Coupling Atomistic and Continuum Hydrodynamics

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Outline

- Introduction
- Triple-Scale AdResS-HybridMD
- Multiscale flow simulation past a Buckyball
- 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

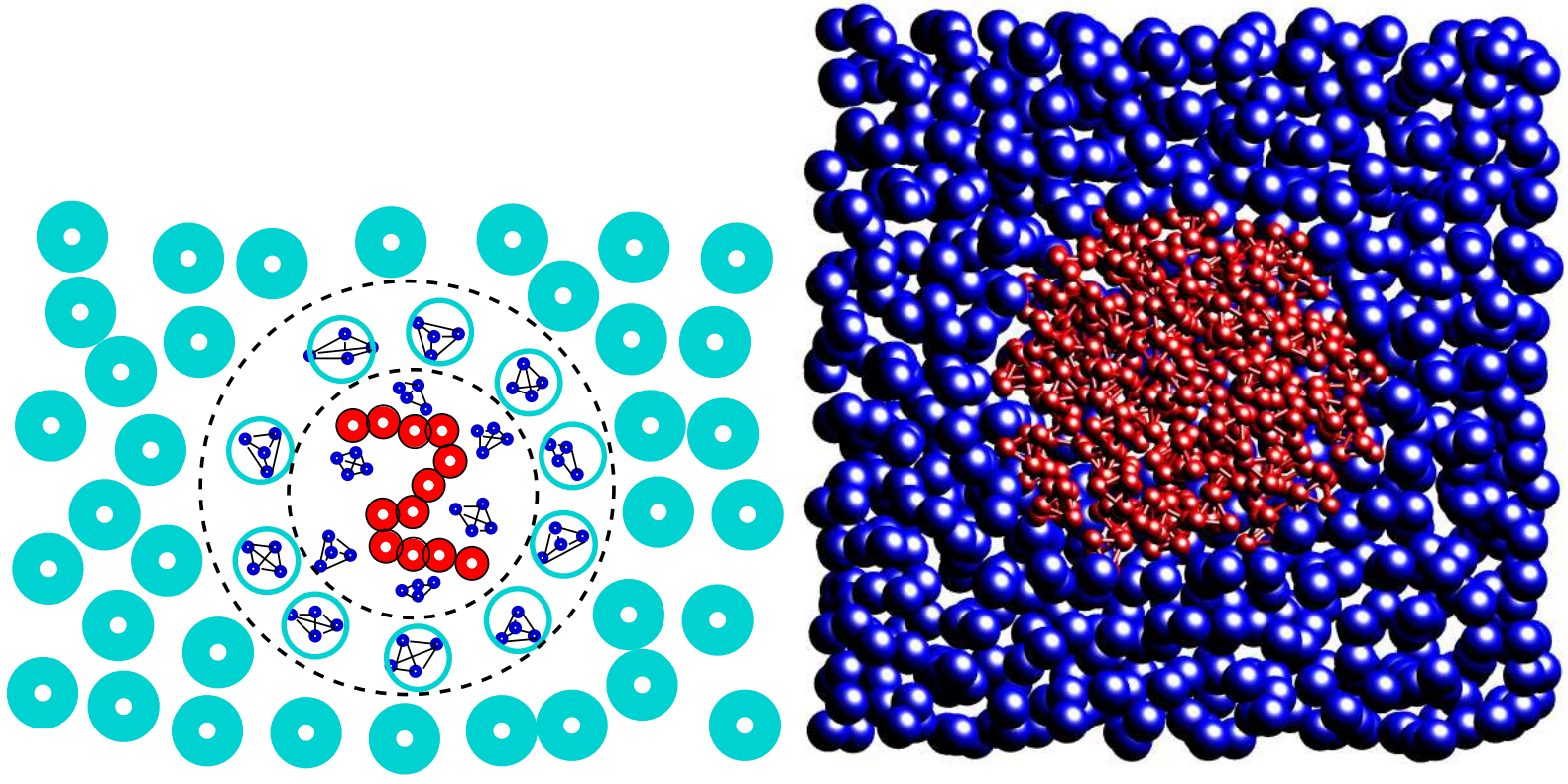
Continuum fluid dynamics (CFD):

- 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

Hybrid Atomistic/Mesoscopic Liquid



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

AdResS

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

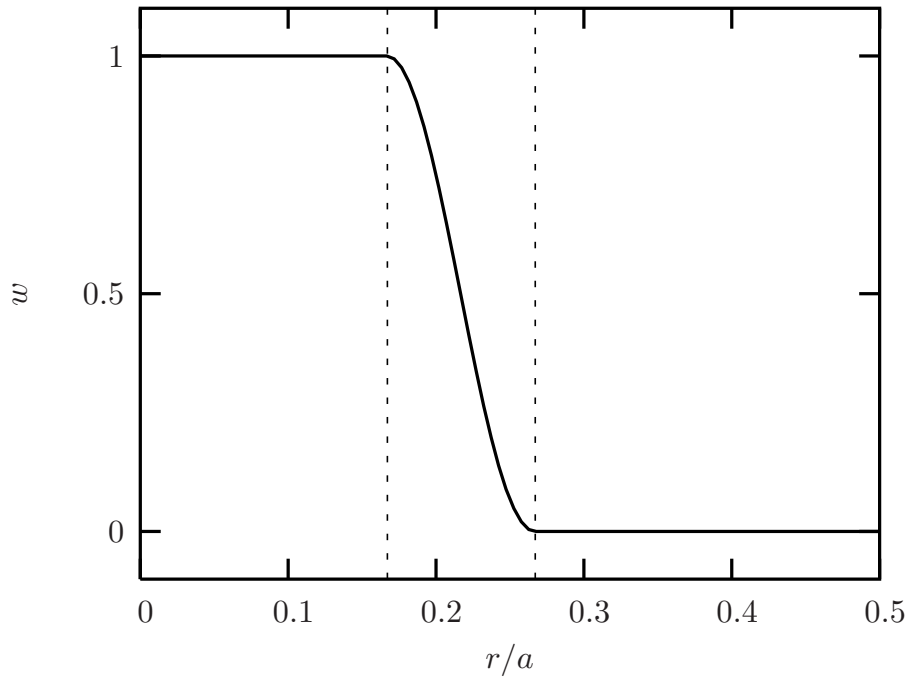
$$\mathbf{F}^{atom}_{\alpha\beta} = \sum_{i\alpha, j\beta} \mathbf{F}^{atom}_{i\alpha j\beta}$$

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

$$\begin{aligned} \mathbf{F}^{atom}_{i\alpha j\beta} &= -\frac{\partial U^{atom}}{\partial \mathbf{r}_{i\alpha j\beta}}, \\ \mathbf{F}^{cm}_{\alpha\beta} &= -\frac{\partial U^{cm}}{\partial \mathbf{R}_{\alpha\beta}}. \end{aligned}$$

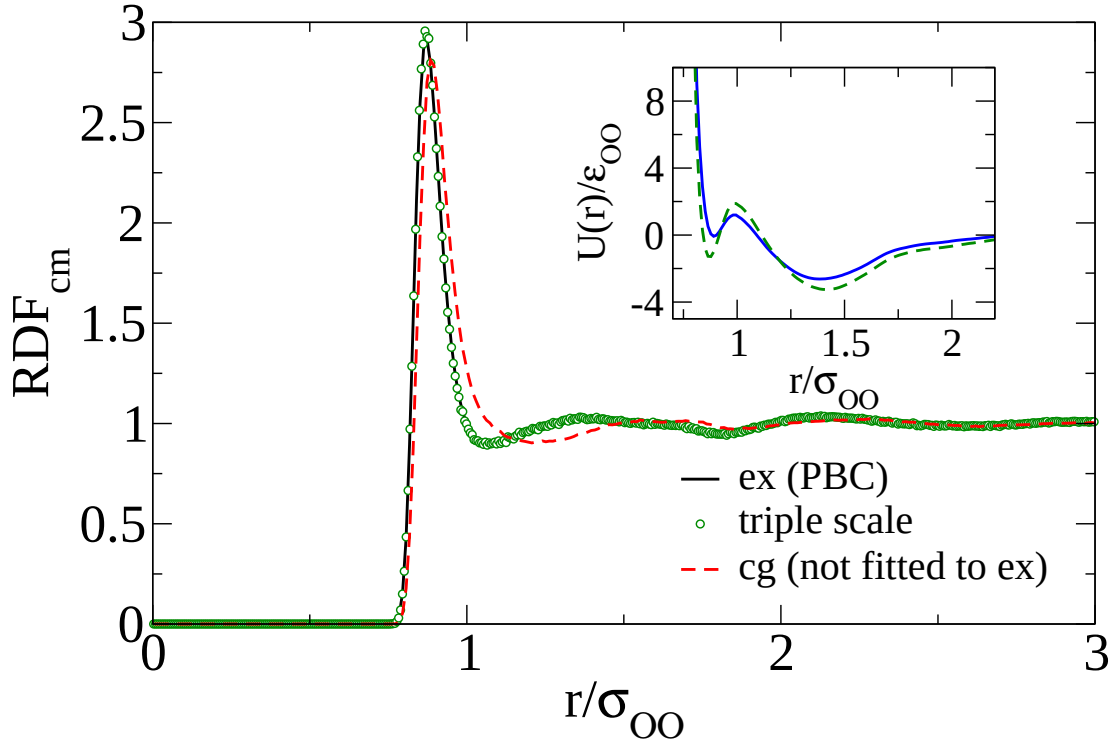
M. Praprotnik, L. Delle Site, K. Kremer, J. Chem. Phys. **123**, 224106 (2005).

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.

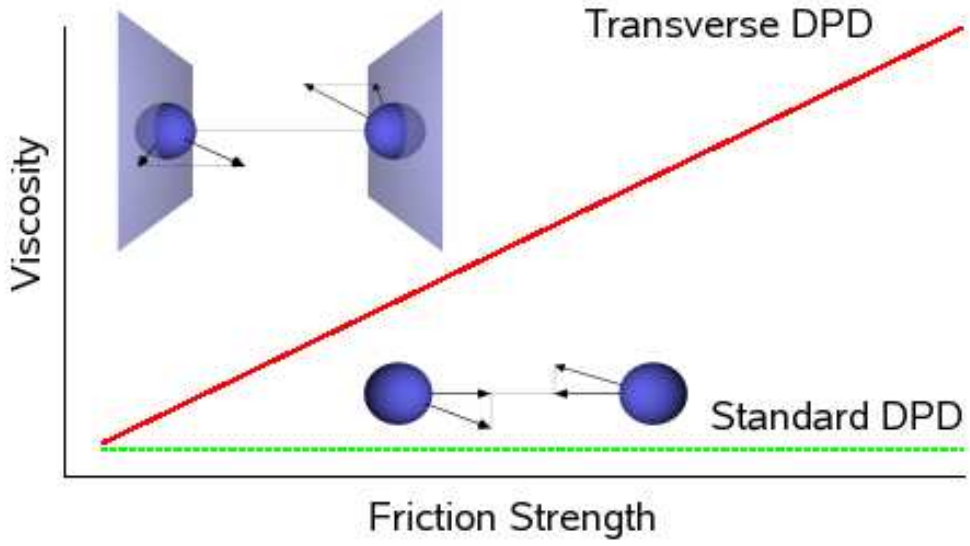
Coarse-Grained Model



- 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).

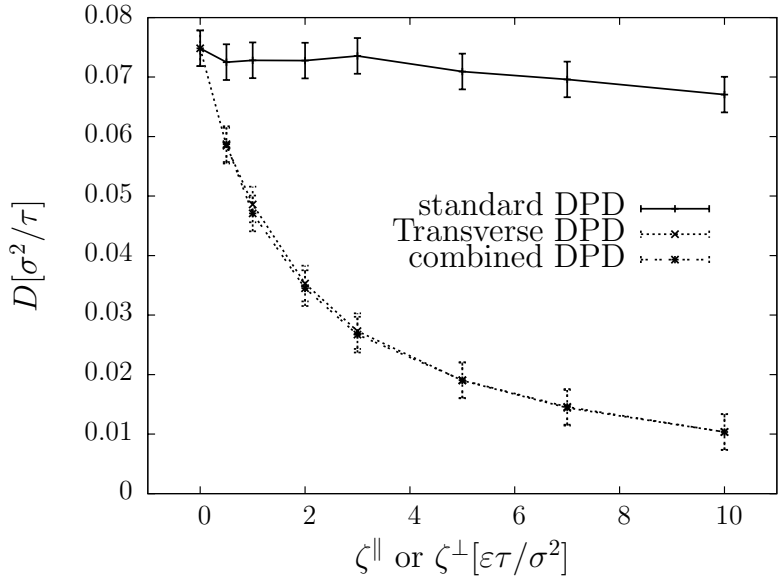
Transverse DPD Thermostat



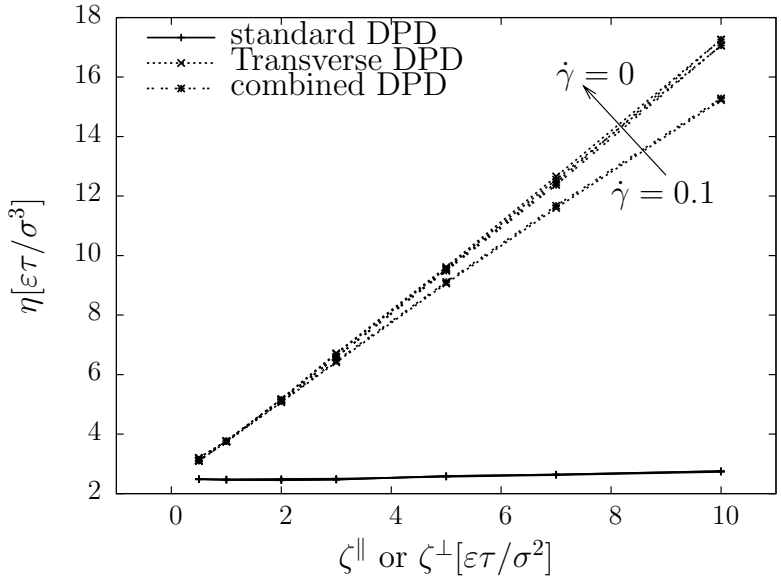
- The **variation** of the **dissipative particle dynamics (DPD)** thermostat includes the damping of the **perpendicular** components of the relative velocity, yet keeping the advantages of conserving **Galilei invariance** and within our error bar also **hydrodynamics**. It allows for **controlling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

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

Tuning Transport Coefficients

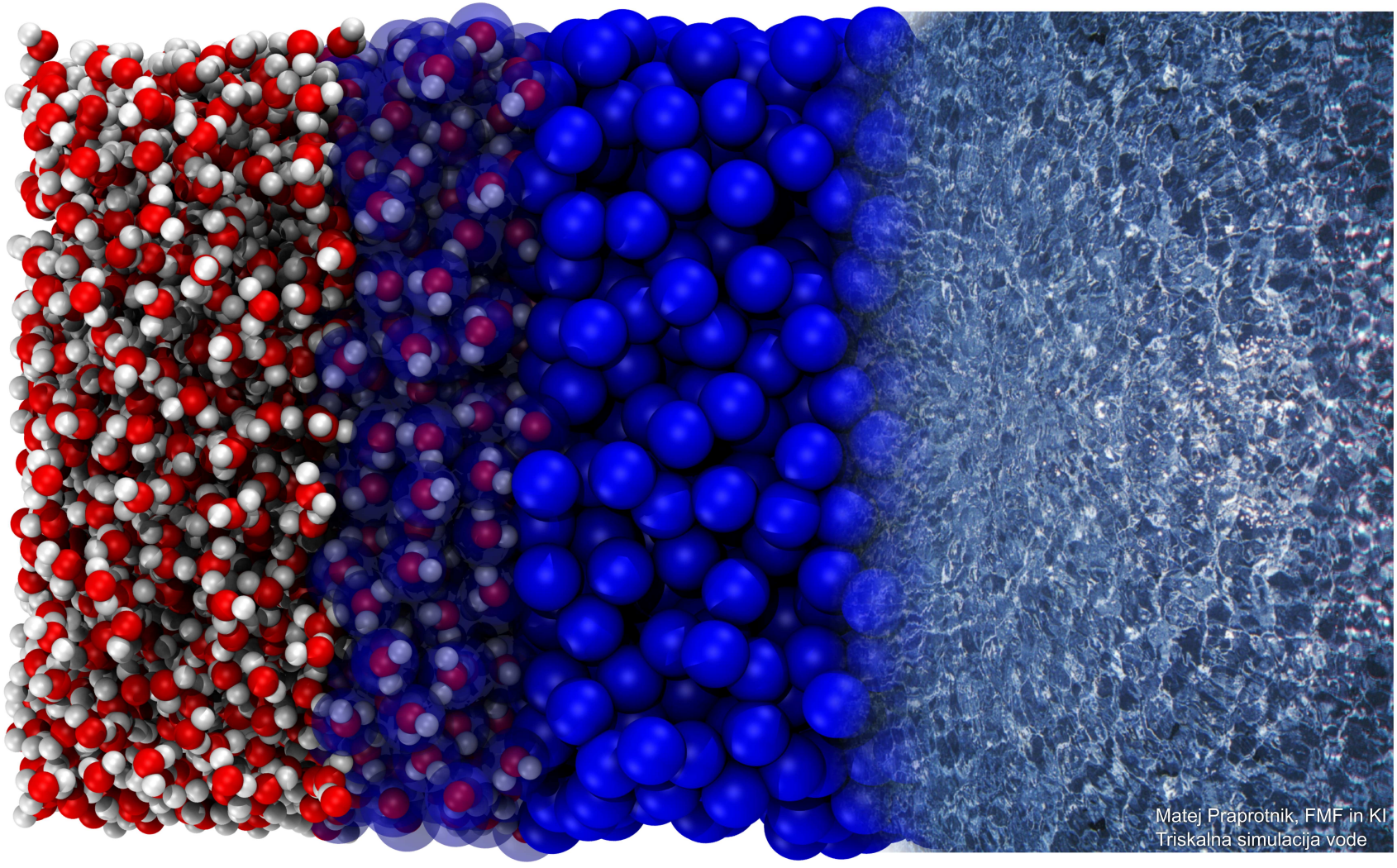


(c) Diffusion constant

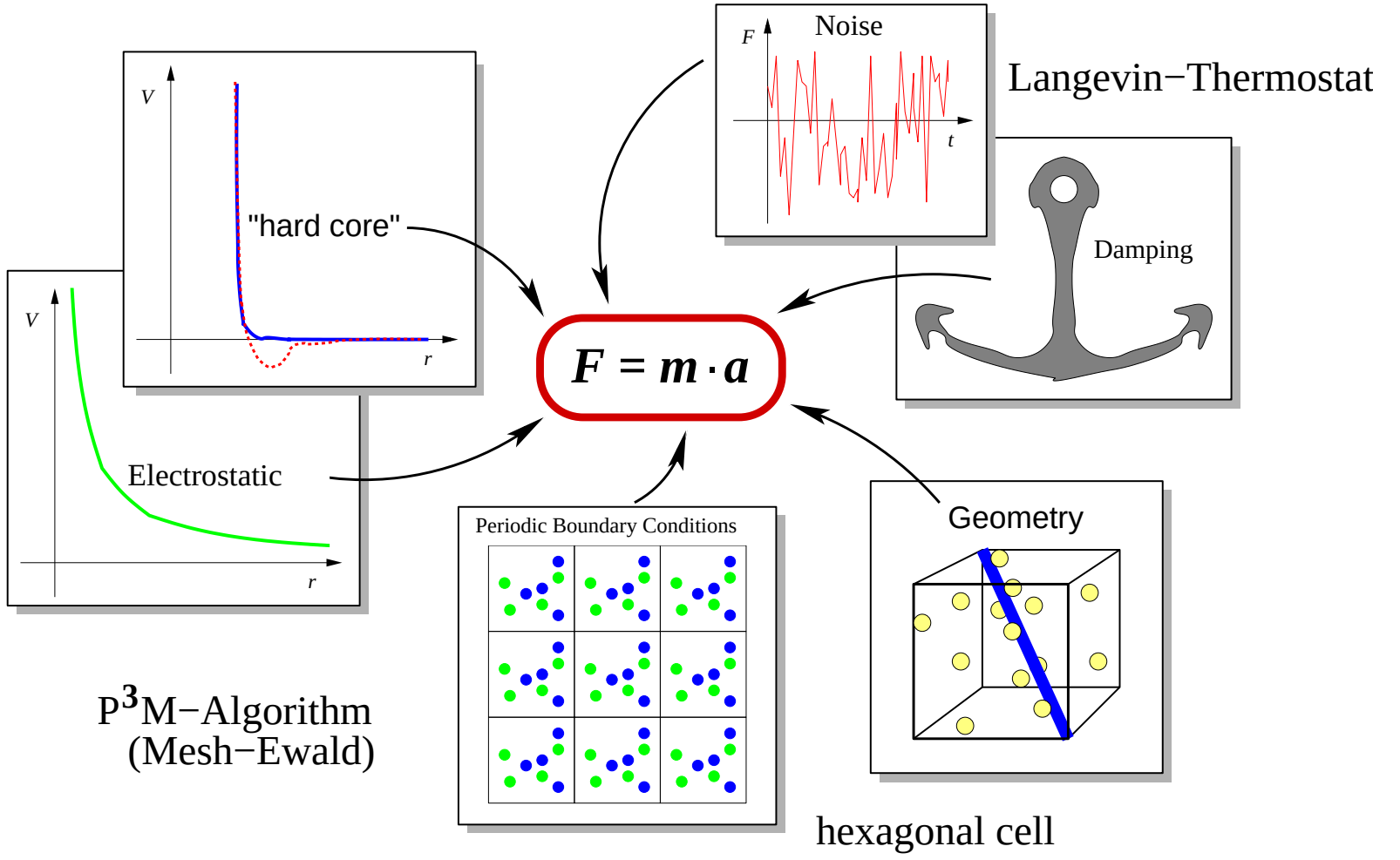


(d) Shear viscosity

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)

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

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

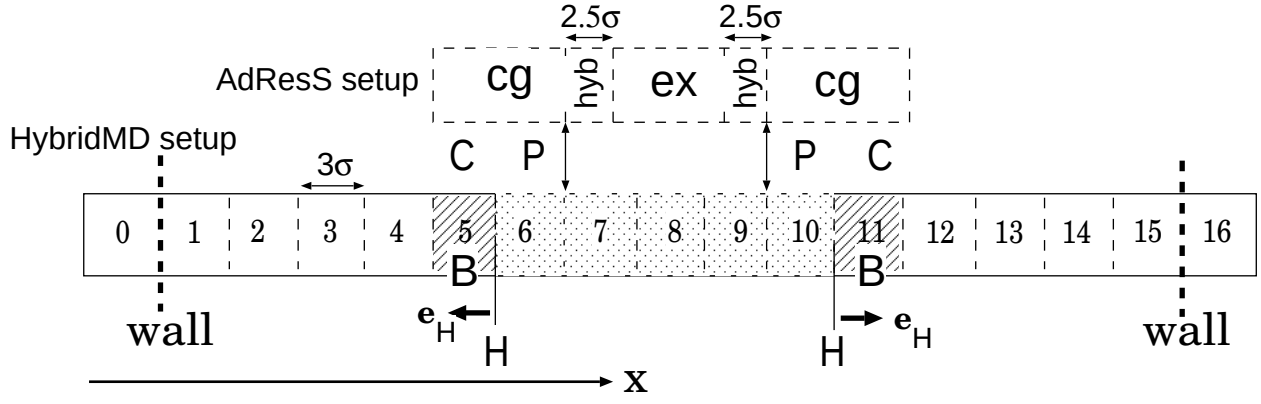
- **Constitutive relations**:
  - Equation of state: $p = p(\rho)$
  - Stress tensor: $\mathbf{\Pi} = -\eta[\nabla\mathbf{u}]^S - \xi\nabla \cdot \mathbf{u}\,\mathbf{I}$

Finite Volume Method

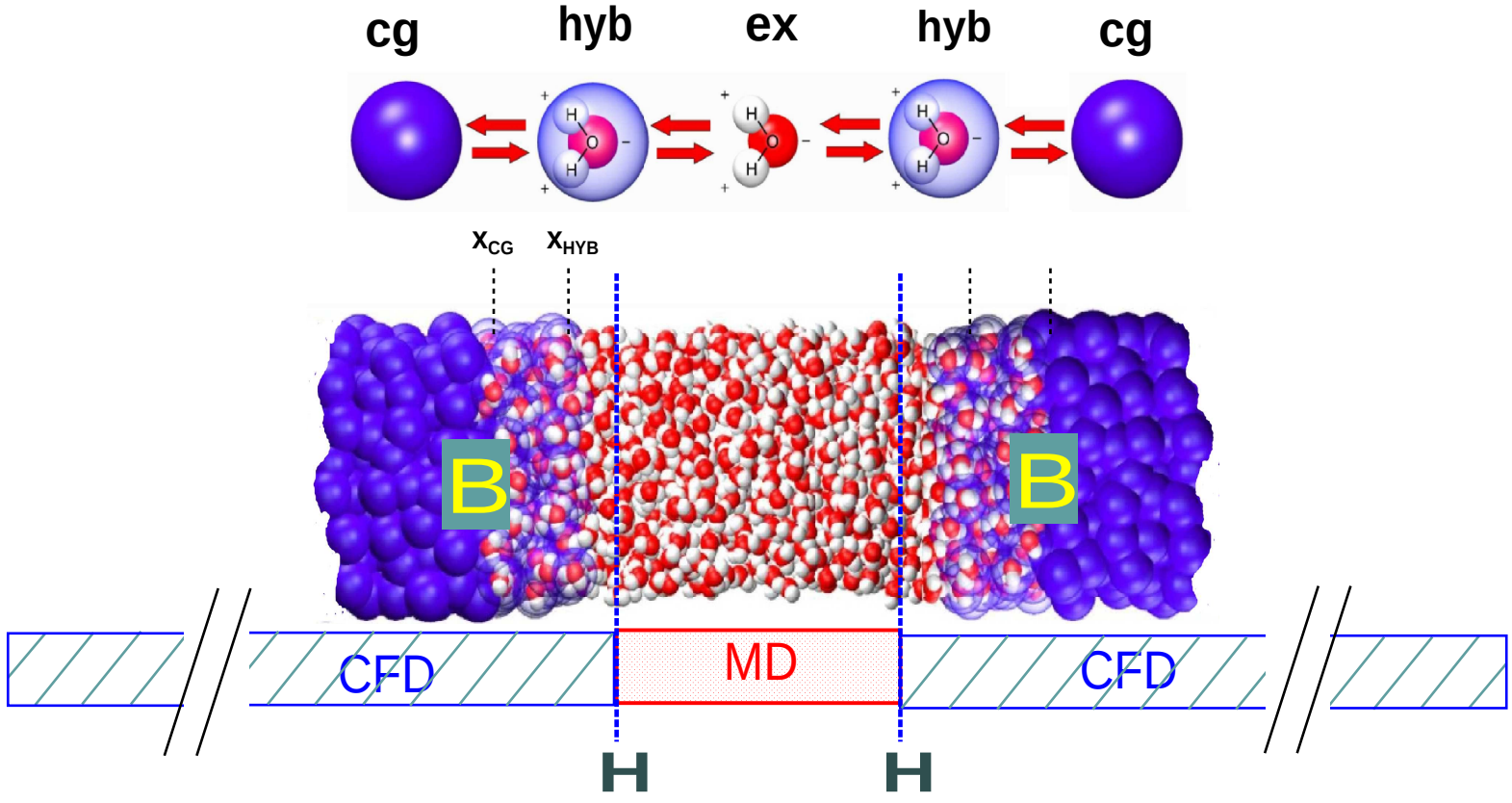
$$\int_{V_C} \partial\phi/\partial t \, dV = -\int_{V_C} \nabla \cdot \mathbf{J}^{\phi} \, dV = -\oint_S \mathbf{J}^{\phi} \cdot dS$$

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

$\Phi_C = \int_{V_C} \phi(\mathbf{r}, t) d\mathbf{r}^3$. 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

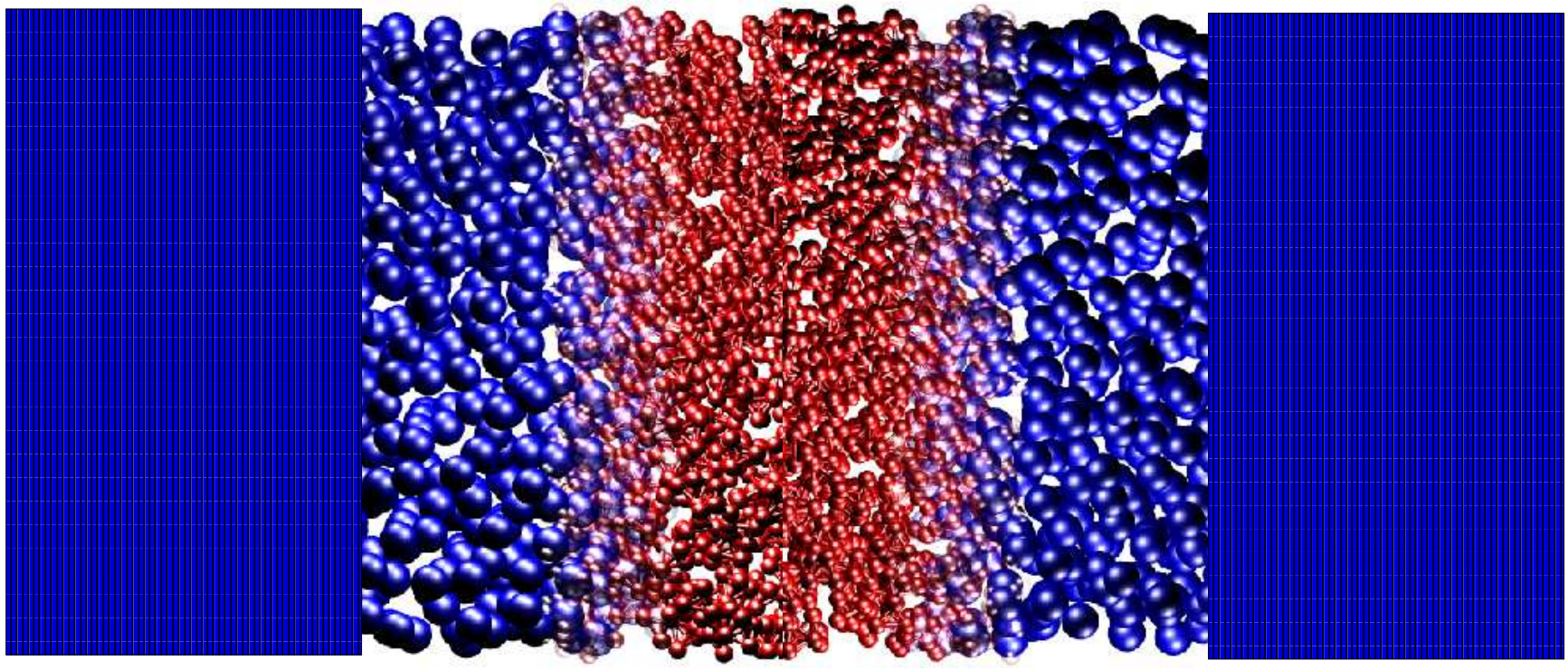


B=buffer (overlap domain) serves to impose fluxes into the particle region.

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**

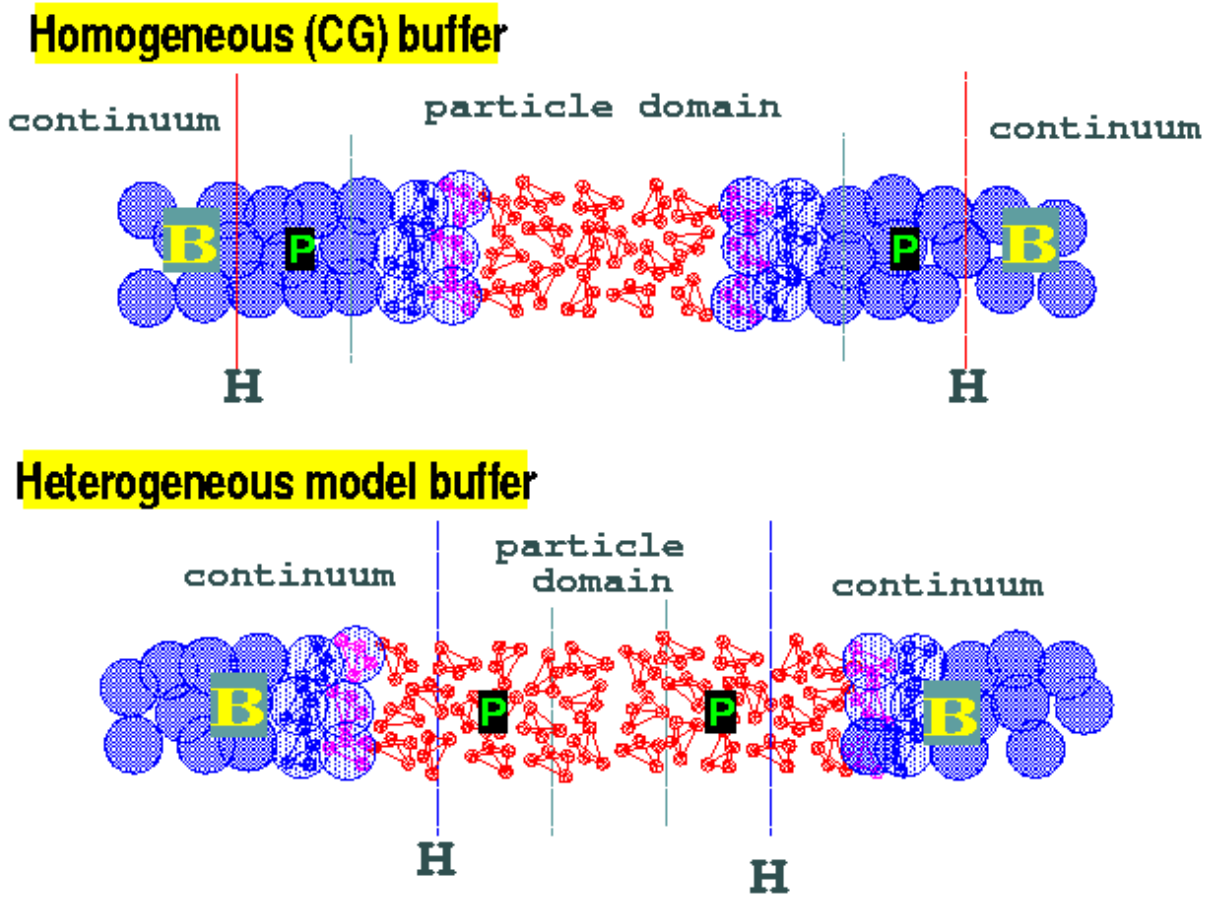
Triple-Scale Method



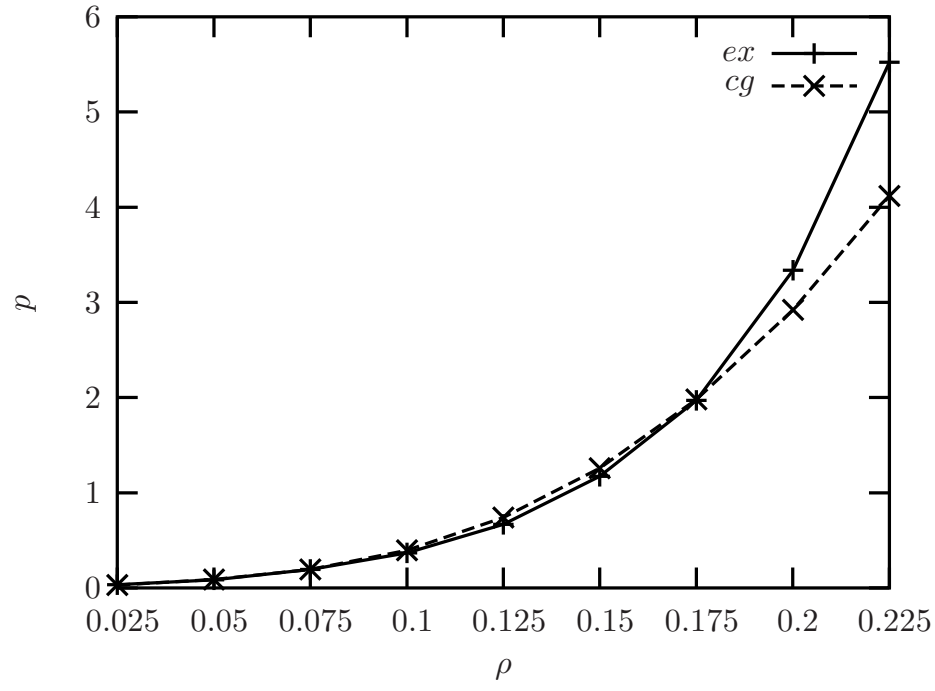
- to allow for insertion of larger molecule into a dense liquid
- to allow for grand canonical MD simulation of open molecular systems

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

Buffer: Two Possible Setups



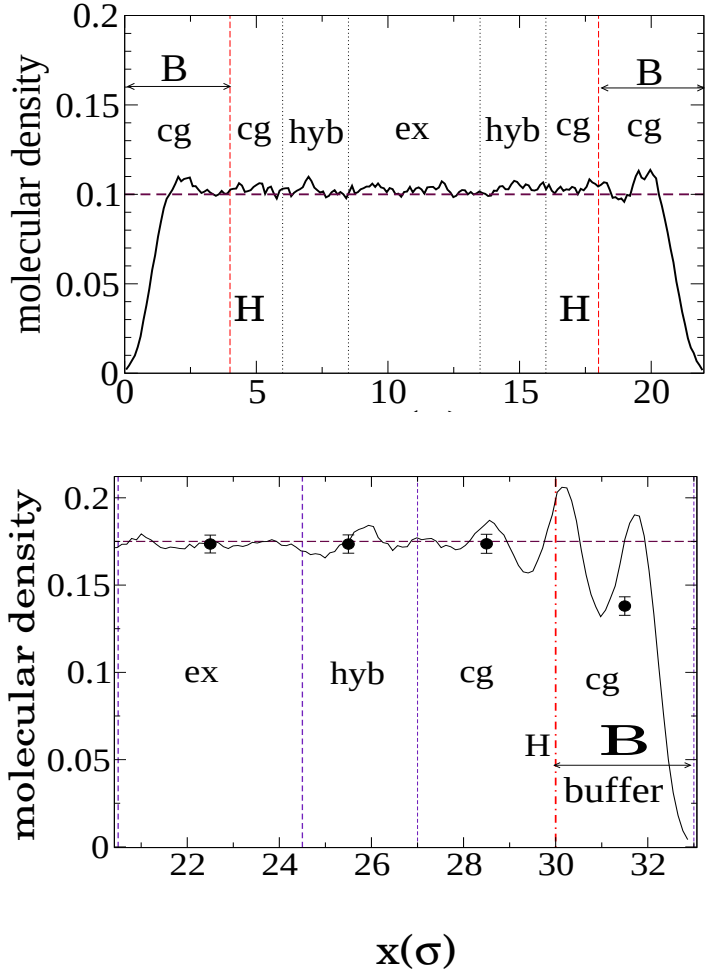
Equation of State



The pressure tensor:

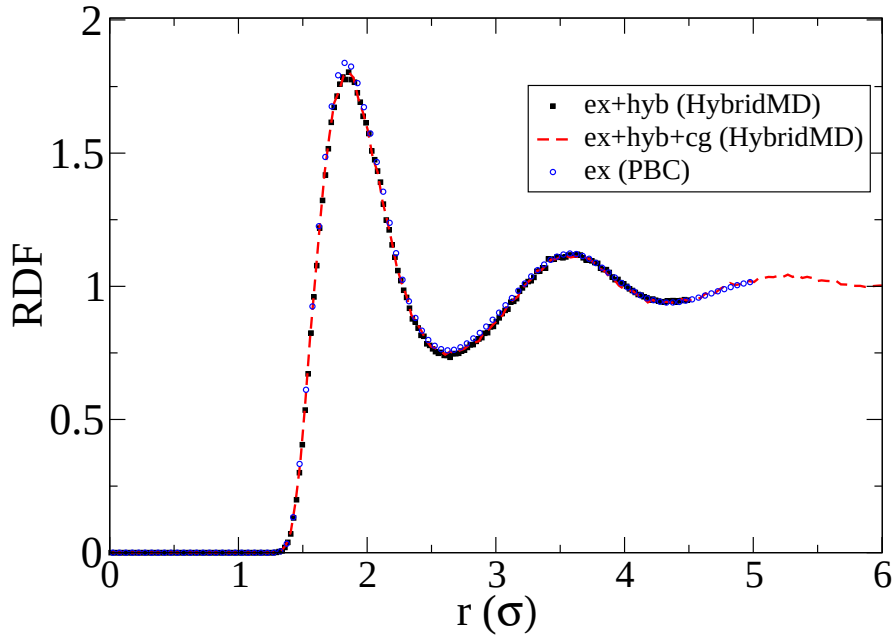
$$\mathbf{J} = p\,\mathbf{I} + \rho \mathbf{v}\mathbf{v} + \mathbf{\Pi}$$

Molecular Density Profile



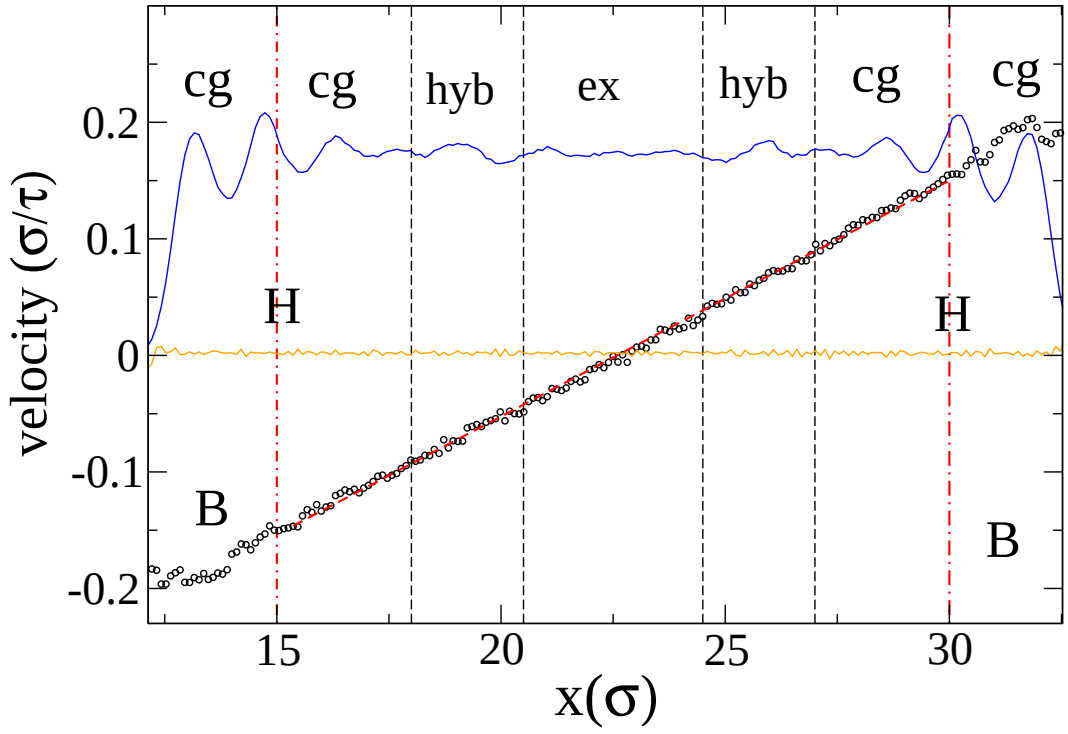
- (a) $\rho_m = 0.1\sigma^{-3}$. (b) $\rho_m = 0.175\sigma^{-3}$.

RDFs: Equilibrium



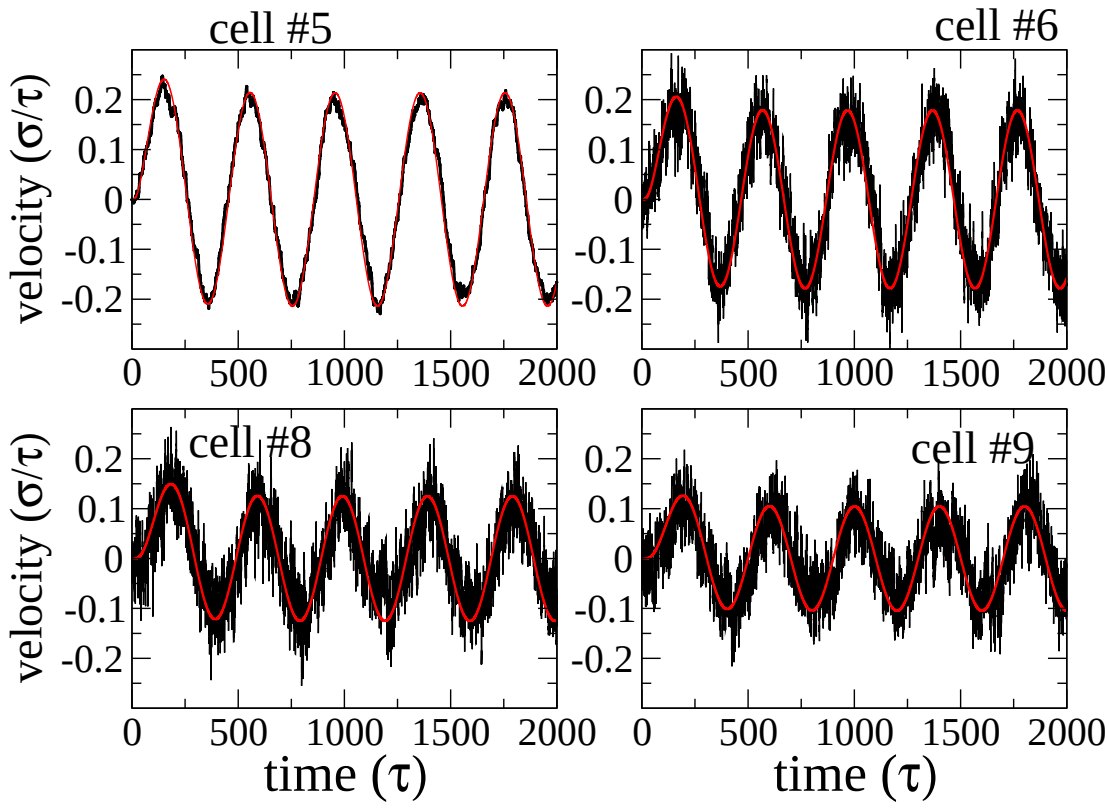
- RDF$_{cm}$s of the liquid in the atomistic and transition domains ($ex + hyb$) and in the total molecular region ($ex + hyb + cg$) of the triple-scale model together with the reference RDF$_{cm}$ of the all-atom system (ex(PBC)) at $\rho = 0.175/\sigma^3$.

Couette Flow



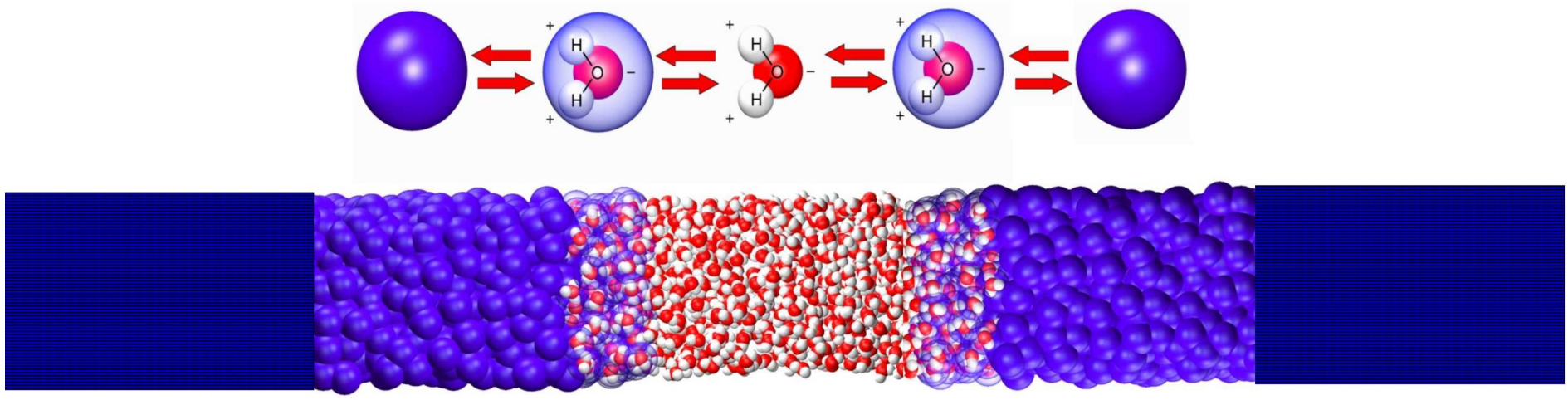
- Velocity profile at the particle region of an hybrid simulation of a Couette flow.

Stokes Flow



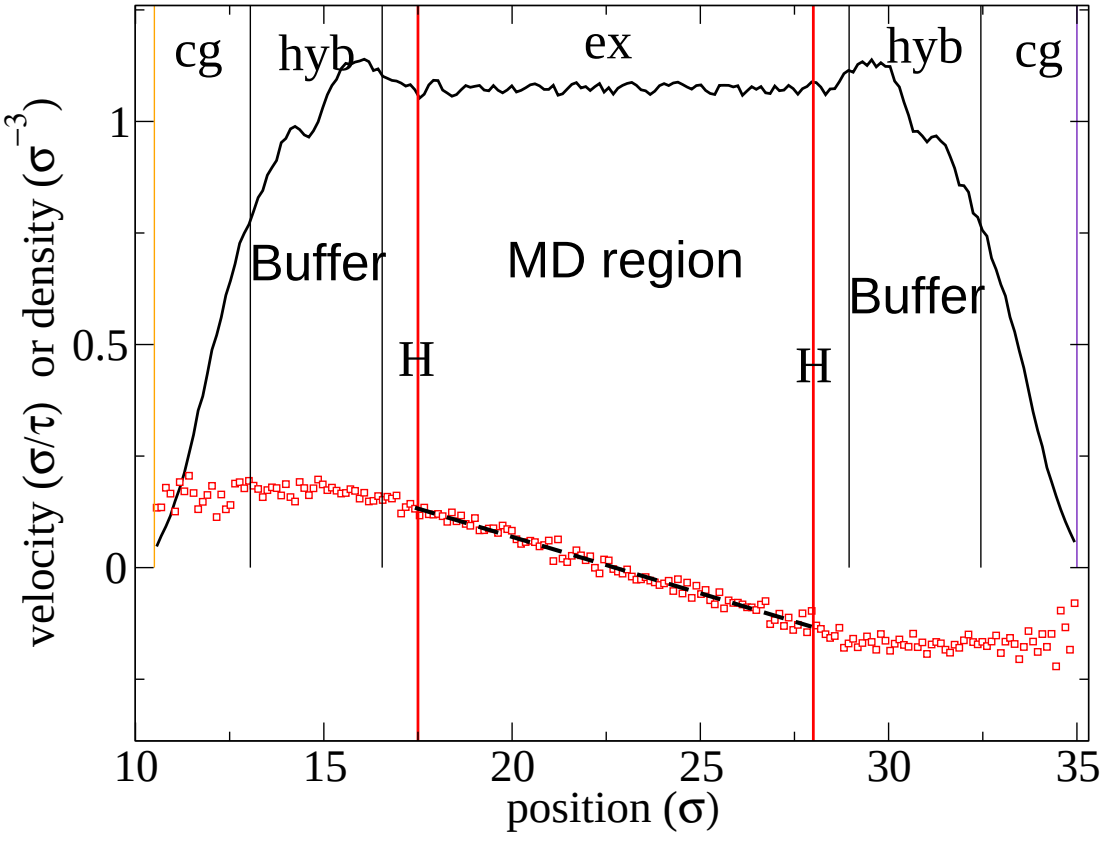
- Velocity in the y-direction at some selected cells in a hybrid simulation of a Stokes flow.

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.

Grand-Canonical Ensemble

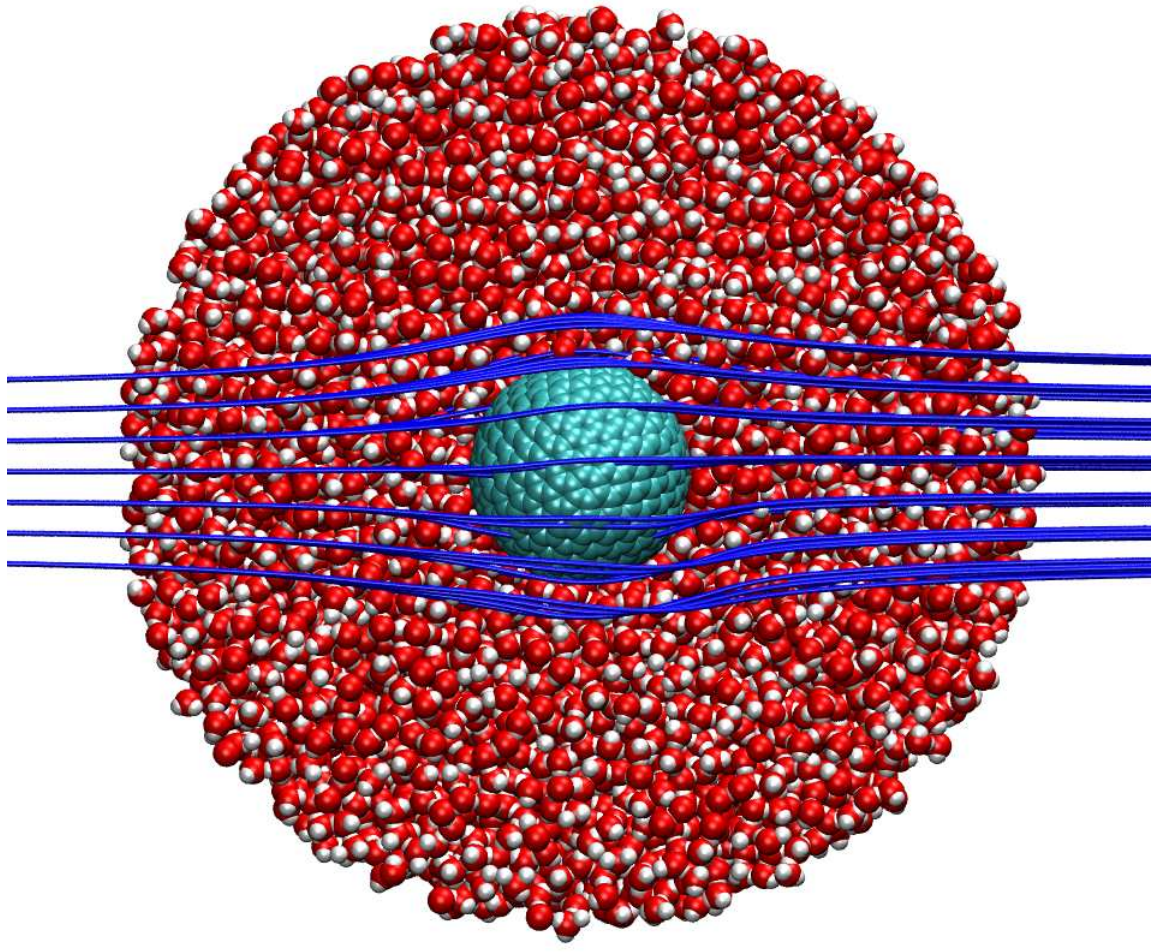
Mass fluctuations

Standard deviation of mass $Var[\rho] = \rho k_B T/(V c_T^2)$, $c_T^2 = \left(\frac{\partial p}{\partial \rho}\right)_T$, $\beta_T = (c_T^2 \rho)^{-1}$

Flexible TIP3P: $c_T = 7.38(\varepsilon_{OO}/m_O)^{1/2}$, $\rho = 1.20 m_O/\sigma_{OO}^3$

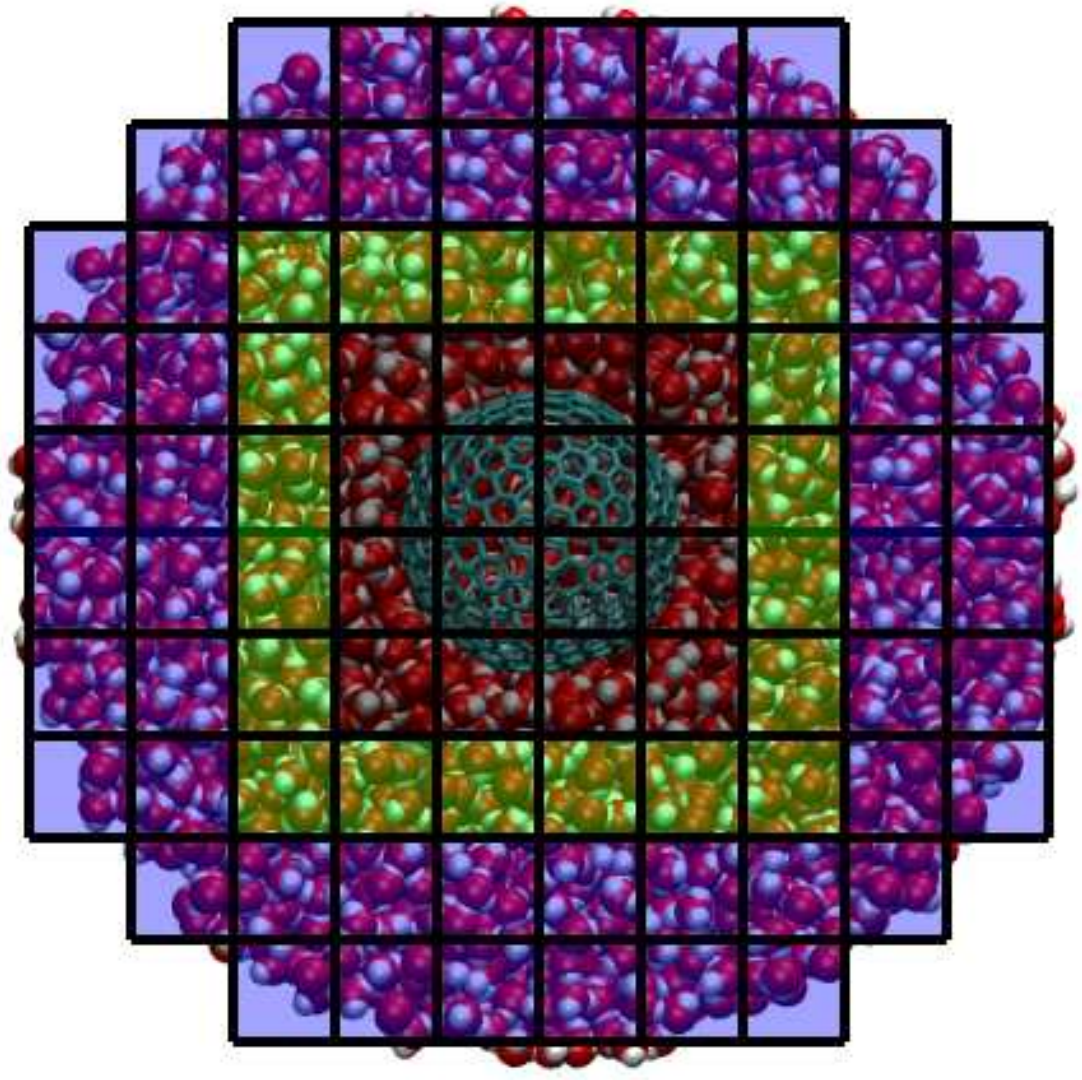
- $V = 3.50 \times 6.18 \times 11.12\, \sigma_{OO}^3$:
  grand canonical: $Var[\rho] = 0.0187$, **simulation**: $Var[\rho] = 0.020 \pm 0.002$
- $V = 10.50 \times 6.18 \times 11.12\, \sigma_{OO}^3$:
  grand canonical: $Var[\rho] = 0.0108$, **simulation**: $Var[\rho] = 0.011 \pm 0.005$

Multiscale Flow Past Fullerene



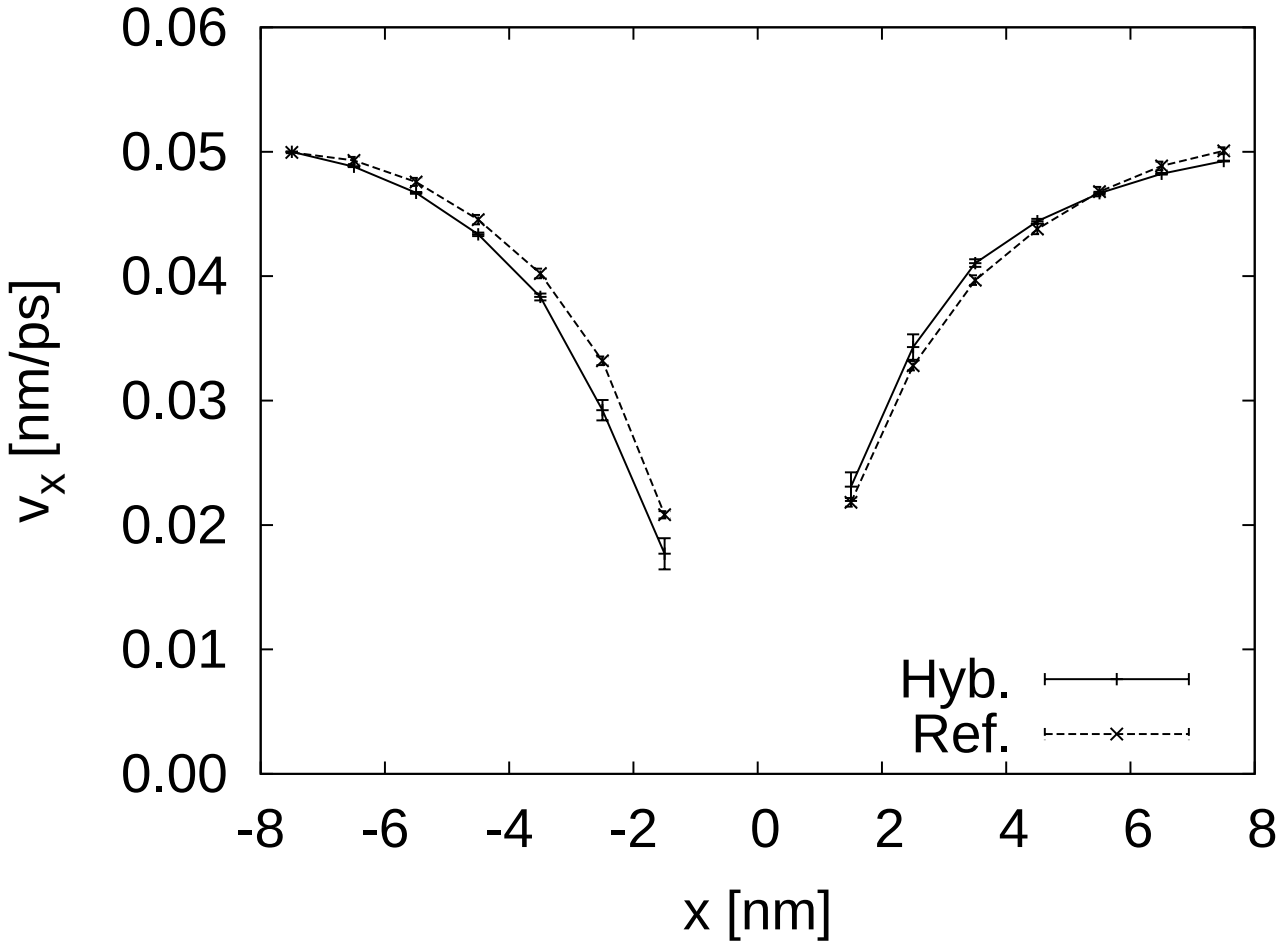
J. H. Walther, M. Praprotnik, E. M. Kotsalis, P. Koumoutsakos, J. Comput. Phys. **231**, 2677-2681, 2012.

Overlap Domain



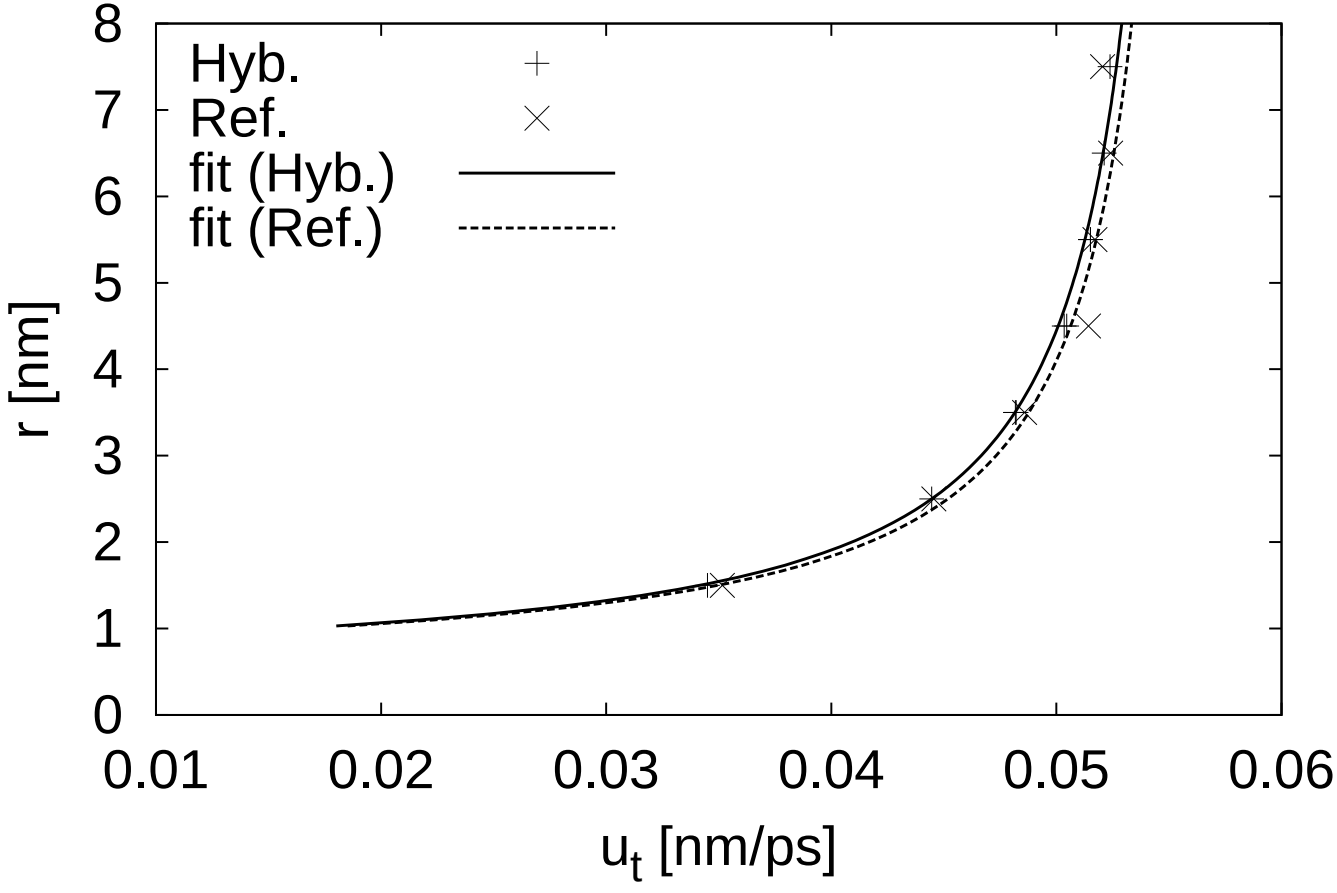
Cross-section through the overlap region.

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 $R \approx 1.03\mathrm{nm}$.

Partial Slip Boundary Conditions

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

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

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

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

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

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

Conclusions

- **AdResS:**
  - Allows for a **dynamical switching** between **atomistic** and **coarse-grained** molecular descriptions.
- **AdResS-HybridMD Scheme:**
  - We performed a **triple-scale simulation** of a molecular liquid.
  - 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**.
- **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.
- **Future work:**
  - Applications to study phenomena involving flow-matter interactions at multiple length scales.

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