Weierstrass Institute for
Applied Analysis and Stochastics

Leibniz Association

The Lippmann equation for liquid metal electrodes

Wolfgang Dreyer, Clemens Guhlke, Manuel Landstorfer, **Rüdiger Müller**

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Lippman's equation

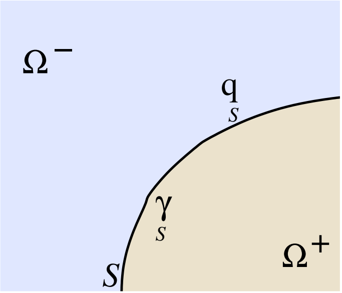
An equation which gives the electric charge per unit area of an interface (electrode):

$$\left(\frac{\partial \gamma}{\partial E_{\mathrm{A}}}\right)_{T,p,\mu_i \neq \mu} = -Q_{\mathrm{A}}$$

where γ is the interfacial tension, E_{A} is the potential of a cell in which the reference electrode has an interfacial equilibrium with one of the ionic components of A, Q_{A} is the charge on unit area of the interface, μ_i is the chemical potential of the combination of species i whose net charge is zero, T is the thermodynamic temperature and p is the external pressure. Since more than one type of reference electrode may be chosen, more than one quantity Q may be obtained. Consequently Q cannot be considered as equivalent to the physical charge on a particular region of the interphase. It is in fact an alternative way of expressing a surface excess or combination of surface excess of charged species.

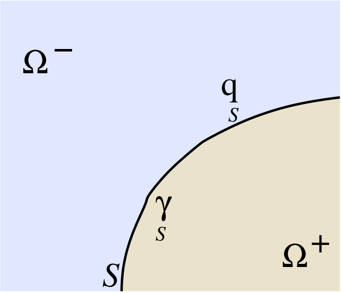
Source:

PAC, 1974, *37*, 499 *(Electrochemical nomenclature)* on page 508
PAC, 1986, *58*, 437 *(Interphases in systems of conducting phases (Recommendations 1985))* on page 445



Lippmann

$$\frac{d\gamma}{dE} = -Q$$



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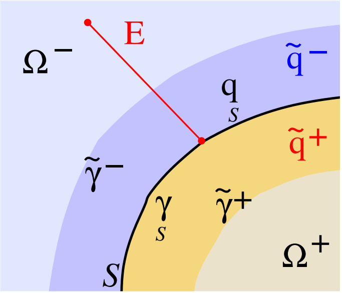
E well defined ?

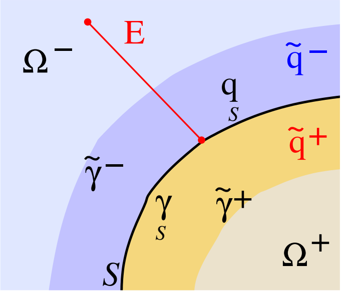


Lippmann

$$\frac{d\gamma}{dE} = -Q$$

E well defined ?

$$Q = Q(\underset{s}{q}, \widetilde{q}^+, \widetilde{q}^-)$$
$$\gamma = \gamma(\underset{s}{\gamma}, \widetilde{\gamma}^+, \widetilde{\gamma}^-)$$



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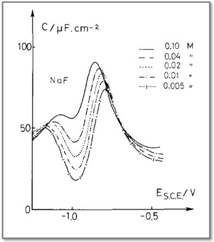


differential capacity

$$C := \frac{dQ}{dE} = -\frac{d^2\gamma}{dE^2}$$

1 Ion transport in electrolyte bulk

- Shortcomings of Nernst-Planck model
- General continuum model for the bulk

2 Electrochemical double layer

- Surface balances and adsorption
- Free energy models for metals
- Double-layer capacity

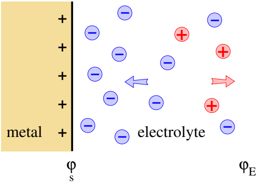
3 Lippmann equation for liquid mercury electrode

- Matched asymptotic analysis
- Numerical results

diluted solution of anions A, cations C in solvet S

$$\partial_t(m_\alpha n_\alpha) + \operatorname{div}(m_\alpha n_\alpha v + J_\alpha) = 0 \quad \text{for } \alpha = A, C$$

$$-\varepsilon\Delta\varphi = z_A n_A + z_C n_C$$



Nernst-Plack (1890):

$$J_\alpha = -M(\nabla n_\alpha + z_\alpha n_\alpha \nabla\varphi) \quad \text{for } \alpha = A, C$$

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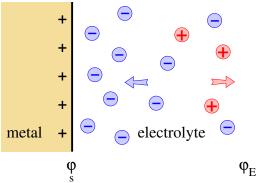

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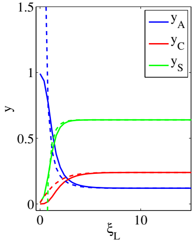
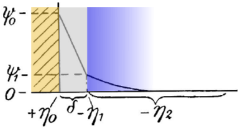
equilibrium → Poisson-Boltzmann

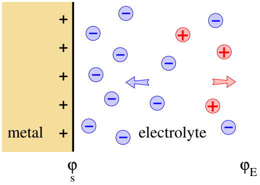
$$0 = \nabla n_\alpha + z_\alpha n_\alpha \nabla\varphi \quad \text{for } \alpha = A, C$$

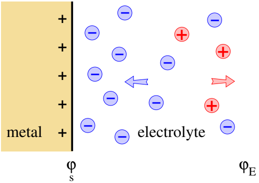
$$-\varepsilon\Delta\varphi = z_A \bar{n}_A \exp(-z_A\varphi) + z_C \bar{n}_C \exp(-z_C\varphi)$$



- postulated layer structure
  [Stern:1924]







- postulated layer structure
  [Stern:1924]
- finite size of ions, volume exclusion
  [Bikerman:1942], [Eigen,Wicke:1952], [Carnahan,Starling:1969], [Borukhov,Andelman,Orlando:1997], [Ajdari,Bazant,Kilic:2007]
  ... molecular dynamics, statistical mechanics,
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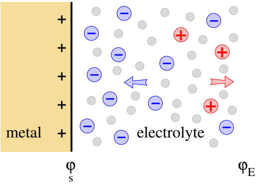
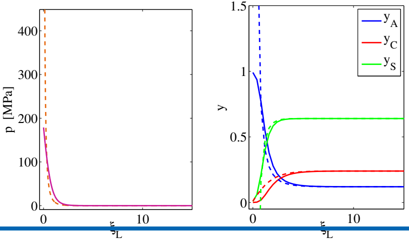


- layers not diluted
- pressure dependence, momentum balance
- [Freise:1952], [Sanfeld:1968], [DGM13]



non-equilibrium thermodynamics distinguishes

- general balance laws
- material dependent constitutive equations

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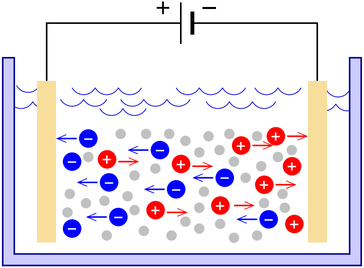
constitutive equations restricted by

- 2nd law of thermodynamics (cf. [Bothe,Dreyer:2014])
- principle of material frame indifference



constituents: $A_0, A_1, \cdots, A_N$

atomic mass: $m_0, m_1, \cdots, m_N$

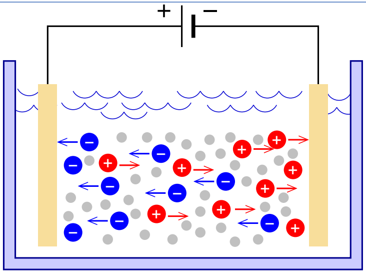
charge number: $z_0, z_1, \cdots, z_N$

fields of matter

$\rho_0, \cdots, \rho_N$	mass density
$\rho\boldsymbol{v}$	momentum
ρu	internal energy

electromagnetic fields

$\boldsymbol{E}$	electric field
$\boldsymbol{B}$	magnetic field



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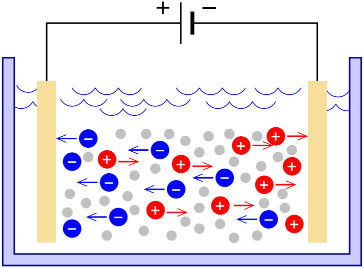

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partial mass balances $\quad \partial_t \rho_\alpha + \operatorname{div}(\rho_\alpha \boldsymbol{v} + \boldsymbol{J}_\alpha) = 0 \quad$ for $\alpha = 0, 1, \cdots, N$

quasi-static momentum $\quad -\operatorname{div}(\boldsymbol{\Sigma}) = \rho\boldsymbol{b}$

electrostatic Poisson eqn. $\quad -\varepsilon_0(1+\chi)\Delta\varphi = n^{\mathrm{F}}$

$$
\begin{aligned}
\xi = \frac{1}{T}\Bigg[& t^{ij} + \tfrac{1}{2}(\mathcal{M}^i B^j + \mathcal{M}^j B^i) - \tfrac{1}{2}(\mathcal{E}^i P^j + \mathcal{E}^j P^i) + \frac{T}{2}\left(\frac{\partial h}{\partial F^{\mathrm{uni}}_{ik}} F^{\mathrm{uni}}_{jk} + \frac{\partial h}{\partial F^{\mathrm{uni}}_{jk}} F^{\mathrm{uni}}_{ik}\right) \\
& - \left(\rho u - Th - \sum_{\alpha=1}^{N} \rho_\alpha \mu_\alpha + \frac{T}{3}\frac{\partial h}{\partial F^{\mathrm{uni}}_{kl}} F^{\mathrm{uni}}_{kl} - \mathcal{E}^k P^k + \mathcal{M}^k B^k\right)\delta^{ij}\Bigg] \frac{1}{2}\left(\frac{\partial v^i}{\partial x^j} + \frac{\partial v^j}{\partial x^i}\right) \\
& + (q^i + (\boldsymbol{\mathcal{E}} \times \boldsymbol{\mathcal{M}})^i)\frac{\partial}{\partial x^i}\left(\frac{1}{T}\right) \\
& - \sum_{\alpha=1}^{N-1} J^i_\alpha \left(\frac{\partial}{\partial x^i}\left(\frac{\mu_\alpha}{T} - \frac{\mu_N}{T}\right) - \frac{1}{T}\left(\frac{z_\alpha e_0}{m_\alpha} - \frac{z_N e_0}{m_N}\right)\mathcal{E}^i\right) \\
& - \frac{1}{T}\sum_{a=1}^{M}\left(\sum_{\beta=1}^{N} \gamma^a_\beta m_\beta \mu_\beta\right) R^a \\
& + \left(\frac{\partial h}{\partial P^i} + \frac{1}{T}\mathcal{E}^i\right)\left(\dot{P}^i - \frac{1}{2}P^j\left(\frac{\partial v^i}{\partial x^j} - \frac{\partial v^j}{\partial x^i}\right)\right) \\
& + \left(\frac{\partial h}{\partial \mathcal{M}^j} + \frac{1}{T}B^j\right)\left(\dot{\mathcal{M}}^j + \frac{1}{2}\mathcal{M}^i\left(\frac{\partial v^i}{\partial x^j} - \frac{\partial v^j}{\partial x^i}\right)\right) .
\end{aligned}
$$

$$
\begin{aligned}
\underset{s}{\xi} = & \left(\underset{s}{\phi}{}^\Delta_\tau - \frac{1}{\underset{s}{T}}\underset{s}{q}{}^\Delta_\tau + \frac{1}{\underset{s}{T}}\sum_{\alpha=1}^{N_s} \underset{s}{J}{}^\Delta_{\tau,\alpha}\underset{s}{\mu_\alpha}\right)_{\|\Delta} \\
& + \frac{1}{\underset{s}{T}}\left(S^{\Gamma\Delta} + \underset{s}{T}\frac{\partial \underset{s}{h}}{\partial \tau^{\mathrm{uni},i}_\Delta}\tau^{\mathrm{uni},i}_\Sigma g^{\Sigma\Gamma} - \left(\underset{s}{\rho}\underset{s}{u} - \underset{s}{T}\underset{s}{h} - \sum_{\alpha=1}^{N_s}\underset{s}{\mu_\alpha}\underset{s}{\rho_\alpha} + \tfrac{1}{2}\underset{s}{T}\frac{\partial \underset{s}{h}}{\partial \tau^{\mathrm{uni},i}_\Sigma}\tau^{\mathrm{uni},i}_\Sigma\right) g^{\Delta\Gamma}\right) \\
& \qquad \cdot \left(\tfrac{1}{2}\left(g_{\Gamma\Lambda}\underset{s}{v}{}^\Lambda_{\tau\|\Delta} + g_{\Delta\Lambda}\underset{s}{v}{}^\Lambda_{\tau\|\Gamma}\right) - b_{\Gamma\Delta}\underset{s}{v}_\nu\right) \\
& - \sum_{\alpha=1}^{N_s-1}\underset{s}{J}{}^\Delta_{\tau,\alpha}\left(\left(\frac{\underset{s}{\mu_\alpha}}{\underset{s}{T}} - \frac{\underset{s}{\mu_{N_s}}}{\underset{s}{T}}\right)_{\|\Delta} - \frac{1}{\underset{s}{T}}\left(\frac{z_\alpha e_0}{m_\alpha} - \frac{z_{N_s} e_0}{m_{N_s}}\right) g_{\Delta\Gamma}\left(\bar{\boldsymbol{E}} + \underset{s}{\boldsymbol{v}} \times \bar{\boldsymbol{B}}\right)^\Gamma_\tau\right) \\
& + \underset{s}{q}{}^\Delta_\tau\left(\frac{1}{\underset{s}{T}}\right)_{\|\Delta} - \frac{1}{\underset{s}{T}}\sum_{a=1}^{M_s}\left(\sum_{\beta=1}^{N_s}\underset{s}{\gamma}{}^a_\beta m_\beta \underset{s}{\mu_\beta}\right)\underset{s}{R}{}^a \\
& + \left[\!\left[\left(q_\nu + (\boldsymbol{\mathcal{E}} \times \boldsymbol{\mathcal{M}})_\nu + \left(T\rho\eta + \sum_{\alpha=1}^{N}\mu_\alpha\rho_\alpha\right)(v_\nu - \underset{s}{v}_\nu)\right)\left(\frac{1}{T} - \frac{1}{\underset{s}{T}}\right)\right]\!\right] \\
& + \frac{1}{\underset{s}{T}}\left[\!\left[\left(t^{ij} - \mathcal{E}^i P^j + \mathcal{M}^i B^j - \left(\rho u - T\rho\eta - \sum_{\alpha=1}^{N}\mu_\alpha\rho_\alpha - \mathcal{E}^k P^k + \mathcal{M}^k B^k\right)\delta^{ij}\right.\right.\right. \\
& \qquad \left.\left.\left. + (\boldsymbol{P} \times \boldsymbol{B})^i(v^j - \underset{s}{v}{}^j) - \left(\tfrac{1}{2}\rho(\underset{s}{\boldsymbol{v}} - \boldsymbol{v})^2 + \underset{s}{T}\rho\left(\frac{\mu_N}{T} - \frac{\underset{s}{\mu_N}}{\underset{s}{T}}\right)\right)\delta^{ij}\right)\nu_j(v^i - \underset{s}{v}{}^i)\right]\!\right] \\
& - \left[\!\left[\sum_{\alpha=1}^{N-1}\left(J_{\nu,\alpha} + \rho_\alpha(v_\nu - \underset{s}{v}_\nu)\right)\left(\frac{1}{T}(\mu_\alpha - \mu_N) - \frac{1}{\underset{s}{T}}(\underset{s}{\mu_\alpha} - \underset{s}{\mu_N})\right)\right]\!\right] \qquad (5.79)
\end{aligned}
$$

[Guhlke:2015]

free energy $\widehat{\rho\psi} = \rho\psi(T, \rho_0, \rho_1, \cdots, \rho_N,) + \chi|\boldsymbol{E}|^2$

$$\mu_\alpha = \frac{\partial \rho\psi}{\partial \rho_\alpha}, \qquad p := -\rho\psi + \sum_{\alpha=0}^{N} \rho_\alpha \mu_\alpha \quad \text{(Gibbs-Duhem)}$$

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$$\boldsymbol{J}_\alpha = -\sum_{\beta=1}^{N} M_{\alpha\beta} \left(\nabla\left(\frac{\mu_\beta - \mu_0}{T}\right) - \frac{1}{T}\left(\frac{z_\beta e_0}{m_\beta} - \frac{z_0 e_0}{m_0}\right)\boldsymbol{E}\right), \qquad \boldsymbol{J}_0 = -\sum_{\alpha=1}^{N} \boldsymbol{J}_\alpha$$

$$\boldsymbol{\Sigma} = -p + \varepsilon_0(1+\chi)(\boldsymbol{E}\otimes\boldsymbol{E} - \tfrac{1}{2}|\boldsymbol{E}|^2\mathbf{1})$$

$$\rho\psi = \underbrace{\sum_{\alpha=0}^{N} \rho_\alpha g_\alpha^{Ref}(T)}_{\text{reference values}} \quad \underbrace{+kT\sum_{\alpha=0}^{N} n_\alpha \ln\frac{n_\alpha}{n}}_{\text{entropy of mixing}} \quad \underbrace{+\rho\psi^M}_{\text{elastic energy}}$$

elastic law: $p = p^{Ref} + K\left(\sum_{\alpha=0}^{N} v_\alpha^{Ref} n_\alpha - 1\right)$

v_α^{Ref}: specific volume of A_α

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incompressible limit $K \to \infty$: $\rho\psi^M = (p - p^{Ref})\left(\sum_{\alpha=0}^{N} v_\alpha^{Ref} n_\alpha - 1\right)$

$$\mu_\alpha = g_\alpha^{Ref} + \frac{kT}{m_\alpha}\ln\frac{n_\alpha}{n} + \frac{v_\alpha^{Ref}}{m_\alpha}(p - p^{Ref})$$

$$\boldsymbol{J}_\alpha = -M_\alpha\left(\nabla n_\alpha - \frac{m_\alpha}{m_0}\frac{n_\alpha}{n_0}\nabla n_0 + v_\alpha^{Ref}\left(1 - \frac{m_\alpha v_0^{Ref}}{m_0 v_\alpha^{Ref}}\right)\nabla p + z_\alpha e_0 \nabla\varphi\right)$$

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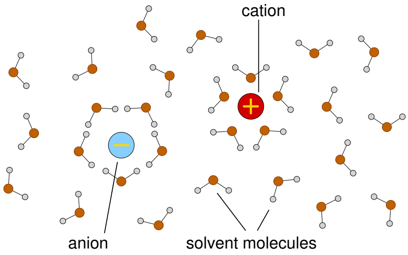
Nernst-Planck: $\boldsymbol{J}_\alpha = -M_\alpha\left(\nabla n_\alpha + z_\alpha e_0 \nabla\varphi\right),$

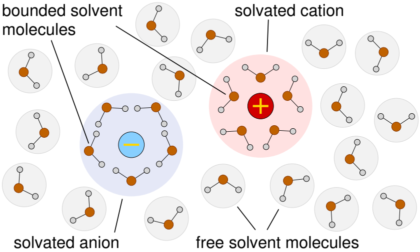


specific volumina:

A: v_A^{Ref}

C: v_C^{Ref}

S: v_S^{Ref}

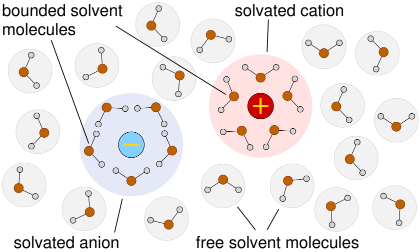


specific volumina:

A: $v_{A^*}^{Ref} + \kappa_A \, v_S^{Ref}$

C: $v_{C^*}^{Ref} + \kappa_C \, v_S^{Ref}$

S: v_S^{Ref}



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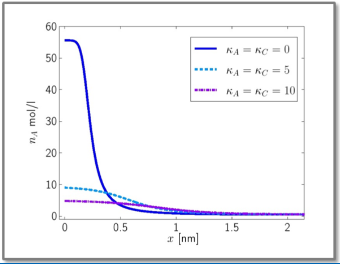

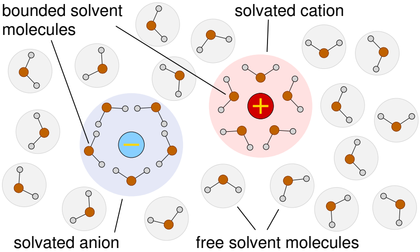

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A: $v_{A^*}^{Ref} + \kappa_A \, v_S^{Ref}$

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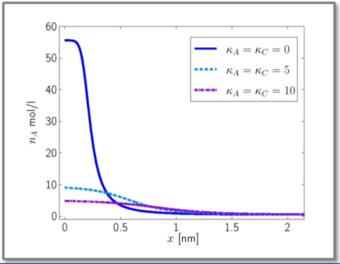
$$\tilde{q} = \int \sum_{\alpha} z_\alpha n_\alpha \, dx$$



at $\varphi_L - \varphi_R = 0.25V$:

experiment: $|\tilde{q}| \approx (0 - 50) \frac{\mu C}{cm^2}$

Nernst-Planck: $|\tilde{q}| \approx 600 \frac{\mu C}{cm^2}$

simple mixture: $|\tilde{q}| \approx 100 \frac{\mu C}{cm^2}$

solvated ions: $|\tilde{q}| \approx 28 \frac{\mu C}{cm^2}$

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volume: $A_0, A_1, \cdots, A_N$

surface: $A_0, A_1, \cdots, A_N, \cdots, A_{N_S}$

bulk $\Omega^{\pm}$

$$\partial_t \rho_\alpha + \operatorname{div}(\rho_\alpha \boldsymbol{v} + \boldsymbol{J}_\alpha) = 0$$

$$-\boldsymbol{\Sigma} = \rho \boldsymbol{b}$$

$$-\varepsilon_0 (1+\chi)\Delta\varphi = n^{\mathrm{F}}$$

surface S

$$\partial_t \underset{s}{\rho_\alpha} + [\![(\rho_\alpha(\boldsymbol{v}-\boldsymbol{w}) + \boldsymbol{J}_\alpha)\cdot\boldsymbol{\nu}]\!] = 0$$

$$-[\![\boldsymbol{\Sigma}\cdot\boldsymbol{\nu}]\!] = \underset{s}{\rho}\,\underset{s}{\boldsymbol{b}} + 2k_M \underset{s}{\gamma}\boldsymbol{\nu}$$

$$-\varepsilon_0 [\![(1+\chi)\partial_n\varphi]\!] = \underset{s}{n}^{\mathrm{F}}$$

volume: $A_0, A_1, \cdots, A_N$ surface: $A_0, A_1, \cdots, A_N, \cdots, A_{N_S}$

bulk $\Omega^\pm$

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$$-\varepsilon_0 (1+\chi) \Delta \varphi = n^{\mathrm{F}}$$

surface S

$$\partial_t \underset{s}{\rho_\alpha} + [\![(\rho_\alpha (\boldsymbol{v} - \boldsymbol{w}) + \boldsymbol{J}_\alpha) \cdot \boldsymbol{\nu}]\!] = 0$$

$$-[\![\boldsymbol{\Sigma} \cdot \boldsymbol{\nu}]\!] = \underset{s}{\rho} \underset{s}{\boldsymbol{b}} + 2k_M \underset{s}{\gamma} \boldsymbol{\nu}$$

$$-\varepsilon_0 [\![(1+\chi) \partial_n \varphi]\!] = \underset{s}{n}^{\mathrm{F}}$$

$$\widehat{\rho\psi} = \rho\psi(T, \rho_0, \rho_1, \cdots, \rho_N) + \chi |\boldsymbol{E}|^2$$

$$\underset{s}{\rho}\underset{s}{\psi} = \underset{s}{\rho}\underset{s}{\psi}(\underset{s}{T}, \underset{s}{\rho_0}, \underset{s}{\rho_1}, \cdots, \underset{s}{\rho_{N_S}})$$

$$\mu_\alpha = \frac{\partial \rho\psi}{\partial \rho_\alpha}$$

$$\underset{s}{\mu_\alpha} = \frac{\partial \underset{s}{\rho}\underset{s}{\psi}}{\partial \underset{s}{\rho_\alpha}}$$

$$p := -\rho\psi + \sum_{\alpha=0}^{N} \rho_\alpha \mu_\alpha$$

$$\underset{s}{\gamma} := \underset{s}{\rho}\underset{s}{\psi} - \sum_{\alpha=0}^{N_S} \underset{s}{\rho_\alpha} \underset{s}{\mu_\alpha}$$

incompressible simple mixture of metal ions M and electrons e

$v_e^{Ref} := 0, \qquad p = p_e + p_M$

goal: $\rho\psi = \rho_M \psi_M(\rho_M) + \rho_e \psi_e(\rho_e), \qquad \underset{s}{\rho}\underset{s}{\psi}(\underset{s}{\rho_0}, \cdots, \underset{s}{\rho_N}, \underset{s}{\rho_e}, \underset{s}{\rho_M})$

$\rho_M \psi_M = p^{Ref} + v_M^{Ref} n_M, \qquad \mu_e = \left(\frac{3}{8\pi}\right)^{2/3} \frac{h}{2m_e} n_e^{2/3}$ (Drude-Sommerfeld) incompressible simple mixture of metal ions M and electrons e

$$v_e^{Ref} := 0, \qquad p = p_e + p_M$$

goal: $\rho\psi = \rho_M \psi_M(\rho_M) + \rho_e \psi_e(\rho_e)$, $\qquad \underset{s}{\rho}\underset{s}{\psi}(\underset{s}{\rho_0}, \cdots, \underset{s}{\rho_N}, \underset{s}{\rho_e}, \underset{s}{\rho_M})$

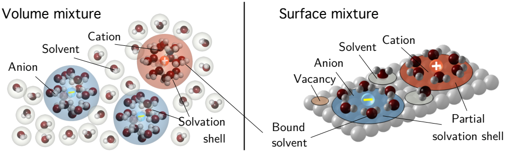
$$\rho_M \psi_M = p^{Ref} + v_M^{Ref} n_M, \qquad \mu_e = \left(\frac{3}{8\pi}\right)^{2/3} \frac{h}{2m_e} n_e^{2/3}$$ (Drude-Sommerfeld)

coupling to surface

Constitutive laws (fast adsoption limit)

$$0 = \frac{\mu_\alpha^\pm - \mu_0^\pm}{T} - \frac{\underset{s}{\mu_\alpha} - \underset{s}{\mu_0}}{\underset{s}{T}}, \qquad 0 = \frac{\mu_0^\pm}{T} - \frac{\underset{s}{\mu_0}}{\underset{s}{T}}$$

Free energy of metal surface



$$\underset{s}{\mu}_\alpha = \underset{s}{\mu}_\alpha^{Ref} + \frac{kT}{m_\alpha} \ln\left(\frac{\underset{s}{n}_\alpha}{\underset{s}{n}_V}\right)$$

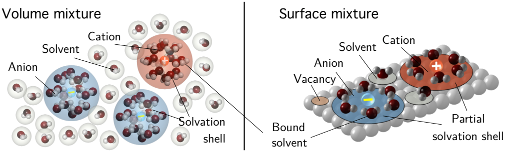
$$\underset{s}{\mu}_M = \underset{s}{\mu}_M^{Ref} - \frac{a_M^{Ref}}{m_M}\underset{s}{\gamma} + \frac{kT}{m_M} \ln\left(\frac{\underset{s}{n}_V}{\underset{s}{n}_M}\right)$$

adsorption sides

$$\underset{s}{n}_M = \underset{s}{n}_M^{Ref}$$

vacancies

$$\underset{s}{n}_V = \underset{s}{n}_M - \sum_\alpha \underset{s}{n}_\alpha$$



adsorption sides

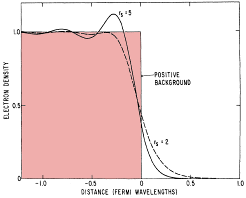
$$\underset{s}{n}_M = \underset{s}{n}_M^{Ref}$$

vacancies

$$\underset{s}{n}_V = \underset{s}{n}_M - \sum_\alpha \underset{s}{n}_\alpha$$

$$\underset{s}{\mu}_\alpha = \underset{s}{\mu}_\alpha^{Ref} + \frac{kT}{m_\alpha} \ln\left(\frac{\underset{s}{n}_\alpha}{\underset{s}{n}_V}\right)$$

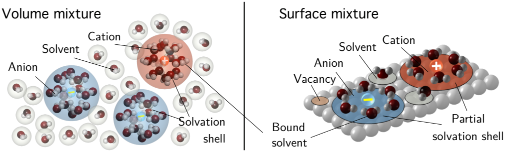
$$\underset{s}{\mu}_M = \underset{s}{\mu}_M^{Ref} - \frac{a_M^{Ref}}{m_M}\underset{s}{\gamma} + \frac{kT}{m_M} \ln\left(\frac{\underset{s}{n}_V}{\underset{s}{n}_M}\right)$$



[Kohn,Lang:1971]

metal – vacuum: $\varphi_M - \varphi_V \sim 7V$

metal – surface: $\varphi_M - \underset{s}{\varphi}_V \sim 2V$



adsorption sides

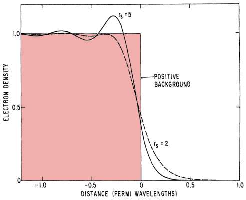
$$\underset{s}{n}_M = \underset{s}{n}_M^{Ref}$$

vacancies

$$\underset{s}{n}_V = \underset{s}{n}_M - \sum_\alpha \underset{s}{n}_\alpha$$

$$\underset{s}{\mu}_\alpha = \underset{s}{\mu}_\alpha^{Ref} + \frac{kT}{m_\alpha} \ln\left(\frac{\underset{s}{n}_\alpha}{\underset{s}{n}_V}\right)$$

$$\underset{s}{\mu}_M = \underset{s}{\mu}_M^{Ref} - \frac{a_M^{Ref}}{m_M}\underset{s}{\gamma} + \frac{kT}{m_M} \ln\left(\frac{\underset{s}{n}_V}{\underset{s}{n}_M}\right)$$



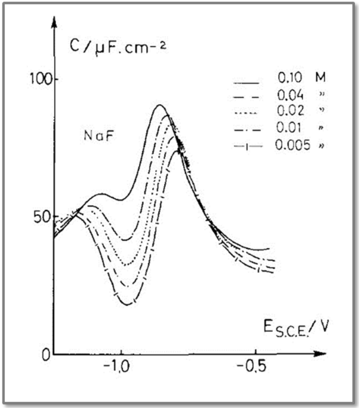
[Kohn,Lang:1971]

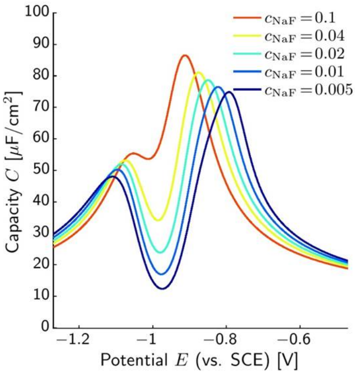
metal – vacuum: $\varphi_M - \varphi_V \sim 7V$

metal – surface: $\varphi_M - \underset{s}{\varphi}_V \sim 2V$

$\underset{s}{\mu}_e = \underset{s}{\mu}_e^{Ref}$ (!) depending on surface orientation

differential capacity: $C := \dfrac{dQ}{dE}$ $\qquad Q := \underset{s}{q} + \tilde{q}$





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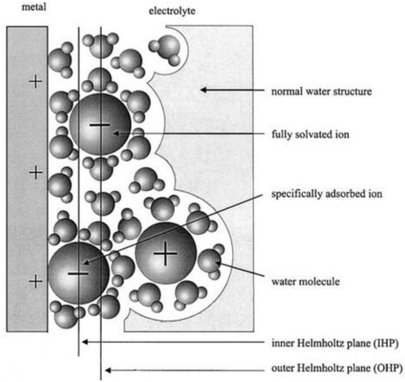

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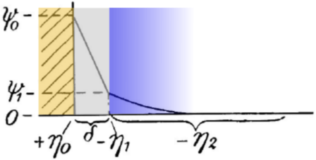

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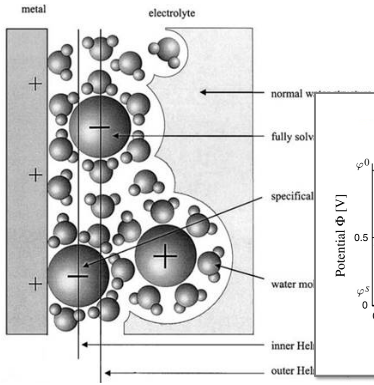
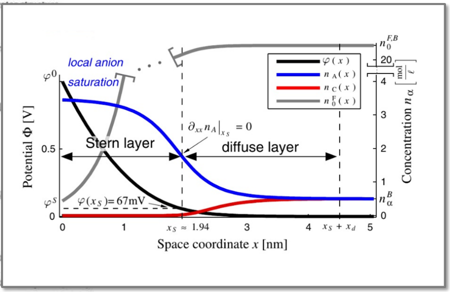
Electrochemical double layer





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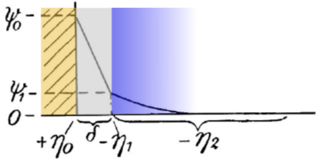

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1 Ion transport in electrolyte bulk

- Shortcomings of Nernst-Planck model
- General continuum model for the bulk

2 Electrochemical double layer

- Surface balances and adsorption
- Free energy models for metals
- Double-layer capacity

3 Lippmann equation for liquid mercury electrode

- Matched asymptotic analysis
- Numerical results

Lippmann $\frac{d\gamma}{dE} = -Q$

Butler-Volmer $\underset{s}{R} = \underset{s}{R_f^0} \exp\left(\alpha_f \frac{e_0}{kT} \eta_S\right) \underset{s}{R_b^0} \exp\left(-\alpha_b \frac{e_0}{kT} \eta_S\right)$

thermodynamic variable: $\boldsymbol{E}$ not φ

Lippmann $\frac{d\gamma}{dE} = -Q$

Butler-Volmer $\underset{s}{R} = \underset{s}{R_f^0} \exp\left(\alpha_f \frac{e_0}{kT} \eta_S\right) \underset{s}{R_b^0} \exp\left(-\alpha_b \frac{e_0}{kT} \eta_S\right)$

thermodynamic variable: $\boldsymbol{E}$ not φ

sharp boundary layers, **Debye length:** λL^{Ref}

$$-(1+\chi)\varepsilon_0 \partial_{xx}\varphi = n^{\mathrm{F}} \quad \rightsquigarrow \quad -\lambda^2(1+\chi)\partial_{\xi\xi}\widehat{\varphi} = \widehat{n}^{\mathrm{F}}$$

$$\lambda = \sqrt{\frac{\varepsilon_0 kT}{e_0^2 n^{Ref} (L^{Ref})^2}}\,, \qquad \lambda\delta = \frac{\underset{s}{n}^{Ref}}{n^{Ref} L^{Ref}}$$

Lippmann $\frac{d\gamma}{dE} = -Q$

Butler-Volmer $\underset{s}{R} = \underset{s}{R_f^0} \exp\left(\alpha_f \frac{e_0}{kT}\eta_S\right) \underset{s}{R_b^0} \exp\left(-\alpha_b \frac{e_0}{kT}\eta_S\right)$

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$$\lambda = \sqrt{\frac{\varepsilon_0 kT}{e_0^2 n^{Ref}(L^{Ref})^2}}\,, \qquad \lambda\delta = \frac{\underset{s}{n}^{Ref}}{n^{Ref} L^{Ref}}$$

$$L^{Ref} = 1\mathrm{cm}, \qquad n^{Ref} = 6.022\cdot 10^{25}\,\mathrm{m}^{-3}, \qquad \underset{s}{n}^{Ref} = 7.3\cdot 10^{18}\,\mathrm{m}^{-2}$$

$$\lambda \approx 1.54\cdot 10^{-8}\,, \qquad \lambda\delta \approx 1.21\cdot 10^{-5}\,, \qquad \lambda|\boldsymbol{b}| \approx 2.38\cdot 10^{-8}\,.$$

Assumptions

- equilibrium: $\partial_t \cdot = 0,\ v = 0$
- $\delta \sim \mathcal{O}(1)$
- $k_M \cdot \lambda L^{Ref} \ll 1$

bulk $\Omega^\pm$

$$\nabla(\mu_\alpha + z_\alpha\varphi) = 0$$

$$\partial_x \Sigma = \lambda \rho \boldsymbol{b}$$

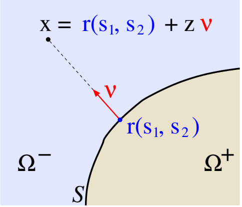
$$-\lambda^2(1+\chi)\partial_{xx}\varphi = n^{\mathrm{F}}$$

surface S

$$(\mu_\alpha + z_\alpha\varphi))^\pm = \underset{s}{\mu}_\alpha + z_\alpha \underset{s}{\varphi}$$

$$[\![\Sigma \cdot \boldsymbol{\nu}]\!] = \lambda\delta(\underset{s}{\rho}\underset{s}{\boldsymbol{b}} + 2k_M\underset{s}{\gamma})$$

$$-[\![\lambda(1+\chi)\partial_x\varphi\nu]\!] = \delta \underset{s}{n}^{\mathrm{F}}$$



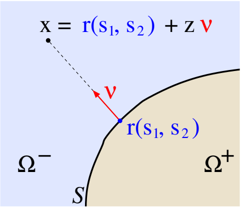
rescale in layer

$$\widetilde{u}(\boldsymbol{r}, z) := u(\boldsymbol{r} + \lambda z \boldsymbol{\nu})$$

formal asymptotics expansions for $0 < \lambda \ll 1$

in bulk: $u = u^{(0)} + \lambda u^{(1)} + \mathcal{O}(\lambda^2)$

in layer: $\widetilde{u} = \widetilde{u}^{(0)} + \lambda \widetilde{u}^{(1)} + \mathcal{O}(\lambda^2)$



rescale in layer

$$\widetilde{u}(\boldsymbol{r}, z) := u(\boldsymbol{r} + \lambda z \boldsymbol{\nu})$$

formal asymptotics expansions for $0 < \lambda \ll 1$

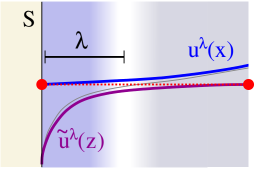
in bulk: $u = u^{(0)} + \lambda u^{(1)} + \mathcal{O}(\lambda^2)$

in layer: $\widetilde{u} = \widetilde{u}^{(0)} + \lambda \widetilde{u}^{(1)} + \mathcal{O}(\lambda^2)$

matching conditions:

$$\widetilde{u}^{(0)}(z) - u^{(0),\pm}(x_S^{(0)}) = o(1/|z|)$$

$$\partial_z \widetilde{u}^{(0)}(z) = o(1/|z|)$$



in higher order

$$\widetilde{u}^{(1)}(z) - z\,\partial_\nu u^{(0),\pm} - u^{(1),\pm} = o(1/|z|)$$

$$\partial_z \widetilde{u}^{(1)}(z) - \partial_\nu u^{(0),\pm} = o(1/|z|)$$

$$
\begin{aligned}
\nabla u &= \lambda^{-1}\partial_z \widetilde{u}\,\boldsymbol{\nu} + |\boldsymbol{\tau_1}|^{-1}\partial_1 \widetilde{u}\,\boldsymbol{\tau}_1 + |\boldsymbol{\tau_2}|^{-1}\partial_2 \widetilde{u}\,\boldsymbol{\tau}_2 + \mathcal{O}(\lambda)\,,\\
\operatorname{div}(\boldsymbol{u}) &= \lambda^{-1}\partial_z \widetilde{\boldsymbol{u}}\cdot\boldsymbol{\nu} + \operatorname{div}_{\boldsymbol{\tau}}(\widetilde{\boldsymbol{u}}) + \mathcal{O}(\lambda)\,,\\
-\Delta u &= -\lambda^{-2}\partial_{zz}\widetilde{u} - \lambda^{-1}2k_M\partial_z\widetilde{u} + \mathcal{O}(1)\,,
\end{aligned}
$$

$$\widetilde{\Sigma}_{\nu\nu} = -\widetilde{p} + \tfrac{1+\chi}{2}|\partial_z\widetilde{\varphi}|^2 + \mathcal{O}(\lambda^2)$$

layer

$$
\begin{aligned}
\lambda^{-1}(\partial_z\widetilde{p} + n^{\mathrm{F}}\,\partial_z\widetilde{\varphi}) + \mathcal{O}(\lambda) &= \lambda\rho\boldsymbol{b}\\
-(1+\chi)(\partial_{zz}\widetilde{\varphi} + \lambda\,2k_M\partial_z\widetilde{\varphi}) + \mathcal{O}(\lambda^2) &= n^{\mathrm{F}}
\end{aligned}
$$

S

$$
\begin{aligned}
-[\![\widetilde{\Sigma}_{\nu\nu}]\!] &= \lambda\,\delta\,2k_M\,\underset{s}{\gamma} + \lambda^2\,\delta\,\underset{s}{\rho}\underset{s}{\boldsymbol{b}}\cdot\boldsymbol{\nu} + \mathcal{O}(\lambda^2)\\
-[\![(1+\chi)\partial_z\varphi]\!] &= \delta\underset{s}{n}^{\mathrm{F}} + \mathcal{O}(\lambda)
\end{aligned}
$$

layer: $\widetilde{\Sigma}_{\nu\nu}^{(0)} = -\widetilde{p}^{(0)} + \frac{1+\chi}{2}|\partial_z \widetilde{\varphi}^{(0)}|^2$

bulk: $\Sigma_{\nu\nu}^{(0)} = -p^{(0)}$

layer

$$-\partial_z \widetilde{\mathbf{\Sigma}}_{\nu\nu}^{(0)} = 0\ ,$$
$$-(1+\chi)\partial_{zz}\widetilde{\varphi}^{(0)} = \widetilde{n}^{\mathrm{F},(0)}.$$

S

$$-[\![\widetilde{\mathbf{\Sigma}}_{\nu\nu}^{(0)}]\!] = 0\ ,$$
$$-[\![(1+\chi)\partial_z \widetilde{\varphi}^{(0)}]\!] = \delta \underset{s}{n}^{\mathrm{F},(0)}$$

$$\widetilde{\mathbf{\Sigma}}_{\nu\nu}^{(0)}(-\infty) = \widetilde{\mathbf{\Sigma}}_{\nu\nu}^{(0)}(\infty) \qquad \Longrightarrow \quad [\![p^{(0)}]\!] = 0$$

layer: $\widetilde{\Sigma}^{(0)}_{\nu\nu} = -\widetilde{p}^{(0)} + \frac{1+\chi}{2}|\partial_z\widetilde{\varphi}^{(0)}|^2$

bulk: $\Sigma^{(0)}_{\nu\nu} = -p^{(0)}$

layer

$$-\partial_z\widetilde{\boldsymbol{\Sigma}}^{(0)}_{\nu\nu} = 0\,,$$
$$-(1+\chi)\partial_{zz}\widetilde{\varphi}^{(0)} = \widetilde{n}^{\mathrm{F},(0)}.$$

S

$$-[\![\widetilde{\boldsymbol{\Sigma}}^{(0)}_{\nu\nu}]\!] = 0\,,$$
$$-[\![(1+\chi)\partial_z\widetilde{\varphi}^{(0)}]\!] = \delta\,\underset{s}{n}^{\mathrm{F},(0)}$$

$$\widetilde{\boldsymbol{\Sigma}}^{(0)}_{\nu\nu}(-\infty) = \widetilde{\boldsymbol{\Sigma}}^{(0)}_{\nu\nu}(\infty) \qquad \Longrightarrow \qquad [\![p^{(0)}]\!] = 0$$

$$\int_{-\infty}^{\infty}\partial_{zz}\widetilde{\varphi}^{(0)}\,\mathrm{d}z \quad = \partial_z\widetilde{\varphi}^{(0)}|_{-\infty}^{0} + \partial_z\widetilde{\varphi}^{(0)}|_{0}^{\infty} \quad = -[\![\partial_z\widetilde{\varphi}^{(0)}]\!]$$

$$\widetilde{q}^{+} := \int_0^{\infty}\widetilde{n}^{\mathrm{F},(0)}\,\mathrm{d}z, \qquad \widetilde{q}^{-} := \int_{-\infty}^{0}\widetilde{n}^{\mathrm{F},(0)}\,\mathrm{d}z$$

global electro-neutrality of double layer: $\delta\,\underset{s}{n}^{\mathrm{F},(0)} + \widetilde{q}^{-} + \widetilde{q}^{+} = 0$

$$\widetilde{\Sigma}^{(1)}_{\nu\nu} = -\widetilde{p}^{(1)} + (1+\chi)\partial_z\widetilde{\varphi}^{(0)}\partial_z\widetilde{\varphi}^{(1)}$$

layer

$$\partial_z\widetilde{p}^{(1)} + \widetilde{n}^{\mathrm{F},(0)}\partial_z\widetilde{\varphi}^{(1)} + \widetilde{n}^{\mathrm{F},(1)}\partial_z\widetilde{\varphi}^{(0)} = 0\,,$$

$$-(1+\chi)\left(\partial_{zz}\widetilde{\varphi}^{(1)} + 2k_M\,\partial_z\widetilde{\varphi}^{(0)}\right) = \widetilde{n}^{\mathrm{F},(1)}$$

S

$$-[\![\widetilde{\Sigma}^{(1)}_{\nu\nu}]\!] = \delta\,2k_M\,\underset{s}{\gamma}$$

$$\widetilde{\Sigma}^{(1)}_{\nu\nu} = -\widetilde{p}^{(1)} + (1+\chi)\partial_z\widetilde{\varphi}^{(0)}\partial_z\widetilde{\varphi}^{(1)}$$

layer

$$\partial_z\widetilde{p}^{(1)} + \widetilde{n}^{\mathrm{F},(0)}\partial_z\widetilde{\varphi}^{(1)} + \widetilde{n}^{\mathrm{F},(1)}\partial_z\widetilde{\varphi}^{(0)} = 0\,,$$

$$-(1+\chi)\left(\partial_{zz}\widetilde{\varphi}^{(1)} + 2k_M\,\partial_z\widetilde{\varphi}^{(0)}\right) = \widetilde{n}^{\mathrm{F},(1)}$$

S

$$-[\![\widetilde{\Sigma}^{(1)}_{\nu\nu}]\!] = \delta\,2k_M\,\underset{s}{\gamma}$$

$$\partial_z\widetilde{\Sigma}^{(1)}_{\nu\nu} = -2k_M\,(1+\chi)(\partial_z\widetilde{\varphi}^{(0)})^2$$

$$\widetilde{\Sigma}^{(1)}_{\nu\nu} = -\widetilde{p}^{(1)} + (1+\chi)\partial_z\widetilde{\varphi}^{(0)}\partial_z\widetilde{\varphi}^{(1)}$$

layer

$$\partial_z\widetilde{p}^{(1)} + \widetilde{n}^{\mathrm{F},(0)}\partial_z\widetilde{\varphi}^{(1)} + \widetilde{n}^{\mathrm{F},(1)}\partial_z\widetilde{\varphi}^{(0)} = 0\,,$$

$$-(1+\chi)\left(\partial_{zz}\widetilde{\varphi}^{(1)} + 2k_M\,\partial_z\widetilde{\varphi}^{(0)}\right) = \widetilde{n}^{\mathrm{F},(1)}$$

S

$$-[\![\widetilde{\Sigma}^{(1)}_{\nu\nu}]\!] = \delta\,2k_M\,\underset{s}{\gamma}$$

$$\partial_z\widetilde{\Sigma}^{(1)}_{\nu\nu} = -2k_M\,(1+\chi)(\partial_z\widetilde{\varphi}^{(0)})^2$$

$$\widetilde{\gamma}^{+} := \int_0^\infty (1+\chi)(\partial_z\widetilde{\varphi}^{(0)})^2\,\mathrm{d}z\,, \qquad \widetilde{\gamma}^{-} := \int_{-\infty}^0 (1+\chi)(\partial_z\widetilde{\varphi}^{(0)})^2\,\mathrm{d}z$$

Young-Laplace $\quad [\![p^{(1)}]\!] = 2k_M\,(\underset{s}{\gamma} + \widetilde{\gamma}^{+} - \widetilde{\gamma}^{-})$

interfacial tension $\gamma := \underset{s}{\gamma} + \widetilde{\gamma}^+ - \widetilde{\gamma}^-$

Ω^+ metal, apply potential $E := \underset{s}{\varphi} - \varphi^-$

$\underset{s}{\mu_e} = const. \to$ constant layer in metal $\Longrightarrow \frac{d}{dE}\widetilde{\gamma}^+ = 0$

interfacial tension $\gamma := \underset{s}{\gamma} + \widetilde{\gamma}^{+} - \widetilde{\gamma}^{-}$

Ω^{+} metal, apply potential $E := \underset{s}{\varphi} - \varphi^{-}$

$\underset{s}{\mu_e} = const.$ $\rightarrow$ constant layer in metal $\Longrightarrow \frac{d}{dE}\widetilde{\gamma}^{+} = 0$

$$\widetilde{\gamma}^{-} = (1+\chi)\int_{-\infty}^{0} (\partial_z \widetilde{\varphi}^{(0)})^2 \,\mathrm{d}z$$

$$= (1+\chi)\int_{E}^{0} \sqrt{p(\widetilde{\varphi} + \varphi^{-})}\, d\widetilde{\varphi} \qquad \text{[DGM13]}$$

$$\frac{d}{dE}\widetilde{\gamma}^{-} = -(1+\chi)\sqrt{p}\big|_{S}^{-} \quad = -\widetilde{q}^{-} \qquad \text{[DGL2014pre]}$$

interfacial tension $\gamma := \underset{s}{\gamma} + \widetilde{\gamma}^{+} - \widetilde{\gamma}^{-}$

Ω^{+} metal, apply potential $E := \underset{s}{\varphi} - \varphi^{-}$

$\underset{s}{\mu_e} = const. \rightarrow$ constant layer in metal $\Longrightarrow \frac{d}{dE}\widetilde{\gamma}^{+} = 0$

$$\widetilde{\gamma}^{-} = (1+\chi)\int_{-\infty}^{0}(\partial_z\widetilde{\varphi}^{(0)})^2\,\mathrm{d}z$$

$$= (1+\chi)\int_{E}^{0}\sqrt{p(\widetilde{\varphi}+\varphi^{-})}\,d\widetilde{\varphi}$$ [DGM13]

$$\frac{d}{dE}\widetilde{\gamma}^{-} = -(1+\chi)\sqrt{p}|_S^{-} = -\widetilde{q}^{-}$$ [DGL2014pre]

$$\frac{d}{dE}\underset{s}{\gamma} = \frac{d}{dE}\left(\underset{s}{\rho}\underset{s}{\psi} - \sum \underset{s}{n_\alpha}\underset{s}{\mu_\alpha}\right)$$

$$= \frac{d}{dE}\left(\underset{s}{\rho}\underset{s}{\psi} - \sum_{\alpha\in\Omega^-} n_\alpha(\mu_\alpha|_S^{-} + z_\alpha E)\right)$$

$$= -\underset{s}{q}$$ [Guhlke2015]

interfacial tension $\gamma := \underset{s}{\gamma} + \widetilde{\gamma}^{+} - \widetilde{\gamma}^{-}$

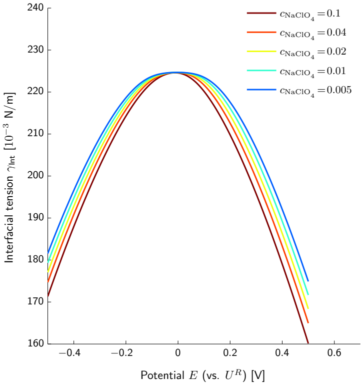
Ω^{+} metal, apply potential $E := \underset{s}{\varphi} - \varphi^{-}$

$\underset{s}{\mu_e} = const. \to$ constant layer in metal $\Longrightarrow \frac{d}{dE}\widetilde{\gamma}^{+} = 0$

$$\begin{aligned}\widetilde{\gamma}^{-} &= (1+\chi)\int_{-\infty}^{0}(\partial_z\widetilde{\varphi}^{(0)})^2\,\mathrm{d}z \\ &= (1+\chi)\int_{E}^{0}\sqrt{p(\widetilde{\varphi}+\varphi^{-})}\,d\widetilde{\varphi} \qquad \text{[DGM13]} \\ \frac{d}{dE}\widetilde{\gamma}^{-} &= -(1+\chi)\sqrt{p}\big|_S^{-} \quad = -\widetilde{q}^{-} \qquad \text{[DGL2014pre]}\end{aligned}$$

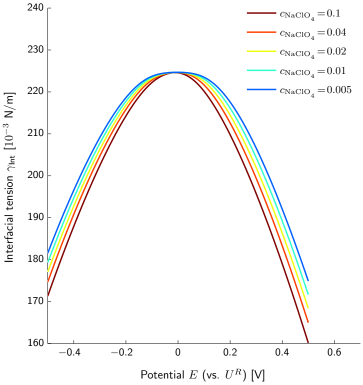
$$\begin{aligned}\frac{d}{dE}\underset{s}{\gamma} &= \frac{d}{dE}\Big(\underset{s}{\rho}\underset{s}{\psi} - \sum \underset{s}{n_\alpha}\underset{s}{\mu_\alpha}\Big) \\ &= \frac{d}{dE}\Big(\underset{s}{\rho}\underset{s}{\psi} - \sum_{\alpha\in\Omega^{-}} n_\alpha(\mu_\alpha|_S^{-} + z_\alpha E)\Big) \\ &= -\underset{s}{q} \qquad \text{[Guhlke2015]}\end{aligned}$$

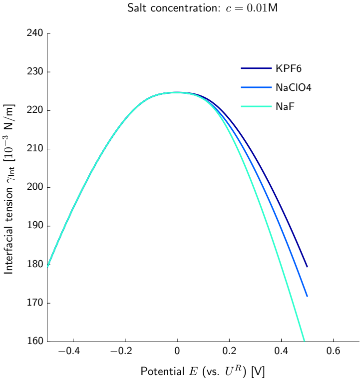
double layer charge: $Q := \underset{s}{q} + \widetilde{q}^{-}$ **Lippmann:** $\frac{d}{dE}\gamma = -Q$

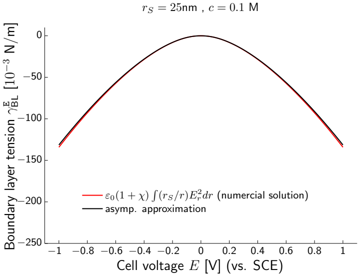


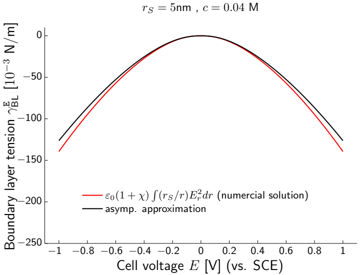
240
230
220
210
200
190
180
170
160
−0.4
−0.2
0
0.2
0.4
0.6
Interfacial tension γ_{Int} $[10^{-3}$ N/m$]$
Potential E (vs. U^R) [V]
$c_{\mathrm{NaClO_4}} = 0.1$
$c_{\mathrm{NaClO_4}} = 0.04$
$c_{\mathrm{NaClO_4}} = 0.02$
$c_{\mathrm{NaClO_4}} = 0.01$
$c_{\mathrm{NaClO_4}} = 0.005$

Numerical results

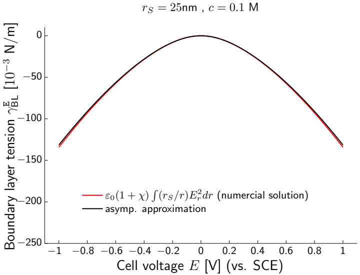


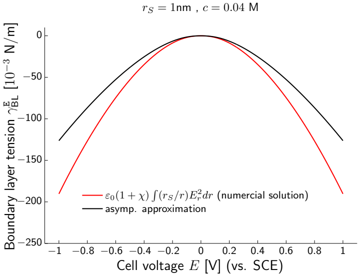



$r_S = 25$nm , $c = 0.1$ M
Boundary layer tension $\gamma^{\mathrm{E}}_{\mathrm{BL}}$ $[10^{-3}$ N/m]
0
−50
−100
−150
−200
−250
−1 −0.8 −0.6 −0.4 −0.2 0 0.2 0.4 0.6 0.8 1
Cell voltage E [V] (vs. SCE)
$\varepsilon_0(1+\chi)\int(r_S/r)E_r^2 dr$ (numercial solution)
asymp. approximation


$r_S = 5$nm , $c = 0.04$ M
Boundary layer tension $\gamma^{\mathrm{E}}_{\mathrm{BL}}$ $[10^{-3}$ N/m]
0
−50
−100
−150
−200
−250
−1 −0.8 −0.6 −0.4 −0.2 0 0.2 0.4 0.6 0.8 1
Cell voltage E [V] (vs. SCE)
$\varepsilon_0(1+\chi)\int(r_S/r)E_r^2 dr$ (numercial solution)
asymp. approximation

Validity of asymptotic results





- pressure dependence, momentum balance necessary
- thermodynamically consistent complete model derived
- incompressible mixture model for metal surface; $\underset{s}{\mu_e} = const.$
- qualitative & quantitative prediction of differential capacity
- jump conditions by formal asymptotic analysis

- electric field contributes to interfacial tension
- Lippmann equation recovered within asymptotic limit
- asymptotic not valid in nm range

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Thank you for your attention! Questions?