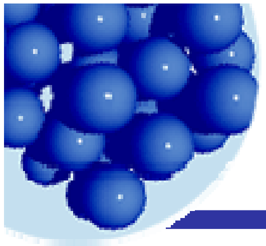
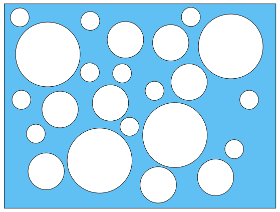
The stability of thin (soft) films

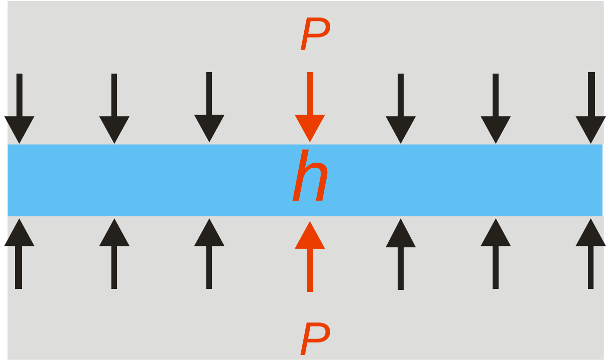
Lecture 3 – Electrostatic effects
November 6, 2009



Review of Lecture 1



The disjoining pressure is a jump in pressure at the boundary. It does not vary between the plates.



$$\Pi(h) = -\frac{1}{A}\frac{\partial G}{\partial h}\bigg|_{T,P,\sigma_1,\sigma_2,N_i}$$

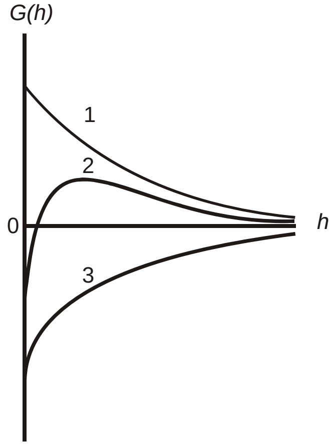
Force between 2 spheres:

$$F_{s-s}(y) \cong \frac{2\pi R_1 R_2}{R_1 + R_2}\int_y^\infty \Pi(h)\,dh$$

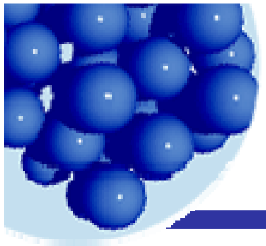
$$\Pi(h) = -\frac{\partial G(h)}{\partial h}$$

$$G(0) = \sigma_{s0} - \sigma_{sl} - \sigma_{lv} = S$$

$$G(\infty) = 0$$



Curve 1 – Stable
Curve 2 – Metastable
Curve 3 - Unstable



Review of Lecture 2

$$\Pi(h) = -\frac{1}{A}\frac{\partial G}{\partial h}\bigg|_{T,P,\sigma_1,\sigma_2,N_i}$$

$$dG = -S^s dT + \sum_{i=1,r} \mu_i dN_i^s + A\left(\Psi_1 d\sigma_1 + \Psi_2 d\sigma_2\right) - A\Pi dh$$

$$dG' = -S^s dT - \sum_{i=1,r} N_i^s d\mu_i - A\left(\sigma_1 d\Psi_1 + \sigma_2 d\Psi_2\right) - A\Pi dh$$

$$\Pi = \frac{1}{A}\int_h^{\infty}\left(\frac{\partial N_i^s}{\partial h}\right)_{\mu_i,\ldots,\Psi_1,\Psi_2} d\mu_i$$

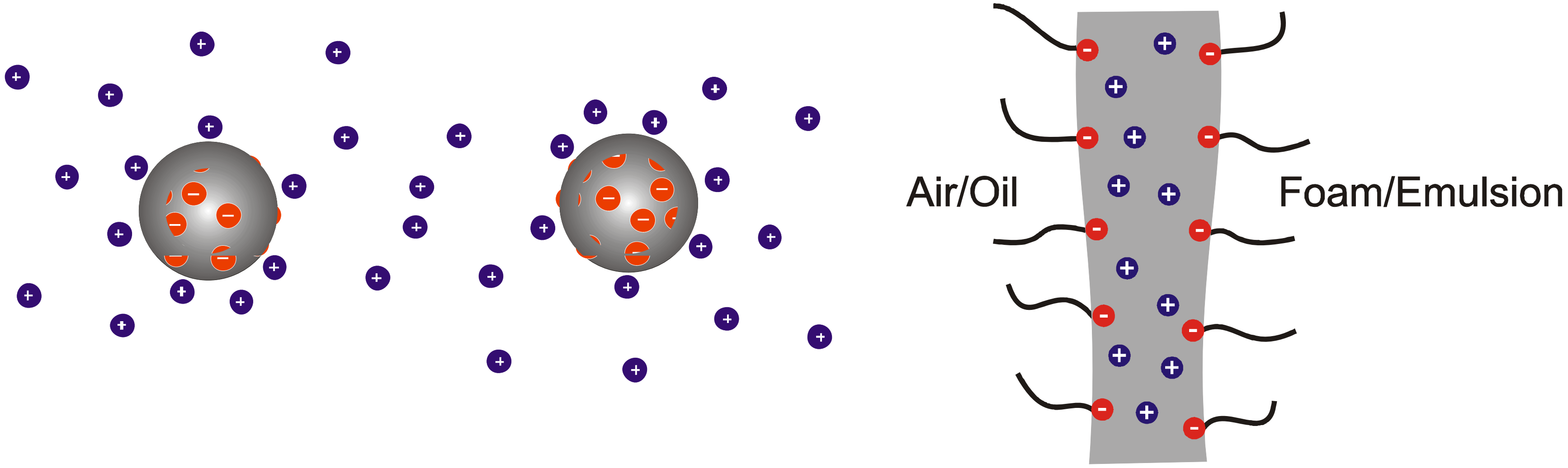
is a ‘modified” Gibbs equation.

$$\left(-d\sigma = \sum \frac{n_i^\sigma}{A} d\mu_i = \sum \Gamma_i d\mu_i\right)$$

$$\frac{N_i^s}{A} - \Gamma_i = A\int_h^{\infty}\left(\frac{\partial \Pi}{\partial \mu_i}\right)_{h,\ldots} dh$$

is the excess adsorption due to disjoining pressure. Note that we do not know how much excess is on either plate!

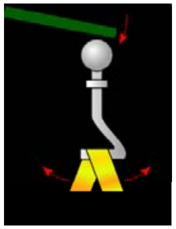
Electrostatic repulsion in thin films



Loosely held countercharges form “electric double layers” next to each surface. The concentration of ions is determined by a balance between the attraction to the surface and kinetic energy.

Electrostatic repulsion results from the interactions of ions around each surface.

The overlap of the electrical double layers is the (electrical component of) disjoining pressure.

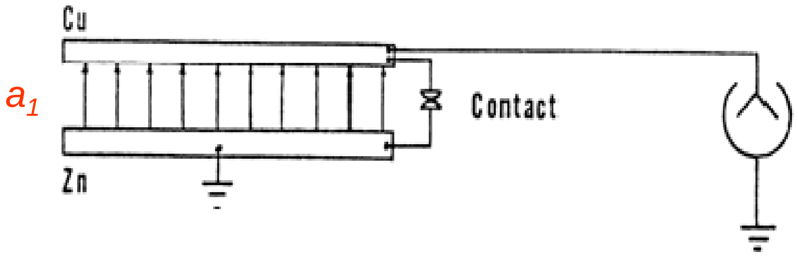


http://en.wikipedia.org/wiki/Electrometer

Contact potentials - 1

> “In a paper of May 21, 1897 (Royal Institution of Great Britain) Lord Kelvin described a demonstration experiment that invites some thoughts, based on hindsight, about the connection between constant potentials and the voltage of galvanic cells.” R.M. Lichtenstien in *Nineteenth-Century Attitudes: Men of Science*, Ross, S. **1991**.

Build a capacitor with two parallel plates of dissimilar metals, say copper and zinc. Ground the zinc plate ground. Isolate the copper plate. Connect the copper plate to the ‘high’-terminal of a (high impedance) electrometer.



$$Ea_1 = \Gamma_{Zn,Cu}$$

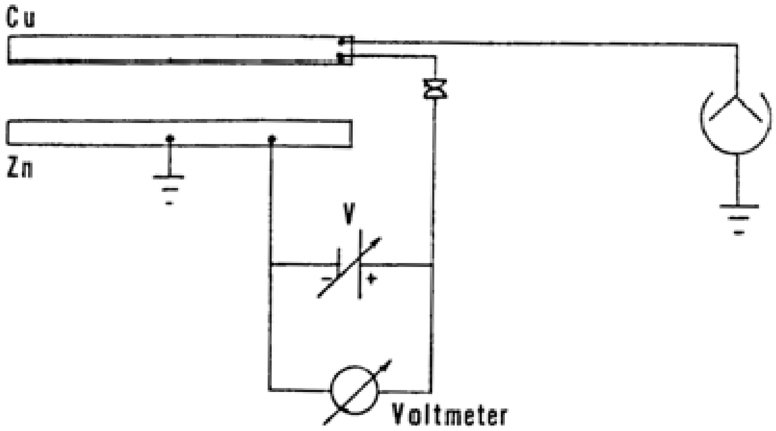
When the plates are moved from contact (at *a*1) to *a*2, the electrometer reads a potential change:

$$E\left(a_2 - a_1\right) = \Gamma_{Zn,Cu} \frac{\left(a_2 - a_1\right)}{a_1}$$

n.b. The contact between plates is broken $a_2 > a_1$

Contact potentials - 2

$$E\left(a_2 - a_1\right) = \Gamma_{Zn,Cu} \frac{\left(a_2 - a_1\right)}{a_1}$$



The experiment can be altered slightly to use Kelvin's null method.

The electric potential at contact is now $Ea_1 - V = \Gamma_{Zn,Cu} - V$

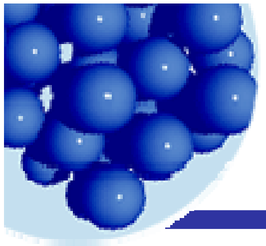
When the copper plate is raised to a2, the electrometer will show the reading

$$\left(E - \frac{V}{a_1}\right)\left(a_2 - a_1\right) = \left(\Gamma_{Zn,Cu} - V\right)\left(\frac{a_2 - a_1}{a_1}\right)$$

n.b. The contact between plates is broken $a_2 > a_1$

Repeated measurements determines the null potential and hence the contact potential:

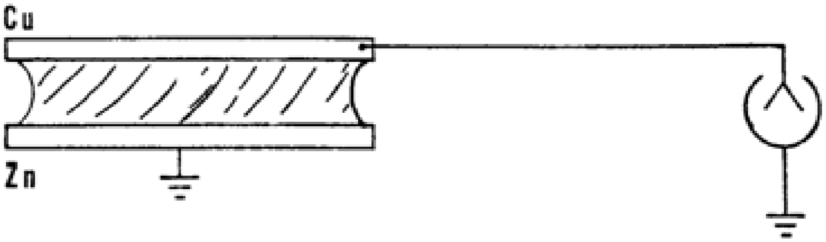
$$\Gamma_{Zn,Cu} = V_{null}$$



Now a remarkable experiment!.

Contact potentials - 3

The dry metallic contact of
is replaced by a wet contact



Before the copper plate is raised the electrometer no longer indicates the metallic zero but a new value, which Kelvin called the electrolytic zero.

Kelvin raised the copper plate, so that the water drop would break, and continued to raise it. The remarkable effect was that the electrometer started and remained at its electrolytic zero! This means there are no field lines across the gap! And ….

$$\Gamma_{Zn,Cu} = \text{ voltage of the cell } Cu / water - drop / Zn$$

Dry contact: Has electric field, but “no” current, **hence no power.**

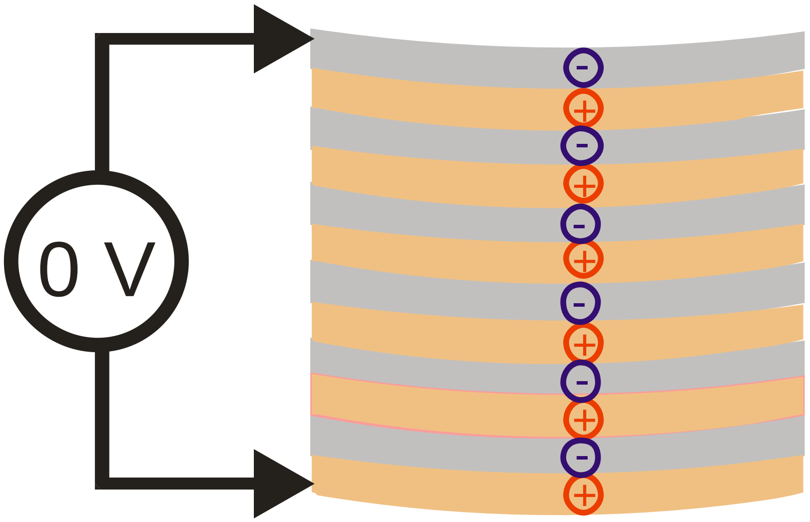
Wet contact: No electric field but has voltage, hence has current, **hence some power**.

How do you get a lot of power?

Lots of power? Make a battery! How?

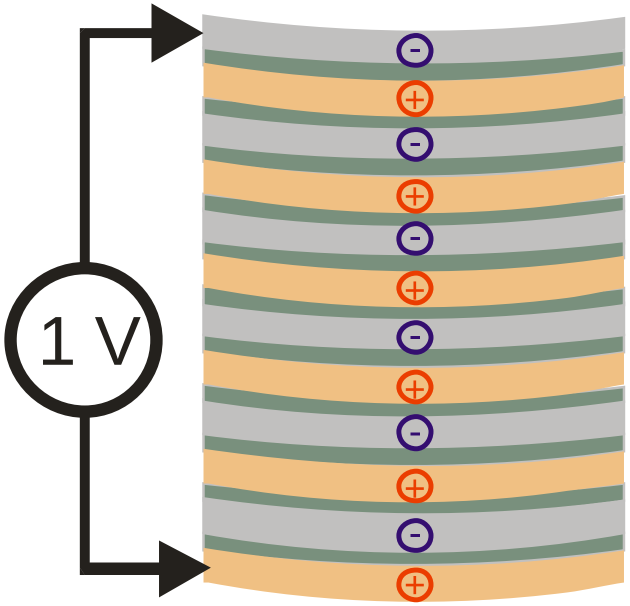
Rubbing or touching two surfaces, say Cu and Zn,
produces some useful power, but not much.

Alternating Cu/Zn plates,
with dry contact.



NDG

Alternating Cu/Zn plates,
with wet contacts.



Equal to just one Cu/Zn set.

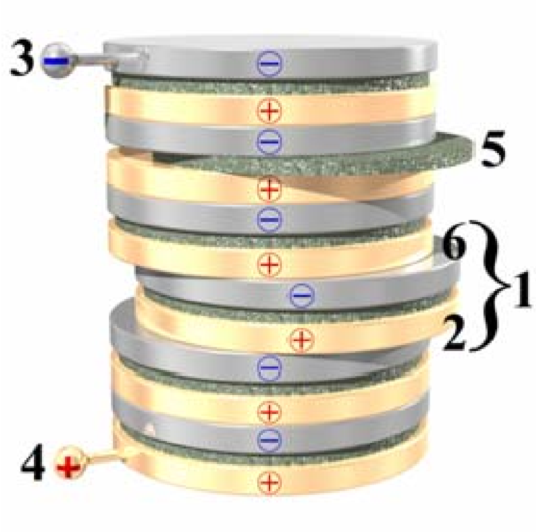
*R.M. Lichtenstien in *Nineteenth-Century Attitudes: Men of Science*, Ross, S. **1991**.

The Voltaic pile

Bottom - *Cu/wet/Zn/dry/Cu/wet/Zn/dry/…Cu/wet/Zn/dry/Cu* – Top

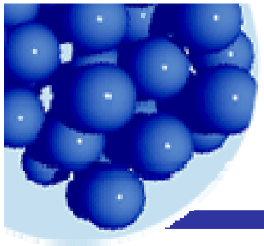
The Voltaic pile has *n* wet contacts and *n* dry contacts

The voltage between the top and the bottom is *n* times the voltage of a single wet contact, $V_{Cu/wet/Zn}$.



There are no voltages across the dry contacts; there are electric fields, all aligned in the same direction.
There are voltages across the wet contacts; there are no electric fields.

Physics in the dry contacts, chemistry in the wet contacts.



Ions near a charged surface - 1

Adsorbed ions determine the surface potential, Φ_0. The counterions (valence z_i) form a diffuse cloud near the surface.

The Guoy-Chapman model assumes the surface potential is uniform and the counterions are point charges.

The concentration of ions, n_i, depends on concentration of ions far from the surface, n_{i0}, and the local electric potential, $\Phi(x)$:

$$n_i = n_{i0} \exp\left(-\frac{z_i e \Phi(x)}{kT}\right)$$

The local charge density, ρ, depends on the charges and the concentrations of ions.

$$\rho = \sum z_i e n_i = \sum z_i e n_{i0} \exp\left(-\frac{z_i e \Phi}{kT}\right)$$

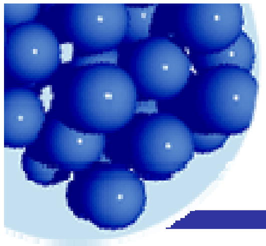
The Poisson equation relates the local charge density to the Laplacean of the electric potential.

$$\nabla^2 \Phi = -\frac{\rho}{D\varepsilon_0}$$

Hence the Poisson-Boltzmann equation, a differential equation to solve with boundary conditions for potential as a function of distance.

$$\nabla^2 \Phi = -\frac{1}{D\varepsilon_0} \sum z_i e n_{i0} \exp\left(-\frac{z_i e \Phi}{kT}\right)$$

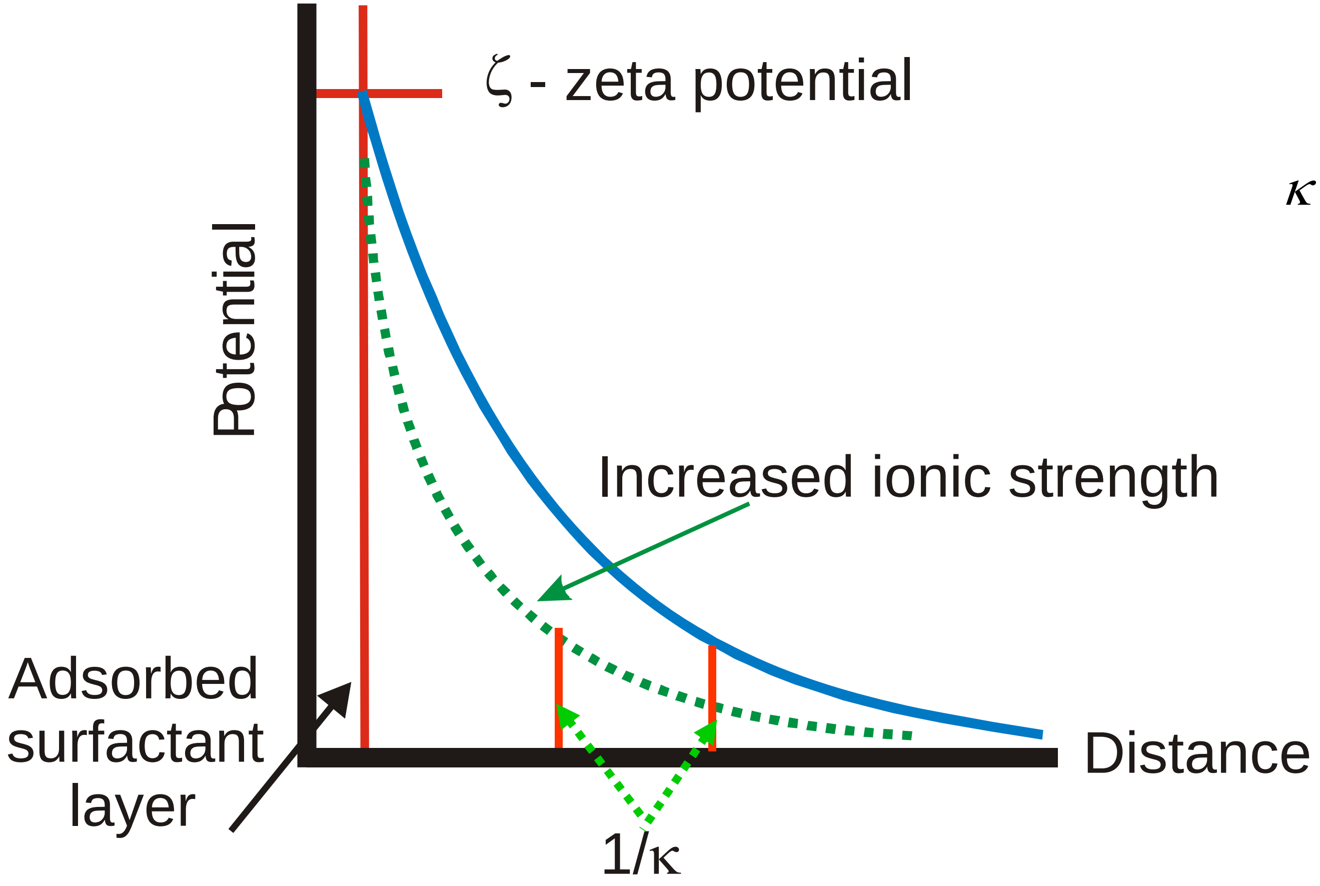
$$\nabla^2\Phi = -\frac{\rho}{D\varepsilon_0}$$



Ions near a charged surface - 2

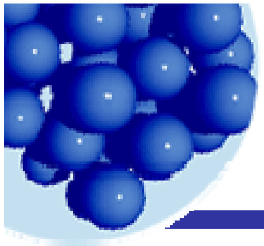
$$\nabla^2\Phi = \kappa^2\Phi \qquad \Phi = \zeta\exp(-\kappa x)$$

(The surface potential is the zeta potential.)



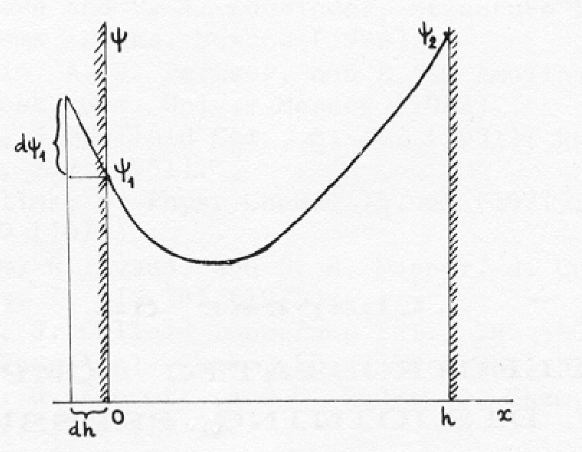
$$\kappa = \sqrt{\frac{e^2\sum_i c_i z_i^2}{D\varepsilon_0 kT}}$$

$$I = \frac{1}{2}\sum_i c_i z_i^2$$



$$\sigma_{ij} = \varepsilon_0 E_i E_j + \frac{1}{\mu_0} B_i B_j - \frac{1}{2}\left(\varepsilon_0 E^2 + \frac{1}{\mu_0} B^2\right)\delta_{ij} \qquad dG = -SdT + VdP - \sum_{i=1}^{r} N_i d\mu_i - A\sum_{j}^{plates} \sigma_j d\Psi_j - A\Pi dh$$

Electrostatic component of disjoining pressure* (1)



Internal field gradients between two flat plates. External walls are assumed to have same potentials as inner. Derjaguin, **1987**, Fig. 6.1.

(1) The disjoining pressure is the excess Maxwell stresses between the field gradients inside (E_h) and the field gradients outside (E_0).

$$\Pi(h) = \frac{\varepsilon}{2}\left(E_h^2 - E_o^2\right)$$

But the gradients are unknown!

(2) Thermodynamics gives:

$$\left.\frac{\partial \Pi}{\partial \psi_1}\right|_{h,\psi_2} = \left.\frac{\partial \sigma_1}{\partial h}\right|_{\psi_1,\psi_2}$$

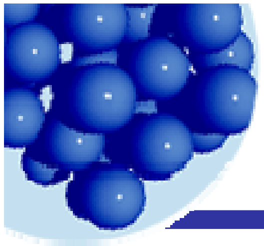
(3) To find the RHS, use the *P-B* equation:

$$-\varepsilon \frac{d^2\psi}{dh^2} = \rho = \sum_i z_i e n_{i0} \exp\left(-\frac{z_i e\psi}{kT}\right)$$

(4) A bit of differential analysis gives:

$$\Pi(h) = -\int_0^{\Psi} \rho(\Psi)\, d\Psi - \frac{\varepsilon}{8\pi}\left(\frac{d\Psi}{dh}\right)^2$$

For symmetric surfaces, the second term is zero at mid-gap.



Electrostatic component of disjoining pressure (2)

First try: same potential on each plate; binary electrolytes.

where $\phi_m = \frac{ze}{kT}\psi_m$ (at the midplane)

$$\Pi(h) = 2kTn\left(\cosh\left[\phi_m(h)\right] - 1\right)$$

and $\left.\frac{d\phi}{dh}\right|_{h=m} = 0$

Manipulating the P-B equation produces:

$$\frac{\kappa h}{2} = \int_{\Phi_m}^{\Phi_0} \frac{d\Phi}{\sqrt{2\left(\cosh\Phi - \cosh\Phi_m\right)}}$$

These two equations give $\Pi(h)$ parametrically through ϕ_m.

For the approach of surfaces at constant potential, Φ_0 is constant.

For the approach of surfaces at constant surface charge density Φ_0 is:

$$\sigma_s = \frac{2zen}{\kappa}\sqrt{2\left(\cosh\Phi_0 - \cosh\Phi_m\right)}$$

(With considerable algebra involving elliptical integrals.)

Electrostatic component of disjoining pressure* (3)

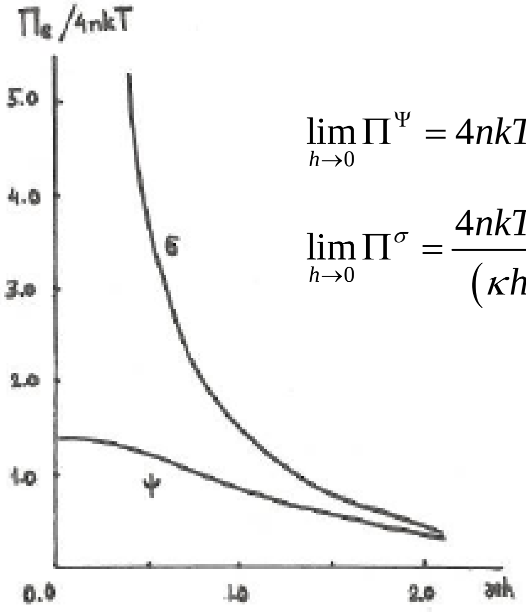
Constant surface potential or constant surface charge?

If two surfaces approach each other and surface potential remain constant, the charge per unit area must decrease. Ions must either adsorb or desorb!

If two surfaces approach each other and the surface charge remain constant (no ion adsorption or desorption), the electric potential must increase!

Disjoining pressure as a function of κ*h* in a symmetrical electrolyte at constant potential (lower curve) and constant surface charge (upper curve).

The difference in behavior is huge!



$$\lim_{h\to 0} \Pi^{\Psi} = 4nkT\sinh^2\left(\frac{\Psi_0}{2}\right)$$

$$\lim_{h\to 0} \Pi^{\sigma} = \frac{4nkT\pi^2}{(\kappa h)^2}$$

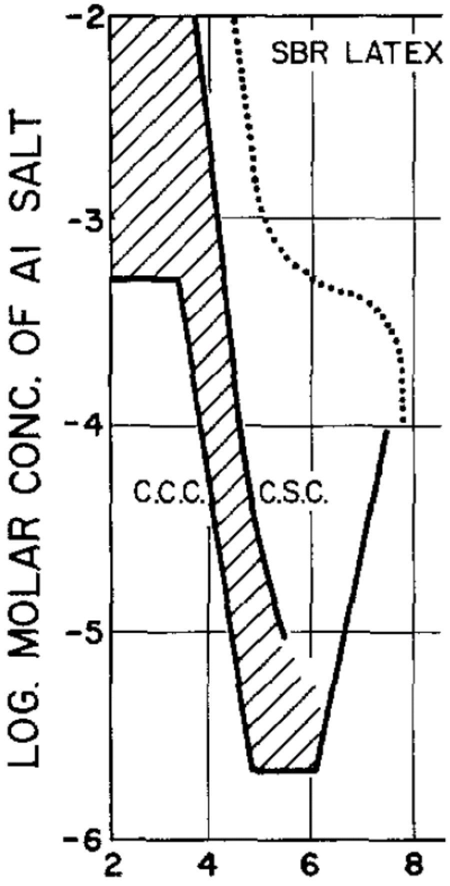
*Following Derjaguin, **1987**, pp. 181 – 183.

Complex ions – phase diagram

Stability domains as a function of $Al(NO_3)_3$ or $AlCl_3$ concentration and pH for styrene-butadiene rubber (SBR).

Shaded area designates the coagulation region; below the *c.c.c.* line the sols remain stable, above the c.s.c. line the sols are restabilized due to charge reversal.

(. . . .) The formation of aluminum hydroxide precipitate in the absence of sol particles.



Matijevic’, *JCIS*, *43*, 217, **1973**.