GEOMETRIC IONIC DIODE: THE ROLE OF CONFINEMENT

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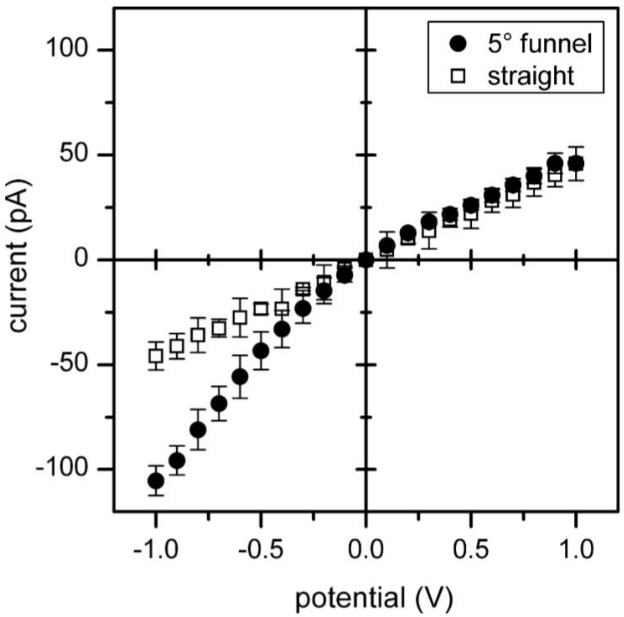
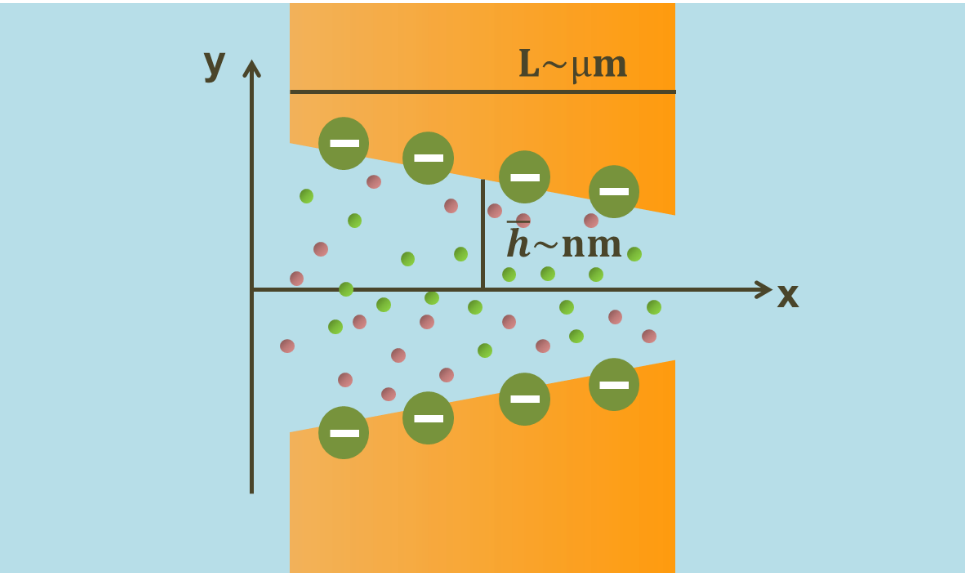
Liquids @ Interfaces – October 2018

IONIC CURRENT RECTIFICATION

Nonlinear current response under voltage reversal

[J. Perry *et Al.* ACSNANO (2010)]





PREFERENTIAL DIRECTION OF MOTION IN THE ABSENCE OF NET FORCING

IONIC CURRENT RECTIFICATION

Nonlinear current response under voltage reversal

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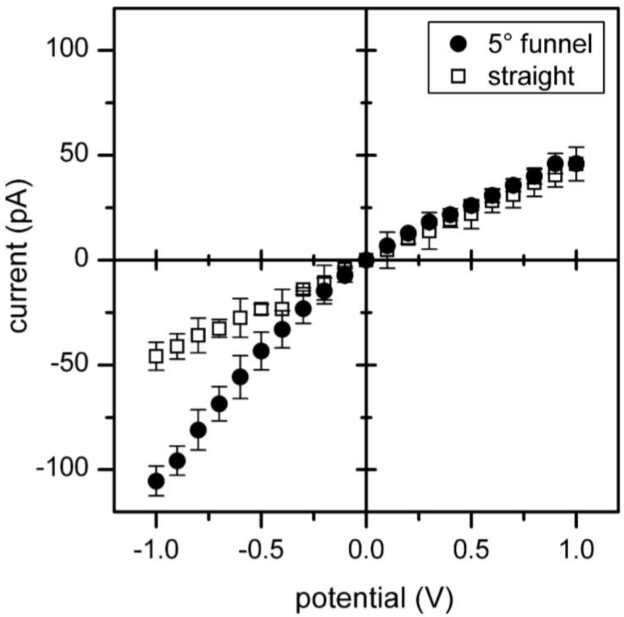
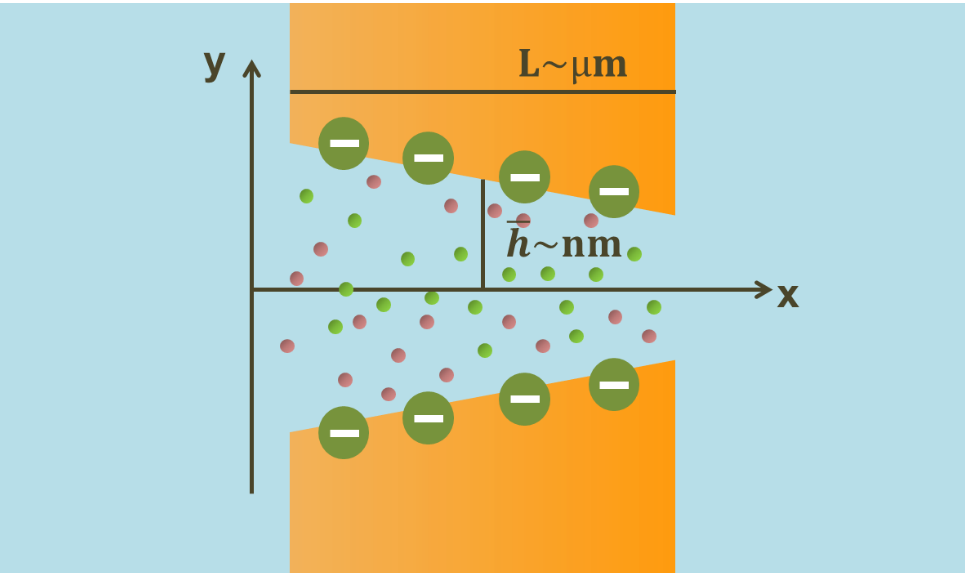
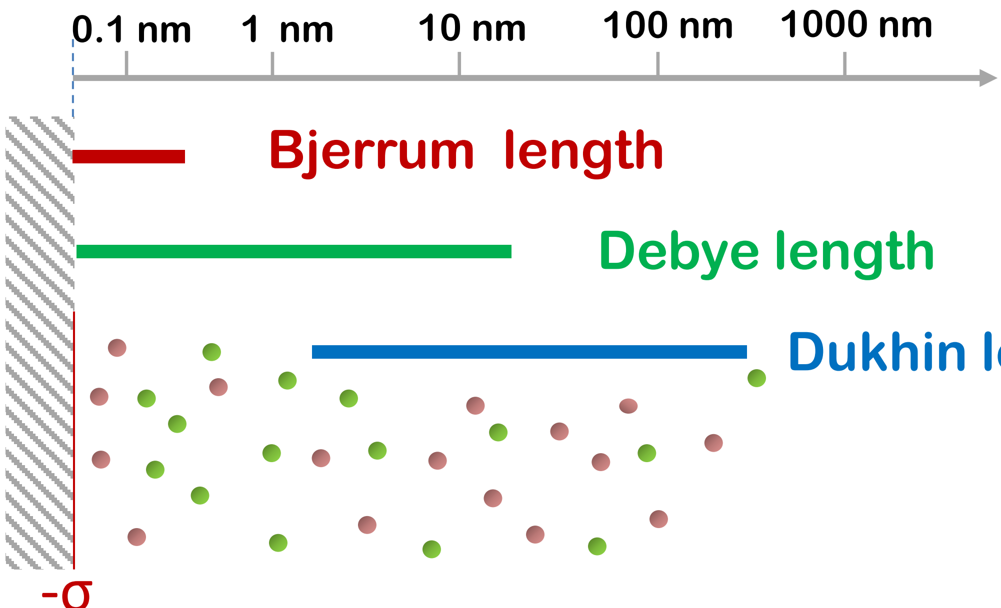




Building blocks:
- **Symmetry breaking**
- **Surface interactions**

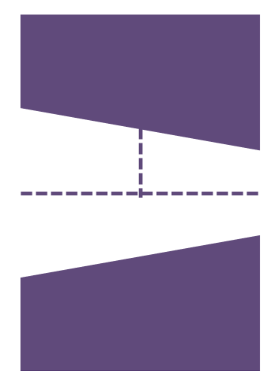
IMPORTANT LENGTHS INTO PLAY

Electrostatic lengths…



Dukhin length $\lambda_{Du} = \dfrac{\sigma}{e\, c_{bulk}}$

…vs geometric lengths



Partial Debye overlap $\dfrac{\lambda_D}{\bar{h}} \sim 1$

Quasi 1D system $\bar{h} \ll L$

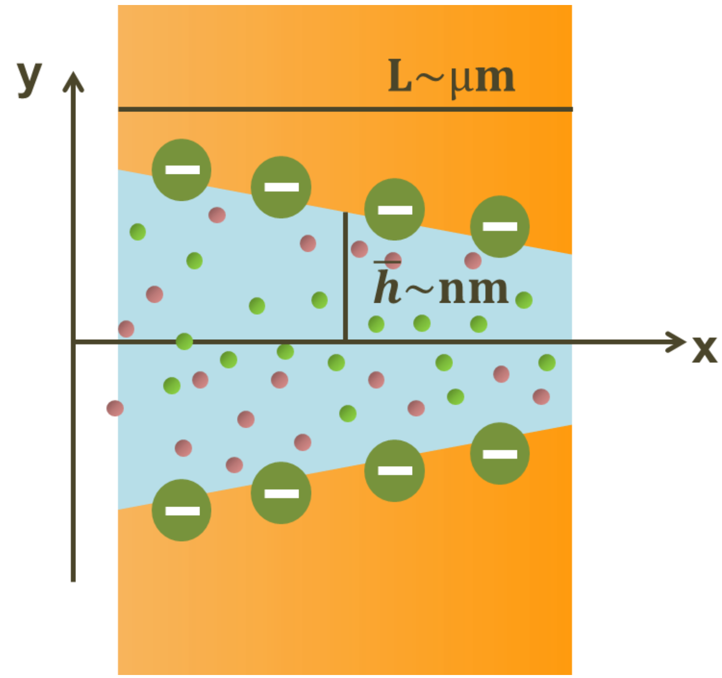
FICK-JACOBS APPROACH

[M. H. Jacobs (1967) , R. Zwanzig (1992)]

Nernst-Planck equation:

$$\partial_t c_\pm + \nabla \cdot \vec{j} = 0$$

$$\vec{j} = \mp c_\pm(x,y,t)\nabla V(x,y) - \nabla c_\pm(x,y,t)$$



Assuming separation of scales:

$$d_x h(x) = \epsilon \ll 1 \quad \Leftrightarrow \quad j_y \ll j_x$$

Channel profile:

$$h(x) = \bar{h} + \epsilon\frac{L}{2} - \epsilon\, x$$

Perturbative expansion in the geometrical parameter ϵ

[S. Martens *et al* PRE (2011)]

FICK-JACOBS APPROACH

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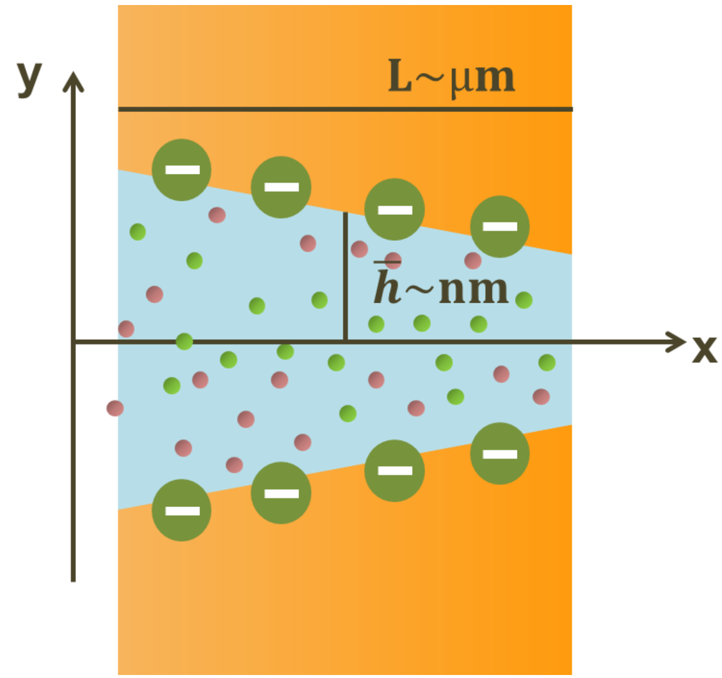


Integrating in the transverse direction:

Marginal concentration: $c_\pm(x) = \int_{-h(x)}^{h(x)} c_\pm(x,y)dy$

Ansatz: $c_\pm(x,y) = \frac{e^{\mp V(x,y)}}{e^{-\beta A_\pm(x)}} c_\pm(x)$

conditional density

Effective free energy:

$$e^{-\beta A_\pm(x)} = \int_{-h(x)}^{h(x)} e^{\mp V(x,y)}\, dy$$

GOVERNING EQUATIONS

Fick-Jacobs equation: $-J_{\pm} = c_{\pm}(x)\frac{d}{dx}\beta A_{\pm}(x) + \frac{d}{dx}c_{\pm}(x)$

Poisson equation: $\partial_y{}^2 V = -\frac{q(x,y)}{\varepsilon}$

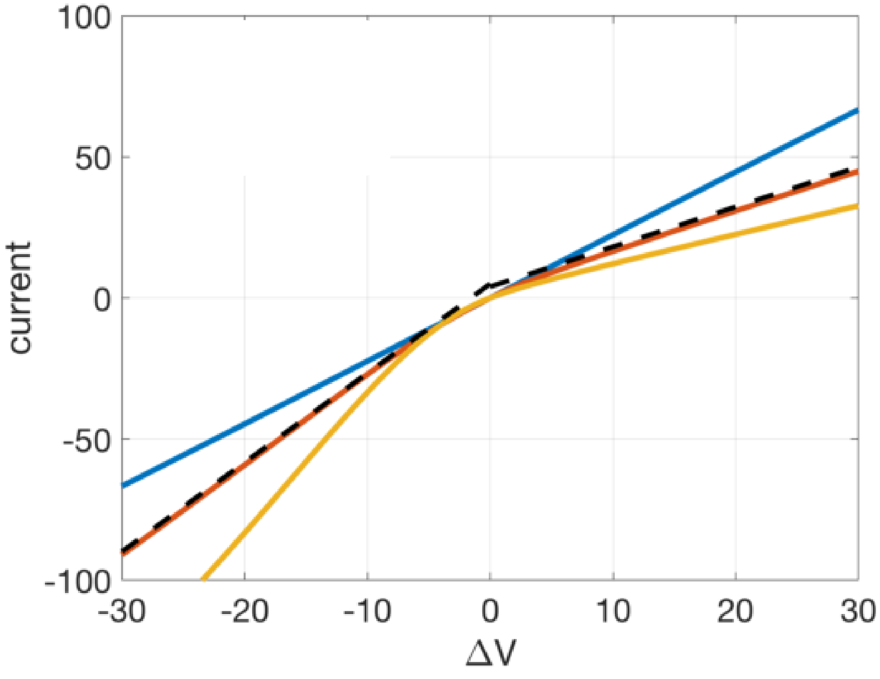
Solving for:

- Small potential variation $\delta V \ll 1$
- Continuity in the chemical potential at the boundaries

$$\mu_{\pm}(x) = \log c_{\pm}(x) + \beta A_{\pm}(x)$$

IONIC CURRENT RECTIFICATION

IV characteristics



- Rectification increasing with the channel corrugation
- Saturation to **limiting conductances** for high field

IN THE LIMIT OF STRONG OVERLAP

In equilibrium:

Non-uniform Donnan potential:

$$V(x) = \frac{1}{2}\log\left[\frac{-Du + \sqrt{Du^2 + h(x)^2}}{+Du + \sqrt{Du^2 + h(x)^2}}\right]$$

Out of equilibrium:

$$\begin{cases} J_{mass} = -\partial_x c_{tot}(x) \cancel{+ c_{tot}(x)\partial_x \log 2h(x)} - 2\,Du\,\partial_x V(x) \\ I_e = -c_{tot}(x)\partial_x V(x) + 2\,Du\,\partial_x \log 2h(x) \end{cases}$$

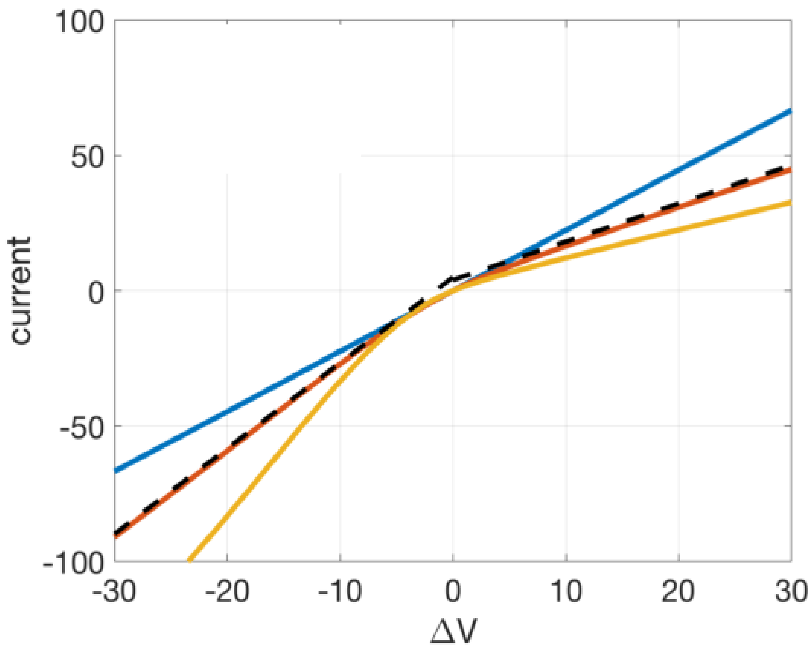
Limit $\Delta V \to \infty$ Neglecting the diffusive contribution to mass flux

$$\boxed{G_{\pm\infty} = \lim_{\Delta V \to \pm\infty} c_{tot}}$$

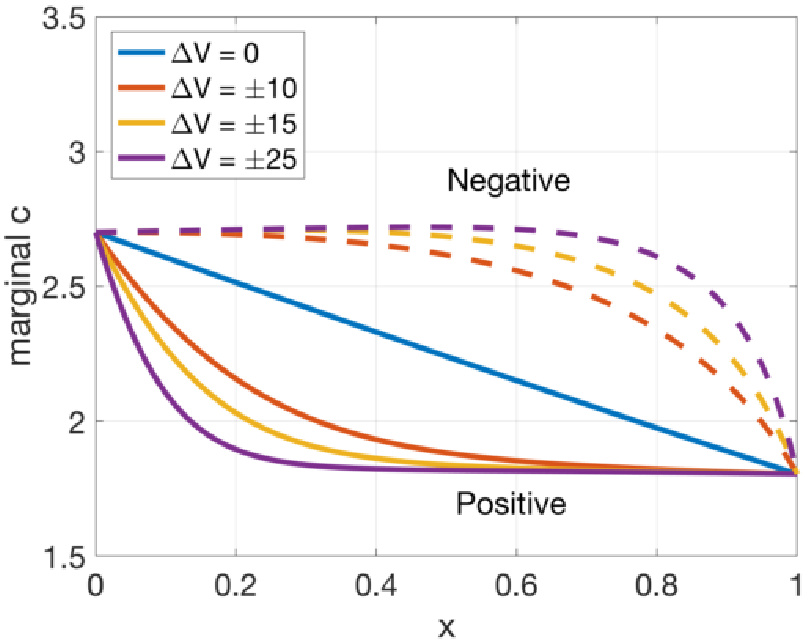
SATURATION OF THE MARGINAL CONCENTRATION

IONIC CURRENT RECTIFICATION

IV characteristics

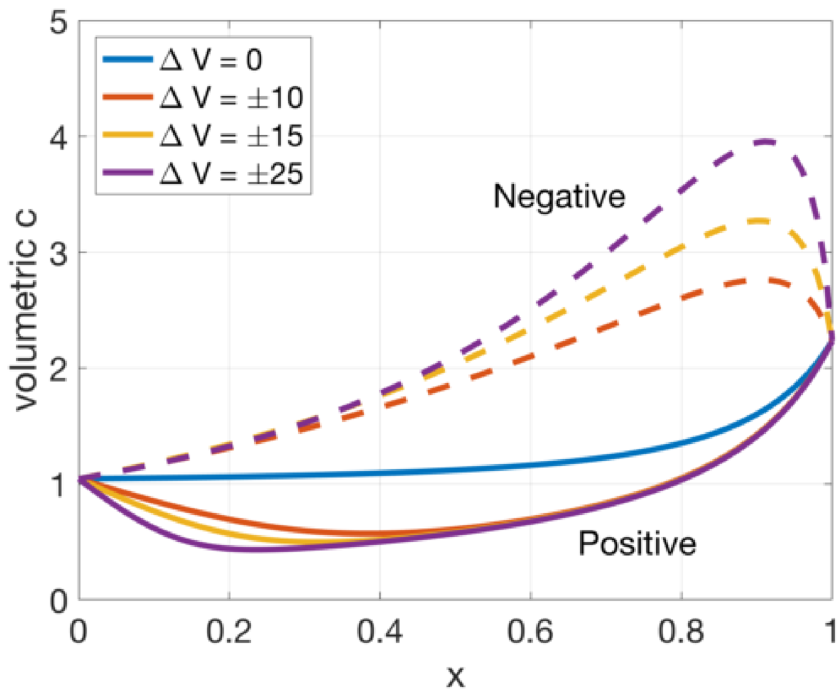


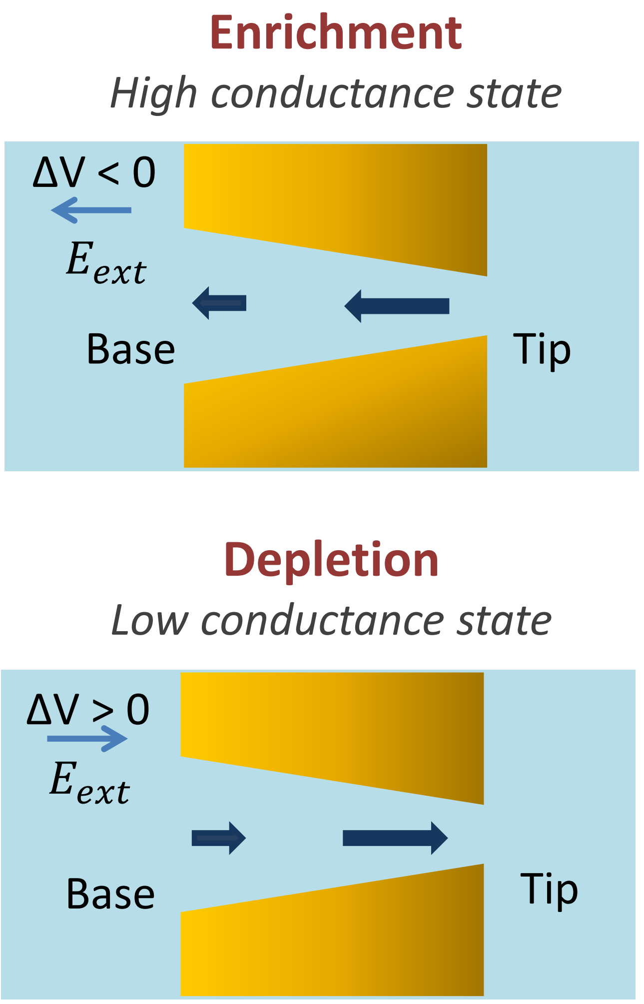
Saturation of the marginal concentration



Analytical prediction for limiting conductances in the limit of strong overlap

ENRICHMENT-DEPLETION

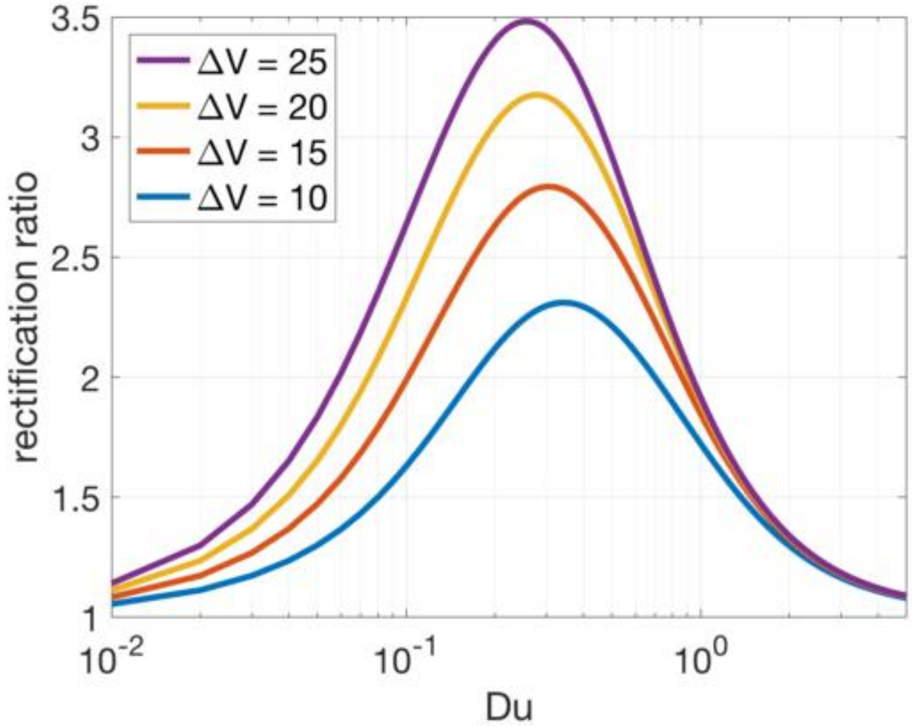




Asymmetric selectivities between tip and base

[Woermann Phys. Chem. Chem. Phys (2003)]

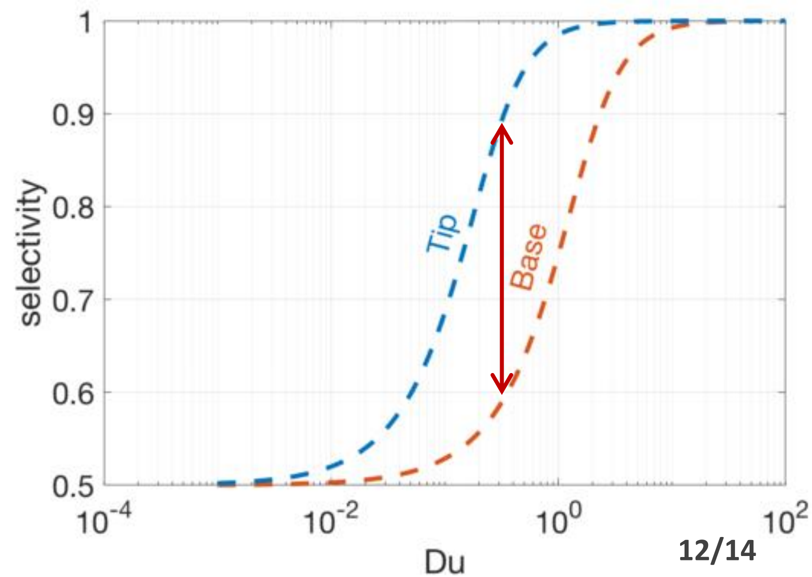
THE IMPORTANCE OF DUKHIN NUMBER



Maximum of rectification for $Du \sim 1$

Dukhin controls the asymmetry in selectivity

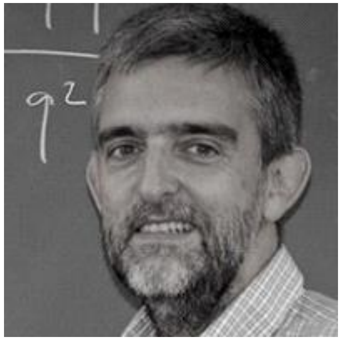
selectivity: $\frac{c_+}{c_+ + c_-}$



CONCLUSION AND PERSPECTIVES

- A general framework capturing rectification property
- Consistent with the enrichment/depletion mechanism
- Rectification controlled by the Dukhin length rather than the Debye length
- Competition between bulk and surface… more to explore!

ACKNOWLEDGEMENT



Ignacio Pagonabarraga

Anthony Poggioli

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NANOTRANS
Transport of Soft Matter at the Nanoscale

MARIE CURIE ACTIONS

GOVERNING EQUATIONS

$$\begin{cases} c_\pm(x) = \frac{1}{2} e^{\pm\frac{\Delta V}{2} - \beta A_\pm(x)} - J_\pm e^{-\beta A_\pm(x)} \int\limits_0^x dx'\, e^{+\beta A_\pm(x')} \\ V(x,y) = -\frac{Du(x)}{\lambda_D(x)} \frac{\cosh\left(\frac{y}{\lambda_D(x)}\right)}{\sinh\left(\frac{h(x)}{\lambda_D(x)}\right)} + \frac{[c_+(x) - c_-(x)]}{[c_+(x) + c_-(x)]} + \langle V \rangle(x) \end{cases}$$

Debye-Hückel like potential

Local electroneutrality

Cross-section averaged potential

Local Debye length:

$$\lambda_D(x) = \frac{\lambda_D}{\sqrt{c_+(x) + c_-(x)}}$$

Local Dukhin number:

$$Du(x) = \frac{Du}{c_+(x) + c_-(x)}$$

Numerical solution of coupled integral equations