Dissipative Particle Dynamics: An Introduction

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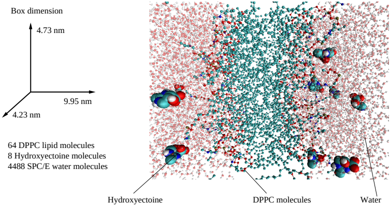
Overview

Dissipative Particle Dynamics (DPD):
A particle based approach to mimic solvent effects

1. Framework: Theoretical background and properties
2. Dissipative Particle Dynamics in ESPResSo
3. Main applications: Solvation properties and flow profiles

Framework:
Theoretical background and properties

Failure of atomistic simulations



Example: DPPC lipid bilayer in hydroxyectoine aqueous solution simulated for 50 ns [Smiatek et. al (2012)]

Study effects for box dimensions of roughly $(100 \times 100 \times 10)$ nm^3:

- $\approx$ 32000 DPPC molecules, 4000 hydroxyectoine molecules and 2244000 water molecules

Typical atomistic simulation time step: 2 fs

Simulating the system for 100 μs:

- 5×10^{10} time steps

A 'little bit' too large for the application of atomistic simulations ...

J. Smiatek, R. K. Harishchandra, H.-J. Galla, A. Heuer, to appear in *Biophys. Chem.* (2012)

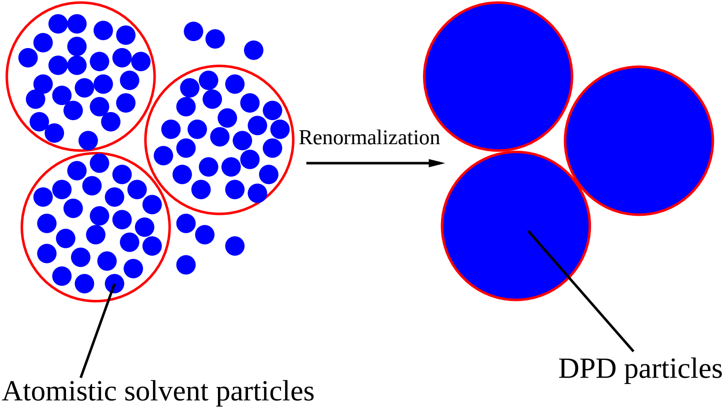
Alternative method: Coarse-graining

- Several effects for macromolecules, membranes, colloids etc. occur on time and length scales that are not accessible to all-atom simulations.
- Most of the computation time is spent into solvent interactions: Negligible? No, not always. Solvent mediated effects (solvation properties, hydrodynamic interactions etc.) are sometimes of main interest

Way out of this dilemma:

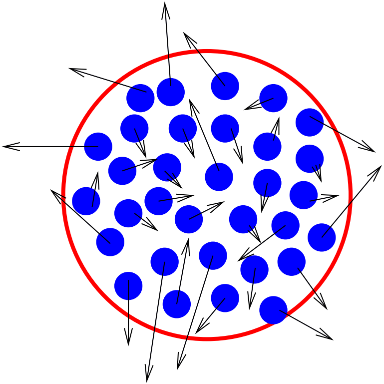
- Coarse-grain the solutes
    - bead-spring models for polymers
- Coarse-grain the solvent
    - Continuum implicit solvent models (GBSA, 'Brownian dynamics')
    - Solve field theory on a grid (*e. g.* Lattice-Boltzmann)
    - Real-space renormalization of solvent particles (DPD, SRD, SPH ...)

Solvent renormalization procedure



- DPD particle represents group of solvent molecules
- molecules are smeared out: corresponding DPD potential should be "soft"
- friction between particles to include dissipation

What about hydrodynamics and coarse-graining?



- Acceleration of enclosed area: sum of forces over the boundary
- Condition leads to Navier-Stokes equation

A small remark...

Coarse-graining means ...

- ... a reduction of the degrees of freedom for particles
- ... an acceleration of computation times
- ... maybe an oversimplification of the system
- ... a neglect of atomistic details

Not everything can be coarse-grained in a simple way...

Example:
MARTINI: coarse-grained force-field biases raft formation in lipid bilayers in contrast to all-atom models [Hakobyan & Heuer (2012)]

D. Hakobyan, A. Heuer, *to appear in Proc. Nat. Acad. Sci. USA (2012)*

Particle based coarse-grained approach: Must haves

Characteristics and obligatory features of a meaningful method which includes hydrodynamic interactions and solvation effects:

- Pair-wise conservative force to generate local thermodynamics (otherwise interpretation as an ideal gas)
- Pair-wise dissipative force to model the viscosity on the mesoscale
- Pair-wise random forces to include Brownian motion
- Fluctuation-dissipation relation should hold for the generation of a canonical ensemble (NVT)

All forces should obey Newtons 3rd law (conservation of momentum)

Dissipative Particle Dynamics

Dissipative Particle Dynamics: History

- Baby years (1992-1995):
  - 1992: First introduction by Hoogerbrugge and Koelman Violation of fluctuation-dissipation relation → no consistent ensemble
- Hype years (1995-2003)
  - 1995: Correction of fluctuation-dissipation relation by Espanol and Warren
  - 1995-1999: Important contributions to the methodology by Espanol, Warren, Marsh, Yeomans, Lowe, Pagonabarraga, Groot, Alvares and others
  - Often used for colloidal systems, polymers, monolayers, mixtures, membranes ...
- After the gold rush (2003-now):
  - What remains: useful for several systems to study varying solvent conditions
  - But: "Out of fashion" compared to Lattice-Boltzmann or Stochastic rotation dynamics → computationally more expensive and slower

Dissipative Particle Dynamics equations

DPD-Forces:

$$\vec{F}_i^{DPD} = \sum_{i \neq j} \vec{F}_{ij}^D + \vec{F}_{ij}^R$$

Dissipative force: $\vec{F}_{ij}^D = -\gamma_{DPD}\, \omega_{DPD}(r_{ij})\, (\hat{r}_{ij} \cdot \vec{v}_{ij}) \cdot \hat{r}_{ij}$

Random force: $\vec{F}_{ij}^R = \sqrt{2\gamma_{DPD}\, k_B T \omega_{DPD}(r_{ij})}\, \chi_{ij} \cdot \hat{r}_{ij}$

- r_{ij} distance and $\hat{r}_{ij}$ unit vector between two particles with relative velocity v_{ij} within a cut-off distance r_c
- friction coefficient γ_{DPD}
- symmetric random number $\chi_{ij} = \chi_{ji}$ with zero mean and unit variance
- weight function

$$\omega_{DPD}(r_{ij}) = \begin{cases} 1 - \frac{r_{ij}}{r_c} & : r_{ij} \leq r_c \\ 0 & : r_{ij} > r_c \end{cases}$$

Conservative force

What about the conservative force?
Often used:

$$\vec{F}_{ij}^{C} = a_{ij}(1 - r_{ij}/r_c)$$

- Parameter a_{ij} regulates strength of repulsive force and solvation properties
- Linear behavior
- Allows large time steps

Requirement of a "soft potential" due to smeared out molecular positions is fulfilled.

A small hidden note ...
Sometimes Lennard-Jones potentials are also in use ...
It is not forbidden!

Complete set of DPD forces

$$\vec{F}_i^{DPD} = \sum_{i \neq j} \vec{F}_{ij}^{D} + \vec{F}_{ij}^{R} + \vec{F}_{ij}^{C}$$

- Pairwise additive forces
- Constructed to conserve local momentum in all force contributions
- Can be integrated by an ordinary integration scheme (Verlet or more refined self-consistent methods ...)

Thermodynamic ensemble: Fluctuation-Dissipation relation

A meaningful method should reproduce the equilibrium distribution of a thermodynamic ensemble...

- Probability to find system at a particular state: $\rho(r^{3N}, p^{3N})$
- Time evolution can be expressed by the Liouville equation:

$$\frac{\partial}{\partial t}\rho(r^{3N}, p^{3N}) = i\mathcal{L}\rho(r^{3N}, p^{3N})$$

with

- Liouville operator $\mathcal{L} = \mathcal{L}_C + \mathcal{L}_D$ (conservative (C) and dissipative contributions (D))

Condition for a stable equilibrium distribution:

$$\frac{\partial}{\partial t}\rho(r^{3N}, p^{3N}) = 0$$

Conservative and dissipative contributions

Conservative contribution:

- $\mathcal{L}_C \rho(r^{3N}, p^{3N}) = 0$ (always fulfilled for conservative interactions)

Dissipative contribution:

- $\mathcal{L}_D \rho(r^{3N}, p^{3N}) = 0$ only fulfilled for
  - $\omega_R(r_{ij})^2 = \omega_D(r_{ij})$ [Espanol & Warren (1995)] (condition for weight function in the dissipative and the random contribution for the DPD equations)

$\omega_R(r_{ij})$ ... kinetic energy input per time
$\omega_D(r_{ij})$ ... kinetic energy dissipation per time
The above relation was violated in the original paper by Hoogerbrugge and Koelman...

P. Espanol, P. B. Warren, *Europhys. Lett.* **30**, 191 (1995)

P. J. Hoogerbrugge, J. M. V. A. Koelman, *Europhys. Lett.* **19**, 155 (1992)

Parameterisation of DPD

Problem:

- Length scales are larger than atomistic scales
- What is the behavior of the physical properties and how to match?

Requirement:

- DPD solvent intends to reproduce the properties of atomistic solutions as far as possible (local thermodynamics)
  - compressibility and density
  - transport properties

Compressibility - matching a_{ij}

The equation of state at high density ($\rho \geq 2\sigma^{-3}$) can be expressed by

- $p = \rho k_B T + \alpha\rho^2$ (virial expansion with pressure p and density ρ)

The standard soft potential gives by matching with experimental or atomistic results

- $\alpha \sim 0.1 a_{ij} r_c^4$

Taking the dimensionless compressibility of water ($\kappa^{-1} \sim 16$) into account:

$$\kappa^{-1} = \frac{1}{k_B T}\frac{\partial p}{\partial \rho} = \frac{1}{k_B T}\frac{\partial p}{\partial n}\frac{\partial n}{\partial \rho}$$

For $\kappa^{-1} \sim 16$

- $a_{ij} = 75\frac{k_B T}{\rho r_c^4}$ [Groot & Warren (1997)]

Due to the purely repulsive force: no liquid-vapour coexistence!

R. D. Groot, P. B. Warren, *J. Chem. Phys.* **107**, 4423 (1997)

A remark on the density

An increase of the solvent density will give better statistics but is computationally more expensive.
Problems for low densities:

- low collision frequency (more a gas than a liquid)
- In more detail: Boltzmann two-particle collisions instead of many particle collisions [Schiller (2005)]

Detailed investigations on boundary conditions and shear viscosity in absence of conservative forces have shown [Schiller (2005), Smiatek et. al (2008)]:

- interplay between density ρ and friction coefficient γ_{DPD}
- acceptable fluid like behavior for $\rho \geq 3\sigma^{-3}$ and $\gamma_{DPD} = 5 - 10\sqrt{(m\epsilon/\sigma^2)}$

U. D. Schiller, Diploma thesis, Bielefeld University, 2005

J. Smiatek, M. P. Allen, F. Schmid, *Europ. Phys. J. E* **26**, 115 (2008)

Transport properties - Shear viscosity

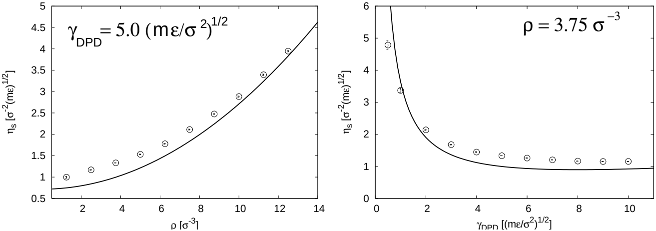
In contrast to Lattice-Boltzmann:

- Shear viscosity in DPD is a function of several parameters

An approximation [Groot & Warren (1997)] is given by

$$\eta_s = \frac{45}{4\pi}\frac{k_B T}{\gamma_{DPD} r_c^3} + \frac{2\pi}{1575}\rho^2 \gamma_{DPD} r_c^5$$

→ More sophisticated theory in [Marsh et. al (1997)]
Simulation results [Smiatek (2009)]:



R. Groot, P. B. Warren, *J. Chem. Phys.* **107**, 4423 (1997)

C. A. Marsh, G. Backx, M. H. E. Ernst, *Phys. Rev. E* **55**, 1676 (1997)

J. Smiatek, PhD thesis, Bielefeld University, Germany (2009)

Intrinsic properties: Schmidt number

The Schmidt number Sc denotes the ratio between momentum transport and mass transport with diffusion constant D:

$$Sc = \frac{\eta_s}{\rho D}$$

Typical values in real fluids: $10^2 - 10^3$
Inserting typical values for DPD:

$$Sc << 100$$

Diffusive transport is as fast as momentum transport
→ DPD is more a gas than a liquid

No problem for Stochastic Rotation Dynamics, Lowe-Andersen thermostat or Lattice-Boltzmann.

Further well-known problems

- Too large time steps ($\delta t > 0.01$) result in wrong temperatures and equilibrium properties [Marsh & Yeomans (1997)]
- Sound velocity too low for large bead sizes
- Clash of intrinsic length scales (surfactants, micelles, oil droplets)
- Lattice-Boltzmann and Stochastic Rotation Dynamics are computationally faster
    - DPD vs. LB (4320 solvent particles vs. 1728 solvent nodes on an Athlon$^{©}$ MP2200+ CPU) [Smiatek et. al (2009)]
    - LB is 9-10 times faster!
    - Forget about comparisons with GPU codes ...

C.A. Marsh, J.M. Yeomans, *Europhys.Lett.* **37**, 511 (1997)

J. Smiatek, M. Sega, U. D. Schiller, C. Holm, F. Schmid, *J. Chem. Phys.* **130**, 244702 (2009)

Why choosing DPD as a method of choice?

There are many problems and it is computationally very slow ...

Why using DPD?

- Solvent is modeled explicitly
  - gives probability to vary between good, theta and poor solvent
  - formation of compounds due to solvophobic interactions (membranes, vesicles and micelles)
  - study of Flory-Huggins behavior (mixtures)
- wall slippage for microchannel flows is well defined

Microflow slippage behavior at channel walls

Consider a fluid in a microchannel:

- external force F_x or pressure gradient induces flow (Plane Poiseuille Flow)
- moving boundaries (rotating cylinders) induce flow (Plane Couette Flow)

How to describe the fluid velocity at the boundaries?

Important question due to large surface to volume ratio ...

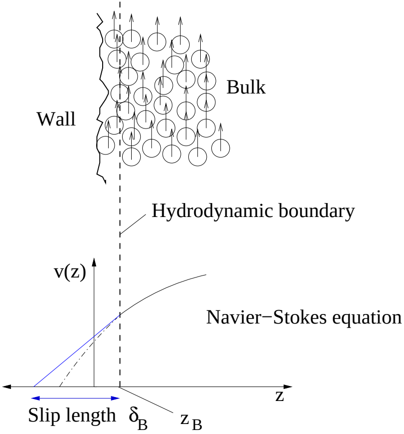
For low Reynolds number:
Possible analytical solution by Stokes equation:

- $\eta_s \frac{\partial^2}{\partial z^2} v_x(z) = -\rho F_x$

Hydrodynamic boundary conditions

- No Slip: $v_x(z)|_{z=z_B} = 0$
- Partial Slip: $v_x(z)|_{z=z_B} = \delta_B \left(\frac{\partial}{\partial z} v_x(z)\right)_{z=z_B}$

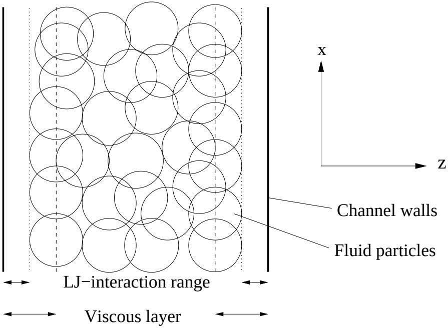
with slip length δ_B and hydrodynamic boundary positions z_B



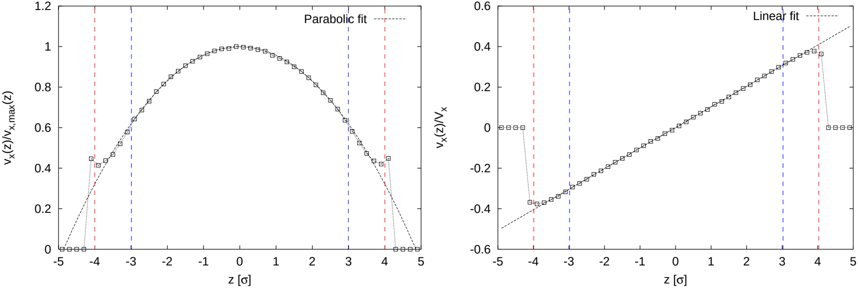
Modelling hydrodynamic boundary conditions in microchannels

Idea:

- Introduction of a viscous layer (described in terms of a Langevin equation) with finite range z_c in close vicinity to the channel walls
- Wall velocity as a reference velocity
  (Moving walls for the simulation of shear flows)



Typical flow profiles with Tunable-Slip Boundaries

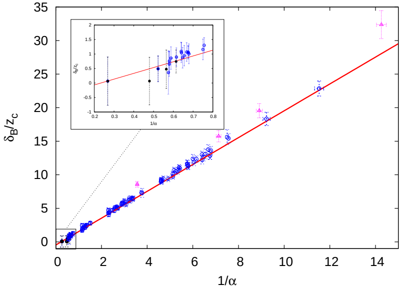


- - - - - - - - - - Range of Tunable−Slip Boundaries

- - - - - - - - - - Range of effective wall−particle interactions

Combination of both flow profiles for different parameter sets allows the calculation of the slip length and of the hydrodynamic boundary positions independently.

Properties of Tunable-slip boundaries



Calculation gives approximation

- $\frac{\delta_B}{z_c} \approx \frac{2\eta_s}{z_c^2 \rho \gamma_L} - \frac{7}{15}$

and exact expression with Airy polynomials [Smiatek et. al (2008)]

- slip length is tunable from full-slip to no-slip
- rotating objects can be modeled as well
- implemented in ESPResSo

J. Smiatek, M. P. Allen, F. Schmid, *Europ. Phys. J. E* **26**, 115 (2008)

Dissipative Particle Dynamics in ESPResSo

Several ways to treat DPD in ESPResSo

ESPResSo treats DPD either as ...

- a global thermostat with no specified conservative interaction (ideal gas [Soddemann et al. (2003)])
- or a thermostat with specified DPD interactions

T. Soddemann, B. Dünweg, K. Kremer, *Phys. Rev. E* **68**, 046702 (2003)

Setting up a DPD thermostat simulation

In *myconfig.h*:

```
#define DPD
```

In the TCL-Script:

```
...
for{set i 0}{$i < N}{incr i}{
set posx [expr $box_x*[t_random]]
...
part $i pos $posx $posy $posz type $solvent_id v $vx $vy $vz
}
galileiTransformParticles
...
set temperature 1.0
set gamma 1.0
set r_cut 1.0
thermostat dpd $temperature $gamma $r_cut
...
```

DPD thermostat simulation plus DPD interaction

In *myconfig.h*:

```
#define inter_DPD
```

In the TCL-Script:

```
...
for{set i 0}{$i < N}{incr i}{
set posx [expr $box_x*[t_random]]
...
part $i pos $posx $posy $posz type $solvent_id v $vx $vy $vz
}
galileiTransformParticles
...
set temperature 1.0
set gamma 1.0
set r_cut 1.0
thermostat inter_dpd $temperature $gamma $r_cut
inter $solvent_id $solvent_id inter_dpd $gamma $r_cut
...
```

Extension: Transverse DPD and mass dependent friction

- Transverse DPD:
    - Dampens the degrees of freedom perpendicular on the axis between two particles [Junghans et. al (2008)]

In *myconfig.h*:
#define TRANS_DPD

- Mass-dependent friction:

In *myconfig.h*:
#define DPD_MASS_RED or #define DPD_MASS_LIN

- for $\gamma_{DPD} \rightarrow \gamma_{DPD} M_{ij}$
    - with reduced mass $M_{ij} = 2m_i m_j / m_i + m_j$
    - with average mass $M_{ij} = 1/2(m_i + m_j)$

C. Junghans, M. Praprotnik, K. Kremer, *Soft Matter* **4**, 156 (2008)

Further remarks

- Integration via Velocity-Verlet algorithm → $\delta t \leq 0.01$ [Marsh & Yeomans (1997)]
- Never forget to set *galileiTransformParticles* because it removes box center of mass motion

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C.A. Marsh, J.M. Yeomans, *Europhys.Lett.* **37**, 511 (1997)

Main applications:
Solvation properties and flow profiles

I. Solvation properties of polymers

Polymers in solution [Spenley (2000)]

End-to-end radius $r_e \sim N^{\nu}$ with N monomers

- Theory: $\nu = 0.588$
- DPD simulation: $\nu = 0.58 \pm 0.04$ for $r_e \sim (N-1)^{\nu}$

Relaxation time of end-to-end distance $\tau \sim r_e^3 \sim N^{3\nu}$

- Theory: $3\nu = 1.77$
- DPD simulation: $3\nu = 1.80 \pm 0.04$

Good reproduction of hydrodynamic properties (Zimm-regime) and static properties of the polymer

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N. A. Spenley, *Europhys. Lett.* **49**, 534 (2000)

Polymers in melt [Spenley (2000)]

End-to-end radius $r_e \sim N^\nu$ with N monomers

- Theory: $\nu = 0.5$
- DPD simulation: $\nu = 0.498 \pm 0.005$ for $r_e \sim (N-1)^\nu$

Relaxation time of end-to-end distance $\tau \sim N^\beta$

- Theory: $\beta = 2$
- DPD simulation: $\beta = 1.98 \pm 0.03$

Good reproduction of screening properties (Rouse-regime) and static properties of the polymer

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N. A. Spenley, *Europhys. Lett.* **49**, 534 (2000)

Influence of solvent conditions for polymer translocation times [Kapahnke et. al (2010)]

- Solvent conditions influence the time scaling behavior for an unbiased polymer translocation process
    - Decreasing solvent quality by increasing a_{ij} values

Theory: Translocation time $\tau \sim N^{\beta}$ with $\beta = 1 + 2\nu = 2.2$ for good solvent conditions

Δa_{ij}	ν	β
0 (good solvent)	$0.60 \pm 0.00(0.588)$	$2.24 \pm 0.03(2.16)$
6	0.57 ± 0.01	2.22 ± 0.03
12	0.44 ± 0.01	2.09 ± 0.08
17	0.27 ± 0.02	1.98 ± 0.08

Reproduction of polymer collapse and change of translocation times

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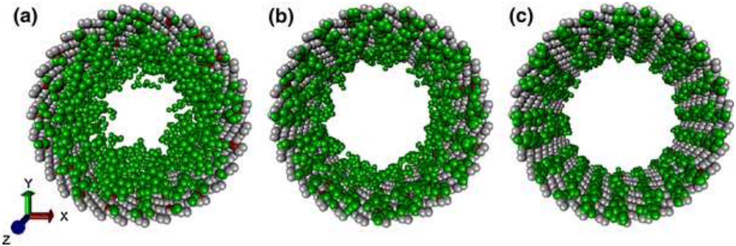
F. Kapahnke, U. Schmidt, D. W. Heermann, M. Weiss, *J. Chem. Phys.* **132**, 164904 (2010)

Solvent conditions for brush coatings [Cao et. al (2010)]



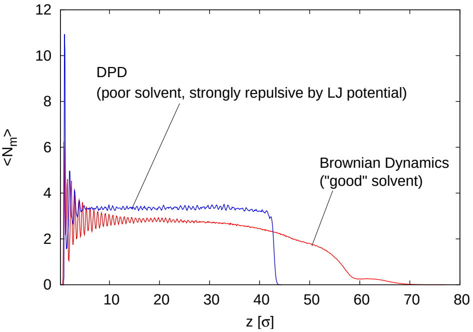
a = 5
Good solvent

a = 25
Athermal solvent

a = 50
Bad solvent

Q. Cao, C. Zuo, L. Li, Y. Yang, N. Li, *Mirofluidics and Nanofluidics* **10**, 977 (2011)

Polymer brushes for different solvent conditions [Hentschel et. al (2012), Smiatek et. al (2012)]



- implicit 'good' solvent conditions by BD simulations leads to a significant swelling

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C. Hentschel, H. Wagner, J. Smiatek, H. Fuchs, X. Zhang, A. Heuer, A. Studer, L. Chi, accepted for publication in *Langmuir* (2012)

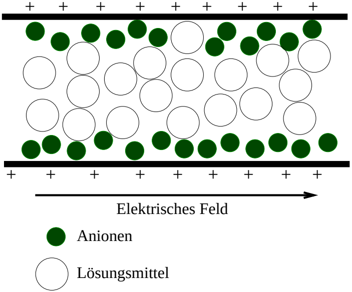
J. Smiatek, H. Wagner, C. Hentschel, L. Chi, A. Studer, A. Heuer, submitted to *J. Chem. Phys.* (2012)

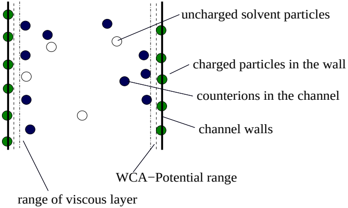
Main applications:
Solvation properties and flow profiles

II. Flow profiles in microchannels

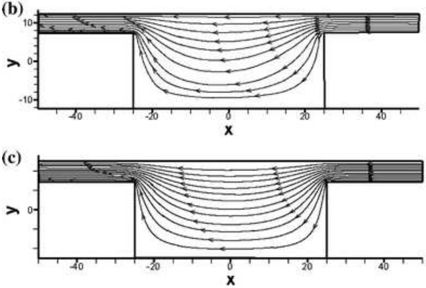
Electroosmotic flow profiles

Typical situation: charged walls, charges in solution and external electric field





Flow profiles in structured microchannels [Duong-Hong et. al (2008)]

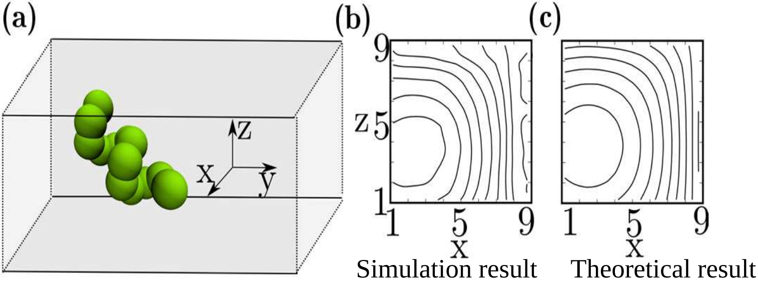


Simulation results

Theoretical results

D. Duong-Hong, J.-S. Wang, G. R. Liu, Y. Z. Chen, J. Han, N. G. Hadjiconstantinou, *Microfluidics and Nanofluidics* **4**, 219 (2008)

Chiral separation by microflows [Meinhardt et. al (2012)]



Simulation result Theoretical result

- Different slip lengths are responsible for asymmetric flow profiles

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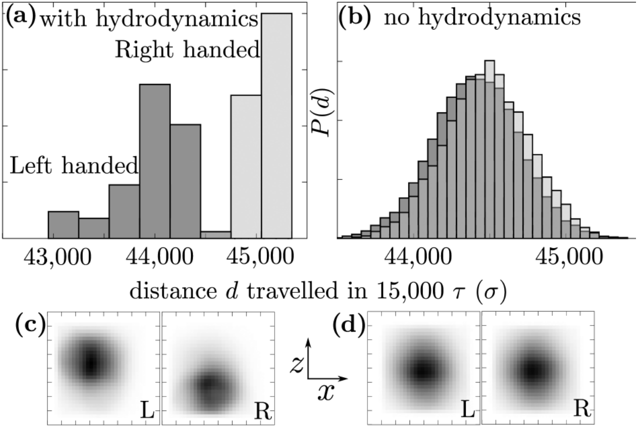
S. Meinhardt, J. Smiatek, R. Eichhorn, F. Schmid, *Phys. Rev. Lett.* **108**, 214504 (2012)

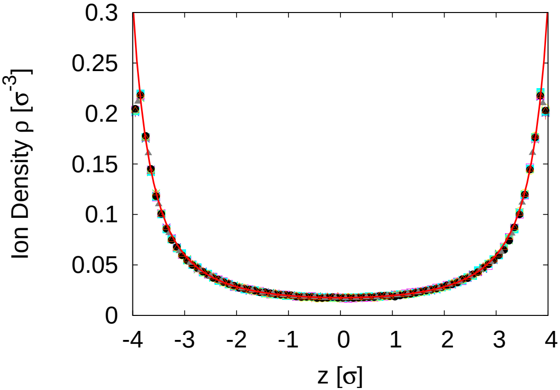
Chiral separation by microflows [Meinhardt et. al (2012)]



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

Counterion-induced electroosmotic flow [Smiatek et. al (2009)]

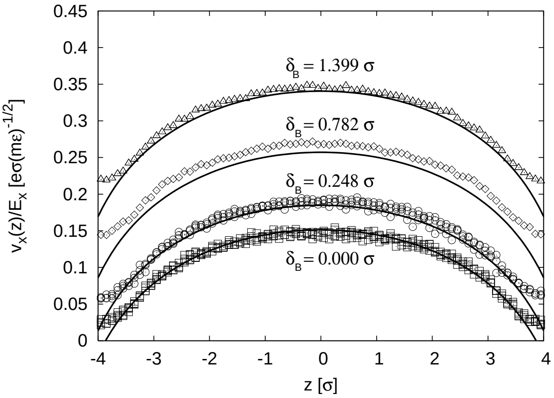
Counterion densities:



J. Smiatek, M. Sega, U. D. Schiller, C. Holm, F. Schmid, *J. Chem. Phys.* **130**, 244702 (2009)

Counterion-induced electroosmotic flow [Smiatek et. al (2009)]

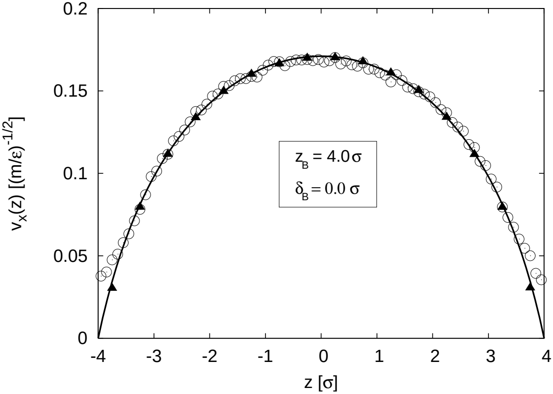
Electrosmotic flow profiles for different slip lengths:



J. Smiatek, M. Sega, U. D. Schiller, C. Holm, F. Schmid, *J. Chem. Phys.* **130**, 244702 (2009)

Counterion-induced electroosmotic flow [Smiatek et. al (2009)]

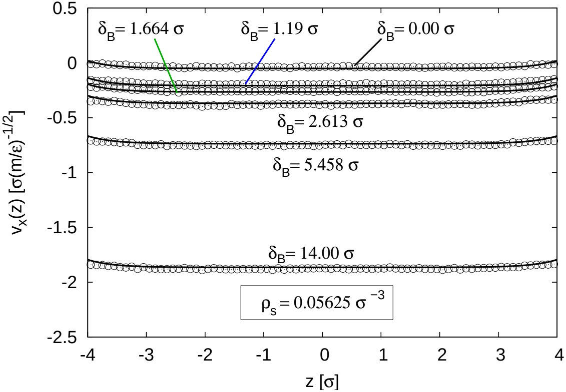
Comparison with Lattice-Boltzmann for no-slip boundary conditions (bounce-back):



J. Smiatek, M. Sega, U. D. Schiller, C. Holm, F. Schmid, *J. Chem. Phys.* **130**, 244702 (2009)

Full electroosmotic flow [Smiatek & Schmid (2010)]

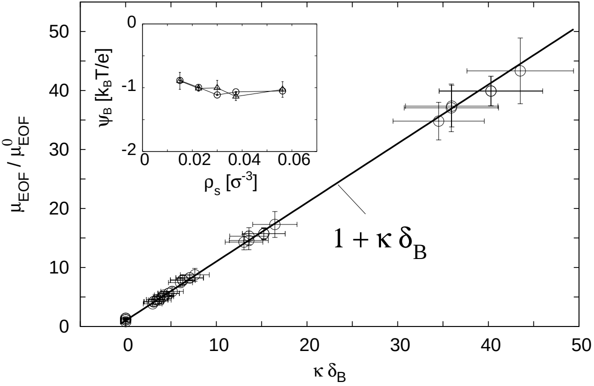
Salt and counterions → 'plug-like' flow profile



J. Smiatek, F. Schmid, *J. Phys. Chem. B* **114**, 6266 (2010)

Electroosmotic mobility [Smiatek & Schmid (2011)]

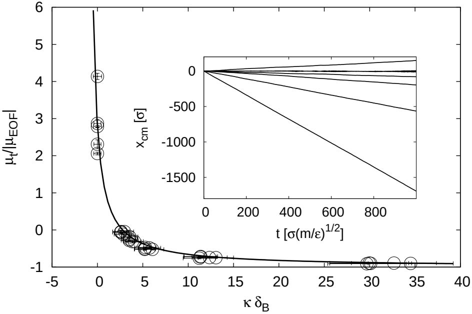
Salt-induced solvent electroosmotic mobility can be expressed by $\mu_{EOF} = \mu^0_{EOF}(1 + \kappa\delta_B)$ with inverse electrostatic screening length κ and slip length δ_B.



J. Smiatek, F. Schmid, *Comp. Phys. Comm.* **182**, 1941 (2011)

Total electrophoretic mobility for polyelectrolytes [Smiatek & Schmid (2010)]

Total electrophoretic mobility compared to the electroosmotic mobility of the solvent for different slip and inverse screening lengths



- Varying parameters: slip length and electrostatic screening length

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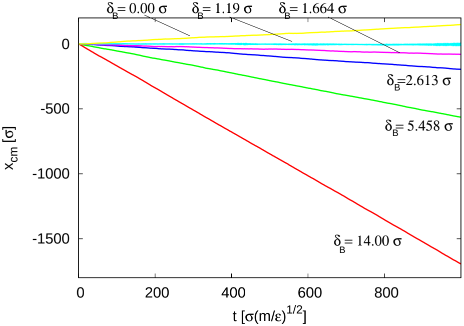
J. Smiatek, F. Schmid, *J. Phys. Chem. B* **114**, 6266 (2010)

Center-of-mass motion for polyelectrolytes [Smiatek & Schmid (2010)]



- Boundary parameters are important: Change of direction due to EOF magnitude increase

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J. Smiatek, F. Schmid, *J. Phys. Chem. B* **114**, 6266 (2010)

Summary

Dissipative Particle Dynamics is a powerful tool to ...

- qualitatively investigate solvation behavior
- treat boundary conditions in microchannel flows
- analyze mixing behavior of different species

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Thank you for your attention!