

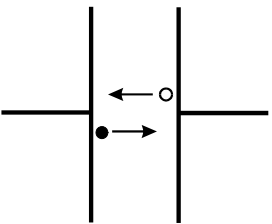
Session 3: The Physics of Imaging

- Capacitance-Resistance model
- Mechanical model
- Bistability of the image
- Chemical model
- The Canonical internal phase
- Imaging with dual particles

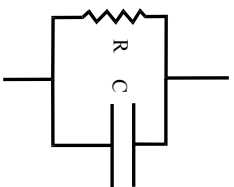
Ian Morrison
Cabot Corporation

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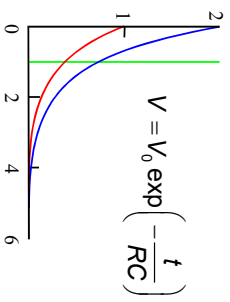
The Capacitance-Resistance Model



Internal Phase



Electrical Model



Exponential decay
with characteristic
time: RC

V = voltage

V_0 = applied voltage

R = resistance

C = capacitance

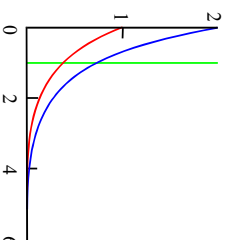
t = time

But ...

- “RC” is independent of voltage and gap
- Switching depends on absolute change in voltage not percent change.

- Therefore “RC” is not directly related to the switching time.

$$\begin{aligned} RC &= \frac{\text{gap}}{\text{conductivity}} \cdot \frac{\text{dielectric constant}}{\text{gap}} \\ &= \frac{D\epsilon_0}{\lambda} \\ &\sim \frac{2.2 \times 8.854 \times 10^{-12} \text{CV}^{-1}\text{m}^{-1}}{50 \times 10^{-12} \Omega^{-1}\text{cm}^{-1}} \\ &\sim 4 \text{ msec} \end{aligned}$$



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D = dielectric constant

ϵ_0 = permittivity of free space

λ = conductivity

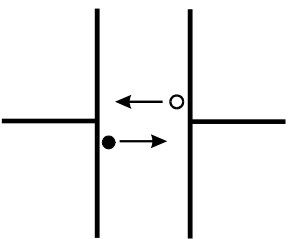
And

The characteristic time “RC” is also not directly related to important internal phase properties such as:

- Particle size
- Particle charge
- Capsule thickness
- Voltage
- Rheology

A Mechanical Model:

First order approximation.



$$v = \mu E = \frac{\mu V}{d}$$

$$v = \frac{d}{t}$$

$$\therefore t = \frac{d^2}{\mu V}$$

$$\mu = \frac{q}{6\pi\eta a}$$

$$\therefore t = \frac{6\pi\eta a d^2}{qV}$$

The characteristic time, t , is directly related to the viscosity, the particle radius, the gap, the particle charge, and the applied voltage as expected.

v = particle velocity

μ = particle electrophoretic mobility

E = electric field

d = gap

t = time

V = applied voltage

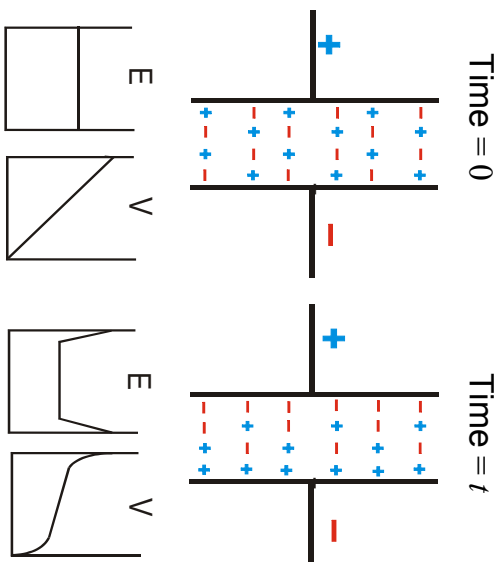
q = charge on particle

η = viscosity of medium

a = particle radius

The blocking electrode and space charge

In nonpolar systems, ions build up at electrodes.



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E = electric field

V = voltage

A Mechanical Model:

Second order approximation – in progress

Variables: The concentration of positive charges, negative charges, and the electric field as a function position and time.

$$\rho_+(x,t) \quad \rho_-(x,t) \quad E(x,t)$$

Relationships between the variables:

$$\begin{aligned}\frac{\partial E}{\partial x} &= \frac{\rho_+ + \rho_-}{D} \\ \frac{\partial \rho_+}{\partial t} &= -\frac{\partial}{\partial x} \mu_+ \rho_+ E \\ \frac{\partial \rho_-}{\partial t} &= -\frac{\partial}{\partial x} \mu_- \rho_- E\end{aligned}$$

Initial conditions: Depend on the problem.

Boundary conditions: No loss or gain of charge at electrodes.

$\rho_+(x,t)$ = the concentration of positive species at position, x , and time, t
 $\rho_-(x,t)$ = the concentration of negative species at position, x , and time, t

$E(x,t)$ = the electric field at position, x , and time, t

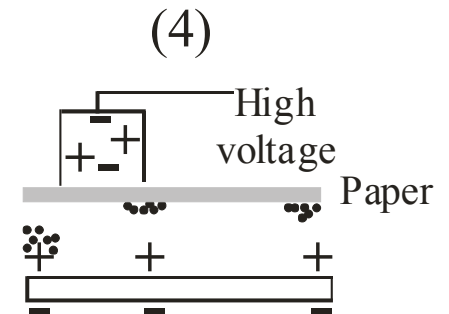
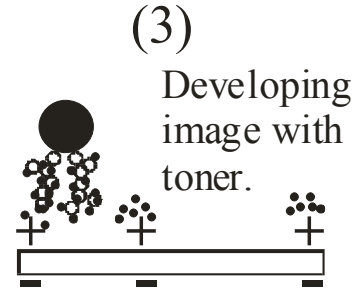
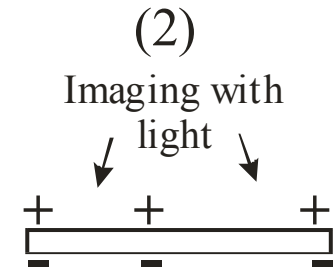
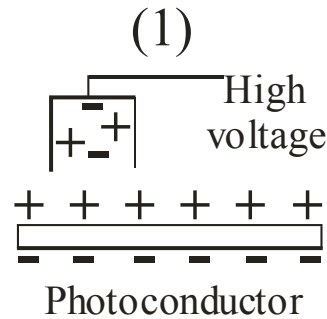
D = dielectric constant (times permittivity of free space)

μ_+ = electrophoretic mobility of positive species

μ_- = electrophoretic mobility of negative species

Steps of the xerographic cycle - dry development

“Complete” models for development including space charge effects have been published in the xerographic literature.

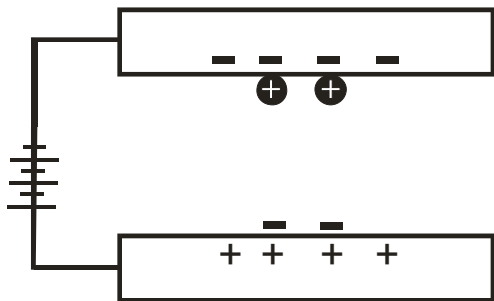


A Mechanical Model:

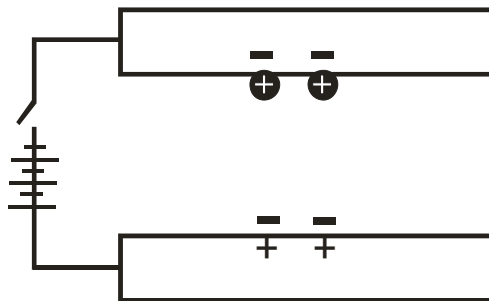
Third order approximation

- Co-ions.
- Field-dependent electrophoretic mobilities.
- Field-dependent conductivity
- Charge injection and electrochemistry at the electrodes.
- Etc.

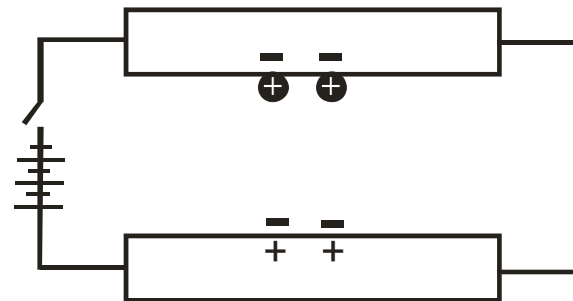
The bistability of the image



An applied voltage plates the particles.



When the voltage is removed, the charged particles are held against the electrode by their image charges.



The electric field is zero outside the particles and their image charges. Shorting the electrodes does not release the particles.

Bistability is possible when no charge is injected from the electrodes and ions do not diffuse between the particle and the electrode – common conditions for nonaqueous dispersions.

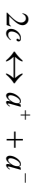
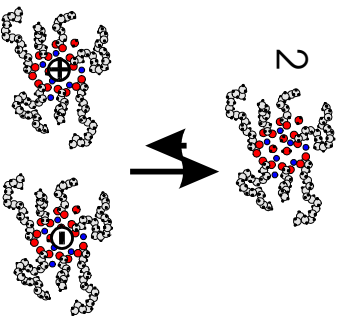
Bistability by other means

- Particle-particle or particle-wall adhesion
- Structures in fluid (particles or a wide variety of polymer gels)
- “Inverse” electrorheological fluids
- Field dependence of zeta potential
- AC electric fields – time dependencies

A Chemical Model:

- The concentration of electric charge in nonpolar liquids is low.
- The ions are charged “micelles” created by disproportionation between micellar cores.
- Particles are charged by disproportionation of surface sites with micellar cores.
- The rates and equilibria are described by simple kinetics, thermodynamics and acid-base scales.

Creation of charged micelles:



$$K_{eq} = \frac{a^+ a^-}{c^2} = \frac{\alpha n_m \alpha n_m}{(1-2\alpha)^2 n_m^2} = \frac{\alpha^2}{(1-2\alpha)^2}$$

$$n_0 = 2[\alpha n_m]$$

$$\lambda = \mu n_0 = 2\mu\alpha n_m \approx 2\mu K_{eq}^{1/2} n_m$$

c = concentration of uncharged micelles

a^+ = concentration of positive micelles

a^- = concentration of negative micelles

K_{eq} = equilibrium constant for micelle charging

n_m = total concentration micelles, charged and uncharged

α = degree of charging

n_0 = concentration of charged micelles

λ = solution conductivity

μ = electrophoretic mobility of charged micelles

Thermodynamics of ionization

Calculate the enthalpy, ΔH^0 , from the temperature dependence of the viscosity and conductivity.

Calculate the free energy, ΔG^0 , from the micelle size, the viscosity, conductivity, charge per micelle, and concentration of micelles.

Calculate the entropy, ΔS^0 , from the enthalpy and the free energy.

$$\lambda = 2q\mu K_{eq}^{1/2} n_0 \text{ and } \mu = \frac{q}{6\pi\eta a}$$

gives

$$K_{eq} = \left[\frac{\lambda}{2q\mu n_0} \right]^{1/2} = \left[\frac{3\pi a\eta\lambda}{q^2 n_0} \right]^{1/2}$$

From

$$\frac{\partial \log K_{eq}}{\partial(1/T)} = -\frac{\Delta H^0}{R}$$

and assuming that the number, size, and charge of micelles are independent of temperature:

$$\Delta H^0 = \frac{-R}{2} \left[\frac{\partial \log \eta}{\partial(1/T)} + \frac{\partial \log \lambda}{\partial(1/T)} \right]$$

also

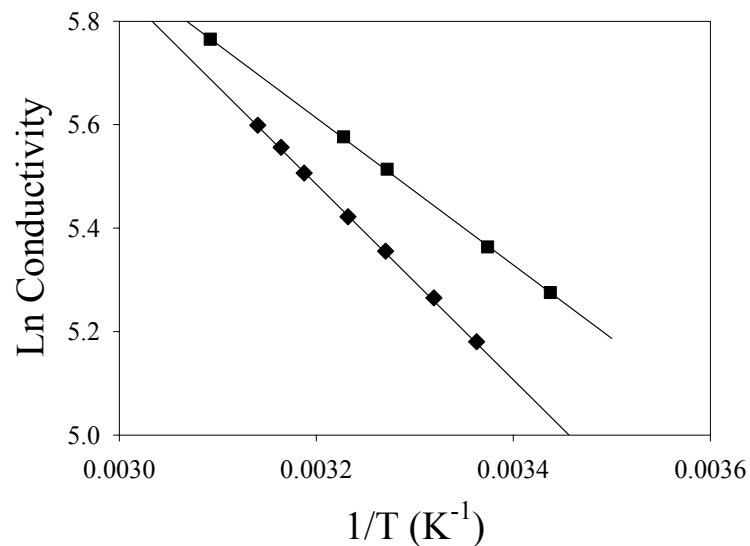
$$\Delta G^0 = -RT \log K_{eq} = -RT \log \left[\frac{3\pi a\eta\lambda}{q^2 n_0} \right]^{1/2}$$

and

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}$$

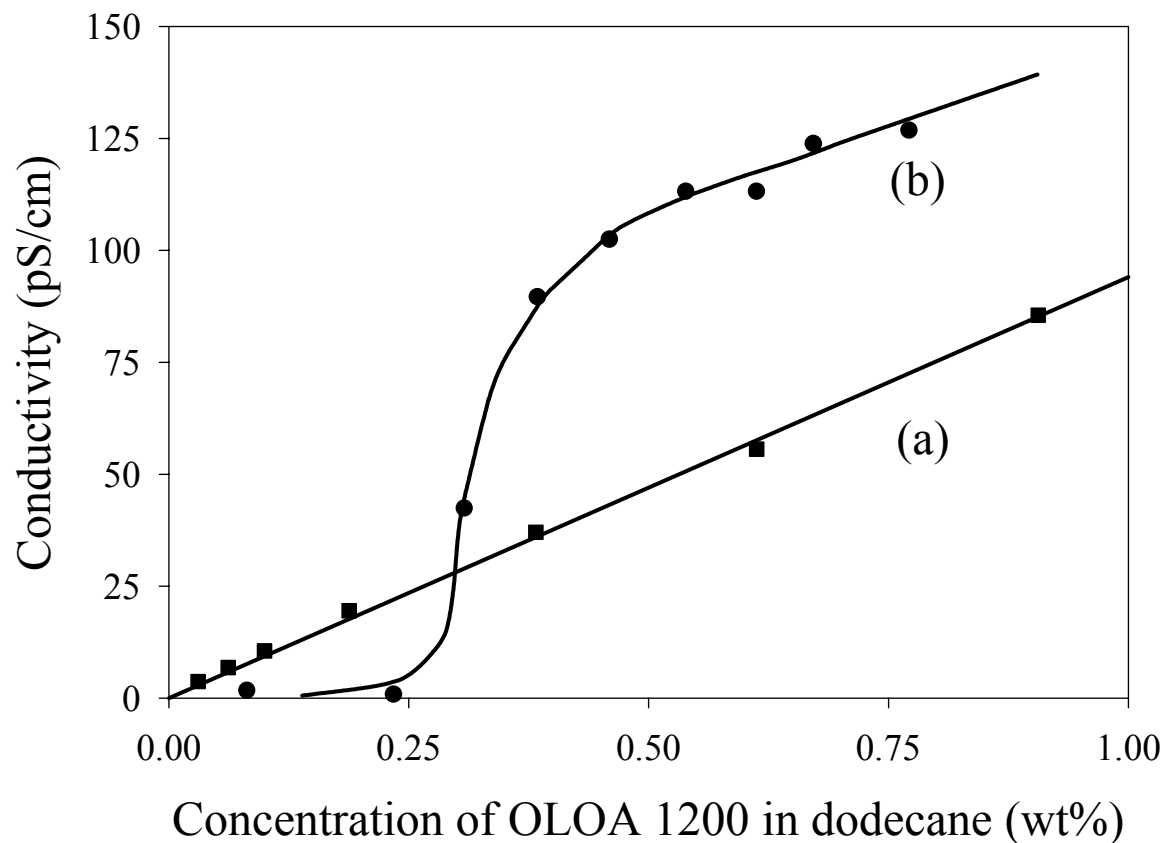
Thermodynamics from “viscosity”

Neutral Ba-petronate in Isopar-L



Function (kcal/mol)	Neutral Ba-petronate in Isopar-L	Lecithin in Isopar-H
ΔH^0	1.6	3.9
ΔG^0	5.2	7.8
$T\Delta S^0$	-3.6	-3.9

Charging equilibria with particles



A simple model of particle charging

- The micelles are in equilibrium with each other: $K1 = \frac{M^+ \cdot M^-}{M^2}$
- Micelles are adsorbed by the surface:
$$K2 = \frac{SM}{M \cdot S}$$
- Some micelles charge exchange with the surface:
$$Kch = \frac{M^+ \cdot S^-}{M \cdot S}$$
- The number of micelles is constant, the number of surface sites (occupied or not) is conserved, and the system is electrically neutral. (3 equations)
- A system of 6 simultaneous equations whose solutions are the roots of 6th order polynomials.

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$K1$ = equilibrium constant for micelle charging

M^+ = concentration of positive micelles

M^- = concentration of negative micelles

M = concentration of uncharged micelles

$K2$ = equilibrium constant of micelle adsorption

SM = concentration of surface sites occupied by micelles

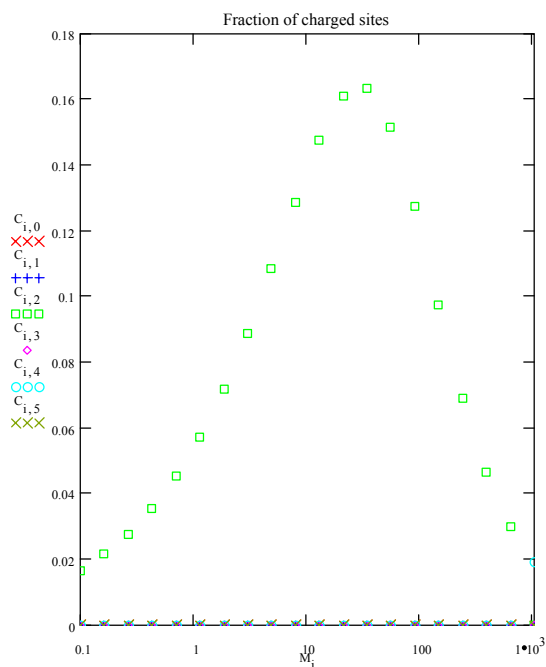
S = concentration of surface sites

Kch = equilibrium constant for surface charging

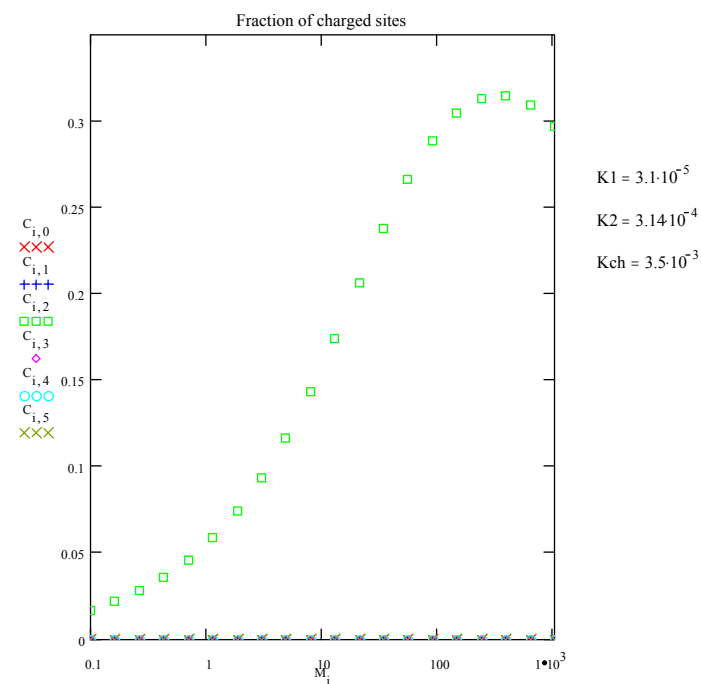
S^- = concentration of negatively charged surface sites

Modeling along.

Fraction of sites charged vs micelle concentration



Arbitrary choice.



Less adsorption of
Neutral micelles.

A Canonical internal phase

- Only use as much pigment per unit area as necessary for the reflectivity.
- Use all the applied charge to move the particles to the viewing surface.

A Canonical IP

The number of particles per unit volume is the mass per unit area divided by the volume of each particle times the density times the gap:

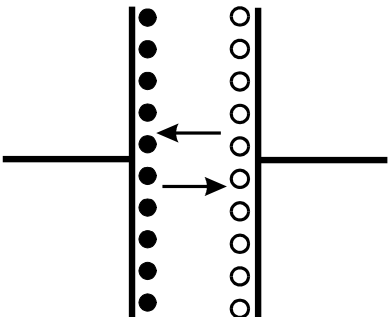
$$n_0 = \frac{M}{\frac{4}{3}\pi a^3 \rho L_s}$$

The charge per unit area is the capacitance times the applied voltage:

$$Q = \frac{DV_0}{L_s}$$

The charge on each particle is the charge per area divided by the number of particles times the gap:

$$q = \frac{DV_0}{n_0 L_s^2}$$



n_0 = number of particles per unit volume

M = mass of particles per unit area (to form an image)

a = radius of particle

ρ = density of particle

L_s = gap

Q = charge per unit area (supplied to make the image)

D = dielectric constant

V_0 = applied voltage

q = charge per particle

A few useful relations: *for the simplest cases.*

The zeta potential of the particles: $\zeta = \frac{q}{4\pi D a}$

The conductivity: $\lambda = 2\mu n_0 q$

Material constants: $M = 8 \times 10^{-3} \frac{\text{kg}}{\text{m}^2}$

$$\eta = 2 \times 10^{-3} \text{ Pa} \cdot \text{s}$$

$$D = 2.2 \times 8.854 \times 10^{-12} \text{ C} \cdot \text{V}^{-1} \cdot \text{m}^{-1}$$

$$L_s = 4 \times 10^{-5} \text{ m}$$

$$\rho = 3.9 \times 10^3 \frac{\text{kg}}{\text{m}^3}$$

ζ = zeta potential

q = charge per particle

D = dielectric constant

a = radius of particle

λ = conductivity of solution

μ = electrophoretic mobility of the particles

n_0 = number of charged particle per unit volume

q = charge per particle

Scaling Relations:

The voltage is:

$$V_0 = \frac{3\zeta M L_s}{\rho a^2}$$

The characteristic time is:

$$t = \frac{3\eta L_s^2}{2D\zeta V_0}$$

An interesting relation is:

$$tV_0 = \frac{3\eta L_s^2}{2D\zeta}$$

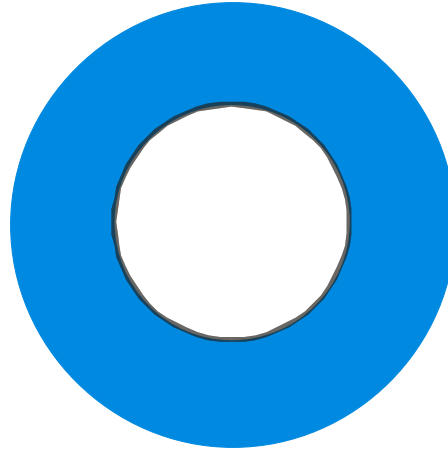
Particle size effect

For 20V across a 40 micron capsule:

Radius (μm)	Transit time (s)
0.3	1.7
0.5	0.61
1.0	0.15
2.0	0.04

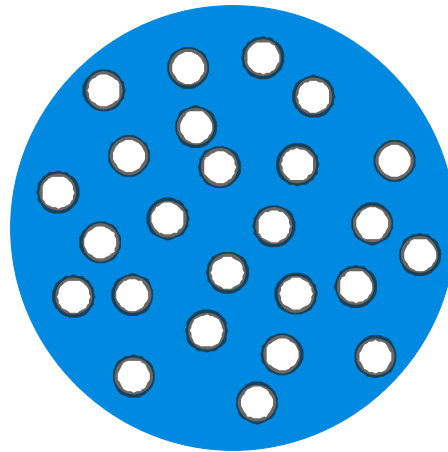
Particle Morphology

Not:



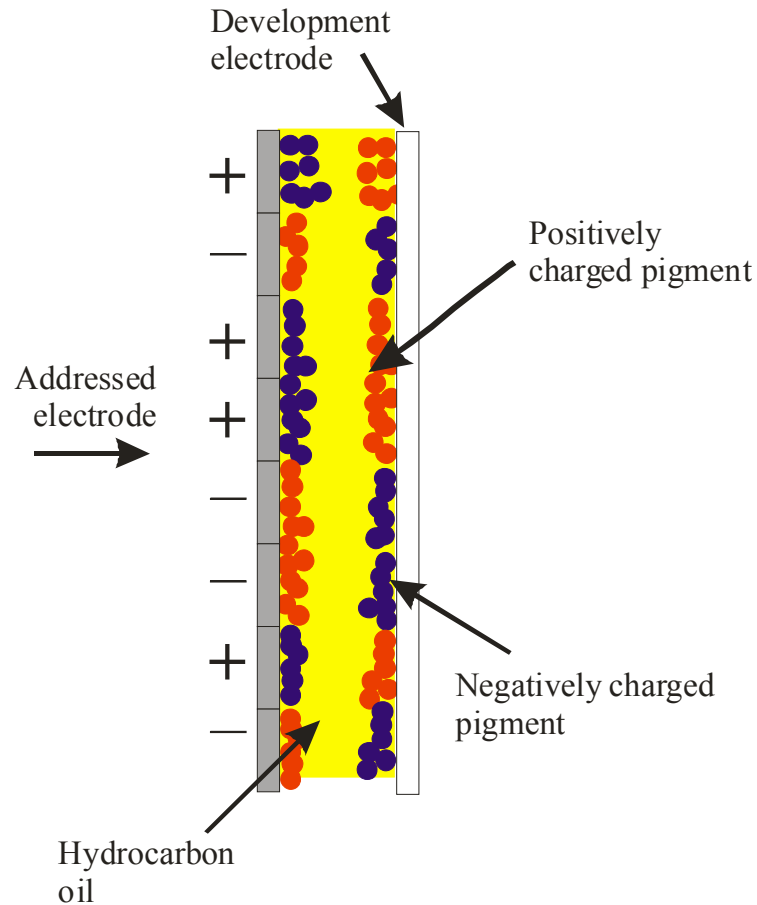
Large TiO₂ particle
With grafted polymer.

But:



0.3 micron TiO₂
particles at 30 percent
by volume in a
polymer matrix.

Imaging with dual particles



How to image with flocculated particles

The field necessary to separate charged particles is:

$$Field^{separation} = \frac{Force^{total}}{|q_1 - q_2|} = \frac{Force^{vdw} + Force^{elec}}{|q_1 - q_2|}$$

n.b. The force varies with the product of particle charges, but the field also varies with the difference.

Practical considerations set an upper limit of about 0.5 V/ μm .

A steric barrier is necessary to limit the maximum attractive force.

The approach

- Take the minimum necessary steric thickness as the independent variable.
- Calculate the **force** between particles as a function of distance.
- Determine the distance between particles that just equals the applied electric field.
- Calculate the energy of particles at that distance.
- Calculated how much closer the particles can come before the energy increases by kT .
- Half of that distance is the minimum steric barrier.

Dispersion force attraction

The usual van der Waals attraction:

$$\text{Energy}^{vdw} = \frac{-A_{121}}{6} \left[\frac{2a_1a_2}{R^2 - (a_1 + a_2)^2} + \frac{2a_1a_2}{R^2 - (a_1 - a_2)^2} + \ln \left[\frac{R^2 - (a_1 + a_2)^2}{R^2 - (a_1 - a_2)^2} \right] \right]$$

The force is the derivative with respect to R :

$$\text{Force}^{vdw} = \frac{32}{3} A_{121} a_1^3 a_2^3 \frac{R}{(R^2 - a_1^2 - 2a_1a_2 - a_2^2)^2 (R^2 - a_1^2 + 2a_1a_2 - a_2^2)^2}$$

A_{121} = Hamaker (Lifshitz) constant for the particles (1) in medium (2)

a_1 = radius of particle (1)

a_2 = radius of particle (2)

R = center to center distance between particles

Electrostatic energies and forces

Two charged spheres at low conductivity:

$$Energy^{elec} = \frac{q_1 q_2}{4\pi D_{\epsilon_0} R} \exp \left[- \left(\frac{2e^2 n_0}{D_{\epsilon_0} k T} \right)^{1/2} (R - a_1 - a_2) \right]$$

The force is the derivative with respect to R :

$$Force^{elec} = - \left[\frac{1}{R} + \left(\frac{2e^2 n_0}{D_{\epsilon_0} k T} \right)^{1/2} \right] E^{elec}$$

The particles are oppositely charged so the energy becomes more negative as they approach and the force becomes more positive.

q_1 = charge on particle (1)

q_2 = charge on particle (2)

D = dielectric constant

ϵ_0 = permittivity of free space

R = center to center distance between particles

e = charge on an electron

n_0 = number of charged ions (micelles) per unit volume

k = Boltzmann constant

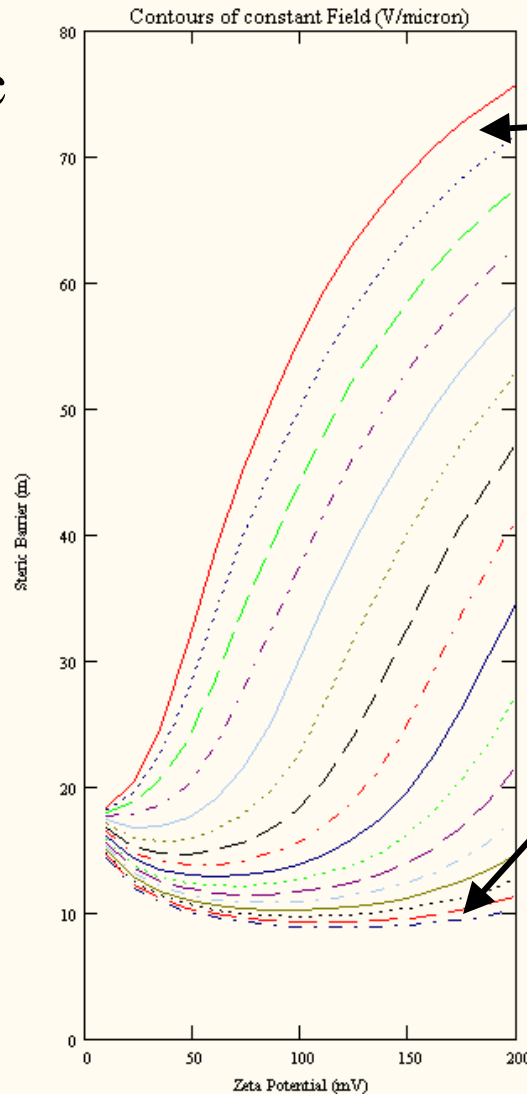
T = absolute temperature

a_1 = radius of particle (1)

a_2 = radius of particle (2)

Requirements on steric barrier

For low electric field, the necessary thickness increases with particle charge.



	0
0	0.01
1	0.023
2	0.035
3	0.048
4	0.061
5	0.073
6	0.086
7	0.099
8	0.111
9	0.124
10	0.137
11	0.149
12	0.162
13	0.175
14	0.187
15	0.2

EMax =

At high field, the necessary thickness decreases with particle charge.