \cancel{A}}{\cancel{A}\cdot \Delta z}$$

$\uparrow$ how ρ is changing inside box over time

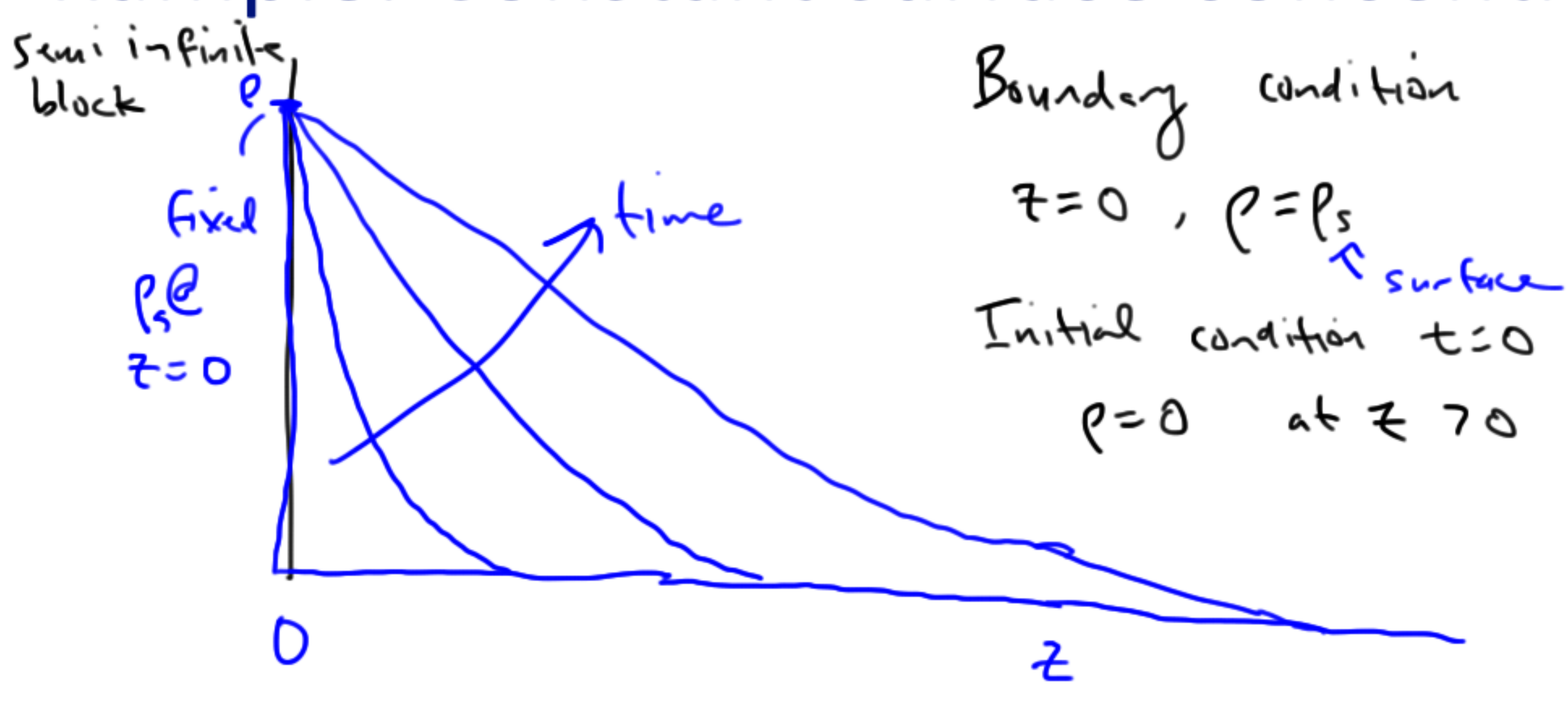
let $\Delta z \rightarrow 0$

Fick's First law: $J = -D\frac{d\rho}{dz}$

$$\frac{d\rho}{dt} = -\frac{dJ}{dz}$$

$$= -\frac{d}{dz}\left(-D\frac{d\rho}{dz}\right) = \boxed{D\frac{d^2\rho}{dz^2} = \frac{d\rho}{dt}}$$

Example: Constant surface concentration



Boundary condition

$z=0\ ,\ \rho=\rho_s$ ← surface

Initial condition $t=0$

$\rho=0$ at $z>0$

$$\frac{d\rho}{dt} = D\frac{d^2\rho}{dz^2}$$

change of variables $\eta = \dfrac{z}{(4Dt)^{1/2}}$

$$\frac{\partial\rho}{\partial\eta}\cdot\frac{\partial\eta}{\partial z}$$

$$\frac{d\rho}{dt} = \frac{d\rho}{d\eta}\cdot\frac{\partial\eta}{\partial t} = D\cdot\frac{d}{d\eta}\left(\frac{d\rho}{dz}\right)\frac{d\eta}{dz} = D\,\frac{\partial^2\rho}{\partial\eta^2}\cdot\left(\frac{\partial\eta}{\partial z}\right)^2$$

$$\frac{\partial\eta}{\partial t} = \frac{\partial}{\partial t}\left(\frac{z}{(4Dt)^{1/2}}\right) = \frac{-z}{2\,(4Dt)^{1/2}\,t} = -\frac{\eta}{2t}$$

$$\frac{\partial\eta}{\partial z} = \frac{1}{(4Dt)^{1/2}}$$

$$\frac{-\eta}{2\cancel{t}} = \cancel{D}\cdot\frac{\partial^2\rho}{\partial\eta^2}\left[\frac{1}{(4\cancel{D}\cancel{t})^{1/2}}\right]^2$$

$$-2\eta\frac{d\rho}{d\eta} = \frac{d^2\rho}{d\eta^2} = \frac{d}{d\eta}\left(\frac{d\rho}{d\eta}\right) \qquad \text{let } \frac{d\rho}{d\eta} = f$$

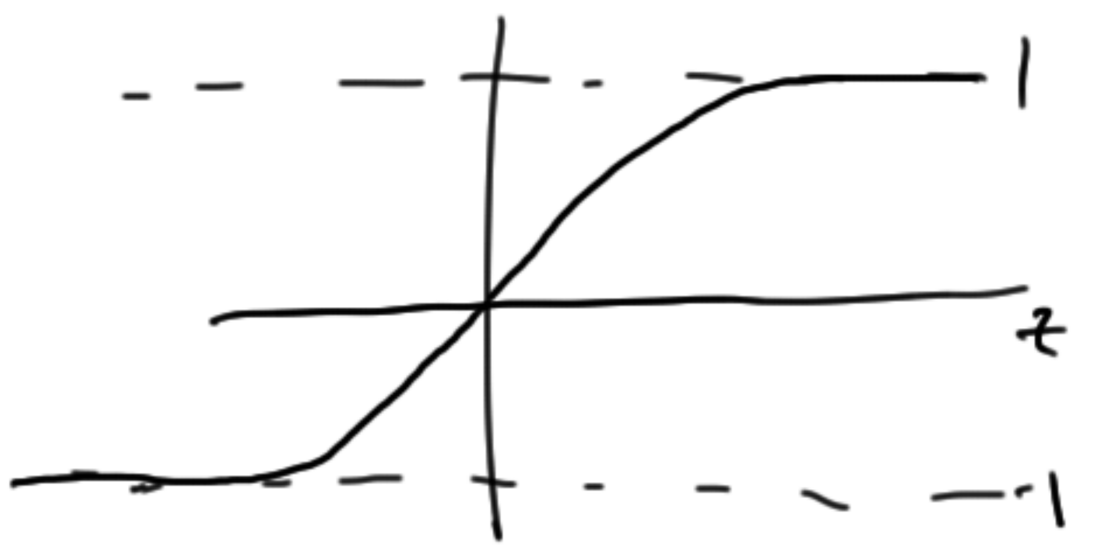
$$-2\eta\cdot f = \frac{df}{d\eta}$$

$$\frac{1}{f}\,df = -2\eta\, d\eta$$

$$\ln f = \ln\left(\frac{d\rho}{dz}\right) = -\eta^2 + c_1$$

$$\frac{d\rho}{dz} = c_1 e^{-\eta^2}$$

$$\rho = c_1 \underbrace{\int_0^{\eta} e^{-\eta'^2}\,d\eta'}_{\text{error function}} + c_2$$



$$\rho = c_1\frac{\sqrt{\pi}}{2}\,\mathrm{erf}(\eta) + c_2$$

$\eta = \dfrac{z}{(4Dt)^{1/2}}$ B.C. $z=0,\ \rho=\rho_s$

$\eta = 0$

Plug in B.C

$$\rho_s = c_1\frac{\sqrt{\pi}}{2}\,\cancel{\mathrm{erf}}(0) + c_2 \quad\Rightarrow\quad c_2 = \rho_s$$

$$\rho = c_1\frac{\sqrt{\pi}}{2}\,\mathrm{erf}(\eta) + \rho_s$$

I.C. $t=0,\ \rho=0$ @ $z>0$

$\eta=\infty$

Plug in: $0 = c_1\dfrac{\sqrt{\pi}}{2}\,\overbrace{\mathrm{erf}(\infty)}^{=1} + \rho_s$

$$c_1 = \frac{-2\rho_s}{\sqrt{\pi}}$$

$$\boxed{\rho = -\rho_s\,\mathrm{erf}(\eta) + \rho_s}$$

solution for semi infinite slab w/ constant surface concentration

Sedimentation

Downwards force = $F_{gravity}$ (corrected for buoyancy)

Upwards force = $F_{viscosity} = -fv$ velocity

frictional coefficient (depends on shape (size/interaction w/ solvent)

$F_{visc} = F_g \Rightarrow$ constant v_{ss}

steady state velocity

Centrifuge increases gravitational force up to 10^6 times

angular velocity

$$F_{cent} = (m - m_0)\omega^2 r = m\omega^2 r b \qquad b = \left(1 - \frac{m_0}{m}\right)$$

mass of solute

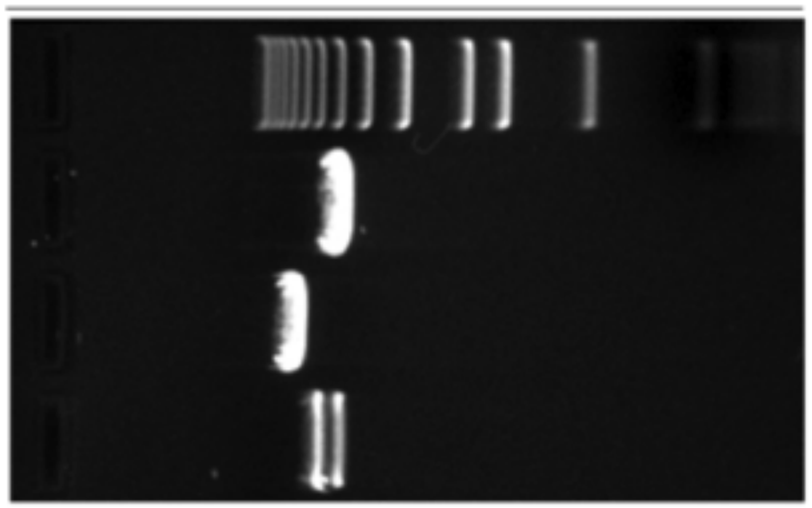
mass of solvent

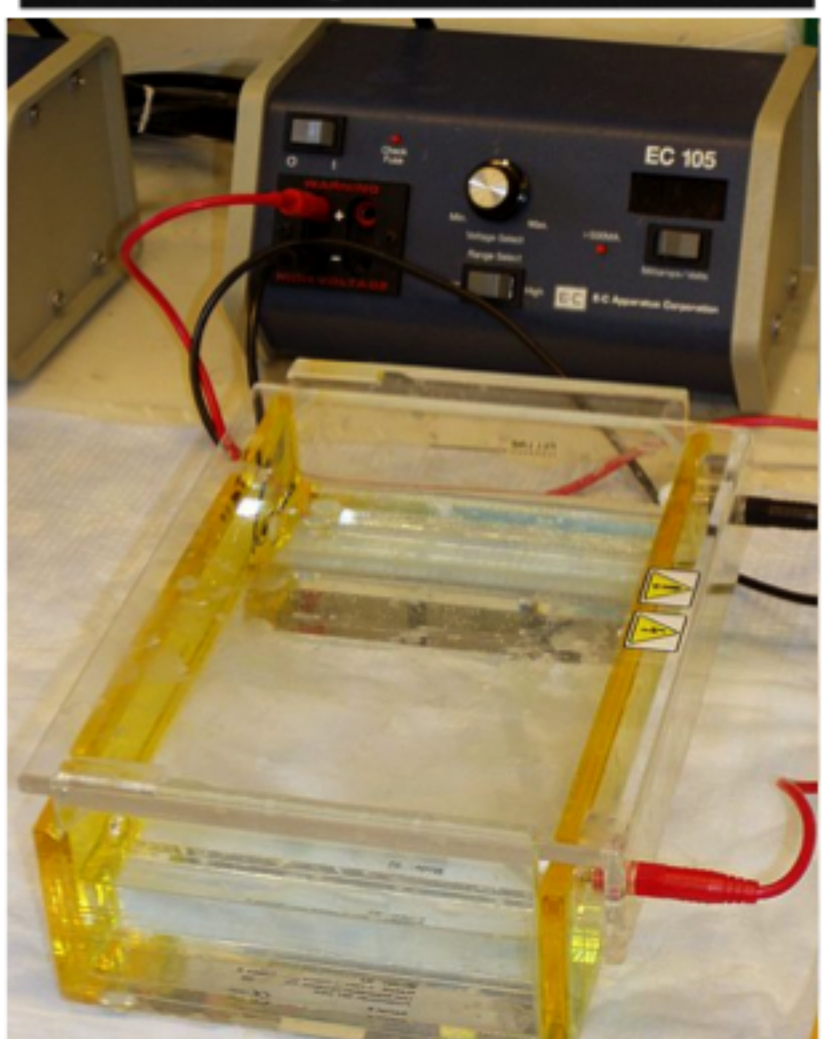
distance from the center of rotation

$F_{vis} = F_{cent} \Rightarrow$ can solve for steady state velocity

Electrophoresis

- The frictional force due to viscosity opposes an electrostatic force acting on a charged molecule moving through an electric field





velocity, $v \propto \ln m$

mass

http://en.wikipedia.org/wiki/Gel_electrophoresis

Convection

- Net flow of a gas or liquid, usually through another fluid, without mixing
- In additional to movement from diffusion, molecules have a net velocity in a specific direction

$$\langle v_{conv} \rangle = \frac{dz}{dt}$$

Fick's 2nd Law

$$\frac{d\rho}{dt} = \left(\frac{d\rho}{dt}\right)_{diff} + \left(\frac{d\rho}{dt}\right|_{conv} = D\frac{d^2\rho}{dz^2} + \langle v_{conv} \rangle \frac{d\rho}{dz}$$

$$P(z,t) = (4\pi Dt)^{-1/2} e^{-(z - \langle v_{conv} \rangle t)^2/4Dt)}$$

1st law of thermodynamics - conservation of energy

$$\Delta E = w + q$$

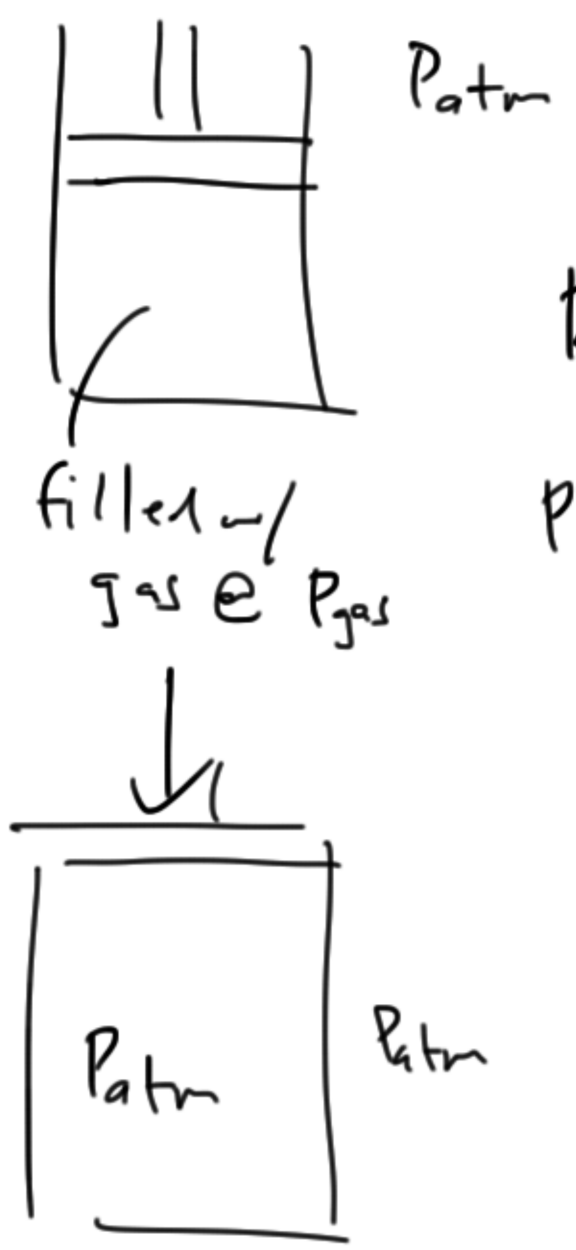
w: work $\quad$ q: heat

$\Delta E = E_2 - E_1$ state function (path/process independent)

work and heat are path dependent

sum of work and heat is a state function

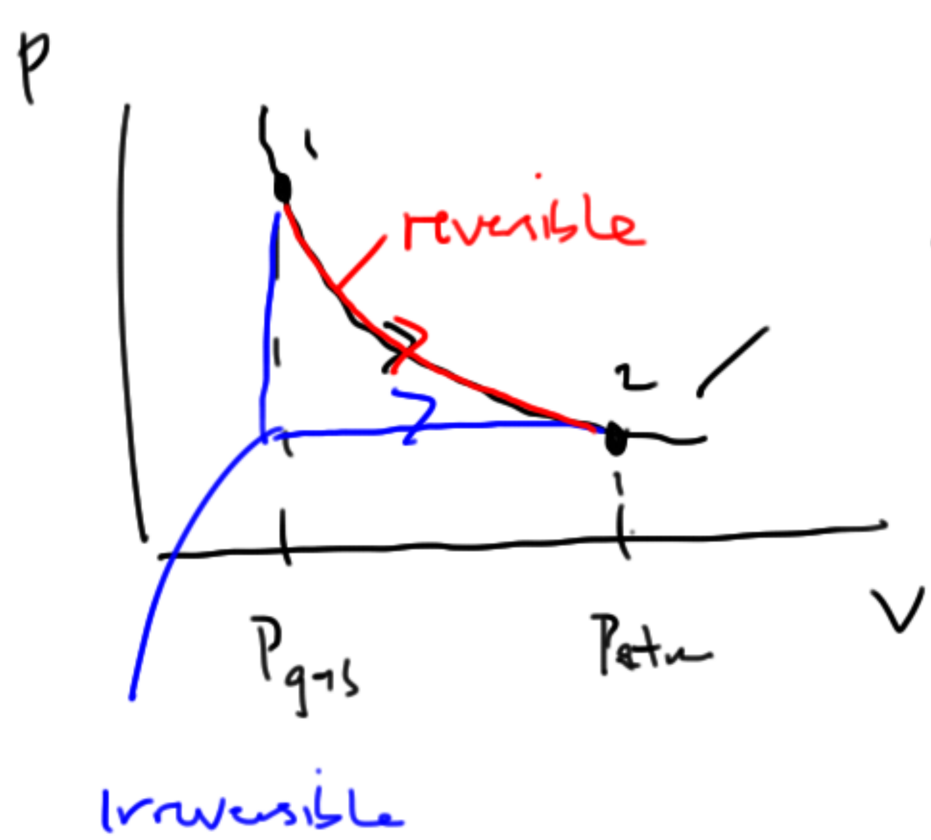
Reversible versus Irreversible processes



$P_{gas} > P_{atm}$

Constant T process

Release piston, it will move up (does work)



$$P = \frac{nRT}{V}$$

$$w = -\int P\,dV$$

Reversible: $w = -\int_{V_1}^{V_2} \frac{nRT}{V}\,dV$

$$w = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$w = -P_{atm}\int dV$$

$$w = -P_{atm}(V_2 - V_1)$$

$$\Delta E = \frac{3}{2} nR(T_2 - T_1)$$