Tools for multiscale simulations of liquid matter

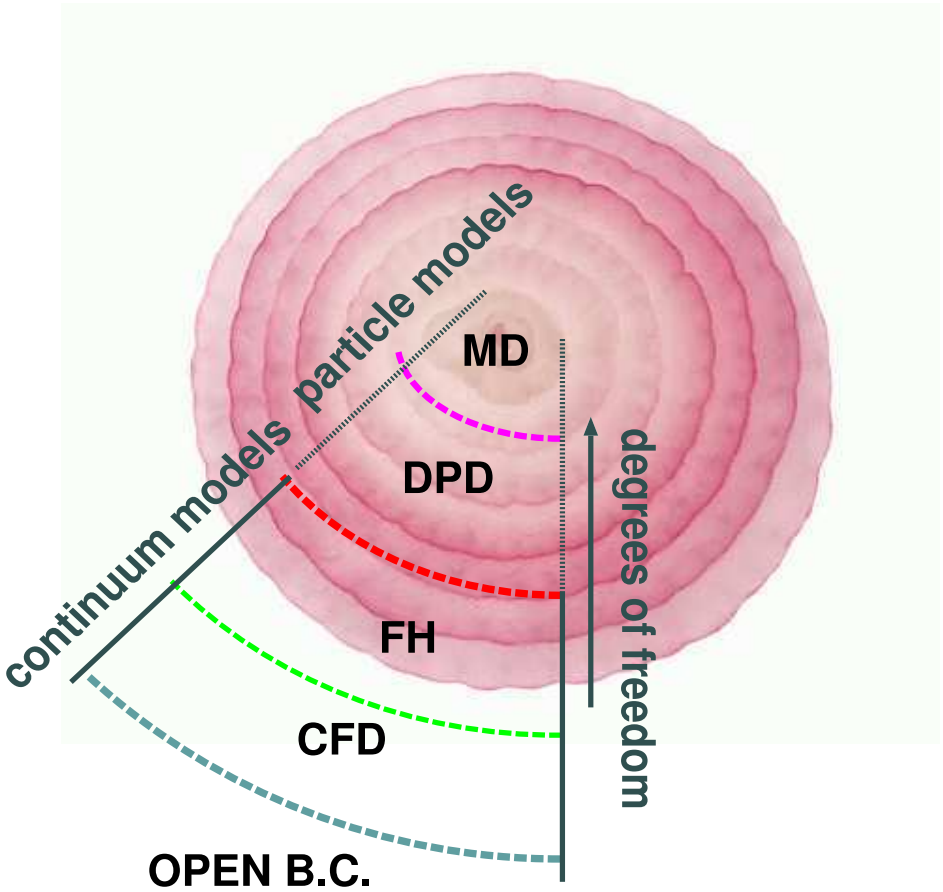
Rafael Delgado-Buscalioni

Universidad Autónoma de Madrid

Banff, December 2009

- Open MD, Hybrid particle-continuum
  - Gianni De Fabritiis (U. Pompeu Fabra, Barcelona)
  - P. Coveney (UCL, London)
  - E. Flekkoy (Oslo Univ.)
- Adaptive resolution
  - Matej Praprotnik (National Inst. Chem. Ljubljana)
  - Kurt Kremer (Max-Plank, Mainz)
- Coarse grained dynamics
  - Pep Español (UNED, Madrid)
  - Eric vanden-Eijnden (Courant Institute, NY)

Interfacing models with different degrees of freedom



Open boundary conditions:
OUTSIDE WORLD
steady state,
thermodynamic reservoir

Some methods for soft matter simulation

Particle methods	Continuum methods
QM = Quantum mechanics **MD** = Molecular dynamics **MC** = Monte Carlo **DPD** = Dissipative Particle Dynamics **DSMC** = Direct simulation Monte Carlo	**CFD** = Computational fluid dynamics **FD** = Finite Differences **SMFD** = Spectral methods **LB** = Lattice Boltzmann **FH** = Fluctuating hydrodynamics **SRD** = Stochastic Rotation Dynamics **MPM** = Mass point method

Multiscale modelling for different states of matter

SOLIDS	QM-MD	PRL **93**, 175503 (2004)
	MD-FD	PRL **87**(8),086104 (2001)
	QM-MD-FD	Abraham
GASES	DSMC-CFD	AMAR [A. Garcia]
	MC-CFD	PRB, **64** 035401.(2001)
MEMBRANES	MD-MPM	Ayton et al. J.Chem.Phys **122**, 244716 (2005)

LIQUIDS

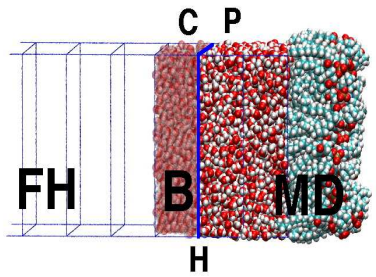
Domain decomposition	MD-CFD, MD-FH	PRL **97**, 134501 (2006)
Eulerian-Lagrangian	MD-LB, MD-FH	Ladd, Dunweg,...
Velocity-Stress coupling	MD-SMFD, MD-FD	
Stochastic Rotation Dynamics	MD-SRD	Malevanets-Kapral
Adaptive Resolution	AdResS	JChemPhys, **123** 224106 (2005)

Multiscale/Hybrid aproaches for complex liquids

Domain decomposition

type A

Molecular detail,
interfases, surfaces,
macromolecule -fluid interaction



shear flows ✓
sound, heat
large molecules
multispecies ✗
electrostatics

Eulerian-Lagrangian Solute-solvent hydrodynamic coupling

Suspensions
of colloids or polymers,
small particles in flow

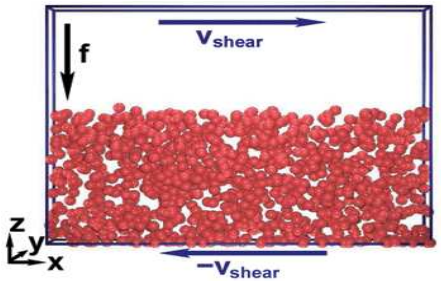


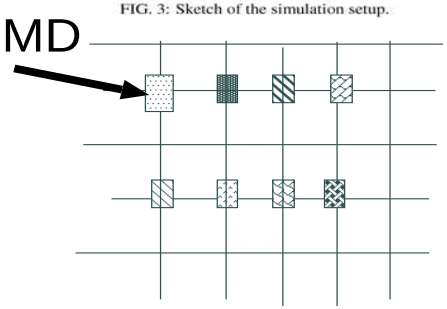
FIG. 3: Sketch of the simulation setup.

Point particle aproximation:
Stokes drag (point particle),
Faxen terms (finite size effects)
Basset memory effects...
Force Coupling
particles of finite size
Direct simulation
Immersed boundaries

Patch dynamics HMM Velocity-Stress coupling

type B

Non-Newtonian fluids
Unknown constitutive relation
polymer mels...



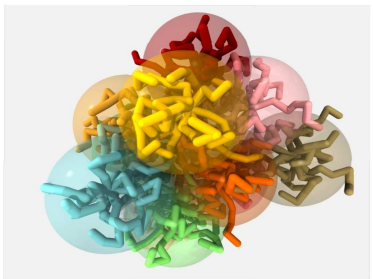
MD nodes used to evaluate the **local stress** for the Continuum solver.

Continuum solver provides the local **velocity gradient** imposed at each MD node.

how to "lift MD" ✗

Coarse-grained dynamics

How to reduce the degrees of freedom and keep the underlying dynamics



diffusion ✓
viscosity
anisotropy ✗
(nematics...)

Imposition of a macroscopic state into a microscopic simulation box

Imposition of a macroscopic state into a microscopic simulation box

Related issues (Patch dynamics): How to "lift" the desired macroscopic state into the microscopic domain.

Also related: Fast equilibration

Imposition of a macroscopic state into a microscopic simulation box

Related issues (Patch dynamics): How to "lift" the desired macroscopic state into the microscopic domain.
Also related: Fast equilibration

- **State coupling**

Imposition of a macroscopic state into a microscopic simulation box

Related issues (Patch dynamics): How to "lift" the desired macroscopic state into the microscopic domain.
Also related: Fast equilibration

- **State coupling**
  - Schwartz iterative method

Imposition of a macroscopic state into a microscopic simulation box

Related issues (Patch dynamics): How to "lift" the desired macroscopic state into the microscopic domain.
Also related: Fast equilibration

- **State coupling**
  - Schwartz iterative method
  - Constrained molecular dynamics (velocity coupling)

Imposition of a macroscopic state into a microscopic simulation box

Related issues (Patch dynamics): How to "lift" the desired macroscopic state into the microscopic domain.
Also related: Fast equilibration

- **State coupling**
  - Schwartz iterative method
  - Constrained molecular dynamics (velocity coupling)
  - DOLLS/SLLOD: Molecular dynamics in the inertial frame

Imposition of a macroscopic state into a microscopic simulation box

Related issues (Patch dynamics): How to "lift" the desired macroscopic state into the microscopic domain.
Also related: Fast equilibration

- **State coupling**
  - Schwartz iterative method
  - Constrained molecular dynamics (velocity coupling)
  - DOLLS/SLLOD: Molecular dynamics in the inertial frame
- **Flux coupling**

Imposition of a macroscopic state into a microscopic simulation box

Related issues (Patch dynamics): How to "lift" the desired macroscopic state into the microscopic domain.
Also related: Fast equilibration

- **State coupling**
  - Schwartz iterative method
  - Constrained molecular dynamics (velocity coupling)
  - DOLLS/SLLOD: Molecular dynamics in the inertial frame
- **Flux coupling**
- **Control algorithms**

Imposition of a macroscopic state into a microscopic simulation box

Related issues (Patch dynamics): How to "lift" the desired macroscopic state into the microscopic domain.
Also related: Fast equilibration

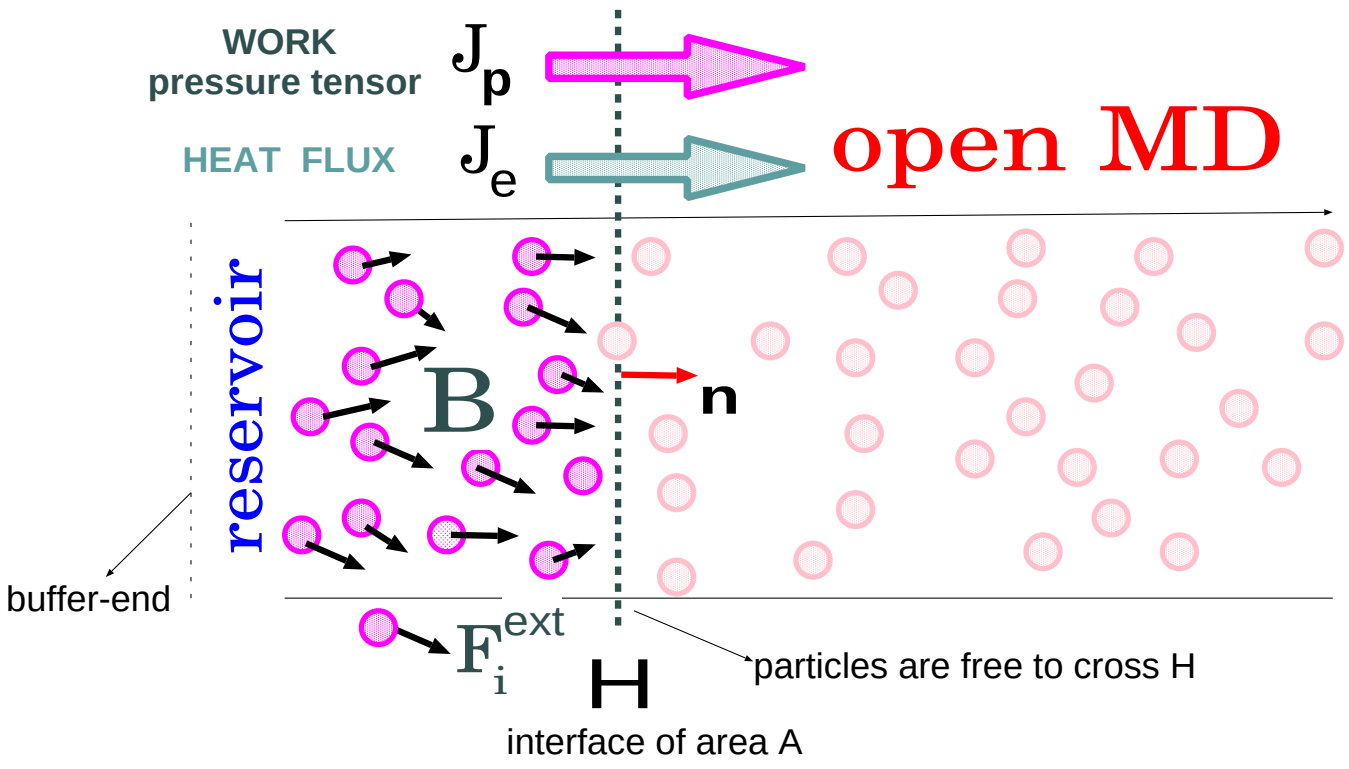
- **State coupling**
  - Schwartz iterative method
  - Constrained molecular dynamics (velocity coupling)
  - DOLLS/SLLOD: Molecular dynamics in the inertial frame
- **Flux coupling**
- **Control algorithms**
  - Density profile

Imposition of a macroscopic state into a microscopic simulation box

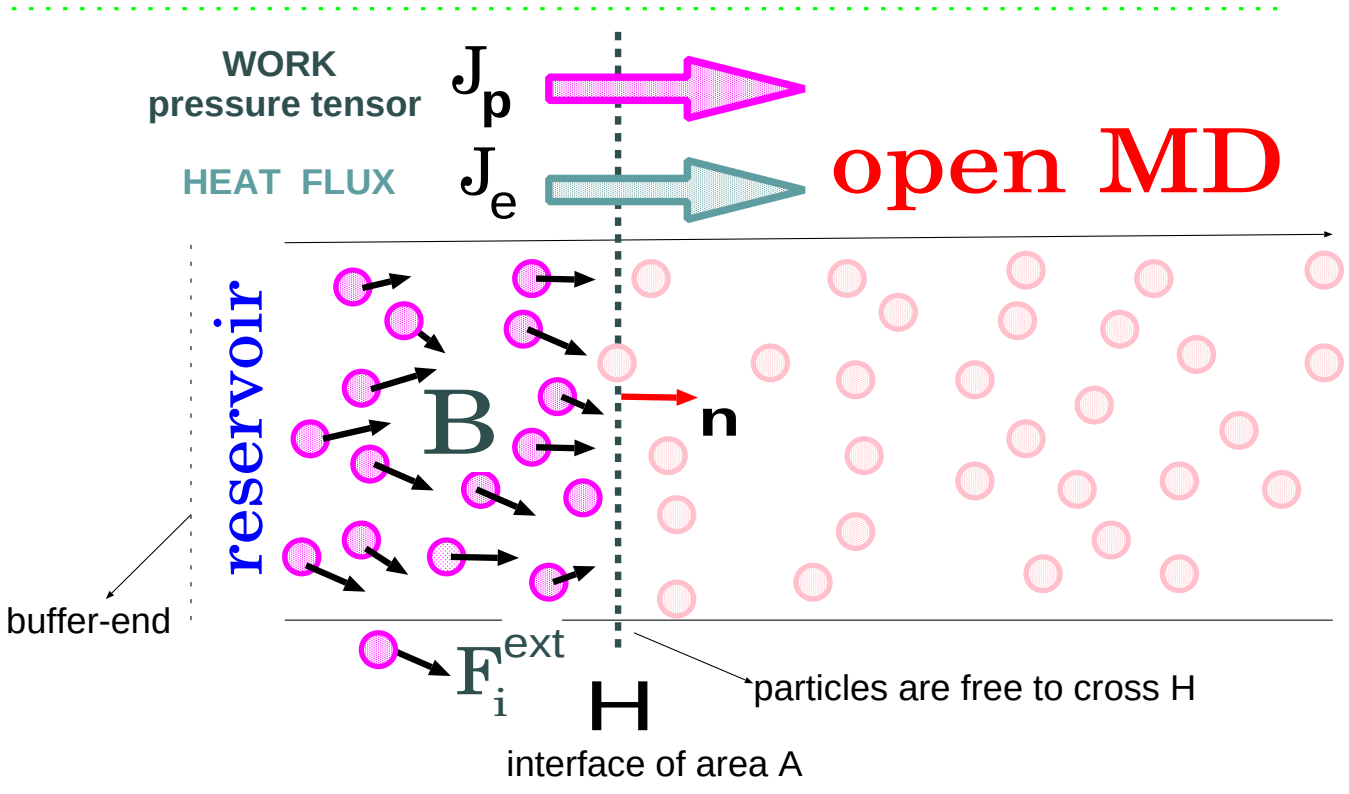
Related issues (Patch dynamics): How to "lift" the desired macroscopic state into the microscopic domain.
Also related: Fast equilibration

- **State coupling**
  - Schwartz iterative method
  - Constrained molecular dynamics (velocity coupling)
  - DOLLS/SLLOD: Molecular dynamics in the inertial frame
- **Flux coupling**
- **Control algorithms**
  - Density profile
  - Mass (particle insertion)

Open MD: flux boundary conditions for molecular dynamics



Open MD: flux boundary conditions for molecular dynamics



$$\mathbf{F}_i^{ext} = \frac{g_i A}{\sum_{i\in B} g_i} \mathbf{J_p} \cdot \mathbf{n} \simeq \frac{A}{N_B} \left(p\,\mathbf{n} + \mathbf{T} \cdot \mathbf{n} \right)$$

p pressure, **T** shear stress tensor.

Open MD
Task to be solved at the buffer

- Mass control: particle insertion/deletion.

Open MD

Task to be solved at the buffer

- Mass control: particle insertion/deletion.
- Density profile: controlled by external force distribution.

Open MD
Task to be solved at the buffer

- Mass control: particle insertion/deletion.
- Density profile: controlled by external force distribution.
- Imposition of momentum and energy flux
  Mass flux across H arises naturally a consequence of the imposed momentum flux.

Open MD
Mass control at the buffer

- The average buffer mass is controlled to a fixed value $\langle M_B \rangle$ by a simple relaxation algorithm:

$$\frac{\Delta M_B}{\Delta t} = \frac{1}{\tau_B} \left(\langle M_B \rangle - M_B \right)$$

  with $\tau_B \simeq [10 - 100] fs$ (faster than any hydrodynamic time).
- Particle deletion/insertion
  - `Delete particle if` : $\Delta M_B < 0$ or if it crosses the buffer-end.
  - `Insert particle if` : $\Delta M_B > 0$
    USHER algorithm [J. Chem. Phys, **119**, 978 (2003)]

Open MD
Mass control at the buffer
Particle insertion by the USHER algorithm

J. Chem. Phys **119**, 978 (2003) for Lennard-Jones fluids
J. Chem. Phys. **121**, 12139 (2004) for water

- Insert a new molecule at target potential energy E_T (usually $E_T = e(\rho, T)$ mean energy per particle)

Open MD
Mass control at the buffer
Particle insertion by the USHER algorithm

J. Chem. Phys **119**, 978 (2003) for Lennard-Jones fluids
J. Chem. Phys. **121**, 12139 (2004) for water

- Insert a new molecule at target potential energy E_T (usually $E_T = e(\rho, T)$ mean energy per particle)
- Easy to implement Based on a modified Newton-Raphson method in the potential energy landscape.

Open MD
Mass control at the buffer
Particle insertion by the USHER algorithm

J. Chem. Phys **119**, 978 (2003) for Lennard-Jones fluids
J. Chem. Phys. **121**, 12139 (2004) for water

- Insert a new molecule at target potential energy E_T (usually $E_T = e(\rho, T)$ mean energy per particle)
- Easy to implement Based on a modified Newton-Raphson method in the potential energy landscape.
- Thermodynamic control: local ENERGY, TEMPERATURE and PRESSURE are kept at the proper equation of state.

Open MD
Mass control at the buffer
Particle insertion by the USHER algorithm

J. Chem. Phys **119**, 978 (2003) for Lennard-Jones fluids
J. Chem. Phys. **121**, 12139 (2004) for water

- Insert a new molecule at target potential energy E_T (usually $E_T = e(\rho, T)$ mean energy per particle)
- Easy to implement Based on a modified Newton-Raphson method in the potential energy landscape.
- Thermodynamic control: local ENERGY, TEMPERATURE and PRESSURE are kept at the proper equation of state.
- Negligible insertion cost $< 1\%$ total CPU (LJ), $\sim 3\%$ (water).

Open MD
Mass control at the buffer
Particle insertion by the USHER algorithm

J. Chem. Phys **119**, 978 (2003) for Lennard-Jones fluids
J. Chem. Phys. **121**, 12139 (2004) for water

- Insert a new molecule at target potential energy E_T (usually $E_T = e(\rho, T)$ mean energy per particle)
- Easy to implement Based on a modified Newton-Raphson method in the potential energy landscape.
- Thermodynamic control: local ENERGY, TEMPERATURE and PRESSURE are kept at the proper equation of state.
- Negligible insertion cost $< 1\%$ total CPU (LJ), $\sim 3\%$ (water).
- Very fast: water into water at low energy ($E_T = e$) requires 100 iterations (10^5 fater than random insertion)

Open MD
Density profile at the buffer

- The external force on a molecule i in the buffer:

$$\mathbf{f}_i^{ext} = \frac{g(x_i)}{\sum_{i\in B} g(x_i)}\mathbf{F}^{ext} \quad (\text{with } \mathbf{F}^{ext} = A_H \mathbf{J}_H \cdot \mathbf{e}_H)$$

Open MD
Density profile at the buffer

- The external force on a molecule i in the buffer:

$$\mathbf{f}_i^{ext} = \frac{g(x_i)}{\sum_{i\in B} g(x_i)}\mathbf{F}^{ext} \quad (\text{with } \mathbf{F}^{ext} = A_H \mathbf{J}_H \cdot \mathbf{e}_H)$$

- The buffer density profile is controlled by the force distribution $g(x)$.

Open MD
Density profile at the buffer

- The external force on a molecule i in the buffer:

$$\mathbf{f}_i^{ext} = \frac{g(x_i)}{\sum_{i\in B} g(x_i)}\mathbf{F}^{ext} \quad (\text{with } \mathbf{F}^{ext} = A_H \mathbf{J}_H \cdot \mathbf{e}_H)$$

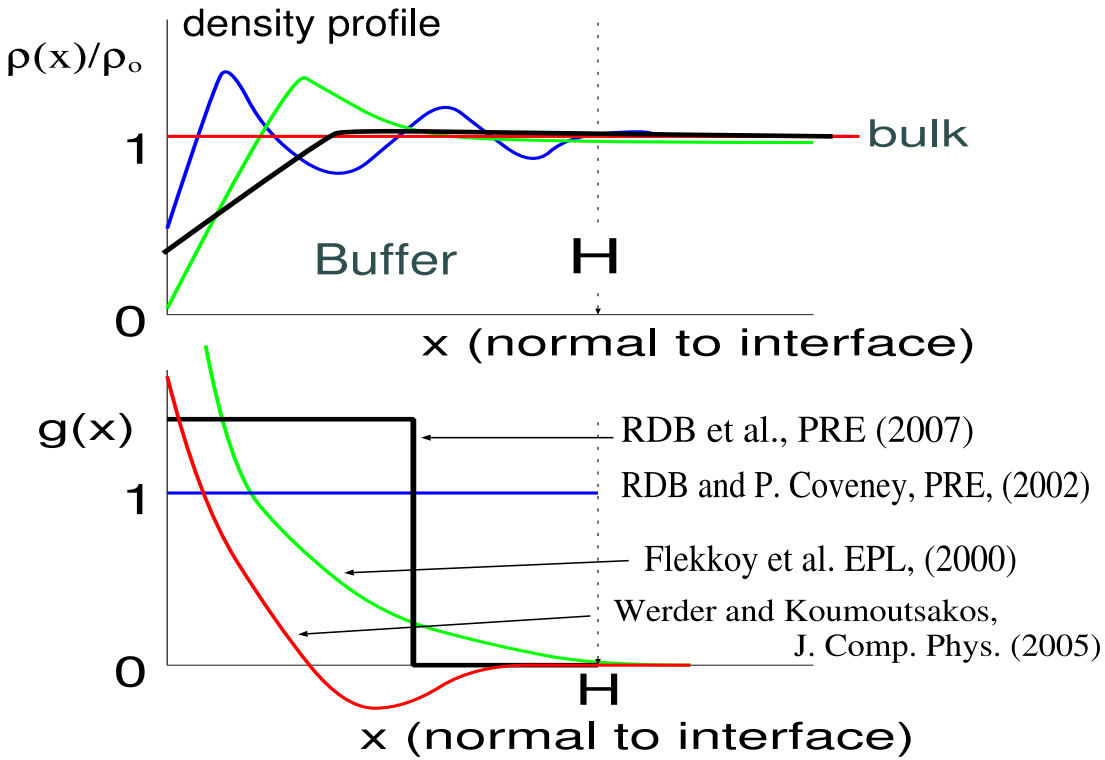
- The buffer density profile is controlled by the force distribution $g(x)$.

Open MD
Density profile at the buffer

- The external force on a molecule i in the buffer:

$$\mathbf{f}_i^{ext} = \frac{g(x_i)}{\sum_{i\in B} g(x_i)} \mathbf{F}^{ext} \quad (\text{with } \mathbf{F}^{ext} = A_H \mathbf{J}_H \cdot \mathbf{e}_H)$$

- The buffer density profile is controlled by the force distribution $g(x)$.



Open MD

Imposition of momentum and energy flux

Flekkoy, RDB, Coveney, PRE **72**, 026703 (2005)

Impose:

Open MD

Imposition of momentum and energy flux

Flekkoy, RDB, Coveney, PRE **72**, 026703 (2005)

Impose: momentum flux $\mathbf{J_p}$

Open MD

Imposition of momentum and energy flux

Flekkoy, RDB, Coveney, PRE **72**, 026703 (2005)

Impose: momentum flux $\mathbf{J_p}$ and energy flux J_e across H

Open MD

Imposition of momentum and energy flux

Flekkoy, RDB, Coveney, PRE **72**, 026703 (2005)

Impose: momentum flux $\mathbf{J_p}$ and energy flux J_e across H
Over Δt

Open MD

Imposition of momentum and energy flux

Flekkoy, RDB, Coveney, PRE **72**, 026703 (2005)

Impose: momentum flux $\mathbf{J_p}$ and energy flux J_e across H

Over Δt

$$\mathbf{J_p} A \Delta t = \sum_{i \in B} \mathbf{F}_i^{ext} \Delta t + \sum_{i'} \Delta(m \mathbf{v}_{i'})$$

$$\underbrace{J_e A \Delta t}_{\text{Total input}} = \underbrace{\sum_{i \in B} \mathbf{F}_i^{ext} \cdot \mathbf{v}_i \Delta t}_{\text{External force}} + \underbrace{\sum_{i'} \Delta \epsilon_{i'}}_{\text{Particle insertion/removal}}$$

Open MD

Imposition of momentum and energy flux

Flekkoy, RDB, Coveney, PRE **72**, 026703 (2005)

Impose: momentum flux $\mathbf{J_p}$ and energy flux J_e across H

Over Δt

$$\mathbf{J_p} A \Delta t = \sum_{i \in B} \mathbf{F}_i^{ext} \Delta t + \sum_{i'} \Delta(m \mathbf{v}_{i'})$$

$$\underbrace{J_e A \Delta t}_{\text{Total input}} = \underbrace{\sum_{i \in B} \mathbf{F}_i^{ext} \cdot \mathbf{v}_i \Delta t}_{\text{External force}} + \underbrace{\sum_{i'} \Delta \epsilon_{i'}}_{\text{Particle insertion/removal}}$$

External force: $\mathbf{F}_i^{ext} = \langle \mathbf{F}_i^{ext} \rangle + \tilde{\mathbf{F}}_i^{ext}$ (particle $i \in B$)

Open MD

Imposition of momentum and energy flux

Flekkoy, RDB, Coveney, PRE **72**, 026703 (2005)

Impose: momentum flux $\mathbf{J_p}$ and energy flux J_e across H

Over Δt

$$\mathbf{J_p} A \Delta t = \sum_{i\in B} \mathbf{F}_i^{ext} \Delta t + \sum_{i'} \Delta(m\mathbf{v}_{i'})$$

$$\underbrace{J_e A \Delta t}_{\text{Total input}} = \underbrace{\sum_{i\in B} \mathbf{F}_i^{ext} \cdot \mathbf{v}_i \Delta t}_{\text{External force}} + \underbrace{\sum_{i'} \Delta\epsilon_{i'}}_{\text{Particle insertion/removal}}$$

External force: $\mathbf{F}_i^{ext} = \langle \mathbf{F}_i^{ext} \rangle + \tilde{\mathbf{F}}_i^{ext}$ (particle $i \in B$)

Momentum introduced by the mean external force $\langle \mathbf{F}_i \rangle$

$$\langle \mathbf{F}^{ext} \rangle = \frac{A}{N_B} \tilde{\mathbf{j}}_p \quad \text{where } \tilde{\mathbf{j}}_p \equiv \mathbf{J_p} - \frac{\sum_{i'} \Delta(m\mathbf{v}_{i'})}{A\, dt} \ .$$

Open MD

Imposition of momentum and energy flux

Flekkoy, RDB, Coveney, PRE **72**, 026703 (2005)

Impose: momentum flux $\mathbf{J_p}$ and energy flux J_e across H

Over Δt

$$\mathbf{J_p} A \Delta t = \sum_{i\in B} \mathbf{F}_i^{ext} \Delta t + \sum_{i'} \Delta(m\mathbf{v}_{i'})$$

$$\underbrace{J_e A \Delta t}_{\text{Total input}} = \underbrace{\sum_{i\in B} \mathbf{F}_i^{ext} \cdot \mathbf{v}_i \Delta t}_{\text{External force}} + \underbrace{\sum_{i'} \Delta\epsilon_{i'}}_{\text{Particle insertion/removal}}$$

External force: $\mathbf{F}_i^{ext} = \langle \mathbf{F}_i^{ext} \rangle + \tilde{\mathbf{F}}_i^{ext}$ (particle $i \in B$)

Momentum introduced by the mean external force $\langle \mathbf{F}_i \rangle$

$$\langle \mathbf{F}^{ext} \rangle = \frac{A}{N_B} \tilde{\mathbf{j}}_p \quad \text{where } \tilde{\mathbf{j}}_p \equiv \mathbf{J_p} - \frac{\sum_{i'} \Delta(m\mathbf{v}_{i'})}{A\, dt} \ .$$

Energy introduced via dissipative work of the fluctuating forces $\tilde{\mathbf{F}}_i^{ext}$

$$\tilde{\mathbf{F}}_i^{ext} = \frac{A\mathbf{v}_i'}{\sum_{i=1}^{N_B} \mathbf{v}_i'^2} \left[\tilde{j}_e - \tilde{\mathbf{j}}_p \cdot \langle \mathbf{v} \rangle \right] \quad \text{with } \tilde{j}_e \equiv J_e - \frac{\sum_{i'} \Delta\epsilon_{i'}}{A dt}.$$

Open MD

Imposition of momentum and energy flux

Flekkoy, RDB, Coveney, PRE **72**, 026703 (2005)

Impose: momentum flux $\mathbf{J_p}$ and energy flux J_e across H

Over Δt

$$\mathbf{J_p} A \Delta t = \sum_{i\in B} \mathbf{F}_i^{ext} \Delta t + \sum_{i'} \Delta(m\mathbf{v}_{i'})$$

$$\underbrace{J_e A \Delta t}_{\text{Total input}} = \underbrace{\sum_{i\in B} \mathbf{F}_i^{ext} \cdot \mathbf{v}_i \Delta t}_{\text{External force}} + \underbrace{\sum_{i'} \Delta\epsilon_{i'}}_{\text{Particle insertion/removal}}$$

External force: $\mathbf{F}_i^{ext} = \langle \mathbf{F}_i^{ext} \rangle + \tilde{\mathbf{F}}_i^{ext}$ (particle $i \in B$)

Momentum introduced by the mean external force $\langle \mathbf{F}_i \rangle$

$$\langle \mathbf{F}^{ext} \rangle = \frac{A}{N_B} \tilde{\mathbf{j}}_p \quad \text{where } \tilde{\mathbf{j}}_p \equiv \mathbf{J_p} - \frac{\sum_{i'} \Delta(m\mathbf{v}_{i'})}{A\, dt} \ .$$

Energy introduced via dissipative work of the fluctuating forces $\tilde{\mathbf{F}}_i^{ext}$

$$\tilde{\mathbf{F}}_i^{ext} = \frac{A\mathbf{v}_i'}{\sum_{i=1}^{N_B} \mathbf{v}_i'^2} \left[\tilde{j}_e - \tilde{\mathbf{j}}_p \cdot \langle \mathbf{v} \rangle \right] \quad \text{with } \tilde{j}_e \equiv J_e - \frac{\sum_{i'} \Delta\epsilon_{i'}}{A dt}.$$

Mass flux across H arises naturally from momentum flux

Open MD

Imposition of momentum and energy flux

Flekkoy, RDB, Coveney, PRE **72**, 026703 (2005)

Impose: momentum flux $\mathbf{J_p}$ and energy flux J_e across H

Over Δt

$$\mathbf{J_p} A \Delta t = \sum_{i\in B} \mathbf{F}_i^{ext} \Delta t + \sum_{i'} \Delta(m\mathbf{v}_{i'})$$

$$\underbrace{J_e A \Delta t}_{\text{Total input}} = \underbrace{\sum_{i\in B} \mathbf{F}_i^{ext} \cdot \mathbf{v}_i \Delta t}_{\text{External force}} + \underbrace{\sum_{i'} \Delta\epsilon_{i'}}_{\text{Particle insertion/removal}}$$

External force: $\mathbf{F}_i^{ext} = \langle \mathbf{F}_i^{ext} \rangle + \tilde{\mathbf{F}}_i^{ext}$ (particle $i \in B$)

Momentum introduced by the mean external force $\langle \mathbf{F}_i \rangle$

$$\langle \mathbf{F}^{ext} \rangle = \frac{A}{N_B} \tilde{\mathbf{j}}_p \quad \text{where } \tilde{\mathbf{j}}_p \equiv \mathbf{J_p} - \frac{\sum_{i'} \Delta(m\mathbf{v}_{i'})}{A\, dt} \ .$$

Energy introduced via dissipative work of the fluctuating forces $\tilde{\mathbf{F}}_i^{ext}$

$$\tilde{\mathbf{F}}_i^{ext} = \frac{A\mathbf{v}_i'}{\sum_{i=1}^{N_B} \mathbf{v}_i'^2} \left[\tilde{j}_e - \tilde{\mathbf{j}}_p \cdot \langle \mathbf{v} \rangle \right] \quad \text{with } \tilde{j}_e \equiv J_e - \frac{\sum_{i'} \Delta\epsilon_{i'}}{A dt}.$$

Mass flux across H arises naturally from momentum flux

Respects second law

Open MD: Molecular dynamics at different ensembles

- The amount of HEAT and WORK done into the MD system is exactly controlled

Open MD: Molecular dynamics at different ensembles

- The amount of HEAT and WORK done into the MD system is exactly controlled
- The system comunicates with the exterior at its boundaries, like a real system.

Open MD: Molecular dynamics at different ensembles

- The amount of HEAT and WORK done into the MD system is exactly controlled
- The system comunicates with the exterior at its boundaries, like a real system.

Open MD: Molecular dynamics at different ensembles

- The amount of HEAT and WORK done into the MD system is exactly controlled
- The system comunicates with the exterior at its boundaries, like a real system.

Possible MD-ensembles

Open MD: Molecular dynamics at different ensembles

- The amount of HEAT and WORK done into the MD system is exactly controlled
- The system comunicates with the exterior at its boundaries, like a real system.

Possible MD-ensembles

Grand canonical

μ_BVT

Open MD: Molecular dynamics at different ensembles

- The amount of HEAT and WORK done into the MD system is exactly controlled
- The system comunicates with the exterior at its boundaries, like a real system.

Possible MD-ensembles

Grand canonical

μ_BVT

Isobaric ensemble

$\mathbf{J_p} = P\hat{\mathbf{n}}.$

Open MD: Molecular dynamics at different ensembles

- The amount of HEAT and WORK done into the MD system is exactly controlled
- The system comunicates with the exterior at its boundaries, like a real system.

Possible MD-ensembles

Grand canonical

μ_BVT

Isobaric ensemble

$\mathbf{J_p} = P\hat{\mathbf{n}}.$

Constant enthalpy

$\mathbf{J}_e = M\langle \mathbf{v} \rangle \cdot F = -p\Delta V$

$\Delta N = 0$

$\Delta E + p\Delta V = \Delta H = 0$

Open MD: Molecular dynamics at different ensembles

- The amount of HEAT and WORK done into the MD system is exactly controlled
- The system comunicates with the exterior at its boundaries, like a real system.

Possible MD-ensembles

Grand canonical

$$\mu_B \mathrm{VT}$$

Isobaric ensemble

$$\mathbf{J_p} = P\hat{\mathbf{n}}.$$

Constant enthalpy

$$\mathbf{J}_e = M\langle \mathbf{v} \rangle \cdot F = -p\Delta V$$
$$\Delta N = 0$$
$$\Delta E + p\Delta V = \Delta H = 0$$

Constant heat flux, Q

$$\mathbf{J}_e = Q$$

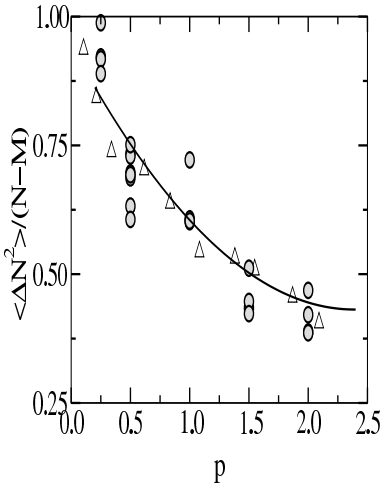
Open MD: Mass fluctuations at grand canonical ensemble

$$\texttt{Var}[\rho] = k_B T \rho / (V c_T^2) \text{ with } c_T^2 = (\partial p / \partial \rho)_T$$

Flux particle BC´s are thermodynamically consistent

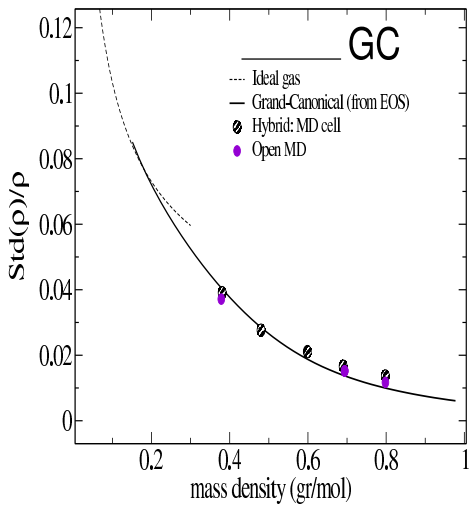
with the Grand Canonical ensemble

Soft-particles
DPD-like



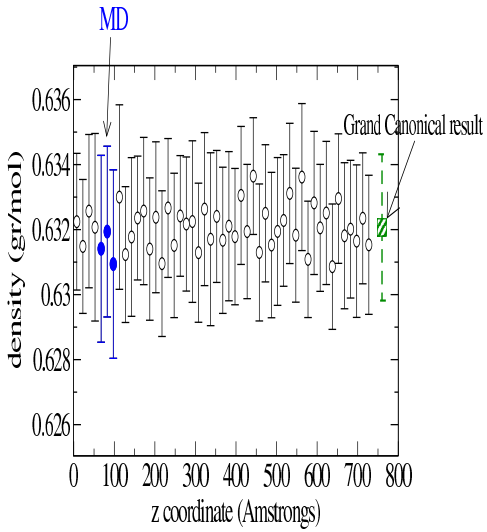
pressure

Liquid argon



density

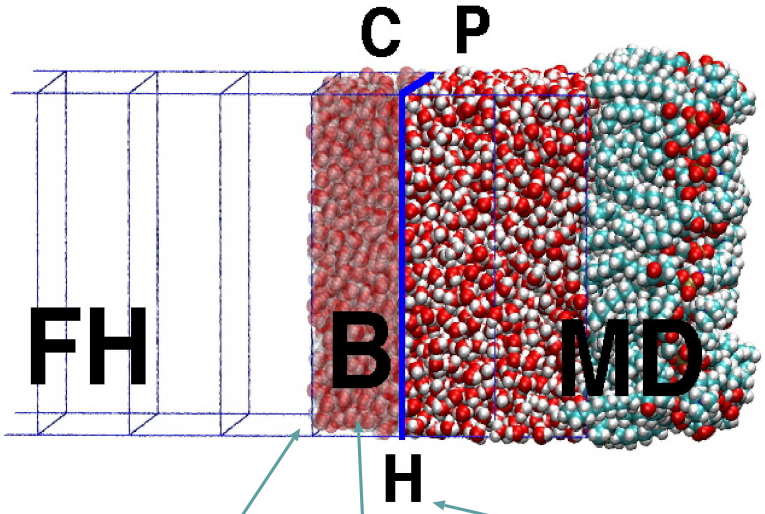
Water (T=300 K)



cell-coordinate

Hybrid particle-continuum dynamics

Coupling molecular dynamics (MD)
and fluctuating hydrodynamics (FH)
General issues concerning particle-continuum coupling



Information exchanged
variables / fluxes

Time dependence
Steady / Unsteady

Fluctuations
Deterministic CFD or
Fluctuating Hydrodynamics (**FH**)

End of particles box
open / closed

Particle buffer B
Maxwell daemons or
External forces

Continuity at interface H
- imposed to P / imposed to C
- continuity in fluctuations

Continuum fluid dynamics

- Conservation law $\partial\Phi/\partial t = -\boldsymbol{\nabla}\cdot\mathbf{J}^{\phi}$

Continuum fluid dynamics

- Conservation law $\partial\Phi/\partial t = -\boldsymbol{\nabla}\cdot\mathbf{J}^{\phi}$

mass	$\Phi = \rho$	$\mathbf{J}^{\rho} = \rho\mathbf{u}$
momentum	$\Phi = \boldsymbol{g} \equiv \rho\mathbf{u}(\mathbf{r},\mathbf{t})$	$\mathbf{J}^{\boldsymbol{g}} = \rho\mathbf{u}\mathbf{u} + \boldsymbol{P}$
energy	ρe	$\mathbf{J}^{e} = \rho\mathbf{u}e + \boldsymbol{P}:\mathbf{u} + \boldsymbol{Q}$

Continuum fluid dynamics

- Conservation law $\partial\Phi/\partial t = -\boldsymbol{\nabla}\cdot\mathbf{J}^{\phi}$

mass	$\Phi = \rho$	$\mathbf{J}^{\rho} = \rho\mathbf{u}$
momentum	$\Phi = \boldsymbol{g} \equiv \rho\mathbf{u}(\mathbf{r},\mathbf{t})$	$\mathbf{J}^{\boldsymbol{g}} = \rho\mathbf{u}\mathbf{u} + \boldsymbol{P}$
energy	ρe	$\mathbf{J}^{e} = \rho\mathbf{u}e + \boldsymbol{P}:\mathbf{u} + \boldsymbol{Q}$

- Closure relations

Equation of state $p = p(\rho)$

Constitutive relations

Pressure tensor $\boldsymbol{P} = p\mathbf{1} + \boldsymbol{\Pi} + \tilde{\boldsymbol{\Pi}}$

Viscous tensor $\boldsymbol{\Pi} = -\eta\left(\nabla\boldsymbol{u} + \nabla\boldsymbol{u}^{T}\right) + (2\eta/3 - \xi)\,\nabla\cdot\boldsymbol{u}$

Conduction heat flux $\boldsymbol{Q} = -\kappa\nabla T + \tilde{Q}$

Fluctuating heat and stress *a la Landau*

Stress fluctuations $\langle\tilde{\boldsymbol{\Pi}}(\boldsymbol{r}_1,t)\tilde{\boldsymbol{\Pi}}(\boldsymbol{r}_2,0)\rangle = 2k_BTC_{\alpha\beta\gamma\delta}\delta(\boldsymbol{r}_2-\boldsymbol{r}_1)\delta(t)$

$C_{\alpha\beta\gamma\delta} = \left[\eta(\delta_{\alpha\delta}\delta_{\beta\gamma} + \delta_{\alpha\gamma}\delta_{\beta\delta} + (\zeta - \tfrac{2}{3}\eta)\delta_{\alpha\beta}\delta_{\delta\gamma}\right]$

Heat flux fluctuations $\tilde{Q}$

CFD: The finite volume scheme

Finite volume schemes for fluctuating hydrodynamics

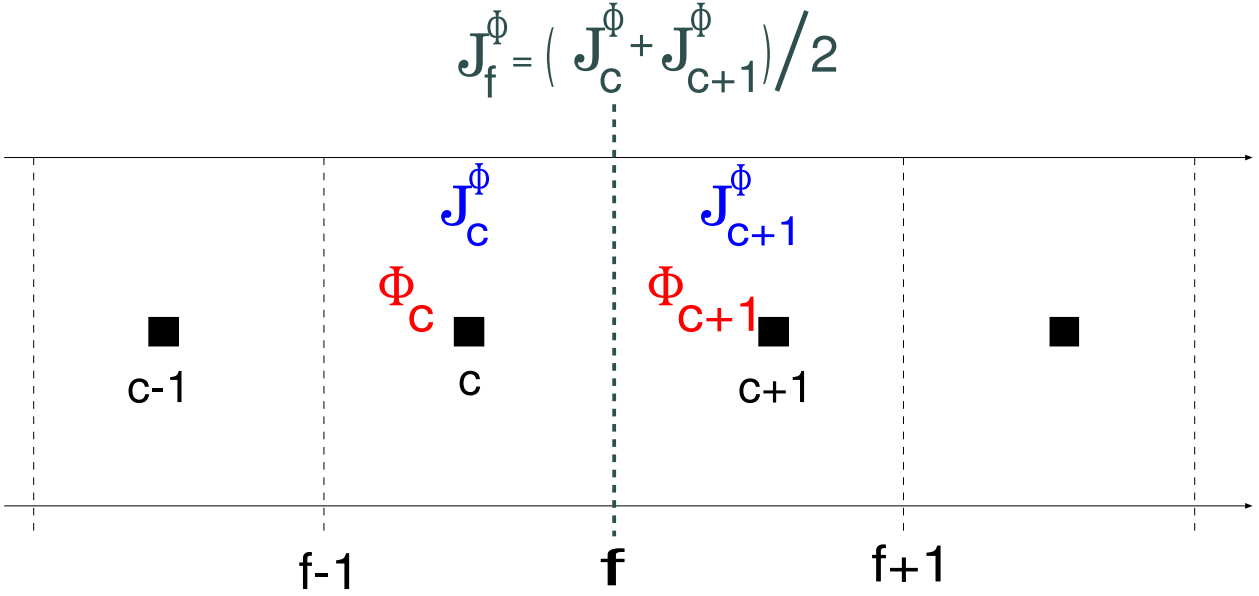
- Alejandro Garcia et al. Phys. Rev. E, **76**, 016708, (2007) energy,chemical species
- Pep Español. Phys. Rev. E, **64**, 046115, (2001) Lagrangian on Voronoi cells
- G. De Fabritiis et al Phys Rev E, **75** 026307 (2007) FH for argon and water
- RDB and A. Dejoan, Phys Rev E ,**78** 046708 (2008) Open BC for FH

$$\int_{V_c} \partial\Phi/\partial t = -\oint_{S_\alpha} \mathbf{J}^\phi \cdot \boldsymbol{ds}$$

$$V_c \frac{\Delta\Phi_c}{\Delta t} = -\sum_{f=\text{faces}} A_f \mathbf{J}_f^\phi \cdot \boldsymbol{e}_f \quad \text{(explicit Euler scheme)}$$

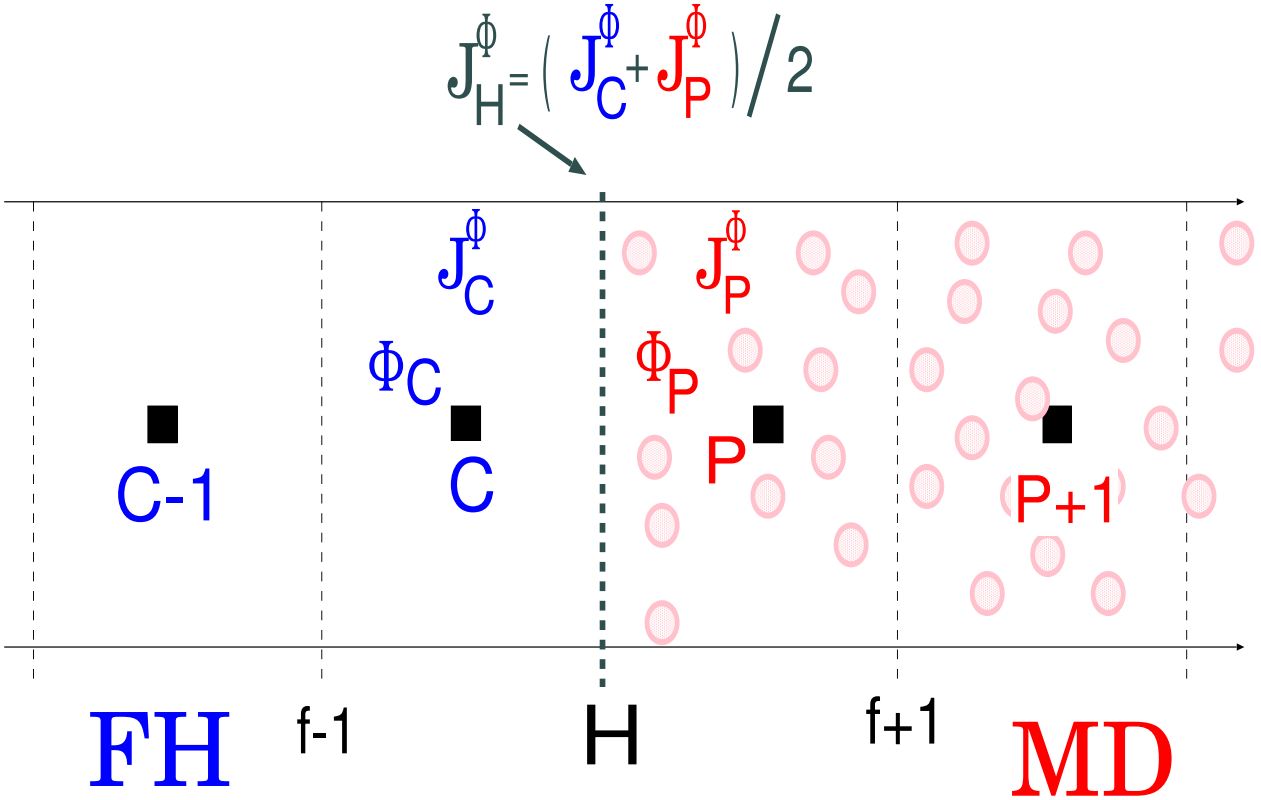
Hybrid MD

CFD: Finite volume



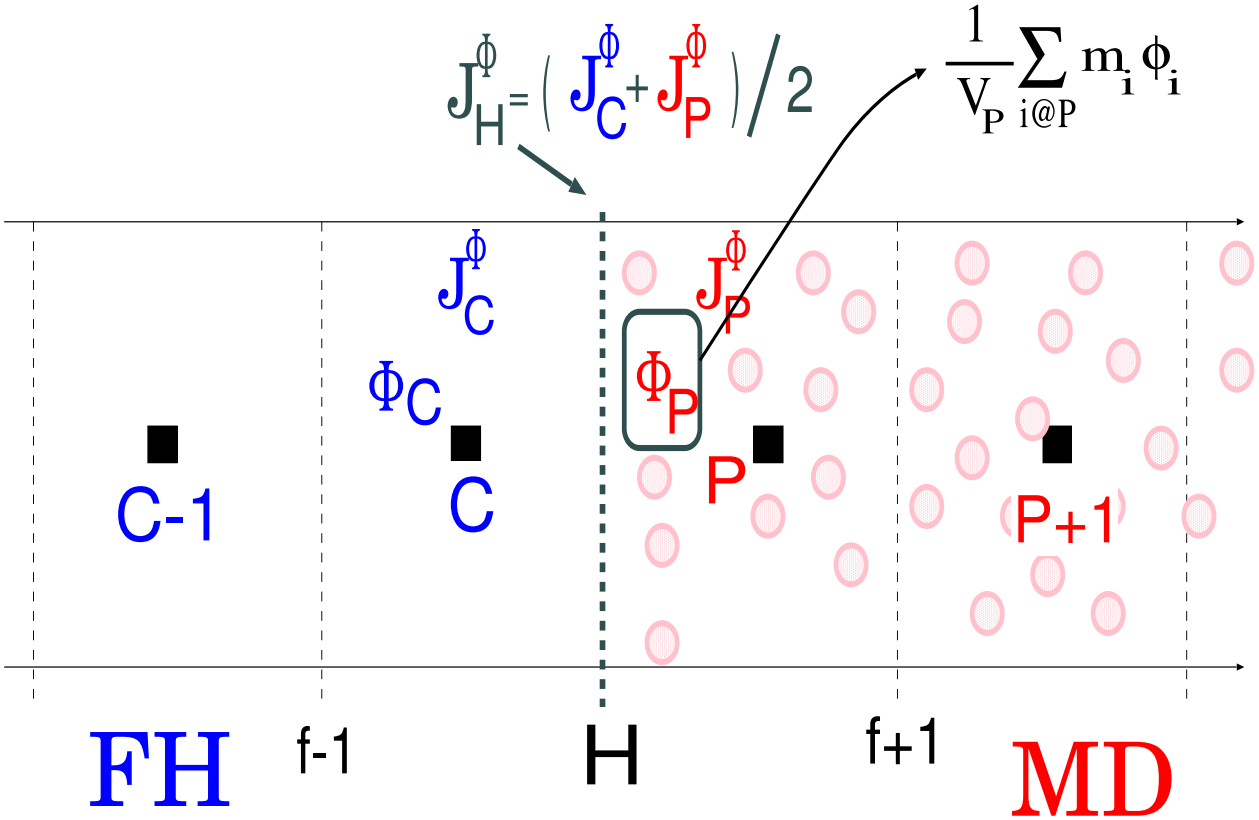
Hybrid MD

Flux at interface H



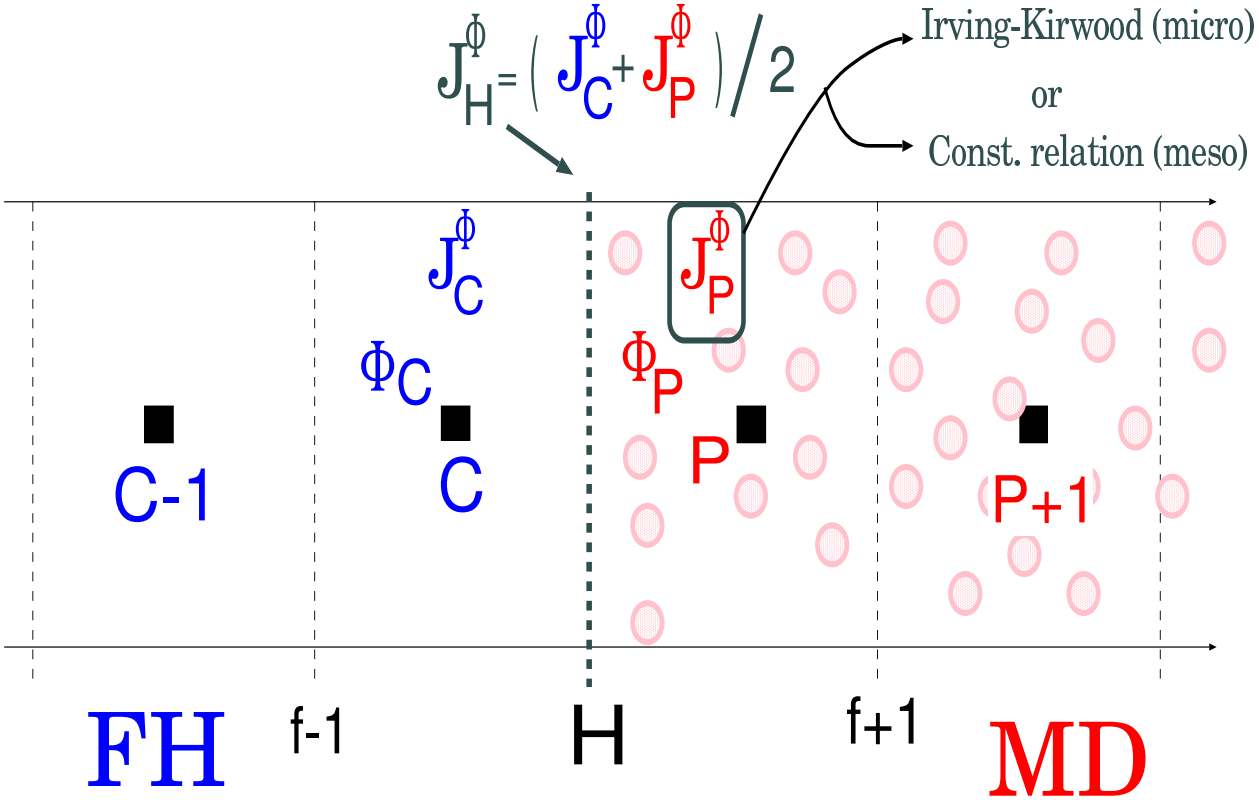
Hybrid MD

Local P variables



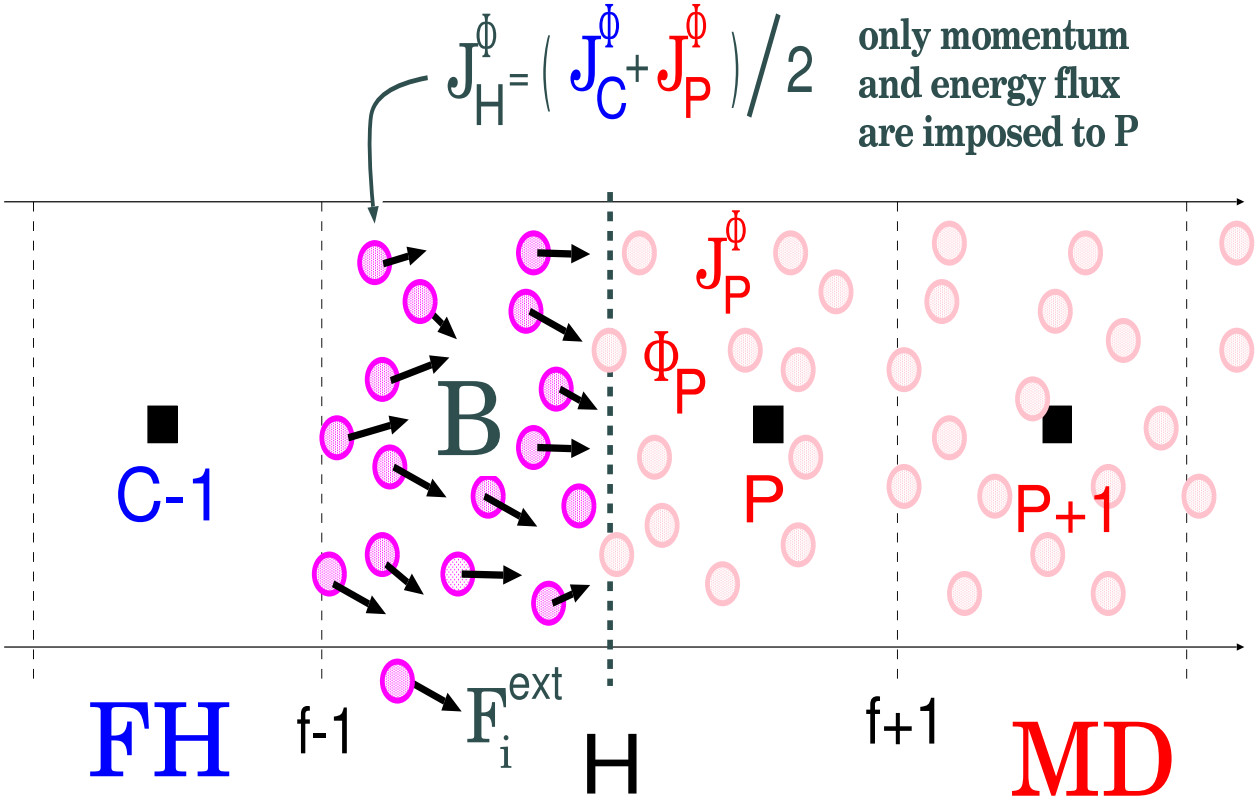
Hybrid MD

Local P fluxes



Hybrid MD

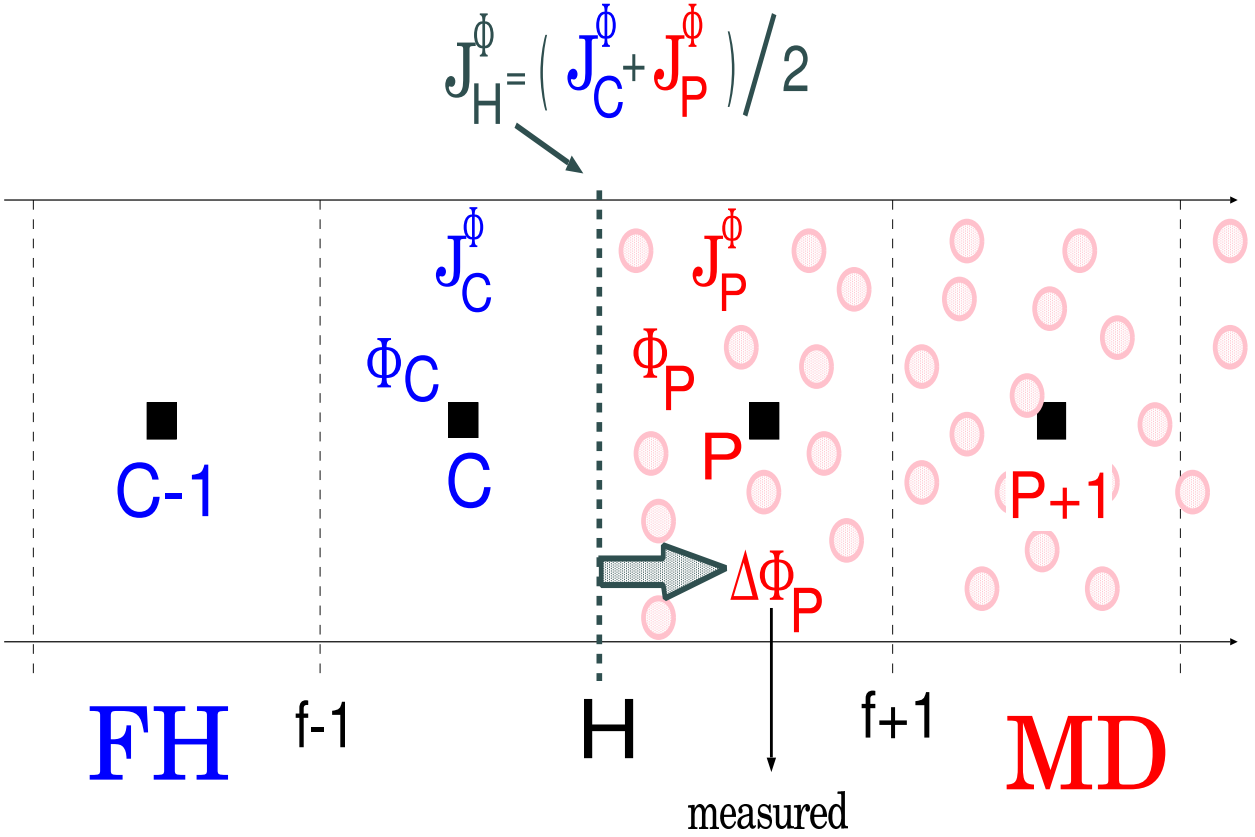
Send fluxes to MD



flux correction

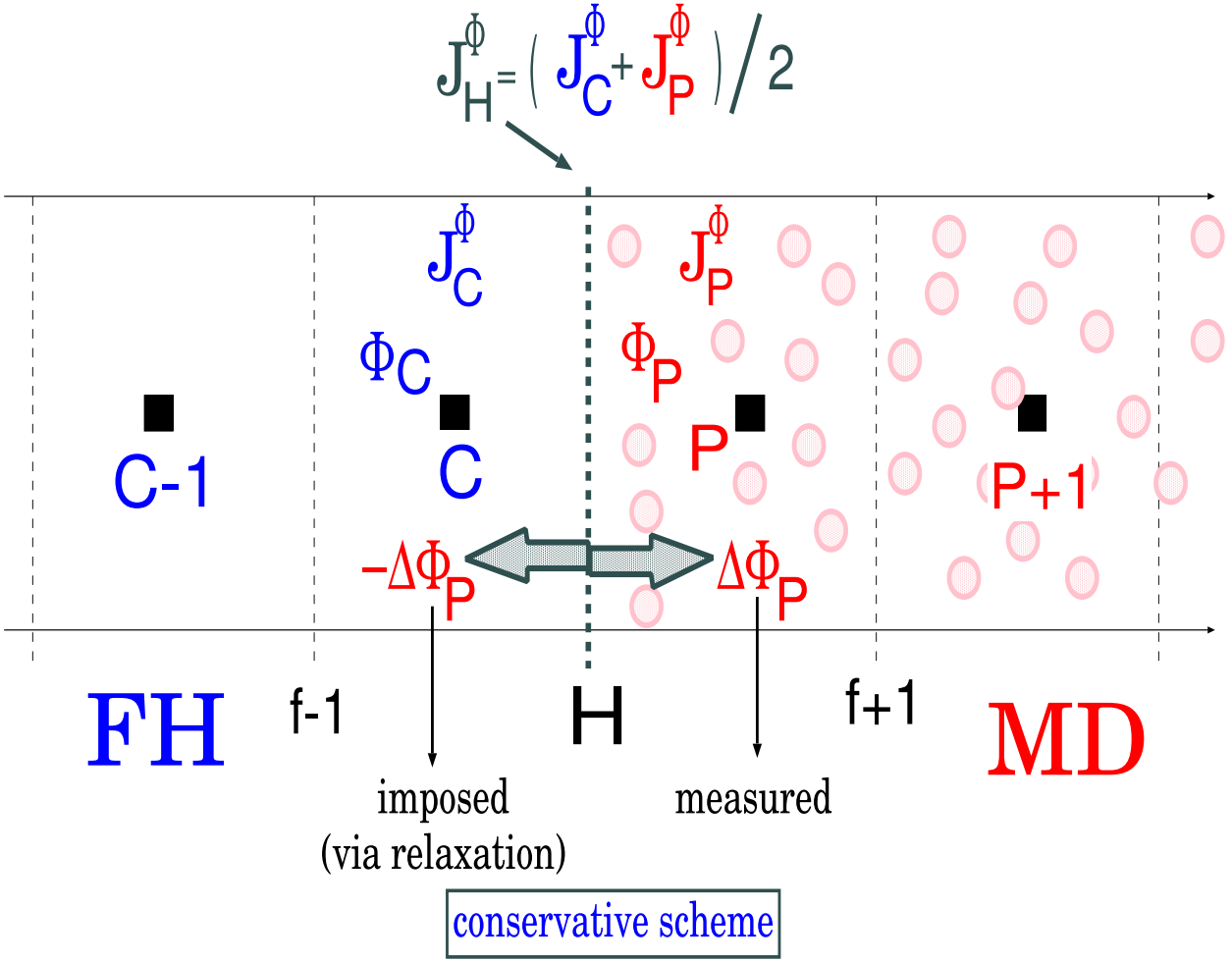
Hybrid MD

Flux balance

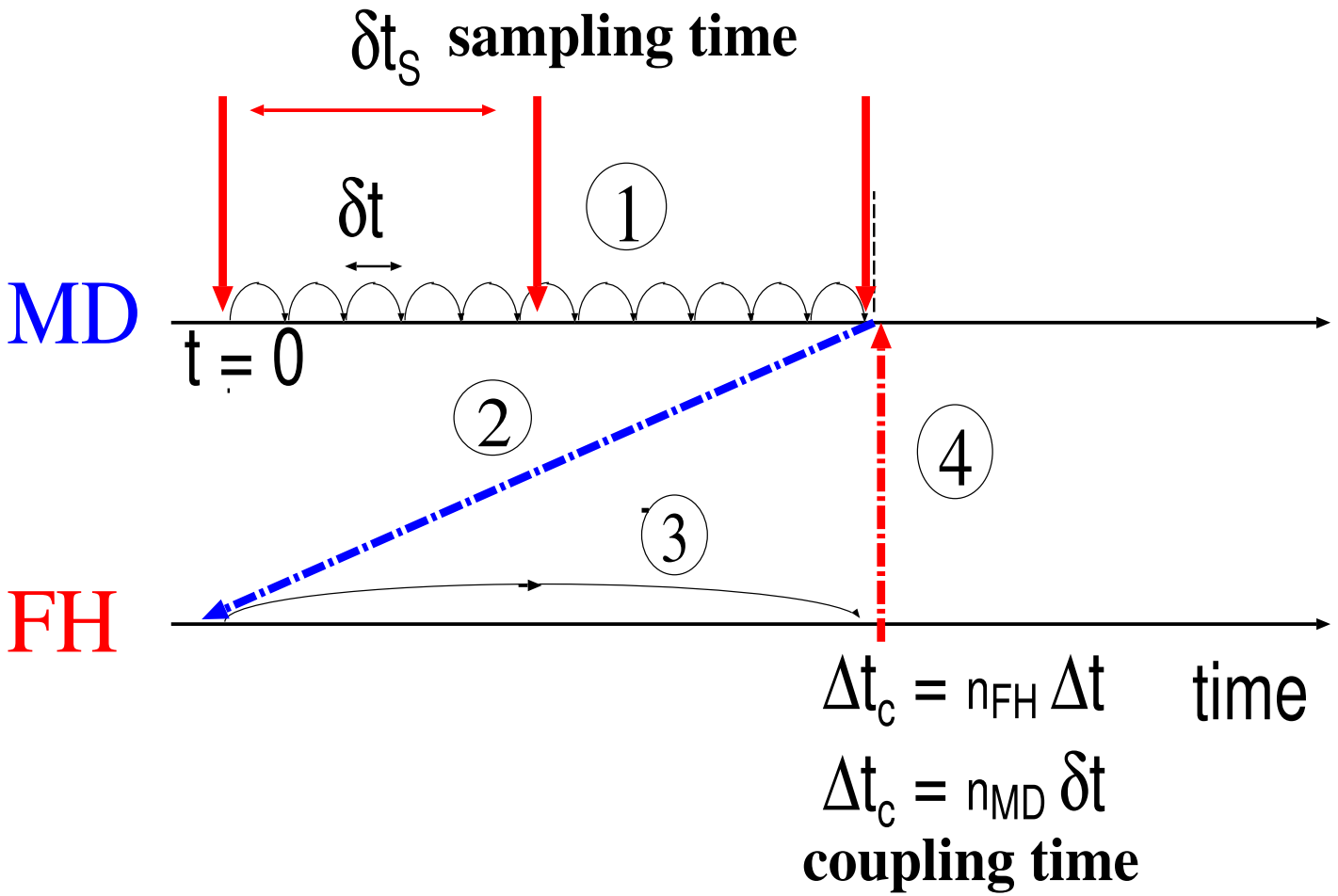


Hybrid MD

Conservative scheme



Hybrid MD
Time coupling



Hybrid MD
Coupling time and stress fluctuations

Green-Kubo relations

- Molecular dynamics: decorrelation time $\tau_c \sim 100$fs (simple liquids)

$$\langle J^2_{MD} \rangle = \frac{\eta k_B T}{V \tau_c} \text{ with, } \tau_c \equiv \frac{\int_0^\infty \langle J(t) J(0) \rangle dt}{\langle J(0)^2 \rangle}$$

- Fluctuating hydrodynamics, decorrelation time $\Delta t_{FH}/2$

$$\langle J^2_{FH} \rangle = \frac{2\eta k_B T}{V \Delta t_{FH}}$$

- Balance the stress fluctuations $\langle J^2_{MD} \rangle = \langle J^2_{FH} \rangle$:

$\Delta t_{FH} = 2\tau_c = \delta t_S$ Sampling time = twice MD decorrelation time

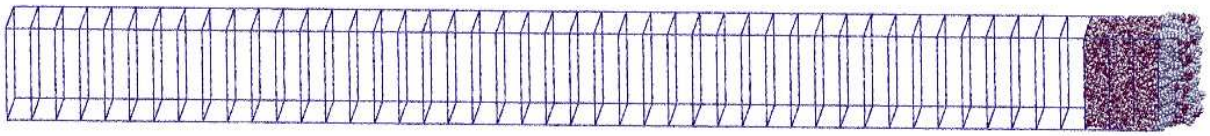
- Coupling time (in general) $\boxed{\Delta t_c = n_{FH} \Delta t_{FH} = N_s \delta t_s}$

Hybrid MD : Simulations

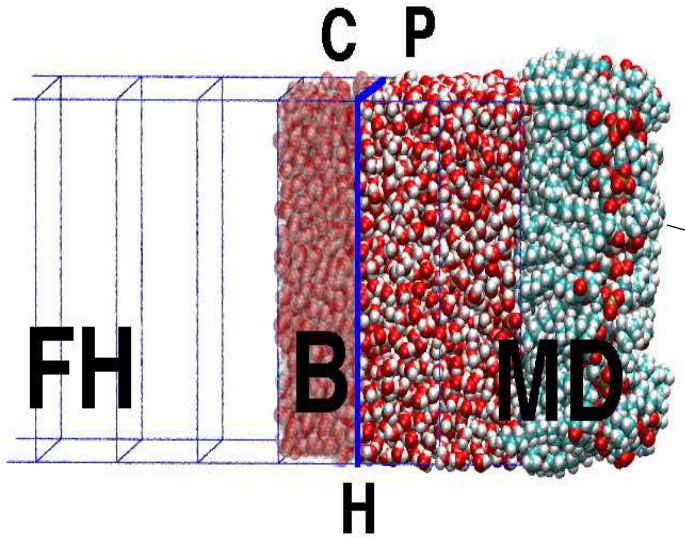
- Shear flow (steady/unsteady) PR E, 67, 046704 (2003)
- Sound waves across MD box. PRL, 97, 134501 (2006)
- Heat
- Open systems with proper mass fluctuations: PRE 76, 036709 (2007)
- Flow-soft matter interaction
  Water sound wave colliding against a lipid layer [PRL, **97** (2006)].

Hybrid MD

Embedding TIP3P water with a fluctuating hydrodynamics solver

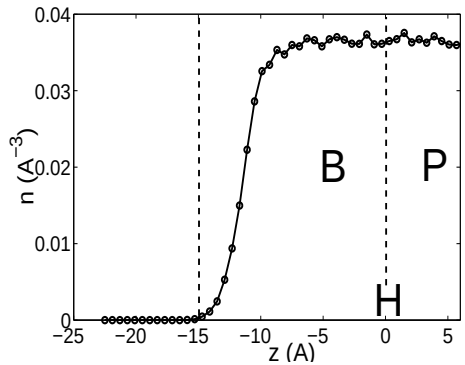


Hybrid MD-FH setup



DMPC (lipid layer)

water density profile

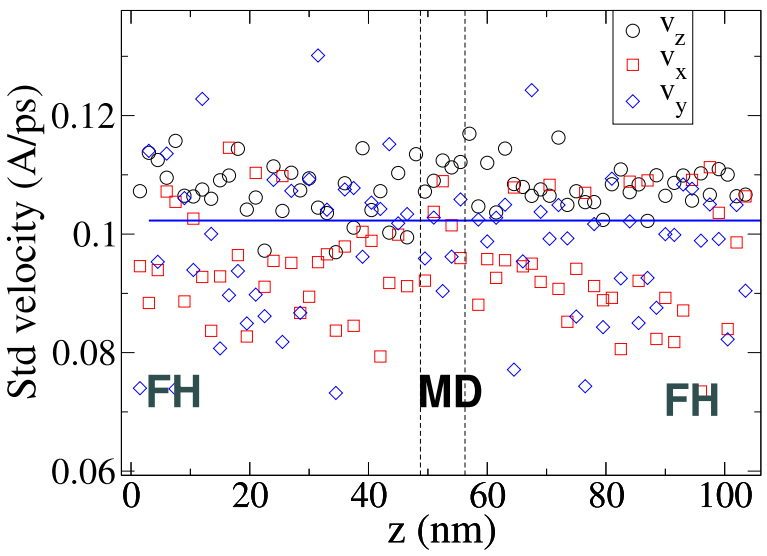


PRL, 97, 134501 (2006)

PRE, 76, 036709 (2007)

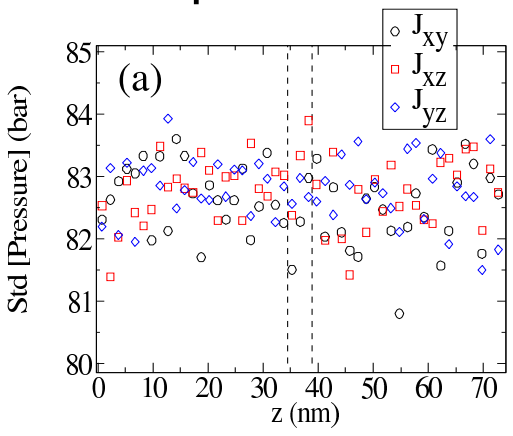
Hybrid MD @ equilibrium state: velocity and stress fluctuations

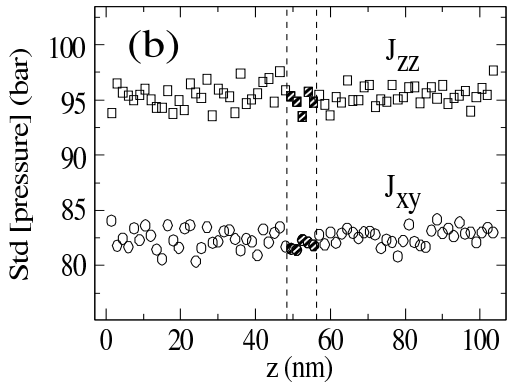
STD velocity



position

STD Stress tensor components

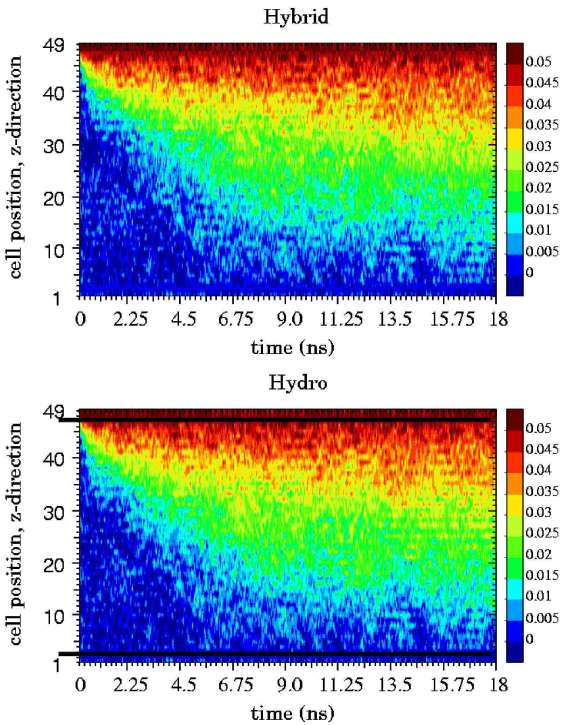




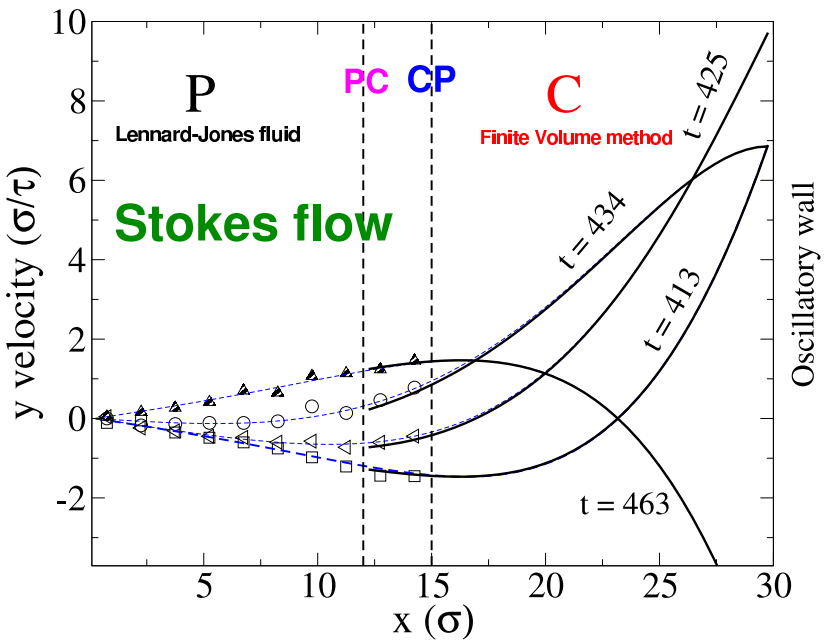
position

Hybrid MD @ non-equilibrium: shear flow

Start-up Couette

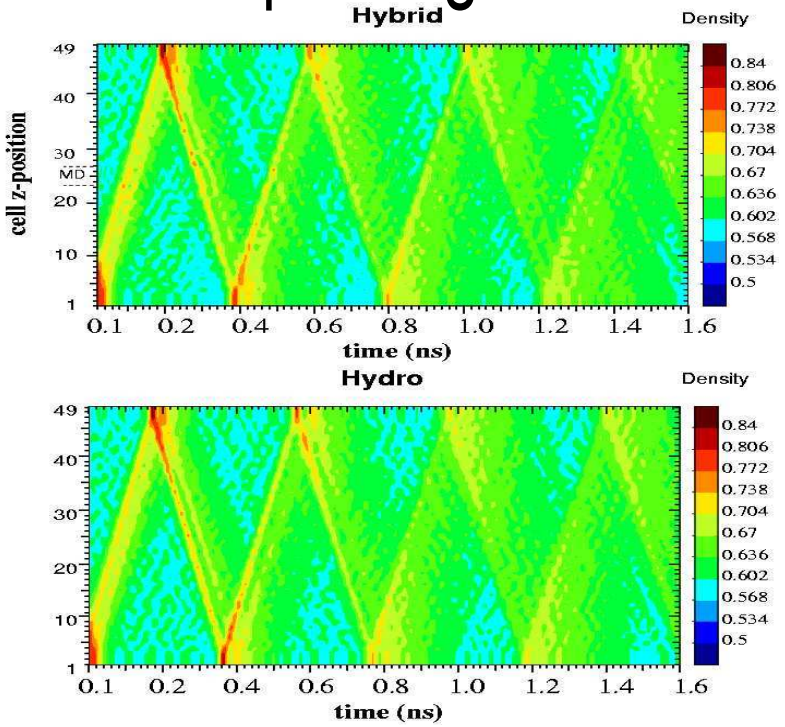


Oscillatory shear

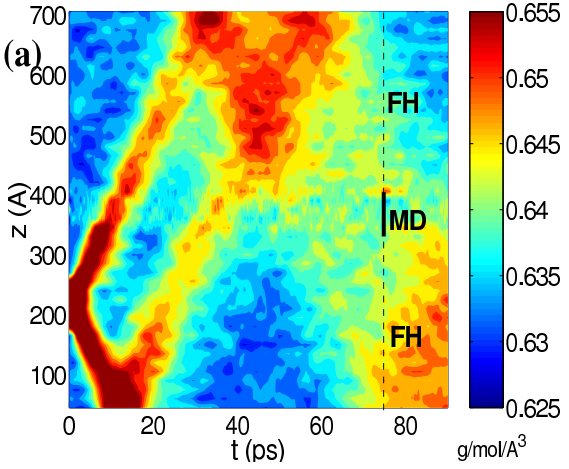


Hybrid MD @ non-equilibrium: sound waves

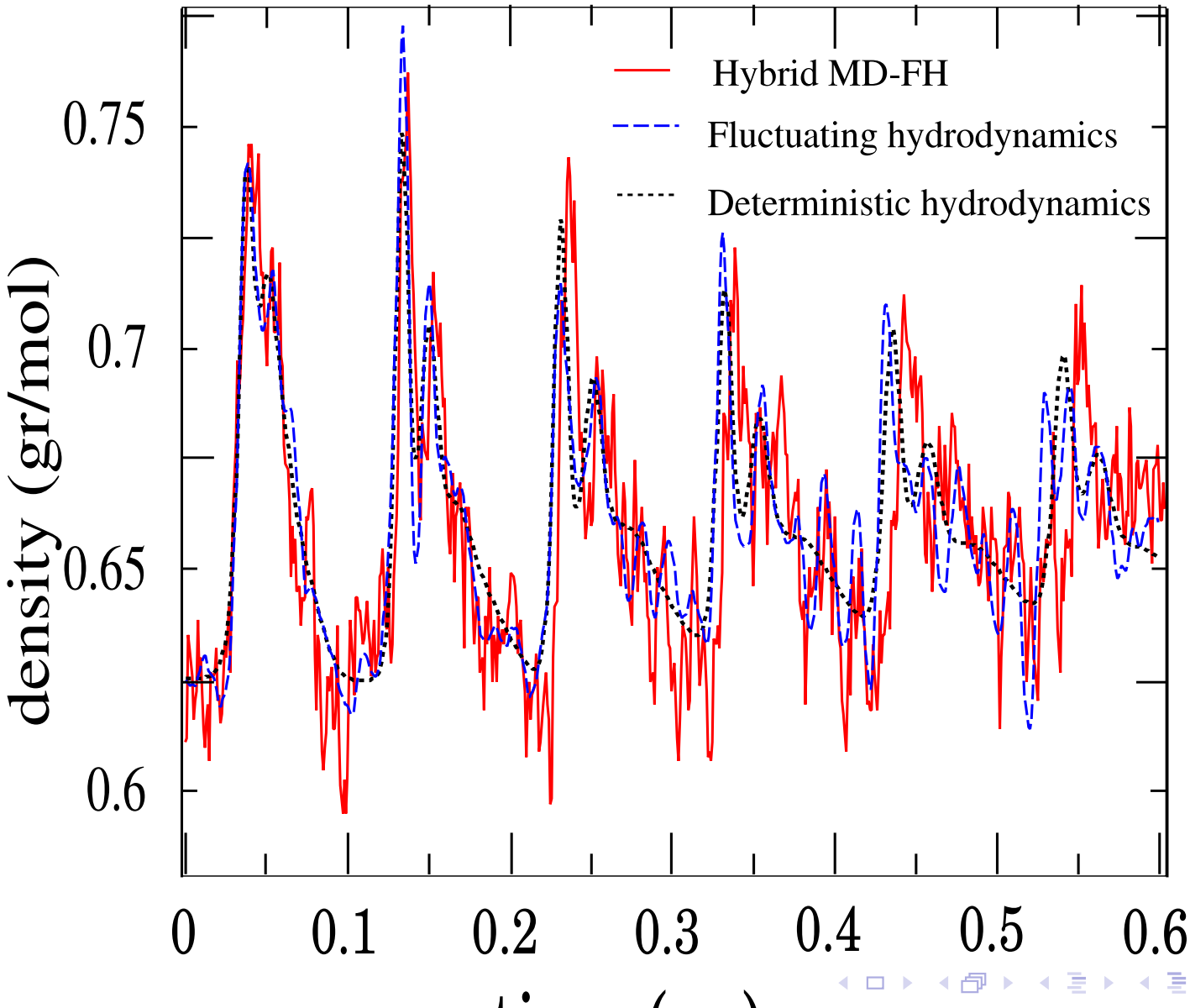
liquid argon



water

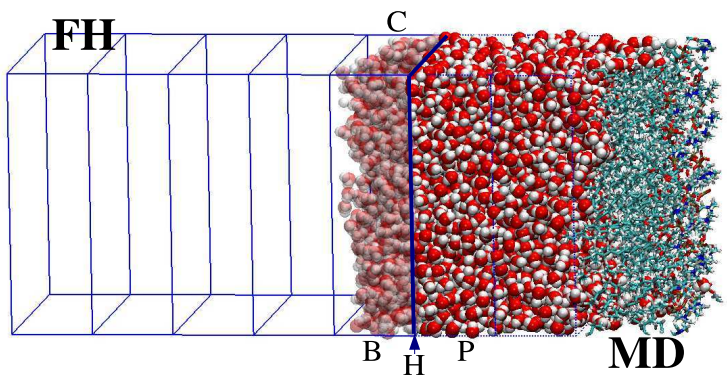


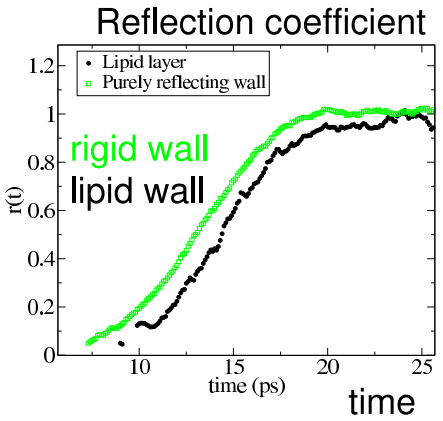
Hybrid MD @ non-equilibrium: sound waves

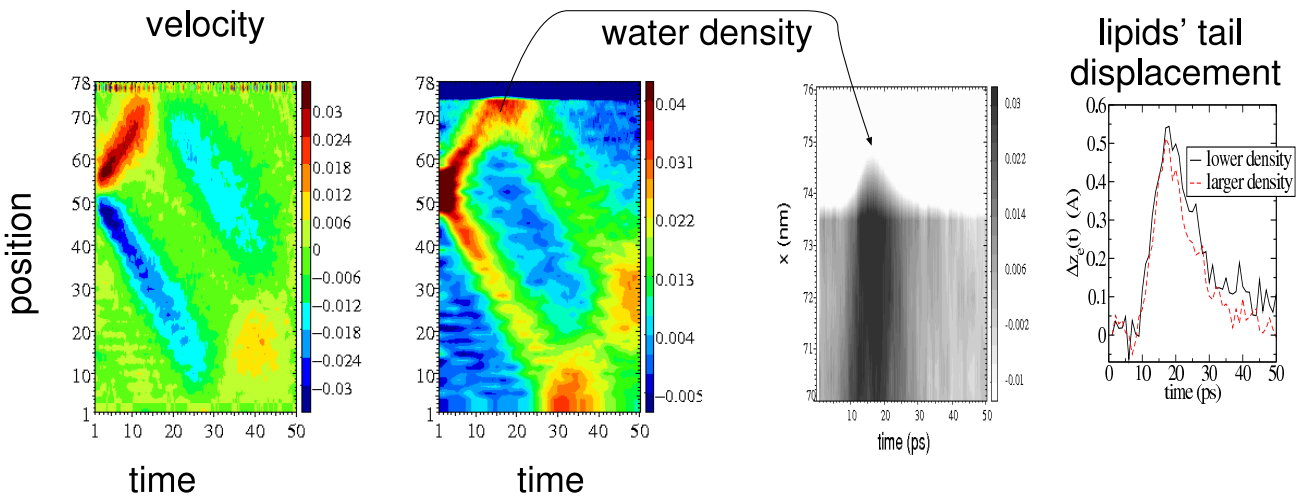


Sound - (soft) mattter interaction

RDB et al, J. Mech. Engineering Sci. (2008)







Adaptive Resolution

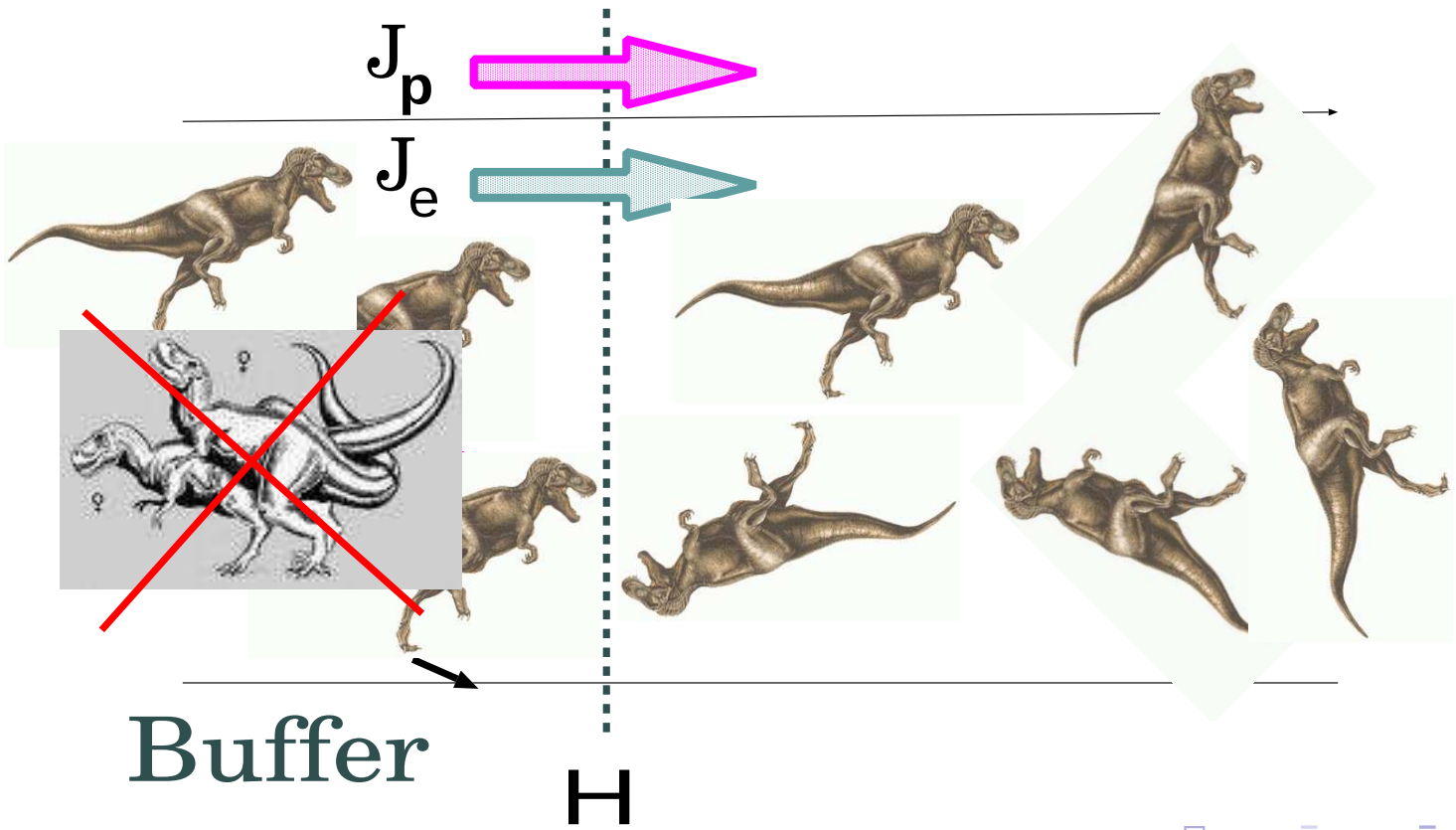
one motivation

Adaptive Resolution

one motivation

USHER cannot insert large molecules

open MD for complex molecules

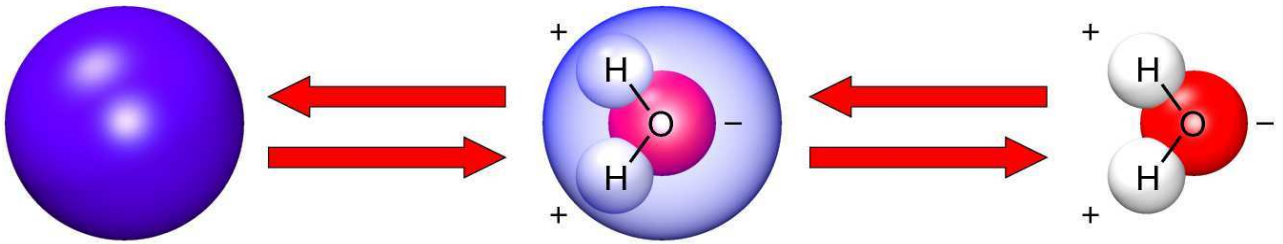


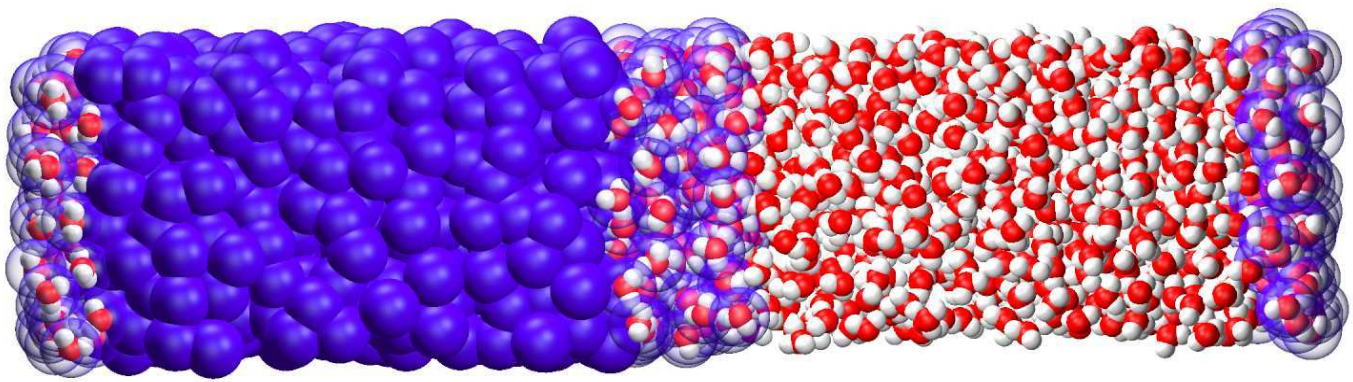
Adaptive Resolution Scheme

Praprotnik, Delle Site, Kremer, J. Chem. Phys **123** 224106 (2005)
Ann. Rev. Phys. Chem. **59** 545 (2008)

Adaptive Resolution Scheme

Praprotnik, Delle Site, Kremer, J. Chem. Phys **123** 224106 (2005)
Ann. Rev. Phys. Chem. **59** 545 (2008)



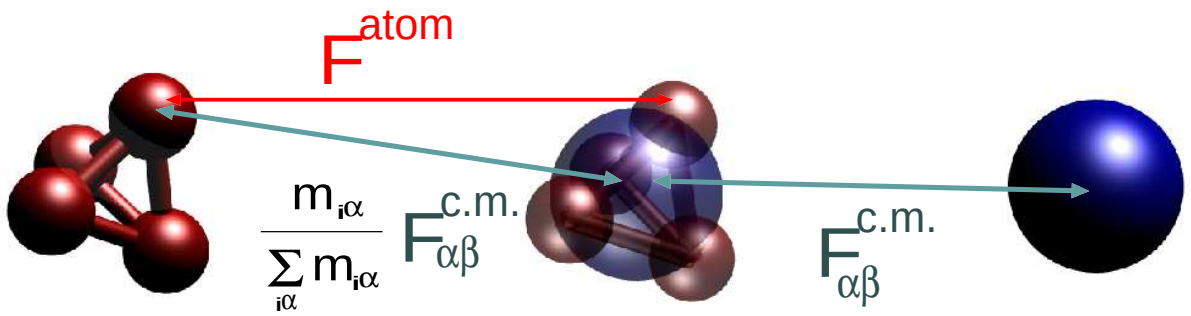


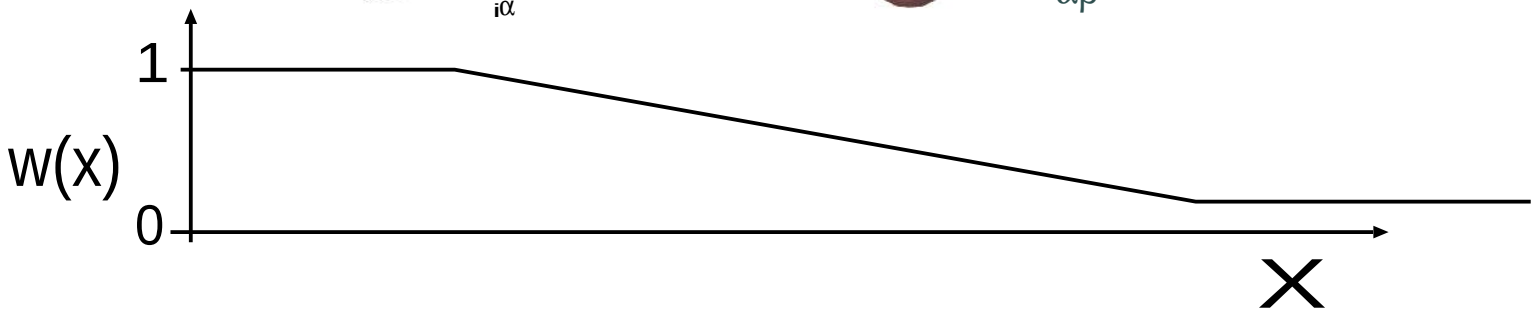
Adaptive Resolution Scheme

center of mass

$$R_\alpha = \frac{\sum_{i\alpha} m_{i\alpha} r_{i\alpha}}{M_\alpha}$$

$$V_\alpha = \frac{\sum_{i\alpha} m_{i\alpha} v_{i\alpha}}{M_\alpha}$$



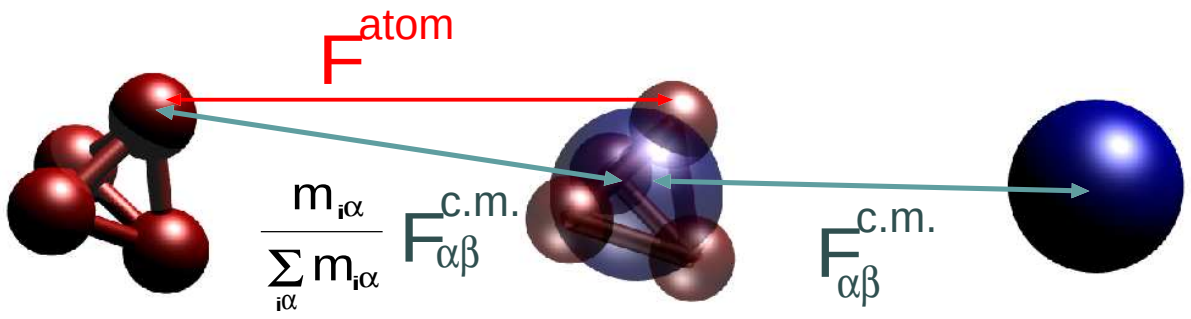


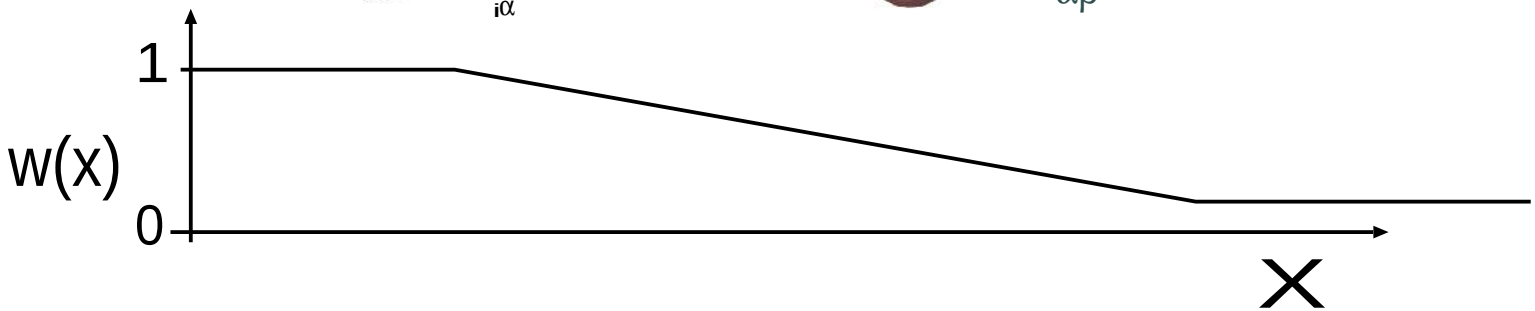
Adaptive Resolution Scheme

center of mass

$$R_\alpha = \frac{\sum_{i\alpha} m_{i\alpha} r_{i\alpha}}{M_\alpha}$$

$$V_\alpha = \frac{\sum_{i\alpha} m_{i\alpha} v_{i\alpha}}{M_\alpha}$$





$$\mathbf{F}_{\alpha\beta} = w(x_\alpha)w(x_\beta)\sum_{i\alpha j\beta}\mathbf{F}^{\rm atom}_{i\alpha j\beta} + [1 - w(x_\alpha)w(x_\beta)]\mathbf{F}^{\rm c.m.}_{\alpha\beta}$$

$$\mathbf{F}^{\rm atom}_{i\alpha j\beta} = -\frac{\partial U^{\rm atom}}{\partial \mathbf{r}_{i\alpha j\beta}} \quad \textbf{Atomistic}$$

$$\mathbf{F}^{\rm c.m.}_{\alpha\beta} = -\frac{\partial U^{\rm c.m.}}{\partial \mathbf{R}_{\alpha\beta}} \quad \textbf{Coarse} - \textbf{Grained}$$

AdResS

pros

- Reduction of degrees of freedom for the liquid outside the region of interest.

AdResS

pros

- Reduction of degrees of freedom for the liquid outside the region of interest.
- Conserves momentum (3rd Newton Law by construction)

AdResS

pros

- Reduction of degrees of freedom for the liquid outside the region of interest.
- Conserves momentum (3rd Newton Law by construction)
- Fluid structure and pressure can be recovered in the coarse-grained domain.

AdResS

pros

- Reduction of degrees of freedom for the liquid outside the region of interest.
- Conserves momentum (3rd Newton Law by construction)
- Fluid structure and pressure can be recovered in the coarse-grained domain.
- Self-diffusion of atomistic and coarse-grained domains can be *somehow* matched (a first-principles theory is lacking in the literature).

AdResS

pros

- Reduction of degrees of freedom for the liquid outside the region of interest.
- Conserves momentum (3rd Newton Law by construction)
- Fluid structure and pressure can be recovered in the coarse-grained domain.
- Self-diffusion of atomistic and coarse-grained domains can be *somehow* matched (a first-principles theory is lacking in the literature).

AdResS

pros

- Reduction of degrees of freedom for the liquid outside the region of interest.
- Conserves momentum (3rd Newton Law by construction)
- Fluid structure and pressure can be recovered in the coarse-grained domain.
- Self-diffusion of atomistic and coarse-grained domains can be *somehow* matched (a first-principles theory is lacking in the literature).

cons

- It does not conserves energy $\Longrightarrow$ cannot describe heat transfer

AdResS

`pros`

- Reduction of degrees of freedom for the liquid outside the region of interest.
- Conserves momentum (3rd Newton Law by construction)
- Fluid structure and pressure can be recovered in the coarse-grained domain.
- Self-diffusion of atomistic and coarse-grained domains can be *somehow* matched (a first-principles theory is lacking in the literature).

`cons`

- It does not conserves energy $\Longrightarrow$ cannot describe heat transfer
- Substantial work for fine-tunning both `cg` and `hyb` models (effective potentials, pressure, viscosities)

AdResS

pros

- Reduction of degrees of freedom for the liquid outside the region of interest.
- Conserves momentum (3rd Newton Law by construction)
- Fluid structure and pressure can be recovered in the coarse-grained domain.
- Self-diffusion of atomistic and coarse-grained domains can be *somehow* matched (a first-principles theory is lacking in the literature).

cons

- It does not conserves energy $\Longrightarrow$ cannot describe heat transfer
- Substantial work for fine-tunning both cg and hyb models (effective potentials, pressure, viscosities)
- Restricted to a single thermodynamic state

AdResS combined with open MD or Hybrid MD
A triple-scale hybrid

RDB, K. Kremer, M. Praprotnik

J. Chem. Phys, 128 114110, (2008); J. Chem. Phys -in press- (2009)

AdResS combined with open MD or Hybrid MD
A triple-scale hybrid

RDB, K. Kremer, M. Praprotnik

J. Chem. Phys, 128 114110, (2008); J. Chem. Phys -in press- (2009)

- Enables hybrid description of large molecules with large scale hydrodynamics

AdResS combined with open MD or Hybrid MD
A triple-scale hybrid

RDB, K. Kremer, M. Praprotnik

J. Chem. Phys, 128 114110, (2008); J. Chem. Phys -in press- (2009)

- Enables hybrid description of large molecules with large scale hydrodynamics
- Eliminates the need for fine-tunning both `cg` and `hyb` models (effective potentials, pressure, viscosities)

AdResS combined with open MD or Hybrid MD
A triple-scale hybrid

RDB, K. Kremer, M. Praprotnik

J. Chem. Phys, 128 114110, (2008); J. Chem. Phys -in press- (2009)

- Enables hybrid description of large molecules with large scale hydrodynamics
- Eliminates the need for fine-tunning both `cg` and `hyb` models (effective potentials, pressure, viscosities)
- Can be extended to work along a thermodynamic process (at constant temperature)

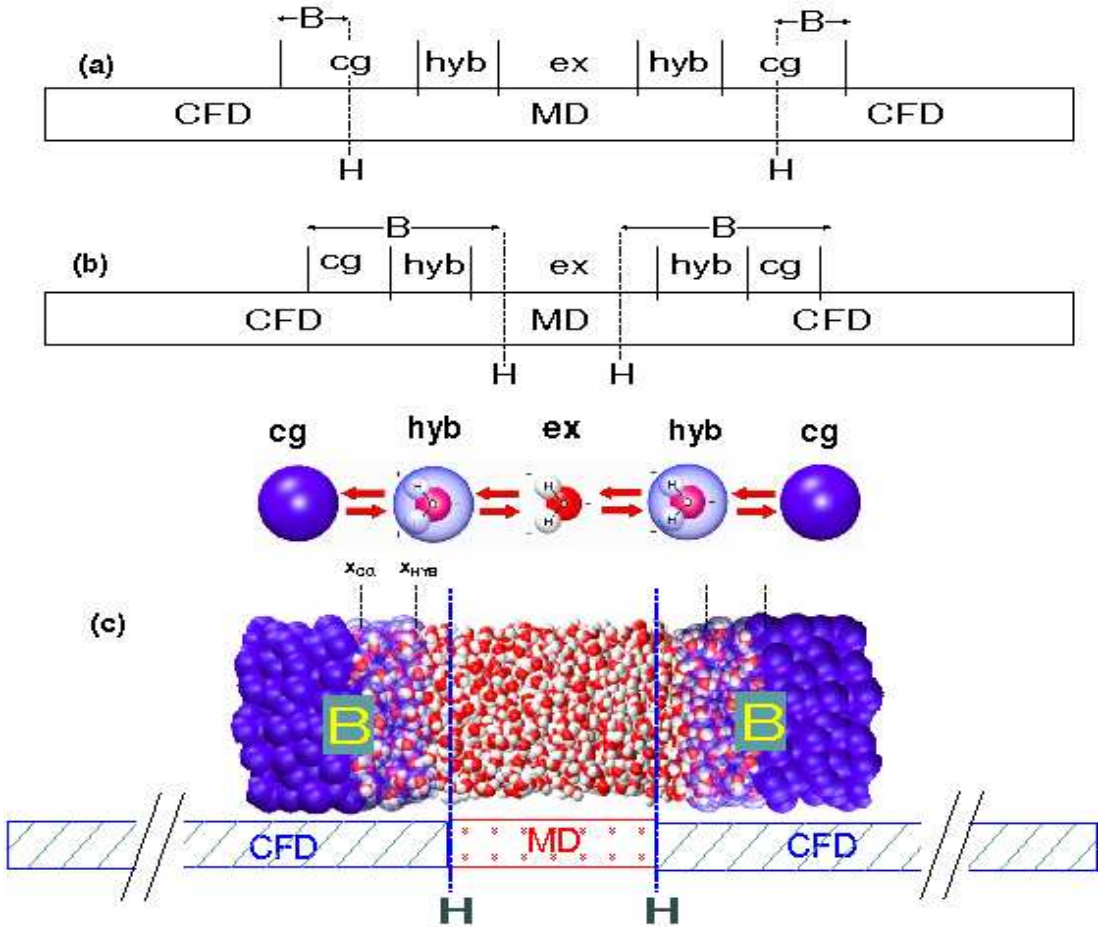
AdResS combined with open MD or Hybrid MD
A triple-scale hybrid

RDB, K. Kremer, M. Praprotnik

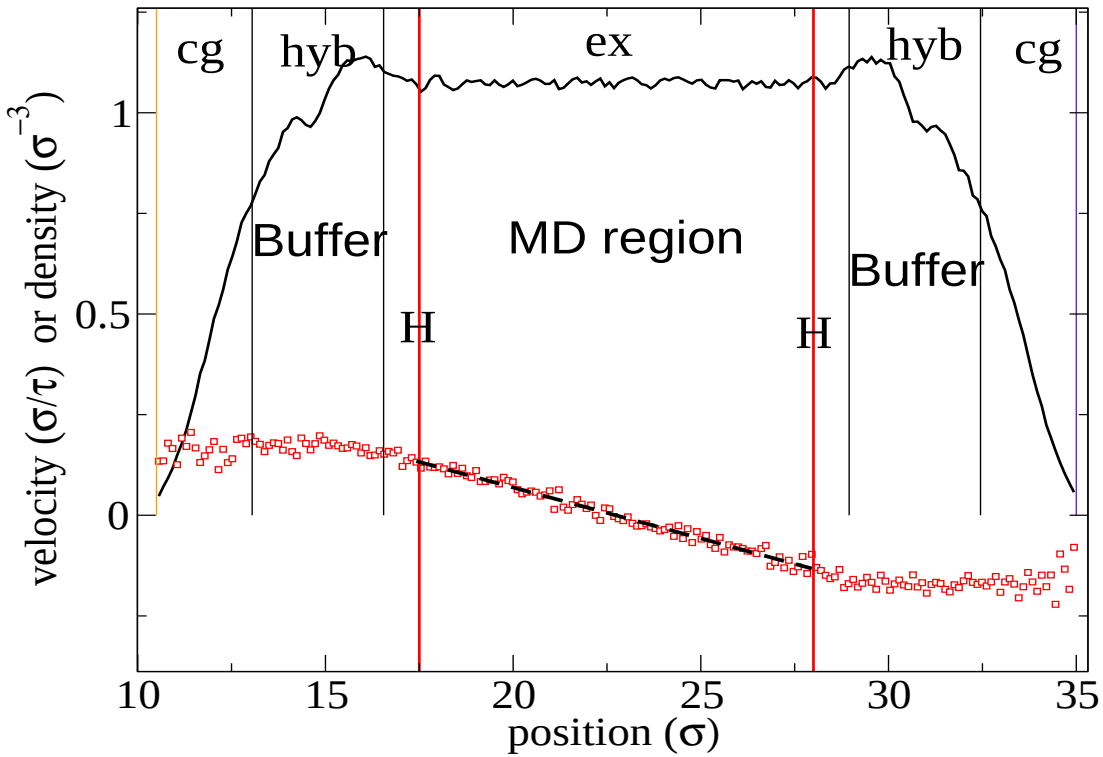
J. Chem. Phys, 128 114110, (2008); J. Chem. Phys -in press- (2009)

- Enables hybrid description of large molecules with large scale hydrodynamics
- Eliminates the need for fine-tunning both `cg` and `hyb` models (effective potentials, pressure, viscosities)
- Can be extended to work along a thermodynamic process (at constant temperature)
- Opens a route to describe heat transfer (still to be solved)

HybridMD-AdResS triple scale

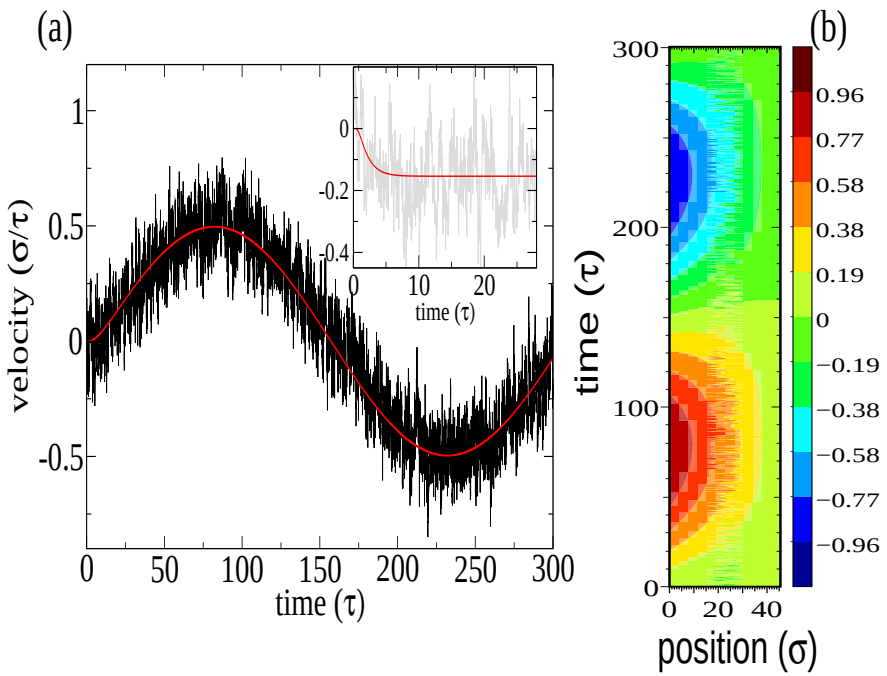


HybridMD-AdResS triple scale

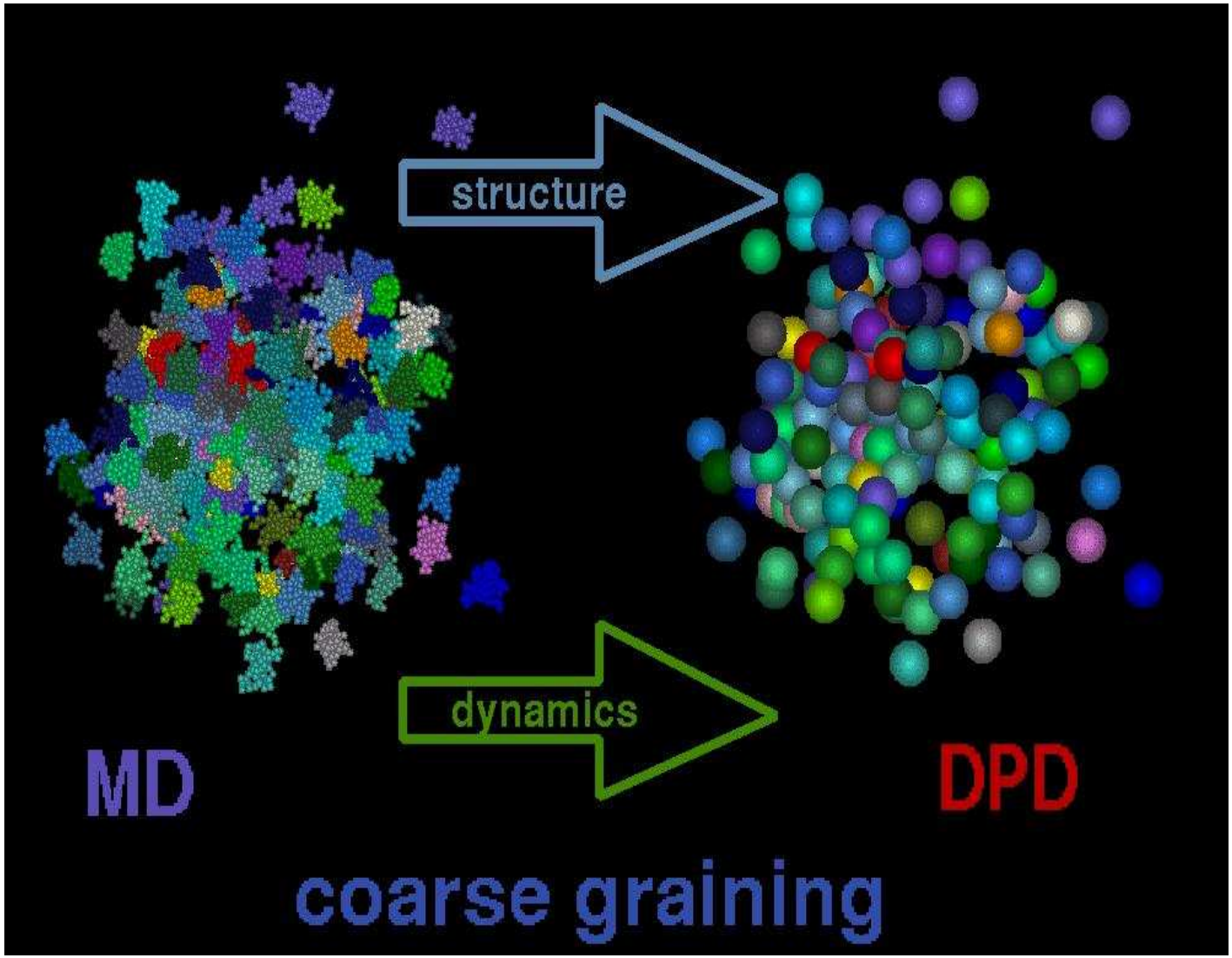


HybridMD-AdResS triple scale

Simulation of TIP3P water under oscillatory shear



Coarse graining dynamics



The state of the art

- The current idea is to obtain effective potentials from the distribution probability of distances between CoM.

The state of the art

- The current idea is to obtain effective potentials from the distribution probability of distances between CoM.
- The hope is that this effective potential allows for realistic simulations.

The state of the art

- The current idea is to obtain effective potentials from the distribution probability of distances between CoM.
- The hope is that this effective potential allows for realistic simulations.
- For static equilibrium properties the method works, but dynamic properties like diffusion are badly represented.

The state of the art

- The current idea is to obtain effective potentials from the distribution probability of distances between CoM.
- The hope is that this effective potential allows for realistic simulations.
- For static equilibrium properties the method works, but dynamic properties like diffusion are badly represented.
- The eliminated degrees of freedom should appear as dissipation and noise.

Faraday Discuss., **144**, *301, (2010)*

- A well-defined method for coarse-graining exists:
  Zwanzig projection

Faraday Discuss., **144**, *301, (2010)*

- A well-defined method for coarse-graining exists: Zwanzig projection
- Deemed as a "formal" procedure (and therefore useless...).

Faraday Discuss., **144**, *301, (2010)*

- A well-defined method for coarse-graining exists: Zwanzig projection
- Deemed as a "formal" procedure (and therefore useless...).
- How to make Zwanzig Projection Operator a practical useful tool.

Faraday Discuss., **144**, *301, (2010)*

- A well-defined method for coarse-graining exists: Zwanzig projection
- Deemed as a "formal" procedure (and therefore useless...).
- How to make Zwanzig Projection Operator a practical useful tool.
- Demonstrate the procedure for the case of star polymer melts.

Outline of Zwanzig theory

The microscopic state is $z = (\cdots, \mathbf{q}_i, \mathbf{p}_i, \cdots)$. Its dynamics is

$$\partial_t z_t = L z_t \qquad\qquad z_t = \exp\{tL\} z_0$$

where z_t is the microscopic state at time t and L is the Liouville operator.

Outline of Zwanzig theory

The microscopic state is $z = (\cdots, \mathbf{q}_i, \mathbf{p}_i, \cdots)$. Its dynamics is

$$\partial_t z_t = L z_t \qquad\qquad z_t = \exp\{tL\} z_0$$

where z_t is the microscopic state at time t and L is the Liouville operator.

The macroscopic state of the system is represented by a set of functions $A(z)$.

Outline of Zwanzig theory

The microscopic state is $z = (\cdots, \mathbf{q}_i, \mathbf{p}_i, \cdots)$. Its dynamics is

$$\partial_t z_t = L z_t \qquad\qquad z_t = \exp\{tL\} z_0$$

where z_t is the microscopic state at time t and L is the Liouville operator.

The macroscopic state of the system is represented by a set of functions $A(z)$.
Its dynamics is

$$\partial_t A(z_t) \quad = \quad LA(z_t) = \exp\{tL\} LA(z_0)$$

Outline of Zwanzig theory

The microscopic state is $z = (\cdots, \mathbf{q}_i, \mathbf{p}_i, \cdots)$. Its dynamics is

$$\partial_t z_t = L z_t \qquad\qquad z_t = \exp\{tL\} z_0$$

where z_t is the microscopic state at time t and L is the Liouville operator.

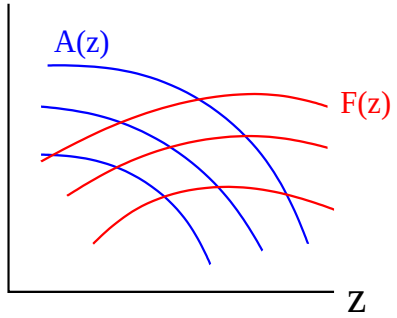
The macroscopic state of the system is represented by a set of functions $A(z)$.
Its dynamics is

$$\partial_t A(z_t) \quad = \quad L A(z_t) = \exp\{tL\} L A(z_0) \qquad \text{Not closed!}$$

The projector

The essence of Zwanzig theory is the projection operator P

$$PF(z) = \langle F \rangle^{A(z)}$$



where

$$\langle \cdots \rangle^{\alpha} = \frac{1}{\Omega(\alpha)} \int dz \rho^{\mathrm{eq}}(z) \delta(A(z) - \alpha) \cdots$$

$$\Omega(\alpha) = \int dz \rho^{\mathrm{eq}}(z) \delta(A(z) - \alpha)$$

and $\rho^{\mathrm{eq}}(z)$ is the equilibrium ensemble.

The tricks

From

$$\partial_t A(z_t) \quad = \quad LA(z_t) = \exp\{tL\}LA(z_0)$$

The tricks

From

$$\partial_t A(z_t) \quad = \quad LA(z_t) = \exp\{tL\}LA(z_0)$$

insert $1 = P + Q$

$$\partial_t A(z_t) \quad = \quad \exp\{tL\}PLA(z_0) + \exp\{tL\}QLA(z_0)$$

The tricks

From

$$\partial_t A(z_t) \quad = \quad LA(z_t) = \exp\{tL\}LA(z_0)$$

insert $1 = P + Q$

$$\partial_t A(z_t) \quad = \quad \exp\{tL\}PLA(z_0) + \exp\{tL\}QLA(z_0)$$

and use Duhamel-Dyson identity

$$\exp\{tL\} \quad = \quad \exp\{tQL\} + \int_0^t ds \exp\{(t-s)L\}PL\exp\{sQL\}$$

The macro dynamics

By using the form of the projector we obtain the exact equation

$$\partial_t A(z_t) = \langle LA \rangle^{A(z_t)} + \int_0^t ds M(A(z_{t-s}), s) \frac{\partial S}{\partial \alpha}(A(z_{t-s})) + \tilde{R}_t(z)$$

The macro dynamics

By using the form of the projector we obtain the exact equation

$$\partial_t A(z_t) = \langle LA \rangle^{A(z_t)} + \int_0^t ds M(A(z_{t-s}), s) \frac{\partial S}{\partial \alpha}(A(z_{t-s})) + \tilde{R}_t(z)$$

where

$$S(\alpha) = k_B \ln \Omega(\alpha) = k_B \ln \int \rho^{\mathrm{eq}}(z) \delta(A(z) - \alpha) dz$$

$$M(\alpha, t') = \frac{1}{k_B} \langle \tilde{R}_0 \tilde{R}_{t'} \rangle^{\alpha}$$

$$\tilde{R}_t(z) = \exp\{tQL\} QLA(z)$$

The macro dynamics

By using the form of the projector we obtain the exact equation

$$\partial_t A(z_t) = \langle LA \rangle^{A(z_t)} + \int_0^t ds M(A(z_{t-s}), s) \frac{\partial S}{\partial \alpha}(A(z_{t-s})) + \tilde{R}_t(z)$$

where

$$S(\alpha) = k_B \ln \Omega(\alpha) = k_B \ln \int \rho^{\mathrm{eq}}(z) \delta(A(z) - \alpha) dz$$

$$M(\alpha, t') = \frac{1}{k_B} \langle \tilde{R}_0 \tilde{R}_{t'} \rangle^{\alpha}$$

$$\tilde{R}_t(z) = \exp\{tQL\} QLA(z) \qquad \text{Not closed!}$$

Markovian approximation

$$M(\alpha, t') = \frac{1}{k_B}\langle \tilde{R}_0 \tilde{R}_{t'} \rangle^{\alpha} \approx M(\alpha)\delta(t')$$

$$M(\alpha) = \frac{1}{k_B}\int_0^{\infty} \langle \tilde{R}_0 \tilde{R}_s \rangle^{\alpha} ds \qquad \text{Green-Kubo}$$

Then

$$\partial_t \alpha_t = \langle LA \rangle^{\alpha_t} + M(\alpha_t)\frac{\partial S}{\partial \alpha}(\alpha_t) + \tilde{R}_t(z)$$

Closed equation! (R_t is a known white noise).

How to compute the objects from MD?

The three basic objects to compute in Zwanzig's theory are $\langle LA \rangle^{\alpha}$, $S(\alpha)$, and $M(\alpha)$.

How to compute the objects from MD?

The three basic objects to compute in Zwanzig's theory are $\langle LA \rangle^{\alpha}$, $S(\alpha)$, and $M(\alpha)$.
We need to compute constrained averages.

$$\begin{aligned} \langle \cdots \rangle^{\alpha} &= \frac{1}{\Omega(\alpha)} \int dz \rho^{\mathrm{eq}}(z) \delta(A(z) - \alpha) \cdots \\ \Omega(\alpha) &= \int dz \rho^{\mathrm{eq}}(z) \delta(A(z) - \alpha) \end{aligned}$$

To compute the friction matrix through Green-Kubo, we need

$$\tilde{R}_t = \exp\{tQL\} QLA(z_0)$$

How to compute the objects from MD?

The three basic objects to compute in Zwanzig's theory are $\langle LA \rangle^{\alpha}$, $S(\alpha)$, and $M(\alpha)$.
We need to compute constrained averages.

$$\begin{aligned} \langle \cdots \rangle^{\alpha} &= \frac{1}{\Omega(\alpha)} \int dz \rho^{\mathrm{eq}}(z) \delta(A(z) - \alpha) \cdots \\ \Omega(\alpha) &= \int dz \rho^{\mathrm{eq}}(z) \delta(A(z) - \alpha) \end{aligned}$$

To compute the friction matrix through Green-Kubo, we need

$$\tilde{R}_t = \exp\{tQL\} QLA(z_0)$$

Zwanzig theory is formal...

How to compute the objects from MD?

From the exact equation

$$\partial_t A(z_t) \quad = \quad \langle LA \rangle^{A(z_t)} + \int_0^t ds M(A(z_{t-s}), s) \frac{\partial S}{\partial \alpha}(A(z_{t-s})) + \tilde{R}_t(z)$$

At "short times", we may approximate the projected current by

$$\tilde{R}_t \quad \approx \quad LA(z_t) - \langle LA \rangle^{A(z_t)}$$

How to compute the objects from MD?

From the exact equation

$$\partial_t A(z_t) \quad = \quad \langle LA \rangle^{A(z_t)} + \int_0^t ds M(A(z_{t-s}), s) \frac{\partial S}{\partial \alpha}(A(z_{t-s})) + \tilde{R}_t(z)$$

At "short times", we may approximate the projected current by

$$\tilde{R}_t \quad \approx \quad LA(z_t) - \langle LA \rangle^{A(z_t)}$$

$$\exp\{tQL\}QLA(z_0) \quad \approx \quad \exp\{tL\}QLA(z_0)$$

How to compute the objects from MD?

From the exact equation

$$\partial_t A(z_t) \quad = \quad \langle LA \rangle^{A(z_t)} + \int_0^t ds M(A(z_{t-s}), s) \frac{\partial S}{\partial \alpha}(A(z_{t-s})) + \tilde{R}_t(z)$$

At "short times", we may approximate the projected current by

$$\tilde{R}_t \quad \approx \quad LA(z_t) - \langle LA \rangle^{A(z_t)}$$

$$\exp\{tQL\}QLA(z_0) \quad \approx \quad \exp\{tL\}QLA(z_0)$$

This is not very systematic.

How to compute the objects from MD?

From the exact equation

$$\partial_t A(z_t) = \langle LA \rangle^{A(z_t)} + \int_0^t ds M(A(z_{t-s}), s) \frac{\partial S}{\partial \alpha}(A(z_{t-s})) + \tilde{R}_t(z)$$

At "short times", we may approximate the projected current by

$$\tilde{R}_t \approx LA(z_t) - \langle LA \rangle^{A(z_t)}$$

$$\exp\{tQL\}QLA(z_0) \approx \exp\{tL\}QLA(z_0)$$

This is not very systematic. Worst: the friction matrix vanish!! (Plateau problem).

A more systematic approach

From the exact equation

$$\partial_t A(z_t) = \langle LA \rangle^{A(z_t)} + \int_0^t dt' M(A(z_{t-t'}), t') \frac{\partial S}{\partial \alpha}(A(z_{t-t'})) + \tilde{R}_t(z)$$

A more systematic approach

From the exact equation

$$\partial_t A(z_t) = \langle LA \rangle^{A(z_t)} + \int_0^t dt' M(A(z_{t-t'}), t') \frac{\partial S}{\partial \alpha}(A(z_{t-t'})) + \tilde{R}_t(z)$$

Perform the change of variables $t' = \epsilon^2 \tau$,

$$\partial_t \alpha_t = \langle LA \rangle^{\alpha_t} + \int_0^{t/\epsilon^2} d\tau \epsilon^2 M(\alpha_{t-\epsilon^2\tau}, \epsilon^2 \tau) \frac{\partial S}{\partial \alpha}(\alpha_{t-\epsilon^2\tau}) + \tilde{R}_t(z)$$

A more systematic approach

From the exact equation

$$\partial_t A(z_t) \quad = \quad \langle LA \rangle^{A(z_t)} + \int_0^t dt' M(A(z_{t-t'}), t') \frac{\partial S}{\partial \alpha}(A(z_{t-t'})) + \tilde{R}_t(z)$$

Perform the change of variables $t' = \epsilon^2 \tau$,

$$\partial_t \alpha_t \quad = \quad \langle LA \rangle^{\alpha_t} + \int_0^{t/\epsilon^2} d\tau \epsilon^2 M(\alpha_{t-\epsilon^2\tau}, \epsilon^2 \tau) \frac{\partial S}{\partial \alpha}(\alpha_{t-\epsilon^2\tau}) + \tilde{R}_t(z)$$

Assume

$$\lim_{\epsilon \to 0} \epsilon^2 M(\alpha_{t-\epsilon^2\tau}, \epsilon^2 \tau) \quad \equiv \quad m(\alpha_t, \tau)$$

A more systematic approach

From the exact equation

$$\partial_t A(z_t) = \langle LA \rangle^{A(z_t)} + \int_0^t dt' M(A(z_{t-t'}), t') \frac{\partial S}{\partial \alpha}(A(z_{t-t'})) + \tilde{R}_t(z)$$

Perform the change of variables $t' = \epsilon^2 \tau$,

$$\partial_t \alpha_t = \langle LA \rangle^{\alpha_t} + \int_0^{t/\epsilon^2} d\tau \epsilon^2 M(\alpha_{t-\epsilon^2\tau}, \epsilon^2 \tau) \frac{\partial S}{\partial \alpha}(\alpha_{t-\epsilon^2\tau}) + \tilde{R}_t(z)$$

Assume

$$\lim_{\epsilon \to 0} \epsilon^2 M(\alpha_{t-\epsilon^2\tau}, \epsilon^2 \tau) \equiv m(\alpha_t, \tau)$$

Then

$$\partial_t \alpha_t = \langle LA \rangle^{\alpha_t} + \int_0^{\infty} m(\alpha_t, \tau) d\tau \frac{\partial S}{\partial \alpha}(\alpha_t) + \tilde{R}_t(z)$$

A more systematic approach

When the limit exists?

$$\epsilon^2 M(\alpha_{t-\epsilon^2\tau}, \epsilon^2\tau) = \frac{1}{k_B}\langle(\epsilon QLA)\exp\{\tau\epsilon^2 QLQ\}(\epsilon QLA)\rangle^{\alpha_{t-\epsilon^2\tau}}$$

A more systematic approach

When the limit exists?

$$\epsilon^2 M(\alpha_{t-\epsilon^2\tau}, \epsilon^2\tau) = \frac{1}{k_B}\langle(\epsilon QLA)\exp\{\tau\epsilon^2 QLQ\}(\epsilon QLA)\rangle^{\alpha_{t-\epsilon^2\tau}}$$

Assume

$$L = L_0 + \frac{1}{\epsilon}L_1 + \frac{1}{\epsilon^2}L_2$$

A more systematic approach

When the limit exists?

$$\epsilon^2 M(\alpha_{t-\epsilon^2\tau}, \epsilon^2\tau) = \frac{1}{k_B}\langle(\epsilon QLA)\exp\{\tau\epsilon^2 QLQ\}(\epsilon QLA)\rangle^{\alpha_{t-\epsilon^2\tau}}$$

Assume

$$L = L_0 + \frac{1}{\epsilon}L_1 + \frac{1}{\epsilon^2}L_2$$

with

$$\begin{aligned} L_2 A &= 0 \\ P L_1 A &= 0 \end{aligned}$$

A more systematic approach

When the limit exists?

$$\epsilon^2 M(\alpha_{t-\epsilon^2\tau}, \epsilon^2\tau) = \frac{1}{k_B}\langle(\epsilon QLA)\exp\{\tau\epsilon^2 QLQ\}(\epsilon QLA)\rangle^{\alpha_{t-\epsilon^2\tau}}$$

Assume

$$L = L_0 + \frac{1}{\epsilon}L_1 + \frac{1}{\epsilon^2}L_2$$

with

$$\begin{aligned} L_2 A &= 0 \\ PL_1 A &= 0 \end{aligned}$$

Then the limit exists

$$\epsilon^2 M(\alpha_{t-\epsilon^2\tau}, \epsilon^2\tau) = \frac{1}{k_B}\langle L_1 A\exp\{\tau L_2\}L_1 A\rangle^{\alpha} + \mathcal{O}(\epsilon)$$

A more systematic approach

Therefore, if $L = L_0 + \frac{1}{\epsilon}L_1 + \frac{1}{\epsilon^2}L_2$, with $L_2 A = 0$ and $PL_1 A = 0$ then for $\epsilon \longrightarrow 0$, we have a Markovian SDE

$$\partial_t \alpha_t \quad = \quad \langle L_0 A \rangle^{\alpha_t} + \overline{M}(\alpha_t)\frac{\partial S}{\partial \alpha}(\alpha_t) + \tilde{R}_t(z)$$

where the Green-Kubo friction matrix is given by

$$\overline{M}(\alpha_t) \quad = \quad \frac{1}{k_B}\int_0^\infty \langle L_1 A \exp\{\tau L_2\} L_1 A \rangle^{\alpha} d\tau$$

A more systematic approach

However, $L \neq L_0 + \frac{1}{\epsilon}L_1 + \frac{1}{\epsilon^2}L_2$ in general...

A more systematic approach

However, $L \neq L_0 + \frac{1}{\epsilon}L_1 + \frac{1}{\epsilon^2}L_2$ in general...
Introduce an evolution operator $\mathcal{R}$ "similar" to L and such that

$$\begin{aligned} \mathcal{R}A(z) &= 0 \\ \mathcal{R}H(z) &= 0 \end{aligned}$$

A more systematic approach

However, $L \neq L_0 + \frac{1}{\epsilon}L_1 + \frac{1}{\epsilon^2}L_2$ in general...
Introduce an evolution operator $\mathcal{R}$ "similar" to L and such that

$$\begin{aligned} \mathcal{R}A(z) &= 0 \\ \mathcal{R}H(z) &= 0 \end{aligned}$$

It is always possible to decompose the Liouville operator as

$$L = L_0 + L_1 + L_2$$

$$\begin{aligned} L_0 &= P(L - \mathcal{R}) \\ L_1 &= Q(L - \mathcal{R}) \\ L_2 &= \mathcal{R} \end{aligned}$$

A more systematic approach

However, $L \neq L_0 + \frac{1}{\epsilon}L_1 + \frac{1}{\epsilon^2}L_2$ in general...
Introduce an evolution operator $\mathcal{R}$ "similar" to L and such that

$$\begin{aligned} \mathcal{R}A(z) &= 0 \\ \mathcal{R}H(z) &= 0 \end{aligned}$$

It is always possible to decompose the Liouville operator as

$$L = L_0 + L_1 + L_2$$

$$\begin{aligned} L_0 &= P(L - \mathcal{R}) \\ L_1 &= Q(L - \mathcal{R}) \\ L_2 &= \mathcal{R} \end{aligned}$$

By construction, $L_2 A = 0$ and $PL_1 A = 0$.

A more systematic approach

Now, instead of $L = L_0 + L_1 + L_2$, *model* the system with L^ϵ

$$L^\epsilon \equiv L_0 + \frac{1}{\epsilon} L_1 + \frac{1}{\epsilon^2} L_2$$

This is not the real dynamics except when $\epsilon = 1$. Hopefully, it is very similar, even in the $\epsilon \to 0$ limit.

A more systematic approach

Now, instead of $L = L_0 + L_1 + L_2$, *model* the system with L^ϵ

$$L^\epsilon \equiv L_0 + \frac{1}{\epsilon} L_1 + \frac{1}{\epsilon^2} L_2$$

This is not the real dynamics except when $\epsilon = 1$. Hopefully, it is very similar, even in the $\epsilon \to 0$ limit.

Instead of perpetrating unsystematic approximation errors, we prefer to perpetrate systematic modelling errors.

A more systematic approach

In terms of the new operator $\mathcal{R}$

$$\begin{aligned} \langle L_0 A \rangle^\alpha &= \langle LA \rangle^\alpha \\ \overline{M}(\alpha) &= \frac{1}{k_B} \int_0^\infty \langle (LA - \langle LA \rangle^\alpha) \exp\{\tau \mathcal{R}\} (LA - \langle LA \rangle^\alpha) \rangle^\alpha d\tau \end{aligned}$$

A more systematic approach

In terms of the new operator $\mathcal{R}$

$$\begin{aligned} \langle L_0 A\rangle^\alpha &= \langle LA\rangle^\alpha \\ \overline{M}(\alpha) &= \frac{1}{k_B}\int_0^\infty \langle (LA - \langle LA\rangle^\alpha)\exp\{\tau\mathcal{R}\}(LA - \langle LA\rangle^\alpha)\rangle^\alpha d\tau \end{aligned}$$

The basic difference with the "usual" aproximation (plateau-problematic) is that instead of

$$\exp\{QLt\} \approx \exp\{Lt\}$$

we now approximate

$$\exp\{QLt\} \approx \exp\{\mathcal{R}t\}$$

A more systematic approach

Note that because $\mathcal{R}A = 0, \mathcal{R}H = 0$, the dynamics $\exp\{\tau\mathcal{R}\}$ samples $\rho^{\mathrm{eq}}(z)\delta(A(z) - \alpha)$.

A more systematic approach

Note that because $\mathcal{R}A = 0, \mathcal{R}H = 0$, the dynamics $\exp\{\tau\mathcal{R}\}$ samples $\rho^{\mathrm{eq}}(z)\delta(A(z) - \alpha)$.
By ergodicity, we have now a *practical* method for computing constrained averages and correlations with time averages

$$\langle F\rangle^{\alpha} = \lim_{T\to\infty}\frac{1}{T}\int_0^T d\tau \exp\{\tau\mathcal{R}\}F(z)$$

$$\begin{aligned}\langle \delta J \exp\{\tau\mathcal{R}\}\delta J\rangle^{\alpha} &= \lim_{T\to\infty}\frac{1}{T}\int_0^T d\tau_0 \exp\{\tau_0\mathcal{R}\}\delta J(z)\\ &\times \exp\{(\tau_0+\tau)\mathcal{R}\}\delta J(z)\end{aligned}$$

where the initial condition z satisfies $A(z) = \alpha$.

A more systematic approach

Yet, we need to define $\mathcal{R}$.

A more systematic approach

Yet, we need to define $\mathcal{R}$.

Take the Hamiltonian dynamics constrained with Lagrange multipliers to give $\dot{A} = 0$:

$$\begin{aligned} \dot{q}_i &= \frac{\partial H}{\partial p_i} - \lambda_\mu \frac{\partial A^\mu}{\partial p_i} \\ \dot{p}_i &= -\frac{\partial H}{\partial q_i} + \lambda_\mu \frac{\partial A^\mu}{\partial q_i} \end{aligned}$$

The Lagrange multipliers can be obtained explicitly from $\dot{A} = 0$

$$\lambda_\nu = \{A_\mu, A_\nu\}^{-1} L A^\mu$$

Summary

The equivalent Fokker-Planck equation

$$\partial_t \rho(\alpha, t) = \frac{\partial}{\partial \alpha} \mathbf{v}(\alpha) \rho(\alpha, t) + k_B \frac{\partial}{\partial \alpha} \Omega(\alpha) \mathbf{M}(\alpha) \cdot \frac{\partial}{\partial \alpha} \frac{\rho(\alpha, t)}{\Omega(\alpha)}$$

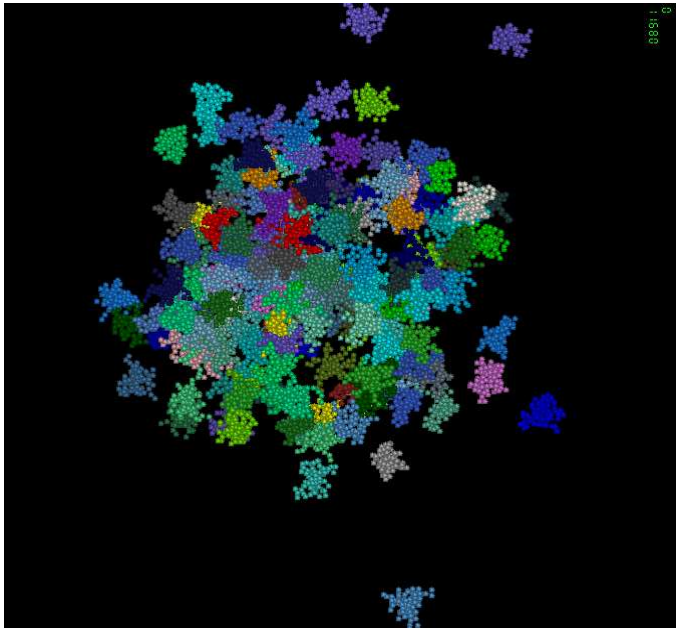
where

$$\begin{aligned} \Omega(\alpha) &= \int dz \rho^{\mathrm{eq}}(z) \delta(A(z) - \alpha) \\ \mathbf{v}(\alpha) &= \langle LA \rangle^{\alpha} \\ \mathbf{M}(\alpha) &= \frac{1}{k_B} \int_0^{\infty} \langle (LA - \langle LA \rangle^{\alpha}) \exp\{\tau \mathcal{R}\} (LA - \langle LA \rangle^{\alpha}) \rangle^{\alpha} d\tau \end{aligned}$$

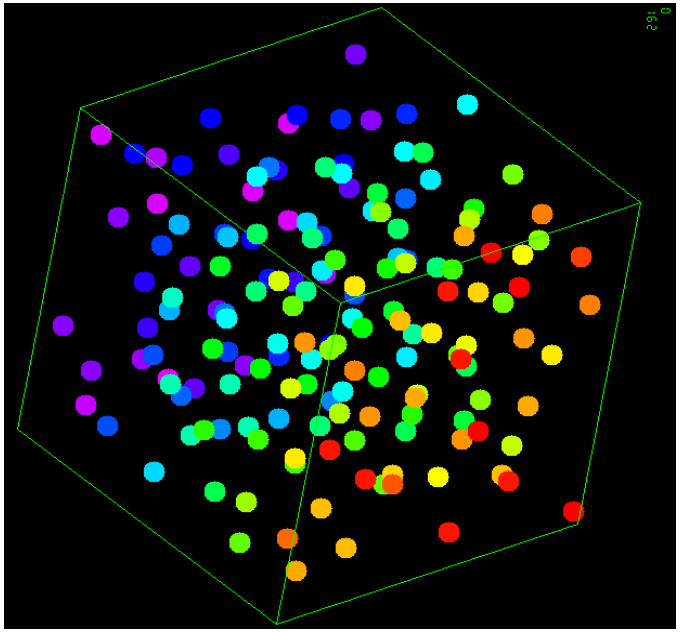
All these objects may be computed from simulating the constrained dynamics

Coarsening star polymers

MD



CoM



160 star molecules: 12 arms, 6 monomers each. L-J non-bonded interaction, FENE bonded interaction

Coarsening star polymers

Level	Variables	Dynamics
Micro	$z = \{\mathbf{r}_{i_\mu}, \mathbf{p}_{i_\mu}\}$	$\dot{z} = Lz$
Macro	$A(z) = \begin{cases} \mathbf{R}_\mu(z) = \frac{1}{m_\mu}\sum_{i_\mu} m_{i_\mu}\mathbf{r}_{i_\mu} \\ \mathbf{P}_\mu(z) = \sum_{i_\mu} \mathbf{p}_{i_\mu} \end{cases}$	SDE

Coarsening star polymers

Level	Variables	Dynamics
Micro	$z = \{\mathbf{r}_{i_\mu}, \mathbf{p}_{i_\mu}\}$	$\dot{z} = Lz$
Macro	$A(z) = \begin{cases} \mathbf{R}_\mu(z) = \frac{1}{m_\mu}\sum_{i_\mu} m_{i_\mu}\mathbf{r}_{i_\mu} \\ \mathbf{P}_\mu(z) = \sum_{i_\mu} \mathbf{p}_{i_\mu} \end{cases}$	SDE

So we need to find out $\Omega(\alpha)$, $v(\alpha)$ and $M(\alpha)$ of the SDE.

Coarsening star polymers

The equilibrium distribution $\Omega(\alpha)$ is

$$\Omega(R,P) = \int dz \rho^{\mathrm{eq}}(z)\delta(R-\hat{R}(z))\delta(P-\hat{P}(z))$$

Integrating out momenta

$$\Omega(R,P) = \Omega(R)\frac{1}{\sqrt{2\pi T\prod_\mu M_\mu}}\exp\left\{-\beta\sum_\mu \frac{P_\mu^2}{2M_\mu}\right\}$$

The effective potential is defined through

$$\Omega(R) = \frac{1}{Q}\exp\left\{-\frac{V^{\mathrm{eff}}(R)}{k_B T}\right\}$$

Coarsening star polymers

The drift term $v(\alpha) = \langle LA \rangle^{\alpha}$ is now

$$\left\langle L\hat{\mathbf{R}}_{\mu} \right\rangle^{RP} = \frac{\mathbf{P}_{\mu}}{M_{\mu}} \rightarrow L\mathbf{R} - \left\langle L\hat{\mathbf{R}}_{\mu} \right\rangle^{RP} = 0$$

$$\left\langle L\hat{\mathbf{P}}_{\mu} \right\rangle^{RP} = \langle \mathbf{F}_{\mu} \rangle^{RP} \rightarrow \langle \mathbf{F}_{\mu} \rangle^{R} = -\frac{\partial V^{\text{eff}}}{\partial \mathbf{R}_{\mu}}$$

Coarsening star polymers

The friction matrix $M(\alpha)\frac{1}{k_B}\int_0^\infty \langle \delta LA \exp\{\tau\mathcal{R}\}\delta LA\rangle^\alpha d\tau$ is now

$$\mathbf{M}_{\mu\nu}(R,P) = \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \\ \mathbf{0} & \boldsymbol{\gamma}_{\mu\nu}(R,P) \end{pmatrix}$$

The mutual friction coefficients between molecules μ,ν are

$$\boldsymbol{\gamma}_{\mu\nu}(R,P) = \int_0^\infty dt \langle \delta\mathbf{F}_\nu \exp\{\mathcal{R}t\}\delta\mathbf{F}_\mu\rangle^{RP}$$

$$\delta\mathbf{F}_\mu = \hat{\mathbf{F}}_\mu - \left\langle \hat{\mathbf{F}}_\mu \right\rangle^{RP}$$

Coarsening star polymers

The SDE for the CoM provided by Zwanzig theory are

$$\begin{aligned} \partial_t \mathbf{R}_\mu &= \mathbf{V}_\mu \\ \partial_t \mathbf{P}_\mu &= \sum_\nu \langle \mathbf{F}_{\mu\nu} \rangle^R - \sum_\nu \gamma_{\mu\nu}(R)\mathbf{V}_{\mu\nu} + \tilde{\mathbf{F}}_\mu \end{aligned}$$

where $\mathbf{V}_{\mu\nu} = \mathbf{V}_\mu - \mathbf{V}_\nu$.

Coarsening star polymers

The SDE for the CoM provided by Zwanzig theory are

$$\begin{aligned} \partial_t \mathbf{R}_\mu &= \mathbf{V}_\mu \\ \partial_t \mathbf{P}_\mu &= \sum_\nu \langle \mathbf{F}_{\mu\nu} \rangle^R - \sum_\nu \gamma_{\mu\nu}(R)\mathbf{V}_{\mu\nu} + \tilde{\mathbf{F}}_\mu \end{aligned}$$

where $\mathbf{V}_{\mu\nu} = \mathbf{V}_\mu - \mathbf{V}_\nu$.

These are the equations of Dissipative Particle Dynamics.

Coarsening star polymers

The constrained dynamics $\mathcal{R}$ is now simply

$$\begin{aligned} \dot{\mathbf{r}}_{i_\mu} &= \mathbf{v}_{i_\mu} - \mathbf{V}_\mu \\ \dot{\mathbf{p}}_{i_\mu} &= \mathbf{F}_{i_\mu} - \frac{m_{i_\mu}}{M_\mu}\mathbf{F}_\mu \end{aligned}$$

That, obviously, satisfy $\dot{\mathbf{R}}_\mu = 0$ and $\dot{\mathbf{P}}_\mu = 0$.

Coarsening star polymers

The constrained dynamics $\mathcal{R}$ is now simply

$$\begin{aligned} \dot{\mathbf{r}}_{i_\mu} &= \mathbf{v}_{i_\mu} - \mathbf{V}_\mu \\ \dot{\mathbf{p}}_{i_\mu} &= \mathbf{F}_{i_\mu} - \frac{m_{i_\mu}}{M_\mu}\mathbf{F}_\mu \end{aligned}$$

That, obviously, satisfy $\dot{\mathbf{R}}_\mu = 0$ and $\dot{\mathbf{P}}_\mu = 0$.

By running this dynamic equations and performing time averages we may compute

$$\begin{aligned} &\langle \mathbf{F}_{\mu\nu} \rangle^R \\ \gamma_{\mu\nu}(R) &= \frac{1}{k_B T}\int_0^\infty dt \langle \delta\mathbf{F}_\mu \exp\{t\mathcal{R}\}\delta\mathbf{F}_\nu \rangle^R \end{aligned}$$

Coarsening star polymers

We assume pair-wise additivity

$$\begin{aligned} \langle \mathbf{F}_{\mu\nu} \rangle^{R} &= \langle \mathbf{F}_{\mu\nu} \rangle^{R_{\mu\nu}} \\ \gamma_{\mu\nu}(R) &= \frac{1}{k_B T} \int_0^\infty dt \langle \delta\mathbf{F}_\mu \exp\{t\mathcal{R}\} \delta\mathbf{F}_\nu \rangle^{R_{\mu\nu}} \end{aligned}$$

Coarsening star polymers

We assume pair-wise additivity

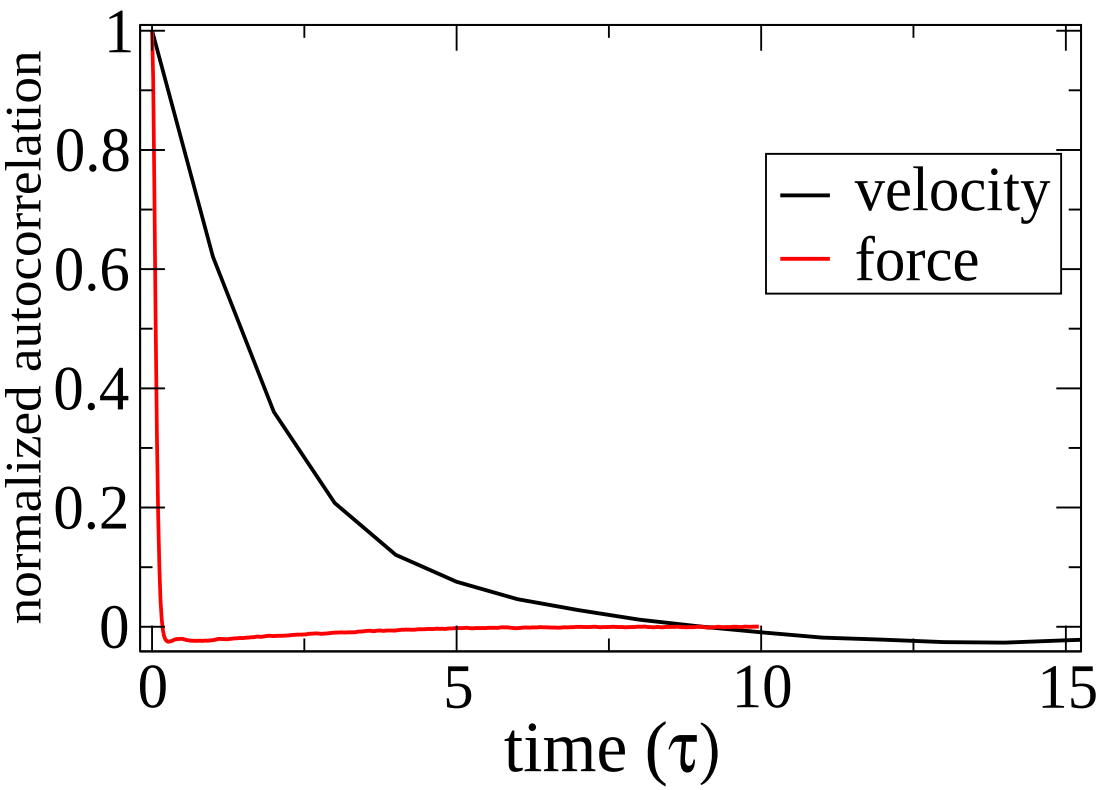
$$\begin{aligned} \langle \mathbf{F}_{\mu\nu} \rangle^{R} &= \langle \mathbf{F}_{\mu\nu} \rangle^{R_{\mu\nu}} \\ \gamma_{\mu\nu}(R) &= \frac{1}{k_B T} \int_0^\infty dt \langle \delta \mathbf{F}_\mu \exp\{t\mathcal{R}\} \delta \mathbf{F}_\nu \rangle^{R_{\mu\nu}} \end{aligned}$$

$$\langle \mathbf{F}_{\mu\nu} \rangle^{R_{\mu\nu}} = \langle \mathbf{F}_{\mu\nu} \cdot \mathbf{e}_{\mu\nu} \rangle^{R_{\mu\nu}} \mathbf{e}_{\mu\nu}$$

$$\gamma_{\mu\nu}(R_{\mu\nu}) = A(R_{\mu\nu})\mathbf{1} + B(R_{\mu\nu})\mathbf{e}_{\mu\nu}\mathbf{e}_{\mu\nu}$$

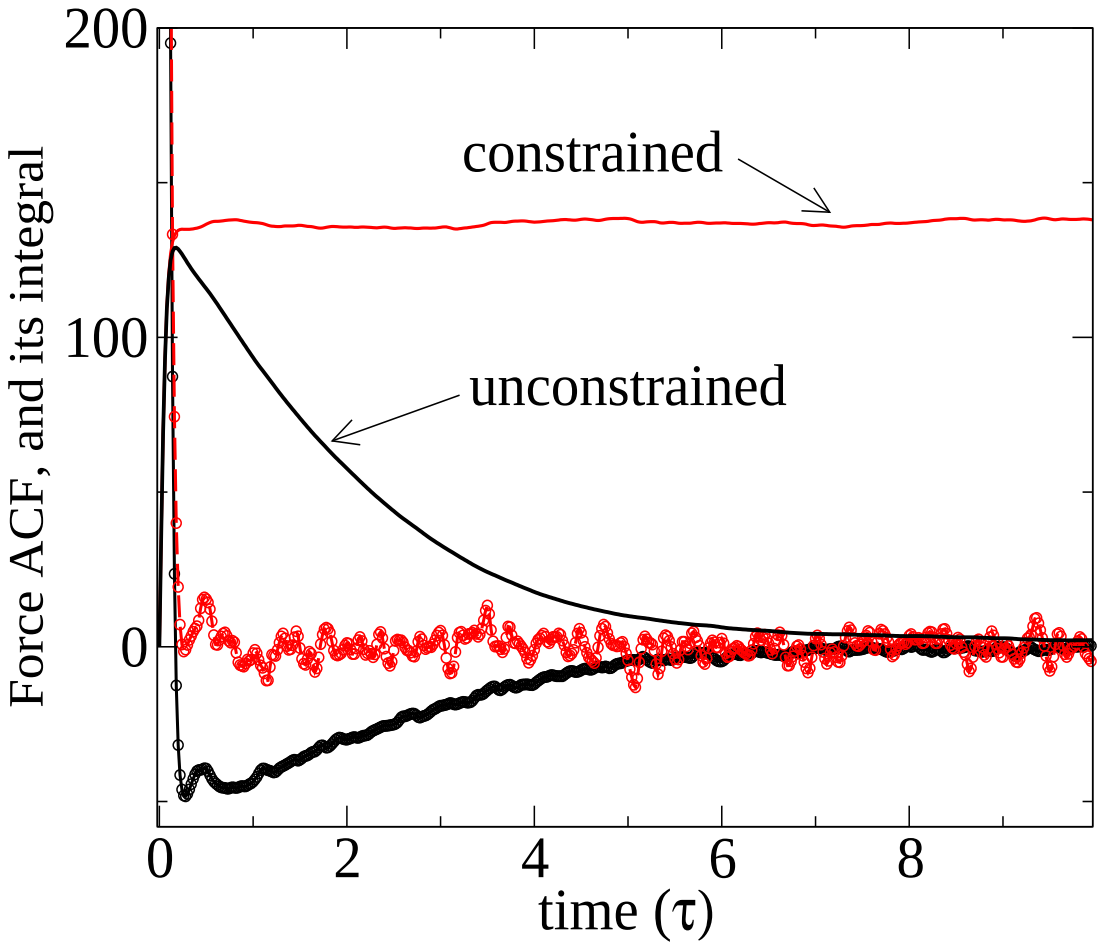
Coarsening star polymers

Markovian behaviour expected?



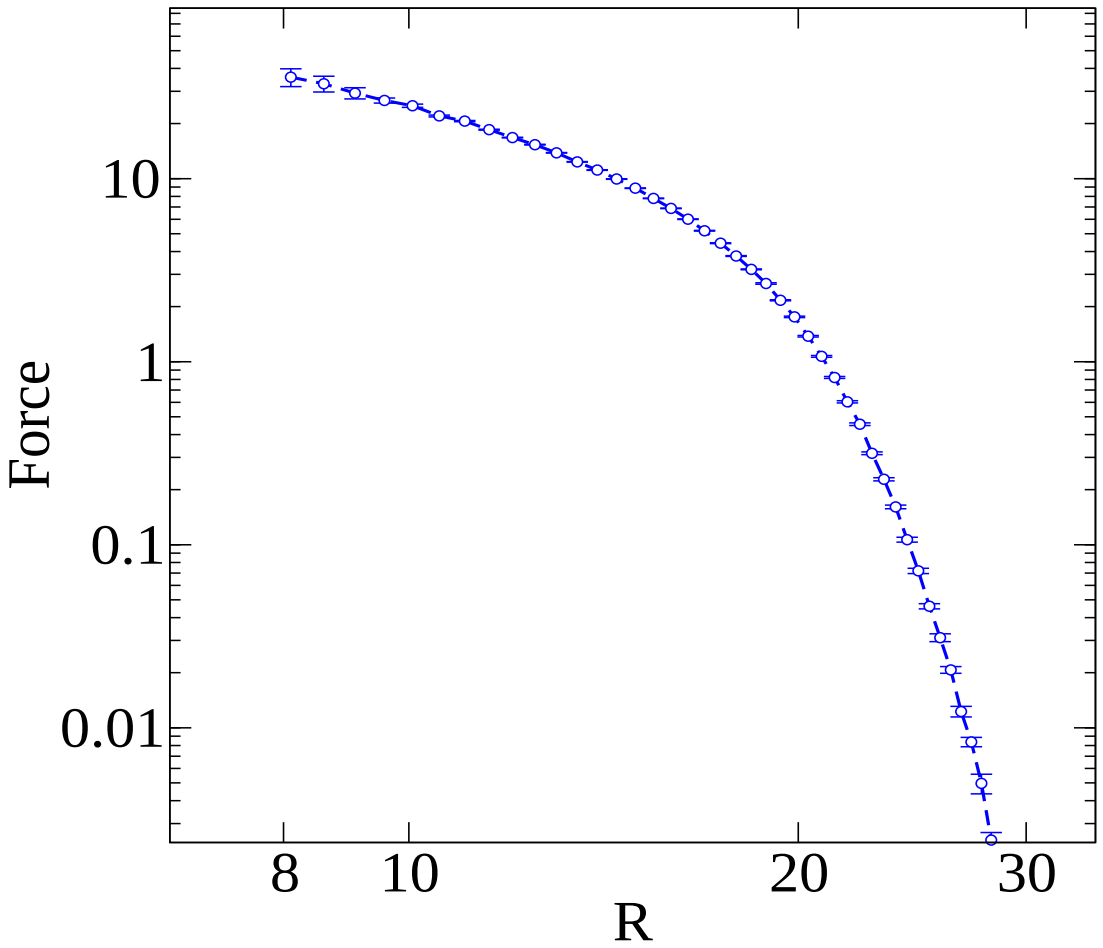
Coarsening star polymers

The plateau problem



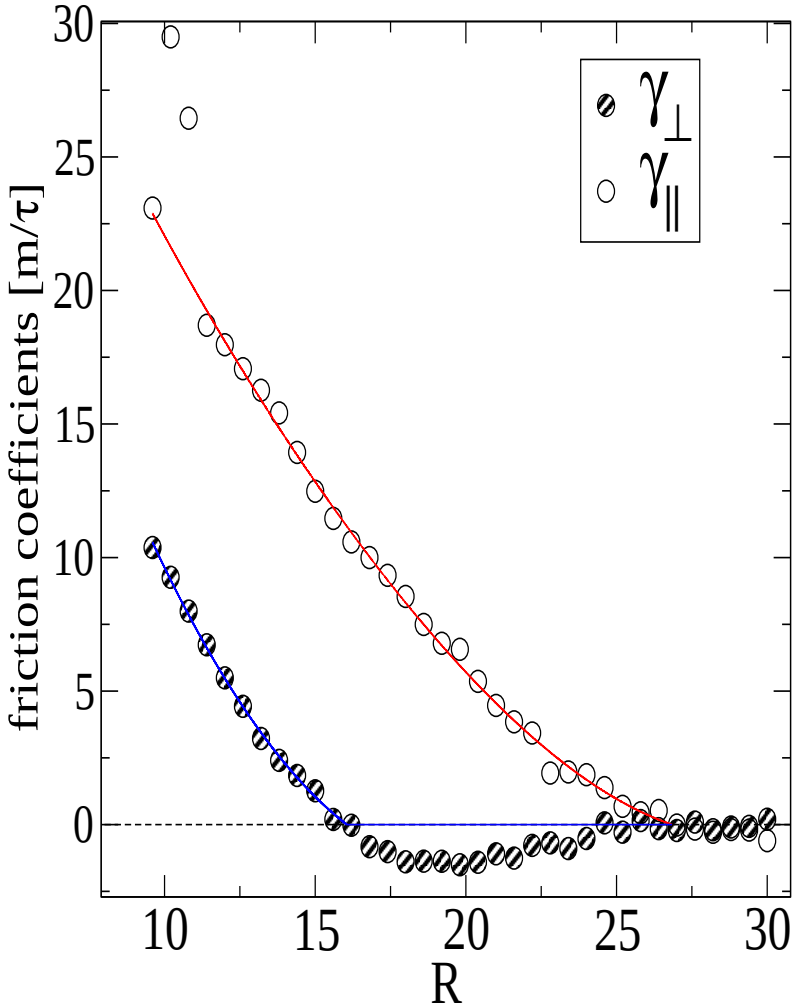
Coarsening star polymers

The average force $\langle \mathbf{F}_{\mu\nu} \rangle^{R_{\mu\nu}}$



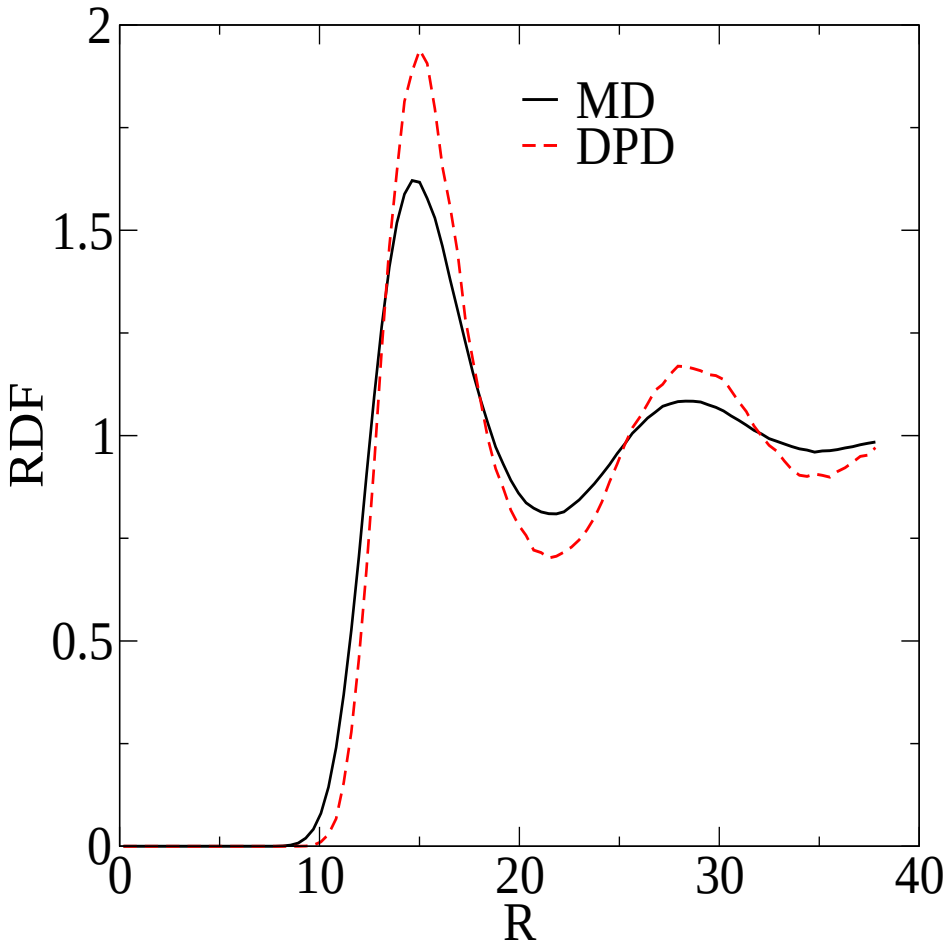
Coarsening star polymers

The friction coefficient $\gamma(R_{\mu\nu}) = A(R_{\mu\nu})\mathbf{1} + B(R_{\mu\nu})\mathbf{e}_{\mu\nu}\mathbf{e}_{\mu\nu}$



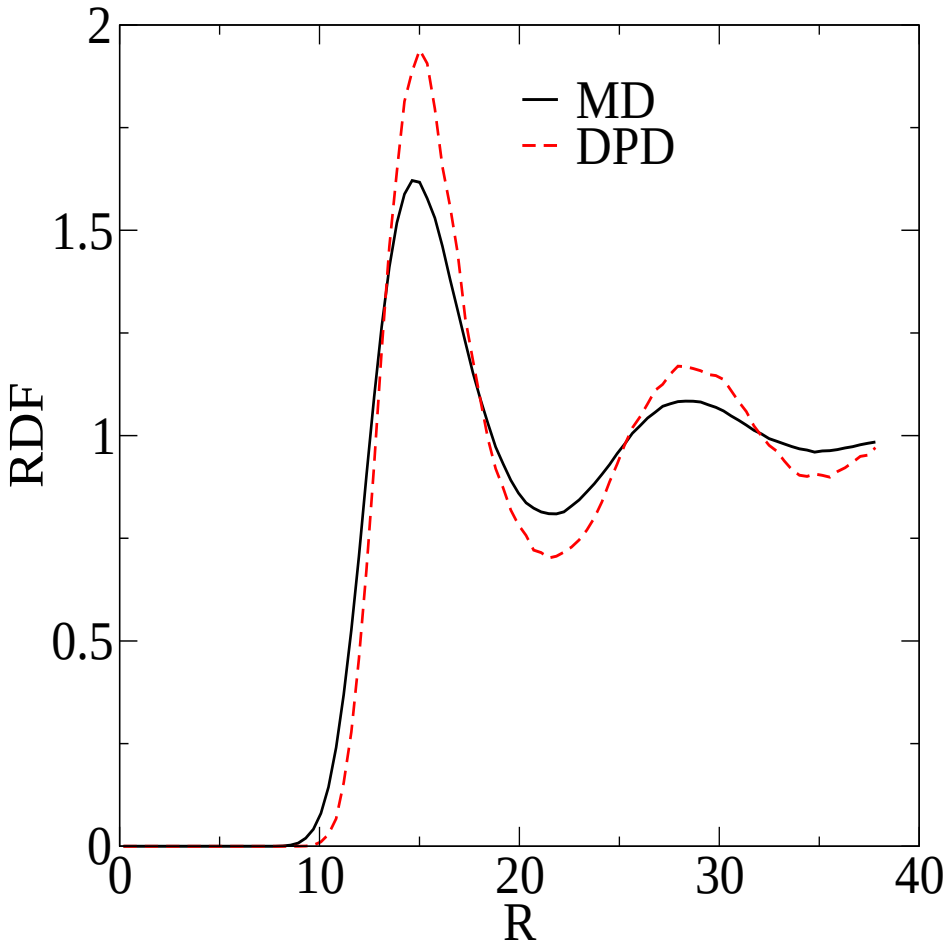
Result of the comparison

The radial distribution function of the CoM



Result of the comparison

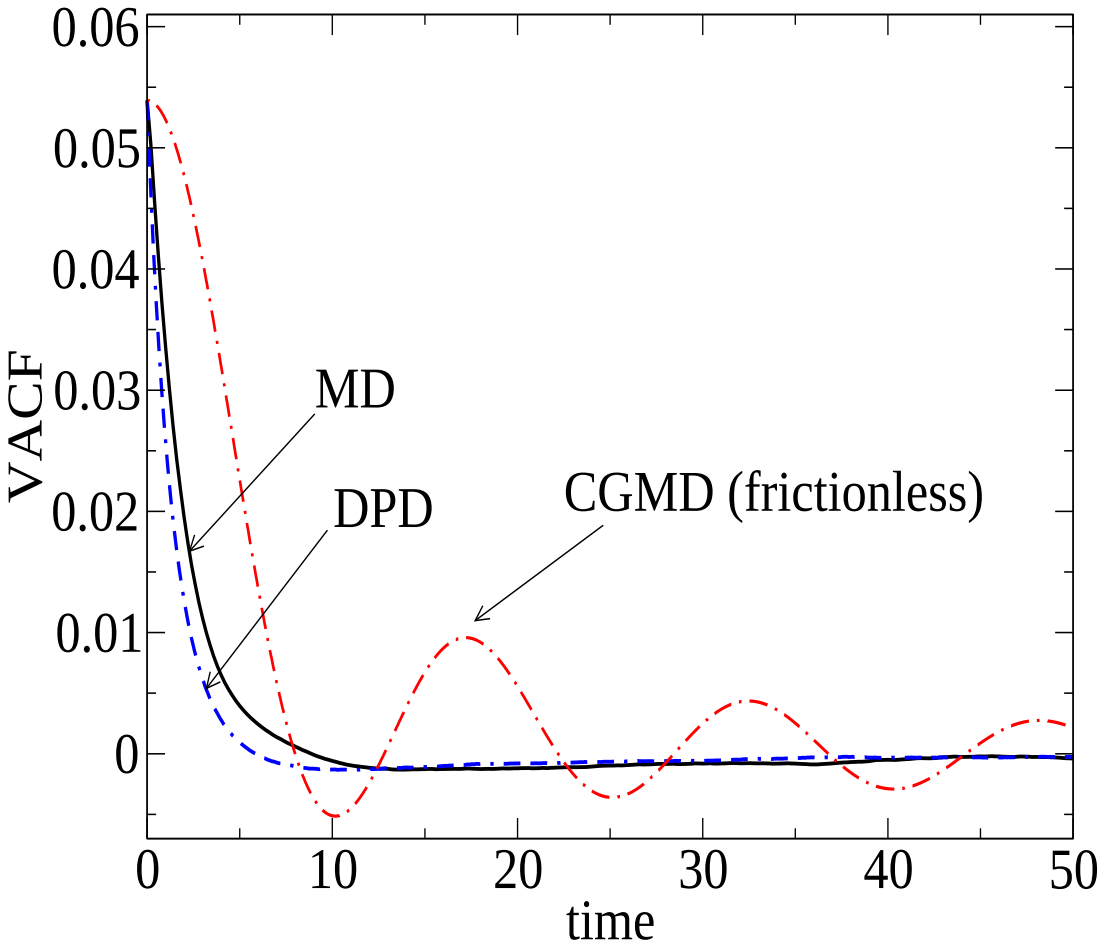
The radial distribution function of the CoM



The pressure and the temperature of the DPD and MD differ in less than 1%.

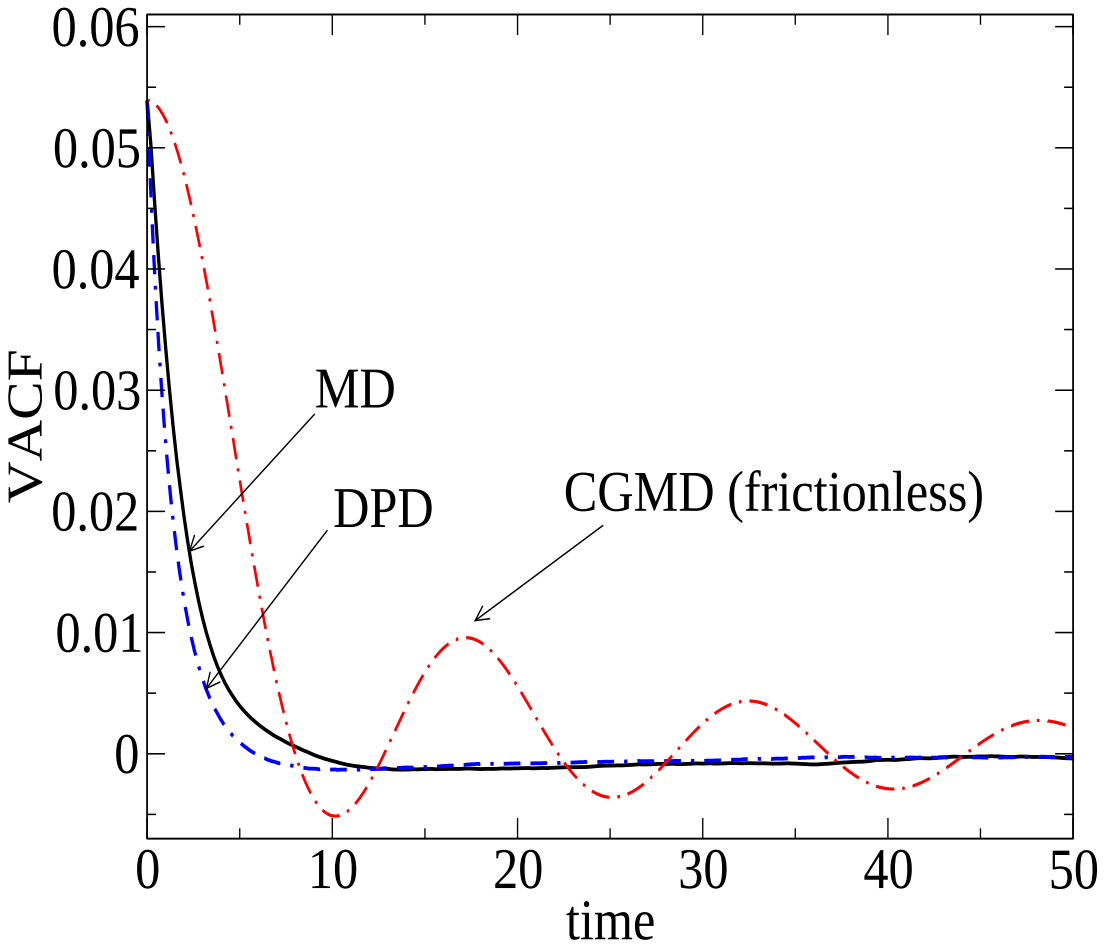
Result of the comparison

The velocity autocorrelation function of the CoM



Result of the comparison

The velocity autocorrelation function of the CoM



Friction is crucial.

Conclusions

- Hybrid MD: particle-continuum scheme for liquid matter based on domain decomposition.

Conclusions

- Hybrid MD: particle-continuum scheme for liquid matter based on domain decomposition.
  - It can solve: Shear flow, sound waves and heat transfer

Conclusions

- Hybrid MD: particle-continuum scheme for liquid matter based on domain decomposition.
  - It can solve: Shear flow, sound waves and heat transfer
  - Can be equipped with **adaptive resolution** (AdResS-HybridMD) to treat large molecules.

Conclusions

- Hybrid MD: particle-continuum scheme for liquid matter based on domain decomposition.
  - It can solve: Shear flow, sound waves and heat transfer
  - Can be equipped with **adaptive resolution** (AdResS-HybridMD) to treat large molecules.
  - Remains to be solved: multispecies and electrostatics across the hybrid interface, energy-conserving adaptive resolution

Conclusions

- Hybrid MD: particle-continuum scheme for liquid matter based on domain decomposition.
  - It can solve: Shear flow, sound waves and heat transfer
  - Can be equipped with **adaptive resolution** (AdResS-HybridMD) to treat large molecules.
  - Remains to be solved: multispecies and electrostatics across the hybrid interface, energy-conserving adaptive resolution
  - Efficient deployment will require: high performance computing, **parallelization.**

Conclusions

- Hybrid MD: particle-continuum scheme for liquid matter based on domain decomposition.
  - It can solve: Shear flow, sound waves and heat transfer
  - Can be equipped with **adaptive resolution** (AdResS-HybridMD) to treat large molecules.
  - Remains to be solved: multispecies and electrostatics across the hybrid interface, energy-conserving adaptive resolution
  - Efficient deployment will require: high performance computing, **parallelization.**
- Coarse graining with proper dynamics

Conclusions

- Hybrid MD: particle-continuum scheme for liquid matter based on domain decomposition.
  - It can solve: Shear flow, sound waves and heat transfer
  - Can be equipped with **adaptive resolution** (AdResS-HybridMD) to treat large molecules.
  - Remains to be solved: multispecies and electrostatics across the hybrid interface, energy-conserving adaptive resolution
  - Efficient deployment will require: high performance computing, **parallelization.**
- Coarse graining with proper dynamics
  - A well-defined method for coarse-graining exists: Zwanzig projection

Conclusions

- Hybrid MD: particle-continuum scheme for liquid matter based on domain decomposition.
  - It can solve: Shear flow, sound waves and heat transfer
  - Can be equipped with **adaptive resolution** (AdResS-HybridMD) to treat large molecules.
  - Remains to be solved: multispecies and electrostatics across the hybrid interface, energy-conserving adaptive resolution
  - Efficient deployment will require: high performance computing, **parallelization.**
- Coarse graining with proper dynamics
  - A well-defined method for coarse-graining exists: Zwanzig projection
  - A practical recipe has been formulated to compute the macroscopic dynamics from microscopic simulations.

Conclusions

- Hybrid MD: particle-continuum scheme for liquid matter based on domain decomposition.
  - It can solve: Shear flow, sound waves and heat transfer
  - Can be equipped with **adaptive resolution** (AdResS-HybridMD) to treat large molecules.
  - Remains to be solved: multispecies and electrostatics across the hybrid interface, energy-conserving adaptive resolution
  - Efficient deployment will require: high performance computing, **parallelization.**
- Coarse graining with proper dynamics
  - A well-defined method for coarse-graining exists: Zwanzig projection
  - A practical recipe has been formulated to compute the macroscopic dynamics from microscopic simulations.
  - Demonstrated the procedure for the case of star polymer melts.

Possible connexions with Heterogeneous Multiscale Modelling

- Open MD can be used to reconstruct a macroscopic state given based on the fluxes across boundaries ("lift" operation for dense liquids).

Possible connexions with Heterogeneous Multiscale Modelling

- Open MD can be used to reconstruct a macroscopic state given based on the fluxes across boundaries ("lift" operation for dense liquids).
- It could be easily adapted to impose Dirichlet boundary conditions (state coupling).

Possible connexions with Heterogeneous Multiscale Modelling

- Open MD can be used to reconstruct a macroscopic state given based on the fluxes across boundaries ("lift" operation for dense liquids).
- It could be easily adapted to impose Dirichlet boundary conditions (state coupling).
- Alternative methods (accelerated MD: tune $\epsilon > 1$ to accelerate slow variables) may also enhance the lift operation (work in progress).