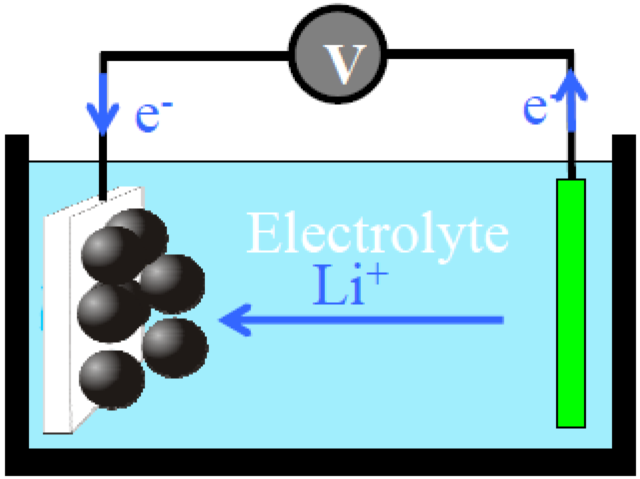
Weierstrass Institute for Applied Analysis and Stochastics

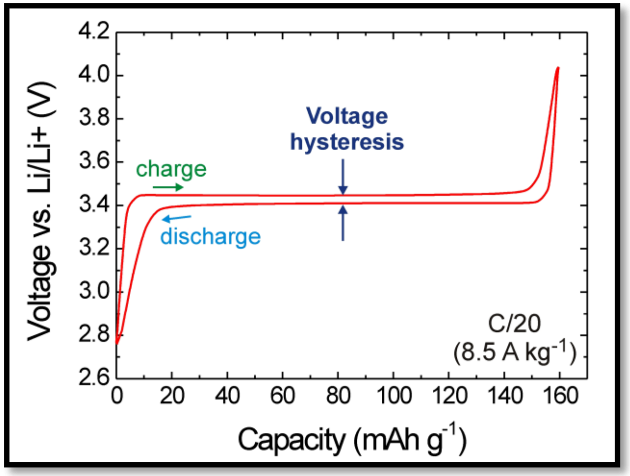
Leibniz Association

Models of Lithium-Ion Batteries: A Paradigm for Consistent Modeling

Wolfgang Dreyer   Clemens Guhlke   Manuel Landstorfer   Rüdiger Müller

Selected Phenomena in Li-Ion Batteries





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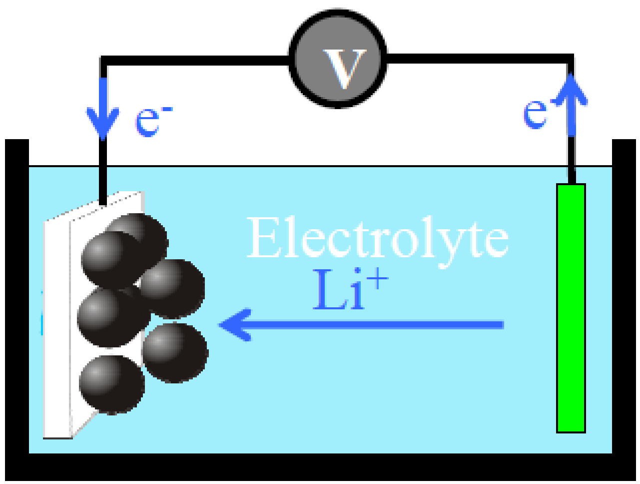

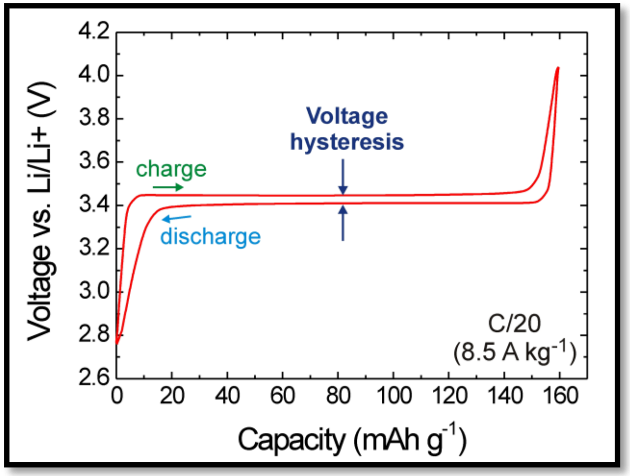

- Phase transition within particle ensemble
- Ion transport
- Adsorption
- Electron transfer reaction
- Double layers

Electrochemistry

Max Planck
(1858-1947)

Otto Stern
(1888-1969)

Alexander N.
Frumkin
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David C.
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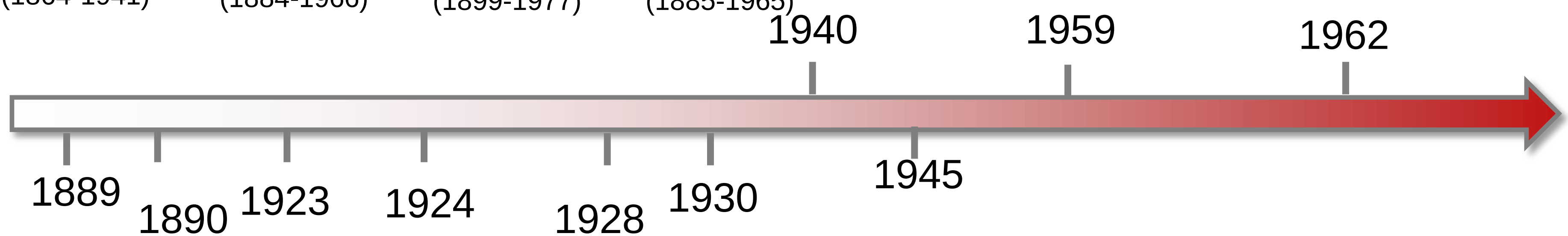

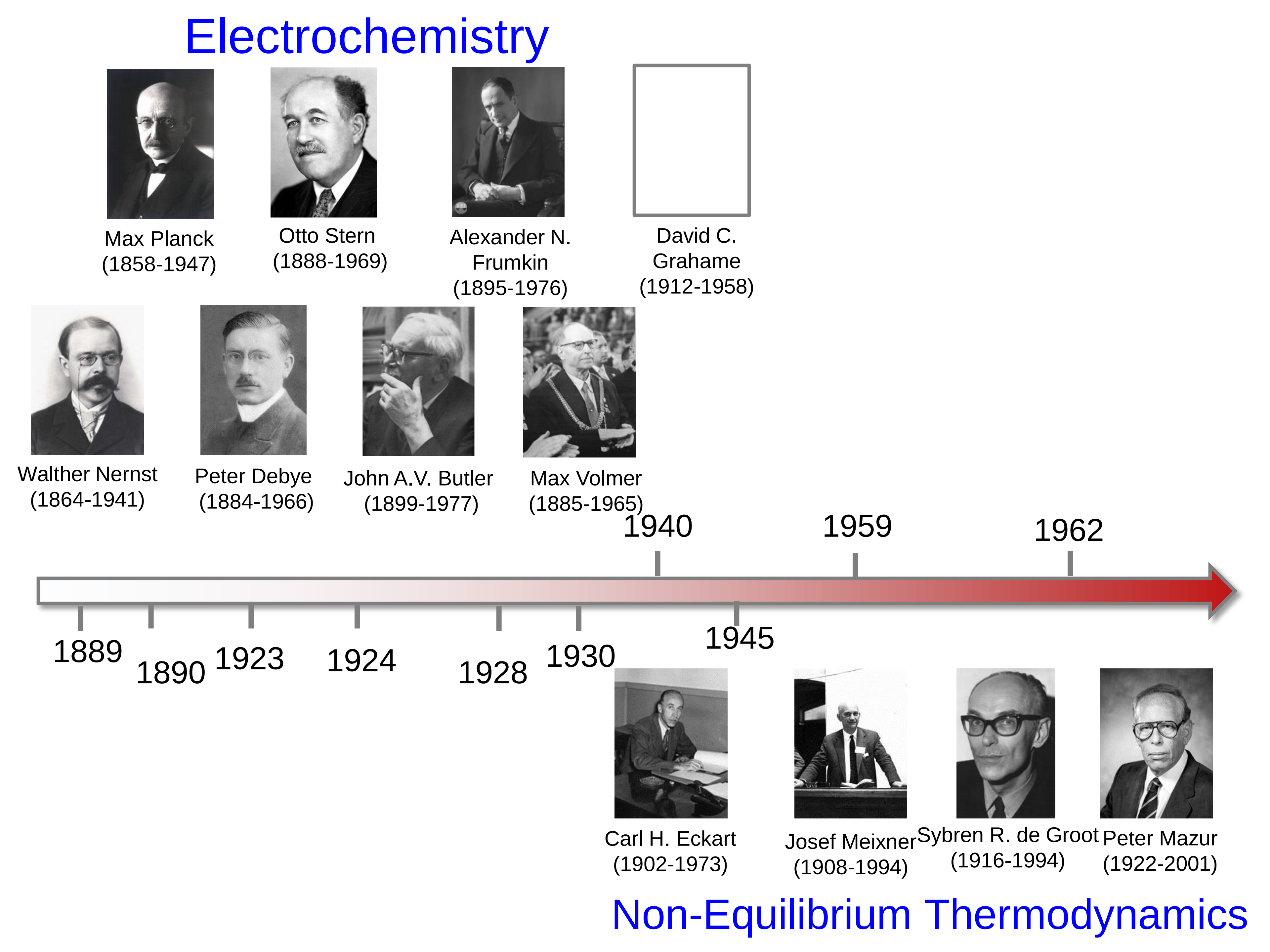
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Josef Meixner
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Peter Mazur
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Non-Equilibrium Thermodynamics

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No separation between universal laws and material depending relations ⇒ Models limited to specific

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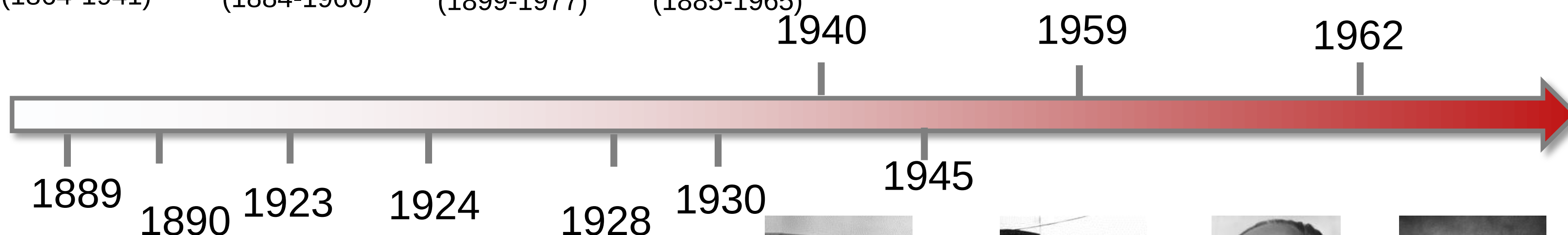
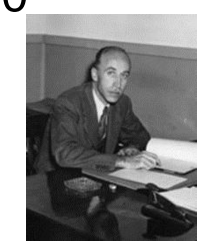


Missing coupling of electro- and thermodynamics for surfaces



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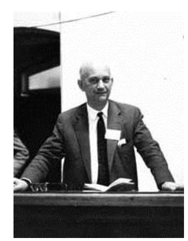

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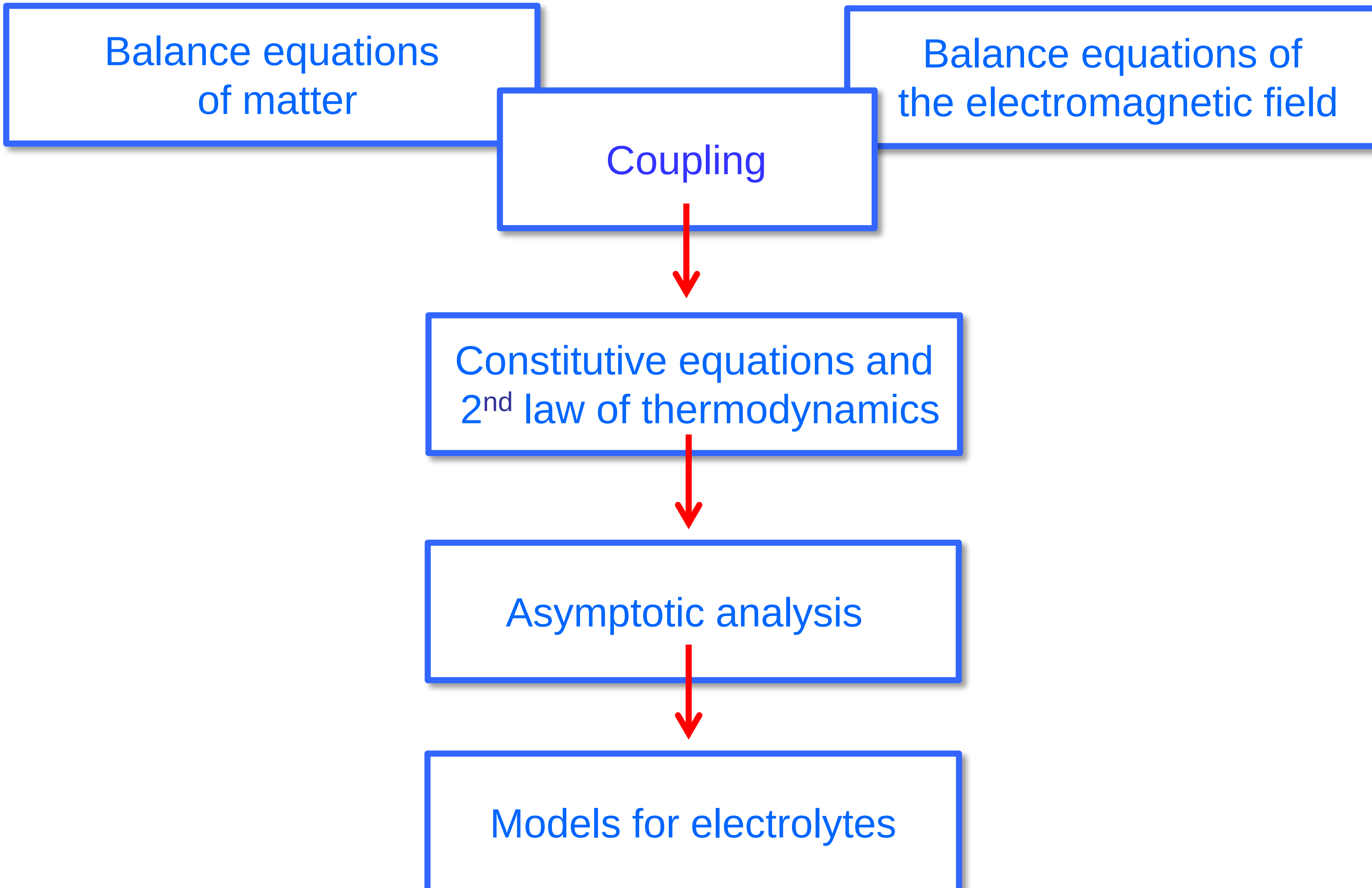
Non-Equilibrium Thermodynamics

Structure of Models



Variables

φ	electric potential
$(n_\alpha)_{\alpha=1,2,\ldots,N-1,N}$	particle densities
$\mathbf{v}$	barycentric velocity

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$(n_\alpha)_{\alpha=1,2,\ldots,N-1,N}$ particle densities

$\mathbf{v}$ barycentric velocity

Essential flaws of the Nernst-Planck model

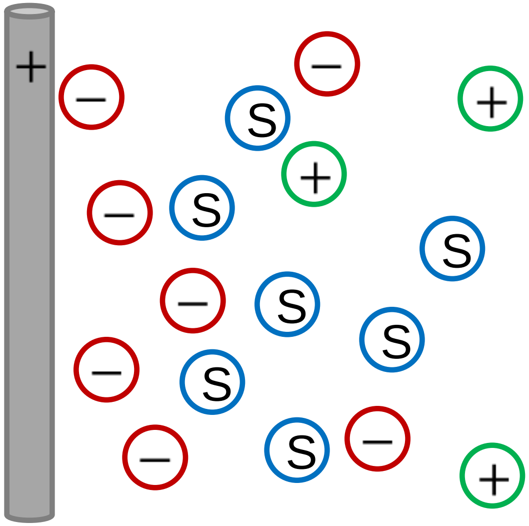
- The solvent and the barycentric velocity are ignored
- The pressure due to the constituents of the electrolyte is ignored
- The diffusion fluxes do not reflect the interaction of anions and cations with the solvent

Nernst-Planck, 1890

$$\mathbf{J}_\alpha = -M_\alpha^{\mathrm{NP}} \left(\nabla n_\alpha + \frac{z_\alpha e_0}{kT} n_\alpha \nabla \varphi\right) \qquad \text{for} \qquad \alpha = 1,2,\ldots,N-1$$

Dreyer, Guhlke, Müller, 2012

$$\mathbf{J}_\alpha = -M_\alpha^{\mathrm{NP}} \left(\nabla n_\alpha + \frac{z_\alpha e_0}{kT} n_\alpha \nabla \varphi - \frac{m_\alpha}{m_N}\frac{n_\alpha}{n_N}\nabla n_N + \frac{1}{kT}\left(1-\frac{m_\alpha}{m_N}\right)\frac{n_\alpha}{n^{\mathrm{R}}}\nabla p\right)$$



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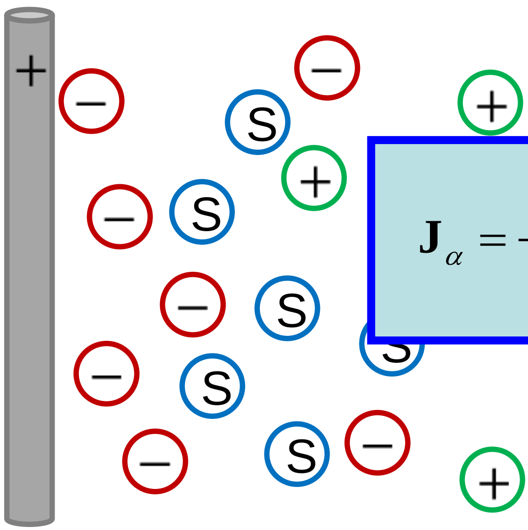

$$\mu_\alpha = \frac{\partial \rho\psi(T, n_1, n_2, \ldots, n_N, \nabla\varphi)}{\partial n_\alpha}$$

$$\mathbf{J}_\alpha = -\sum_{\beta=1}^{N-1} M_{\alpha\beta}\left(\nabla\left(\frac{\mu_\beta}{T} - \frac{\mu_N}{T}\right) + \frac{1}{T}\left(\frac{z_\beta}{m_\beta} - \frac{z_N}{m_N}\right)\nabla\varphi\right) \qquad \mathbf{J}_N = -\sum_{\alpha=1}^{N-1}\mathbf{J}_\alpha$$

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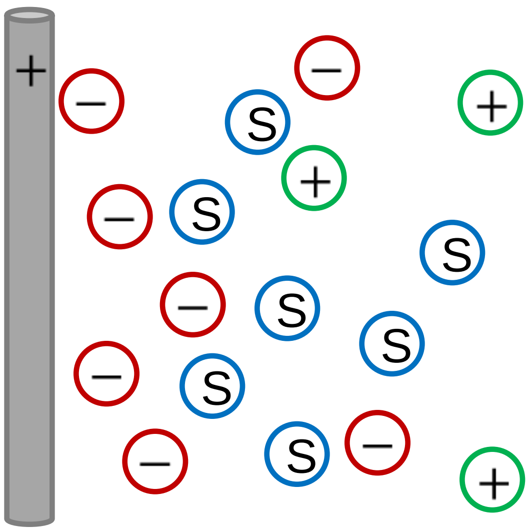

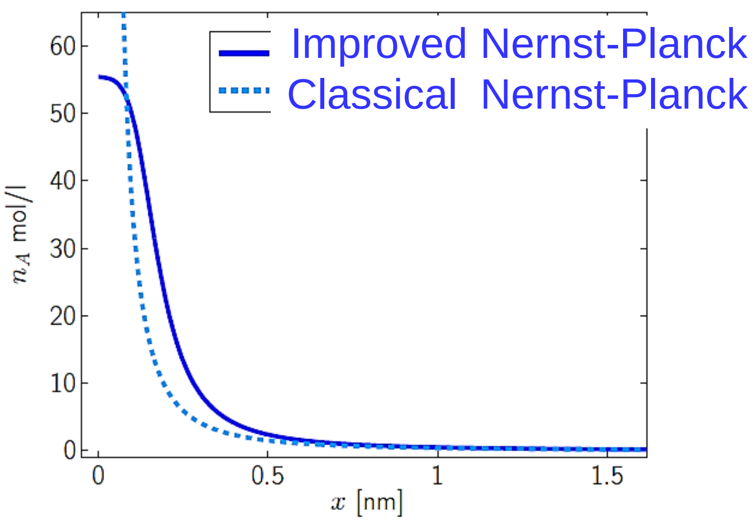

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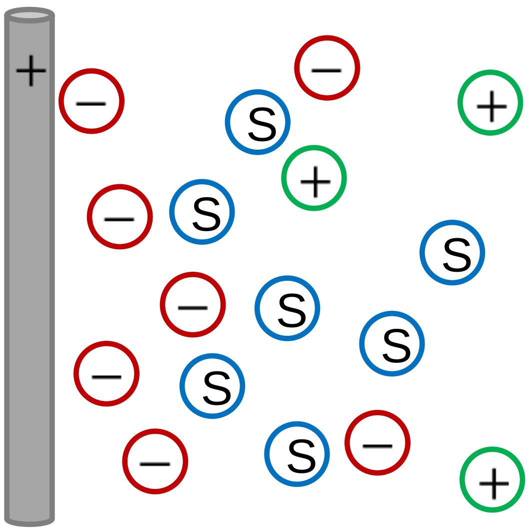

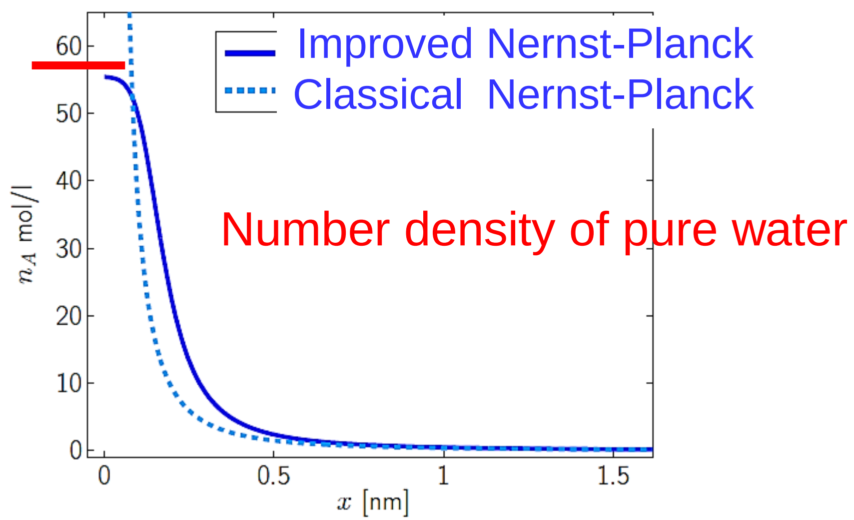

Example: Boundary Layer

Nernst-Planck, 1890

$$\mathbf{J}_\alpha = -M_\alpha^{\mathrm{NP}}\left(\nabla n_\alpha + \frac{z_\alpha e_0}{kT} n_\alpha \nabla\varphi\right) \qquad \text{for} \qquad \alpha = 1,2,\ldots,N-1$$

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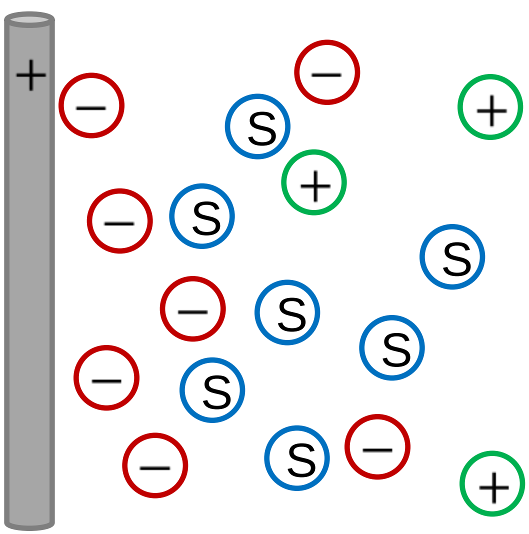
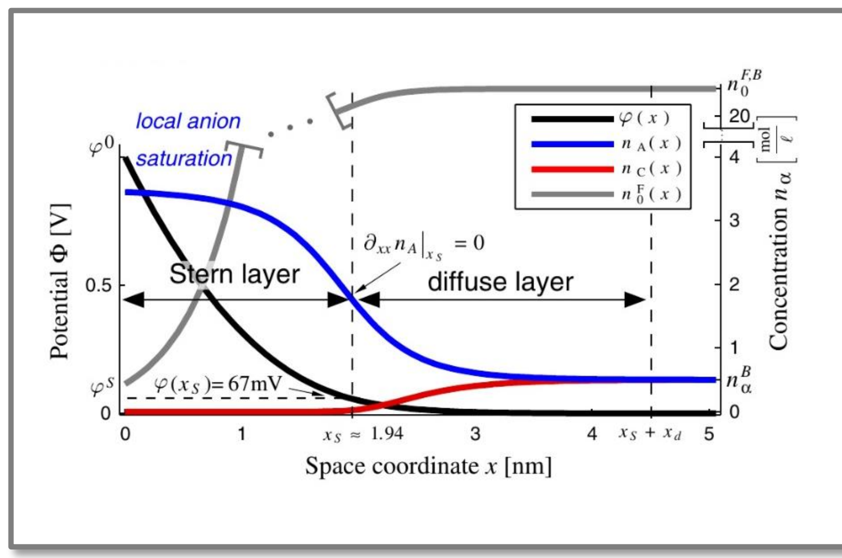




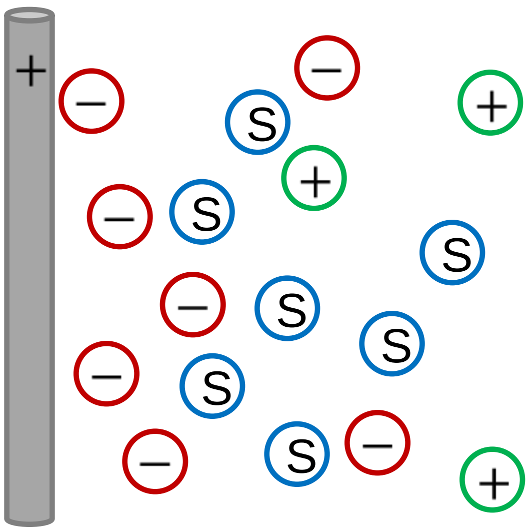
Example: Role of Elastic Pressure

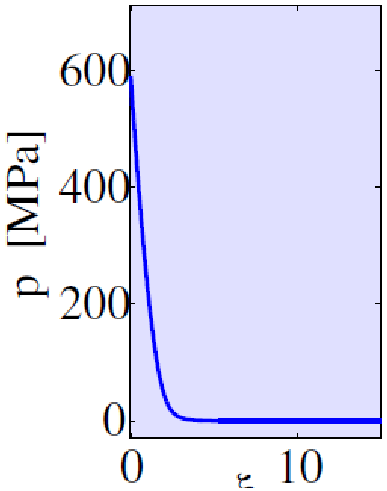
Nernst-Planck, 1890

$$\mathbf{J}_\alpha = -M_\alpha^{\mathrm{NP}} \left(\nabla n_\alpha + \frac{z_\alpha e_0}{kT} n_\alpha \nabla \varphi \right) \qquad \text{for} \qquad \alpha = 1, 2, \ldots, N-1$$

Dreyer, Guhlke, Müller, 2012

$$\mathbf{J}_\alpha = -M_\alpha^{\mathrm{NP}} \left(\nabla n_\alpha + \frac{z_\alpha e_0}{kT} n_\alpha \nabla \varphi - \frac{m_\alpha}{m_N} \frac{n_\alpha}{n_N} \nabla n_N + \frac{1}{kT} \left(1 - \frac{m_\alpha}{m_N}\right) \frac{n_\alpha}{n^{\mathrm{R}}} \nabla p \right)$$





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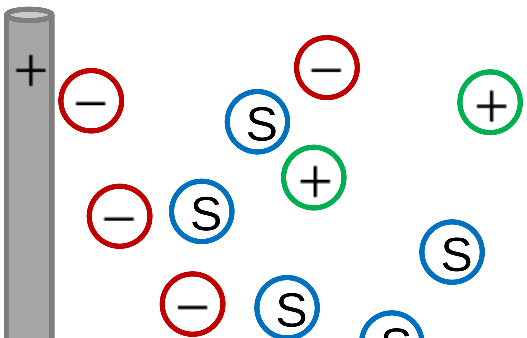
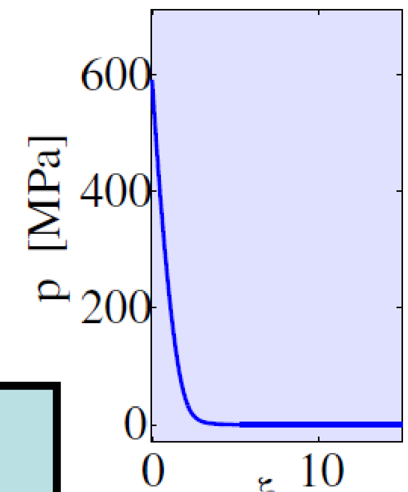


Recall

$$\mathbf{\Sigma} = -p + \varepsilon_0(1+\chi)\left(\nabla\varphi\otimes\nabla\varphi - \frac{1}{2}\left|\nabla\varphi\right|^2\mathbf{1}\right) = \text{constant} = 0.1\,\mathrm{MPa}$$



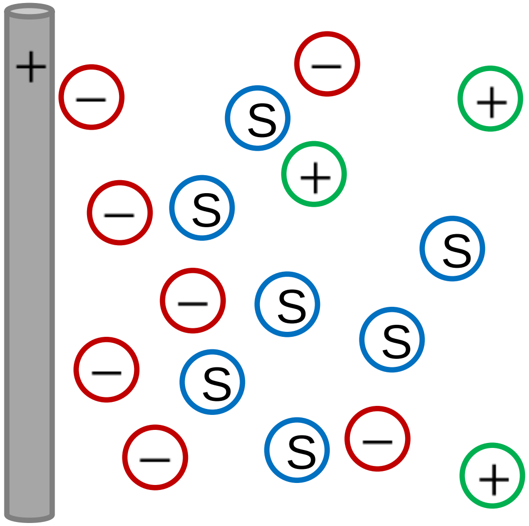
Example: Solvation Phenomenon

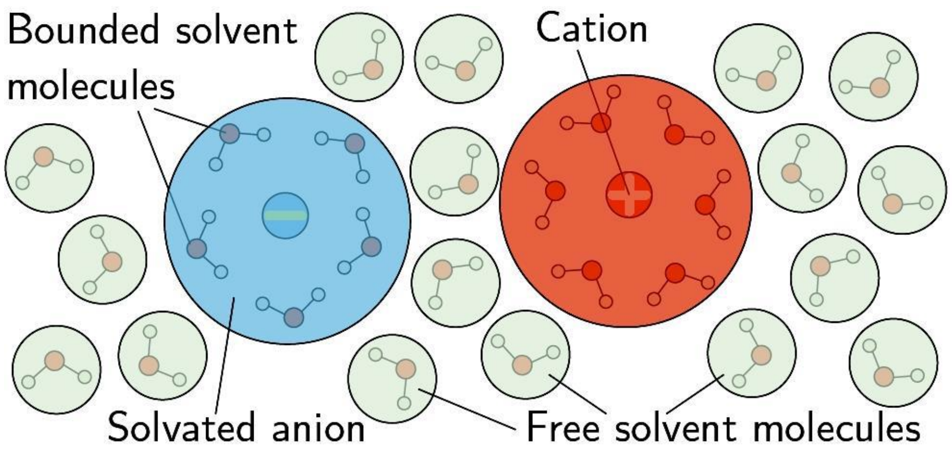
Nernst-Planck, 1890

$$\mathbf{J}_\alpha = -M_\alpha^{\mathrm{NP}} (\nabla n_\alpha + \frac{z_\alpha e_0}{kT} n_\alpha \nabla \varphi) \qquad \text{for} \qquad \alpha = 1,2,\ldots, N-1$$

Dreyer, Guhlke, Müller, 2012

$$\mathbf{J}_\alpha = -M_\alpha^{\mathrm{NP}} (\nabla n_\alpha + \frac{z_\alpha e_0}{kT} n_\alpha \nabla \varphi - \frac{m_\alpha}{m_N} \frac{n_\alpha}{n_N} \nabla n_N + \frac{1}{kT} (1 - \frac{m_\alpha}{m_N}) \frac{n_\alpha}{n^{\mathrm{R}}} \nabla p)$$





$$\Delta\varphi = -\frac{1}{\varepsilon_0} n^e \quad \text{with} \quad n^e = \sum_{\alpha=1}^{N} z_\alpha n_\alpha - \mathrm{div}(\mathbf{P})$$

$$\partial_t \rho\boldsymbol{\upsilon} + \mathrm{div}(\rho\boldsymbol{\upsilon} \otimes \boldsymbol{\upsilon} - \boldsymbol{\sigma}) = -n^e \nabla\varphi$$

$$\partial_t m_\alpha n_\alpha + \mathrm{div}(m_\alpha n_\alpha \boldsymbol{\upsilon} + \mathbf{J}_\alpha) = \sum_{i=1}^{N_\mathrm{R}} \mathrm{m}_\alpha \nu_\alpha^i (R_\mathrm{f}^i - R_\mathrm{b}^i) \qquad \alpha \in \{1, 2, \ldots, N\}$$

Variables

φ	electric potential
$(n_\alpha)_{\alpha=1,2,\ldots,N}$	particle densities
$\boldsymbol{\upsilon}$	barycentric velocity

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$$\rho = \sum_{\alpha=1}^{N} m_\alpha n_\alpha \qquad \rho\boldsymbol{\upsilon} = \sum_{\alpha=1}^{N} m_\alpha n_\alpha \boldsymbol{\upsilon}_\alpha \qquad \mathbf{J}_\alpha = m_\alpha n_\alpha (\boldsymbol{\upsilon}_\alpha - \boldsymbol{\upsilon}) \implies \sum_{\alpha=1}^{N} \mathbf{J}_\alpha = 0$$

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$$\partial_t \rho\boldsymbol{\upsilon} + \operatorname{div}(\rho\boldsymbol{\upsilon} \otimes \boldsymbol{\upsilon} - \boldsymbol{\Sigma}) = 0$$

$$\boldsymbol{\Sigma} = \boldsymbol{\sigma} + \varepsilon_0 (\nabla\varphi \otimes \nabla\varphi - \frac{1}{2} |\nabla\varphi|^2 \mathbf{1})$$

Constitutive model and 2nd law of thermodynamics

$$\Delta\varphi = -\frac{1}{\varepsilon_0}\left(\sum_{\alpha=1}^{N} z_\alpha n_\alpha - \operatorname{div}(\mathbf{P})\right)$$

$$\partial_t \rho\boldsymbol{\upsilon} + \operatorname{div}(\rho\boldsymbol{\upsilon}\otimes\boldsymbol{\upsilon} - \boldsymbol{\sigma}) = \left(\sum_{\alpha=1}^{N} z_\alpha n_\alpha - \operatorname{div}(\mathbf{P})\right)\nabla\varphi$$

$$\partial_t m_\alpha n_\alpha + \operatorname{div}(m_\alpha n_\alpha \boldsymbol{\upsilon} + \mathbf{J}_\alpha) = \sum_{i=1}^{N_\mathrm{R}} \mathrm{m}_\alpha \nu_\alpha^i (R_\mathrm{f}^i - R_\mathrm{b}^i) \qquad \alpha\in\{1,2,\dots,N\}$$

Variables

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$(n_\alpha)_{\alpha=1,2,\dots,N}$	particle densities
$\boldsymbol{\upsilon}$	barycentric velocity

$$\rho\psi = \rho\hat{\psi}(T,\rho_1,\rho_2,\dots,\rho_N,\nabla\varphi)$$

$$\mathbf{P} = \frac{\partial\rho\psi}{\partial\nabla\varphi} \qquad \mu_\alpha = \frac{\partial\rho\psi}{\partial\rho_\alpha}$$

$$\boldsymbol{\sigma} = -p\mathbf{1} - \nabla\varphi\otimes\mathbf{P} \qquad p = -\rho\psi + \sum_{\beta=1}^{N}\rho_\beta\mu_\beta$$

$$\mathbf{J}_\alpha = -\sum_{\beta=1}^{N-1} M_{\alpha\beta}\left(\nabla\left(\frac{\mu_\beta}{T} - \frac{\mu_N}{T}\right) + \frac{1}{T}\left(\frac{z_\beta}{m_\beta} - \frac{z_N}{m_N}\right)\nabla\varphi\right) \qquad \alpha\in\{1,2,\dots,N-1\}$$

$$R_\mathrm{b}^i = R_\mathrm{f}^i \exp\left(\frac{1}{kT}\sum_{\beta=1}^{N}\mathrm{m}_\beta \nu_\beta^i \mu_\beta\right)$$