COMSOL CONFERENCE
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Non-linear DC Electrophoresis in High Electric Field Conditions

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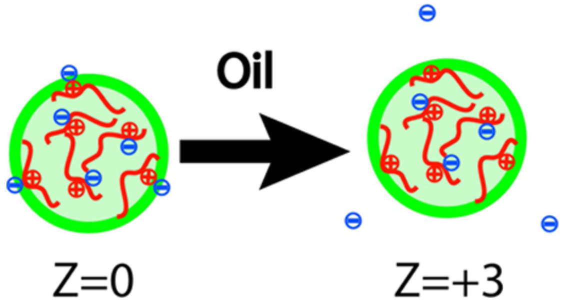
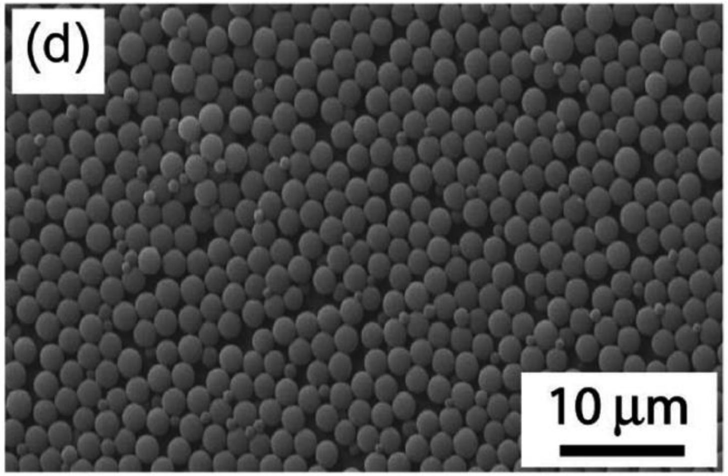
Experimental systems (Bartlett *et al.*)

Colloidal charged solid particles in liquid medium

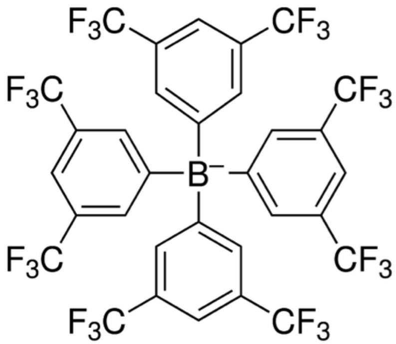


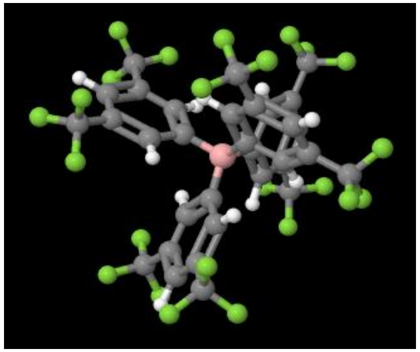


PMMA charged particles in Dodecane, non-polar solvent.

Salt-free suspension: only added counterions.

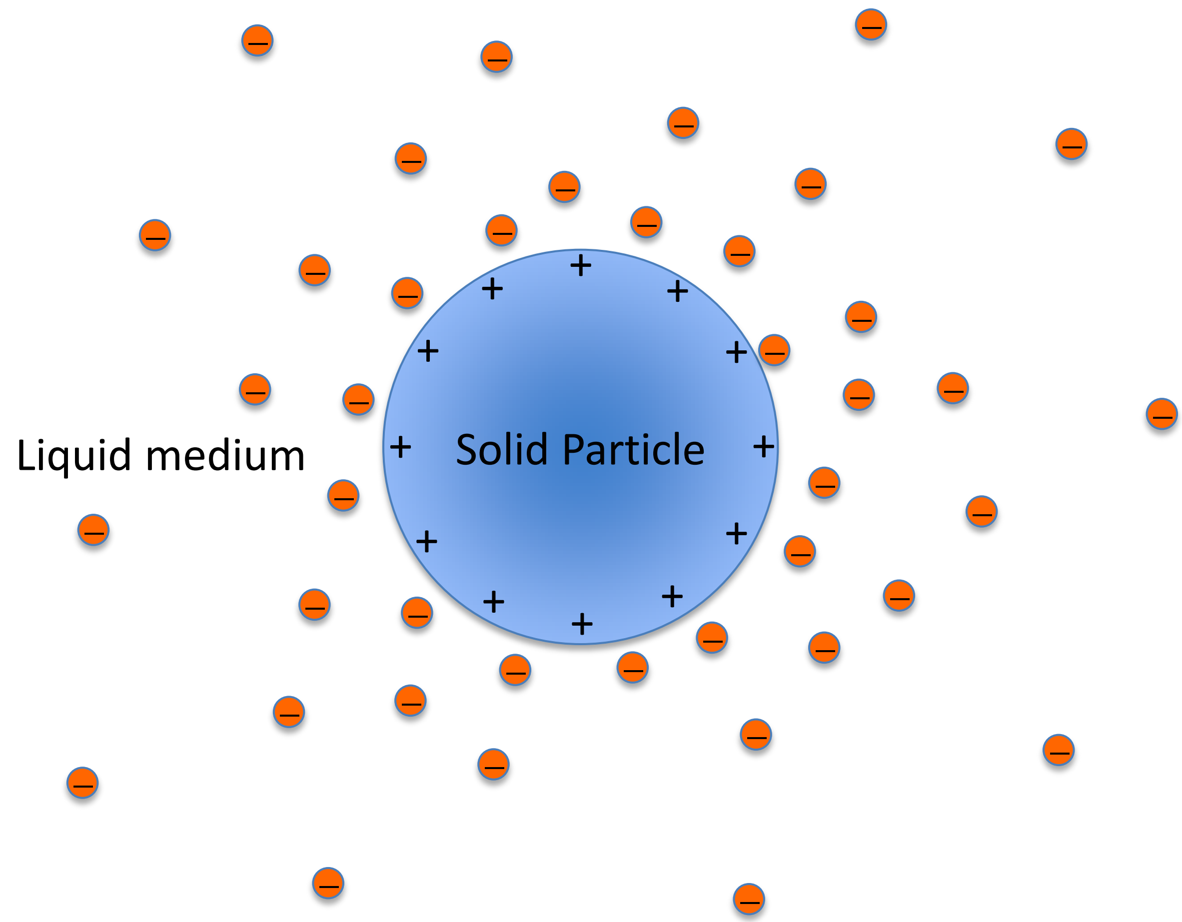
Added Counterions: TFPhB$^-$





Applications: paints, inks, cosmetics, food industry, electrophoretic displays (EDP), renewable energy, nanoparticulate materials, etc…

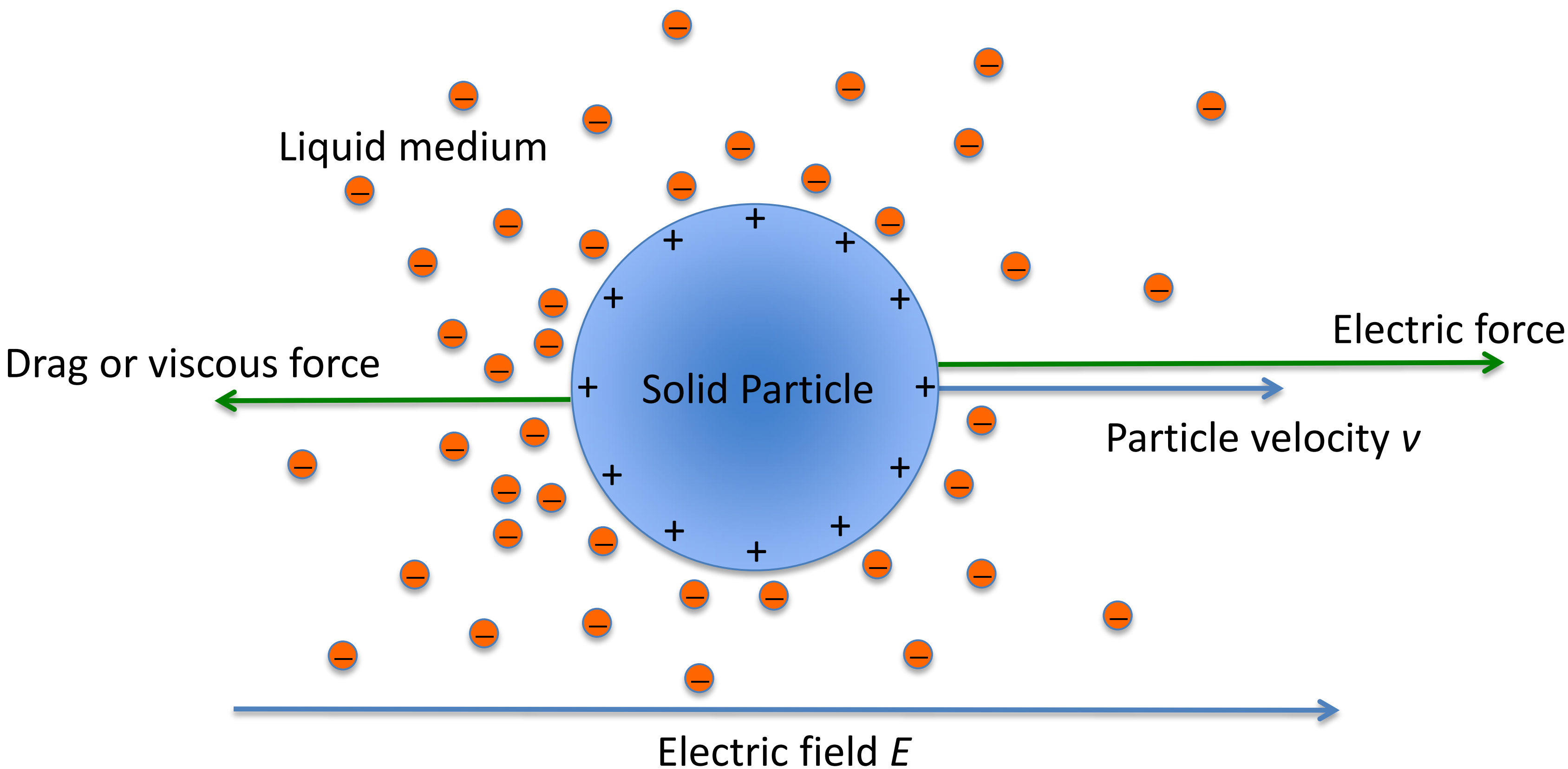
Equilibrium Electric Double Layer (EDL)



Equilibrium between diffusive and electrostatic force over ions: Poisson-Boltzmann equation

Spherical symmetry of the ionic concentration and electric potential

Electrophoresis: Applied Electric Field



Electrophoretic mobility: $m = \frac{v}{E}$

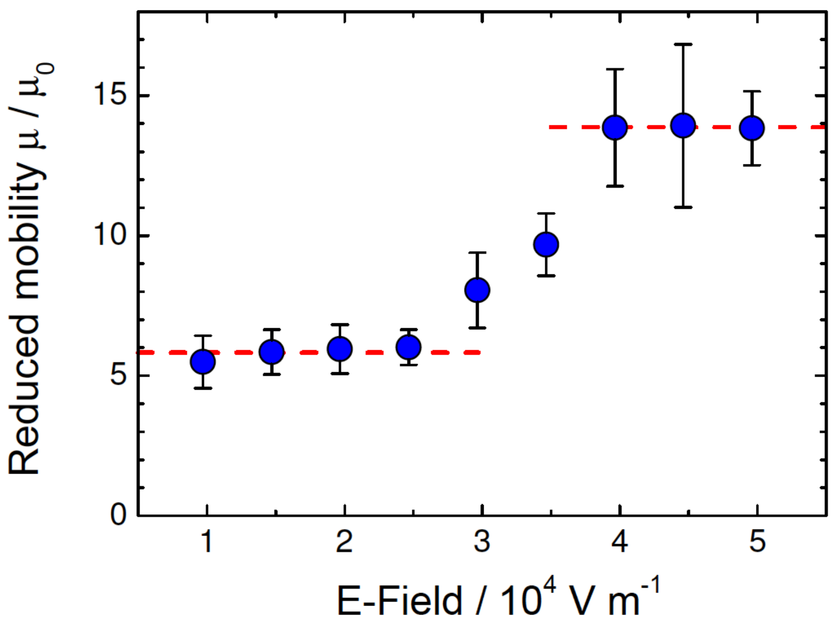
The applied electric field produces a distortion of the EDL: induced dipole moment

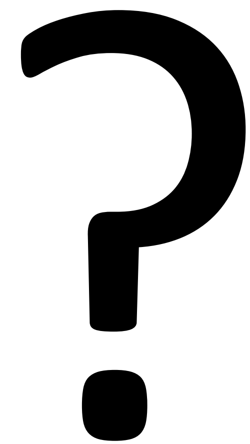
Cylindrical symmetry of the ionic concentration and electric potential

Standard theories of electrophoresis:

- Valid for **weak electric fields**, *i.e.*, low distortion of the EDL in comparison with the equilibrium state.
- **Linearization** of all fields (electric potential, ionic distribution, flow field, …) to first order in the applied electric field.
- Within this approximation, the **electrophoretic mobility is independent of the applied electric field**.

Non-linear effects observed that cannot be described with the standard theories.





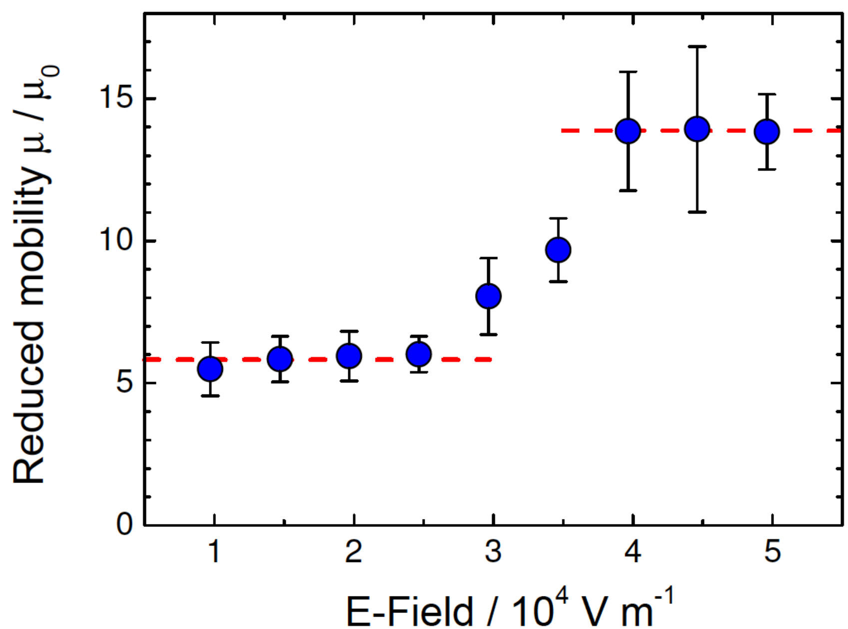
Goals:

- Make non-linear calculations with the full non-linear set of governing equations

  → COMSOL Multiphysics.

- Test the validity range of the linear theory and…
- Try to understand the observed mechanism and compare with experimental data

Non-linear effects observed that cannot be described with the standard theories.



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Governing Equations

Poisson's equations for the electric potential.

Fick's second law with diffusion, flow convection and electromigration for the counterionic concentration.

Navier-Stokes equations for incompressible fluid flow with an electric body force.

Newton's second law for the particle motion.

Governing equations

Poisson: $$\vec{\nabla}^2\Psi(\vec{r}) = -\frac{\rho_{el}(\vec{r})}{\varepsilon_r\varepsilon_0} \qquad \rho_{el}(\vec{r}) = z_c e c(\vec{r})$$

Ionic balance: $$\frac{\partial c(\vec{r})}{\partial t} + \vec{\nabla}\cdot\left(-D\vec{\nabla}c(\vec{r}) - z_c e\mu_c c(\vec{r})\vec{\nabla}\Psi(\vec{r})\right) + \vec{u}(\vec{r})\cdot\vec{\nabla}c(\vec{r}) = 0$$

Navier-Stokes: $$\rho\frac{\partial \vec{u}(\vec{r})}{\partial t} + \rho\left(\vec{u}(\vec{r})\cdot\vec{\nabla}\right)\vec{u}(\vec{r}) = \vec{\nabla}\left[-p(\vec{r})\mathbf{I} + \eta\left(\vec{\nabla}\vec{u}(\vec{r}) + (\vec{\nabla}\vec{u}(\vec{r}))^T\right)\right] + \vec{f}(\vec{r})$$

$$\vec{\nabla}\cdot\vec{u}(\vec{r}) = 0 \qquad \vec{f}(\vec{r}) = -z_c e c(\vec{r})\vec{\nabla}\Psi(\vec{r})$$

Particle motion: $$\vec{F} = \vec{F}_{visc} + \vec{F}_{elec} = m\vec{a} \qquad \vec{F}_{visc} = \oint_{S_P}\mathbf{T}\cdot d\vec{S} \qquad \vec{F}_{elec} = \oint_{S_P}\mathbf{M}\cdot d\vec{S}$$

Numerical parameters

GEOMETRICAL VALUES USED

Particle radius: a = 775 nm

Cell radius: $b = a\phi^{-1/3}$

Volume fraction: $\phi = 10^{-3}$

PHYSICAL VALUES USED

Surface charge density: $\sigma = 1.14 \cdot 10^{-5}$ C/m^2

Temperature: T = 25 ºC

Relative electric permittivity: $\varepsilon_r = 2.01$

Medium density: $\rho = 0.745$ g/cm^3

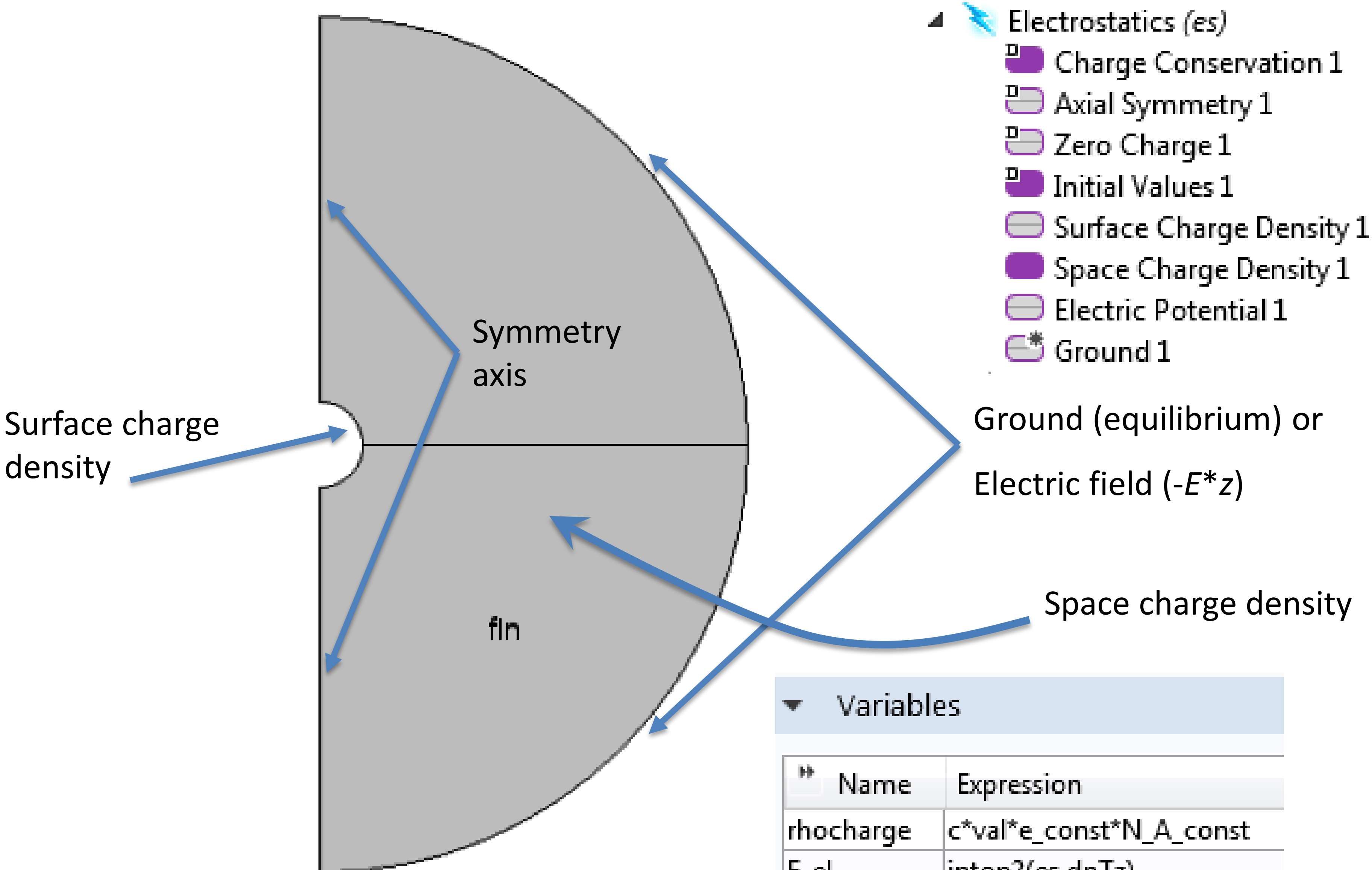
Medium viscosity: $\eta = 1.34 \cdot 10^{-3}$ Pa·s

Added Counterions: $TFPhB^-$

Limiting molar conductivity: 20.8 S·cm^2/mol

Applied electric field: ***Variable***

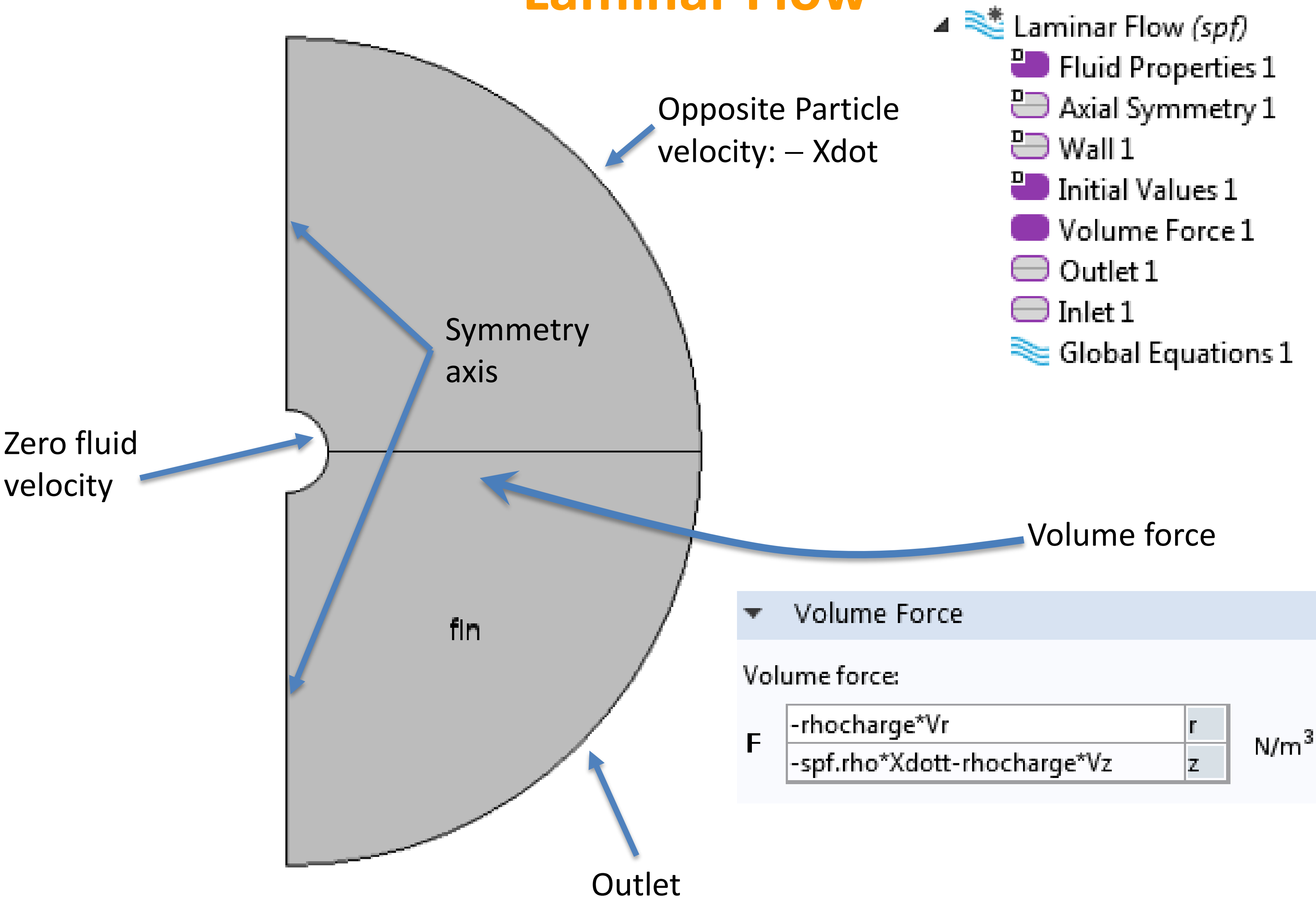
Electrostatics



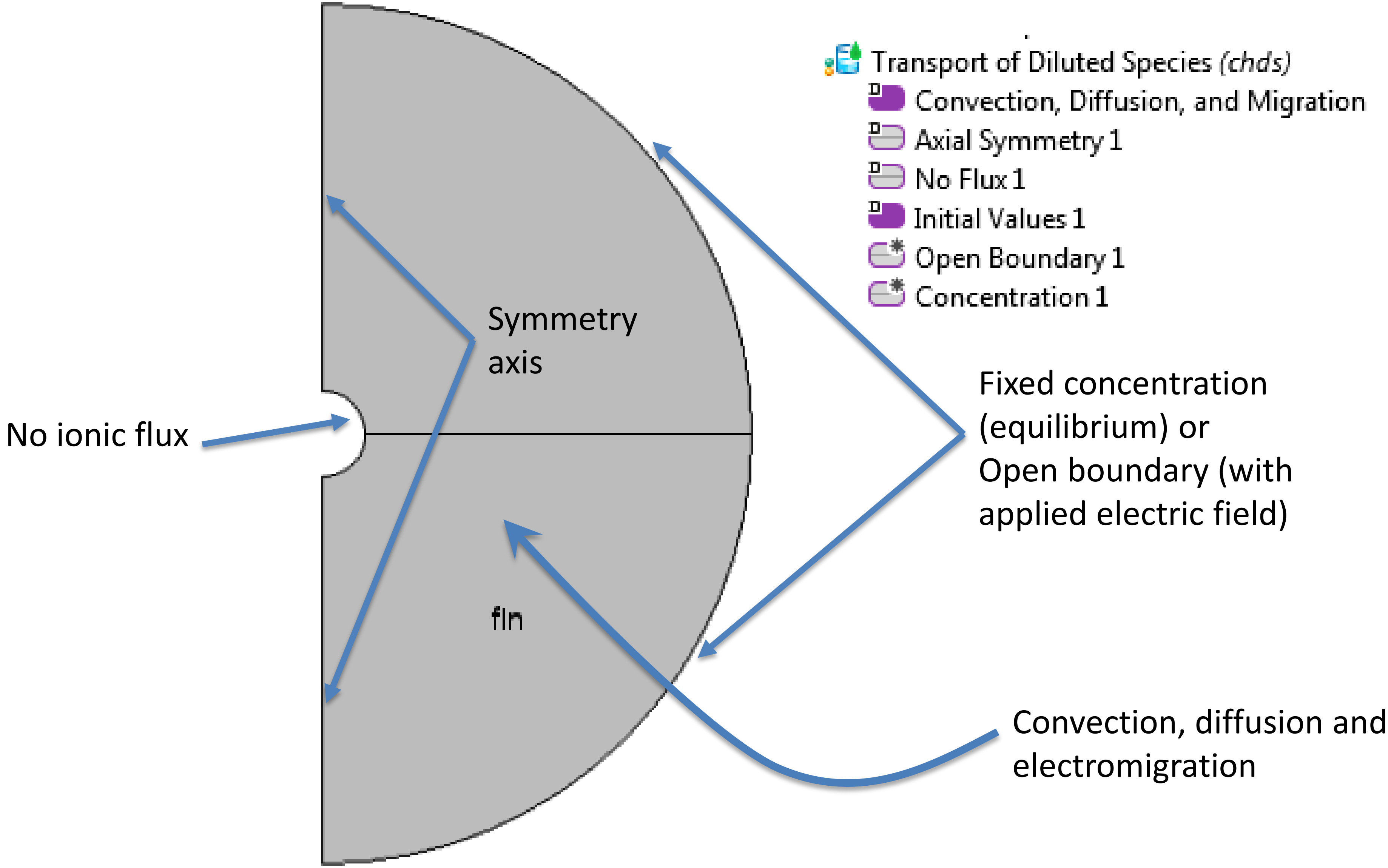
Variables

Name	Expression
rhocharge	c*val*e_const*N_A_const
F_el	intop2(es.dnTz)
F_z	intop2(-spf.T_stressz)

Laminar Flow



Counterion Concentration



ODE for the particle velocity

Global Equations

Global Equations

$f(u, u_t, u_{tt}, t) = 0, \; u(t_0) = u_0, \; u_t(t_0) = u_{t0}$

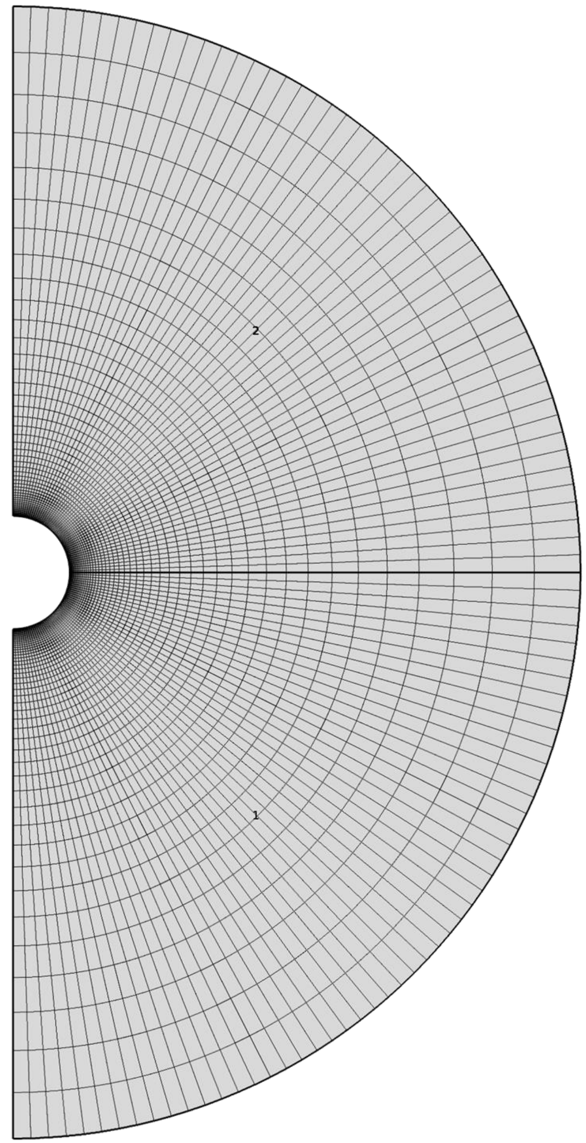
Name	f(u,ut,utt,t) (m/s)	Initial value (u0) (	Initial value (ut0)	Description
Xdot	Xdott-(F_z+F_el)/mass_part	0	0	Electrophoretic velocity
		0	0	

- Laminar Flow *(spf)*
  - Fluid Properties 1
  - Axial Symmetry 1
  - Wall 1
  - Initial Values 1
  - Volume Force 1
  - Outlet 1
  - Inlet 1
  - Global Equations 1

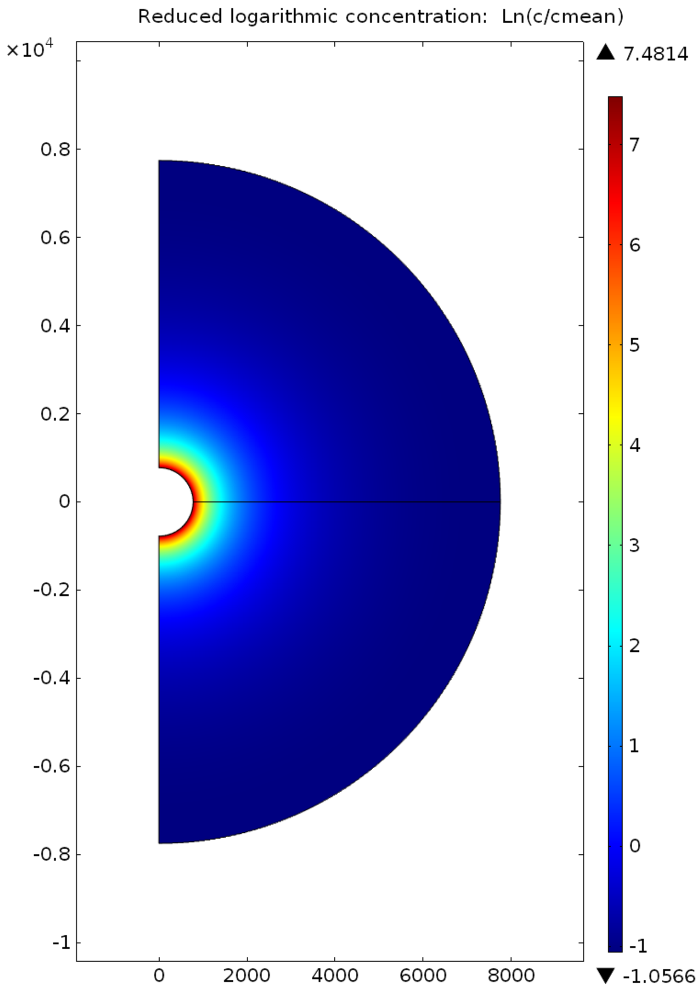
Variables

Name	Expression
rhocharge	c*val*e_const*N_A_const
F_el	intop2(es.dnTz)
F_z	intop2(-spf.T_stressz)

Mesh

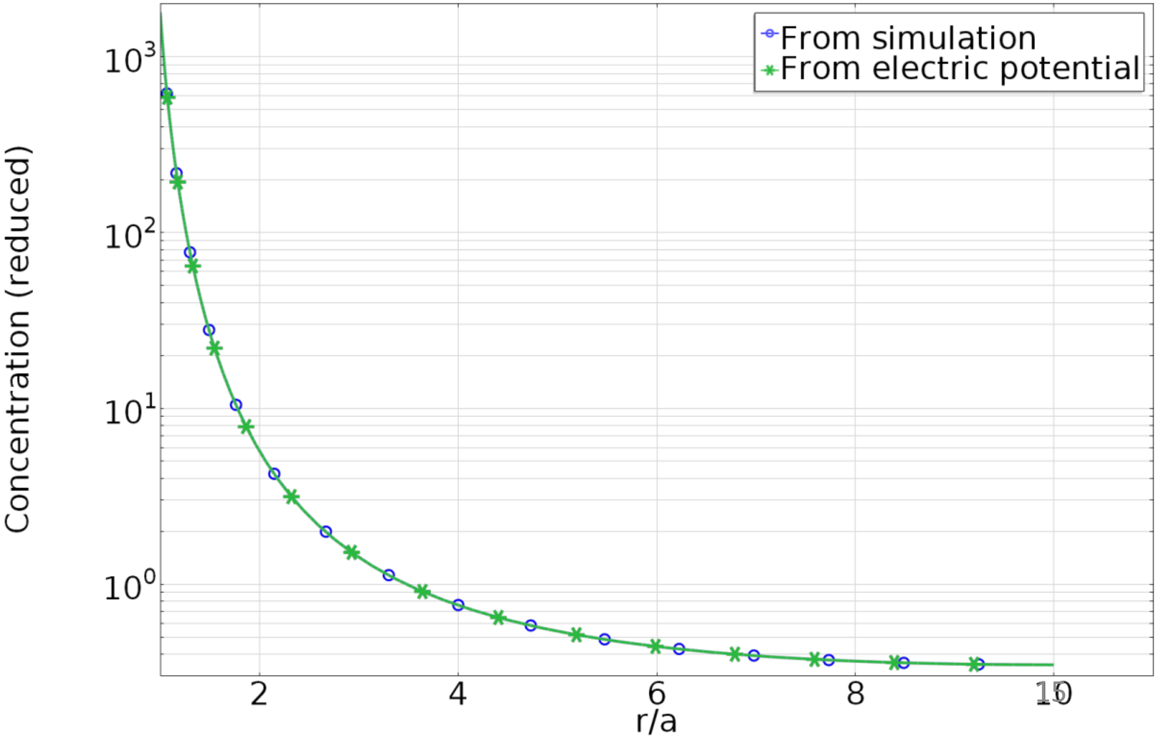


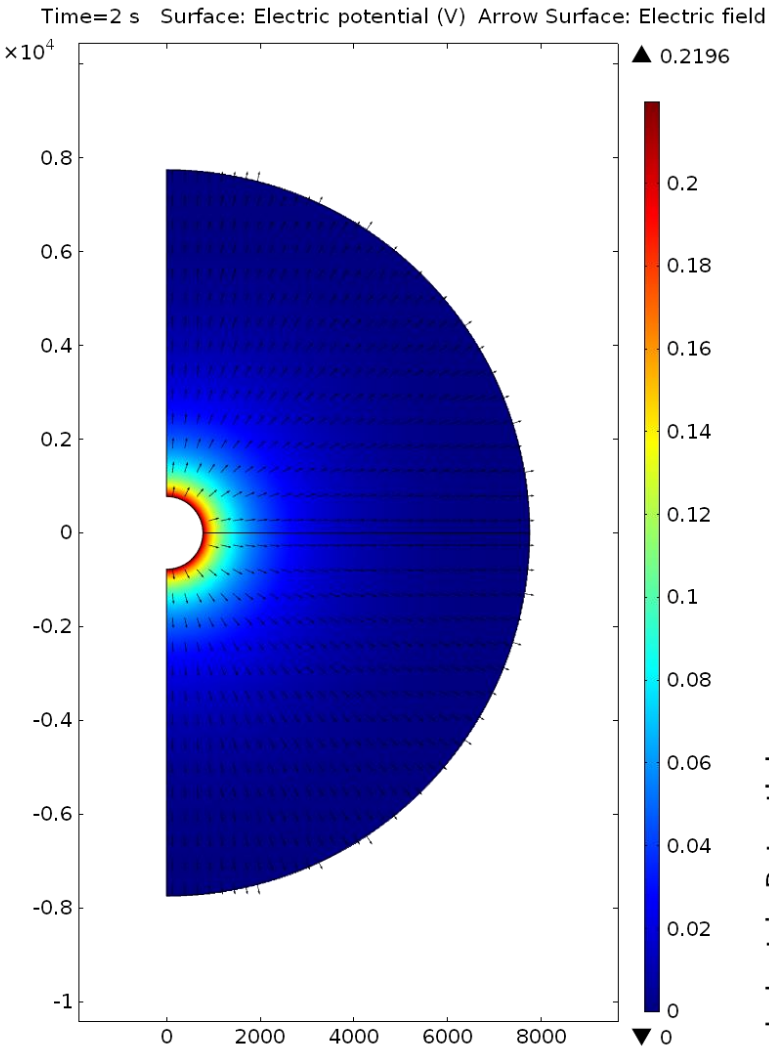
Quad mesh used in the simulations.



Equilibrium EDL:

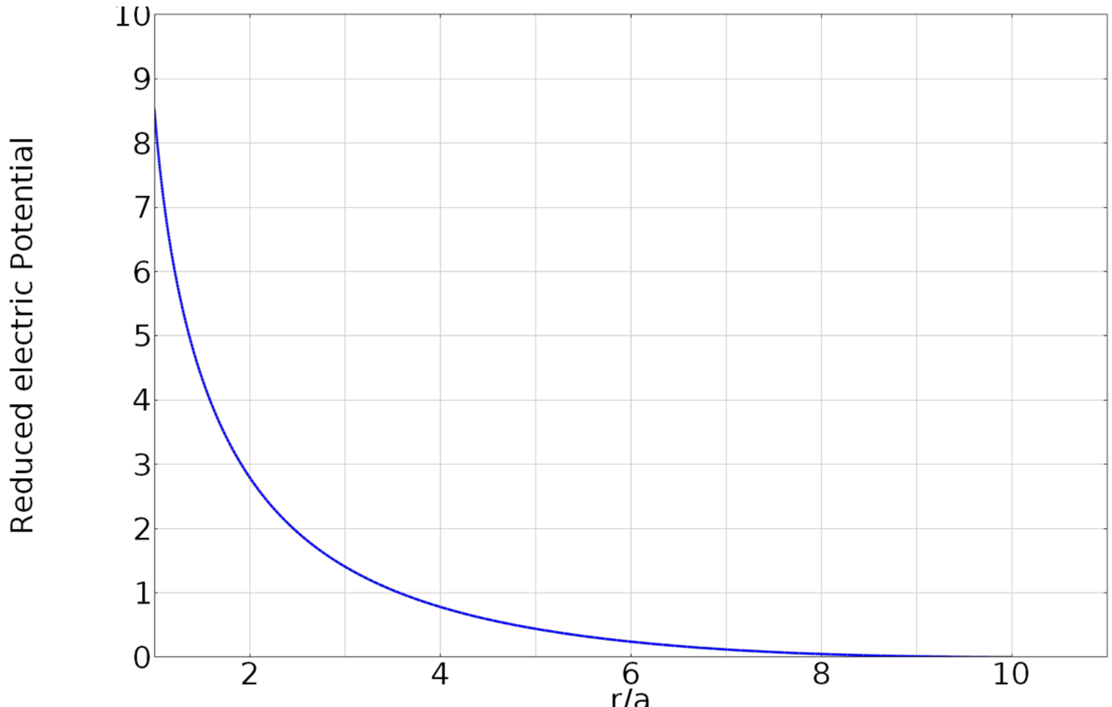
Concentration distribution



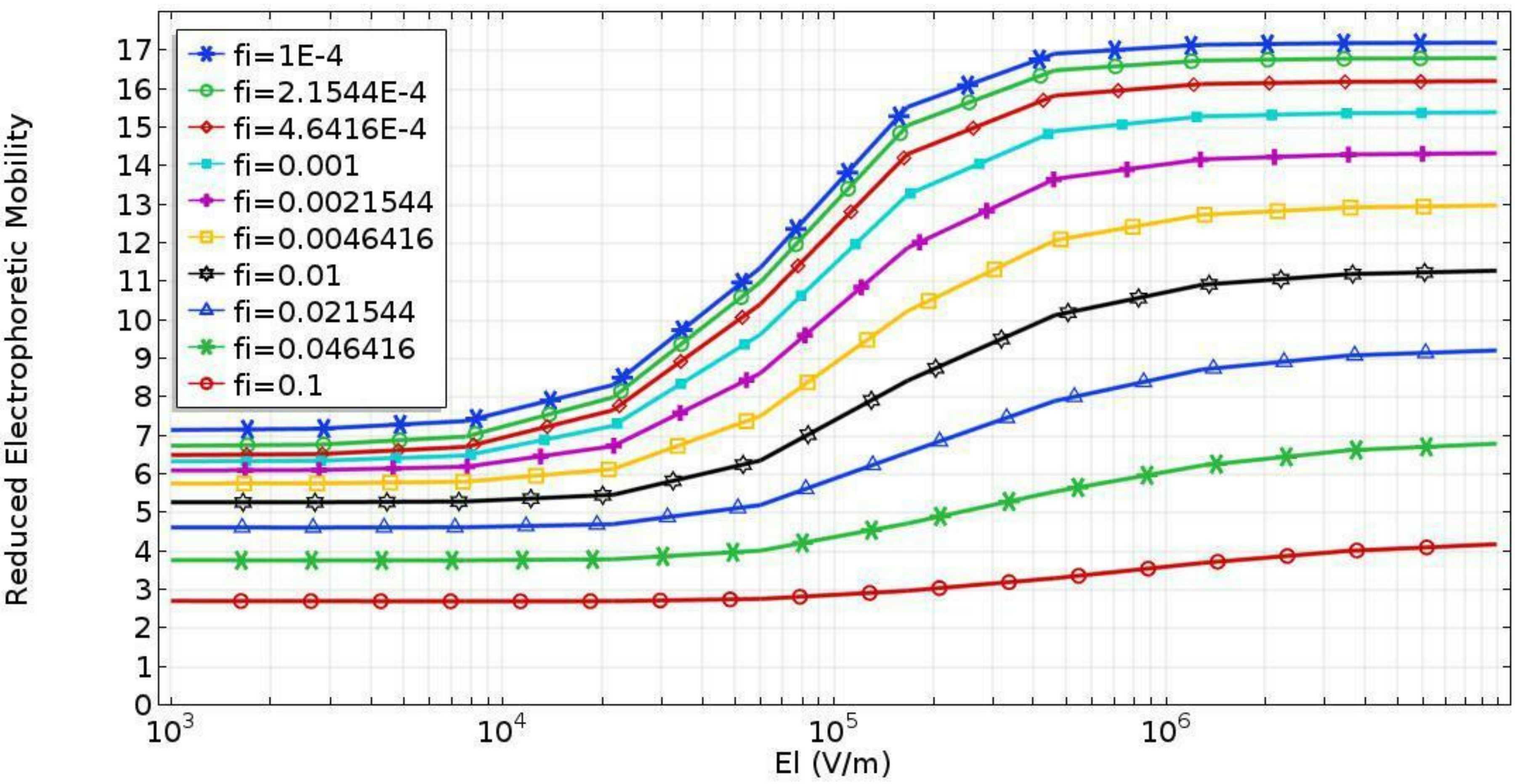


Equilibrium EDL:

Electric Potential

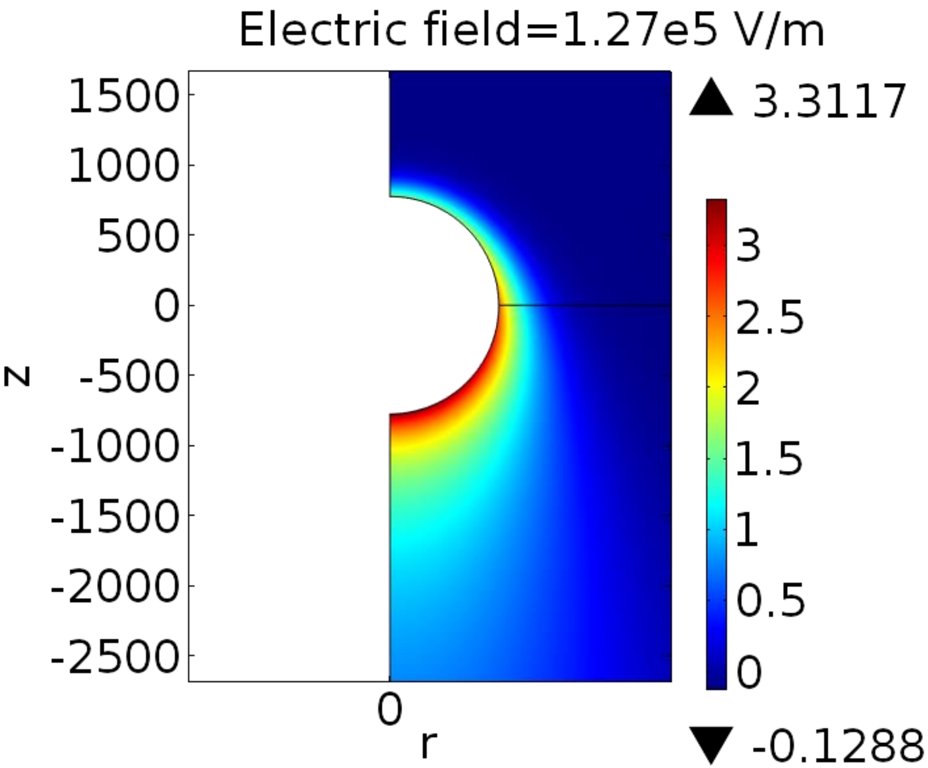


Electrophoretic mobility numerical results

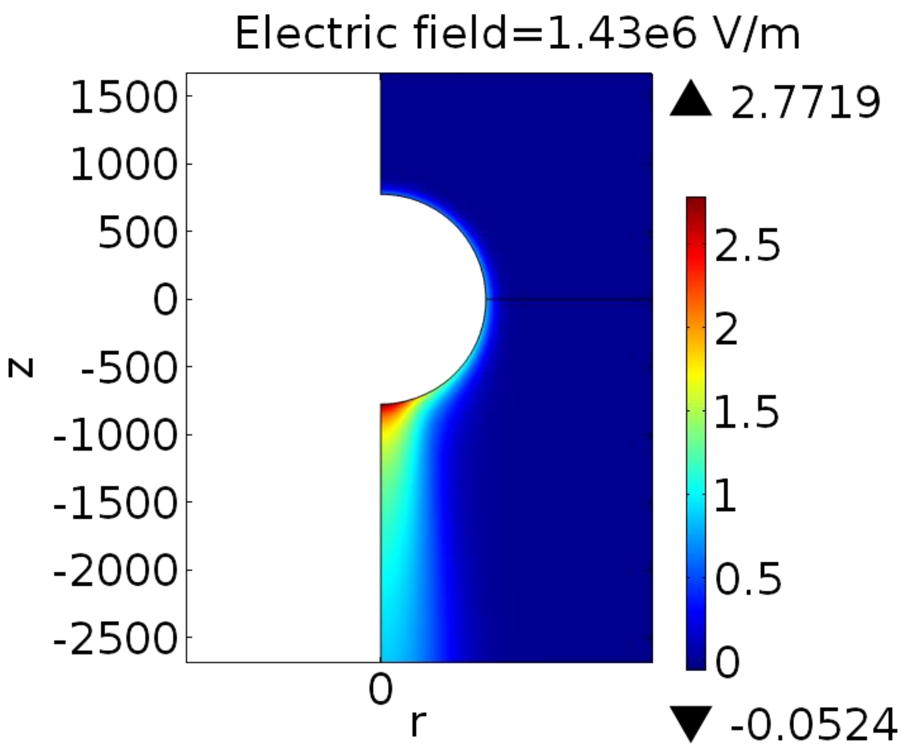


Stationary reduced electrophoretic mobility for different volume fractions.

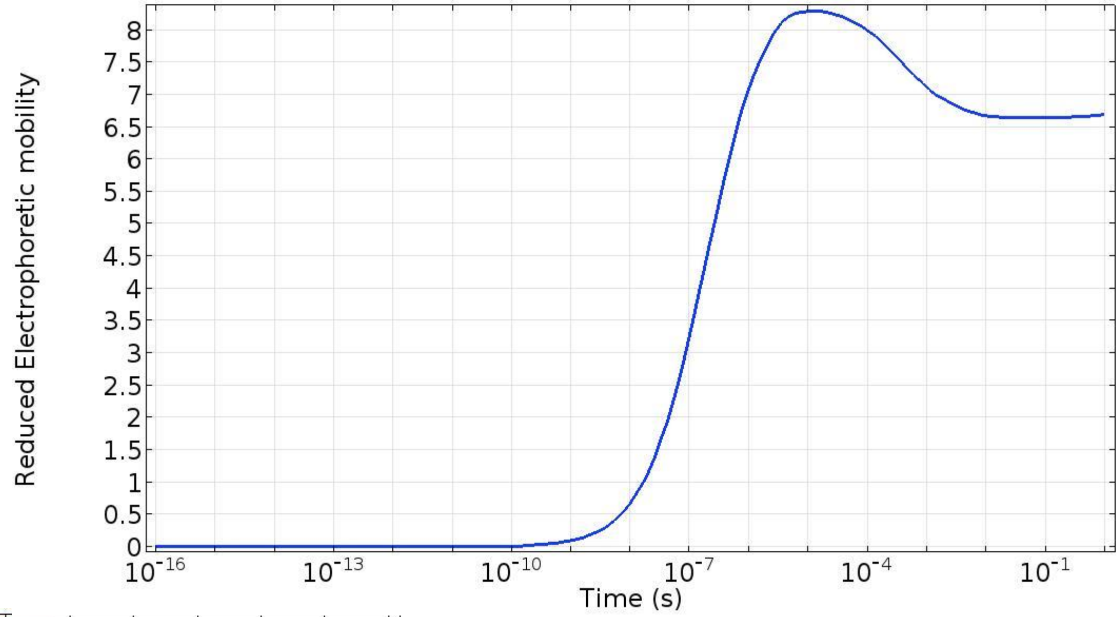
EDL distortion

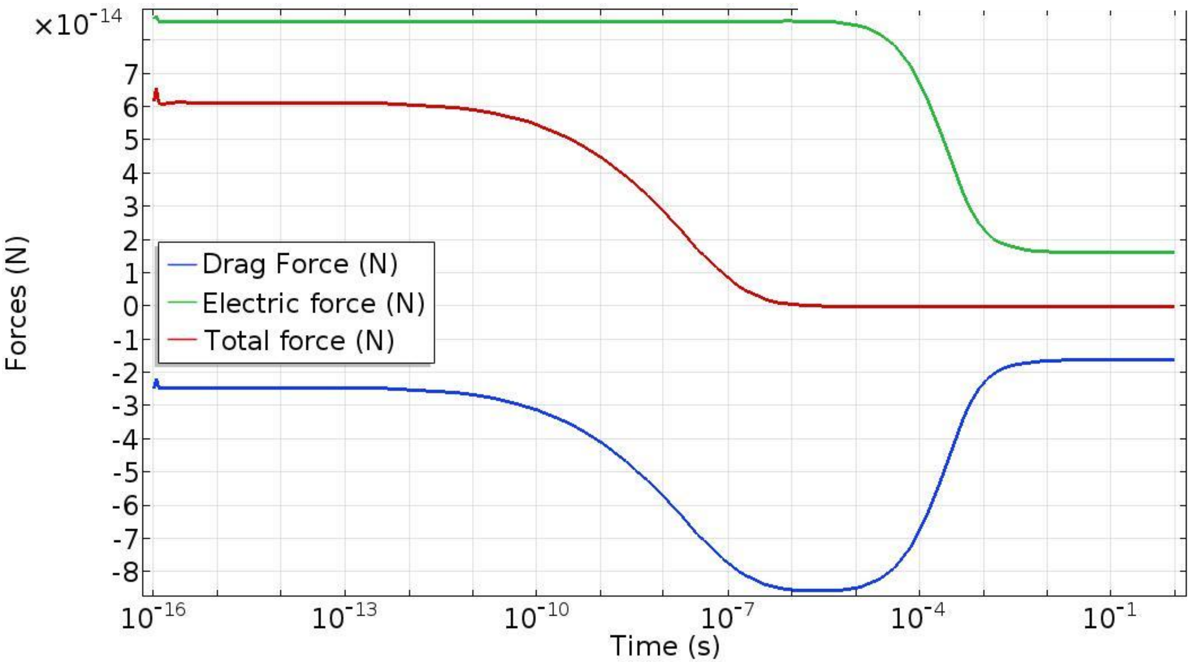


Stationary ionic distributions for different electric field values.

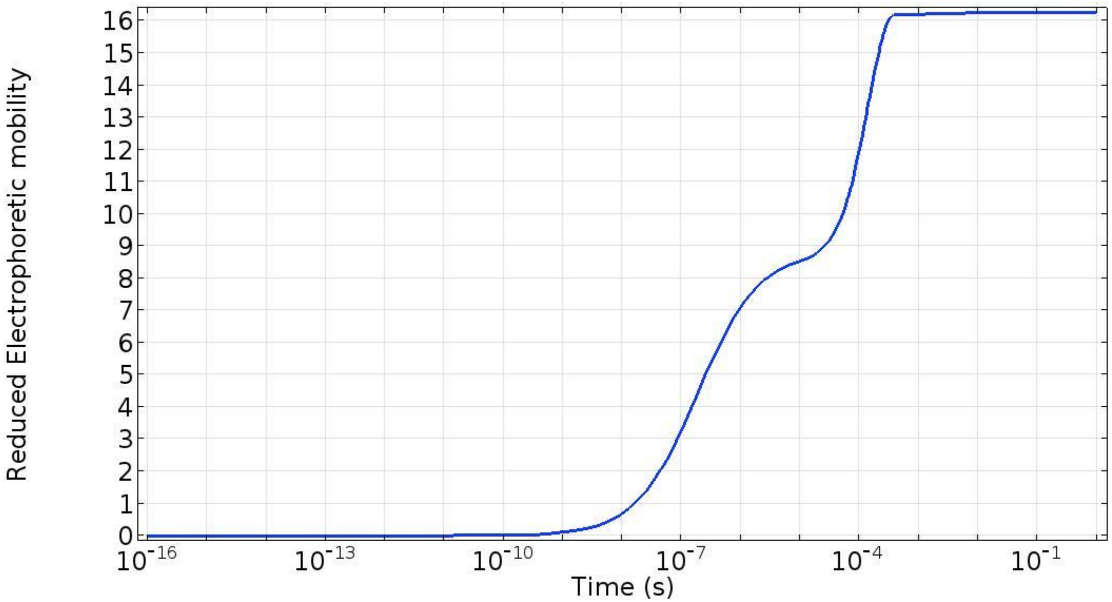


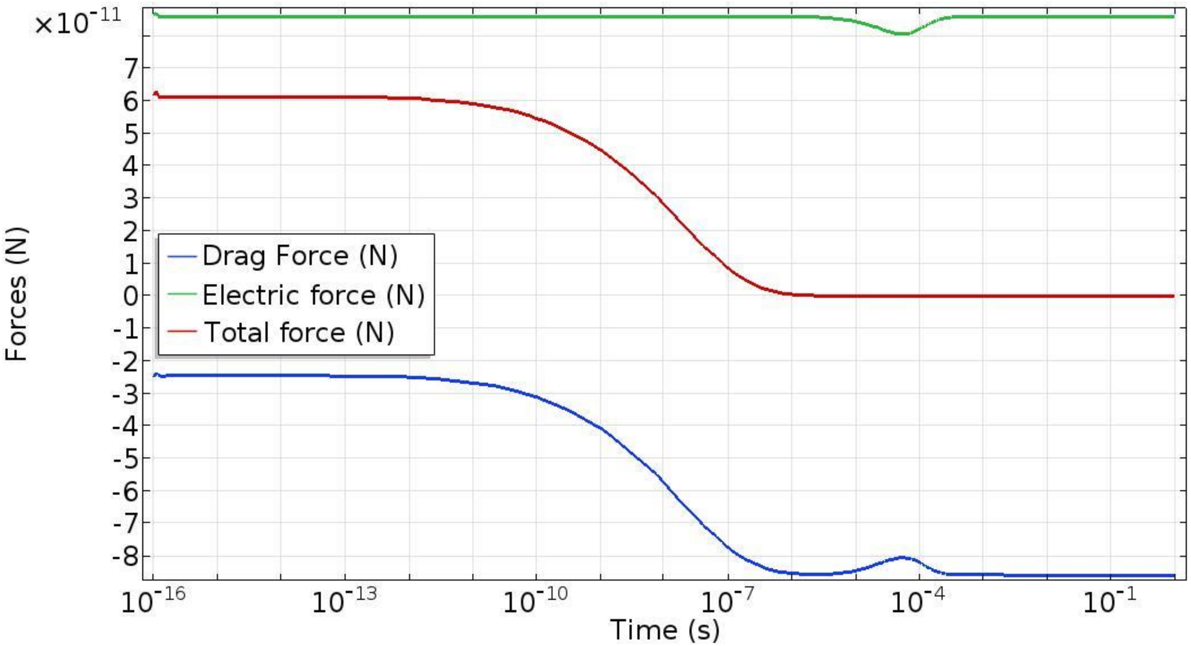
Time behaviour low electric field El = 10^3 V/m



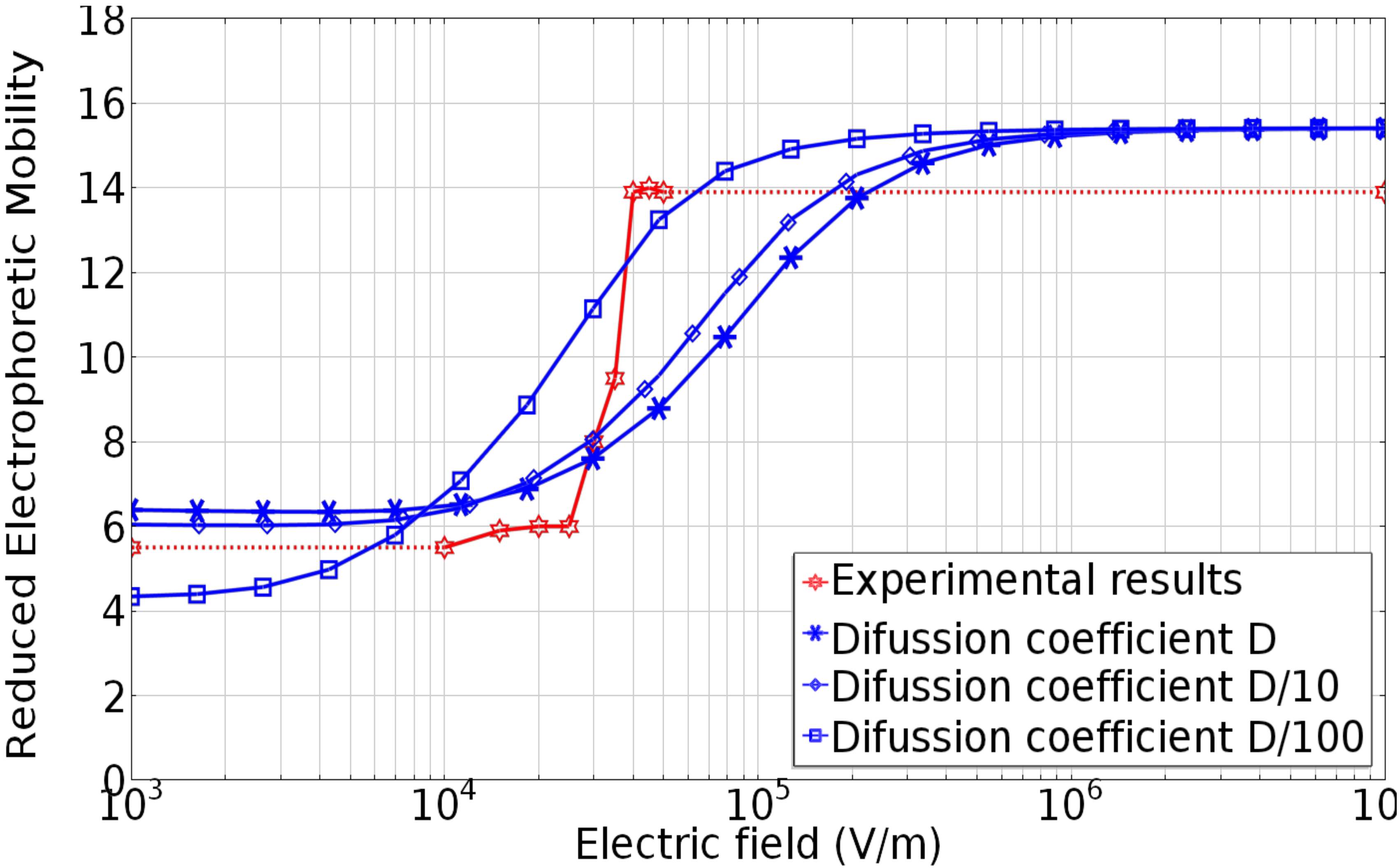


Time behaviour high electric field El = 10^6 V/m





Comparison with experiments



Stationary reduced electrophoretic mobility as a function of applied electric fields.

The electric field is applied at time t = 0 s over the equibrium electric double layer.

Conclusions

- We have made time-dependent calculations using COMSOL Multiphysics to solve the full non-linear set of equations that governs the elctrophoresis of nanoparticles.
- The results of the non-linear model coincides with the predictions of the standard linear theories up to $4 \cdot 10^4$ V/m in the applied electric field.
- We obtain numerical results that reproduce qualitetively the experimental behavior observed and can explain the unbinding of counterions under a high electric field, which is a non-linear effect.
- The predicted numerical electric field onset of the non-linear regime ($\approx 4 \cdot 10^4$ V/m) is significantly higher than the one observed in the experimental results ($\approx 4 \cdot 10^4$ V/m) . We think that this discrepancy is due to the finite ionic size. We will include this correction in future work.

Acknowledgements

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References

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2. G. Hussain, A. Robinson, P. Bartlett, *Charge Generation in Low-Polarity Solvents: Poly(ionic liquid)-Functionalized Particles*, Langmuir, **29**, 4204 (2013).

3. F. Carrique, E. Ruiz-Reina, F. J. Arroyo, M. L. Jiménez, A. V. Delgado, *Dynamic electrophoretic mobility of spherical colloidal particles in salt-free concentrated suspensions*, Langmuir, **24**, 2395 (2008).

Thank you very much for your attention!!

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