# Open Molecular Dynamics

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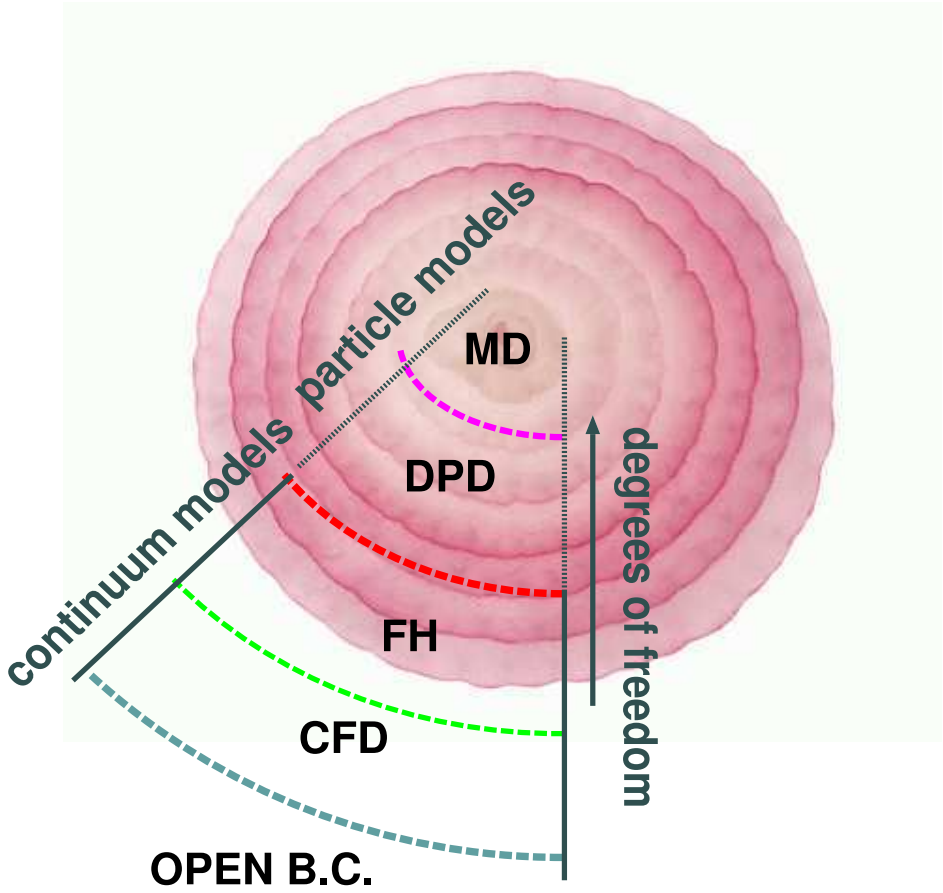
# Domain decomposition: connecting models, connecting open systems



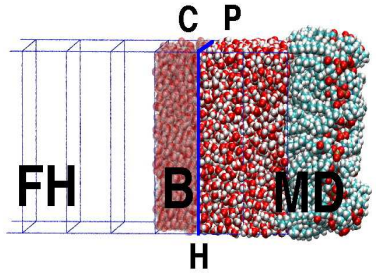

Open boundary conditions:
OUTSIDE WORLD
steady state,
thermodynamic reservoir

# Multiscale approaches 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

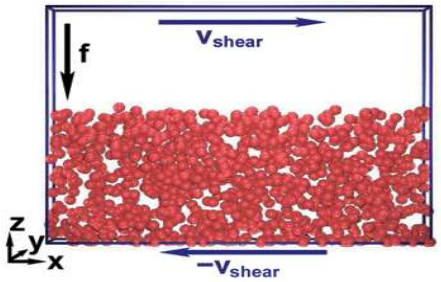


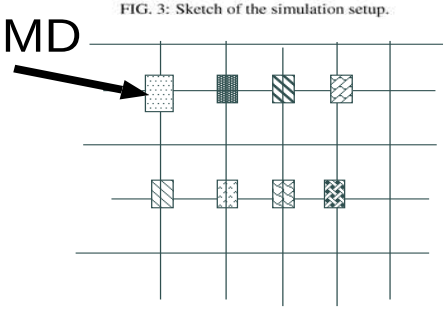

FIG. 3: Sketch of the simulation setup.

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...



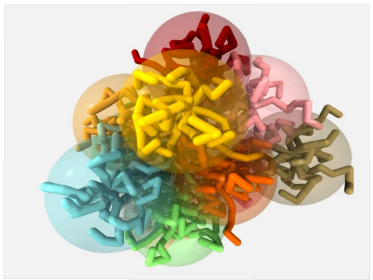

MD nodes used to evaluate the **local stress** for the Continuum solver.

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...)

# Open systems
# Beyond periodic boundary conditions

## Objetives

- Avoid finite size effects (wrapped hydrodynamic fields)

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**Purpose:** reduce unphysical artifacts at boundaries.

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  - Imposing fluxes
  - The particle buffer
  - Using Adaptive Resolution: the *mesoscopic layer*.

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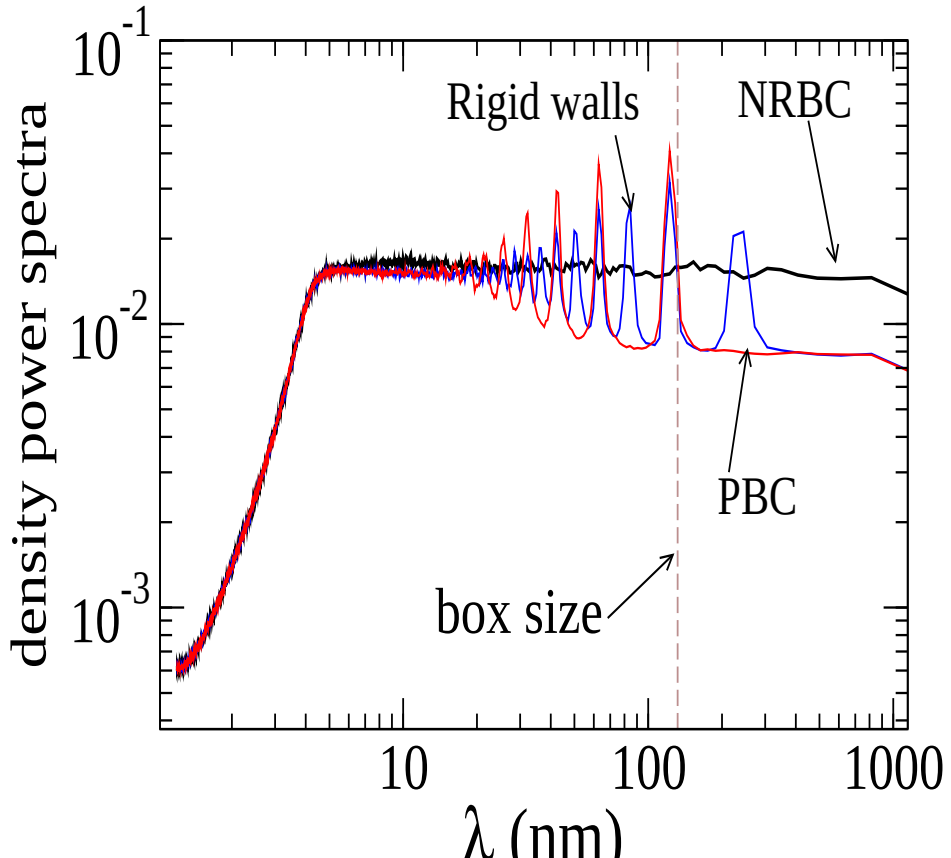
- **Open Fluctuating Hydrodynamics** OPEN FH
- **Open Molecular Dynamics:** OPEN MD
  - Imposing state variables
  - Imposing fluxes
  - The particle buffer
  - Using Adaptive Resolution: the *mesoscopic layer*.
- **Conection with a continuum solver: the hybrid particle-continuum scheme**

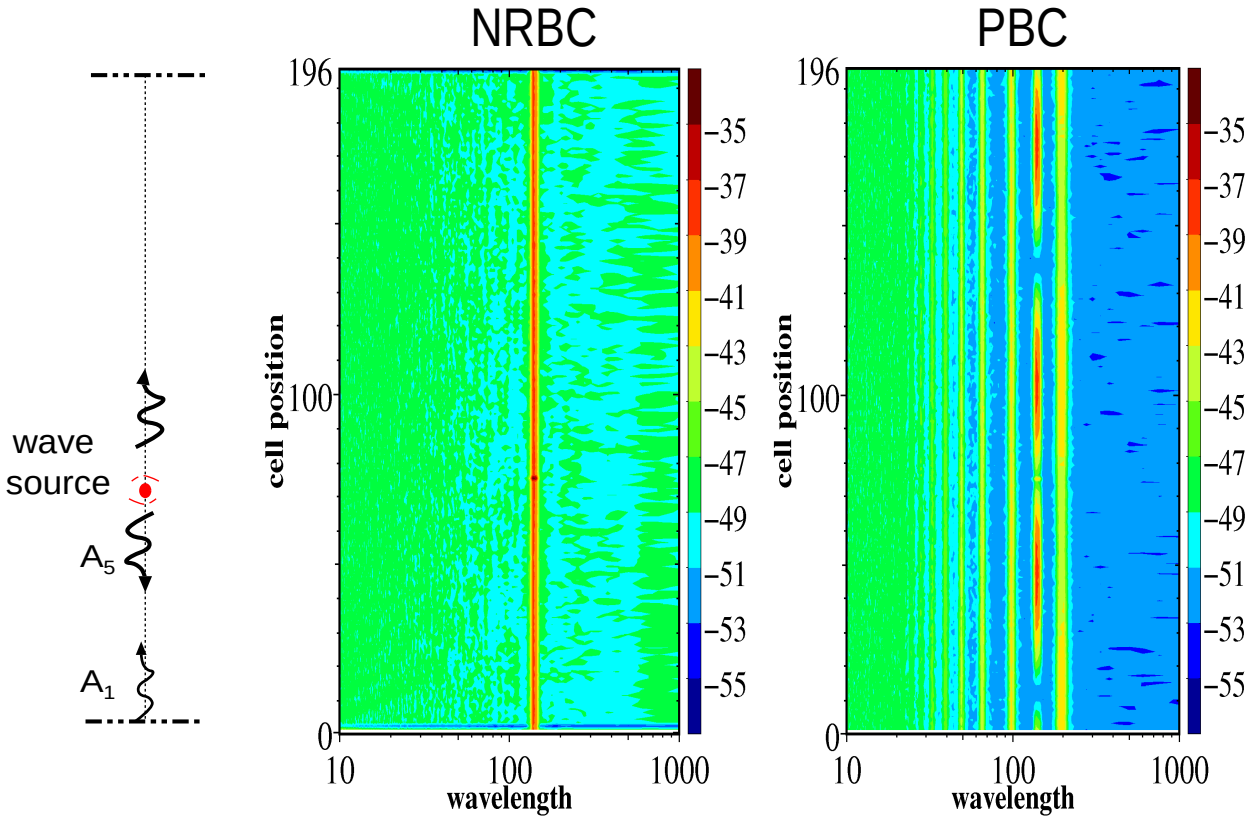
# Open Fluctuating hydrodynamics

RDB & Dejoan, Phys. Rev. E **78**, 046708 (2008)
Power spectra of density fluctuations: liquid argon @ equilibrium
NRBC=Non-Reflecting boundary conditions



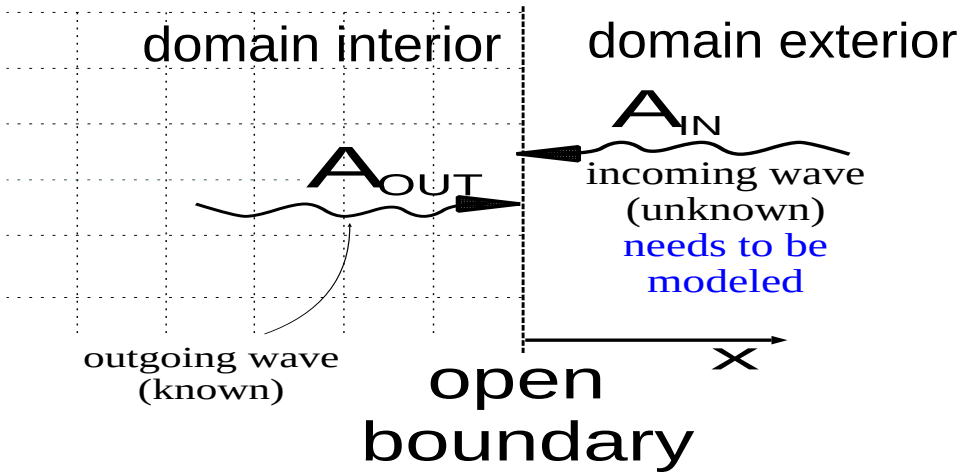
# Open Fluctuating hydrodynamics
## Evacuation of sound waves using non-reflecting boundaries

RDB & Dejoan, Phys. Rev. E **78**, 046708 (2008)



# Open Fluctuating hydrodynamics

Non-reflecting boundary conditions in terms of sound modes.




- Amplitude of **sound waves**

$$A_{IN} = \frac{1}{2}\left(\frac{\delta p}{\rho_e c} - \delta u\right) \quad \text{moving} \leftarrow$$

$$A_{OUT} = \frac{1}{2}\left(\frac{\delta p}{\rho_e c} + \delta u\right) \quad \text{moving} \rightarrow$$

with $\delta p = p - p_e$, $\delta u = u - u_e$, pressure and velocity fluctuations.

# Open Fluctuating hydrodynamics
## Non-reflecting boundary conditions for sound modes

- **Linear Navier-Stokes Eqs.**, normal-to-boundary direction,

$$\frac{\partial A_i}{\partial t} = (u \pm c)\frac{\partial A_i}{\partial x} \pm \frac{1}{\rho_e}\frac{\partial P_{xx}}{\partial x}$$

  with $i = IN \rightarrow +$ and $i = OUT \rightarrow -$

- Amplitude variations:

$$\frac{L_i}{\rho_e c} = (u \mp c)\frac{\partial A_i}{\partial x}$$

# Open Fluctuating hydrodynamics

$$\frac{\partial A_i}{\partial t} + \frac{L_i}{\rho_e c} = \pm \frac{1}{\rho_e} \frac{\partial P_{xx}}{\partial x}$$

Amplitude variations,

$$\begin{aligned} L_{OUT} &= (u-c)\frac{\partial A_{OUT}}{\partial x} \text{ Measured within domain} \\ L_{IN} &= K(\rho c A_{IN}) \quad \text{Modelled} \\ K &= \frac{\nu_L}{(0.4\Delta x)^2} \text{ Satisfies FD balance} \end{aligned}$$

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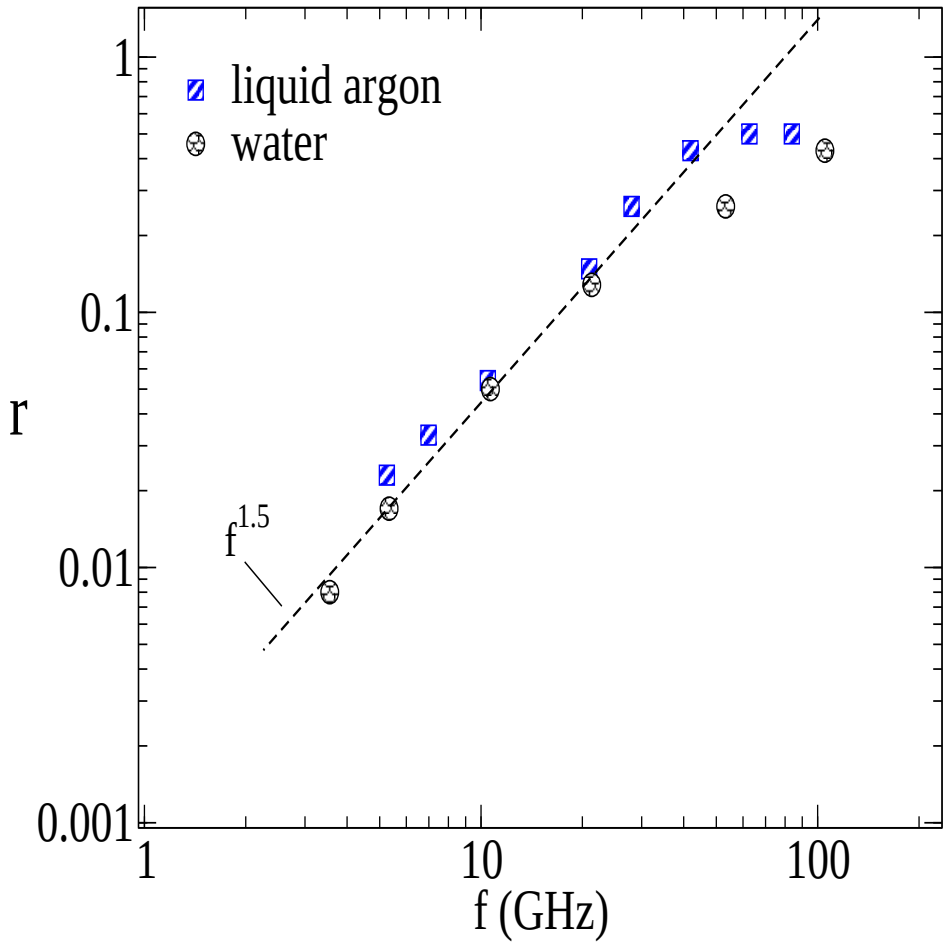
**NRBC Eqs. for boundary cells,**

$$\begin{aligned} \text{density} &: \frac{\partial \rho}{\partial x} = 0 \\ \text{velocity} &: \frac{\partial u}{\partial t} + \frac{1}{2\rho_e c}(L_{OUT} - L_{IN}) = 0 \end{aligned}$$

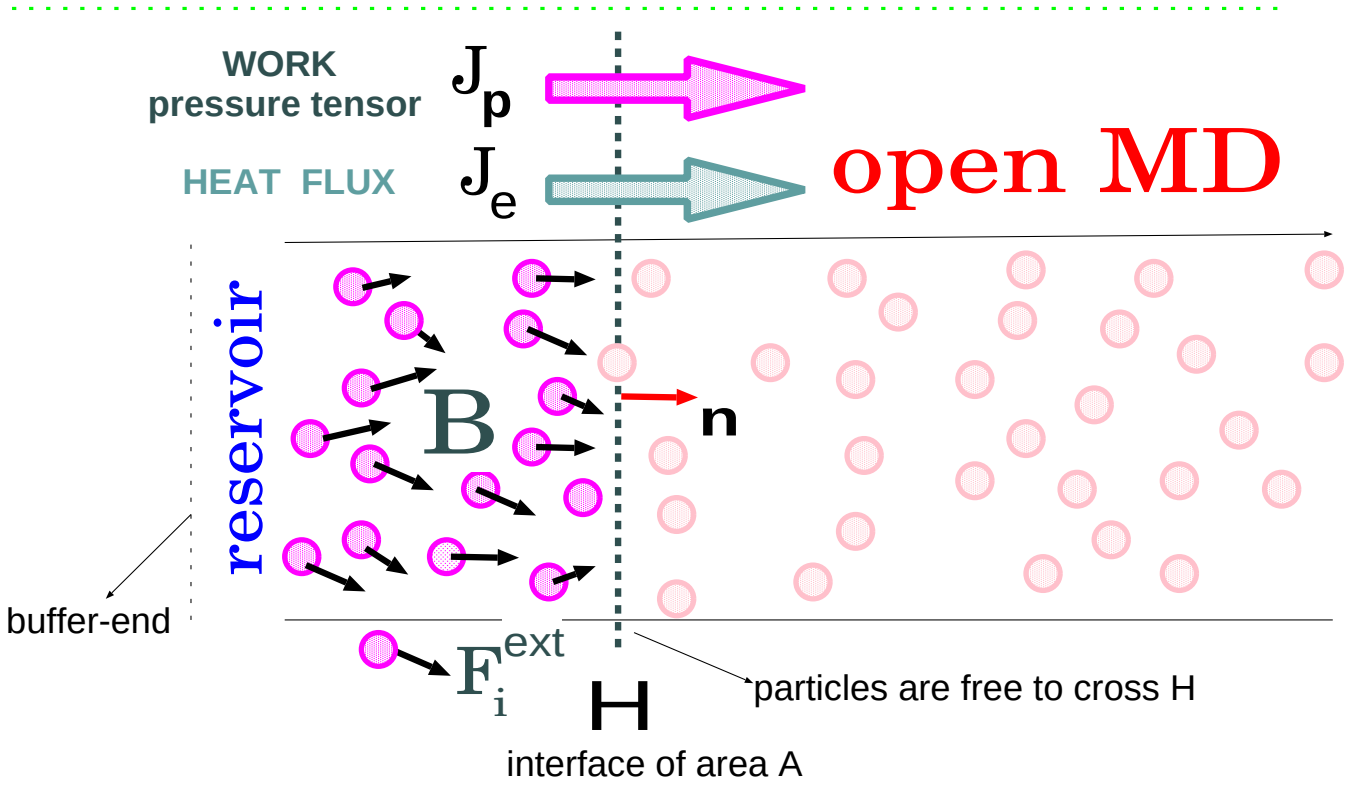
# Open Fluctuating hydrodynamics

NRBC Reflection coefficient.



# Open MD
## via external forces

$$m\ddot{\mathbf{r}}_i = \mathbf{f}_i(\{\mathbf{r}\}) + \mathbf{f}_i^{\text{ext}}$$



# State-Coupling

(see: Thomsom and O'Connel and Mark Robbins' group)

**Scope**

- **CFD Research:** effects of molecular domain onto the mean flow.
- **Priority:** The external flow imposed into the molecular region.
- **Mass flux**: Imposed to MD using continuum expression: $A\rho V_n$.
- **NO molecular fluctuations**
- **Impose** external velocity $\mathbf{V}$ at the buffer $\bar{\mathbf{v}} \equiv \frac{1}{N_B} \sum_{i \in B} \mathbf{v}_i$

# State-Coupling

## Method

- Constrained dynamics: $m\ddot{\mathbf{r}}_i = \left(\mathbf{f}_i - \bar{\mathbf{f}}\right) - \xi\left(\mathbf{v}_i - \mathbf{V}\right)$
- External force: $\mathbf{f}_i^{\text{ext}} = -\bar{\mathbf{f}} - \xi\left(\mathbf{v}_i - \mathbf{V}\right)$
- Mean buffer velocity:

$$\frac{d\bar{\mathbf{v}}}{dt} = -\gamma\left(\bar{\mathbf{v}} - \mathbf{V}\right)$$

$\bar{\mathbf{v}}$ converges to $\mathbf{V}$ exponentially (at rate $\gamma = \xi/M_B$); and instantaneously if $\gamma = 1/\Delta t$

# Thermodynamics of State-Coupling

Input power

$$\dot{E} = \sum_{i \in B} \mathbf{f}_i^{\text{ext}} \cdot \mathbf{v}_i$$

External force

$$\begin{aligned} \mathbf{f}_i^{\text{ext}} &= -\bar{\mathbf{f}} - \xi \left( \mathbf{v}_i - \mathbf{V} \right) \\ \text{where} \qquad & \bar{\mathbf{f}} = \frac{1}{N} \sum_{i \in B} \mathbf{f}_i = M \frac{d\bar{\mathbf{v}}}{dt} \end{aligned}$$

# Thermodynamics of State-Coupling

Assume $\bar{\mathbf{v}} \simeq \mathbf{V}$

$$\dot{E} = -N\bar{\mathbf{f}} \cdot \bar{\mathbf{v}} - \xi \sum_{i \in B} (\mathbf{v}_i - \bar{\mathbf{v}})^2$$

Use equipartition $3kT = \langle (\mathbf{v}_i - \bar{\mathbf{v}})^2 \rangle$ and $\langle \bar{\mathbf{f}} \bar{\mathbf{v}} \rangle = M \langle \frac{d\bar{\mathbf{v}}}{dt} \bar{\mathbf{v}} \rangle = 0$ to get:

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$$\frac{d\langle E \rangle}{dt} = -3\frac{\xi}{m} NkT$$

Exponential freezing (very fast, $\xi/m >> \xi/M = \gamma$).
**Hard thermostatting is required** (simple velocity rescaling!)

# Flux-Coupling

(See: Flekkoy, RD-B and Coveney, Phys. Rev. E, 72, 026703 (2005)

## Scope

- **Molecular research:** effects of flow on molecular domain.
- **Priority:** avoid external artifacts into molecular domain
- **Mass flux**: Measured from MD; naturally arises from pressure gradient across the interface
- **Molecular fluctuations** (mass,momentum, energy)
- **Imposes:** Flux across interface of area A and (inwards) surface vector $\mathbf{n}$
- **Momemtum** flux (force/area) $\mathbf{P}_n = \mathbf{P} \cdot \mathbf{n}$
- **Heat** flux (energy/time) $\dot{Q}_e = \mathbf{q} \cdot \mathbf{n}$

# Flux-Coupling

(PRE, 72, 026703 (2005) **Method**

- External force to buffer particles: $\mathbf{f}_i^{\text{ext}} = \bar{\mathbf{f}}_{\text{ext}} + \tilde{\mathbf{f}}_{\text{ext}}$
- Momentum transfer by the average external force

$$\bar{\mathbf{f}}_{\text{ext}} = \mathbf{P}_n A / N_B$$

- Heat transfer by the fluctuating external force

$$\tilde{\mathbf{f}}_{\text{ext}} = \frac{\mathbf{v}_i}{\sum_{i \in B} v_i^2} \dot{Q}_e$$

- Momentum and energy due to particle insertion/deletions can be taken into account (**exact balance**).

# Thermodynamics of Flux-Coupling

Energy input over $\Delta t$

$$
\begin{aligned}
\Delta E &= \sum_{i \in B} \mathbf{f}_i^{\text{ext}} \cdot \mathbf{v}_i \Delta t + \sum_k e_k \\
\mathbf{f}_i^{\text{ext}} &= A\mathbf{P}_n/N + \frac{\mathbf{v}_i}{\sum_{i \in B} v_i^2} \dot{Q}_e \\
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Entropy change (quasi-statiorary, $\dot{Q}_e$ not so large)

$$\begin{aligned}
T\Delta S' &= \sum_k e_k - \mu \Delta N \text{ Particle insertions} \\
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# Thermodynamics of Flux-Coupling

Energy input

$$\Delta E = A\mathbf{P}_n \cdot \bar{\mathbf{v}}\Delta t + T\Delta S + \mu\Delta N$$

Pressure and stress (tangential external force)

$$\begin{aligned} \mathbf{P}_n &= p\mathbf{n} + P_t\mathbf{t} \\ A\mathbf{P}_n \cdot \bar{\mathbf{v}}\Delta t &= p(A\bar{\mathbf{v}} \cdot \mathbf{n}\Delta t) + AP_t\bar{\mathbf{v}} \cdot \mathbf{t}\Delta t \end{aligned}$$

Hence,

$$\Delta E = -p\Delta V + T\Delta S + \mu\Delta N + \text{Heat dissipated by shear}$$

Flux coupling is consistent with equilibrium thermodynamics for open systems.

## Flux-coupling: OPEN MD in generalized ensembles

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Grand canonical $\mu_B$VT

Dynamics of confined systems

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Dynamics of confined systems

Isobaric ensemble $\mathbf{P}_n = p\mathbf{n}$

Outlet B.C., Hybrids

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Grand canonical $\mu_B$VT — Dynamics of confined systems

Isobaric ensemble $\mathbf{P}_n = p\mathbf{n}$ — Outlet B.C., Hybrids

Constant enthalpy $\dot{Q}_e = 0$ — Joule-Thompson, MD-calorimeter

$(\Delta N = 0)$

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

# Flux-coupling: OPEN MD in generalized ensembles

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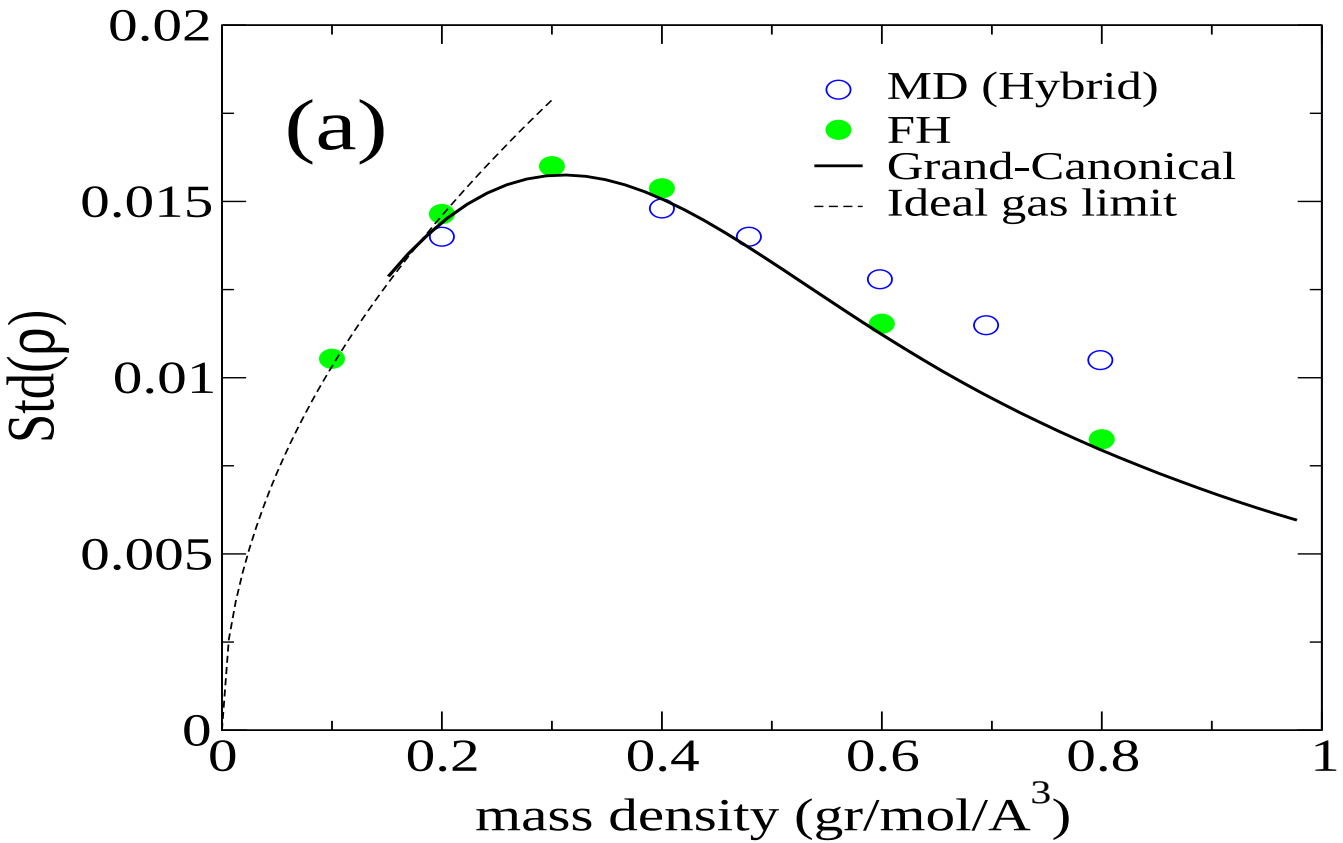
|---|---|
| Grand canonical $\mu_B$VT | Dynamics of confined systems |
| Isobaric ensemble $\mathbf{P}_n = p\mathbf{n}$ | Outlet B.C., Hybrids |
| Constant enthalpy $\dot{Q}_e = 0$ $(\Delta N = 0)$ $\Delta H = \Delta E + p\Delta V = 0$ | Joule-Thompson, MD-calorimeter |
| Constant heat flux: $\dot{Q}_e$ | Melting, ice formation, heat exchange at complex surfaces |

# Density fluctuations (MD-FH hybrid)

Standard deviation of argon density, $T = 300K$

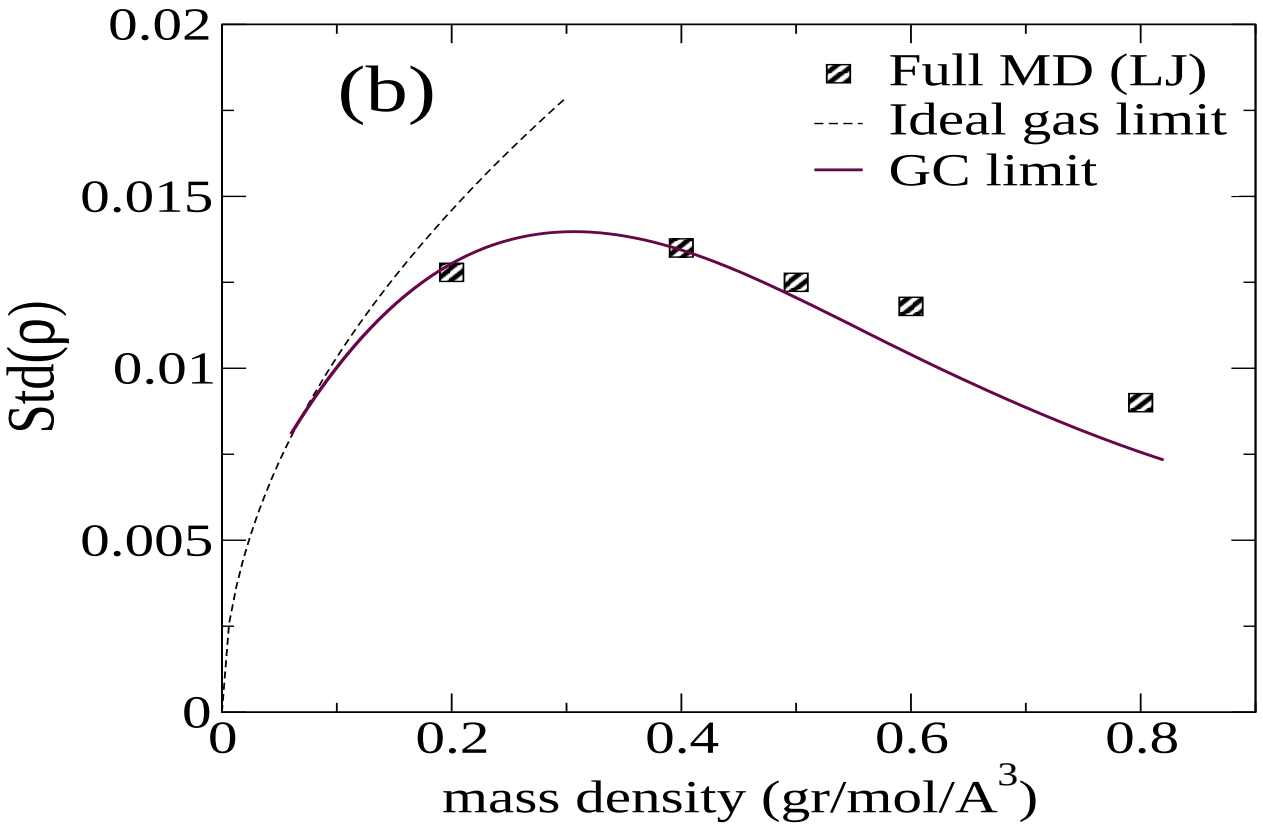
RDB and G.Fabritiis et al. PRE, **76** (2007)



# Density fluctuations (Full MD)

Standard deviation of argon density, $T = 300K$

Subvolume of a large PBC box



# Open MD
## Density profile at the buffer

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

$$\mathbf{f}_i^{ext} = \frac{g(x_i)}{\sum_{i \in B} g(x_i)} \mathbf{F}^{ext} \quad (\text{with } \mathbf{F}^{ext} = A\mathbf{P} \cdot \mathbf{n})$$

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- The buffer density profile is controlled by the force distribution $g(x)$.
- Any $g(x) \neq$cte introduces **spurious heat** into the system and requires thermostats.

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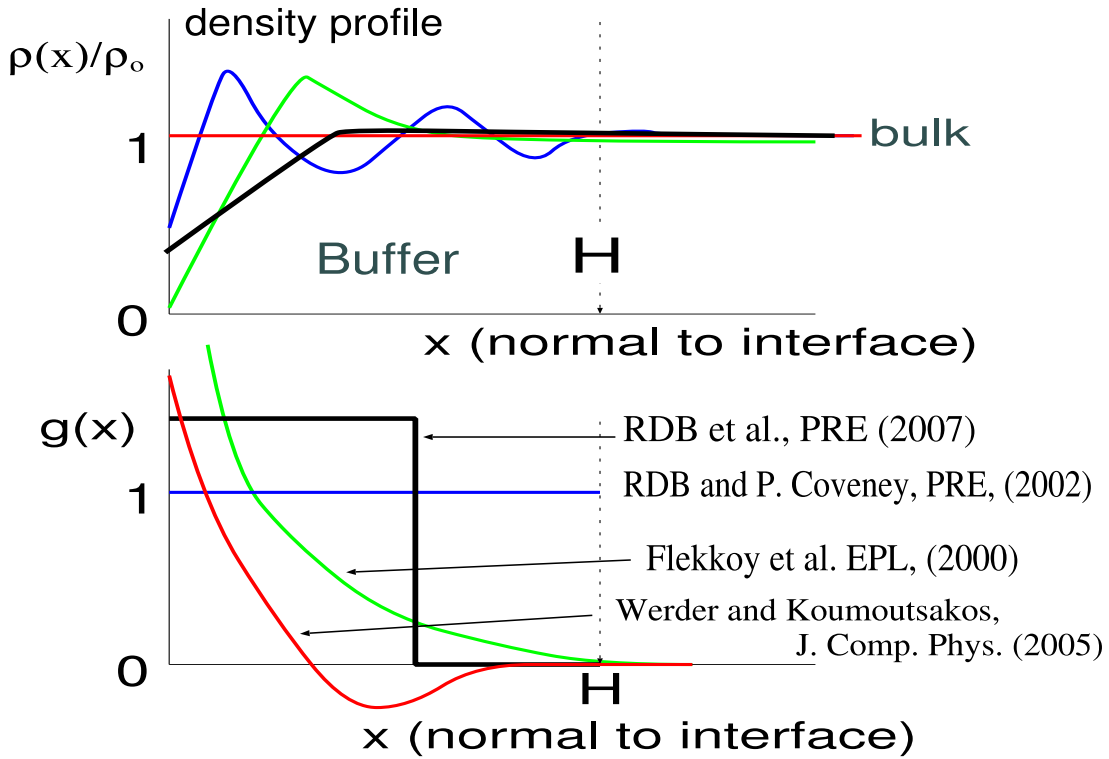

# Open MD
## Mass control at the buffer

The average buffer mass is controlled to a fixed value $\langle M_B \rangle$

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

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

- `Deletion`: $\Delta M_B < 0$ (also particles crossing the buffer-end)
- `Insertion`: $\Delta M_B > 0$
  - Small solvent molecules: USHER algorithm for
  - Large molecules (star polymers): **Adaptive Resolution**

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

J. Chem. Phys **119**, 978 (2003) spherical molecules
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)

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J. Chem. Phys **119**, 978 (2003) spherical molecules
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## Particle insertion by the USHER algorithm

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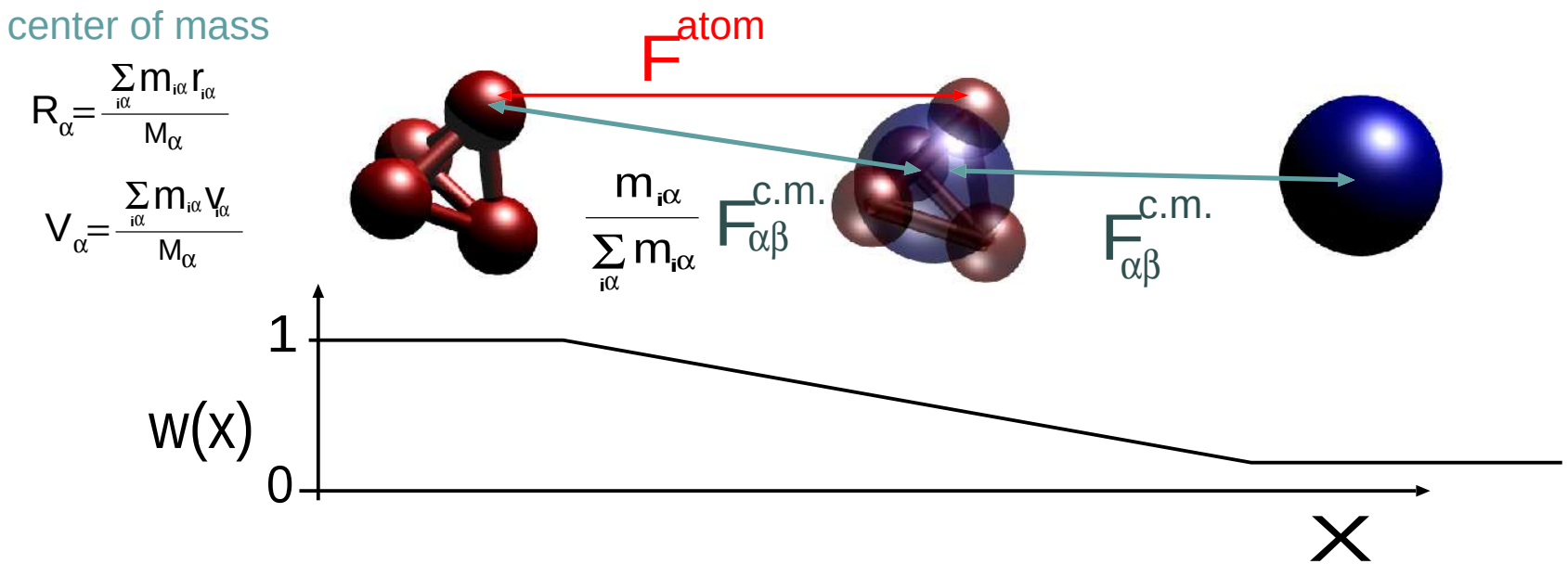
- Negligible insertion cost $< 1\%$ total CPU (LJ), $\sim 3\%$ (water).
- Very fast: water into water at low energy ($E_T = e$) requires 100 iterations ($10^5$ fater than random insertion)

# Adaptive Resolution Scheme

Praprotnik, Delle Site, Kremer, Annu. Rev. Phys. Chem. 59, 545 (2008)

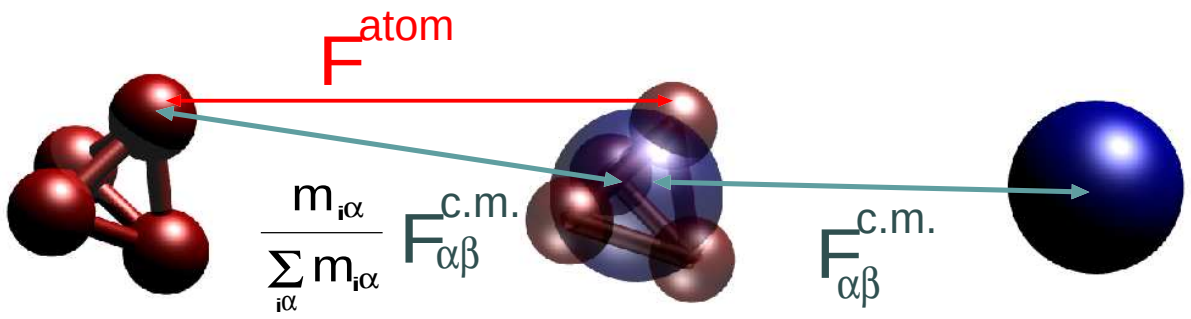


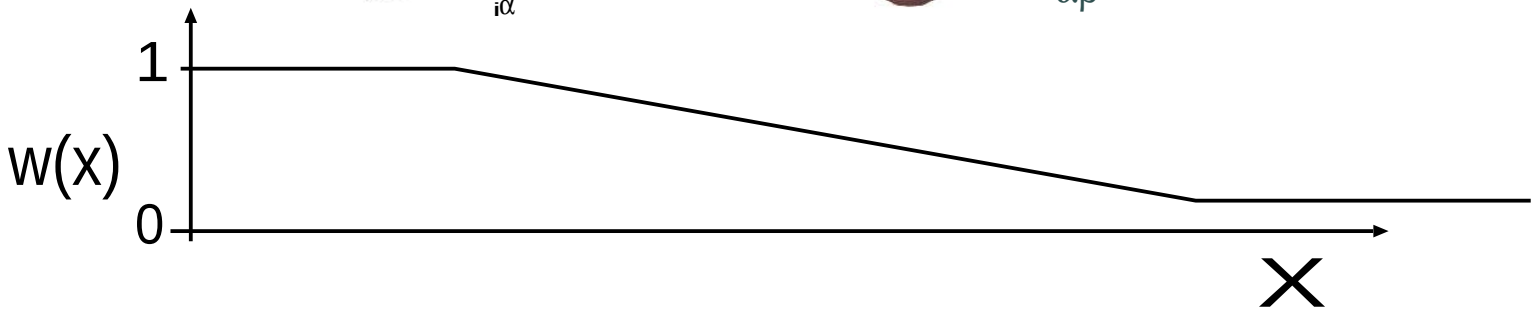
# Adaptive Resolution Scheme

center of mass

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

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



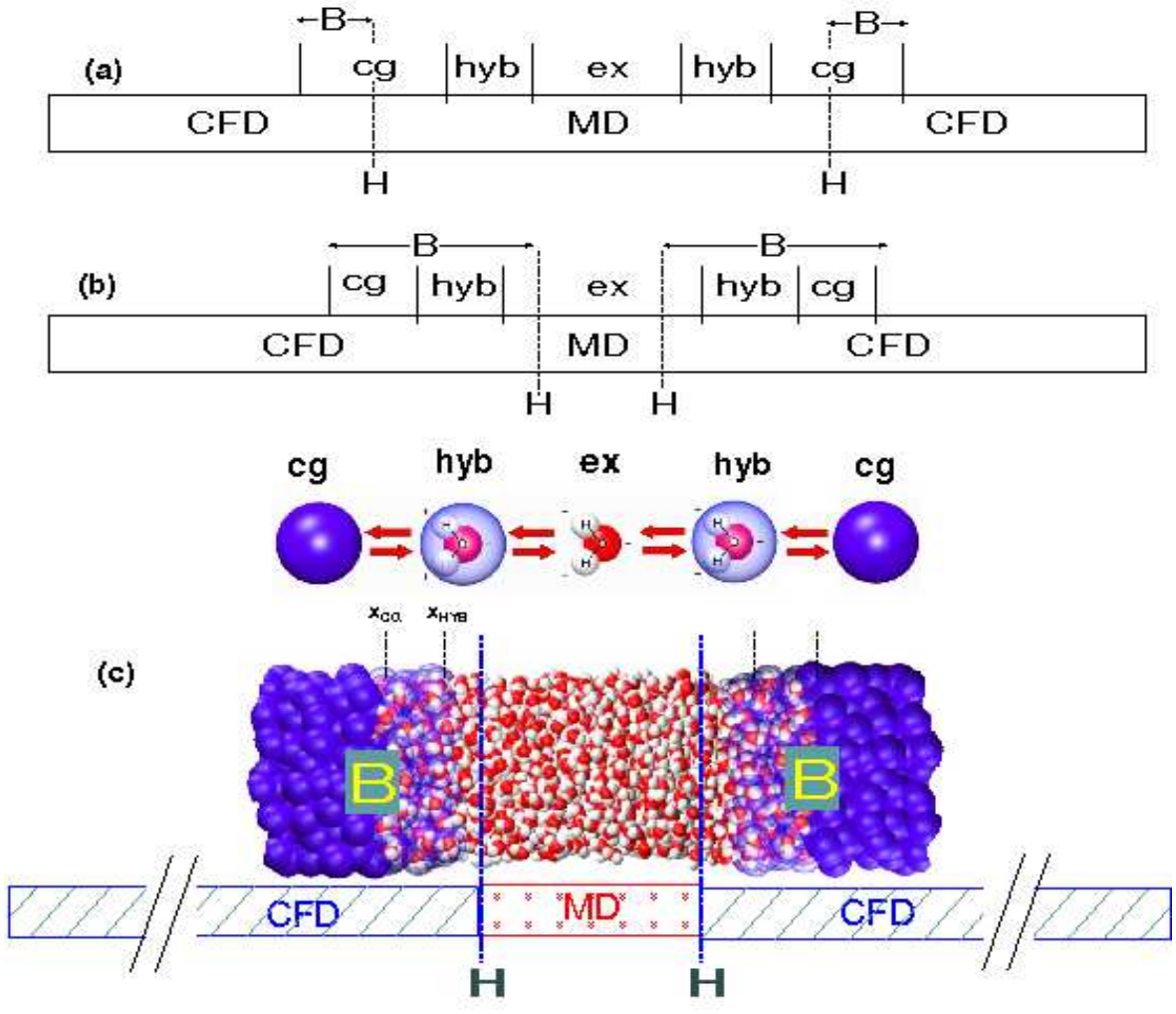

$$\mathbf{F}_{\alpha\beta} = w(x_\alpha)w(x_\beta)\sum_{i\alpha j\beta}\mathbf{F}^{\text{atom}}_{i\alpha j\beta} + [1 - w(x_\alpha)w(x_\beta)]\mathbf{F}^{\text{c.m.}}_{\alpha\beta}$$

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

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

# HybridMD-AdResS triple scale

(a) Coarse-grained buffer
(b) Adaptive buffer



# Open MD with AdResS

The *adaptive* buffer

does not require accurate fits for the CG and HYB models

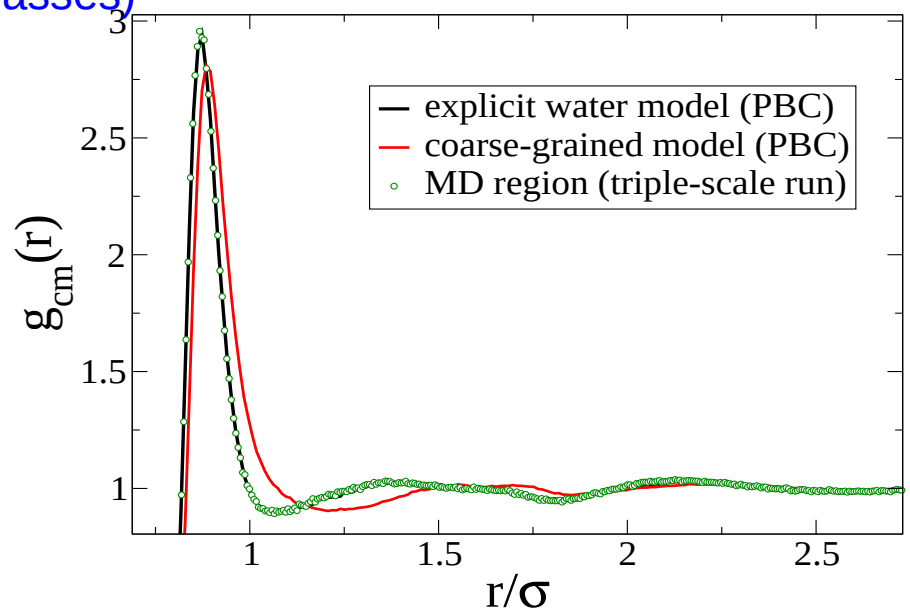
RDB, Kremer, Praprotnik, J.Chem.Phys. **131**, 244107 (2009)

Viscosities
(oxigen-LJ units)

CG $\eta$=20

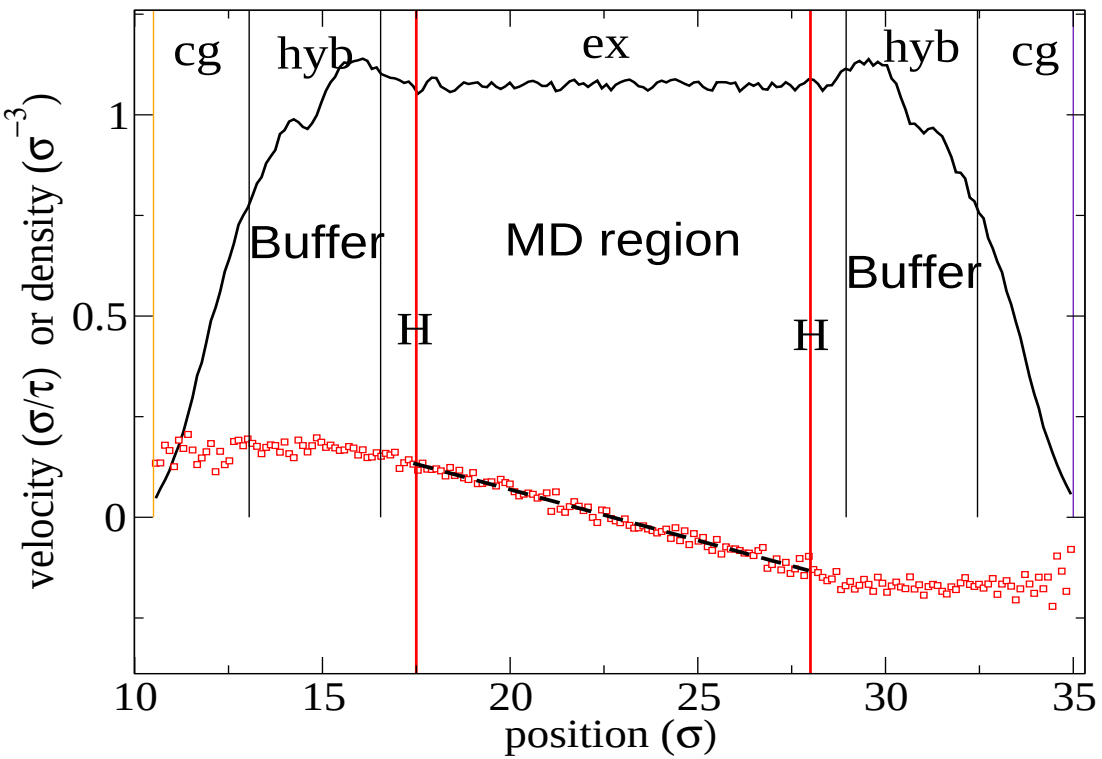
EX $\eta$=45 —— **Flexible TIP3P water model**

Radial distribution funcions
(center of masses)



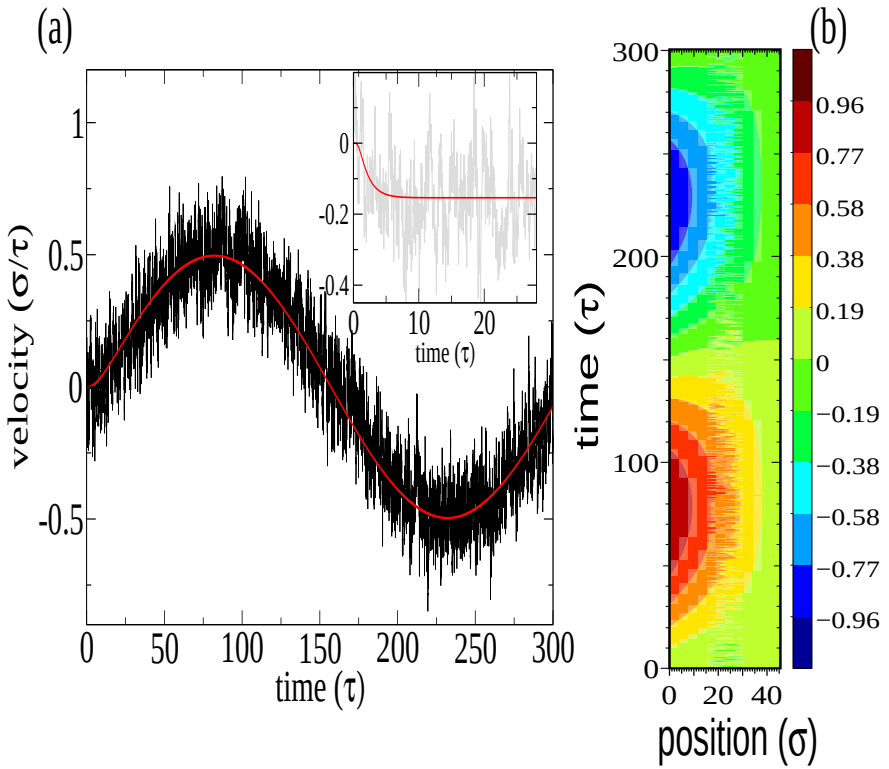
# HybridMD-AdResS triple scale

RDB, Kremer, Praprotnik, J.Chem.Phys. **131**, 244107 (2009)

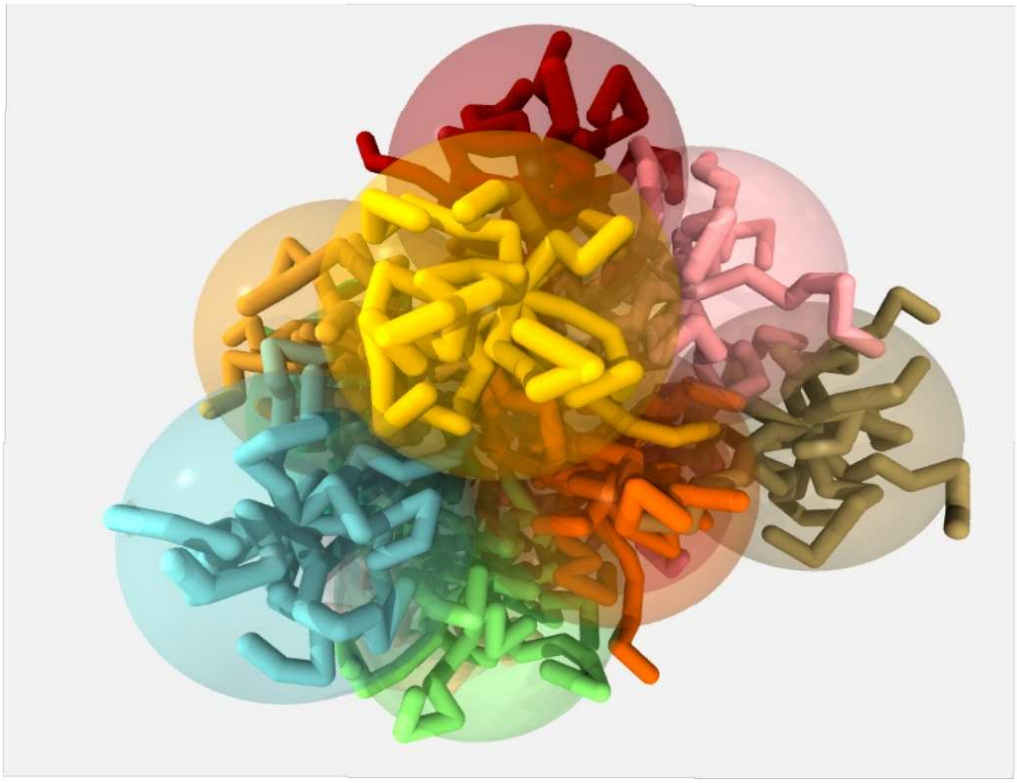


# HybridMD-AdResS triple scale

Simulation of TIP3P water under oscillatory shear RDB, Kremer, Praprotnik, J.Chem.Phys. **131**, 244107 (2009)

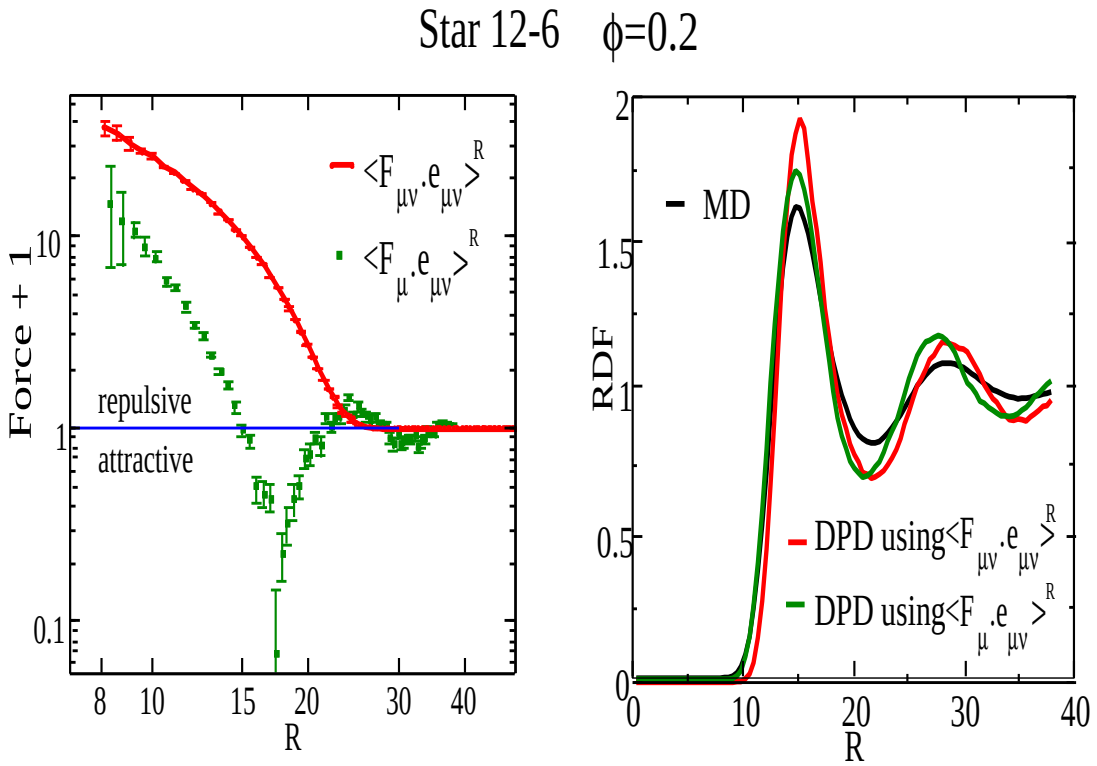


# Melts of star polymers via Open MD-AdResS



# Melts of star polymers via OPEN MD-AdResS

(to be submitted)

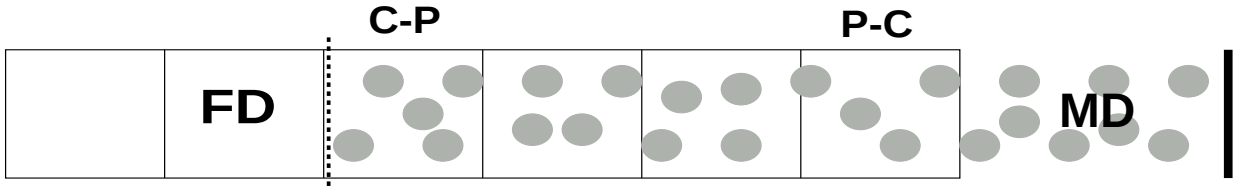


# Hybrid particle-continuum schemes: alternatives

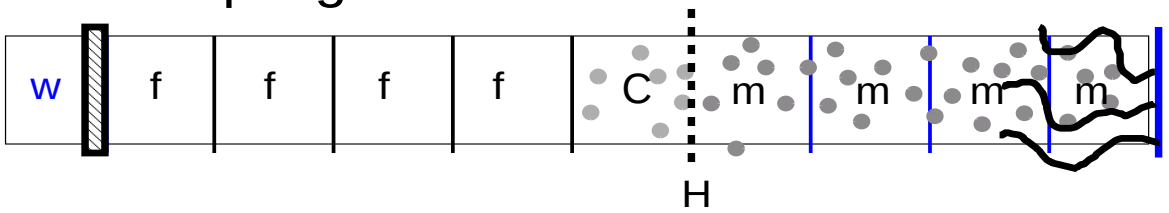
- **State scheme:** Non-conservative, no fluctuations (requires averaging), incompressible.
- **Flux scheme:** Conservative, fluctuations, compressible.

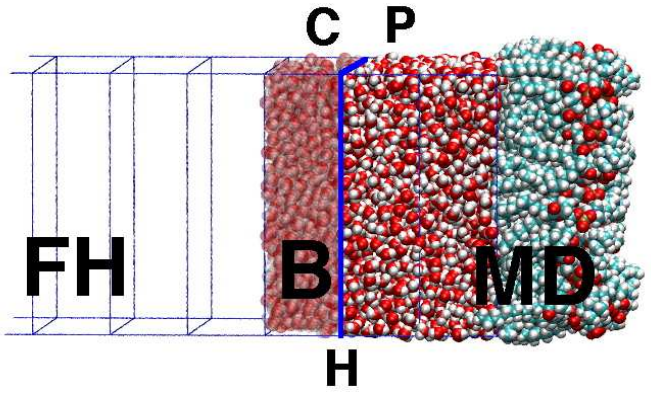
# Hybrid particle-continuum schemes: set-up

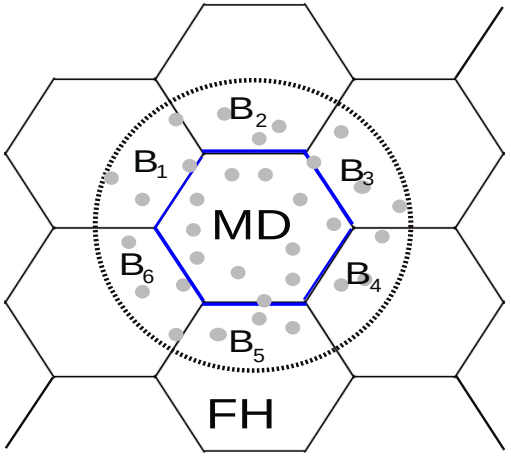
State-coupling



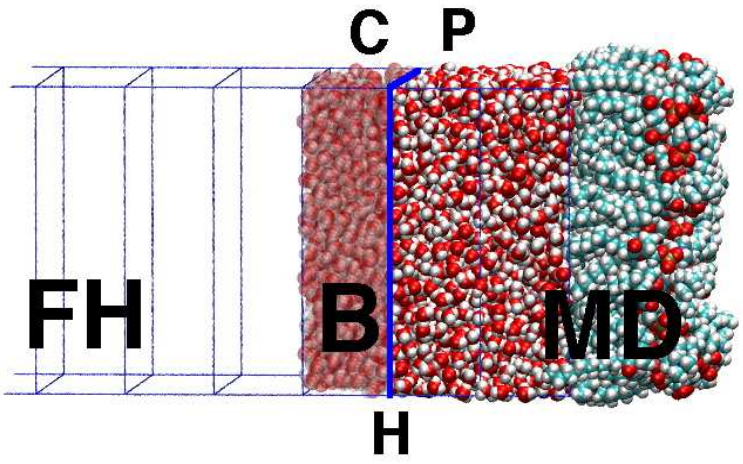

Flux-coupling



# Continuity in flux schemes



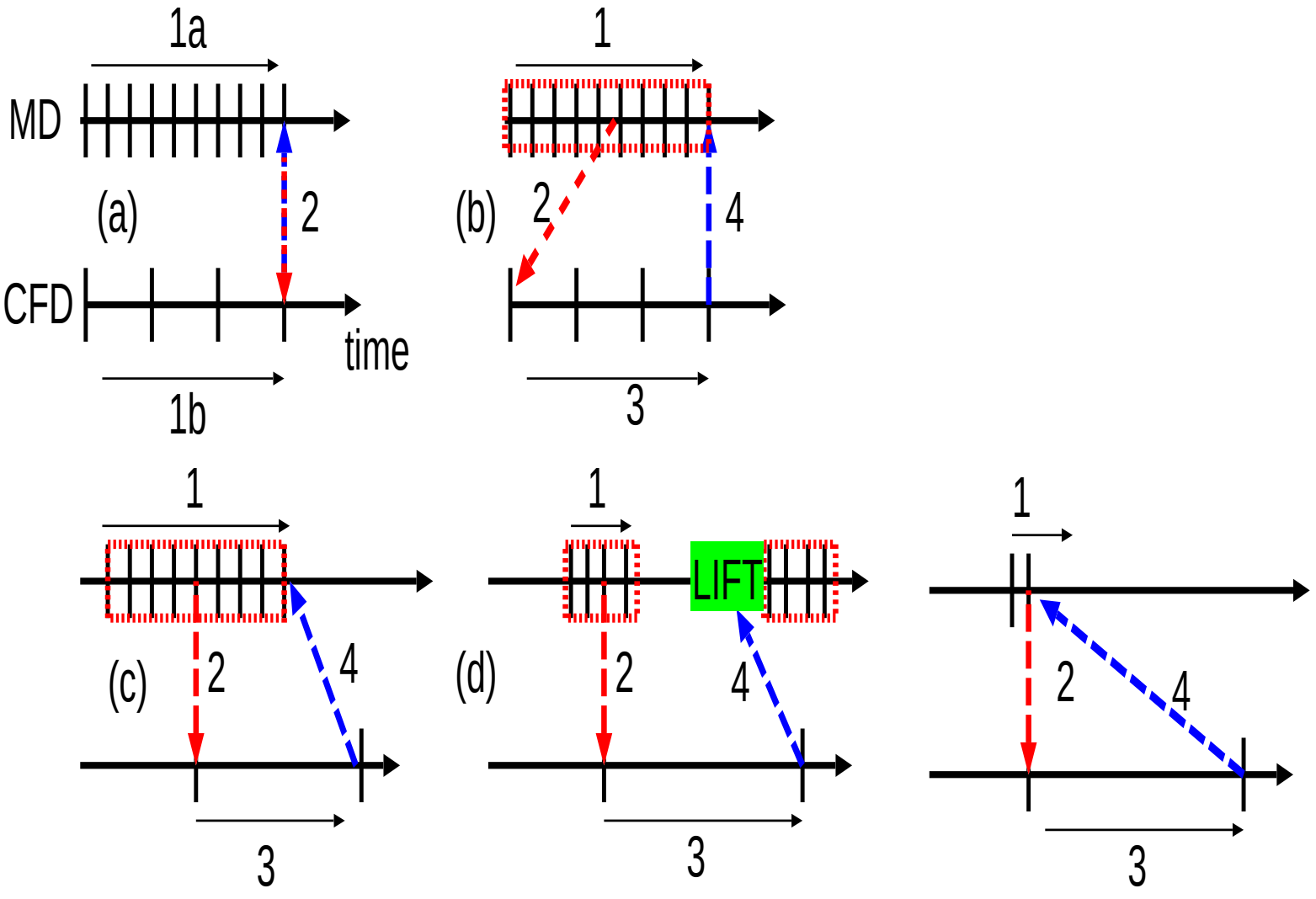

The continuum solver, schematically

$$\Delta\Phi_i = \Delta t\, \mathtt{NS}\left[\{\Phi_j\}\right] + \delta_{fC}\Delta\phi^{MD}$$

Relaxation of particle transfers towards C

$$\begin{aligned}
\Delta M^{MD} &= \frac{\Delta t_c}{\tau_M}\left(\Delta M_H^{MD} - \Delta M_H^{NS}\right) \\
\text{where} \quad & \Delta M_H^{NS} = -A\rho_H \mathbf{V}_H \cdot \mathbf{n}\,\Delta t \\
\Delta \mathbf{V}^{MD} &= \frac{\Delta t_c}{\tau_v}\left(\langle \mathbf{v}_C^{MD}\rangle_{[\delta t,\tau]} - \langle \mathbf{V}_C\rangle_{[\Delta t,\tau]}\right)
\end{aligned}$$

# Hybrid particle-continuum schemes: Time coupling



# Hybrid MD-Fluctuating Hydrodynamics
## Matching stress fluctuations via 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 stress fluctuations, $\boxed{\langle J^2_{MD} \rangle = \langle J^2_{FH} \rangle}$:

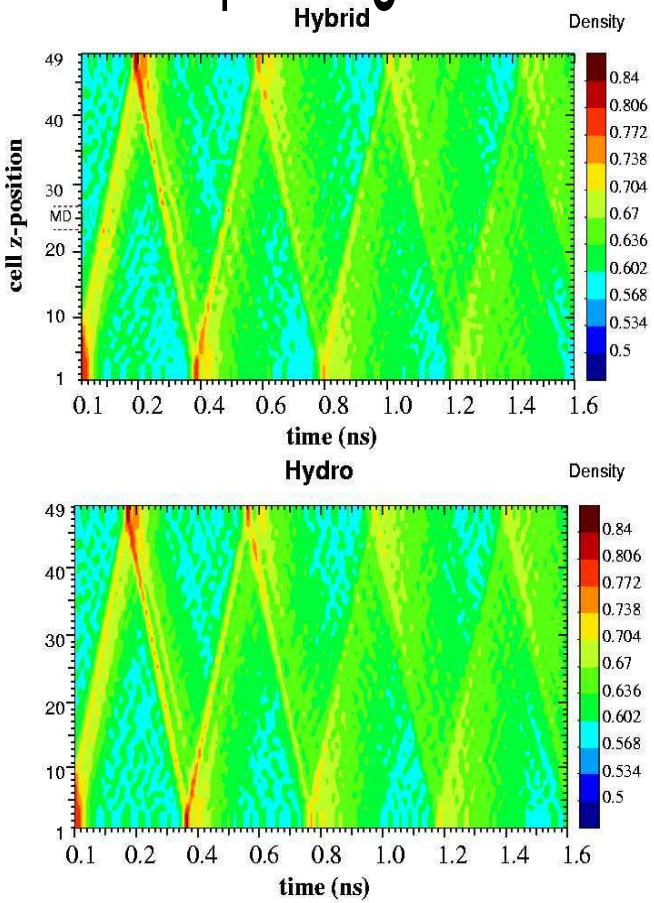
$\Delta t_{FH} = 2\tau_c = \delta t_S$ Sampling time = twice MD decorrelation time

In general, $\boxed{\Delta t_c = n_{FH} \Delta t_{FH} = N_s \delta t_s}$

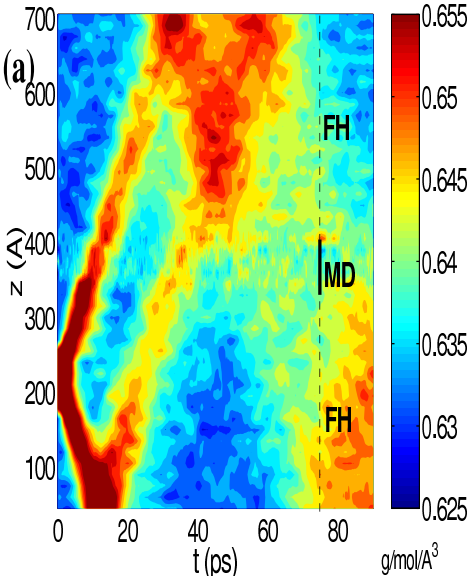
# Hybrid MD-Fluctuating Hydrodynamics

## Some test cases: sound

liquid argon




water



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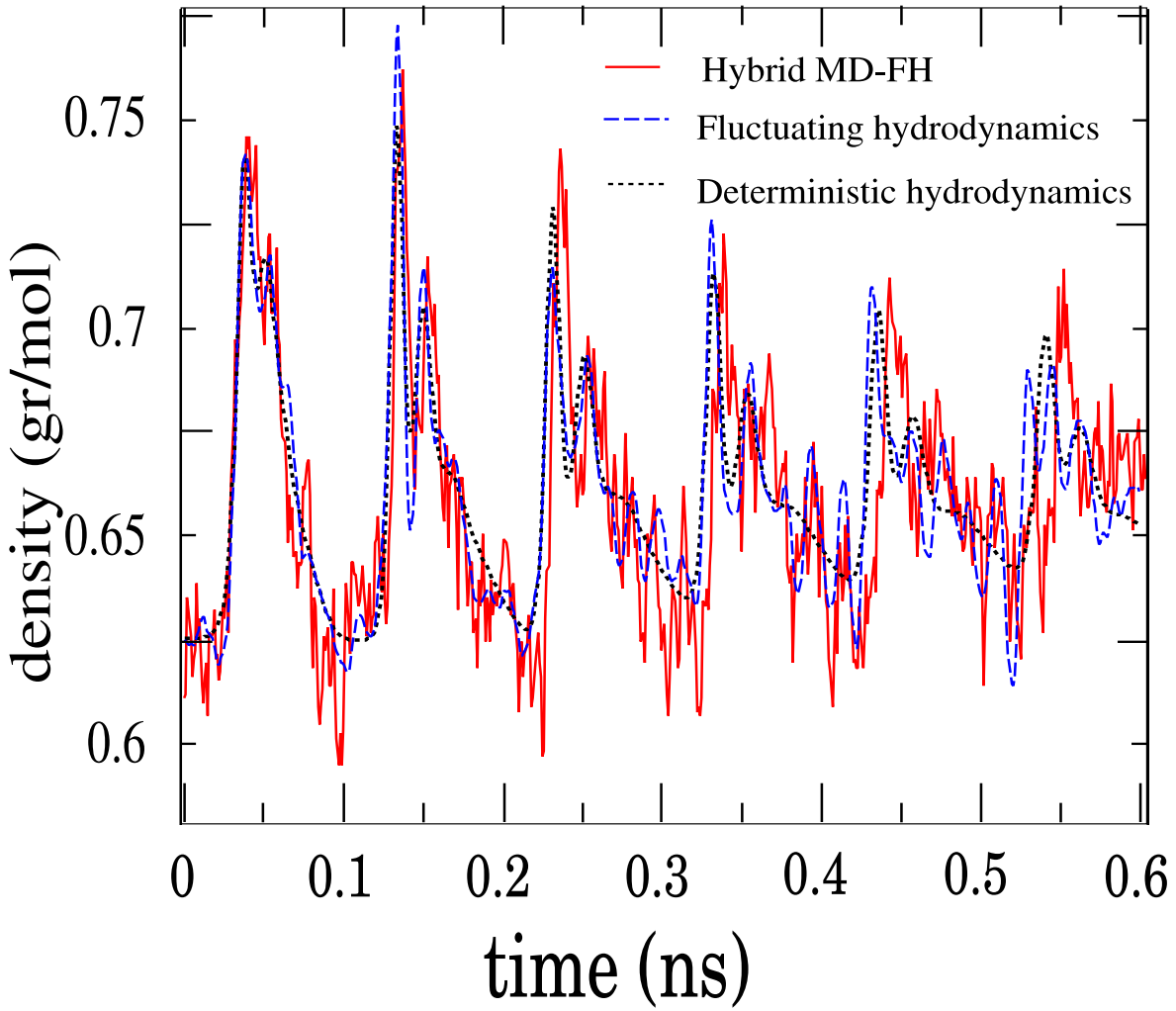
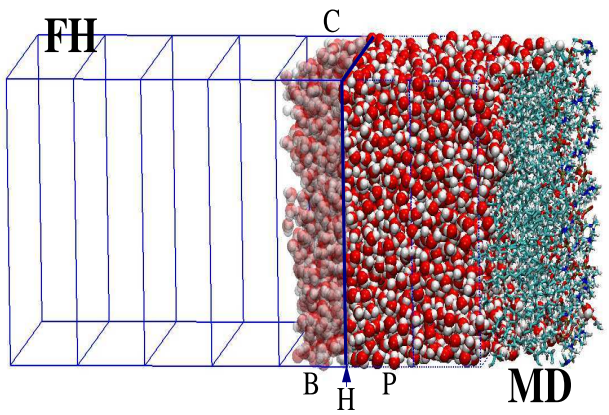
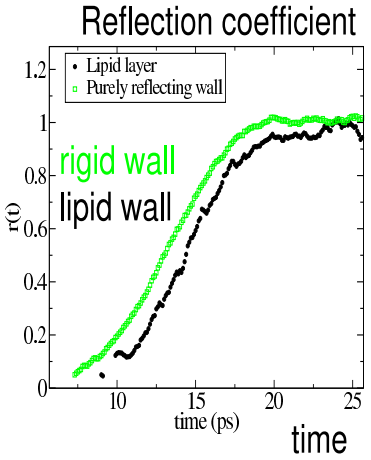
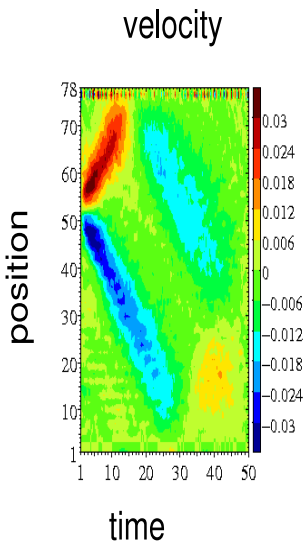


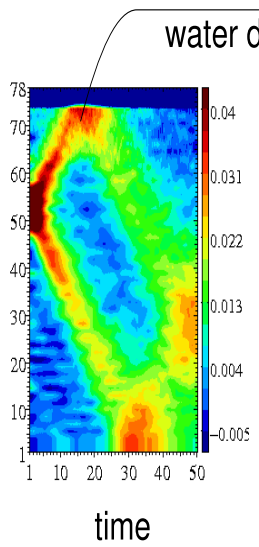
# Hybrid MD-Fluctuating Hydrodynamics
## Collision of sound waves against DMPC lipid layer

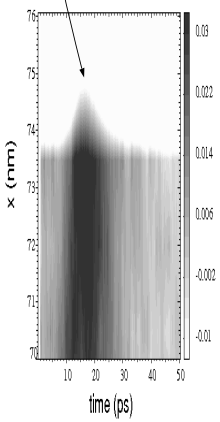
RDB et al, Proc IMechE, Part C: J Mech. Eng. Sci. **222** (2008)

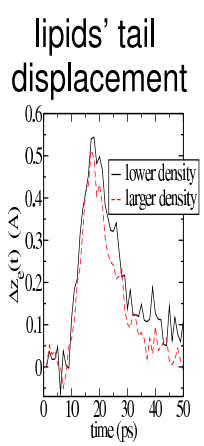


# *Conclusions*

- Simulations of open systems is required for many applied problems: Confined systems, flow in nanotubes, sound-soft matter interaction, melting...
- Open FH
- Open MD
- Hybrid MD
- Use in combination with AdResS to work with large molecules