Electrophoresis of Charged Macromolecules

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The analytical description of charged colloidal suspensions is problematic:

- Long ranged interactions: electrostatics/hydrodynamics
- Inhomogeneous/asymmetrical systems
- Many-body interactions

**Alternative**: the relevant microscopic degrees of freedom are simulated via Molecular Dynamics!

- Explicit particles (ions) with charges
- Implicit solvent approach, but hydrodynamic interactions of the solvent are included via a Lattice–Boltzmann algorithm
Test of LB implementation for Poiseuille

Simulation box of size $80 \times 40 \times 10$. Velocity profile for a Poiseuille flow in a channel, which is tilted by $45^\circ$ relative to the Lattice-Boltzmann node mesh. Computed using ESPResSo.

Profile of the absolute fluid velocity of the Poiseuille flow in the $45^\circ$ tilted channel. Red crosses represent simulation data, the blue line is the theoretical result and the dashed blue line represents the theoretical result, using the channel width as a fit parameter.
EOF in a Slit Pore

Simulation results for a water system. Solid lines denote simulation results, the dotted lines show the analytical results for comparison. Red stands for ion density in particles per nm$^3$, blue stands for the fluid velocity in x-direction, green denotes the particle velocity. All quantities in simulation units.
Colloidal Electrophoresis

Electric field $E$

Local force balance $F_E = F_{\text{Drag}}$ leads to stationary state

$$F_E = Z_{\text{eff}} E$$

Observable: mobility $\mu$

$$\mu = \frac{\nu}{E} = \frac{Z_{\text{eff}}}{\gamma_{\text{eff}}}$$

Reduction mobility $\mu_{\text{red}} = 6\pi \eta \ell_B \mu$

Viscosity $\eta$  
Bjerrum length $\ell_B = \frac{e^2}{4\pi \varepsilon k_B T}$
Dimensional Analysis

\[ \mu_{\text{red}} = \mu_{\text{red}}(\kappa R, \tilde{Z}, \tilde{D}_i, f_i, l_B/R) \]

dependence seems weak:
effects of salt and of counterions are similar

\[ \tilde{Z} = Zl_B / R \]

\( D_i \): collective diffusion coefficient

\[ \kappa^2 = 4\pi l_B \sum z_i^2 c_i \]

\[ f_i = c_i \left( \frac{\sum z_j^2 c_j}{\sum c_j} \right) \]
Fig. 3.—Reduced mobility $E$ of a spherical colloidal particle in a KCl solution as a function of reduced zeta potential $y$, for $\kappa a \leq 2.75$. In this regime the mobility appears to increase monotonically with zeta potential.
The point is academic however since the method, presented in the previous sections of this paper, enables a rapid, exact numerical solution to the general mobility problem.* Thus the chemist, armed with this computer program can generate mobility as a function of zeta potential for the Ka value, the particular electrolyte solution, and temperature of interest to himself. In view of this, the utility of displaying graphs of $p(\zeta, K_a)$ for restricted electrolyte systems, as a conversion aid for the experimentalist, seems marginal.

![Figure 4](image-url)

**Fig. 4.**—Variation of mobility in KCl with zeta potential for $\kappa a > 3$. In this case the mobility curves have a maximum.
Fig. 5.—Maximum mobility of a spherical particle in KCl as a function of $\kappa a$.

$a=R$ in lecture notes notation
FIG. 6.—Effect of counterion valency on the form of the mobility against zeta potential curves, for $\kappa a = 5$. 

![Graph showing the effect of counterion valency on mobility against zeta potential for KCl, Ba(NO$_3$)$_2$, and LaCl$_3$.](image)
Electro-Hydrodynamical Model

- charged colloid
- driven system (external constant E-field)
- 1 central Lennard-Jones (LJ) bead
- 100 LJ monomers on the surface, connected to a network via FENE bonds
- counterions: LJ beads

simulation=> lattice (implicit) hydrodynamics
Langevin MD + Lattice-Boltzmann algorithm
periodic boundary conditions
Ewald sum: $P^3M$

Ionic Distribution around the Colloid
the ions within the shear plane renormalize the charge \( Z \) to \( Z_{\text{eff}} \)
Mobility is calculated at zero field with the Green-Kubo integral: linear regime

\[ \mu = \frac{1}{3k_B T} \sum_i Z_i \int_0^\infty dt \langle \vec{v}_c(t) \cdot \vec{v}_i(0) \rangle \]
Comparison to Experiments

\[ Z_{\text{Eff}} = 20 - 30, \ R = 2.2 \ \text{nm} \]

\[ \kappa R_{\text{eff}}^2 = 4 \pi \ell_B \left(n_{\text{salt}} + n_M Z_{\text{eff}} + n_{H,OH} \right) \]

V. Lobaskin, B. Dünweg, M. Medebach, T. Palberg, CH, PRL 98, 176105 (2007)
Salt and Concentration Effects

Salt-free Simulations at finite $\Phi$ can be mapped to simulations including salt
Colloidal Electrophoresis

Simulation snapshot
Ionic Strength, [M]

Planar

R = 5 nm
R = 20 nm
R = 100 nm
R = 400 nm

reduced ζ-potential
The simulation results with and without LJ attraction are shown via lines indicating SEM calculations using GC and spherical PB solutions, whereas the dashed and dotted lines indicate calculations based on GC solutions, respectively. The decrease out of phase (phase offset is 225 degrees) with respect to the potential drop between the bulk and the location of the shear plane, which is in agreement with the SEM and previous findings.

The measurements for each valency are carried out with the very same negatively charged PS colloid (diameter: 2 µm). The field strength is varied in the range 1–18 V/m. The laser power is 0.2 W. The field strength is observed for CaCl₂ trivalent salt, the experimental results show a mobility reversal, which is in agreement with the SEM and previous findings.

Using the experimentally determined colloidal surface charge density, the counterion valency, needs to be larger than 10 to produce charge inversion by pure electrostatic correlation effects, while obviously, the colloidal surface charge density is too low to produce the experimentally observed mobility reversal. This could have been expected, however, no model in the monovalent and divalent cases [see Fig. 5(a)] successfully describes the experimental results significantly. The electrophoretic mobility is eventually pronounced monotonic decrease of the mobility with increasing ionic strength is observed in the trivalent case. This could have been expected, however, no model in the monovalent and divalent cases [see Fig. 5(a)]. Squares represent the peak area and the full curves are at least qualitatively reproducible without further amendments to the restricted primitive model in the monovalent and divalent cases [see Fig. 5(a)], whereas the decrease out of phase (phase offset is 225 degrees) with respect to the potential drop between the bulk and the location of the shear plane, which is in agreement with the SEM and previous findings.

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Figure 2: Electrophoretic mobility as a function of ionic strength for monovalent (KCl), divalent (CaCl$_2$) and trivalent (LaCl$_3$) salt solutions. Experimental results, black squares, are from Semenov et al.$^{10,31,32}$ for latex colloids of diameter 2.23 µm and surface charge density $-0.31 \, \mu C/cm^2 \approx -0.02 \, e/nm^2$. Simulation results are represented via blue circles (WCA interaction) and red filled circles (full LJ interaction). The dashed and dotted lines represent calculations based on the numerical solution to the nonlinear planar and spherical PB, respectively. In the trivalent case, the red solid line represents the PB solution including the full LJ interaction between the counterions and the surface. Data taken from.$^{10}$
Comparison to other Experimental Data

Figure 4: Electrophoretic mobility as a function of ionic strength of monovalent (KCl), divalent (CaCl$_2$) and trivalent (LaCl$_3$) electrolyte. Simulation results, represented via blue (WCA) and red filled circles (full LJ), are compared to the experimental results of Elimelech et al. with latex colloids of diameter 0.753 µm and surface charge density $-5.64 \, \mu C/cm^2 \approx -0.35 \, e/nm^2$. The dashed and dotted lines represent calculations based on the numerical solution to the nonlinear planar and spherical PB, respectively. In the trivalent case, the red solid line represents the PB solution including the full LJ interaction between the counterions and the surface.
Conclusions

- Successful mapping of simulations of charged colloidal electrophoresis onto experimental values

- Colloidal concentration can be mapped on salt concentration

- Intriguing minimum observed in $\mu_{\text{red}}$ as function of $\kappa R$

- SEM works well, even for multivalent salt solutions if combined with Simulations for determining the zeta potential

- In specific effects (non-electrostatic attraction) might be important for some ion species (here La$^{3+}$)
Electrophoresis of Polyelectrolytes

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Outline

- Coarse-grained simulation model for electrophoresis with and without HI
- Results on diffusion & mobility compared to experiments
- Effective charge estimators
- Effective friction of polyelectrolytes in free-solution electrophoresis
- ELFSE
- Electrophoresis of charged colloids
Why care about electrophoresis?

- Electrophoretic separation of DNA
  - Crucial step is gene analysis
  - Yields characteristic genetic fingerprints
- Today: Gel Electrophoresis based on entanglement
  - Widely applicable and reliable
  - Slowed down dynamics leads to long elution times
- Future: Novel separation techniques based on hydrodynamic and chemical interactions
  - Micro-fluidic devices with structured surfaces
  - On-going design and development process

**First Goal:** Understand free-flow Electrophoresis
Free-Flow Electrophoresis

- Charged polymers move in solution under the influence of an external electric field.
- Local force balance leads to constant velocity.
  - Electrical driving force
  - Solvent friction force
- Electrophoretic mobility $\mu$
  - Size dependence of $\mu$ (N) determines separation process.

$$F_E = Q_{\text{eff}} E$$
$$F_{\text{Drag}} = \Gamma_{\text{eff}} \nu$$

$$\mu = \frac{\nu}{E} = \frac{Q_{\text{eff}} (N)}{\Gamma_{\text{eff}} (N)}$$
Short and long polyelectrolytes

- **Short PE chains:**
  - Extended rod-like conformation
  - Length dependent mobility

- **Long PE chains:**
  - Random coil conformations
  - Screening of long range hydrodynamic interactions
  - Length independent mobility (free-draining)

**Experimental observations:**

- Crossover:
  - DNA: $N_{FD} \sim 170$ bp
  - PSS: $N_{FD} \sim 100$ units
Short and long polyelectrolytes

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**Experimental observations:**

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  - DNA: $N_{FD} \sim 170$ bp
  - PSS: $N_{FD} \sim 100$ units

**Not understood**
Model

- No chemical details
  - Charged subgroups connected along a backbone by elastic springs
  - Ions modeled as free mobile charges

- Implicit solvent model
  - Continuous dielectric background
  - Explicit charges treated with full electrostatics via P3M in p.b.c.
  - Explicit hydrodynamics by frictionally coupling the beads to a Lattice-Boltzmann fluid
  - Can simulate with HI and without HI (Langevin)
LB-Hydrodynamics

- Lattice Boltzmann equation
  - streaming and collision
  - discrete set of velocity populations
- D3Q18 scheme
- hydrodynamic fields from populations
Hydrodynamics via LB

- Frictional coupling of MD particles to Lattice Boltzmann fluid [1]
  - Modified Langevin equation:
    \[
    m \frac{\vec{v}_i}{dt} = \vec{F}_i - \Gamma (\vec{v}_i - \vec{u}_{LB}) + \vec{F}_r(t)
    \]
  - Momentum exchange between immersed particles and fluid
  - Total momentum conservation

Hydrodynamic interactions


Current D3Q19 Version with correct fluctuation spectrum due to Schiller, Duenweg implemented in ESPResSo
Observables

- (Self-)Diffusion $D$

\[
D = \frac{k_B T}{\gamma_{\text{eff}}} \quad D = \frac{1}{3} \int_0^\infty d\tau \langle \vec{v}(\tau) \vec{v}(0) \rangle
\]

- Electrophoretic mobility $\mu$

\[
\mu = \frac{\nu}{E} = \frac{q_{\text{eff}}}{\gamma_{\text{eff}}} \quad \mu = \frac{\langle \nu_{PE} \rangle}{E}
\]

- Zero-field mobility (Green-Kubo):

\[
\mu = \frac{1}{3k_B T} \sum_i \int_0^\infty \langle \vec{V}_i(0) \cdot \vec{v}_{PE}(\tau) \rangle d\tau
\]
Simulation parameters

- Mapping on **sulfonated polystyrene** (PSS)
- All beads have diameter of 2.5 Ångström
- Chain length $N=1 \ldots 64$
- $l_b = 7.1$ Ångström ($\text{H}_2\text{O}$ at $20^\circ \text{C}$)
- Monomer concentration 100 mMol
- No added salt
- Experimental conditions:
  - Böhme, Scheler, IPF Dresden, PFG-NMR
Results 1: Diffusion

Electrophoretic mobility

Effect of HI

Salt dependence $c_s$ of Mobility

with hydrodynamical interactions (HI)

Maximum reproduced

No maximum

Independent of $c_s$
Polyelectrolyte-ion-complex
Hydrodynamic Friction

- Important quantity to characterize PEs
- Effective friction for polymers

\[ D = \frac{k_B T}{\Gamma_{\text{eff}}} \quad \Rightarrow \quad \Gamma_{\text{eff}} = \frac{k_B T}{D} \]

- Obtainable from mobility measurements

\[ \mu = \frac{Q_{\text{eff}}}{\Gamma_{\text{eff}}} \quad \Rightarrow \quad \bar{\Gamma}_{\text{eff}} = \frac{Q_{\text{eff}}}{\mu} \]

Q1: How to estimate the effective charge?
Q2: Can we use \( \Gamma_{\text{eff}} = \bar{\Gamma}_{\text{eff}} \) to measure \( Q_{\text{eff}} \)?
3 Estimators for $Q_{\text{eff}}$

(1) Ion velocity distribution to find co-moving counter ions

$$Q_{\text{eff}}^{(1)} = N_{\text{PE}} - N_{\text{CI}} \left( d_{CM} < d(v_{CI} = 0) \right)$$

(2) Calculation from Langevin (no HD) mobility

$$Q_{\text{eff}}^{(2)} = N_{\text{PE}} \left( 1 - \frac{1 - \mu \Gamma_0}{1 + \mu \Gamma_0} \right)$$

(3) Counter ions within $2\sigma$ of PE chain

$$Q_{\text{eff}}^{(3)} = N_{\text{PE}} - N_{\text{CI}} \left( d_{CM} < 2\sigma \right)$$
Co-moving counter ions reduce effective charge of PE-Ion complex

Look at the ion velocity distribution to find co-moving counterions

\[ Q_{\text{eff}}^{(1)} = N_{\text{PE}} - N_{\text{CI}} \left( d_{\text{CM}} < d(v_{\text{CI}} = 0) \right) \]
Ion Velocity Distribution

Simulations with and without HD yield almost identical threshold => similar $Q_{eff}$

$v_{ion}$: relative velocity to center of mass (PE + Cl) frame
Langevin Simulation (No HI)

- The mobility measures the combined movement of PE and co-moving counter ions.

- Local friction of each particle is given in Langevin simulation as $\Gamma_0$

\[
\begin{align*}
Q_{\text{eff}} &= (N_{\text{PE}} - N_{\text{CI}}) \\
\Gamma_{\text{eff}} &= \Gamma_0(N_{\text{PE}} + N_{\text{CI}}) \\
\mu &= \frac{N_{\text{PE}} - N_{\text{CI}}}{\Gamma_0(N_{\text{PE}} + N_{\text{CI}})} \\
Q_{\text{eff}}^{(2)} &= N_{\text{PE}} \left(1 - \frac{1 - \mu \Gamma_0}{1 + \mu \Gamma_0}\right)
\end{align*}
\]
Estimator Comparison

\[ Q_{\text{eff}}^{(3)} > Q_{\text{eff}}^{(2)} \approx Q_{\text{eff}}^{(1)} \]

Manning fraction \( f_M = 1 - \frac{b}{\lambda_B} \) based on one infinite rod at infinite dilution
dynamic \( Q_{\text{eff}} \) = static \( Q_{\text{eff}} \)
Effective Friction

PE effective friction deviates from single chain D for longer N! Influence of condensed counterions

Debye length ≈ hydrodynamic screening length
Effective Charge and Friction

Constant friction and charge per monomer for long PEs.

Debye length ≈ hydrodynamic screening length

\[ Q_{\text{eff}}^{(2)}/N \]

\[ \tilde{\Gamma}_{\text{eff}}^{(2)}/(\Gamma_1 N) \]
3 Estimators for $Q_{\text{eff}}$

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(2) Ion velocity distribution to find co-moving counter ions

$$Q_{\text{eff}}^{(2)} = N \left( 1 - I (d_0) \right)$$

(3) Counter ions within $2\sigma$ of PE chain

$$Q_{\text{eff}}^{(3)} = N_{\text{PE}} - N_{\text{CI}} (d < d_0)$$
Ion velocity with respect to CM
Effective charge vs. \(N\)

Only the dynamical estimators \(Q^{(1)}_{\text{eff}}\) and \(Q^{(2)}_{\text{eff}}\) are compared.

Effective charge estimators \(Q^{(1)}_{\text{eff}}\) and \(Q^{(2)}_{\text{eff}}\) are numerically equivalent! No dependence on hydrodynamical interactions, weak salt dependence for small \(N\), \(Q_{\text{eff}}\) is independent of salt for large \(N\), and \(Q_{\text{eff}}/N = \text{constant}\).
Contrary to the dynamical estimators we observe a strong salt dependence.
Effective friction vs. $N$

$$\Gamma_{\text{eff}} = \frac{Q_{\text{eff}}}{\mu} \quad \text{versus} \quad \Gamma = 6\pi \eta R_h$$

Zimm (?) scaling with hydrodynamical interactions

Rouse (?) scaling without hydrodynamical interactions
Effective friction vs. chain length

Hydrodynamic shielding

Independant. of $c_s$

With hydrodynamical interactions.

For large $N$ \( \frac{\Gamma}{N} = \text{constant} \)
Hydrodynamic coupling scheme

Influence of surrounding ions on hydrodynamic screening length

Debye length $\approx$ hydrodynamic screening length

unscreened  medium screening by counterions  large screening by counterions
Intermediate conclusion on FSE

- Coarse-grained MD with full electrostatic and explicit hydrodynamic interactions reproduce experimental results on bulk electrophoresis of polyelectrolytes, with and without salt.
- Mobility maximum due to hydrodynamic shielding.
- Dynamic charge estimators do not depend on HI, and are independent of salt (the static one is, however, salt dependent!)
- Effective friction is strongly influenced by co-moving ions and salt concentration:
  - Hydrodynamic shielding for short N, constant friction per monomer for long chains due to hydrodynamic screening.

How to separate long chains?

- Attaching a label to the PE changes the scaling of effective friction („Molecular parachute“) ELFSE (End-Labelled Free Solution Electrophoresis) principle

- Size-dependent free-solution mobility of long PE chains


• Ren, H., et. al.; Electrophoresis 1999, 20, 2501-2509
End-labeles

- Linear tags
- Branched tgs
- Micellar tags
Mobility influenced by label

End-labeling restores size dependence of mobility

⇒ separation possible
Theoretically expected slowdown

\[ \mu = \mu_0 \frac{M_{PE}}{M_{PE} + \alpha M_L} \]

\[ \alpha = \frac{b_L l_L}{b_{PE} l_{PE}} \]

- Calculate persistence length
  \[ l_L = 1.9, \ l_{PE} = 4.7 \rightarrow \alpha M_L \approx 0.4 \times 20 \approx 8 \]

- Calculate \( \alpha \) from simulation according to

\[ \frac{\mu_0}{\mu} = 1 + \alpha M_L \frac{1}{M_{PE}} \]

- Desruisseaux, C. et. al.; Macromolecules 2001, 34, 44-52
Slow down as expected!

Results for linear labels, no free fit parameters
Conclusions on ELFSE

- ELFSE works according to the theoretical predictions
- Size dependant separation can be pushed to longer chain lengths
- The insight gained by analyzing this process can lead to optimized experimental setups

For more details see:

Governing Physics for Bare Colloids

Stokes equation:

\[ \rho_s \frac{\partial \vec{u}}{\partial t} = \eta \nabla^2 \vec{u} - \nabla P - \sum_{j=1}^{N} n_j z_j e \nabla \psi \]

Poisson-Nernst-Planck equation:

\[ \lambda_j (\vec{u} - \vec{v}_j) - z_j e \nabla \psi - k_B T \nabla \log n_j = \vec{0} \]

Incompressibility:

\[ \nabla \cdot \vec{u} = \vec{0} \]

\( \rho_s, \vec{u}, \eta \) : Solvent’s density, velocity and viscosity

\( P \) : Pressure

\( \vec{V} \) : Particle’s velocity

\( \nabla \psi \) : Electric field due to ions of charge \( z_j \) and concentration \( n_j \) and the applied field

\( \lambda_j \) : Ionic drag coefficient
The Darcy-Brinkman equation:

\[
\rho_s \frac{\partial \vec{u}}{\partial t} = \eta \nabla^2 \vec{u} - \vec{\nabla} P + \underbrace{\frac{\eta}{l^2}(\vec{V} - \vec{u})}_{\text{drag force of the layer}} - \sum_{j=1}^{N} n_j z_j e \vec{\nabla} \psi
\]

Poisson-Nernst-Planck equation:

\[
\lambda_j (\vec{u} - \vec{v}_j) - z_j e \vec{\nabla} \psi - k_B T \vec{\nabla} \log n_j = \vec{0}
\]

Incompressibility:

\[
\vec{\nabla} \cdot \vec{u} = \vec{0}
\]

\(l^2\) : permeability of the grafted polymer layer

\(l(r)\) : Brinkman length related to the monomer distribution, decreases with increasing monomer density
Soft Colloid Electrophoresis

- Canonical ensemble (NVT)
- $L$: Simulation box size ($L=48\sigma_{ij}$)
- Raspberry-like colloid
- $R_{col}$: colloid radius ($R=3\sigma_{ij}$)
- $Q_{col}$: colloid charge
- $N$: number of grafted polymers ($N=20$)
- $M$: degree of polymerization of each chain ($M=20$)
- $H$: layer thickness $\sim 4.5\sigma_{ij}$
- $\lambda$: fraction of charged monomers
- $c_s$: monovalent salt concentration
- $\lambda_D$: Debye length
- $HI$ via LB fluid

$$\mu_{\text{red}} = \frac{3}{2} \frac{\eta e}{\epsilon_{rs} \epsilon k_B T} \mu_e$$

Hill's numerical solver based on Darcy-Brinkman formalism*
Monomer density parameters found from fit to simulation

Mobility of Neutral Soft Colloid

\[ \lambda = 0.1 \]
\[ Q_{\text{col}} = -40 \text{ e} \]
\[ Q_{\text{net}} = 0 \text{ e} \]

\( \mu_{\text{red}} \) vs. \( c_s/M \) for different values of \( \lambda_D/\sigma \):
- \( 10^1 \)
- \( 10^0 \)

Simulation vs. Theory
Mobility of Neutral Soft Colloid

- Let us start by considering the effect of an applied field
- We want to address the situation where the surface
- For weak electric fields, the surface-generated electro-osmotic
- Increasing rapidly with
- Nonmonotonic dependence on the applied electric field
- and strong deformation regimes for the isolated grafted
- Polymers maybe treated on an individual (noninteracting)
- Grafted to a flat surface at low densities in which the
- Density (Figure 1).
- Consider separately the limits of low and high grafting
- Coverage estimates from electrokinetic data. We will
- Of the coating). Moreover, this would facilitate polymer
- A grafted wall and consequently the electrophoretic

**Figure 1**

- EOF I
- EOF II
- $\lambda_D > H$
- $\mu_{red}$
- $c_s/M$
- $\lambda_D/\sigma$
- $\lambda = 0.1$
- $Q_{col} = -40$ e
- $Q_{net} = 0$ e
- Simulation
- Theory
Mobility of Charged Soft Colloid

\[ \mu_{\text{red}} = \frac{n_{\text{ion}} e}{
u} \]

\[ \lambda = 0.1 \]

\[ Q_{\text{col}} = -90 \text{ e} \]

\[ Q_{\text{net}} = -50 \text{ e} \]

\begin{align*}
\lambda_D > H &\quad \text{EOF II} \\
\lambda_D < H &\quad \text{EOF I}
\end{align*}

\[ \frac{\lambda D}{\sigma} \]

\[ c_s / M \]

\[ 10^{-3} \quad 10^{-2} \quad 10^{-1} \quad 10^0 \]

\[ 10^1 \quad 10^0 \]

Simulation

Theory
Mobility of Charged Soft Colloid

Experimentally realizable!

\[ \lambda_D / \sigma \]

\[ R_{\text{col}} = 1 \, \mu m \]

\[ c_s / M \]
Mobility of Charged Soft Colloid: Charge Effect

Simulation

\[ \lambda = 0.1 \]
\[ c_s = 0.5 \text{ M} \]
Conclusion

- Neutral soft colloids electrophoreose at high salt concentration
- Mobility *reversal* of a charged composites in *monovalent* salt
- This can be used as a measure of the *local* salt concentration
- Good agreement with the numerical results via Hill’s solver
- Darcy-Brinkman is applicable to soft surfaces