CBE-521, Fall 2015

Homework No. 1 (third assignment of year)

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In [1]:
```
from pint import UnitRegistry
ureg = UnitRegistry()
import numpy as np
import math
np.set_printoptions(precision=4)
```

Problem 1

Calculate the average linear velocity and the bulk flow rate of water at 293oK for a cylindrical nanocapillary with diameter 500 nm and length 1 cm. The applied pressure is 5 atm. (The viscosity of water is 9.93×10^{-4} Pa s).

Apply the Hagen-Poiseuille equation for flow in a cylindrical cappillary:

$$v_{avg} = \frac{\int_0^{2\pi} \int_0^R v_z r dr d\theta}{\int_0^{2\pi} \int_0^R r dr d\theta} = \frac{\Delta P R^2}{8 \eta L}$$

In [2]:
```
R = 500./2. * ureg.nanometer;
P = 5. * ureg.atm; P
eta = 9.93*10**-4 * ureg.pascal *ureg.second; eta
L = 1. * ureg.centimeter; L
v = P*R**2/(8*eta*L)
```

In [3]:
```
v.to(ureg.meter / ureg.second)
```

Out[3]: 0.000398590917674 meter/second

The average linear velocity is:

$$v_{avg} = 3.99 \times 10^{-4} \frac{m}{sec}$$

The bulk flow rate is calculated by:

$$Q = \int_0^{2\pi} \int_0^R v_z r dr d\theta = \pi R^2 v_z$$

In [4]:
```
Q = np.pi * R**2 * v; Q.to(ureg.meter**3 / ureg.seconds);
```

The bulk flow rate is:

$$Q = 7.83 \times 10^{-17} \frac{m^2}{sec}$$

Problem 2

Washburn equation for a horizontal capillary can be written in the form: $$ = \frac{dL}{dt}=\frac{\gamma R}{4 \mu L}$$

Derive expression for the time dependencies of the length of travel L(t) and the average velocity of capillary driven fluid motion.

Derive $L(t)$

1. The change in pressure across a gas-liquid interface is given by:
$$\Delta P = \frac{2\gamma}{R}$$
2. Substitue this expression into the Hagen-Poiseuille equation:
$$v_{avg} = \frac{\Delta P R^2}{8\eta L} = \frac{\gamma R}{4\eta L}$$
3. write the average velocity in terms of a differential:
$$v_{avg} = \frac{dL}{dt}$$
4. Integrage this differential equation to obtain an expression for average length of travel (L) as a function of time (t):
$$\int L dL = \frac{\gamma R}{4\eta} \int dt$$
$$\frac{L^2}{2} = \frac{\gamma R t}{4\eta}$$
$$L(t) = \sqrt{\frac{\gamma R t}{2\eta}}$$

Derive $v_{avg}(t)$

Substitue this expression into the expression for average velocity to obtain an expression for velocity (v_{avg}) as a function of time (t):

$$v_{avg}(t) = \frac{\gamma R}{4\eta L} \; v_{avg}(t) \qquad = \frac{\gamma R}{4\eta \sqrt{\frac{\gamma R t}{2\eta}}}$$

Problem 3

The surface tension of pure water at room temperature is equal to 72 mN/m. Calculate the pressure drop at the water surface in a capillary with radius 0.5 mm. Assume perfect wetting of the walls.

In [5]:
```
gamma = 72 * ureg.millinewton / ureg.meter
R = 0.5 * ureg.millimeter
```

Substitute the given values into the Washburn equation:

$$\Delta P = \frac{2\gamma}{R}$$

In [6]:
```
delta_P = 2*gamma/R
delta_P.to(ureg.newton / ureg.meter**2);
```

The pressure drop (ΔP) at the water surface in the capillary is:

$$\Delta P = 288.0\frac{N}{m^2}$$

Problem 4

Using the correct expression for the potential distributions (and low potential approximations), derive relationships for the surface charges at the solid liquid interface for a geometries given below.

The governing equation for the electrostatic potential when assuming low potential is:

$$\nabla^2\psi = \kappa^2\psi$$

Where κ is the inverse Debeye length:

$$\kappa = \left(\frac{e^2 \sum_i z_i^2 n_i^0}{\epsilon\epsilon_0 kT}\right)^{\frac{1}{2}}$$

Low potential approximations may be applied when:

$$\frac{z_i e\psi}{kT} \ll 1$$

where z_i $=$ elementary charge on ion, -1.602×10^{-19}Coulombs e $=$ elementary charge on

The surface charge at a solid-liquid is given by:

$$\sigma = -\epsilon\epsilon_0 \nabla\psi$$

Therefore, for a one-dimenisional flat surface:

$$\sigma = -\epsilon\epsilon_0 \left(\frac{d\psi}{dx}\right)_{x=0}$$

For a one-dimenisional spherical or cylindrical surfaces:

$$\sigma = -\epsilon\epsilon_0 \left(\frac{d\psi}{dr}\right)_{r=R}$$

Boundary conditions on the electrostatic potential(ψ) for flat surfraces are:

$$\psi(x=\infty) = 0 \; \psi(x=0) \qquad = \psi_0$$

And for spherical or cylindrical surfaces:

$$\psi(r=\infty) = 0$$
$$\psi(r=0) = \psi_0$$

single double layer

First, solve for the electrostatic potential via the governing equation: $\frac{d^2\psi}{dx^2} = \kappa^2\psi$

1. rewrite in standard form: $\psi'' - \kappa^2\psi = 0$
2. write the characteristic equation: $m^2 - \kappa^2 = 0$
3. solve for the roots of the characteristic equation:
$$m_n = \pm\frac{\sqrt{4\kappa^2}}{2} = \pm\kappa$$
4. assume a general form of the solution:
$$\psi = C_1 exp(m_1 x) + C_2 exp(m_2 x)$$
5. substitute the roots of the characteristic equation into ψ:
$$\psi = C_1 exp\,(\kappa x) + C_2 exp\,(-\kappa x)$$
6. because of the boundary condition at $x = 0$, we can assume $C_1 = 0$:
$$\psi = C_2 exp\,(-\kappa x)$$
7. solve for C_2 by applying the boundary condition at $x = 0$:
$$\psi = \psi_0 exp(-\kappa x)$$
8. calculate the derivative of ψ :
$$\frac{d\psi}{dx} = \psi_0 \kappa exp(-\kappa x)$$
9. solve for the surface charge by substituting in $\left(\frac{d\psi}{dx}\right)_{x=0}$ into σ:
$$\sigma = -\epsilon\epsilon_0\psi_0\kappa$$

spherical double layer

By following a similar approach as for the single double layer, an equation for the electrostatic potential (ψ) and its derivative are obtained:

$$\psi = \psi_0\frac{exp\,[-\kappa(r-R)]}{r} \quad \left(\frac{d\psi}{dr}\right) \qquad = \frac{-\psi_0(\kappa r + 1)exp\,[-\kappa(r-R)]}{r^2} \quad \left(\frac{d\psi}{dr}\right)_{r=R} = \frac{-(\psi_0\kappa R + \psi_0}{R^2}$$

Therefore, the surface charge (σ) is given by:

$$\sigma = \frac{\epsilon\epsilon_0(\psi_0\kappa R + \psi_0)}{R^2}$$

single cylindrical double layer

The expression for the electrostatic potential (ψ) and its derivative are:

$\psi = \psi_0 \dfrac{K_0(\kappa r)}{K_0(\kappa R)}$ where $K_0(\kappa r)$ is the K_0 Bessel function, which is a function of κr $\left(\dfrac{d\psi}{dr}\right) =$

Therefore, the surface charge (σ) is given by:

$$\sigma = \epsilon\epsilon_0 \frac{\psi_0 \kappa K_1(\kappa R)}{K_0(\kappa R)}$$

slit shaped channel

The expression for the electrostatic potential (ψ) and its derivative are:

$\psi = \psi_0 \dfrac{cosh\left[\kappa\left(\frac{h}{2} - x\right)\right]}{cosh\left[\kappa\frac{h}{2}\right]}$ $\left(\dfrac{d\psi}{dx}\right) = -\psi_0\kappa \dfrac{sinh\left[\kappa\left(\frac{h}{2} - x\right)\right]}{cosh\left[\kappa\frac{h}{2}\right]}$ $\left(\dfrac{d\psi}{dx}\right)_{x=0} = -\psi_0\kappa \dfrac{sinh\left[\kappa\left(\frac{h}{2}\right)\right]}{cosh\left[\kappa\frac{h}{2}\right]}$

Therefore, the surface charge (σ) is given by:

$$\sigma = \epsilon\epsilon_0\psi_0\kappa \frac{sinh\left[\kappa\left(\frac{h}{2}\right)\right]}{cosh\left[\kappa\frac{h}{2}\right]}$$

cylindrical capillary

The expression for the electrostatic potential (ψ) and its derivative are:

$\psi = \psi_0 \dfrac{I_0(\kappa r)}{I_0(\kappa R)}$ where $I_0(\kappa r)$ is the I_0 Bessel function, which is a function of κr $\left(\dfrac{d\psi}{dr}\right) = \dfrac{-\psi}{}$

Therefore, the surface charge (σ) is given by:

$$\sigma = \epsilon\epsilon_0 \frac{\psi_0 \kappa I_1(\kappa R)}{I_0(\kappa R)}$$

Problem 5

A particle is suspended in KCl solution with ionic strength equal to $0.001M$. When subjected to electric field with strength of $2000V/m$ the particle moves with a velocity of $130\mu m/s$. Calculate the ζ-potential at room temperature ($T = 298^o K$) if the particle radius is

In [7]:
```
eta = 0.001 * ureg.pascal * ureg.second # viscosity
E_z = 2000 * ureg.volt / ureg.meter # electric field strength
v_ep = 130 * ureg.micrometer / ureg.second # electrophoresis veloci
ty

e = 1.6021766 * 10**-19 * ureg.coulomb # elementary charge
Na = 6.0223 * 10**23 / ureg.mol #Avogadros number
k_b = 1.3806488 * 10**-23 * ureg.joule / ureg.kelvin # boltzman's c
onstant
C_0 = 0.001 * ureg.mole / ureg.liter #ionic strength (molar concent
ration) (M) of the electrolyte
T = 298 * ureg.kelvin #absolute temperature of electrolyte
epsilon = 78.25 # relative permitivity
epsilon_0 = 8.854*10**-12 * ureg.farad / ureg.meter #permitivity of
free space

kappa_inv = np.sqrt((epsilon * epsilon_0 * k_b * T)/(2* Na* e**2 *
C_0)); # inverse Debye length (lambda)
kappa = 1.0 / kappa_inv
kappa_inv_app = 0.304 / np.sqrt(0.001) #approximate kappa inverse f
or a 1:1 electroly at 298 K in water
```

Evaluate the inverse Debye length (κ):

In [8]:
```
kappa.dimensionality; #check units
kappa.to(1 / ureg.nanometer)
```

Out[8]: 0.104146553262 1/nanometer

Evaluate the dimensionless parameter κR to determine which approximation to use for ζ:

- $\kappa R \gg 1 \implies$ Smoluchowski
- $\kappa R \ll 1 \implies$ Huckel
- $\kappa R \approx 1 \implies$ Henry

a. $500nm$

$\kappa R = (500nm)(0.104nm^{-1}) \approx 52 \implies$ Smoluchowski, $\zeta = \frac{\eta v_{ep}}{E_z \epsilon \epsilon_0}$

In [9]:
```
R = 500. * ureg.nanometer
kR = kappa * R;
zeta = eta * v_ep / (E_z * epsilon * epsilon_0); zeta.to(ureg.volt)
```

Out[9]: 0.0938187177002 volt

zeta potential is 0.0938 volt

b. 1nm

$\kappa R = (1nm)(0.104nm^{-1}) \approx 0.1 \implies$ Huckel,

$$Q = \frac{v_{ep} 6\pi R\eta}{E_z}\zeta \qquad = \frac{Q}{(1+\kappa R)4\pi\epsilon\epsilon_0}$$

In [10]:
```
R = 1 * ureg.nanometer
kR = kappa * R; kR;
Q = v_ep * 6 * np.pi * R * eta / E_z
mu_ep = Q / (6 * np.pi * eta * R)
zeta = mu_ep * 3 * eta / (2 * epsilon * epsilon_0); zeta.to(ureg.vo
lt)
```

Out[10]: 0.14072807655 volt

zeta potential is 0.141 volt

c. $10nm$

$\kappa R = (10nm)(0.104nm^{-1}) \approx 1 \implies$ Henry;

$$zeta = \frac{\mu_{ep} 3\eta\kappa R}{2\epsilon\epsilon_0}\frac{1}{f_1\kappa R} \qquad \text{Ohshima's approximation for } f_1\kappa R:\ f_1\kappa R = 1 + \frac{1}{2\left[1 + \left(\frac{5}{2\kappa R}(1 + 2ex\right.\right.}$$

In [11]:
```
R = 10 * ureg.nanometer
f1kR = 1 + 1 / (2 *(1 + ((5/(2*kappa*R))*(1 + 2 * np.exp(-kappa *
R)))**3)) # Ohshima's expression
mu_ep = v_ep / E_z # electrophoretic mobility
zeta = mu_ep * 3 * eta* kappa * R / (2 * epsilon * epsilon_0 *f1kR)
```

In [12]:
```
zeta.to(ureg.volt)
```

Out[12]: 0.14551899977 volt

zeta potential is 0.146 volt

Problem 6

A cylindrical capillary filled with 0.01 M NaCl solution and has ζ-potential equal to 80 mV. The length of the capillary is 1m and its diameter is 1 mm.

Check the validity of the Smoluchowski model for this dimensions and ionic strength.

The Smoluchowski model is valid when $\kappa R \gg 1$; therefore, check κ and R:

In [13]:
```
R = 1 * ureg.millimeter / 2
R = R.to(ureg.nanometer)
M = 0.01
kappa_inv_app = 0.304 / np.sqrt(M) * ureg.nanometer #approximate ka
ppa inverse for a 1:1 electroly at 298 K in water
kappa = 1./kappa_inv_app; kappa
```

Out[13]: 0.328947368421 1/nanometer

In [14]:
```
kappa * R
```

Out[14]: 164473.684211 dimensionless

$\kappa R \approx 164,000$ which is much greater than 1; therefore, the Smouchowski model is valid

Calculate the electroosmotic linear and volumetric flow rates if a potential difference of 1000 V is applied at both ends.

from Smoluchowski:

$$v_{eo} = -\frac{\epsilon \epsilon_0 \zeta E_z}{\eta}$$

assumed that $\eta = 0.001 Pa - s$, as in Problem 5

In [15]:
```
eta = 0.001 * ureg.pascal * ureg.second # viscosity
E_z = 1000 * ureg.volt / ureg.meter # electric field strength
T = 298 * ureg.kelvin #absolute temperature of electrolyte
zeta = 80 * ureg.millivolt
epsilon = 78.25 # relative permitivity
epsilon_0 = 8.854*10**-12 * ureg.farad / ureg.meter #permitivity of free space

v_eo = - epsilon * epsilon_0 * zeta * E_z / eta; v_eo.dimensionality;
v_eo.to(ureg.meter / ureg.second)
```

Out[15]: -5.542604e-05 meter/second

In [16]:
```
q_eo = v_eo * np.pi * R**2; q_eo.to(ureg.meter**3 / ureg.second)
```

Out[16]: -4.35315100204e-11 meter^3/second

The electroosmotic linear and volumetric flow rates are $-5.54 \times 10^{-5} m/sec$ and $-4.35 \times 10^{-11} m^3/sec$, respectively.