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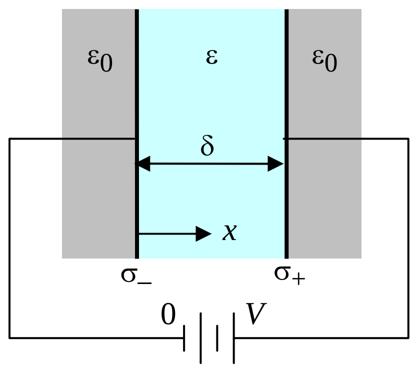
DC Polarization of Planar Electrodes Separated by Low-Dielectric Fluid

In this Note, we review the derivation of the equations used by Jun Kim *et al. Langmuir* **21**, 8620 (2005).

Capacitance with Neutral Fluid



Consider a parallel plate capacitor consisting of two parallel plates, located at x=0 and at x=δ. The fluid in between the plates has permittivity ε while the plates themselves have permittivity ε_0. Suppose we apply a voltage drop V between the two plates. What charge will accumulate on the plates at steady state after any electrical current has subsided?

Assuming that $\mathbf{E} = E_x(x)\mathbf{e}_x$ and no free charges in any of the media [i.e. $\rho(x) = 0$], then Gauss's equation [see (12) in Electrostatics of Continuous Media.doc]* becomes

$$\frac{dE_x}{dx} = 0 \qquad \text{or} \qquad E_x(x) = \text{const} = -V/\delta \tag{1}$$

The value of the integration constant is set by the boundary conditions on the electrostatic potential. Assuming that V>0, this means that E_x is pointing in the –x direction. From (anti-)symmetry (or overall electroneutrality), we expect that equal but opposite surface charge densities arise on the two surfaces:

$$\sigma_- = -\sigma_+$$

$\sigma_- > 0$ and $\sigma_+ < 0$ if V>0. The electric field outside the two surfaces vanishes according to EofCM-(8) and (9):

for x<0 or x>δ: $\qquad E_x(x) = 0$

The magnitude of the charge density is related to the electric field strength by EofCM-(7):

$$E_x = \frac{\sigma_- - \sigma_+}{2\varepsilon} = \frac{-\sigma_+ - \sigma_+}{2\varepsilon} = -\frac{\sigma_+}{\varepsilon} \tag{2}$$

* Files referred to in this document can be found online at http://www.andrew.cmu.edu/user/dcprieve/Notes/.

Eliminating E_x between (1) and (2): $\sigma_+ = \frac{\varepsilon V}{\delta}$

The ***capacitance*** of the device is defined as the charge separated per unit area per unit voltage applied:

$$c = \frac{\sigma_+}{V} = \frac{\varepsilon}{\delta}$$

Capacitance with Thin Double Layers

Jun uses the differential capacitance calculated from the Gouy-Chapman model. The surface charge density in the Gouy-Chapman model is given by [see (16) from Electrohydrodynamics.doc]:

$$\sigma = \frac{2\kappa\varepsilon kT}{ze}\sinh\left(\frac{ze\psi_0}{2kT}\right) \tag{3}$$

The differential capacitance is defined as

$$c_{dl} = \frac{d\sigma}{d\psi} = \frac{ze}{2kT}\frac{2\kappa\varepsilon kT}{ze}\cosh\left(\frac{ze\psi_0}{2kT}\right) = \underbrace{\kappa\varepsilon}_{c_{dl}^0}\cosh\left(\frac{ze\psi_0}{2kT}\right) \tag{4}$$

In particular, Jun used the differential capacitance corresponding to $\psi_0 \to 0$:

$$c_{dl}^0 = \kappa\varepsilon \tag{5}$$

Comparing (5) with (3), we see that the differential capacitance from the Gouy-Chapman theory corresponds to an apparent plate spacing equal to the Debye length: $\delta = \kappa^{-1}$.

The rationale for using the differential capacitance to interpret Jun's experiments is not obvious, although it seems like a good guess. Below we develop a model for slow changes in current during polarization of the double layers.

Slow Polarization of Thin Double Layers

Suppose in the absence of any applied voltage, the electrodes are not charged. Following a step application of voltage V across the electrodes, separated by distance δ (see sketch on page 1), the initial current density is given by Ohm's law as

$$i_x = KE_x = -\frac{KV}{\delta}$$

In the absence of any Faradaic reaction to convert ionic charge to electronic charge, electric current causes charges to build up next to the electrode at a rate given by

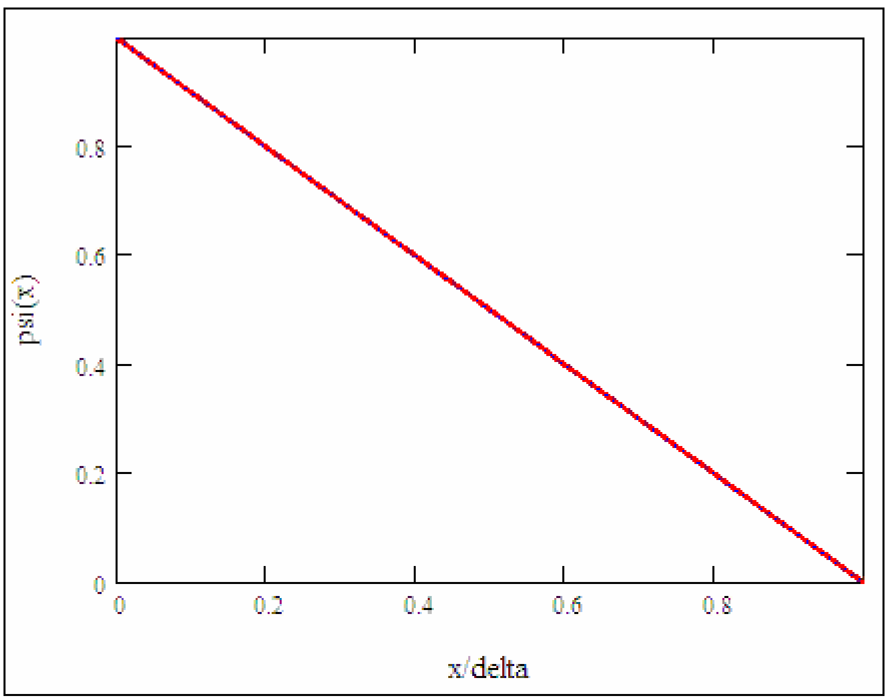
$$\frac{d\sigma_+}{dt} = i_x \tag{6}$$

Once a diffuse layer of charge builds up, a potential drop across the layer occurs which reduces the electric field in the electrically neutral bulk solution, and therefore a decay in the current density. The potential drop is given ψ_0 by (3) and the resulting current is given by

$$i_x = -\frac{K}{\delta}\left(V + 2\psi_0\right) \tag{7}$$

The sign of ψ_0 will generally be opposite to the sign of V, which explains adding ψ_0 instead of subtracting; the factor of 2 arises because we have two layers of charge, one next to either electrode.

The graph below is an animation intended to convey how the electrostatic potential profile between two parallel plate electrodes evolves with time as polarization of the counterion clouds proceeds.* The initial state is unpolarized (maximum current) and the final state is completely polarized (zero current).



Now we continue with the analysis of the dynamics. Substituting (3) and (7) into (6):

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* If clicking on this figure does not start animation, go to website http://www.andrew.cmu.edu/user/dcprieve/Notes/ and click on Polarization.avi.

$$\underbrace{\frac{d\sigma_+}{d\psi_0}}_{c_{dl}}\frac{d\psi_0}{dt} = -\frac{K}{\delta}\left(V + 2\psi_0\right) \tag{8}$$

or
$$\frac{d\psi_0}{dt} + \frac{2K}{\delta c_{dl}}\psi_0 = -\frac{KV}{\delta c_{dl}}$$

If we assume that the differential capacitance c_{dl} is constant (which would occur is ψ_0 remains small), then this equation can be integrated to give a general solution of

$$\psi_0(t) = A\exp\left(-\frac{2Kt}{\delta c_{dl}^0}\right) - \frac{V}{2}$$

If the initial potential vanishes, then the particular solution is

$$\psi_0(t) = \frac{V}{2}\left[\exp\left(-\frac{2Kt}{\delta c_{dl}^0}\right) - 1\right]$$

This predicts that ψ_0 decays from 0 to $-V/2$ with a decay time of

$$\tau = \frac{\delta c_{dl}^0}{2K}$$

Indeed this is exactly Jun's model (although the derivation is not presented in Jun's paper).

Since $V/2$ is not usually small, we expect that these simple dynamics are not valid except possibly near the beginning of the decay. Using (4) in (8) instead of a constant c_{dl}, we have

$$\underbrace{\underbrace{\kappa\varepsilon}_{c_{dl}^0}\cosh\left(\frac{ze\psi_0}{2kT}\right)}_{c_{dl}}\frac{d\psi_0}{dt} + \frac{2K}{\delta}\left(\psi_0 + \frac{V}{2}\right) = 0$$

Unfortunately, this ODE is <u>not</u> linear. Dividing by $2K/\delta$:

$$\underbrace{\frac{\delta c_{dl}^0}{2K}}_{\tau}\cosh\left(\frac{ze\psi_0}{2kT}\right)\frac{d\psi_0}{dt} + \psi_0 + \frac{V}{2} = 0$$

and multiplying by $ze/2kT$:

$$\tau \cosh\left(\frac{ze\psi_0}{2kT}\right)\frac{d}{dt}\left(\frac{ze}{2kT}\psi_0\right)+\frac{ze}{2kT}\left(\psi_0+\frac{V}{2}\right)=0$$

or in dimensionless form:

$$\cosh y\frac{dy}{dt'}+y+V'=0 \tag{9}$$

where $y \equiv \dfrac{ze\psi_0}{2kT}$ $t' \equiv \dfrac{t}{\tau}$ and $V' \equiv \dfrac{zeV}{4kT}$

Initially the diffuse layer is not polarized but the surfaces might still bear a nonzero zeta potential. So as a more general initial condition, let's impose

$$y(0) = y_0$$

As $t'\to\infty$, $dy/dt' \to 0$ and (9) yields $y(\infty) = -V'$

Let $u = y + V'$ so that $dy = du$

and $\cosh y = \cosh(u - V') \equiv f(u)$

Then (9) becomes

$$f(u)\frac{du}{dt'}+u=0$$

which is now a first-order separable ODE. The transformed initial condition is

$$u(0) = y_0 + V'$$

Separating

$$f(u)\frac{du}{u}=-dt'$$

Integrating $\displaystyle\int_{u(0)}^{u(t')}\frac{f(u)}{u}du=-t'$ or $\displaystyle\int_{u(t')}^{u(0)}\frac{f(u)}{u}du=t'$

Substituting $f(u)$, we can write this as

$$\int_{u(t')}^{y_0+V'}\frac{\cosh(u-V')}{u}du=t' \tag{10}$$

We are interested in how the current decays with time. The current is given by (7).

$$i_x=-\frac{K}{\delta}\left(V+2\psi_0\right)=-\frac{K}{\delta}\frac{4kT}{ze}\left(V'+y\right)=-\frac{4KkT}{\delta ze}u$$

Dividing by the initial value: $$\frac{i_x(t)}{i_x(0)} = \frac{u}{u_0}$$

As $t'\to\infty$, $y \to -V'$ and $u \to 0$. The integral in (10) is singular in this limit owing to the zero in the denominator. One way to deal with this is to add and subtract one in the numerator:

$$\int_{u(t')}^{u_0} \frac{\cosh(u-V')}{u} du = \int_{u(t')}^{u_0} \frac{\cosh(u-V')-1}{u} du + \int_{u(t')}^{u_0} \frac{du}{u}$$
$$= \ln\frac{u_0}{u(t')} + \int_{u(t')}^{u_0} \frac{\cosh(u-V')-1}{u} du$$

As $u\to0$, the integral converges to some constant (call it $\ln A$) while the logarithm continues to grow. Then exponentiating both sides of (10) yields

as $t'\to\infty$: $$A\frac{u_0}{u(t')} = e^{t'} \quad \text{or} \quad u(t') \to \frac{u_0}{A} e^{-t'}$$

The graph below (computed by numerical integration) confirms this behavior, but the time required to reach this limit grows exponentially with u_0.

n := last(t)   i := 0, 1.. n   j := 0.. 2   n = 12

u0 = 5.8 $to\tau_{i,j}$:= tfn$(u0, IoI0_{i,j})$ $\tau J := (0.68\ \ 1.04\ \ 1.77)^T$

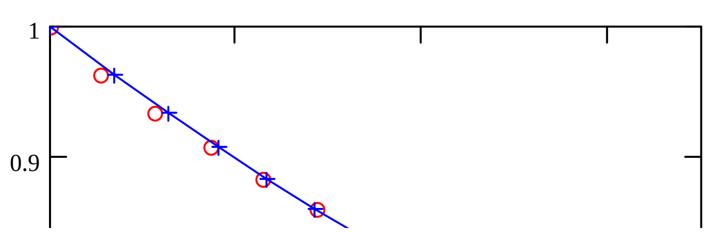
J := 2

$\tau := \tau J_J$ $\tau = 1.77$

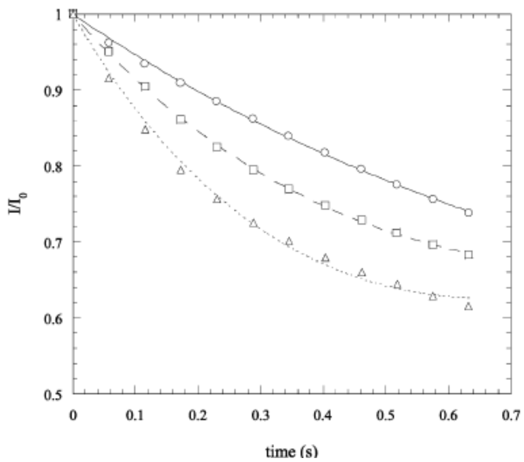
$$SSE(\tau, u0) := \sum_i \left(\tau \cdot tfn(u0, IoI0_{i,J}) - t_i\right)^2$$

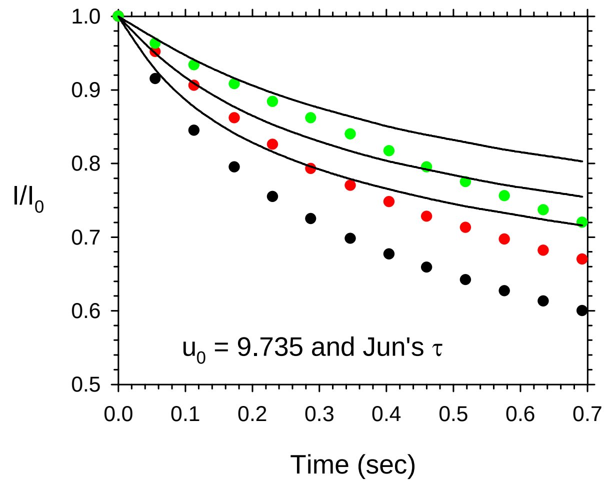
$$\begin{pmatrix}\tau\\ u0\end{pmatrix} := Minimize(SSE, \tau, u0)$$ $\tau = 1.859$

u0 = 3.085



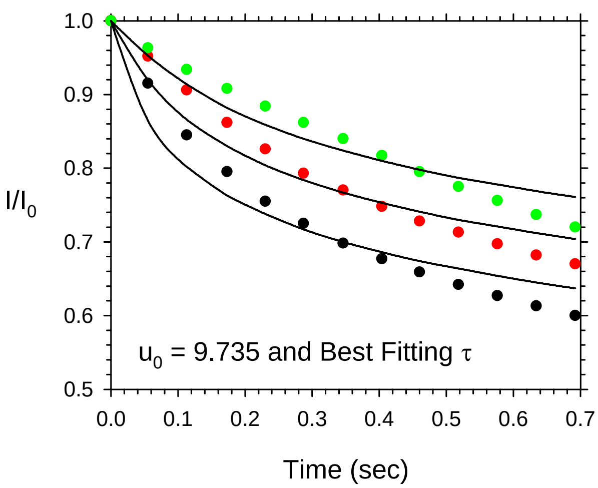
Below is Jun's experimental data for V = 1 volt applied across a gap of δ = 190 nm. Assuming z=1, we convert V=1 volt into V' = 19.47 and u_0 = 9.735. The second parameter is τ and in the above plot, we used the values reported by Jun.

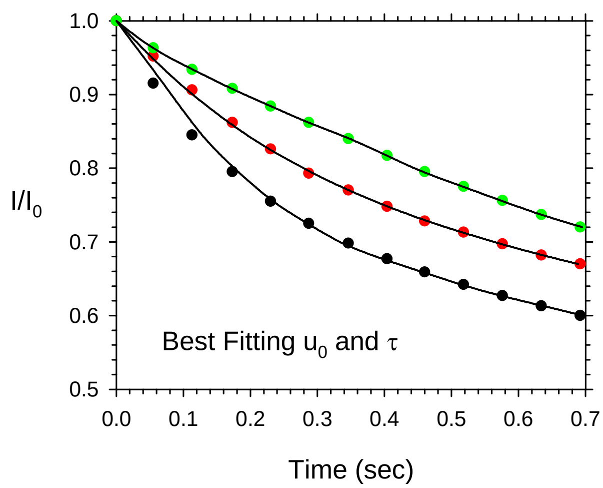




The solid curves in the figure on the right, which are predicted from (10), are not very good fits to the experimental data points. Of course, Jun used a different fitting function (having a more arbitrary functional form) to obtain the good fits shown on the left.

Below are best fits of (10) to Jun's data. On the left, we have set u_0 = 9.735 and varied τ to give the best fit. The functional form is not quite right: the solid lines display more upward curvature than the experimental data, regardless of τ. Thus (10) underestimates I/I_0 at short times and overestimates them at long times. The best-fitting τ (see table below figures) is about half of Jun's values for each concentration of OLOA. In the figure on the right, we have varied both u_0 and τ to obtain the best fit. The fits are much better using τ's close to those used by Jun; however the best fitting value of u_0 is substantially less than 9.735.





	1-parameter fit (τ only)			2-parameter fit (u_0 and τ)	
wt% OLOA	u_0	τ_{Jun} (sec)	τ_{best} (sec)	u_0	τ (sec)
0.5	9.735	1.77	0.866	3.09	1.86

1.57	9.735	1.04	0.467	5.35	1.03
3.63	9.735	0.68	0.216	5.71	0.594