Streaming Potential And Streaming Current of a Particle Covered Surface

Part 2: virial expansion and simulations

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Overview

- Repetition
- System/Assumptions/Model
- Averaged streaming current/details

- Results
- Comparison with experiment
- Conclusions

Inspirers, Co-Workers

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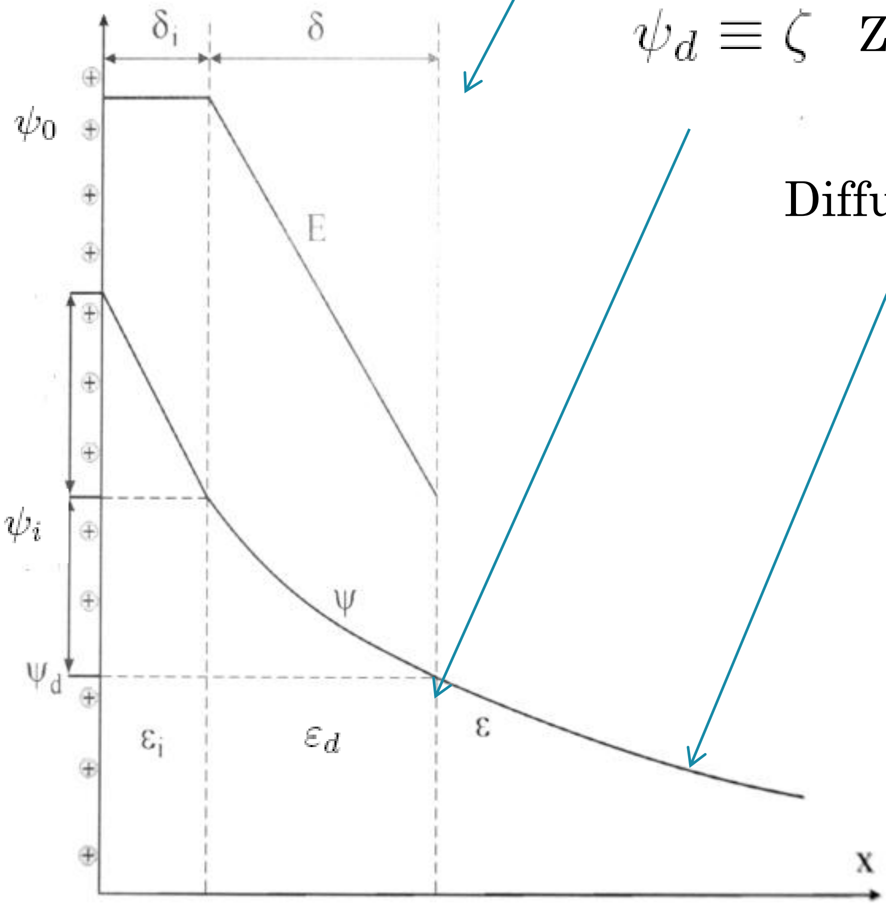
Repetition: Electrical Double Layer (EDL)



Stern layer

$\psi_d \equiv \zeta$ Zeta-potential

Diffuse layer

$$I_1 = -\frac{e\zeta}{\eta}\frac{\pi a^2}{L}\Delta p$$

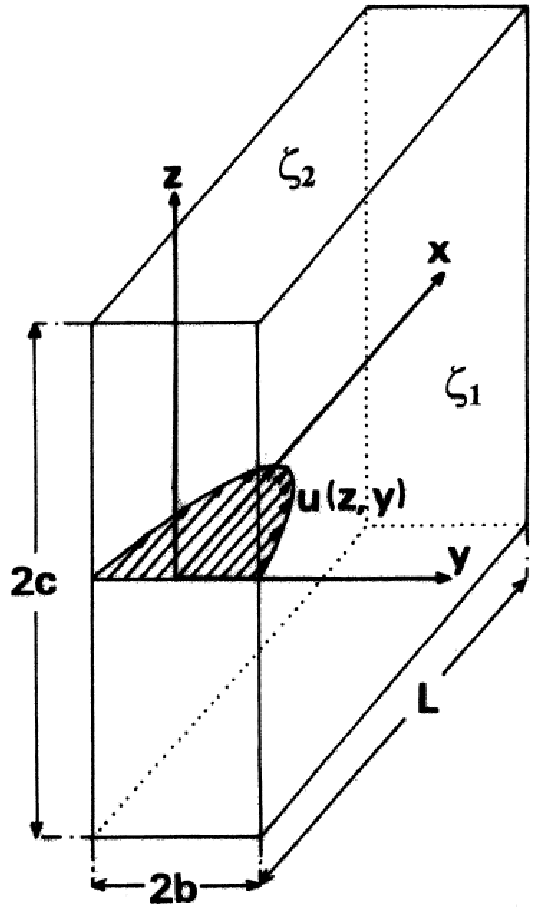
$$I_2 = K\pi a^2 E$$

Electrolite conductivity

$$E = \frac{\varepsilon\zeta}{\eta K}\frac{\Delta p}{L}$$

Streaming potential $\Delta\psi = \frac{\varepsilon\zeta}{\eta K}\Delta p$

SYSTEM

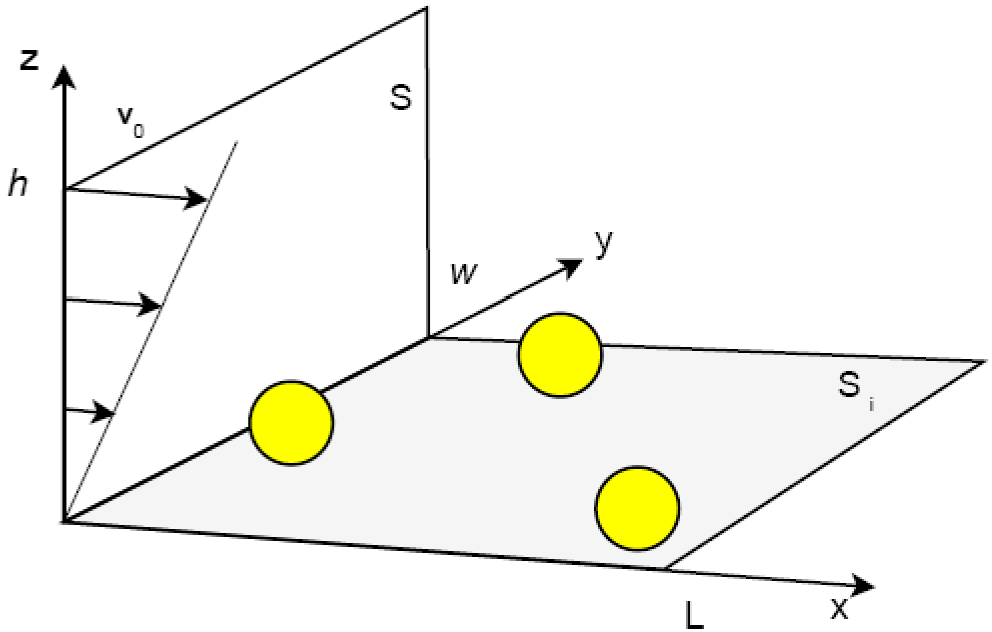


$$v = u(y, z)\boldsymbol{e}_x$$

Assumptions

- Charge density is a simple sum of the density induced due to the charged interface and charged particles.
- The induced electrostatic potential is nonzero only in the nearest vicinity of the charged surfaces. The Poisson equation is used separately for the interface and the individual sphere surfaces.
- The potential is a function only of the scalar distance from the considered surface (interface or sphere surface).
- The streaming current is generated in the vicinity of the wall only, therefore the ambient flow is well approximated by the shear flow
- The Poisson equation and the equation governing fluid motion are decoupled.
- $Re \ll 1$

Model



$$\mathbf{v}_0 = \dot{\gamma} z \mathbf{e}_{\mathbf{x}}.$$

Fundamental equations

Poisson equation:

$$\triangle\psi = -\frac{4\pi}{\epsilon}\rho,$$

Stokes equations:

$$\eta\boldsymbol{\nabla}^2\mathbf{v} - \boldsymbol{\nabla}p = \mathbf{0}, \quad \boldsymbol{\nabla}\cdot\mathbf{v} = 0,$$

$$I = \int_S \rho\mathbf{v}\cdot\mathbf{e_x}dS,$$

Streaming current

Particle-free surface

Integral over channel cross-section

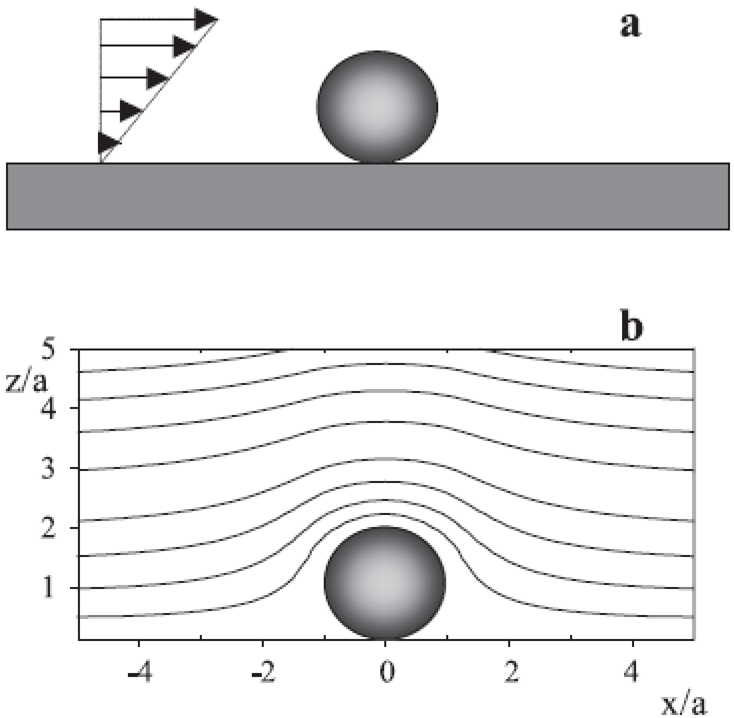
Streaming current:

$$
\begin{aligned}
I_0 &= -\frac{\epsilon}{4\pi}\int_S \frac{d^2\psi}{dz^2}\mathbf{v_0}(\mathbf{r})\cdot\hat{\mathbf{e}}_{\mathbf{x}}dydz \\
&= -\frac{\epsilon}{4\pi}\int_0^h \frac{d^2\psi}{dz^2}zdz\int_0^w \dot{\gamma}dy \\
&= -\frac{\epsilon\zeta_i\dot{\gamma}}{4\pi}w,
\end{aligned}
$$

Cross-section width

Particles adsorbed at surface

$$\mathbf{v}_0 = \dot{\gamma} z \mathbf{e_x}.$$



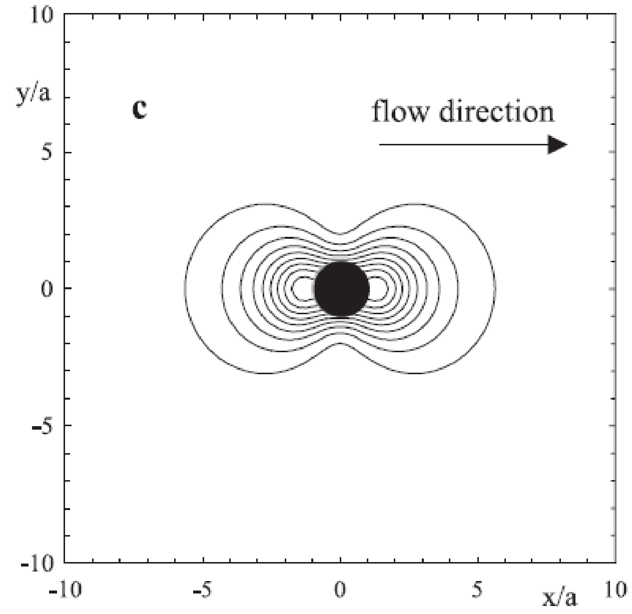
$$\mathbf{v} = \mathbf{v}_0 + \delta\mathbf{v},$$

Streaming current

$$I = \int_S \rho \mathbf{v} \cdot \mathbf{e_x} dS,$$

$$I = -\frac{\epsilon}{4\pi}\frac{1}{L}\int_0^L dx \int_0^w dy \int_0^h dz \frac{d^2\psi}{dz^2}\,\mathbf{v}(\boldsymbol{r})\cdot\boldsymbol{e}_x.$$

Expansion of fluid velocity



$$I = I_0 - \frac{\epsilon}{4\pi}\frac{1}{L}\left(\zeta_i \int_{S_i} \boldsymbol{e}_z\cdot\nabla\delta\mathbf{v}(\boldsymbol{r})\cdot\boldsymbol{e}_x dS_i + \zeta_p \sum_{k=1}^{N}\int_{S_{p_k}} \boldsymbol{n}_k(\boldsymbol{r})\cdot\nabla\mathbf{v}(\boldsymbol{r})\cdot\boldsymbol{e}_x dS_{p_k}\right),$$

Averaged streaming current

$$\frac{\langle I \rangle}{I_0} = 1 - B_i(\Theta)\Theta + \frac{\zeta_p}{\zeta_i} B_p(\Theta)\Theta,$$

$$B_i(\Theta) \; = \; -\frac{1}{\pi a^2 \dot{\gamma}} \left\langle \frac{1}{N} \int_{S_i} \boldsymbol{e}_z \cdot \nabla \delta \mathbf{v}(\boldsymbol{r}) \cdot \boldsymbol{e}_x dS_i \right\rangle ,$$

$$B_p(\Theta) \; = \; \frac{1}{\pi a^2 \dot{\gamma}} \left\langle \frac{1}{N} \sum_{k=1}^{N} \int_{S_{p_k}} \boldsymbol{n}_k(\boldsymbol{r}) \cdot \nabla \mathbf{v}(\boldsymbol{r}) \cdot \boldsymbol{e}_x dS_{p_k} \right\rangle$$

Calculation details

$$B_i(\Theta) = \frac{1}{\pi \eta a^2 \dot{\gamma}} \left\langle \frac{F}{N} \right\rangle$$

$$F = \sum_{i=1}^{N} F_k, \qquad \boldsymbol{F}_k = \int \boldsymbol{f}_k(\boldsymbol{r}) d\boldsymbol{r},$$

$$F_k = \boldsymbol{F}_k \cdot \boldsymbol{e}_x. \qquad \boldsymbol{f}_k(\boldsymbol{r}) = \delta(|\boldsymbol{r} - \boldsymbol{R}_k| - a)\ \boldsymbol{\sigma} \cdot \boldsymbol{n}_k.$$

Calculation details

$$B_p(\Theta) = \frac{1}{\pi \eta a^2 \dot{\gamma}} \left\langle \frac{H}{N} \right\rangle$$

$$H_k = \frac{1}{3a^2} Q_k - F_k \qquad Q_k = \boldsymbol{Q}_k \cdot \boldsymbol{e}_x,$$

$$\boldsymbol{Q}_k = 3 \int \left[2(\boldsymbol{r} - \boldsymbol{R}_k)^2 \boldsymbol{f}_k(\boldsymbol{r}) - (\boldsymbol{r} - \boldsymbol{R}_k)(\boldsymbol{r} - \boldsymbol{R}_k) \cdot \boldsymbol{f}_k(\boldsymbol{r}) \right] d\boldsymbol{r},$$

$$\boldsymbol{f}_k(\boldsymbol{r}) = \delta(|\boldsymbol{r} - \boldsymbol{R}_k| - a)\, \boldsymbol{\sigma} \cdot \boldsymbol{n}_k.$$

Virial expansion

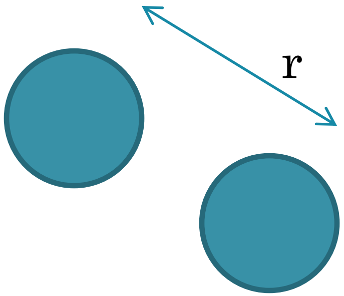
$$B_i(\Theta) = C_{1i}^0 - C_{2i}^0\Theta + \left(C_{3i}^0 - C_{3i}^1\right)\Theta^2 + \mathcal{O}(\Theta^3),$$

$$B_p(\Theta) = C_{1p}^0 - C_{2p}^0\Theta + \left(C_{3p}^0 - C_{3p}^1\right)\Theta^2 + \mathcal{O}(\Theta^3).$$

Surface particle coverage: $\Theta = \dfrac{\pi a^2 N}{S_i}.$

Pair-Correlations

$$g(\boldsymbol{r}) = g_0(\boldsymbol{r}) + \Theta g_1(\boldsymbol{r}) + \dots,$$



$$g_0(\boldsymbol{r}) = \begin{cases} 1 & \text{for} \quad r \geq 2a, \\ 0 & \text{for} \quad r < 2a, \end{cases}$$

$$g_1(\boldsymbol{r}) = \begin{cases} 0 & \text{for} \quad 0 \leq r < 2a, \\ \frac{8}{\pi} \arccos(\frac{r}{4a}) - \frac{1}{\pi}\frac{r}{a}\sqrt{4 - (\frac{r}{2a})^2} & \text{for} \quad 2a \leq r < 4a, \\ 0 & \text{for} \quad r \geq 4a. \end{cases}$$

Cluster expansion

$$\mathcal{F}_1(1,\ldots,N) = \mathcal{F}_1^{(1)}(1) + \sum_{l=2}^{N} \mathcal{F}_1^{(2)}(1,l) + \\ + \sum_{1<l<m}^{N} \mathcal{F}_1^{(3)}(1,l,m) + \ldots,$$

$$\begin{aligned}
\mathcal{F}_1^{(1)} &= \mathcal{F}_1(1), \\
\mathcal{F}_1^{(2)}(1,l) &= \mathcal{F}_1(1,l) - \mathcal{F}_1(1), \\
\mathcal{F}_1^{(3)}(1,l,m) &= \mathcal{F}_1(1,l,m) - \mathcal{F}_1(1,l) + \\
&\quad - \mathcal{F}_1(1,m) + \mathcal{F}_1(1),
\end{aligned}$$

Virial Coefficients

$$C_{1i}^{0} = 6\mathcal{F}_1,$$
$$C_{1p}^{0} = 6\mathcal{H}_1,$$

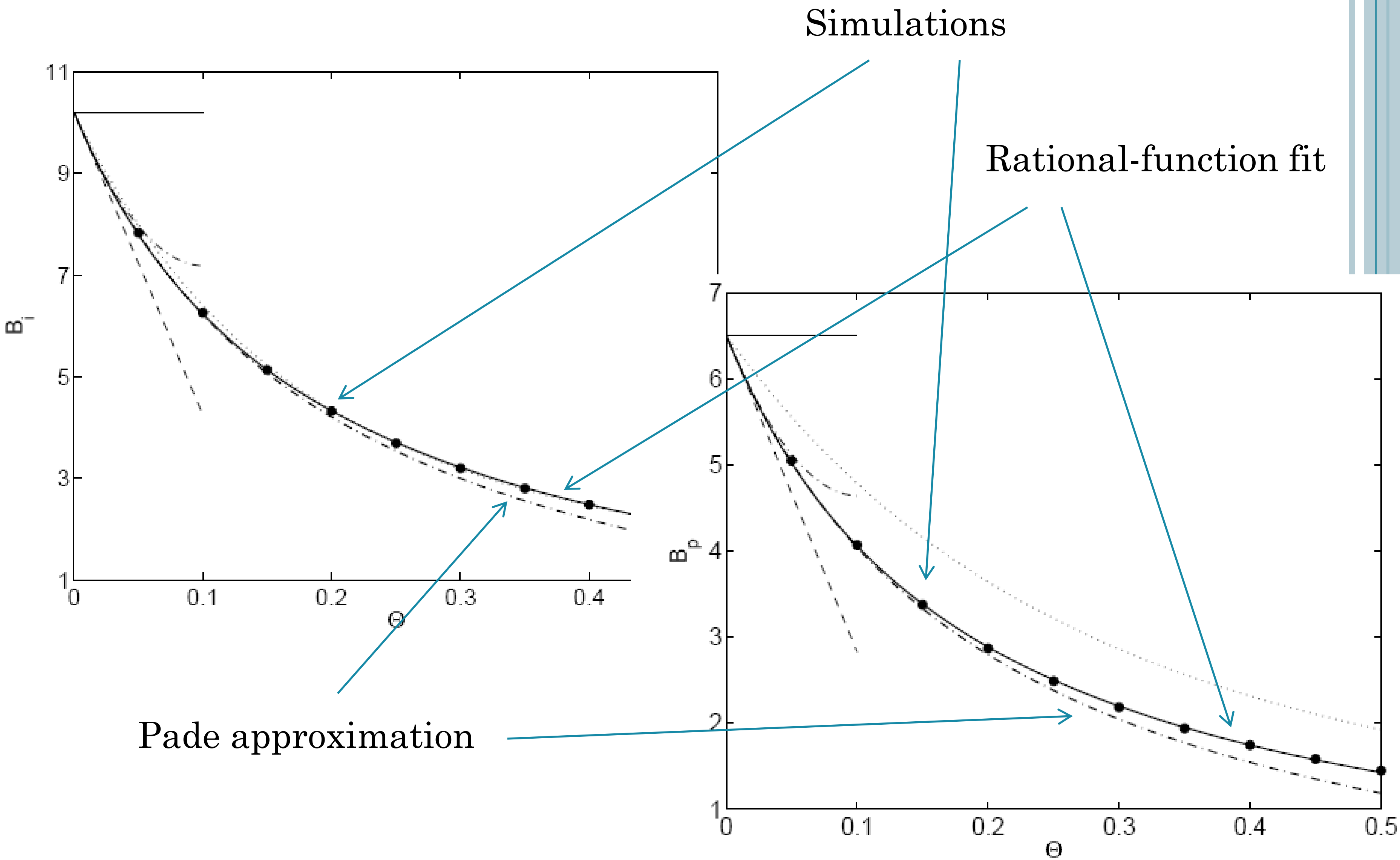
Multipole method
HYDROMULTIPOLE algotithm

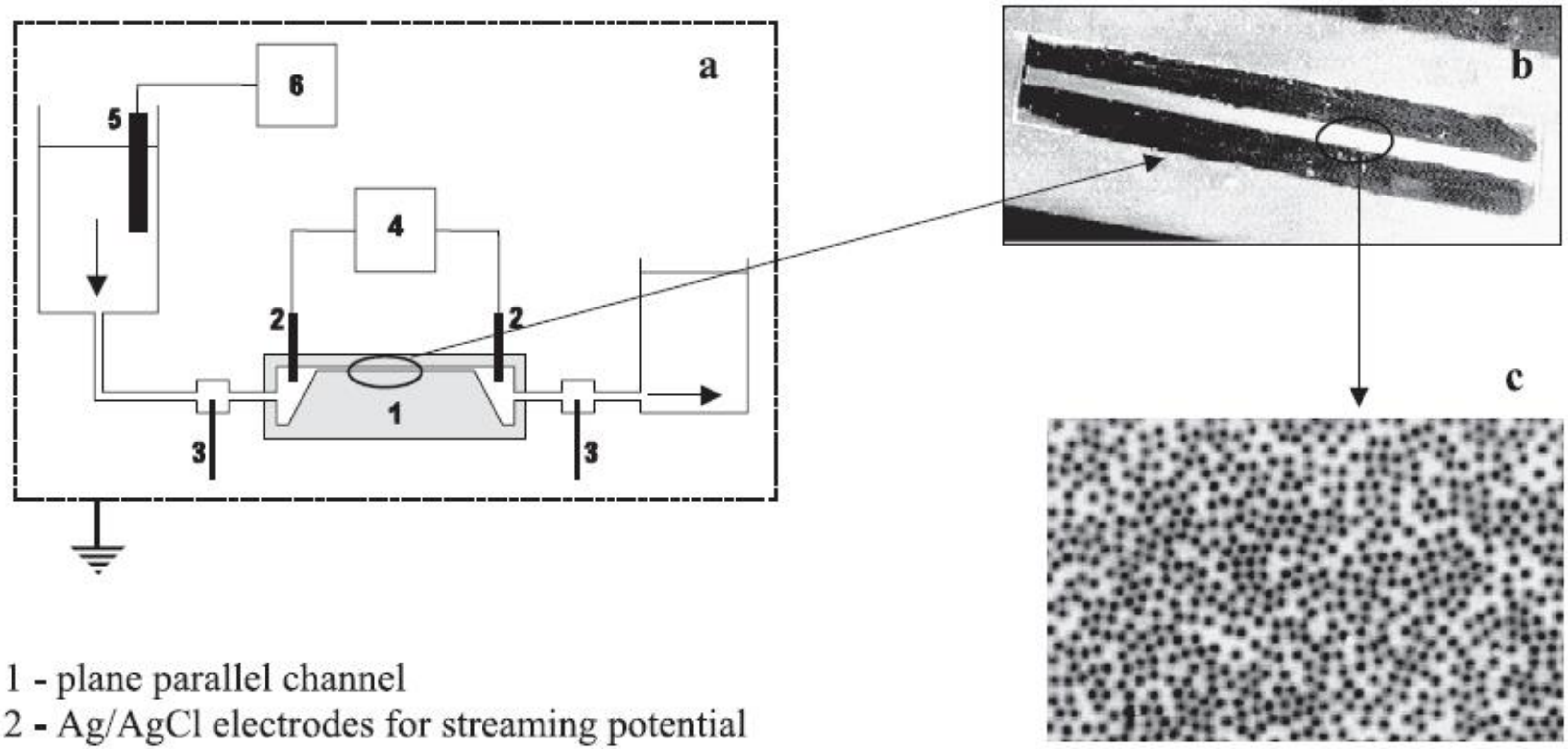
$$C_{2i}^{0} = -\frac{3}{\pi}\int d\boldsymbol{r}_{12} g_0(\boldsymbol{r}_{12})\left(\mathcal{F}_1^{(2)}(12)+\mathcal{F}_2^{(2)}(12)\right)$$
$$C_{2p}^{0} = -\frac{3}{\pi}\int d\boldsymbol{r}_{12} g_0(\boldsymbol{r}_{12})\left(\mathcal{H}_1^{(2)}(12)+\mathcal{H}_2^{(2)}(12)\right)$$

$$C_{3i}^{1} = -\frac{3}{\pi}\int_{2\le r_{12}\le 4} d\boldsymbol{r}_{12} g_1(\boldsymbol{r}_{12})\left(\mathcal{F}_1^{(2)}(12)+\mathcal{F}_2^{(2)}(12)\right)$$
$$C_{3p}^{1} = -\frac{3}{\pi}\int_{2\le r_{12}\le 4} d\boldsymbol{r}_{12} g_1(\boldsymbol{r}_{12})\left(\mathcal{H}_1^{(2)}(12)+\mathcal{H}_2^{(2)}(12)\right)$$

RESULTS

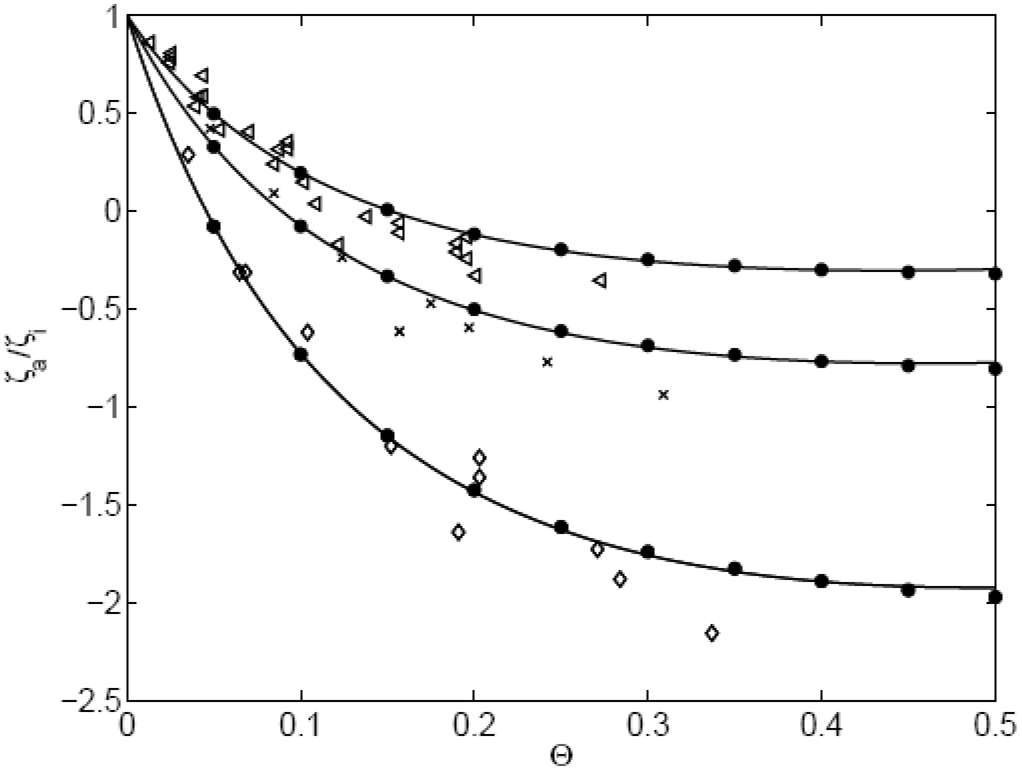
$$B_q(\Theta) = \frac{C^0_{1q} + a_q\,\Theta}{1 + b\,\Theta},$$
$$b \;=\; 5.46 \pm 0.02.$$





1 - plane parallel channel
2 - Ag/AgCl electrodes for streaming potential measurements
3 - electrodes for cell resistance determination
4 - Keithley electrometer
5 - conductivity cell
6 - conductometer

Comparison with experiment



$$\zeta_p/\zeta_i = -0.44, -1.11, -2.72$$

$$\frac{\zeta_a}{\zeta_i} = 1 - B_i(\Theta)\Theta + \frac{\zeta_p}{\zeta_i}B_p(\Theta)\Theta$$

Conclusions

- Adsorbed particles change the streaming current/potential significantly, even if the particles are not charged
- Virial expansion is slowly covergent – this behaviour well described by the Pade approximation
- Simulation results fit rational function with pole at negative particle surface coverage