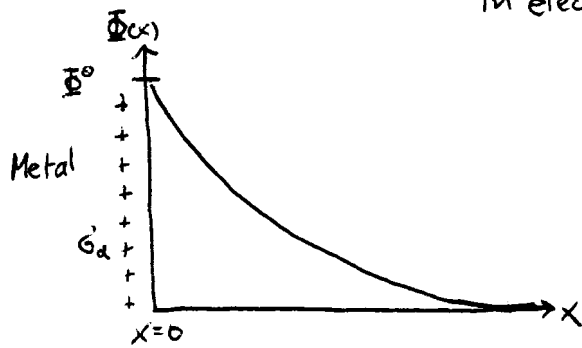


Problem 1.3.3 - Equilibrium potential & space charge distribution in electrolytes.



δd = net surface charge at $x=0$

A = surface area of metal

Wish to find equilibrium potential and space charge distribution in the electrolyte.

(steady-state / no time dependence)

a) Combining Gauss' Law $\nabla \cdot \epsilon \underline{E} = \rho$
 and EQS Faraday's Law $\nabla \times \underline{E} = 0 \Rightarrow \underline{E} = -\nabla \Phi$

$$\Rightarrow \nabla \cdot (\epsilon (-\nabla \Phi)) = \rho \quad \text{With constant } \epsilon$$

$$\nabla^2 \Phi = -\frac{\rho}{\epsilon}$$

For 1-D model, x -direction only,

$$\boxed{\frac{\partial^2 \Phi}{\partial x^2} = -\frac{\rho}{\epsilon}}$$

Assuming ion distribution by Boltzmann statistics (derived in class),
 for species i with valence z_i ,

$$c_i = c_{i0} e^{-\frac{z_i F \Phi(x)}{RT}}$$

Since $\rho_i = z_i F c_i$, $\rho_i = z_i F c_{i0} e^{-\frac{z_i F \Phi(x)}{RT}}$

With $\rho = \sum_i \rho_i$

$$\boxed{\frac{\partial^2 \Phi}{\partial x^2} = -\frac{F}{\epsilon} \sum_i c_{i0} z_i e^{-\frac{z_i F \Phi(x)}{RT}}}$$

b) For ^{mono-}monovalent, symmetrical electrolyte, $z_+ = -z_- = z_0$ (eventually, $z_0 = 1$)
 $C_{+0} = C_{-0} = C_0$

$$\frac{d^2\Phi}{dx^2} = -\frac{F}{\epsilon} \left[z_+ C_{+0} e^{-\frac{z_+ F \Phi(x)}{RT}} + z_- C_{-0} e^{-\frac{z_- F \Phi(x)}{RT}} \right]$$

$$= -\frac{F z_0 C_0}{\epsilon} \left[e^{-\frac{z_0 F \Phi(x)}{RT}} - e^{\frac{z_0 F \Phi(x)}{RT}} \right]$$

Taylor series for $\frac{z_0 F \Phi(x)}{RT} \ll 1$

$$e^{\frac{z_0 F \Phi(x)}{RT}} \approx 1 + \frac{z_0 F \Phi(x)}{RT} + \text{higher order terms} \rightarrow 0$$

$$\Rightarrow \frac{d^2\Phi}{dx^2} = \frac{F}{\epsilon} z_0 C_0 \left[1 + \frac{z_0 F \Phi(x)}{RT} - 1 + \frac{z_0 F \Phi(x)}{RT} \right]$$

$$= \frac{2 z_0^2 F^2 C_0}{\epsilon RT} \Phi(x)$$

$$\boxed{\frac{d^2\Phi}{dx^2} = \kappa^2 \Phi(x)} \quad \text{with} \quad \boxed{\kappa^2 = \frac{2 z_0^2 F^2 C_0}{\epsilon RT}}$$

linearized Poisson-Boltzmann equation

The Debye length is then

$$\boxed{\frac{1}{\kappa} = \left(\frac{2 z_0^2 F^2 C_0}{\epsilon RT} \right)^{-1/2}}$$

$$F = 96485 \frac{\text{C}}{\text{mol}} \quad R = 8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

$$\epsilon_0 = 8.85 \cdot 10^{-12} \frac{\text{F}}{\text{m}} \quad \epsilon = 80 \epsilon_0 \text{ (for NaCl solution)}$$

$$C_0 = 0.1 \text{M} / 0.001 \text{M} \quad z_0 = 1$$

0.1 M NaCl solution, $C_0 = 0.1 \text{M}$

$$\frac{1}{\kappa} = \left(\frac{2(1)^2 (96485 \text{ C/mol})^2 (0.1 \text{ mol/l}) (1 \text{ l} / 0.001 \text{ m}^3)}{80 \times 8.85 \cdot 10^{-12} \frac{\text{F}}{\text{m}} \cdot 8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \cdot 310 \text{ K}} \right)^{-1/2} = \boxed{9.9 \cdot 10^{-10} \text{ m}}$$

0.001 M NaCl solution, $c_0 = 0.001 \text{ M}$

$$\frac{1}{\kappa} = \left(\frac{2(1)^2 (96485 \text{ C/mol})^2 \cdot (0.001 \text{ mol/L}) \cdot (1^2 / 0.001 \text{ m}^2)}{80 \cdot 8.85 \cdot 10^{-12} \text{ F/m} \cdot 8.314 \text{ J/mol} \cdot \text{K} \cdot 310 \text{ K}} \right)^{-1/2} = \boxed{9.9 \cdot 10^{-9} \text{ m}}$$

c) Solve $\frac{d^2\Phi}{dx^2} = \kappa^2\Phi$ with B.C.s $\Phi(0) = \Phi_0$
 $\Phi(x \rightarrow \infty) = 0$

$$\Rightarrow \Phi(x) = Ae^{\kappa x} + Be^{-\kappa x}$$

Apply B.C.s: $\Phi(x \rightarrow \infty) = Ae^{x \rightarrow \infty} + Be^{x \rightarrow \infty} = 0 \Rightarrow A = 0$
 $\Phi(0) = B = \Phi_0$

$$\Rightarrow \boxed{\Phi(x) = \Phi_0 e^{-\kappa x}}$$

The Debye length is the characteristic length over which spatial decay of potential occurs due to a source of charge.

At the scale of $1/\kappa$, charge/species separation occurs in the electrolyte.

$$\rho_u(x) = \nabla \cdot \epsilon \underline{E} = -\epsilon \nabla^2 \Phi = -\epsilon \frac{d^2\Phi}{dx^2}$$

$$\boxed{\rho_u(x) = -\epsilon \kappa^2 \Phi_0 e^{-\kappa x}}$$

d) Surface boundary condition:

$$\underline{n} \cdot (\epsilon_1 \underline{E}_1 - \epsilon_2 \underline{E}_2) = \sigma_s \text{ (surface charge density)} = \frac{\sigma_d}{A}$$

$$\underline{E}_1 = -\nabla\Phi \quad \underline{E}_2 = -\nabla\Phi_{\text{metal}} = 0 \text{ (no electric field in metal)}$$

$$\Rightarrow \epsilon \frac{d\Phi}{dx} \Big|_{x=0} = \frac{\sigma_d}{A} \Rightarrow \frac{d\Phi}{dx} \Big|_{x=0} = -\frac{\sigma_d}{\epsilon A}$$

$$\Rightarrow -\Phi_0 K e^{-K(x=0)} = -\frac{Q_d}{\epsilon A}$$

$$\boxed{Q_d = \epsilon A K \Phi_0} \quad \text{for small } \Phi_0$$

The capacitor charge-potential relationship: $q = C \cdot V$
charge ↑ ↓ capacitance ↑ potential

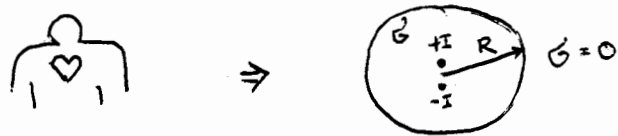
where $C \equiv \frac{\epsilon A}{d}$ for planar capacitor. (d = thickness of capacitor)

$$\text{Here, } C = \epsilon A K \hat{=} \frac{\epsilon A}{d} \quad (q \hat{=} Q_d, V \hat{=} \Phi_0)$$

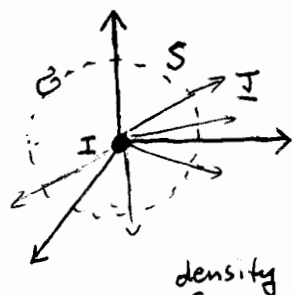
$$\Rightarrow \boxed{d \hat{=} 1/K = \text{Debye length}}$$

The "thickness" of a capacitor in this model is the Debye length.

Problem 1.3.4 - Centric dipole model



a) Current monopole (point charge), spherically symmetric
Uniformly conducting medium



S : surface of sphere
 I : current source
 \underline{J} : current density

All current ^{density} integrated over the surface of an imaginary sphere of any size will arise due to the current sources inside the sphere, i.e. due to I :

$$\oint_S \underline{J} \cdot d\mathbf{A} = I$$

$$\Rightarrow \int_0^{2\pi} \int_0^\pi J_R \cdot r^2 \sin\theta \, d\theta \, d\phi = I$$

$J_\theta = J_\phi = 0$ due to symmetry

$$\Rightarrow \boxed{J_R = \frac{I}{4\pi r^2}}$$

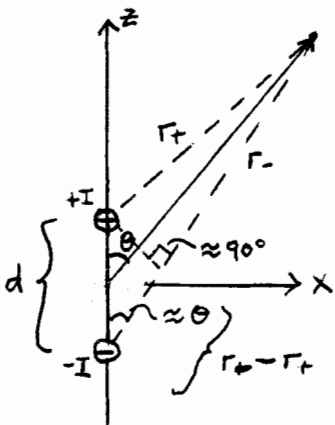
Since $\underline{J} = G\underline{E}$,

$$\Rightarrow \boxed{E_R = \frac{I}{4\pi G r^2}}$$

Since $E = -\nabla\Phi \Rightarrow \Phi = \int E_R dr$

$$\Rightarrow \boxed{\Phi = \frac{I}{4\pi G r}}$$

b) Current dipole where $d \ll$ characteristic length



By superposition of two current monopoles

$$\begin{aligned}\Phi(r) &= \frac{I}{4\pi\epsilon r_+} + \frac{-I}{4\pi\epsilon r_-} = \frac{I}{4\pi\epsilon} \left(\frac{1}{r_+} - \frac{1}{r_-} \right) \\ &= \frac{I}{4\pi\epsilon} \left(\frac{r_- - r_+}{r_+ r_-} \right)\end{aligned}$$

Assuming $r_+, r_- \gg d$. $r_+ \approx r_-$

$$r_+ \cdot r_- \approx r^2$$

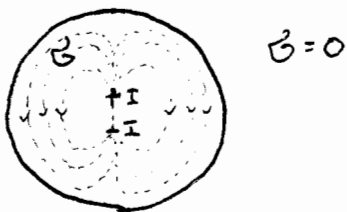
$$r_- - r_+ \approx d \cos \theta$$

$$\Rightarrow \boxed{\Phi(r) = \frac{I d \cos \theta}{4\pi\epsilon r^2}}$$

Potential arising from a dipole both r and θ

(There are many ways to solve this problem)

c) Current dipole inside a conducting sphere, ϵ , $R \gg d$



We consider steady dipole current.

In a homogeneous material, we have $\rho_{net} = 0$, Poisson equation becomes the Laplace's equation:

$$\nabla^2 \Phi = 0$$

In spherical coordinates, the solution can be written as

$$\Phi(r, \theta) = \frac{A}{r} + B r \cos \theta + C \frac{\cos \theta}{r^2}$$

We can throw out the monopole term right away if you want.

We cannot eliminate the dipole term for obvious reasons.

Due to the electric fields arising from the dipole, charge separation will occur at the sphere surfaces leading to uniformly induced field. Therefore, the uniform field term stays as well. (see (f) for more)

On a more mathematical basis, we will deduce boundary conditions.

$$1. \text{ at } r=R \quad \underline{n} \cdot (\underline{J}_1 - \underline{J}_2) = \frac{\partial \sigma}{\partial t} \begin{matrix} \nearrow \\ \text{steady} \\ \text{state} \end{matrix}$$

$$\Rightarrow \underline{n} \cdot (\underbrace{\epsilon_1 \underline{E}_1}_{\text{sphere}} - \underbrace{\epsilon_2 \underline{E}_2}_{\text{outside}}) = 0 \quad \epsilon_2 = 0$$

$$\Rightarrow \underline{n} \cdot \epsilon_1 \underline{E}_1 = 0 \quad (\text{no normal component of electric field at boundary})$$

$$\Rightarrow E_r = -\frac{\partial \Phi}{\partial r} = 0$$

$$\frac{\partial \Phi}{\partial r} = 0 \text{ at } r=R$$

2. as $r \rightarrow 0$ the system is mostly affected by dipole

$$\Rightarrow \Phi(r \rightarrow 0) = \frac{I d \cos \theta}{4\pi \epsilon r^2} \quad \text{as deduced in b)}$$

3. at $\theta = 90^\circ$ the potential is zero due to symmetry.

(For $\theta > 90^\circ$, potential is negative; for $\theta < 90^\circ$, potential is positive)

$$\begin{matrix} \theta < 90^\circ \\ - - \frac{+I}{-I} - - - \theta = 90^\circ \\ \theta > 90^\circ \end{matrix}$$

$$\Phi(\theta = 90^\circ) = 0$$

Applying B.C.s

$$3. \Phi(r, \theta=90^\circ) = \frac{A}{r} + B r \cos 90^\circ + C \frac{\cos 90^\circ}{r^2} = 0$$

$$\Rightarrow A=0$$

$$2. \Phi(r \rightarrow 0, \theta) = B \cdot 0 \cdot \cos \theta + C \frac{\cos \theta}{r^2} = \frac{Id \cos \theta}{4\pi \epsilon r^2}$$

$$\Rightarrow C = \frac{Id}{4\pi \epsilon}$$

$$1. \left. \frac{\partial \Phi}{\partial r} \right|_{r=R} = B \cos \theta \frac{2Id \cos \theta}{4\pi \epsilon R^3} = 0$$

$$\Rightarrow B = \frac{Id}{2\pi \epsilon R^3}$$

$$\Rightarrow \boxed{\Phi(r, \theta) = \frac{Id \cos \theta}{2\pi \epsilon} \left(\frac{1}{2r^2} + \frac{r}{R^3} \right)}$$

$$\underline{J} = \epsilon E = -\epsilon \frac{\partial \Phi}{\partial r} \underline{e}_R - \epsilon \left(\frac{1}{r} \frac{\partial \Phi}{\partial \theta} \right) \underline{e}_\theta \quad (\text{Note: } \frac{\partial \Phi}{\partial \phi} = 0 \text{ due to symmetry})$$

$$= -\frac{Id \cos \theta}{2\pi} \left(-\frac{1}{r^3} + \frac{1}{R^3} \right) \underline{e}_R + \frac{Id \sin \theta}{2\pi r} \left(\frac{1}{2r^2} + \frac{r}{R^3} \right) \underline{e}_\theta$$

$$\boxed{\underline{J} = \frac{Id \cos \theta}{2\pi} \left(\frac{1}{r^3} - \frac{1}{R^3} \right) \underline{e}_R + \frac{Id \sin \theta}{2\pi} \left(\frac{1}{2r^3} + \frac{1}{R^3} \right) \underline{e}_\theta}$$

On the surface, $r=R$

$$\boxed{\underline{J} = \frac{3Id \sin \theta}{4\pi R^3}} \quad \text{at } r=R$$

\underline{J} is independent of $\underline{e}_R \Rightarrow$ no radial component. \underline{J} is independent of ϕ .

d) The heart beats at 1 Hz

$$\Rightarrow T_{\text{heart}} = \frac{1}{\omega_{\text{heart}}} \sim 1 \text{ sec}$$

$$\tau_{\text{charge relaxation}} \sim \frac{\epsilon}{\sigma} \sim 1 \text{ nsec}$$

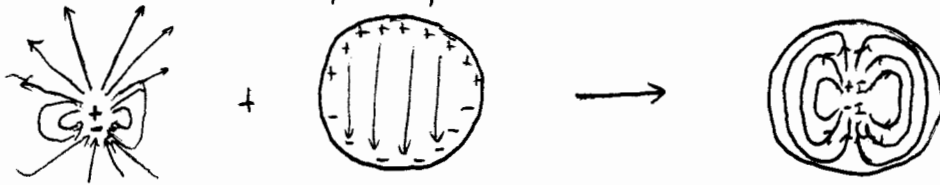
$$\Rightarrow T_{\text{heart}} \gg \tau_{\text{charge relaxation}}$$

Charge relaxation occurs much faster than the heart beat. So, we can assume that the field/current establishment is at steady-state in the time scale of interest:

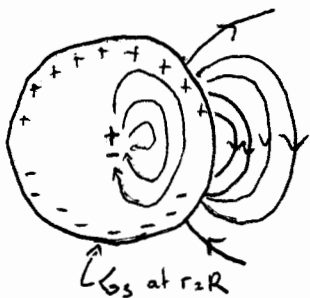
$$\nabla \cdot (\epsilon_1 \underline{E}_1 - \epsilon_2 \underline{E}_2) = -\frac{\partial \rho_s}{\partial t}$$

This allows us to solve for Φ inside the sphere without solving for Φ outside the sphere.

e) Note that inside the sphere, the fields arise due to the dipole and the induced uniform field:



Now, we are interested in the fields outside the sphere



$$G=0$$

$$E=E_0$$

Since we know Φ inside the sphere and at the boundary, we can solve for Φ^{out} .

If you were trying to make measurements in the lab, Φ^{out} and $\underline{E}^{\text{out}}$ produced by the heart beat would constitute "noise" produced by the body.

Again, $\Phi^{\text{out}} = \frac{A}{r} + Br \cos \theta + C \frac{\cos \theta}{r^2}$

B.C.s (a) as $r \rightarrow \infty$, $\Phi^{\text{out}} \rightarrow 0$

(only source of fields should be the heart)

$\Rightarrow B = 0$

(b) at $r = R$, $\Phi^{\text{out}}(R) = \Phi^{\text{in}}(R) = \frac{3}{4} \frac{Id \cos \theta}{\pi \epsilon_0 R^2}$ (from c)

$\Rightarrow A = 0$ (point charge solution can't satisfy B.C. for all θ)

$\Rightarrow C = \frac{3Id}{4\pi\epsilon_0}$

$\Rightarrow \Phi^{\text{out}} = \frac{3Id}{4\pi\epsilon_0} \left(\frac{\cos \theta}{r^2} \right)$

\mathbf{E}^{out} = dipole field produced by body.

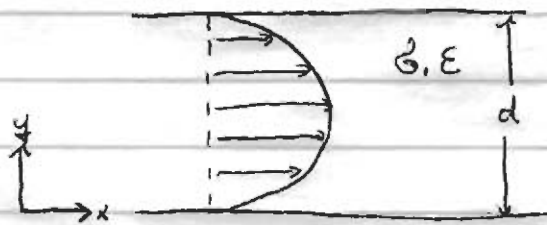
$\mathbf{J}^{\text{out}} = 0$ since $\mathcal{B}^{\text{out}} = 0$

Now, we can calculate

$\mathcal{G}_s(r=R) = \underline{n} \cdot (\epsilon_1 \underline{E}_1 - \epsilon_2 \underline{E}_2)$
 $\epsilon_0 \underline{E}^{\text{out}}$

So, the body does produce "noise" in region outside the body.

Problem 1.6.1 - Blood flow-measuring technique
(see Figures 1.6.3 and 1.6.4)



$\sigma_0 \epsilon$ constant

$$\underline{v} = v_x(y) \underline{e}_x \quad (\text{no } v_y, v_z)$$

$$= U \frac{y}{d} \left(1 - \frac{y}{d}\right) \underline{e}_x \quad U = 4 \text{ cm/sec}$$

$$\nabla \cdot \underline{v} = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} = 0$$

Method I: at $t=0$ $p_u = p_0 e^{-(x/d)^2}$ ($\sigma_0 \approx 1 \frac{\text{mho}}{\text{m}}$)

a) 1.6.30: $\frac{Dp_u}{Dt} + \frac{\sigma_0}{\epsilon} \nabla \cdot \epsilon \underline{E} = -\underline{E} \cdot \nabla \sigma_0$
 $\sigma_0 = \text{const.}$

$$\nabla \cdot \epsilon \underline{E} = \rho_u$$

$$\Rightarrow \frac{Dp_u}{Dt} + \frac{\sigma_0}{\epsilon} p_u = 0 \quad \left(\frac{Dp_u}{Dt} = \frac{\partial p_u}{\partial t} + \underline{v} \cdot \nabla p_u \right)$$

In moving frame: $\frac{\partial p_u'}{\partial t} + \frac{\sigma_0}{\epsilon} p_u'(x', y', t) = 0$

Solving: $p_u'(x', y', t) = \underbrace{p_u'(x', y', t=0)}_{= p_0 e^{-(x'/d)^2}} e^{-t/\tau} \quad \tau = \frac{\epsilon}{\sigma_0}$

Transforming to fixed frame: $x' = x - v_x(y)t$

$$p_u(x, y, t) = p_0 e^{-[x - v_x(y)t]^2/d^2} e^{-t/\tau}$$

Check to see if 1.6.30 is satisfied:

$$\frac{\partial \rho_u}{\partial t} + \underline{v} \cdot \nabla \rho_u + \frac{\sigma}{\epsilon} \rho_u \stackrel{?}{=} 0$$

$$\Rightarrow \rho_0 e^{-t/\tau} \frac{\partial}{\partial t} \left(e^{-\frac{(x-v_x(y)t)^2}{d^2}} \right) - \frac{1}{\tau} \left[\rho_0 e^{-\frac{(x-v_x(y)t)^2}{d^2}} e^{-t/\tau} \right] + v_x(y) \cdot \frac{\partial \rho_u}{\partial x} + \frac{1}{\tau} \rho_u \stackrel{?}{=} 0$$

↑ cancel ↑

$$\Rightarrow \rho_0 e^{-t/\tau} e^{-\frac{(x-v_x(y)t)^2}{d^2}} \left[v_x(y) \cdot \frac{2[x-v_x(y)t]}{d^2} \right] + v_x(y) e^{-t/\tau} e^{-\frac{(x-v_x(y)t)^2}{d^2}} \left[-\frac{2(x-v_x(y)t)}{d^2} \right] \stackrel{?}{=} 0$$

↔ cancel ↔

⇒

$$0 = 0 \quad \checkmark$$

Solution satisfies 1.6.30.

b) It is important to compare the time scales of charge relaxation and convection:

$$\tau_{\text{ch. relax}} \sim 1 \text{ nsec} \quad \tau_{\text{conv.}} \sim \frac{d}{u} = \frac{1 \text{ cm}}{4 \text{ cm/s}} = 0.25 \text{ s}$$

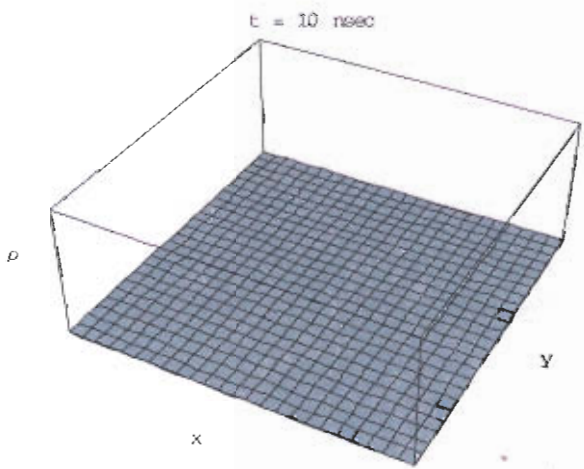
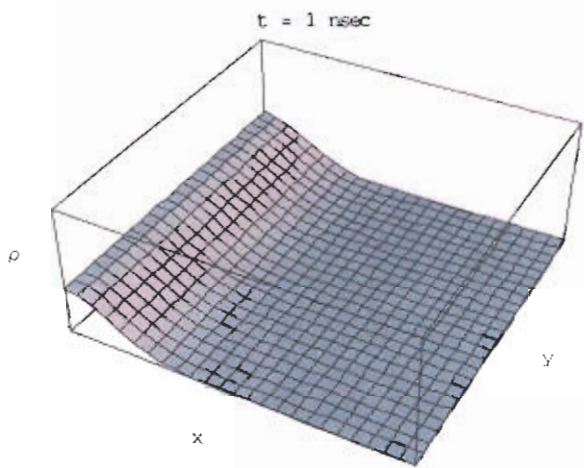
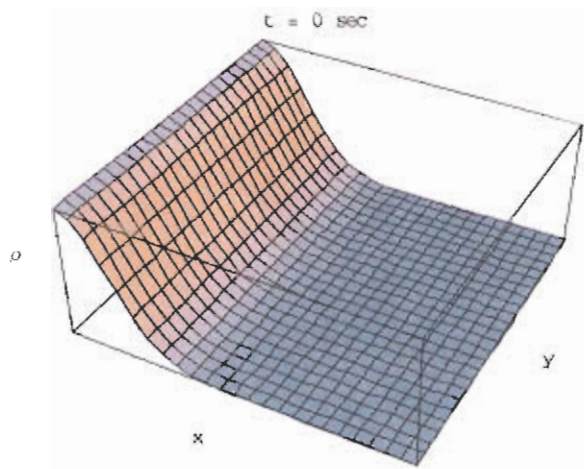
$$\Rightarrow \tau_{\text{conv.}} \gg \tau_{\text{ch. relax.}}$$

Charge relaxation will occur so that $\rho_u \approx 0$ by the time the velocity profile develops.

It is also important to note that charge will not spread in x-direction for the same reasons.

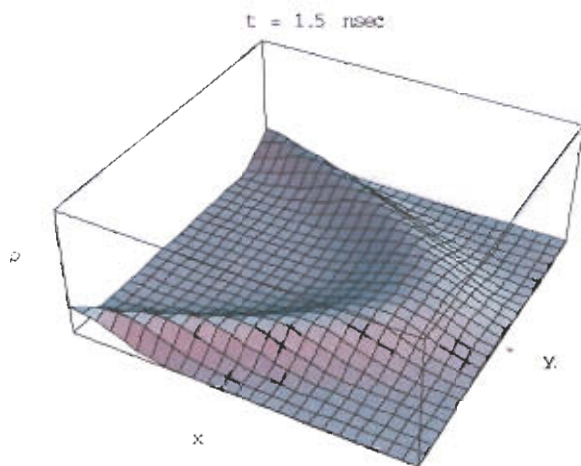
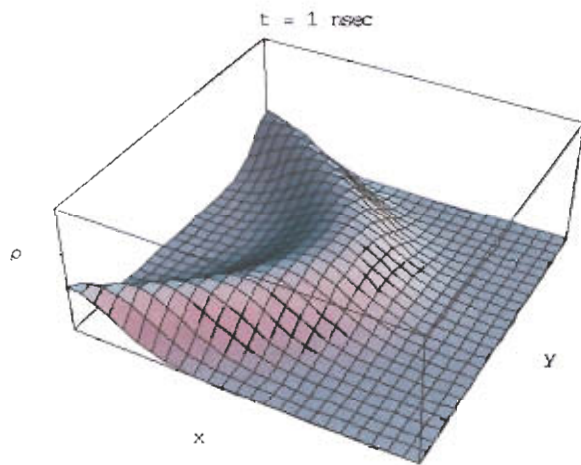
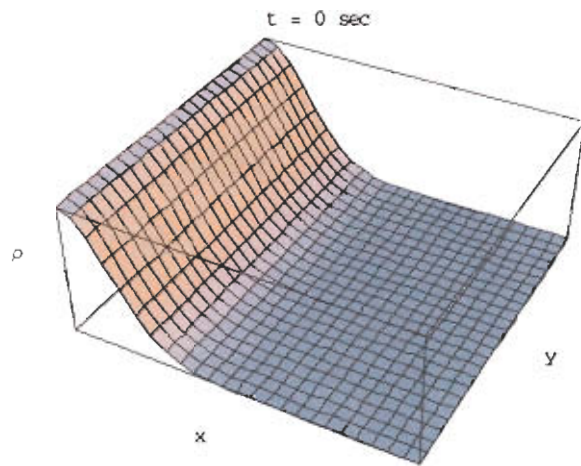
The next two pages show the actual profile for $d=1 \text{ cm}$, $u=4 \text{ cm/s}$ and an unrealistic profile for $d=1 \text{ cm}$, $u=10^{10} \text{ cm/s}$.

Here is the actual profile for $d = 1$ cm and $U = 4$ cm/s. Charge relaxation occurs so fast that the velocity profile is never developed in the time scale of charge relaxation.

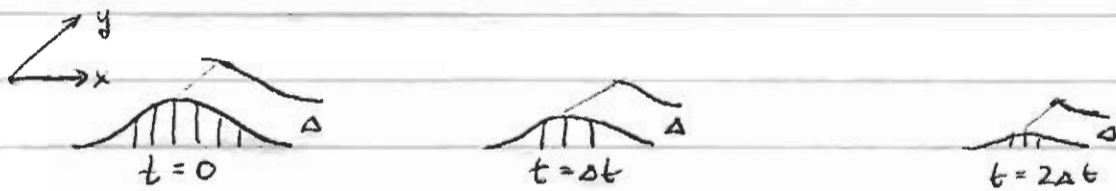


Here are the profiles if $U = 10^{10}$ cm/s so that the convection time scale is slightly smaller than the charge relaxation time scale ($t_{\text{conv}} > t_{\text{ch.rel}}$). Note this is just for illustration.

Since convection occurs faster, charge profile can develop according to the velocity profile.



$$c) \rho_u(x, y, t) = \begin{cases} 0 & x \leq \Delta, d - \Delta \leq x \\ \rho_0 e^{-[x - v_x(y)t]^2 / d^2} e^{-t/\tau} & \Delta \leq x \leq d - \Delta \end{cases}$$



The pulse does not spread out in x - or y -direction!
 The diffusion time scale is much \gg than the charge relaxation constant.

$$\tau_{\text{diff}} = \frac{\Delta^2}{2D} \gg \tau_{\text{ch. rel}} = \frac{\epsilon}{\sigma_0}$$

Net charge ρ_u relaxes in time $\tau = \epsilon/\sigma$ by means of conduction currents ($\vec{J} = \sigma \vec{E}$), where \vec{E} is the field produced by ρ_u in the conductor, in a time much shorter than typical diffusion times, for most σ of interest to us. In any case, the net charge ρ_u (as opposed to charge carriers, such as ions) does not spread at all in an ohmic conductor where 1.6.21 and 1.6.30 are valid and σ is uniform.

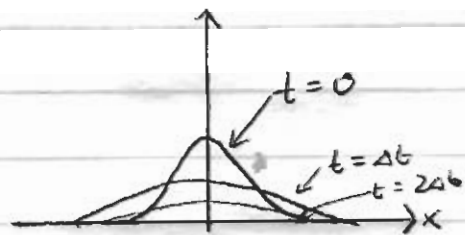
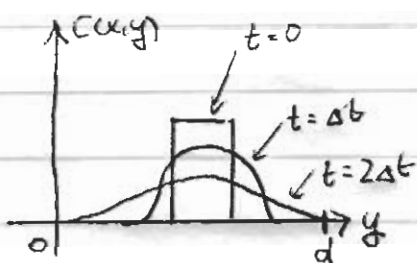
There is never any net charge in the bulk in regions where there was no net charge at $t=0$. Conduction currents do not transport net charge, although charge carriers move!

(\vec{E} acts on all carriers in conductor; Diffusion acts "locally" where there is ∇C).

$$d) \tau_{ch. rel.} = \frac{\epsilon}{\sigma} \ll \tau_{conv.} = \frac{l = 5 \text{ cm}}{u \sim 4 \text{ cm/s}}$$

Net Charge would relax well before the carriers reach the electrodes. Therefore, this method is not feasible.

e) In absence of convection, ordinary diffusion would look like:



This problem falls into convective diffusion (chapter 7).

For this method to be feasible,

- we must know B.C. at walls on chemical constituents
- we assume that ~~put~~ slowly diffuses or spreads out in the x-direction but becomes uniform in the y-direction if d is small, such that diffusion times in y-direction are short compared to distance between $x=0$ and that of the electrode.
- Can measure conductivity or concentration of labelled ions, etc., but placement of electrode in y-direction maybe important.