Adaptive Resolution Molecular Dynamics Simulation

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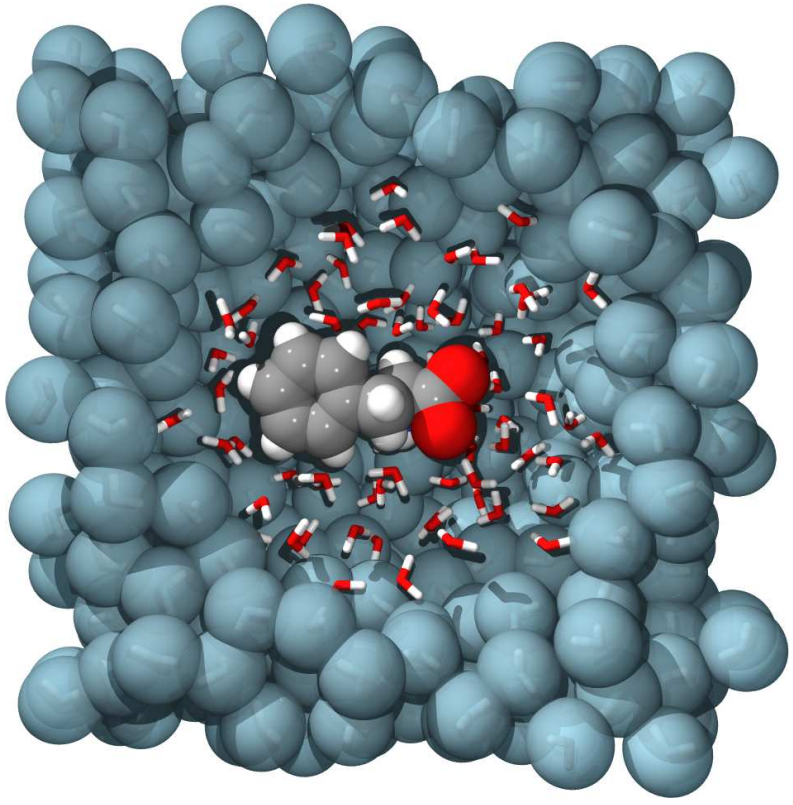
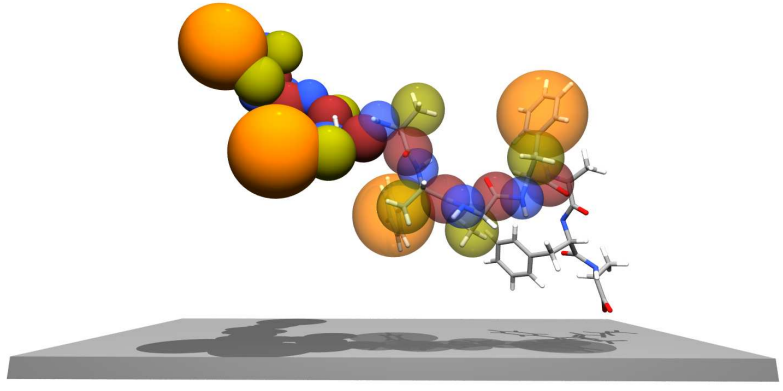
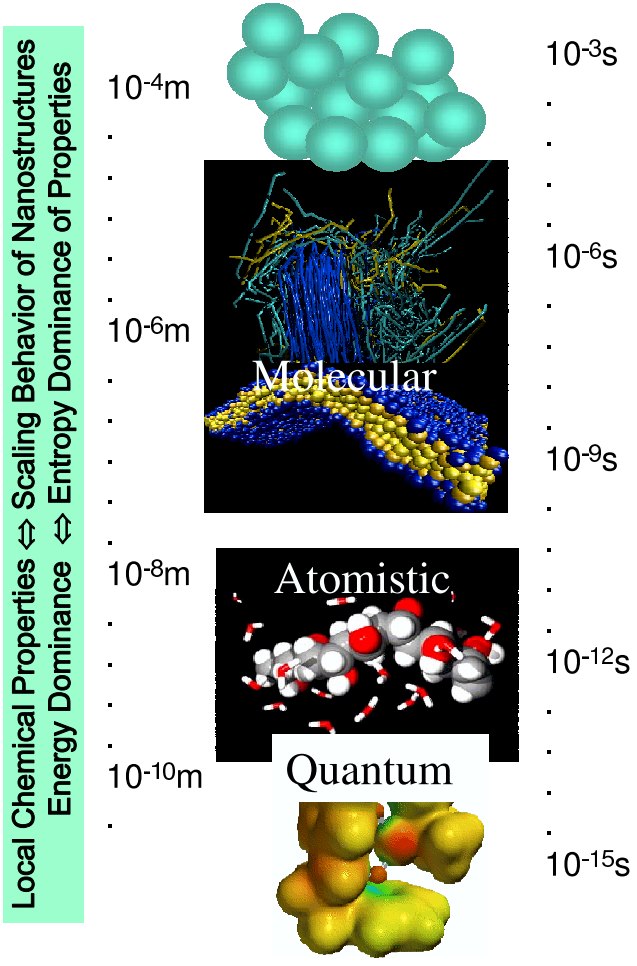
Multiscale Phenomena





Multiscale Modeling



MACRO Finite Element Calculations,

Continuum hydrodynamics,

Dissipative Particle Dynamics (DPD)

MD-MC-Lattice Boltzmann

MESO MC statics/dynamics,

MD, NEMD,

MICRO Classical Force Field MD, MC,

Embedded Atomistic-Quantum methods,

Car-Parrinello MD,

Quantum MC,

Quantum Chemical Methods

Adaptive resolution simulation

- **Motivation:**
  - to simplify the model to the largest extent possible while keeping all the necessary details where this is required.
- **Method:** *AdResS (Adaptive Resolution Scheme)*
  - allows for an dynamical switching between the atomistic and mesoscopic levels of detail $\Longrightarrow$ on-the-fly changing of the number of DOFs
  - tailor-made for molecular systems where spatially localized domains with the required atomistic resolution exchange particles with the remainder of the system sufficiently described on the mesoscopic scale.
- **Results:**
  - accurately reproduces the statistical properties of the reference all-atom system.

MD simulation

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

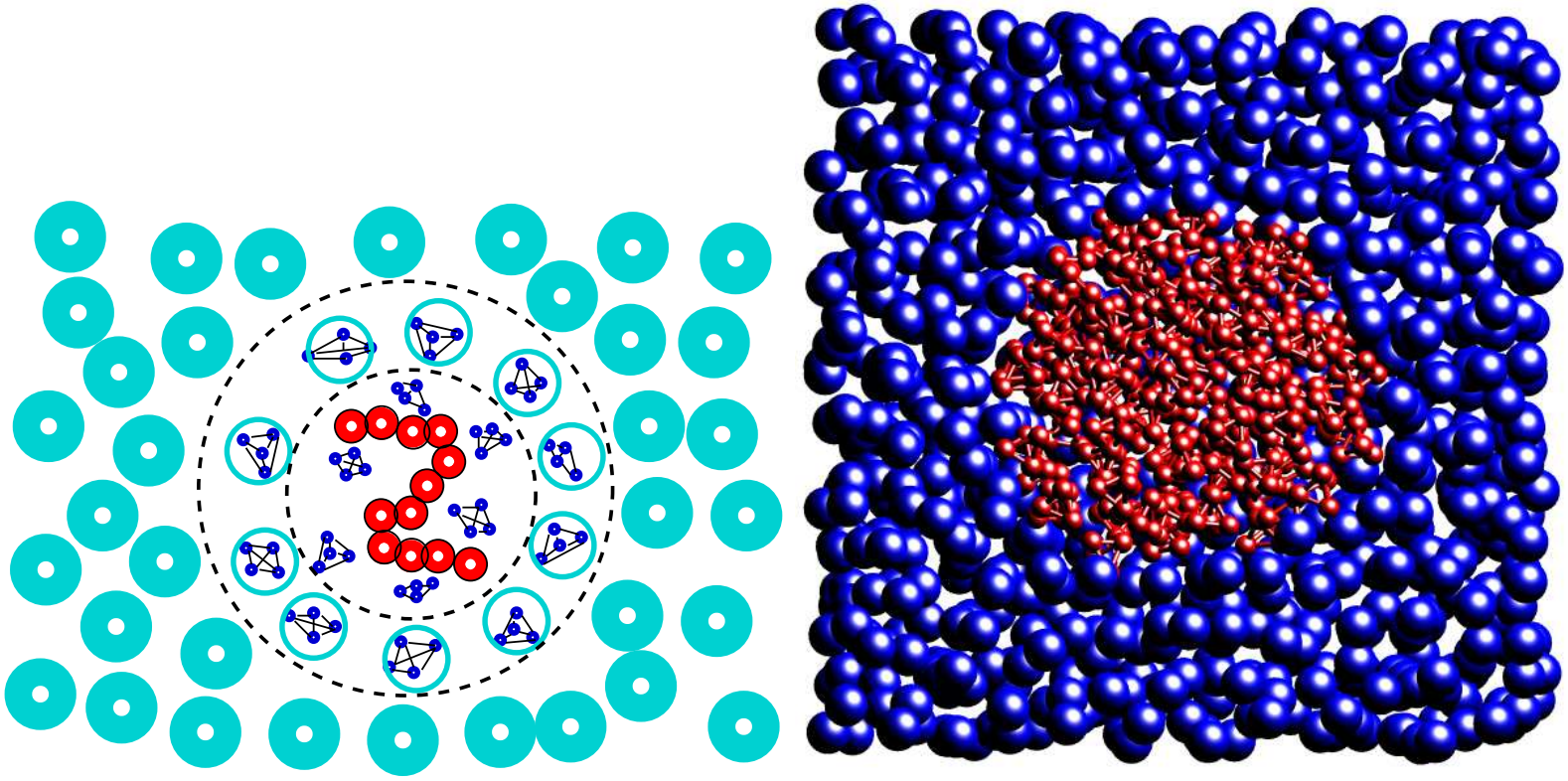
Mesoscopic MD simulation:

- 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

Combining the best from both approaches:

- Hybrid Adaptive MD Schemes

Hybrid atomistic/mesoscopic liquid

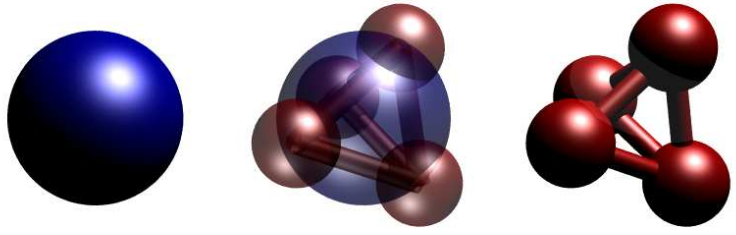


MP, L. Delle Site, K. Kremer, J. Chem. Phys. **126**, 134902 (2007).

MP, L. Delle Site, K. Kremer, Phys. Rev. E **73**, 066701 (2006).

Changing Number of Degrees of Freedom

- A tetrahedral molecule has a defined spatial orientation and $3N = 12$ DOFs:
  - 3 translational
  - 3 rotational
  - $3N - 6 = 6$ vibrational
- One particle mesoscopic molecule has no defined spatial orientation and only 3 translational DOFs.



MP, L. Delle Site, K. Kremer, J. Chem. Phys. **123**, 224106 (2005).
MP, L. Delle Site, K. Kremer, Annu. Rev. Phys. Chem. **59**, 545 (2008).

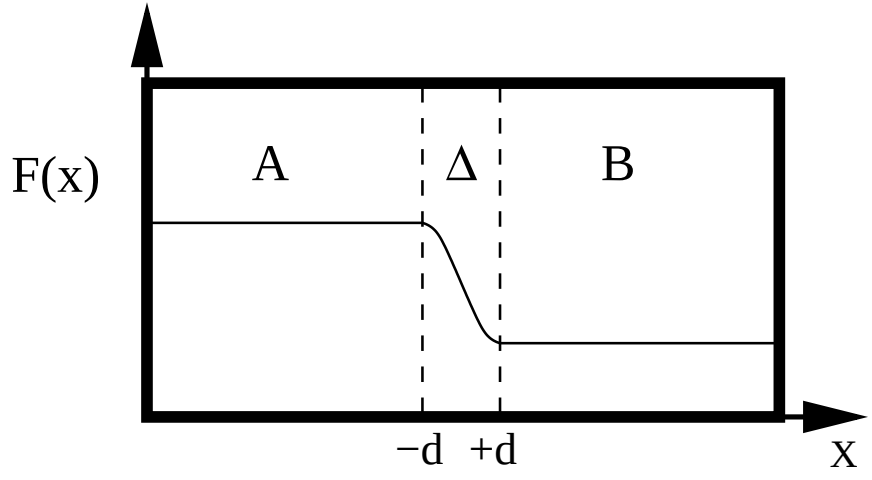
Geometrically induced phase transition

In thermodynamical equilibrium, `boundary conditions` analogous to to two-phase coexistence must be satisfied:

$$\mu_{ex} = \mu_{cg}, \quad p_{ex} = p_{cg}, \quad T_{ex} = T_{cg}.$$

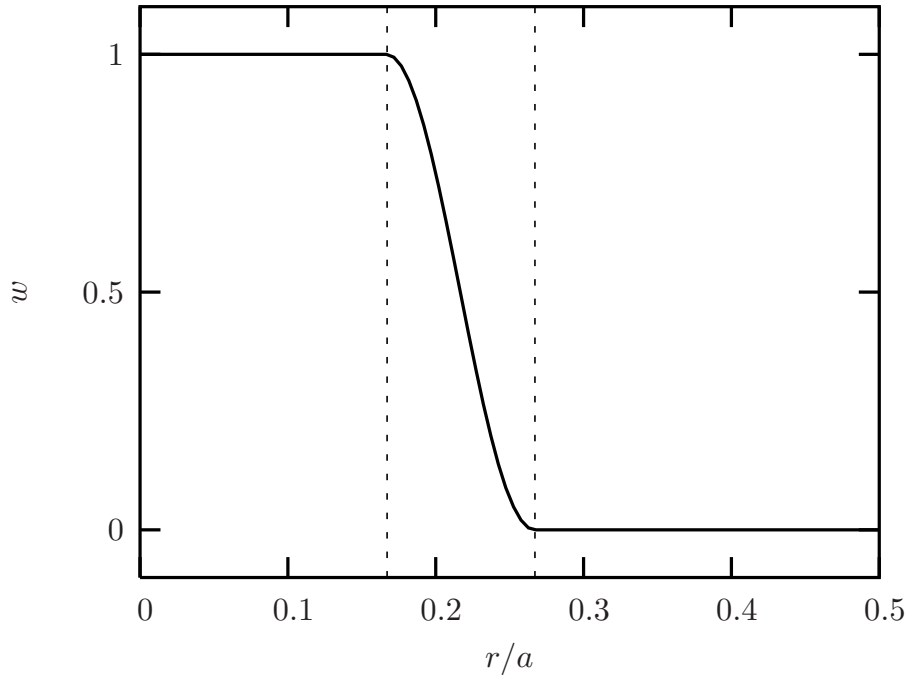
The rotational and vibrational parts of the free energy can be viewed as the `latent heat`, which is supplied or taken by the thermostat, at this transition.

Transition region



- Molecules in A and B are **physically identical** but **differently represented**.
- The number of DOFs is $n = n(x)$ with: $n_A = const_A$; $n_B = const_B$; and $n_\Delta = n(x)$
- The system is in equilibrium which implies:
  $\lim_{x \to d-} \frac{\partial F_A(x)}{\partial x} = \lim_{x \to d+} \frac{\partial F_B(x)}{\partial x} = 0 \Longrightarrow$
  $\lim_{x \to d-} \frac{\partial n_A(x)}{\partial x} = \lim_{x \to d+} \frac{\partial n_B(x)}{\partial x} = 0$

Weighting Function = Order Parameter



- 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.

AdResS: Linking Atomic and Mesoscopic Length Scales

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

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

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

May the Force be with you

One must interpolate the **forces** and not the interaction potentials if the **Newton's Third Law** is to be satisfied!

MP, K. Kremer, L. Delle Site, J. Phys. A: Math. Theor. **40**, F281, 2007.

The extension of equipartition theorem to non-integer DOFs

- For the fractional quadratic DOF Θ with the weight $w = \alpha$ we can write the **partition function** as:

$$\exp(-\beta F_\alpha) = C \int \exp(-\beta f(\alpha) p_\Theta^2/2)\, dV_\alpha =$$

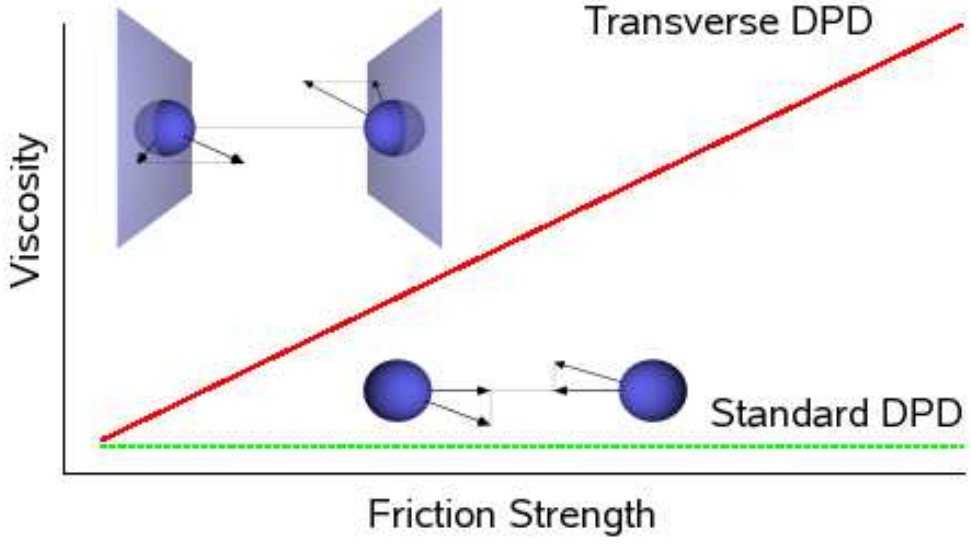
$$= 2C \int_0^\infty \exp(-\beta f(\alpha) p_\Theta^2/2)\, |p_\Theta|^{\alpha-1} \frac{dp_\Theta}{\Gamma(\alpha)} =$$

$$= \frac{2^{\alpha/2} C \Gamma(\alpha/2)}{\Gamma(\alpha)} f(\alpha)^{-\alpha/2} \beta^{-\alpha/2} \sim \beta^{-\alpha/2}.$$

- $\langle K_\alpha \rangle = \frac{d(\beta F_\alpha)}{d\beta} = \frac{\alpha}{2\beta} = \frac{\alpha k_B T}{2}$.
- In equilibrium $T_A = T_B = T_\Delta = T$ and thus: $n_\alpha \sim \alpha$.

MP, K. Kremer, L. Delle Site, Phys. Rev. E **75**, 017701 (2007).

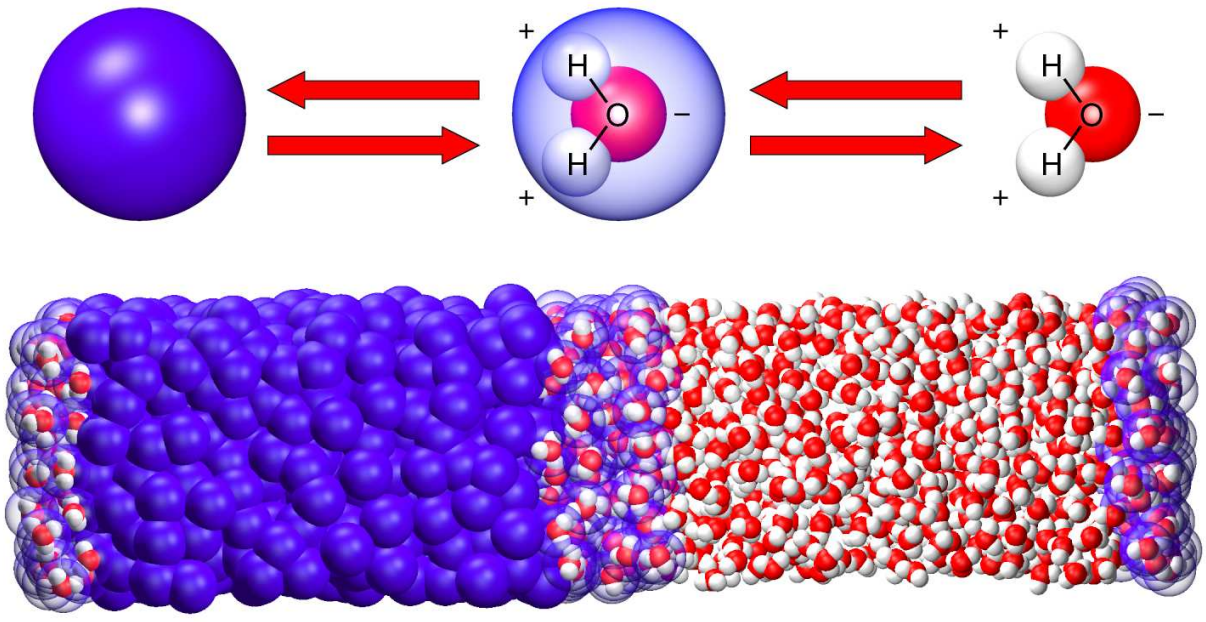
Transverse DPD Thermostat



- 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, MP, K. Kremer, Soft Matter **4**, 156 (2008).

Liquid Water



- MP, S. Matysiak, L. Delle Site, K. Kremer, C. Clementi, J. Phys.: Condens. Matter **19**, 292201 (2007).
- S. Matysiak, C. Clementi, MP, K. Kremer, L. Delle Site, J. Chem. Phys. **128**, 024503 (2008).

Electrostatics: Reaction field method

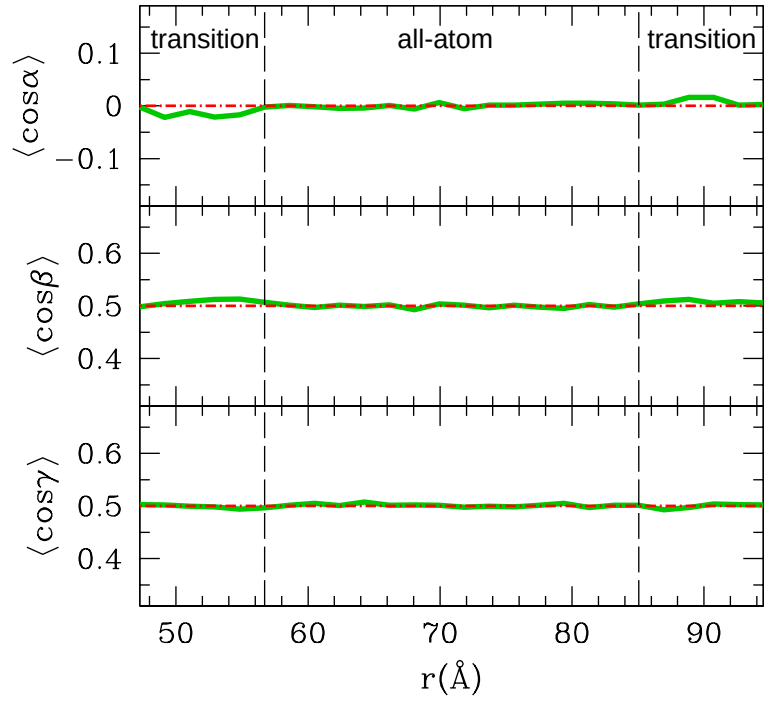
The electrostatic forces interactions are described using the Reaction field (RF) method:

$$\mathbf{F}^{atom}_{C_{i_\alpha j_\beta}}(\mathbf{r}_{i_\alpha j_\beta}) = \frac{e_{i_\alpha} e_{j_\beta}}{4\pi\epsilon_0}\left[\frac{1}{r^3_{i_\alpha j_\beta}} - \frac{1}{R_c^3}\frac{2(\epsilon_{RF}-1)}{1+2\epsilon_{RF}}\right]\mathbf{r}_{i_\alpha j_\beta}.$$

The RF is suitable to be used with AdResS because:

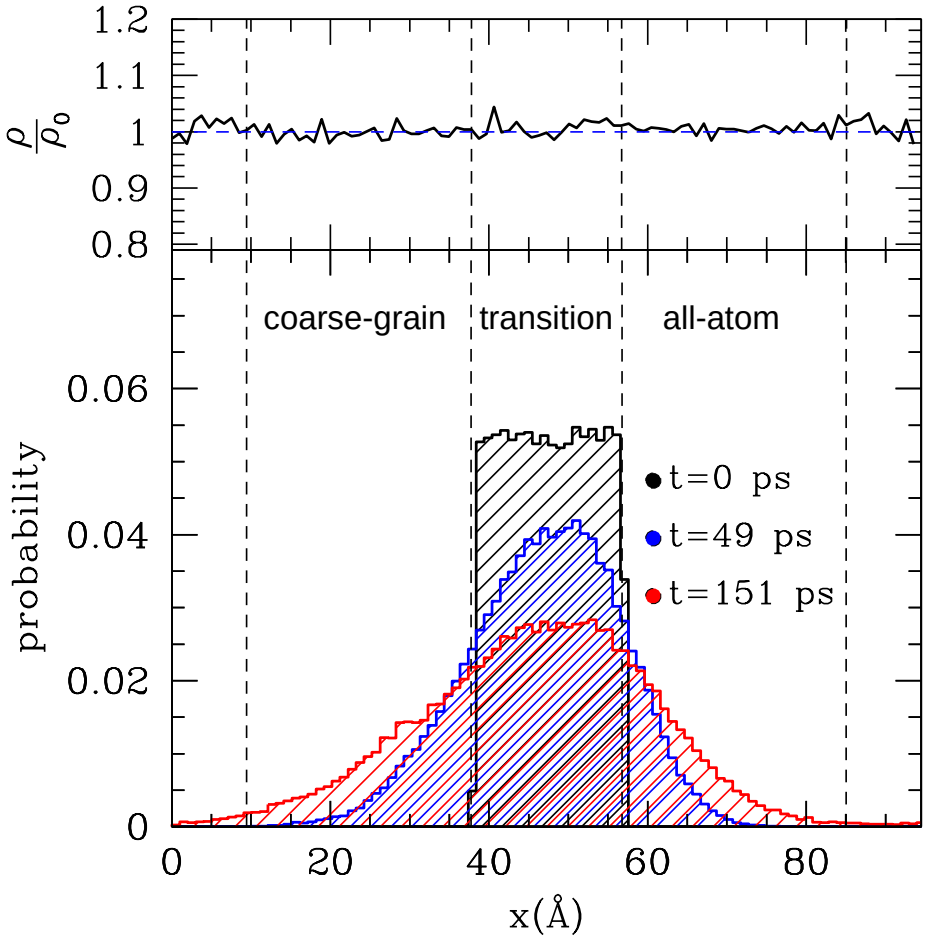
- it is pairwise
- like AdResS it must also be applied with a thermostat

Interface effect of the cg water



The transition regime neutralizes the interface effect of the *c*g water $\Longrightarrow$ the structure of water in the explicit regime is the same as in the bulk.

Diffusion across the transition regime



AdResS: Conclusions

Adaptive Resolution MD simulation:

- Changing resolution is formally equivalent to a phase transition $\longrightarrow$ latent heat.
- For a smooth variation of the resolution we introduce a transition regime.
- The temperature in the transition region can be obtained by extending the equipartition theorem to non-integer dimensions.

Hybrid method AdResS:

- Allows for a dynamical switching of the spatial resolution.
- We treat only as many DOFs as absolutely necessary for the problem considered.
- AdResS was so far applied to MD simulations of a simple tetrahedral liquid, a macromolecule in an explicit solvent, and liquid water at standard conditions.

Future work:

- Application to different soft matter systems and molecular liquids.

Concurrent Triple-Scale Simulation

Motivation:

- to perform MD of **open domains** with relatively large molecules, either in the **grand canonical ensemble** or under **non-equilibrium conditions**.

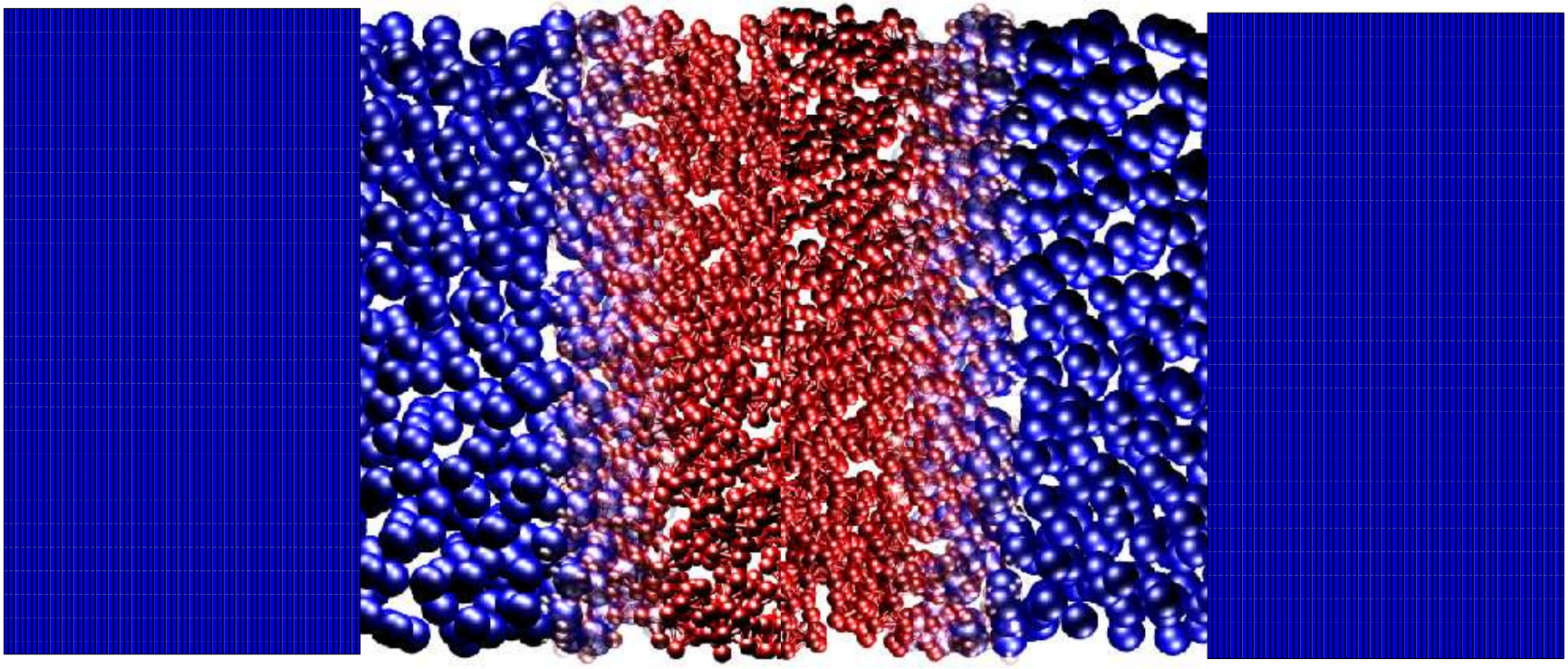
Method: *Triple-scale AdResS-HybridMD scheme*

- 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)**
- covers the **length-scales** ranging from the **micro-** to **macro**-scale
- 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 Model



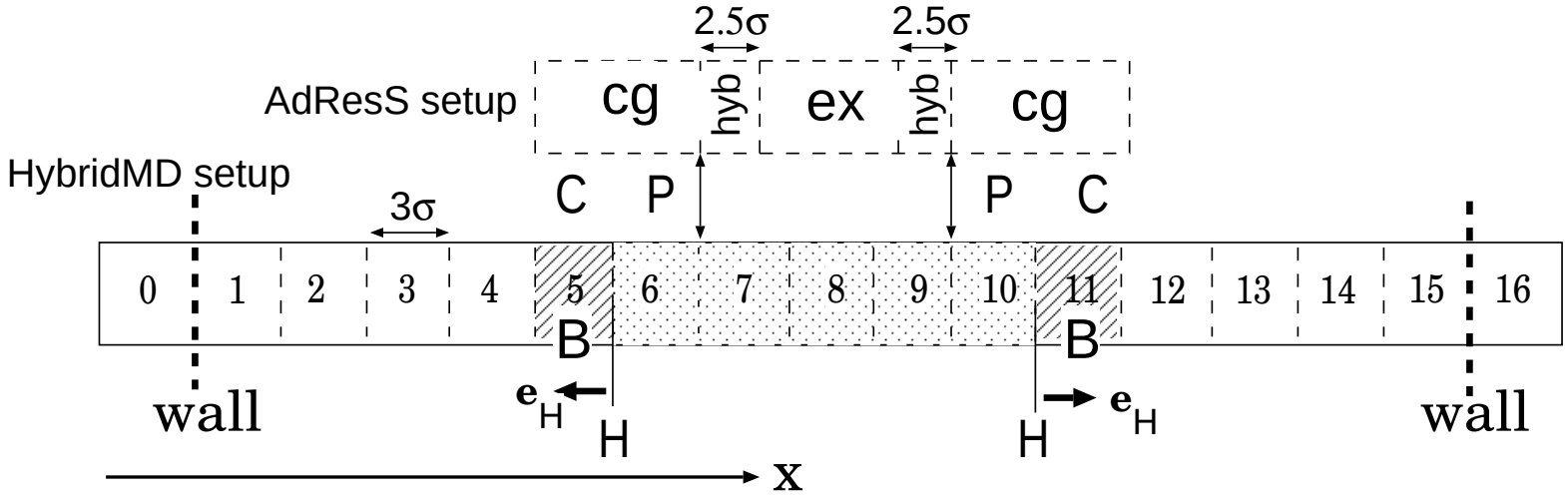
R. Delgado Buscalioni, K. Kremer, MP, J. Chem. Phys. **128**, 114110 (2008).

HybridMD: Coupling Particle-Based and Continuum Descriptions

- 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.

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

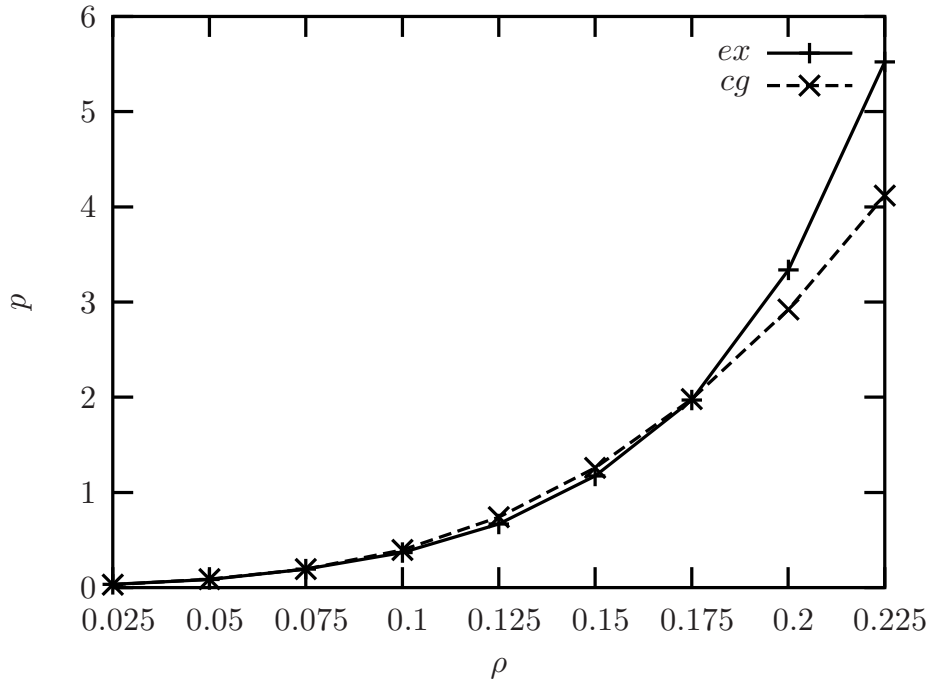
AdResS-HybridMD: Combined Scheme



Domain decomposition of the combined scheme. The top part of the figure shows the location of the fluid model layers (cg, hyb and ex) within the HybridMD setup. The bottom part of the figure shows the set of control cells used in the HybridMD setup.

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

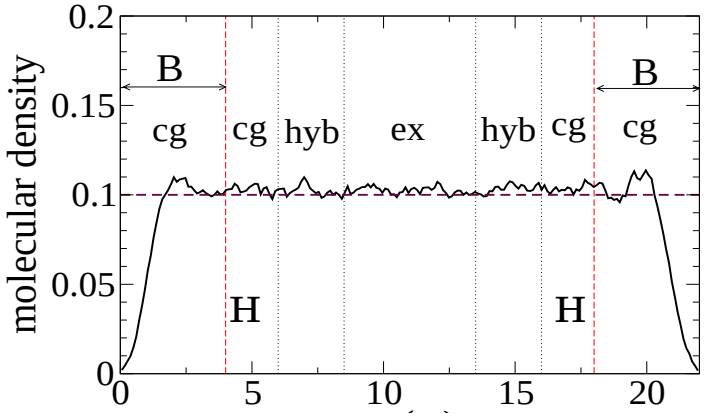
Equation of state

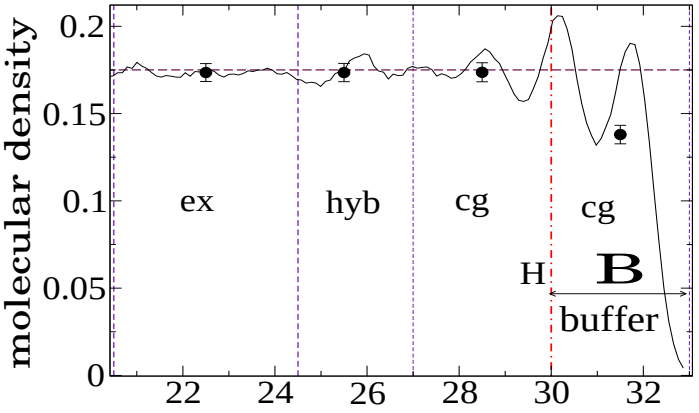


The pressure tensor:

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

Molecular Density Profile

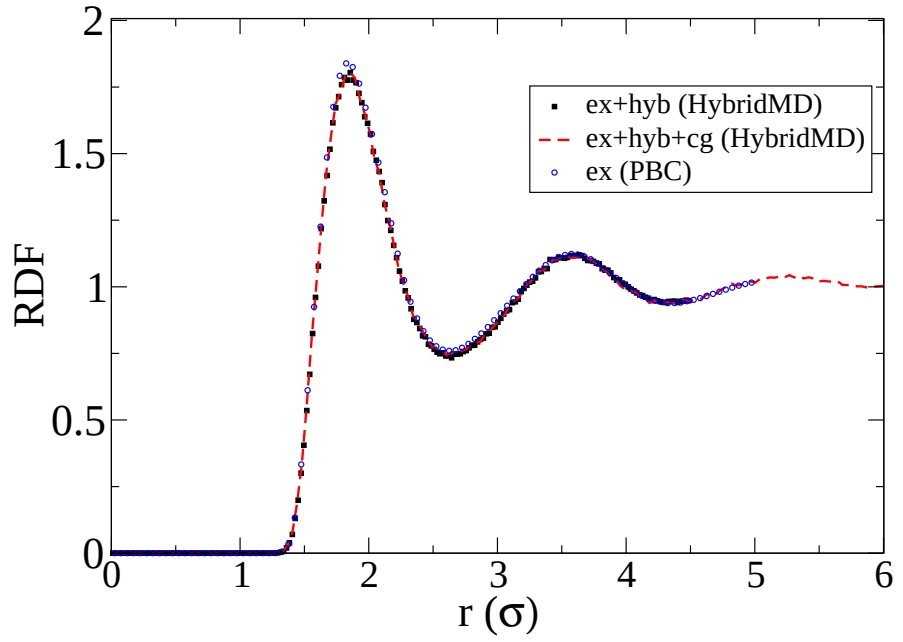




x(σ)

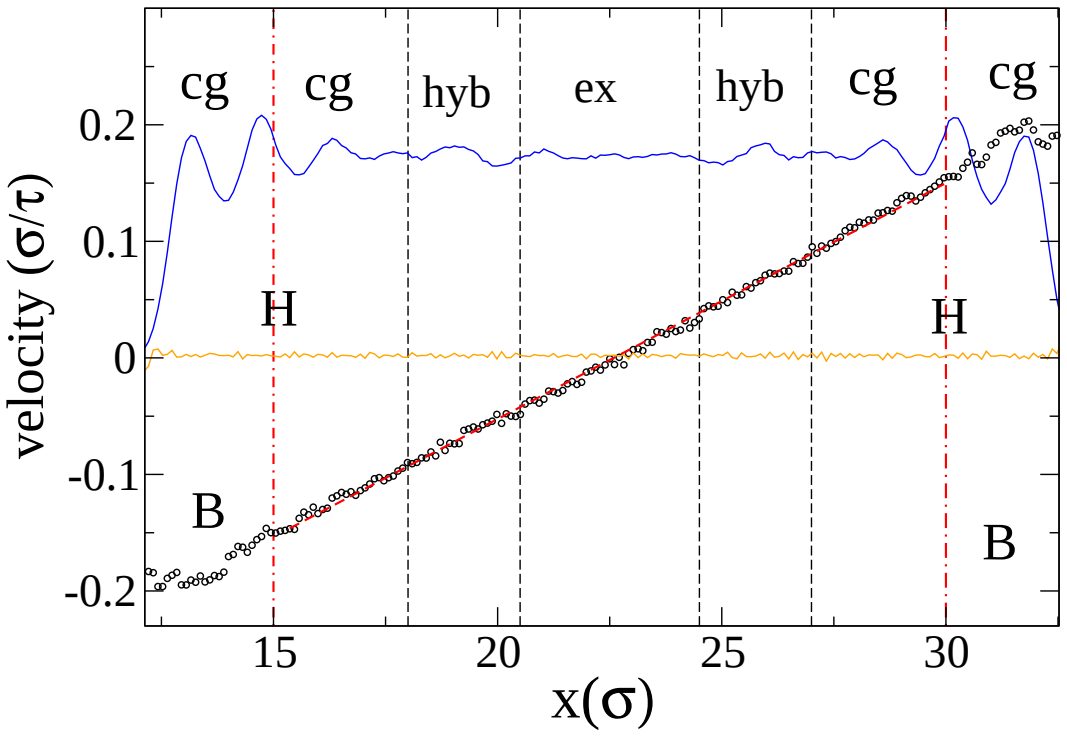
(a) $\rho_m = 0.1\sigma^{-3}$. (b) $\rho_m = 0.175\sigma^{-3}$.

Radial Distribution Functions: Equilibrium



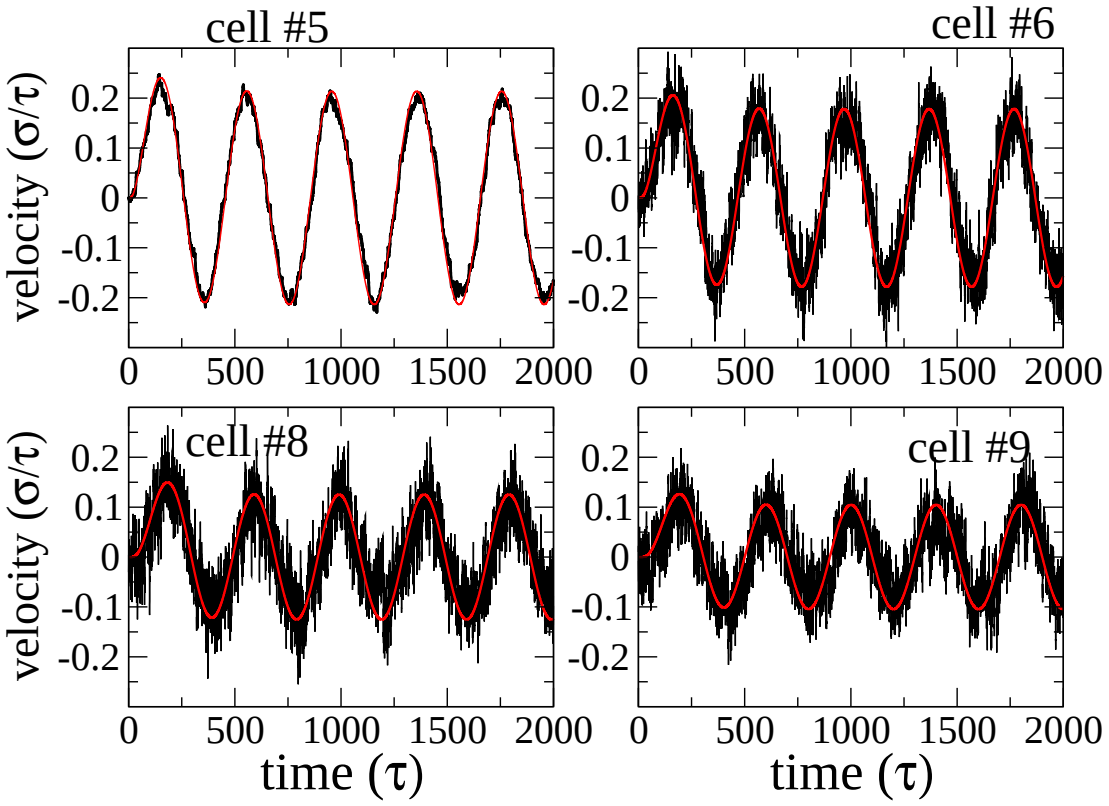
- RDF$_{cm}$s of the liquid in the atomistic and transition domains ($ex + hyb$) and in the total molecular region ($ex + hyb + cg$) of the triple-scale model together with the reference RDF$_{cm}$ of the all-atom system (ex(PBC)) at $\rho = 0.175/\sigma^3$.

Couette Flow



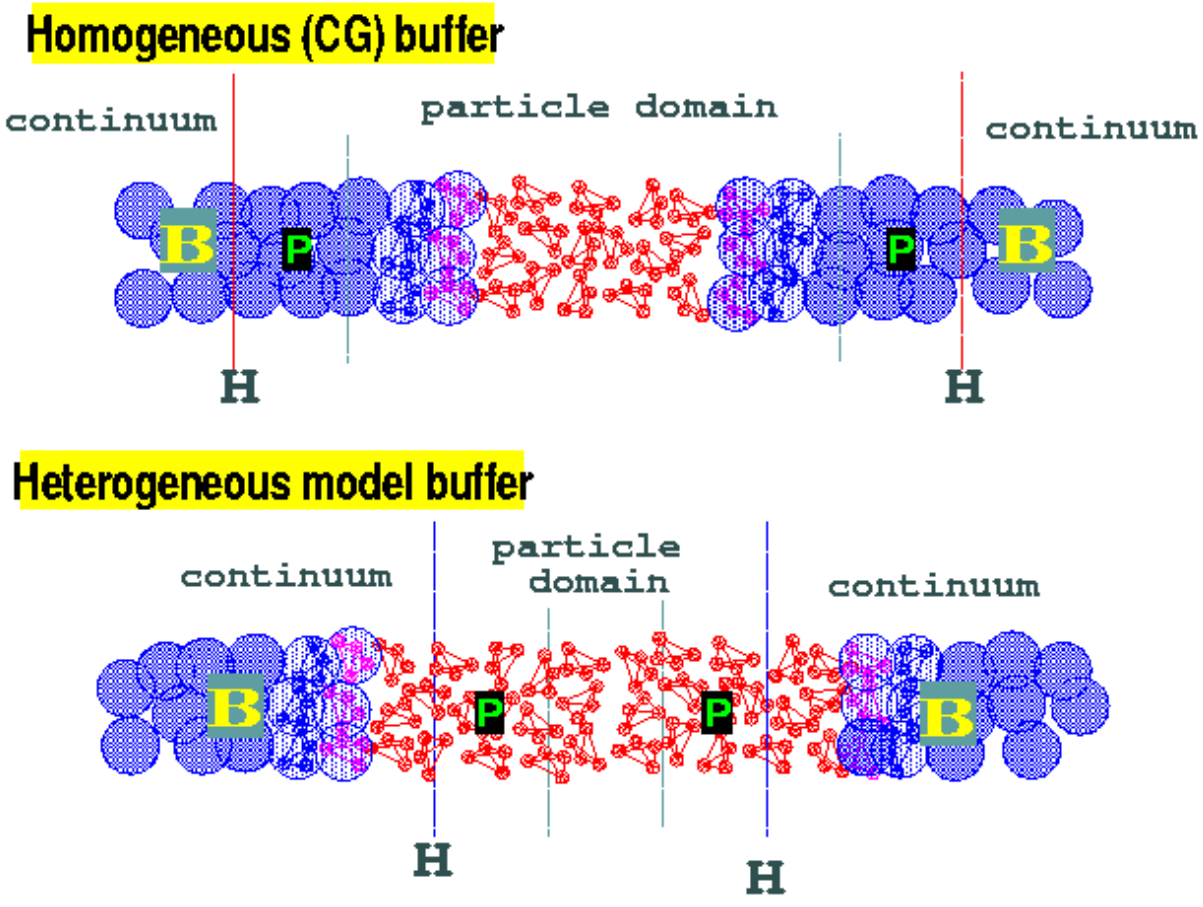
Velocity profile at the particle region of an hybrid simulation of a Couette flow.

Stokes Flow



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

Triple-Scale Simulation: Two Possible Setups

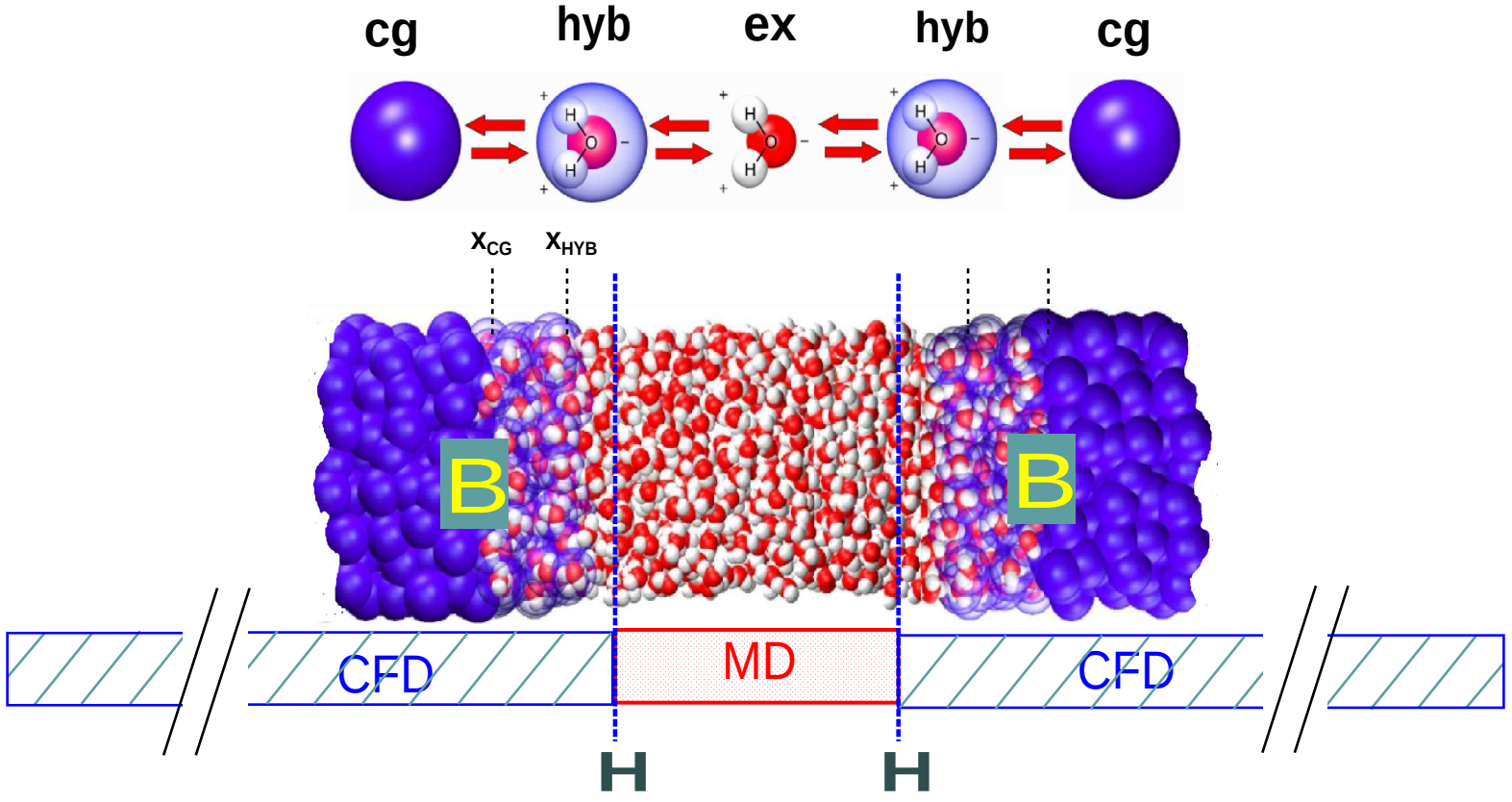


R. Delgado Buscalioni, K. Kremer, MP, J. Chem. Phys. **128**, 114110 (2008).

Buffer: Two Possible Setups

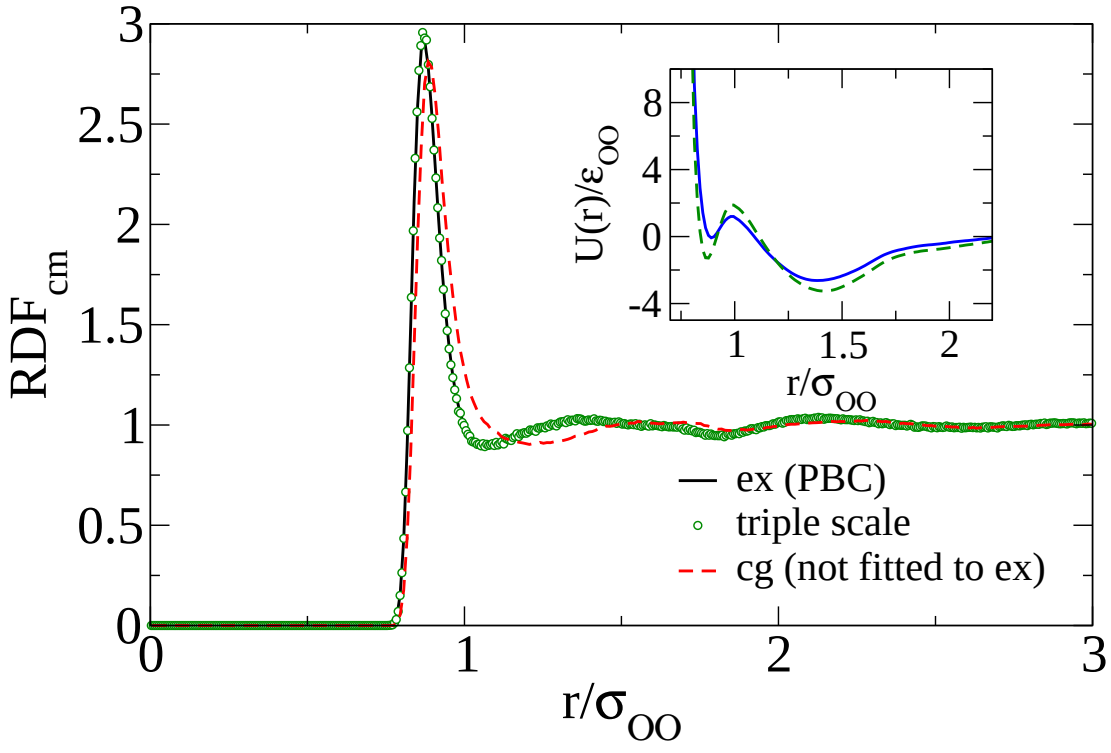
- **Homogeneous buffer:**
  - *pro*: Requires small buffer size.
  - *pro*: Allows us to introduce CG molecular information into the explicit MD region (structure, diffusion rates, etc.)
  - *con*: Requires fine tuning of CG model ,i.e., EOS, viscosity or diffusion coefficient: *Transversal DPD*; C. Junghans, MP, K. Kremer, Soft Matter **4**, 156 (2008).
- **Heterogeneous buffer:**
  - *pro*: All-atom MD region: correct viscosity, EOS, fluctuations.
  - *pro*: Does not requires fine tuning of CG and HYB models.
  - *pro*: Enables energy exchange, as the MD region is fully explicit.
  - *con*: Larger buffer size.

Triple-Scale Simulation: Liquid Water



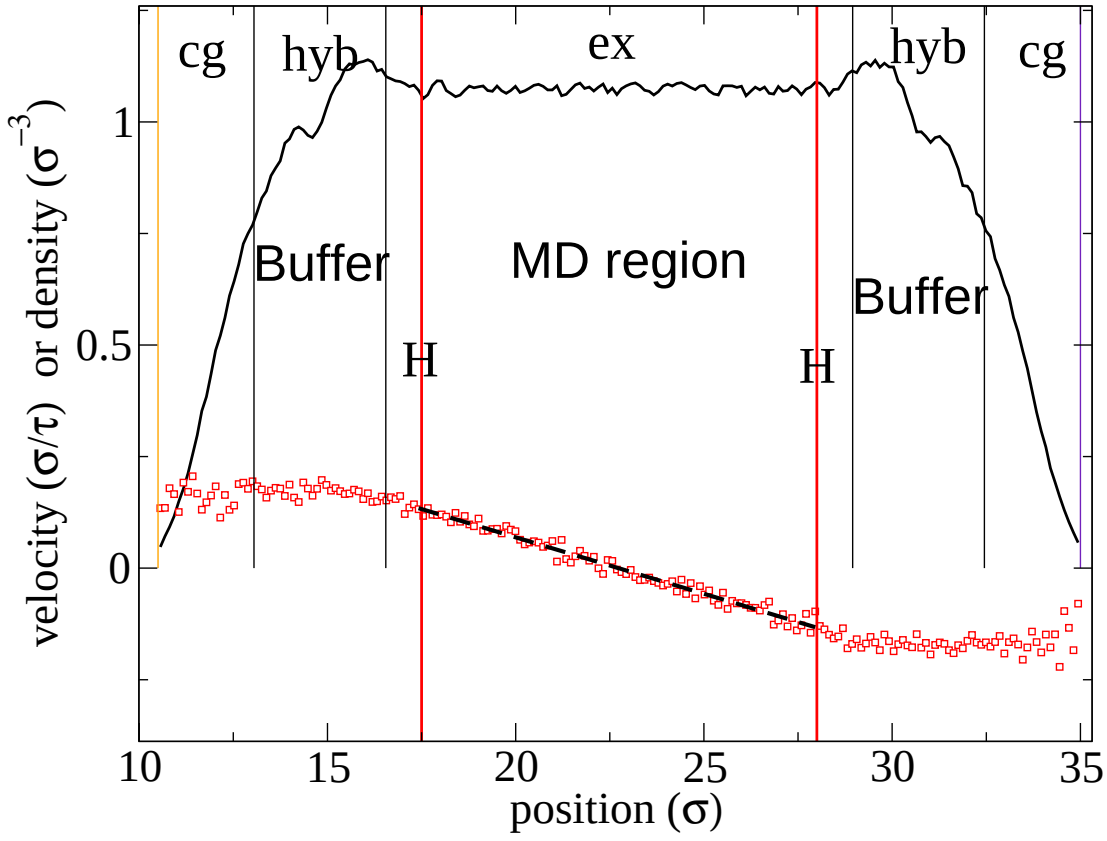
R. Delgado Buscalioni, K. Kremer, MP, submitted.

Coarse-Grained Model



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

Couette Flow: Liquid Water



- Density profile and velocity distribution across the particle domain.

Grand Canonical Ensemble

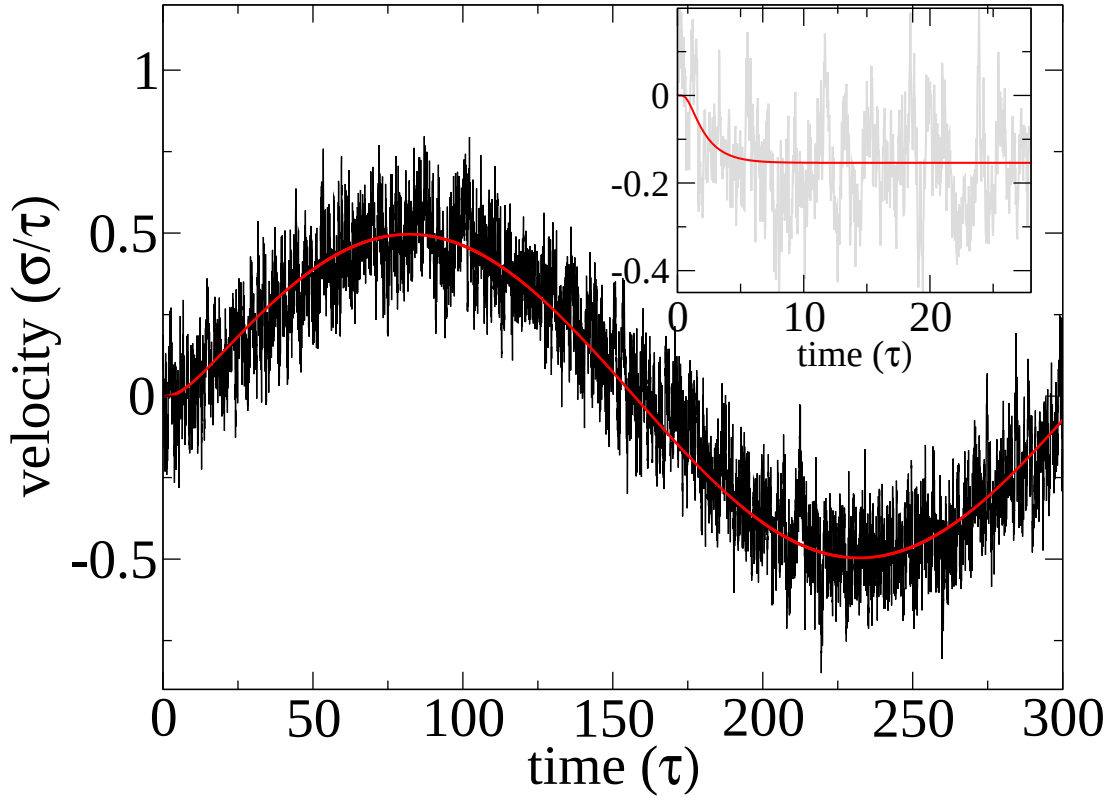
Mass fluctuations

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: $Var[\rho] = 0.011 \pm 0.005$

Oscillatory Shear Flow



- Time evolution of the velocity. For comparison, the deterministic Navier-Stokes solution is shown.

Conclusions

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 triple-scale scheme is **robust** against the details of the mesoscopic model.
- 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.
- Grand canonical molecular simulations involving complex molecules.