Studying Mesoscale Flow with Dissipative Particle Dynamics

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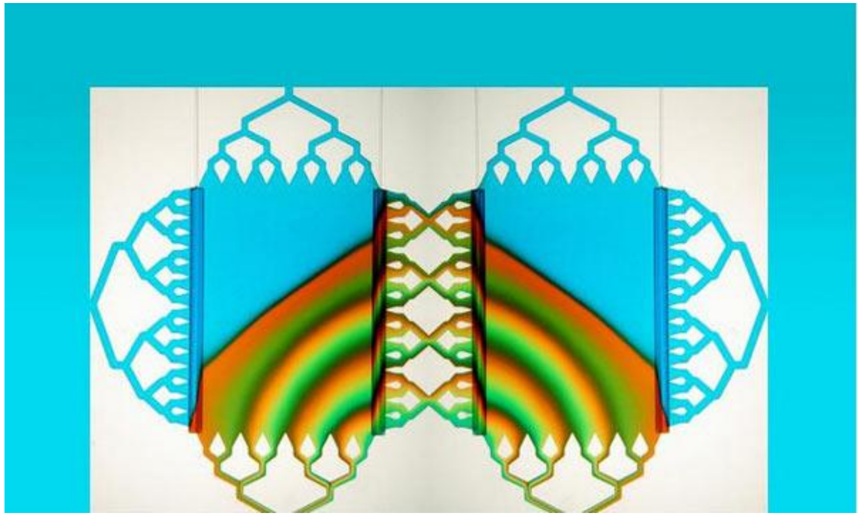
Mesoscale Flows

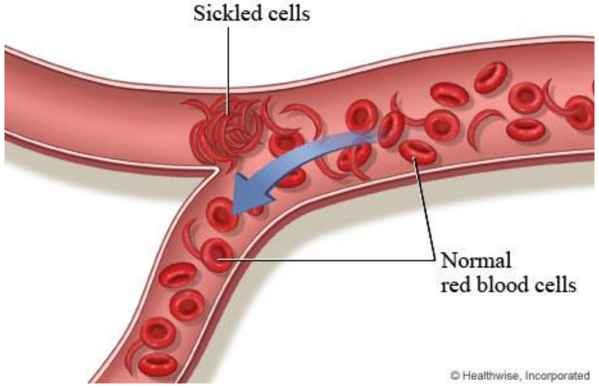
Examples

Microfluidic systems

Lab on a Chip
Art gallery

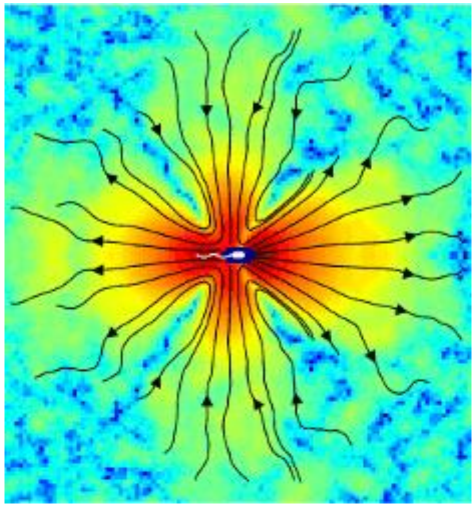


Blood in capillaries



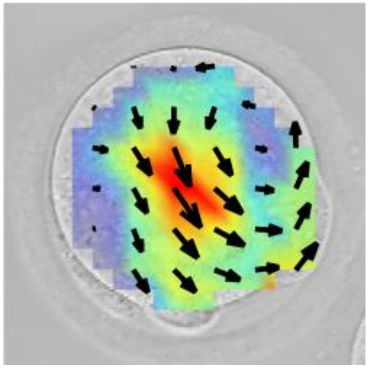
© healtwise, incorporated

Bacteria



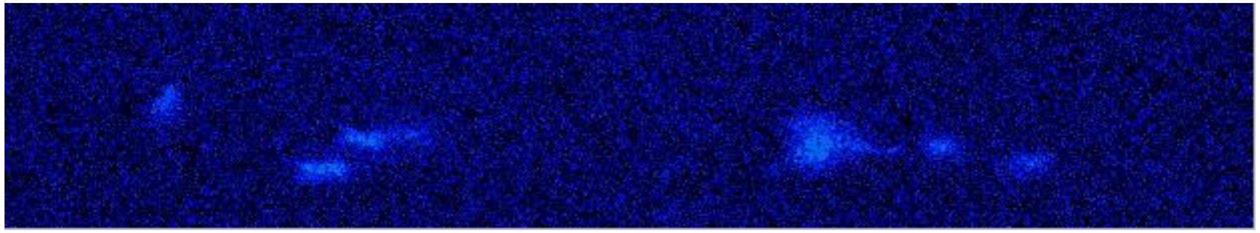
R. Goldstein, Web site

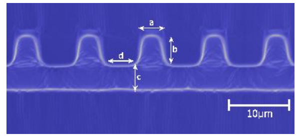
Flow in Cells



S. Windsor, Web site

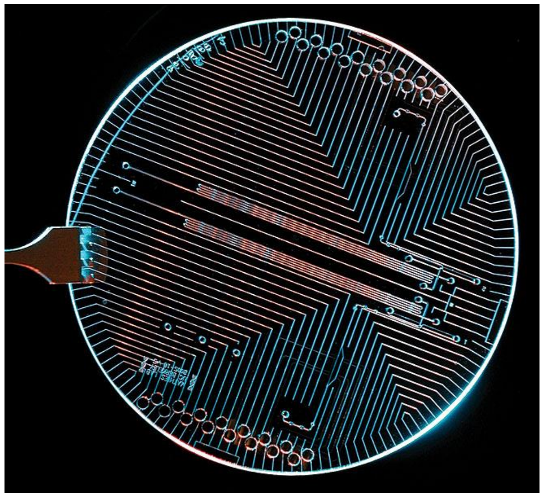
Flow and Transport in Electric Fields





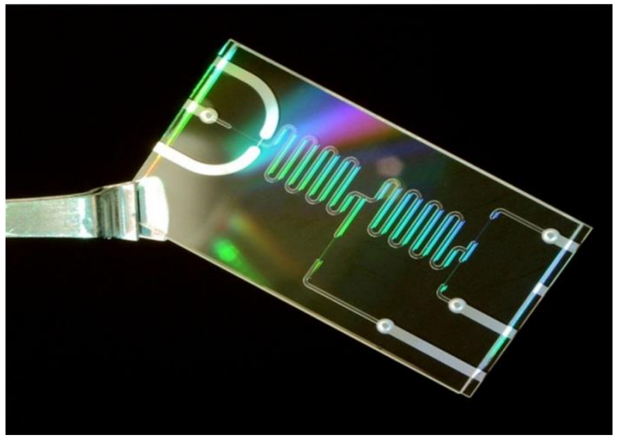
λ-DNA in a microchannel

(T.T. Duong et al, MEE 67, 905 (2003))



(Blazej et al, PNAS 2006)

Integrated microfluidic bioprocessors



LioniX

Flow on the micro- and nanoscale

On the nanoscale, things are special …

… Reynolds numbers are tiny → Flows are laminar.

… Thermal fluctuations are important

… Boundary effects are important

- Fluids slip at surfaces
  (can usually be neglected on the macroscale)
- Surfaces may be charged

Surfaces can be used to manipulate flows.

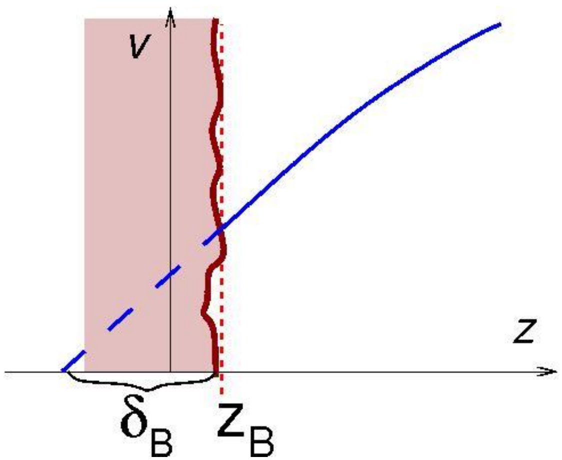
Flows can be used to manipulate particles.

Hydrodynamic Boundary Conditions

<u>Macroscopically</u>: most common assumption:

Stick boundaries: Fluid velocity ***v*** vanishes at walls

<u>Microscopically</u> more appropriate: Partial slip



$$\delta_B \left.\frac{\partial v}{\partial z}\right|_{z=z_B} = v(z)\Big|_{z=z_B}$$

z_B : Hydrodynamic boundary

δ_B : Slip length

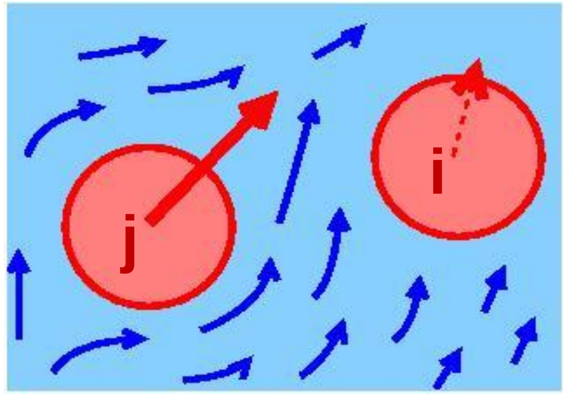
Hydrodynamic Interactions

Force on solute j

→ Solvent flow

→ Convective transport

→ Induced motion of solute i



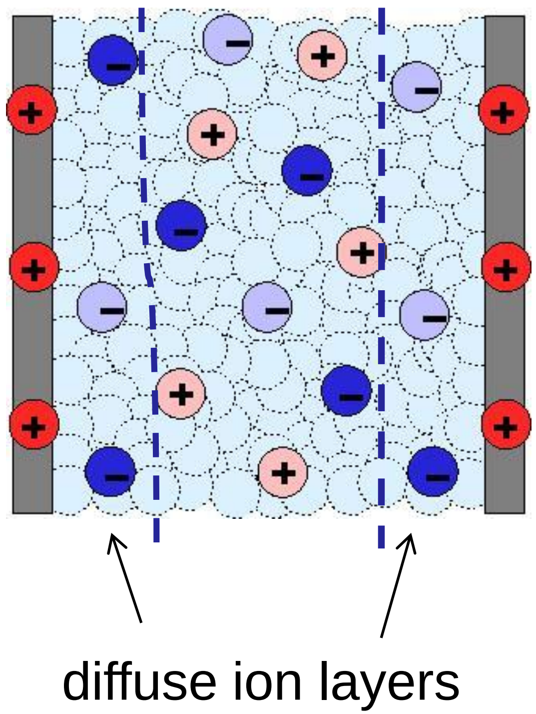
Stokes regime: Response to external force

$$\mathbf{v}_i = \frac{1}{k_B T} D_0 \; \mathbf{F}_i + \frac{1}{k_B T} \sum_{j \neq i} \mathbf{D}(\mathbf{r}_{ij}) \; \mathbf{F}_j$$

with mobility matrix: $\mathbf{D}(\mathbf{r}) = \frac{k_B T}{8\pi\eta r}\left(\mathbf{1} + \mathbf{rr}/r^2\right) + O(\frac{1}{r^2})$

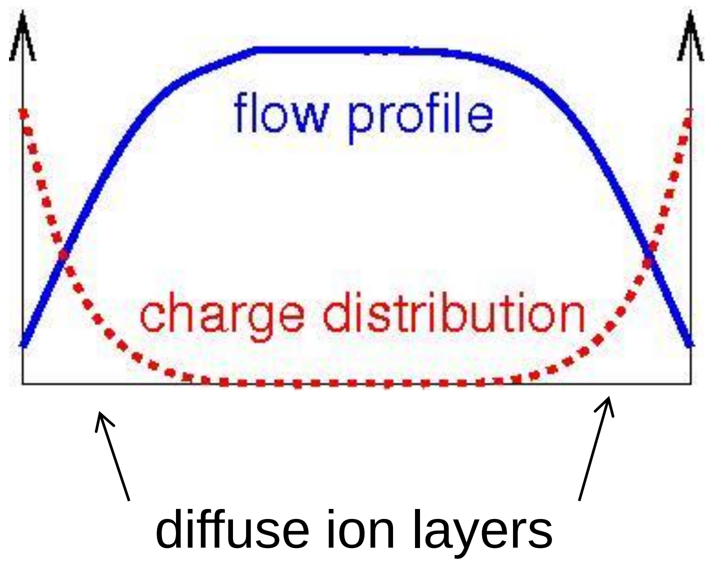
⇒ Long-range "Hydrodynamic interaction"

Electrostatic boundary conditions



Electric double layer

Apply electric field



Electroosmotic flow

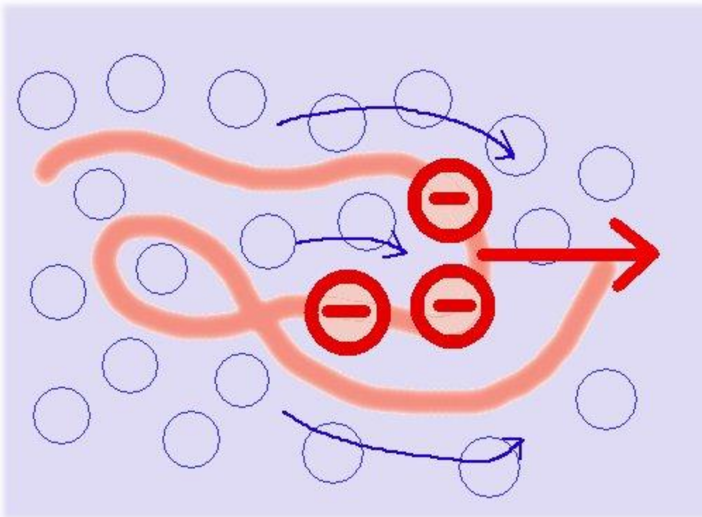
Electric field drags mobile ion layer along

$\Rightarrow$ Induces flow!

Electrohydrodynamic „Screening“

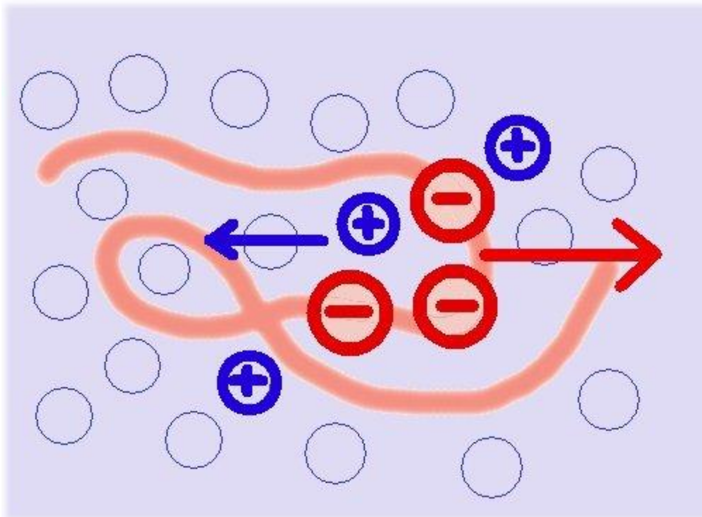
Example: Polyelectrolyte chain in a static electric field

Hydrodynamic drag



Hydrodynamic interactions

Electroosmosis



Counterions: opposite force

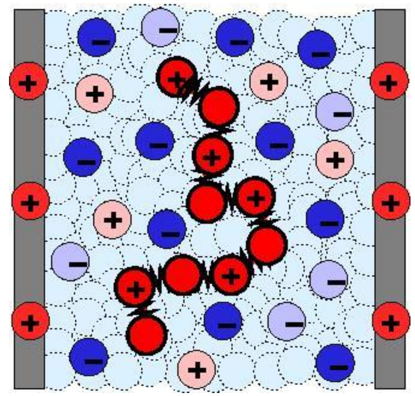
⇒ Hydrodynamic interactions are screened (leading order)

BUT … only with respect to static fields, only for long chains

Challenges for Computer Simulations

Study in full the interplay of

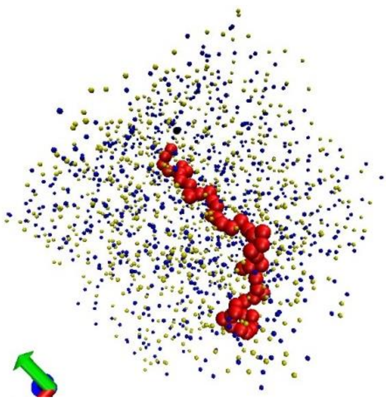
- Hydrodynamics
- Charges
- Flow and boundary conditions



… ideally under physiological conditions

- Ion concentration ~ 0.2 M or more
- Debye length < 1 nm

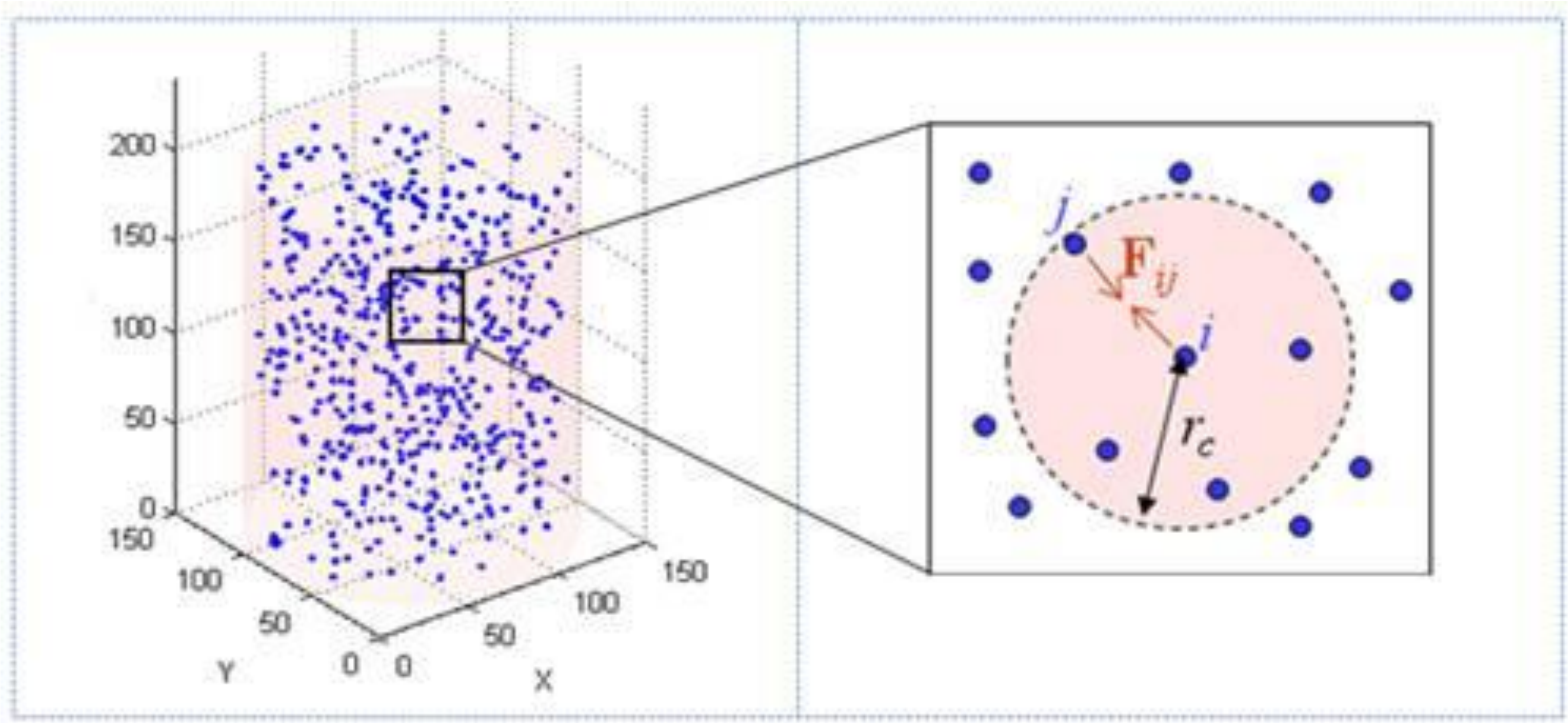
→ Fluid full with ions



→ Devise strategies how to manipulate flows and transport

Method: Dissipative Particle Dynamics

A type of particle-based coarse-grained model for fluids



Source: M.E. Kutay, Web site

Structure of a Standard DPD Model

(Koelman, Hoogerbrugge 1993, Espanol, Warren, 1995)

Pairwise forces between particles i and j: $(\mathbf{e}_{ij} = \mathbf{r}_{ij} / r_{ij})$

$\mathbf{F}_{ij} = \mathbf{F}_{ij}^{C} + \mathbf{F}_{ij}^{D} + \mathbf{F}_{ij}^{R} = -\mathbf{F}_{ji}$ with

$\mathbf{F}_{ij}^{C}$: conservative pair force
(conservative multibody forces are also possible)

$\mathbf{F}_{i}^{D} = -\gamma\, \omega(r_{ij}/r_c)\, (\mathbf{e}_{ij}\, \mathbf{v}_{ij})\, \mathbf{e}_{ij}$: dissipative force

$\mathbf{F}^{R}$: random, satisfies fluctuation-dissipation theorem

⇒ Momentum conserving thermostat

⇒ **Can be used to simulate hydrodynamic flows**

Why use DPD?

- Physical motivation:
  simplest Ansatz for coarse-grained model
  with dissipative dynamics
  that preserves momentum conservation
- Useful as off-lattice solver for hydrodynamics
  → Easy with curved boundaries
  → Easy with constant pressure (fluctuating box)
- Can be combined naturally with other particle based
  models (i.e., molecular dynamics models)
- "Smoothed dissipative particle dynamics" (SDPD)
  → Equation of state of fluid is put in

(but: admittedly slower than Lattice Boltzmann methods)

Outline of this Talk

- **Part 1: Surface slip**
  - Implementing (no)-slip boundaries in DPD simulations
  - Example: Effective slip on structured surfaces
- **Part 2: An applicaton**
  - Separation of chiral particles in microfluidic channels
- **Part 3: An efficient DPD algorithm for electrolyte fluids**
  - The condiff-DPD method
  - Example: Electroosmotic flow on patterned surfaces

Part I: Tunable slip boundaries

Jens Smiatek, *M.P. Allen, FS,*
Eur. Phys. J. E 26, 115 (2008).

***J. Zhou**, A. Belyaev, FS, O. Vinogradova, JCP 136, 194706 (2012).*

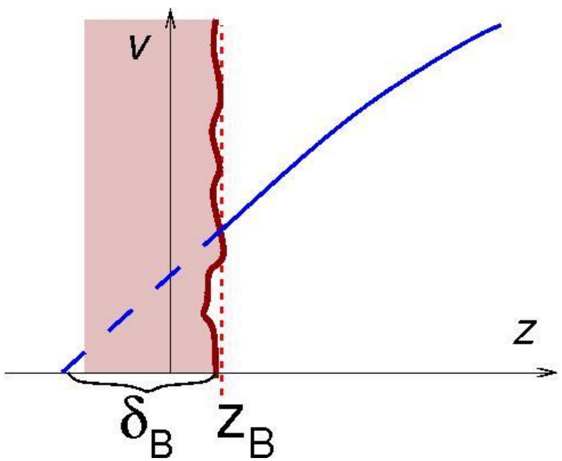
*E.S. Asmolov, **J. Zhou**, FS, O.I. Vinogradova, PRE 88, 023004 (2013).*

***J. Zhou**, E.S. Asmolov, FS, O.I. Vinogradova, JCP 139, 1748708 (2013).*

*T.V. Nizkaya, E. Asmolov, **J. Zhou**, FS, O.I. Vinogradova, submitted (2014).*

Recall: Hydrodynamic boundaries

Partial slip boundary condition



$$\delta_B \left.\frac{\partial v}{\partial z}\right|_{z=z_B} = v(z)\big|_{z=z_B}$$

z_B : Hydrodynamic boundary

δ_B : Slip length

Task: Implement this in DPD simulations

Tunable-slip boundaries

Idea: *Jens Smiatek, M.P. Allen, FS, Eur. Phys. J. E 26, 115 (2008)*

Represent wall-fluid friction by an effective viscous force
→ Viscous layer of finite thickness.

$\mathbf{F}_i = \mathbf{F}_i^D + \mathbf{F}_i^R$ with $\mathbf{F}_i^D = -\gamma\, \omega(z_i / z_c)\, (\mathbf{v}_i - \mathbf{v}_{wall})$

$\mathbf{F}^R$: random, satisfies fluctuation-dissipation theorem

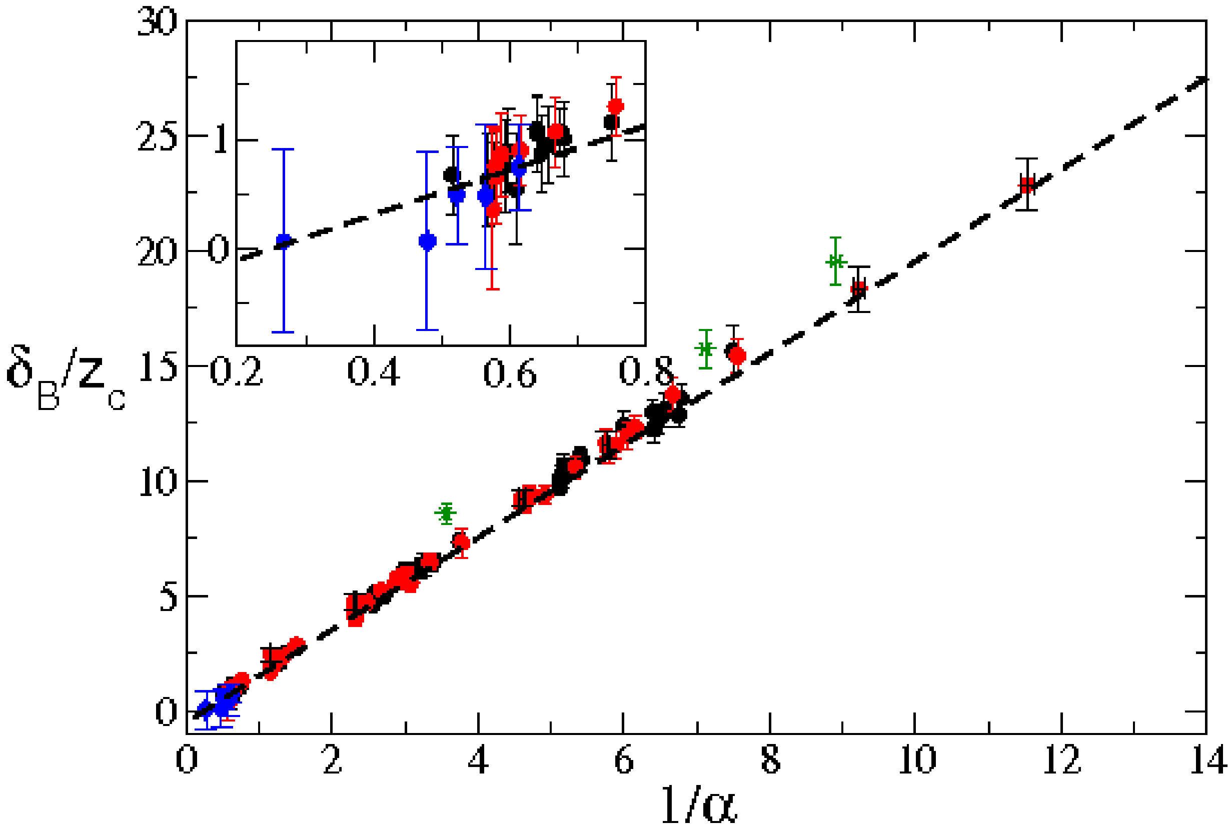
Advantages:

- Slip length can be tuned by tuning γ
- By solving Stokes equation, one can derive an analytical expression for δ_B

→ depends on $\omega(x)$ and dimensionless parameter

$$\alpha = \frac{z_c^2 \gamma \rho}{\eta}$$

Results: Tunable slip boundary method



Data for
γ = 0.1 - 1
ρ = 3.75 - 12.3
η = 1 – 5

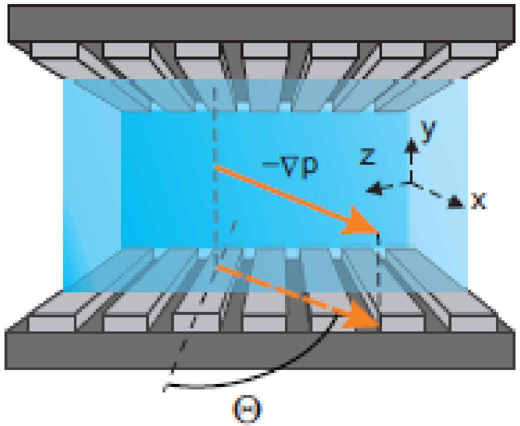
Dashed line:
theory

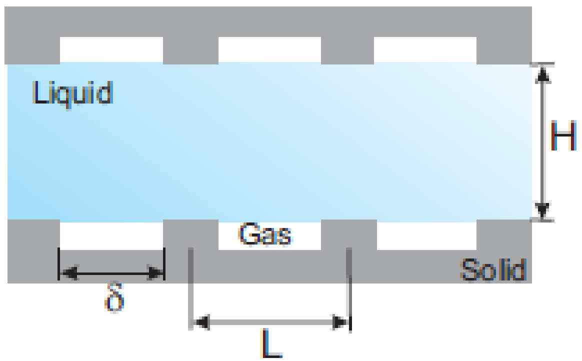
$\Rightarrow$ Data collapse, good agreement with theory.

Slip length δ_B can be tuned from 0 to ∞ !

Effective slip on structured surfaces

J. Zhou, A. Belyaev, FS, O. Vinogradova, J. Chem. Phys. 136, 194706 (2012).
E.S. Asmolov, J. Zhou, FS, O.I. Vinogradova, Phys. Rev. E 88, 023004 (2013).
J.Zhou, E.S. Asmolov, FS, O.I. Vinogradova, J. Chem. Phys. 139, 1748708 (2013).





Goal: Use structured surfaces
to control flows

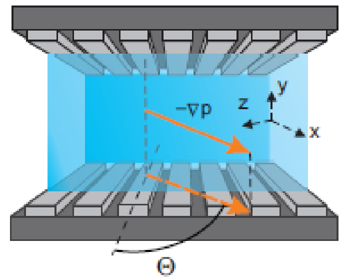
Here: Alternating stripes slip / no slip
(≅ superhydrophobic surface, Cassie state)

Expectation:

Surface tunes effective slip
(Cottin-Bizonne et al, 2005)

Theory: Slip Tensor

(Bazant & Vinogradova, J. Fluid Mech. 2008;
Belyaev & Vinogradova, J. Fluid Mech. 2010)



On anisotropic surfaces, slip becomes a **tensorial** quantity!

$$\delta_B \left.\frac{\partial v}{\partial z}\right|_{z=z_B} = v(z)\big|_{z=z_B} \quad \rightarrow \quad b_{ij} \left.\frac{\partial v_j}{\partial z}\right|_{z=z_B} = v_i(z)\big|_{z=z_B}$$

Stripe pattern ⇒ Eigendirections are || and ⊥ to the stripes

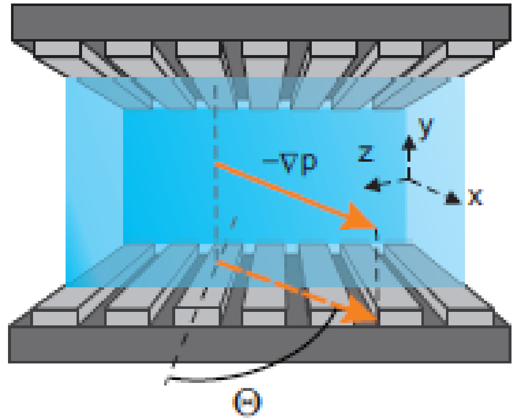
Analytical predictions for b_{ij} for arbitrary channel width L

e.g., at $L \rightarrow \infty$

$$b_{\text{eff}}^{\|,\perp} = \frac{L}{2\pi} \frac{\ln\left(\sec\left(\pi\phi/2\right)\right)}{1 + \frac{L}{2\pi\delta}\ln\left(\sec\left(\pi\phi/2\right) + \tan\left(\pi\phi/2\right)\right)}$$

(ϕ: Fraction of hydrophobic surface area; δ: slip length there)

Simulation Details

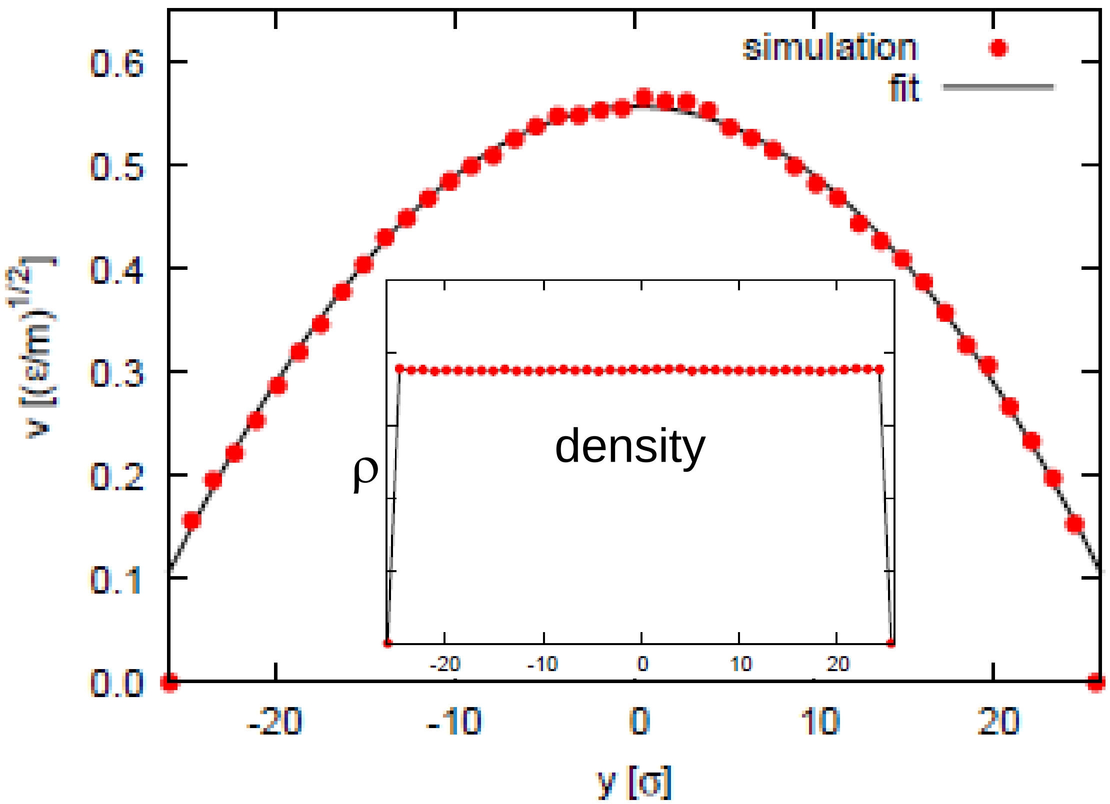


- DPD fluid without conservative interactions,
  DPD density ρ=3.75 $\rightarrow$ viscosity η=1.35
- Simulation box: One period L=50. Box size 20 x H x L
- Flat surface, Tunable slip boundaries
- Periodic boundary conditions except in y direction
- Pressure driven flow (volume force)
- ESPResSo package (Holm group, Stuttgart)

(Simulation units: DPD interaction range, thermal energy $k_B T$)

Average Flow Profile

Typical in-plane average of flow profile under pressure

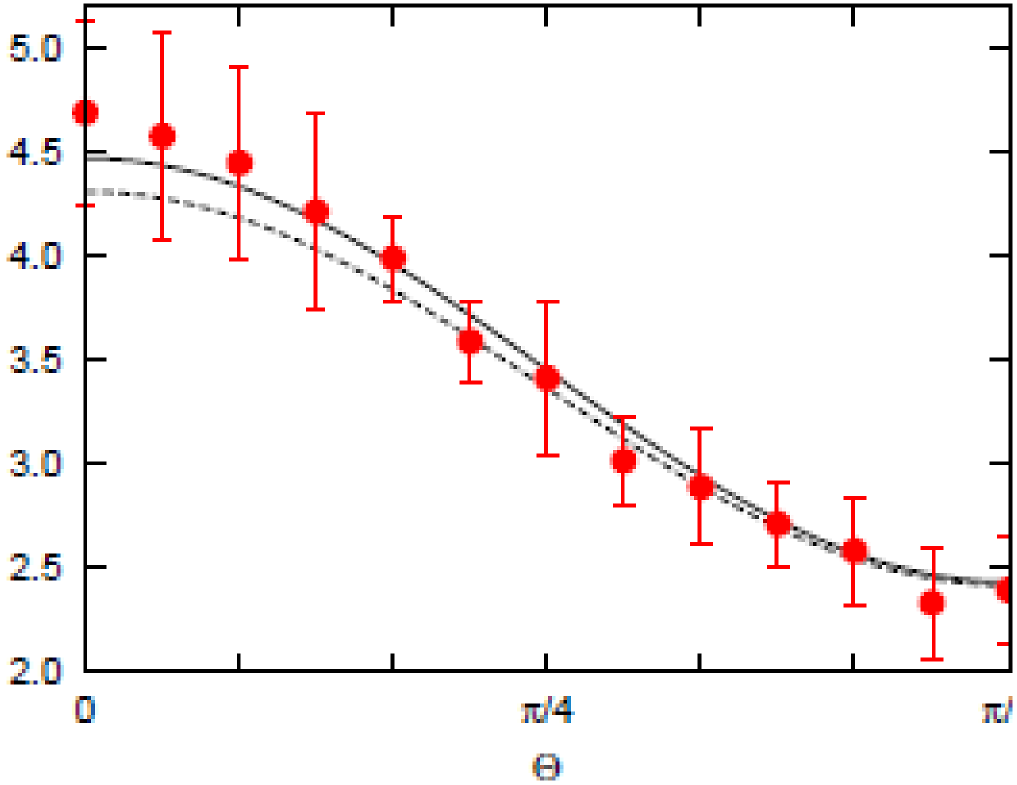


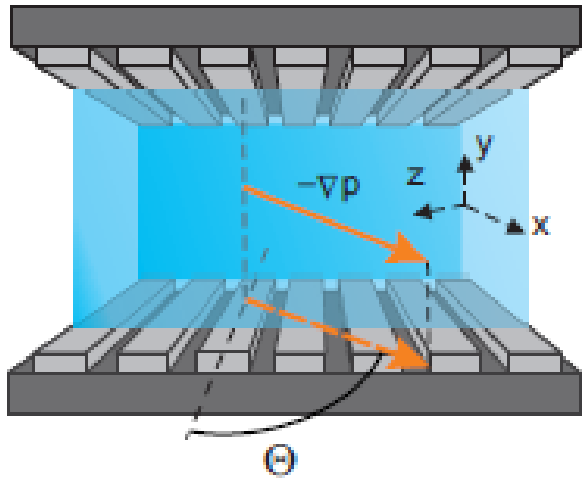
Longitudinal flow,
L=H=b=50
50:50 coverage

⇒ Parabolic Poiseuille-type flow

⇒ Effective slip length can be extracted.

Effective slip lengths



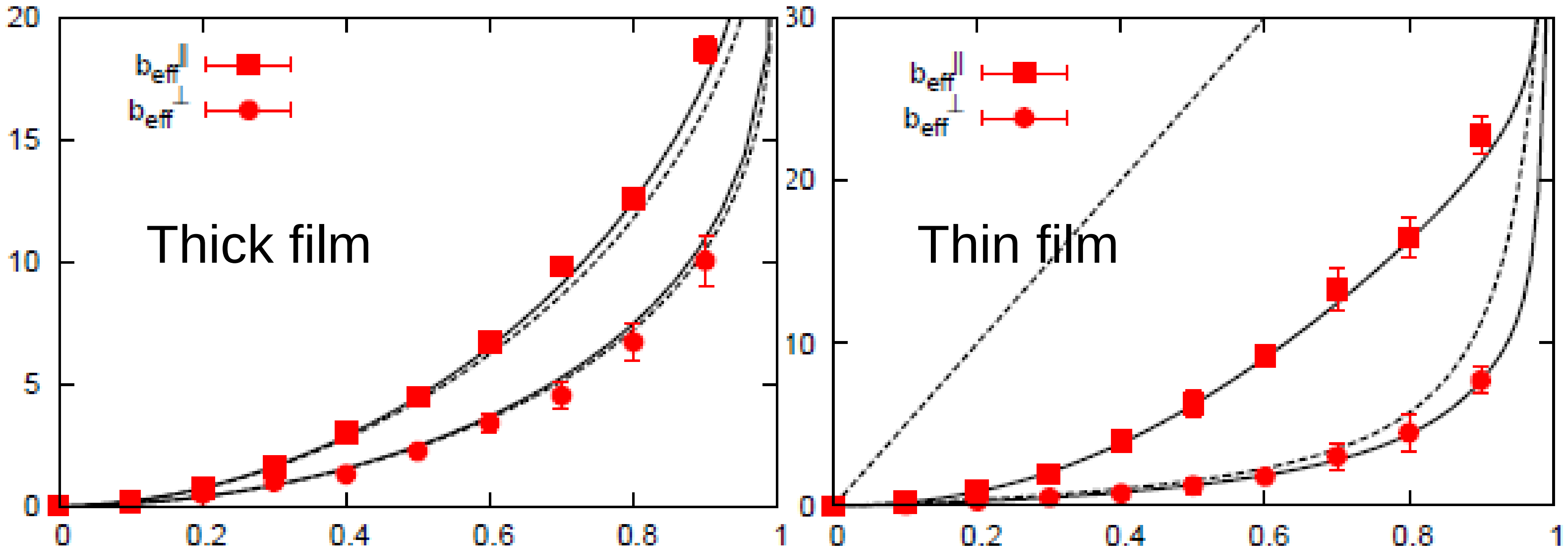


(50:50 coverage)

⇒ Good agreement with theory by Vinogradova & coworkers

⇒ Theory works ! Tunable slip algorithm works !

Parallel and Perpendicular Slip Lengths

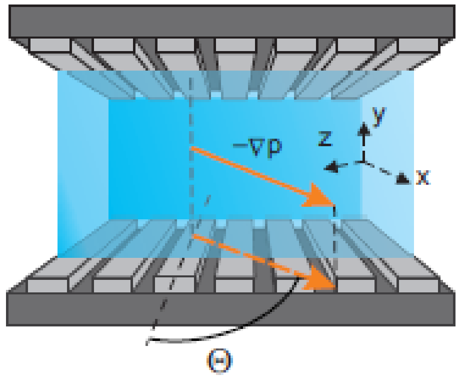


Fraction ϕ of hydrophobic surface area

$\Rightarrow$ Again very good agreement with theory

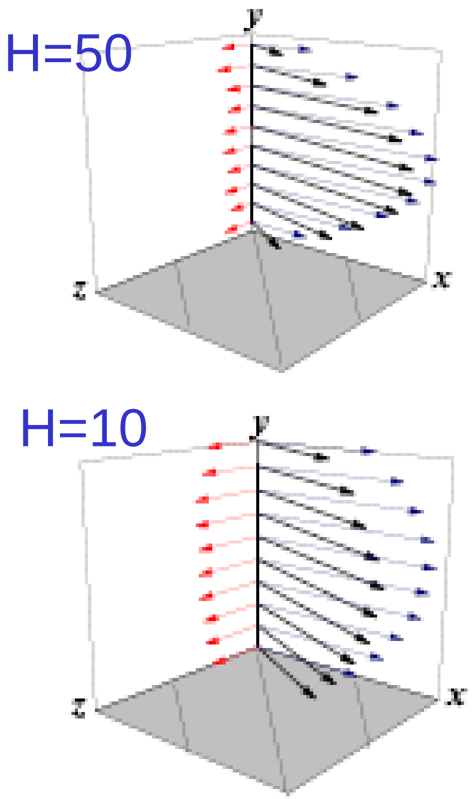
Surface slip can be tuned over wide range by patterning

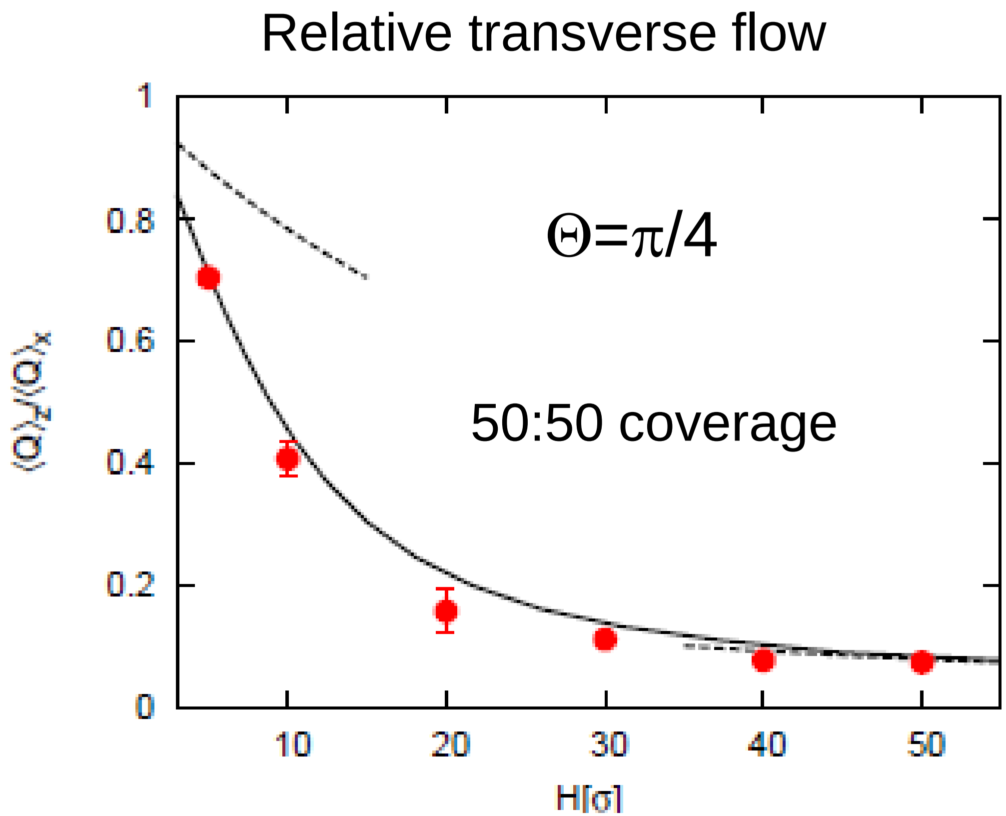
Flow at Intermediate Angles



Poiseuille flow that is not aligned with stripes

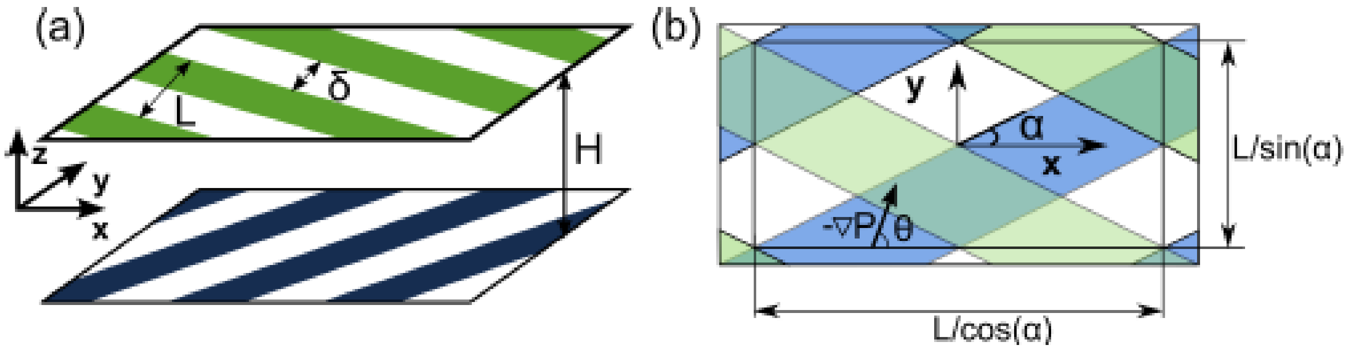
⇒ Generation of **transverse flow**





Flow in Channels with Misaligned Stripes

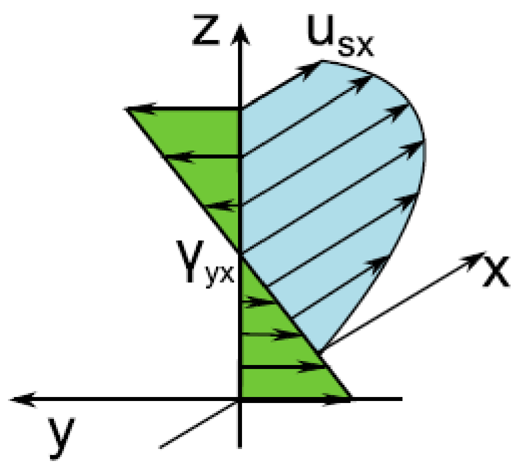
*T.V. Nizkaya, E. Asmolov, **J. Zhou**, FS, O.I. Vinogradova, PRE 2015.*



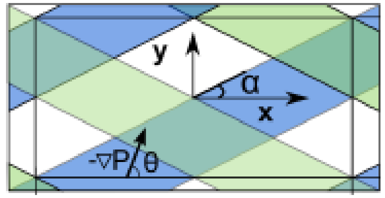
Theoretical prediction:

Superposition of Poiseuille flow and shear flow

Question: Can this be useful ?



Flow versus Shear

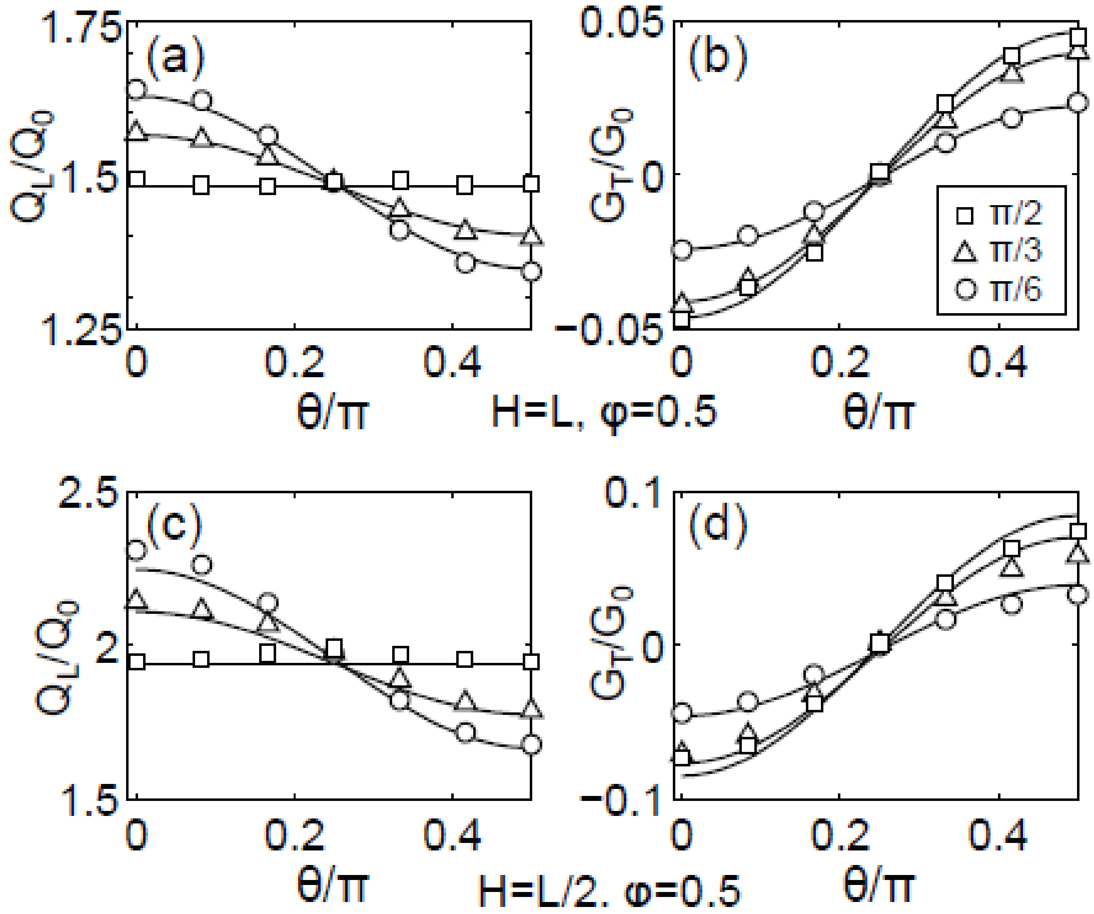


Flow rate

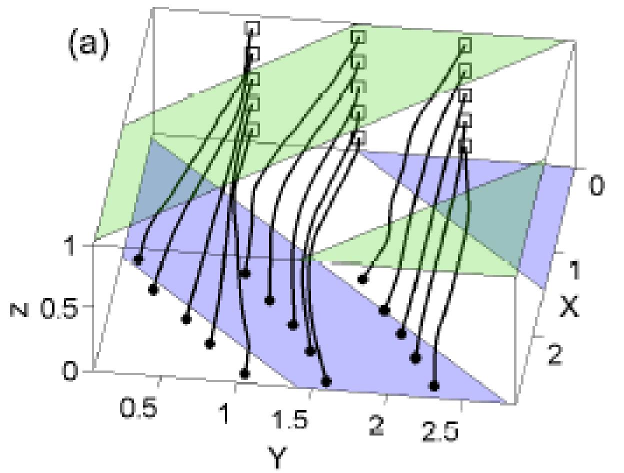
Shear rate

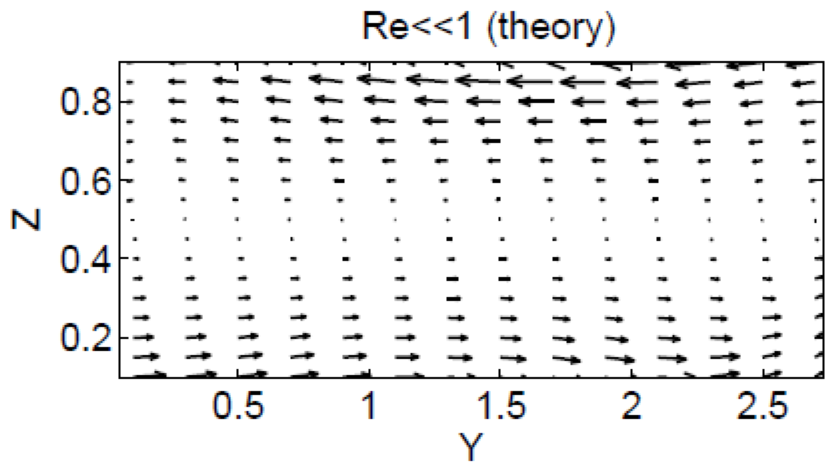
Thick film

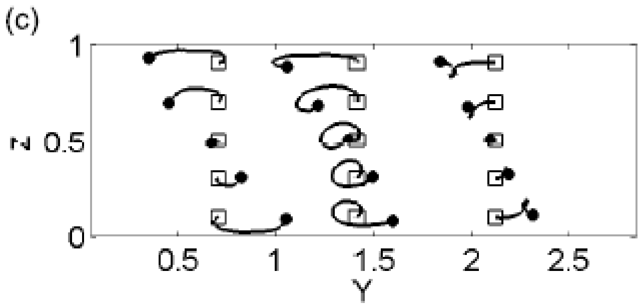
Thinner film

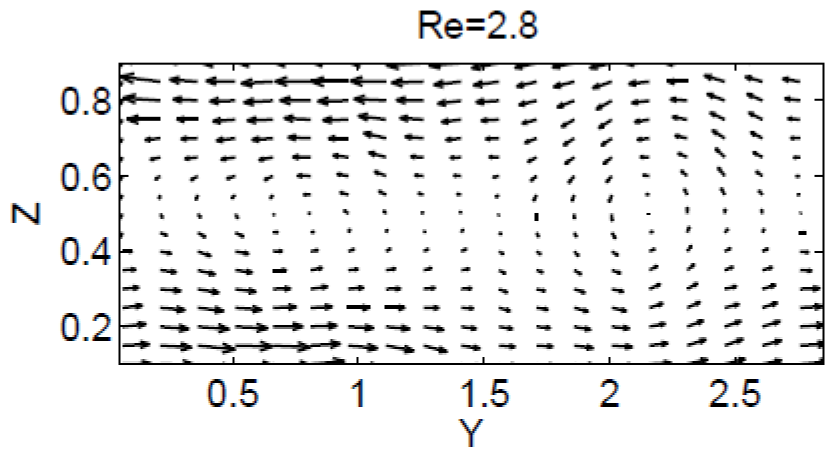


Particle Displacements after one Period









Potential as micromixers?

Conclusion of Part 1: Surface Slip

On nanoscales, fluids may slip on surfaces

We have devised a way to implement arbitrary slip boundary conditions in DPD simulations.

Surface slip can be controlled by patterning surfaces.

Patterned surfaces with variable surface slip can possibly be exploited in lab-on-a chip technologies, e.g., for mixing of fluids on microscales

… or for particle separation

Part 2:

Separation of Chiral Particles in Microfluidic Channels

S. Meinhardt, J. Smiatek, R. Eichhorn, F. Schmid,
Phys. Rev. Lett. 108, 214504 (2012).

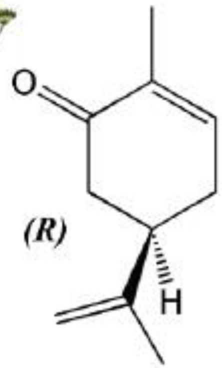
The Challenge

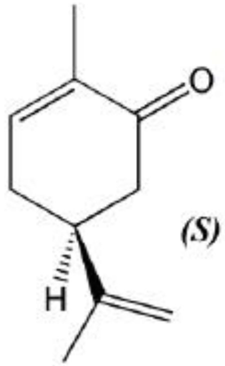
Distinguish between particles
with different chirality

Why bother ?

- Nature is chiral
  (e.g., proteins, sugars, DNA)
- Biological response depends on chirality

Example: Carvone

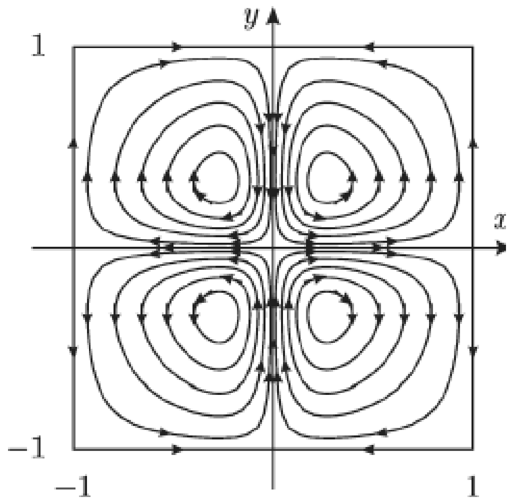




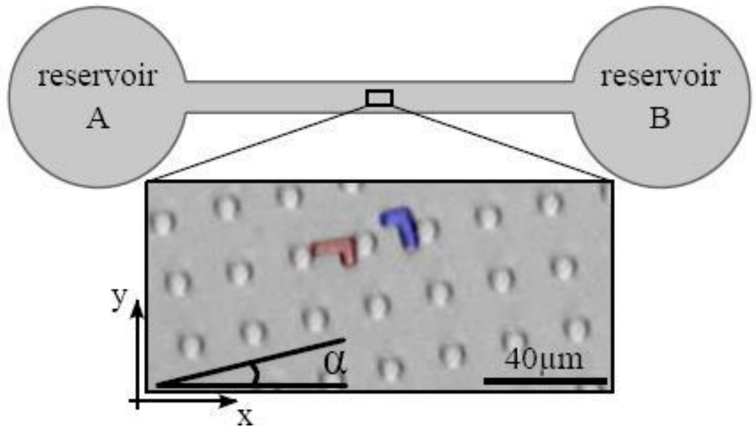
Idea : To separate chiral partners ...

Use **microfluidic devices**
with **asymmetric flow patterns**

Examples in two dimensions



Kostur et al, PRL 2006

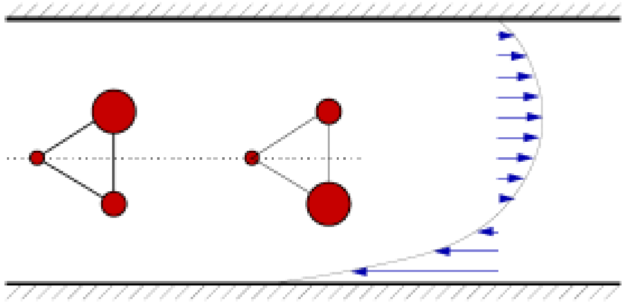


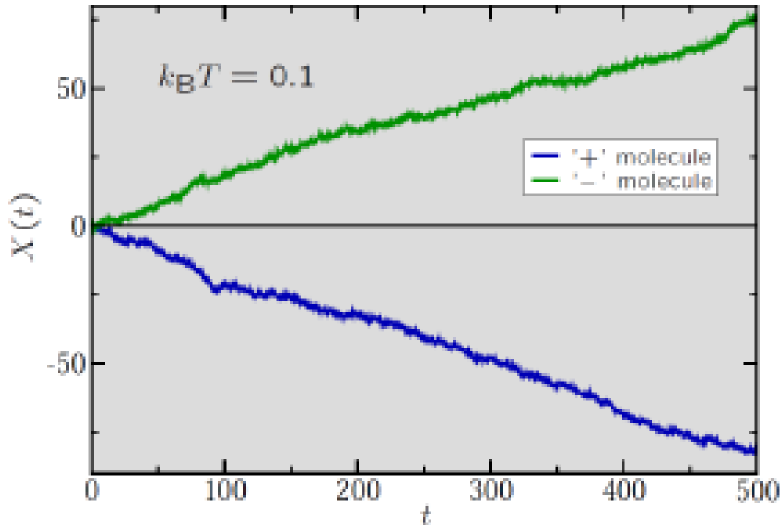
Speer et al, PRL 2010
Bogunovic et al, PRL 2012

Separation in Asymmetric Poiseuille Flow

Ralf Eichhorn, PRL 2010

2D asymmetric flow
Langevin simulations





⇒ Different enantiomers can be separated !

Our Question

Can asymmetric Poiseuille flow also be used for chiral separation in more realistic situations ?

- three spatial dimensions
- taking account of hydrodynamics

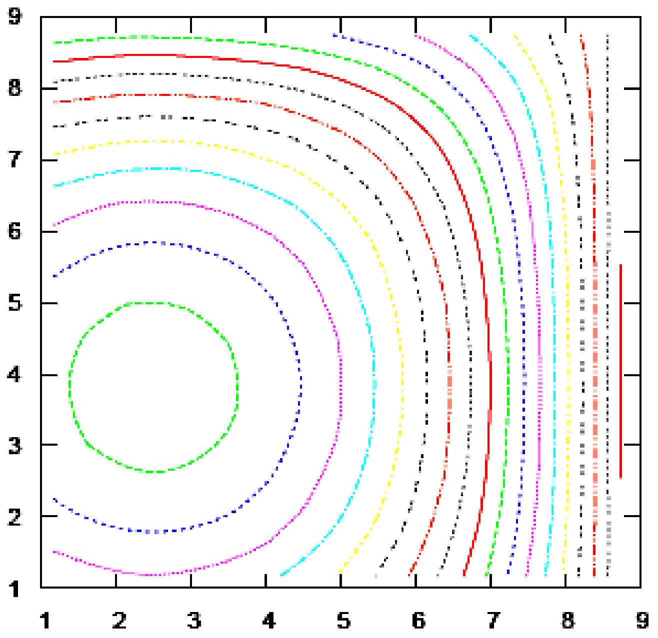
Methods

Dissipative particle dynamics (DPD) simulations.

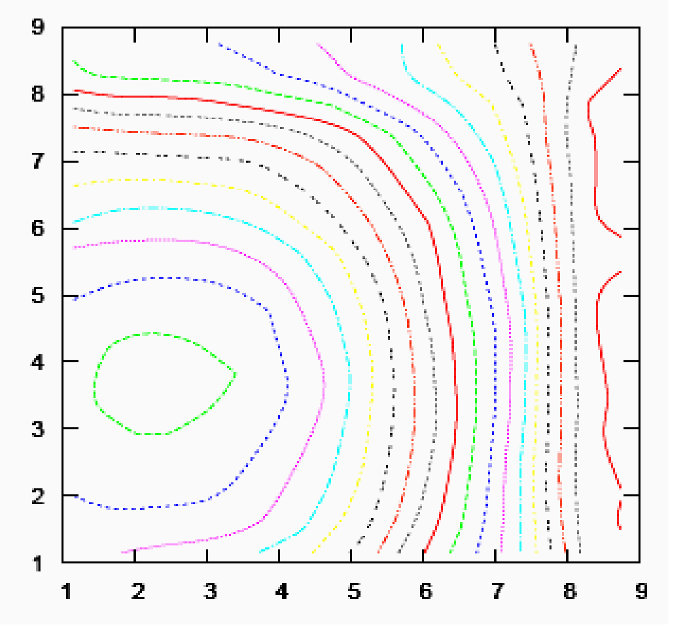
Langevin dynamics (LD) in an imposed flow profile.
(for comparison, to assess hydrodynamic effects)

Asymmetric Poiseuille Profile in 3 D

Square channel,
different slip lengths at all four walls

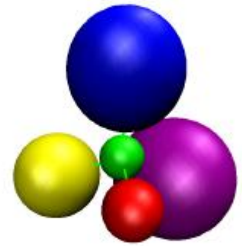


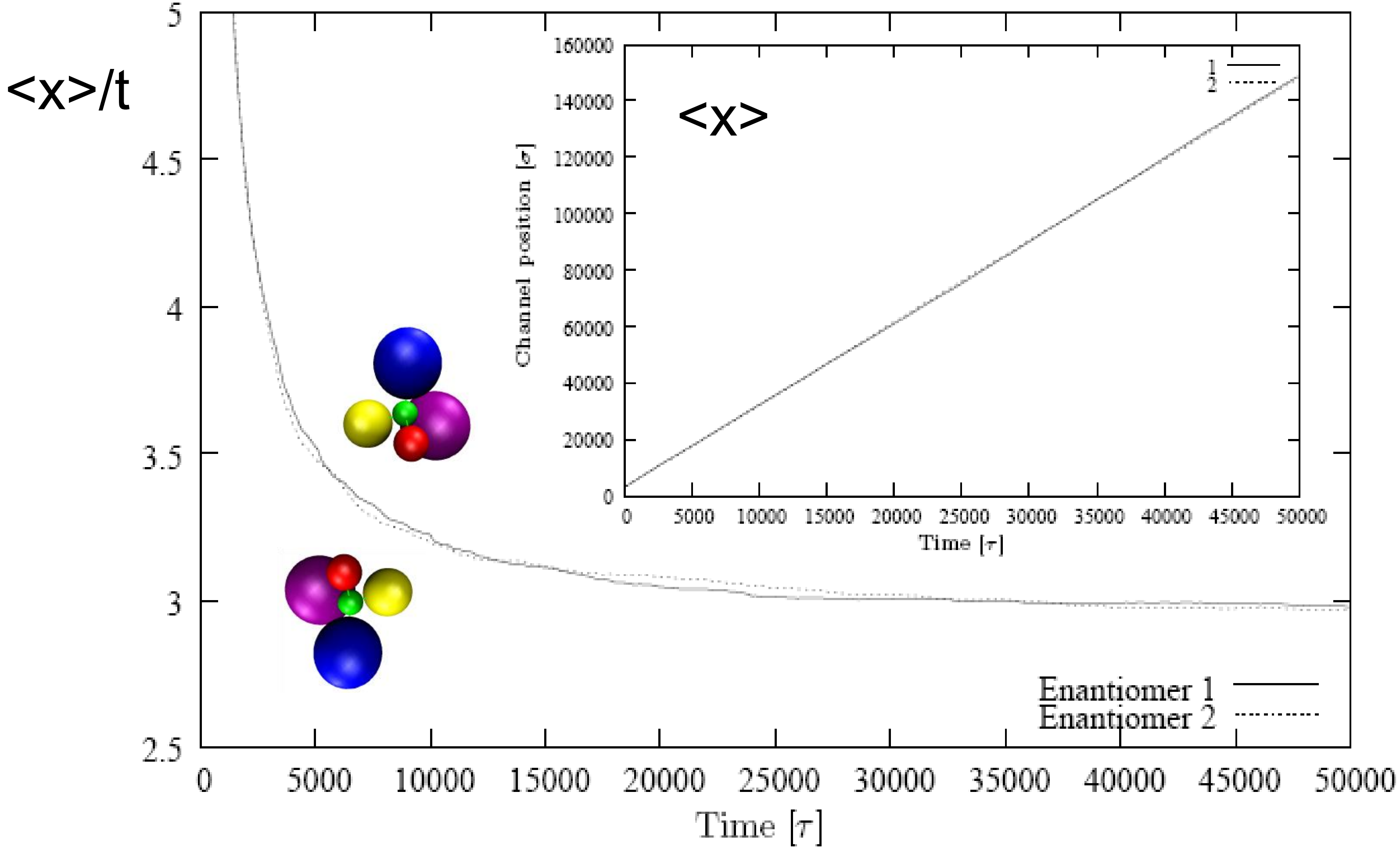
Theoretical profile



DPD profile

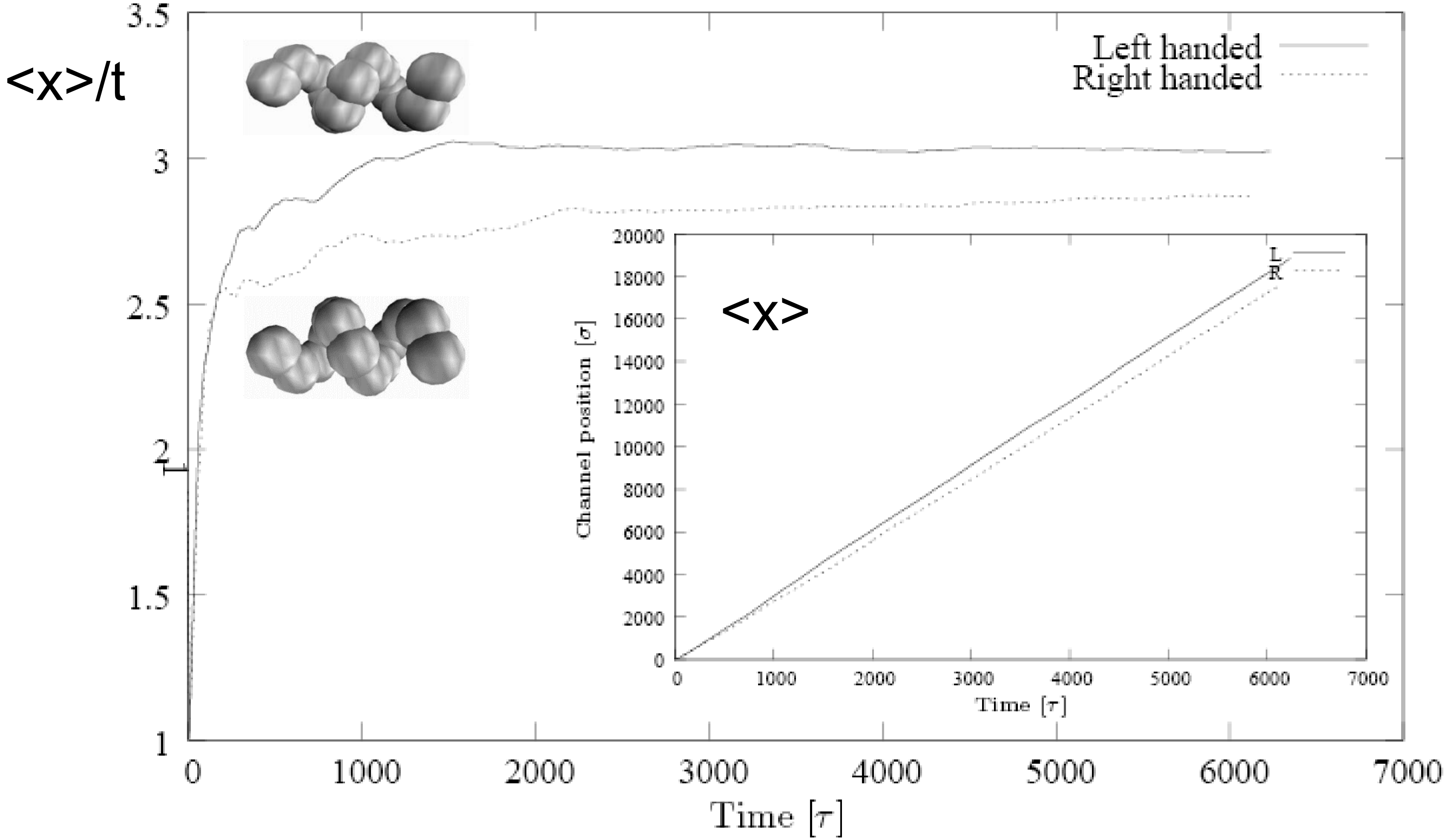
Result I: Chiral Tetrahedra

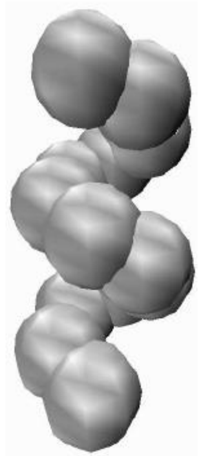




⇒ **No Separation ☹**

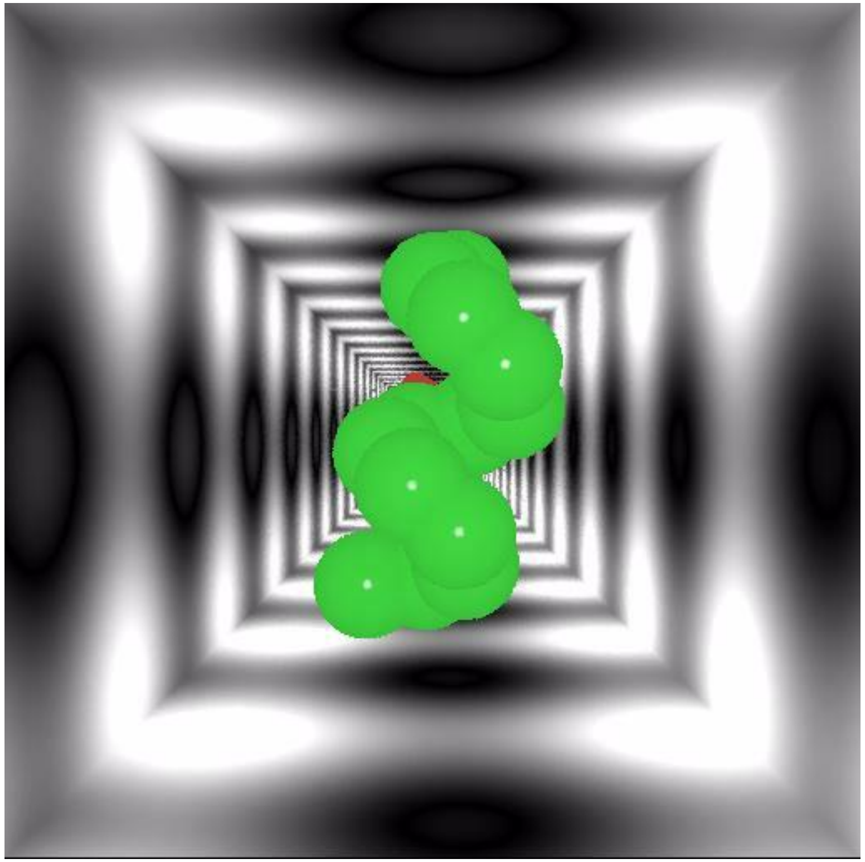
Result II: Helices





⇒ Separation Works ☺

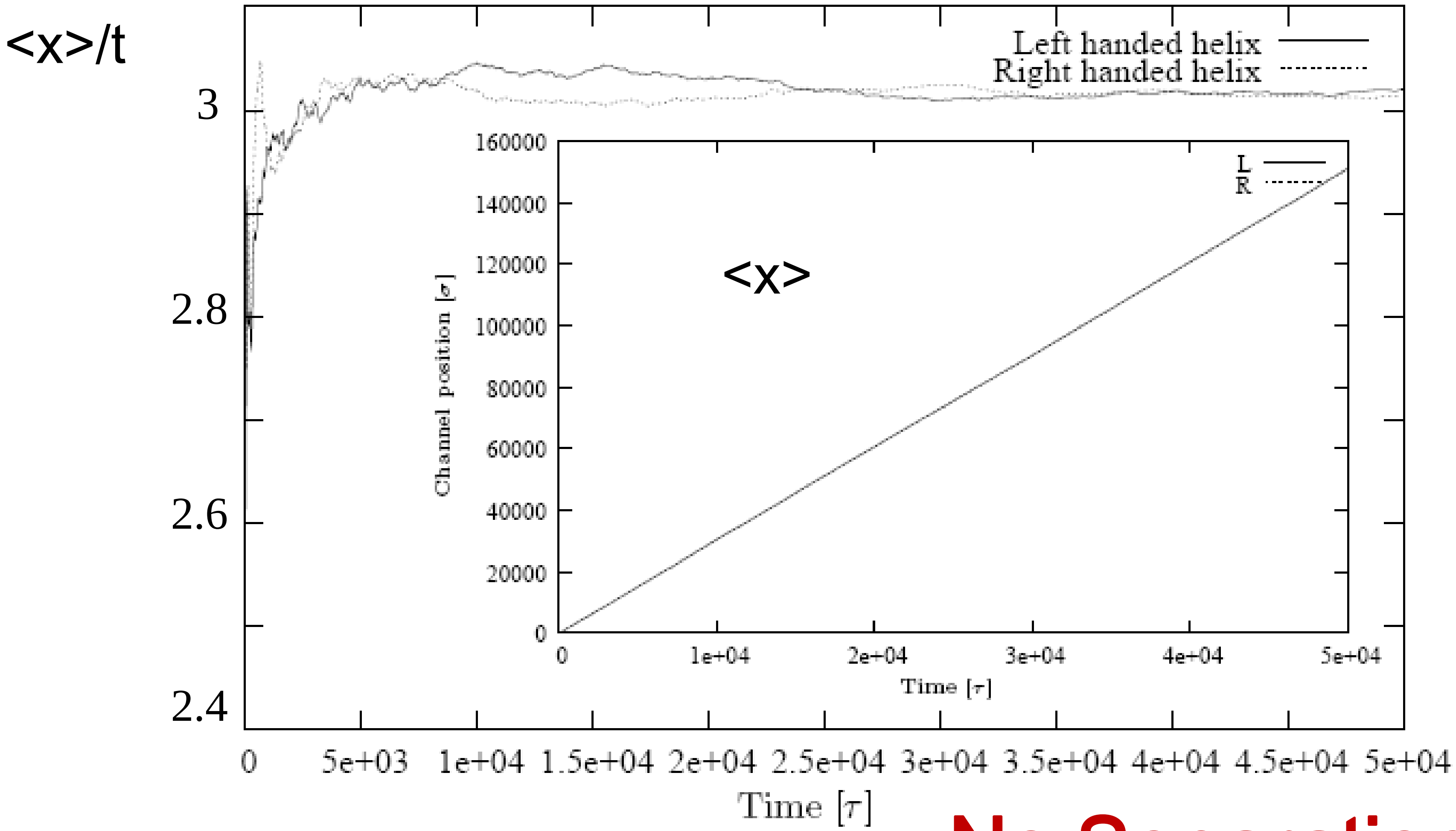
Particle Motion in Microchannel

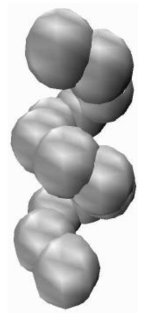


Different chirality => Different speed

Two particles pass each other without problems.

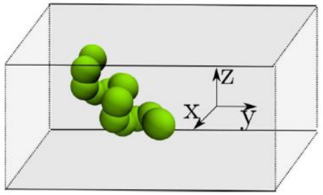
Helices: Langevin Simulations

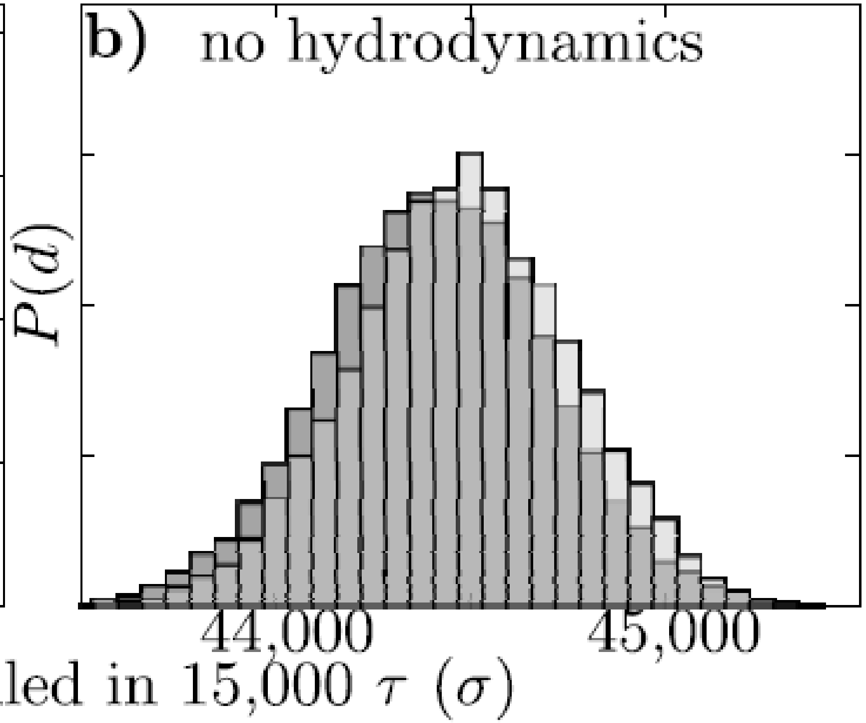




No Separation !?!

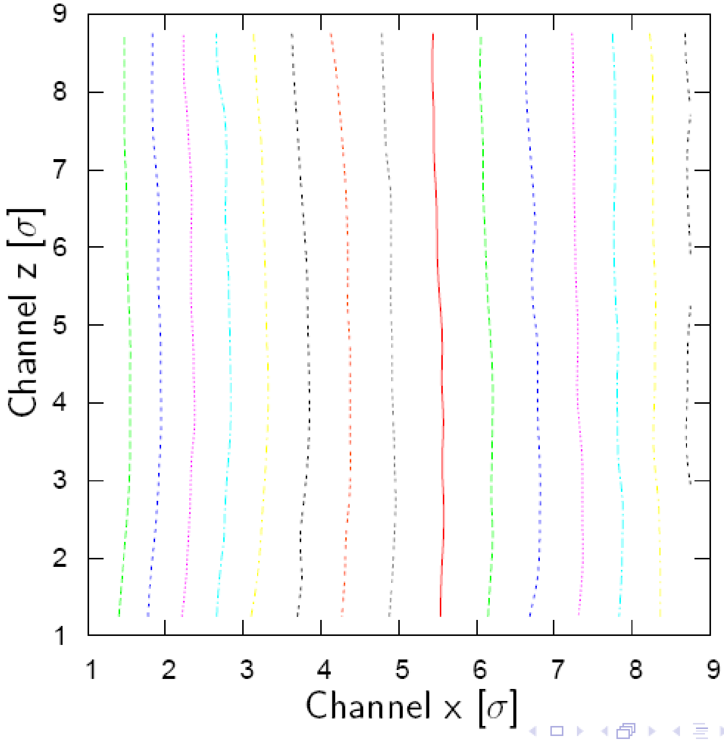
Separation along the channel

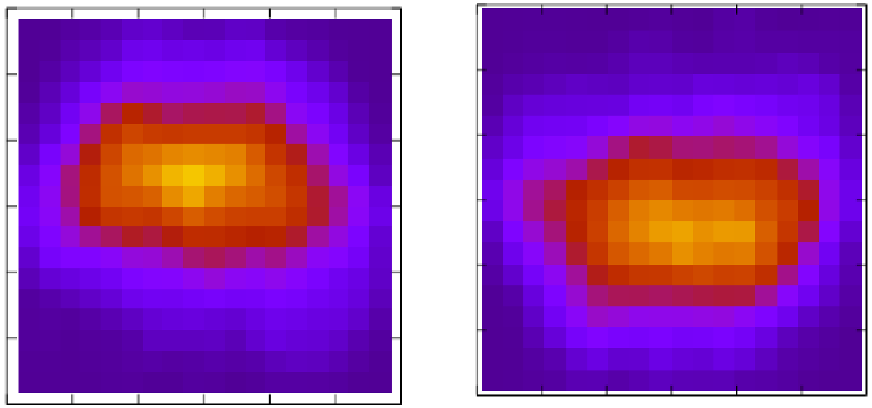




$\Rightarrow$ Good separation in the presence of hydrodynamics
Very weak separation without.

Try Symmetric Couette Flow (DPD)

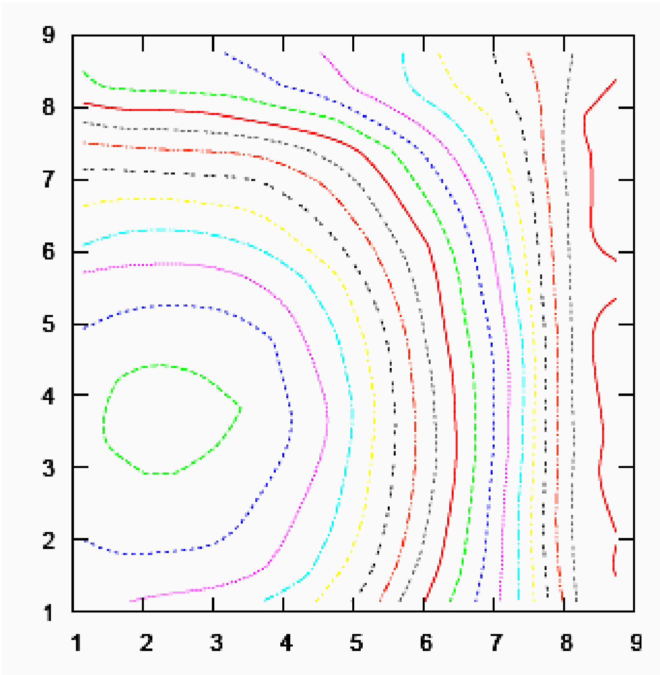


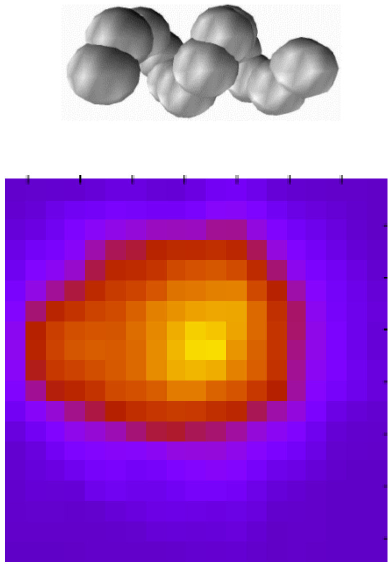


⇒ Enantiomers have the same speed (not shown) ...

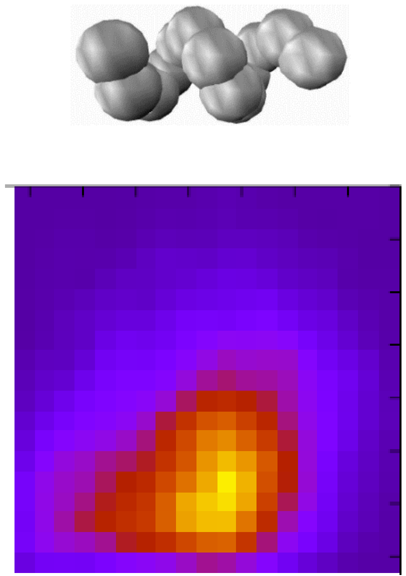
... but different center-of-mass distribution!

Distribution in Asymmetric Flow





faster



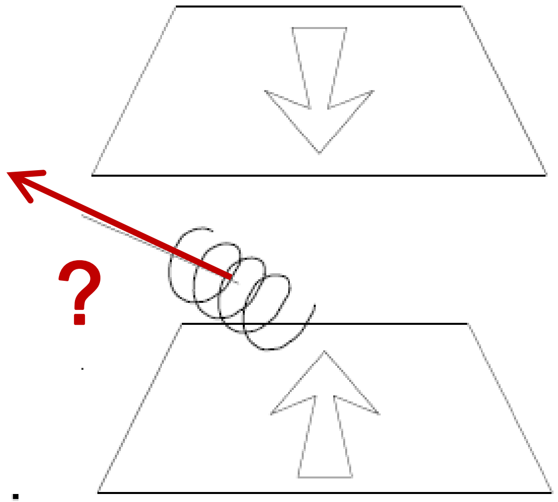
slower

⇒ Separation mechanism: Separation by shear !

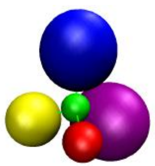
Chiral Particles in Planar Couette Flow

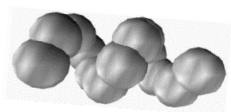
(Kim and Rae, 1991; Makino and Doi, 2005-2008)

For chiral particles, shear can induce motion in the vorticity direction.

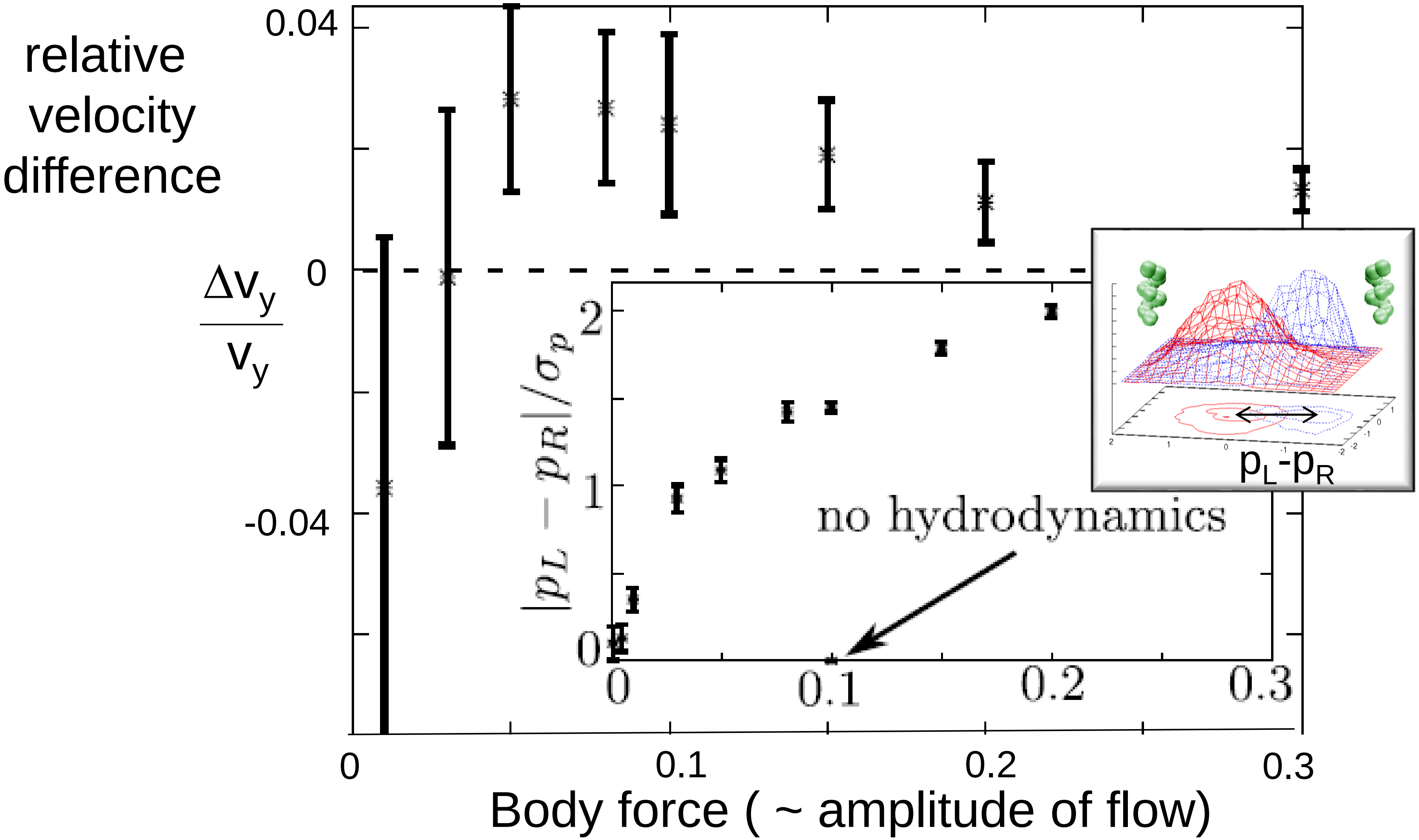


- Hydrodynamic effect
- Nonlinear effect
  (forbidden in linear response regime)
- Depends on Peclet number: $Pe = \frac{\dot{\gamma}}{D_R}$

 : Pe=15

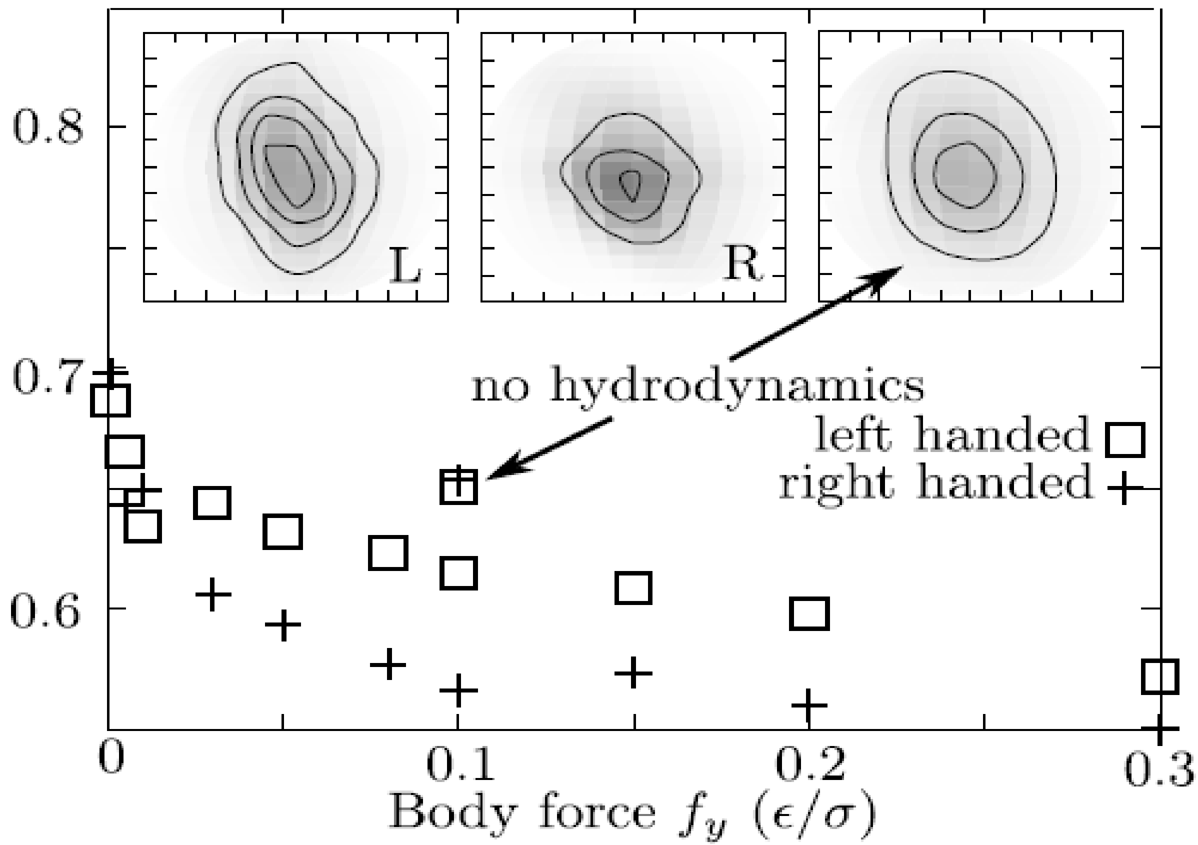
 : Pe=120

Varying Pe systematically



Orientational distribution of particles

width of distribution



Helices are first oriented by shear, then they migrate

Two step mechanism $\Rightarrow$ nonlinear

Conclusion of Part 2

Chiral particles can be separated in microfluidic channels with asymmetric flow profiles.

The separation is driven by a nonlinear hydrodynamic mechanism, which induces vorticity motion in shear flow.

Other separation mechanisms don't seem to work very well in 3 dimensions.
(but maybe we have not tried hard enough!)

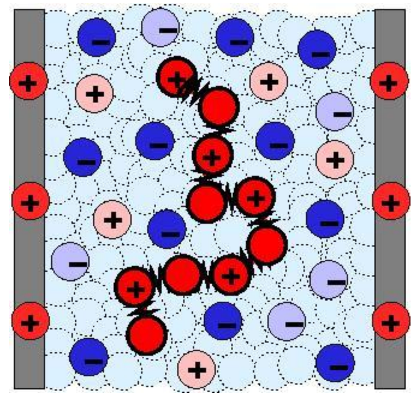
Part 3:
An efficient DPD algorithm for electrolyte fluids

S. Medina , J. Zhou, Z.-G. Wang, FS.,
J. Chem. Phys. 2015.

Motivation: back to our “grand challenge”

Study in full the interplay of

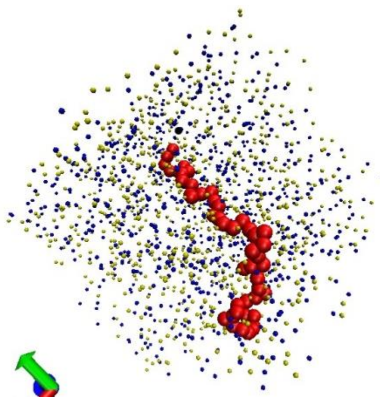
- Hydrodynamics √
- Charges
- Flow and boundary conditions √



… ideally under physiological conditions

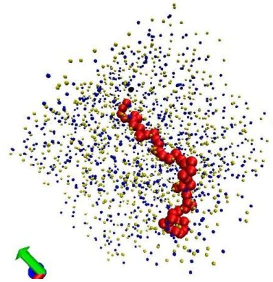
- Ion concentration ~ 0.2 M or more
- Debye length < 1 nm

→ Fluid full with ions



→ Devise strategies how to manipulate flows and transport

The problem



Simulations of electrolyte fluids at high salt concentrations (i.e., physiological conditions): Most of the computing time goes in the evaluation of electrostatic interactions

Ions mostly screen each other (electrostatically, electro-hydrodynamically)

However, just replacing them by short range interactions will not reproduce correct dynamics

⇒ Search for algorithm without explicit ions, but with full ion dynamics

Our solution: ConDiff-DPD" algorithm

Explicit treatment of ions not possible (high concentrations, large systems)

⇒Development of a new hybrid algorithm
which treats micro-ions at the level of **density fields**.

Based on electrokinetic equations

$$\rho_m \left(\partial_t \mathbf{v} + \mathbf{v}(\nabla \mathbf{v}) \right) = \nabla (\boldsymbol{\sigma} - \mathbf{P}) - k_B T \sum_i z_i \rho_i \nabla \hat{\Phi}$$

Navier-Stokes equation → DPD fluid

$$\frac{\partial \rho_i}{\partial t} + \nabla (\mathbf{v} \rho_i) = \nabla D_i \left(\nabla \rho_i + z_i \rho_i \nabla \hat{\Phi} \right)$$

Nernst-Planck equation for ions → **Brownian particles**
"pseudo-ions"

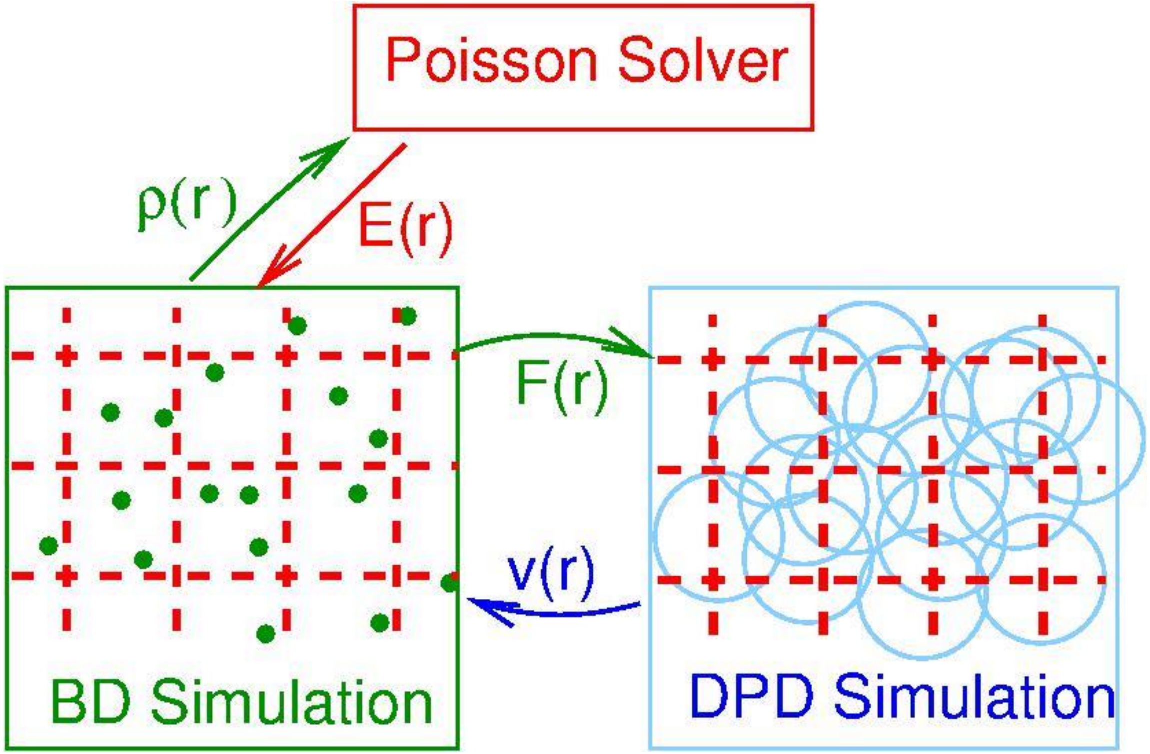
$$\Delta \hat{\Phi} = -4\pi l_B \left(\sum_i z_i \rho_i + \rho_{\text{ext}} \right)$$

Poisson equation → Particle-mesh Ewald method

Basic Idea of "Condiff-DPD" Algorithm II

Pseudo-ions

DPD fluid



$$\frac{d\mathbf{r}_i^c}{dt} = \mathbf{v} + \mu_c \mathbf{F}_c + \sqrt{2k_B T \mu_c}\,\xi$$

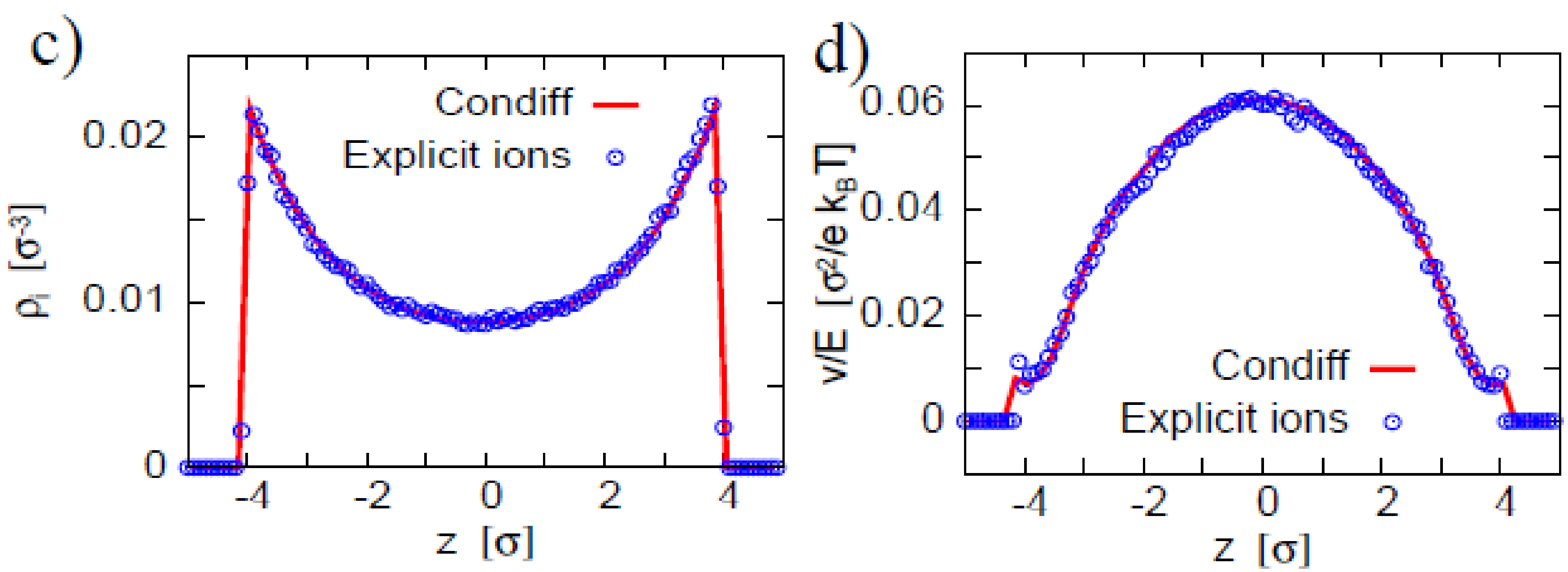
with $\mathbf{F}_c = eZ_c \mathbf{E}\left(\mathbf{r}_i^c\right)$

DPD equations

with $\rho_{\mathrm{DPD}} \mathbf{F} = \sum_c \rho_c \mathbf{F}_c$

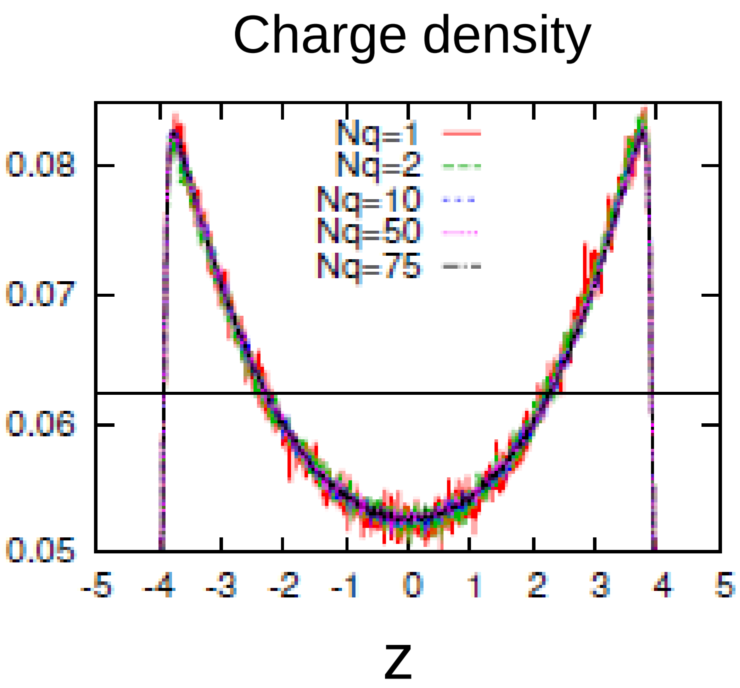
Simple Test: Electroosmotic Flow

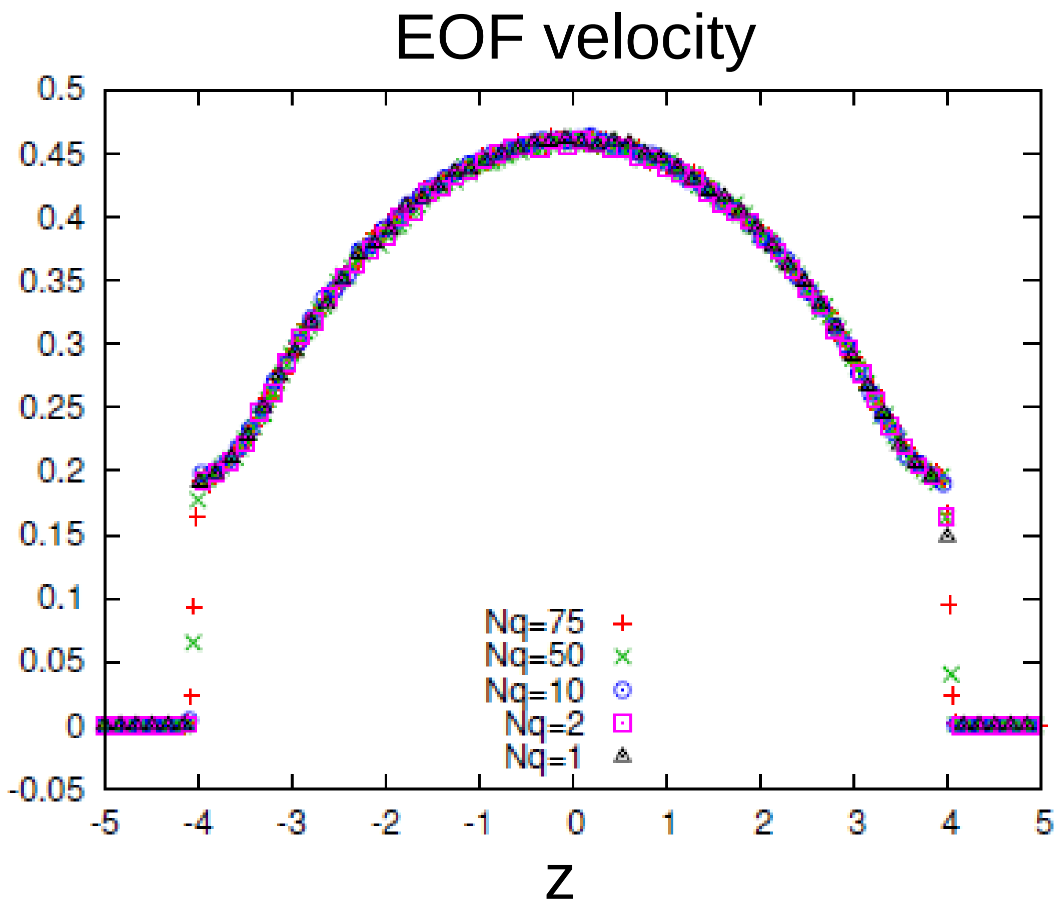
Counterion-induced electroosmotic flow in slit channel



Simple Test: Electroosmotic Flow

Varying the number of pseudo-ions per charge





Condiff-DPD algorithm: Pros and Cons

Pros

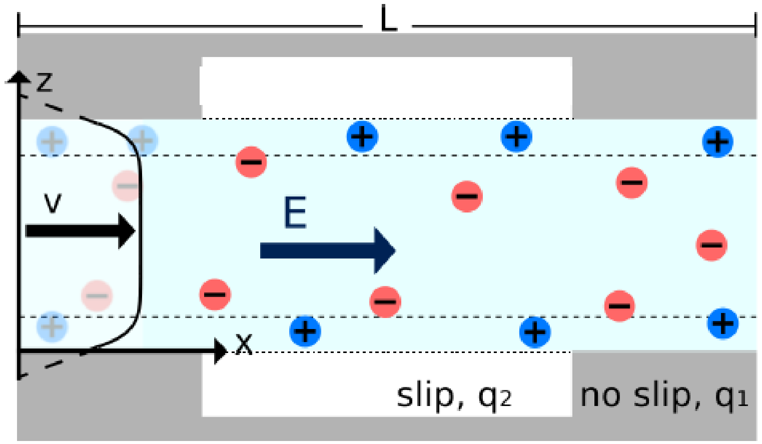
- Run time independent of ion concentration
- At physiological salt concentrations:
  Speedup by one order of magnitude
  compared to fully explicit simulations
- Ions have no (unphysical) inertia (as they should)
  Ion diffusion constant is an input parameter.
- Ions have no (unphysical) hard core interactions
  $\rightarrow$ No unphysical ion structure, fast equilibration times

Cons

- Local ion correlation effects are neglected

Application: EOF on structured surfaces

S. Medina et al., submitted (2014).



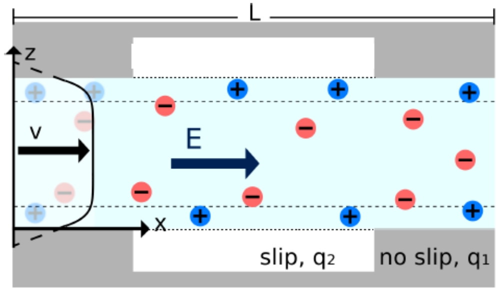
Goal: Use structured surfaces to control EOF flows

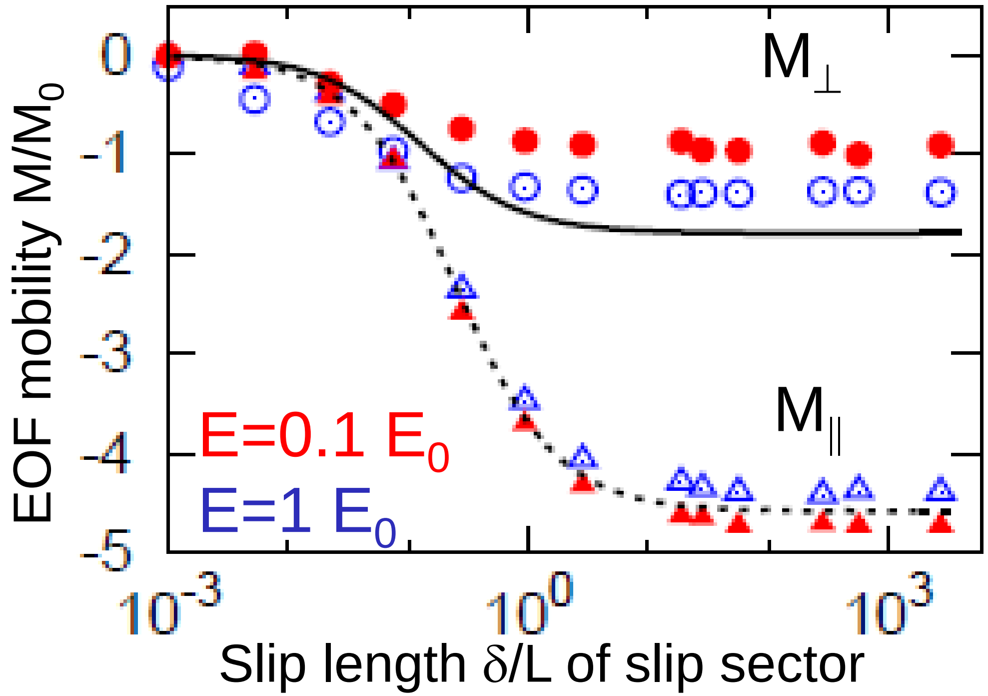
Here: Alternating stripes slip / no slip varying surface charge density

Expectations: Surface tunes effective EOF mobility
Anisotropic, tensorial EOF mobility
(Squires 2008, Belyaev and Vinogradova, 2011)

Results: EOF on patterned surfaces (I)

Oppositely charged stripes with equal width





⇒ Good agreement with theory of Belyaev & Vinogradova

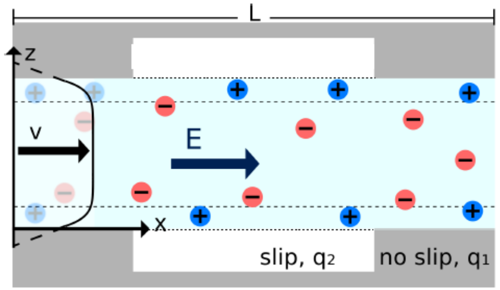
(PRL 107, 98301 (2011))

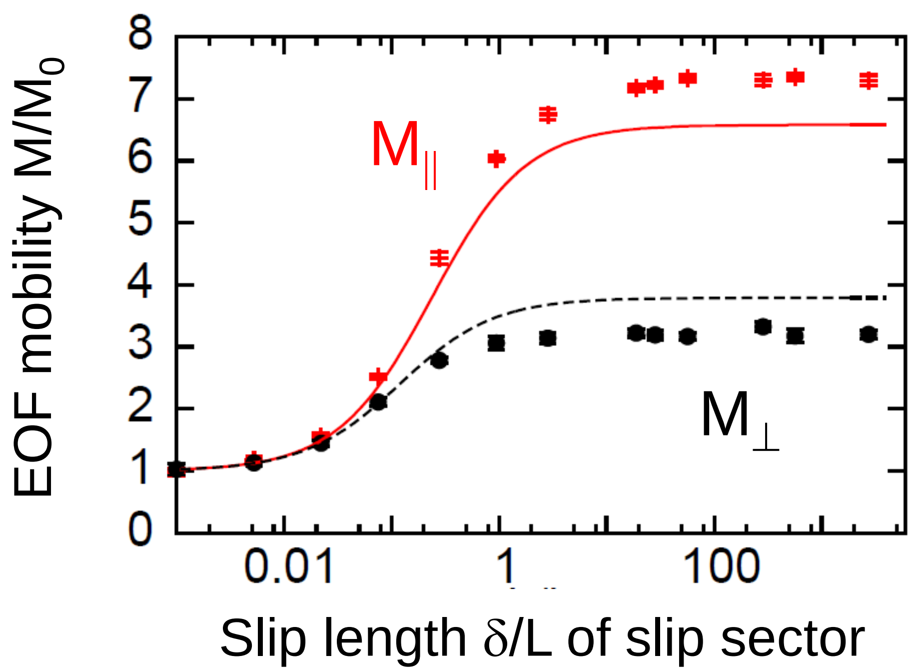
⇒ Tensorial mobility, slip length highest in parallel direction

($1E_0 \sim 3 \cdot 10^5$ V/cm)

Results: EOF on patterned surfaces (I)

Equally charged stripes with equal width





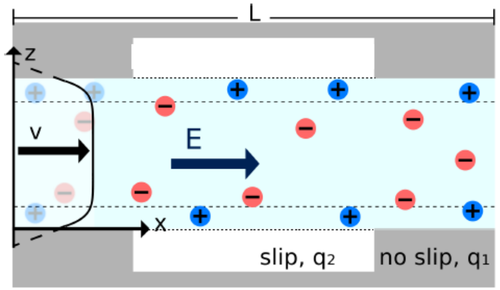
$\Rightarrow$ Still good agreement with theory of Belyaev & Vinogradova

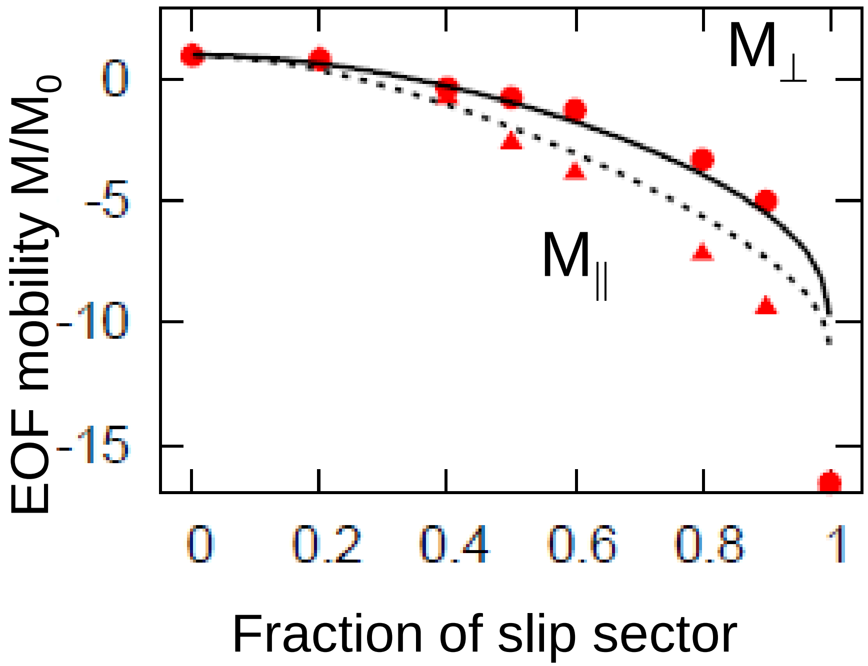
(PRL 107, 98301 (2011))

($E=0.1E_0 \sim 3\cdot10^4$ V/cm)

Results: EOF on patterned surfaces (II)

Oppositely charged stripes
with variable width





⇒ Mobility reversal

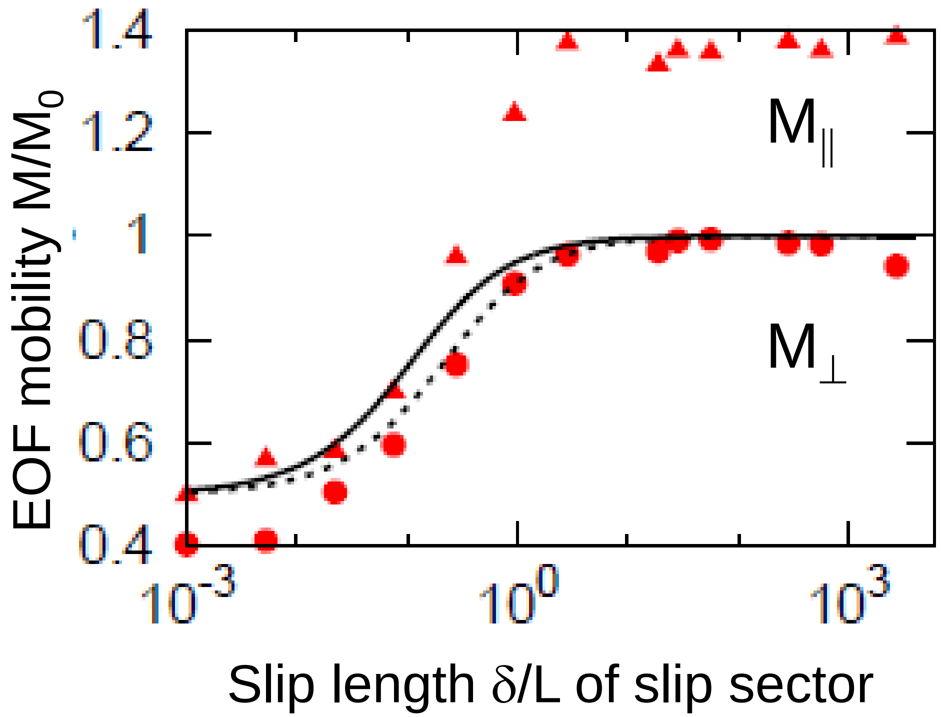
⇒ Mobility becomes large
for large slip fraction

⇒ Still good agreement
with theory

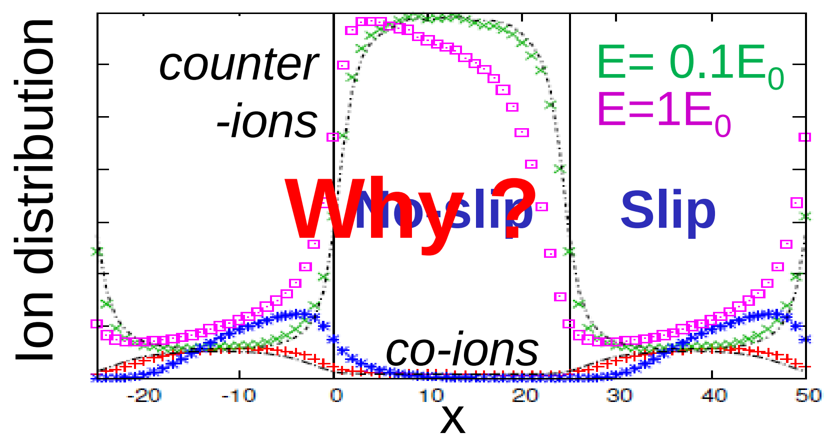
(E= $0.1E_0 \sim 3\cdot10^4$ V/cm, $\delta/L=0.27$)

Results: EOF on patterned surfaces (III)

Only no-slip sector charged



$\Rightarrow$ Theory qualitatively correct, but underestimates slip for parallel EOF flow



Charge overhanging into slip sector, contributes to EOF

($E= 0.1E_0 \sim 3\cdot10^4$ V/cm)

Conclusion of Part 3: Condiff-DPD Method

We have devised a new efficient method to simulate electrohydrodynamic effects in electrolytes with high salt concentration with DPD simulations

The method can easily be adapted to other situations where convection-diffusion is important
(e.g., diffusiophoresis, chemical reactions)

Application to electroosmotic flow on patterned surfaces

A rich flow behavior is observed on patterned surfaces with varying slip length and charge density.
Much of it, but not all, is in good agreement with the theoretical predictions ob Belyaev & Vinogradova.

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PC²

Paderborn

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