Homework 3

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CBE-521, Fall 2015
Homework No. 1 with Prof. Petsev (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)
```

1 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]:

$$0.000398590917674 \frac{meter}{second}$$

1.1 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);
```

1.2 The bulk flow rate is:

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

2 Problem 2

Washburn equation for a horizontal capillary can be written in the form:

$$< v >= \frac{dL}{dt} = \frac{\gamma R}{4\mu L}$$

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

2.1 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):

$$\int L dL = \frac{\gamma R}{4\eta} \int dt \tag{1}$$

$$\frac{L^2}{2} = \frac{\gamma R t}{4\eta} \tag{2}$$

$$L(t) = \sqrt{\frac{\gamma R t}{2\eta}} \tag{3}$$

2.2 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):

$$v_{avg}(t) = \frac{\gamma R}{4\eta L} \tag{4}$$

$$v_{avg}(t) = \frac{\gamma R}{4\eta \sqrt{\frac{\gamma R t}{2\eta}}} \tag{5}$$

3 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:

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

4 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:

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

Low potential approximations may be applied when:

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

$$\begin{aligned}
&\text{where} && (6)\\
z_i &= \text{elementary charge on ion, } -1.602 \times 10^{-19} \text{Coulombs} && (7)\\
e &= \text{elementary charge on proton, } 1.602 \times 10^{-19} \text{Coulombs} && (8)\\
\psi &= \text{electrostatic potential} && (9)\\
k &= \text{Boltzman constant} && (10)\\
T &= \text{absolute temperature} && (11)
\end{aligned}$$

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:

$$\psi(x = \infty) = 0 \tag{12}$$
$$\psi(x = 0) = \psi_0 \tag{13}$$

And for spherical or cylindrical surfaces:

$$\psi(r = \infty) = 0 \tag{14}$$
$$\psi(r = 0) = \psi_0 \tag{15}$$

4.1 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:
$$\psi = C_1 exp\left(\kappa x\right) + C_2 exp\left(-\kappa x\right)$$
6. because of the boundary condition at $x = 0$, we can assume $C_1 = 0$:
$$\psi = C_2 exp\left(-\kappa x\right)$$
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:
$$\sigma = -\epsilon\epsilon_0\psi_0\kappa$$

4.2 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:

$$\psi = \psi_0 \frac{exp\left[-\kappa(r-R)\right]}{r} \tag{16}$$

$$\left(\frac{d\psi}{dr}\right) = \frac{-\psi_0(\kappa r+1)exp\left[-\kappa(r-R)\right]}{r^2} \tag{17}$$

$$\left(\frac{d\psi}{dr}\right)_{r=R} = \frac{-(\psi_0\kappa R+\psi_0)}{R^2} \tag{18}$$

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

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

4.3 single cylindrical double layer

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

$$\psi = \psi_0 \frac{K_0(\kappa r)}{K_0(\kappa R)} \tag{19}$$

where $K_0(\kappa r)$ is the K_0 Bessel function, which is a function of κr (20)

$$\left(\frac{d\psi}{dr}\right) = \frac{-\psi_0 K_1(\kappa r)\kappa}{K_0(\kappa R)} \tag{21}$$

$$\left(\frac{d\psi}{dr}\right)_{r=R} = \frac{-\psi_0\kappa K_1(\kappa R)}{K_0(\kappa R)} \tag{22}$$

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

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

4.4 slit shaped channel

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

$$\psi = \psi_0 \frac{cosh\left[\kappa\left(\frac{h}{2}-x\right)\right]}{cosh\left[\kappa\frac{h}{2}\right]} \tag{23}$$

$$\left(\frac{d\psi}{dx}\right) = -\psi_0\kappa \frac{sinh\left[\kappa\left(\frac{h}{2}-x\right)\right]}{cosh\left[\kappa\frac{h}{2}\right]} \tag{24}$$

$$\left(\frac{d\psi}{dx}\right)_{x=0} = -\psi_0\kappa \frac{sinh\left[\kappa\left(\frac{h}{2}\right)\right]}{cosh\left[\kappa\frac{h}{2}\right]} \tag{25}$$

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

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

4.5 cylindrical capillary

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

$$\psi = \psi_0 \frac{I_0(\kappa r)}{I_0(\kappa R)} \tag{26}$$

$$\text{where } I_0(\kappa r) \text{ is the } I_0 \text{ Bessel function, which is a function of } \kappa r \tag{27}$$

$$\left(\frac{d\psi}{dr}\right) = \frac{-\psi_0 I_1(\kappa r)\kappa}{I_0(\kappa R)} \tag{28}$$

$$\left(\frac{d\psi}{dr}\right)_{r=R} = \frac{-\psi_0 \kappa I_1(\kappa R)}{I_0(\kappa R)} \tag{29}$$

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

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

5 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 velocity

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 constant
C_0 = 0.001 * ureg.mole / ureg.liter #ionic strength (molar concentration) (M) of the electroly
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 lengt
kappa = 1.0 / kappa_inv
kappa_inv_app = 0.304 / np.sqrt(0.001) #approximate kappa inverse for a 1:1 electroly at 298 K
```

Evaluate the inverse Debye length (κ):

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

Out[8]:

$$0.104146553262 \frac{1}{nanometer}$$

Evaluate the dimensionless parameter κR to determine which approximation to use for ζ: - $\kappa R >> 1 \implies$ Smoluchowski - $\kappa R << 1 \implies$ Huckel - $\kappa R \approx 1 \implies$ Henry

5.1 a. 500 nm

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

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

5.2 b. 1nm

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

$$Q = \frac{v_{ep} 6\pi R\eta}{E_z} \tag{30}$$
$$\zeta = \frac{Q}{(1+\kappa R)4\pi\epsilon\epsilon_0} \tag{31}$$

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.volt)
```

Out[10]:

$$0.14072807655 volt$$

zeta potential is 0.141 volt

5.3 c. $10nm$

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

$$zeta = \frac{\mu_{ep} 3\eta\kappa R}{2\epsilon\epsilon_0}\frac{1}{f_1\kappa R} \tag{32}$$
$$\text{Ohshima's approximation for } f_1\kappa R: \tag{33}$$
$$f_1\kappa R = 1 + \frac{1}{2\left[1 + \left(\frac{5}{2\kappa R}(1+2exp(-\kappa R))\right)^3\right]} \tag{34}$$

In [11]:
```
R = 10 * ureg.nanometer
f1kR = 1 + 1 / (2 *(1 + ((5/(2*kappa*R))*(1 + 2 * np.exp(-kappa * R)))**3)) # Ohshima's expres
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

6 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.

6.1 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 kappa inverse for a 1:1 elect
kappa = 1./kappa_inv_app; kappa
```

Out[13]:

$$0.328947368421 \frac{1}{nanometer}$$

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

6.2 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]:

$$-5.542604e-05 \frac{meter}{second}$$

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

Out[16]:

$$-4.35315100204e-11 \frac{meter^3}{second}$$

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.