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Highly Nonlinear Electrokinetic Simulations Using a Weak Form

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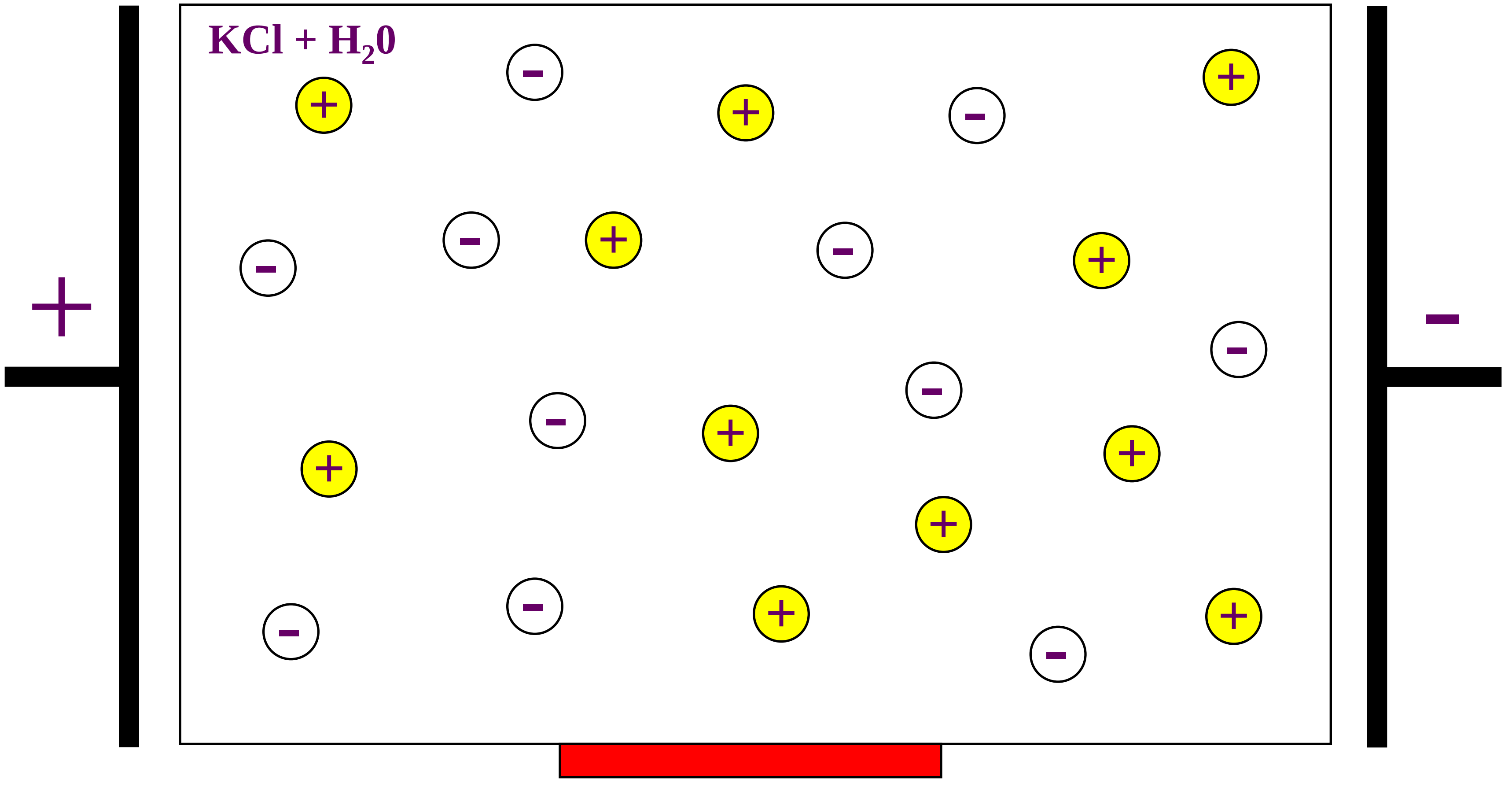
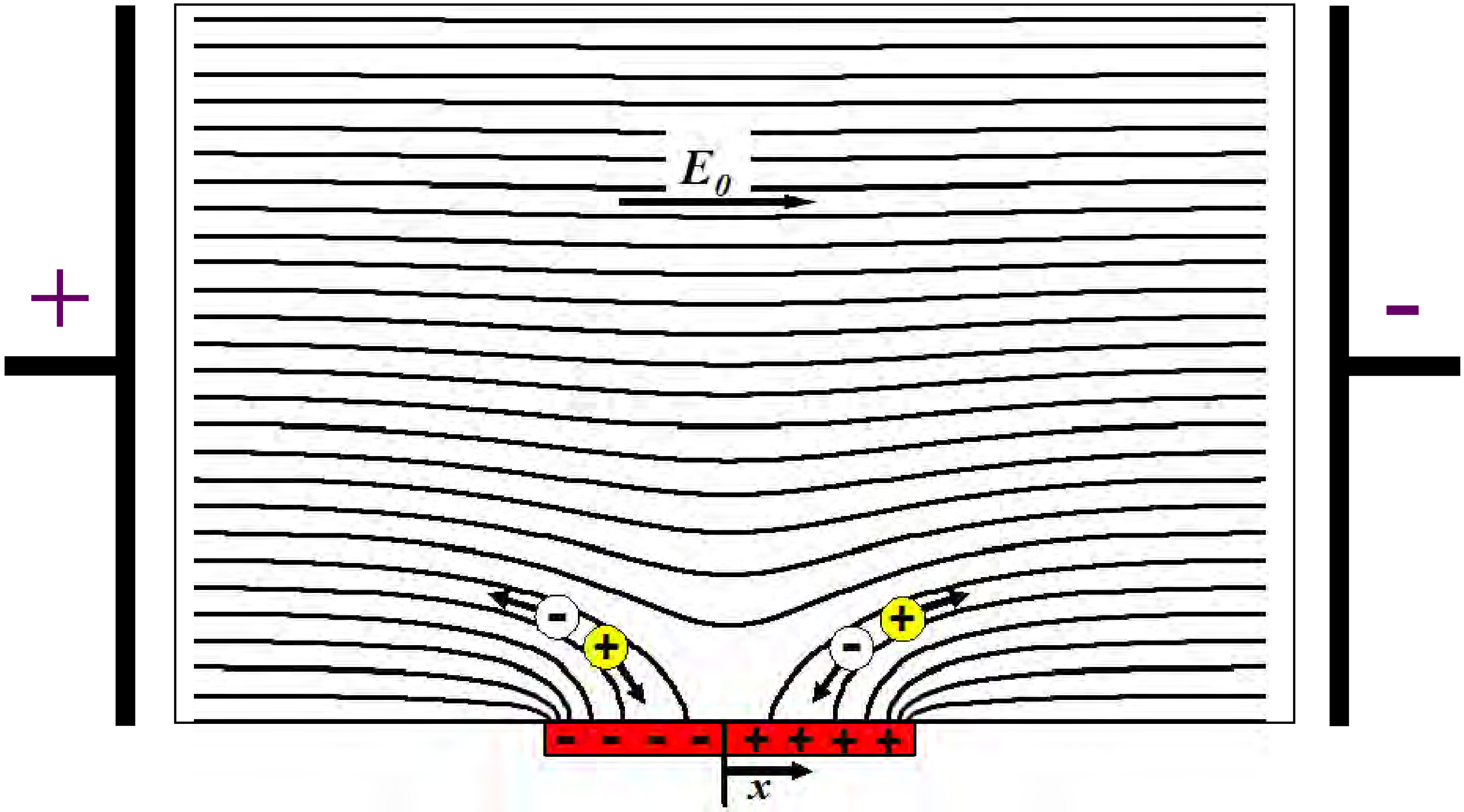
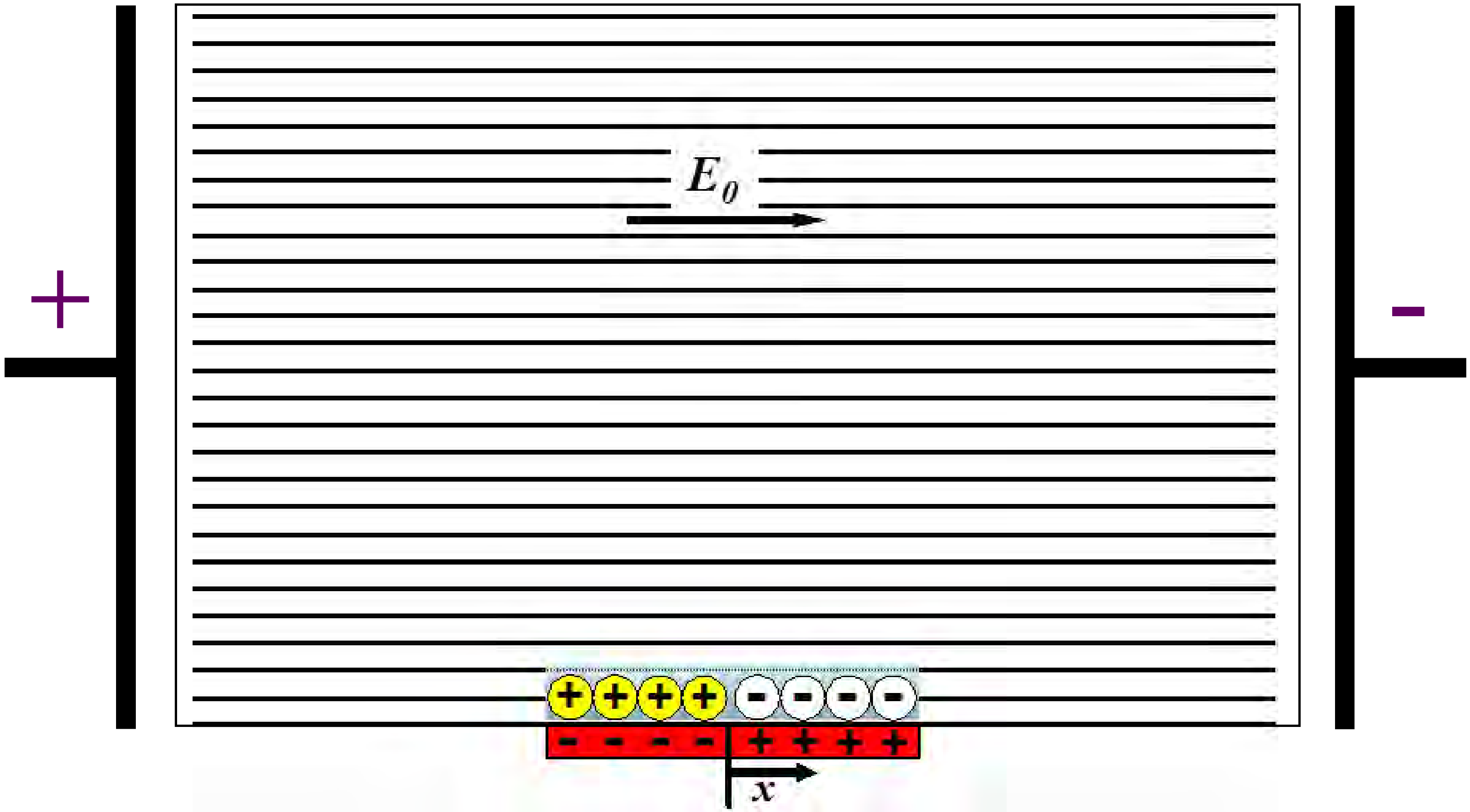
Induced Charge Electroosmosis



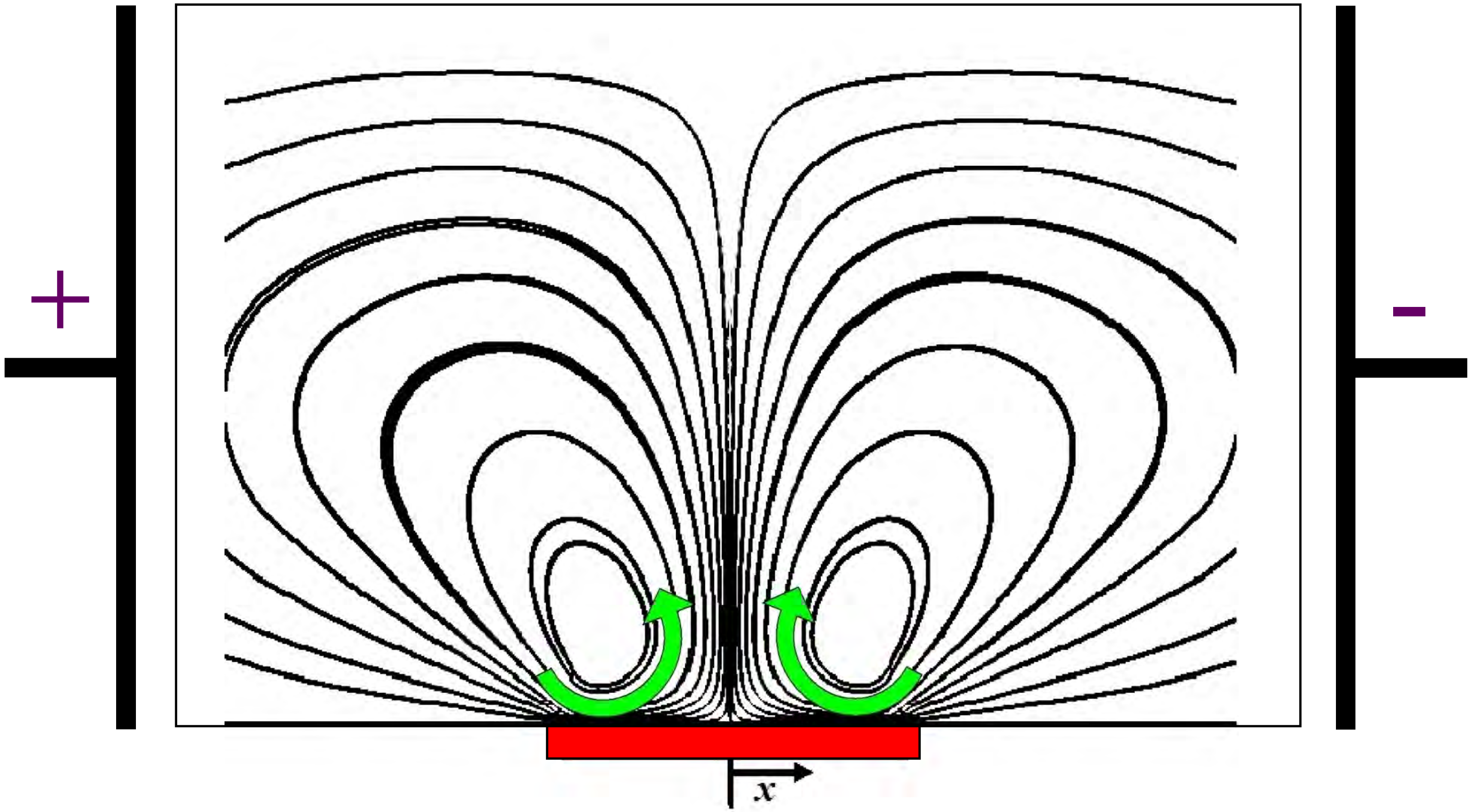
Induced Charge Electroosmosis



Induced Charge Electroosmosis



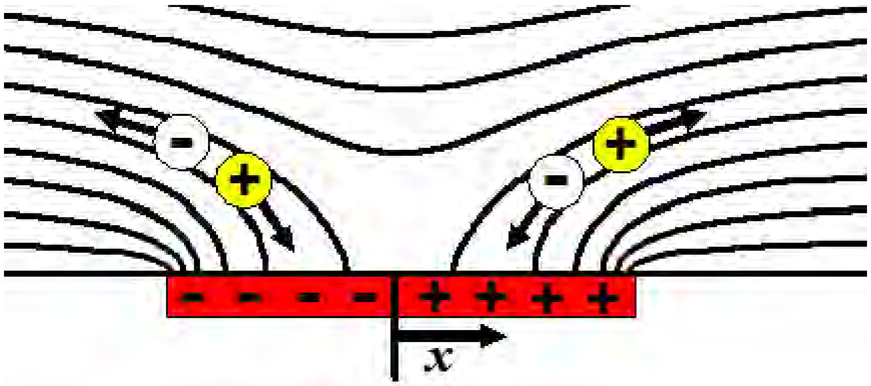
Induced Charge Electroosmosis



Effective Boundary PDE

- Conservation of double layer surface charge

$$\frac{\partial q}{\partial t} = \frac{\partial \phi}{\partial y} + \frac{\partial}{\partial x}\left(Du \frac{\partial \phi}{\partial x} \right)$$



Non-linear Capacitance

$$q = -2\sinh(\zeta/2)$$

$$Du = 4\varepsilon(1+m)\sinh^2(\zeta/4)$$

Transformation for Stability

- Double layer charge grows exponentially and causes numerical errors.

$$\frac{\partial q}{\partial t} = \frac{\partial \phi}{\partial y} + \frac{\partial}{\partial x}\left(Du \frac{\partial \phi}{\partial x} \right)$$

- To make the solution stable, a variable transformation is required.

$$q = -2\sinh(\zeta/2) \Rightarrow \frac{dq}{dt} = -\cosh\left(\frac{\zeta}{2}\right)\frac{d\zeta}{dt}$$

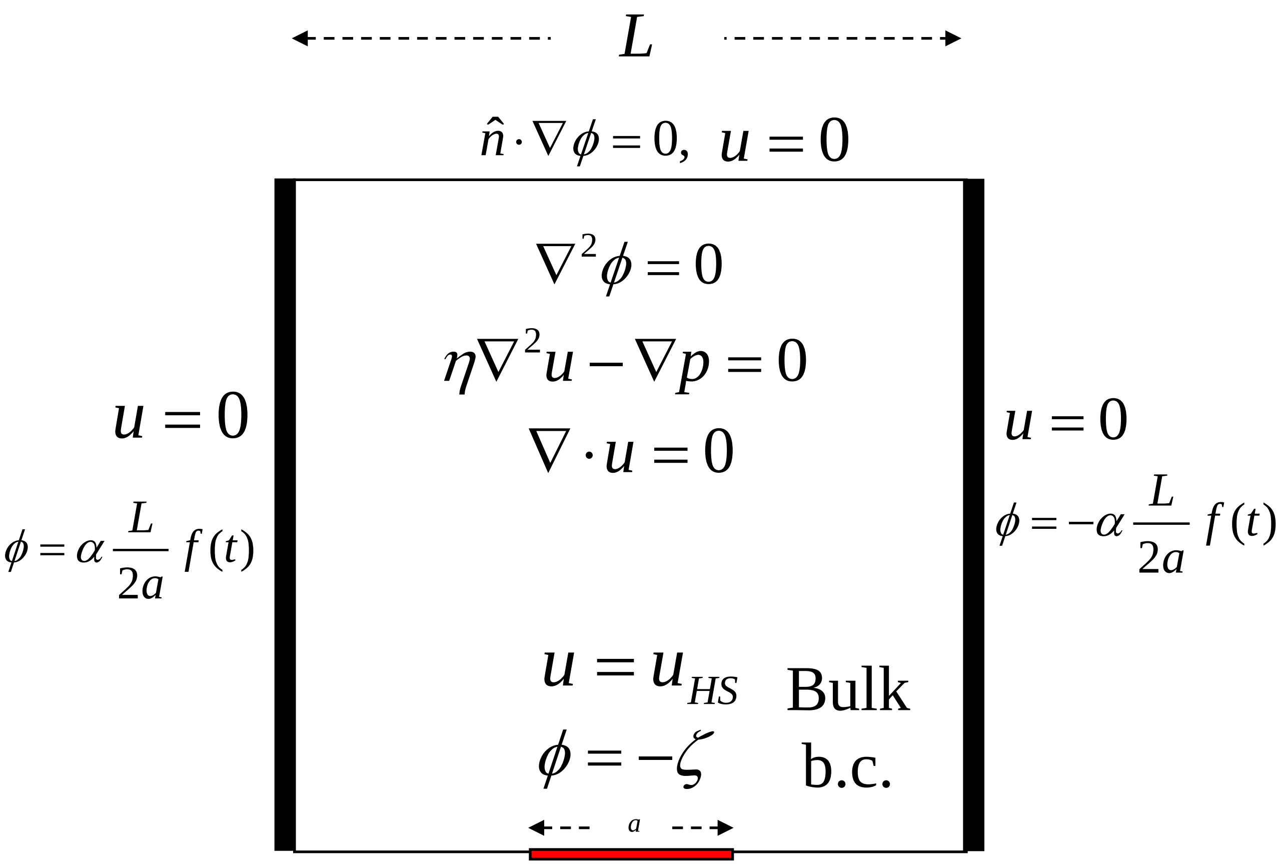
$$\phi = -\zeta$$

$$\Downarrow$$

- Stability is improved by creating diffusion without losing accuracy.

$$\frac{\partial \zeta}{\partial t} = -\frac{1}{\cosh(\zeta/2)}\left[\frac{\partial \phi}{\partial y} - \frac{\partial}{\partial x}\left(Du \frac{\partial \zeta}{\partial x} \right) \right]$$

Nonlinear Electrokinetic Model



$$\frac{\partial q}{\partial t} = \frac{\partial\phi}{\partial y} + \frac{\partial}{\partial x}\left(Du\frac{\partial\phi}{\partial x}\right)$$ Boundary PDE

$$q = -2\sinh(\zeta/2) \qquad u_{HS} = 2/\alpha^2\,\zeta\,\partial\phi/\partial x$$

$$Du = 4\varepsilon(1+m)\sinh^2(\zeta/4) \qquad \varepsilon = \lambda_D/a$$

Non-Dimensional Simulation Parameters

Voltage Scaling

$$\alpha = \frac{\text{zeta magnitude}}{\text{thermal voltage}} = \frac{ze}{kT}\frac{a}{L}V_{ext}$$

Length scale ratio

$$\varepsilon = \frac{\text{debye length}}{\text{electrode length}} = \frac{\lambda_D}{a}$$

Weak Form in COMSOL

- Weak form
  - An integral form equivalent to the original PDE.
  - Derived by multiplying the PDE with a test function and then integrating over the domain.

- Weak form advantages
  - Create custom equations on with dimension
  - Implement PDEs on boundaries
  - Mixed time and space derivative

Weak Form: Example

Consider Diffusion Equation $$\frac{\partial C}{\partial t} = \nabla \cdot \left(D \nabla C \right) + R$$

Weak Form: multiply with test function *v* and integrate over domain

$$\int_{\Omega} v \frac{\partial C}{\partial t} d\Omega = \int_{\Omega} v \nabla \cdot \left(D \nabla C \right) d\Omega + \int_{\Omega} v R d\Omega$$

Simplify $$\int_{\Omega} v \frac{\partial C}{\partial t} d\Omega = \int_{\Omega} \nabla \cdot \left(v D \nabla C \right) d\Omega - \int_{\Omega} D \nabla v \cdot \nabla C d\Omega + \int_{\Omega} v R d\Omega$$

Apply Green's Theorem

$$\int_{\Omega} v \frac{\partial C}{\partial t} d\Omega \;=\; \int_{\partial\Omega} v \hat{n} \cdot \left(D \nabla C \right) d\partial\Omega \;-\; \int_{\Omega} D \nabla v \cdot \nabla C d\Omega \;+\; \int_{\Omega} v R d\Omega$$

Time dependent term Boundary fluxes Diffusive term Source term

Weak Form Contributions

Time dependent or *dweak* terms:

$$\int_{\Omega} v \frac{\partial C}{\partial t} d\Omega$$

weak terms for Ω

$$-\int_{\Omega} D\nabla v \cdot \nabla C d\Omega + \int_{\Omega} vRd\Omega$$

weak terms for $\partial\Omega$

$$\int_{\partial\Omega} v\hat{n} \cdot \left(D\nabla C\right) d\Omega$$

Double Layer Boundary PDE

$\partial\Omega$ —— Ω, Boundary —— $\partial\Omega$, Points

Boundary PDE

$$\frac{\partial \zeta}{\partial t} = -\frac{1}{\cosh(\zeta/2)}\left[\frac{\partial \phi}{\partial y} - \frac{\partial}{\partial x}\left(Du\,\frac{\partial \zeta}{\partial x}\right)\right]$$

Weak Form

$$\int_\Omega v\frac{\partial \zeta}{\partial t}d\Omega = -\int_\Omega \frac{v}{\cosh(\zeta/2)}\frac{\partial \phi}{\partial y}d\Omega + \underbrace{\int_\Omega \frac{v}{\cosh(\zeta/2)}\frac{\partial}{\partial x}\left(Du\,\frac{\partial \zeta}{\partial x}\right)d\Omega}_{K}$$

Simplify

$$K = \underbrace{\int_{\partial\Omega}\left(v\frac{Du}{\cosh(\zeta/2)}\frac{d\zeta}{dx}\right)\cdot\hat{n}\,d\partial\Omega}_{\partial\Omega \text{ Contribution}} - \underbrace{\int_\Omega \frac{Du}{\cosh(\zeta/2)}\left[\frac{\partial \zeta}{\partial x}\frac{\partial v}{\partial x} - \frac{v}{2}\tanh(\zeta/2)\left(\frac{\partial \zeta}{\partial x}\right)^2\right]d\Omega}_{\Omega \text{ Contribution}}$$

Weak Form Contributions

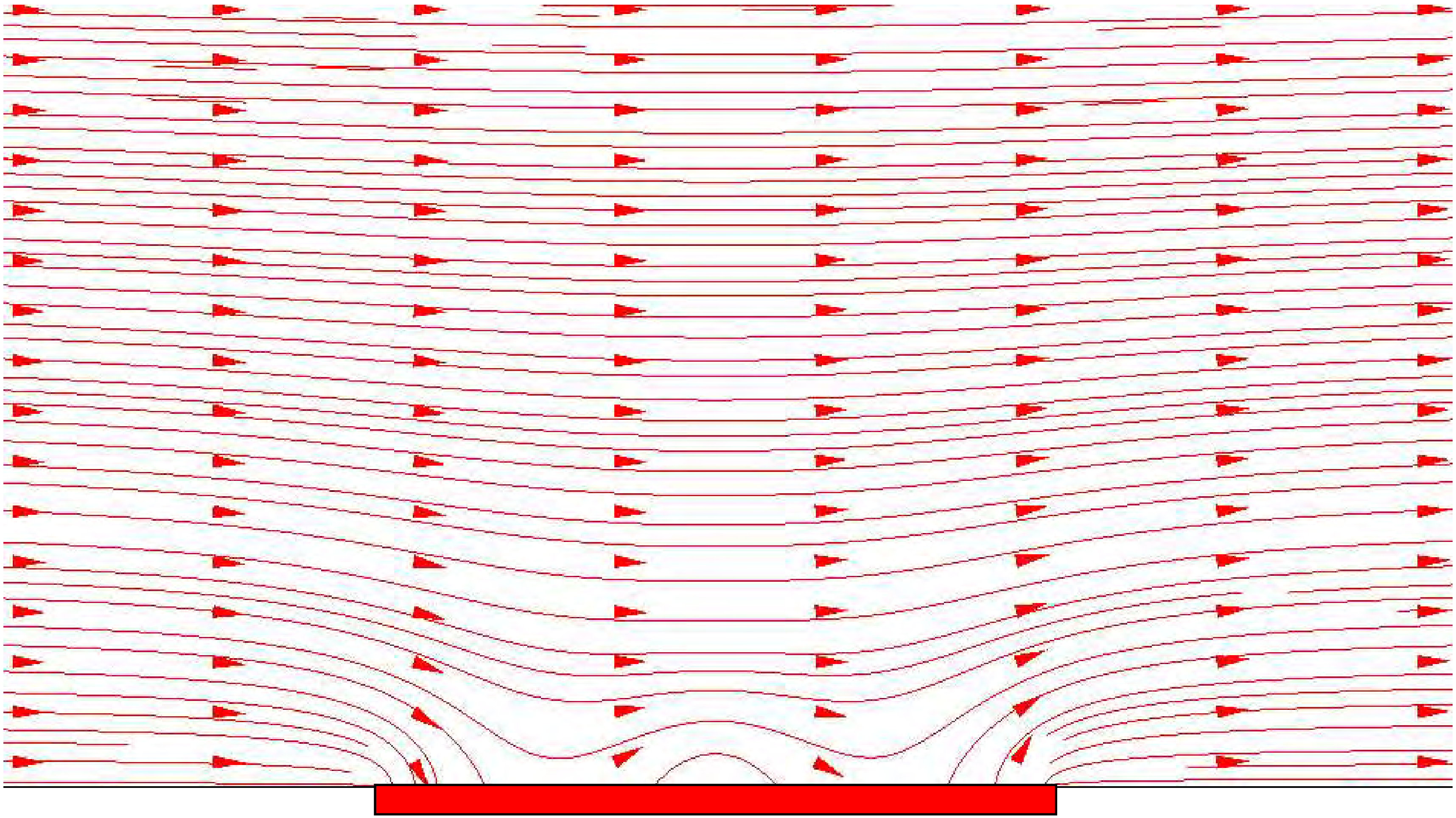
Time dependent or *dweak* terms: $$\int_\Omega v\frac{\partial\zeta}{\partial t}d\Omega$$

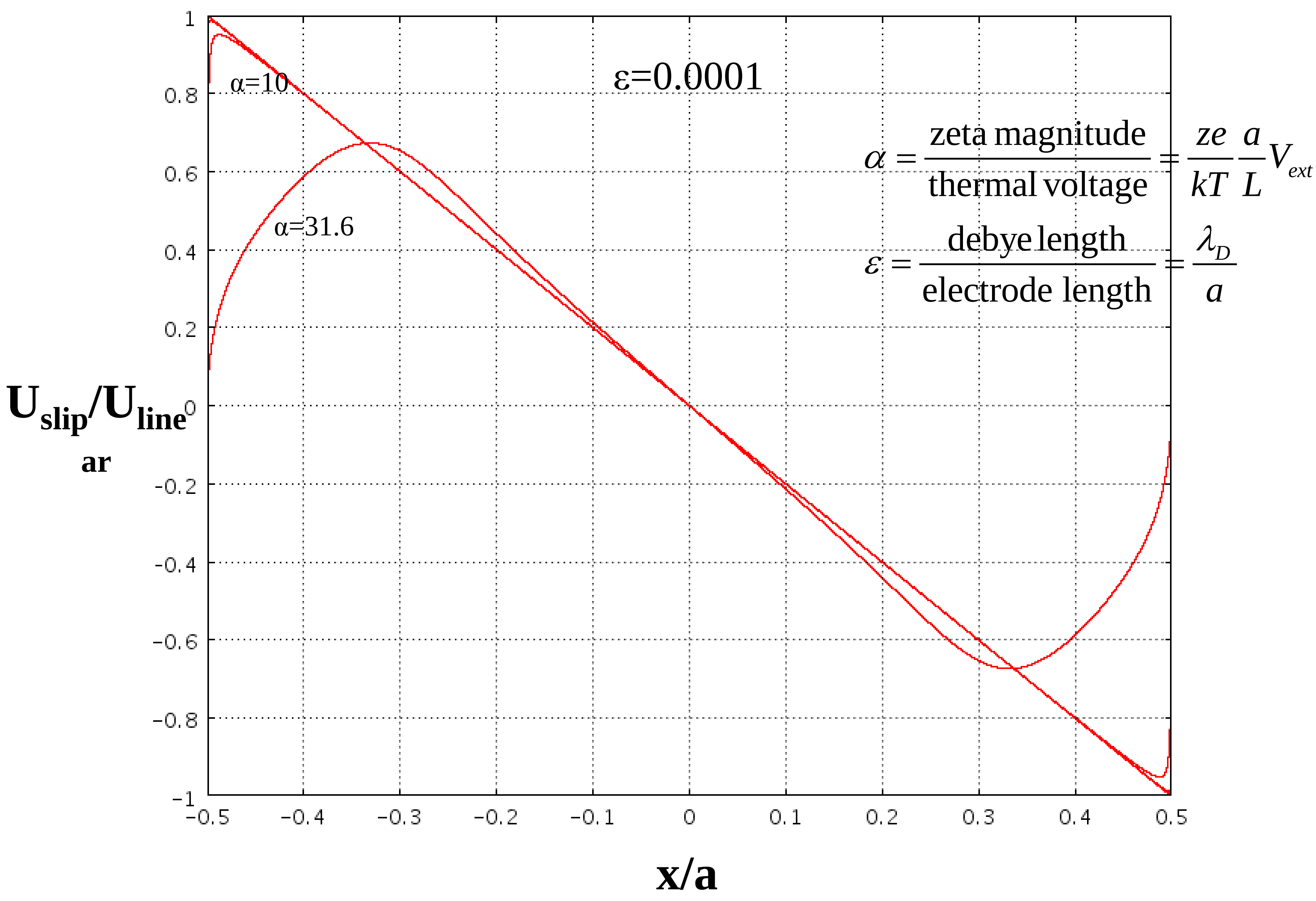
weak terms for boundary Ω

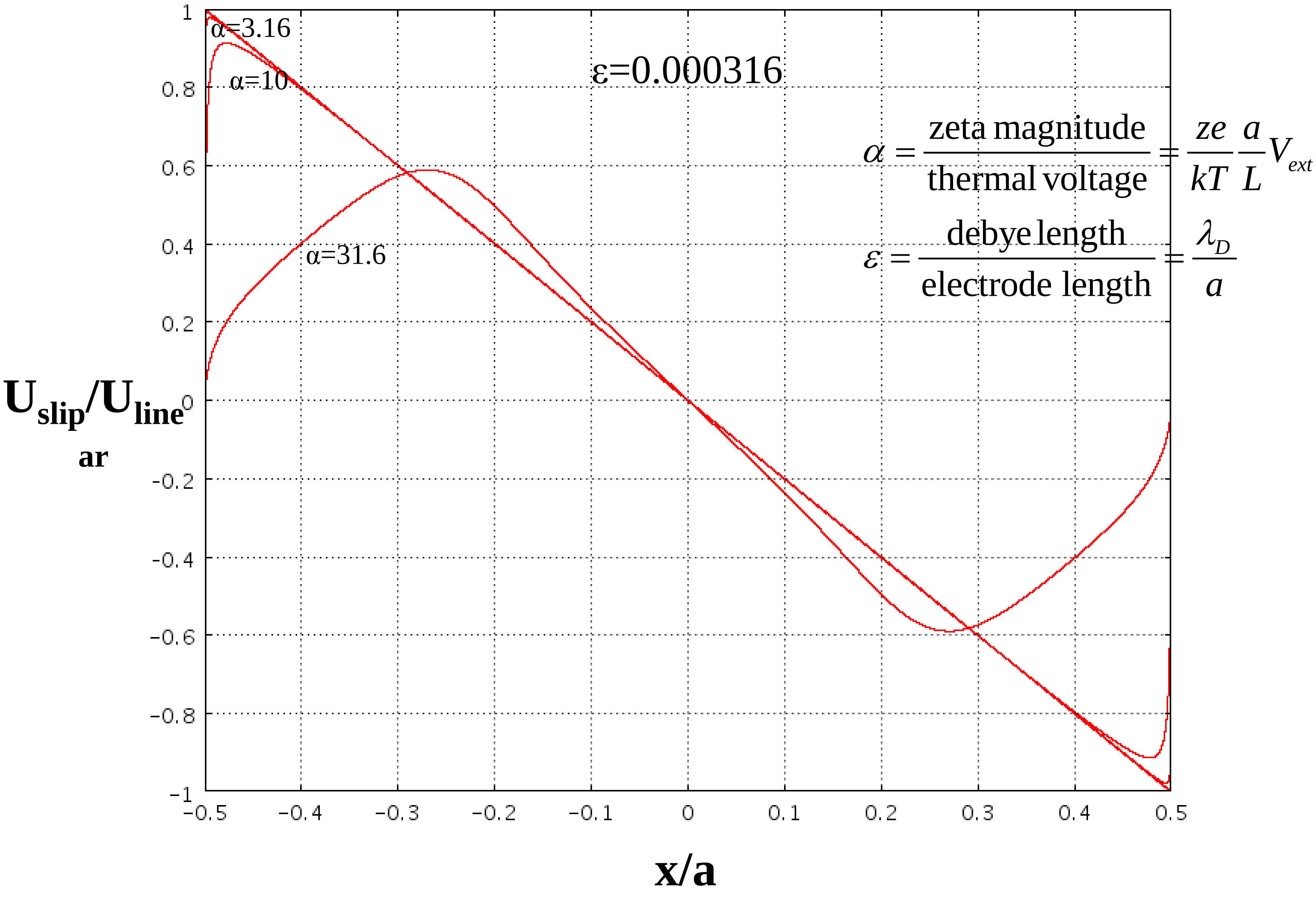
$$\underbrace{-\int_\Omega \frac{v}{\cosh(\zeta/2)}\left[\frac{\partial\phi}{\partial y}-\frac{Du}{2}\tanh(\zeta/2)\left(\frac{\partial\zeta}{\partial x}\right)^2\right]d\Omega}_{\text{Sources}}-\underbrace{\int_\Omega \frac{Du}{\cosh(a\zeta)}\frac{\partial\zeta}{\partial x}\frac{\partial v}{\partial x}d\Omega}_{\text{Diffusion}}$$

weak terms for Points ∂Ω $$\int_{\partial\Omega}\left(v\frac{Du}{\cosh(\zeta/2)}\frac{d\zeta}{dx}\right)\cdot\hat{n}d\partial\Omega$$

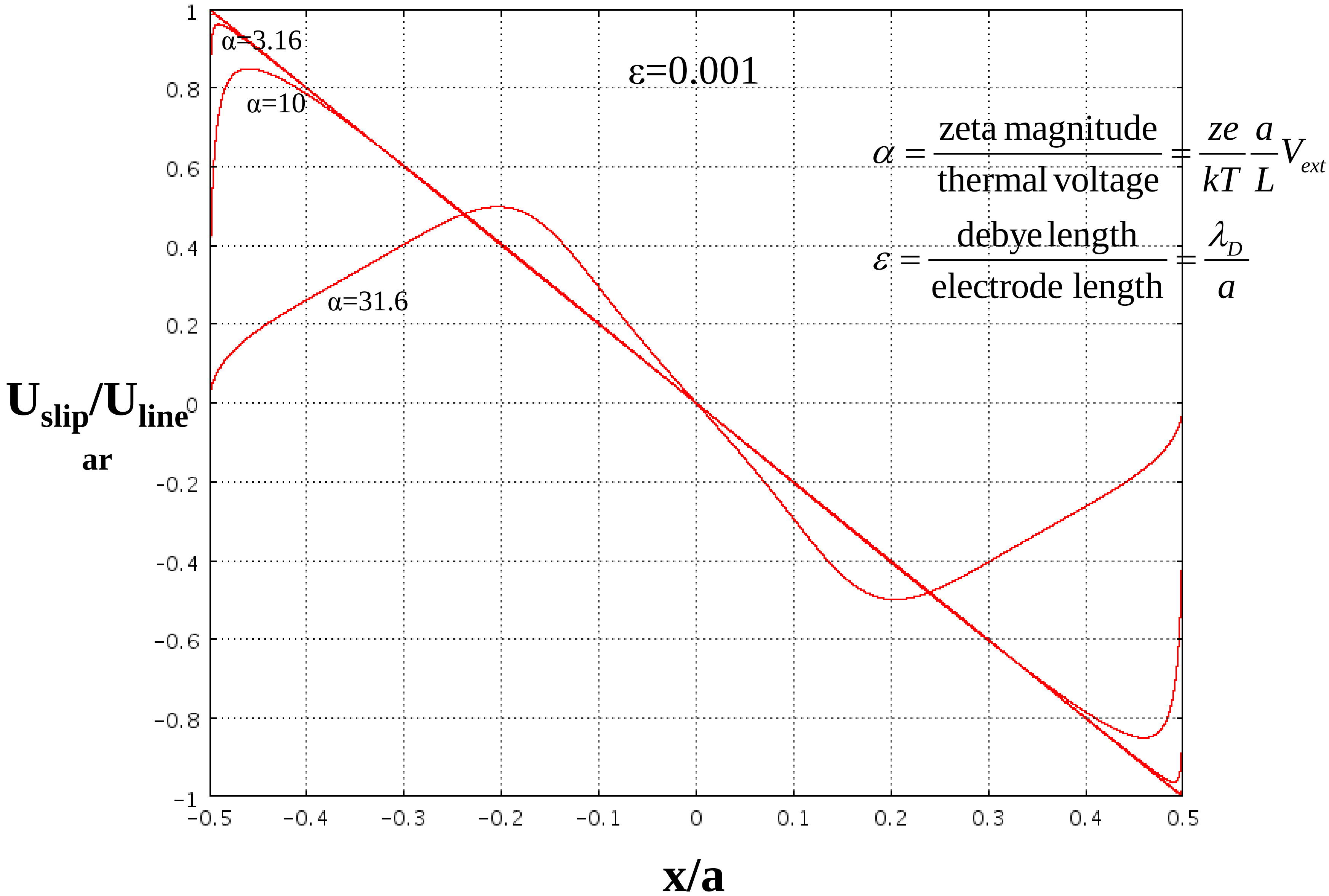
Effect of Surface Conduction



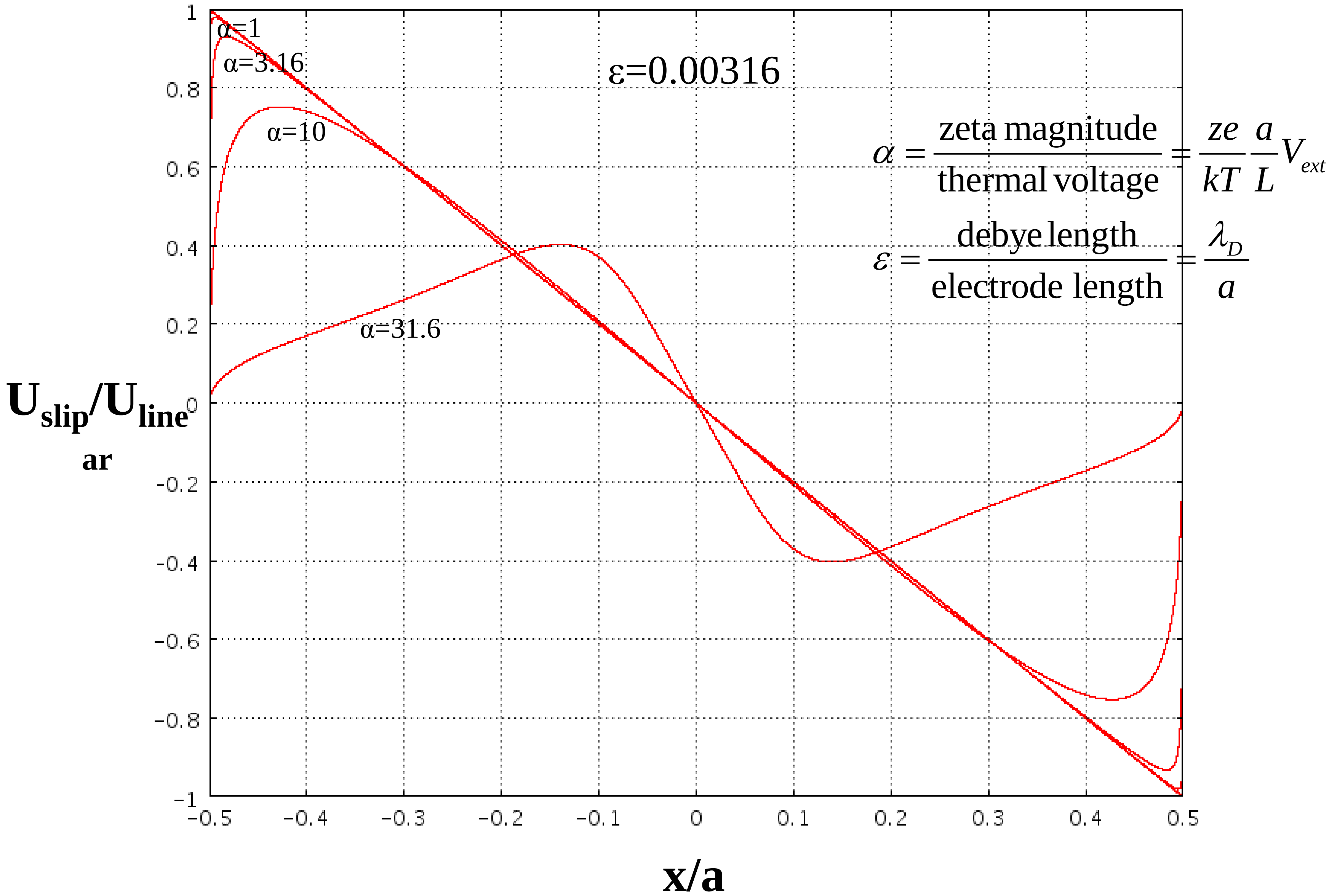

ε=0.0001
α=10
α=31.6
$\alpha = \frac{\text{zeta magnitude}}{\text{thermal voltage}} = \frac{ze}{kT}\frac{a}{L}V_{ext}$
$\varepsilon = \frac{\text{debye length}}{\text{electrode length}} = \frac{\lambda_D}{a}$
U_{slip}/U_{linear}
x/a
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-0.5
-0.4
-0.3
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5



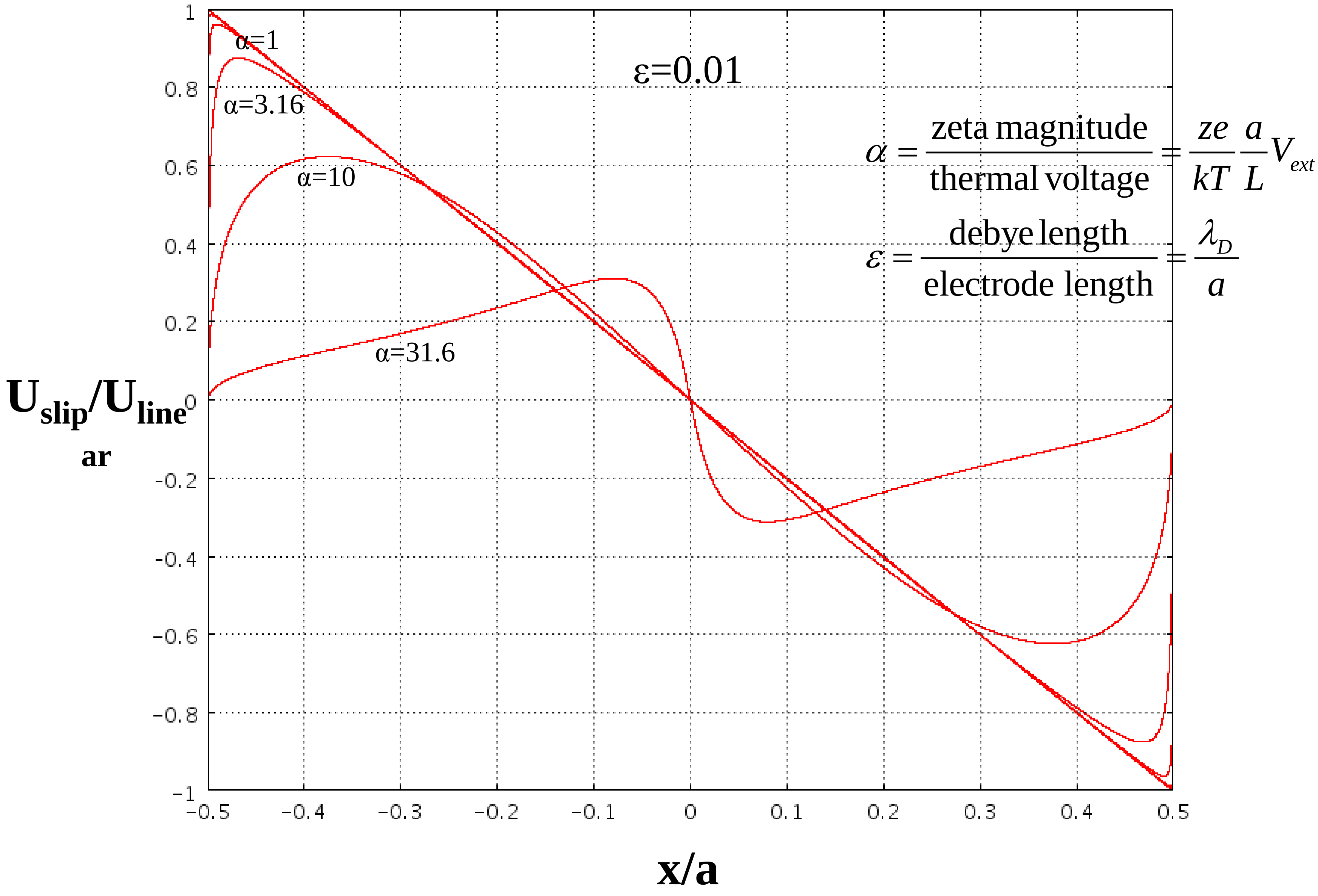
α=3.16
α=10
α=31.6
ε=0.000316
$\alpha = \frac{\text{zeta magnitude}}{\text{thermal voltage}} = \frac{ze}{kT}\frac{a}{L}V_{ext}$
$\varepsilon = \frac{\text{debye length}}{\text{electrode length}} = \frac{\lambda_D}{a}$
U_{slip}/U_{linear}
x/a
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-0.5
-0.4
-0.3
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5



ε=0.001
α=3.16
α=10
α=31.6
$\alpha = \frac{\text{zeta magnitude}}{\text{thermal voltage}} = \frac{ze}{kT}\frac{a}{L}V_{ext}$
$\varepsilon = \frac{\text{debye length}}{\text{electrode length}} = \frac{\lambda_D}{a}$
U_{slip}/U_{linear}
x/a
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-0.5
-0.4
-0.3
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5



ε=0.00316
$\alpha = \frac{\text{zeta magnitude}}{\text{thermal voltage}} = \frac{ze}{kT}\frac{a}{L}V_{ext}$
$\varepsilon = \frac{\text{debye length}}{\text{electrode length}} = \frac{\lambda_D}{a}$
α=1
α=3.16
α=10
α=31.6
U_{slip}/U_{line}
ar
x/a
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-0.5
-0.4
-0.3
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5



ε=0.01
α=1
α=3.16
α=10
α=31.6
$\alpha = \frac{\text{zeta magnitude}}{\text{thermal voltage}} = \frac{ze}{kT}\frac{a}{L}V_{ext}$
$\varepsilon = \frac{\text{debye length}}{\text{electrode length}} = \frac{\lambda_D}{a}$
U_{slip}/U_{linear}
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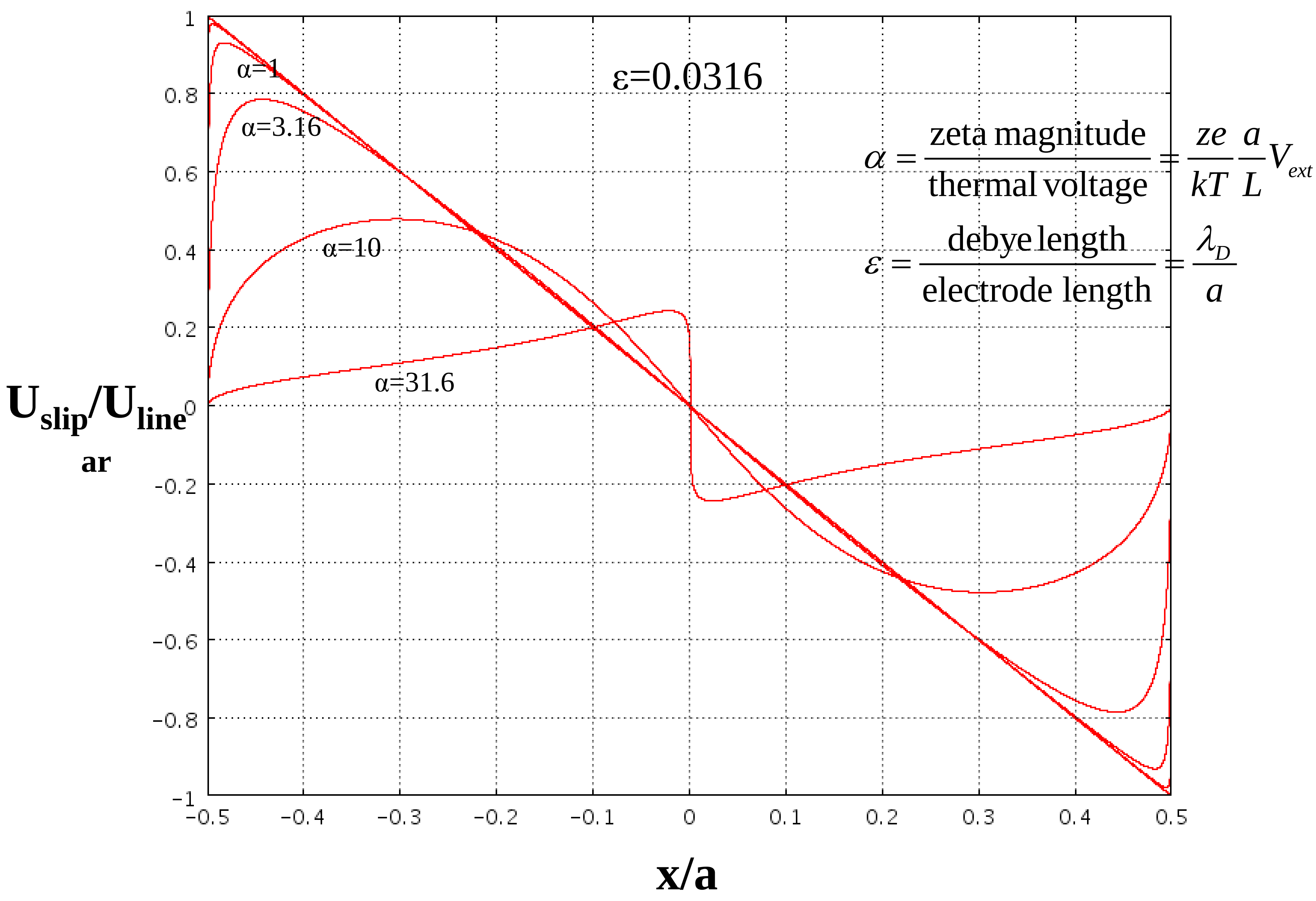
-0.3
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5



ε=0.0316
α=1
α=3.16
α=10
α=31.6
$\alpha = \frac{\text{zeta magnitude}}{\text{thermal voltage}} = \frac{ze}{kT}\frac{a}{L}V_{ext}$
$\varepsilon = \frac{\text{debye length}}{\text{electrode length}} = \frac{\lambda_D}{a}$
1
0.8
0.6
0.4
0.2
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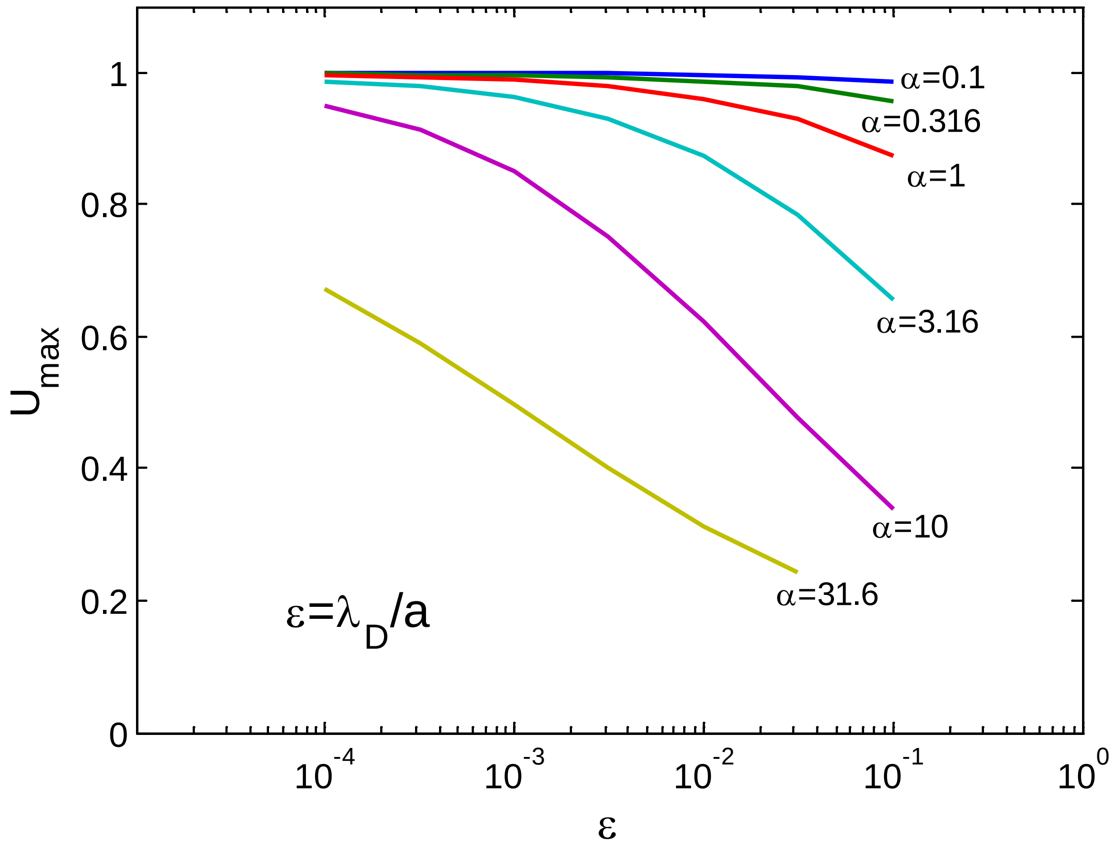
-0.2
-0.4
-0.6
-0.8
-1
-0.5
-0.4
-0.3
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
U_{slip}/U_{linear}
x/a

Normalized Velocity: Nonlinear Effects

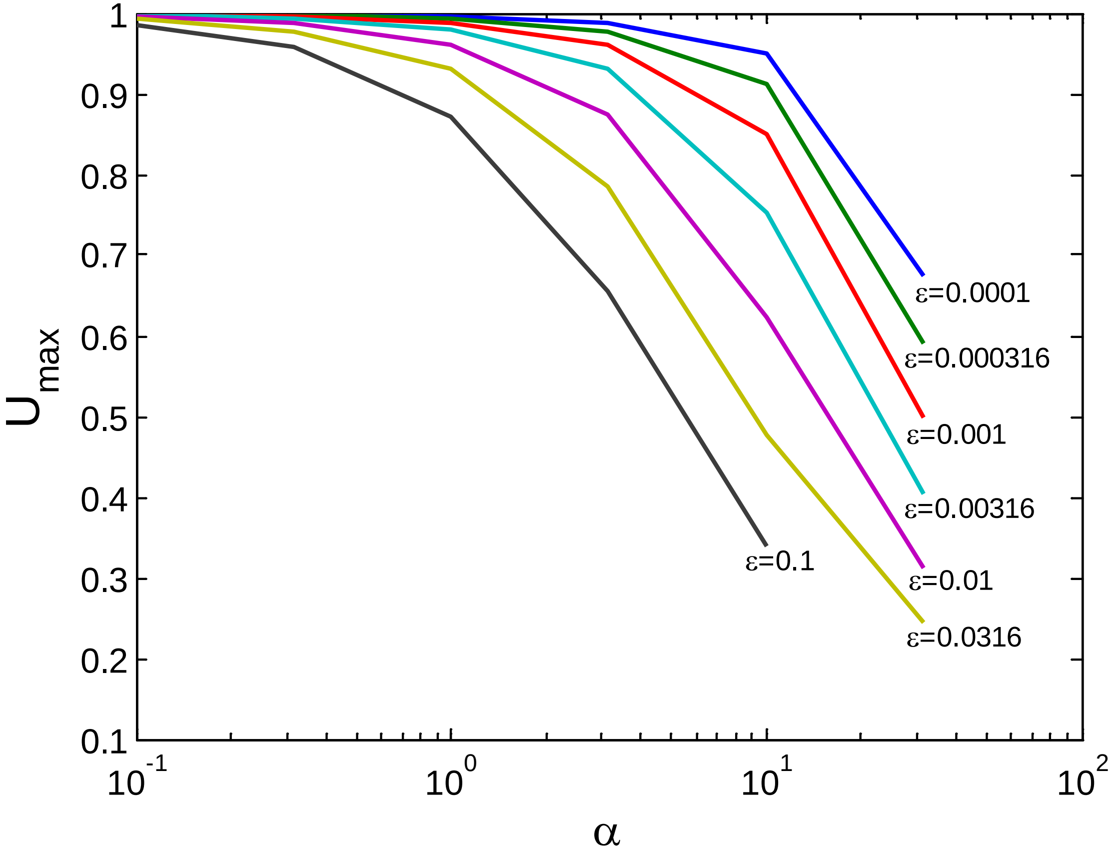


$$\alpha = \frac{\text{zeta magnitude}}{\text{thermal voltage}} = \frac{ze}{kT}\frac{a}{L}V_{ext}$$

$$\varepsilon = \frac{\text{debye length}}{\text{electrode length}} = \frac{\lambda_D}{a}$$

As double layer gets thicker, the normalized velocity decreases due to higher surface conduction.

Normalized Velocity: Nonlinear Effects



$$\alpha = \frac{\text{zeta magnitude}}{\text{thermal voltage}} = \frac{ze}{kT}\frac{a}{L}V_{ext}$$

$$\varepsilon = \frac{\text{debye length}}{\text{electrode length}} = \frac{\lambda_D}{a}$$

As zeta potential increases, the normalized velocity decreases due to higher surface conduction.

Conclusions

- An effective boundary PDE was used for simulation electroosmosis.
- Nonlinear effects such as exponential capacitance and surface conduction were simulated.
- The boundary PDE was made stable by variable transformations.
- Results for high zeta potentials (~30x thermal voltage) were obtained.
- The dimensionless velocity decreases with increasing zeta potentials and increasing double layer thickness, because surface conduction effects become prominent for high zeta potentials and thicker double layers.