Electrovariable liquid interfaces for optical applications: structure and dynamics

by

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A thesis submitted in partial fulfillment for the degree of Doctor of Philosophy in the Faculty of Natural Sciences Department of Chemistry

January 2012
Declaration of Originality

I herewith certify that all material in this dissertation which is not my own work has been properly acknowledged.

Signed: Monica Marinescu

Date: January 2, 2012


The material presented in Chapter 6 has been partially published in Marinescu M, Urbakh M, Barnea T, Kucernak A R and Kornyshev A A J. Phys. Chem. C (2010).


Abstract

Due to their versatility, liquid/liquid interfaces are currently of great interest for a variety of optical applications, such as variable-focus lenses, microfluidics, optical switches and display elements. This thesis explores the properties of the electrified interface between two immiscible electrolytic solutions (ITIES) in two types of systems.

The ITIES formed between a droplet and the surrounding liquid, supported on an electrode, has been shown to provide a viable ultra-low-voltage alternative to currently used systems. Due to the electrowetting effect, significant changes in the contact angle are obtained as the result of small variations in the applied voltage, $\approx 1$ V. On real electrodes, chemical and physical inhomogeneities were found to lead to significant hysteresis of the contact angle variation. Pulsed voltage was used to reduce hysteresis and increase the interval of angles reached. A theoretical model of the droplet dynamics is developed by analogy to the harmonic oscillator. The predicted time-dependent motion of the system rationalises the behaviour observed experimentally, and helps in the design of viable systems. The developed model could also provide a new framework for the study of the role of friction in wetting dynamics.

Beside changing its shape, another way to functionalise the ITIES is by allowing nanoparticles to spontaneously assemble at the interface. Once localised, their arrangement greatly influences the response of the system to incident light. An external voltage can control the response time and the structure of this assembly, as well as make it reversible. Such systems are of great interest for controllable optics and sensing applications. There are few independent characterisation methods of populated interfaces. A model is developed for the capacitance of an ITIES populated by metal nanoparticles. Model predictions allow to extract important information from capacitance measurements on the structure of the adsorbed layer, promoting this method as a quantitative characterisation tool.

The Faraday rotation from a monolayer of dielectric nanoparticles at an ITIES is calculated in a dipolar approximation. The particle density is assumed to be reversibly controlled by an applied potential. The difference between the angle of rotation caused by particles dissolved in the bulk and that caused by a monolayer arrangement is predicted to be large enough to make low-energy switchable Faraday isolators possible.
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<th>Definition</th>
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<tr>
<td>CL</td>
<td>(three phase) contact line</td>
</tr>
<tr>
<td>EWOD</td>
<td>Electrowetting on dielectric</td>
</tr>
<tr>
<td>GC</td>
<td>Gouy Chapman (model for diffuse layers)</td>
</tr>
<tr>
<td>ITIES</td>
<td>Interface (between) Two Immiscible Electrolyte Solutions</td>
</tr>
<tr>
<td>MWT</td>
<td>Mott Watts Tobin (model for the inner layer)</td>
</tr>
<tr>
<td>NP</td>
<td>nanoparticle</td>
</tr>
<tr>
<td>PZC</td>
<td>point of zero charge</td>
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<table>
<thead>
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<th>Symbol</th>
<th>Value with units</th>
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<tr>
<td>Speed of Light</td>
<td>$c$</td>
<td>$2.998 \times 10^8 \text{ m s}^{-1}$</td>
</tr>
<tr>
<td>Electronic Charge</td>
<td>$e$</td>
<td>$1.602 \times 10^{-19} \text{ C}$</td>
</tr>
<tr>
<td>Vacuum Permittivity</td>
<td>$\varepsilon_0$</td>
<td>$8.854 \times 10^{-12} \text{ F m}^{-1}$</td>
</tr>
<tr>
<td>Faraday Constant</td>
<td>$F$</td>
<td>$96.485 \times 10^3 \text{ C mol}^{-1}$</td>
</tr>
</tbody>
</table>
| Boltzmann Constant            | $k_B$  | $1.380 \times 10^{-23} \text{ J K}^{-1}$  
|                               |        | $8.617 \times 10^{-5} \text{ eV K}^{-1}$ |
| Gas Constant                  | $R$    | $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ |
|                               |        | $5.189 \times 10^{19} \text{ eV K}^{-1} \text{ mol}^{-1}$ |
| Avogadro’s Number             | $N_A$  | $6.022 \times 10^{23} \text{ mol}^{-1}$ |
| Gravity acceleration          | $g$    | $9.8 \text{ m s}^{-2}$                |
## Glossary of symbols

<table>
<thead>
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<th>Symbol</th>
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<tr>
<td>$A$</td>
<td>total apparent area of the ITIES</td>
</tr>
<tr>
<td>$a$</td>
<td>fixed lattice constant for maximum coverage</td>
</tr>
<tr>
<td>$A_{ab}$</td>
<td>area of the liquid$_a$/liquid$_b$ interface</td>
</tr>
<tr>
<td>$A_b$</td>
<td>complex function of bulk material leading to Faraday rotation</td>
</tr>
<tr>
<td>$A_{bl}$</td>
<td>off-diagonal term of $\hat{\epsilon}_{bl}$</td>
</tr>
<tr>
<td>$A_{de}$</td>
<td>apparent area of the droplet/electrode interface</td>
</tr>
<tr>
<td>$A_{ds}$</td>
<td>apparent area of the droplet/surrounding interface</td>
</tr>
<tr>
<td>$A_{ma}$</td>
<td>area of the metal/liquid$_a$ interface</td>
</tr>
<tr>
<td>$A_{mb}$</td>
<td>area of the metal/liquid$_b$ interface</td>
</tr>
<tr>
<td>$\hat{\alpha}_{NP}$</td>
<td>tensor for polarisability volume of one spherical NP</td>
</tr>
<tr>
<td>$\alpha_{NP}$</td>
<td>polarisability volume of one spherical NP</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>contact angle inside the droplet</td>
</tr>
<tr>
<td>$\alpha_0$</td>
<td>contact angle in the absence of applied potential</td>
</tr>
<tr>
<td>$\alpha_{|}$</td>
<td>in-plane polarisability of a monolayer</td>
</tr>
<tr>
<td>$\alpha_{\perp}$</td>
<td>out-of-plane polarisability of a monolayer</td>
</tr>
<tr>
<td>$\hat{\alpha}_{ml}$</td>
<td>tensor of polarisability volume for a monolayer of NPs</td>
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<td>$\beta_a$</td>
<td>inner layer thickness inside the ligand layer in liquid$_a$</td>
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<tr>
<td>Symbol</td>
<td>Description</td>
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<tr>
<td>$\beta_b$</td>
<td>inner layer thickness inside the ligand layer in liquid$_b$</td>
</tr>
<tr>
<td>$C$</td>
<td>specific differential capacitance</td>
</tr>
<tr>
<td>$C_{de}$</td>
<td>specific differential capacitance of the droplet/electrode interface</td>
</tr>
<tr>
<td>$C_{ds}$</td>
<td>specific differential capacitance of the droplet/surrounding interface</td>
</tr>
<tr>
<td>$C_{se}$</td>
<td>total specific differential capacitance of the surrounding/electrode interface</td>
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<tr>
<td>$C_{se}^{il}$</td>
<td>the specific differential capacitance of the inner layer part of the surrounding/electrode interface</td>
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<tr>
<td>$c_0$</td>
<td>speed of light in vacuum</td>
</tr>
<tr>
<td>$C_a$</td>
<td>specific diffuse layer capacitance in liquid$_a$</td>
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<tr>
<td>$C_b$</td>
<td>specific diffuse layer capacitance in liquid$_b$</td>
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<tr>
<td>$C_{ab}$</td>
<td>specific differential capacitance of the liquid$_a$/liquid$_b$ interface</td>
</tr>
<tr>
<td>$C_{all}$</td>
<td>specific differential capacitance of the occupied interfaces</td>
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<tr>
<td>$c_a$</td>
<td>electrolyte concentration in liquid$_a$</td>
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<tr>
<td>$c_b$</td>
<td>electrolyte concentration in liquid$_b$</td>
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<td>$C_{dl}$</td>
<td>specific differential capacitance of the diffuse layer</td>
</tr>
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<td>$C_{ma}$</td>
<td>specific differential capacitance of the metal/liquid$_a$ interface</td>
</tr>
<tr>
<td>$C_{mb}$</td>
<td>specific differential capacitance of the metal/liquid$_b$ interface</td>
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<tr>
<td>$\tilde{c}_{np}$</td>
<td>dimensionless initial bulk concentration of NPs</td>
</tr>
<tr>
<td>$C_{tot}$</td>
<td>total specific differential capacitance</td>
</tr>
<tr>
<td>$c$</td>
<td>molar electrolyte concentration</td>
</tr>
<tr>
<td>$C_{il}$</td>
<td>specific differential capacitance of the inner layer</td>
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<td>$\chi_0$</td>
<td>ratio of available dipoles in the inner layer, MWT theory</td>
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<td>$\chi_{0,d}$</td>
<td>$\chi_0$ in the droplet</td>
</tr>
<tr>
<td>$\chi_{0,s}$</td>
<td>$\chi_0$ in the surrounding</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
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<td>---------------------------------------------------------------------------</td>
</tr>
<tr>
<td>$c_{np}$</td>
<td>initial NP bulk concentration</td>
</tr>
<tr>
<td>$c_{np}^*$</td>
<td>reference NP bulk concentration</td>
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<tr>
<td>$c_d$</td>
<td>molar concentration in the droplet</td>
</tr>
<tr>
<td>$c_s$</td>
<td>molar concentration in the surrounding</td>
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<td>$D$</td>
<td>effective thickness of the inner layer</td>
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<td>$D$</td>
<td>diffusion constant of ions</td>
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<td>$D_a$</td>
<td>effective thickness of inner layer in liquid$_a$</td>
</tr>
<tr>
<td>$D_b$</td>
<td>effective thickness of inner layer in liquid$_b$</td>
</tr>
<tr>
<td>$D_{\text{dieI}}$</td>
<td>thickness of the dielectric layer, EWOD</td>
</tr>
<tr>
<td>$\delta$</td>
<td>penetration parameter of a NP into the oil phase</td>
</tr>
<tr>
<td>$\theta_{\text{bl}}$</td>
<td>Faraday rotation angle for NPs dispersed in bulk liquid</td>
</tr>
<tr>
<td>$e$</td>
<td>elementary charge</td>
</tr>
<tr>
<td>$E_{ext}$</td>
<td>external electric field due to electromagnetic radiation</td>
</tr>
<tr>
<td>$E_o$</td>
<td>Eötvös (or Bond) number</td>
</tr>
<tr>
<td>$E(x_i)$</td>
<td>total electric field at lattice point $i$</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>diagonal term of the permittivity tensor of bulk material</td>
</tr>
<tr>
<td>$\epsilon_{\text{de}}$</td>
<td>specific free electrostatic energy at the droplet/electrode interface</td>
</tr>
<tr>
<td>$\epsilon_{\text{ds}}$</td>
<td>specific free electrostatic energy at the droplet/surrounding interface</td>
</tr>
<tr>
<td>$\epsilon_{\text{il}}$</td>
<td>relative permittivity in the inner layer</td>
</tr>
<tr>
<td>$\epsilon_{\text{se}}$</td>
<td>specific free electrostatic energy at the surrounding/electrode interface</td>
</tr>
<tr>
<td>$\hat{\epsilon}$</td>
<td>permittivity tensor of bulk material</td>
</tr>
<tr>
<td>$\epsilon_0$</td>
<td>permittivity of vacuum</td>
</tr>
<tr>
<td>$\epsilon_a$</td>
<td>bulk permittivity in liquid$_a$</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$\epsilon_b$</td>
<td>bulk permittivity in liquid</td>
</tr>
<tr>
<td>$\epsilon_{bl}$</td>
<td>diagonal term of $\hat{\epsilon}_{bl}$</td>
</tr>
<tr>
<td>$\hat{\epsilon}_{bl}$</td>
<td>effective dielectric permittivity tensor of bulk liquid with dispersed NPs</td>
</tr>
<tr>
<td>$\epsilon_i$</td>
<td>bulk relative permittivity of solvent $i$</td>
</tr>
<tr>
<td>$\epsilon_{il}^a$</td>
<td>the relative permittivity in the inner layer of liquid $a$</td>
</tr>
<tr>
<td>$\epsilon_{il}^b$</td>
<td>the relative permittivity in the inner layer of liquid $b$</td>
</tr>
<tr>
<td>$\hat{\epsilon}_{ml}$</td>
<td>effective dielectric permittivity tensor for a monolayer of NPs</td>
</tr>
<tr>
<td>$\epsilon_s$</td>
<td>scalar bulk permittivity of the surrounding liquid</td>
</tr>
<tr>
<td>$\epsilon_{\beta a}$</td>
<td>bulk permittivity in inner layer $\beta_a$</td>
</tr>
<tr>
<td>$\epsilon_{\beta b}$</td>
<td>bulk permittivity in inner layer $\beta_b$</td>
</tr>
<tr>
<td>$\epsilon_{\gamma a}$</td>
<td>bulk permittivity in inner layer $\gamma_a$</td>
</tr>
<tr>
<td>$\epsilon_{\gamma b}$</td>
<td>bulk permittivity in inner layer $\gamma_b$</td>
</tr>
<tr>
<td>$\epsilon_{\text{diel}}$</td>
<td>relative permittivity of the dielectric layer, EWOD</td>
</tr>
<tr>
<td>$\epsilon_d$</td>
<td>relative permittivity in the droplet</td>
</tr>
<tr>
<td>$\epsilon_s$</td>
<td>relative permittivity in the surrounding</td>
</tr>
<tr>
<td>$\eta$</td>
<td>damping coefficient due to viscosity</td>
</tr>
<tr>
<td>$\eta_{\text{bulk}, d}$</td>
<td>bulk viscosity in the droplet</td>
</tr>
<tr>
<td>$\eta_{\text{bulk}, s}$</td>
<td>bulk viscosity in the surrounding</td>
</tr>
<tr>
<td>$\eta_{\text{surf}}$</td>
<td>surface viscosity</td>
</tr>
<tr>
<td>$f$</td>
<td>volume fraction of NPs in liquid</td>
</tr>
<tr>
<td>$F_0$</td>
<td>static friction force</td>
</tr>
<tr>
<td>$F_{\text{el}}$</td>
<td>electric force on an ion</td>
</tr>
<tr>
<td>$F_f$</td>
<td>friction force</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>$F_d$</td>
<td>driving force</td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>Gibbs free energy of the system compared to a droplet-free one</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>interfacial coverage by NPs</td>
</tr>
<tr>
<td>$\gamma_{de}$</td>
<td>PZC surface tension at the droplet/electrode interface</td>
</tr>
<tr>
<td>$\gamma_{ds}$</td>
<td>PZC surface tension at the droplet/surrounding interface</td>
</tr>
<tr>
<td>$\gamma_{se}$</td>
<td>PZC surface tension at the surrounding/electrode interface</td>
</tr>
<tr>
<td>$\gamma_a$</td>
<td>inner layer thickness outside of ligand layer in liquid_a</td>
</tr>
<tr>
<td>$\gamma_b$</td>
<td>inner layer thickness outside of ligand layer in liquid_b</td>
</tr>
<tr>
<td>$h$</td>
<td>penetration depth of a NP into the oil phase</td>
</tr>
<tr>
<td>$h_d$</td>
<td>height of the droplet</td>
</tr>
<tr>
<td>$j$</td>
<td>flux of charge due to ion migration</td>
</tr>
<tr>
<td>$K$</td>
<td>specific integral capacitance</td>
</tr>
<tr>
<td>$k$</td>
<td>equivalent elastic constant of the system</td>
</tr>
<tr>
<td>$K_\infty$</td>
<td>capacitance of the inner layer in the high-frequency limit, MWT theory</td>
</tr>
<tr>
<td>$k_+$</td>
<td>wave number of the left circularly polarised light</td>
</tr>
<tr>
<td>$k_-$</td>
<td>wave number of the right circularly polarised light</td>
</tr>
<tr>
<td>$k_{b,p}$</td>
<td>$k$ during bias or pulse</td>
</tr>
<tr>
<td>$K_{dl}$</td>
<td>specific integral capacitance of the diffuse layer</td>
</tr>
<tr>
<td>$K_{\infty,d}$</td>
<td>$K_\infty$ in the droplet</td>
</tr>
<tr>
<td>$K_{\infty,s}$</td>
<td>$K_\infty$ in the surrounding</td>
</tr>
<tr>
<td>$K_{il}$</td>
<td>specific integral capacitance of the inner layer</td>
</tr>
<tr>
<td>$l$</td>
<td>dimension of bulk liquid perpendicular to the ITIES</td>
</tr>
<tr>
<td>$\lambda_c$</td>
<td>capillary length</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>-------</td>
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</tr>
<tr>
<td>$\lambda_a$</td>
<td>Debye screening length in liquid a</td>
</tr>
<tr>
<td>$\lambda_b$</td>
<td>Debye screening length in liquid b</td>
</tr>
<tr>
<td>$\lambda_i$</td>
<td>Debye screening length in phase $i$</td>
</tr>
<tr>
<td>$L$</td>
<td>Characteristic length of the system</td>
</tr>
<tr>
<td>$m$</td>
<td>Accelerated mass in the system</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Coefficient of friction for solids</td>
</tr>
<tr>
<td>$\mu_{ion}$</td>
<td>Ion mobility</td>
</tr>
<tr>
<td>$N$</td>
<td>Number of NPs piercing the interface</td>
</tr>
<tr>
<td>$N_{ch}$</td>
<td>Number of electron charges on one NP</td>
</tr>
<tr>
<td>$n_i$</td>
<td>Bulk number concentration of ion type $i$</td>
</tr>
<tr>
<td>$N_{max}$</td>
<td>Maximum number of NPs at the interface</td>
</tr>
<tr>
<td>$N_r$</td>
<td>Normal force, reaction to the gravitational force</td>
</tr>
<tr>
<td>$n_s$</td>
<td>Number density of NPs at the interface</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Angular frequency of the electromagnetic radiation</td>
</tr>
<tr>
<td>$\Delta p$</td>
<td>Laplace pressure drop over a curved interface</td>
</tr>
<tr>
<td>$p_j$</td>
<td>Induced dipole moment on sphere $j$</td>
</tr>
<tr>
<td>$\tilde{\phi}_{dl}$</td>
<td>$\tilde{\phi}$ in the droplet</td>
</tr>
<tr>
<td>$\tilde{\phi}_s$</td>
<td>$\tilde{\phi}$ in the surrounding</td>
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<tr>
<td>$\tilde{\phi}$</td>
<td>Dimensionless energy required for dipole reorientation, MWT theory</td>
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<tr>
<td>$Q$</td>
<td>Existing charge in the diffuse layer</td>
</tr>
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<td>$Q_{de}$</td>
<td>Charge density during bias at the droplet/electrode interface</td>
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<td>$Q_{se}$</td>
<td>Charge density during bias at the surrounding/electrode interface</td>
</tr>
<tr>
<td>$\delta Q$</td>
<td>Extra charge density accumulated at an electrode/liquid interface during the pulse</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>$\delta Q_d$</td>
<td>extra charge density accumulated during the pulse at the droplet/electrode interface</td>
</tr>
<tr>
<td>$\delta Q_s$</td>
<td>extra charge density accumulated during the pulse at the droplet/surrounding interface</td>
</tr>
<tr>
<td>$R$</td>
<td>radius of the triple CL</td>
</tr>
<tr>
<td>$r_d$</td>
<td>radius of the droplet curvature</td>
</tr>
<tr>
<td>$R_{eq(b,p)}$</td>
<td>$R_{eq}$ during bias or pulse</td>
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<tr>
<td>$R_L$</td>
<td>ligand length</td>
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<tr>
<td>$R_S$</td>
<td>radius of the spherical NP</td>
</tr>
<tr>
<td>$R_{pin(b,p)}$</td>
<td>equilibrium $R$ in the presence of static friction</td>
</tr>
<tr>
<td>$R_s$</td>
<td>edge length of hexagonal unit cell of the NP</td>
</tr>
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<td>$R_{eq}$</td>
<td>equilibrium radius of the CL in the absence of friction</td>
</tr>
<tr>
<td>$\rho$</td>
<td>bulk density of fluid</td>
</tr>
<tr>
<td>$\rho_d$</td>
<td>bulk density in the droplet</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>bulk density in the surrounding fluid</td>
</tr>
<tr>
<td>$\Delta \rho$</td>
<td>difference between densities of two fluids</td>
</tr>
<tr>
<td>$S$</td>
<td>area of a unit cell on the interface</td>
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<tr>
<td>$S_0$</td>
<td>diametral cross sectional area of an NP</td>
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<td>$\sigma$</td>
<td>surface charge density on one NP</td>
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<tr>
<td>$\sigma_a$</td>
<td>surface charge density of ligands in liquid$_a$</td>
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<td>$\sigma_b$</td>
<td>surface charge density of ligands in liquid$_b$</td>
</tr>
<tr>
<td>$\sigma_{dl}$</td>
<td>surface charge density</td>
</tr>
<tr>
<td>$T$</td>
<td>absolute temperature</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
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</table>
Physical Constants

\( \tau \) relaxation time of the double layer \[64\]

\( \tau_d \) time for ion migration in the droplet \[64\]

\( \tau_s \) time for ion migration in the surrounding fluid \[64\]

\( \tau_p \) duration of pulse \[64\]

\( \Theta \) Heaviside step function \[112\]

\( \theta_b \) angle of rotation of linear polarisation in the bulk material \[109\]

\( U \) dimensionless electrostatic potential \[26\]

\( U_{ds} \) dimensionless potential drop over the droplet/surrounding interface \[66\]

\( \Delta U \) dimensionless potential drop between two points, e.g. electrodes \[27\]

\( \hat{U} \) dipolar interaction term \[111\]

\( U_\delta \) dimensionless potential around which the penetration function is centred \[93\]

\( U_0 \) lattice-type dependent factor for dipolar interaction \[111\]

\( \Delta U_\delta \) steepness of the penetration function \[93\]

\( U_{dl} \) dimensionless potential drop over the inner layer \[65\]

\( U_\Gamma \) dimensionless potential around which the coverage function is centred \[93\]

\( \Delta U_\Gamma \) steepness of the coverage function \[93\]

\( U_m \) dimensionless potential on a localised NP \[99\]

\( U_{il} \) dimensionless potential drop over the inner layer \[31\]

\( U_{int} \) dimensionless potential at the ITIES \[28\]

\( V \) electrostatic potential \[26\]

\( v \) ion velocity \[65\]

\( V_{ds} \) potential drop over the droplet/surrounding interface \[44\]

\( \delta V \) potential screened by charge \( \delta Q \) \[65\]
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<th>Symbol</th>
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<td>difference in potential between two points, e.g. two electrodes</td>
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<tr>
<td>$V_a$</td>
<td>potential in the bulk of liquid $a$</td>
<td>93</td>
</tr>
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<td>$V_{1a}$</td>
<td>potential at the plane of ligand charges inside the inner layer in liquid $a$</td>
<td>93</td>
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<td>$V_{2a}$</td>
<td>potential between the diffuse and inner layer in liquid $a$</td>
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<td>potential in the bulk of liquid $b$</td>
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<td>$V_{1b}$</td>
<td>potential at the plane of ligand charges inside the inner layer in liquid $b$</td>
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<td>potential between the diffuse and inner layer in liquid $b$</td>
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<td>$V_{bp}$</td>
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<td>$V_{dl}$</td>
<td>potential drop over the diffuse layer</td>
<td>50</td>
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<tr>
<td>$V_{il}$</td>
<td>potential drop over the inner layer</td>
<td>50</td>
</tr>
<tr>
<td>$V_m$</td>
<td>potential on the localised NP</td>
<td>93</td>
</tr>
<tr>
<td>$V_{pzc}$</td>
<td>potential at the point of zero charge</td>
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<td>$V_{eff}$</td>
<td>total screened potential at the end of a pulse</td>
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<td>volume of the droplet</td>
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<td>$x$</td>
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<td>$x_i$</td>
<td>position of lattice point $i$</td>
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<tr>
<td>$\xi$</td>
<td>ratio of free-to-occupied area in an occupied unit cell</td>
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<td>$z_i$</td>
<td>charge of ion type $i$, multiple of the elementary charge</td>
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To my parents
Chapter 1

Introduction

Liquid interfaces provide a huge range of possible applications. Although they have been studied since the turn of the 19th century, the phenomena in such systems continue to be implemented in new ways, many times completely unrelated to the purpose for which they were initially studied. In an era of miniaturisation and speed, liquid/liquid interfaces offer a robust two dimensional system that can be functionalised in multiple ways; its properties are as diverse as the choice of liquid phases, electrolyte, dispersed colloids, or geometrical setup. Gradual technological advances made it possible to accurately design the physical and chemical properties of these elements. Theory and experiment need to take turns in catching up with each other.

Marketed and prototype devices are based on the interaction between the functionalised liquid/liquid interface and the incoming light. Two main types of systems can be identified based on a liquid/liquid interface: (i) those using the electrowetting effect, where the interface changes area and, due to geometrical constraints, shape as a result of applied potential, and (ii) those using the tendency of colloids or particles to spontaneously assemble at the interface. Both types of systems are considered when formed at the interface between two immiscible electrolytic solutions (ITIES). In the case of electrowetting, this type of interface is chosen because it promises to provide a viable alternative to systems currently used. In the case of populated interfaces, it is in ITIES that reversibility of the assembly has been observed experimentally and described theoretically, such that these systems, again, become of crucial importance for applications, such as those benefiting from switchability and tunability.

The benefits of using liquid interfaces for variable optical devices have been recognised as early as the 1870’s, when astronomers were using rotating pools of mercury as telescopic mirrors (Gibson 1991). Around the same time, voltage was shown to affect the shape of liquid/fluid interfaces. The electrocapillary phenomenon, observed and described by Lippmann and Gibbs (McBain & Mills 1938), suggests that polarisable liquid/liquid interfaces under applied voltage have the tendency to change their area as to maximise the total capacitance. This effect, together with the observation that droplets tend to form spheroidal interfaces, hints towards
using liquid/liquid interfaces towards electrovariable lenses (Quilliet & Berge 2001, Mugele & Baret 2005). Diverse optofluiddic technologies (Shamai et al. 2008) were developed based on the phenomenon of electrowetting, beside variable-focus lenses (Berge & Peseux 2000, Hendriks et al. 2005, Dong et al. 2006). Prototype and marketed devices also include microfluidic systems (Cho & Moon 2008) and electronic displays (Hayes & Feenstra 2003). The rapid development of applications in the area of electrovariable optics (Wheeler 2008) is caused by the many benefits of systems based on liquid/liquid interfaces, such as a self-healing surface, smooth at the molecular level, and lack of mechanical moving parts.

The existing devices are based on a system known as electrowetting on dielectric, where electrolyte is introduced only in one of the liquid phases, and the electrode surface needs to be protected by a thin polymeric layer. We are interested in using the electrowetting effect without the polymeric coating, which leads to significant voltage drops, corresponding power loss, and makes their specifications non-ideal. To this end, we study electrowetting in a system based on \textit{ITIES} as proposed and investigated theoretically by Monroe et al. (2006b), and experimentally by Kornyshev et al. (2010). Significant electrowetting responses were obtained, for voltages below 1 V, still within the range for which little electrochemical reactions take place (Girault & Schiffrin 1989).

In the absence of the dielectric layer, pinning played an important role: surface roughness and heterogeneity of the electrode caused contact angle hysteresis and reduced reproducibility (Kornyshev et al. 2010). Such effects are a major obstacle to the operation of microfluidic low-voltage devices. The addition of vibrational energy was successfully used to reduce hysteresis in wetting (Andrieu et al. 1994), and to move droplets along inclined surfaces (Daniel et al. 2005). Producing mechanical shaking reproducibly, however, is experimentally difficult; moreover, this technique relies on inertial energy, and is of little use in small scale devices. ‘Electric shaking’ provided by sinusoidal voltage modulation emerged as a viable method to reduce hysteresis in high-voltage electrowetting (Li & Mugele 2008). Instead, Kucernak et al. used a pulse-assisted technique with ultra-short voltage pulses to effectively combat pinning in the \textit{ITIES}-based low-voltage electrowetting (Kornyshev et al. 2010).

Although the effects of surface roughness on the statics of wetting have been intensively studied (Buguin et al. 2006), its impact on the dynamics is not well understood. Inspired by the experimental results of Kornyshev et al. (2010), we developed the first model to describe the dynamics of electrowetting, and to help rationalise the interplay between pinning, as caused by effective friction forces, and voltage pulsing.

As mentioned above, the functionality of systems based on the liquid/liquid interface is not limited to electrowetting-induced shape changes. Liquid/liquid interfaces present an ideal support for the spontaneous self-assembly of particles. This phenomenon was first studied at the beginning of the 20\textsuperscript{th} century within the framework of emulsion stability (Ramsden 1903, Pickering 1907). The system has been used since then intensively for this purpose, especially in the food
Chapter 1. Introduction

and oil industries. It was only much later, when the mechanisms of this adsorption and the properties of the two-dimensional layer were understood, that the possibility of using such systems for their optical properties became apparent. Intensive research in the area of liquid interfaces populated with nanoparticles (NPs) is driven by the desire to build self-assembled, flexible nanostructures for diverse applications (Binder 2005), but also for their unique properties regarding ion and electron transport (Dryfe 2006). Populated ITIES are used for catalytic applications (Su et al. 2010, Mendez et al. 2010), while potential applications to molecular machines (Kornyshev et al. 2007), optical applications (Flatte et al. 2008a, Flatte et al. 2010), and sensing applications are at an incipient stage.

Recent experimental studies showed that the interfacial layer can be re-adsorbed in the bulk by applying an external voltage, for assemblies of small metal NPs by Su et al. (2004), and of semiconductor NPs by Su et al. (2005). The possibility of obtaining a reversible system opens the field to applications that benefit from or are based on switchability. Voltage-controlled reversibility was theoretically modelled in Flatte et al. (2008b) and Flatte et al. (2010). Although the predicting power of their numerical results suffer from the simplifying assumptions that need to be made, the model shows valid qualitative results: reversibility should be possible in most systems, conditional on the appropriate choice of system parameters.

Having reliable techniques for characterising the populated interface is increasingly important, as the experimental and theoretical interest in populated liquid/liquid interfaces in general, and populated ITIES in particular, grows. Detailed knowledge about the structure and position of the interfacial layer would allow the degree of control required for the design in most applications. The thickness and in-plane organisation of the NP layer greatly influence the optical and magnetic response of the system.

NP assemblies at the liquid/liquid interface cannot be studied by standard AFM, STM, or transmission electron spectroscopy. The interface is elastic, supports capillary waves, and the structural features to be measured are in the range of nanometres. When they form microscopic aggregates, interfacial structures can be studied by optical microscopy (Campbell et al. 2009). Some information has been obtained by removing the layer and depositing it on a solid, some degree of reorganisation will always occur in this process. Identifying which of the measured features reflect the structure in situ is practically impossible, making this method far from ideal.

The populated ITIES was investigated by UV-vis spectroscopy (Girault 2006), surface plasmon resonance (Hojeij et al. 2010), and second harmonic generation spectroscopy (Galletto et al. 2007). The reflection and transmission coefficients for visible light incident on a monolayer of localised metallic NPs were calculated by (Flatte et al. 2010) in the dipolar approximation. The results showed a frequency shift and linewidth broadening signature of the surface plasmon resonance. Semiconductor NPs at the ITIES have been predicted to experience large electric fields, which can produce dramatic room-temperature Stark shifts in the optical transmission (Flatte et al. 2008b). From an experimental perspective, however, extracting detailed information from interface-averaged optical data remains problematic.
Girault and co-workers have recently used an alternative technique to detect metal NPs at the ITIES: impedance measurements, (Younan et al. 2010). This method provides an independent means for interface characterisation, to be used alongside information gathered from optical measurements. The capacitance measurements proved to be sufficiently sensitive to the spatial arrangement of the NPs relative to the interface. We are providing a model for the capacitance of such an interface partially or fully occupied by NPs, enabling, thus, the extraction of information about the structure of the adsorbed layer from such data.

The interaction of light with assembled particles has been experimentally and theoretically studied, both to characterise the structure of the layer and to take advantage of the system’s properties, for applications such as tunable mirrors. The properties of magnetic NPs at an ITIES interface, however, have not been explored to date. This despite the extensive existing literature on metallic and insulating magnetic NPs in solution, including studies on iron, cobalt, ferrite, and magnetite ferrofluids, (Odenbach 2010). Measurements of Faraday rotation have been performed by Davies & Llewellyn (1980) and Pang et al. (2003). Theoretical models (Hui & Stroud 1987) and experimental studies (Smith et al. 2005) showed that the Faraday rotation by magnetic NPs in a nonmagnetic matrix depends on the NP density.

As voltage was shown to provide control of the NP population at the interface, we explore the possibility of using ITIES systems for applications requiring Faraday rotation, such as Faraday isolators. These devices currently require energies that are orders of magnitude higher than in the liquid system. We develop a model that calculates the Faraday rotation response obtained from NPs dissolved in solution and assembled at the interface. Interactions between localised particles are modelled in the dipolar approximation.

**Structure of thesis**

The topic of electrowetting with ITIES is treated in Part I, starting with a brief introduction to the type of system currently used in electrovariable applications, and the need to an alternative system. The initial theoretical treatment of electrowetting with ITIES in equilibrium as developed by Monroe et al. (2009) is given in Chapter 4. Following the chronological sequence of events, Chapter 5 summarises the experimental findings of (Kornyshev et al. 2010), which highlighted the need for a model of electrowetting dynamics. The model developed, its predictions and how they relate to experimental data is described in Chapter 6.

Part II of this thesis presents studies done on the second type of system: ITIES populated by NPs. In Chapter 7 spontaneous and driven self-assembly are briefly discussed, together with the theory of reversibility of assemblies at the ITIES by Flatte et al. (2010). Chapter 8 presents the developed capacitance model, its predictions and a comparison with the experimental data of Younan et al. (2010). Calculations for the Faraday rotation to be obtained from NPs dissolved or localised is sketched in Chapter 9. As this work is still in progress, only preliminary results are available.
Bibliography


Chapter 1. Introduction


Chapter 2

Electrolyte interfaces

We review the basic phenomena and models needed to describe electrified interfaces between two immiscible electrolytes, and between an electrolyte and an electrode. We consider two ways of expressing information about the interfacial structure: by the spatial potential distribution and the corresponding accumulated charge, or by effective specific capacitances. Electrified interfaces between two phases, where at least one is an electrolyte, are characterised by the presence of free ions that move as a result of thermal energy and external electric field, in what is called diffusion and migration motion, respectively. Although the models described below are too simplistic to provide an accurate description of real interfaces, they do offer a general framework for understanding and predicting the properties of interfacial systems.

2.1 The diffuse layer

Placing a charged object in contact with an electrolyte solution leads to the rearrangement of ions in solution as a result of electrostatic forces. Opposite sign ions assemble on the liquid side of the interface with the solid, while a net depletion of same sign ions is present in the interfacial region. If no ions are allowed to penetrate the interface, the electrolyte as a whole remains electroneutral. Due to thermal motion, the interfacial ionic arrangement is diffuse, configuration known as the electrical double layer. Any viable model of such an interface must account for the temperature in the system and for the number of ions available in the bulk. The first description to fulfill these conditions was developed by Gouy (1910) and Chapman (1913), is known as the Gouy-Chapman theory (GC), and is described below.
2.1.1 Diffuse layer potential

The electrostatic potential profile $V(x)$ is calculated from the Poisson-Boltzmann equation, relating it self-consistently to the ionic distribution. The latter depends on the temperature of the system and on the availability of ions. For a flat interface:

$$\frac{d^2V}{dx^2} = -\frac{1}{\epsilon_0 \epsilon} \sum_j n_j z_j e \exp \left(-\frac{z_j e V}{k_B T}\right), \quad (2.1.1)$$

for $j$ types of ions present in solution, of charge $z_j$ and number per unit volume $n_j$ in bulk; $\epsilon$ is the bulk relative dielectric permittivity of the solvent. In systems where the thermal energy is considerably larger than the electrostatic one, $k_B T \gg |z_j e V|$, the solution in the Debye-Hückel approximation is obtained

$$V(x) = \Delta V \exp \left(-\frac{x}{\lambda}\right), \quad (2.1.2)$$

$\Delta V$ denotes the potential at the interface, in this case equal to the total potential drop over the diffuse layer, and $x$ the distance from it. The Debye screening length

$$\lambda = \left(\sum_j \frac{z_j^2 e^2 n_j}{\epsilon_0 \epsilon k_B T}\right)^{-\frac{1}{2}} \quad (2.1.3)$$

is a measure of the efficiency of screening. As the concentration of ions in the bulk increases or the temperature decreases, the potential is screened over a shorter distance.

An analytical solution of Equation 2.1.1 is not available for most systems. In the case of symmetric, monovalent electrolytes: $z_- = z_+ = \pm 1$, $j = 2$ and $n_1 = n_2 = n$, an implicit solution for $V(x)$ can be obtained:

$$\tanh \left(\frac{e V}{4k_B T}\right) = \tanh \left(\frac{e \Delta V}{4k_B T}\exp \left(-\frac{x}{\lambda}\right)\right), \quad (2.1.4)$$

and the Debye length defined in Equation 2.1.3 reduces to

$$\lambda = \sqrt{\frac{\epsilon_0 \epsilon k_B T}{2e^2 n}}. \quad (2.1.5)$$

Other expressions for $\lambda$ can be produced by using $R/F = k_B / e$ and the molar concentration $c$ instead of the number concentration $c = n / N_A$.

It is useful at this point to introduce the dimensionless potential

$$U \equiv \frac{e V}{k_B T}, \quad (2.1.6)$$

such that the potential distribution through a diffuse layer from Equation 2.1.4 becomes

$$\frac{U}{2} = \ln \frac{\alpha \exp \left(-\frac{x}{\lambda}\right) + 1}{\alpha \exp \left(-\frac{x}{\lambda}\right) - 1}, \quad \text{with} \quad \alpha = \frac{\exp \left(\Delta U / 2\right) + 1}{\exp \left(\Delta U / 2\right) - 1}. \quad (2.1.7)$$
\( \Delta U \) is the dimensionless potential drop over the diffuse layer, defined analogously to the definition in Equation 2.1.6 in terms of \( \Delta V \).

### 2.1.2 Diffuse layer capacitance

The experimentally measurable property is usually the specific differential capacitance, defined as

\[
C \equiv \frac{d\sigma_{dl}}{d\Delta V},
\]

as it is easier to determine changes in the potential drop than its absolute value. The surface charge density \( \sigma_{dl} \) in the diffuse layer is equal to the counter charge, since the net charge in a double layer is zero. The specific integral capacitance is given by \( K = \sigma_{dl}/\Delta V \), such that the relations between the two are:

\[
C(V) = K(V) + (V - V_{pzc}) \frac{dK(V)}{dV},
\]

\[
K(V) = \frac{1}{V - V_{pzc}} \int_{V_{pzc}}^{V'} C(V') \, dV'.
\]

In systems where the capacitance is independent of potential, the two capacitances are equivalent \( C(V) = K(V) \). The applied potential for which there is zero charge density accumulated at the interface is not necessarily 0 V. The point of zero charge, \( V_{pzc} = V(\sigma_{dl} = 0) \neq 0 \) accounts, amongst other factors, for specific adsorption of ions at the interface.

The capacitance of a diffuse layer with potential distribution given by Equation 2.1.7 is (Lyklema 1991):

\[
C = \frac{\varepsilon_0 \varepsilon}{\lambda} \cosh \frac{\Delta U}{2}.
\]

### 2.2 The electrolyte/electrolyte interface

Applying a potential over the interface between two immiscible electrolytic solutions (ITIES) leads to the formation of a double layer on either side of the interface, described by the Verwey Niessen theory, (Verwey & Niessen 1939). Although the *immiscible* attribute refers to the solvents, it is also assumed that no ions transfer through the interface. The potentials we consider are indeed below the transfer energy of ions. As before, we look first at the potential distribution across the ITIES, and then at its capacitance.
2.2.1 Potential distribution across the ITIES

The Poisson-Boltzmann equation is solved separately for the two diffuse layers on either side of the interface. If the applied potential \( \Delta V \) drops over the ITIES, the boundary conditions are:

\[
\begin{align*}
\text{medium}_a \quad & \quad \left. \frac{dV}{dx} \right|_{x \to -\infty} = 0, \quad V(x \to -\infty) = \Delta V, \\
\text{medium}_b \quad & \quad \left. \frac{dV}{dx} \right|_{x \to \infty} = 0, \quad V(x \to \infty) = 0.
\end{align*}
\]

In terms of the dimensionless potential, the solution can be obtained from that of a single diffuse layer in the gc theory, Section 2.1.1, with the appropriate coordinate rotation and translation. The potential distribution on the two sides of the interface is:

\[
\begin{align*}
\exp\left(\frac{\Delta V}{2} - \frac{U(x)}{2}\right) = 1 + \frac{\beta^{-1}}{\beta + 1} \exp\frac{x}{\lambda_1}, & \quad x \leq 0 \quad (2.2.1a) \\
\exp\left(\frac{U(x)}{2}\right) = 1 + \frac{\beta^{-1}}{\beta + 1} \exp\frac{-x}{\lambda_2}, & \quad 0 < x, \quad (2.2.1b)
\end{align*}
\]

with \( \epsilon_j, \lambda_j \) the bulk relative permittivity and Debye length of medium \( j \), and \( \beta = \exp(\Delta U/2 - U_{int}/2) \). At the interface the potential \( U_{int} \equiv U(x = 0) \) and its first derivative are continuous, due to electric field continuity and absence of adsorbed charge. From these conditions, the potential at the interface is obtained:

\[
\sinh\left(\frac{U_{int}}{2}\right) = \left(\frac{\epsilon_a^2}{\epsilon_b^2} + 1\right)^{-\frac{1}{2}} \sinh\left(\frac{\Delta U}{2}\right).
\]

2.2.2 Capacitance of ITIES

The total capacitance of an ITIES can be considered the result of two gc capacitors in series, corresponding to the potential drops on either side of the interface:

\[
C_a = \frac{\epsilon_0 \epsilon_a}{\lambda_a} \cosh\left(\frac{\Delta U - U_{int}}{2}\right), \quad C_b = \frac{\epsilon_0 \epsilon_b}{\lambda_b} \cosh\left(\frac{U_{int}}{2}\right), \quad C_{ab} = \frac{C_a C_b}{C_a + C_b}. \quad (2.2.2)
\]

Limitations of the Gouy-Chapman theory

The gc theory was developed as an improvement to the Helmholtz’s description of the electrified interface as a simple capacitor, with a capacitance independent of the applied potential and electrolyte concentration. In the gc model, the ion arrangement at an electrified interface is
calculated while accounting for thermal motion and the limited availability of ions. The relatively straightforward predictions presented so far come at the cost of important assumptions:

1. all ions are point charges,
2. the electrostatic forces are the only type of interaction present,
3. each ion interacts with a mean potential field caused by all ions around it and by the screened electrode charge,
4. the solvent is a structureless continuum, characterised solely by its bulk dielectric constant, and
5. the interface is flat and impermeable to ions.

For strong enough electric fields or high electrolyte concentrations, the Debye screening length can become similar to the size of the counterions in the double layer. This is especially the case in non-aqueous electrolytes, when large organic ions are dissolved. In this case, finite size ions pack tightly close to the interface, leading to oscillations in the ion density, even for relatively low concentrations, as shown by Monte Carlo simulations (Torrie & Valleau 1982). Its effects on the potential and charge distribution in the double layer cannot be modelled by a theory of point-like charges. Even for small ions, at high enough potentials the density of charge near the interface is, eventually, overestimated: \( C(V \to \infty) \to \infty \), as given by Equation 2.1.10. Moreover, the GC model only distinguishes between ions of different charge; non-electrostatic interactions leading to specific adsorption at the interface are not included.

Finally, at the microscopic scale the interface is not sharp with respect to the density profile and, implicitly to other medium properties such as the dielectric permittivity. Interfaces are also rarely flat: liquid/liquid interfaces are flexible and support capillary waves, such as those produced by thermal motion, while the liquid/solid interface profile will greatly depend on the surface roughness of the solid. In both cases, depending on the characteristic size of roughness compared to the Debye screening length, the effective area of the interface can be significantly larger than its apparent area, and the assumption of a flat interface breaks.

Some effects become increasingly important at the solid/liquid interface and can be accounted for by modelling an extra layer at the interface, as described in Section 2.3. Others, such as the microscopic profile of the interface, the size of the counterions, and specific adsorption, are equally relevant for electrolyte/electrolyte interfaces. Modified versions of classical models are used to capture the effects enumerated above. A modified Verwey Niesen model assigning specifically adsorbed ions and solvent molecules to an extra layer between the two diffuse layers was introduced by Gavach et al. (1977). This model improves the fit between theoretical predictions and experimental data of the capacitance of a water/nitrobenzene interface, especially when the layer is considered of mixed solvent (Senda et al. 1991). Such a model is similar to
the Stern layer presented in Section 2.3.1. Modified Poisson-Boltzmann solutions, developed to account for exclusion volume of ions and fluctuation potential (Outhwaite et al. 1980), as well as models of diffuse rather than sharp boundaries between the layers further improve the description (Samec et al. 1984).

2.3 The electrolyte/electrode interface

The GC model often provides a poor fit to experimental data. As a result, models of the interface between an electrolyte and an electrode greatly benefit from the introduction of an extra region between the solid surface and the diffuse layer, called the Stern layer. The most naive Stern layer is the region at the electrode that contains solvent molecules, no ions, with thickness given by the finite counterion size (Lyklema 1991). A common improvement is to account for specific adsorption. This layer, thus, improves the description of real double layers, by including the effects of those properties that cannot be retrieved from the idealised diffuse layer. Such properties relevant to most systems include: the finite size of ions and their effect on the electrostatic field, the effect of image charges across the interface, non-electrostatic interactions of ions with the solid surface leading to specific adsorption, and the polarisability of the solvent molecules when close to the surface. In practice, such a comprehensive model is rarely possible, as it requires ab initio quantum mechanical calculations, and detailed information about system parameters.

We are considering two simple models of the inner layer: the Stern, and the Mott Watts-Tobin (MWT) model. The first describes an ideal molecular capacitor, while the second includes the effect of solvent polarisability towards a voltage-dependent capacitance. In both cases, the total capacitance of the interface is given by two capacitors in series. As such, both models presented for the inner layer, as most feasible models assume that the inner and diffuse double layers can be partitioned by an equipotential dividing surface.

2.3.1 The Stern model

The Stern layer is the region depleted of charge between the solid surface and the centre-plane of the first row of solvated ions, known as the outer Helmholtz plane. In this way the finite size of counterions is accounted for. The layer is modelled as an ideal capacitor, with one plate at the potential of the electrode, and the other at the imposed equipotential plane between the inner and diffuse layers. The potential distribution inside the layer is linear, and the capacitance is independent of ion concentration and applied voltage:

\[ C = \frac{\epsilon_0 \epsilon_{\text{il}}}{D} \] (2.3.1)
where $\epsilon_{il}$ and $D$ are associated with the effective relative dielectric permittivity and thickness of the inner layer. In general, $D$ is on the scale of one or two molecular diameters, and $\epsilon_{il}$ is expected to be smaller than the bulk permittivity of the solvent, due to the effect of confinement on the liquid dipoles. Since both parameters are difficult to assess, the capacitance is usually left as a single parameter; the ratio $\epsilon_{il}/D$ is measured at high salt concentrations. As the capacitance of the diffuse layer increases, at high voltages the total capacitance of the series arrangement is determined by that of the inner layer exclusively.

### 2.3.2 The MWT model

Extensive theoretical and experimental studies searched for better models of the inner layer, especially for the water/electrode system (Bockris & Jeng 1990), as it became apparent that a microscopic model is required. A relatively simplistic model in the mean field approximation was developed by Mott & Watts-Tobin (1961) (MWT). The relative dielectric constant of the inner layer becomes dependent on the electric field, as the dipoles of the solvent are allowed to reorient in the inner layer. In their model, the water molecules form a regular two-dimensional lattice and can take one of two possible states: their dipole aligns with the applied electric field, either parallel or anti-parallel to it. The average dipole moment of the lattice starts from zero at zero electrode charge, and increases with applied potential until it reaches a saturation value, corresponding to the potential for which all available dipoles are oriented opposite to the external electric field.

Within this model, and in the absence of adatoms and specific adsorption, the integral and differential capacitances calculated for a voltage drop $U_{il}$ over the inner layer are

$$C_{il}(U_{il}) = K_\infty \left( 1 + \chi_0 \text{sech}^2 \frac{U_{il}}{\tilde{\phi}} \right),$$

$$K_{il}(U_{il}) = K_\infty \left( 1 + \chi_0 \tanh \left( \frac{U_{il}/\tilde{\phi}}{U_{il}/\tilde{\phi}} \right) \right),$$

with the following parameters: $\tilde{\phi}$ the dimensionless energy needed to reorient the dipoles, $K_\infty$ the capacitance of the inner layer in the high-frequency limit, and $\chi_0$ a dimensionless parameter quantifying the number of dipoles available in the inner layer. The three parameters depend on the molar concentration of the pure solvent, the bulk dipole moment, and the bulk permittivity. Their values can be obtained by fitting experimental data, especially in the case of aqueous electrolytes; Monroe et al. (2009) describes such a fitting procedure. Although rather antiquated, this model provides a good fit to experimental data for the interface between some aqueous solutions and gold, and provided a voltage-dependent capacitance of the inner layer with the price of only few fitting parameters.
2.4 Real interfaces

Real interfaces are not sharp, their point of zero charge is not the same as that of zero voltage, can support capillary waves, are penetrated by ions, and are the place of irreversible processes, such as ion transfer. Some of the complications in describing real interfaces are briefly discussed below.

Specific ion adsorption

Specific adsorption takes place especially at the liquid/electrode interface as a result of non-electrostatic interactions between ions and the solid surface. The surface density of adsorbed charge, as well as its distance from the electrode is highly sensitive to the electrode/salt pair in the system. Specific adsorption can have a significant effect on the potential distribution inside the inner layer, and on the arrangement of ions in the diffuse layer. Advanced models that account for specific adsorption are triple layer models, since adsorbed, non-hydrated ions come closer to the surface than the ones in the diffuse layer can. The three layers cannot be considered in series. Multiple system parameters need to be approximated from experimental data, once adsorption isotherms are derived (Lyklema 1991).

Solvent polarisation

The MWT theory give a simplistic account of water polarisation properties. Rather than the step function between an effective inner layer permittivity and the bulk permittivity of the diffuse layer, the real permittivity of the medium is expected to vary continuously with distance from the planar electrode surface. Solvent molecules beyond the first layer interact with those in the first one, and with the applied electric field; the first monolayer of molecules is not bounded by two perfectly conducting surfaces. Moreover, dipoles are allowed to orient in arbitrary directions, leading to a more complicated function for the average dipole moment (Bockris et al. 1963). Neighbouring molecular dipoles in a layer are interacting, not least through hydrogen bonds (Guidelli 1981), leading to an effective value for the dipole of a water molecule, which is significantly different from the value of the non-interacting dipole (Bockris et al. 1963). Changes in the local effective dielectric permittivity directly influence the value of the voltage dependent capacitance.

Point of zero charge crystal structure dependent

As in the case of liquid/liquid interfaces, the point of zero charge is influenced by specific adsorption, caused by the dissolved ions. For liquid/solid interfaces, it also depends on the polarisation of the solvent molecules close to the electrode (Lyklema 1991). Finally, there is experimental proof of the variation of $V_{pz}$ with the structure of the electrode surface, such as its crystal plane (Hamelin & Stoicoviciu 1987b, Hamelin & Stoicoviciu 1987a).
While no classical theory can explain all main features of experimental results (Bockris & Jeng 1990), numerical models shed more light onto the cases when classical top-bottom approaches do not hold. The interface-bulk continuity has been studied via statistical mechanical methods (Torrie & Patey 1993), and Monte Carlo simulations (Torrie & Valleau 1982). Molecular dynamics simulations have been used to retrieve the known behaviour in limiting cases (Guidelli & Schmickler 2000).
Bibliography


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Part I

Electrowetting with ITIES
Chapter 3

Introduction to electrowetting

3.1 A historic perspective

The phenomenon of electrowetting refers to the change in area of the interface between a liquid and a fluid as a result of applied potential. This effect takes place in three-phase systems when at least one contains free ions. As a result of the applied potential, the ions migrate towards different interfaces, changing their effective properties, and thus the equilibrium areas of the three types of interfaces in equilibrium.

Voltage-induced changes in the area of a liquid/fluid interface were first documented by Lippmann (1875) in the framework of his electrocapillarity studies. Long capillaries with liquid mercury were used to measure the relation between small changes in electrostatic charge and capillary forces. These studies stood at the basis of the first electrocardiography machine. The effect of electrowetting was observed by Frumkin while studying chemical reactions on the surface of a liquid mercury electrode supporting an oil droplet immersed in an electrolytic solutions (Frumkin et al. 1932, Frumkin 1936). The practical applications of this phenomenon were at the time overlooked, maybe partly due to the inherent drawbacks of a mercury electrode; the metal’s toxicity and the instability of a liquid electrode surface make the system impractical. Solid electrodes do not display these defects, but lack the inertness of mercury and the smoothness of a liquid surface; as a result corrosion, electrolyte decomposition and pinning become prohibitive.

3.2 Electrowetting on dielectric

These problems were overcome by the possibility of coating a solid electrode with a polymeric film some 50 years later (Holly 1977, Ponter & Yektafard 1984). Gold electrodes coated with insulating alkanethiol layers delivered stable electrowetting effects (Sondaghnuethorst &
Figure 3.1: Schematics of a liquid lens. The path of light (horizontal line) encounters a curved interface that acts as a lens. As a change in the applied voltage modifies the curvature, the focal length of the liquid lens is tunable.

Fokkink 1992, Sondaghuethorst & Fokkink 1994), although response times were slow, of the order of seconds, and hysteresis was large. More recently, electrowetting by liquid hexadecanethiol droplets on coated gold surrounded by electrolyte delivered contact angles between 30° and 120° for voltages of 0 V to 2 V. These results by Gorman et al. (1995) proved the viability of the system for electrovariable liquid lenses and arrays thereof. The reinstated enthusiasm for this phenomenon led to an avalanche of theoretical and experimental studies on electrowetting on dielectric (EWOD) (Quilliet & Berge 2001, Mugele & Baret 2005, Shamai et al. 2008).

Currently there is a variety of prototype and marketed devices, such as electrovariable liquid lenses for cameras, multi-array liquid displays, and lab-on-a-chip microfluidic devices. All these applications benefit from the current EWOD technology; they have low power consumption ~20 V, activation times within ms’s, they lack mechanical moving parts, and have a high degree of miniaturisation with sizes in the µm range, and the resulting absence of gravity effects (Mugele 2009). The more popular devices based on EWOD are presented below.

Liquid lens

A fluorinated organic insulating layer coating the droplet allowed reproducible contact angle variation between 30° and 100° by an applied potential of 0 V to 100 V (Berge 1993). In Berge & Peseux (2000) switching times around 10 ms and operating voltages in the 300 V range were obtained. These specifications made the system feasible for liquid lenses. The lens is formed by the curved interface between an oil droplet and the surrounding electrolyte, as sketched in Figure 3.1. The focal length is determined by the curvature of the interface, that can be tuned by the applied voltage. This voltage is currently in the range of tens of volts. Liquid lenses
marketed by Varioptic Co. for surveillance and phone cameras, are in many ways superior to conventional ones. The active element is a defect-free, self-healing liquid interface, with high optical quality and little sensitivity to mechanical faults (Shamai et al. 2008). The interface is smooth on a molecular scale, and that does not require any polishing. The focal length available is determined by the strength of the electrowetting effect achievable, and does not require any moving mechanical parts, unlike solid lenses.

**Liquid displays**

The electrowetting effect can also be used to move a droplet in and out of the path of light. This action can switch between two reflected colours, if, for example, the droplet is coloured black, while the surrounding liquid and electrodes are transparent in the visible range; a pixel is formed. An array of such pixels mounted on a thin flexible wafer, with voltage controlled independently, exhibits all qualities of reflective displays, including wide viewing angle and the possibility of reading in bright ambient light. Short enough response times have been achieved for a refresh time of 25 pictures per second, a frequency high enough for rendering movies (Shamai et al. 2008).\(^1\)

Liquid displays for polychromatic rendering of images are also possible. Two types of arrangements are currently pursued: RGB cells in parallel with controlled relative brightness and stacked CMY cells (Feenstra & Hayes 2006). The former come with an inherent three-fold decrease in resolution. Various companies are developing electrowetting paper: E-paper by *Liquavista B. V.* with energy consumption currently five times lower than that of LCD displays, and by *Phillips Corporate Labs.*

\(^1\)This aspect is particularly important in the direct competition between electrowetting paper and the electrophoretic displays currently used by E-readers such as the Amazon Kindle, with a response time of $\sim1\text{s.}$
Lab-on-a-chip

Tools based on EWOD that manipulate minute quantities of substance, performing operations such as mixing, dropping and separating (Miller & Wheeler 2009, Wheeler 2008). The droplet motion is achieved by individually controlling electrodes in a purpose-built arrangement. The lab-on-a-chip device, currently developed, amongst others, by Duke University is a critical tool for digitalising various processes (Fair 2007).

3.2.1 EWOD limitations

The effect of the dielectric layer can be modeled by a modified Young Laplace equation that includes the effect of electric polarisation of the layer (Mugele & Baret 2005), Lippmann’s equation:

$\gamma_{ds} \cos \alpha = \gamma_{se} - \gamma_{de} + \frac{C \Delta V^2}{2} \Rightarrow \cos \alpha = \cos \alpha_0 + \frac{C \Delta V^2}{2 \gamma_{ds}}.$ \hspace{1cm} (3.2.1)

The value of the equilibrium contact angle $\alpha_0$ in the absence of electric field depends on the interplay between the surface tensions $\gamma$ between each two of the three phases, denoted by the subscripts ‘d’ - droplet, ‘s’ - surrounding, and ‘e’ - electrode (or dielectric coating atop), as in Figure 3.3. The relation in Equation 3.2.1 is written for $\alpha$ measured inside the droplet, such that for $\gamma_{se} > \gamma_{de}$, it yields $\alpha_0 < 90^\circ$ and $\cos \alpha_0 > 0$. The added term $C \Delta V^2/2$ quantifies the energy stored in the region between the electrolyte and the metal, with specific capacitance $C$, under a potential drop $\Delta V$. According to Equation 3.2.1, a droplet containing electrolyte and surrounded by a dielectric medium, such as air, spreads under the effect of applied voltage, $\alpha < \alpha_0$. If the surrounding liquid rather than the droplet contains electrolyte, then the droplet contracts under applied potential. In either case, Equation 3.2.1 models the condition of energy minimisation in the system: accumulation of charge at one of the liquid/solid interfaces, either ‘de’ or ‘se’, decreases the energy of that interface, and the droplet changes shape as to maximise the respective area. The dimensionless term $C \Delta V^2/2 \gamma_{ds}$ gives the strength of the effect and is known as the electrowetting number.
Equivalently, changes in the shape of the droplet can be seen as the result of capacitance com-
petition in the system: the applied voltage increases the capacitance of the electrolyte/electrode
interface. As the thickness of the dielectric layer is much larger than the dimensions of the double
layer, it is the capacitance of the polymer film that characterises the total capacitance of the se-
ries arrangement. The capacitance of the dielectric layer is simply modelled by \( C = \varepsilon_0 \varepsilon_{\text{diel}} / D_{\text{diel}} \).

It becomes apparent that one needs to increase \( C \) to increase the energy efficiency of a device.
The dielectric permittivity \( \varepsilon_{\text{diel}} \) is limited by the appropriate materials available. Aside manu-
facturing considerations, targeted qualities are endurance to high voltages, and hydrophobicity,
because high \( \alpha_0 \) values allow for a wider range of available contact angles. The layer thickness
\( D_{\text{diel}} \) cannot be indefinitely reduced without losing protection against corrosion.

Besides the perspective of limited possible efficiency improvements, there are other challenges
to EWOD. Lippmann’s equation is only applicable at low voltages; the charge distribution at the
ds interface is neglected, and an ideal parallel capacitor is assumed at the electrolyte/electrode
interface. A saturation of the contact angle at high voltages has been observed experimentally
in all systems, for which no unchallenged theoretical model has been yet proposed (Mugele &
Baret 2005). While saturation voltages lie outside the interval of interest for applications, this
issue highlights deficiencies in the current understanding of the process (Quinn et al. 2005, Peykov
et al. 2000).

Advanced theories of the microscopics of this effect have been developed. Electric field diver-
gences have been found to take place at the triple phase contact line, probably responsible
for the intense Faradaic processes that take place in such systems in the absence of the pro-
tective layer. The presence of such divergences make it difficult to develop a comprehensive
theory of EWODs. Ongoing studies are directed at solving other challenges, such as eliminating
hysteresis that damages the stability of devices, and providing a theoretical description of out-
of-equilibrium dynamic behaviour of the system by describing the flow of liquid films in electric
fields (Drygiannakis et al. 2009).

While applications based on the electrowetting effect have the potential to shape our everyday
life, the EWOD systems are far from having reached ideal specifications. The EWOD setup provides
an ingenious solution to hysteresis and reversibility problems, at the cost of introducing a passive
element with relatively high energy consumption. Even the lowest recorded voltages for shape
deformation in display elements is \( \sim 20 \text{ V} \), not ideal for portable devices, (Kuiper & Hendriks
2004). Additional electronics and extra power required for portable integration increase the
device weight and shorten the battery life.
Bibliography


Chapter 4

Theory of equilibrium

4.1 The ITIES system

As the energy efficiency of EWOD devices is limited by the presence of the dielectric layer, an alternative system is highly desirable. The system obtained at the interface between two immiscible electrolytic solution (ITIES) has recently proved to be a serious contender. Such an interface is obtained by dissolving electrolyte in both droplet and surrounding liquids. The equilibrium theory of electrowetting with ITIES of Monroe et al. (2009) predicts that a contact angle variation similar to that of EWOD occurs for very low voltages (~1 V). In using this system, one also avoids some of the problems encountered in the theoretical study of EWOD. The applied voltage is completely screened at the scale of the Debye screening length, while the bulk of both liquids is electroneutral. As a result, a rigorous analytical framework can be developed under the valid assumption that all interfaces are flat. Due to the screening, no field singularities are present in the vicinity of the contact line, and the risk of chemical reactions is significantly reduced.

In the systems of interest, the droplet size is in the mm range, such that gravity does not play a role. This is confirmed by the dimensionless Eötvös number \( \mathcal{E}_o = \Delta \rho g L^2 / \gamma_{ds} \), a ratio between buoyancy forces and surface tension, where \( \Delta \rho \) is the difference in the densities of the two liquids, and \( L \) the characteristic size of the system. For a nitrobenzene (\( \rho_d \approx 1.197 \cdot 10^3 \text{ kg m}^{-3} \)) or 1,2-dichloroethane (\( \rho_d \approx 1.245 \cdot 10^3 \text{ kg m}^{-3} \)) droplet immersed in water (\( \rho_s \approx 0.997 \cdot 10^3 \text{ kg m}^{-3} \)), of volume \( v_d = 0.1 \mu\text{L} \) (corresponding size or radius \( L = 0.6 \text{ mm} \)), with surface tension \( \gamma_{ds} \approx 2.54 \cdot 10^{-2} \text{ J m}^{-2} \), \( \mathcal{E}_o \approx 0.03 \ll 1 \), and buoyancy effects are negligible.

All density values are given for 25 °C. Comparing \( \mathcal{E}_o \) to 1 is identical to comparing the value of the capillary length, \( \lambda_c = \sqrt{\gamma_{ds} / \rho_d g} \approx 1.5 \text{ mm} \), to the characteristic length in the system, here taken as the droplet radius, \( L = 0.6 \text{ mm} \). As \( L < \lambda_c \), the effect of gravity can be neglected.
Figure 4.1: Two electrowetting systems with the corresponding potential distribution and ion arrangement. In a) a thin insulating film coats the electrode, the oil droplet contains no ions, and the potential drops over the macroscopic dimension of the droplet. EWOD devices where the droplet contains electrolyte are also used. In b) the oil phase contains organic ions, excess charge accumulates in nanometre-thick regions around interfaces and balances the charges in the adjacent phase. Electric fields of $\sim 10^7 \text{V cm}^{-1}$ are present at interfaces. From (Kornyshev et al. 2010).

In the absence of field divergences, and when the droplet is small enough for buoyancy effects to be negligible, the shape of the droplet on a macroscopically smooth surface is a truncated sphere. This was shown by both theoretical calculations in Monroe et al. (2007) and experimental images of Kornyshev et al. (2010). The spherical shape, desirable for electro-variable lens applications, is maintained on a real surface as long as the correlation length of roughness or inhomogeneity is much shorter than the size of the droplet.

Figure 4.1 compares the potential and charge distributions in EWOD and ITIES electrowetting configurations. Unlike in EWOD, in an ITIES system both droplet and surrounding liquids contain electrolytes. In the electric field caused by an applied potential, ions in both electrolytes migrate, until they come in the vicinity of an interface. If the applied potential is lower than the free energy of transfer for ions across the interface, then they accumulate within a narrow region around it, of the thickness of the Debye screening length. At equilibrium, the voltage drops exclusively across these interfacial regions, and the bulk of the droplet becomes electroneutral. In consequence, the equilibrium shape of the droplet can be seen as the result of the competition between the capacitances of the three interfaces. As the applied potential affects the number of ions accumulated at each interface, the equilibrium contact angle is voltage-dependent.

Another feature of this system is the strong electric fields formed at the ITIES. Up to $10^7 \text{V cm}^{-1}$ can be induced by relatively modest applied voltages, $\sim 1 \text{V}$. In a symmetric monovalent electrolyte of concentration $\sim 0.1 \text{m}$, the thickness of the screening layer given by the Debye length, $\lambda \sim 10^{-9} \text{m}$, yields an electric field density $\Delta V/\lambda \approx 10^{14} \text{V cm}^{-2}$. Such fields are of current interest for surface enhanced Raman spectroscopy applications.
Chapter 4. ITIES equilibrium

The two liquids are an aqueous and an organic solvent, and the electrolyte ions of choice are usually small hydrophilic salts and large hydrophobic organic ions. Under this configuration, the ITIES system can sustain up to 0.5 V across the interface. Calculations predict that this range is large enough for a wide interval of angles to be reached. Cousens & Kucernak (2011) recently obtained ITIES with a significantly increased polarisation window, of 1.2 V.

4.2 An equilibrium model

A theoretical model for the equilibrium state of the ITIES system in Figure 4.1(b) has been developed by Monroe et al. (2009). The contact angle of the droplet in equilibrium is determined via minimisation of the system energy for a given applied voltage. The energy contribution of each of the three interfaces is calculated based on the surface charge density at each boundary: droplet/surrounding (‘ds’), droplet/electrode (‘de’) and surrounding/electrode (‘se’). The two back-to-back double layers at the ‘ds’ interface are described by the Verwey Niessen theory, as presented in Section 2.2. The electrical double layers at the ‘de’ and ‘se’ interfaces are described by the non-linear Gouy-Chapman theory of a diffuse double layer, as in Section 2.1, in series with an inner layer, as in Section 2.3.2.

The change in the Gibbs free energy of the system due to the presence of the droplet is given by Equation 1 in (Monroe et al. 2009):

$$\Delta G = \left[ \gamma_{de} - \gamma_{se} + \varepsilon_{de}(\Delta V - V_{ds}) - \varepsilon_{se}(\Delta V) \right] A_{de} + \left[ \gamma_{ds} + \varepsilon_{ds}(V_{ds}) \right] A_{ds} + \nu_d \Delta p. \quad (4.2.1)$$

Included are the contributions of interfacial areas $A_{ij}$, free energy changes per unit area $\varepsilon_{ij}$ induced by the applied voltage, interfacial tensions $\gamma_{ij}$ in the absence of charge, and of the Laplace pressure $\Delta p$ across the curved surface of the droplet of volume $v_d$. The $\varepsilon_{ij}$ terms
corresponding to the three interfaces are given in Appendix A as obtained for this system by Monroe et al. (2007). The applied potential on the working electrode $\Delta V$ drops over the ‘de’ interface to a value of $V_{ds}$ in the bulk of the droplet. All potentials are measured with respect to the bulk of the surrounding electrolyte, as in Figure 4.2. The expressions of the different terms in Equation 4.2.1 are explained in Appendix A.

Minimisation of the free energy in Equation 4.2.1 for a given applied potential leads to the corresponding equilibrium contact angle $\alpha(V)$. The equilibrium shape of the droplet depends on all system parameters, such as dielectric constants, electrolyte concentrations, properties of the double layers, and surface tensions.

### 4.2.1 Assumptions

There are two assumptions made in this model that deserve particular attention.

1. The properties of the interface between aqueous electrolytes and gold electrodes have been extensively studied, both theoretically and experimentally, such that one can predict with a certain confidence the properties of the inner layer and of its capacitance. The capacitance of the electrode/organic electrolyte interface is highly dependent on the solvent-ion pair; little information is available for the system of experimental interest, gold/nitrobenzene. The model of Monroe et al. (2009) assumes that the inner layer in the organic phase has the same characteristics as that in the aqueous phase:

   - the properties of the aqueous electrolyte/gold inner layer are obtained by fitting MWT-GC model predictions to measured capacitance curves of 0.1 M aqueous potassium perchlorate on polycrystalline gold;
   - the properties of the nitrobenzene/gold inner layer are obtained under the assumption that this layer maintains the following properties identical to those of the water/gold inner layer: the ratio between the inner layer thickness and the size of a solvent molecule, the fraction of electrode surface occupied by dipoles that can reorient, and the high frequency dielectric constant of the solvent. For a detailed discussion of the procedure and its caveats, see Monroe et al. (2009).

2. The energy minimisation in Equation 4.2.1 is performed with respect to the geometry of the droplet, while all other system properties are considered to be in equilibrium. Ions are assumed to instantaneously reach their equilibrium configuration, such that the droplet bulk is permanently electroneutral. This is the case only at times longer than the characteristic time needed for the ions to reach equilibrium under the given applied potential.
Chapter 4.  ITIES equilibrium

4.3 Model predictions

The model developed by Monroe et al. (2009) allows for a detailed analysis of the system’s behaviour; ideally, the theory can be proven (or disproven) by testing its predictions experimentally. We present model predictions of the strength of the electrowetting effect with respect to electrolyte concentration, a parameter easy to control experimentally. These predictions also help rationalise the mechanism of the droplet behaviour.

The system parameters used in the plotted results are listed in Table 4.1. The bulk dielectric permittivities correspond to a nitrobenzene droplet surrounded by an aqueous electrolyte. Both electrolytes are symmetric and monovalent; their size and chemical characteristics are ignored.

<table>
<thead>
<tr>
<th>From (Monroe et al. 2009)</th>
<th>From (Kornyshev et al. 2010)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon_s$</td>
<td>78.33</td>
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<tr>
<td>$\epsilon_d$</td>
<td>34.82</td>
</tr>
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<td>$K_{\infty,s}$ (F m$^{-2}$)</td>
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</tr>
<tr>
<td>$K_{\infty,d}$ (F m$^{-2}$)</td>
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</tr>
<tr>
<td>$\gamma_{d,s}$ (J m$^{-2}$)</td>
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<tr>
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</tr>
</tbody>
</table>

Table 4.1: Parameter values for a nitrobenzene droplet surrounded by an aqueous electrolyte. The values of the inner layer parameters are considered independent of electrolyte concentration.

4.3.1 Contact angle

Model predictions show that a strong electrowetting effect can be obtained for very low voltages, Figure 4.3. As the applied voltage increases, the droplet contracts and eventually detaches, or dewets. The equilibrium contact angle depends on electrolyte concentration in the droplet and surrounding. Increasing $c_d$, the electrolyte concentration in the droplet, while keeping $c_s$ fixed, is predicted to decrease the strength of the electrowetting effect; dewetting takes place at lower potentials. This effect is rather counterintuitive and is briefly discussed below. In Monroe et al. (2006a), an analysis of the electrowetting effect as predicted by the model is presented in the limit of no inner layers.
Figure 4.3: The electrowetting effect becomes weaker for increasing electrolyte concentration in the droplet. Parameters: $c_s = 0.5\, \text{M}, \alpha_0 = 1^\circ$.

### 4.3.2 Capacitances

As previously mentioned, the electrowetting effect can be rationalised as the outcome of the competition of capacitances at the three interfaces. The total capacitance across the droplet and that of the ‘se’ interface are effectively in parallel. Minimisation of the system free energy is equivalent to a variation of interfacial areas in the direction of increasing the area of the strongest capacitor.

In the case of the EWOD system, the intuition gained from the capacitance perspective is an accurate prediction of the ideal system behaviour. For the ITIES, however, the presence of the electrolyte inside both droplet and surrounding liquids adds significant complexity to the capacitance model, such that the value of the equilibrium contact angle relative to $\alpha_0$ is not easily predictable. In series are now the capacitances of the ‘ds’ and ‘de’ interfaces, of similar magnitude. The droplet volume is constrained, such that the ‘de’ and ‘ds’ areas are not independent: as the contact angle increases, the ‘de’ area decreases, while both ‘ds’ and ‘se’ areas must increase. As higher applied potentials lead to larger contact angles, a larger charge density accumulates at the ‘ds’ interface. Due to the condition of net droplet electroneutrality, the same amount of charge must gather at the ‘de’ interface. If $A_{de} \ll A_{ds}$ then the charge density at the ‘de’ interface is much larger, and so is its differential capacitance.

The capacitance of the ‘se’ interface is not influenced by changes in the electrolyte concentration in the droplet. Figure 4.4(c) illustrates a typical relation between the inner layer, diffuse layer and total capacitance, exemplified for $C_{se}$. Since the value of $c_s$ is relatively high, the low capacitance of the compact layer dominates $C_{se} \approx C_{se}^{il}$. 
Figure 4.4: Capacitances at the three interfaces for a droplet in equilibrium. Parameters: $c_s = 0.5 \text{ M}$, $\alpha_0 = 1^\circ$. 
Capacitances for the ‘de’ and ‘ds’ interfaces for equilibrium configurations of the droplet are shown in Figure 4.4(a) and Figure 4.4(b) for a range of voltages. The potential drop across each of them is smaller than that of the applied potential, shown on the x-axis. $C_{de}$ exhibits the predicted features of an electrified solid/liquid interface: as the electrolyte concentration increases, so does the diffuse layer capacitance, and the inner layer begins to dominate the total capacitance. This is visible in the peak centred around $V = 0$ that forms for $c_d = 0.5 \text{m}$. As the voltage is increased, the total capacitance eventually reaches the saturated value of the inner layer. For the range of voltages needed for a significant electrowetting effect in this system (nitrobenzene/water), both diffuse and compact layers contribute.

$C_{ds}$ increases with electrolyte concentration, as expected. Its relatively flat shape with voltage can be explained by the fact that the voltage drop over it varies only ‘slowly’, $dV_{ds}/d\Delta V$, as shown in Figure 4.5(b) as $\Delta V$ changes from 0 V to 1 V, the ‘ds’ interface only experiences a maximum of 0.12 V. On the equivalent ‘stretched’ axis, $C_{ds}$ would have the familiar shape of a Verwey Niessen capacitance.

The capacitance of the ‘ds’ interface increases with higher $c_d$, as $C_{ds}$ is described according to the GC theory, as in Equation 2.2.2. In terms of the ‘ds’ interface, the presence of higher electrolyte concentration in the droplet amplifies the electrowetting response. Conversely, in the competition between the ‘de’ and the ‘se’ interfaces, the presence of electrolyte in the droplet weakens the response. $C_{de}$ increases with increased $c_d$, such that the tendency of the ‘se’ to increase its area is hindered; higher $c_d$ weaken the electrowetting response. For the chosen parameter values, the model predicts that this second effect is stronger, as illustrated by Figure 4.3. Calculations show that the difference between the two competing effects in capacitances is only minimal, and could be overcome by competing effects in reality. One consideration is the effect of electrolyte concentration on the liquid/liquid surface tension, briefly discussed in Section 5.2.

### 4.3.3 Potential distribution

The details of potential distribution across the individual interfaces determine the capacitance values. The distribution of potential drops in the system is displayed in Figure 4.5. In general, most of the voltage drop occurs over the ‘de’ and ‘se’ interfaces, due to the existence of the inner layer. The fraction becomes larger for higher $c_d$, when the inner layer is dominant. $V_{ds}$ reaches a maximum for intermediate applied voltages; in the extreme case of very low or very high applied voltages, corresponding to the absence of electric field or for dewetting, the potential in the bulk of the droplet becomes zero. The droplet is at the same potential as the surrounding bulk.

As the applied potential increases, a smaller fraction of it drops over the ‘ds’ interface, Figure 4.5(d). The majority of the applied potential drops over the ‘de’ interface, indeed increasingly so at large voltages. This is a consequence of droplet electroneutrality and of $A_{ds} \gg A_{de}$, as explained above.
Chapter 4. ITIES equilibrium

Figure 4.5: Calculated potential drops in equilibrium. Parameters: $c_s = 0.5 \text{ M}$, $\alpha_0 = 1^\circ$.

Figure 4.6: Potential drop across the ITIES positioned at $x = 0$. The distance on either side of the interface is normalised by the inverse Debye length.
Although the fraction of the voltage drop over the ‘ds’ interface is relatively small, the energy of this interface plays a significant role in determining the equilibrium shape of the droplet. Following the calculations in Section 2.2, Figure 4.6 displays the expected behaviour of $V_{ds}$, the potential distribution over two diffuse layers in series.

Conclusion

The equilibrium theory developed in Monroe et al. (2009) predicts a strong electrowetting effect in systems based on ITIES and allows the tuning of different system parameters in order to increase the effect. These theoretical predictions, however, can only be validated by experimental evidence.
Bibliography


Chapter 5

An experiment

5.1 Experimental procedure and results

The viability of the ITIES system for applications requiring strong electrowetting effect and ultra-low voltages was experimentally investigated by Kucernak and coworkers, (Kornyshev et al. 2010). The system studied consisted of a sub-millimetre droplet of nitrobenzene of 0.1 µL with dissolved TBA⁺-TPB⁻ (tetrabutylammonium tetraphenylborate) electrolyte, on a sputtered gold electrode, in an aqueous solution of lithium chloride. Voltages were measured in an electrochemical cell vs. Ag/AgCl. They found that pinning on the electrode surface led to frequently open hysteresis loops in the contact angle measurements with cyclic voltammetry.

A technique was devised to help alleviate the effect of roughness: voltage pulses were superimposed onto the bias voltage. As their duration was \( \sim 50\mu s \), the pulses were shorter than the response time of ions, and could not lead to significant Faradaic processes. As a result, a strong electrowetting effect and reproducible contact angles for any bias within the stability window were obtained.

Their procedure is best understood by following the changes in the contact angle of the droplet, as depicted in Figure 5.1(a):

- at open circuit, measured independently as 0.005 V, the contact angle is 70°;
- a constant bias voltage of 0 V is applied, followed by a \(-0.650\) V bias;
- ten 50µs pulses of amplitude \(-2.0\) V are applied, each two seconds apart; these intervals were chosen much longer than the time required for the geometry to stabilise so that the effect of each pulse can be observed; every pulse brings the droplet to a more contracted geometry; the steps, however, decrease in size;
- the contact angle saturates at 118°;
Figure 5.1: a) The contact angle hysteresis can be eliminated by pulsed-voltage control. During the periods 0–4.5 s and 24–32 s, the electrode was disconnected and so the potential is uncontrolled. The upper part displays the recorded contact angle, while the lower one the applied potential profile. b) Sample photographs obtained by a CCD camera with videozoom microscope. The contact angle was measured by fitting the digital images to spherical sections. c) Contact angle reached after every subsequent pulse, replotted with data from Kornyshev et al. (2010). Parameters: $c_d = 0.1$ M, $c_s = 0.5$ M.
disconnecting the potentiostat brings the angle down to 88°;

- the potential is set to 0 V;

- ten 50µs pulses of amplitude +2.0 V are applied; as a result, the contact angle returns, gradually, to the initial value of 70°.

Images of the static droplet were taken throughout this procedure; as it can be seen in Figure 5.1(c) the shape is a truncated sphere. The evolution of the cosine of the pinned contact angle with every subsequent pulse is close to exponential, Figure 5.1(b). The pulsing technique was used for a range of bias voltages and for different electrolyte concentrations. Figure 5.2 summarises the largest contact angle obtained for every applied potential.

The experimental results prove that, due to an original pulsing technique, it is possible to eliminate pinning and greatly improve the reproducibility of the measured contact angle values. This is a first proof of principle study that shows that ultra low voltage electrowetting based on ITIES is possible: large angle variations of ∼60° were produced by bias voltages below 1 V. As it will be shown next, the study also highlighted the need for a theoretical description of the dynamics of electrowetting.
5.2 Comparison to theoretical predictions

Although the experiment was designed, in part, to test the validity of the model in Monroe et al. (2009), a comparison between experimental data and theoretical predictions proved difficult. The obtained trend in contact angle in Figure 5.2 seems to oppose the model predictions: as the concentration of either electrolyte is increased, the range of achievable contact angles increases, as does the highest achievable angle. Attempts to predict the behaviour in Figure 5.2 for reasonable system parameters were unsuccessful. An increase in the electrowetting effect with higher $c_d$ can be obtained is varying $\gamma_{ds}$, as discussed below. Other features of the measured contact angle that are particularly difficult to accommodate within the equilibrium model, such as the extended regions in which increasing the applied voltage has little or no effect on $\alpha$.

Interfacial tension

The model contains two parameters that describe the geometry of the droplet in the absence of electric field (or at $V_{pzc}$): the Young Laplace contact angle and the interfacial tension of the liquid/liquid interface. While the influence of the contact angle is mainly to shift the curve $\alpha(V)$ vertically, $\gamma_{ds}$ has a strong impact on the strength of the electrowetting effect, as it dictates the effective stiffness of the liquid/liquid interface. The smaller the value of $\gamma_{ds}$, the more the droplet shape changes as a result of varying potential. By splitting the interfacial energy into a concentration-independent $\gamma$ term and a concentration-dependent $\tilde{\varepsilon}$ term, it was assumed that this elasticity is independent of the electrolyte concentration even at the high charge densities surrounding the electrified ities. Qualitatively, one expects that the value of $\gamma_{ds}$ is reduced by the presence of electrolyte in the oil droplet, the phase with lower dielectric constant. This would be in line with the trend seen in Figure 5.2 with respect to concentration variations. For system parameters corresponding to Kornyshev et al. (2010), a change in $\gamma_{ds}$ of 20% leads to changes in $\alpha$ of $\approx 25\%$.

The effect of dissolved electrolyte onto the surface tension of the air/electrolyte interface was studied by Onsager & Samaras (1934), who theoretically modelled the increase in $\gamma$ with electrolyte concentration. A similar mixing rule as that in the Onsager-Samaras model could be derived for the electrolyte/electrolyte interface. This result, unfortunately, would only be an instructive estimate, as its validity is limited to cases in which the Debye-Hückel approximation holds. This approximation assumes concentrations below 0.01 $\text{M}$.

Experimental evidence of the electrolyte concentration having an effect on the liquid/liquid surface tension was provided by Kakiuchi & Senda (1983). Measured capillary curves showed a variation in $\gamma_{ds}$ from 25.8 mN m$^{-1}$ to 26.8 mN m$^{-1}$ (only 4%) when the concentration of LiCl$_{aq}$ was changed from 0.01 $\text{M}$ to 1 $\text{M}$, while that of the TBA$^+\text{-TPB}^-$ in nitrobenzene was kept at
For the concentration of the aqueous electrolyte fixed and that of nitrobenzene varied, the change in $\gamma_{ds}$ was slightly smaller. The effect of other assumptions on the model results was also tested. The roughness of the electrode surface can have a significant impact on the effective area of both the $de$ and $se$ interfaces, considered flat in the theoretical model. A theory to account for this effect on the capacitance of electrolyte/electrode interfaces was developed by Daikhin et al. (1998). The value of $V_{\text{pzc}}$ can, in principle, change as a result of surface reorganisation with voltage. As the gold electrode used is sputtered, this effect was not considered.

5.3 Conclusion

The experiment of Kucernak and coworkers proves that ultra-low voltage electrowetting with ITIES is possible, due to their original pulsing technique. A few fundamental questions are raised by the attempt to fit the data of Kornyshev et al. (2010) with any theoretical model. What is the Young Laplace contact angle $\alpha_0$ in a real system and can it be measured? What is the point of zero charge in a three phase system, with three interfaces and two electrolytes? These are topics that go beyond the subject of electrowetting and that will require, most probably, much coordinated theoretical and experimental investigation to solve. Other questions are more specific to this experiment. What is the role of pulsing in combating pinning? What is the relation between the equilibrium geometry of a droplet in an ideal system and that measured after the pulsing and recorded in Figure 5.2? It is these latter questions that we are trying to answer with a theory of dynamics of electrowetting, rather than with that of (Monroe et al. 2009).

\footnote{Markin et al. (2005) obtained more striking differences in different systems of non-polarisable water/nitrobenzene interfaces, i.e. in which the electrolyte is distributed between the two phases, e.g. TBA$^+$-Cl$^-$.}
Bibliography


Chapter 6

Theory of dynamics

Attempts to correlate the theoretical predictions with the experimentally observed trends failed, even when accounting, at least qualitatively, for the effects of electrolyte concentration on the liquid/liquid surface tension, of electrode roughness on capacitor area, and of surface reorganisation on the point of zero charge. Does this mean that the theory of Monroe et al. (2009) is fundamentally wrong? Let us put aside the promising results of Figure 5.2 and concentrate instead on the evolution of the droplet through one single pulsing cycle as given in Figure 5.1(a).

This study of the time response is invaluable for understanding the details of the dynamics of electrowetting on real surfaces. It was shown that, in the absence of pulsing, surface roughness and heterogeneity create pinning forces strong enough to stop the droplet from reaching its equilibrium position. The effective friction forces are thus not negligible. Under pulsed voltage, the dynamics and range of contact angle variation were found to be significantly different, including seemingly perfect reproducibility. These observations lead to the conclusion that a theory that describes the dynamics of the ITIES system is needed. In the least, such a theory should rationalise the effect of pulsing on the droplet dynamics and its interplay with surface roughness, i.e. the stick-slip motion of the droplet, as well as the fact that initial and final angles for a pulsing cycle are the same.

A theory of pulse-assisted electrowetting in ITIES can be developed based on the existing equilibrium model in Monroe et al. (2009). A first such theory is detailed in the present chapter, together with its main predictions, and a comparison with the experimental data, as in Marinescu et al. (2010). It is a phenomenological model built on the assumption that the motion of the droplet is determined by two competing forces: a driving and a resisting force. The first is caused by the applied voltage, when the droplet is not in the equilibrium configuration, while the second is caused by the friction with the surface of the metal electrode. Changes in the droplet geometry are described by the motion of the triple phase contact line (CL). Seen from this perspective, the effect of the applied pulses is to facilitate the depinning of the CL.
6.1 Model formulation

As mentioned before, the shape of the macroscopic droplet is a truncated sphere, proven both by experimental images in Kornyshev et al. (2010) and by calculations (Monroe et al. 2007). The CL is a perfect circle if the electrode roughness correlation length is small compared to the size of the droplet. In this case, the geometry of the droplet is unambiguously characterised by the instantaneous size of the wetting spot, in other words by the radius $R$ of the CL. Equations describing the dynamics of the droplet in Figure 6.1 are formulated in terms of the time-dependent function $R(t)$. Geometrical considerations and the constraint of constant $v_d$ yield an implicit relation between the instantaneous contact angle $\alpha(t)$ and $R(t)$:

$$\sin \alpha = \frac{R}{r_d}, \quad \cos \alpha = 1 - \frac{h_d}{r_d}, \quad r_d = \frac{v_d}{\pi h_d^2} + \frac{r_d}{3},$$

(6.1.1)

where $h_d$ is the height of the droplet and $r_d$ the radius of its curvature, as defined in Figure 4.2.

6.1.1 Acting forces

Two forces act on the CL when a voltage $V$ is applied:

- a driving force $F_d$ that tends to bring the droplet to the new equilibrium contact angle corresponding to $V$, and
- a friction force $F_f$ that opposes the motion caused by $F_d$.

$F_f$ may be considered homogeneous and isotropic as long as the electrode surface exhibits no macroscopic patterning.
6.1.1.1 The friction force $F_f$

$F_f$ includes two contributions: the static friction $F_0$, independent of velocity, is caused by the chemical and geometrical roughness of the electrode surface, while the other contribution, dependent on velocity, accounts for the viscous dissipation through the rheological flow:

$$F_f = -F_0 \text{sign} (\dot{R}) - \eta \dot{R}.$$  \hfill (6.1.2)

Here $\eta$ is a damping coefficient determined by the fluid viscosity close to the electrode surface, $\dot{R} = \frac{dR}{dt}$, and sign is the signum function, defined as

$$\text{sign}(x) = \begin{cases} -1 & \text{if } x < 0, \\ 0 & \text{if } x = 0, \\ 1 & \text{if } x > 0. \end{cases}$$

The limiting value at vanishing velocity is given by the static friction $F_0$, as in Buguin et al. (2006) and Mueser et al. (2003). From rest, the cl starts moving when $F_d$ becomes larger than $F_0$.

Throughout this analysis, $F_0$ is assumed constant, a characteristic of the electrode roughness. It can be argued, however, that this is not the case; modified expressions for $F_0$ and their effect on the model predictions are discussed briefly in Section 6.1.2.

6.1.1.2 The driving force $F_d$

$F_d$ acts when the droplet is not in the ideal equilibrium configuration $R_{eq}(V)$ dictated by the potential applied, and is expected to decrease as the cl approaches this radius. The driving force experienced in a configuration $R$ can be calculated as $F_d = \partial \Delta G(V,R) / \partial R$, where $\Delta G$ is the Gibbs free energy of the system, as in Equation 4.2.1. At fixed $V$, the variation of $\Delta G(R)$ close enough to its minimum at $R_{eq}$ can be approximated by a parabola, as illustrated in Figure 6.2. In this range, $F_d$ is linear with displacement, and a relation resembling Hooke’s law can be written:

$$F_d(V) = k(V)(R_{eq}(V) - R), \quad \text{with} \quad k(V) = -\frac{\partial^2 \Delta G}{\partial R^2} \bigg|_{R=R_{eq}(V)}.$$  \hfill (6.1.3)

The effective stiffness $k$ and equilibrium configuration $R_{eq}$ constitute thus the link with the equilibrium model of electrowetting with ITIES in Monroe et al. (2009).

As $\Delta G(R)$ is derived from an equilibrium model, its value is strictly valid only at the minimum; the accumulation of charge at each interface is assumed to screen fully the applied potential. $\Delta G$ at geometries around equilibrium are calculated by fixing $R$, and assuming that the ion distribution responds instantaneously, i.e. the bulks of the two liquids are electroneutral. The
Figure 6.2: The free energy of the system $\Delta G(R)$ is calculated from Equation 4.2.1 as detailed in Appendix A. Around its minimum, $\Delta G(R)$ is approximated by a parabola. Parameter values: $\alpha_0 = 1^\circ$, $c_d = 0.1 \text{ m}$, $c_s = 0.5 \text{ m}$, and voltage $V$. As a result, $k \approx 0.1 \text{ N m}^{-1}$.

6.1.2 Equation of motion

The equation governing the motion of the CL under applied potential, subject to the two acting forces, resembles that used by Buguin et al. (2006) to model mechanical shaking:

$$F_f + F_d = m\ddot{R} \Rightarrow m\ddot{R} + \eta\dot{R} = k_{(b,p)}(R_{eq(b,p)} - R) - F_0 \text{sign}(\dot{R}),$$

where $m$ is the accelerated mass in the system, and the subscripts $b$ and $p$ denote characteristic parameters during the applied bias $V_b$ and pulse $V_p$. A pulse of amplitude $V_p$ of the same sign as the bias voltage enhances the driving force, and can affect the droplet motion. $k_b(V)$ increases with $V$, Figure 6.2, as does the distance between an initial set position $R$ and the equilibrium one $R_{eq}(V_p)$; thus $F_d$ increases with $V_p$.

The first term in Equation 6.1.4 is inertial, unusual for a model of the wetting dynamics of droplets (Berge & Peseux 2000, Hendriks et al. 2005). This mass-dependent term, however, contributes significantly to the motion of a droplet under short voltage pulses, similar to the response of a solid/solid system to mechanical shaking (Buguin et al. 2006).
During the short pulse, the droplet displacement is negligible, but the CL may acquire a finite velocity due to the increased driving force. After the pulse is turned off, the CL continues to move due to inertia. During this motion, $F_d$ is proportional to the distance from the equilibrium position under the bias, while the inertial force is decreasing due to viscosity. When the sum of these forces is balanced by $F_0$, the CL stops. When $R \in [R_{eq}(V_p), R_{eq}(V_b)]$, $F_d$ during bias points in the opposite direction from $F_d$ during pulse. Each further pulse drives the contact line to move further, but the sliding distance is shorter.

The equilibrium CL radius in the presence of friction is obtained from Equation 6.1.4 for zero acceleration and velocity:

$$R_{pin(b,p)} = R_{eq(b,p)} - \frac{F_0 \text{sign}(\dot{R})}{k_{(b,p)}} = R_{eq(b,p)} \pm \frac{F_0}{k_{(b,p)}},$$

(6.1.5)

with ‘+’ for contracting motion ($\text{sign}(\dot{R}) = -1$), and ‘−’ for spreading ($\text{sign}(\dot{R}) = 1$). $R_{pin}$ are hence the limiting radii for infinitely slow contraction or spreading. From Equation 6.1.5 one can conclude that the maximum contact angle hysteresis is caused by surface roughness, here characterised by the static friction force, $R_{pin+} - R_{pin−} = 2F_0/k$. This result is in line with the conclusion of Tadmor (2008), based on experimental results of advancing and receding angles of liquid droplets.

**Contact dependent friction force**

As mentioned, buoyancy does not play a role for the system considered here, and $F_0$ does not depend on the weight of the droplet. Its independence of $R$, however, is less certain. Bowden & Tabor (2001) and Gao et al. (2004) assume the static friction in liquid drops is independent of the contact area, in analogy to the friction force between solids: $F_0 = \mu N_r$ with $\mu$ the coefficient of friction and $N_r$ the normal force.

For a droplet on a solid surface the friction is caused by the molecular interactions taking place at the liquid/solid interface, rather than by the droplet weight. It is reasonable, for example, to expect the static friction force acting on the droplet when close to dewetting to be significantly smaller than that close to complete wetting. A relation $F_0 = \beta R^n$ might be appropriate, where $\beta$ is the proportionality constant. $n = 1$ if the relevant interactions are those along the moving CL, and $n = 2$ if the contact area rather than the CL is the determining factor. Determining which of these approaches is correct when modelling friction in liquid dynamics is beyond the scope of the current model.

Assuming that most of the resistance to the motion of spreading or contracting is met within a narrow region around the three phase CL, the relation $F_0 = \beta R$ can be substituted in the equation of motion, Equation 6.1.4 giving

$$m\ddot{R} + \eta\dot{R} = \tilde{k}_{(b,p)}(R_{eq(b,p)} - R) - \tilde{F}_0 \text{sign}(\dot{R}).$$

(6.1.6)
with \( \tilde{k} = k + \beta \text{sign}(\tilde{R}) \) and \( \tilde{F}_0 = \beta R_{\text{eq}(b,p)} \). In the case of a first order proportionality relation between \( F_1 \) and \( R \), the motion of the droplet maps onto that for \( R \)-independent \( F_1 \), with modified values for the stiffness coefficient and static friction. If the contact area rather than length of the cl are the determining factor, \( F_0 = \beta R^2 \), this mapping is not possible.

### 6.1.3 Effect of a voltage pulse

After a time \( \tau \) equal to the relaxation time of the double layer, the applied voltage is completely screened by the charge accumulation at interfaces. This is the case during most of the time in which the bias voltage acts, and the equilibrium model in Monroe et al. (2009) can be used to obtain a value for \( k(V_b) \) and \( R_{\text{eq}}(V_b) \). The pulses used, however, are extremely short, 50\( \mu \)s, such that only partial relaxation takes place. The times for ionic migration to charge the double layers can be estimated according to \( \tau = L \cdot \lambda / D \) where \( \lambda \approx 10^{-7} \) cm is the Debye length in the nitrobenzene droplet of \( c_d = 0.1 \) m, \( D \approx 10^{-5} \) cm\(^2\) s\(^{-1}\) the diffusion constant, and \( L \) the distance over which the ions migrate; \( L_d \approx 0.1 \) cm in the droplet, and \( L_s \approx 1 \) cm between the working and counter electrodes in the surrounding phase. The corresponding migration times are \( \tau_d \approx 10^{-3} \) s and \( \tau_s \approx 10^{-2} \) s. Times for reaching equilibrium in the droplet and surrounding media are different; the effect of this on the droplet dynamics at such short timescales is not explored. We only conclude that the double layers do not have the time to re-arrange and reach equilibrium during the applied pulse, as \( \tau_p \ll \tau_{d,s} \), and the voltage drop extends throughout the droplet and surrounding for the duration of the pulse. The pulses are seen to have a strong effect on the final position of the droplet, as seen in the experimental results of Kornyshev et al. (2010). Can the same equilibrium model be used to obtain equivalent \( k \) and \( R_{\text{eq}} \) values during a pulse?

Let us consider the first moments after applying a higher voltage, at times that are orders of magnitude shorter than \( \tau_p \). An increase from \( V_b \) to \( V_p \) has the immediate effect of setting a potential drop \( V_p - V_b \) across the entire system, a distance of \( \sim 1 \) cm between the working and counter electrodes. Under the influence of this relatively weak electric field, the ion species in both electrolytes start drifting towards the respective interfaces, where they accumulate, and contribute to the screening of the newly applied potential. The quantity of charge reaching the double layers depends both on the intensity of the applied potential that determines the intensity of the electric field, and on the duration of the pulse. The latter dependence is not straightforward: as more ions reach the double layer and screen the potential, the electric field in the system decreases, and with it decrease the ion currents reaching each interface. For an accurate description of the effect of pulsing on charge distribution, the non-linear electrokinetics of the ion motion through the solution should be modelled (Bazant et al. 2009). Instead of developing a detailed model for the time dependence of ionic drift velocity \( v(t) \) in the first moments after a voltage is applied, the upper limit of \( v(t) = \text{const.} \cdot v(0^+) \) is considered in the following.
The ion velocity \( v(t) \) caused by the fraction of the applied potential that is unscreened at the end of the pulse is estimated as

\[
v = \frac{zeDV_p - V_b}{k_BT} L, \tag{6.1.7}
\]

with \( ze \) the ion charge, here \( z = \pm 1 \). The corresponding extra charge density \( \delta Q \) accumulated at each liquid/electrode interface during the pulse is

\[
\delta Q = \frac{(ze)^2eNADV_p - V_b}{k_BT} \tau_p, \tag{6.1.8}
\]

where \( c \) is the bulk molar concentration of the electrolyte. In arriving to the expression above, one uses: \( j = nev, D = \mu_{i\text{on}}k_BT, \mu_{i\text{on}} = v/F_{\text{el}}, \) and \( F_{\text{el}} = eE = eV/L \). It is assumed for simplicity that all ions have the same hydrodynamic radius in both media. For typical values of system parameters: \( \alpha_0 = 1^\circ, V_p = 1 \text{ V}, V_b = 0.65 \text{ V}, V_{\text{pzc}} = 0.3 \text{ V}, D = 10^{-5} \text{ cm}^2\text{s}^{-1}, L = 1 \text{ cm} \) in surrounding, \( \tau_p = 50 \mu\text{s}, T = 295 \text{ K}, c_s = 0.5 \text{ M}, \) and \( c_d = 0.1 \text{ M} \), one obtains \( \delta Q_s = 32.8 \mu\text{C cm}^{-2} \) for the ‘se’ interface and \( \delta Q_d = 6.57 \mu\text{C cm}^{-2} \) for the ‘de’ one.

An extra charge \( \delta Q \) gathered per unit area of an interface screens an extra potential \( \delta V \)

\[
\delta V = \frac{\delta Q}{K} = \delta Q \left( \frac{1}{K_{\text{dl}}} + \frac{1}{K_{\text{il}}} \right), \tag{6.1.9}
\]

with \( K_{\text{dl}} \) and \( K_{\text{il}} \) the diffuse and inner layer specific integral capacitances. Because the diffuse layer does not rearrange under \( V_p \), \( K_{\text{dl}} \) and \( K_{\text{il}} \) are assumed to maintain their values from during the bias voltage.

\( K_{\text{il}} \) is calculated as in Section 2.3.2 while \( K_{\text{dl}} \) is calculated as in Equation 2.1.9 from the known form of the differential capacitance for a Gouy-Chapman diffuse layer:

\[
K_{\text{dl}}(U_{\text{dl}}) = \frac{1}{U_{\text{dl}}} \cdot \int_0^{U_{\text{dl}}} C_{\text{dl}} \text{d}V = \frac{Q}{V_{\text{dl}}}, \tag{6.1.10}
\]

where \( Q \) is the existing charge at the respective liquid/electrode interface, contained exclusively by the diffuse layer, and the dimensionless potentials \( U_{\text{dl,il}} = zFV_{\text{dl,il}}/(RT) \) are obtained as described below. For the ‘se’ interface, \( Q \) is calculated through the following steps:

1. solve Equation 14 in (Monroe et al. 2009) for \( U_{\text{se,il}} \), given in Equation A.2a
2. obtain \( U_{\text{se,dl}} = \Delta U - U_{\text{se,il}} \)
3. calculate the differential capacitance of the diffuse layer according to the Gouy-Chapman model in Equation 2.1.10

\[
C_{\text{dl}} = \frac{\epsilon_0\epsilon_s}{\lambda_s} \frac{U_{\text{dl}}}{\cosh \frac{U_{\text{dl}}}{2}}, \tag{6.1.11}
\]

\(^1\)Voltage values in the theoretical analysis are given as absolute values; in some model predictions, however, it is instructive to consider the effect of a nonzero \( V_{\text{pzc}} \).
4. calculate the total charge in the diffuse layer by integrating the capacitance over potentials from 0 to the total voltage drop over the diffuse layer

\[ Q = \int_0^{V_{\text{eff}}} C_{\text{dl}} \, dV. \] (6.1.12)

The charge in the ‘de’ diffuse layer is obtained analogously, with the substitution \( \Delta U \rightarrow \Delta U - U_{\text{ds}} \).

For the set of parameter values given above: \( Q_{\text{se}} = 160 \mu\text{C cm}^{-2} \) and \( Q_{\text{de}} = 74.3 \mu\text{C cm}^{-2} \). As expected, a higher charge density is reached at the se interface than at the ‘de’ one, because \( \epsilon_s > \epsilon_d \), water versus nitrobenzene, and \( c_s > c_d \). The extra charge accumulated under the pulse and the corresponding extra screened potential are each approximately a quarter of their value under \( V_b \). The integral capacitance of the diffuse layer is significantly higher than that of the inner layer, as the charge is stored in the former.

The extra screened voltage due to changes in charge density at the three interfaces, leads to an instantaneous driving force different from that in the absence of the pulse. The driving force during the pulse is assumed to be equal to that acting on the contact line under a bias voltage \( V_{\text{eff}} = V_b + \delta V \), with \( \delta V \) given by Equation 6.1.9 corresponding \( k(V_{\text{eff}}) \) and \( R_{\text{eq}}(V_{\text{eff}}) \) are calculated.

This analysis provides an upper limit of the effect of the pulse, since the flux of charge towards the interfaces decreases with time, as the unscreened voltage in the bulk of both liquids decreases. This effect is not included in the estimations above, as can be seen in the naive character of Equation 6.1.7.

6.1.4 System parameters

The exact time evolution of the contact angle of a pulsed droplet can be followed by solving Equation 6.1.4. First, however, values need to be assigned to all model parameters. It has been shown that \( k \) and \( R_{\text{eq}} \) can be obtained from the equilibrium theory. Using the model of Monroe et al. (2009) implies, of course, full knowledge of the electrochemical properties of the system, such as \( V_{\text{pzc}} \) and properties of the inner layers, not always possible. Besides, there are three extra parameters from the phenomenological considerations of dynamics: \( m \), \( \eta \), and \( F_0 \). Their values or even exact physical interpretation is not straightforward. Further quantitative information experimentally obtained for a specific system is highly desirable. If the number of unknowns is reduced, considering them as fitting parameters becomes feasible. Until then, only a discussion of possible values of these parameters is possible.
6.1.4.1 Viscosity and damping

The viscosity involved in the CL motion is an effective property of a liquid film during slip, and can be different from the bulk value by up to two orders of magnitude (Klein 2007). The damping coefficient in the model is related to viscosity through \( \eta = \eta_{surf} \cdot L \), where \( L \) is a characteristic length of the system, such as the droplet radius \( L = 1 \text{ mm} \). At 25°C the bulk viscosity of water is \( \eta_{bulk, w} = 9 \cdot 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1} \) and of nitrobenzene is \( \eta_{bulk, d} = 2 \cdot 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1} \). Thus, \( \eta \approx 10^{-6} \text{ kg s}^{-1} \) to \( 10^{-3} \text{ kg s}^{-1} \).

6.1.4.2 Moving mass

The parameter \( m \) characterises the fraction \( p \) of liquid mass, from both droplet and surrounding, that rearranges when the CL changes radius infinitesimally. Both \( p \cdot \rho_d \cdot v_d \) and \( p \cdot (\rho_d - \rho_s) \cdot v_d \) seem reasonable assumptions; a correct approach must reflect the droplet motion at the microscopic level. The two expressions give similar results for the system studied experimentally; at 25°C, 1 atm: water, \( \rho_s = 997.0 \text{ kg m}^{-3} \), and nitrobenzene, \( \rho_d = 1199 \text{ kg m}^{-3} \). For \( p = 0.1 \) and droplet volume \( v_d \approx 10^{-10} \text{ m}^3 \), \( m \approx 10^{-9} \text{ kg} \) to \( 10^{-8} \text{ kg} \).

6.1.4.3 Static friction

The static friction is a macroscopic characteristic of the electrode surface and should be related to the degree of roughness and inhomogeneity. A relation between the geometrical characteristics of roughness, such as correlation length and peak height, and the value of \( F_0 \) does not exist. In the system considered here, one expects that \( F_0 \) values are comparable with those measured for the lateral friction forces for sessile liquid droplets of hexadecane on Teflon and OTA treated mica. For this system, Tadmor et al. (2009) found \( F_0 \approx 10^{-5} \text{ N} \). In the present model, the static friction term is considered independent of the CL radius.

6.1.4.4 Point of zero charge

A nonzero value of \( V_{pzc} \) is an ubiquitous phenomenon in electrochemistry. For example, values of the \( V_{pzc} \) measured on a single crystal gold surface for KPF_{6} solution, varied between between 0V and 0.3V, depending on the crystal phase and the concentration of the solution (Hamelin & Stoicoviciu 1987b). The value of the apparent \( V_{pzc} \) shifted towards more positive values as concentrations increased from 0.001 m to 0.030 m. In the experimental setup of Kucernak and coworkers, the electrode surface is polycrystalline and the solution concentrations are at least one order of magnitude larger. A value of 0.3 V is chosen here, in order to illustrate the effects of a non-zero \( V_{pzc} \). It is expected that \( V_{pzc} > 0 \) in the experimental system, since positive pulses on top of a zero bias lead to spreading of the droplet, indicating that \( \alpha_0 \) had not been yet reached.
In the case of pulsing, the value of $V_{pzc}$ is particularly important, as the droplet motion may be triggered only if

\[
\begin{align*}
\text{contracting} & \quad R_{eq,b} + \frac{F_0}{k_p} < R_{eq,b} + \frac{F_0}{k_b}, \\
\text{spreading} & \quad R_{eq,b} - \frac{F_0}{k_b} < R_{eq,b} - \frac{F_0}{k_p}.
\end{align*}
\]

Since $R_{eq,b}$ is largest for $V_b = V_{pzc}$, a pulse on top of $V_b$ causes a driving force towards increasing $R$ only when $|V_b - V_{pzc}| > |V_{eff} - V_{pzc}|$.

In-depth studies of the $V_{pzc}$ value for particular interfaces do not answer all questions, however, in the absence of a meaningful interpretation of the $pzc$ in a three-phase system. The pulsing technique could provide a tool for identifying the existence and value of an effective $V_{pzc}$.

### 6.1.4.5 Young Laplace contact angle

The equilibrium contact angle of the system, a parameter difficult to measure on a real surface, is dependent on the properties of all three phases, and on the presence of dissolved ions. Measurements performed by Yoshida et al. (2003) on a nitrobenzene droplet, surrounded by aqueous electrolyte on a glassy carbon electrode, indicate an equilibrium angle around 95°, with a dependence on electrolyte concentration: more concentrated electrolyte in the polar phase increases its hydrophilicity. These studies, however, were performed on a different electrode material, and with different electrolytes (sodium perchlorate and sodium dodecylsulfonate in water, tetrabutylammonium perchlorate and ferrocene in nitrobenzene). Studies more relevant to the system considered by Kornyshev et al. (2010) are unknown to us. In the following, complete wetting of the gold surface by nitrobenzene was considered, with $\alpha_0 = 1^\circ$, in reality, this value is expected to be larger. As friction plays an important role, $\alpha_0$ is expected to be smaller than the value of the initial and final angle of 70° in Figure 5.1(a), the most spread geometry obtained during the cycle.

### 6.2 Model predictions - an analytical result

A closed-form analytical solution to the equation of motion in Equation 6.1.4 is calculated for a set of simplifying assumptions. Although it has limited validity, this result helps rationalise the contact motion and exhibits the main characteristics of the system dynamics measured by Kornyshev et al. (2010). The model predicts the stick-slip motion under successive pulsing, as well as the decreasing step size of the contact angle evolution with each subsequent pulse.

The notations used are listed below:
• $m$ - accelerated/moving mass in the system, \textit{i.e.} the fraction of liquid mass, in the droplet or/and surrounding, rearranging when the CL moves;

• $\eta$ - viscosity of the moving liquid, could be a special surface property, much larger than bulk viscosity; it has the units of viscosity per length; the characteristic size of the system is taken as $r$, the minimum radius of the droplet;

• $F_0$ - the static friction between liquid and the rough electrode;

• $k_{b,p}$ - elastic constants in the driving force;

• $\tau_p$ - pulse duration;

• $R(t)$ - instantaneous radius of the CL;

• $R_{eq(b,p)}$ - equilibrium radii on an ideal surface, \textit{i.e.} in the absence of friction: $R_{eq,b} = R_{eq}(V_b)$, $R_{eq,b} = R_{eq}(V_b + \delta V)$;

• $R_{pin(b,p)}$ - pinning radii in the presence of friction, \textit{i.e.} equilibrium under the action of driving and friction forces, for infinitesimally slow motion; it is taken as the initial position, before the first pulse is applied.
6.2.1 Initial position

At $t = 0$ the droplet is brought from a zero volt bias to $V_b < 0$. As a result, the CL radius decreases, $\dot{R} < 0$ and the CL is pinned at,

$$ R_{\text{pin},b} \equiv R(0) = R_{\text{eq},b} + \frac{F_0}{k_b}, \quad \dot{R}(0) = 0, \quad (6.2.1) $$

for a CL moving infinitely slowly, from Equation 6.1.5. $R_{\text{pin},b}$ in Equation 6.2.1 is considered the initial radius of the CL. In reality, this need not be the case, as $R_{\text{pin},b}$ can be overshot due to non-zero inertia and velocity. The assumption does not affect the main predictions of the approximate solution.

6.2.2 During the pulse

During the first pulse, $0 < t < \tau_p$, the equation of motion reads

$$ m \ddot{R} + \eta \dot{R} = k_p (R_{\text{pin},p} - R) - F_0 \text{sign}(\dot{R}). \quad (6.2.2) $$

As the pulse is very short, the condition $\dot{R} < 0$ remains valid throughout, and the exact solution is:

$$ R(t) = R_{\text{pin},p} - \left( A_1 \cdot e^{-\lambda_1 t} + A_2 \cdot e^{-\lambda_2 t} \right), \quad (6.2.3a) $$

$$ \lambda_{1,2} = \frac{\eta}{2m} \left( 1 \pm \sqrt{1 - \frac{4k_p m}{\eta^2}} \right). \quad (6.2.3b) $$

$R_{\text{pin},p}$ is defined analogously to $R_{\text{pin},b}$ in Equation 6.1.5, and the coefficients $A_{1,2}$ are derived from the initial conditions in Equation 6.2.1

$$ A_{1,2} = \frac{1}{2} (R_{\text{pin},p} - R_{\text{pin},b}) \left( 1 \mp \frac{1}{\sqrt{1 - \frac{4k_p m}{\eta^2}}} \right). \quad (6.2.4) $$

By substituting Equation 6.2.4 into Equation 6.2.3 the closed-form solution after the first pulse becomes

$$ R(t) = R_{\text{pin},p} + (R_{\text{pin},b} - R_{\text{pin},p}) f(t), \quad (6.2.5a) $$

$$ f(t) = \frac{1}{2} \left( 1 - \frac{1}{\sqrt{1 - \frac{4k_p m}{\eta^2}}} \right) e^{-\lambda_1 t} + \frac{1}{2} \left( 1 + \frac{1}{\sqrt{1 - \frac{4k_p m}{\eta^2}}} \right) e^{-\lambda_2 t}. \quad (6.2.5b) $$

The radius of the CL at the end of the pulse, $R(\tau_p)$ and its velocity, $\dot{R}(\tau_p)$ form the initial conditions for the motion during the next bias interval.
6.2.3 After the pulse

At times $t > \tau_p$, the applied voltage is $V_b$, and the equation of motion reads

$$m\ddot{R} + \eta \dot{R} = k_b(R_{eq,b} - R) - F_0 \text{sign}(\dot{R}). \tag{6.2.6}$$

The CL continues to contract in a decelerated motion, due to a weaker driving force than during the pulse. When the CL velocity reaches zero, the direction of the motion could, in principle change, similar to the oscillatory motion of a harmonic oscillator: $R$ has passed beyond its equilibrium value $R_{eq,b}$. Under the effect of the driving force, the CL would start expanding. As soon as the velocity changes sign however, so does the friction term in the expression governing $R_{pin,b}$, Equation 6.1.5.

An analysis of the equation of motion shows that if the CL velocity reaches zero while within the interval $[R_{eq,b} - F_0/k_b, R_{eq,b} + F_0/k_b]$, the droplet is trapped for any realistic values of the static friction. This interpretation is supported by experimental evidence, where no oscillatory motion is visible.

Although the system is in nature oscillatory for the chosen parameter values, the CL is effectively pinned as soon as $\dot{R} = 0$ due to the change in sign of $\dot{R}$. This becomes apparent when Equation 6.1.4 is rewritten for the damping term:

$$\eta \dot{R} = k_{(b,p)} \left( R_{eq(b,p)} - \dot{R} \right) + F_0 - m\ddot{R}, \quad t \to t^*_+, \dot{R} < 0$$

$$\eta \dot{R} = k_{(b,p)} \left( R_{eq(b,p)} - \dot{R} \right) - F_0 - m\ddot{R}, \quad t \to t^*_+, \dot{R} > 0;$$

with $t^*$ denoting the time at which the $\dot{R}$ changes direction; the second equation cannot be fulfilled. With this finding, $\dot{R} < 0$ throughout, and the solution during the first bias interval can be written as:

$$R(t) = R_{pin,b} - \left( B_1 \cdot e^{-\omega_1(t-\tau_p)} + B_2 \cdot e^{-\omega_2(t-\tau_p)} \right), \tag{6.2.7a}$$

$$\omega_{1,2} = \frac{\eta}{2m} \left( 1 \pm \sqrt{1 - \frac{4k_b m}{\eta^2}} \right). \tag{6.2.7b}$$

Initial conditions ensure that the CL displacement and velocity are continuous at time $\tau_p$, when the pulse voltage is switched off. From Equation 6.2.5

$$R(\tau_p) = R_{pin,p} + (R_{pin,b} - R_{pin,p}) f(\tau_p), \tag{6.2.8a}$$

$$\dot{R}(\tau_p) = - (R_{pin,b} - R_{pin,p}) \dot{f}(\tau_p). \tag{6.2.8b}$$
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Figure 6.3: Time dependence of $cl$ motion. Although typical values of the system parameters allow for oscillations, the $cl$ is effectively pinned at $R(t = t^*)$, when the velocity first reaches zero. Parameters: $F_0 = 1.65 \cdot 10^{-5}$ N, $m = 1.2 \cdot 10^{-10}$ kg, $\eta = 0.3 \cdot 10^{-5}$ kg s$^{-1}$, $\alpha_0 = 1^\circ$, $V_{pzc} = 0.3$ V, $c_d = 0.1$ m, $c_s = 0.5$ m, $\tau_p = 50$ μs.

By substitution in Equation (6.2.8) it follows that

$$B_{1,2} = (R_{pin, p} - R_{pin, b}) \left\{ (f(\tau_p) - 1) \left( 1 + \frac{\omega_1 + \omega_2}{\omega_1 - \omega_2} \right) + \frac{2\dot{f}(\tau_p)}{\omega_1 - \omega_2} \right\},$$

(6.2.9)

and the solution after the first pulse and bias interval becomes

$$R(t) = R_{pin, b} + (R_{pin, b} - R_{pin, p}) g(t),$$

(6.2.10a)

$$g(t) = \frac{1}{2} \left\{ (f(\tau_p) - 1) \left( 1 + \frac{\omega_1 + \omega_2}{\omega_1 - \omega_2} \right) + \frac{2\dot{f}(\tau_p)}{\omega_1 - \omega_2} \right\} e^{-\omega_1(t - \tau_p)}$$

$$+ \left[ (f(\tau_p) - 1) \left( 1 + \frac{\omega_1 + \omega_2}{\omega_1 - \omega_2} \right) + \frac{2\dot{f}(\tau_p)}{\omega_1 - \omega_2} \right] e^{-\omega_2(t - \tau_p)} \right\}.$$

(6.2.10b)

$t^* > \tau_p$ denotes the time at which the $cl$ stops, with $R_{f,1} = R(t^*)$. An equation for $t^*$ is obtained from the condition $\dot{R}(t^*) = 0$:

$$e^{(\omega_1 - \omega_2)(t^* - \tau_p)} = \frac{B_1\omega_1}{B_2\omega_2} \Rightarrow t^* = \frac{1}{\omega_1 - \omega_2} \cdot \ln \left( -\frac{B_1\omega_1}{B_2\omega_2} \right) + \tau_p,$$

(6.2.11)

and Equation (6.2.10) can be rewritten as an expression for $R_{f,1}$

$$R_{f,1} = R_{pin, b} + (R_{pin, b} - R_{pin, p}) g(t^*).$$

(6.2.12)

The motion of the $cl$ during a pulse and a bias interval as in Equation (6.2.5) and Equation (6.2.10) is shown in Figure 6.3. As discussed, the $cl$ is pinned at $R_{f,1}$.
6.2.4 Subsequent pulsing

During the second pulse, the time dependence of $R(t)$ is similar to that during the first one. With initial conditions $R = R(t^*)$ and $\dot{R}(t^*) = 0$, one obtains:

$$R(t) = R_{\text{pin},p} + (R_{f,1} - R_{\text{pin},p})f(t) = R_{\text{pin},p} + (R_{\text{pin},b} - R_{\text{pin},p}) (1 + g(t^*)) f(t). \quad (6.2.13)$$

By comparing this expression to that for the displacement after the first pulse in Equation 6.2.5, a substitution can be inferred for all subsequent pulses $i$:

$$f_{i+1}(t) \rightarrow (1 + g(t^*)) f_i(t), \quad \dot{f}_{i+1}(t) \rightarrow (1 + g(t^*)) \dot{f}_i(t). \quad (6.2.14)$$

This expression is valid only under the assumption that the time before the CL stops after each applied pulse is the same, independent of the pulse number. The full numerical analysis shows this is not the case; the motion time after each subsequent pulse decreases exponentially. In the absence of this assumption no closed-form solution can be obtained. The final position of the CL after the second pulse becomes

$$R_{f,2} = R_{f,1} + (R_{\text{pin},b} - R_{\text{pin},p}) g(t^*) (p(t^*) - 1) = R_{\text{pin},b} + (R_{\text{pin},b} - R_{\text{pin},p}) p(t^*) g(t^*), \quad (6.2.15)$$

$$p(t^*) = \frac{1}{2} \left[ f(\tau_p) \left( 1 - \frac{\omega_1 + \omega_2}{\omega_1 - \omega_2} \right) - \frac{2\dot{f}(\tau_p)}{\omega_1 - \omega_2} \right] e^{-\omega_1(t^* - \tau_p)} + \frac{1}{2} \left[ f(\tau_p) \left( 1 + \frac{\omega_1 + \omega_2}{\omega_1 - \omega_2} \right) + \frac{2\dot{f}(\tau_p)}{\omega_1 - \omega_2} \right] e^{-\omega_2(t^* - \tau_p)}. \quad (6.2.15)$$

The position reached after $n$ pulses can be deduced

$$R_{f,n} = R_{\text{pin},b} + (R_{\text{pin},b} - R_{\text{pin},p}) g(t^*) \sum_{i=1}^{n} p(t^*)^{i-1}, \quad (6.2.16)$$

and the displacement of the CL caused by pulse $i$ is

$$\Delta_i = (R_{\text{pin},b} - R_{\text{pin},p}) g(t^*) p(t^*)^{i-1}. \quad (6.2.17)$$

The value of $R$ after an infinite number of pulses is obtained in the limit of $n \rightarrow \infty$ for the geometric progression of Equation 6.2.16:

$$R_{f,\infty} = R_{\text{pin},b} + (R_{\text{pin},b} - R_{\text{pin},p}) \frac{g(t^*)}{1 - p(t^*)}. \quad (6.2.18)$$

for reasonable parameter values it can be shown that $0 < p(t^*) < 1$. 
An analogous set of expressions can be derived for the spreading motion of a droplet under the effect of positive pulses on top of a positive bias. In this case, the expressions obtained in Equation 6.2.5, Equation 6.2.10, Equation 6.2.16, Equation 6.2.17, and Equation 6.2.18 remain valid, with the modified notations according to Equation 6.1.5

\[ R_{\text{pin},b} \equiv R(0) = R_{\text{eq},b} - F_0 \frac{k_b}{k}, \quad R_{\text{pin},p} = R_{\text{eq},b} - F_0 \frac{k_p}{k}, \]

and Equation 6.2.16 provides values for the complete bias and pulse cycle, which are displayed in Figure 6.7.

### 6.2.5 Limitations

The closed-form solution comes at the price of several approximations that must be adopted.

- The time-interval between two consecutive pulses is long enough to allow the droplet to come to rest before the next pulse is applied. This condition is easy to control and warrant experimentally.

- The time needed for the \( \text{cl} \) to stop after each pulse is assumed to be the same for each pulse in order for Equation 6.2.16 to be obtained. Exact numerical calculations show that this time decreases exponentially with each pulse. This is the reason for the difference between the two theoretical curves in Figure 6.7 apparent from the second pulse on. The closed-form solution however catches many of the important physical features that govern droplet motion in pulse-assisted electrowetting, and does so in a more transparent fashion than numerical solutions can. Equation 6.2.18 predicts that the final geometry of the droplet after pulsing is between the equilibrium position under pulse and that under the bias voltage. The exact position is given by the interplay between the system parameters.

### 6.3 Model predictions - the complete solution

While the analytical results are invaluable in understanding the main features of the droplet motion, they come at the price of unwarranted approximations. The full predicted behaviour can be calculated. Equation 6.1.4 presents an initial value problem that can be solved numerically as a system of two ordinary differential equations of first order. The numerical results are obtained with ode45 in the MATLAB library (MATLAB version 7.10.0.499(R2010a)). The function uses an explicit Runge-Kutta formula based on the Dormand-Prince method (Inc. 2010). The motion of the droplet can be calculated for any sequence of applied biases and pulses, if the respective driving forces are known.

The predicted change in contact angle for a pulsed droplet is illustrated in Figure 6.4. The expected features of the \( \text{cl} \) motion are apparent here. As the bias voltage is applied, the droplet
Figure 6.4: Mitigation of the contact angle hysteresis under pulsing and the strong dependence of the evolution of the droplet geometry on the static friction force. Parameters used: \( m = 1.2 \cdot 10^{-10} \) kg, \( \eta = 0.3 \cdot 10^{-5} \) kg s\(^{-1} \), \( \alpha_0 = 1^\circ \), \( V_{\text{pzc}} = 0.3 \) V, \( c_d = 0.1 \) M, \( c_s = 0.5 \) M, \( \tau_p = 50 \mu\)s.

Following the steps of the experimental study, values on the x-axis mark the following events: -1 - droplet brought to a halt by positive pulsing on top of a 0 V bias, 0 - bias of \(-0.65\) V applied, 1 to 10 - pulses of \(-1\) V applied, 11 - bias of 0 V applied, 12 to 21 - pulses of 1 V applied. From Marinescu et al. (2010).

contracts due to the electrowetting effect. The CL is pinned before reaching equilibrium due to the existence of a friction force; successive applications of a pulse of the same sign as the bias voltage can provide enough energy to overcome this hindrance temporarily via inertial energy. Key features of pulse-assisted electrowetting are reproduced, such as the step-wise contraction and spreading of the droplet, the asymptotic change in the contact angle, and the retrieval of a final position equal to the initial one.

The contact angle variation in Figure 6.4 shows a qualitatively different behaviour in the contracting and spreading stages. Two factors contribute to this difference:

1. The equilibrium contact angle curve \( \alpha(V) \) is symmetric around \( V_{\text{pzc}} \) rather than around 0 V. The effects of the positive and negative pulses are comparable when their amplitudes are equidistant from \( V_{\text{pzc}} \).

2. The driving force during bias depends on the distance between the instantaneous \( R \) and the equilibrium one \( R_{eq} \), as well as on the stiffness coefficient \( k \); both \( R_{eq} \) and \( k \) depend, in turn, on the applied voltage. The interplay results in a complex behaviour, in which the driving force during spreading is usually significantly weaker than during contraction.

6.3.1 Elimination of hysteresis

It is found that the apparent hysteresis-free behaviour observed experimentally by Kucernak and coworkers (Kornyshev et al. 2010) is a result of the system preparation prior to the bias
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6.3.2 Effect of the static friction force

Figure 6.4 shows that the range of CL variation with pulsing decreases as $F_0$ increases. $F_0$ creates an interval of metastable positions around the ‘ideal’ equilibrium value, defined as the position reached on a frictionless electrode. After any number of negative pulses, the $R$ lies inside this range, irrespective of the bias, as shown in Figure 6.5. The final position is not an intrinsic characteristic of the system, as in the case of frictionless electrowetting; it depends on the amplitude, duration and number of pulses.

The larger the value of $F_0$, the narrower the interval of values taken by $R$; the droplet geometry changes less compared to its hysteresis-free configuration. A large enough $F_0$ can prevent the CL from moving altogether, despite pulsing. In the case of a very small $F_0$, the net effect of pulsing becomes zero as well; all energy accumulated during a pulse is dissipated through oscillatory

**Figure 6.5:** Pulsing affects the ultimate contact angle. Calculated contact angle values after 10 ($-1$ V) pulses for the indicated values of the friction force, in comparison to the frictionless case (thick line). Each time the contact line reaches zero velocity, if the resulting angle lies inside the grey area of metastable droplet geometries, it remains pinned. The area of metastability is shown for the smallest friction force, $F_0 = 10^{-5}$ N; for larger values of $F_0$, the area widens. From Marinescu et al. (2010).
Figure 6.6: The dramatic effect of friction on the net change of the contact angle after the pulsing procedure. The net change in contact angle is shown as the difference between that reached after 10 pulses of −1 V and the initial equilibrium contact angle for the indicated values of the bias. From Marinescu et al. (2010).

motion, and the CL eventually reaches the same position as before the pulse, the friction free, equilibrium one.

For a set of different values of $F_0$, the net change in the contact angle caused by pulsing on top of different biases is plotted in Figure [6.6]. The initial contact angle of the droplet corresponds to that after a set of negative pulses on top of a 0 V bias, similarly to the experimental procedure. As expected, the interval of contact angles reached during the bias-pulsing procedure becomes narrower for larger $F_0$ or lower bias voltages. The dependence is approximately linear. In the limit of an ideal, frictionless electrode, the net change in the CL radius is given by the difference between the equilibrium contact angle under the respective bias and the Young Laplace contact angle.

6.3.3 Comparison to the experimental data

In Figure [6.7] the curves obtained from the exact numerical solution of the model are displayed together with those from the simplified analytical solution in Section [6.2], and the experimental data in Kornyshev et al. (2010). The analytical solution captures only the qualitative character of the CL motion. For reasonable values of the system parameters, the exact solution reproduces well the experimental data. There are minor quantitative differences between the exact theoretical results and the experimental data. Factors such as the onset of secondary processes affecting the surface of the electrode may be present, voltage induced surface reconstruction, for example (Kornyshev & Vilfan 1995). More probable, however, the cause lies in model assumptions such as that of parabolic $\Delta G(R)$, leading to an $R$-independent $k$ value, and in the large number of unknown parameters. Since the maximum measured angles depend on the amplitude of the
Figure 6.7: Exact numerical solution of the model can reproduce experimental data for reasonable parameter values. Parameters: -0.65/0 V biases, -1/1 V pulses, $F_0 = 1.65 \cdot 10^{-5}$ N, $m = 1.2 \cdot 10^{-10}$ kg, $\eta = 0.3 \cdot 10^{-5}$ kg s$^{-1}$, $\alpha_0 = 1^\circ$, $V_{pzc} = 0.3$ V, $c_d = 0.1$ m, $c_s = 0.5$ m. Labeling of the x-axis as in Figure 6.4. From Marinescu et al. (2010).

pulse, an analysis of the experimental data for the different concentrations in Figure 5.2 is not feasible; results there were obtained for pulses of different voltages.

6.4 Conclusion

The model developed here for the dynamics of electrowetting with ITIES has enabled to explain the effects of electric pulsing on the spreading and contracting of a droplet on a real electrode. The phenomenological theory describes the characteristics of the experimentally observed stick-slip motion of the droplet, as well as the apparent removal of contact angle hysteresis.

A few improvements to the model developed here should increase the accuracy of its predictions:

- develop a detailed description of the non-linear effects of the pulse on the motion of ions in the two liquids, rather than taking the upper limit impact scenario used presently;
- model the elastic coefficient $k$ as both voltage and position dependent, especially for low applied bias voltages, where the equilibrium model predicts $\Delta G(R)$ is not ideally parabolic; this would improve the fit between theoretical predictions and experimental data, at the price of less transparent model parameters;
- investigate whether a dependence of $F_0$ on $R$ is to be expected.

Most of these studies are meaningful only under the assumption that the developed model is an accurate description of pulsed electrowetting with ITIES. While preliminary testing of its
predictions against available data supports its validity, in-depth experimental studies are needed for comprehensive testing. Most model parameters have not been independently measured, or are difficult to interpret in the system, such that a precise evaluation is not possible:

- the roughness of the electrode surface, as characterised, for example, by scanning probe techniques,
- the liquid/liquid surface tension, and its dependence on electrolyte concentration,
- the Young Laplace contact angle,
- the electrode/liquid potentials of zero charge.

The interpretation of the latter in a system with three competing interfaces is, in itself, conceptually challenging. Values for most of these parameters can be experimentally evaluated, at least in principle. Reaching an exact fit cannot be a target before diminishing the number of parameters.

Studies of electrowetting with ITIES were sparked by an interest in developing low-power optofluidic devices. The significance of the present description of pulse-assisted electrowetting, however, extends beyond this purely utilitarian view. The dynamic model should aid in more fundamental studies of the friction force at the liquid/electrode interface and its dependence on the applied voltage, as well as in studies of the effective potential of zero charge in a three phase system. In an even wider context, the dynamics model provides a framework for the study of wetting dynamics, pinning, and friction in systems with real solid substrates.
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Part II

Nanoparticles at Interactions
Chapter 7

Particles at liquid/liquid interfaces

Applications on the basis of changing the properties of the liquid/liquid interface by applying an electric field are not limited to those making use of the electrowetting effect. Functionalising liquid/fluid interfaces with particles allows for a variety of applications; the system is extremely versatile, as the particles have different geometrical and physical properties (Boker et al. 2007). Studies are not limited to spherical particles; hexagonal tiles have been self assembled at a curved oil/water interface towards building electrotunable mirrors (Bucaro et al. 2009). We are interested in functionalising the ities, here assumed as flat, with charged NPs.

7.1 Self-assembly

At the basis of all applications is the propensity of colloid particles to self-assemble at a liquid/fluid interface. Particles are dissolved in the bulk, and charged, usually negatively, to avoid agglomeration. The charging is obtained by attaching, via linkers, ligands with terminal groups that dissociate in solution. Due to surface tension properties, they self-assemble spontaneously at the interface. The time in which this occurs is governed by the time of migration of NPs through the bulk. Once at the interface, they can agglomerate irreversibly due to high screening, depending on their size and charge, but also on the concentration of ions in the liquid. When the attractive van der Waals forces are stronger than the screened Coulomb repulsion in the double layer, and the spontaneous, irreversible formation of multilayer films takes place (Yogevo & Eframa 1988).

Metallic NPs have been observed to self-assemble spontaneously at the liquid/liquid interface by Duan et al. (2004) and Reincke et al. (2004). The effect has been experimentally investigated and theoretically described by Reincke et al. (2006), who found that the interfacial coverage decreased with increasing surface charge density on the NPs.
7.2 Reversibility at the ITIES

When the surface charge density on the NPs is large enough to prevent agglomeration inside the double layer, multilayers are not expected to form. The charge on NPs could, in principle, allow the control of the interface population by varying an applied electric field. If this field is strong enough to delocalise the charged particles, the system should become reversible. Experimental studies done at the ITIES formed between water and 1,2-dichloroethane found reversibility for low voltage ranges $-0.2\,\text{V}$ to $0.2\,\text{V}$ and small NPs 1 nm to 3 nm: Su et al. (2004) for assemblies of metal NPs, and Su et al. (2005) for semiconductor NPs.

Reversibility was shown to be possible by the theoretical model developed by Flatte et al. (2008b) and improved by Flatte et al. (2010): charged metal NPs can be brought to and from an ITIES by tuning the external voltage. Adsorption isotherms were calculated for various values of NP radius and charge, and electrolyte concentration. The free energy of one particle, as a function of its distance from the interface, includes four contributions:

- the interfacial surface tension,
- the solvation energy, i.e. electrostatic energy related to the transfer of a charged particle between two media of different permittivities,
- the potential energy of a charged particle in the applied external field, here localised at the interface, and
- the three-phase line tension.

The single particle energy as a function of NP position relative to the interface is illustrated in Figure 7.1, as obtained from the model developed in Flatte et al. (2010). The applied voltage tunes the depth of the energy well at the interface and the relative magnitudes of the two barriers on either side of the well. System parameters such as the NP size and charge, the contact angle with the two liquids, and the magnitude and polarity of the applied field, influence both the position of the minimum, and the depth of the well, which is to be compared with the thermal energy. The interplay of parameter values leads to a stable or metastable bound state of the NP at the interface. In particular, increasing the NP size increases the depth of the potential well, such that high negative potentials might be required if reversibility is to be achieved.

Localised NPs are allowed to interact pairwise via screened electrostatic forces. Together with the details of the single particle energy, this interaction leads to the formulation of an adsorption isotherm. Positive polarisation of the organic phase relative to the aqueous one increases the coverage of the interface, whereas sufficiently negative polarisations repel the NPs away from the interface into the aqueous phase.

In principle, this model allows one to obtain a value of the coverage and the exact position of NPs at the interface for any set of parameter values in the ITIES system. The behaviour in real
Figure 7.1: The energy of a charged 20 nm NP as a function of its position in a system where water occupies $x < 0$ and oil $x > 0$, for three values of the applied potential, measured as the potential in the oil bulk with respect to that in water. The minimum at the ITIES can be stable or metastable. Hysteretic behaviour would be observed with respect to populating/unpopulating the interface, due to the difference in barrier sizes on either side of the well. The size of the well and that of the barriers on either side strongly depend on the polarity and value of the applied potential. Parameter values: NP charge = 1000e, NP radius = 10 nm, line tension = $10^{-11}$ N, contact angle through oil = 0.55π, water/oil interfacial tension = 30 mN m$^{-1}$, water: $\epsilon_a = 5.0$ mM, $c_a = 78.8$; oil (1,2-dichloroethane): $c_b = 5.0$ mM, $\epsilon_b = 10.7$.

Systems, however, is expected to be more complicated; among the ignored contributions are: van der Waals forces between NPs, forces between localised NPs caused by a non-flat liquid/liquid interface, and entropic effects. The many assumptions inherent in the model, together with its dependence on system parameters that are difficult to measure experimentally, reduce the applicability of its quantitative predictions. The theoretical prediction, however, is both important and general: depending on the system parameters, reversibility and tuning of the number of particles at the interface should be possible. There are still many hindrances to obtaining reversibility experimentally:

- stability of charge on NPs in the bulk,
- stability of charge on NPs when at the interface, in contact with oil, in contact with high charge density from ions in the double layer,
- possible flexibility and reorganisation of charge on the surface of the NPs, in bulk and especially at the interface.
Bibliography


Chapter 8

The capacitance of NPs at ITIES

As reversibility has been experimentally obtained in electrified populated ITIES for specific combinations of parameter values, there is strong interest in characterising their structure. A recently used method to characterise the interfaces: Younan et al. (2010) detected the presence of NPs at the ITIES. The system is formed by the flat interface between aqueous NaCl and 1,2-dichloroethane with bis(triphenylphosphoranylidene) ammonium tetrakis-(pentauorophenyl)borate (BTPPATPFB). Gold NPs with an average radius of 16 nm are stabilised by citrates and dissolved in the water phase. Capacitance curves are measured at a frequency of 2 Hz and plotted as a function of bias voltage, from $-0.15 \text{ V}$ to $0.25 \text{ V}$. A significant dependence on the concentration of NPs in the bulk is obtained, leading to the conclusion that this method is suitable to monitor assemblies of NPs.

8.1 Model formulation

A theoretical framework is required so that more information can be extracted from capacitance data obtained by impedance measurements. The model developed here helps describe the effect that charged metal NPs localised at the ITIES have on the voltage dependent capacitance.

Figure 8.1(a) schematically illustrates the system considered: NPs localised at a perfectly flat ITIES. All NPs are assumed identical, perfectly spherical, covered by a homogeneous surface charge distribution. At the interface, they all penetrate the oil phase to the same depth, forming a mono- or submonolayer.

In order to describe the capacitance of a populated ITIES, the interfacial plane is divided into unoccupied and occupied areas. The unoccupied regions are formed by the flat sections of the interface where the liquids are in direct contact. An applied electric field leads to the formation of two back-to-back diffuse layers in series. The occupied regions correspond to those sections of the interface, which are pierced by NPs. Across these regions four layers are identified, one
Chapter 8. Capacitance of NPs at ITIES

Figure 8.1: (a) NPs at the ITIES in a simplified geometry. b) The equivalent capacitor circuit; subscripts: ‘m’ - metal, ‘a’ - liquid_a (oil), ‘b’ - liquid_b (water); superscripts: ‘dl’ - diffuse layer, ‘il’ - inner (or compact) layer. The area of each capacitor is determined by the total area of the respective interfaces. From Marinescu et al. (2012).

diffuse layer and one inner layer on either side of the metal NP, forming the metal/electrolyte interfaces. These four layers are in series, and the metal particle is equipotential. The total capacitance of the interface is the result of the parallel arrangement of the capacitances of the occupied and unoccupied regions. The equivalent circuit is illustrated in Figure 8.1(b).

All diffuse double layers in this system are modelled by the non-linear Gouy-Chapman theory, as in Section 2.1, such that the unpopulated regions have a Verwey-Niessen capacitance, Section 2.2. The inner layers at the metal/electrolyte interfaces are described by the voltage-independent Stern model, Section 2.3.1.

In order to calculate the effective areas of capacitors, the total ITIES is divided into two-dimensional unit cells, such that one cell can enclose exactly one NP. At maximum surface coverage all unit cells are occupied. This model accommodates for the fact that NPs do not come in direct contact, due to electrostatic repulsion and volume exclusion of ligands: the size of a unit cell is larger than that needed to circumscribe an NP.

8.1.1 Parameters and variables

The ITIES has a total area $A$, and is divided into hexagonal unit cells of edge length $R_a$. All NPs are of radius $\mathcal{R}$ and carry charge $eN_{\text{ch}}$, assumed to be homogeneously and continuously distributed; the surface charge density is $\sigma = eN_{\text{ch}}/(4\pi R^2)$. The coverage of an interface at which $N \leq N_{\text{max}}$ particles are localised is $\Gamma = N/N_{\text{max}}$. Thus, $\Gamma$ takes values between...
0: no particles present at the interface; and 1: maximum number of particles present at the interface. At full coverage, the surface-to-surface separation between two NPs is shortest, given by $2 \left( \sqrt{3}/2 \cdot R_s - R \right)$ which is strictly greater than zero. This distance is fixed to twice the length of the functionalisation ligand $R_L$. Under this assumption, the area of a unit cell is $S = 3/2 \cdot \sqrt{3} R_s^2$, and the maximum number of particles that can populate the interface in a monolayer is given by $N_{\text{max}} = A/S$. Their position with respect to the interfacial plane is described by the penetration parameter $\delta = h/(2R)$, where $h$ is the height of the spherical cap immersed in the oil phase, as denoted in Figure 8.1(a).

In a unit cell occupied by an NP placed with its centre on the interface $\delta = 1/2$, the ratio of free-to-occupied areas is $\xi = (S - S_0)/S$ for $S_0 = \pi R^2$, the diametral cross sectional area of the particle. The applied voltage $\Delta V$ is defined as the potential of liquid_a (oil) relative to that of liquid_b (water). The notations used throughout this model, with comments on parameter dependencies, are summarised in Table 8.1.

### 8.1.2 The total capacitance

The capacitance of the system is directly affected by the interfacial coverage and by the depth to which the NPs pierce the interface, both of which are voltage dependent. The surface areas of the different capacitors depend themselves on coverage and depth of penetration, and are voltage dependent.

Following the equivalent capacitor arrangement in Figure 8.1(b), the specific differential capacitance of the system is modelled as

$$C_{\text{all}} = \frac{1}{A} \left[ A_{\text{ab}} C_{\text{ab}} + \left( \frac{1}{A_{\text{ma}} C_{\text{ma}}} + \frac{1}{A_{\text{mb}} C_{\text{mb}}} \right)^{-1} \right].$$

(8.1.1)

$A$’s are surface areas and $C$’s are specific differential capacitances; the subscripts ‘ab’, ‘ma’, and ‘mb’ denote the liquid/liquid, metal/liquid_a and metal/liquid_b interfaces. Two types of regions contribute towards $A_{\text{ab}}$: the unoccupied cells, and a small portion of interface inside occupied cells, around NPs. The areas of the three types of capacitors are calculated by geometrical considerations

$$\frac{A_{\text{ab}}}{A} = 1 - \Gamma \left[ 1 - \xi - (1 - \xi) (1 - 2\delta)^2 \right],$$

(8.1.2a)

$$\frac{A_{\text{ma}}}{A} = \Gamma \cdot 4\delta (1 - \xi),$$

(8.1.2b)

$$\frac{A_{\text{mb}}}{A} = \Gamma \cdot 4\delta (1 - \xi) (1 - \delta).$$

(8.1.2c)
<table>
<thead>
<tr>
<th>Notation</th>
<th>Description</th>
<th>Assumptions and dependencies</th>
</tr>
</thead>
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<tr>
<td>$C_{\text{all}}$</td>
<td>Total capacitance of the occupied sites</td>
<td></td>
</tr>
<tr>
<td>$C_{ab}$</td>
<td>Capacitance of the liquid/liquid interface</td>
<td>$\Delta U, (U_{\text{int}}), \epsilon_a, \lambda_a, \epsilon_b, \lambda_b$</td>
</tr>
<tr>
<td>$C_a, C_b$</td>
<td>Capacitances of the diffuse layers in electrolytes</td>
<td>$\Delta U, (U_{\text{int}}), \epsilon_a, \lambda_a$; $\Delta U, (U_{\text{int}}), \epsilon_b, \lambda_b$</td>
</tr>
<tr>
<td>$C_{ma}, C_{mb}$</td>
<td>Capacitances of the metal/electrolyte interfaces</td>
<td>$\Delta U, U_m, \epsilon_a, \lambda_a; U_m, \epsilon_b, \lambda_b$</td>
</tr>
<tr>
<td>$\Delta V$</td>
<td>Voltage drop between oil and water, in volts</td>
<td></td>
</tr>
<tr>
<td>$\Delta U = \epsilon \Delta V/k_B T$</td>
<td>Voltage drop in units of $k_B T/\epsilon$ ($\approx 25 \text{ mV}$ at room temperature)</td>
<td></td>
</tr>
<tr>
<td>$U_{\text{int}}$</td>
<td>Dimensionless potential at the interfacial plane, for unoccupied sites</td>
<td>$\Delta U, \epsilon_a, \lambda_a, \epsilon_b, \lambda_b$</td>
</tr>
<tr>
<td>$U_m$</td>
<td>Dimensionless potential on an equipotential metal NP at the interface</td>
<td>$\Delta U, \epsilon_a, \lambda_a, \epsilon_b, \lambda_b, \sigma$</td>
</tr>
<tr>
<td>$\epsilon_a, \lambda_a; \epsilon_b, \lambda_b$;</td>
<td>Bulk dielectric constants and Debye lengths in electrolytes</td>
<td>$\epsilon$’s are constant, $\lambda$’s depend on electrolyte concentration</td>
</tr>
<tr>
<td>$\epsilon_{\text{il}}^a, D_a; \epsilon_{\text{il}}^b, D_b$</td>
<td>Dielectric constants and thicknesses of the compact layers at the metal/ electrolyte interfaces</td>
<td>$\epsilon$’s are constant; $D_a = D_b = R_L$</td>
</tr>
<tr>
<td>$\sigma = -e N_{\text{ch}} / (4\pi R^2)$</td>
<td>Surface charge density on a NP</td>
<td></td>
</tr>
<tr>
<td>$N_{\text{ch}}$</td>
<td>Number of electron charges on a NP</td>
<td>Homogeneously distributed</td>
</tr>
<tr>
<td>$A$</td>
<td>Apparent area of the populated sites</td>
<td>Flat, voltage independent</td>
</tr>
<tr>
<td>$A_{ab}$</td>
<td>Area of the free liquid/liquid interface</td>
<td>$\Gamma, R, h, R_L, A$</td>
</tr>
<tr>
<td>$A_{ma}, A_{mb}$</td>
<td>Areas of the metal/liquid interfaces</td>
<td>$\Gamma, R, h, R_L, A$</td>
</tr>
<tr>
<td>$S = \frac{3\sqrt{3}}{2} R_s^2$</td>
<td>Area of the hexagonal unit cell of the sites</td>
<td>$\mathcal{R}, R_L$, packing geometry</td>
</tr>
<tr>
<td>$R_s = \frac{2 \sqrt{3}}{3} (R + R_L)$</td>
<td>Side length of hexagonal unit cell</td>
<td>$\mathcal{R}, R_L$</td>
</tr>
</tbody>
</table>
\[ R \]

Radius of a NP

Perfectly spherical

\[ R_L \]

Length of charged ligand

Perfectly spherical

\[ S_0 = \pi R^2 \]

Area of the NP diametral cross-section

\[ \xi = (S - S_0)/S \]

Ratio of free to occupied ITIES in a unit cell for an NP piercing the interface half way

Neglected: dependence of distance of the closest approach with voltage

\[ \Gamma = N/N_{\text{max}} \]

Surface coverage of ITIES

\[ \Delta V, c_{np}; \text{Neglected: } R, \lambda_a, \lambda_b \]

\[ c_{np} \]

Bulk concentration of NPs

\[ N \]

Number of NPs piercing the ITIES

\[ N_{\text{max}} \]

Maximum number of NPs piercing the ITIES

\[ \delta = h/(2R) \]

Degree by which NPs penetrate the ITIES

\[ V; \text{Neglected: } R, \lambda_a, \lambda_b \]

\[ h \]

Depth of penetration into the oil phase

\[ \Delta V \]

---

**Table 8.1:** Parameter notation in capacitance model. All capacitances are specific differential capacitances; all dielectric permittivities are relative; the subscripts refer to \(a\) - liquid, \(b\) - liquid, \(m\) - metal.

By substituting the expressions of Equations 8.1.2 into Equation 8.1.1, the specific differential capacitance is

\[ C_{all} = (1 - \Gamma) C_{ab} + \Gamma \left\{ C_{ab} \left[ \xi + (1 - \xi) (1 - 2\delta)^2 \right] + 4 (1 - \xi) \left[ \frac{1}{\delta C_{ma}} + \frac{1}{(1 - \delta) C_{mb}} \right]^{-1} \right\} . \tag{8.1.3} \]

The details of the voltage dependence of \( C_{all} \) are thus determined by the properties of the compact and diffuse layers, and by the behaviour of the coverage and penetration functions. These functions are detailed below.
The free ities

$C_{ab}$ obeys the Vervey-Niessen model, and contains two back-to-back double layers in series, one on either side of the interface. For convenience, the results of Section 2.2, where the capacitance of such an interface was derived, are reiterated here:

\begin{align}
C_{ab} &= \left( \frac{1}{C_a} + \frac{1}{C_b} \right)^{-1}, \quad (8.1.4a) \\
C_a &= \frac{\varepsilon_0 \varepsilon_a}{\lambda_a} \cosh \left( \frac{U - U_{\text{int}}}{2} \right), \quad (8.1.4b) \\
C_b &= \frac{\varepsilon_0 \varepsilon_b}{\lambda_b} \cosh \left( \frac{U_{\text{int}}}{2} \right), \quad (8.1.4c) \\
\exp (U_{\text{int}}) &= \frac{1 + \frac{\varepsilon_a \lambda_b}{\varepsilon_b \lambda_a} \exp (\Delta U/2)}{1 + \frac{\varepsilon_a \lambda_b}{\varepsilon_b \lambda_a} \exp (-\Delta U/2)}, \quad (8.1.5)
\end{align}

with $U = \frac{zF}{RT} (V_a - V_b)$ a dimensionless measure of the Galvani potential drop between the bulks of liquid $a$ and $b$. $U_{\text{int}}$ is the dimensionless potential at the interface, obtained by imposing the standard electrostatic boundary conditions.

The occupied ities

$C_{ma}$ and $C_{mb}$ are comprised each of two capacitors in series, corresponding to the diffuse and compact layers. $D_a$, $D_b$ are the effective thicknesses of the compact layers. $\varepsilon_{il}^a$ and $\varepsilon_{il}^b$, the relative dielectric permittivities in the compact layers, are expected to have values lower than the corresponding bulk ones, but higher than those of a dense layer of ligands. The reorientation of liquid molecules inside the ligand layer could be spatially limited and effectively frozen by the ligands’ terminal charge. A value $\varepsilon_{il}^{a,b} = 6$ was generally chosen in model predictions, reflecting the considerations above and allowing for both inner and diffuse layer contributions to be apparent.

8.1.3 Coverage and penetration

$\Gamma$ and, to a smaller degree, $\delta$ depend on various system parameters; the depth and positioning of the energy well for a single NP near the interface is affected by the amount of charge on the NP, by the particle size, and by the concentration of electrolytes, as shown by Flatte et al. (2008b). Increasing the positive potential of liquid $b$ with respect to liquid $a$ increases both $\Gamma$ and $\delta$, since the NPs are negatively charged and initially reside in liquid $a$. As many details of the experimental system are unknown, there is little to be gained from importing the complex isotherm in Flatte et al. (2010). In the current model, we introduce phenomenological Fermi-like
functions for both coverage and NP position at the ITIES:

\[
\frac{1}{\Gamma} = 1 + \frac{1}{\tilde{c}_{\text{np}}} \exp \left( \frac{U_{\Gamma} - U}{\Delta U_{\Gamma}} \right), \tag{8.1.6}
\]

\[
\frac{1}{\delta} = 1 + \exp \left( \frac{U_{\delta} - U}{\Delta U_{\delta}} \right), \tag{8.1.7}
\]

where \( \tilde{c}_{\text{np}} = c_{\text{np}}/c_{\text{np}}^* \), \( c_{\text{np}} \) is the initial concentration of NPs in the bulk, and \( c_{\text{np}}^* \) a reference concentration, here a fitting parameter. Calculated adsorption isotherms indicate that \( \Gamma \) depends on \( c_{\text{np}} \) only for relatively shallow minima in the single particle potential profile (\(< 15k_B T\)). \( U_{\Gamma} \) and \( U_{\delta} \) are the dimensionless potentials at which \( \Gamma = c_{\text{np}}/(c_{\text{np}} + c_{\text{np}}^*) \) and \( \delta = 1/2 \), respectively. \( \Delta U_{\Gamma} \) and \( \Delta U_{\delta} \) characterise the steepness of the smeared step-like functions. The values of \( \Gamma \) and \( \delta \) influence the value of \( C_{\text{all}} \) in Equation 8.1.3 significantly: \( \Gamma \) weighs the relative contributions of the free and occupied interfaces, while \( \delta \) weighs the contributions of the capacitances on either side of a localised NP. The value of \( \delta \) becomes increasingly important when the two electrolytes have different compact and double layer properties.

### 8.1.4 Potential distribution

In order to obtain the total capacitance for an applied potential, calculations are performed in two stages:

1. The potential profile \( V(x) \) across the entire system is calculated according to the assumed structure of the different layers, and subject to the standard electrostatic boundary conditions at the boundaries between layers: continuity of potential and electrostatic induction.

2. The total capacitance of the system is calculated according to Equation 8.1.3, Equation 8.1.4 and a diffuse layer/compact layer series arrangement for \( C_{\text{ma}} \) and \( C_{\text{mb}} \) for the respective potential drops.

The potential profile over an unoccupied ITIES has been calculated in Section 2.2. The interfacial areas occupied by NPs are modelled as in Figure 8.2, the applied potential drops across six layers. From \( a \) to \( b \) they are: diffuse layer in \( a \), inner layer in \( a \) outside the ligand region, inner layer in \( a \) inside the charged ligands region, inner layer in \( b \) inside the charged ligands region, inner layer in \( b \) outside the ligand region, diffuse layer in \( b \). The ligand layers can be penetrated by the two solvents, as they are not dense.

The potential profiles in the two diffuse layers 1 and 6 follow the Gouy-Chapman model; the spatial distribution \( V(x') \) is given by Equation 2.2.1. With the coordinate transformations \( x'_a \rightarrow x + (\gamma_a + \beta_a) \) in liquid \( a \), and \( x'_b \rightarrow x - (\gamma_b + \beta_b) \) in liquid \( b \), the potential distribution
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Figure 8.2: Regions of the system (1–6) with their characteristic lengths ($\lambda_{a,b}$, $\gamma_{a,b}$, $\beta_{a,b}$). Liquid a: 1 - diffuse layer, 2 - compact layer outside charge plane with surface charge density $\sigma$, 3 - compact layer between charge plane and NPs; Liquid b: 4 - compact layer between NPs and charge plane, 5 - compact layer outside the charge plane, 6 - diffuse layer. The voltage in the two liquid bulk is denoted by $V_a$ and $V_b$, while $V_{2a}$, $V_{1a}$, $V_m$, $V_{1b}$, $V_{2b}$ are the potentials at the respective boundaries. From Marinescu et al. (2012).

becomes:

\[
V_1(x) = V_a - \frac{2k_B T}{e} \ln \left[ \frac{\alpha_a \exp \left( -\frac{(x + \gamma_a + \beta_a)}{\lambda_a} \right)}{\alpha_a \exp \left( -\frac{(x + \gamma_a + \beta_a)}{\lambda_a} \right) - 1} \right],
\]

where $\alpha_a = \frac{\exp \left( \frac{e(V_a - V_{2a})}{2k_B T} \right) + 1}{\exp \left( \frac{e(V_a - V_{2a})}{2k_B T} \right) - 1}$.

\[
V_b(x) = V_b + \frac{2k_B T}{e} \ln \left[ \frac{\alpha_b \exp \left( \frac{(x - \gamma_b - \beta_b)}{\lambda_b} \right) + 1}{\alpha_b \exp \left( \frac{(x - \gamma_b - \beta_b)}{\lambda_b} \right) - 1} \right],
\]

where $\alpha_b = \frac{\exp \left( \frac{e(V_{2b} - V_b)}{2k_B T} \right) + 1}{\exp \left( \frac{e(V_{2b} - V_b)}{2k_B T} \right) - 1}$.

In the four compact layers, whose properties do not depend on voltage, the potential varies linearly with $x$:

\[
V_2(x) = \frac{V_{1a} - V_{2a}}{\gamma_a} x + V_{2a} + \left( V_{1a} - V_{2a} \right) \left( 1 + \frac{\beta_a}{\gamma_a} \right),
\]

\[
V_3(x) = \frac{V_m - V_{1a}}{\beta_a} x + V_m,
\]

\[
V_4(x) = \frac{V_{1b} - V_m}{\beta_b} x + V_m,
\]

\[
V_5(x) = \frac{V_{2b} - V_{1b}}{\gamma_b} x + V_{1b} + \left( V_{1b} - V_{2b} \right) \frac{\beta_b}{\gamma_b}.
\]

$V(x)$ is continuous throughout the system, and the NP surface is equipotential. The boundaries between the diffuse and compact layers, as well as those between the two inner compact layers,
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... on the NP, allow no accumulation of charge; \( \frac{dV}{dx} \) is continuous. The positions of the interfaces between the outer and inner compact layers are defined by the positions of the charges on the ligands’ ends, at \( x = -\beta_a \) and \( x = \beta_b \). Continuity of the displacement field across such an interface imposes that a discontinuity in \( \frac{dV}{dx} \) is present, proportional to the existing continuous surface charge density \( \sigma \). The five boundary conditions are:

\[
\begin{align*}
  x &= -\gamma_a - \beta_a \\
  -\epsilon\gamma_a \frac{dV_2}{dx} + \epsilon \frac{dV_1}{dx} &= 0 \quad \Rightarrow \quad -\frac{\epsilon\gamma_a}{\gamma_a} (V_1a - V_{2a}) + \frac{\epsilon_a 4k_BT}{\lambda_a e} \frac{\alpha_a}{\alpha_a^2 - 1} = 0, \\
  x &= -\beta_a \\
  -\epsilon\beta_a \frac{dV_3}{dx} + \epsilon\gamma_a \frac{dV_2}{dx} &= \frac{\sigma_a}{\epsilon_0} \Rightarrow \quad \frac{\epsilon\beta_a}{\beta_a} (V_{1a} - V_m) - \frac{\epsilon\gamma_a}{\gamma_a} (V_{2a} - V_{1a}) = \frac{\sigma_a}{\epsilon_0}, \\
  x &= 0 \\
  -\epsilon\beta_b \frac{dV_4}{dx} + \epsilon\beta_a \frac{dV_3}{dx} &= 0 \quad \Rightarrow \quad -\frac{\epsilon\beta_b}{\beta_b} (V_m - V_{1b}) - \frac{\epsilon\beta_a}{\beta_a} (V_{1a} - V_m) = 0, \\
  x &= \beta_b \\
  -\epsilon\gamma_b \frac{dV_5}{dx} + \epsilon\beta_b \frac{dV_4}{dx} &= \frac{\sigma_b}{\epsilon_0} \Rightarrow \quad -\frac{\epsilon\gamma_b}{\gamma_b} (V_{1b} - V_{2b}) + \frac{\epsilon\beta_b}{\beta_b} (V_m - V_{1b}) = \frac{\sigma_b}{\epsilon_0}, \\
  x &= \gamma_b + \beta_b \\
  -\epsilon\gamma_b \frac{dV_6}{dx} + \epsilon\gamma_b \frac{dV_5}{dx} &= 0 \quad \Rightarrow \quad \frac{\epsilon\gamma_b}{\gamma_b} \frac{4k_BT}{\lambda_b e} \frac{\alpha_b}{\alpha_b^2 - 1} - \frac{\epsilon\gamma_b}{\gamma_b} (V_{1b} - V_{2b}) = 0.
\end{align*}
\]

Equations (8.1.10) form a non-linear system from which the potential values at each interface can be calculated by following the sequence of steps:

1. The conditions at the boundaries 1/2 and 5/6 are in the form of a transcendental-linear mix, which can be rewritten as \( V_{1a} = f_1(V_{2a}, V_a) \), \( V_{1b} = f_2(V_{2b}, V_b) \), with \( f_1 \) and \( f_2 \) transcendental functions.

2. The conditions at boundaries 2/3, 3/4, and 4/5 form a linear system that can be solved for \( V_{1a} = g_1(V_{2a}, V_{2b}) \), \( V_{1b} = g_2(V_{2a}, V_{2b}) \), and \( V_m = g_3(V_{2a}, V_{2b}) \), with \( g_1, g_2, \) and \( g_3 \) linear functions.

3. The \( V_{1a} \) and \( V_{1b} \) expressions in (i) and (ii) must be respectively equal: \( f_1(V_{2a}, V_a) = g_1(V_{2a}, V_{2b}) \), and \( f_2(V_{2b}, V_b) = g_2(V_{2a}, V_{2b}) \); this is a system of non-linear equations that can be solved numerically for \( V_{2a} \) and \( V_{2b} \).

4. \( V(x) \) at the other three interfaces can be calculated from the expressions in (ii).

Once the values of the potential profile at all boundaries are known, the specific capacitances of the various layers can be calculated.

The model presented here can be adapted to treat more complex situations, such as non-uniform charge density, and various positions of the charged plane inside the compact layer. The inner
layers at the metal/electrolyte interfaces are due to trapped solvent molecules in the ligand coating. The terminal carboxyl groups and hydrogen bonding form a region of high charge density. It is reasonable to assume that the position of terminal charges of the ligands form the outer boundary of the compact layer, rather than lying inside it. From here on, no additional compact layer is considered outside the position of $\sigma$, because this interface is neither rigid nor sharp.

8.1.5 Two limiting cases

Let us also consider two limiting cases, when the metal/electrolyte capacitances $C_{ma}$ and $C_{mb}$ are determined solely by diffuse layers or by inner layers. These limits correspond to the cases in which the inner layer capacitances are either substantially (i) larger or (ii) smaller than the diffuse layer ones.

If the effect of diffuse layers is dominating, then the specific capacitances due to the presence of NPs have the same form as in Equations 8.1.4. Since $R_L \ll \lambda_{a,b}$ for all concentrations of interest here, the charge is effectively placed at the boundary between the two liquids. The dimensionless potential on the equipotential metal particle can be calculated analogously to the Verwey Niessen model, accounting however for the presence of a surface charge density $\sigma$ on the particle. The result is

$$\exp\left(\frac{U_m}{2}\right) = \sigma + \sqrt{\frac{\epsilon_0 \epsilon_a}{\lambda_a \lambda_b}} \exp\left(-\frac{U}{2}\right) + \frac{\epsilon_0 \epsilon_a}{\lambda_a} \exp\left(\frac{U}{2}\right) + \frac{\epsilon_0 \epsilon_b}{\lambda_b}$$

(8.1.11)

The predicted total capacitance of a system with this property, or, conversely, with metal/electrolyte capacitance dominated by compact layers, is illustrated in Section 8.2.1.

8.1.5.1 Limitations

Before looking at the predicted voltage-dependence of the system capacitance, let us identify the main assumptions made in this model, starting with the two most important:

- All specific capacitances and potential distributions are calculated as for flat interfaces, i.e. the double layers are not modelled for curved interfaces. The increase in the total surface area of the interface due to piercing by NPs is included by weighting the individual capacitances by the surface area of the curved interface. This approach is fully justified when $R/\lambda_{a,b} \gg 1$. In the experimental setup of Younan et al. (2010) electrolyte concentrations of $\approx 5$ mM are used, corresponding to $\lambda_{a,b} = 1.6$ nm and 4.3 nm in oil and water, respectively; the NPs used have $R = 16$ nm, giving a minimum ratio $R/\lambda_{a,b} \approx 5$.
The capacitors entering the model are characterised by their differential capacitances. Rigorously, the total differential capacitance should be obtained by

1. combining the different integral capacitances in series and parallel, and
2. differentiating the total integral capacitance of the interface over voltage.

The voltage dependence of the capacitor areas would, in that case, also influence the specific differential capacitance of the interface. Such an analysis would be cumbersome, without granting extra physical insight. A comparison between theoretical predictions and experimental data from impedance measurements is valid only for measurements at sufficiently low frequencies. This condition ensures that the ions fully respond to the modulated potential, while the NPs do not react.

Defining the surface coverage by dividing the interface in identical unit cells is, in fact, a mean-field approximation; an inhomogeneous distribution of NPs at the interface could be present.

Interface deformations caused by the three-phase contact angle and thermal fluctuations are not considered (Bresme & Oettel 2007). The ITIES is assumed to be flat for all possible positions of NPs at the interface.

The inner layer capacitance is independent of voltage, according to the naive Stern model. While including a potential-dependent model, such as the MWT, is in principle desirable, the extra parameters brought along by such a theory need to be fit to experimental data describing the particular metal/electrolyte interface, currently unavailable. From a theoretical point of view, it is difficult to establish the relation between $\epsilon_{\gamma a}$ and $\epsilon_{\gamma b}$ in the $V(x)$ profile and the parameters used by the MWT model. Finally, it is expected that the potential dependence of the compact layer capacitance becomes negligible if the charged groups at the end of ligands trap the solvent molecules close to the NP wall.

At high coverages $\Gamma \approx 1$, the diffuse layers around neighbouring NPs are expected to overlap. Only in systems where $R \gg \lambda_{a,b}$ is the overlap region small enough compared to the total area of the effective capacitor, that this effect is negligible. The condition of thin diffuse layers, for which the model presented is exclusively valid, is fulfilled by the experimental setup of Younan et al. (2010), with $R = 16$ nm, $\lambda_a = 1.6$ nm, and $\lambda_b = 4.3$ nm (electrolyte concentrations of 5 mM). A simplified theoretical approach is also possible in the opposite limit of $R \ll \lambda_{a,b}$, for relatively low electrolyte concentrations. In that case, one must consider a different capacitor arrangement, where the diffuse layer envelopes all localised NPs. For intermediate cases, the effect of the overlap is significant and must be considered in detail.
8.2 Model predictions

Model predictions are calculated for the case of the 1,2-dichloroethane/water interface, to enable a direct comparison to the experimental findings reported by Younan et al. (2010). Calculations are made under the assumption that the ligands charge defines the boundary between inner and diffuse layers; there is a single compact layer on either side of the localised NPs, with thickness equal to the length of ligands.

8.2.1 Two limiting cases

![Figure 8.3](image)

**Figure 8.3:** Model predictions for the total specific differential capacitances in two limiting cases: the capacitances of the metal/electrolyte interfaces are determined by the diffuse layers (dl) or the compact layers (cl) only. The Vervey-Niessen capacitance (vn) of the ITIES in the absence of NPs is included as a reference. Parameter values: \( \sigma_1 = -0.75 \mu \text{C cm}^{-2} \) \( (N_{ch,1} = 150) \), \( \sigma_2 = -1.50 \mu \text{C cm}^{-2} \) \( (N_{ch,2} = 300) \), \( R = 16 \text{ nm} \), \( U_\delta = 0(0 \text{ V}) \), \( \Delta U_\delta = 5(0.13 \text{ V}) \), \( U_\Gamma = 0(0 \text{ V}) \), \( \Delta U_\Gamma = 2(0.05 \text{ V}) \), \( c_{np}^a = 1 \text{ mM} \), \( c_{np}^b = 0.67 \text{ mM} \), \( c_a = 5.0 \text{ mM} \), \( c_b = 5.1 \text{ mM} \), \( \epsilon_a = 10.7 \) (1,2-dichloroethane), \( \epsilon_b = 78.3 \) (water), \( R_L = 2 \text{ Å} \); inner layer: \( \epsilon_a^{ill} = \epsilon_b^{ill} = 6 \), \( D_a = D_b = R_L \). From Marinescu et al. (2012).

Results for the case when the metal/electrolyte capacitances are determined by the diffuse or compact layers exclusively are presented in Figure 8.3. Their dependence on the applied potential provides information about the behaviour of the different layers. How much of the features here apparent can be distinguished in the general case depends on the relative contribution of each layer to the total capacitance.

As the voltage is increased, more particles populate the interface, and are centred increasingly into the oil phase. Both \( \Gamma \) and \( \delta \) are centred here around zero bias voltage. It is expected that the coverage is more sensitive to variations in voltage than is penetration (Flatte et al. 2010); to reflect this \( \Delta U_\Gamma < \Delta U_\delta \). The capacitance of the ITIES in the absence of NPs, the ‘vn’ curve, is included as a reference. It can be concluded that the presence of NPs at the interface leads to
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a higher system capacitance, compared to that of the unoccupied interfaces. The increase is partly due to the implicitly larger effective area of the capacitor.

**Diffuse layer effects**

When the diffuse layers alone contribute, the interfacial capacitance behaviour strongly depends on $\sigma$, due to the boundary condition. The value of $\sigma$ influences the distribution of the the potential drop over the two diffuse layers in series. The distribution of potential strongly affects the total capacitance, since the Gouy-Chapman capacitance grows exponentially with voltage.

The presence of charged NPs increases the specific capacitance of the diffuse double layers. The effect of the variation in $\sigma$ on the capacitance curves in Figure 8.3 is understood by considering the distribution of potentials across the double layers.

1. The potential $U_m$ on a localised metal NP in Equation 8.1.11 increases when the applied voltage is increased, or when $N_{ch}$ is decreased (less negative charge).

2. The diffuse layer capacitance of the metal/liquid$_a$ interface, in Equation 8.1.4b with $U_{int} \rightarrow U_m$, reaches its minimum when the applied voltage drops entirely over liquid$_b$, $U - U_m = 0$.

3. The diffuse layer capacitance of the metal/liquid$_b$ interface, in Equation 8.1.4c with $U_{int} \rightarrow U_m$, reaches its minimum when the applied voltage drops entirely over liquid$_a$, $U_m = 0$.

The minima of the capacitances of the two diffuse layers on either side of a localised NP correspond to different applied voltages, and their separation increases as the NPs are charged more negatively. This leads to the formation of a second local minimum in the capacitance with increased $N_{ch}$, as well as to the intersection between capacitance curves corresponding to different charge numbers.

Variation of $\sigma$ was achieved here by increasing the charge on the NP while keeping its radius fixed. Similar observations can be made in the case of decreasing the NP size at a fixed charge number, since $\sigma \propto N_{ch}/R^2$. The total capacitance curve in that case would also be affected by changes in the effective interfacial area.

From an experimental point of view, the homogeneous distribution and the stability of charges on an NP are not guaranteed. Depending on the length and flexibility of ligands, it is also possible that the total charge on the NP remains constant, but is redistributed when at the interface. If citrate stabilisation or other weakly bound groups are used, as in Younan et al. (2010), charge can be lost, especially when in contact with the oil phase. In this case the second minimum in capacitance, appearing at the higher potential, would become less deep and eventually completely disappear. For increasingly positive polarisation of the oil side, leading to increased penetration, the behaviour of the capacitance should transit from high-charge to low-charge curves.
Inner layer effects

If the voltage drops over the metal/electrolyte inner layers exclusively, then all dependence on the NP charge is eliminated, since capacitances of the inner layer are voltage independent in the Stern model. This feature determines the shape of the total capacitance curve ‘c1’ in Figure 8.3; its voltage dependence is inherited from the capacitance of unoccupied interface regions. When the two compact layers have similar capacitances, the value of the penetration parameter becomes less important. The intersection between the capacitances of the unpopulated and populated interfaces occurs at the voltage where the Verwey Niessen capacitance reaches the value of the series capacitance of the inner layers.

8.2.2 Comparison with experimental observations

![Figure 8.4: a) Calculated capacitance curves (lines) and data reported by Younan et al. (2010) in the system described on page 90 with \( c_a = 5.0 \text{ mM}, c_b = 5.1 \text{ mM} \). Various concentrations of NPs in the bulk aqueous electrolyte (c_{np}): \( c_1 = 0.42 \text{ nM}, c_2 = 0.67 \text{ nM}, c_3 = 1.26 \text{ nM} \), and for an unpopulated interface (vn). The measurements are sampled in increments of 0.05 V. b) The capacitance of a localised multilayer ‘metallic’ film of NPs is calculated, accounting for the increased effective surface area, under the assumption of hexagonal close packing of particles. Parameter values: \( N_{ch} = 300, V_{pzc} = 0.015 \text{ V}, R = 16 \text{ nm}, U_\delta = 5(0.13 \text{ V}), \Delta U_\delta = 10(0.26 \text{ V}), U_\Gamma = 1(-0.026 \text{ V}) \Delta U_\Gamma = 10(0.26 \text{ V}), c_{np}^a = 1 \text{ nM}, c_a \text{ and } c_b \text{ as specified above, } \epsilon_a = 10.7, \epsilon_b = 78.3, R_L = 2 \text{ Å}; \) inner layer: \( \epsilon_a^\text{IL} = \epsilon_b^\text{IL} = 8, D_a = D_b = R_L \). From Marinescu et al. (2012).](Image 86x368 to 291x521)

8.2.2.1 The effect of NP concentration

Total capacitance curves obtained in the general case, where both compact and diffuse layers contribute towards the metal/electrolyte interfacial capacitance, are displayed in Figure 8.4(a). As the availability of NPs in the bulk increases, so does \( \Gamma \) for an applied voltage, affecting the total capacitance. The concentration of NPs in the bulk is expected to have an effect on the interfacial coverage only at low voltages, and correspondingly low coverages. At such voltages,
the energy well that captures an NP at the interface is expected to be relatively shallow. As the bias on the oil side is increased, the potential well deepens, and both $\Gamma$ and $C_{\text{all}}$ are expected to become independent of the concentration of NPs in the bulk.

### 8.2.2.2 The capacitance of a multilayer

While the capacitance of the free interface offers one limiting behaviour, that of a multilayer lies at the other extreme. The capacitance of a multilayer of touching spherical NPs at the ITIES was calculated under the assumption that no liquid penetrates the film, and is displayed in Figure 8.4(b). The NPs are arranged in a hexagonal close-packed lattice at the interface with $\delta = 1/2$, corresponding to the minimum roughness coefficient, $A_{na}/A = A_{mb}/A = 1.9$. The resulting capacitance exhibits two minima, from the two diffuse layer capacitances in series. For a thin gold foil at the ITIES, the total capacitance can be obtained by setting the roughness coefficient to one; the behaviour is similar to that of a multilayer.

### 8.2.2.3 Comparison

The experimental data reported by Younan et al. (2010), is included in Figure 8.4(b). The point of zero charge in the experimental system, as given by the minimum of the capacitance of the unoccupied interface, is positioned at $\Delta V < 0$. Three other features are of interest.

1. In the presence of NPs the measured capacitance increases, as predicted in Section 8.2.1.
2. The measured capacitance depends strongly on $c_{\text{np}}$. A higher concentration of NPs in the bulk leads to higher $\Gamma$ at a given voltage and an increase in the measured capacitance. The presence of a $c_{\text{np}}$ dependence is a sign of shallow interfacial energy wells and corresponds to submonolayer coverages.
3. The minimum of the total capacitance shifts towards more negative voltages as $c_{\text{np}}$ increases.

The second observation, together with the pronounced difference between the experimentally measured capacitance and the predicted response of a multilayer, is a strong indication that a submonolayer rather than a monolayer is present in the reported experiments. Independent tools for surface characterisation are needed to confirm this conclusion.

The value of $\varepsilon_{a,b}^{\text{ill}}$ had to be chosen higher than for the other calculated predictions, in order for the theoretical and experimental data to correspond. This could be a sign that the compact layer effects are not as strong as predicted by the model. Without more information on the experimental values of $N_{\text{ch}}$ and $R_L$, however, this remains an assumption.
While the main qualitative features of the capacitance are well reproduced by the model predictions, a quantitative fit with the experiment is not yet viable. There is a pronounced difference between the theoretically predicted Verwey Niessen capacitance and the experimentally observed capacitance of the unpopulated ITIES. This difference, independent of the effect of localised NPs on the capacitance, emphasises the need to study other relevant factors in the system, such as the specific adsorption of ions.

8.2.3 The effect of the NP position

Depending on the system parameters, the exact position of NPs at the ITIES could significantly affect the measured capacitance of the interface. Their exact location, however, is difficult to detect or control; it is instructive to consider the predicted dependence. The effect of changing the value of $V_\delta$, the potential at which the NPs are immersed halfway in each liquid, is illustrated in Figure 8.5. $V_\delta$ is expected to be affected by the wetting properties of the NP material and the two liquids, and by the functionalisation of NPs. If the two liquids have significantly different dielectric properties or electrolyte concentrations, the degree of penetration becomes increasingly important.

The capacitance curves of the populated ITIES exhibit features of the compact layers, as described in Section 8.2.1. As the potential is increased, the capacitance becomes first higher, then lower than that of the unpopulated interface. $V_\delta$ affects the total capacitance only through the geometric weighing terms; specific capacitances do not depend on the exact position of localised NPs. As the NP advances into liquid$_a$, $A_{ma}$ becomes larger than $A_{mb}$. The capacitances of the interfaces on the two sides of a NP have minima at different potentials, dictated by the diffuse...
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layer. These voltage dependent contributions lead to the gradual formation of a second minimum in the total capacitance curve. For $\delta \approx 0$ and $\delta \approx 1$ the capacitance approaches that of an unpopulated interface.

### 8.2.4 The effect of the NP radius

A study of the effects of NP size on the capacitance of a populated interface is presented in Figure 8.6. The NP size is a parameter readily controlled experimentally, such that model predictions regarding its effect are relevant for testing of the presented theory. This study is only preliminary, as $R$ could significantly affect the depth of the interfacial well, and thus the value of $\Gamma$, as well as that of $\delta$. No $R$-dependence is considered in the simplistic definition of these functions, in Section 8.1.3 used for the predictions of Figure 8.6. The effects would emerge from a detailed adsorption isotherm for the particular experimental system.

Figure 8.6: Effect of the NP radius on the capacitance of the populated interface. NP radii $R$ given by: $R_1 = 2$ nm, $R_2 = 20$ nm. The charge on NPs is chosen such that $\sigma$ is constant, equivalent to $N_{ch} = 300$ on an $R = 16$ nm particle. The capacitance of the unpopulated interface ($v_{un}$) is given as a reference. Parameter values: $U_{\delta} = 0$ (0 V), $\Delta U_{\delta} = 5$ (0.13 V), $U_{\Gamma} = 0$ (0 V), $\Delta U_{\Gamma} = 2$ (0.05 V), $\epsilon_{np}^c = 1$ nM, $\epsilon_{np}^d = 0.67$ nM, $\epsilon_a = 5.0$ mM, $\epsilon_b = 5.1$ mM, $\epsilon_a = 10.7$, $\epsilon_b = 78.3$, $R_L = 2$ Å; inner layer: $\epsilon_a^{il} = \epsilon_b^{il} = 6$, $D_a = D_b = R_L$. From Marinescu et al. (2012).

The NP size is varied for constant surface charge density $\sigma$, assumed to be determined by the method of NP functionalisation. $R$ affects $C_{all}$ through $\xi$, Equation 8.1.3. For hexagonal unit cells the ratio of occupied to unoccupied interface per cell is $\xi = 1 - (\pi R^2) / \left( 2\sqrt{3}(R + R_L)^2 \right)$, such that the dependence on NP radius vanishes for $R \gg R_L$, and is noticeable only otherwise, as apparent from Figure 8.6.
8.2.5 The effect of electrolyte concentration

Figure 8.7: Effect of electrolyte concentration on the capacitance of the populated interface. Electrolyte concentrations: \((c_a, c_b) = 1: (5, 5), 2: (20, 5), 3: (5, 20) \text{ mM}\). The capacitances of the unpopulated interface \((v_n)\) at the corresponding concentrations are given as a reference.

Parameter values: \(N_{ch} = 300, \mathcal{R} = 16 \text{ nm}, U_\delta = 0(0 \text{ V}), \Delta U_\delta = 5(0.13 \text{ V}), U_\Gamma = 0(0 \text{ V}), \Delta U_\Gamma = 2(0.05 \text{ V}), c_{np}^* = 1 \text{ nM}, c_{np} = 0.67 \text{ nM}, \epsilon_a = 5.0 \text{ mM}, c_b = 5.1 \text{ mM}, \epsilon_a = 10.7, \epsilon_b = 78.3, R_L = 2 \text{ Å}; \) inner layer: \(\epsilon_{il}^a = \epsilon_{il}^b = 6, D_a = D_b = R_L\). From Marinescu et al. (2012).

This study is only preliminary for the same reasons as those discussed in the previous section: the electrolyte concentration, albeit easy to control experimentally, plays a complex role in the adsorption isotherm. Its value will affect both \(\Gamma\) and \(\delta\), and a detailed model is needed to describe this effect.

The predicted effect of the concentration variation in the absence of such dependence is illustrated in Figure 8.7. An increase in the concentration of either electrolyte leads to the increase of the capacitances of the corresponding diffuse layers, both at the liquid/liquid and at the metal/electrolyte interfaces. As a result, the total capacitance is increased. The intersection between the capacitance of the occupied interface and that of the unoccupied one is a sign of strong compact layer contributions, as explained in Section 8.2.1. Extreme variations in concentration should change the balance between diffuse and compact layer contributions.

8.3 Conclusion

The theoretical model developed here supports the use of capacitance measurements as a quantitative method for characterising NP assemblies at liquid/liquid interfaces in general, and ITIES in particular. The model was used to rationalise the effects of different system parameters; its predictions correspond well to the experimental data available. The thickness and structural integrity of the NP layer remain debatable, as distinguishing between a monolayer and a multilayer is experimentally challenging. The possibility of multilayer formation can be assessed
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theoretically, in principle, based on the current understanding of the adsorption isotherm. Preliminary estimates of the capacitance of a NP multilayer localised at an ITIES suggest that the measurements of Younan et al. (2010) were performed on a submonolayer, not a multilayer. The capacitance of the system is sensitive to the value of the coverage parameter, and this sensitivity can, in principle, be tuned by varying the system parameters appropriately.

Theoretical predictions and experimental data can be better matched by:

- choosing solvents and salts for experimental systems such that specific adsorption of ions at the interface is negligible; otherwise, adsorption must be included in the theoretical model of both the occupied and unoccupied ITIES,

- measuring capacitance via high frequency impedance or, alternatively, developing a more cumbersome but accurate model based on integral capacitances.

Many predictions of the model can be checked by experimental studies; parameters other than the bulk concentration of NPs should be varied, such as the electrolyte concentration, the NP radius, and the ligand size and charge.

Finally, independent experimental studies of several system parameters would help improve our understanding of the system behaviour and advance our ability to tune it for particular applications. The average charge on NPs immersed in the aqueous solution, as well as the stability of the charge with time and when the NPs are in contact with the oil phase, or the expected length and flexibility of ligand chains are crucial pieces of information in this regard.
Bibliography


Chapter 9

Faraday rotation by NPs at ITIES

Theoretical (Hui & Stroud 1987) and experimental (Smith et al. 2005) studies showed that the Faraday rotation induced by a colloidal dispersion of magnetised particles depends on their density. The ITIES system provides a way to electrically tune the density of NPs in the bulk and on the surface in a reversible manner. We are interested in the possibility of designing a tunable Faraday rotator, by using modest voltages, with applications in spectroscopy and for electrically switchable Faraday devices, such as optical isolators. The Faraday effect has multiple applications for instruments measuring optical rotation power, sensing remote magnetic fields, detecting the polarisation of electron spins in semiconductors. The effect is also at the bases of optical isolators, common in optical communications; they allow electromagnetic waves to travel in one direction only, reducing the signal noise due to backscatter.

9.1 Two systems

Let us consider a flat ITIES, with magnetic NPs dispersed in one of the electrolytes, the aqueous one, similar to that considered in Chapter 8. When the aqueous phase is polarised positively with respect to the oil phase, the NPs are dispersed in the bulk, whereas for negative voltages they are confined to the interface. We explore two systems: normal incidence light within a high Q optical cavity, i.e. low dissipation, and grazing incidence in a waveguide geometry, as displayed in Figure 9.1. The electrodes are transparent, and an optical clad provides optical confinement. A constant magnetic field is applied to the system, which causes the magnetisation of the NPs to be oriented parallel or perpendicular to the interface, aligned with the direction of propagation of light.

The direction of linear polarisation of an incident light is rotated to some degree as a result of its passing through the system. Different rotation angles are expected when the NPs are dissolved in the electrolyte than when they are assembled at the interface; in a monolayer, interactions
Figure 9.1: Schematic drawing of the main features of the two geometries. Two immiscible liquids, each with dissolved ions, share a common interface and are placed between two electrodes. The aqueous solution contains negatively charged, magnetic NPs. The incident light is (a) perpendicular and (b) parallel to the ITIES. i) Potential is applied such that the NPs remain in the bulk of the liquid. ii) Potential applied such that the NPs migrate to the liquid/liquid interface. In each case, a constant magnetic field is applied parallel to the incident light and the NPs are magnetised as indicated by arrows. Not drawn to scale.
between neighbouring NPs can enhance the response. The viability of the ITIES system as a Faraday insulator depends on the difference between these two responses.

9.2 The model

9.2.1 Faraday rotation

An anisotropic dielectric medium interacts differently with light, depending on its direction of propagation. This is mathematically expressed by a dielectric permittivity tensor with non-equal diagonal elements, which give different speeds for propagation along the three Cartesian axes. Optical activity and Faraday rotation properties refer to materials that have the property of circular anisotropy: left and right circularly polarised light propagates with different velocities. Since a plane polarised light can be seen as the superposition of one left circular and one right circular polarised components, the plane of polarisation of such a wave is rotated as it passes through an optically active medium. The magneto-optical Faraday effect takes place when the circular anisotropy is caused by an external magnetic field.

The Faraday rotation under a constant magnetic field in the $z$ direction is produced by an anti-symmetric dielectric permittivity tensor of the form

$$\hat{\epsilon} = \begin{pmatrix} \epsilon_{\alpha\alpha} & iA_b & 0 \\ -iA_b & \epsilon_{\beta\beta} & 0 \\ 0 & 0 & \epsilon_{\gamma\gamma} \end{pmatrix},$$

(9.2.1)

where $A_b$ is a complex function that depends on material properties, magnitude of the magnetic field, and on the wavelength. When the material is not ferromagnetic, $A$ is linear in the magnetic intensity. For moderate magnetic fields two further assumptions hold:

$$\epsilon_{\alpha\alpha} = \epsilon_{\beta\beta} = \epsilon_{\gamma\gamma} = \epsilon, \quad A_b \ll \epsilon.$$

The polarisation angle of linearly-polarised light propagating through a medium with the dielectric tensor in Equation 9.2.1 is rotated by an angle per unit length given by

$$\theta_b = \left( k_+ - k_- \right) / 2,$$

proportional to the difference between the wave numbers of the left and right circularly polarised components:

$$k^2 = \left( \omega^2 / c_0^2 \right) (\epsilon \pm A_b),$$

(9.2.2)

$\omega$ is the angular frequency of the electromagnetic radiation, and $c_0$ the speed of light in vacuum. For $A_b \ll \epsilon$ the rotation angle per unit length of the light path becomes

$$\theta_b = \frac{1}{2} \frac{\omega}{c_0} \frac{A_b}{\epsilon^{1/2}}.$$

(9.2.3)
9.2.2 Single sphere polarisability

The effective polarisability of a sphere of radius $R$, made of material of dielectric permittivity $\epsilon$, surrounded by medium $\epsilon_s$, is given by the Clausius Mossotti expression (Myers 1990):

$$\alpha_{np} = R^3 \epsilon_s \frac{\epsilon - \epsilon_s}{\epsilon + 2\epsilon_s}. \quad (9.2.4)$$

The expression was shown to hold for tensorial permittivities by Sihvola (1994), such that $\alpha_{np} \rightarrow \hat{\alpha}_{np}$, with $\epsilon \rightarrow \hat{\epsilon}$, $\epsilon_s \rightarrow \epsilon_s \mathbb{1}$, where $\mathbb{1}$ is the unit matrix. The surrounding medium is assumed to have a scalar dielectric function and must be homogeneous around the particle.

The polarisability of an isolated $np$ with dielectric permittivity characterised by a diagonal term $\epsilon_b$ and off-diagonal function $A_b$

$$\hat{\epsilon} = \begin{pmatrix} \epsilon & iA_b & 0 \\ -iA_b & \epsilon & 0 \\ 0 & 0 & \epsilon \end{pmatrix} = \epsilon \mathbb{1} + \hat{\alpha} \quad (9.2.5)$$

can be calculated as

$$\hat{\alpha}_{np} = \frac{R^3 \epsilon_s}{\gamma} \begin{pmatrix} 1 & iB & 0 \\ -iB & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (9.2.6a)$$

$$\gamma = \frac{\epsilon + 2\epsilon_s}{\epsilon - \epsilon_s} \quad (9.2.6b)$$

$$B = \frac{3\epsilon_s A_b}{(\epsilon - \epsilon_s)(\epsilon + 2\epsilon_s)}. \quad (9.2.6c)$$

This result is obtained under the assumption that $A_b \ll \epsilon - \epsilon_s$ and $A_b \ll \epsilon + 2\epsilon_s$, such that the expansion:

$$\frac{m + x}{n + x} \xrightarrow{x \ll m, n} \frac{m}{n} + \frac{n - m}{n^2} x + ... \quad (9.2.7)$$

can be used to the first order in $x$ for

$$m \rightarrow (\epsilon - \epsilon_s) \mathbb{1}, \quad (9.2.8)$$

$$n \rightarrow (\epsilon + 2\epsilon_s) \mathbb{1}, \quad (9.2.9)$$

$$x \rightarrow \hat{\alpha}. \quad (9.2.10)$$
9.2.3 Faraday rotation from a monolayer

The rotation angle induced by a monolayer is calculated by following the steps:

1. calculate the effective polarisability $\alpha_{ml}$ of a monolayer or submonolayer of spheres with individual polarisability given by Equation 9.2.4, allowing for dipolar interactions between particles,

2. obtain the effective dielectric permittivity $\epsilon_{ml}$ of the structure with polarisability $\alpha_{ml}$,

3. extract the rotation angle $\theta_{ml}$, of the form of Equation 9.2.3

9.2.3.1 Polarisability of a monolayer

Persson & Liebsch (1983) have studied the optical properties of a two-dimensional system of identical plasma spheres within the dipole-dipole approximation. Following their approach we calculate the effective polarisability for a monolayer or submonolayer of spherical NPs in a hexagonal lattice. The local field at a NP at lattice position $i$ is given by the sum between the external field of the incoming electromagnetic wave and that scattered by all other spheres in the lattice. In a dipolar approximation, the electric field is

$$E(x_i) = E_{ext} - \sum_{j \neq i} \hat{U}(x_i - x_j)p_j.$$  \hspace{1cm} (9.2.11)

$p_j$ is the induced dipole moment on sphere $j$, proportional to its polarisability $\hat{\alpha}_{NP,j}$ and to the local field:

$$p_j = \hat{\alpha}_{NP,j} E(x_j).$$  \hspace{1cm} (9.2.12)

The dipole field at particle $i$ due to particle $j$ in Equation 9.2.11 depends on the interaction term

$$\hat{U}(x) = \frac{1}{\epsilon_s} \left( \frac{1}{|x|^3} - \frac{3x \cdot x}{|x|^5} \right).$$  \hspace{1cm} (9.2.13)

In the limit of long wavelengths compared to the lattice constant $a$, $a/\lambda \ll 1$, $\hat{U}$ can be calculated in the reciprocal space:

$$\hat{U} = \begin{pmatrix} -1/2 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \frac{\Gamma^{3/2} U_0}{a^3} \frac{U_0}{\epsilon_s}, \quad U_0 = \frac{a^3}{\Gamma^{3/2}} \sum_j |x_j|^{-3}.$$  \hspace{1cm} (9.2.14)

As before, $\Gamma = N/N_{\text{max}}$ is the interfacial coverage interface, defined as the ratio between the number of localised particles and the total number of NPs that can populate the interfaces. $a$ is a fixed lattice constant, corresponding to the maximum coverage of the interface $N = N_{\text{max}}$. The centre-to-centre distance between particles in a mono- or submonolayer is given by $a/\sqrt{\Gamma}$. $U_0$
is constant for a given lattice type; for a hexagonal lattice the sum is calculated as $U_0 = 11.03$ (Hurley & Singer 1992). Equation 9.2.11 and Equation 9.2.12 can be used to find an expression for the dipole moment in the reciprocal space. By defining the effective polarisability of the layer as the proportionality factor analogous to Equation 9.2.12, Persson & Liebsch (1983) obtain:

$$\hat{\alpha}_{ml} = \begin{pmatrix} \alpha_\parallel & 0 & 0 \\ 0 & \alpha_\parallel & 0 \\ 0 & 0 & \alpha_\perp \end{pmatrix},$$  

(9.2.15)

with $\alpha_\parallel$ the in-plane and $\alpha_\perp$ the out of plane polarisation of the layer:

$$\alpha_\parallel = \frac{\alpha_{NP}}{1 - \frac{1}{2} \alpha_{NP} \frac{U_0 R^{3/2}}{a^3 \epsilon_s}},$$  

(9.2.16)

$$\alpha_\perp = \frac{\alpha_{NP}}{1 + \alpha_{NP} \frac{U_0 R^{3/2}}{a^3 \epsilon_s}}.$$  

(9.2.17)

As in our system $\hat{\alpha}_{NP}$ is itself a tensor, $\hat{\alpha}_\parallel$ and $\hat{\alpha}_\perp$ are also tensors.

By substituting the expression of $\hat{\alpha}_{NP}$ from Equation 9.2.6, the effective polarisability of the monolayer becomes:

$$\hat{\alpha}_{\parallel} = \frac{R^3 \epsilon_s}{\gamma} \left(1 - \frac{\Delta}{\gamma}\right)^{-1} \begin{pmatrix} 1 & iC \\ -iC & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \Delta = \frac{\Gamma^{3/2} U_0 R^3}{2a^3 R}$$  

(9.2.18)

$$C = \frac{3\epsilon_s A_b}{(\epsilon - \epsilon_s)(\epsilon + 2\epsilon_s)} + \frac{3\epsilon_s A_b}{(\epsilon + 2\epsilon_s)^2} \left(1 - \frac{\Delta}{\gamma}\right)^{-1},$$  

(9.2.19)

with $\gamma$ defined as in Equation 9.2.6.

### 9.2.3.2 Dielectric permittivity of a monolayer

The dielectric permittivity of the monolayer of NPs at an ITIES interface can be written as in (Flatte et al. 2010):

$$\epsilon_{ml} = \left(1 - n_s \pi R^2\right) \left[\epsilon_a \Theta(-z) + \epsilon_b \Theta(z)\right] \mathbb{1} + \frac{4\pi n_s}{2R} \hat{\alpha}_{ml},$$  

(9.2.20)

where $\Theta$ is the Heaviside step function, and $n_s$ the number density of particles at the interface $n_s = N/A$. For a hexagonal lattice of NPs at the interface $n_s = \Gamma/(2\sqrt{3}R^2)$. The first term in Equation 9.2.20 accounts for the unoccupied interface, while the second one weighs the contribution from localised NPs.
For the case of $\epsilon_a \simeq \epsilon_b = \epsilon_s$, the dielectric permittivity becomes

$$\hat{\epsilon}_{ml} = \left(1 - n_\pi R^2\right) \epsilon_s + \frac{4\pi n_s}{2R} \hat{\alpha}_{ml}. \quad (9.2.21)$$

The thickness of the functionalisation layer can be accounted for by making the substitution: $R \rightarrow R + \delta$. In the following, however, the assumption $R \gg \delta$ is made.

The diagonal and off-diagonal elements of $\hat{\epsilon}_{ml}$ are obtained by substituting Equation 9.2.18:

$$\epsilon_{ml} = \frac{2\pi n_s R^2 \epsilon_s}{\gamma - \Delta} + \left(1 - n_\pi R^2\right) \epsilon_s, \quad (9.2.22a)$$

$$A_{ml} = \frac{6\pi n_s R^2 \epsilon_s A_{b}}{\gamma - \Delta} \frac{1}{(\epsilon - \epsilon_s)(\epsilon + 2\epsilon_s)} \left(1 + \frac{\Delta}{\gamma - \Delta}\right), \quad (9.2.22b)$$

with $\gamma$ defined as in Equation 9.2.6 and $\Delta$ as in Equation 9.2.18. For light incident perpendicularly to the interface, $\hat{\alpha}_{ml} = \hat{\alpha}_\parallel$.

For the waveguide geometry shown in Figure 9.1(b) where the light travels parallel to the monolayer, both perpendicular and parallel polarisabilities play a role in the system response, and a mathematical treatment is complex. When the NPs are localised, the highly anisotropic polarisability causes

$$|\epsilon_{\alpha\alpha} - \epsilon_{\beta\beta}| \gg |A_b| \quad (9.2.23)$$

for Equation 9.2.1, such that the Faraday rotation is fully quenched, and no rotation is expected to take place.

### 9.2.4 Faraday rotation from bulk

When the particles are dispersed in the bulk electrolyte, no significant inter-particle interaction takes place for reasonable NP concentrations. Equivalent to Equation 9.2.21, the effective dielectric permittivity of the bulk dispersion of the same number of particles as were present at the interface can be written as

$$\epsilon_{bl} = \epsilon_s + \frac{4\pi n_s}{l} \hat{\alpha}_{NP}, \quad (9.2.24)$$

with $l$ the dimension of the bulk in the $z$ direction and $n_s$ as before, to conserve the number of particles in the system. Substituting $\hat{\alpha}_{NP}$ for an isolated NP from Equation 9.2.6, the diagonal and off-diagonal elements of the effective bulk permittivity are calculated:

$$\epsilon_{bl} = \epsilon_s + \frac{4\pi n_s R^3 \epsilon_s}{l} \frac{\epsilon_s}{\gamma}, \quad (9.2.25a)$$

$$A_{bl} = \frac{4\pi n_s R^3}{l} \frac{3\epsilon_s^2 A_{b}}{(\epsilon + 2\epsilon_s)^2}. \quad (9.2.25b)$$

As in the case of the monolayer, the corresponding Faraday rotation per unit length for a bulk region with dispersed NPs ($\theta_{bl}$) can be calculated analogously to $\theta_b$ in Equation 9.2.3.
These expressions are similar to those obtained by Hui & Stroud (1987) for a dilute suspension of small particles that are homogeneously distributed in a liquid. They calculated the effective dielectric tensor in the case of small volume fraction of inclusions $f \ll 1$ via the Maxwell-Garnett approximation (Maxwell-Garnett 1904, Landau et al. 1984). In the limit of low magnetic fields such that $A_b \ll \epsilon$, they obtain

\begin{align}
\epsilon_{bl} &= \epsilon_s \left(1 + 3f/\gamma\right), \\
A_{bl} &= \frac{9\epsilon_s^2 f A_b}{(\epsilon + 2\epsilon_s)^2}.
\end{align}

In order to compare their results to those in Equation 9.2.25, $f$ is calculated for the case in which the number of NPs in the bulk is exactly that required to completely cover the interface:

\begin{equation}
f = \frac{4}{3} \pi R^3 n_s / T.
\end{equation}

With this identity, the expressions in Equation 9.2.26 and Equation 9.2.25 become identical.

### 9.2.4.1 Limiting cases

A few simple checks can be done of the consistency of the developed approach.

- For bulk and monolayer results, in the trivial case of no magnetic field $A_b \to 0 \Rightarrow A_{ml} \to 0$, no rotation occurs.

- The results for monolayer and bulk rotations, Equation 9.2.22 and Equation 9.2.25, become identical in the limit of vanishing dipole-dipole interaction $U_0/a^3 \to 0$, and identifying the surface volume fraction as $f = 2\pi R^2 n_s / 3$.

- Matching the diagonal term requires one more condition, namely that the surface is sparsely populated $n_s \ll (\pi R^2)^{-1}$. This constraint is required because of the use of the Maxwell Garnett limit, that requires the volume fraction of inclusions to be small.

### 9.3 Limitations

The interaction between NPs in the lattice is considered in the dipole approximation. As no multipole interactions are considered, the results are strictly valid for an average distance between neighbouring particles of a few radii and in the limit of $\lambda \gg a$. However, in the case of Faraday rotation, multipole interactions are not expected to play a significant role, unlike for the transmission/reflection response of a monolayer.

The interface must be part of the system, as it allows for the reversible localisation of NPs, which provides the low-power switchability of the rotation effect. The interaction between
the interface and the incoming light, however, have not been considered in the response model. As mentioned, the polarisation of a single NP as given by the Clausius Mossoti formula in Equation 9.2.4 is derived for a homogeneous and isotropic surrounding medium. While this is the case when NPs are dispersed in the bulk electrolyte, it is certainly not providing a generally accurate description for NPs localised at the interface. The result presented here is valid only for systems in which \( \epsilon_a \approx \epsilon_b \) at the frequency of interest. To account for the exact position of the NP at the interface, \( \alpha_{\text{NP}} \) must become a function of both \( \epsilon_a, \epsilon_b \), the two liquids in the system.

9.4 Model predictions (preliminary results)

Parameter values

The parameters are taken for the visible spectrum, when available. The NP material is taken as yttrium iron garnet (YIG), a transparent magnetic material commonly used in magnetic bubble memories. The static dielectric constant of YIG was calculated by Hofmeister & Campbell (1992), \( \epsilon \approx 20 \) from infrared measurements. The bulk Faraday rotation per unit length for macroscopic YIG in the visible spectrum was measured by Wettling et al. (1973); for wavelengths \( \approx 500 \text{ nm} \), \( \theta_b \leq 5 \cdot 10^4 \text{ rad m}^{-1} \). The permittivity of both solvents is taken as that for water, within this wavelength region \( \epsilon_s = 1.77 \).

9.4.1 Normal incidence

![Graph of particle radius vs. Faraday rotation](image)

**Figure 9.2:** Ratio of Faraday rotation per unit length from NPs assembled at a monolayer to that from NPs dispersed in the bulk, with conserved number of particles. \( \Gamma \) and \( R \) are independently varied. The rotation angle increases with \( \Gamma \); at fixed \( \Gamma \) the rotation from a monolayer increases with decreasing \( R \), as this case corresponds to more material available to interact with the incident light. In b) the \( \ln (\theta_{\text{ml}}/\theta_{\text{bl}}) \) values are given in the colour bar.

Figure 9.2(a) displays the ratio between the Faraday rotation per unit length for a localised monolayer and that for the same number of NPs dispersed in the bulk, in the case of perpendicular
incidence in Figure 9.1(a). The sizable rotation difference between the occupied and unoccupied interface states is not limited to full monolayer coverages.

For a system with thickness \( l = 1 \text{ cm} \), \( R = 40 \text{ nm} \) and \( \epsilon = 20 \), the rotation per unit length of dispersed NPs in the bulk is \( \theta_{\text{bl}} = 4 \cdot 10^{-2} \text{ rad m}^{-1} \), and that of NPs in a monolayer, \( \theta_{\text{ml}} = 10^4 \text{ rad m}^{-1} \). The net rotation when all particles are dispersed in the bulk liquid is given by \( l \cdot \theta_{\text{bl}} = 4 \cdot 10^{-4} \text{ rad} \), while from the monolayer by \( 2R \cdot \theta_{\text{ml}} = 10^{-3} \text{ rad} \). The difference in polarisation angle is \( 6 \cdot 10^{-4} \text{ rad} \) for a single pass of the wave through the system. Although this rotation of the polarisation angle is modest compared to the 0.78 rad required for an isolator, the effect can be amplified in a high quality factor optical cavity with quality factor \( Q \simeq 10^4 \).

**Voltage dependence**

![Figure 9.3](image)

**Figure 9.3:** a) For a small variation in the applied potential, the interface coverage \( \Gamma \) is predicted to change dramatically (Flatte et al. 2010). b) Ratio between the Faraday rotation obtained from a monolayer and that from the bulk dispersion, as a function of applied voltage, for the coverage relation illustrated in a). The curves correspond to various NP radii. The absorption isotherm was calculated as for \( N_{\text{ch}} = 4000 \), \( c_a = c_b = 5 \text{ mM} \), \( \epsilon_a = 78.8 \) (aqueous), \( \epsilon_b = 10.7 \) (1,2-dichloroethane), liquid/liquid surface tension =0.03 N m\(^{-1}\), triple phase contact angle =0.55\( \pi \) rad, line tension =10\(^{-11}\) N, as in Flatte et al. (2008b).

A proof of principle study of the way in which the system would switch between rotations is given in Figure 9.3(b), the description of the effect of the electric potential on the Faraday rotation per unit length for the normal-incidence geometry. The curves are calculated assuming a \( \Gamma(V) \) dependence given by the the model in Flatte et al. (2010), summarised in Chapter 7. \( \Gamma(V) \) is given by the combined result of the energy profile of a single NP and the electrostatic interaction between two NPs at the interface. Under these assumptions, the gradual population of the ITIES for the system considered here is depicted in Figure 9.3(a).
9.4.2 Parallel incidence

In the case of grazing incidence, Figure 9.1(b), the thickness of the cell perpendicular to the interface is of the order of a wavelength of light, \( l \sim 1 \mu m \). In order to have enough NPs to cover the interface with a monolayer, the concentration in the bulk must be \( 10^4 \) times larger than in the case considered previously, of cell thickness \( \approx 1 \text{ cm} \). For parallel propagation of light in the bulk \( \theta_{bl} \sim 4 \text{ rad cm}^{-1} \), leading to the \( \pi/4 \) rotation required for a Faraday isolator within a lateral distance of \( \sim 2 \text{ mm} \). For a small electrochemical cell a few microns thick and a few millimetres long, accumulation and depletion of NPs from an ITIES should be sufficient to switch a Faraday isolator constructed in a waveguide geometry.

9.5 Discussion

A framework was developed for calculating the electrically-controllable Faraday rotation achieved due to the reversible NP accumulation at an ITIES. In principle, the same approach can be used for metal NPs, with a frequency dependent \( \epsilon(\omega) \) and \( A_h(\omega) \) in Equation 9.2.5, given, in a simple model, by the Drude free electron gas model.

Two types of systems were considered for use in a first electrically switchable Faraday isolator.

1. For normal incidence and low concentrations of NPs in the bulk, the response, and thus Faraday rotation, are enhanced when NPs are localised at the interface. This effect is a result of high effective particle concentration at the ITIES and inter-particle interactions. For high enough monolayer-to-bulk rotation ratios, a switch between the covered/uncovered states of the interface could become a tunable interference filter for frequencies in the visible spectrum. The difference in the net rotation of the two states is small, such that the device would require a high quality factor (\( Q \approx 10^4 \)) optical cavity for a \( \pi/4 \) rotation.

2. A second geometry with grazing incident light is considered, in which an efficient quenching of the Faraday rotation should take place when the NPs are localised. This quenching is caused by the intrinsic anisotropy of the system. For a small electrochemical cell, a high enough concentration in the bulk could provide significant rotation compared to the localised state. If reversibility between the two states of the system can be reached for voltages \( \sim 1 \text{ V} \), low-power electrical switching of a Faraday isolator can be achieved in this waveguide geometry. Such a device would be highly regarded for use in communication systems. In an optical device, the linear birefringence would be compensated for with other linear birefringent elements, such that the signal is not distorted.

Reversibility with voltage changes is essential for both geometries considered. While reversible assemblies have been obtained experimentally and rationalised theoretically, the applicability of
the present theoretical model remains dependent on the reversibility of the particular system of interest. For applications based on Faraday rotation, the exact structure of the layer formed by localised NPs is not crucial; important is the possibility of switching between two states, where most particles are confined or dispersed.

**Current work**

Before promoting the effect as described by the model predictions for particular applications, a number of issues need to be addressed:

- Calculations of the Faraday rotation obtained from a monolayer in the case of grazing incidence should be performed, to test the assumption that anisotropy in the system is strong enough to quench the effect. If this is the case, the net rotation caused by the bulk dispersion as opposed to the monolayer assembly will be large enough. An analysis of the allowed modes in a waveguide and of their interaction with the populated interface is needed.

- In both systems, the amount of light that is absorbed is crucial for viable applications and needs to be estimated using the imaginary component of the dielectric permittivity. The choice of liquids, frequency of light, concentration of NPs and size of the system are all parameters that play a role. For perpendicular incidence in an optical cavity, such absorption is significant, especially in a system where water is one of the solvents and frequencies are in the infrared. For this reason, a microfluidic system of \( \mu m \) dimensions might be the better choice if the difference in rotations can be kept large enough.

- The time response of the system is also important for practical applications. While exact predictions cannot be made in the absence of detailed experimental information, estimates of response times inherent to the population/depopulation of the \( \text{ITIES} \) are possible. Pulsed voltages could be used to decrease switching times.

- All above considerations should be targeted towards the types of possible applications; two ranges of frequencies, in the visible (filters) and in the infrared region (telecommunications) are currently targeted for all estimates and predictions.

This work is currently under progress and should provide answers to the above shortly.
Bibliography


Chapter 10

Epilogue

Although well established, the area of electrified liquid/liquid interfaces has seen dramatic changes recently. Technological advances have brought about the possibility of designing liquid systems for a variety of applications that were traditionally reserved to devices with solid active elements. Such developments require and benefit from a detailed quantitative understanding of the relevant phenomena, at levels spanning from nano- to macroscopic.

The three models developed here, in Chapters 6, 8 and 9, provide virtual tools for understanding the behaviour and properties of two systems based on the interface between two electrolytes. All projects were inspired by recent experimental developments and, with the exception of the model for Faraday rotation in Chapter 9, have been developed by interacting closely with experimental teams.

A first model for the dynamics of electrowetting with ities, on a real, microscopically rough electrode is developed. The behaviour is described by a phenomenological model through analogy to a harmonic oscillator. The effects of roughness and pulsing, two principal factors in the observed behaviour of the droplet, are analysed. The time-dependent electrowetting response under pulsing is determined by the following factors: the driving force caused by the applied voltage, the static friction force caused by any morphological non-uniformities of the solid electrode surface, the viscous energy dissipation, and the inertia. Analytical results are obtained for a set of simplifying assumptions, and prove useful in understanding the main trends in the droplet behaviour. The full numerical solution can describe the experimental data quantitatively. Pulsing is shown to be a viable tool for increasing the interval of achievable contact angles via the electrowetting effect in systems with non-ideal electrodes. Besides being a tool for facilitating electrowetting, the pulsing technique could become an electroanalytical method for studying more general topics in wetting dynamics, such as friction.

In the second part, models are developed for quantifying electric and magnetic properties of the ities. The functionalisation is achieved via self-assembled particle layers, reversible with applied potential. A model for the capacitance of the ities fully or partially occupied by charged metal
nanoparticles is developed. The interface is modelled by an equivalent arrangement of capacitors, with specific capacitances given by the respective models for diffuse and inner layers, and areas calculated as a function of the layer geometry. Significant differences in capacitance between a monolayer, a submonolayer and a metallic film are predicted. The effects of different parameters are analysed: the concentration of NPs in the bulk, electrolyte concentrations in the liquids, the depth to which the NPs pierce the interface, their charge and size. The model predictions validates impedance measurements as a tool for quantitative analysis of the interfacial structure, as it allows to extract information about the structure of the adsorbed layer from capacitance measurements.

The possibility of designing a low-power Faraday isolator for optical and communication applications is also investigated. Preliminary calculations show that a microfluidic device formed by an ITIES with assembled magnetic dielectric nanoparticles in a waveguide geometry should exhibit the required properties.

These models offer a basic framework for quantitative analysis in systems of great interest for a variety of optical, magnetic and sensing applications. Although model predictions compare well with the available experimental data, the latter is still limited. Further experimental investigations will provide the categoric validity check, showing whether the models developed here manage to capture all relevant physical phenomena.
Appendix A

Equilibrium of ITIES - Step by step

As mentioned in Section 4.2, the change in the Gibbs free energy of the system due to the presence of the droplet is given by:

\[
\Delta G = \left[ \gamma_{de} - \gamma_{se} + \bar{\varepsilon}_{ds} (\Delta V - V_{ds}) - \varepsilon_{se}(\Delta V) \right] A_{de} + \left[ \gamma_{ds} + \bar{\varepsilon}_{ds}(V_{ds}) \right] A_{ds} + v_d \Delta p,
\]

in terms of interfacial areas, energies, and the Laplace pressure. To calculate the equilibrium contact angle of the droplet in the ITIES system, we follow the path described below, by Monroe et al. (2007) and Monroe et al. (2009).

1. The Young Laplace equation

\[
\cos \alpha_0 = \frac{\gamma_{se} - \gamma_{de}}{\gamma_{ds}}
\]

is used to express the difference \(\gamma_{se} - \gamma_{de}\) in terms of \(\gamma_{ds}\) and \(\alpha_0\). The equilibrium contact angle in the absence of ions corresponds to \(V = 0\) in the model, and to \(V = V_{pzc}\) for any comparisons to experimental data.

2. The droplet volume and the areas of the two droplet interfaces are geometric parameters, functions of droplet radius \(r_d\) and height \(h_d\)

\[
A_{de} = \pi h_d (2r_d - h_d), \quad A_{ds} = 2 \pi h_d r_d, \quad v_d = \frac{\pi h_d^2}{3} (r_d - \frac{1}{3} h_d),
\]

where

(a) \(h_d\) and \(r_d\) are functions of the contact angle, and are related to each other through the conserved droplet volume

\[
r_d = \frac{v_d}{\pi h_d^2} + \frac{h_d}{3};
\]

(b) the ratio between the areas of the two droplet interfaces is expressed in terms of the contact angle for the truncated sphere droplet

\[
\mathcal{A}(\Delta V, V_{ds}) = \frac{A_{de}}{A_{ds}}, \quad \cos \alpha = 2 \cdot \mathcal{A} - 1;
\]
(c) the ratio $A$ is expressed in terms of the surface charge densities at the two droplet interfaces using the constraint of net droplet electroneutrality

$$A(\Delta V, V_{ds}) = -\frac{\sigma_{ds}(V_{ds})}{\sigma_{de}(\Delta V - V_{ds})};$$

(d) the two surface charge densities are obtained via the VN and GC-MWT theories

$$\sigma_{ds}(U_{ds}) = \frac{2RT\epsilon_0\sqrt{\epsilon_d\epsilon_s\kappa_d\kappa_s}\sinh(U_{ds}/2)}{F_z\sqrt{\left(\hat{C} + 1/\hat{C}\right)^2 + 4\sinh^2(U_{ds}/4)},}$$

$$\sigma_{de}(\Delta U - U_{ds}) = -\frac{2RT\epsilon_0\epsilon_d\kappa_d}{F_z}\sinh\left(\frac{\Delta U - U_{ds} - \Delta U_{de}^{\|}}{2}\right),$$

in terms of dimensionless potentials $U$, parameter $\hat{C} = \sqrt{\epsilon_d\kappa_d/\epsilon_s\kappa_s}$, and $\Delta U_{de}^{\|}$ the dimensionless potential drop over the inner layer at the specified interface. $\kappa = 1/\lambda$.

3. The se interface has a charge density

$$\sigma_{se}(\Delta U) = -\frac{2RT\epsilon_0\epsilon_s\kappa_s}{F_z}\sinh\left(\frac{\Delta U - \Delta U_{se}^{\|}}{2}\right).$$

4. The ds interfacial energy is

$$\varepsilon_{ds}(U_{ds}) = 4b\gamma_{ds}\left(\hat{C} + 1/\hat{C}\right)\left(1 - \sqrt{1 + \frac{4\sinh^2(U_{ds}/4)}{(\hat{C} + 1/\hat{C})^2}}\right),$$

with the dimensionless parameter

$$b = \left(\frac{RT}{F_z}\right)^2\frac{\epsilon_0\sqrt{\epsilon_d\epsilon_s\kappa_d\kappa_s}}{\gamma_{ds}}.$$

5. The de and se interfacial energies are given by

$$\varepsilon_{se}(\Delta U) = -2\epsilon_0\epsilon_s\kappa_s\left(\frac{RT}{F_z}\right)\sinh^2\left(\frac{\Delta U - \Delta U_{se}^{\|}}{2}\right)\left[\frac{\epsilon_0\epsilon_s\kappa_s}{K_{se}(\Delta U_{se}^{\|})} + \text{sech}^2\left(\frac{\Delta U - \Delta U_{se}^{\|}}{4}\right)\right],$$

$$\varepsilon_{de}(\Delta U - U_{ds}) = -2\epsilon_0\epsilon_d\kappa_d\left(\frac{RT}{F_z}\right)\sinh^2\left(\frac{\Delta U - U_{ds} - \Delta U_{de}^{\|}}{2}\right)\left[\frac{\epsilon_0\epsilon_d\kappa_d}{K_{de}(\Delta U_{de}^{\|})} + \text{sech}^2\left(\frac{\Delta U - U_{ds} - \Delta U_{de}^{\|}}{4}\right)\right].$$
6. An implicit relation between the applied potential $\Delta U$, the potential drop over the ‘ds’ interface $\Delta U_{ds}$, and that over the inner layer of the ‘de’ interface $U^{il}_{de}$ is obtained by:

(a) assuming that the inner and diffuse double layers can be separated by an equipotential plane

$$\Delta U = \Delta U^{il}_{se} + \Delta U^{dl}_{se},$$
$$\Delta U - U_{ds} = \Delta U^{il}_{de} + \Delta U^{dl}_{de};$$

(b) writing the diffuse layer potential drops under the constraint that no ions from bulk enter the inner layer

$$\Delta U = \Delta U^{il}_{se} + 2 \sinh^{-1} \left[ \frac{K^{il}_{se} \Delta U^{il}_{se}}{\epsilon_0 \epsilon_s \kappa_s} \right];$$
$$\Delta U - U_{ds} = \Delta U^{il}_{de} + 2 \sinh^{-1} \left[ \frac{K^{il}_{de} \Delta U^{il}_{de}}{\epsilon_0 \epsilon_d \kappa_d} \right];$$

(c) writing the integral capacitance of the inner layer as in the mwt model.

7. Parameter values for the ‘se’ interface are obtained by fitting available experimental data for the aqueous solution/gold electrode. Those for the ‘de’ interface are taken by analogy, since no data is available for an oil/gold interface.

8. The Laplace pressure is obtained from the Gibbs free energy of the system, Equation 4.2.1 by means of the Euler-Lagrange relation in terms of the ‘ds’ interfacial tension and energy, and the droplet radius

$$\Delta p = -\frac{2(\gamma_{ds} + \bar{\varepsilon}_{ds})}{r_d}.$$ 

Due to the complicated relations between variables, $V_{ds}$ is taken as the independent one. The equilibrium geometry of the system is obtained by minimising the free energy $\Delta G$ in Equation A.1 with respect to $V_{ds}$ for a given applied voltage. Once the position of the minimum energy is known, all system properties can be calculated, including the equilibrium contact angle $\alpha$. 
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