ELECTROSTATIC CHARGING WHEN CONDUCTIVE LIQUIDS DEWET SOLID SURFACES

Third European Conference on Plant & Process Safety

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ABOUT ME

Aaron Ratschow

Education

BS Ind. Eng. (TU Darmstadt)
BS Mech. Eng. (TU Darmstadt)
MS Proc. Eng. (TU Darmstadt)

Experience

2014-2017	Junior Comtec, Consultant/Project Manager
2018	Bayer PPS EXS, Intern
2018-2020	Bayer PPS EXS, Simulation Specialist
2020-	TU Darmstadt NMF, External PhD Candidate

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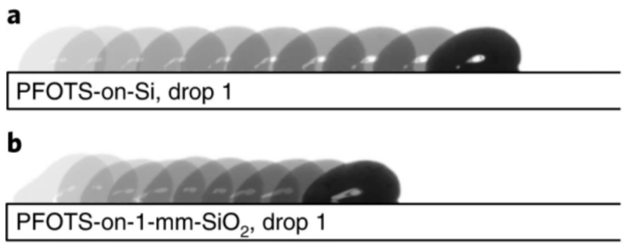
SOLID-LIQUID CONTACT ELECTRIFICATION

		Liquid	
		conductive	insulating
Solid	conductive	No charge separation	Flow electrification
	insulating	Charge separation when dewetting	Flow electrification

Slide electrification?

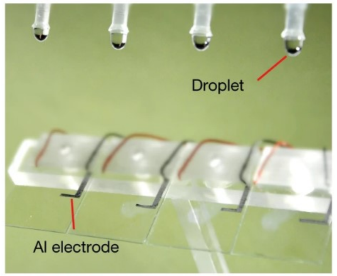
CHARGE SEPARATION AT CONTACT LINES...

...influences drop trajectories



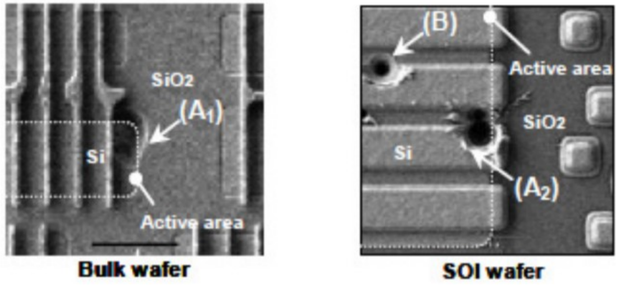
[Li et al., Nat. Phys. 2022]

...can be used for energy harvesting



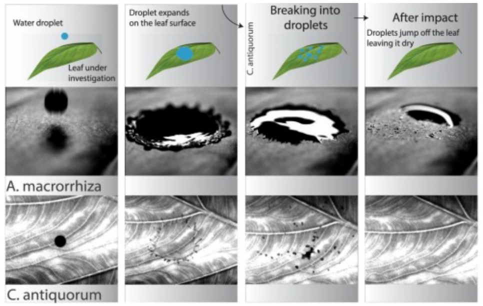
[Xu et al., Nat. 2020]

...damages semiconductors during rinsing



[Hagimoto et al., Solid State Phenom. 2009]

...even happens on plant leafs



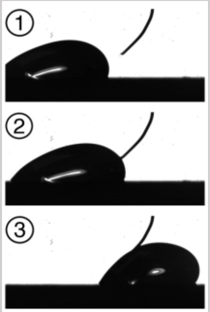
[Armiento et al., Commun. Mat. 2022]

EXPERIMENTS AND SIMULATIONS HELP DEVELOPING A THEORY

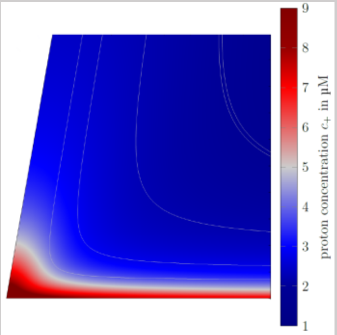
Observation

Prediction

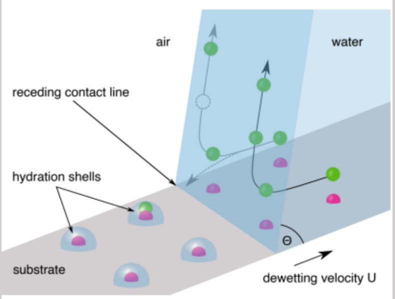
Experiments and Measurements



Numerical Simulations



Theory

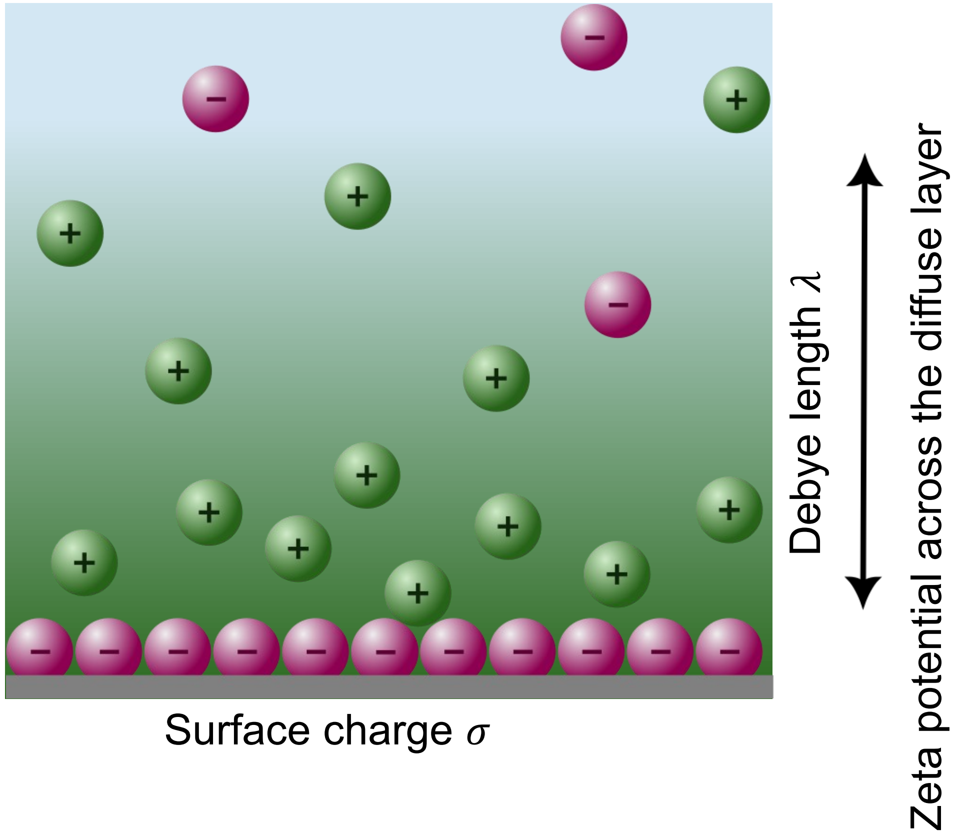


Practicality

Cost

ELECTRIC DOUBLE LAYERS

Electric double layer

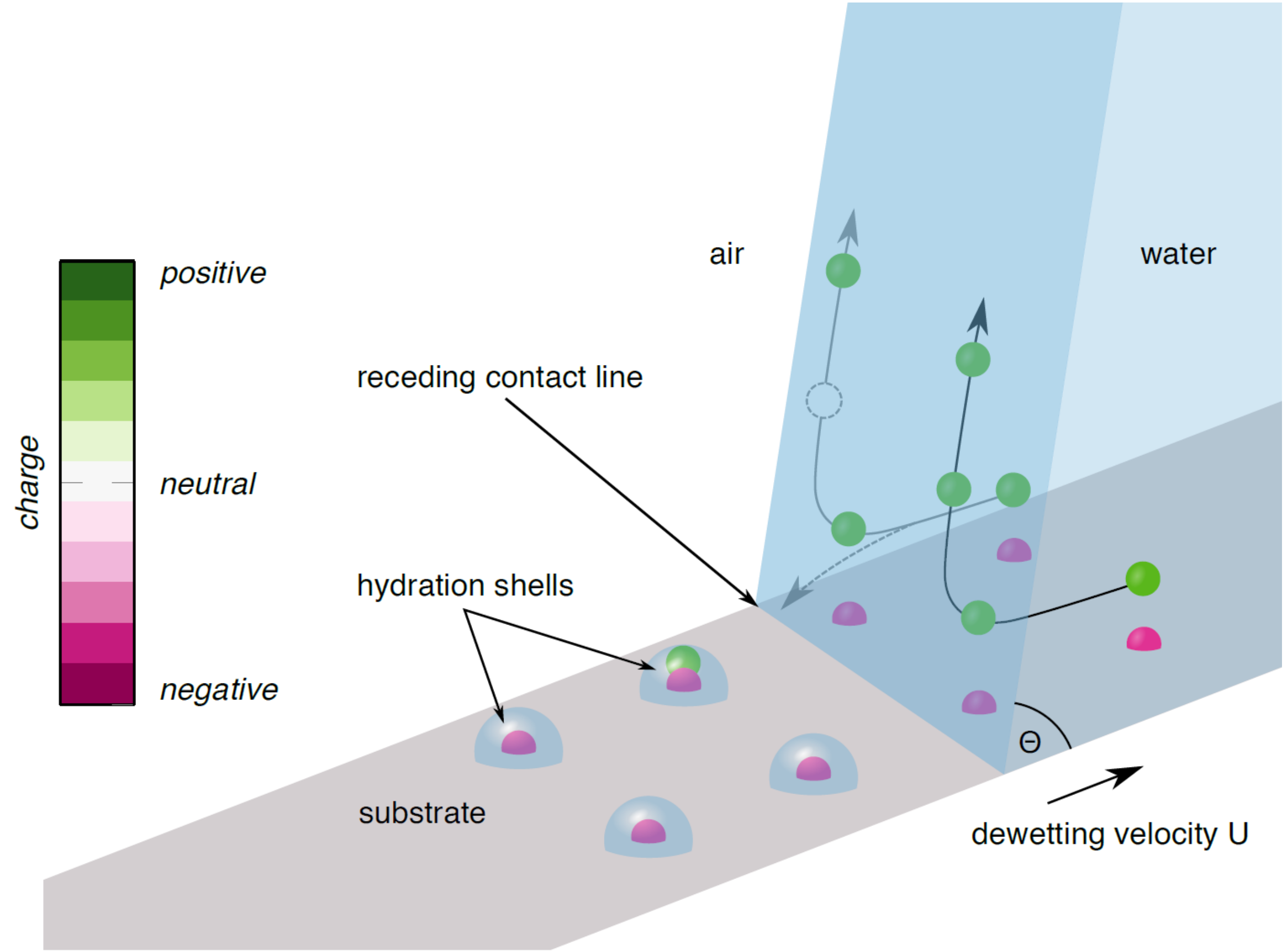


- Charged solid surface surface
  - Characterized by zeta potential
- Diffuse layer of countercharges in liquid
  - Thickness is Debye length ~1-500 nm
  - Described by Poisson-Boltzmann Theory

Origins of surface charge

- Dissociation of surface groups
- Specific adsorption of ions
- Dissolution of the solid

FUNDAMENTAL CHARGE SEPARATION MECHANISM

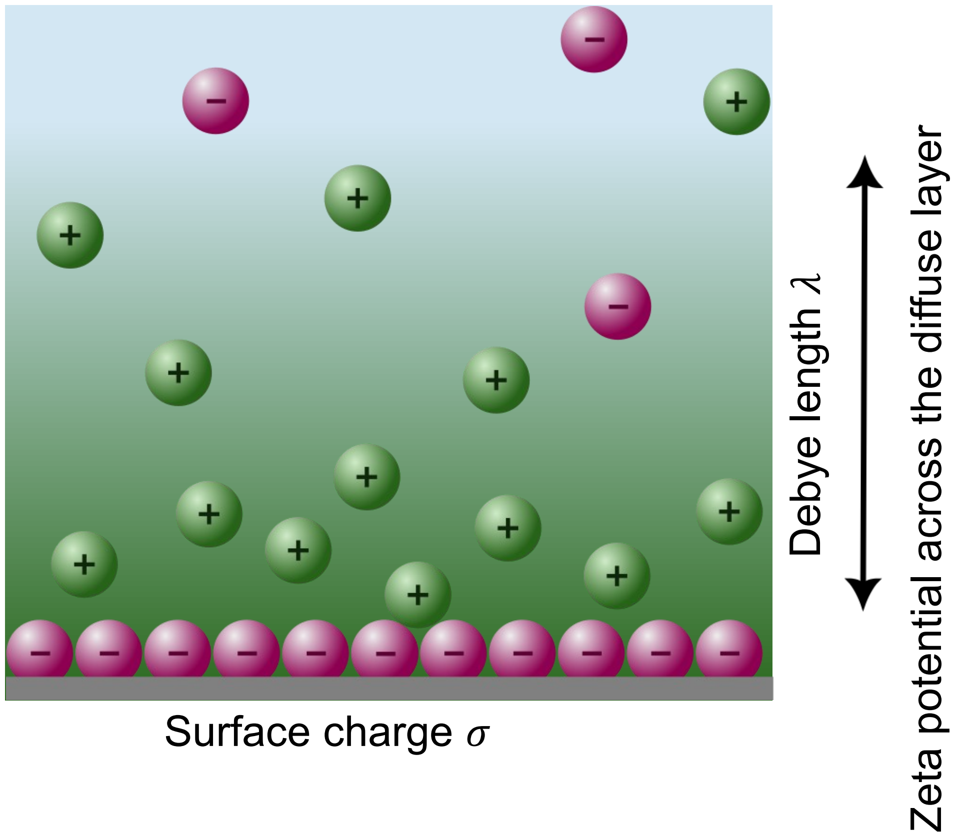


Charge separation mechanism

- Electric double layer of bound surface charge and layer of diffuse charge in liquid
- Receding contact line dewets bound surface charge
- Diffuse charge remains in the liquid

ELECTRIC DOUBLE LAYER AND SURFACE CHEMISTRY

Electric double layer



- Surfaces like glass deprotonate upon contact with liquid

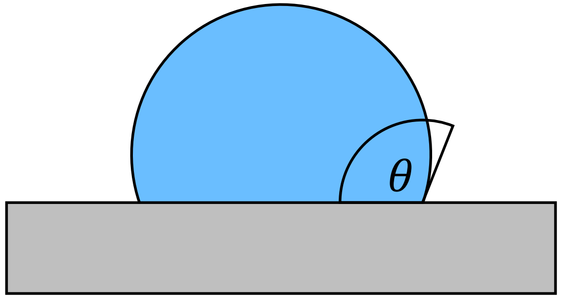
$$\mathrm{R-OH} \overset{K}{\leftrightarrow} \mathrm{R-O^-} + \mathrm{H^+}$$

- Diffuse layer structure and chemical reaction on surface are coupled through concentrations and electric fields
- Equilibrium surface charge depends on diffuse layer and chemistry, well defined for flat surfaces

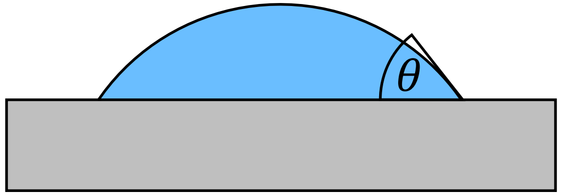
→What determines electric double layer structure at receding contact line?

BACKGROUND: WETTING AND CONTACT ANGLES

Hydrophobic contact angle

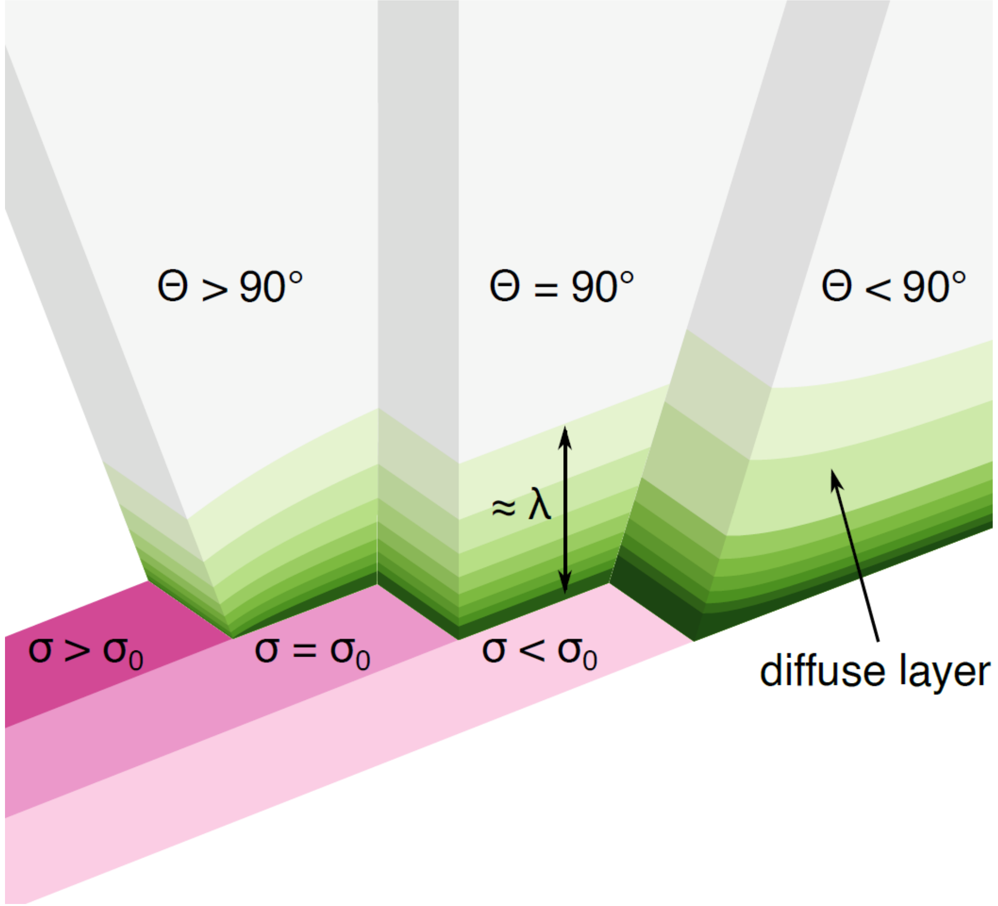


Hydrophilic contact angle



- The contact angle is the angle that forms between a solid surface and that of a drop or puddle at the solid-liquid-gas three-phase contact line
- It depends only on the materials and not on the shape of the liquid drop or puddle
- Surfaces with contact angles >90° are called hydrophobic and <90° hydrophilic
- Movement of the contact line in the direction of the solid is called wetting and in the direction of the liquid is called dewetting
- High wetting velocities increase and dewetting velocities decrease the local contact angle

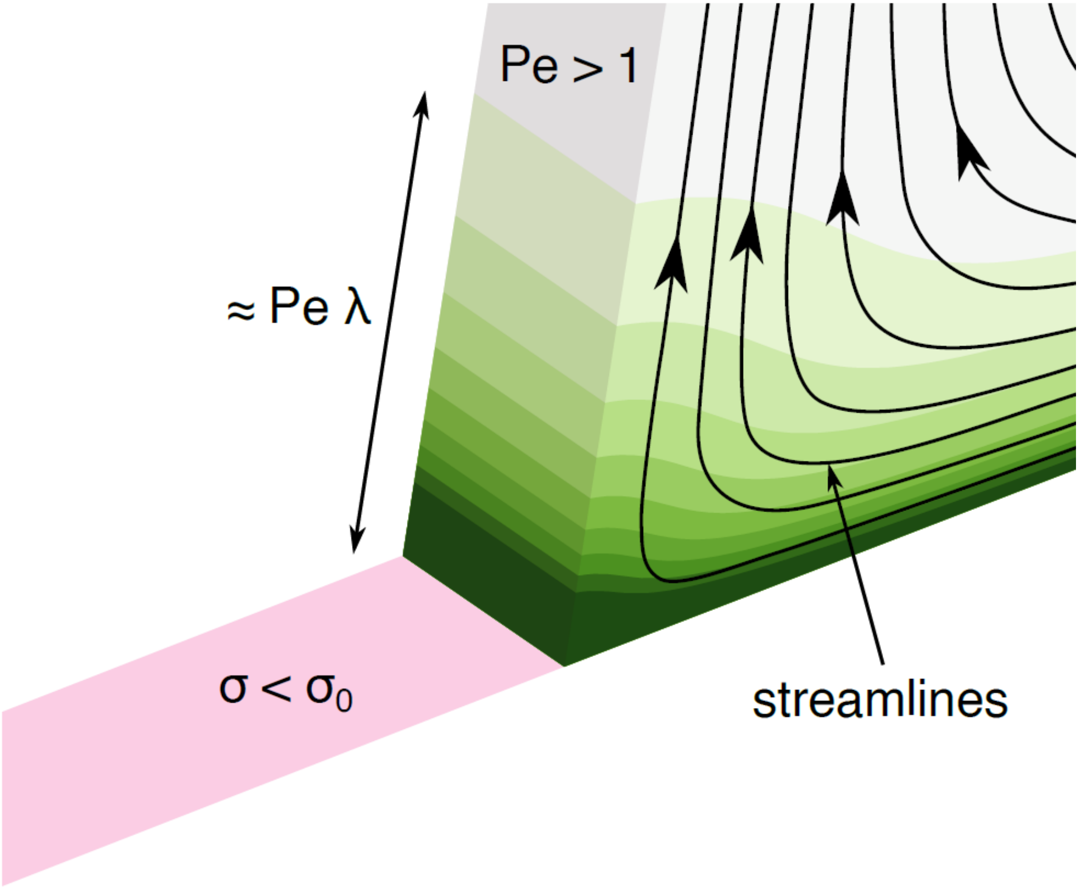
INFLUENCE OF THE CONTACT ANGLE



- Close to the contact line, EDL structure is warped by the liquid-gas interface
- Bound surface charge (pink) increases with the contact angle
- Linearized analytical expression for the effect found by Dörr & Hardt (Phys. Rev. E, 2012)

$$\frac{\sigma_0}{\sigma} = g(\theta) = \frac{2\pi}{\theta}$$

INFLUENCE OF LIQUID FLOW



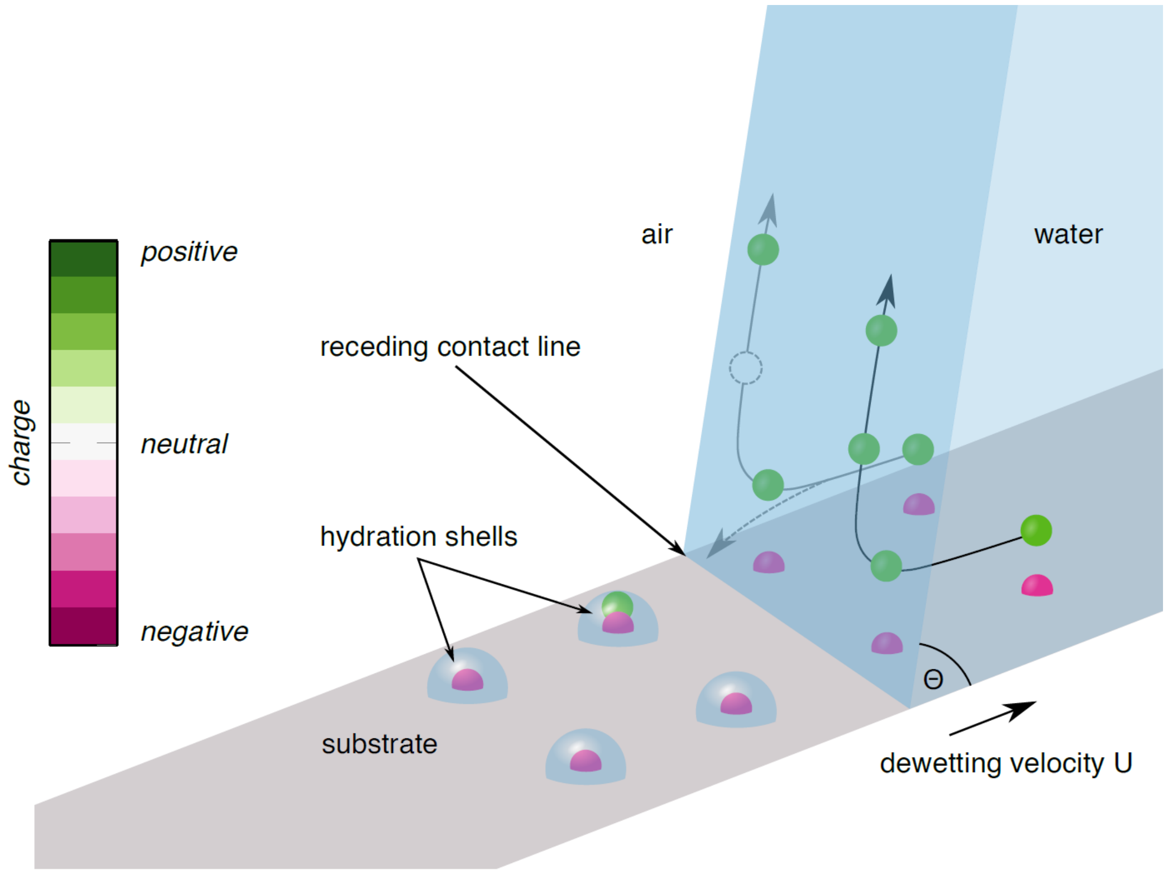
- Substantial wall-normal flow along the liquid-gas interface near the contact line
- Influence of flow is measured by Péclet number

$$Pe = \frac{U\lambda}{D}$$

- Advective transport expands the Debye length to

$$\lambda_{\mathrm{eff}} = \frac{2}{\sqrt{Pe^2 + 4} - Pe}\lambda$$

ANALYTICAL MODEL FOR SURFACE CHARGE



Full analytical model for surface charge at receding contact line

$$\frac{\phi_{CL}(Pe)}{\phi_T} = \frac{1}{2}(K+1) - \sqrt{\frac{1}{4}(K+1)^2 + KC\lambda_{\text{eff}}/\lambda}$$

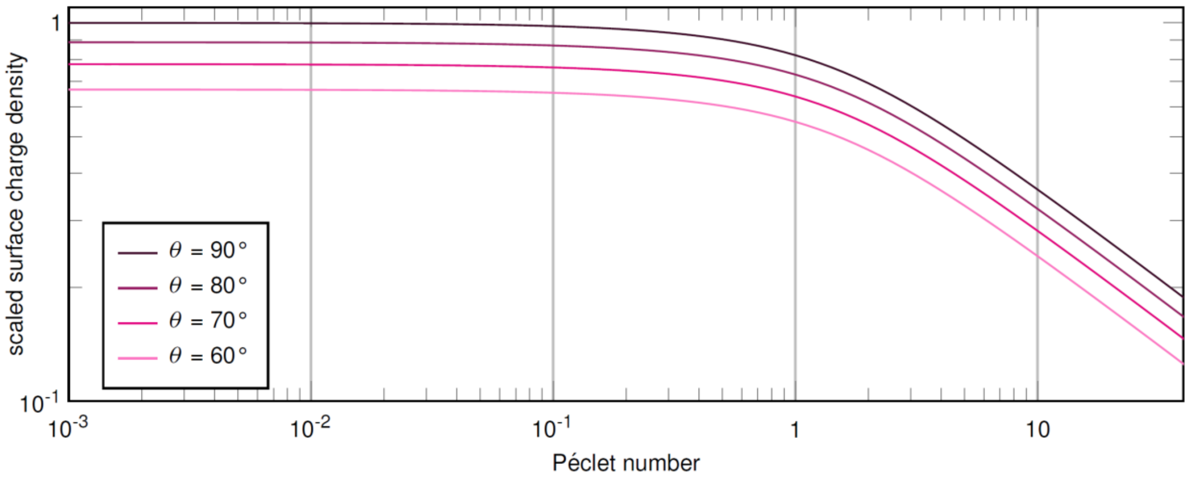
$$\sigma_{CL}(\theta, Pe) = \frac{\varepsilon\phi_{CL}}{\lambda_{eff}\, g(\theta)}$$

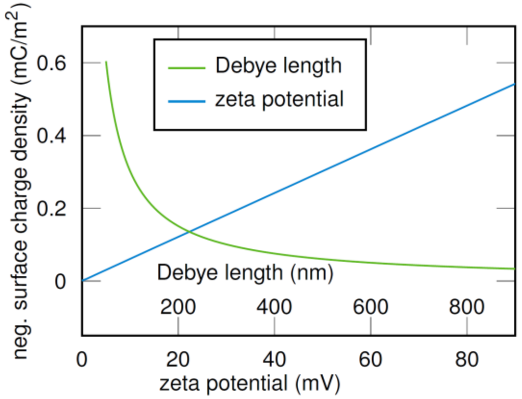
Effects on the atomistic scale

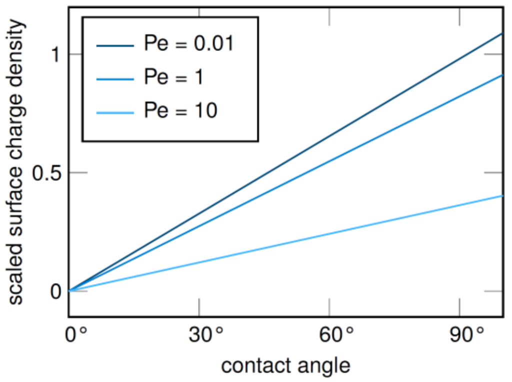
- Dewetted surface charges have hydration shells, some of which carry a counterion
- Net surface charge is thus reduced by factor $\omega = O(0.1 - 1)$ independent of θ, Pe

→ **Model should correctly predict trends**

THEORETICAL PREDICTIONS FOR SURFACE CHARGE DENSITY

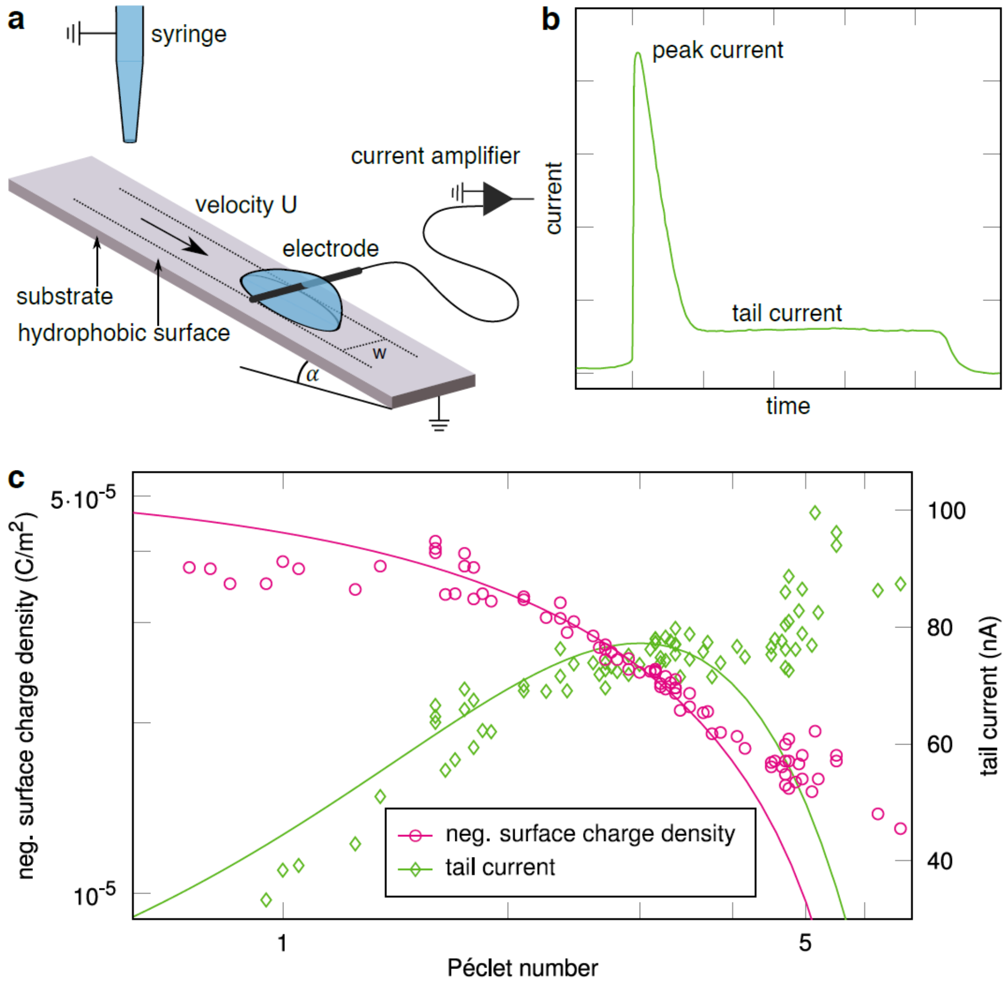






- Two regimes in Pe, high velocities surprisingly reduce charge separation, caused by increased effective Debye length
- Charge separation is strongest on hydrophobic surfaces with high contact angles
- Higher charges on surfaces with higher zeta potential

EXPERIMENTAL VALIDATION



- Validation with sliding drop experiments
- Charge separation during electrode contact measured by tail current
- Analytical calculations use ‚Cox-Voinov model' for dynamic contact angle → loses validity around $Pe = 4$

→ **Model prediction of decreasing charge separation with increasing velocity clearly reflected in experiment**

IMPLICATIONS

- Charge separation even for grounded liquids[1]
- Ungrounded puddles or reservoirs can acquire kilovolt potentials and lead to discharge[2]
- **Universal phenomenon** for dewetting with conductive liquids[1,3]
- Charge separation leads to substantial contact angle hysteresis[3]
- Special relevance for liquids of **medium conductivity**

Condensation processes	Cleaning and rinsing	Draining of equipment

Dewetting **faster is safer**, for Péclet numbers larger than one. Rule of thumb:

$$Pe = \frac{\tilde{U}}{10} * \sqrt{\frac{\varepsilon_r}{\tilde{k}}}$$

$\tilde{U}$: dewetting velocity in m/s, ε_r: dielectric constant of liquid, $\tilde{k}$: liquid conductivity in S/m

UNDERLYING RESEARCH

1. **A. D. Ratschow**, L. S. Bauer, P. Bista, S. A. L. Weber, H.-J. Butt, S. Hardt, *How charges separate when surfaces are dewetted*, 2023, arXiv, https://doi.org/10.48550/arXiv.2305.02172

2. P. Bista*, **A. D. Ratschow***, H.-J. Butt, S. A. L. Weber, *High Voltages in Sliding Water Drops,* 2023, Journal of Physical Chemistry Letters, https://doi.org/10.1021/acs.jpclett.3c02864

3. X. Li*, **A. D. Ratschow***, S. Hardt, H.-J. Butt, *Surface Charge Deposition by Moving Drops Reduces Contact Angles,* 2023, Physical Review Letters, https://doi.org/10.1103/PhysRevLett.131.228201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Wetting Processes

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Any Questions?

THANK YOU FOR YOUR ATTENTION

APPENDIX:
RULE OF THUMB DERIVATION

Péclet number definition

$$Pe = \frac{U\lambda}{D}$$

Debye length as a function of conductivity k

$$\lambda = \sqrt{\frac{\varepsilon_0 \varepsilon_r D}{k}}$$

Putting it together

$$Pe = \sqrt{\frac{U^2 \varepsilon_0 \varepsilon_r D}{D^2 k}} = U \sqrt{\frac{\varepsilon_r}{k}} \sqrt{\frac{\varepsilon_0}{D}} = \tilde{U} * \sqrt{\frac{\varepsilon_r}{\tilde{k}}} * 0.0941 \approx \frac{\tilde{U}}{10} * \sqrt{\frac{\varepsilon_r}{\tilde{k}}}$$

Here, we used the fact that $D \approx 10^{-9}\mathrm{m}^2/s$ for nearly all electrolytes. $\tilde{U}$ and $\tilde{k}$ are the dewetting velocity and the liquid conductivity in SI units, m/s and S/m respectively.

APPENDIX:
FULL ANALYTICAL MODEL FOR CHARGE SEPARATION

Details in our paper: https://arxiv.org/pdf/2305.02172.pdf

$$\frac{\phi_{\mathrm{CL}}(Pe)}{\phi_{\mathrm{T}}} = \frac{1}{2}(K+1) - \sqrt{\frac{1}{4}(K+1)^2 + KC\lambda_{\mathrm{eff}}/\lambda}$$

$$\sigma_{\mathrm{CL}}(\theta, Pe) = \frac{\varepsilon\phi_{\mathrm{CL}}}{\lambda_{\mathrm{eff}}\, g(\theta)}$$

with

$$K = (\zeta/\phi_{\mathrm{T}} - 1)/(C\phi_{\mathrm{T}}/\zeta + 1)$$

$$C = e\Gamma\lambda/(\varepsilon\phi_{\mathrm{T}})$$

$$Pe = U\lambda/D$$

$$g(\theta) = \pi/(2\theta)$$

$$\lambda_{\mathrm{eff}} = \frac{2}{\sqrt{Pe^2+4} - Pe}\lambda$$

APPENDIX: FULL VARIABLE LIST

Symbol	Variable
σ_{CL}	Dewetted surface charge density on the solid surface
ϕ_{CL}	Surface potential at contact line
ϕ_T	Thermal potential, usually 25 mV at ambient conditions
λ	Debye length
ε	Dielectric permittivity of the liquid
ζ	Native zeta potential of the liquid/solid pair
e	Elementary charge
Γ	Active site density of the surface, usually 5/nm² *
U	Dewetting velocity
D	Ion diffusivity, usually $\approx 10^{-9}\mathrm{m}^2/s$
θ	Contact angle

**results are insensitive to this parameter, even when it is off by one or two orders of magnitude.*

APPENDIX: ADDITIONAL READING

Practical handbook on electrostatics:

Static Electricity, Understanding, Controlling, Applying,
Lüttgens, Günter / Lüttgens, Sylvia / Schubert, Wolfgang

https://www.wiley-vch.de/de/fachgebiete/ingenieurwesen/static-electricity-978-3-527-34128-3

Experimental work on the charging of high-pressure water jets:

Elektrostatische Aufladung beim Versprühen von Wasser – Untersuchung praxisrelevanter Prozesse bei der Reinigung kleiner und mittelgroßer Behälter.
Baumann, F., M. Himstedt, D. Möckel, M. Thedens und M. Beyer, 2022.

https://oar.ptb.de/resources/show/10.7795/110.20220629