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Activity based finite volume methods for generalised Nernst-Planck-Poisson systems

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Incompressible isothermal mixture of N ionic species with zero barycentric velocity

- Species N: electroneutral solvent

$$-\nabla\cdot\varepsilon\nabla\phi = q = F\sum_{\alpha=1}^{N} z_\alpha c_\alpha \qquad (1a)$$

$$\partial_t c_\alpha + \nabla\cdot\vec{N}_\alpha = 0 \qquad (\alpha = 1\dots N-1) \qquad (1b)$$

$$\vec{N}_\alpha = -\frac{D_\alpha}{RT} c_\alpha \left(\nabla\tilde{\mu}_\alpha + z_\alpha F\nabla\phi\right). \qquad (\alpha = 1\dots N-1) \qquad (1c)$$

$$\tilde{\mu}_\alpha = \mu_\alpha - \frac{M_\alpha}{M_N}\mu_N. \qquad (\alpha = 1\dots N-1) \qquad (1d)$$

$$\sum_{\alpha=1}^{N} c_\alpha = \bar{c} = \text{const} \qquad \text{species volume balance} \qquad (1e)$$

c_α	molar densities
μ_α	chemical potentials
$\tilde{\mu}_\alpha$	effective chemical potentials
$\mu_\alpha^\circ = \text{const}$	reference chemical potentials
$a_\alpha = \exp(\frac{\tilde{\mu}_\alpha - \mu_\alpha^\circ}{RT})$	activity
$\beta_\alpha = \frac{c_\alpha}{\bar{c}a_\alpha}$	inverse activity coefficient
$\vec{N}_\alpha$	molar fluxes $\left(\sum_{\alpha=1}^{N}\vec{N}_\alpha = 0\right)$
z_α	charge numbers ($z_N = 0$)
$\bar{c}$	summary concentration of mixture
ϕ	electrostatic potential
ε	dielectric permittivity
T	temperature
R	molar gas constant
F	Faraday constant
q	space charge
M_α	molar masses
D_α	diffusion coefficients

Ideal dilute solution ≡ Gouy Chapman double layer model ≡ Boltzmann statistics

$$\mu_\alpha = \mu_\alpha^\circ + RT\ln\frac{c_\alpha}{\bar{c}} \qquad (\alpha = 1\dots N-1)$$

$$\mu_N = 0$$

$$\tilde{\mu}_\alpha = \mu_\alpha^\circ + RT\ln\frac{c_\alpha}{\bar{c}} \qquad (\alpha = 1\dots N-1)$$

$$\beta_\alpha = \beta = 1 \qquad (\alpha = 1\dots N-1)$$

Free energy density which does not take into account the solvent:

$$\psi = \frac{1}{2}\varepsilon|\nabla\phi|^2 + RT\sum_{\alpha=1}^{N-1} c_\alpha\left(\ln\frac{c_\alpha}{\bar{c}} - 1\right).$$

- Ions are point charges
- Overestimation of physical maximum of ion concentrations

Bikerman-Freise model ≡ volume filling model

$$\mu_\alpha = \mu_\alpha^\circ + RT\ln\frac{c_\alpha}{\bar{c}} \qquad (\alpha = 1\dots N)$$

$$\tilde{\mu}_\alpha = \mu_\alpha^\circ + RT\ln\frac{c_\alpha}{\bar{c}} - RT\ln\frac{c_N}{\bar{c}} \qquad (\alpha = 1\dots N-1)$$

$$= \mu_\alpha^\circ + RT\ln\frac{c_\alpha}{\bar{c}} - RT\ln\left(1 - \sum_{\alpha=1}^{N-1}\frac{c_\alpha}{\bar{c}}\right) \qquad \text{due to (1e)}$$

$$\beta_\alpha = \beta = \frac{1}{1+\sum_{i=1}^{N-1} a_i} \qquad (\alpha = 1\dots N-1)$$

Free energy density which does take into account the solvent:

$$\psi = \frac{1}{2}\varepsilon|\nabla\phi|^2 + RT\sum_{\alpha=1}^{N} c_\alpha\left(\ln\frac{c_\alpha}{\bar{c}} - 1\right).$$

- Molar volume of each species is $v_\alpha = \frac{1}{\bar{c}}$
- Intrinsic limitation: $c_\alpha \le \bar{c}$

Activity based formulation

$$-\nabla\cdot\varepsilon\nabla\phi = q = F\bar{c}\sum_{\alpha=1}^{N-1} z_\alpha\beta_\alpha a_\alpha \qquad (2a)$$

$$\partial_t(\bar{c}\beta_\alpha a_\alpha) = -\nabla\cdot\vec{N}_\alpha \qquad (\alpha = 1\dots N-1) \qquad (2b)$$

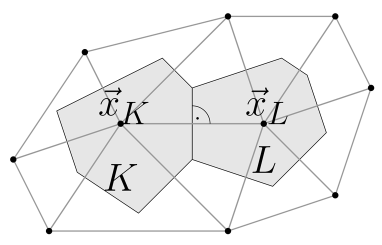
$$\vec{N}_\alpha = -D_\alpha\bar{c}\beta_\alpha\left(\nabla a_\alpha + a_\alpha z_\alpha\frac{F}{RT}\nabla\phi\right). \qquad (\alpha = 1\dots N-1) \qquad (2c)$$

Thermodynamic equilibrium: $\vec{N}_\alpha = 0$

$\mu_\alpha^\circ = 0$, $\psi_\alpha = \text{const}$: quasi-Fermi potential ⇒ nonlinear Poisson equation

$$-\nabla\cdot\varepsilon\nabla\phi = F\bar{c}\sum_{\alpha=1}^{N-1} z_\alpha\beta_\alpha\exp\left(\frac{z_\alpha F}{RT}(\psi_\alpha - \phi)\right)$$

Finite volume scheme consistent with equilibrium



Discrete continuity equation:

$$|K|\frac{c^n_{\alpha,K} - c^{n-1}_{\alpha,K}}{t^n - t^{n-1}} + \sum_{L \text{ neighbour of } K} |\partial K\cap\partial L| N^n_{\alpha,KL} = 0$$

Discrete flux – generalization of Scharfetter-Gummel scheme:

$B(\xi) = \frac{\xi}{\exp(-\xi)-1}$ – Bernoulli function, $Z_\alpha = z_\alpha\frac{F}{RT}$:

$$N_{\alpha,KL} = \bar{c}\overline{\beta_\alpha}_{KL}\frac{D\left(B(Z_\alpha(\phi_L - \phi_K))a_{\alpha,K} - B(Z_\alpha(\phi_K - \phi_L))a_{\alpha,L}\right)}{|\vec{x}_K - \vec{x}_L|}$$

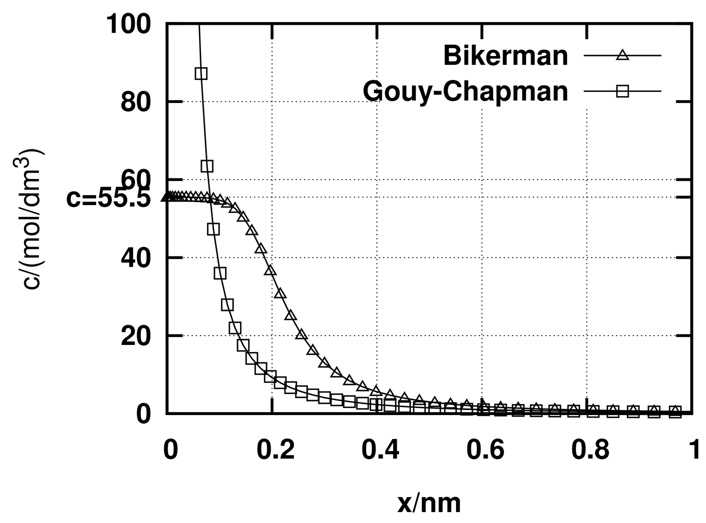
Discrete Poisson equation:

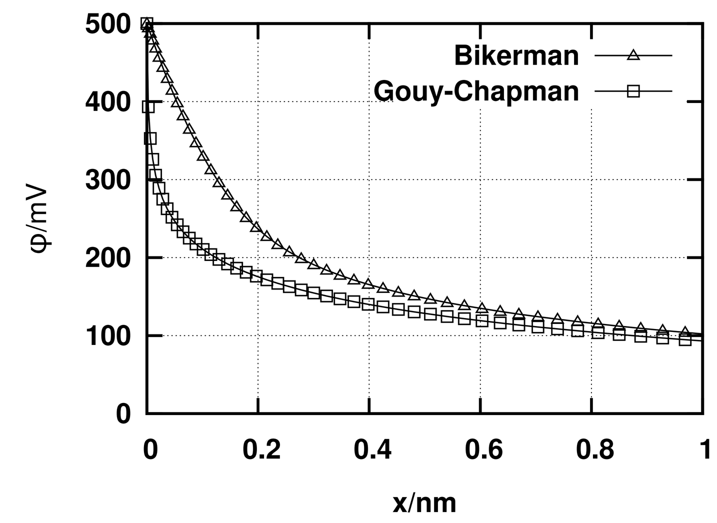
$$\sum_{L \text{ neighbour of } K} |\partial K\cap\partial L|\varepsilon\frac{\phi^n_K - \phi^n_L}{|\vec{x}_K - \vec{x}_L|} = |K|q(a_{1,K}\dots a_{N-1,K})$$

Theorem. *The solution of the discretized Nernst-Planck-Poisson system in thermodynamic equilibrium is equal to the solution of the discretized nonlinear Poisson equation.*

Numerical example: ideally polarizable electrode

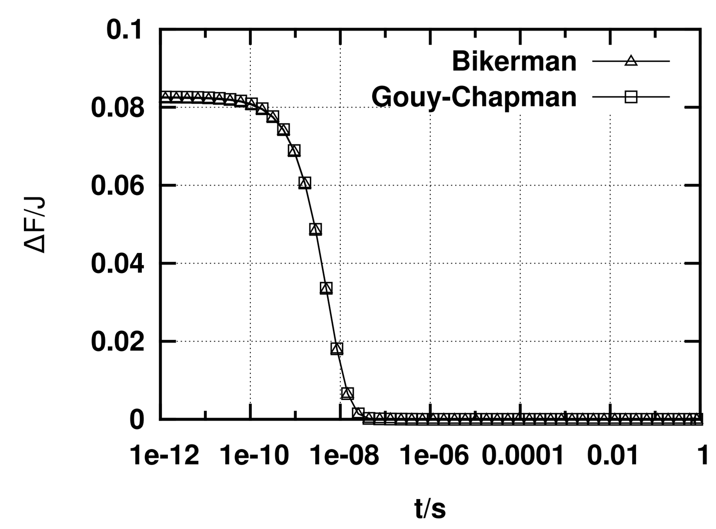
Aqueous binary 1:1 electrolyte with molarity of bulk solution $c_{\alpha,\infty} = c_\infty = 0.01\ mol/dm^3$ for $\alpha = 1,2$. $\bar{c} = 55.508\ mol/dm^3$ – molarity of water at standard conditions.





Negative ion concentration (left) and potential profile (right) with applied voltage $0.5\ V$.

Decay of relative free energy during double layer discharge



Decay of free energy to equilibrium value during discharge of double layer.

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