Concurrent multiple scale simulation of molecular liquids

Combining adaptive coarse-graining and hybrid particle-continuum hydrodynamics schemes.

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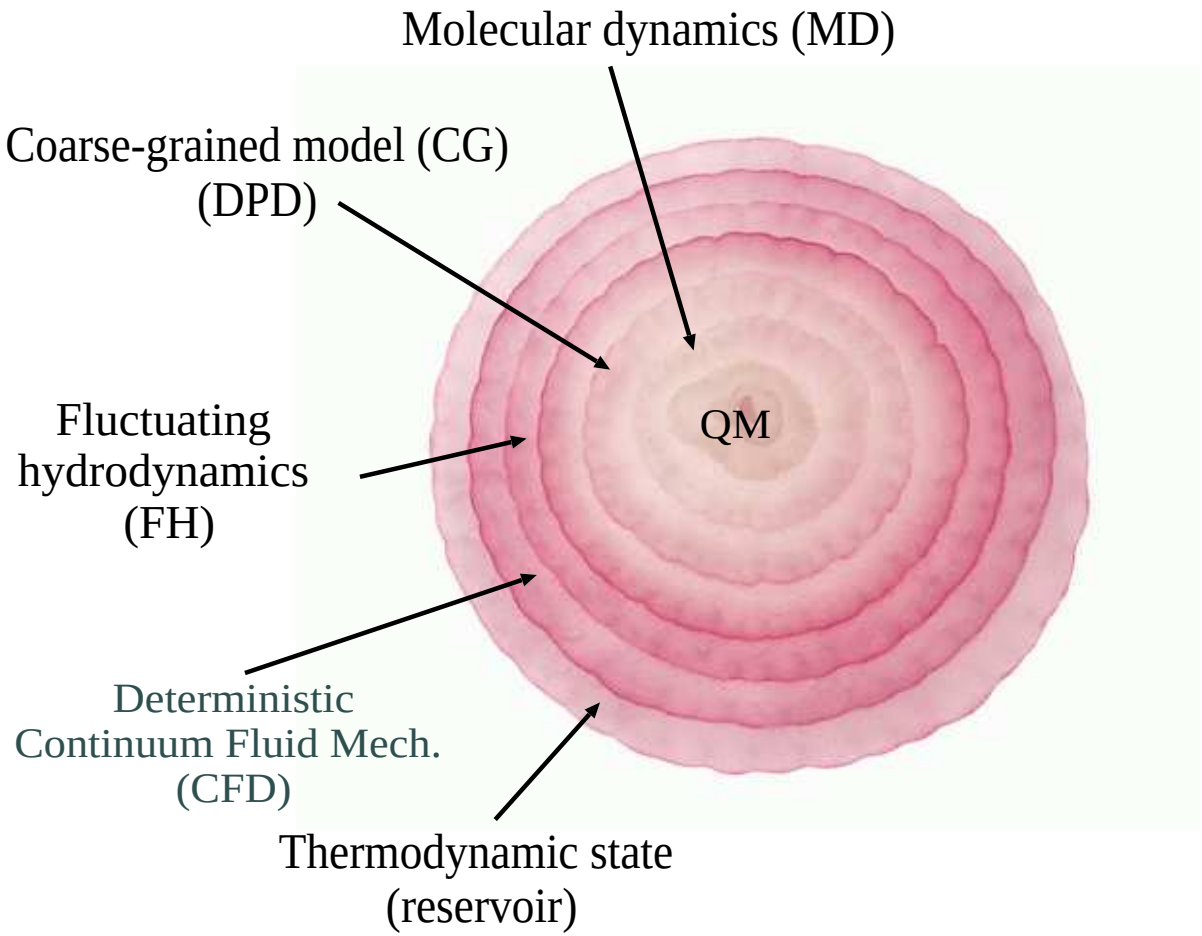
The Onion Project

TOP

The Onion Project

TOP for multiscale domain decomposition



Coworkers

- *MD-CG-continuum*.
  - **Kurt Kremer**, Max-Plank Institute for Polymer Research (Mainz, Germany).
  - **Matej Praprotnik**, Max-Plank Institute for Polymer Research.

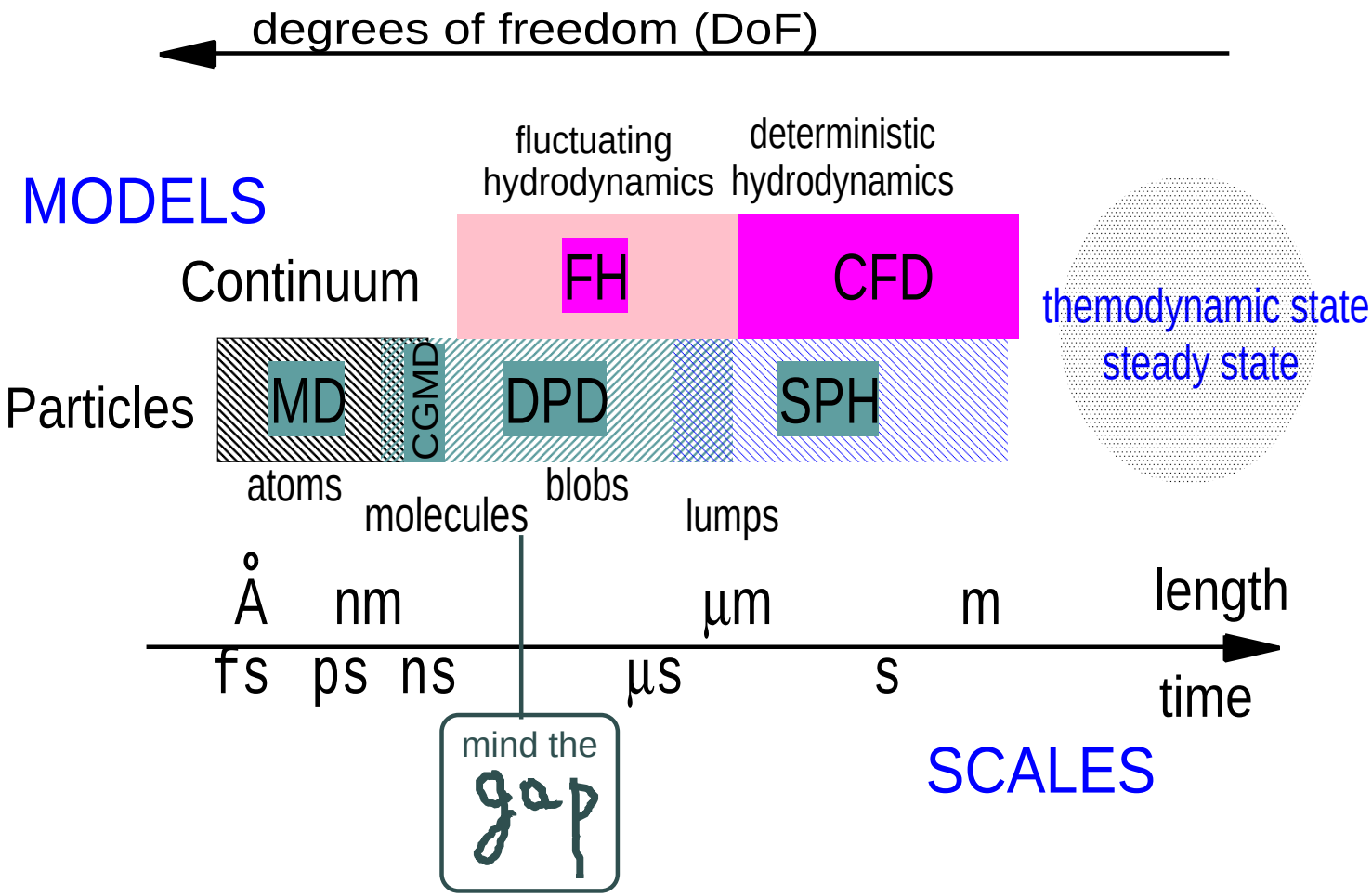
- *MD-continuum hydrodynamics*
  - **Gianni De Fabritiis**, U. Pompeu Fabra (Barcelona)
  - **Peter Coveney**, UCL (London)

- *Open boundaries for Fluctuating hydrodynamics*
  - **Anne Dejoan**, CIEMAT (Madrid)

- *Coarse-graining with proper dynamics*.
  - **Pep Español**, UNED (Madrid).

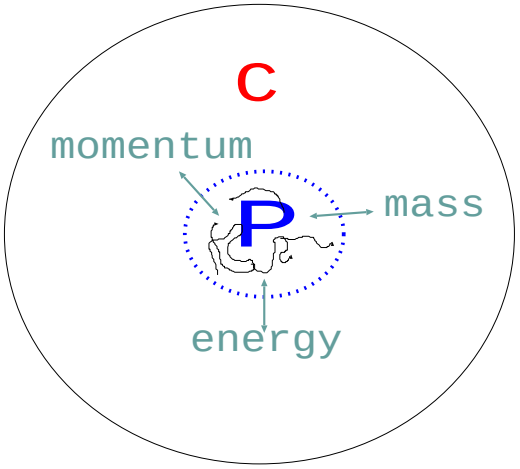
Scales and models

with hydrodynamics



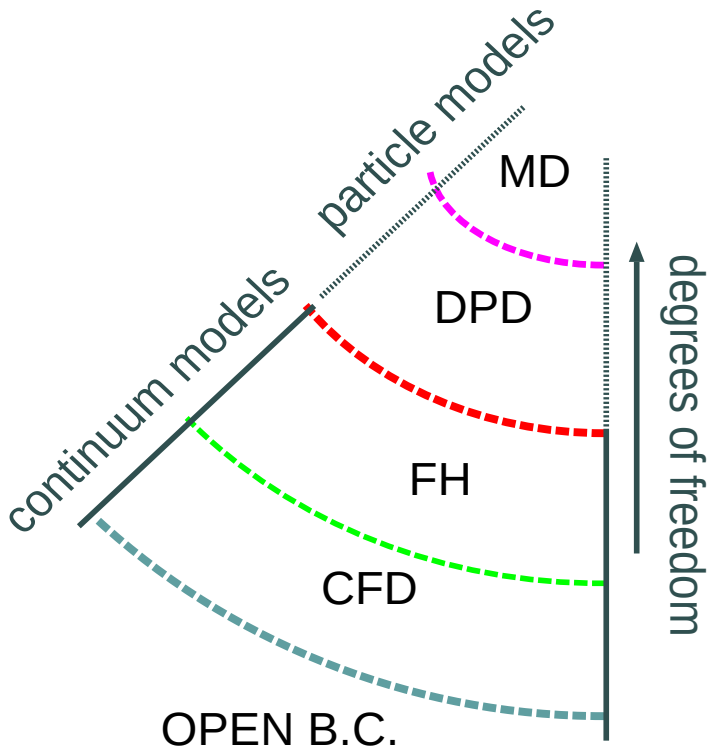
Multiscale modelling: Motivation. Applications.

- Multiscale models: predicted as a scientific milestone in near future by the 2020 Science Group. [$Nature$ **440** (7083): 383 (2006)]
- Complex fluids near interfaces: microfluidics, slip of liquid flow past surfaces.
- Fluid-fluid or soft interfaces (e.g., Rayleigh-Taylor instability, membrane's dynamics)
- Macromolecules-sound interaction (proteins) [*Science*, 309:1096, 2005.]
- Crystal growth from liquid phase.
- Wetting phenomena: microscopic treatment of the wetting front. Lubrication
- Confined systems: driven to chemical equilibrium, osmosis driven flows through membranes, thin films, water between membranes, clays,
- etc...



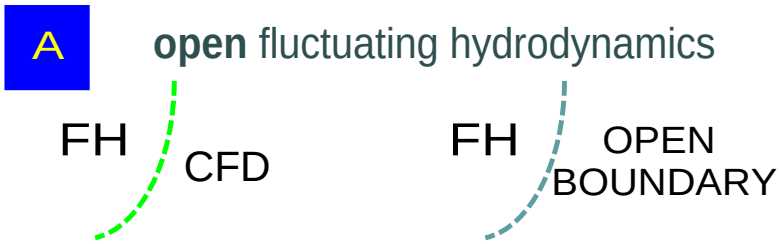
Domain decomposition

Interfacing models with different degrees of freedom

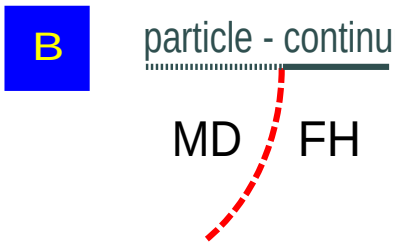


Open boundary conditions:
OUTSIDE WORLD
steady state,
thermodynamic reservoir

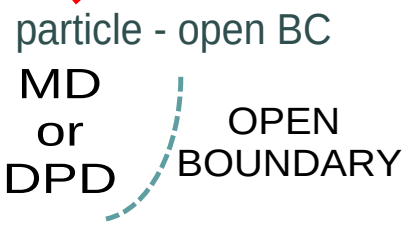
Domain decomposition: talk outline



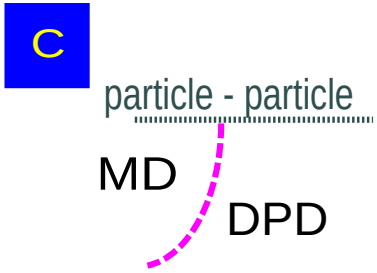
RDB, A. Dejoan, PRE (in press)



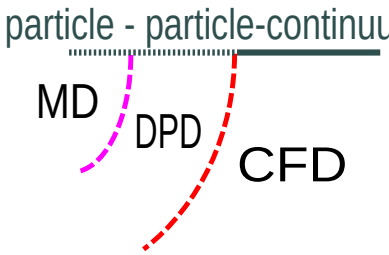
G. De Fabritiis, RDB, P. Coveney, PRL (2006)
RDB, G. De Fabritiis, PRE (2007)



E. Flekkoy, RDB, P. Coveney, PRE (2005)

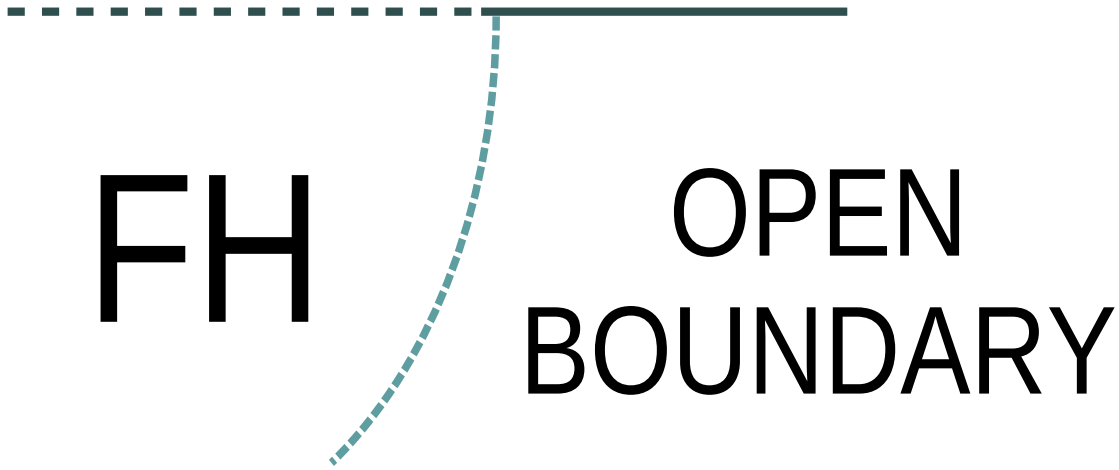


M. Praprotnik, L. Delle Site, K. Kremer, JCP (2005)



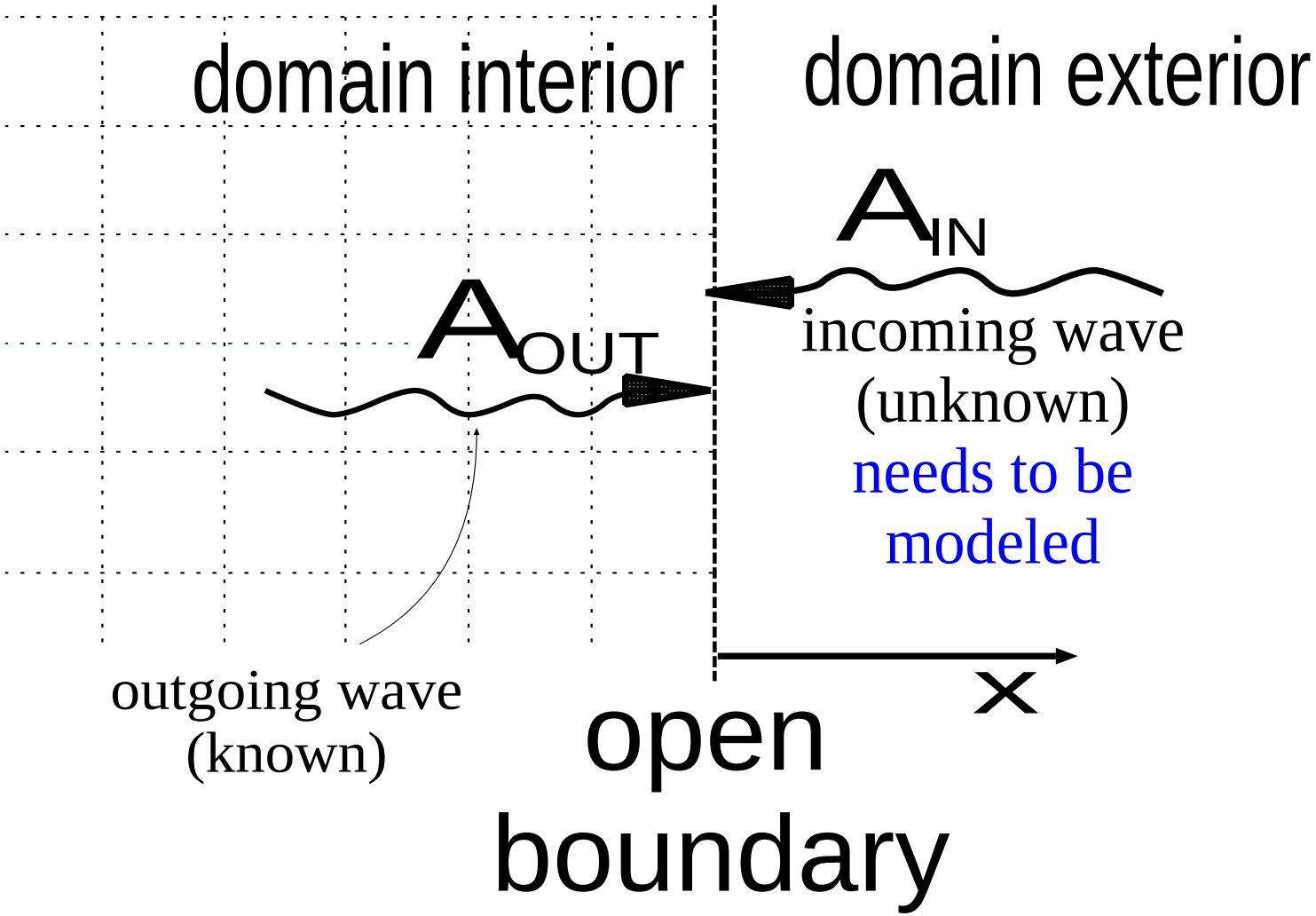
RDB, M. Praprotnik, K. Kremer JCP (2008)

Non-reflecting boundary conditions for fluctuating hydrodynamics



RDB, Anne Dejoan, Phys Rev E. (in press)

Non-reflecting boundary conditions for CFD: set-up



Implementation of non-reflecting boundary conditions.

$$\text{density} \quad : \quad \frac{\partial \rho}{\partial x} = 0$$

$$\text{velocity} \quad : \quad \frac{\partial u}{\partial t} + \frac{1}{2\rho_e c}(L_{OUT} - L_{IN}) = 0$$

Closure models for the incoming waves

$L_{OUT} = \lambda_{OUT}\left(\frac{\partial P}{\partial x} + \rho c \frac{\partial u}{\partial x}\right)$	Evaluated at the interior domain
$L_{IN} = 0$	`cons:` ill posed, overall pressure drift
$L_{IN} = K(p - p_{eq}) \quad K = \frac{\sigma c}{L}$	`cons:` reflection of low freqs.
$\boxed{L_{IN} = K(\rho c A_{IN}) = \frac{K}{2}(\delta p - \rho_e c \delta u)}$	`pros:` *Wave masking*. Enables fluctuation-dissipation balance.

NRBC for FH: Fluctuation-dissipation balance for incoming waves

- Stochastic eq. for incoming wave amplitude:

$$\frac{dA_{IN}(x_b)}{dt} + KA_{IN}(x_b) = F(t)$$

- Fluctuating stress: $F(t) \equiv \frac{1}{\Delta x \rho_e}\left[\tilde{\Pi}_{xx}(x_b + \frac{\Delta x}{2}) - \tilde{\Pi}_{xx}(x_b - \frac{\Delta x}{2})\right]$

$$\langle F(t)F(0)\rangle = 2\Phi\delta(t) = \frac{4k_BT\eta_L}{\Delta x^2\rho_e^2 V_c}\delta(t)$$

- Stochastic boundary **dynamics**: $\langle A_{IN}(t)A_{IN}(0)\rangle = \frac{\Phi}{K}\exp(-Kt)$.

  $\langle A_{IN}\rangle = 0$ and $\boxed{\langle A_{IN}^2\rangle = \frac{\Phi}{K}}$.

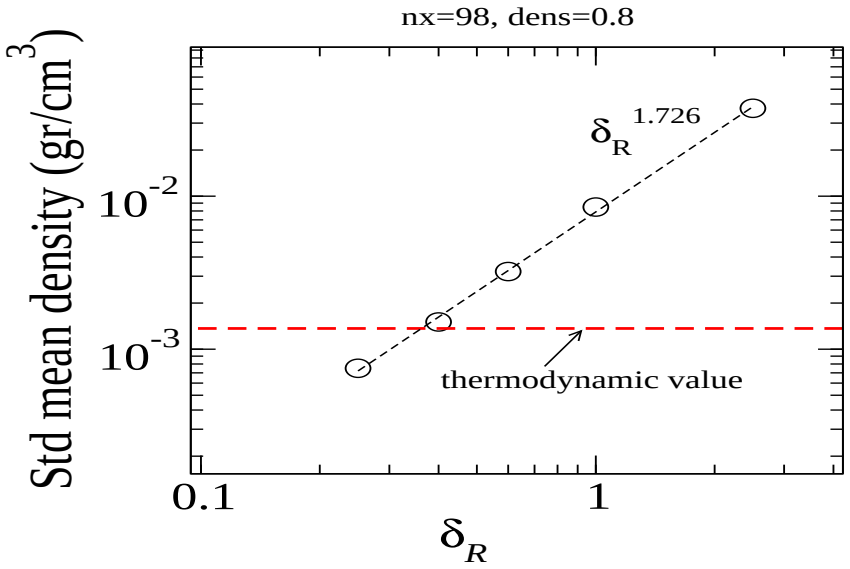
- Sound amplitude variance, **thermodynamics,** $A_{IN} = (1/2)(c\delta\rho/\rho_e - \delta u)$.

  $\boxed{\langle A_{IN}^2\rangle = \frac{1}{2}\frac{k_BT}{\rho_e V_c}}$

- **Relaxation rate**: $\boxed{K = \frac{\nu_L}{(\delta_R\Delta x)^2}}$ with $\delta_R^{(theor)} = 0.5$

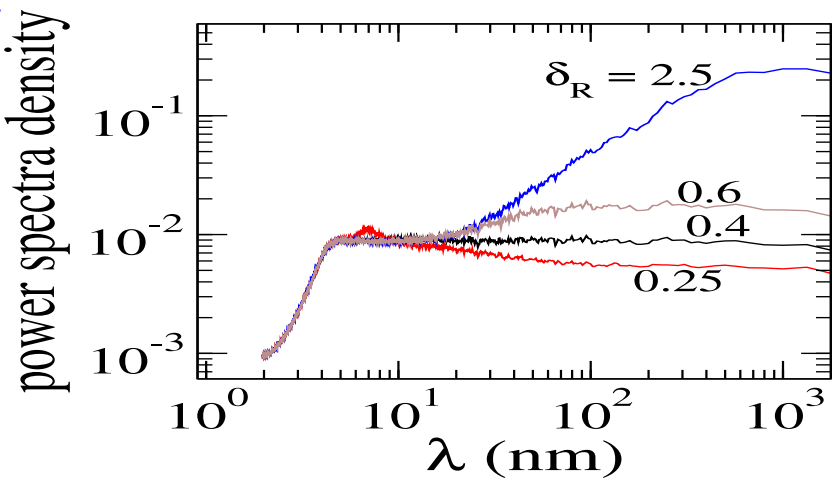
Mean density fluctuation at equilibrium: grand canonical ensemble,

$$\langle (\delta\bar{\rho})^2 \rangle = \frac{k_B T}{c^2 V}$$

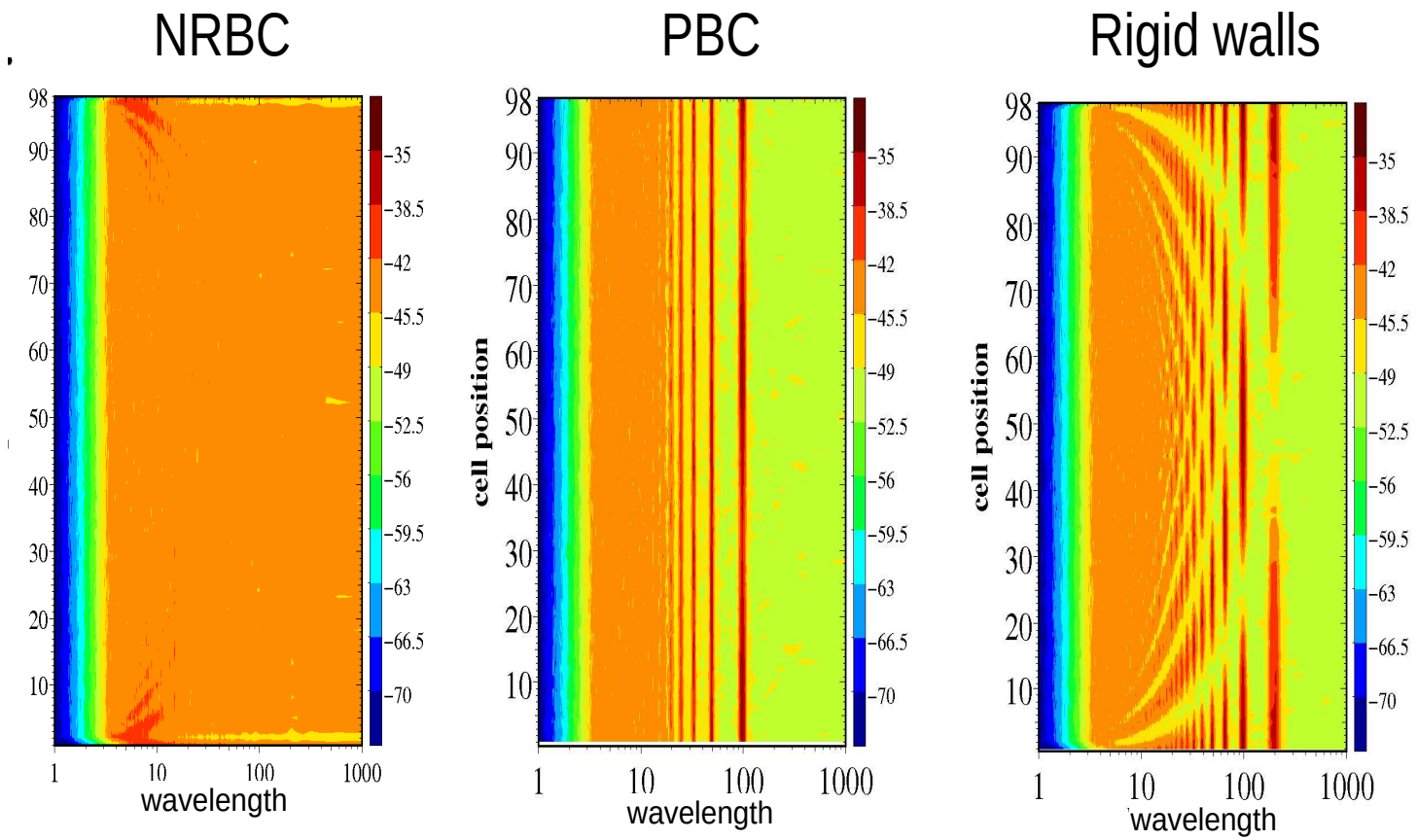


$$\delta_R^{(num)} = 0.4$$

Sound power spectral density within the system interior

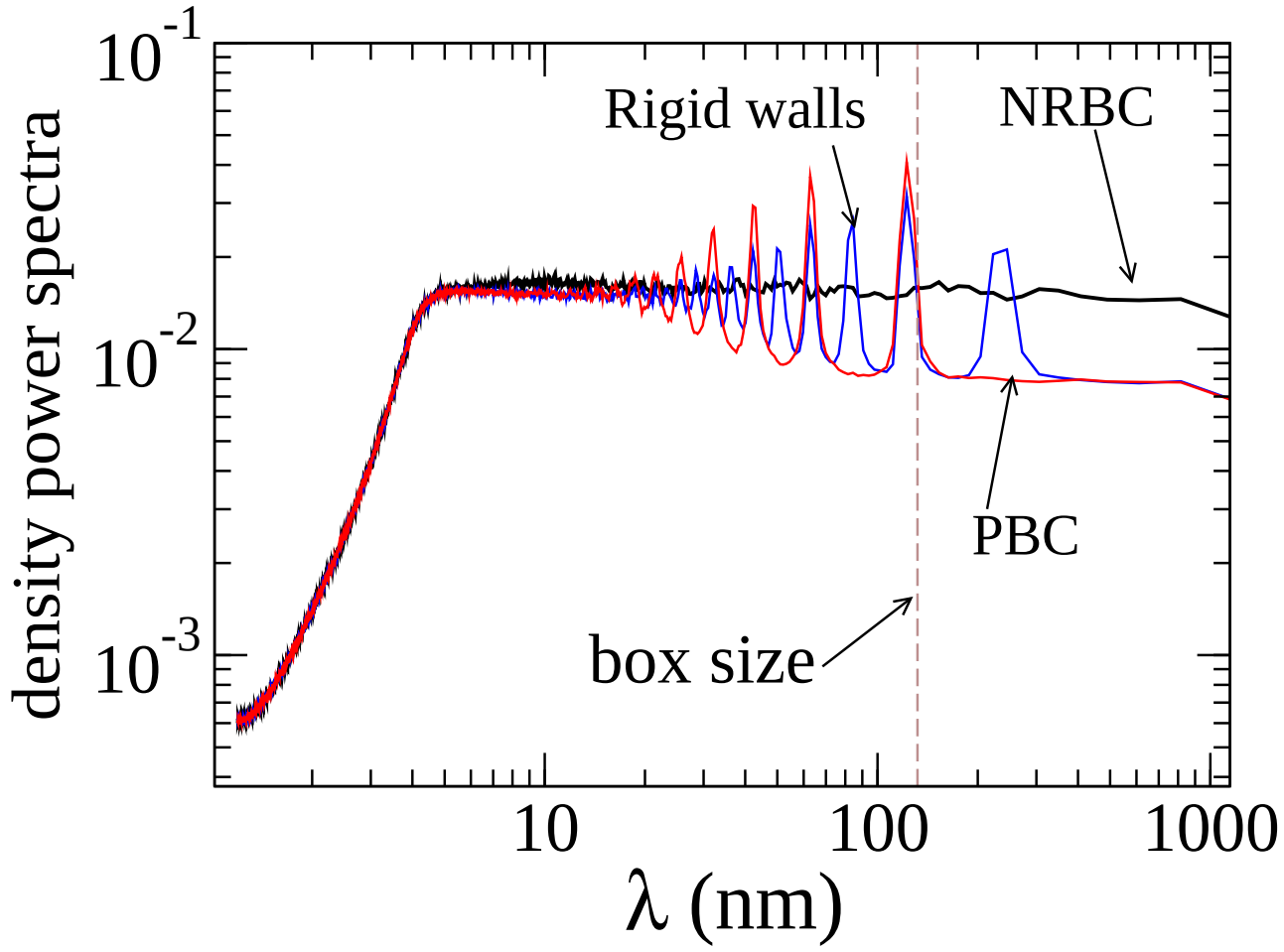


Comparsison between Non-reflecting boundaries (NRBC), periodic (PBC) and rigid walls

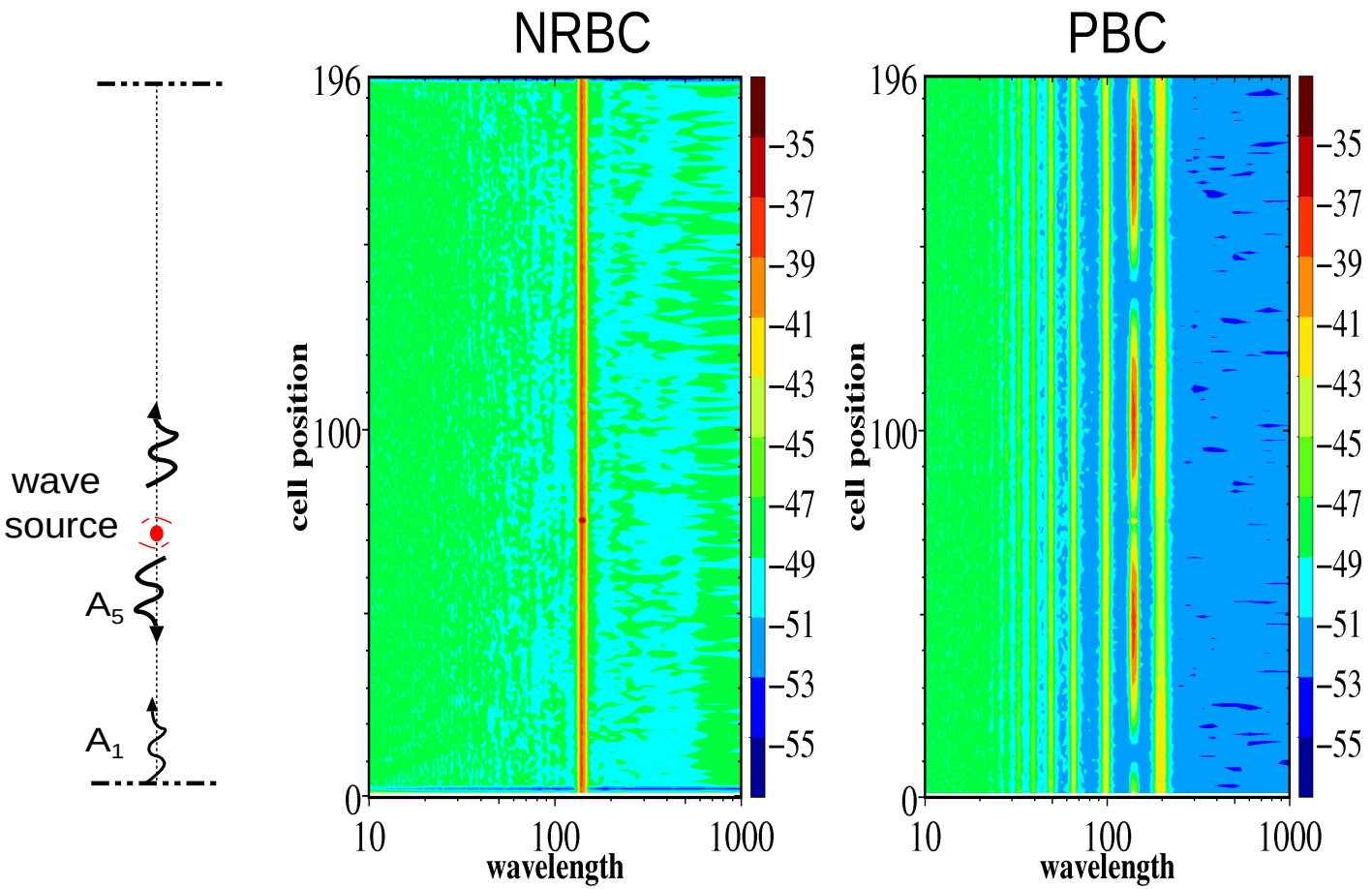


Comparison with PBC and Rigid walls:

PSD of waves within the system

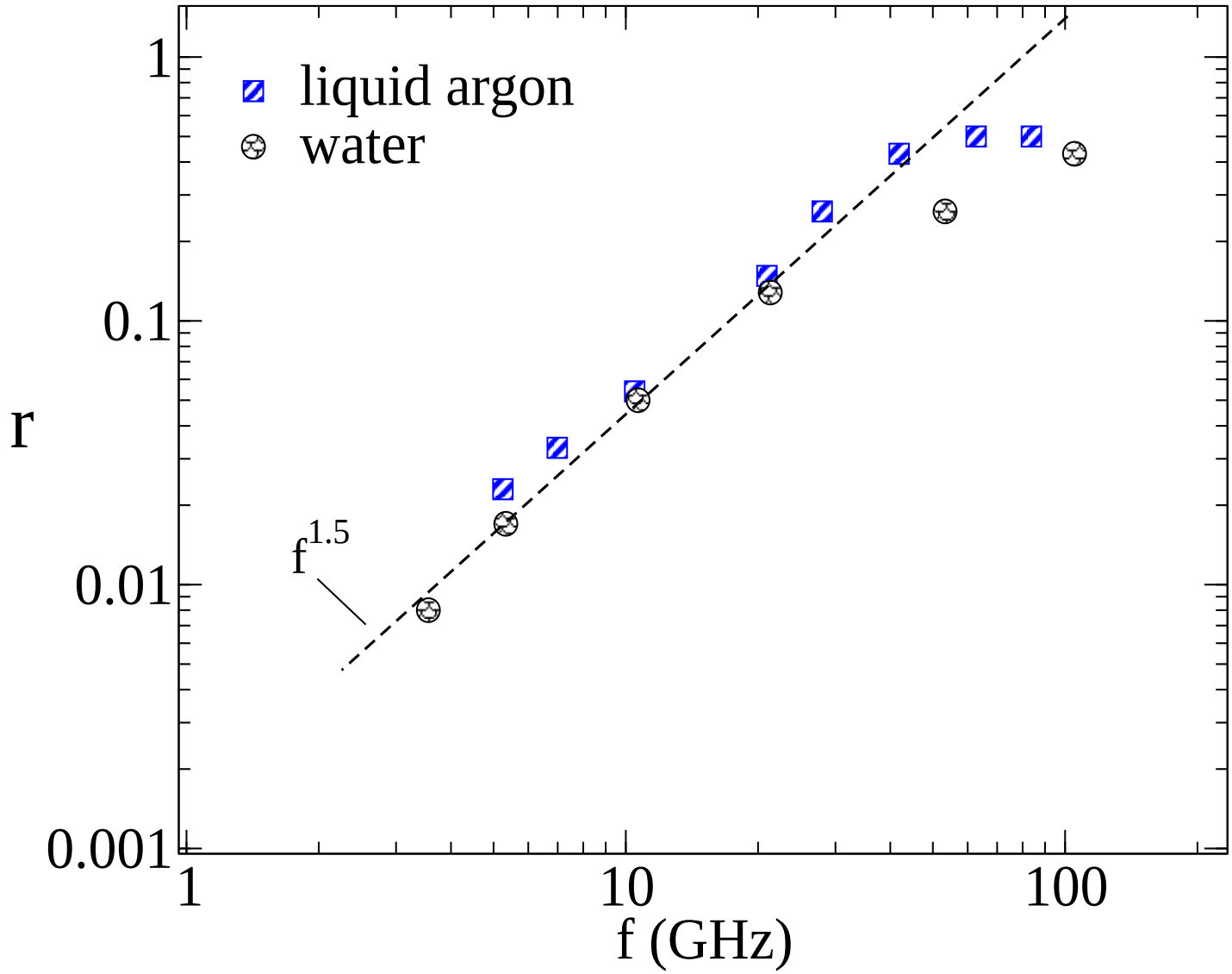


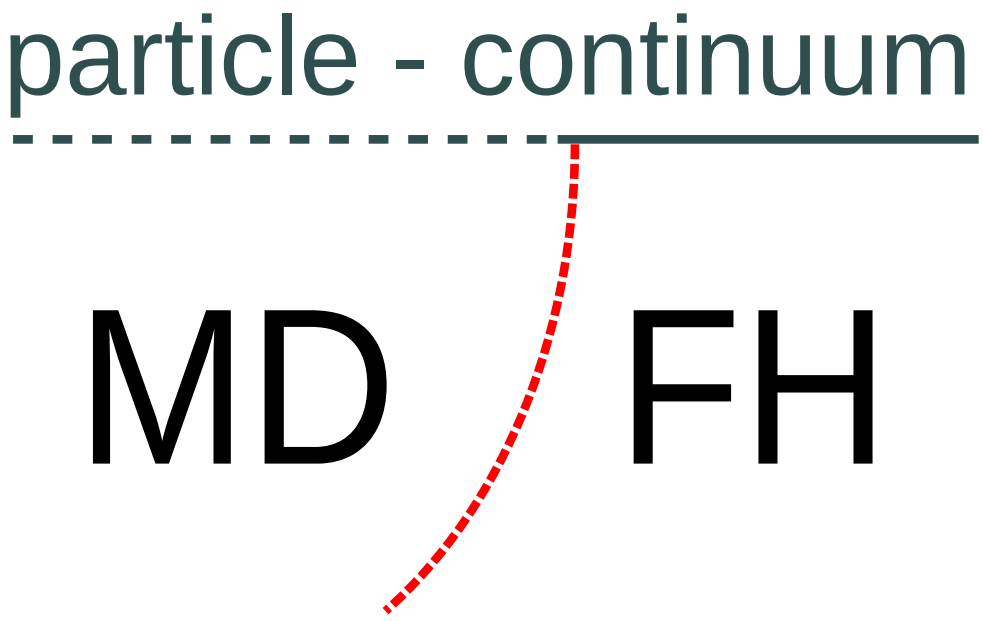
Forced waves: evacuation of sound



Reflection coefficient

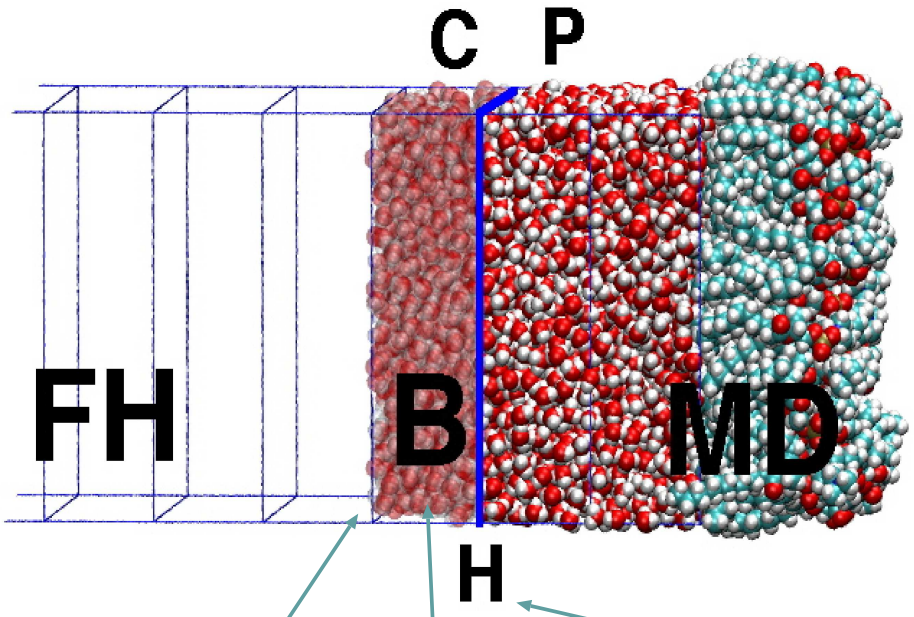
$$r \simeq 10^{-3}(f\Delta x)^{1.5}$$




particle - continuum
MD
FH

MD-CFD **Domain decomposition**

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

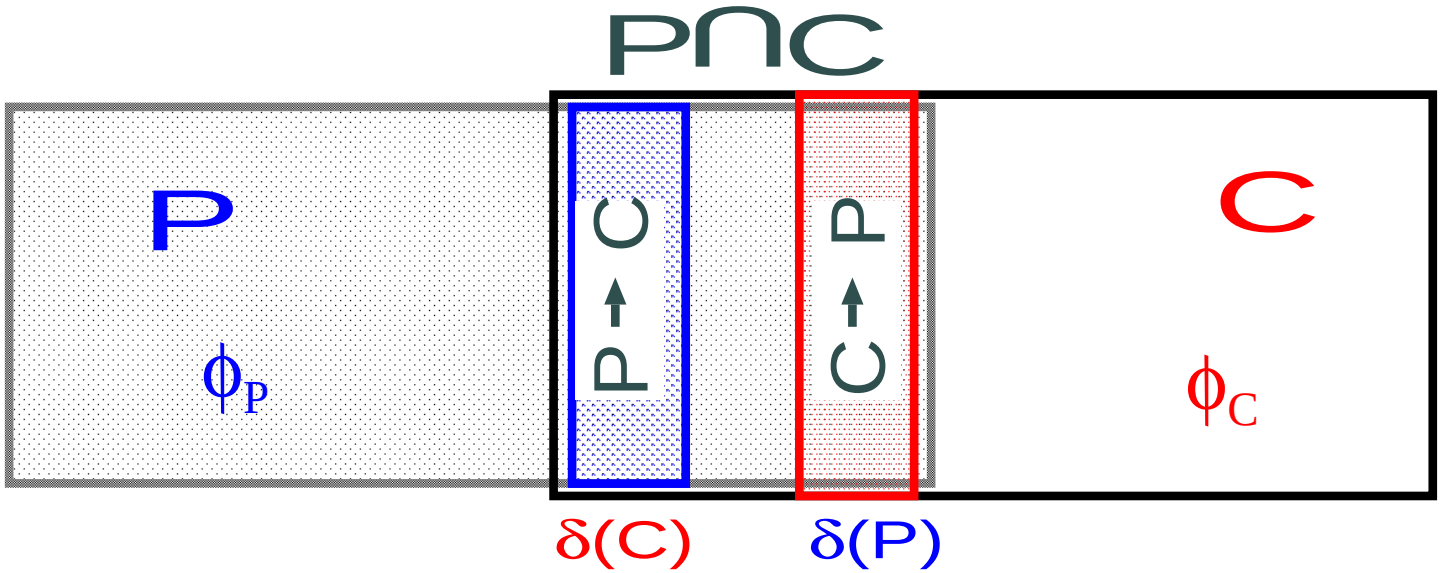
MD-CFD: **Hybrid schemes depending upon the exchanged information**

- **Coupling through variables:**
  - **Schwartz scheme**: steady state, closed system (only shear), no fluctuations.
  - **Constraint particle dynamics** (velocity imposition): unsteady, closed (only shear), no fluctuations.

- **Coupling through fluxes** (of momentum and energy)
  - **Unsteady** flows
  - **Open** molecular dynamics: **grand canonical ensemble**, generalized ensembles for MD.
  - Shear, **sound and heat** transfers (avoid finite size effect)
  - **Fluctuations** included (MD-Fluctuating hydrodynamics)

MD-CFD The Schwartz method

REFS: Hadjiconstantinou, Koumoutsakos



0) Solve C using an initial guess for ϕ_C at δ(C)

loop

1) Solve P imposing ϕ_C at δ(P) Maxwell Daemon for velocity

2) Solve C imposing $\langle\phi_P\rangle$ at δ(C) Dirichlet B.C.

Check for convergence within PNC

Constrained dynamics .vs. velocity continuity

	C imposes to P	P imposes to C
Authors	Nie *et al* (MD-CFD)	RDB (MD-FH); Garcia (DSMC-CFD)
velocity	Contrained particle dynamics	Relaxation BC for C
mass flux	Imposed to P	Measured from P

Constrained particle dynamics: Thompson and O'Connel, PRE, (1995); Nie *et al.* J. Fluid Mech. (2004)

$$\frac{dx_i^2}{dt} = F_i/m + \frac{1}{\tau_r}\left(v_B^C - \langle v \rangle_B^P\right)$$

Continuum velocity relaxation: RDB, Flekkoy, P.Coveney, EuroPhys. Lett. (2005)

$$\frac{[\Delta\rho\mathbf{v}]_H^C}{\Delta t} = [\mathrm{Navier-Stokes}] + \frac{1}{\tau_r}\left(\langle [\rho\mathbf{v}]^P \rangle_H - [\rho\mathbf{v}]_H^C\right)$$

Note: Constraining the particle dynamics affects the particle collective properties. It also destroys energy balance. Relaxation of C is simple and efficient, $\tau_r << \tau_{hydro}$.

Continuum fluid dynamics

- **Conservation law** conserved quantity per unit volume Φ

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

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

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

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

Fluctuating heat and stress a *la Landau*

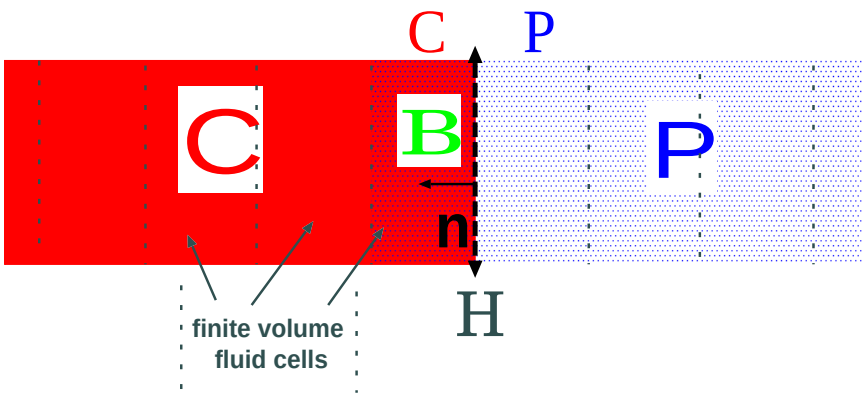
Stress fluctuations $\langle\tilde{\Pi}(\boldsymbol{r}_1,t)\tilde{\Pi}(\boldsymbol{r}_2,0)\rangle = 2k_BTC_{\alpha\beta\gamma\delta}\delta(\boldsymbol{r}_2-\boldsymbol{r}_1)\delta(t)$

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

Heat flux fluctuations $\tilde{Q}$

MD-CFD **Flux exchange**

REFS: E. Flekkoy EPL (2000); A. Garcia (AMAR)m J.Comp.Phys (1999); Delgado-Buscalioni (HybridMD), PRE (2002), PRL (2007).



Continuum sudomain: C
Particle subdomain: P
Particle buffer: B

Total system : C+P
Extended system: C+P+B

Flux of ϕ across hybrid interface H

$$J_\phi^H = \frac{\left(J_\phi^{PC} + J_\phi^{CP}\right)}{2}$$

Conservation

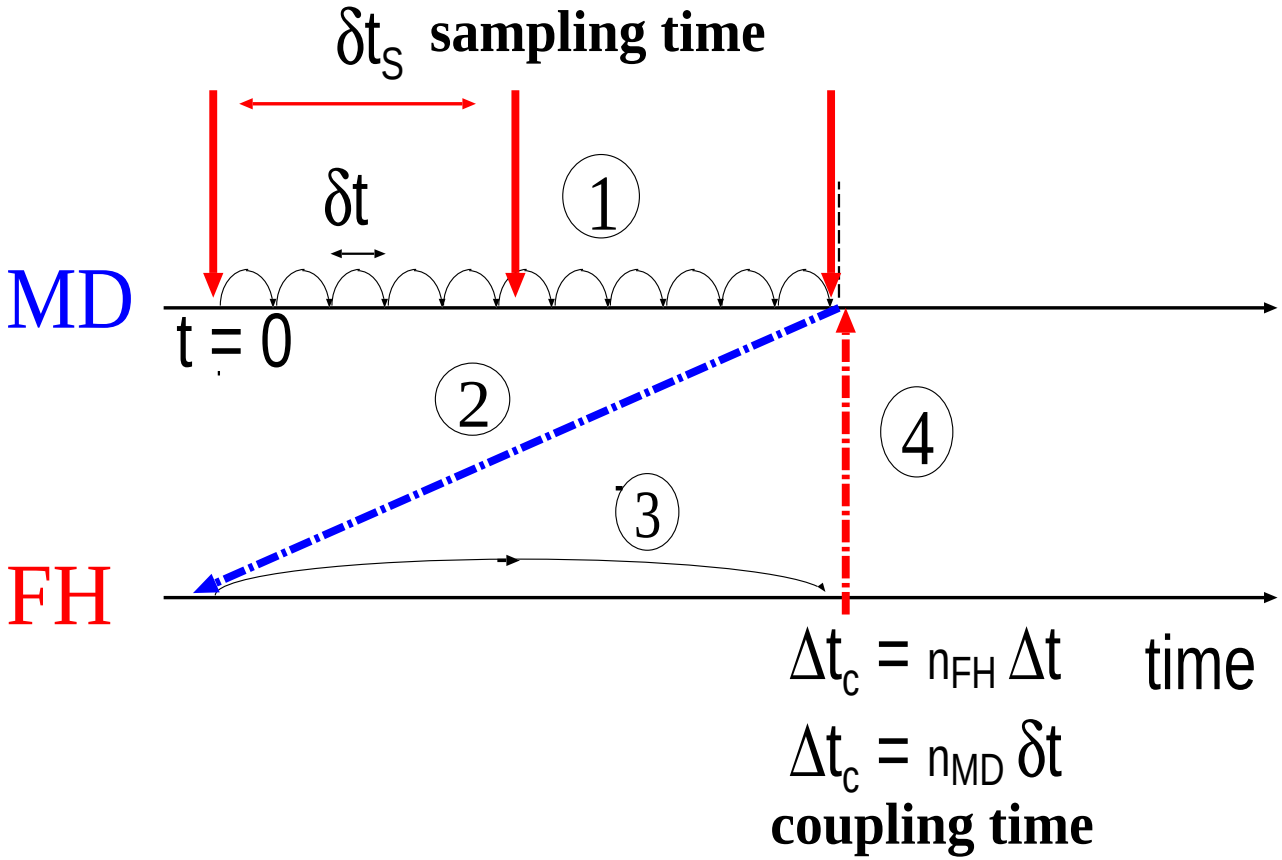
$$\Delta\phi_C = A\, J_\phi^H . \mathbf{n}\, \Delta t$$

$$\Delta\phi_P = -A\, J_\phi^H . \mathbf{n}\, \Delta t$$

Conservation laws apply for the total system: P+C

G. De Fabritiis, RDB, P. Coveney; PRL 97, 134501 (2006)
RDB, G. De Fabritiis; PRE 76, 036709 (2007)

MD-FH Time coupling in flux based scheme



MD-FH 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 $\Delta t/2$,

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

Thus for $\boxed{\langle J^2_{MD} \rangle = \langle J^2_{FH} \rangle}$ the decorrelation times should coincide:

$$\Delta t = 2\tau_c = \delta t_S \;\; \text{Smallest coupling time} = \text{Sampling time}$$

In general,

$$\boxed{\Delta t_c = n_{FH} \Delta t = 2 N_s \tau_c}$$

The finite volume scheme

Finite volume schemes for fluctuating hydrodynamics

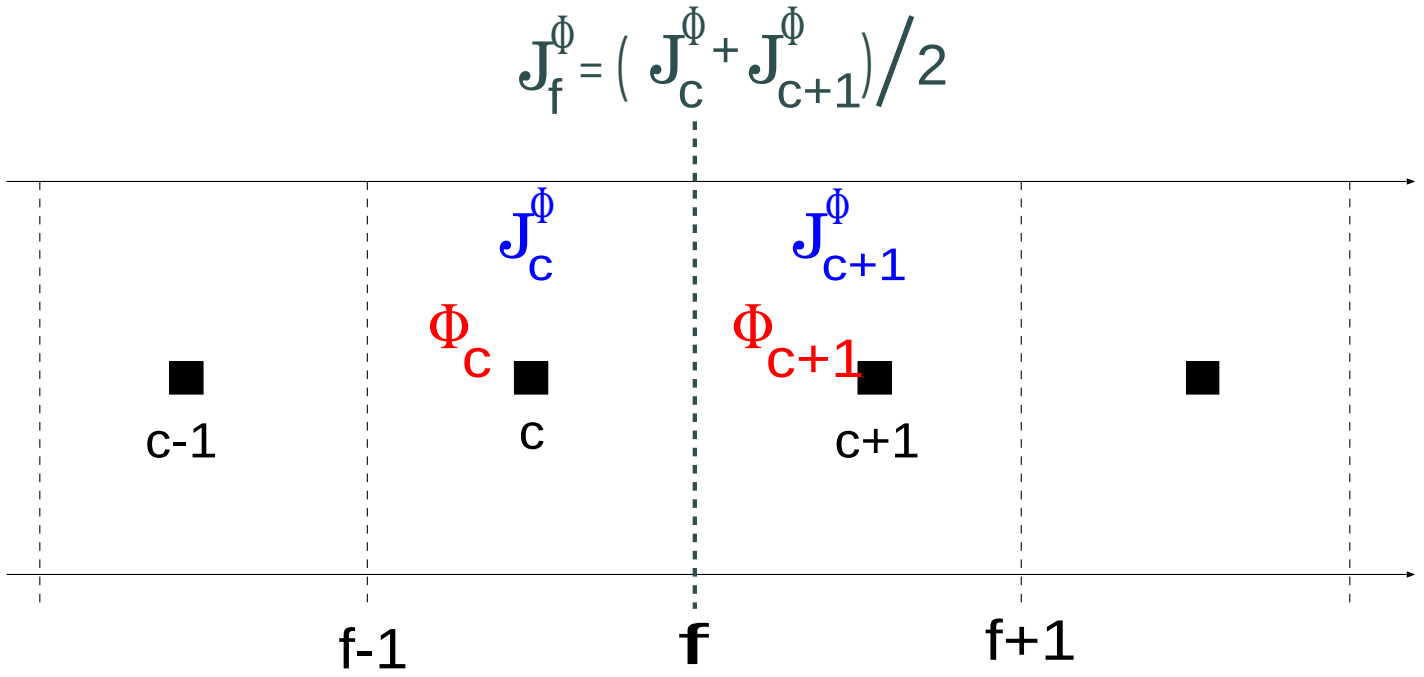
- FH for argon and water: G. De Fabritiis et al PRE, **75** 026307 (2007)
- Open BC for FH: RDB and A. Dejoan, PRE (accepted)
- Staggered grid for FH: RDB and A. Dejoan, (preprint)

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

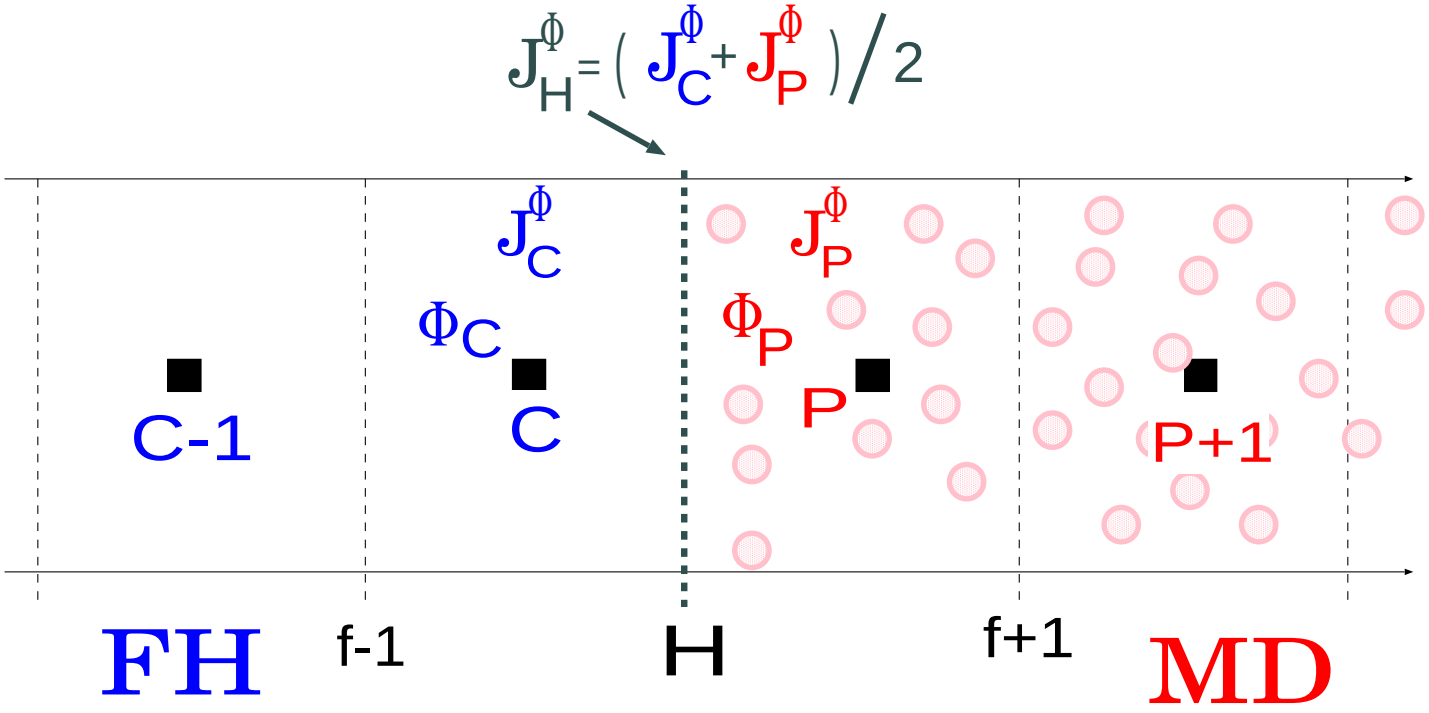
$$V_c \frac{\Delta\Phi_c}{\Delta t} = -\sum_{f=\text{faces}} A_f \mathbf{J}_f^\phi \cdot \boldsymbol{e}_f \quad \text{(explicit Euler scheme)}$$

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	$\mathbf{J}^e = \rho\mathbf{u}e + \boldsymbol{P} : \mathbf{u} + \boldsymbol{Q}$

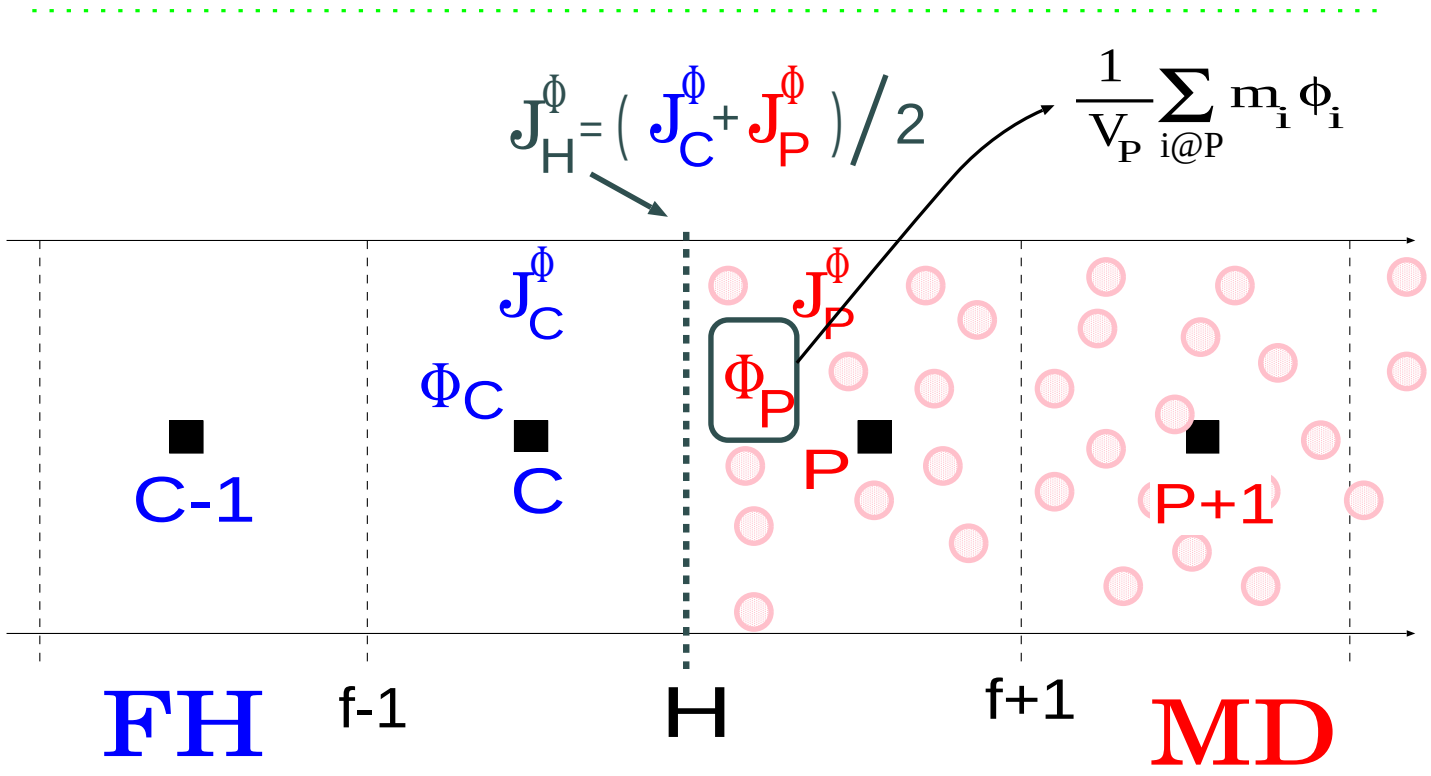
Finite volume scheme



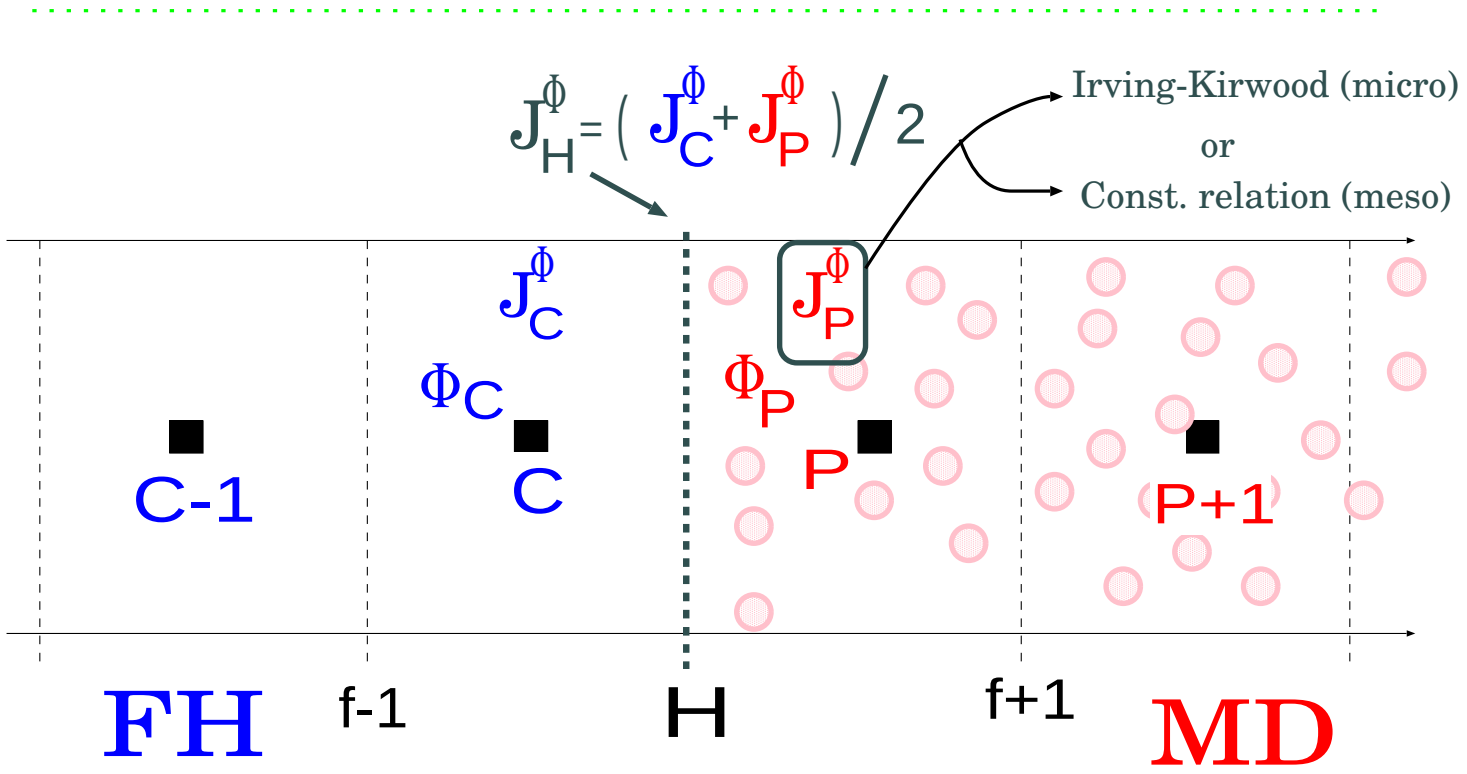
MD-FH: **hybridMD scheme**



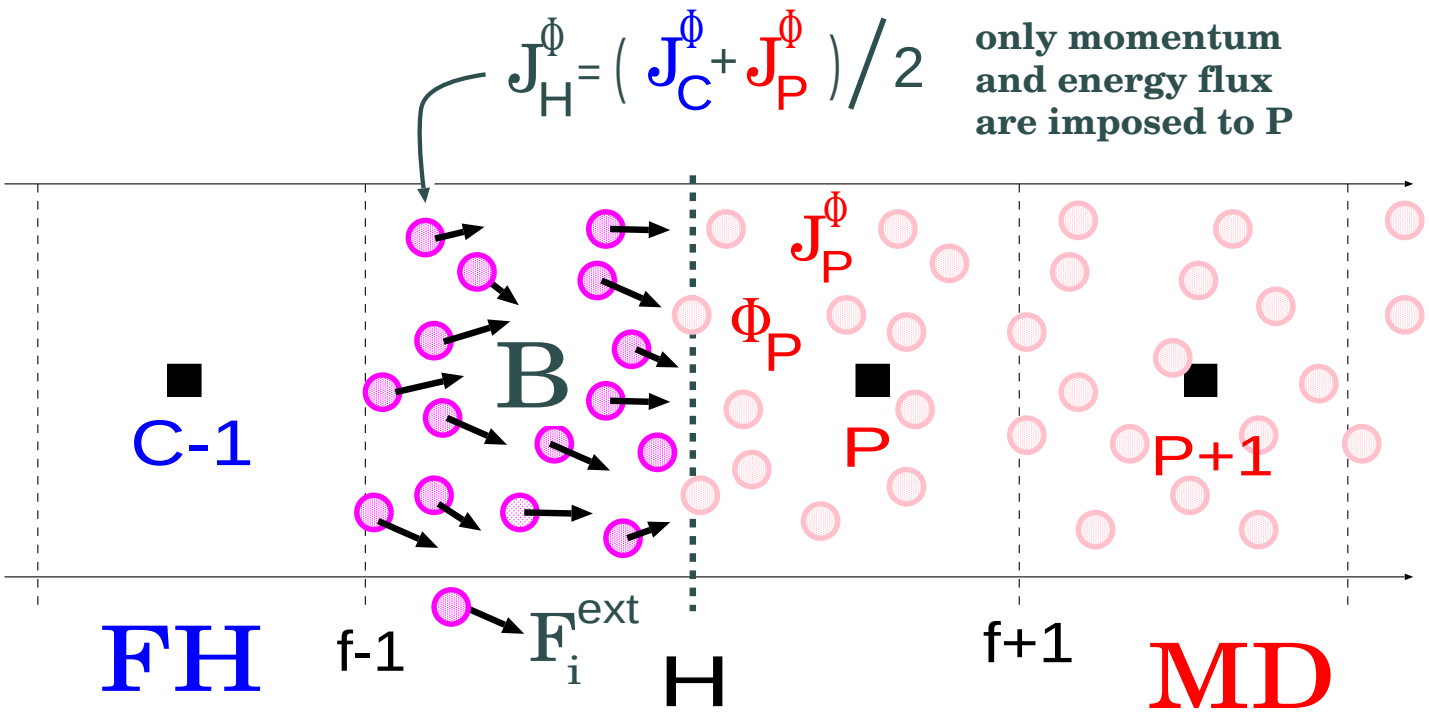
MD-FH: **Local P variables**



MD-FH: **Local P fluxes**

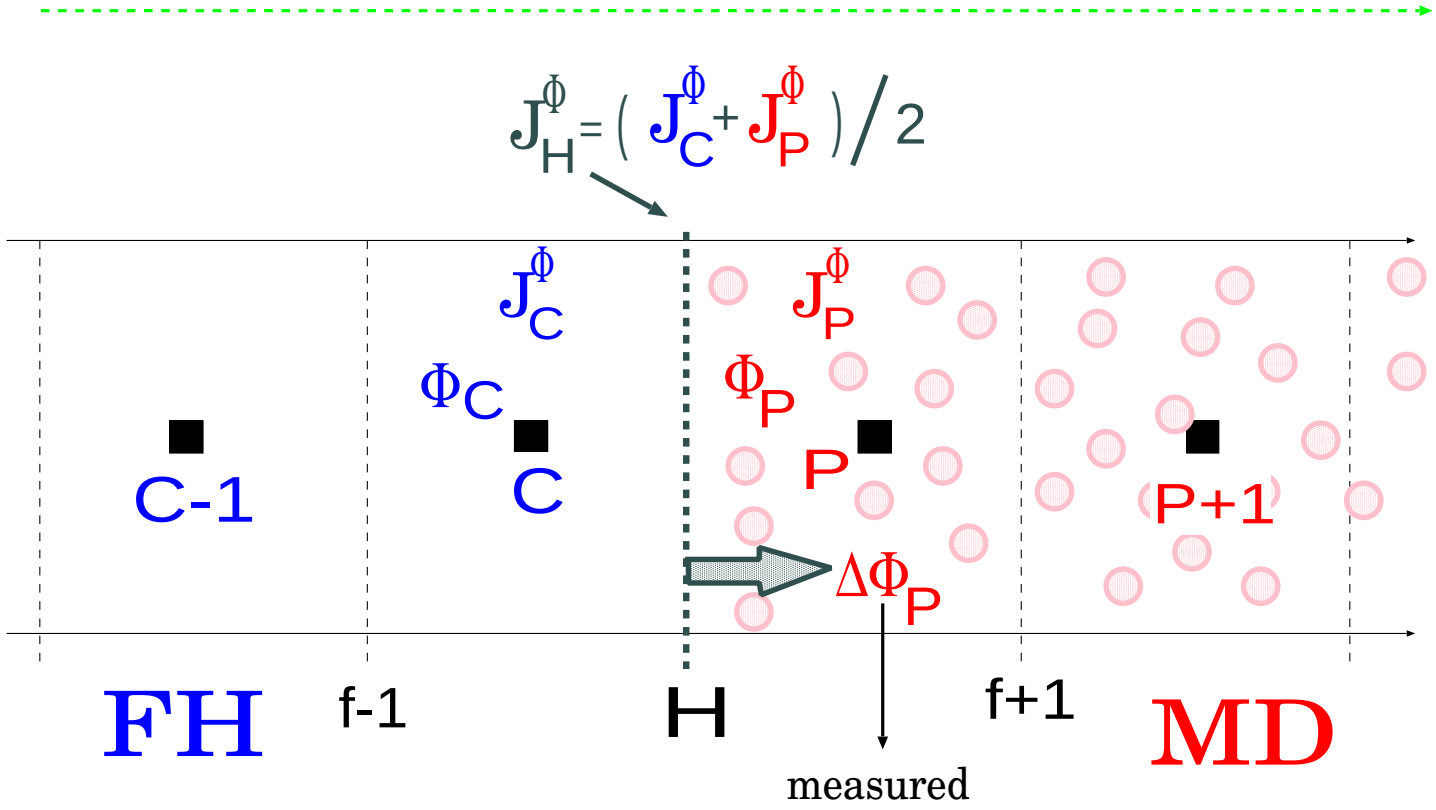


MD-FH: **Imposing fluxes into MD**

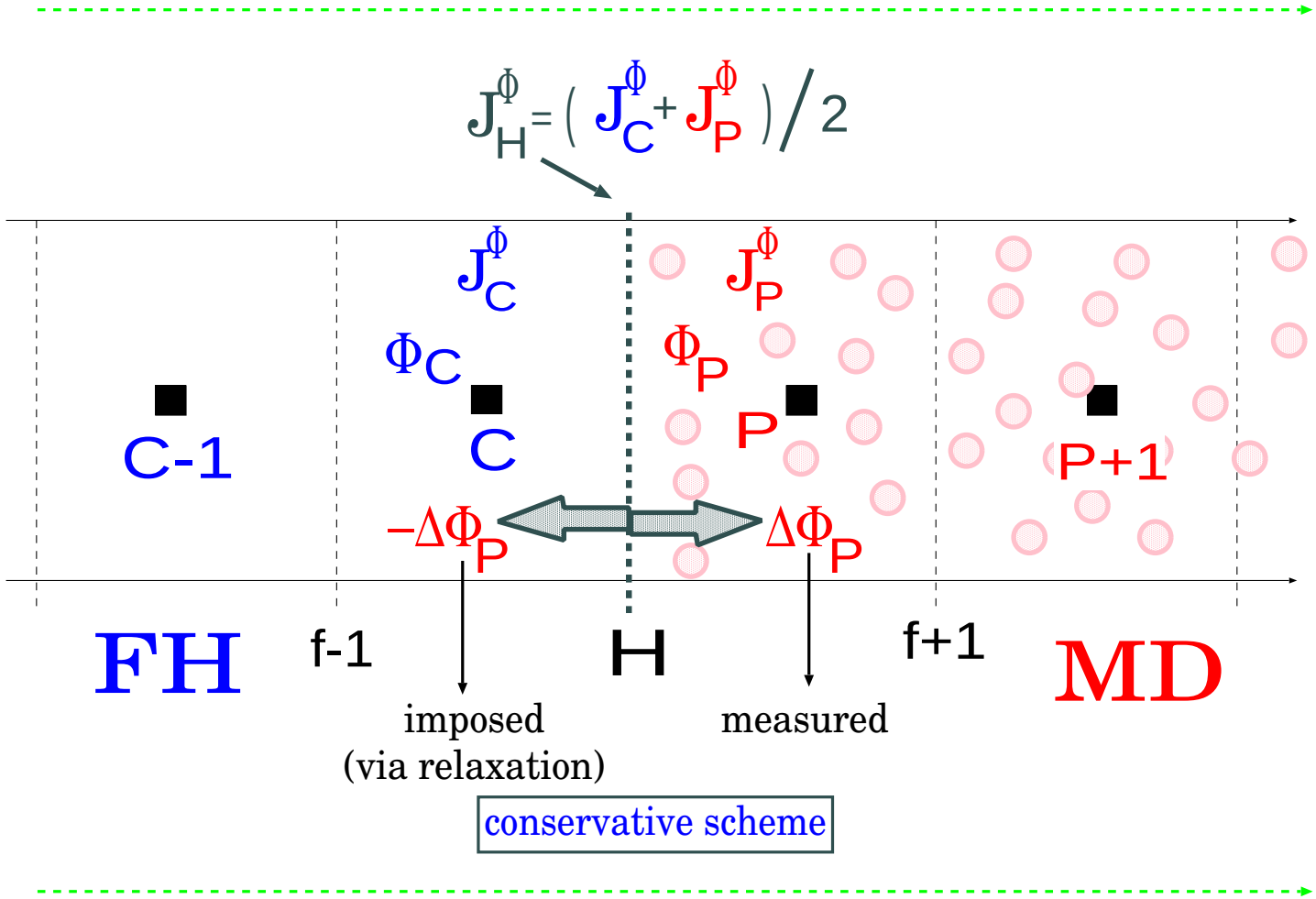


flux correction

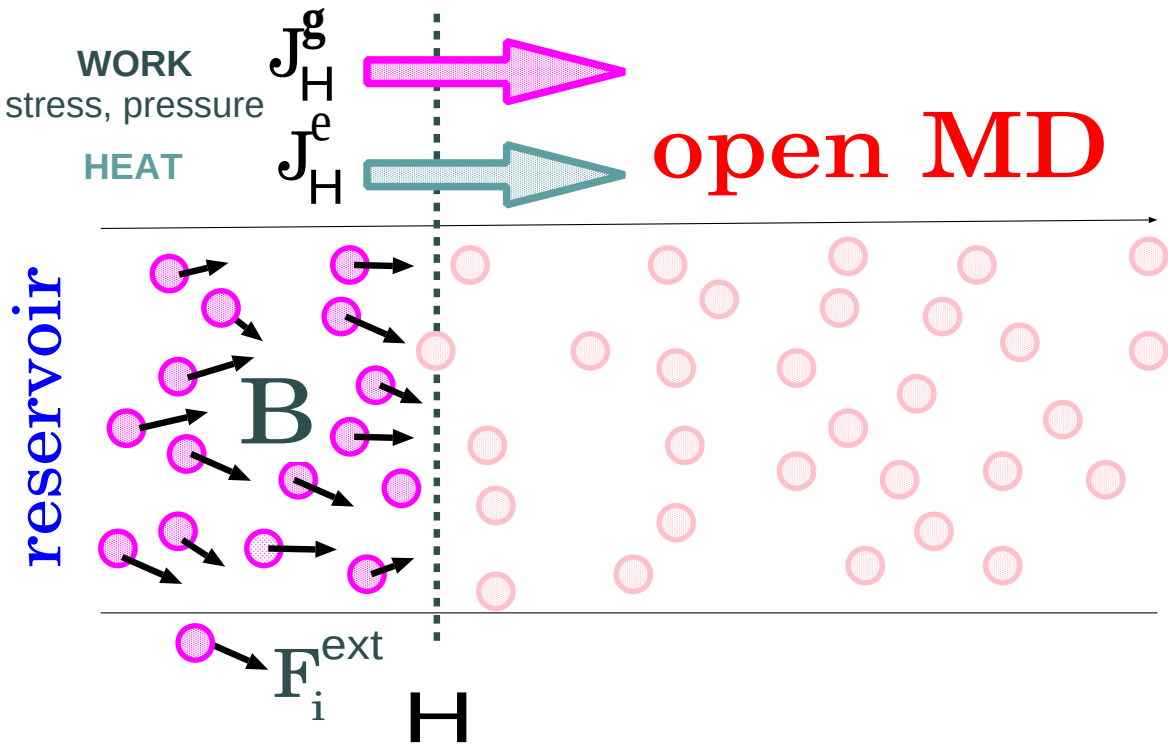
MD-FH: **flux balance**



MD-FH: **flux balance: conservative scheme**



open molecular dynamics



MD-FH **Flux boundary conditions for** `open MD`

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

Energy flux J_e and momentum flux $\mathbf{J_p}$ imposed into MD across H

$$\begin{array}{lrcll} \text{Momentum over } \Delta t & \mathbf{J_p} A \Delta t & = & \sum_{i\in B} \mathbf{F}_i^{ext} \Delta t & + \quad \sum_{i'} \Delta(m\mathbf{v}_{i'}) \\ \text{Energy over } \Delta t & \underbrace{J_e A \Delta t}_{\text{Total input}} & = & \underbrace{\sum_{i\in B} \mathbf{F}_i^{ext} \cdot \mathbf{v}_i \Delta t}_{\text{External force}} & + \quad \underbrace{\sum_{i'} \Delta\epsilon_{i'}}_{\text{Particle insertion/removal}} \end{array}$$

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

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

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

Energy: introduced by the fluctuating force $\tilde{\mathbf{F}}_i^{ext}$ via dissipative work.

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

Molecular dynamics at various ensembles

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

- THE AMOUNT OF HEAT AND WORK INTO THE MD SYSTEM IS EXACTLY CONTROLLED

- The system comunicates with the exterior at its boundaries (B), as a real system does.

- Grand-canonical ensemble. μVT, with $\mu = \mu(p^C, T^C)$ chemical potential at the reservoir B. **Dynamics of confined systems**

- Isobaric ensemble NPT. $\mathbf{J_p} = p\hat{\mathbf{n}}$.

- Constant enthalpy HPT. $\mathbf{J}_e^H = M\langle \mathbf{v} \rangle \cdot F$ and $\Delta N = 0$. $\Delta E + p\Delta V = \Delta H = 0$. (Joule-Thompson), **MD-calorimeter**

- Constant heat flux. $\mathbf{J}_e = cte$. (**melting dynamics**, growth of solid phase -ice-, heat exchange at complex surfaces...)

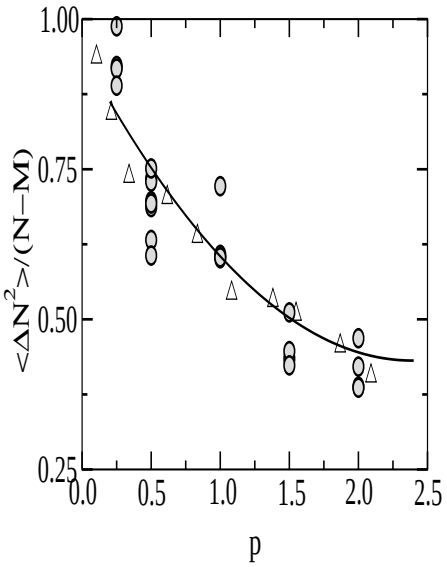
Mass fluctuations: grand canonical ensemble

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

Flux particle BC´s are thermodynamically consistent

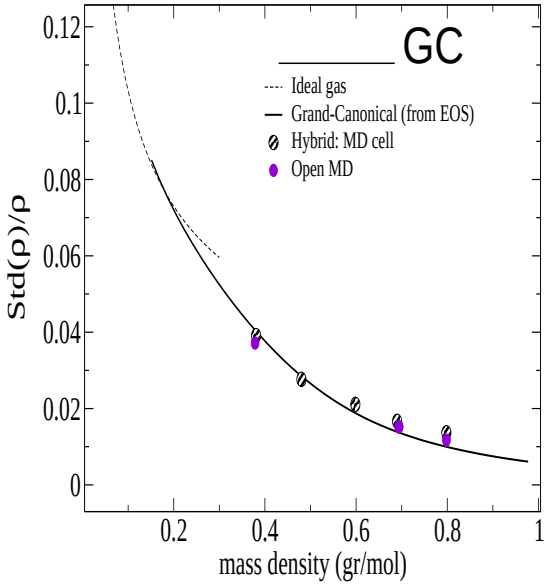
with the Grand Canonical ensemble

Soft-particles
DPD-like



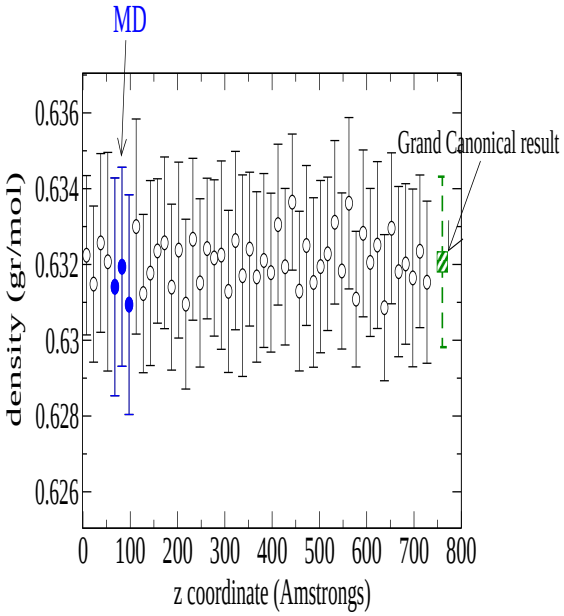
pressure

Liquid argon



density

Water (T=300 K)



cell-coordinate

The particle buffer

- **Distribute external forces** to impose momentum and energy in MD

- **Mass reservoir**: mean buffer mass $\langle M_B \rangle = m \langle N_B \rangle$ controlled by a simple relaxation algorithm:

$$\frac{dN_B}{dt} = \frac{1}{\tau_B} (\alpha N_C - N_B)$$

with $\tau_B \simeq [10 - 100] fs$ (faster than any hydrodynamic time) and $\alpha \simeq 0.75$.

- **Open system:**
  - Particles leaving the buffer end are removed
  - Particle insertion ($\Delta N_B > 0$) using the USHER algorithm [J. Chem. Phys, **119**, 978 (2003)]

USHER energy controlled molecule insertion

J. Chem. Phys **119**, 978 (2003); J. Chem. Phys. **121**, 12139 (2004) (water)

- **Objective**: Insert a new molecule at target potential energy E_T.
- **Method**: Newton-Raphson-like search in the potential energy landscape.
  Succesful insertion $|\Delta E/E_T| < 0.01$ where $\Delta E = E_T - E_i^{(n)}$

Translation of the centre of mass along force direction $\boldsymbol{F}$

$$\mathbf{r}_{cm}^{n+1} = \mathbf{r}_{cm}^{n} + \frac{\mathbf{F}_{cm}^{n}}{F_{cm}^{n}}\delta r$$

Rotation around the torque axis: (water)

$$\mathbf{r}_{cm,i}^{n+1} = \mathcal{R}_{\delta\theta}^{(n)}\mathbf{r}_{cm,i}^{n}$$

$\delta r = \min(\Delta E/F, \Delta R_{\max})$;
$\Delta R_{\max} \simeq$ half distance of first peak of radial distribution
$\delta\theta = \min(\Delta E/\tau, \Delta\Theta_{\max})$
the maximum rotation allowed is $\Delta\Theta_{\max} \sim 45^o$

Thermodynamically controllable process: Local ENERGY, TEMPERATURE and PRESSURE and are kept at the proper equation of state values.

Negligible insertion cost:

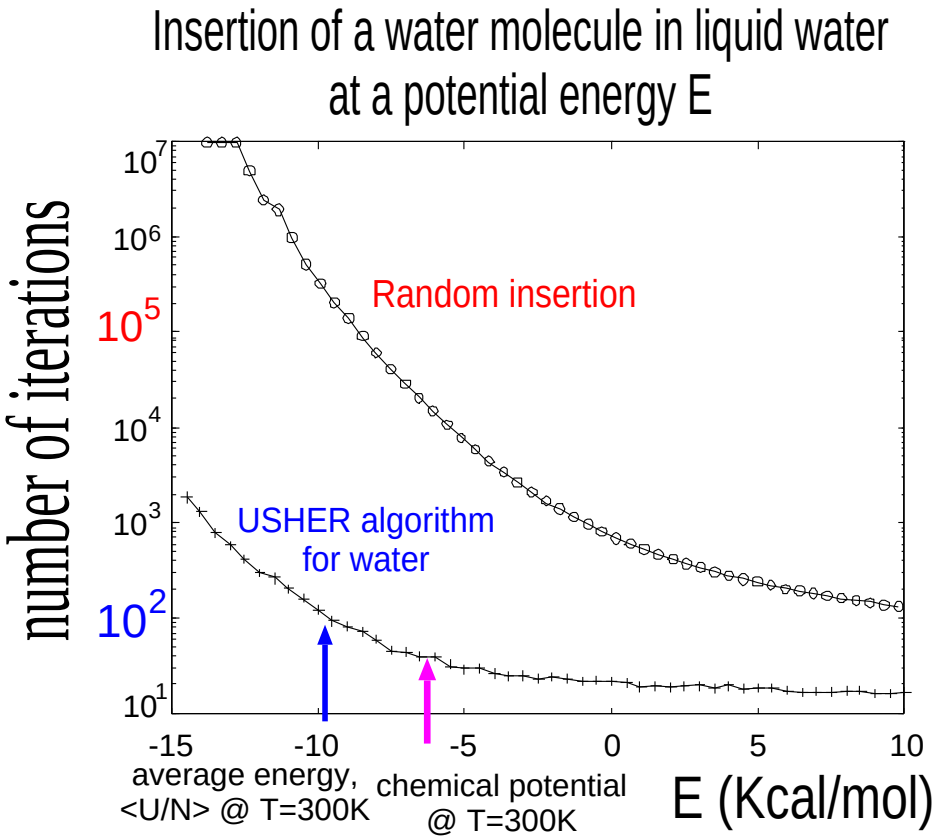
LJ particles ($\rho < 0.85$)	$< 1\%$ total CPU
Water into water	$\sim 3\%$ total CPU

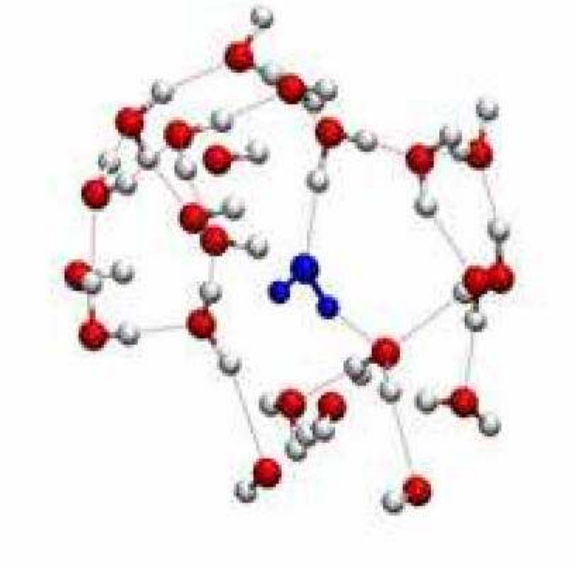
Insertions done at the mean energy/molecule contribution $E_T = 2U_{eos}$

USHER: fast and controlled particle insertion

J. Chem. Phys **119**, 978 (2003); J. Chem. Phys. **121**, 12139 (2004) (water)

Applications: Constant chemical potential simulations, unfolding of proteins via water insertion (Goodfellow), water insertion in confined systems (e.g. proteins).

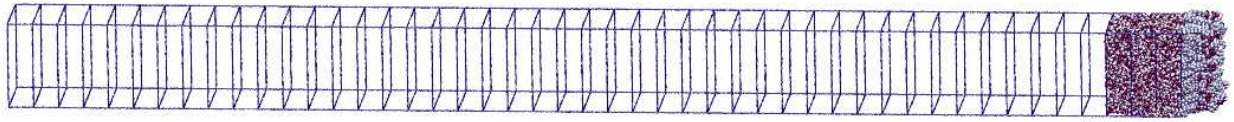




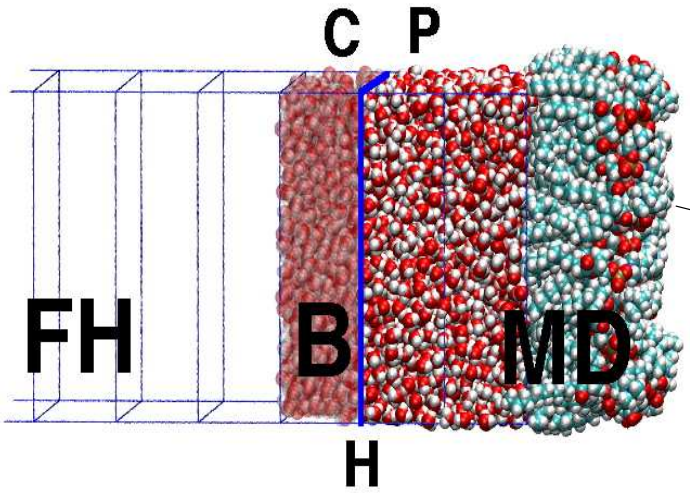
MD-FH Setup for tests

Water against a lipid layer at $T = 300K$
[G.Fabritiis,RDB, Coveney PRL, **97** (2006)].

Multiscale modelling
Embedding molecular dynamics within fluctuating hydrodynamics

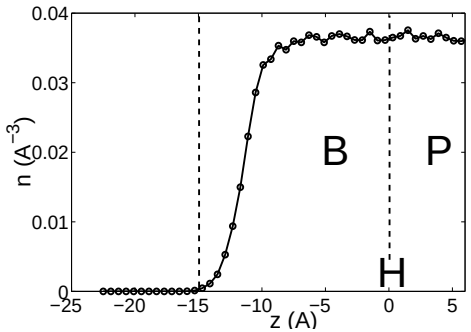


Hybrid MD-FH setup



DMPC
(lipid layer)

water density profile



PRL, 97, 134501 (2006)

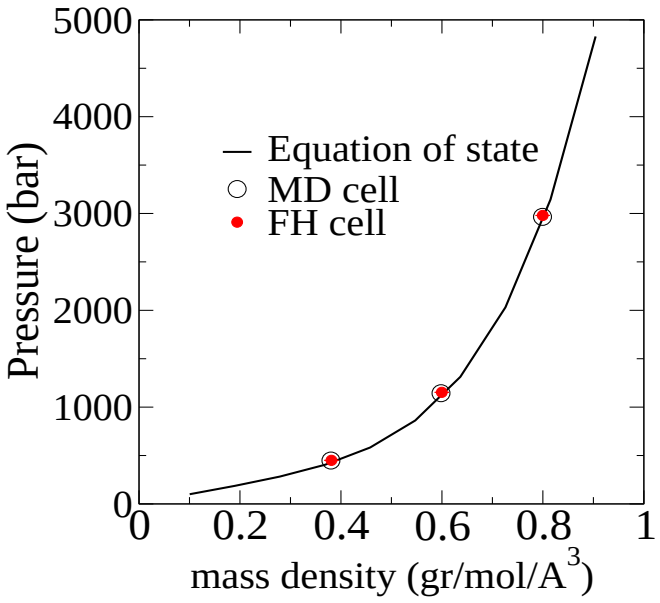
PRE, 76, 036709 (2007)

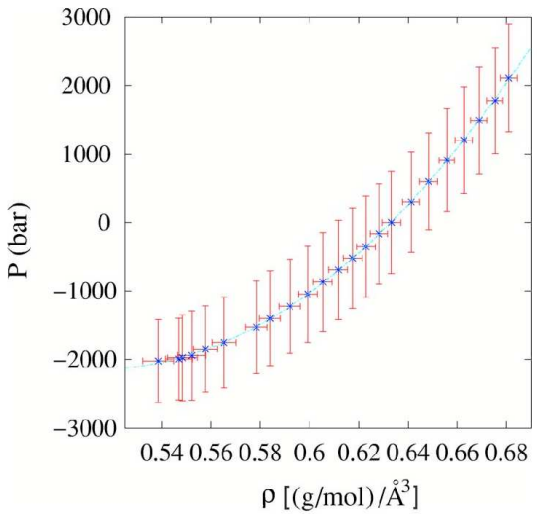
MD-FH Equilibrium

Equation of state $p = p(\rho)$ for argon and water TIP3P, $T = 300K$ [G.Fabritiis et al. PRE, **76** (2007)].

OPEN MD can be used to measure $p = p(\rho)$

argon (LJ) water (TIP3P)

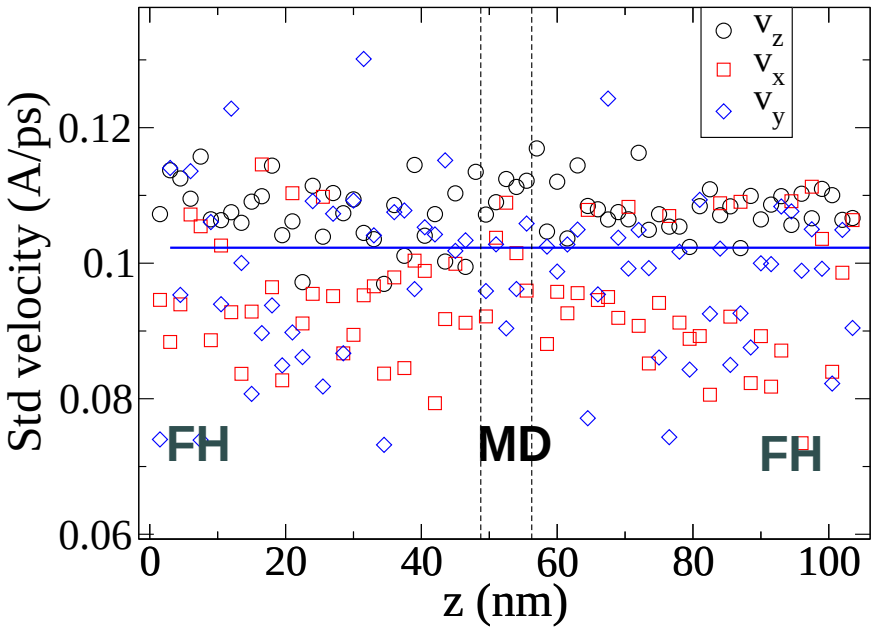




MD-FH Velocity and stress fluctuations

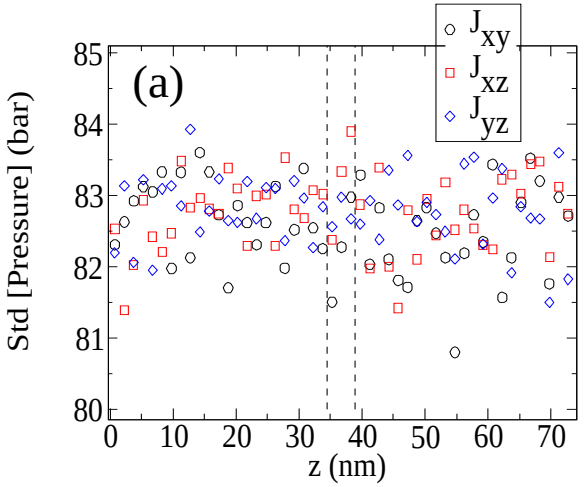
`Standard deviation of velocity` (kinetic temperature)
liquid argon @ $T = 300K$ [RDB and G.Fabritiis et al. PRE, **76** (2007)].

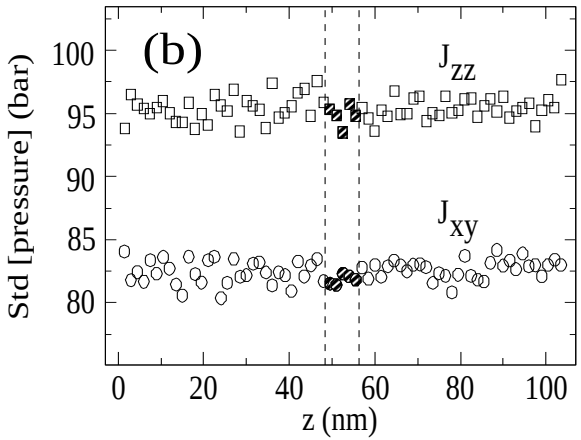
STD velocity



position

STD Stress tensor components





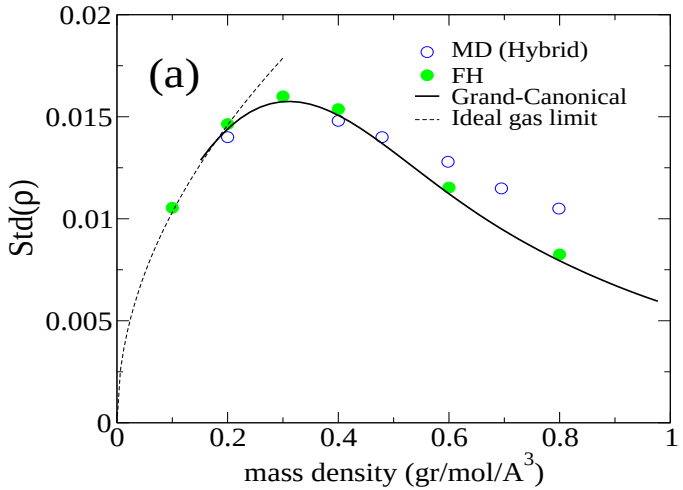
position

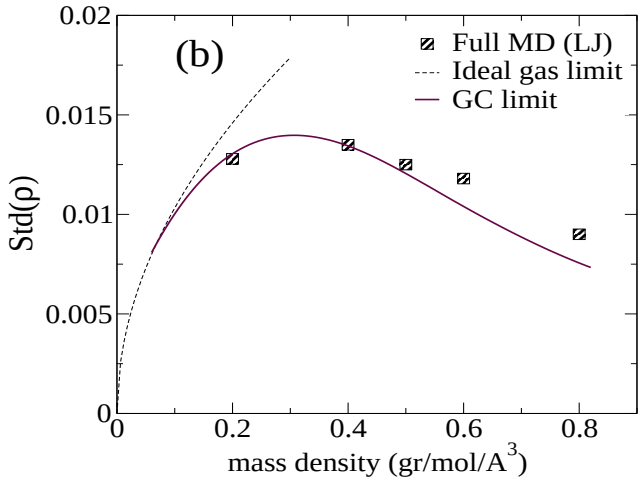
MD-FH Density fluctuations

`Standard deviation of density`

argon at several densities, $T = 300K$

RDB and G.Fabritiis et al. PRE, **76** (2007)





HybridMD

FH

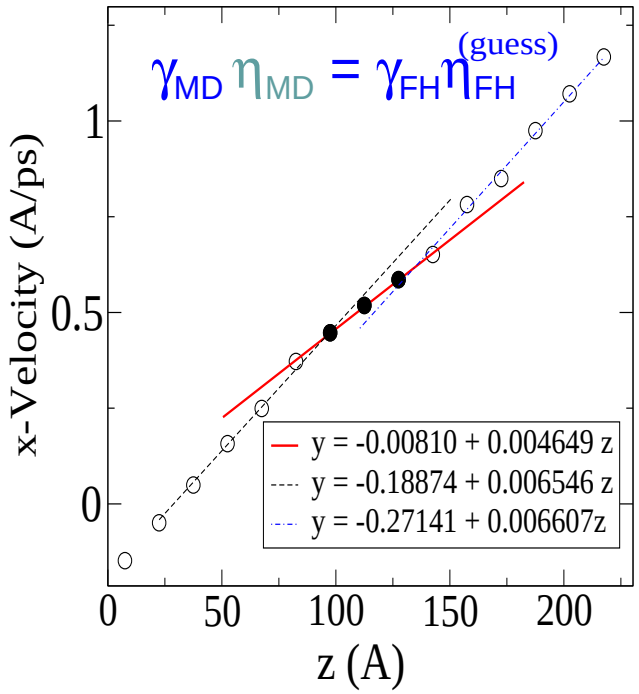
Grand canonical →

full MD

MD-FH **Shear flow**

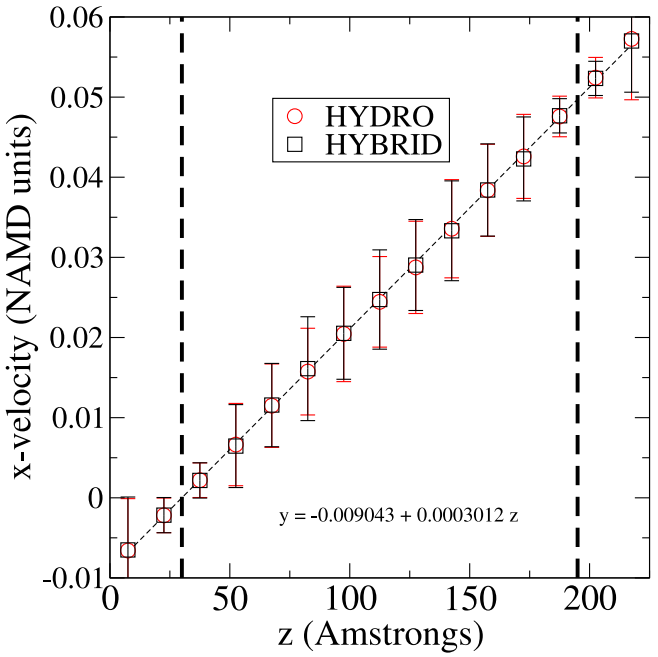
viscosity calibration

hybridMD as a rheometer



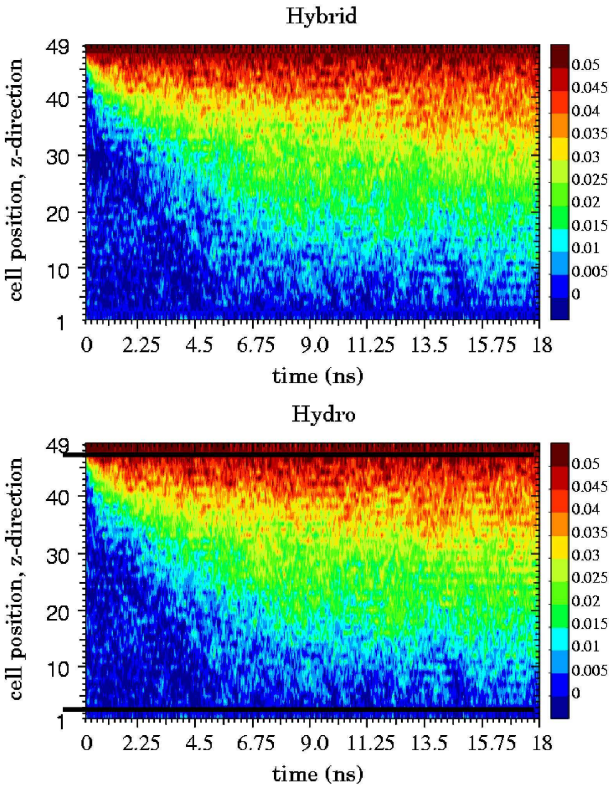
Couette flow

steady solution

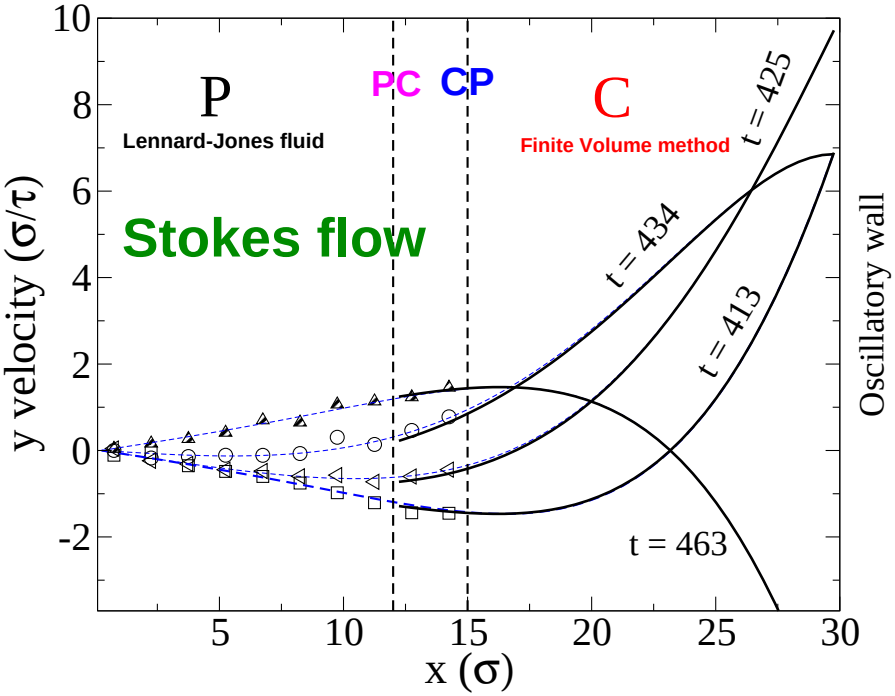


MD-FH **Unsteady shear**

Start-up Couette

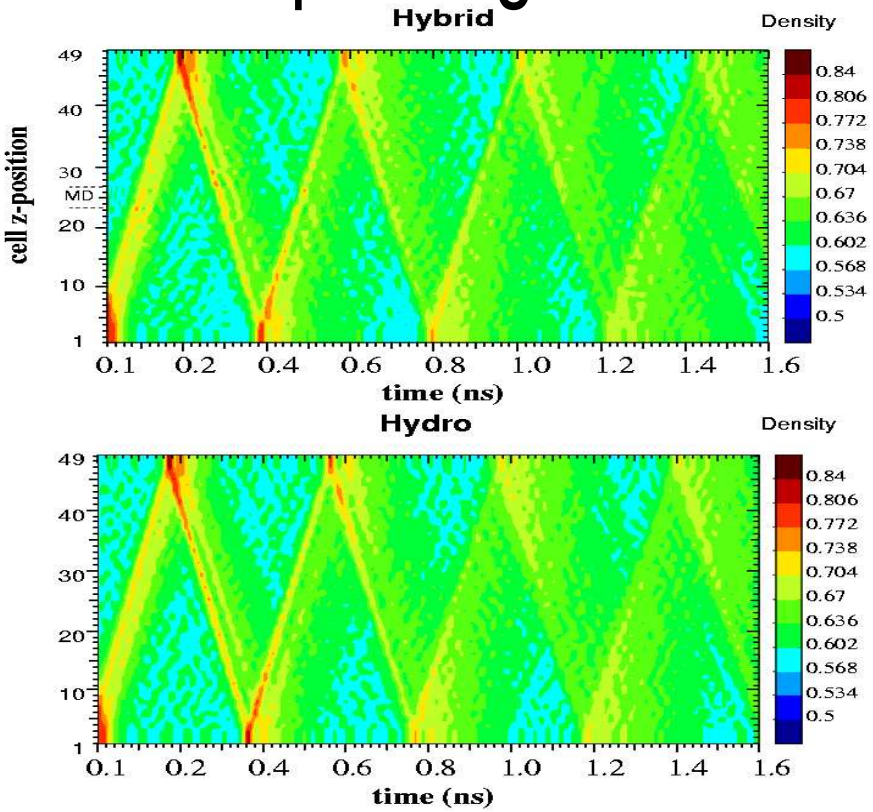


Oscillatory shear

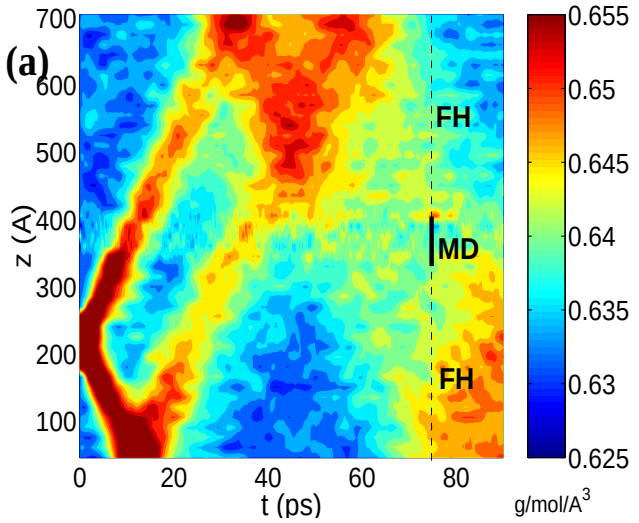


MD-FH **Sound waves**

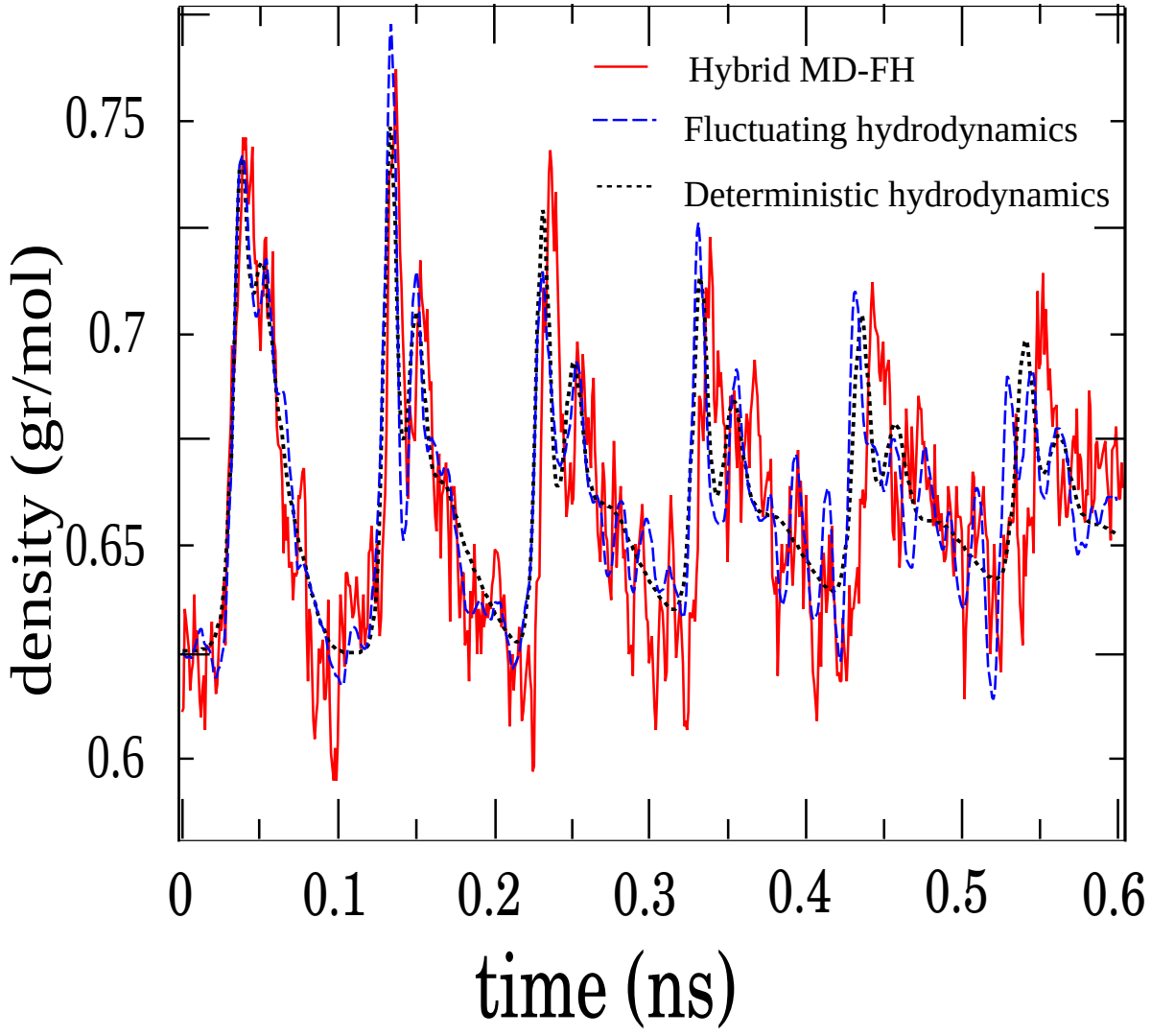
liquid argon



water

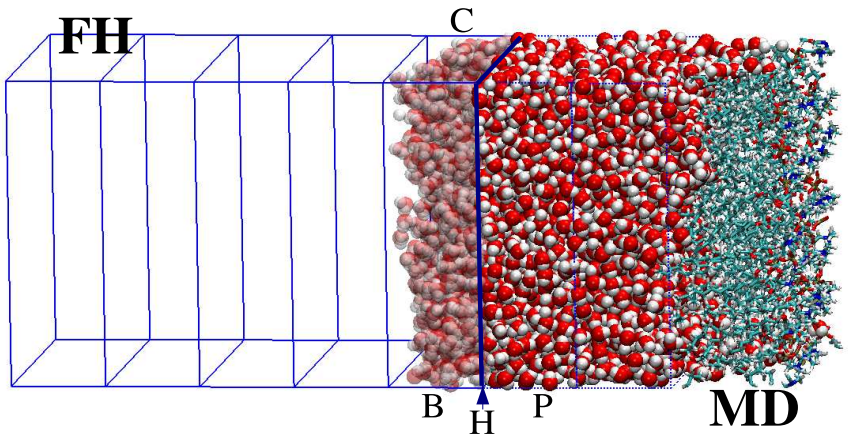


MD-FH **Sound waves: time resolution** ~ 0.02 **ns**

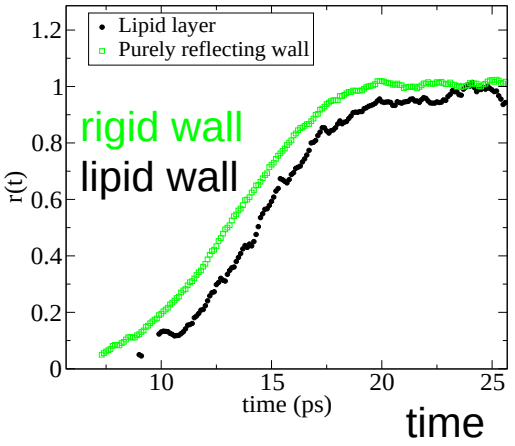


MD-FH **Sound - (soft) mattter interaction**

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

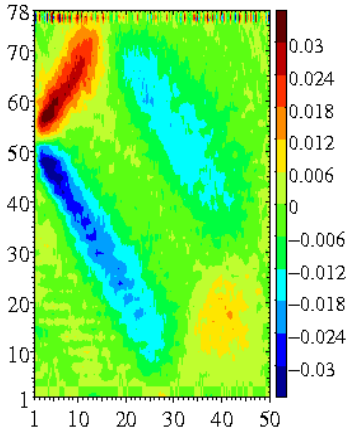


Reflection coefficient

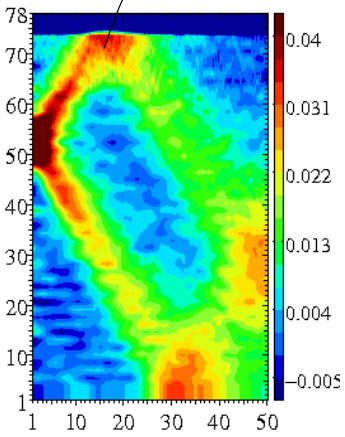


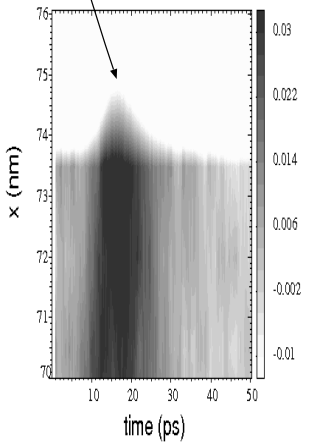
time

velocity

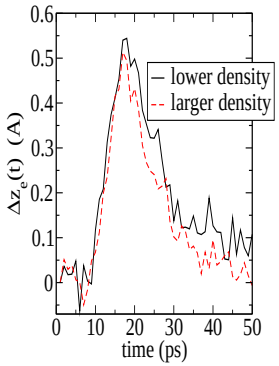


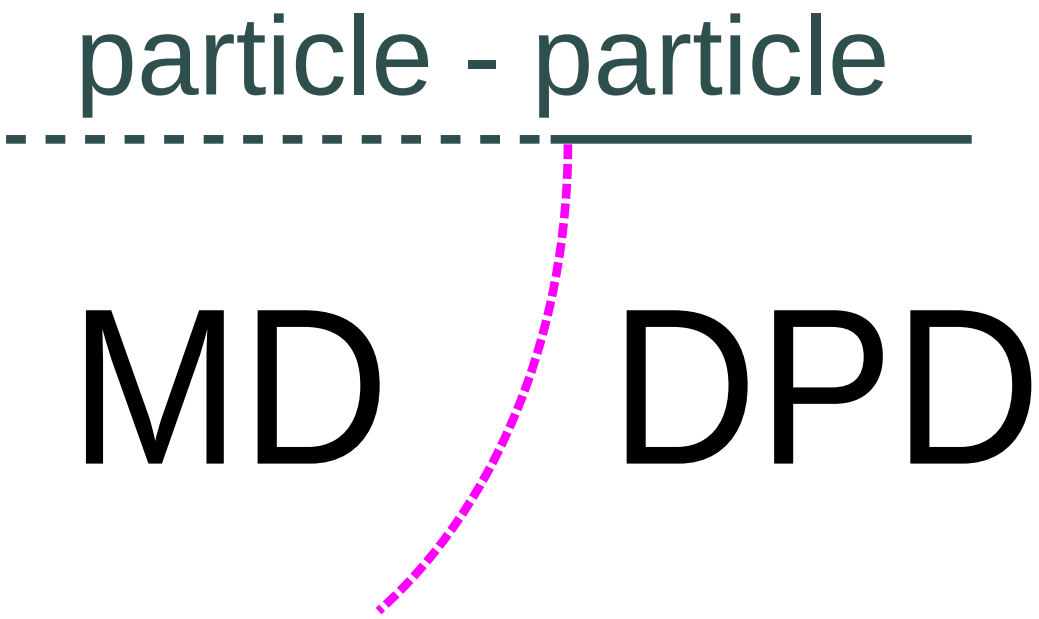
water density





lipids' tail displacement




particle - particle
MD
DPD

Particle models

Dissipative particle dynamics

$$
\begin{aligned}
m_i \frac{d\mathbf{v}_i}{dt} &= \sum_{i \neq j} \mathbf{F^C}_{ij} + \mathbf{F^D}_{ij} + \mathbf{F^R}_{ij} \\
\mathbf{F^D}_{ij} dt &= -m_i \gamma \omega^2(r_{ij}) [\hat{\mathbf{r}}_{ij} \cdot \mathbf{v}_{ij}] \hat{\mathbf{r}}_{ij} dt \\
\mathbf{F^R}_{ij} dt &= m_i \sigma \omega(r_{ij}) \hat{\mathbf{r}}_{ij} dW_{ij} \\
m\sigma^2 &= 2\gamma kT
\end{aligned}
\tag{1}
$$

Molecular dynamics

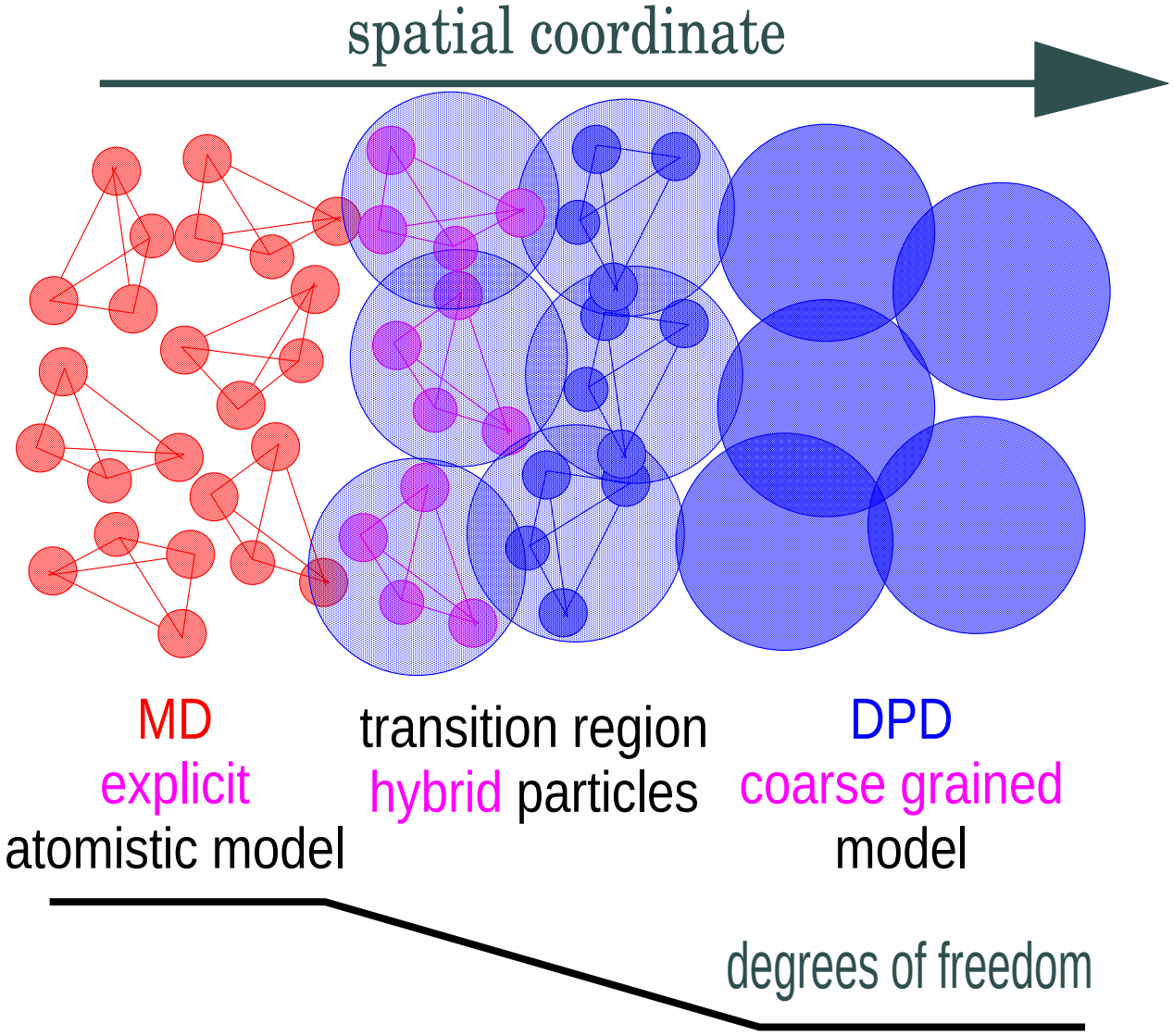
$$
m_i \frac{d\mathbf{v}_i}{dt} = \sum_{i \neq j} \mathbf{F^C}_{ij} + (\text{thermostats})
$$

The essential difference lies in how steep the conservative forces are. **Coarse-grained molecular dynamics** is an intermediate step between soft (linear) forces and hard core repusions in atomistic MD.

Coupling MD to DPD

Adaptive Resolution Scheme (AdResS)

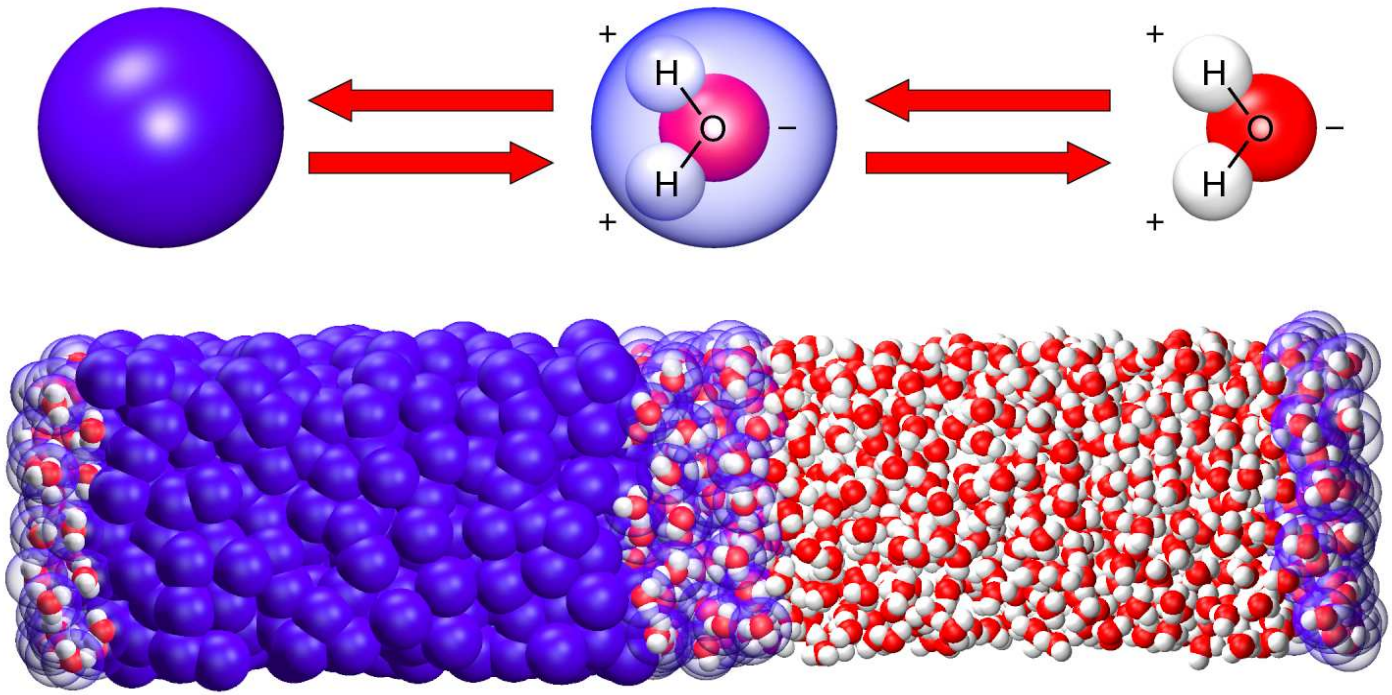
M. Praprotnik, L. DelleSite and K.Kremer, J. Chem.Phys **123** 224106 (2005), Ann. Rev. Phys. Chem. **59** 545 (2008)



Coupling MD to "DPD"

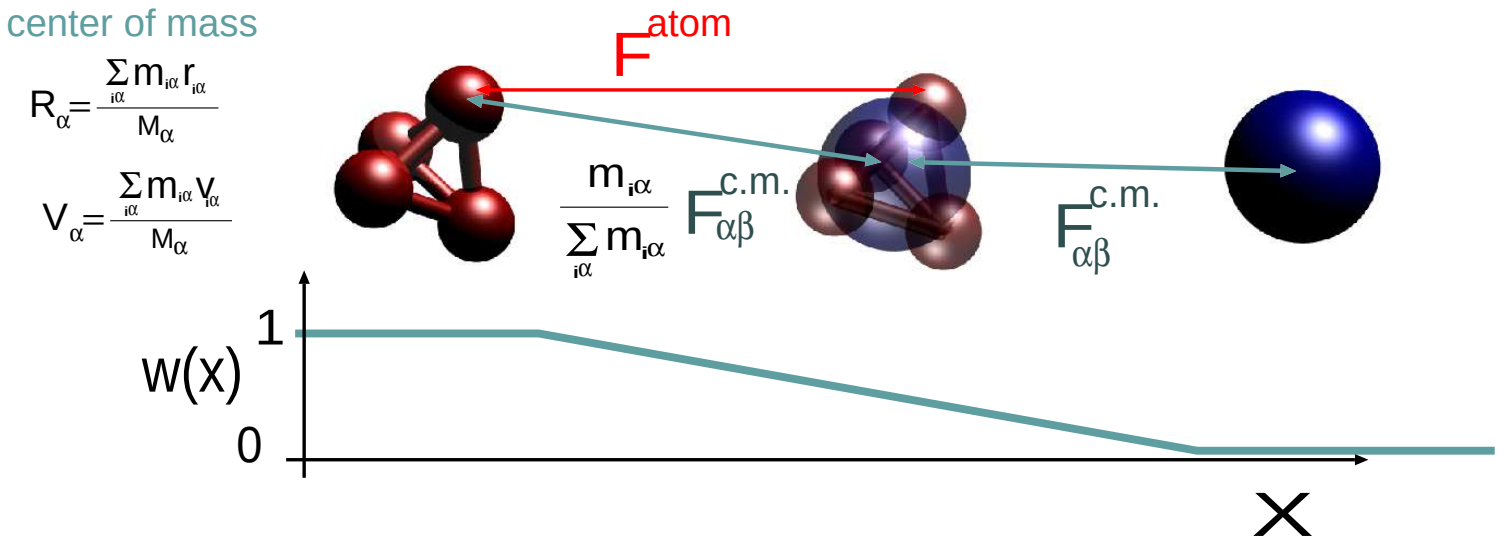
Adaptive Resolution Scheme for liquid water

M. Praprotnik, et a. J.Phys. Condens. Matter **19** (2007)



Coupling MD to "DPD"

Adaptive Resolution Scheme



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

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

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

(2)

Coupling MD to DPD

Effective potential for c.m. interaction

- The effective pair potential $U^{c.m.}$ is determined so as to match the center of mass radial distribution function of the *explicit* atomistic model, ${g^{ex}}_{cm}(r)$.

- This can be done using the `iterative Bolzmann inversion` [J. Comput. Chem. **24**1624 (2003)], which starts from the Potential of Mean Force as initial guess $(k = 0)$.

$$U^{cm}_{k+1}(r) = U^{cm}_{k}(r) + T \log \frac{g^{cg}_{k}(r)}{{g^{ex}}_{cm}(r)} \tag{3}$$

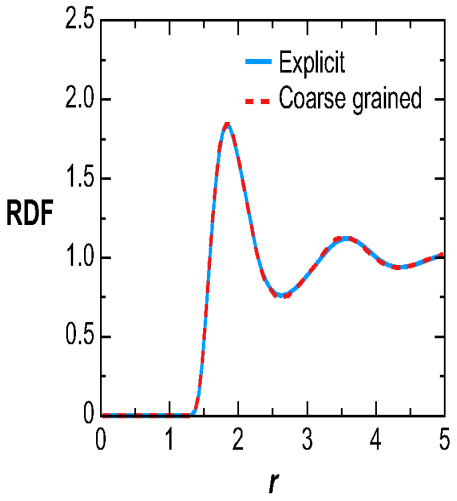
- Small correction $\Delta U^{cm} = U_0(1 - r/r_c)$ to equilibribrate pressures.

Coupling MD and DPD

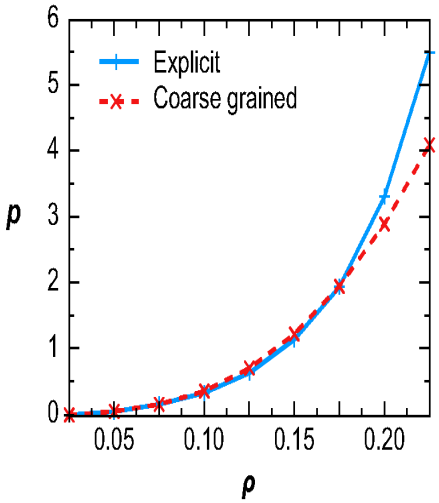
Matching liquid structure and pressure

Tetraedral fluid
kT = 1; ρ=0.175

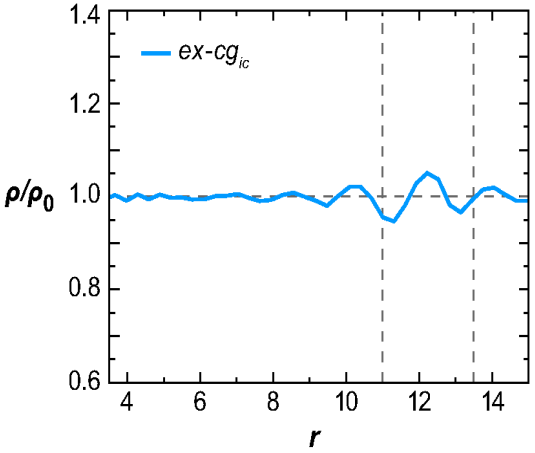
Radial distr. func.



pressure eos



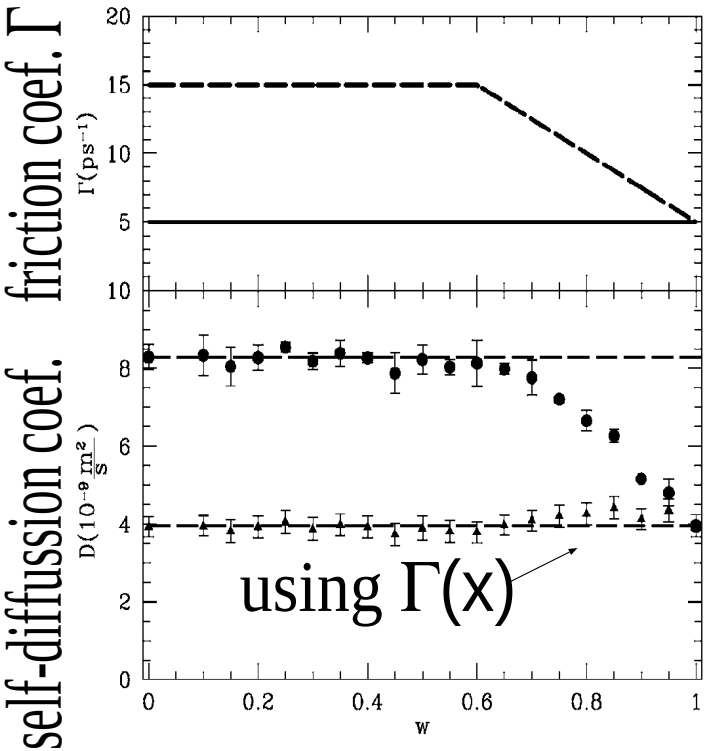
density profile



Coupling MD and DPD

Dynamics: self-diffusion across interfase

Position dependent Langevin thermostat



$$m_i \frac{dv_i}{dt} = F_i - m_i \Gamma(x_i) v_i + W_i(x_i, t)$$

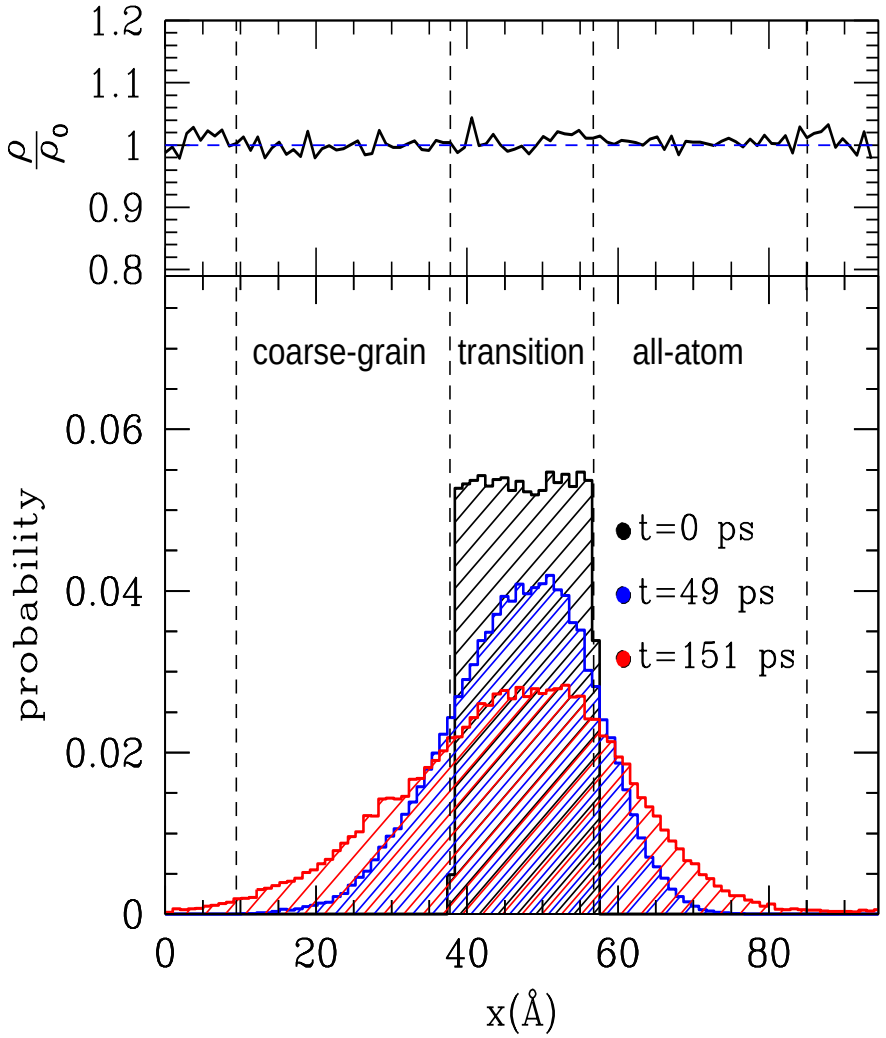
$$\langle W_i(x,0) \rangle = 0$$

$$\langle W_i(x,\tau) W_j(x,0) \rangle = 2\Gamma(x) kT \delta(\tau) \delta_{ij}$$

The thermostat at the "DPD" region is also needed to equilibrate the removed /added degrees of freedom (i.e. to add / remove the latent heat of transition).

Coupling MD and DPD

Dynamics: self-diffusion across interfase



Coupling MD and DPD

AdResS

`pros`

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

Coupling MD and DPD

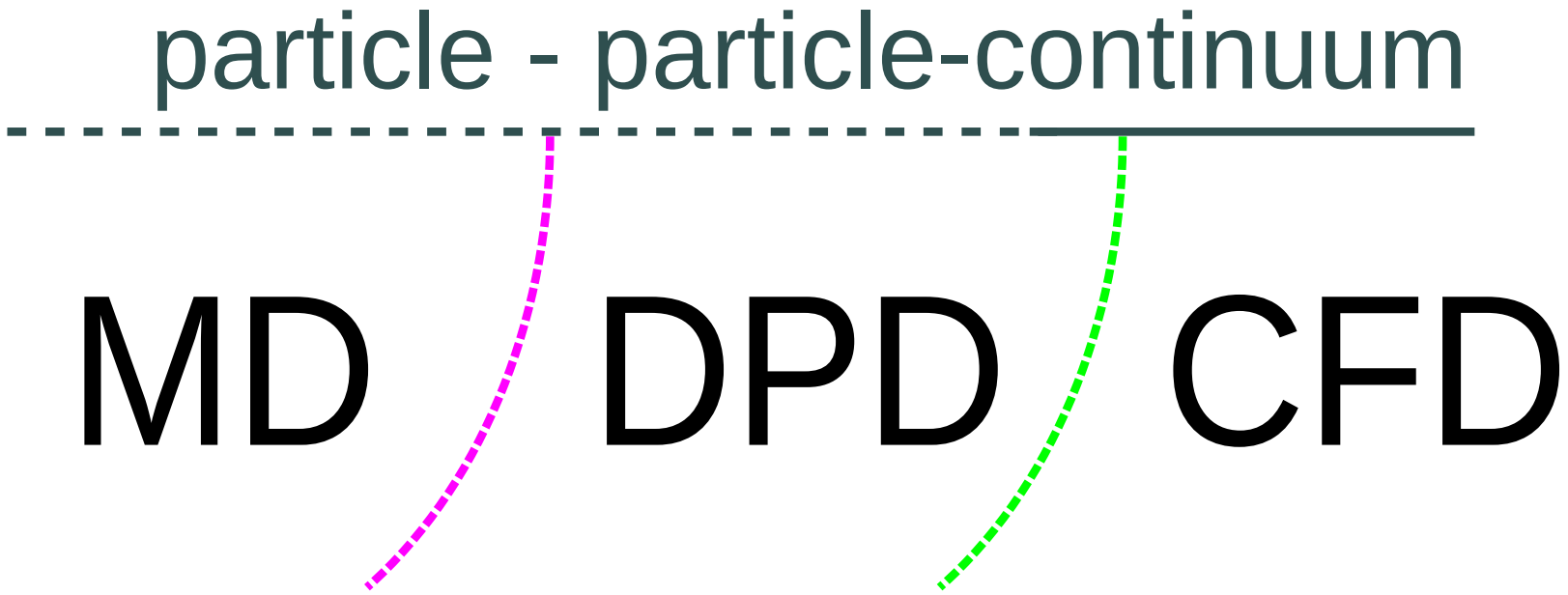
AdResS

`cons`

- It does not conserves energy $\Longrightarrow$ heat transfer is not described.

- Requires substantial pre-evaluation of the effective potential U^{cm} using `iterative Bolzmann inversion` for each fluid and thermodynamic state considered
  - Restricted to homogenous, or near equilibrium states
  - Pressure corrections using `iterative Bolzmann inversion` within the hybrid region might be required to obtain seamless density profiles.

- Viscosity mismatch between coarse-grained and atomistic models $\Longrightarrow$ incorrect shear transfer. This can be (partially) solved by using `transversal DPD` thermostat. C. Junghans et al., SoftMatter (2008).


particle - particle-continuum
MD
DPD
CFD

MD-DPD-CFD

Triple scale coupling

RDB, K. Kremer, M. Praprotnik, J. Chem. Phys, **128** 114110, (2008)

`General motivation`

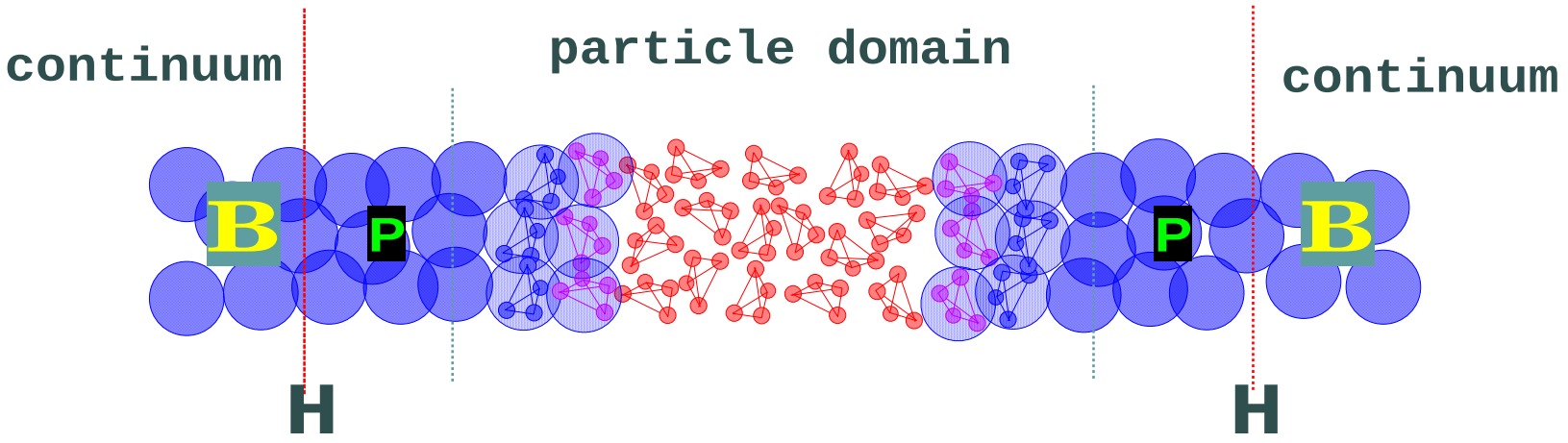
Complex molecules

- Technical issues
  - Generalize the (MD-DPD) AdResS scheme to include **hydrodynamics**
  - Solve the **insertion** of larger molecules in hybridMD
- Applications
  - Phenomena involving flow-matter interaction at multiple length scales complex fluids near surfaces, lubrication, macromolecules in flow,...
  - Grand canonical molecular dynamics involving complex molecules confined systems

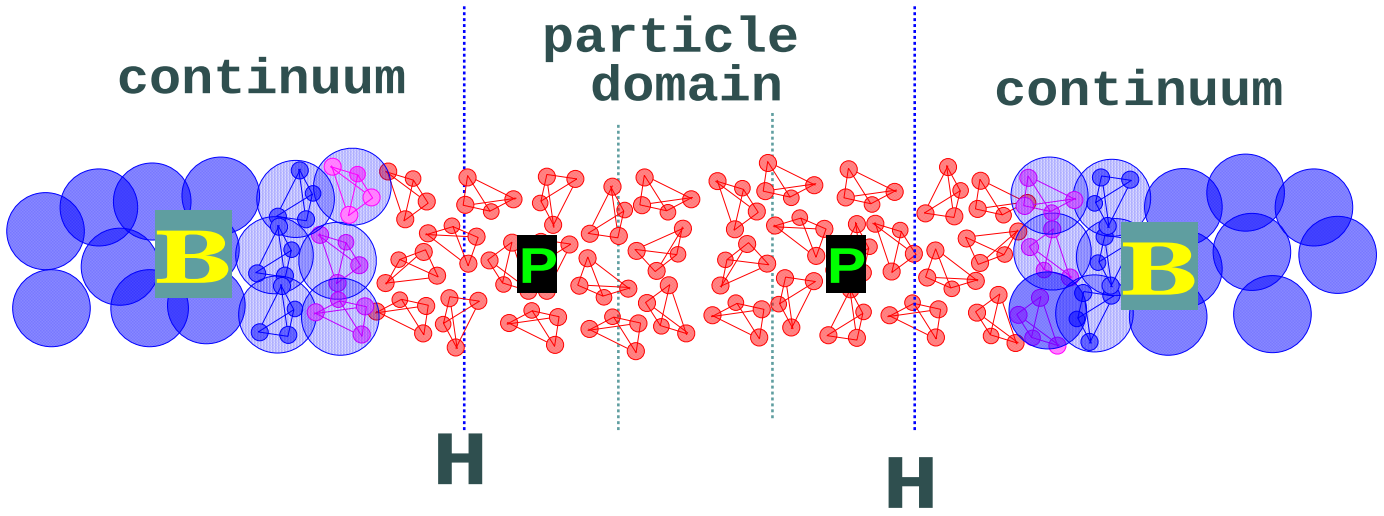
MD-DPD-CFD **Two possible setups**

RDB, K. Kremer, M. Praprotnik, J. Chem. Phys, **128** 114110, (2008)

Homogeneous (CG) buffer



Heterogeneous model buffer



MD-DPD-CFD: **Two possible setups**

RDB, K. Kremer, M. Praprotnik, J. Chem. Phys, **128** 114110, (2008)

- **Homogeneous buffer**
  - `con:` Requires fine tunning of `CG` model
    - Viscosity **or** molecular diffusion coefficient
      Transversal DPD C. Junghans, et al., Soft Matter 4, 156 (2008)
    - Equation of state
  - `pro:` Requires smaller buffer size
  - `pro:` Permits to introduce CG molecular information into the MD (explicit) region (structure, diffusion rates, etc...)

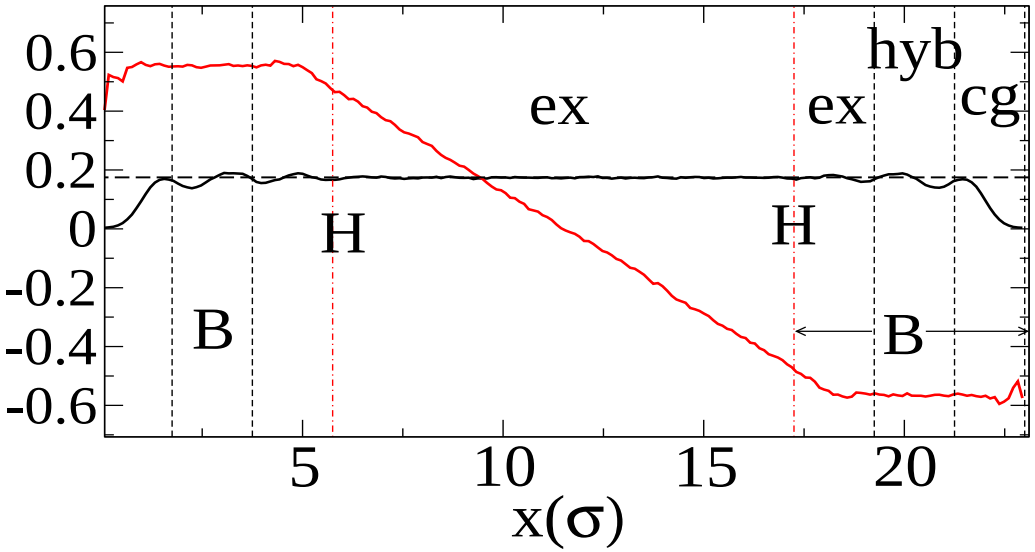
- **Heterogeneous buffer**
  - `con:` Larger buffer size
  - `pro:` The P-cell is fully atomistic (correct viscosity, EOS, fluctuations)
  - `pro:` Does not requires fine tunning of `CG` model and `hyb` models
  - `pro:` Enables **energy exchange**, as the MD region is fully explicit.

MD-DPD-CFD: **Shear flow**

Heterogeneous buffer

high density tetraedral liquid under shear

density and velocity profiles

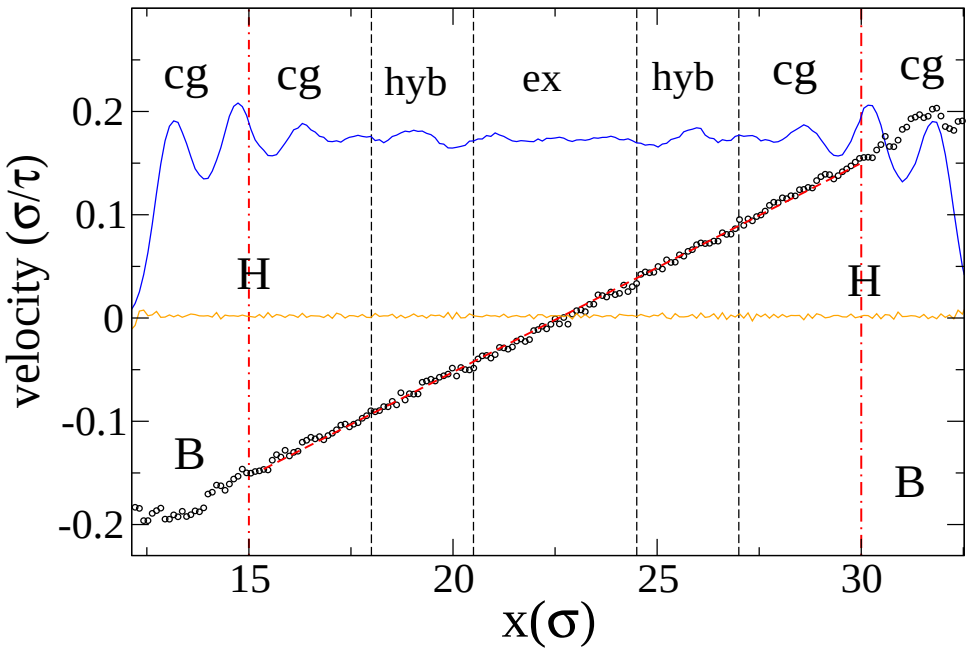


MD-DPD-CFD: **Shear flow**

Homogeneous buffer

high density tetraedral liquid under shear

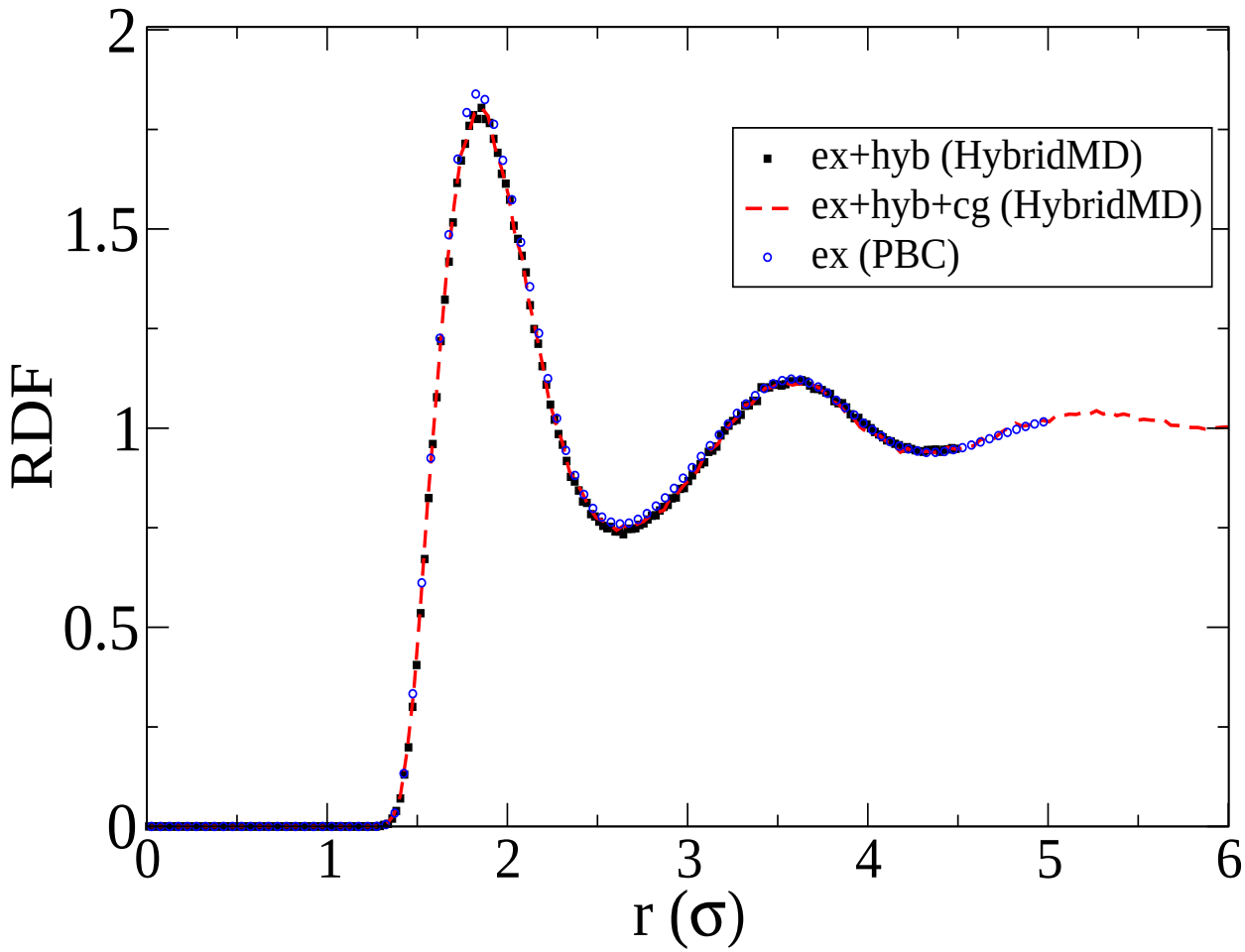
density and velocity profiles



MD-DPD-CFD: **Equilibrium**

liquid structure around the hybrid interface

Radial distribution function
high density tetraedral liquid



MD-DPD-CFD: **Equilibrium: grand canonical**

Mass fluctuations

- Scaled standard deviation of mass $\sigma_N^2/V = \rho k_B T \left(\frac{\partial p}{\partial \rho}\right)_T^{-2}$

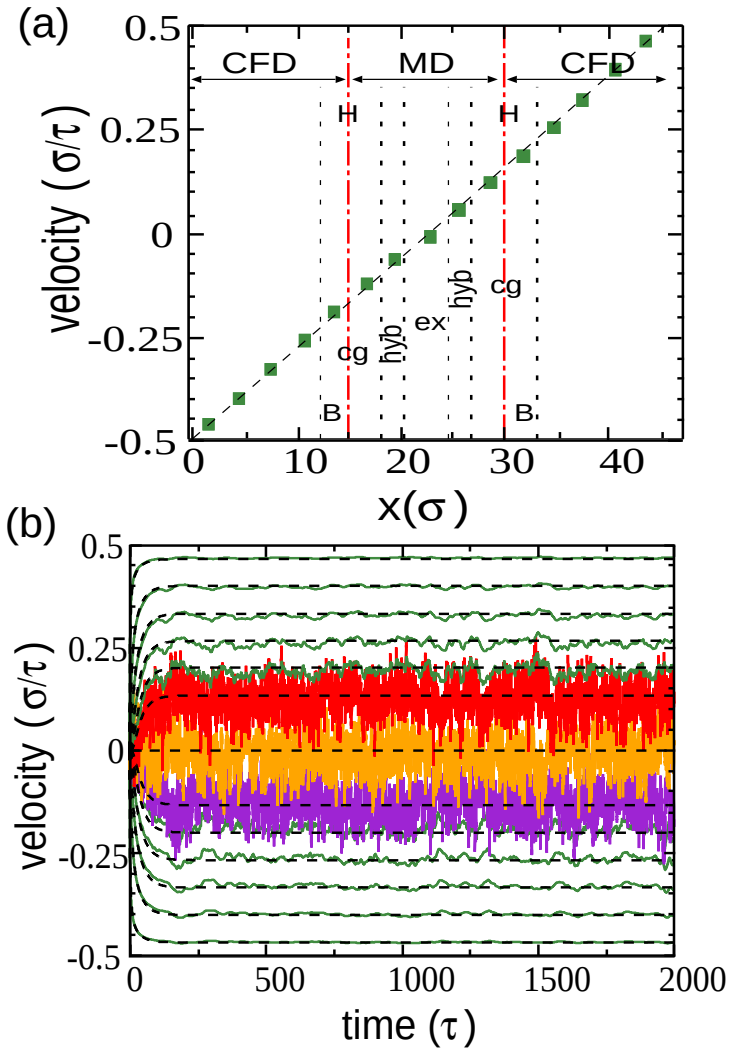
ρ	simulation	Grand canonical
0.1	0.2	0.17
0.175	0.1	0.07

- Standard deviation number of particles in one cell, $V = 15 \times 15 \times 3\sigma^3$ similar values within error bars

Coarse Grained	hyb	atomistic
13.9	14.2	14.5

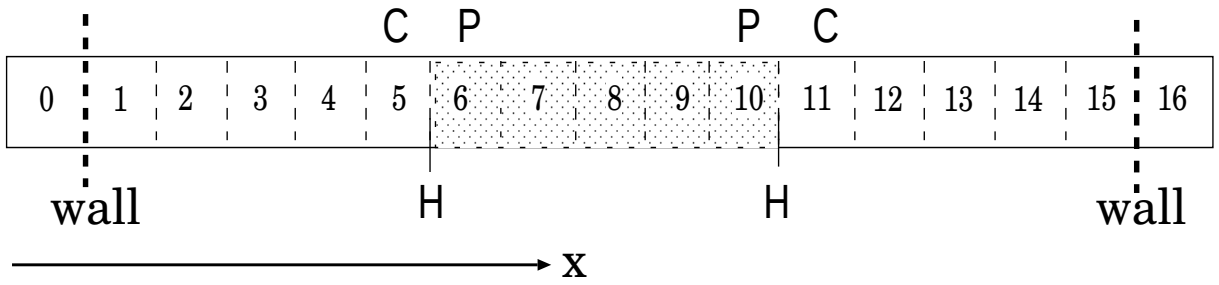
MD-DPD-CFD: **Unsteady flows**

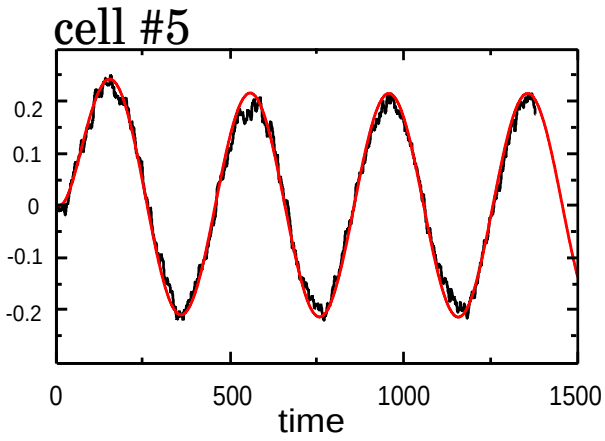
Start Couette flow

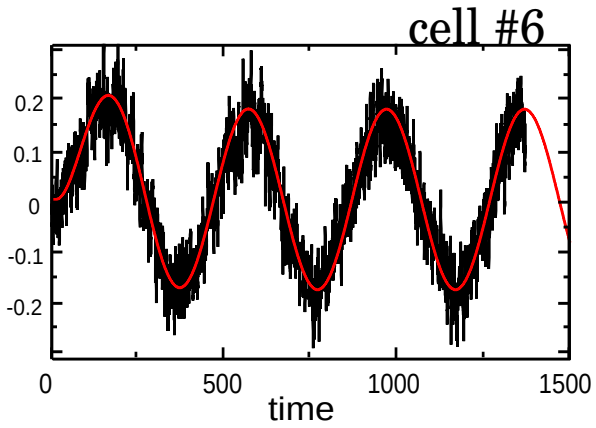


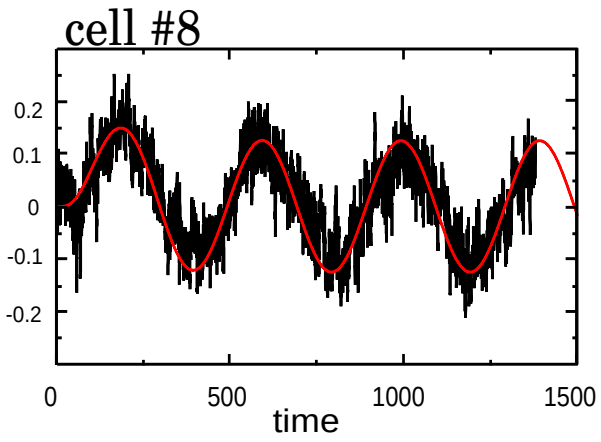
MD-DPD-CFD: **Unsteady flows**

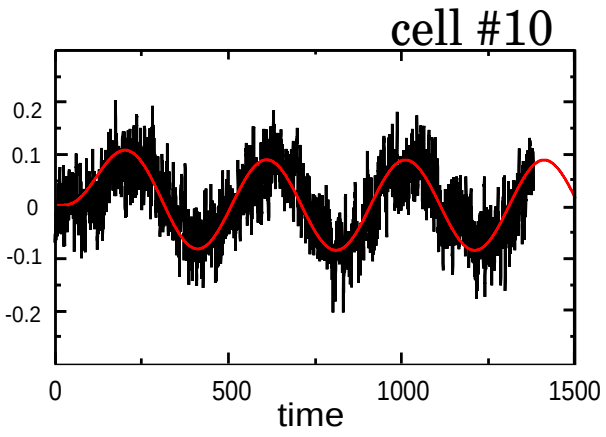
Stokes flow (oscillatory shear)







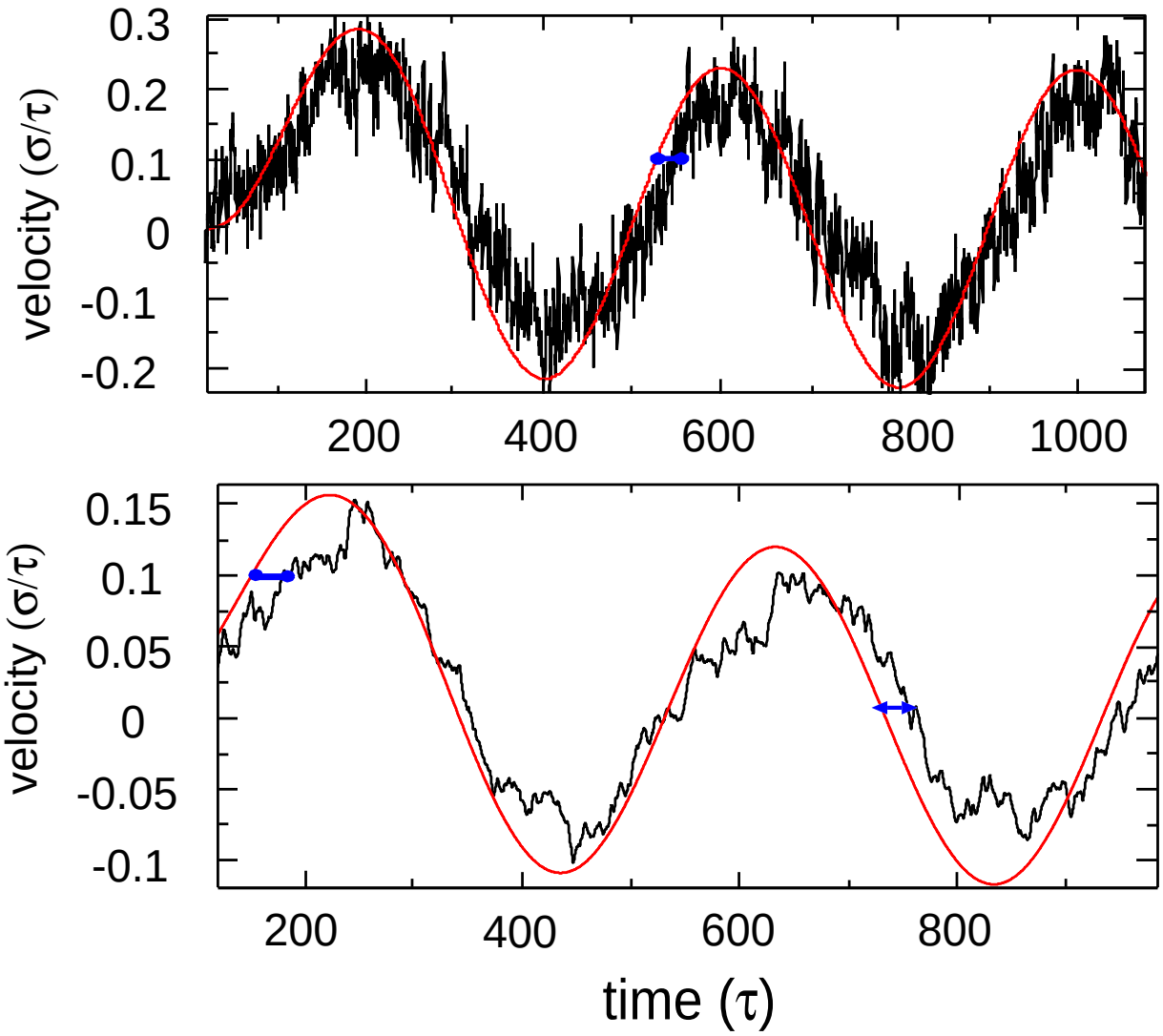




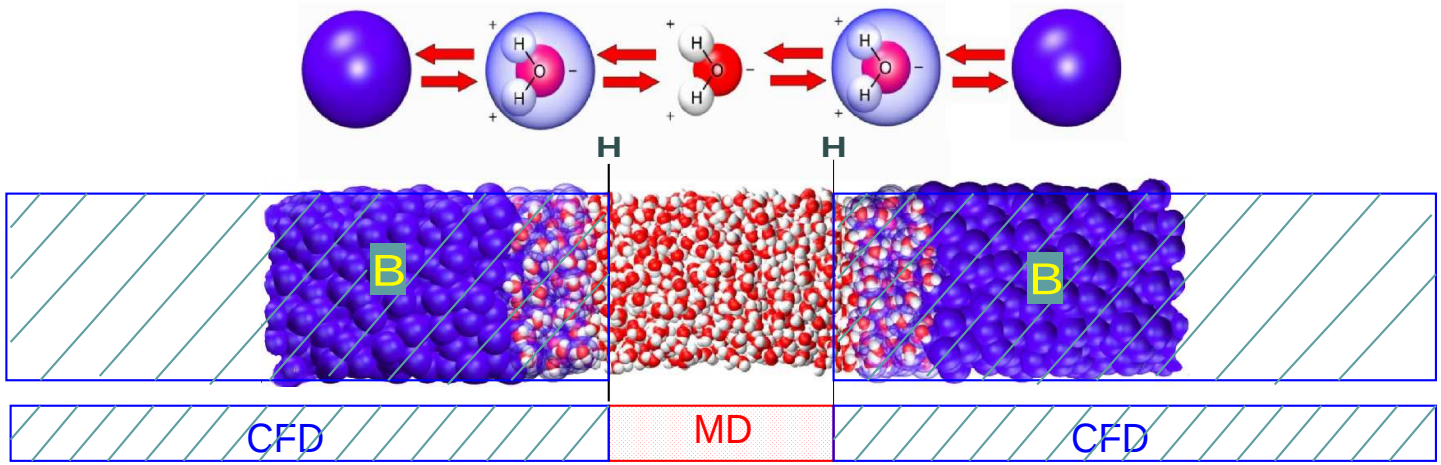
MD-DPD-CFD: **Unsteady flows**

Diffusive delay in long buffers

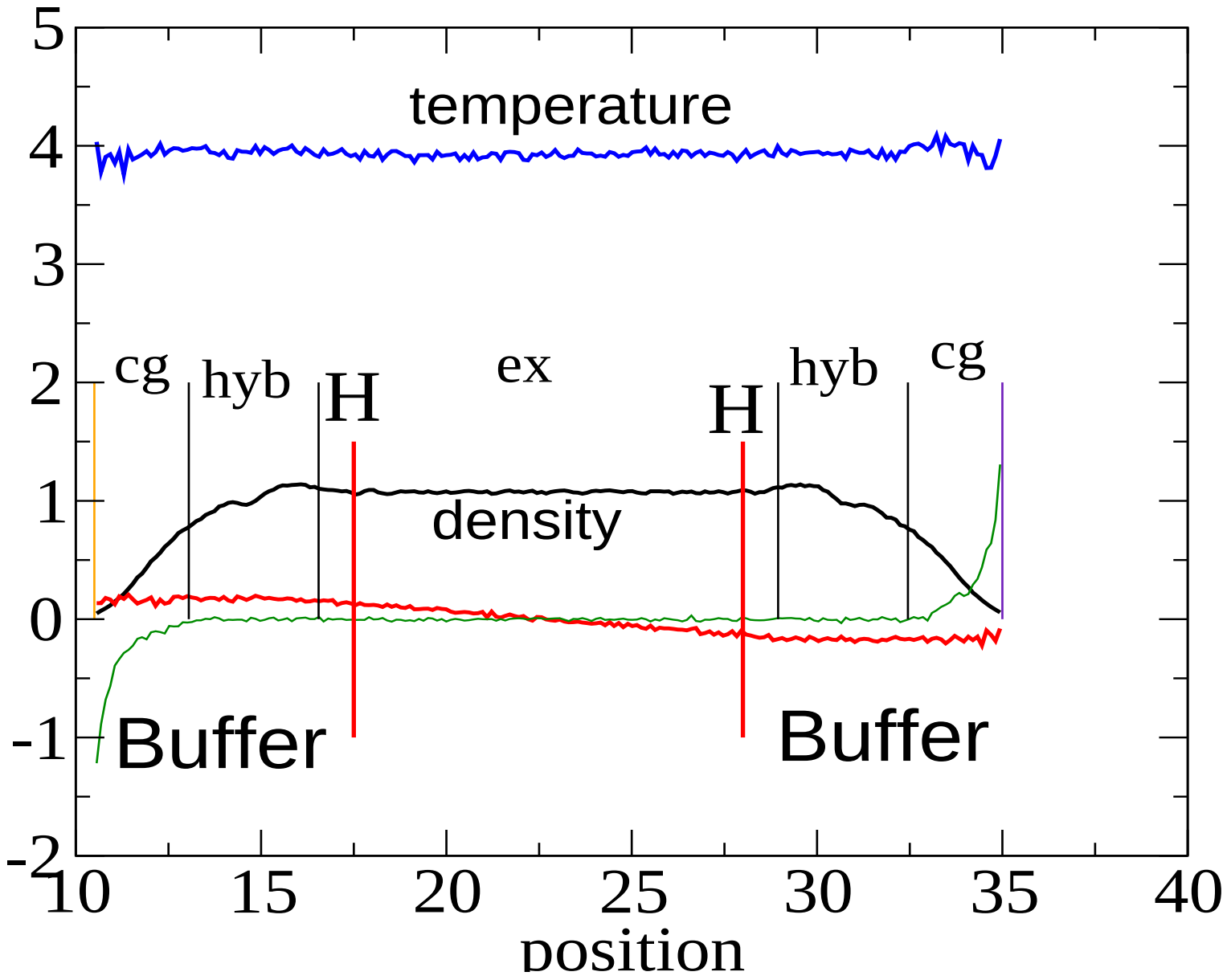
Delay time (due to momentum diffusion along buffer): $\tau_B \simeq \ell_B^2 \rho/\eta$



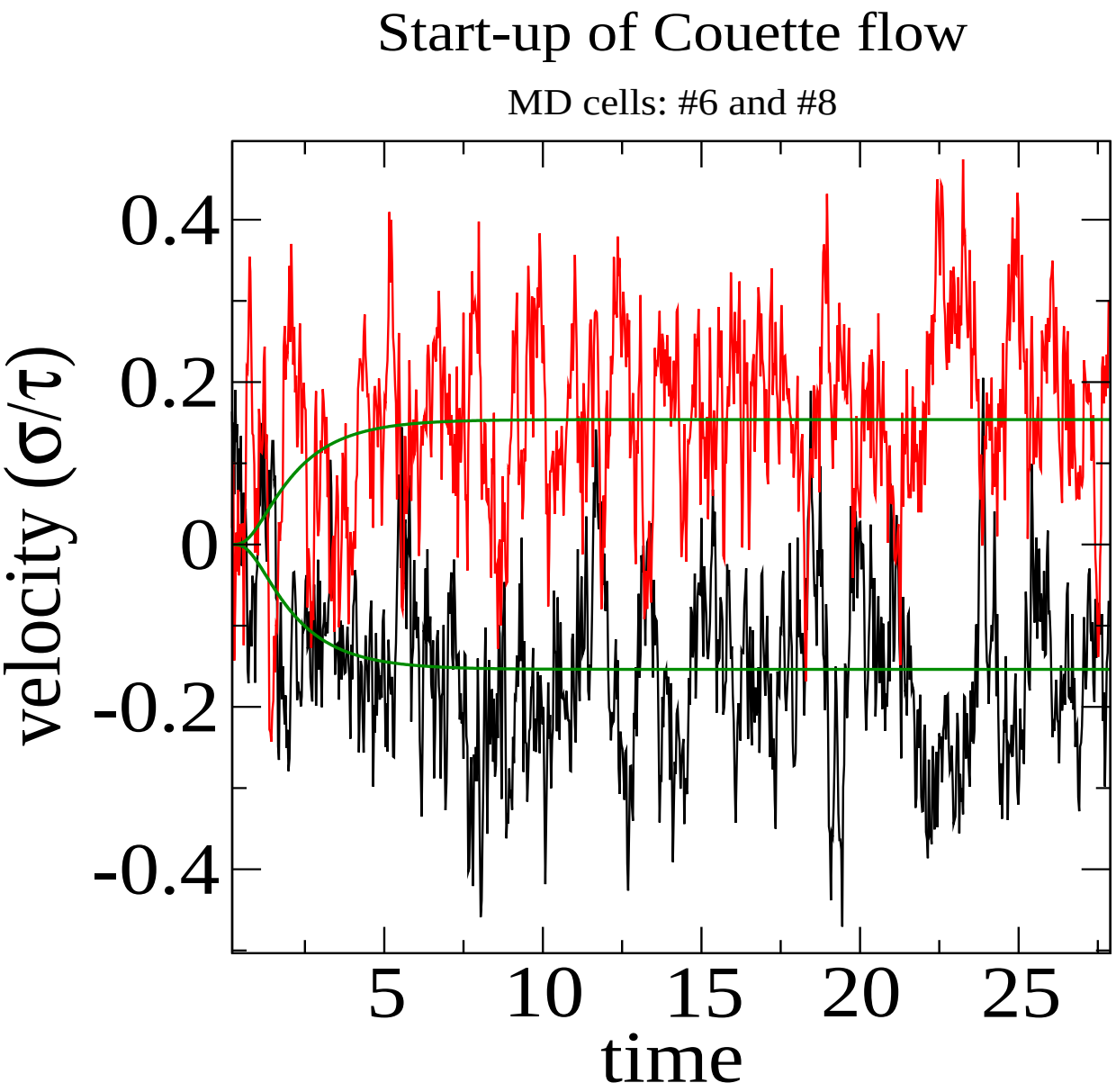
MD-DPD-CFD: **Triple scale for water**



MD-DPD-CFD: **Triple scale for water**



MD-DPD-CFD: **Triple scale for water**



Concluding remarks

- Multiscale modeling based on domain decomposition
  - Open boundaries for fluctuating hydrodynamics:
    - Evacuation of sound waves.
    - Can be generalized to energy and vorticity.
  - HybridMD: MD-Fluctuating hydrodynamics.
    - Sound, heat and energy transfer
    - Open molecular dynamics (grand canonical μVT and other ensembles)
  - Adaptive coarse-graining: MD-CG
    - Proper coarse-grained structure and pressure
    - Diffusive (mass) transport at mesoscale can be (to some extent) matched
  - Triple scale model: MD-CG-continuum
    - Coarse-grained (DPD like) intermediate model
    - Proper hydrodynamics on shear and isothermal sound transport (not heat)
    - Solves insertion of complex molecules in hybrid schemes