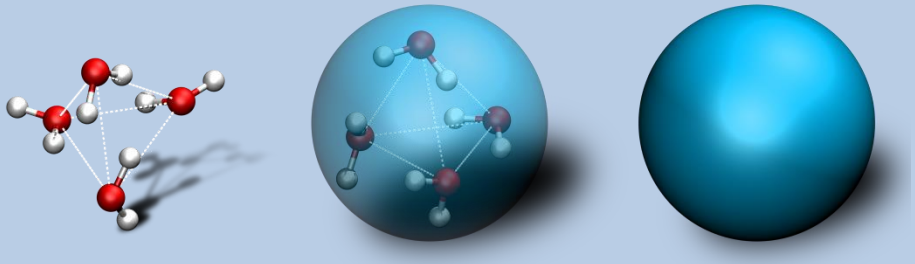

Napredne metode simulacij molekulske dinamike – večskalne simulacije z uporabo polja MARTINI

Matej Praprotnik

National Institute of Chemistry, Slovenia

2. mednarodna spomladanska šola fizike - delavnice iz biofizike

Maribor, maj 2015

Kemijski inštitut
Ljubljana
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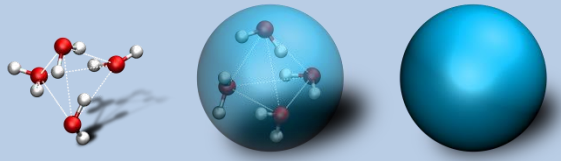
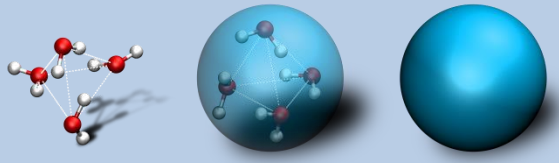
Institute of Chemistry
Slovenia



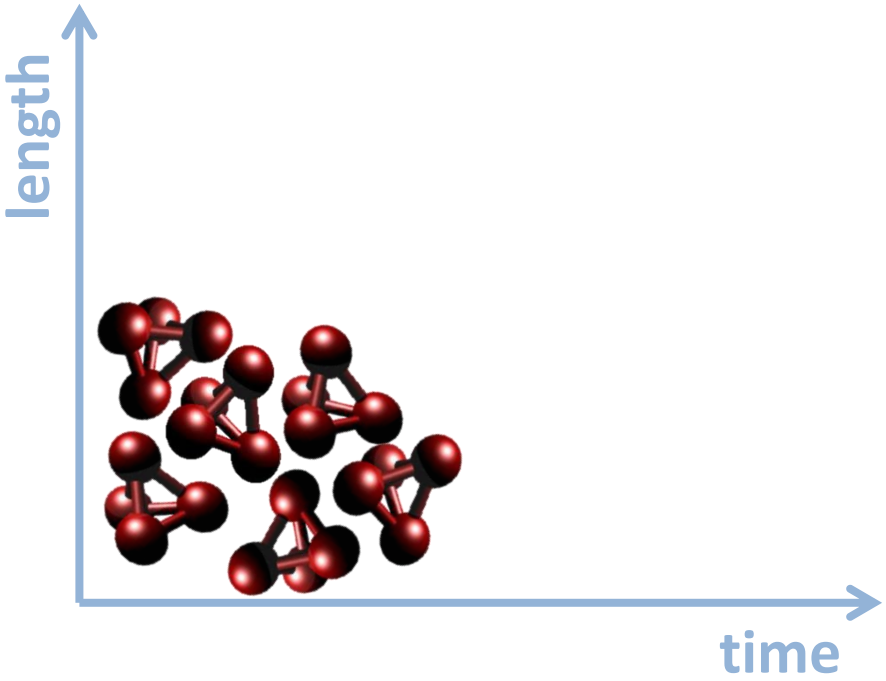
Outline

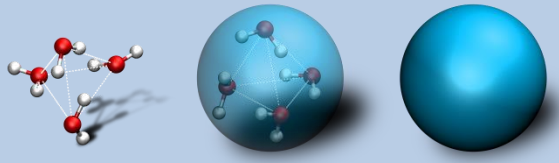
- why multiscale simulations?
- Adaptive Resolution Scheme (AdResS)
- 4-to-1 mapping
- multiscale MARTINI water model
- atomistic protein in multiscale MARTINI water
- polarizable models
- coupling of rotational degrees of freedom



Multiscale simulation

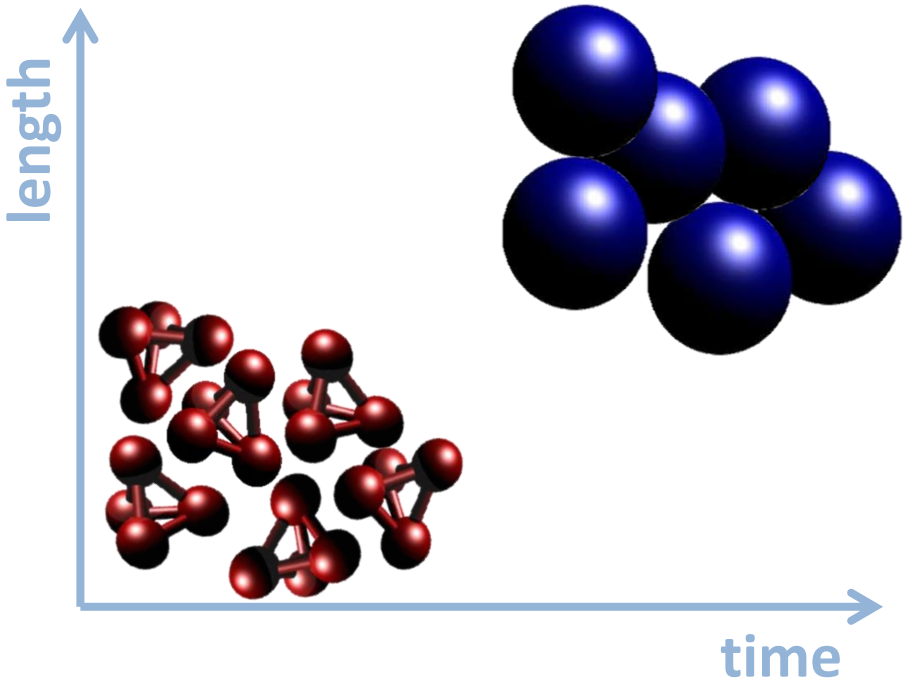
- concurrent multiscale simulation
- atomistic simulation
  - large length and time scales are difficult to capture





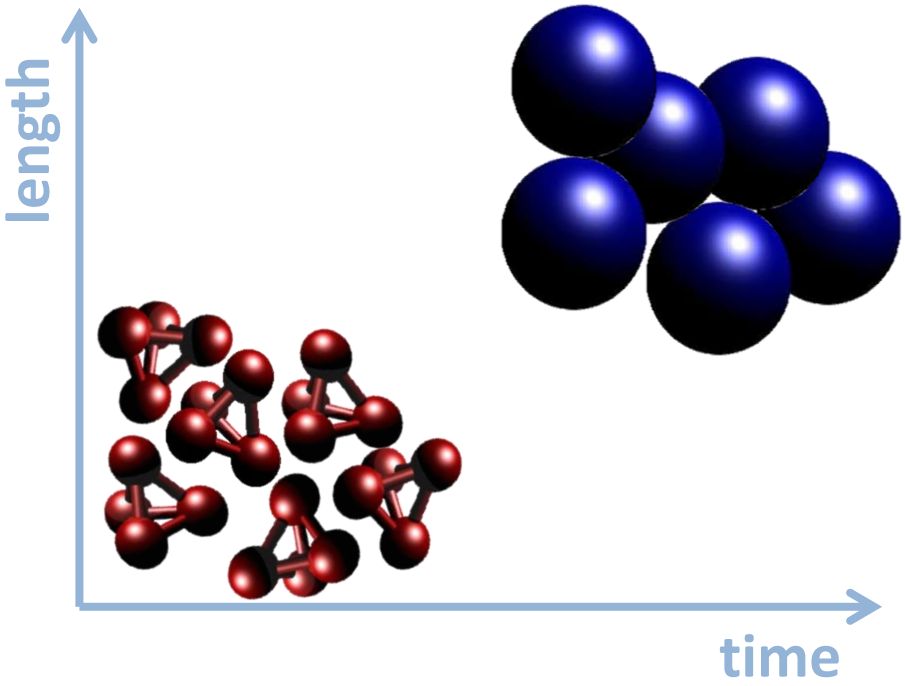
Multiscale simulation

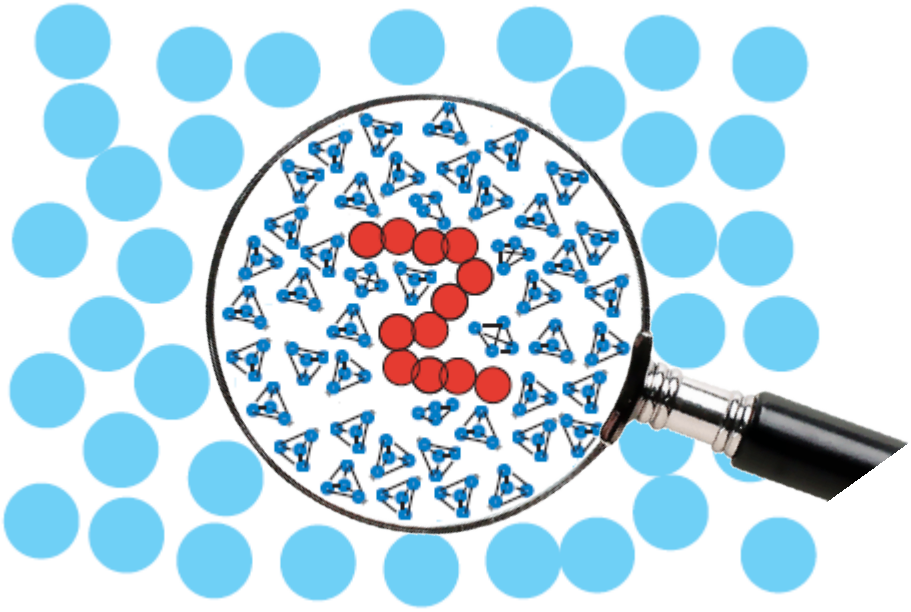
- concurrent multiscale simulation
- atomistic simulation
  - large length and time scales are difficult to capture
- coarse-grain simulation
  - atomistic details are lost



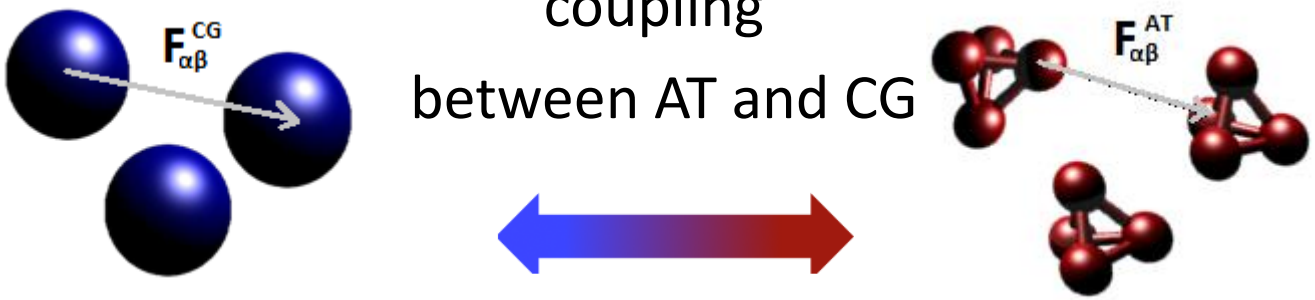
Multiscale simulation

- concurrent multiscale simulation
- atomistic simulation
  - large length and time scales are difficult to capture
- coarse-grain simulation
  - atomistic details are lost
- multiscale simulations





Adaptive Resolution Scheme (AdResS)



coarse-grained (CG) atomistic (AT) region

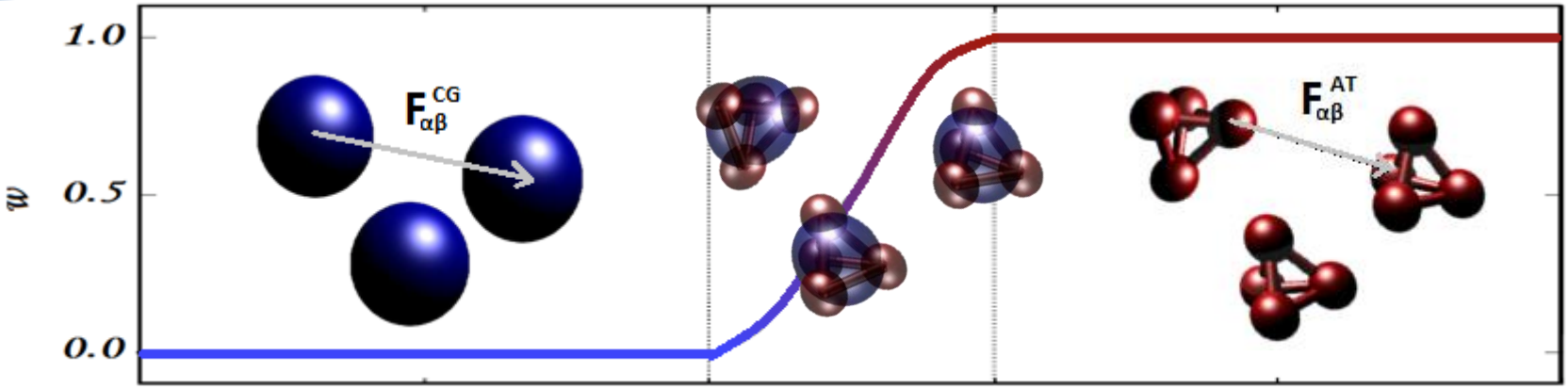
- Boltzmann inversion: effective potential calculated iteratively so that coarse-grained radial distribution function matches the atomistic one

$$U_{i+1}(r) = U_i(r) - k_B T \ln\left[\frac{g_i(r)}{g_{AT}(r)}\right]$$

- atomistic force fields (Amber, Gromos, …)
- nonbonded potentials (Lennard-Jones , electrostatic)
- bonded potentials (bonds, angles, dihedrals)

Praprotnik, Delle Site, Kremer; Annu. Rev. Phys. Chem. (2008)

Adaptive Resolution Scheme (AdResS)



coarse-grained (CG) hybrid (HY) atomistic (AT) region

- force between particle α and β:

$$F_{\alpha\beta} = w(x_\alpha)w(x_\beta)F_{\alpha\beta}{}^{AT} + [1 - w(x_\alpha)w(x_\beta)]\, F_{\alpha\beta}{}^{CG}$$

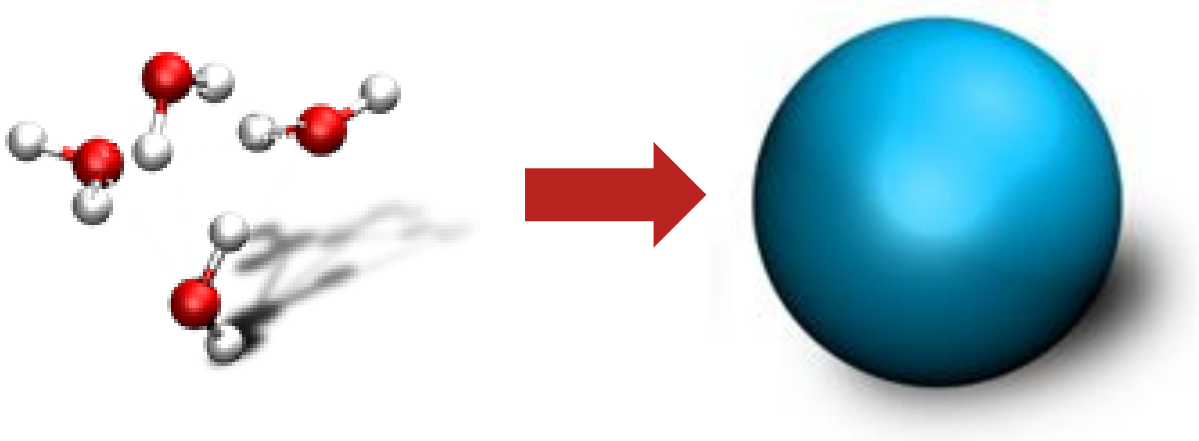
$w(x)$... position dependent weighting function

- the above force coupling scheme obeys Newton's third law
- implementation: ESPRESSO++, GROMACS

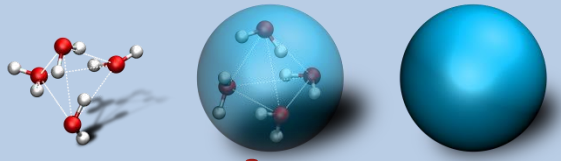
Praprotnik, Delle Site, Kremer; Annu. Rev. Phys. Chem. (2008)

The next step: multi-molecule mapping

- multiple AT molecules mapped to 1 CG bead
- motivation:
  - greater computational speed-up
  - with 4-to-1 mapping the MARTINI force field can be used



Marrink, Risselada, Yefimov, Tieleman, de Vries; Phys. Chem. B (2007)
Fuhrmans, Sanders, Marrink, de Vries; Theor. Chem. Acc. (2010)



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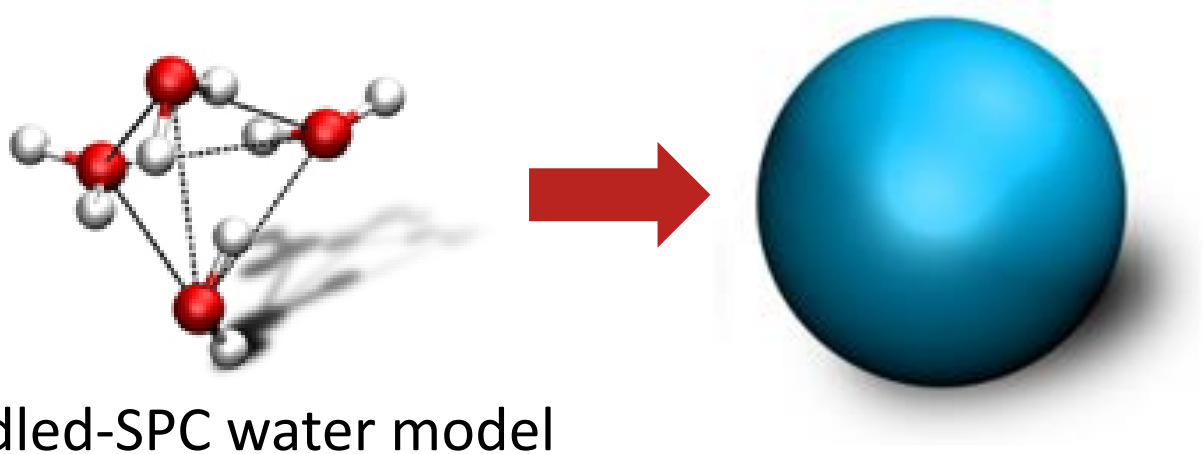
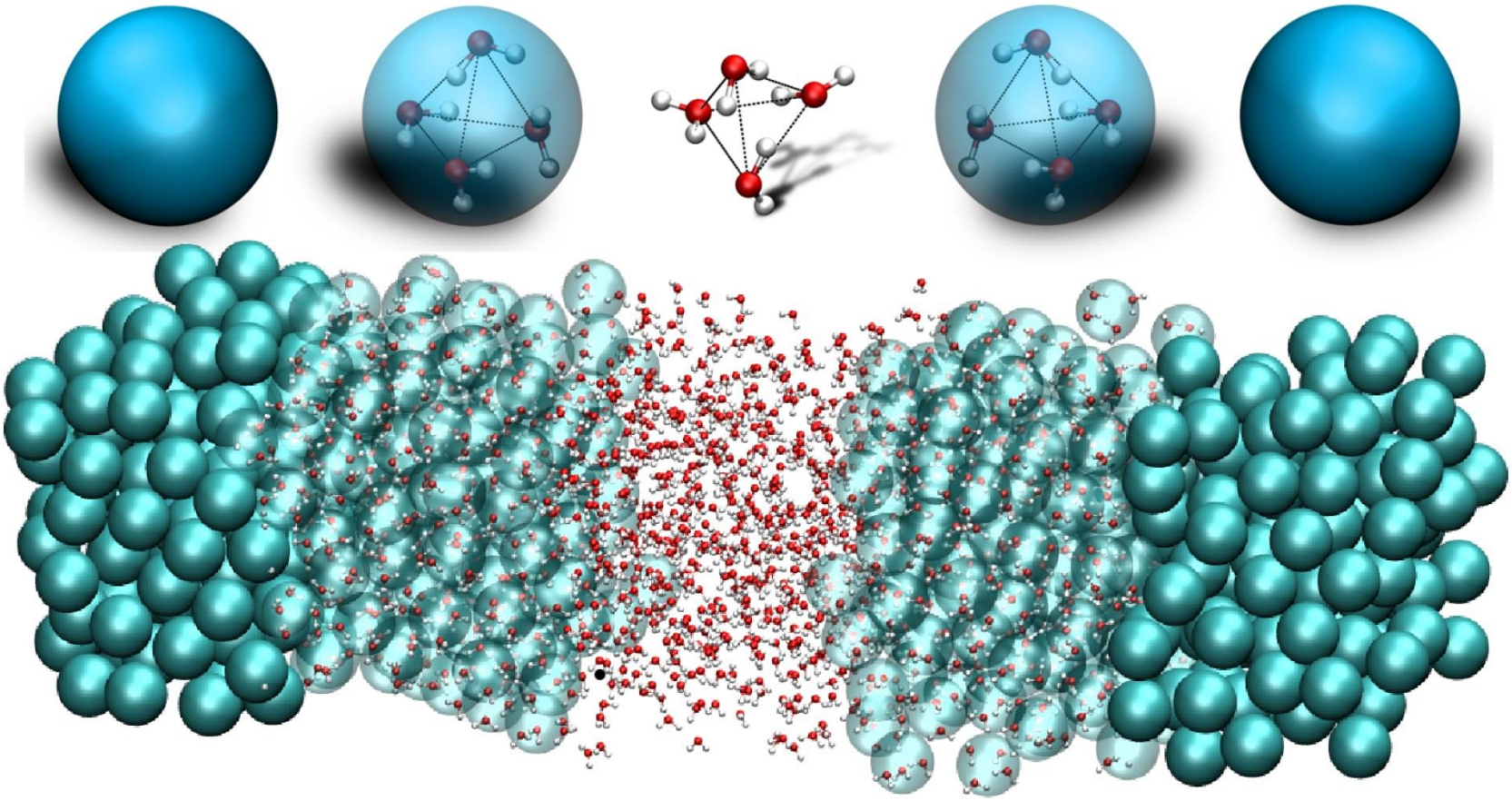


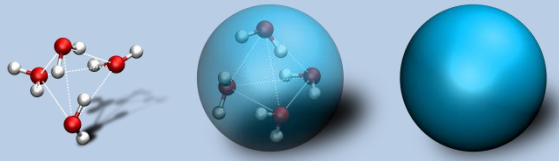
- bundled-SPC water model
  - half harmonic bonds between oxygen atoms
  - different force constants -> model 1 and 2

Marrink, Risselada, Yefimov, Tieleman, de Vries; Phys. Chem. B (2007)
Fuhrmans, Sanders, Marrink, de Vries; Theor. Chem. Acc. (2010)

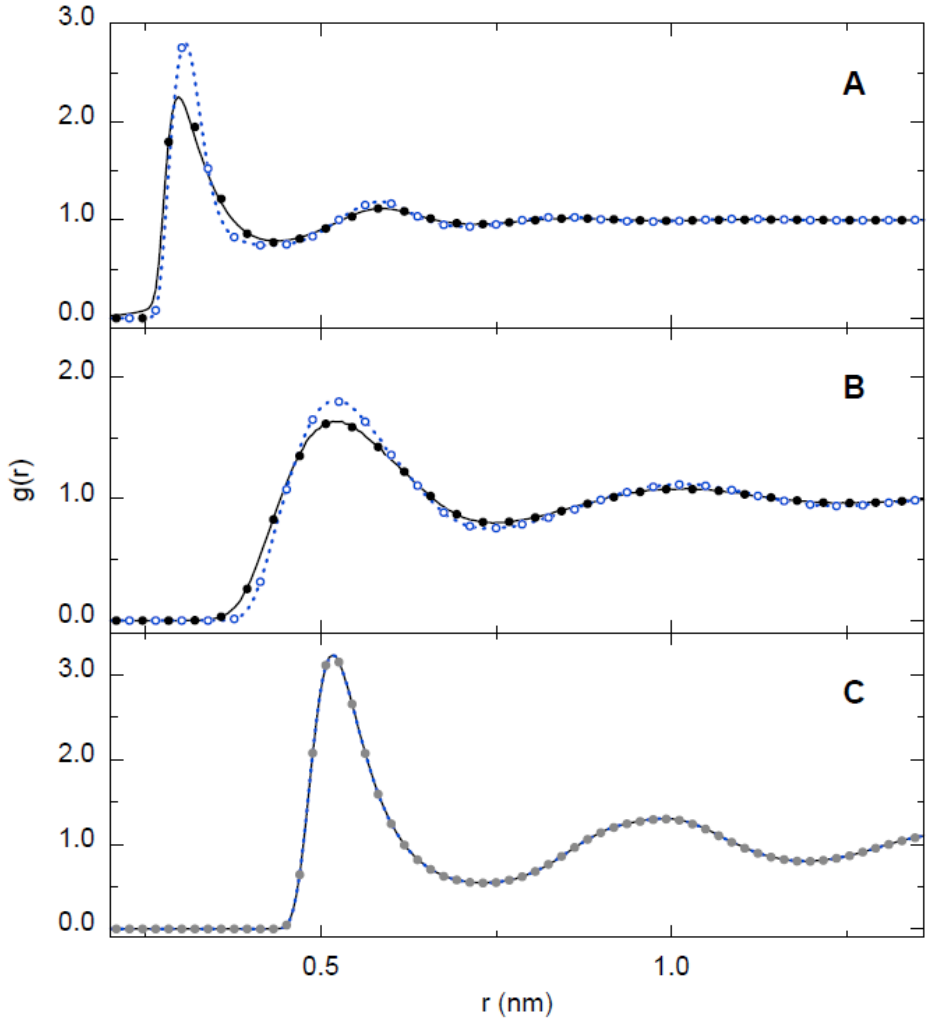
Bundled-SPC/MARTINI water



Zavadlav, Melo, Cunha, de Vries, Marrink, Praprotnik; *J. Chem. Theory Comput*. (2014)

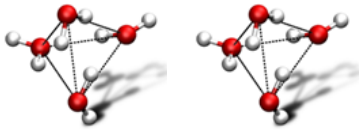


Bundled-SPC/MARTINI water

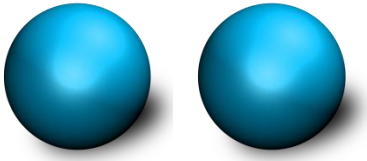


oxygen

bundle COM



CG bead

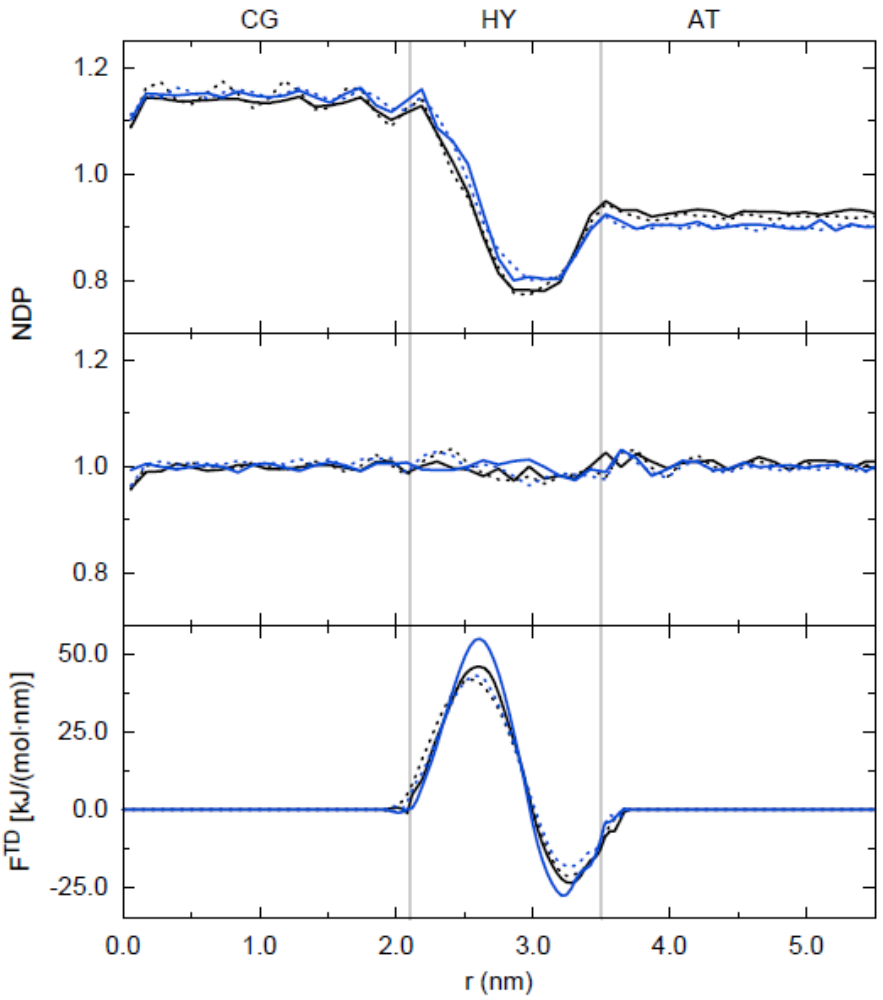


Zavadlav, Melo, Cunha, de Vries, Marrink, Praprotnik; *J. Chem. Theory Comput*. (2014)

Bundled-SPC/MARTINI water

- density profile
- Thermodynamic (TD) force on CG beads in HY region
- calculated iteratively

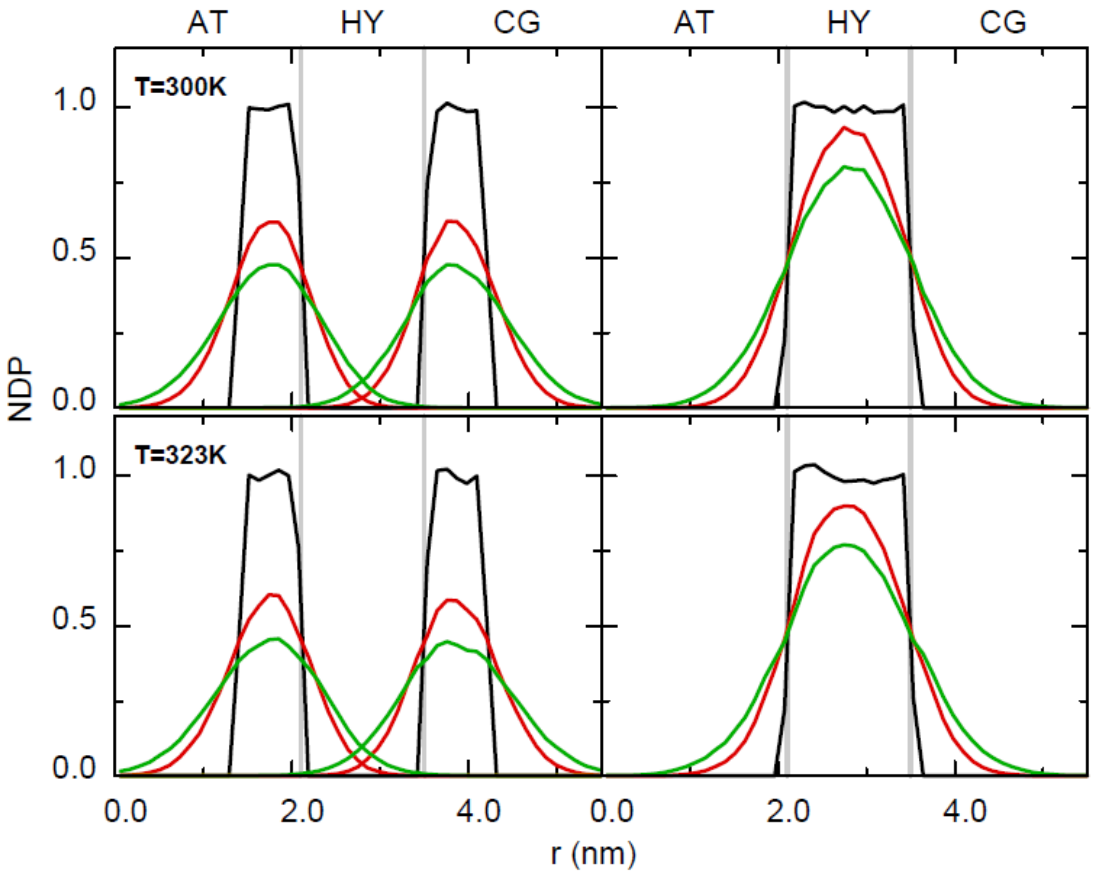
$$F_{TD}{}^{i+1} = F_{TD}{}^{i} - \frac{M_\alpha}{\rho_0{}^2 \kappa_T} \nabla \rho^i(x)$$



Zavadlav, Melo, Cunha, de Vries, Marrink, Praprotnik; *J. Chem. Theory Comput*. (2014)

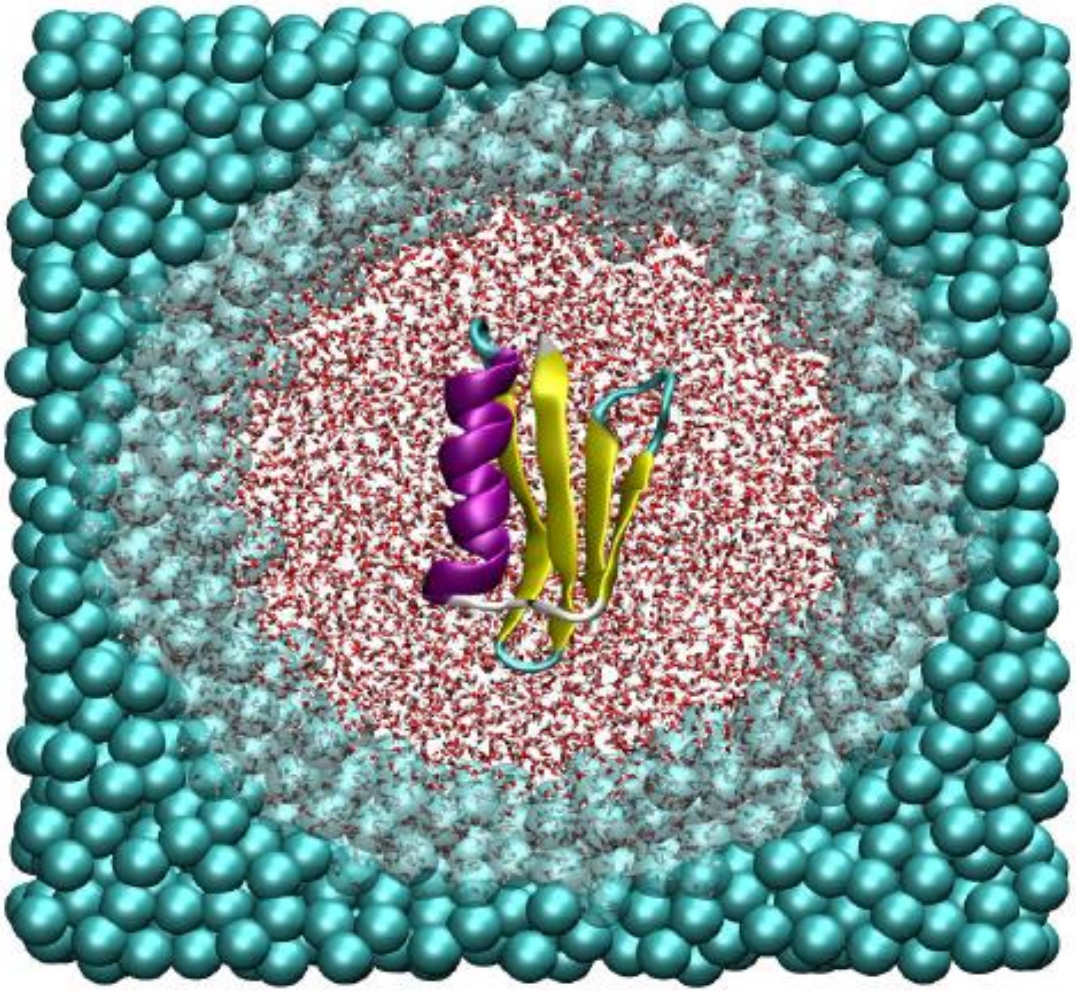
Bundled-SPC/MARTINI water

- Dynamical properties:



Zavadlav, Melo, Cunha, de Vries, Marrink, Praprotnik; *J. Chem. Theory Comput*. (2014)

Protein in Bundled-SPC/MARTINI water



Zavadlav, Melo, Marrink, Praprotnik; *J. Chem. Phys*. (2014)

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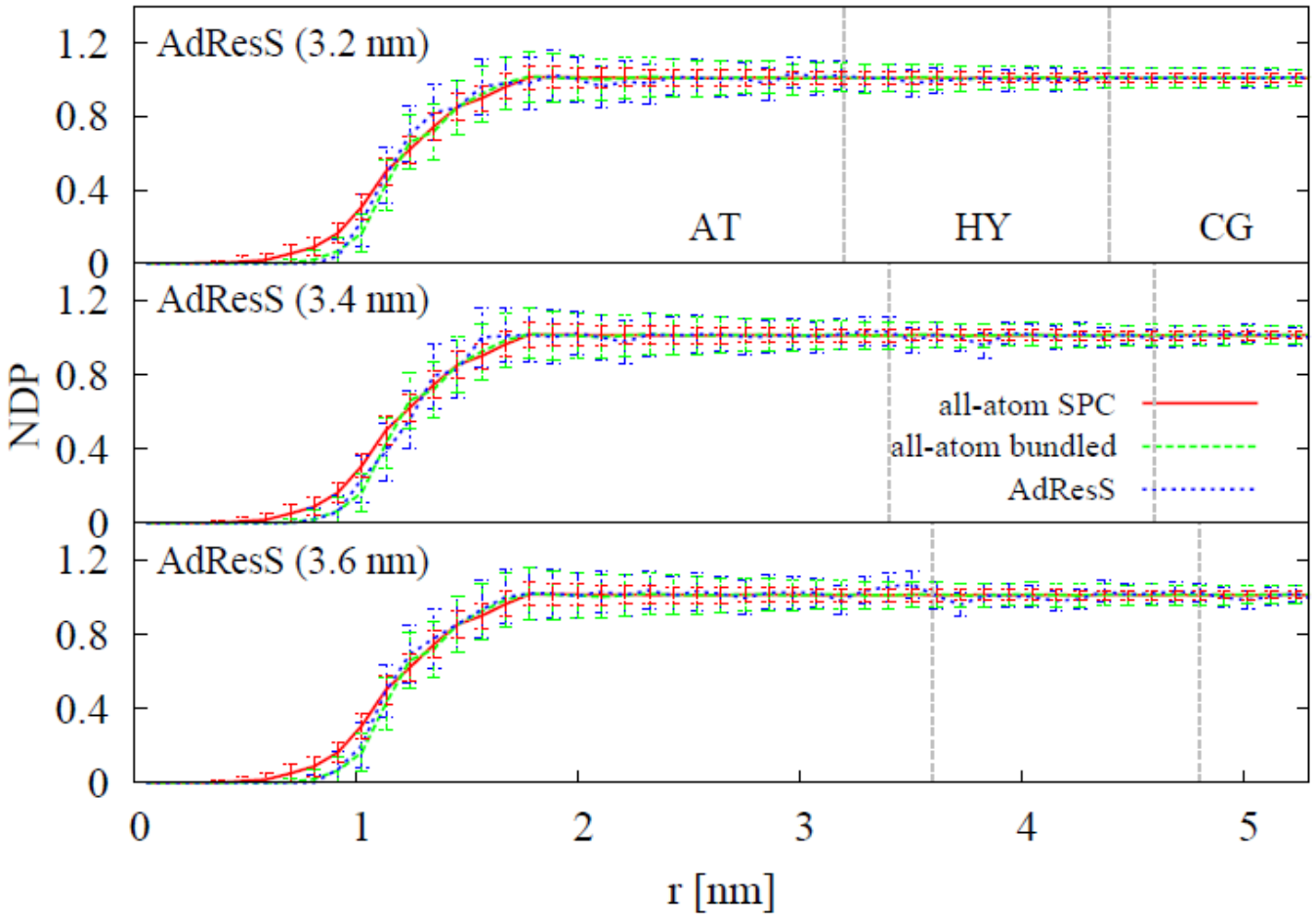
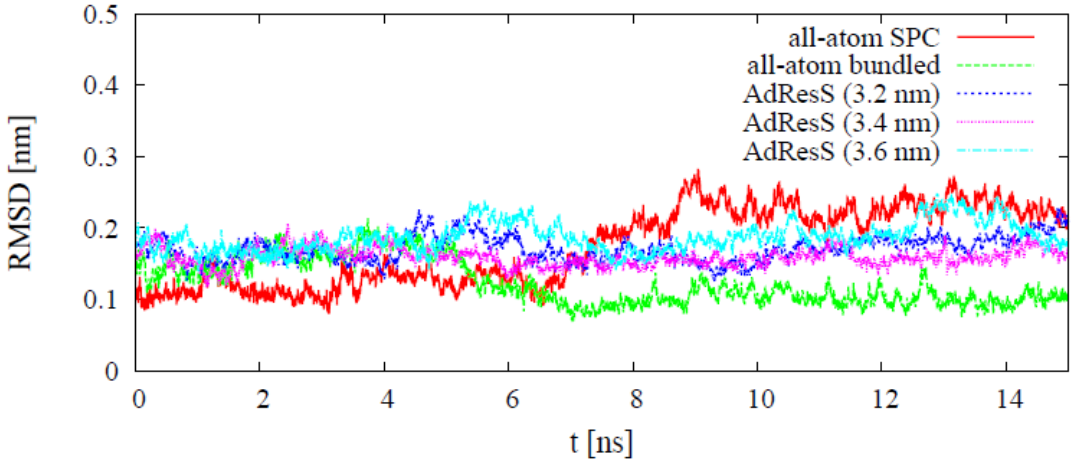


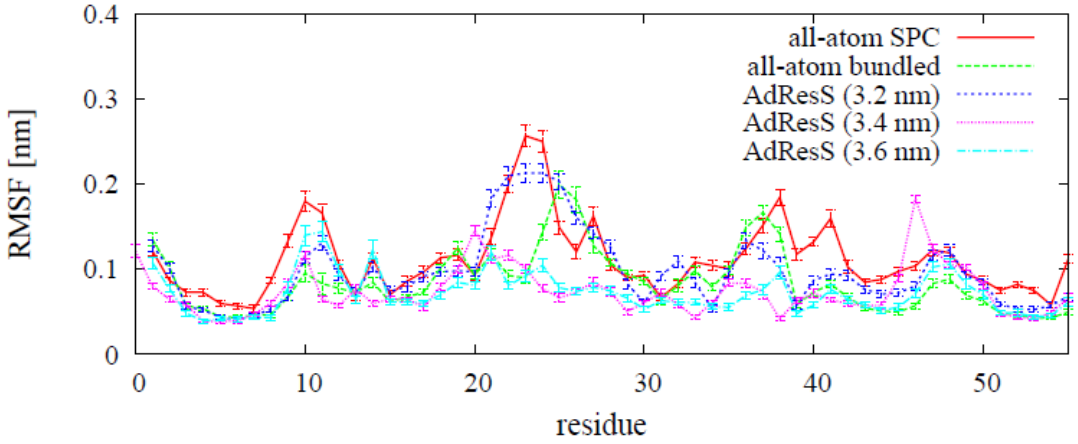
normalized density profile

Zavadlav, Melo, Marrink, Praprotnik; *J. Chem. Phys*. (2014)

Protein in Bundled-SPC/MARTINI water



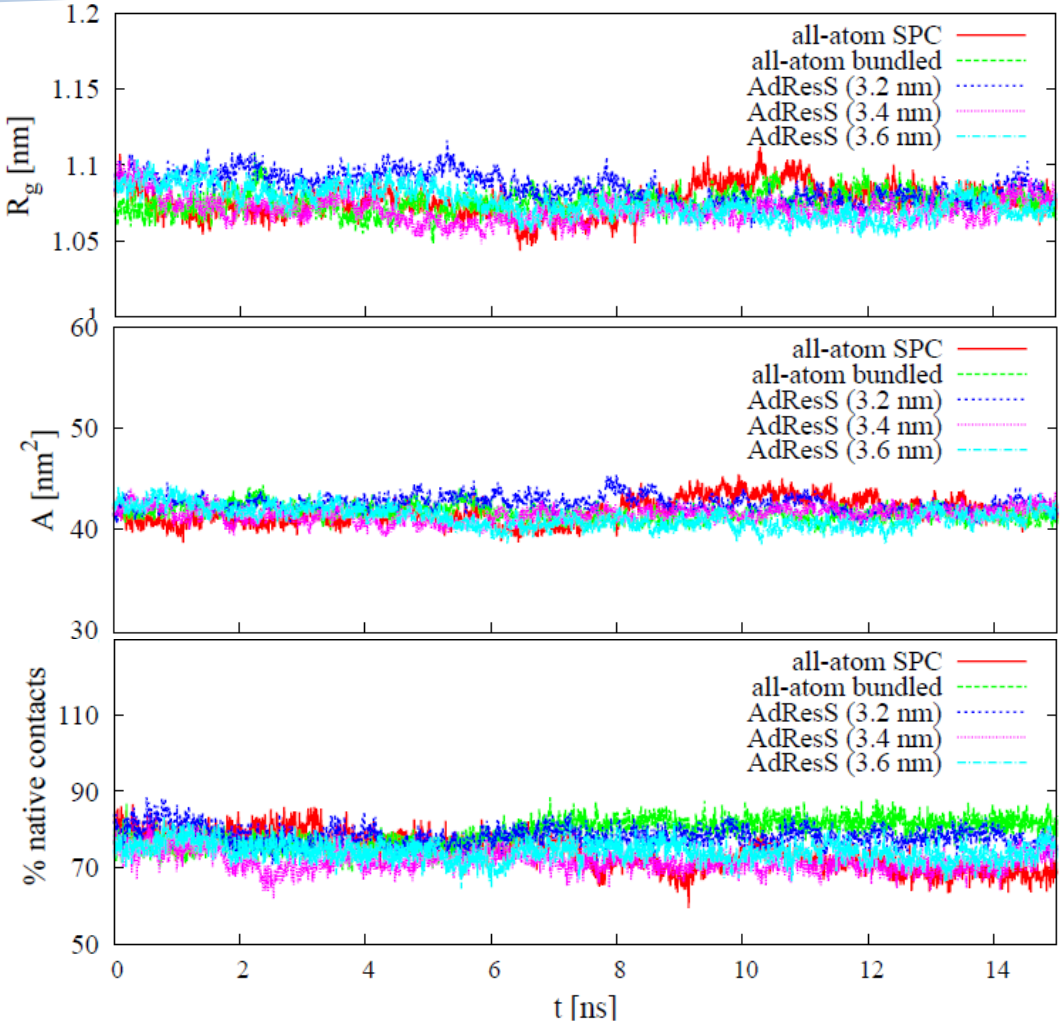
root-mean-square deviation



root-mean-square fluctuations

Zavadlav, Melo, Marrink, Praprotnik; *J. Chem. Phys*. (2014)

Protein in Bundled-SPC/MARTINI water

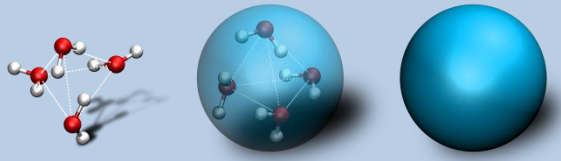


radius of gyration

solvent accessible surface area

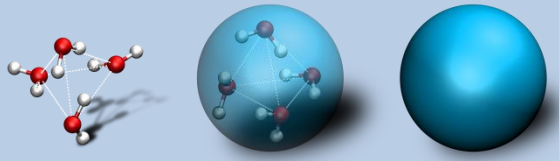
percentage of native contacts

Zavadlav, Melo, Marrink, Praprotnik; *J. Chem. Phys*. (2014)



Conclusions

- AdResS:
  - allows for a dynamical switching between atomistic and coarse-grained molecular descriptions.
  - larger length and time scales can be achieved because of the speed up while keeping all the details in the regions of interest
  - bridge between different models
- future work:
  - studying biophysical phenomena at multiple length scales



Acknowledgements

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- **Siewert J. Marrink**; Groningen Biomolecular Sciences and Biotechnology Institute and Zernike Institute for Advanced Materials, University of Groningen, Groningen, Netherlands

- **Slovenian Research Agency** for funding

Napredne Metode Simulacij Molekulske Dinamike: Odprte Simulacije Molekulske Dinamike

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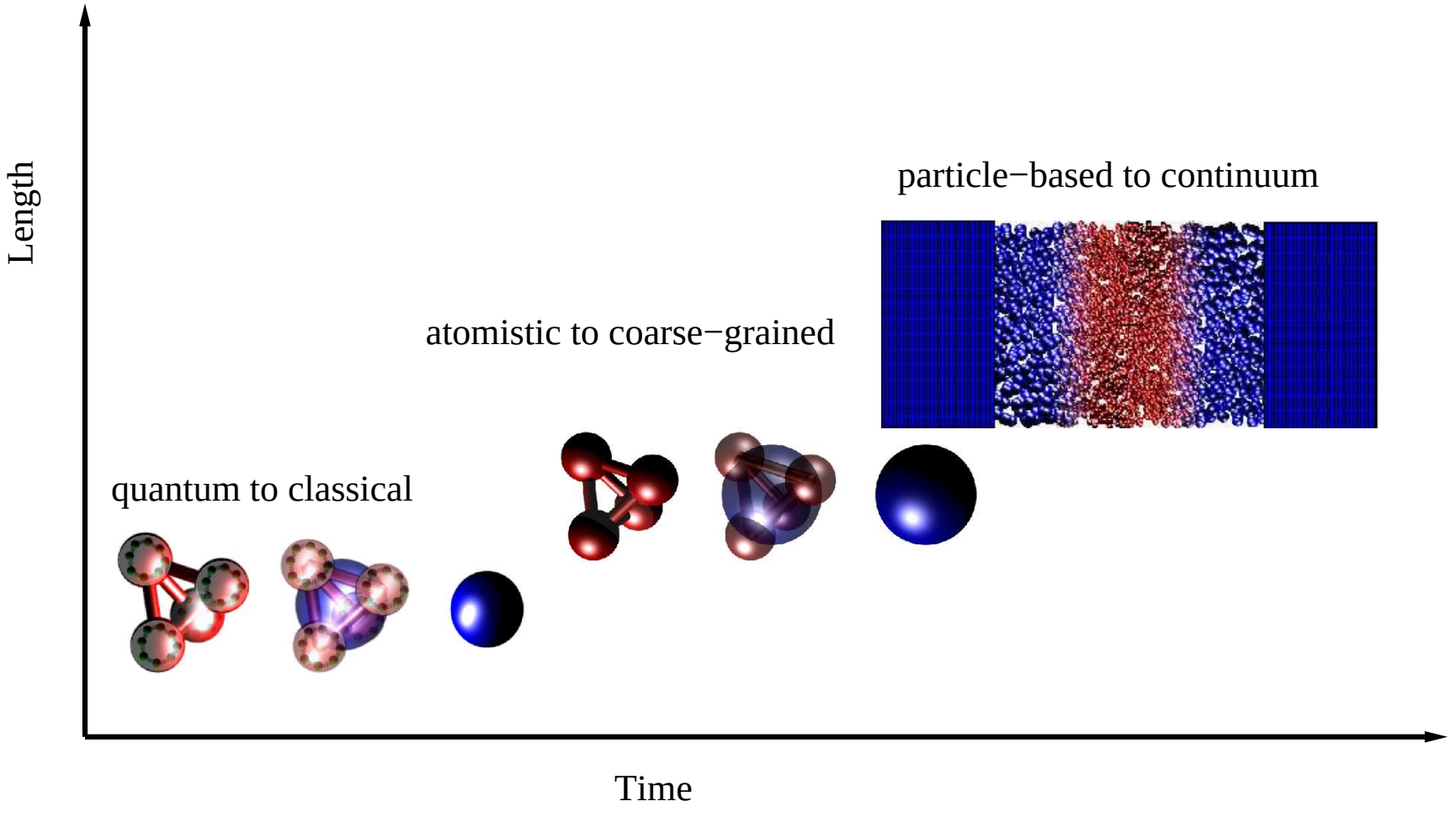
Kemijski inštitut

Ljubljana

Multiscale Modeling



M. Praprotnik, L. Delle Site, Humana Press (2012).

Multiscale Simulation of Liquids

All-Atom MD simulation:

- allows to study processes at the atomic level of detail
- is often incapable to bridge a gap between a wide range of length and time scales involved in molecular systems

Mesoscopic MD simulation:

- reduces the number of DOFs by retaining only those that are relevant for the property of interest $\Longrightarrow$ longer length and time scales can be reached
- specific chemical details are usually lost in the coarse-graining procedure

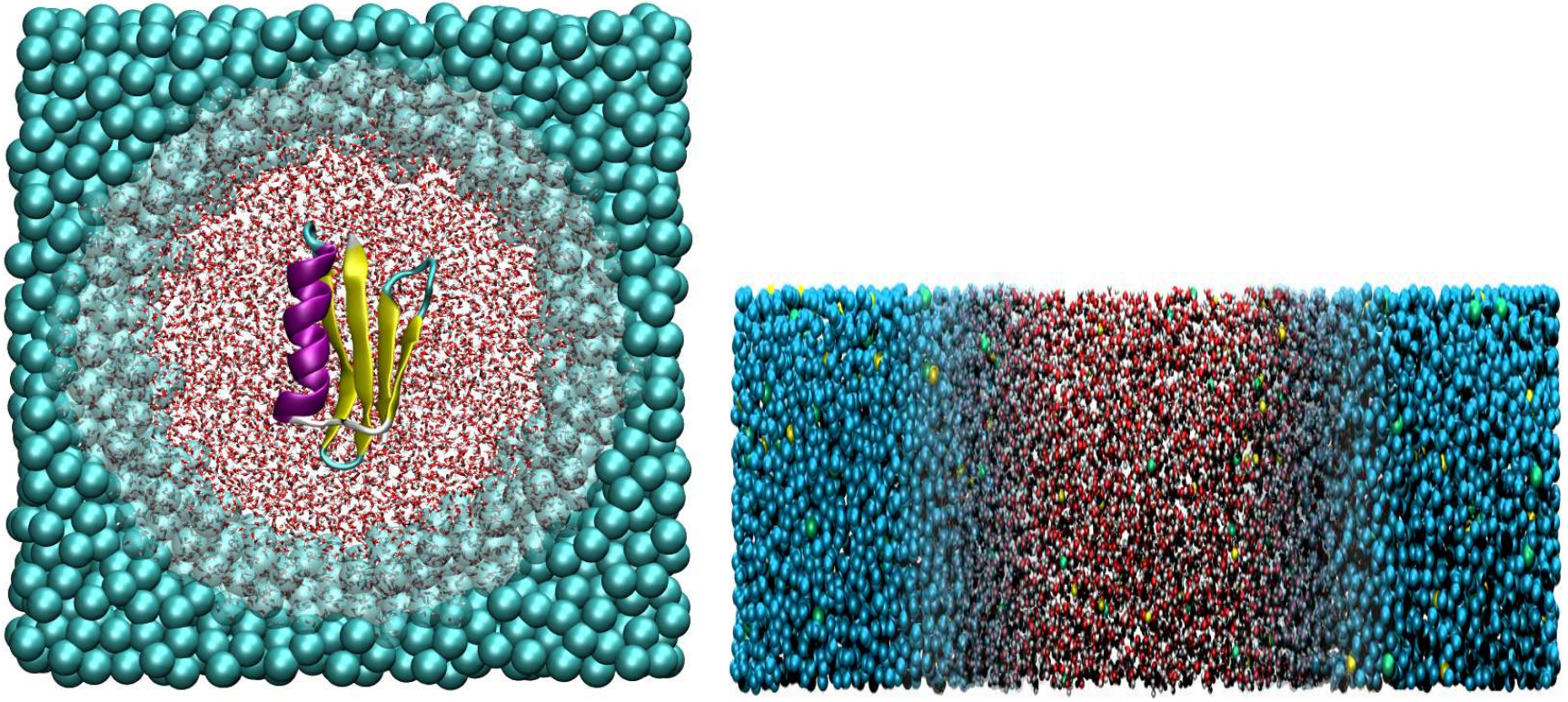
Continuum fluid dynamics (CFD):

- allows to model fluid flows on length scales that are out of scope of MD simulation.
- at lower scales (a few molecular diameters) no-slip boundary condition breaks down.

Combination:

- Hybrid MD-Continuum Methods $\Longrightarrow$ Open Boundary Molecular Dynamics

Hybrid Atomistic/Mesoscopic Liquid



J. Zavadlav, M. N. Melo, S.-J. Marrink, M. Praprotnik, J. Chem. Phys. **140**, 054114 (2014).
S. Bevc, C. Junghans, K. Kremer, M. Praprotnik, New J. Phys. **15**, 105007 (2013).

Adaptive Resolution Simulation

`AdResS` consists of two main steps:

1. Derive the effective pair potential U^{cm} between coarse-grained molecules on the basis of the reference all-atom system.
2. Couple the atomistic and mesoscopic scales:

$$\mathbf{F}_{\alpha\beta} = w(X_\alpha)w(X_\beta)\mathbf{F}^{atom}_{\alpha\beta} + [1 - w(X_\alpha)w(X_\beta)]\mathbf{F}^{cm}_{\alpha\beta},$$

where

$$\mathbf{F}^{atom}_{\alpha\beta} = \sum_{i\alpha,j\beta} \mathbf{F}^{atom}_{i\alpha j\beta}$$

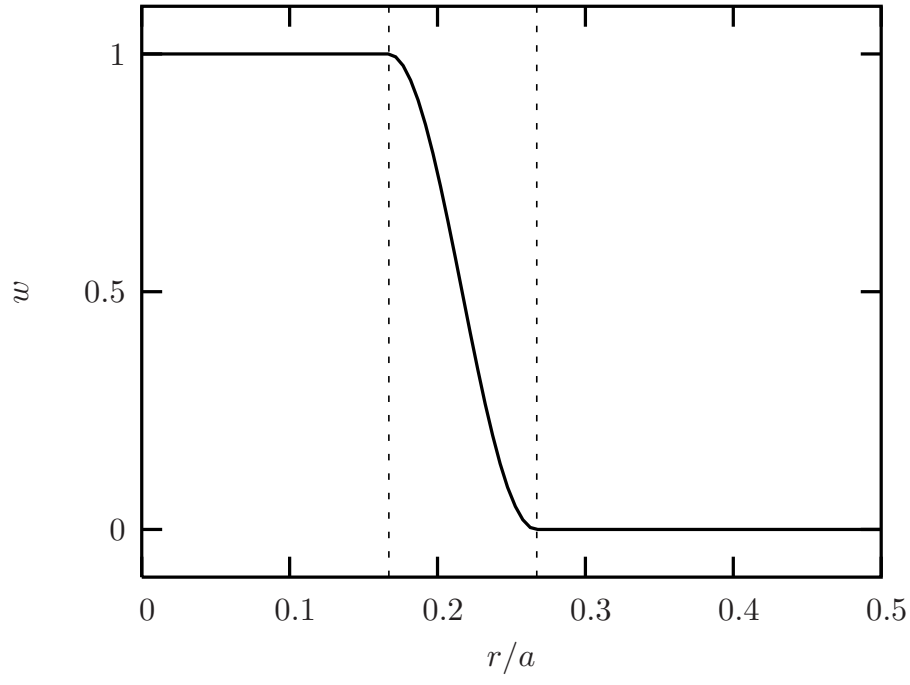
is the sum of all pair interactions between explicit atoms of molecules α and β and

$$\mathbf{F}^{atom}_{i\alpha j\beta} = -\frac{\partial U^{atom}}{\partial \mathbf{r}_{i\alpha j\beta}},$$

$$\mathbf{F}^{cm}_{\alpha\beta} = -\frac{\partial U^{cm}}{\partial \mathbf{R}_{\alpha\beta}}.$$

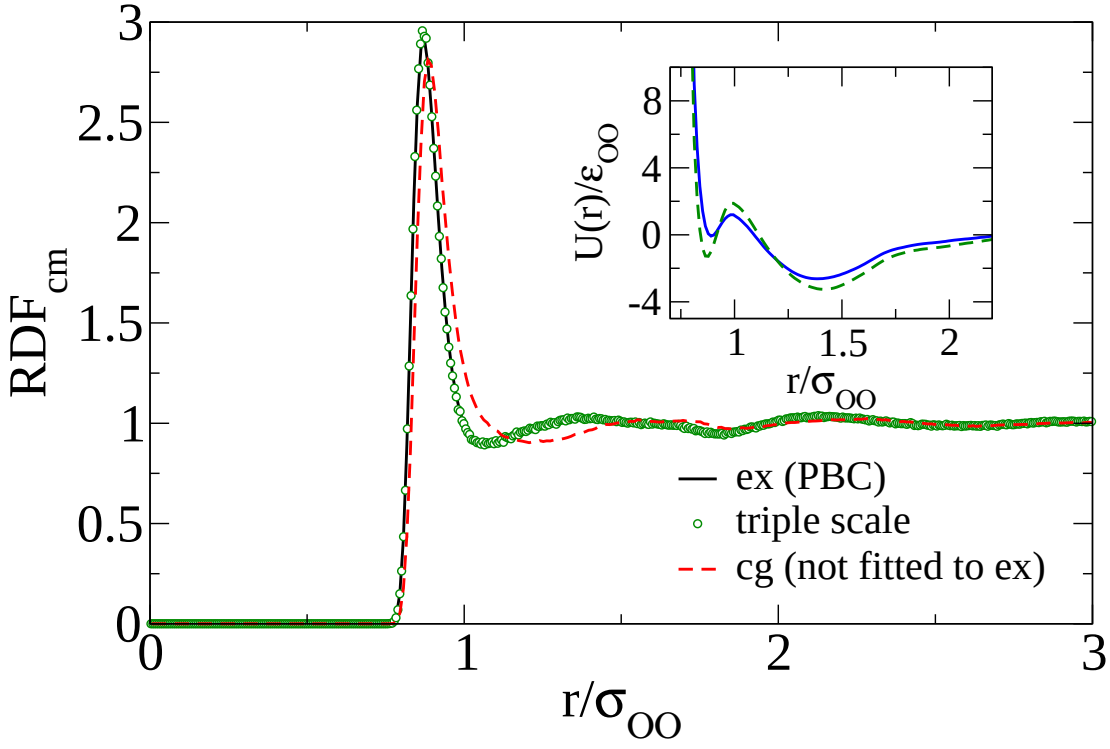
M. Praprotnik, L. Delle Site, K. Kremer, Annu. Rev. Phys. Chem. **59**, 545 (2008).

Weighting Function



- The values $w = 1$ and $w = 0$ correspond to the atomistic and coarse-grained regions, respectively, while the values $0 < w < 1$ correspond to the transition (hyb) regime.

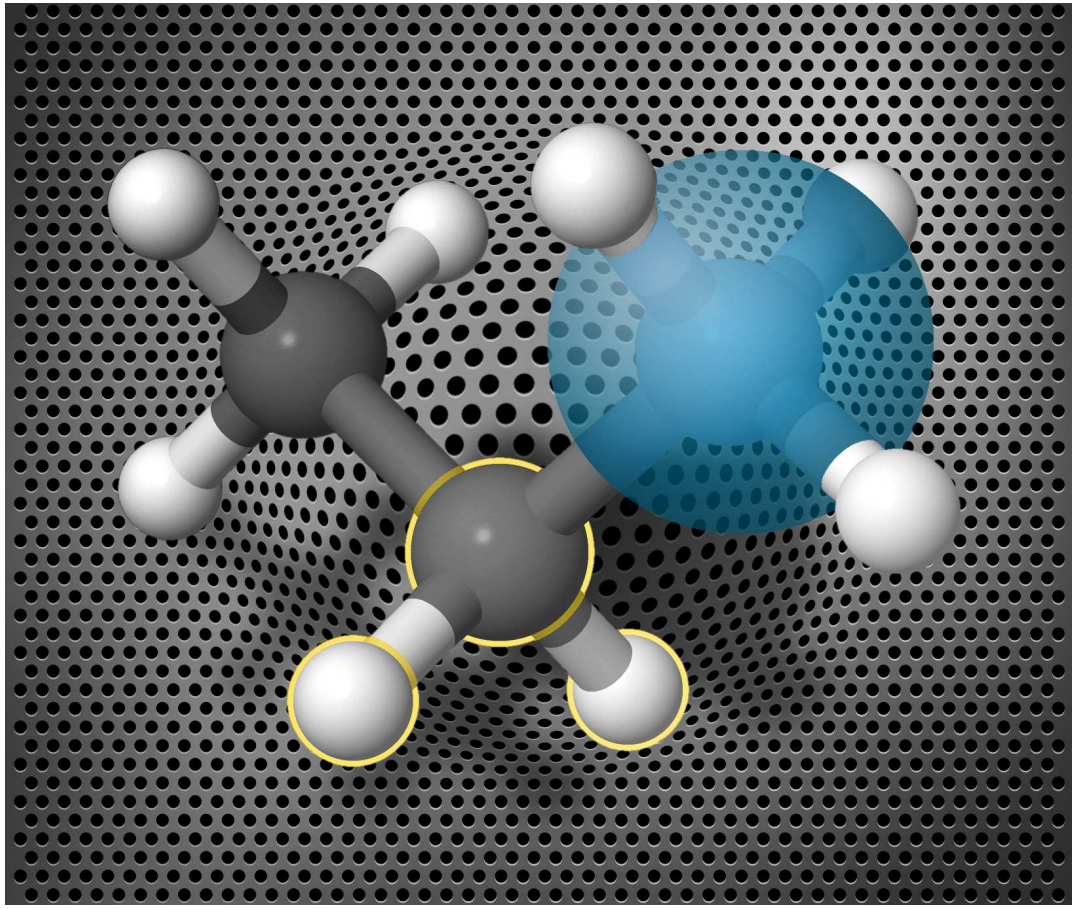
Coarse-Grained Model



- Center-of-mass RDF of the flexible TIP3P water model and the effective potential.

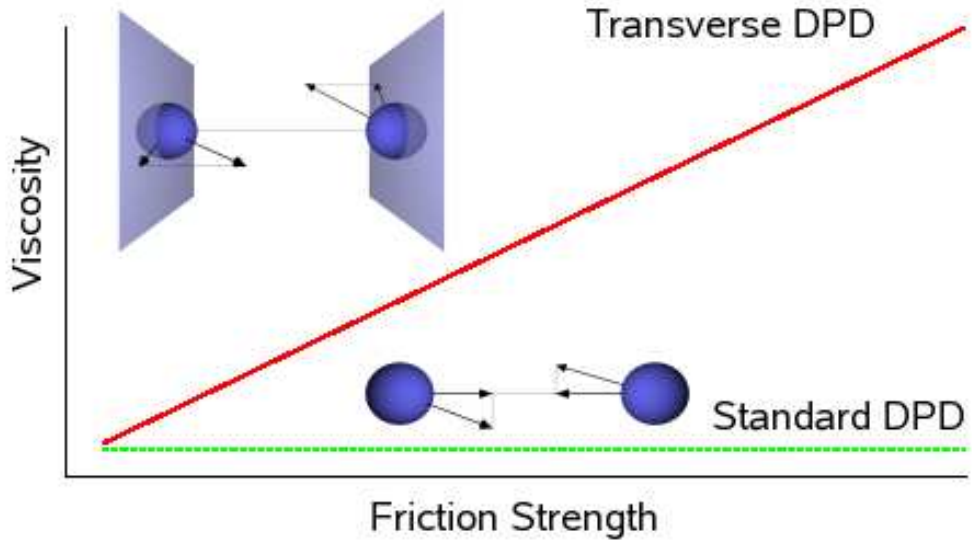
R. Delgado Buscalioni, K. Kremer, M. Praprotnik, J. Chem. Phys. **131**, 244107, (2009).

STOCK (http://stock.cmm.ki.si)



S. Bevc, C. Junghans, M. Praprotnik, J. Comput. Chem., DOI: 10.1002/jcc.23806, (2015).

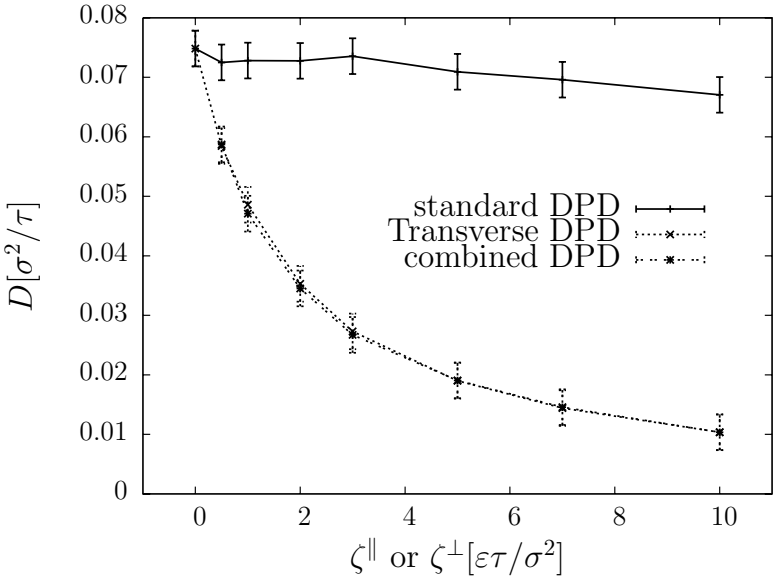
Transverse DPD Thermostat



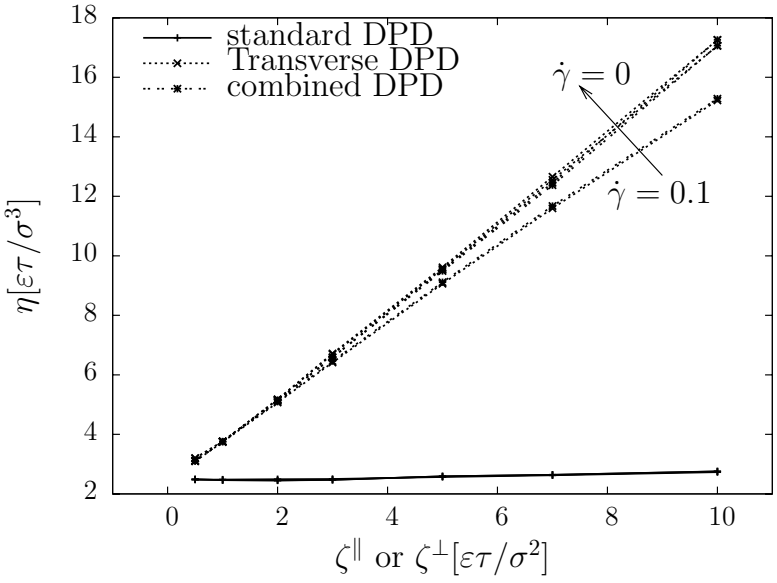
- The **variation** of the **dissipative particle dynamics (DPD)** thermostat includes the damping of the **perpendicular** components of the relative velocity, yet keeping the advantages of conserving **Galilei invariance** and within our error bar also **hydrodynamics**. It allows for **controlling transport properties** of molecular fluids.

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

Tuning Transport Coefficients

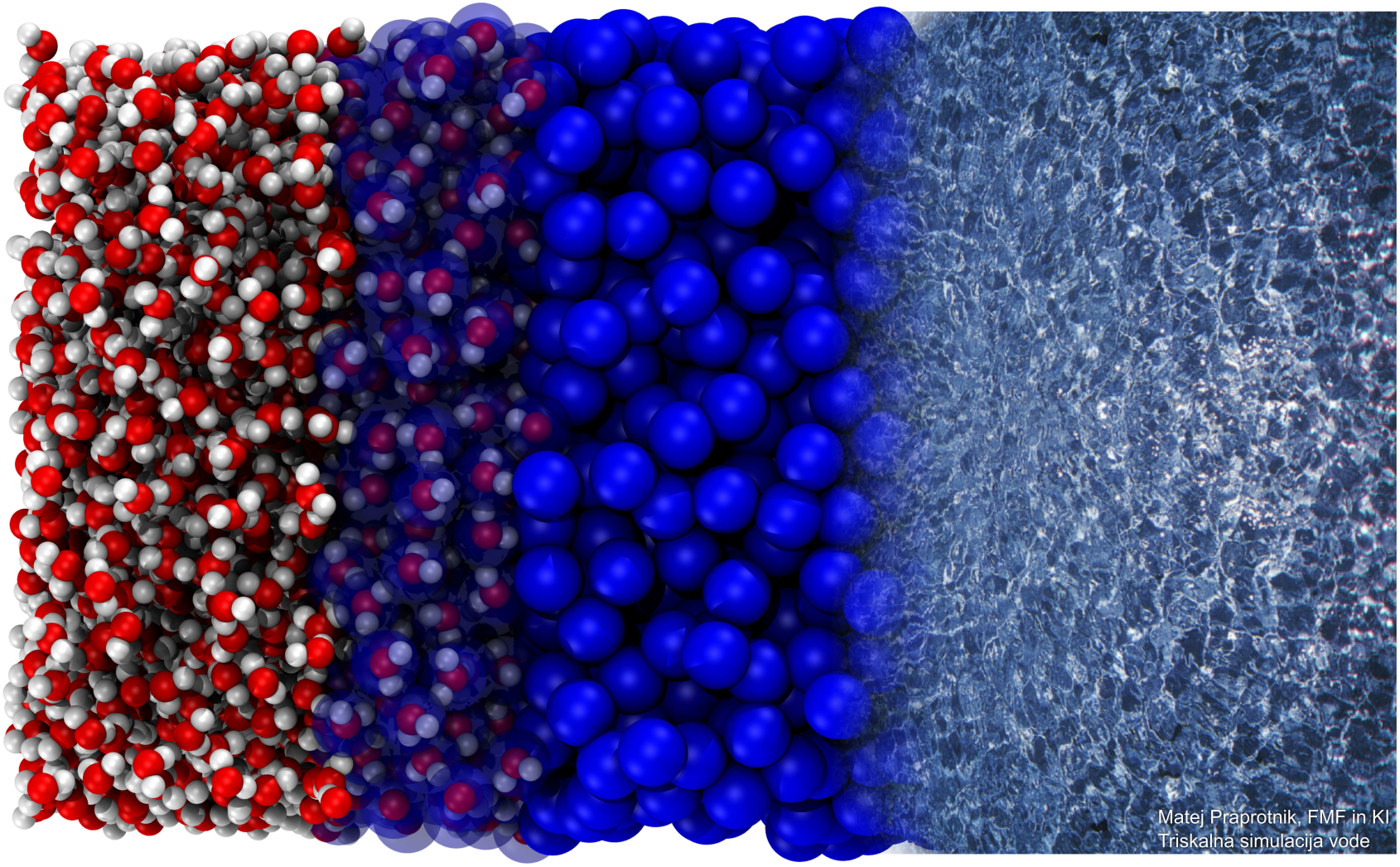


(c) Diffusion constant

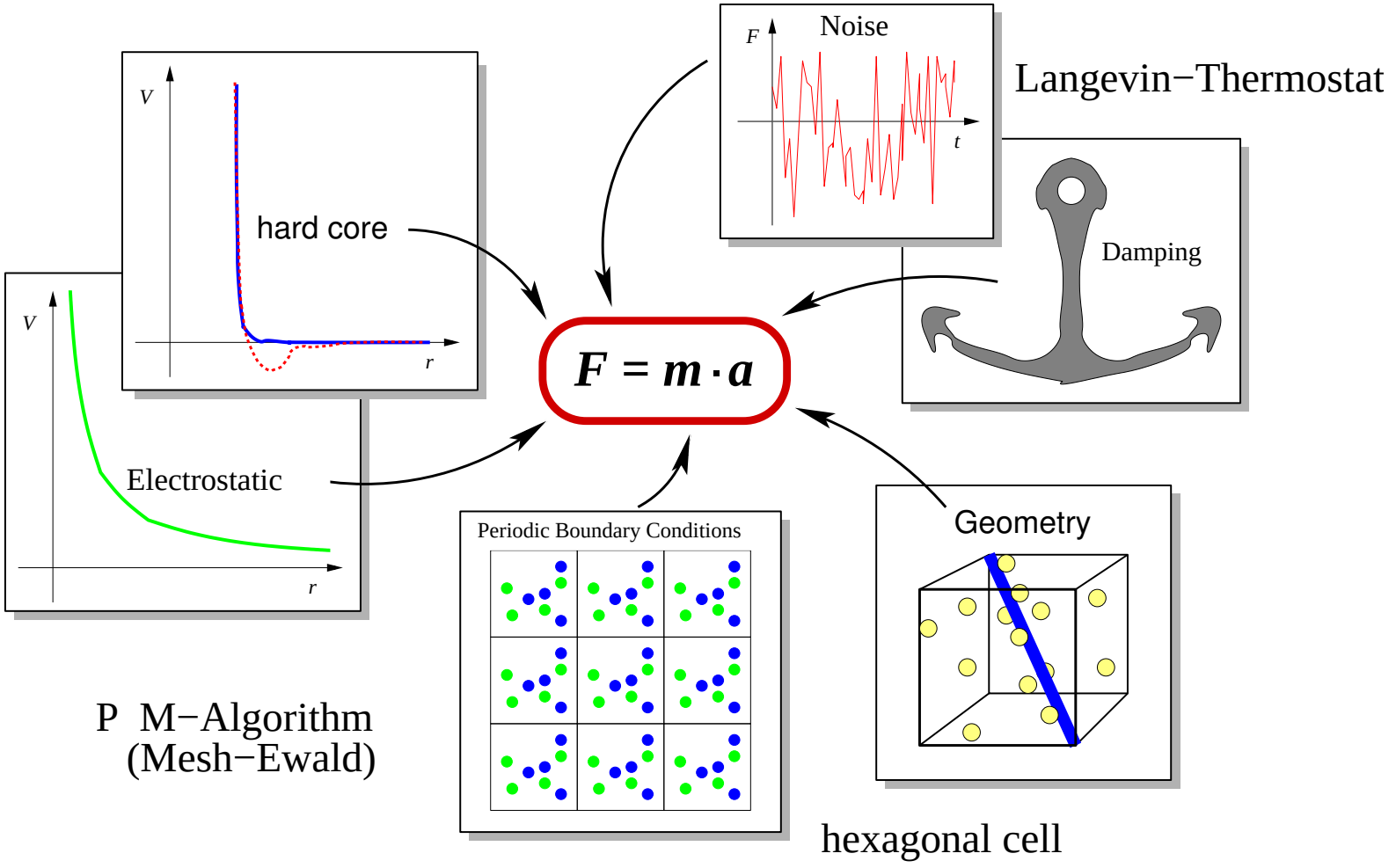


(d) Shear viscosity

Coupling MD with Continuum



Molecular Dynamics (MD) simulation



Navier-Stokes Equation

Conservation of momentum:

$$\rho(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u}) = -\nabla p + \nabla \cdot \mathbf{\Pi} + \mathbf{f}$$

Stress tensor:

$$\mathbf{\Pi} = -\eta[\nabla \mathbf{u}]^S - \xi \nabla \cdot \mathbf{u}\, \mathbf{I}$$

We consider a Newtonian fluid with dynamic viscosity η and bulk viscosity ξ. The traceless symmetric tensor is defined as $A^S_{\alpha\beta} = (A_{\alpha\beta} + A_{\beta\alpha}) - (2/3)A_{\gamma\gamma}$.

Conservation of mass:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0$$

Coupling MD and Continuum

- **Physical quantities**, i.e., density, momentum, and corresponding fluxes must be **continuous across the interface.**
- **Atomistic** and **continuum** domains provide each other with **boundary conditions.**
- To impose boundary conditions from the **MD to continuum** domain is relatively easy since it involves **temporal and spatial averaging.**
- Imposing the **continuum boundary conditions** on the **particle domain** presents the **major challenge** in hybrid methods.

Hybrid Atomistic-Continuum Schemes

- **state variable (Dirichlet) schemes**
  - **Schwartz alternating method**
- **flux-exchange schemes**

S. T. O'Connell, P. A. Thompson, Phys. Rev. E **52**, R5792 (1995)
N. G. Hadjiconstantinou, A. T. Patera, Int. J. Mod. Phys. **8**, 967 (1997)
X. Nie, S. Chen, M. O. Robbins, Physics of Fluids **16**, 3579-3591 (2004)
T. Werder, J. H. Walther, P. Koumoutsakos, J. Comp. Phys. **205**,373 (2005)
E. G. Flekkoy, G. Wagner, J. Feder, Europhys. Lett. **52**, 271 (2000)
G. De Fabritiis, R. Delgado Buscalioni, P. Coveney, Phys. Rev. Lett **97**, 134501 (2006).
W. E, B. Enquist, X. T. Li, W. Q. Ren, E. Vanden-Eijden, CiCP **2**, 367 (2007).
D. A. Fedosov, G. E. Karniadakis, J. Comput. Phys. **228**, 1157 (2009).

HybridMD

- The hybrid particle-continuum scheme (HybridMD) is designed to connect the dynamics of a "**molecular domain**" with that obtained from a **continuum description** of the surrounding fluid flow.
- The method is based on **flux-exchange**.
- The system is divided in (at least) two domains, described via classical **molecular dynamics (MD)** and **continuum fluid dynamics (CFD)**, i.e., solving the **Navier-Stokes** equations.
- The MD and CFD domains share one unique "hybrid interface", H: Flux balance implies the **conservation of mass and momentum** across H.

De Fabritiis, Delgado Buscalioni, Coveney, Phys. Rev. Lett **97**, 134501 (2006).
Delgado Buscalioni, De Fabritiis, Phys. Rev. E **76**, 036709 (2007).

CFD: Flux-Exchange Scheme

- **Conservation law** for any conserved fluid variable $\phi(\mathbf{r}, t)$:

$$\partial\phi/\partial t = -\nabla \cdot \mathbf{J}^{\phi}$$

$\mathbf{J}^{\phi}(\mathbf{r}, t)$ is the associated local flux.

  - mass: $\phi = \rho$, $\mathbf{J}^{\phi} = \rho\mathbf{u}$
  - momentum: $\phi = \rho\mathbf{u}$, $\mathbf{J}^{\phi} = \mathbf{J}_p = p\,\mathbf{I} + \rho\mathbf{u}\mathbf{u} + \mathbf{\Pi}$

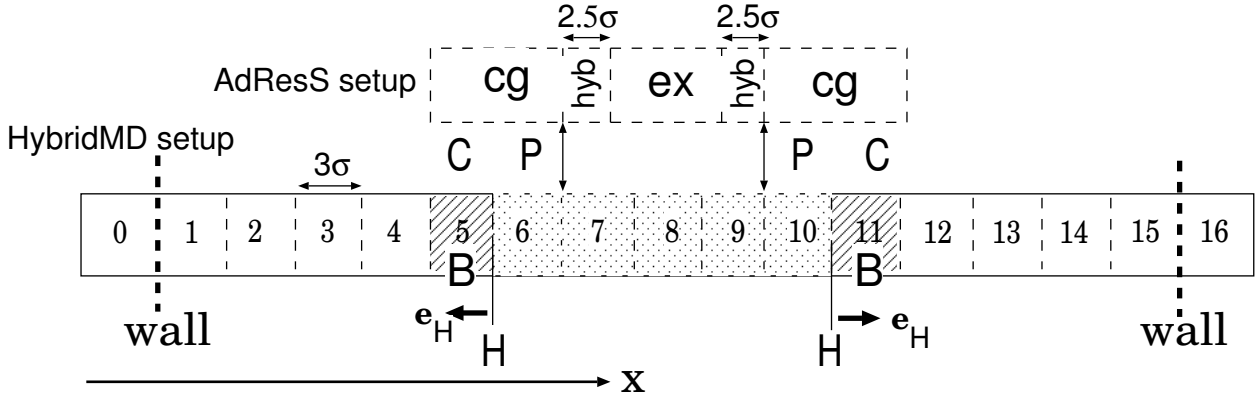
- **Constitutive relations**:
  - Equation of state: $p = p(\rho)$
  - Stress tensor: $\mathbf{\Pi} = -\eta[\nabla\mathbf{u}]^S - \xi\nabla \cdot \mathbf{u}\,\mathbf{I}$

Finite Volume Method

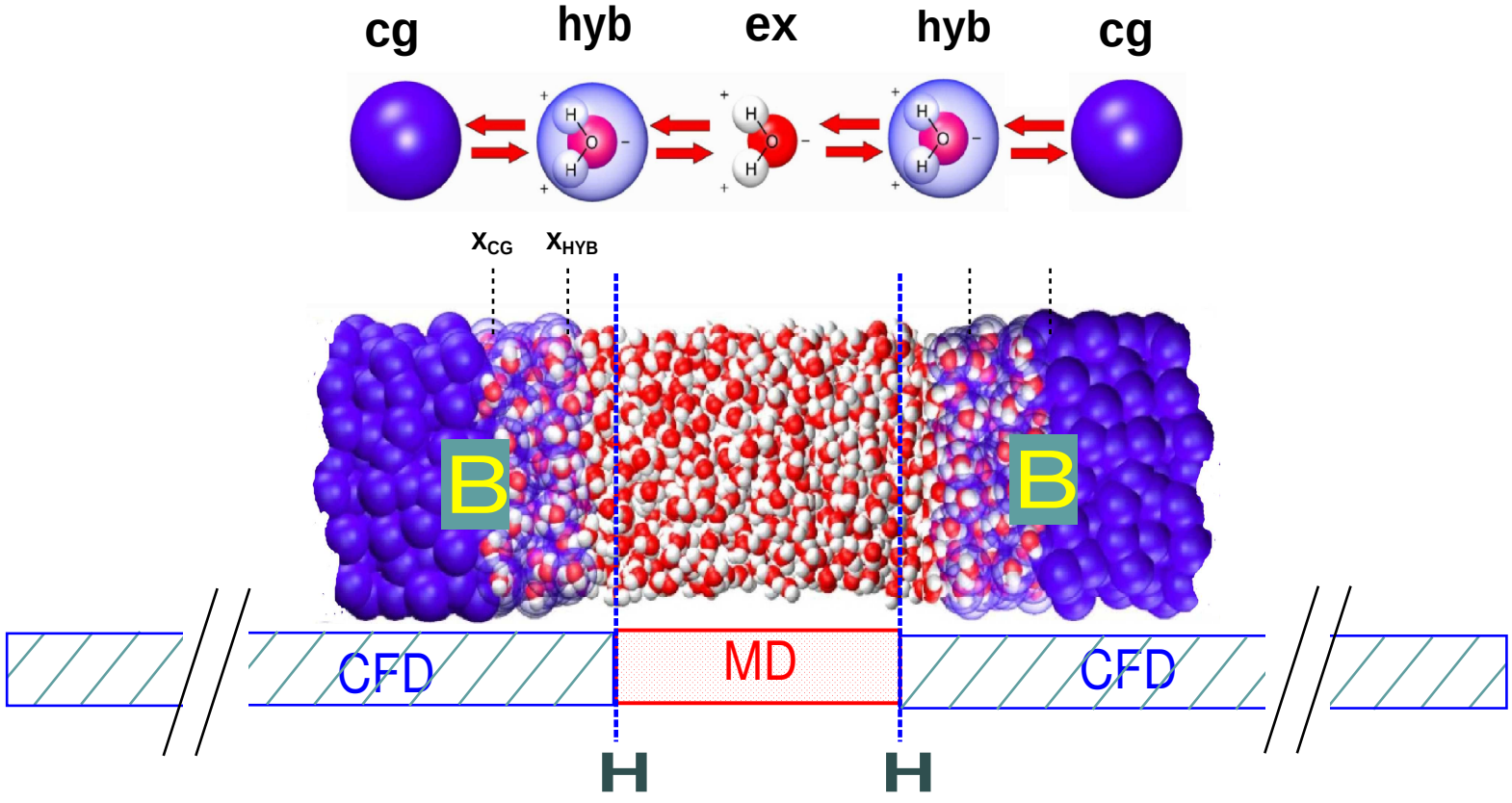
$$\int_{V_C} \partial\phi/\partial t \, dV = -\int_{V_C} \nabla \cdot \mathbf{J}^{\phi} \, dV = -\oint_S \mathbf{J}^{\phi} \cdot dS$$

$$\frac{d\Phi_C}{dt} = -\sum_{f=faces} A_f \mathbf{J}_f^{\phi} \cdot \mathbf{n}_f$$

$\Phi_C = \int_{V_C} \phi(\mathbf{r}, t) d\mathbf{r}^3$. The above eq. is numerically solved by the explicit Euler scheme, where $\mathbf{J}_f^{\phi} = (\mathbf{J}_C^{\phi} + \mathbf{J}_{C+1}^{\phi})/2$.



Buffer

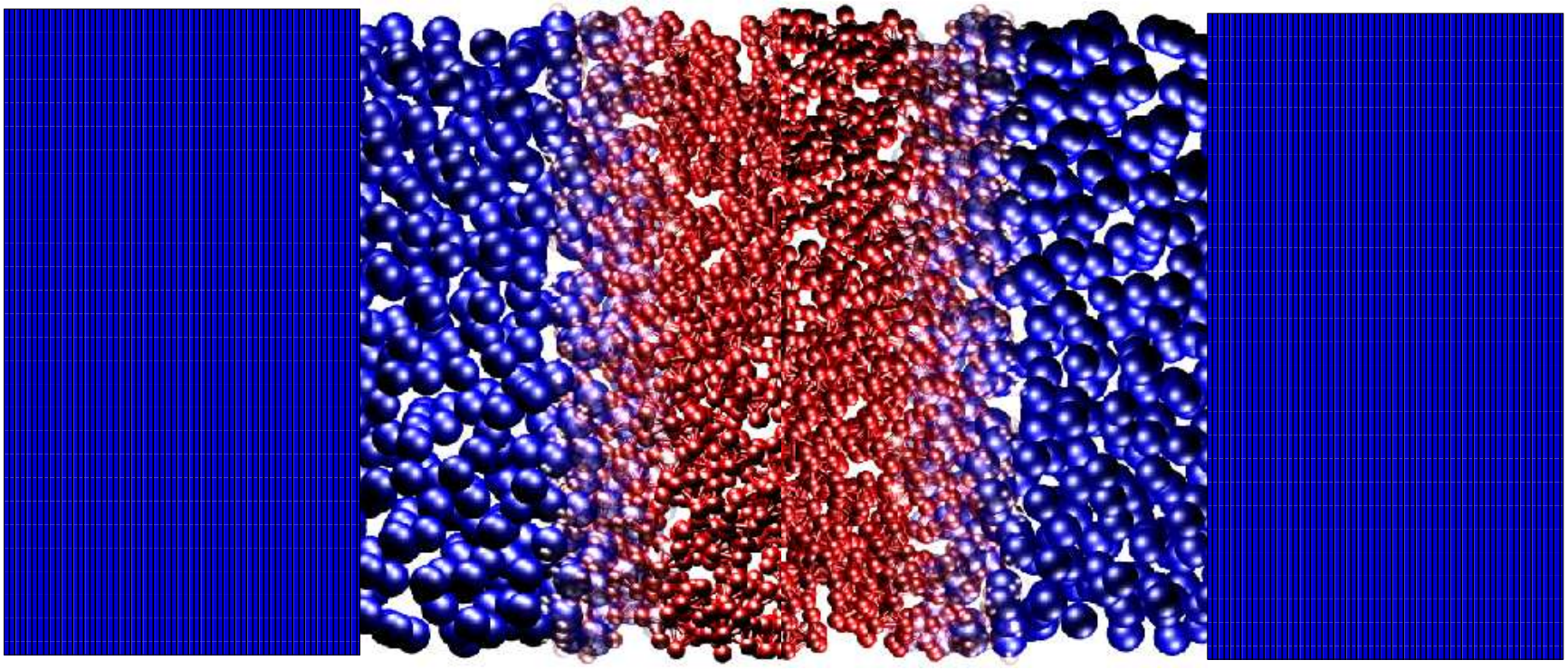


B=buffer (overlap domain) serves to impose fluxes into the particle region.

Concurrent Triple-Scale Simulation

- **Motivation:**
  - to cover the **length-scales** ranging from the **micro-** to **macro**-scale
- **Method:** *Triple-scale AdResS-HybridMD scheme*
  - is a combination of two dual-scale models: a particle-based **Adaptive Resolution Scheme (AdResS)**, which couples the **atomic** and **mesoscopic** scales, and a **hybrid continuum-molecular dynamics scheme (HybridMD)**
  - successfully sorts out the problem of **large molecule insertion** in the hybrid particle-continuum simulations of molecular liquids
  - opens up the possibility to perform efficient **grand-canonical molecular dynamics simulations** of truly open molecular liquid systems
- **Results:**
  - the **structural** and **dynamical** properties of the liquid are **accurately captured**

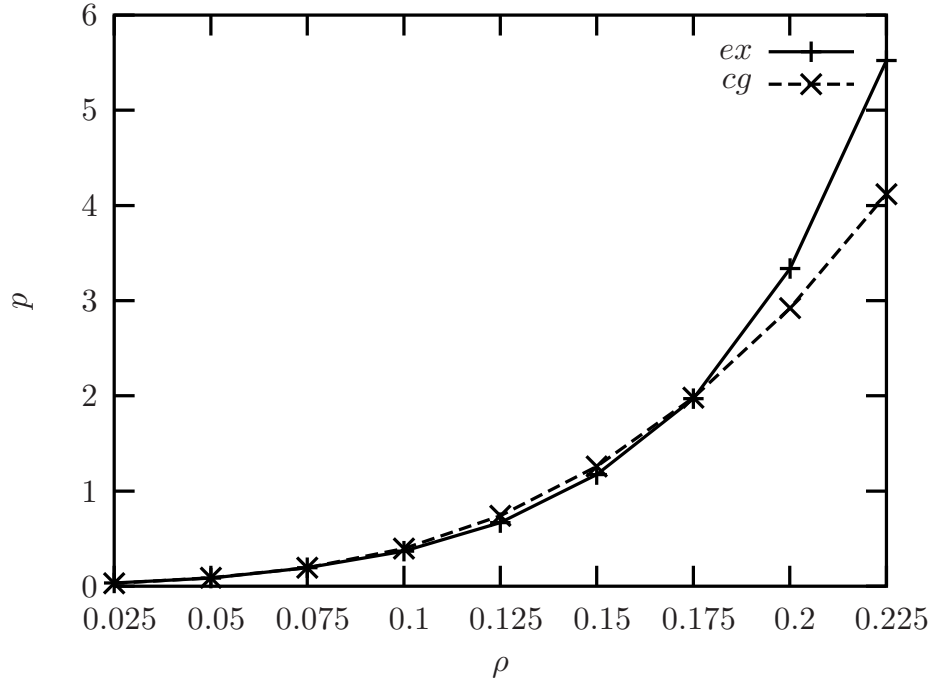
Triple-Scale Method



- to allow for insertion of larger molecule into a dense liquid
- to allow for grand canonical MD simulation of open molecular systems

R. Delgado Buscalioni, K. Kremer, M. Praprotnik, J. Chem. Phys. **128**, 114110 (2008).

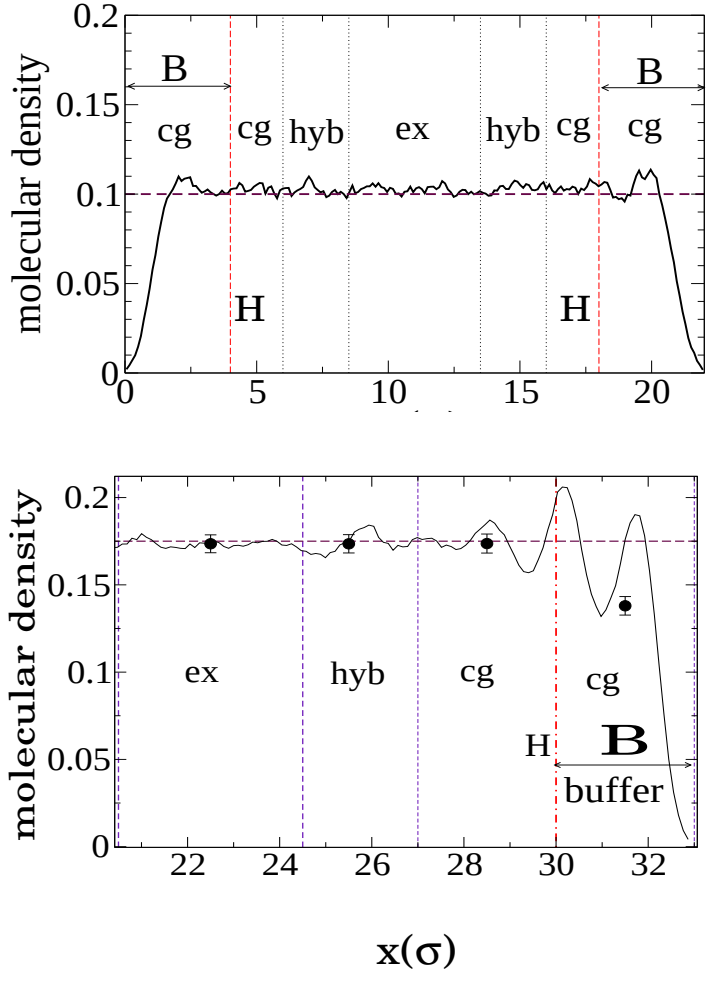
Equation of State



The pressure tensor:

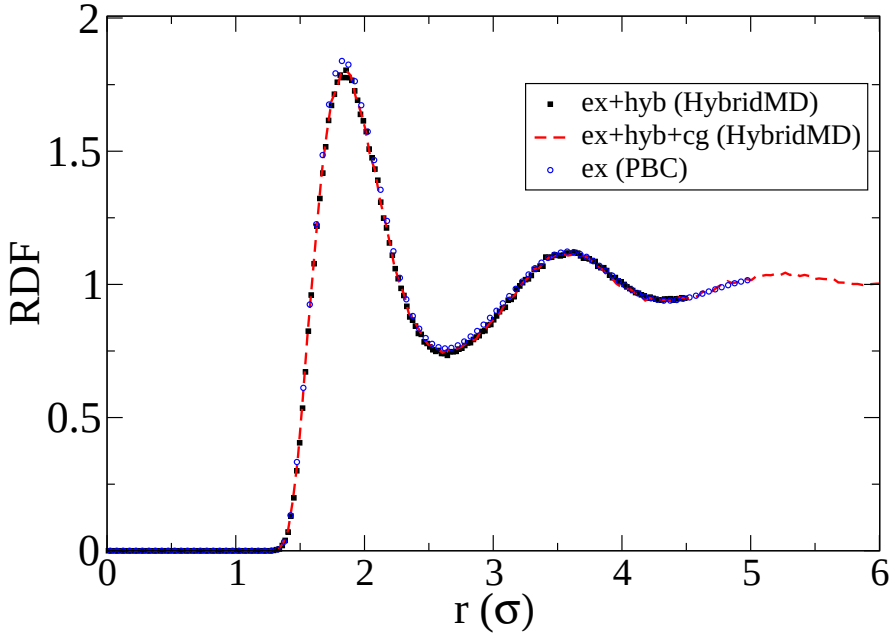
$$\mathbf{J} = p\,\mathbf{I} + \rho \mathbf{v}\mathbf{v} + \mathbf{\Pi}$$

Molecular Density Profile



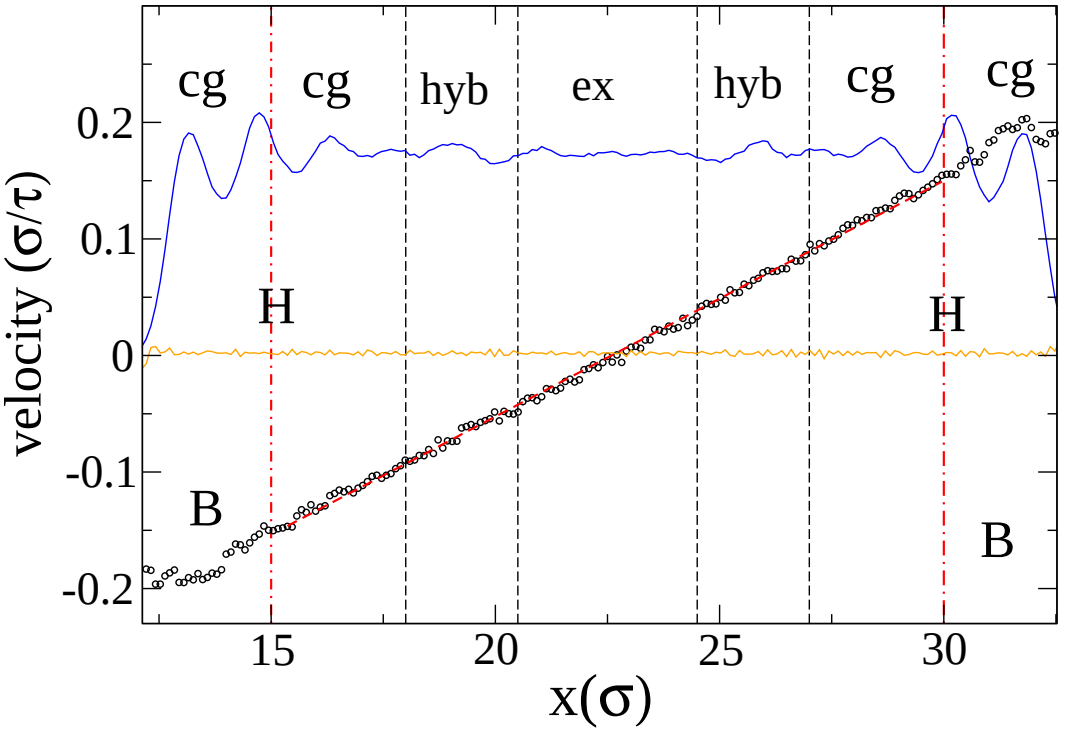
- (a) $\rho_m = 0.1\sigma^{-3}$. (b) $\rho_m = 0.175\sigma^{-3}$.

RDFs: Equilibrium



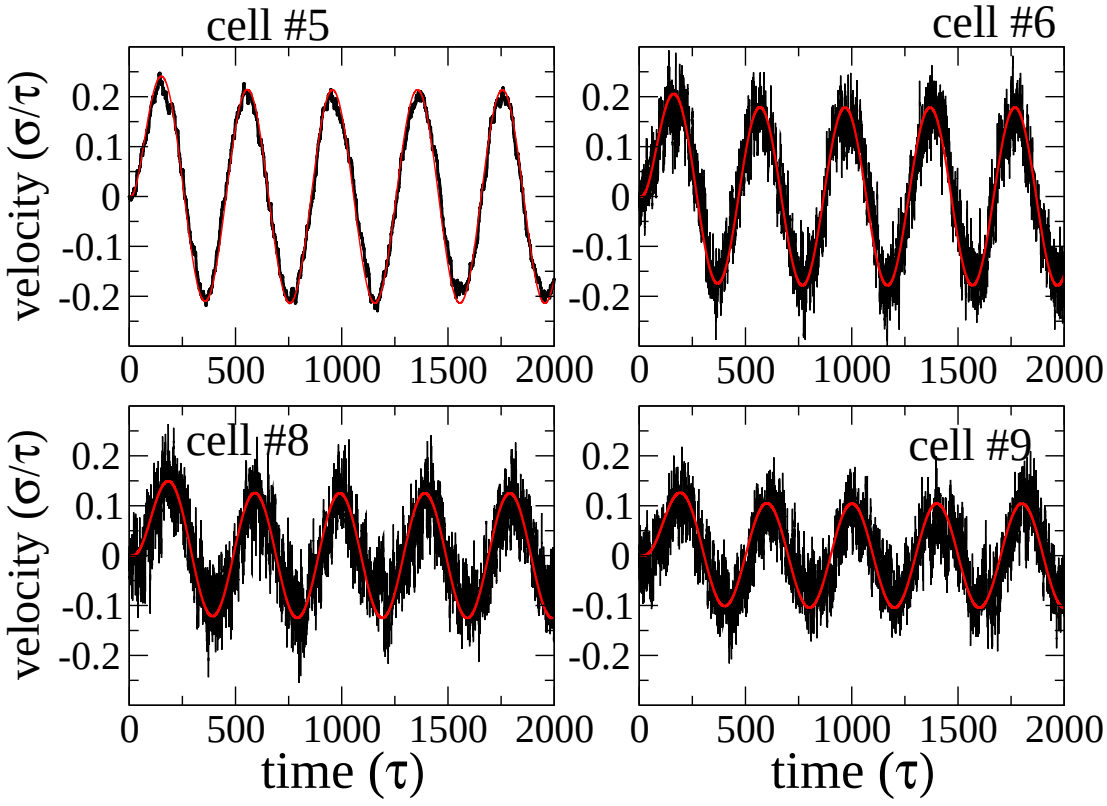
- RDF$_{cm}$s of the liquid in the atomistic and transition domains ($ex + hyb$) and in the total molecular region ($ex + hyb + cg$) of the triple-scale model together with the reference RDF$_{cm}$ of the all-atom system (ex(PBC)) at $\rho = 0.175/\sigma^3$.

Couette Flow



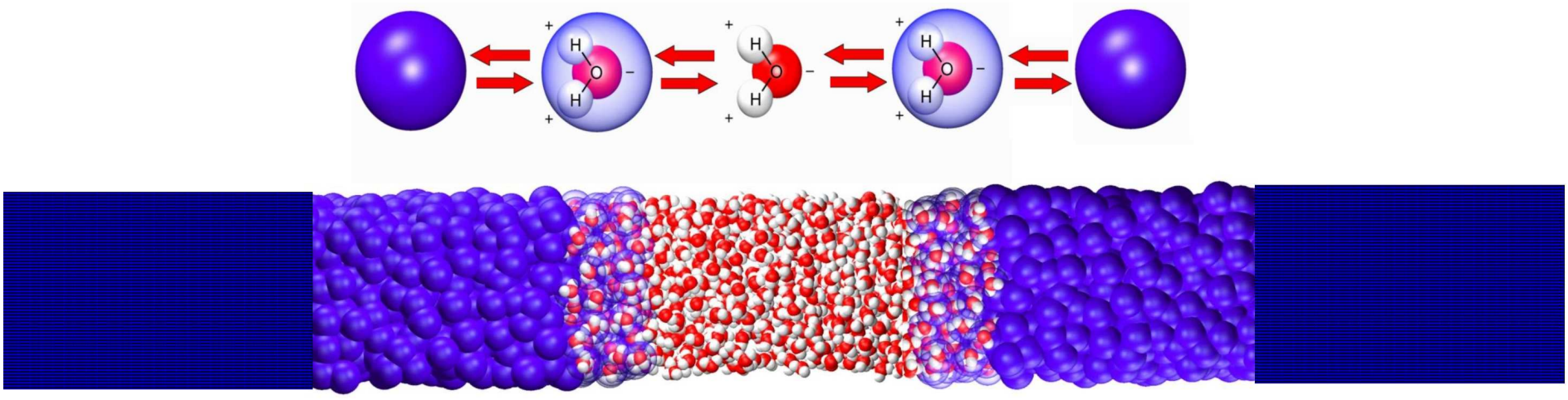
- Velocity profile at the particle region of an hybrid simulation of a Couette flow.

Stokes Flow



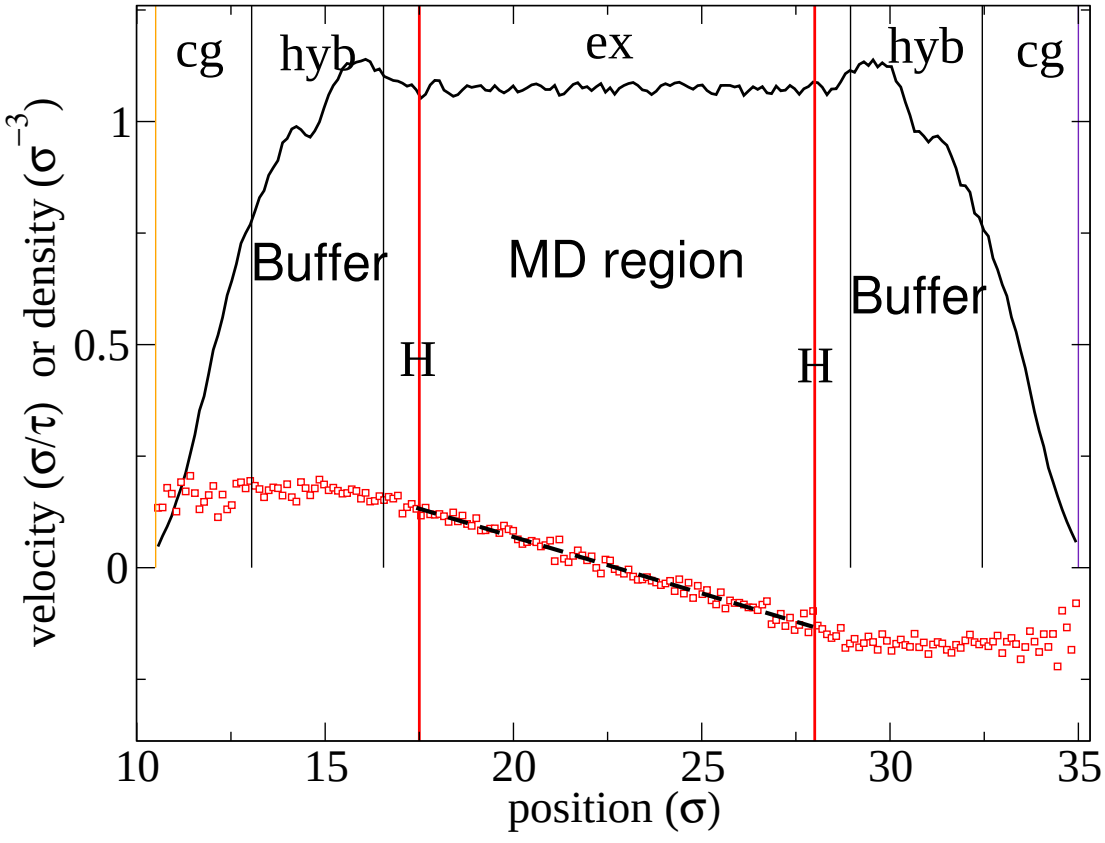
- Velocity in the y-direction at some selected cells in a hybrid simulation of a Stokes flow.

Triple-Scale Simulation: Liquid Water



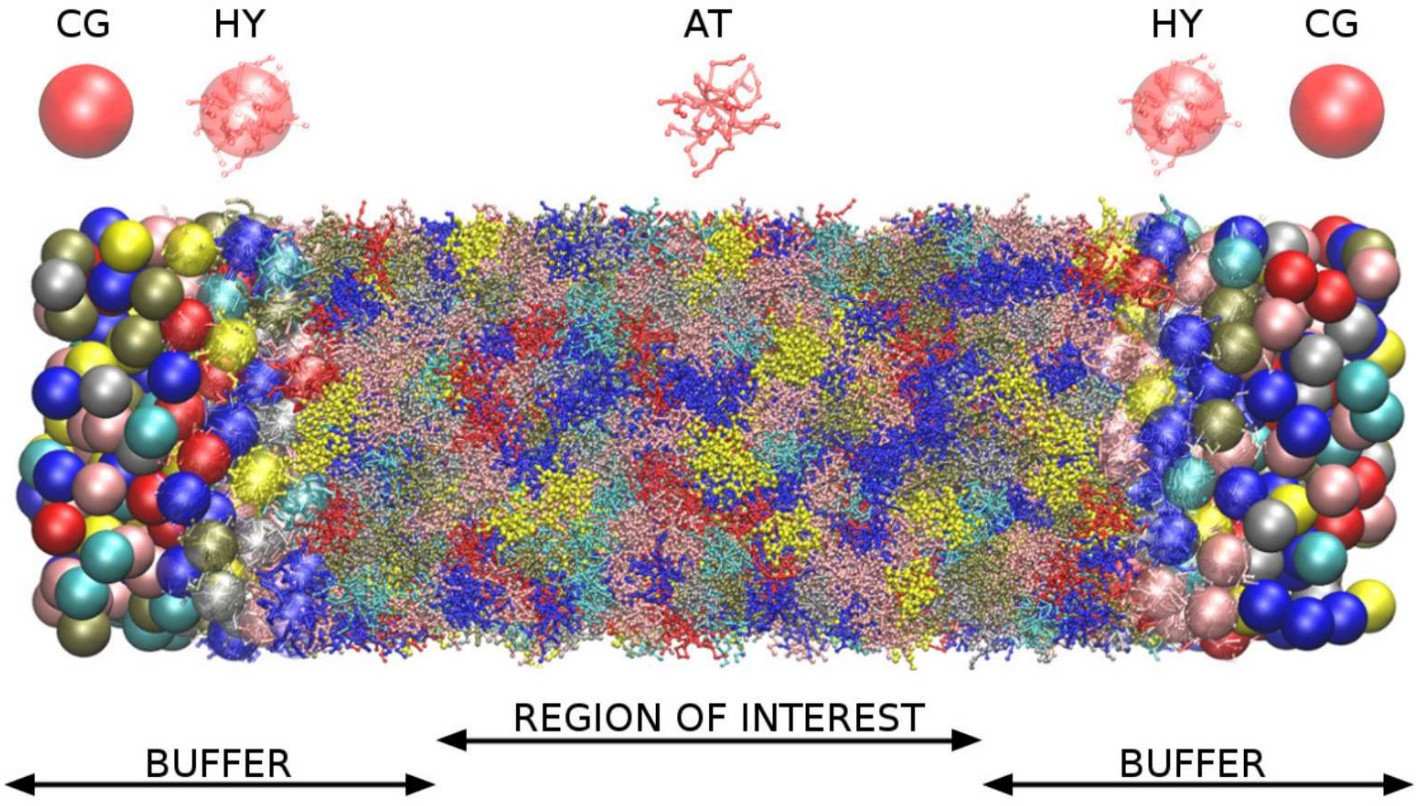
R. Delgado Buscalioni, K. Kremer, M. Praprotnik, J. Chem. Phys. **131**, 244107, (2009).

Couette Flow



- Density profile and velocity distribution across the particle domain.

OBMD - Star-Polymer Melt



R. Delgado Buscalioni, J. Sablic, M. Praprotnik, EPJ ST, submitted.

Conclusions

- **AdResS:**
  - Allows for a **dynamical switching** between **atomistic** and **coarse-grained** molecular descriptions.
- **Triple-scale Scheme $\Longrightarrow$ Open Boundary Molecular Dynamics:**
  - We performed **triple-scale simulations** of molecular liquids.
  - Length scales from the **micro-** to **macro-**scale are concurrently coupled.
  - The method allows us to perform **efficient molecular dynamics simulations** of molecular liquids in the **grand canonical ensemble** or under **non-equilibrium flows**.
- **Future work:**
  - Applications to study phenomena involving flow-matter interactions at multiple length scales.

Acknowledgments

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Slovenian Research Agency for funding

Napredne Metode Simulacij Molekulske Dinamike: Večskalne Simulacije Tekočinskega Toka mimo Nanodelcev

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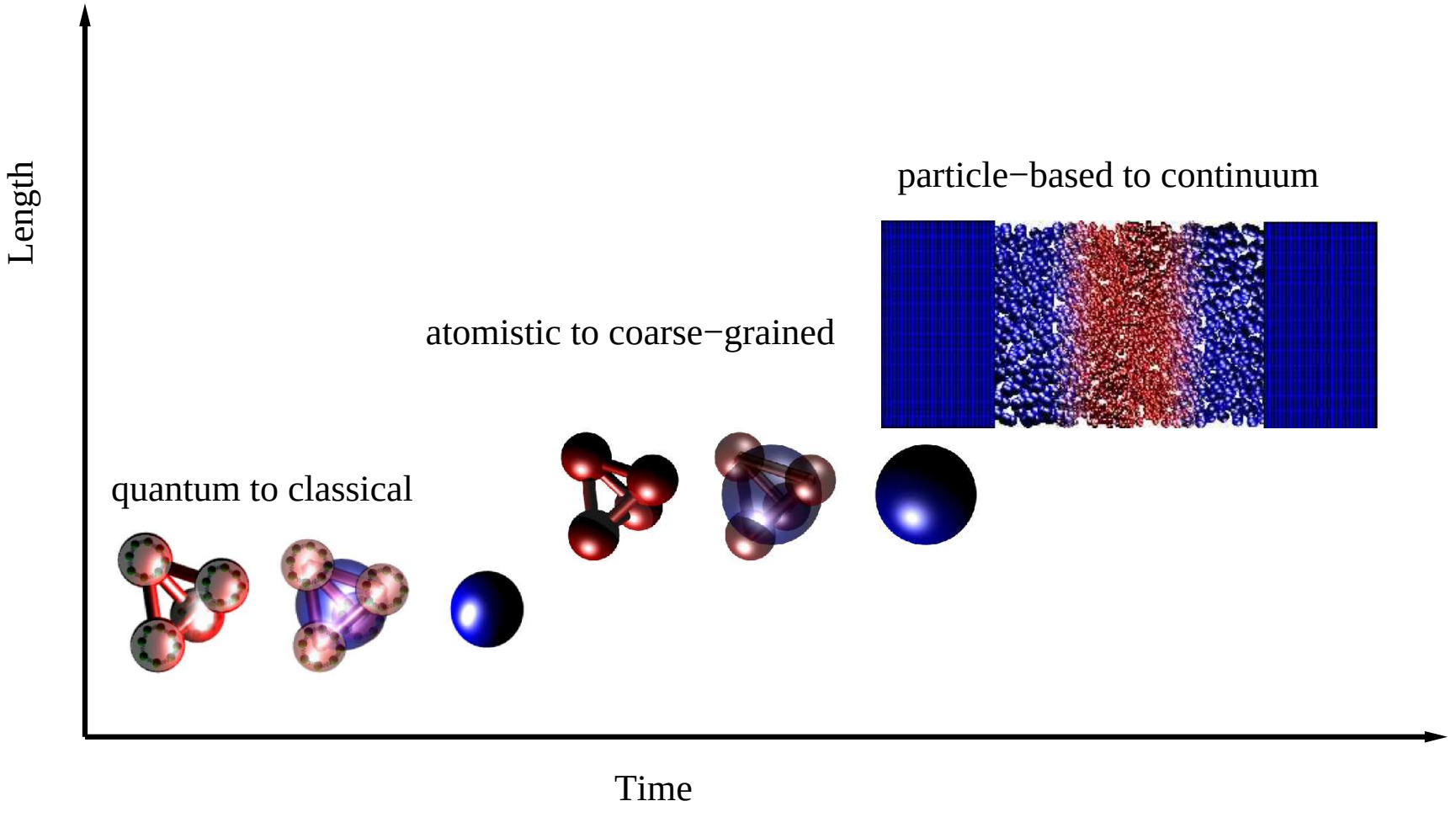
Ljubljana

Multiscale Modeling



M. Praprotnik, L. Delle Site, Humana Press (2012).

Outline

- Introduction
- Multiscale flow simulation past a buckyball
- Continuum simulation of water flow past a fullerene molecule
- Continuum simulations of water flow in carbon nanotube membranes
- Conclusions

Multiscale Simulation of Liquids

All-Atom MD simulation:

- allows to study processes at the atomic level of detail
- is often incapable to bridge a gap between a wide range of length and time scales involved in molecular systems

Mesoscopic MD simulation:

- reduces the number of DOFs by retaining only those that are relevant for the property of interest $\Longrightarrow$ longer length and time scales can be reached
- specific chemical details are usually lost in the coarse-graining procedure

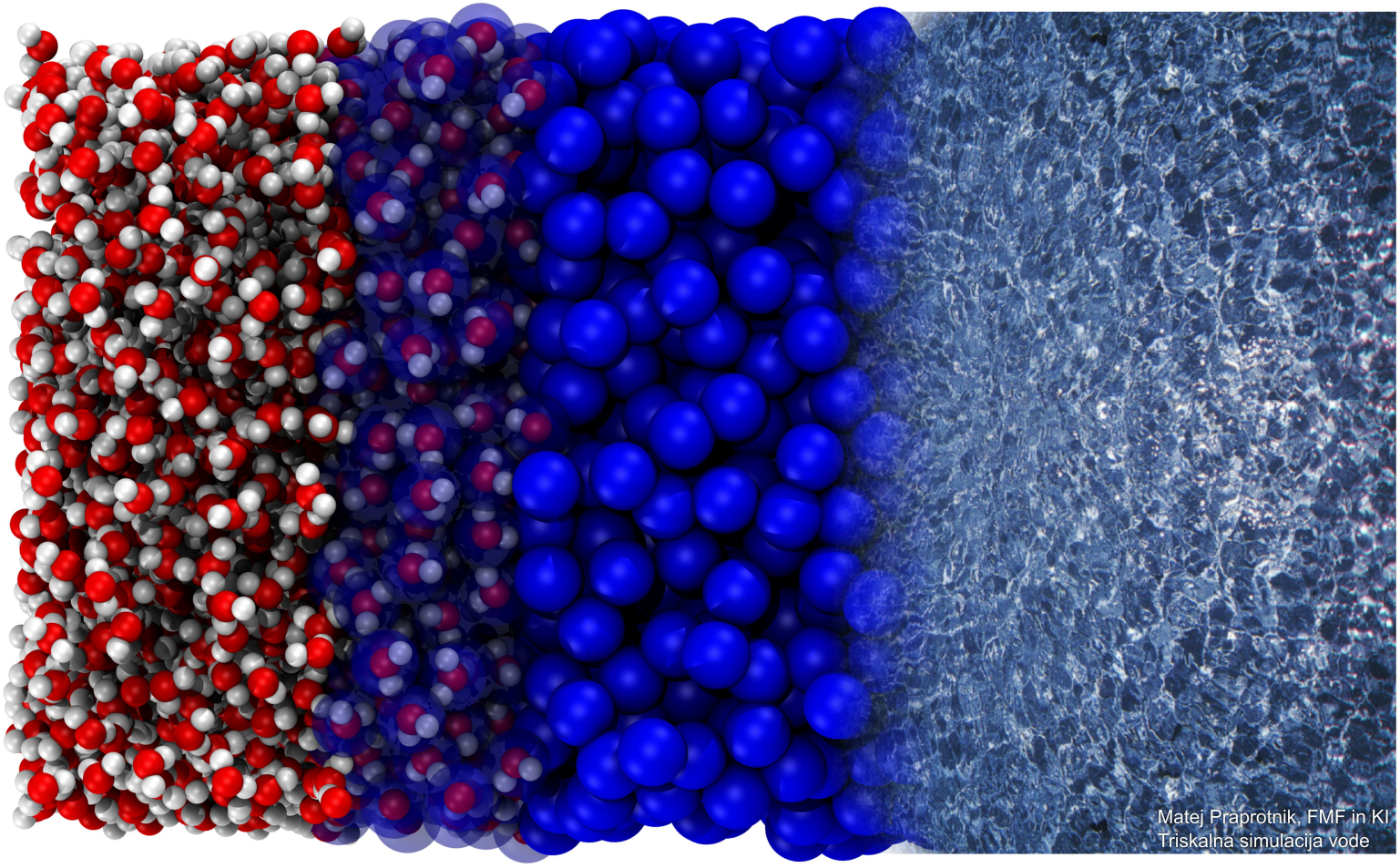
Continuum fluid dynamics (CFD):

- allows to model fluid flows on length scales that are out of scope of MD simulation.
- at lower scales (a few molecular diameters) no-slip boundary condition breaks down.

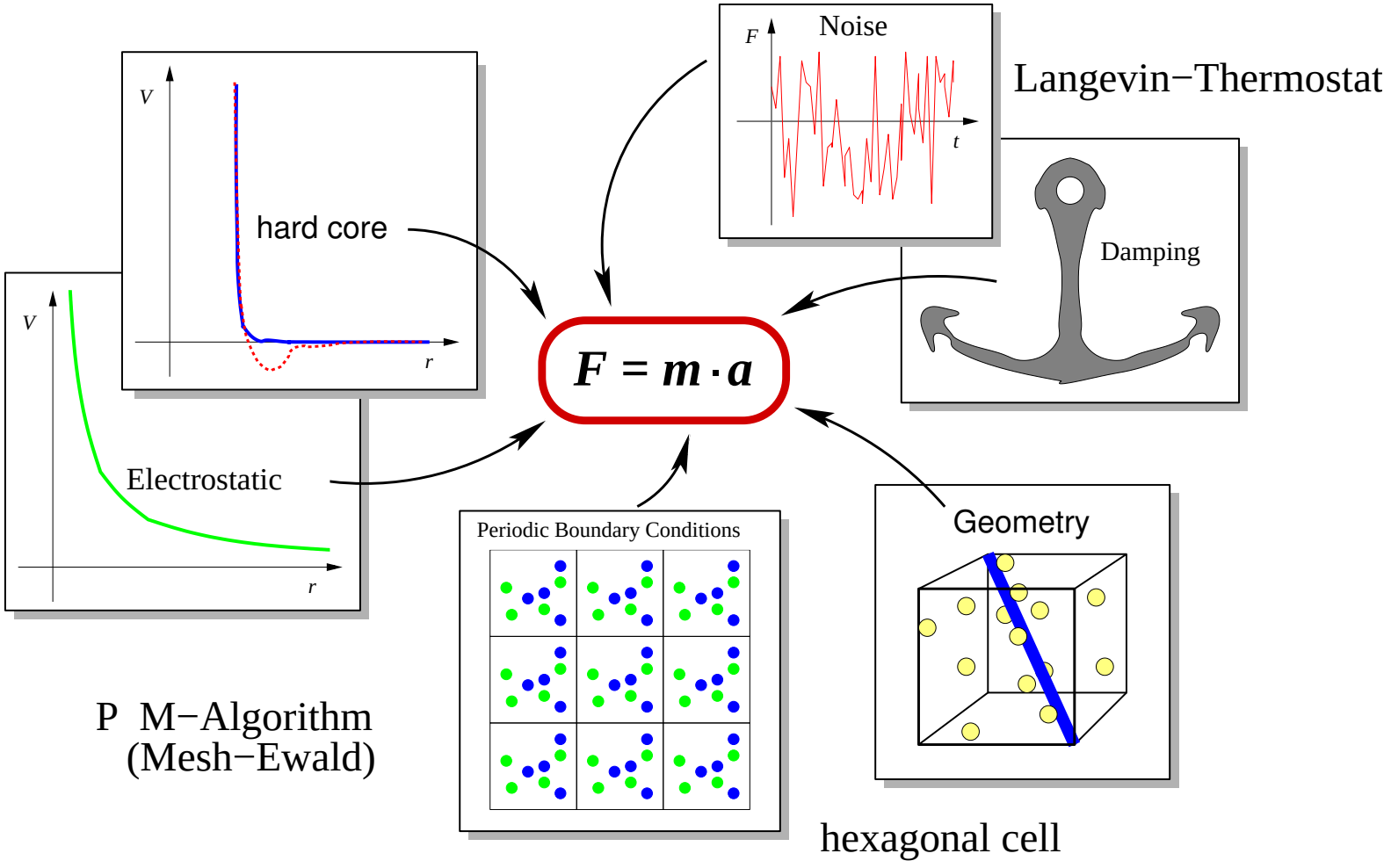
Combination:

- Hybrid MD-Continuum Methods

Coupling MD with Continuum



Molecular Dynamics (MD) Simulation



Navier-Stokes Equation

Conservation of momentum:

$$\rho(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u}) = -\nabla p + \nabla \cdot \mathbf{\Pi} + \mathbf{f}$$

Stress tensor:

$$\mathbf{\Pi} = -\eta[\nabla \mathbf{u}]^S - \xi \nabla \cdot \mathbf{u}\, \mathbf{I}$$

We consider a Newtonian fluid with dynamic viscosity η and bulk viscosity ξ. The traceless symmetric tensor is defined as $A^S_{\alpha\beta} = (A_{\alpha\beta} + A_{\beta\alpha}) - (2/3)A_{\gamma\gamma}$.

Conservation of mass:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0$$

Coupling MD and Continuum

- **Physical quantities**, i.e., density, momentum, and corresponding fluxes must be **continuous across the interface.**
- **Atomistic** and **continuum** domains provide each other with **boundary conditions.**
- To impose boundary conditions from the **MD to continuum** domain is relatively easy since it involves **temporal and spatial averaging.**
- Imposing the **continuum boundary conditions** on the **particle domain** presents the **major challenge** in hybrid methods.

Hybrid Atomistic-Continuum Schemes

- **state variable (Dirichlet) schemes**
  - **Schwartz alternating method**
- **flux-exchange schemes**

S. T. O'Connell, P. A. Thompson, Phys. Rev. E **52**, R5792 (1995)
N. G. Hadjiconstantinou, A. T. Patera, Int. J. Mod. Phys. **8**, 967 (1997)
X. Nie, S. Chen, M. O. Robbins, Physics of Fluids **16**, 3579-3591 (2004)
T. Werder, J. H. Walther, P. Koumoutsakos, J. Comp. Phys. **205**,373 (2005)
E. G. Flekkoy, G. Wagner, J. Feder, Europhys. Lett. **52**, 271 (2000)
G. De Fabritiis, R. Delgado Buscalioni, P. Coveney, Phys. Rev. Lett **97**, 134501 (2006).
W. E, B. Enquist, X. T. Li, W. Q. Ren, E. Vanden-Eijden, CiCP **2**, 367 (2007).
D. A. Fedosov, G. E. Karniadakis, J. Comput. Phys. **228**, 1157 (2009).

CFD: Flux-Exchange Scheme

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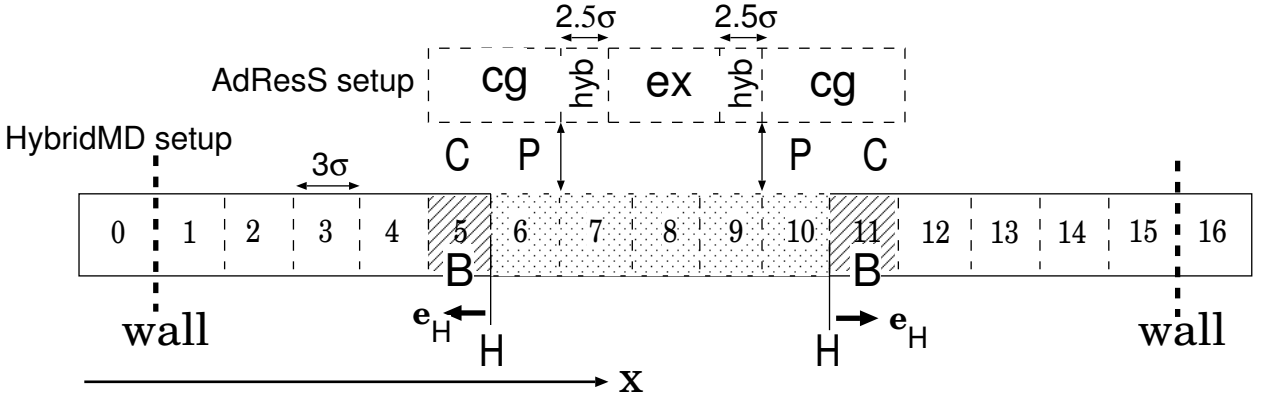
De Fabritiis, Delgado Buscalioni, Coveney, Phys. Rev. Lett **97**, 134501 (2006).

Finite Volume Method

$$\int_{V_C} \partial\phi/\partial t \, dV = -\int_{V_C} \nabla \cdot \mathbf{J}^{\phi} \, dV = -\oint_S \mathbf{J}^{\phi} \cdot dS$$

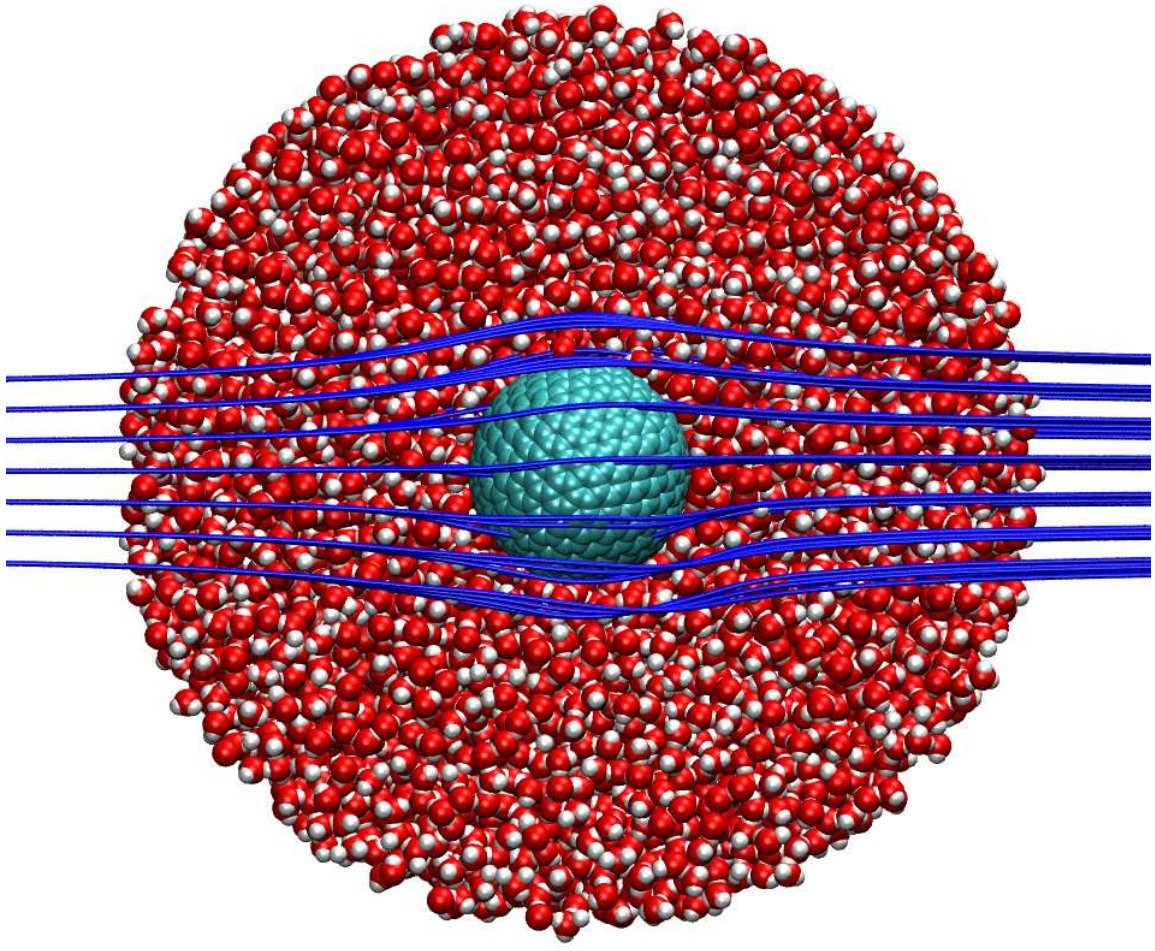
$$\frac{d\Phi_C}{dt} = -\sum_{f=faces} A_f \mathbf{J}_f^{\phi} \cdot \mathbf{n}_f$$

$\Phi_C = \int_{V_C} \phi(\mathbf{r}, t) d\mathbf{r}^3$. The above eq. is numerically solved by the explicit Euler scheme, where $\mathbf{J}_f^{\phi} = (\mathbf{J}_C^{\phi} + \mathbf{J}_{C+1}^{\phi})/2$.



R. Delgado Buscalioni, K. Kremer, M. Praprotnik, J. Chem. Phys. **128**, 114110 (2008).

Multiscale Flow Past Fullerene



J. H. Walther, M. Praprotnik, E. M. Kotsalis, P. Koumoutsakos, J. Comput. Phys. **231**, 2677-2681 (2012).

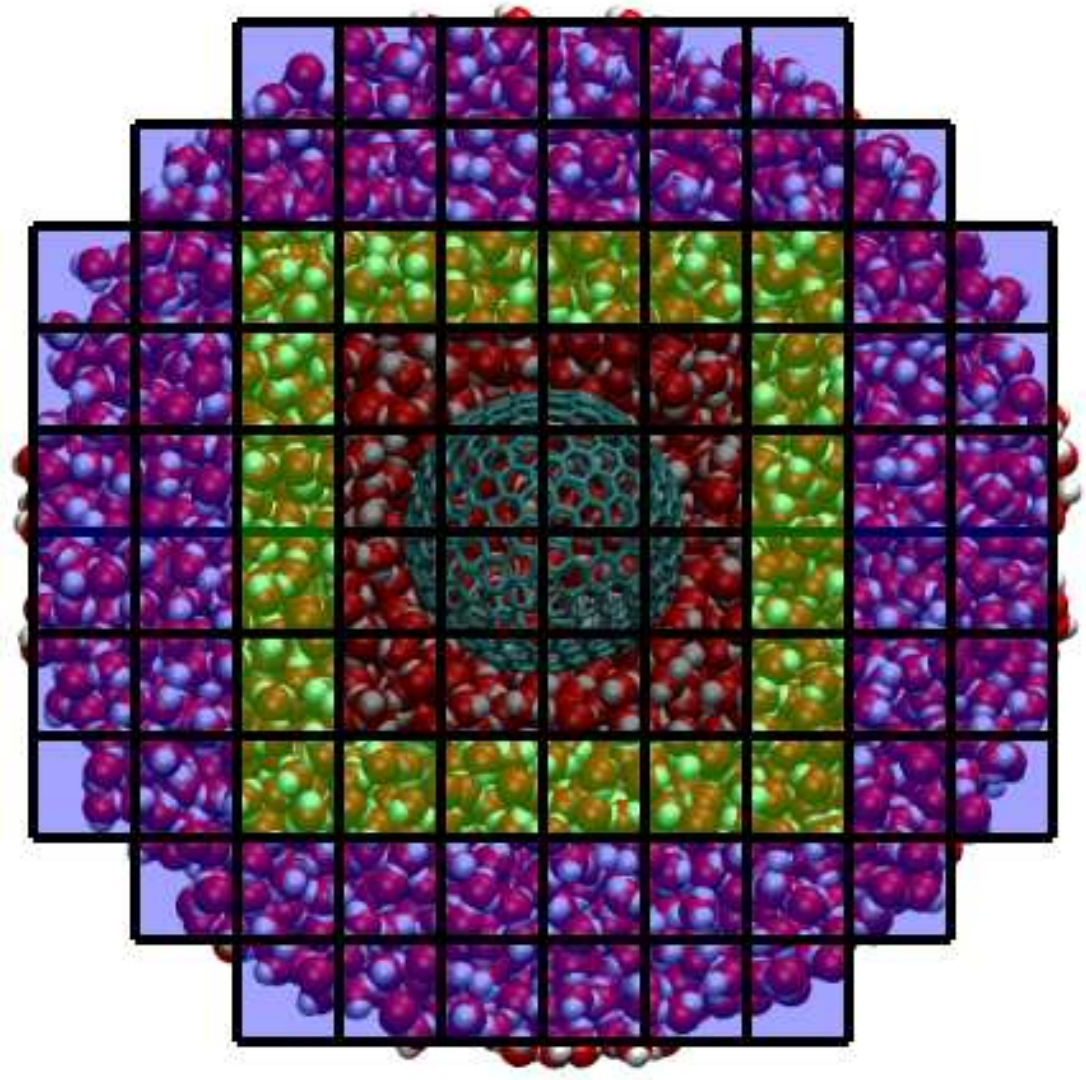
Schwartz Alternating Method

- Solution of one of the domains provides boundary conditions to the other domain (through the overlap domain) and vice versa.
- This procedure is iterated until both solutions in the overlap domain are matched.
- Requirement: fluid variables of MD and continuum domains must match in the overlap domain.

P. L. Lions, In R. Glowinski ed., First International Symposium on Domain Decomposition Methods for Partial Differential Equations, pp. 1-42, SIAM, 1998.

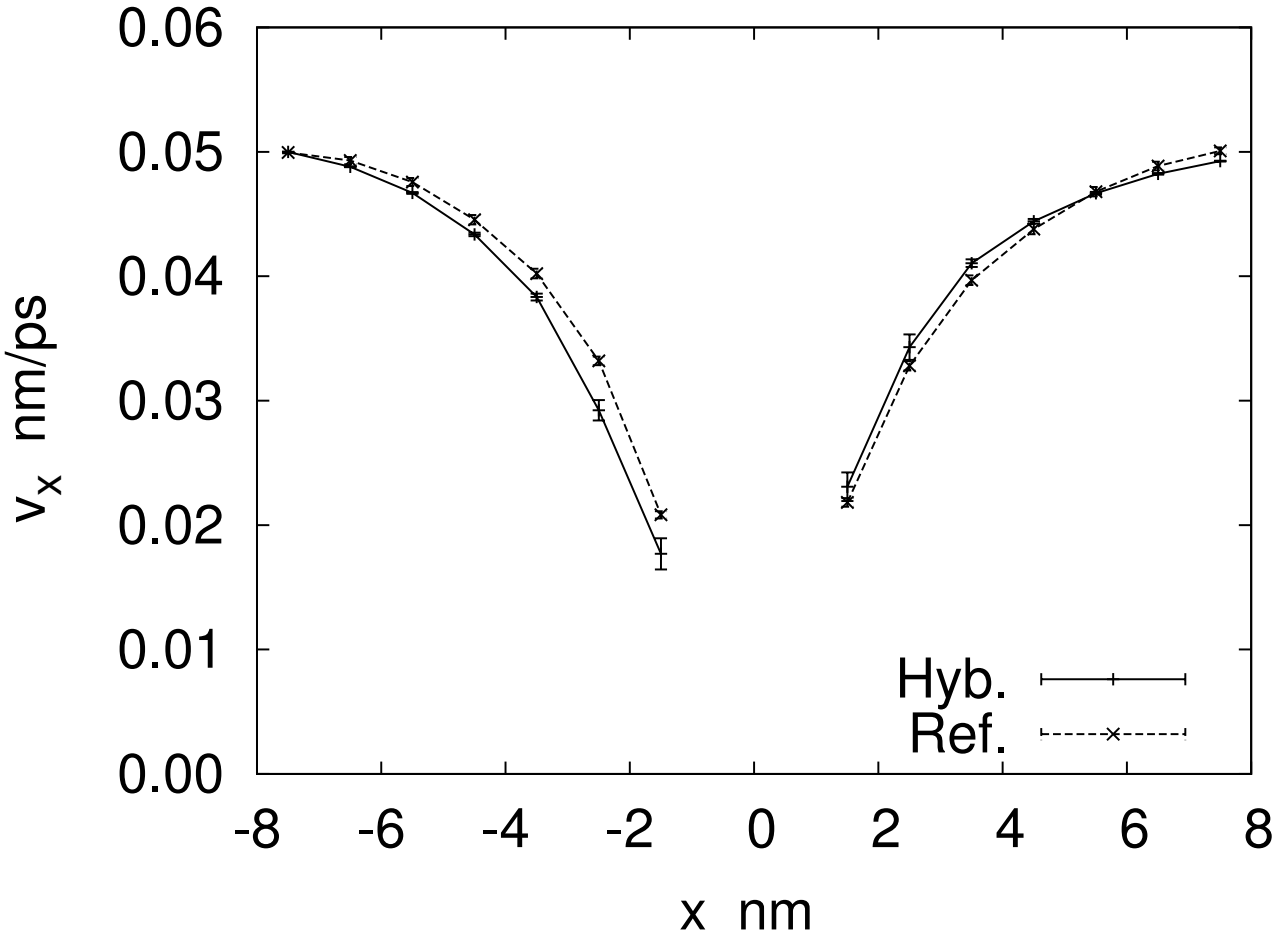
N. G. Hadjiconstantinou, A. T. Patera, Int. J. Mod. Phys. **8**, 967 (1997)

Overlap Domain



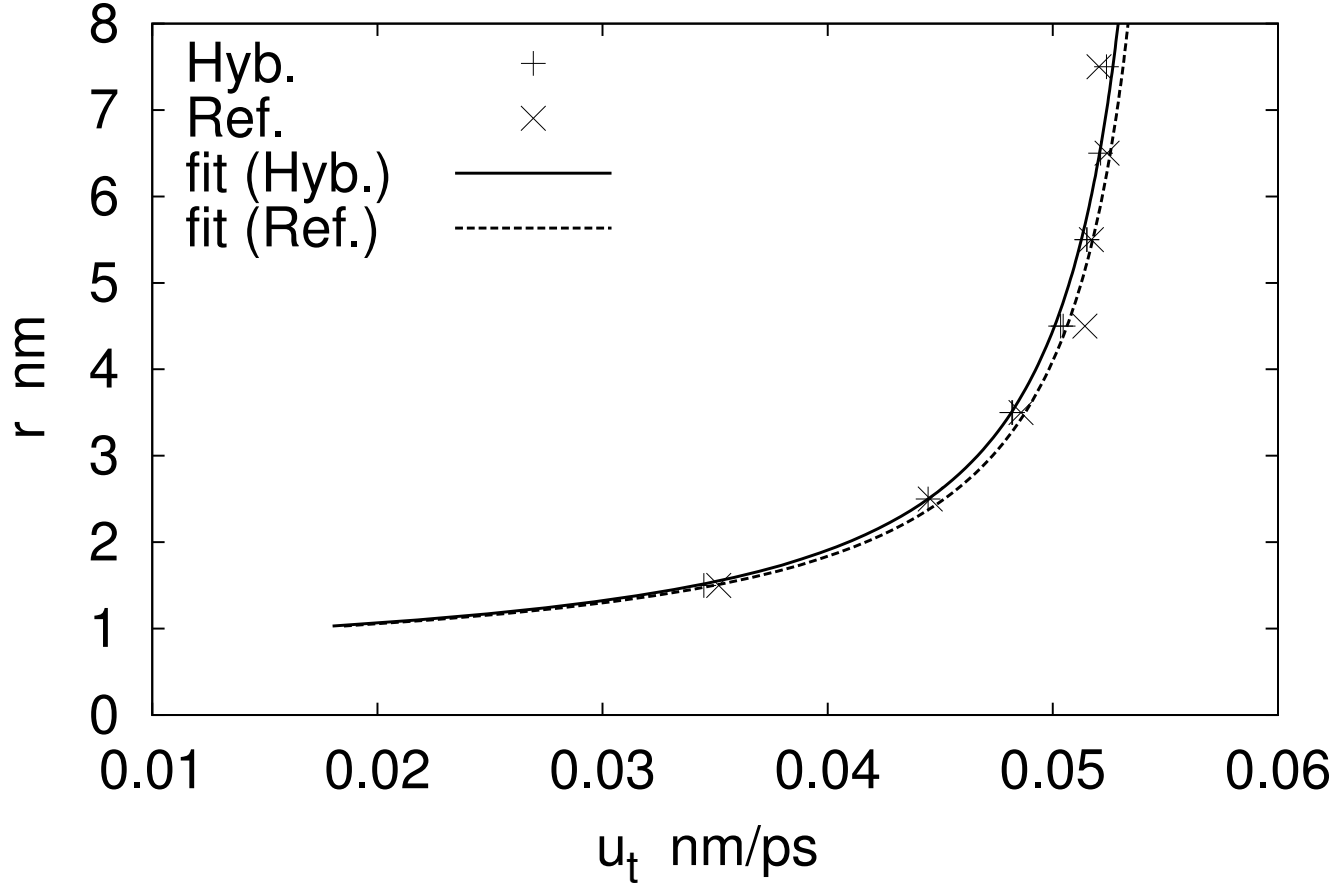
$$\mathbf{J} = p\,\mathbf{I} + \rho \mathbf{v}\mathbf{v} + \mathbf{\Pi}$$

Velocity Profile



The x-component velocity profile along the line passing through the fullerene molecule in the x-direction.

Tangential Velocity Profile



The tangential velocity profile in the radial direction from the fullerene with the radius $R \approx 1.03\text{nm}$.

Partial Slip Boundary Conditions

- The drag force for the Stokes flow past a sphere with partial slip:

$$F_D = 6\pi \left(\frac{R_H + 2l_s}{R_H + 3l_s} \right) \eta R_H u_\infty$$

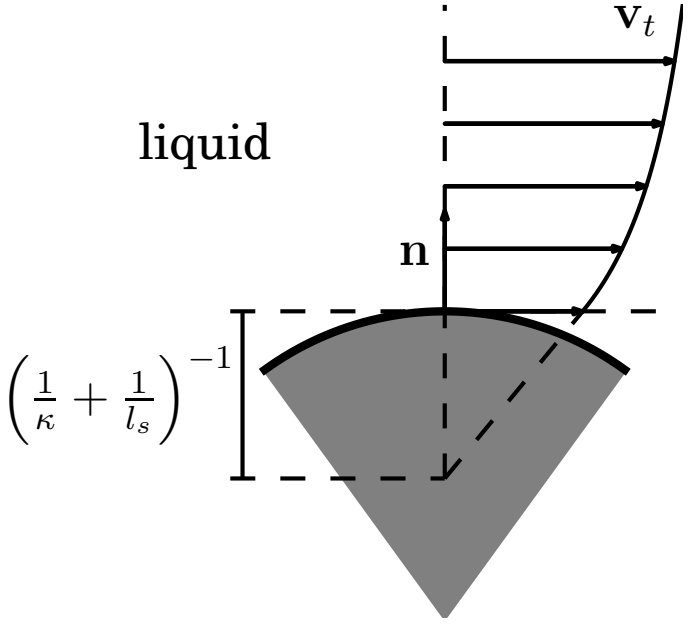
  The freestream velocity is $u_\infty = 0.05\,\mathrm{nm/ps}$.

- We determine the unknown slip length l_s and hydrodynamics radius R_H by an iterative procedure using the tangential velocity radial profile with the initial guess $R_H = R$.

- **hybrid**: $u_s = u_t(R_H) = 0.027 \pm 0.001\,\mathrm{nm/ps}$, $l_s = 0.60 \pm 0.02\,\mathrm{nm}$, $R_H = 1.22 \pm 0.06\,\mathrm{nm}$

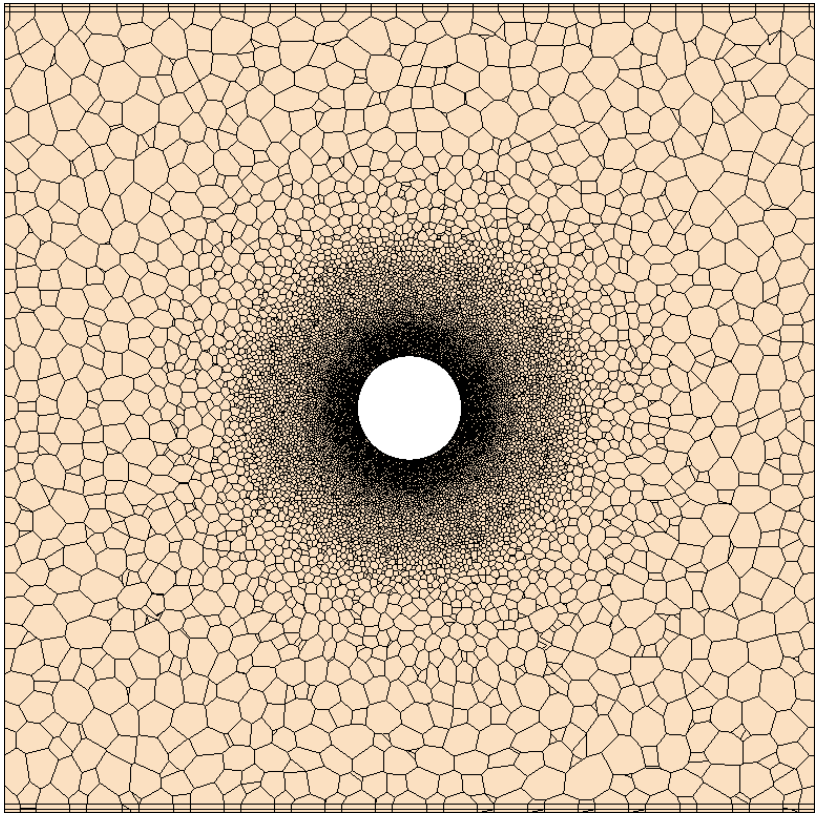
- **all-atom**: $u_s = u_t(R_H) = 0.030 \pm 0.001\,\mathrm{nm/ps}$, $l_s = 0.94 \pm 0.03\,\mathrm{nm}$, $R_H = 1.32 \pm 0.11\,\mathrm{nm}$

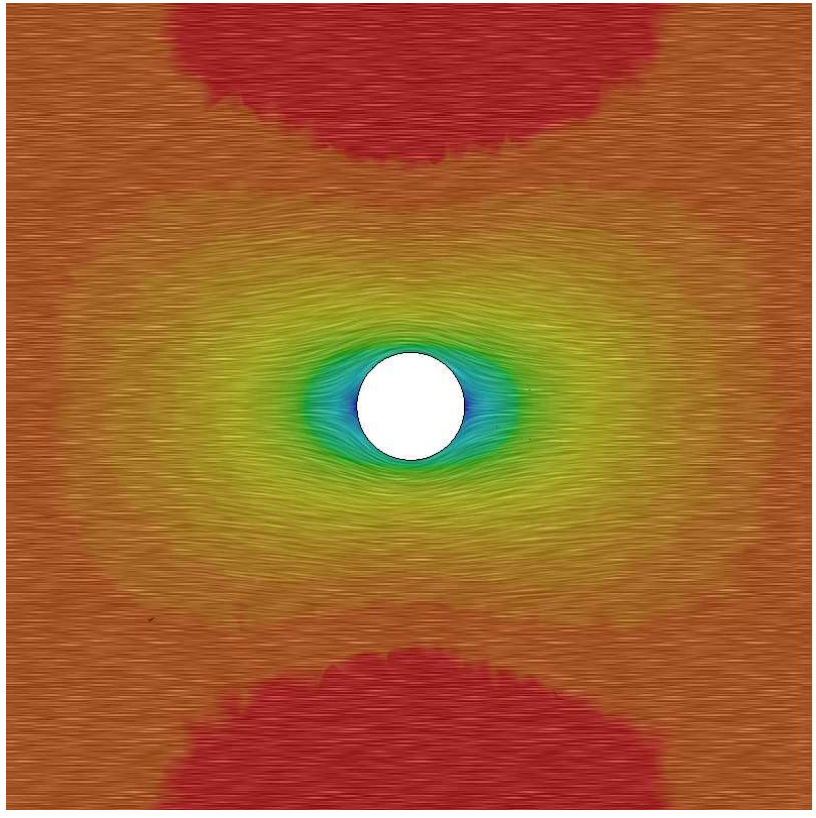
Boundary Conditions Sketch



$$v_t = l_s \left(\frac{\partial v_t}{\partial n} - \frac{v_t}{\kappa} \right)$$

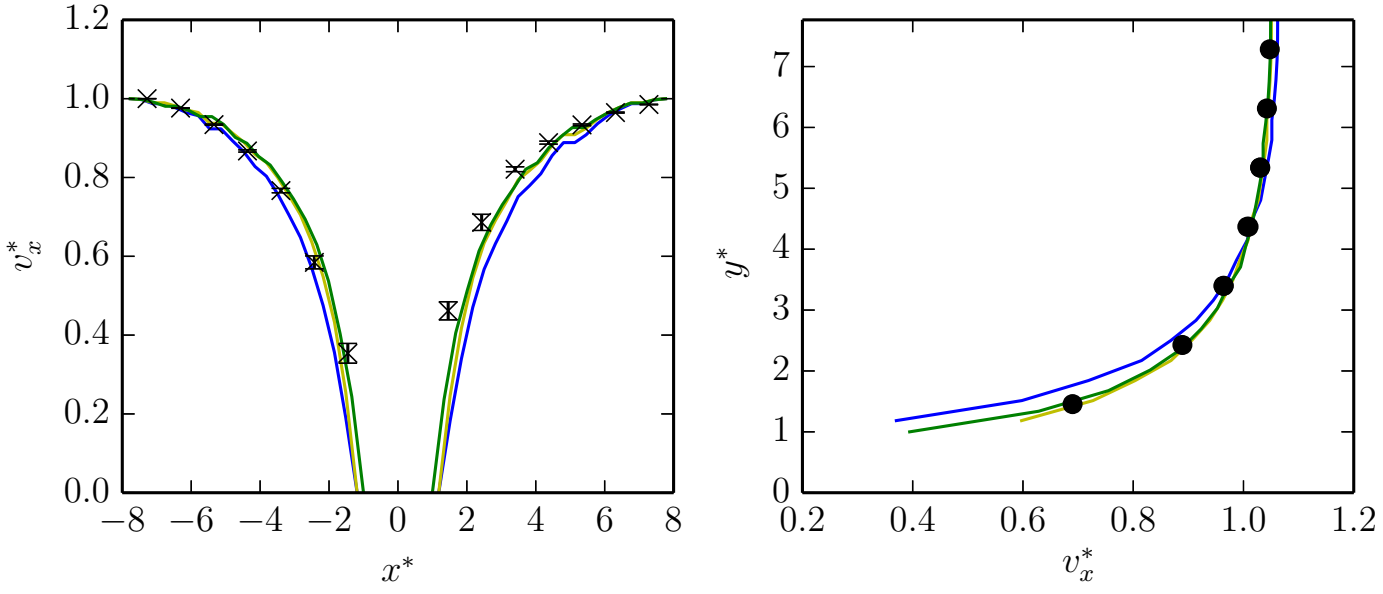
CFD: Buckyball





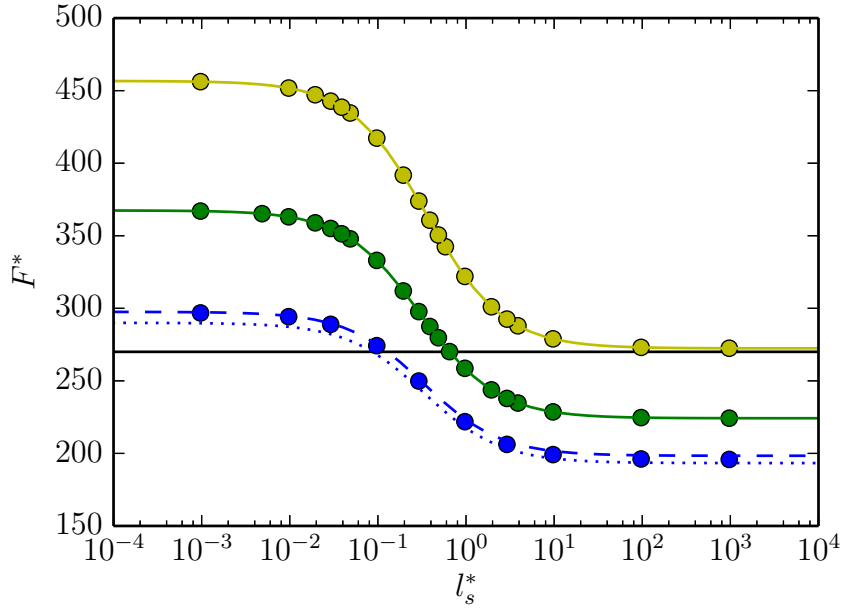
A. Popadić et al, in preparation.

Velocity Profile



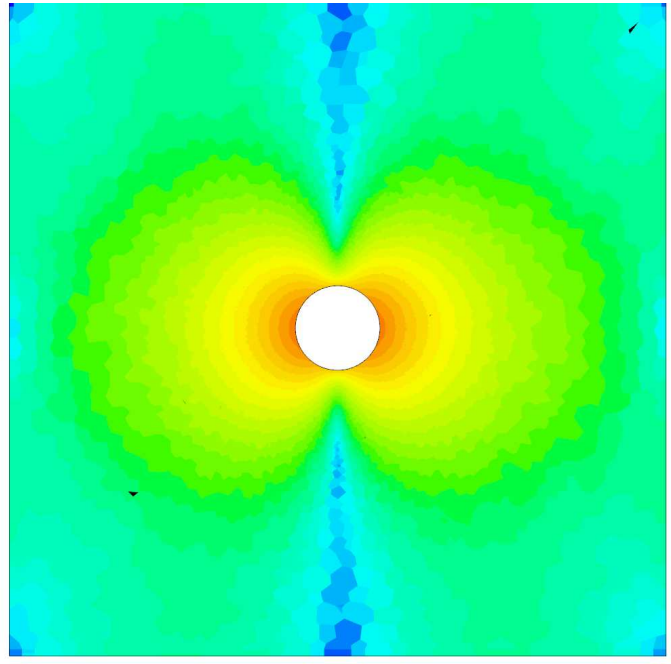
- black: hybrid
- blue: $R_H = 1.22\,\mathrm{nm},\ l_s = 0.60\,\mathrm{nm}$
- green: $R_H = 1.03\,\mathrm{nm},\ l_s = 0.67\,\mathrm{nm}$
- yellow: $R_H = 1.22\,\mathrm{nm},\ l_s \to \infty$

Drag Force



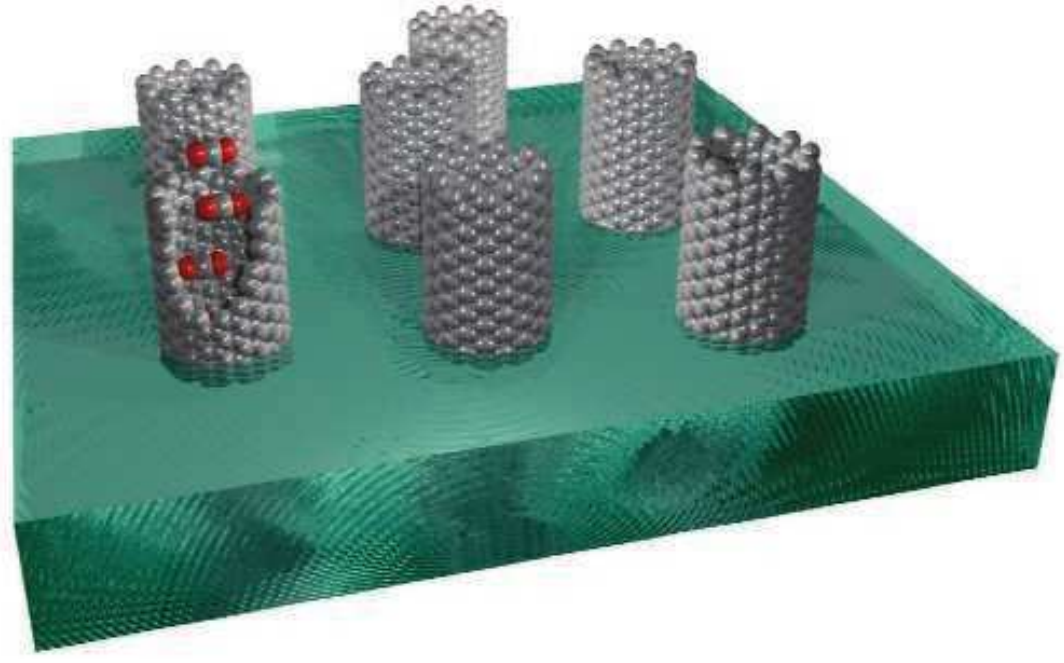
- black: drag force measured in the hybrid simulation
- blue: Stokes problem ($R_H = 1.03\,\mathrm{nm}$)
- green: $R_H = 1.03\,\mathrm{nm}$
- yellow: $R_H = 1.22\,\mathrm{nm}$

Energy Dissipation Rate



$$\dot{e}^* = \frac{1}{2\mathrm{Re}} \left(\frac{\partial v_i^*}{\partial x_k^*} + \frac{\partial v_k^*}{\partial x_i^*} \right)^2$$

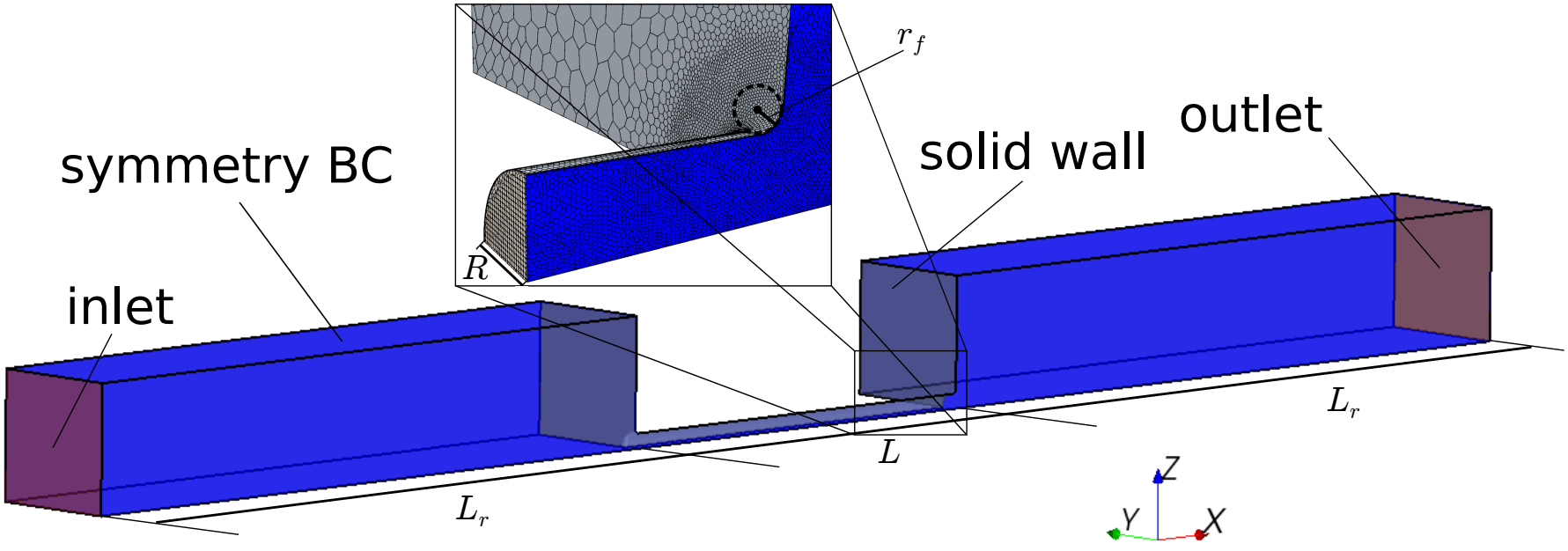
Carbon NanoTube Membrane



J. D. Ho, R. Yeh, A. Sandstrom, I. Chorny, W. E. C. Harries, R. A. Robbins, L. J. W. Miercke, R. M. Stroud, PNAS **106**, 7437 – 7442 (2009).

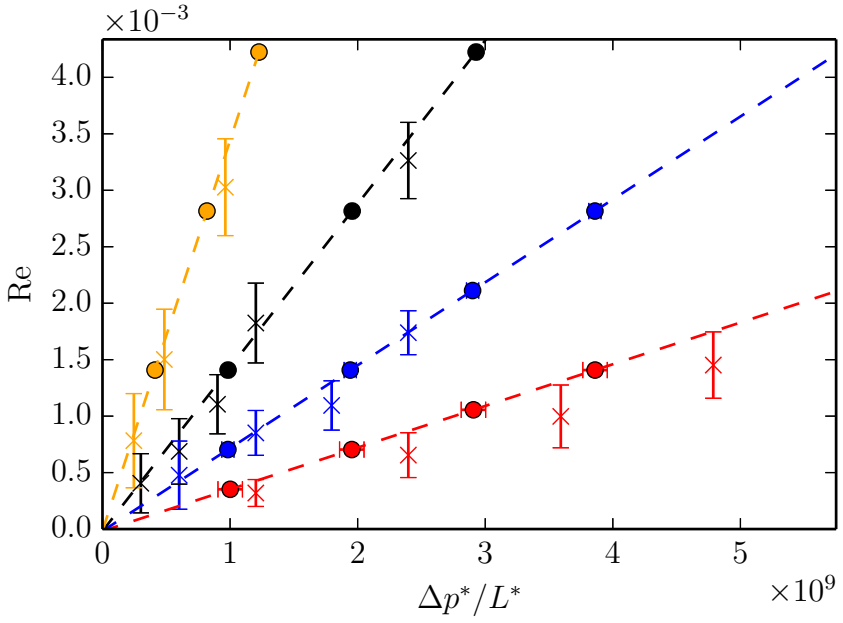
J. H. Walther, K. Ritos, E. R. Cruz-Chu, C. M. Megaridis, P. Koumoutsakos, Nano Lett. **13**, 1910-1914 (2013).

CFD: Carbon NanoTube Membrane



A. Popadić, J. H. Walther, P. Koumoutsakos, M. Praprotnik, New J. Phys. **16**, 082001 (2014).

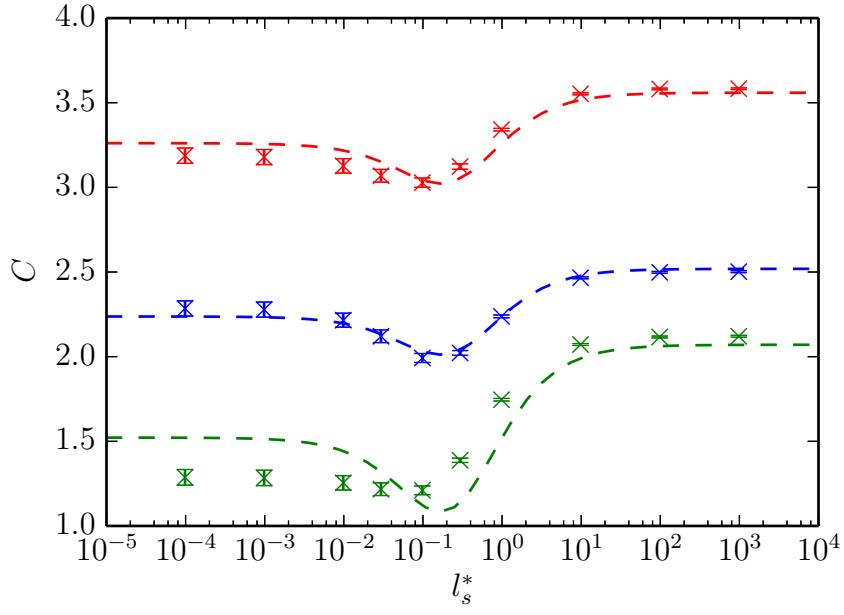
MD/CFD Results Comparison



$l_s = 63\,\mathrm{nm}$

- x: MD
- o: CFD
- yellow: $30\,\mathrm{nm}$
- black: $12\,\mathrm{nm}$
- blue: $6\,\mathrm{nm}$
- red: $3\,\mathrm{nm}$

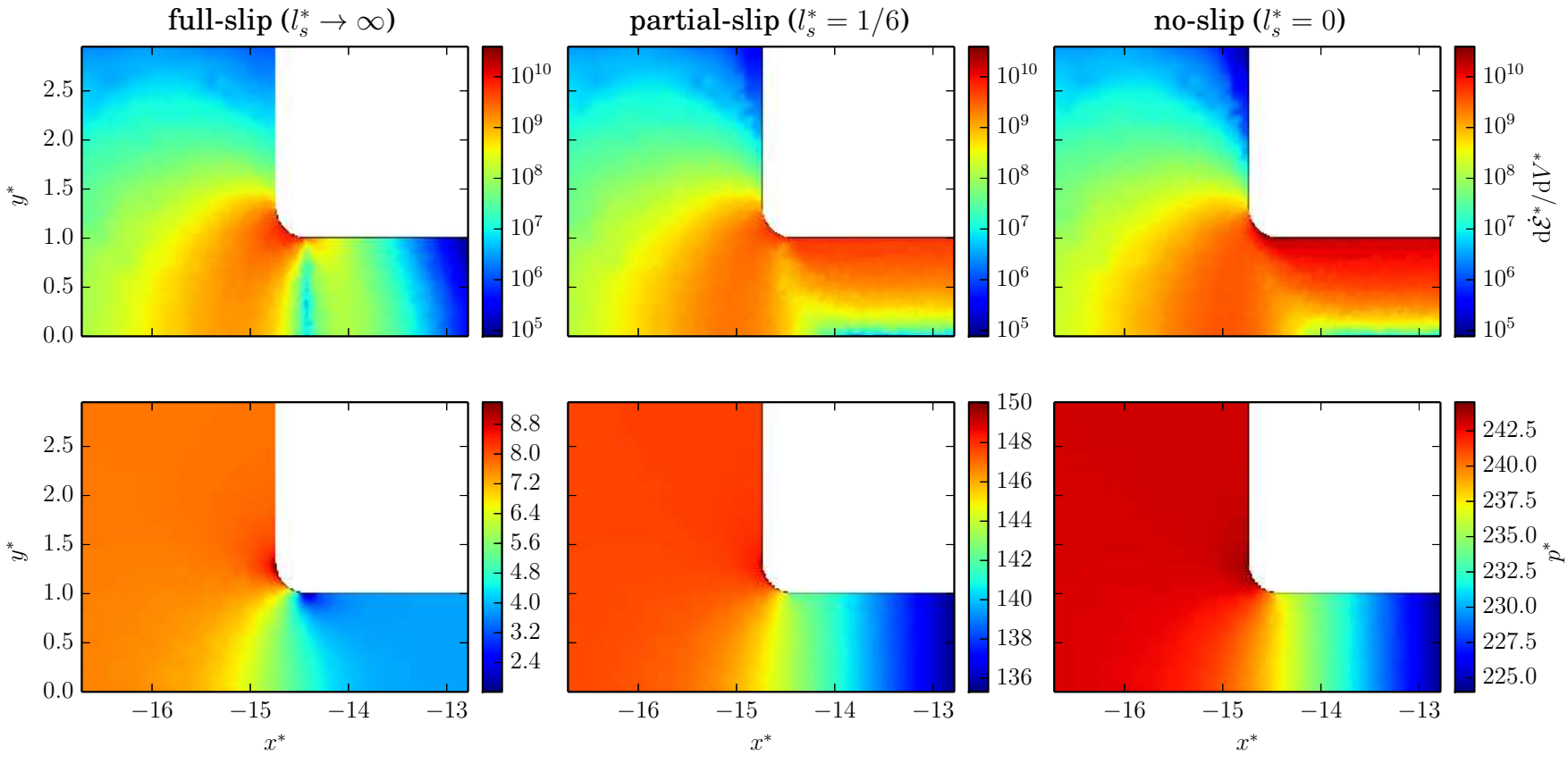
Pressure Drop at CNT Entrance/Exit



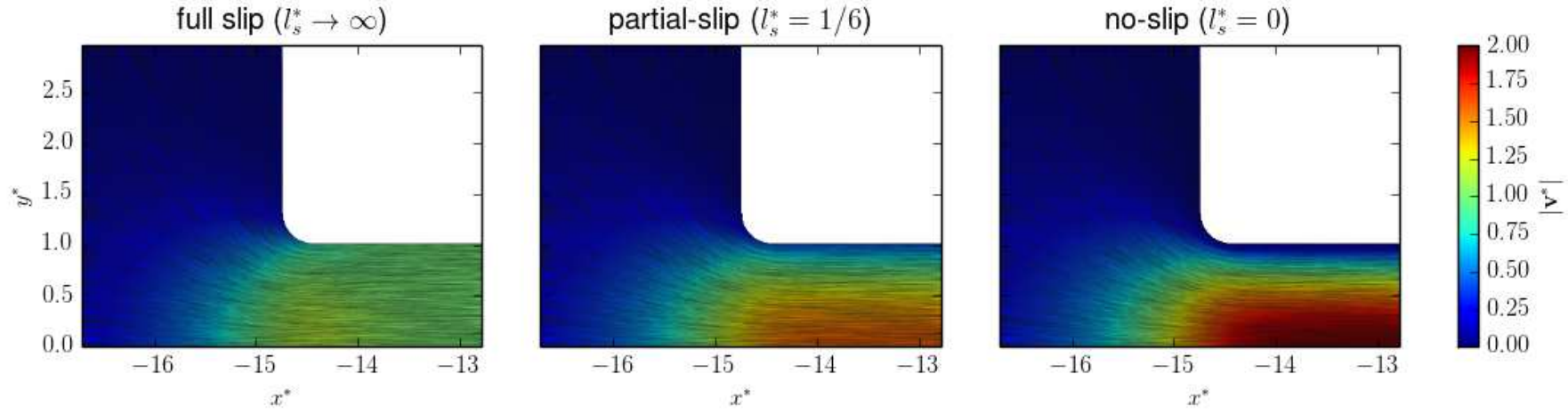
- green: $r_f^* = 0.6$
- blue: $r_f^* = 0.3$
- red: $r_f^* = 0$

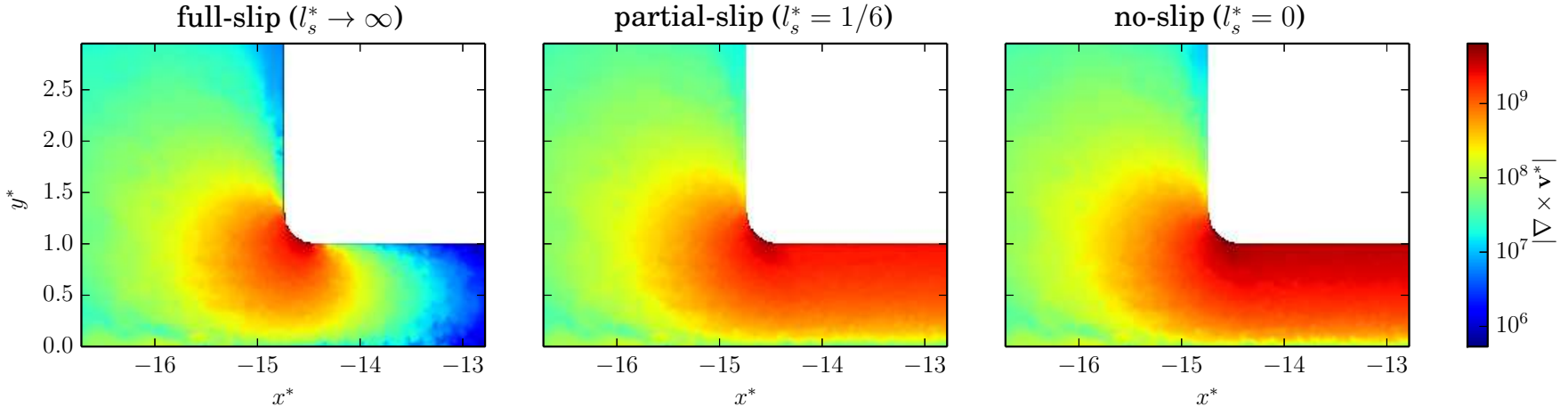
$$\Delta p^* = \pi \left(C_1 + C_2 \frac{240 l_s^{*2} - 72 l_s^* + 7}{(1 + 4 l_s^*)^2} \right) = \pi C$$

Energy Dissipation and Pressure Profile

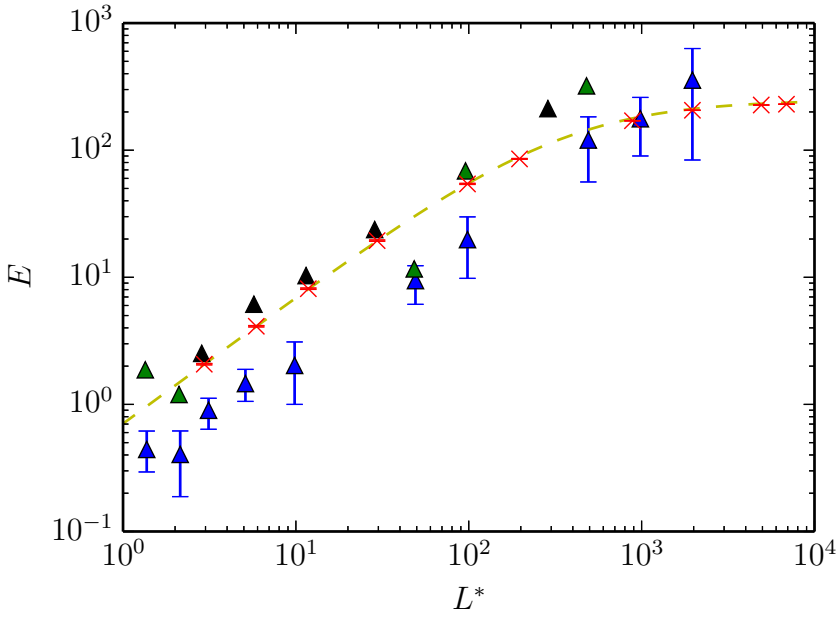


Velocity and Vorticity Fields





Flow Enhancement



$$E = Q^*/Q^*_{HP}$$

- red: CFD ($l^*_s = 62$)
- yellow: $E = \left(\frac{1}{1+4l^*_s} + \frac{C\pi}{8L^*}\right)^{-1}$

Conclusions

- **Multiscale flow past a buckyball:**
  - We simulated **a steady incompressible water flow** past an immobile C_{540} **fullerene molecule** with **partial slip** boundary conditions.
  - it employs a fully **3D coupling** between **atomistic** and **continuum** descriptions.
  - allows for studying **nanoscale flow phenomena** that are out of scope of the pure atomistic simulation.
- **Continuum simulation of water flow past a fullerene molecule:**
  - We compared computational fluid dynamics solutions to the above multiscale simulation of water flow past a fullerene molecule.
  - We employed **the Navier boundary condition** and we showed that the **continuum hydrodynamics** subject to the Navier boundary condition gives an **accurate description** of fluid flow past the fullerene molecule.
- **Continuum simulations of water flow in carbon nanotube membranes:**
  - The flow quantities calculated from the present hybrid approach using **slip lengths extracted from MD simulations** are in **excellent agreement** with pure MD results while they are obtained at **a fraction of the computational cost**.
  - Our simulations provide an **asymptotic flow rate enhancement** and indicate that the pressure losses at the CNT ends can be reduced by reducing their curvature.

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