Modelling sound-matter interaction at different scales

Rafael Delgado-Buscalioni

Universidad Autónoma de Madrid

Ittingen, October 2010

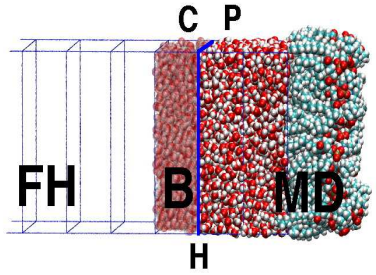
- Particle hydrodynamics
  - Florencio Balboa (Univ. Autonoma Madrid)
  - Ignacio Pagonabarraga (Univ. Barcelona) (new)
  - Anne Dejoan (CIEMAT)
- Open flutuating hydrodynamics
  - Anne Dejoan (CIEMAT)
- Hybrid molecular-continuum hydrodynamics
  - Gianni De Fabritiis (U. Pompeu Fabra, Barcelona)
  - Jason Reese (U. StrathClyde, Glasgow) (new)
- Adaptive resolution in HybridMD
  - Matej Praprotnik (National Inst. Chem. Ljubljana)
  - Kurt Kremer (Max-Plank, Mainz)
- Coarse-grained dynamics
  - Pep Español (UNED)
  - Eric vanden-Eijnden (Courant Institute, NY)

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

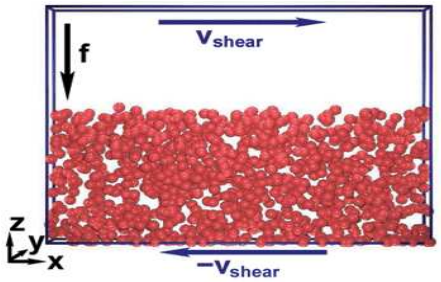


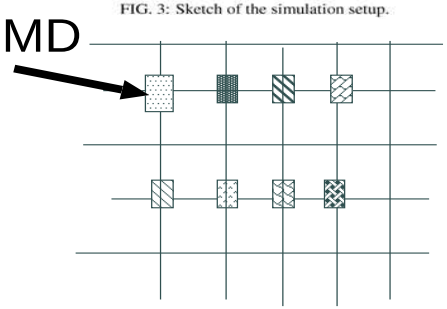
FIG. 3: Sketch of the simulation setup.

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...



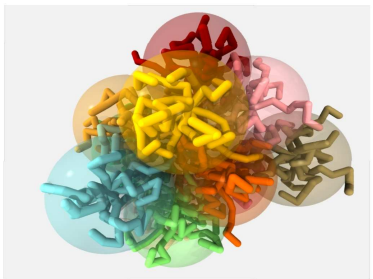
MD nodes used to evaluate the **local stress** for the Continuum solver.

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...)

Outline of the talk

- Direct Forcing: **Sound-particle interactions at microns**

Outline of the talk

- Direct Forcing: **Sound-particle interactions at microns**
- Open FH: **Non-reflecting boundaries for Fluctuating Hydrodynamics**

Outline of the talk

- Direct Forcing: **Sound-particle interactions at microns**
- Open FH: **Non-reflecting boundaries for Fluctuating Hydrodynamics**
- HybridMD: **UltraSound-molecule interaction at nanometers**

Outline of the talk

- Direct Forcing: **Sound-particle interactions at microns**
- Open FH: **Non-reflecting boundaries for Fluctuating Hydrodynamics**
- HybridMD: **UltraSound-molecule interaction at nanometers**
  - Overview of HybridMD: state-coupling vs. flux-couping

Outline of the talk

- Direct Forcing: **Sound-particle interactions at microns**
- Open FH: **Non-reflecting boundaries for Fluctuating Hydrodynamics**
- HybridMD: **UltraSound-molecule interaction at nanometers**
  - Overview of HybridMD: state-coupling vs. flux-couping
  - The particle buffer

Outline of the talk

- DIRECT FORCING: **Sound-particle interactions at microns**
- OPEN FH: **Non-reflecting boundaries for Fluctuating Hydrodynamics**
- HYBRIDMD: **UltraSound-molecule interaction at nanometers**
  - Overview of HybridMD: state-coupling vs. flux-couping
  - The particle buffer
  - Combining with Adaptive Resolution: the *mesoscopic buffer*.

Outline of the talk

- DIRECT FORCING: **Sound-particle interactions at microns**
- OPEN FH: **Non-reflecting boundaries for Fluctuating Hydrodynamics**
- HYBRIDMD: **UltraSound-molecule interaction at nanometers**
  - Overview of HybridMD: state-coupling vs. flux-couping
  - The particle buffer
  - Combining with Adaptive Resolution: the *mesoscopic buffer*.
  - OPENMD: general ensemble

Outline of the talk

- DIRECT FORCING: **Sound-particle interactions at microns**
- OPEN FH: **Non-reflecting boundaries for Fluctuating Hydrodynamics**
- HYBRIDMD: **UltraSound-molecule interaction at nanometers**
  - Overview of HybridMD: state-coupling vs. flux-couping
  - The particle buffer
  - Combining with Adaptive Resolution: the *mesoscopic buffer*.
  - OPENMD: general ensemble
  - **Test cases: Sound across MD domains**

Outline of the talk

- DIRECT FORCING: **Sound-particle interactions at microns**
- OPEN FH: **Non-reflecting boundaries for Fluctuating Hydrodynamics**
- HYBRIDMD: **UltraSound-molecule interaction at nanometers**
  - Overview of HybridMD: state-coupling vs. flux-couping
  - The particle buffer
  - Combining with Adaptive Resolution: the *mesoscopic buffer*.
  - OPENMD: general ensemble
  - **Test cases: Sound across MD domains**
  - **Water wave against lipid layers**

Direct Forcing for Point particle hydrodynamics.

Motivation

- The Stokes drag
$$\mathbf{F}_{fp} = -\xi\left(\mathbf{U} - \mathbf{V}\right)$$
- Limitted to low Reynolds and small velocity gradients [Maxey, Riley]
- A practical way to relax to the zero Reynolds limit $\mathbf{u} = \mathbf{v_p}$ [Ladd, Dünweg].
- Cannot be used to solve sound-matter interaction [Mazur, Bedeaux]
- **Direct Forcing alternative:** Get fluid-particle forces from imposition of no-slip BC at the particle center.

Direct Forcing

based on Uhlmann, J.Comp. Phys. (2005)

Principle: Use a volume force $\mathbf{F}$ to impose the velocity $v(t)$ at one "stick point" of the fluid.
Let $g = \rho u$ the momentum density.

$$
\begin{aligned}
g^{n+1} &= \tilde{g}^{n+1} + f^{n+1}\Delta t \\
\tilde{g}^{n+1} &= g^{n} + \mathtt{NS}^{n}\Delta t \quad \text{explicit solver for NS} \\
f^{n+1} &= \rho^{n+1}\frac{v^{n+1} - \tilde{u}^{n+1}}{\Delta t} \quad \text{At the stick point } f = 0 \text{ elsewhere} \\
\tilde{\rho}^{n+1} &= \rho^{n+1}
\end{aligned}
$$

It is easy to show that this scheme satisfies: $u^{n+1} = v^{n+1}$ at the stick point.

Direct forcing: interpolation

Particle position $\mathbf{R}$ in continuum space
Fluid is solved at a mesh $\{\mathbf{r}_i\}$ $i \in f$
Interpolation is required:

$$\tilde{u}(\mathbf{R}) \simeq \tilde{U} = \sum_{i \in f} \delta_h(|\mathbf{r}_i - \mathbf{R}|)\tilde{u}(\mathbf{r}_i)$$

or in brief

$$\tilde{U} = \sum_i \delta_i \tilde{u}_i$$

The kernel satisfies $\sum_i \delta_i = 1$ and is constructed with a soft function $\delta_h(\mathbf{r}) = \phi(x/h)\phi(y/h)\phi(z/h)$

$$\phi(u) = \begin{cases} \frac{1}{3}(1 + \sqrt{1 - 3u^2}) & 0 \leq |u| \leq \frac{1}{2} \\ \frac{1}{6}(5 - 3|u| - \sqrt{-2 + 6|u| - 3u^2}) & \frac{1}{2} \leq |u| \leq \frac{3}{2} \\ 0 & \frac{3}{2} \leq |u| \end{cases}$$

Direct forcing: fluid-particle force

Total force exchanged between fluid and one particle:

$$\mathbf{F}(\mathbf{R}) = \rho(\mathbf{R})\Delta V \alpha = h^3 \sum_i \rho_i \mathbf{a}_i$$

ΔV is a "volume-particle parameter"
The fluid-particle relative acceleration

$$\alpha = \frac{\mathbf{V} - \tilde{\mathbf{U}}}{\Delta t}$$

is shared as acceleration of local fluid nodes,

$$\mathbf{a}_i = \alpha \delta_i \frac{\Delta V}{h^3}$$

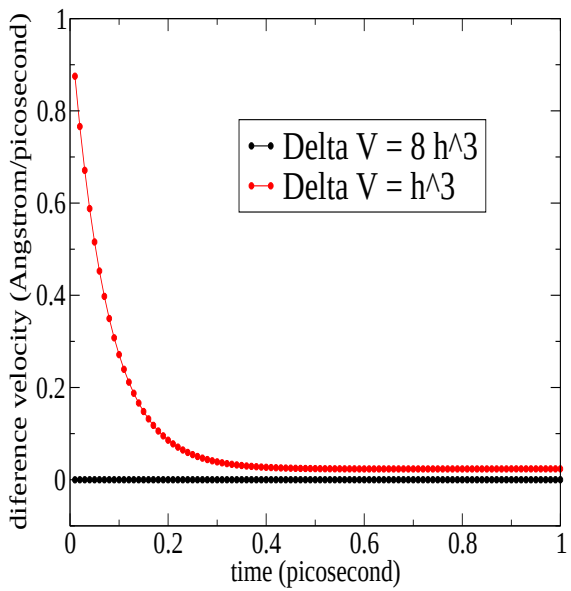
Direct forcing: No-slip

It is easy to show that

$$\mathbf{U}^{n+1} = \mathbf{V} + \left(1 - \sum_i \delta_i^2 \frac{\Delta V}{h^3}\right)\left(\tilde{\mathbf{U}} - \mathbf{V}\right)$$

For a 3D cubic mesh $\sum_i \delta_i^2 = \frac{1}{8}$, so **no-slip** is obtained for $\Delta V = 8h^3$ This determines the **No-slip radius**:

$$\mathbf{R}_{noslip} = (6/\pi)^{1/3} h \simeq 1.241h$$



Direct forcing: fluid-particle force

Fluid momentum eq:

$$\mathbf{g}_i^{n+1} = \tilde{\mathbf{g}}^{n+1} + \rho_i^{n+1}\mathbf{a}_i\Delta t$$

$$\rho_i^{n+1} = \tilde{\rho}^{n+1}$$

Particle eqn:

$$m_p^* \frac{dV}{dt} = -\mathbf{F} + \mathbf{F}_{\text{extra}}$$

with $m_p^* \equiv m_p - m_f$ particle mass excess (wrt. fluid.) RHS depends on V but can be solved directly,

$$\mathbf{V}^{n+1} = \mathbf{V}^n + \frac{m_f}{m_p^* + m_f}\left(\tilde{\mathbf{U}}^{n+1} - \mathbf{V}^n\right) + \frac{\mathbf{F}_{\text{extra}}}{m_p^* + m_f}$$

with $m_f = \Delta V \sum_i \rho_i \delta_i$

Direct forcing: a fast CUDA algorithm

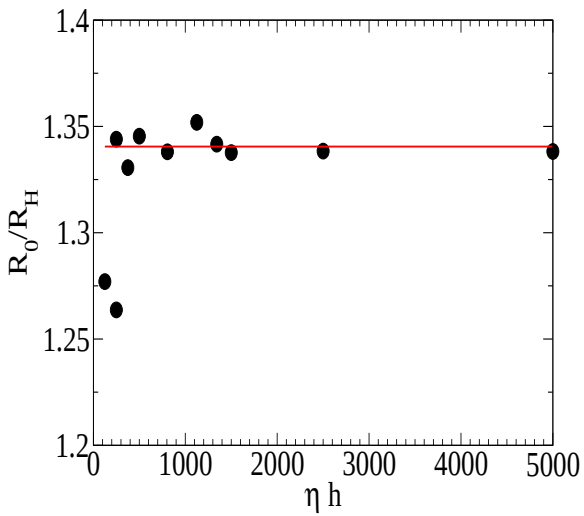
1. Update fluid (without particles): $\tilde{\mathbf{U}}^{n+1}$ and $\tilde{\rho}^{n+1} = \rho^{n+1}$.
2. Update particle position, $\mathbf{R}^{n+1} = \mathbf{R}^n + \mathbf{V}^n \Delta t$
3. Interpolate fluid velocity at $\mathbf{R}$: $\tilde{\mathbf{U}}^{n+1} = \sum_i \delta_i \tilde{\mathbf{u}}_i^{n+1}$
4. Update particle velocity: $\mathbf{V}^{n+1}$
5. Evaluate relative accelerations: α, and node interpolations $\mathbf{a}_i = \alpha \delta_i \Delta V / h^3$.
6. Udate fluid with particle force contributions: $\mathbf{u} = \tilde{\mathbf{u}} + \mathbf{a} \Delta t$
7. **Straightforward generalization to N particles**

Direct forcing: Hydrodynamic Radius from Stokes drag

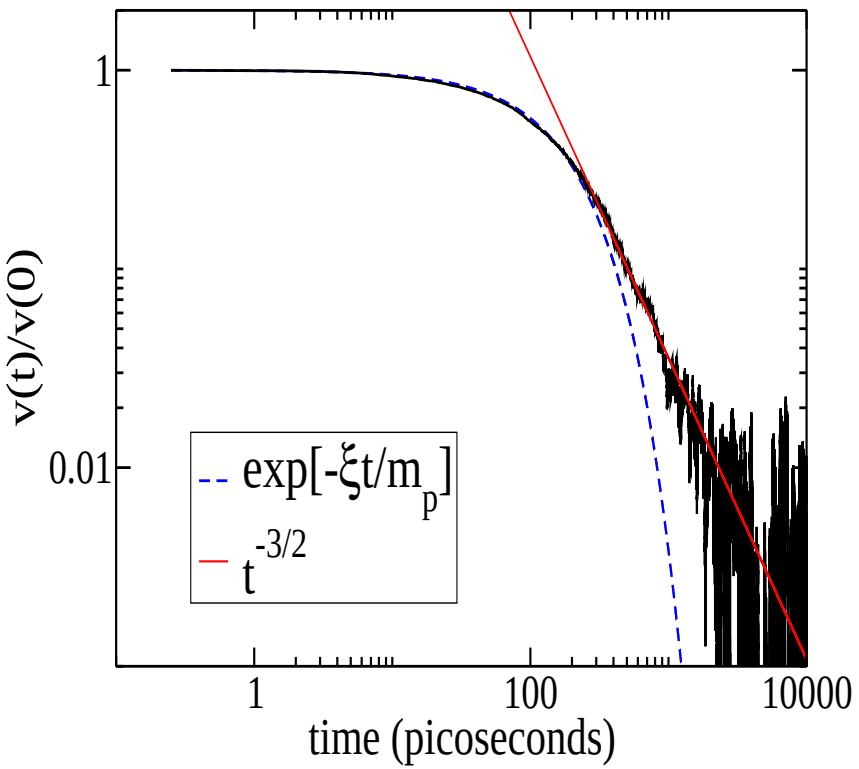
The hydrodynamic radius R_H is defined via the Stokes drag force relation

$$F = 6\pi\eta R_H V_p$$

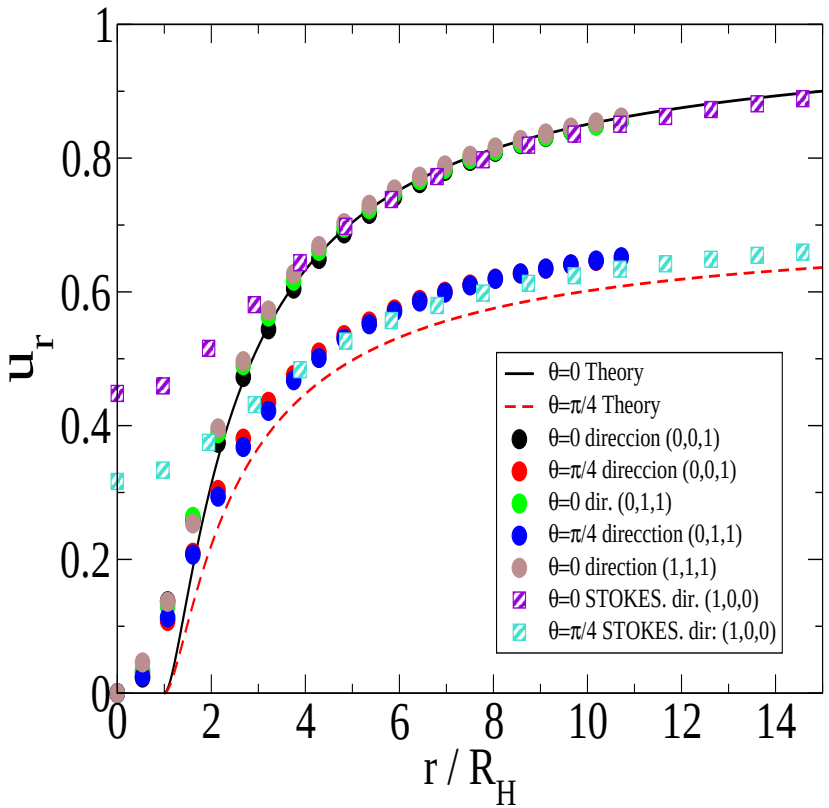
in simulations where V_p is constant and the fluid is at rest $U_\infty = 0$. We find $R_H = R_{ns}/1.34$



Direct forcing: Velocity decay and long-time tail

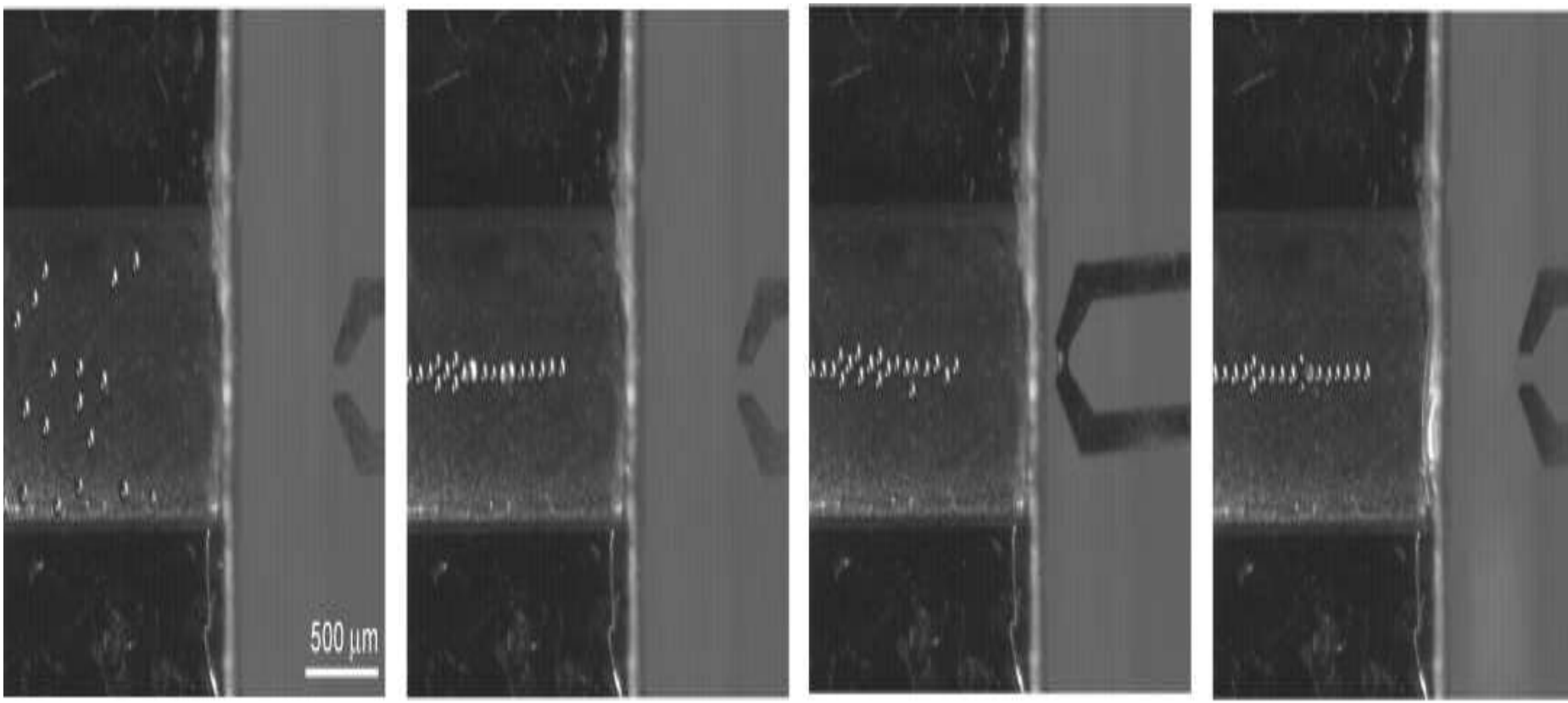


Direct forcing: Flow lines



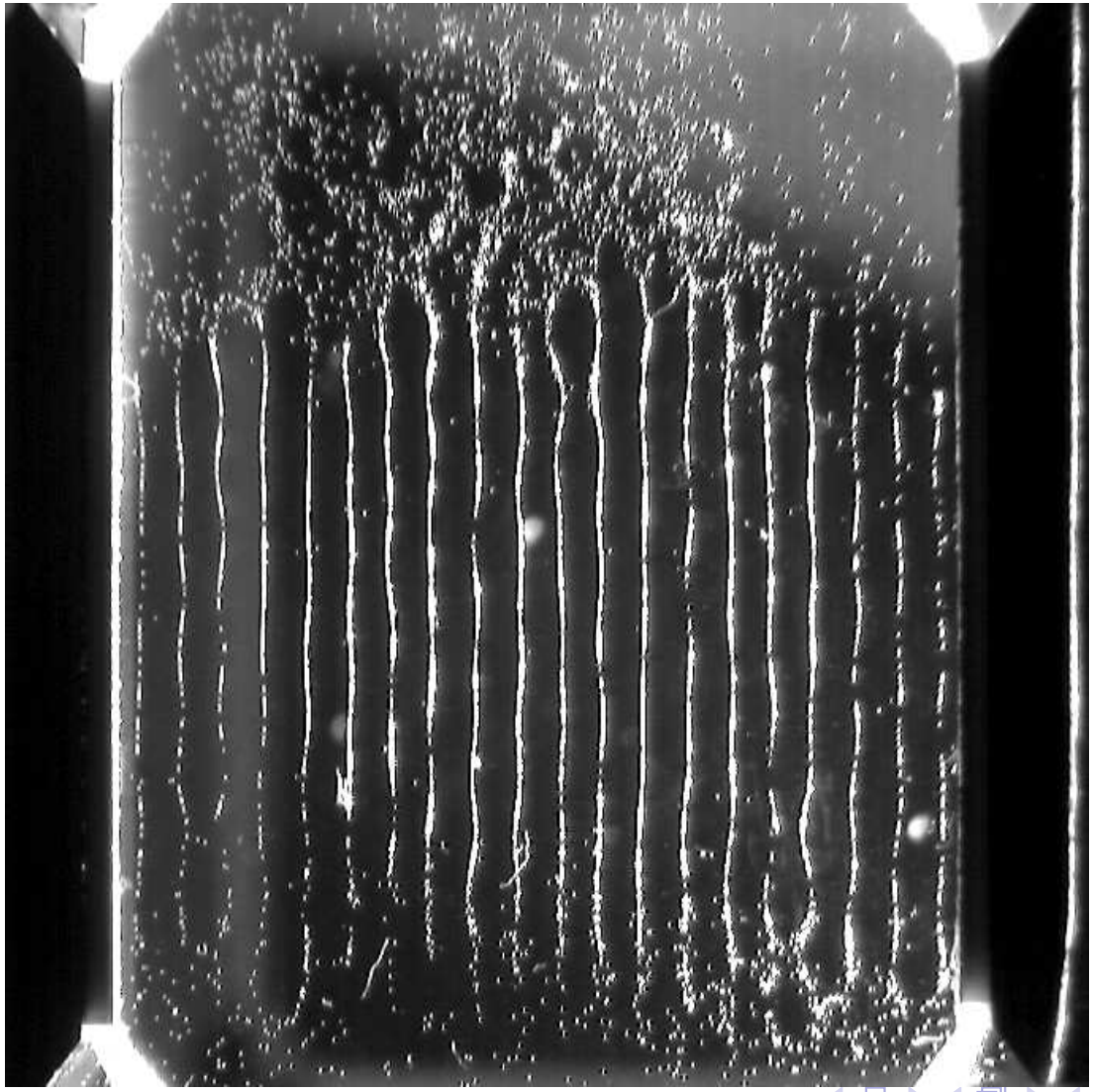
Direct forcing: sound-particle interaction

Micromanipulation of Small Particles with Ultrasound. Jürg Dual group, ETH



Direct forcing: sound-particle interaction

Micromanipulation of Small Particles with Ultrasound. Jürg Dual group, ETH



Direct forcing: sound-particle interaction

Acoustic boundary layer $\delta = \sqrt{(\nu/\omega)}$, with $\nu = \eta/\rho$

Wave number: $\lambda = c\,2\pi/\omega$

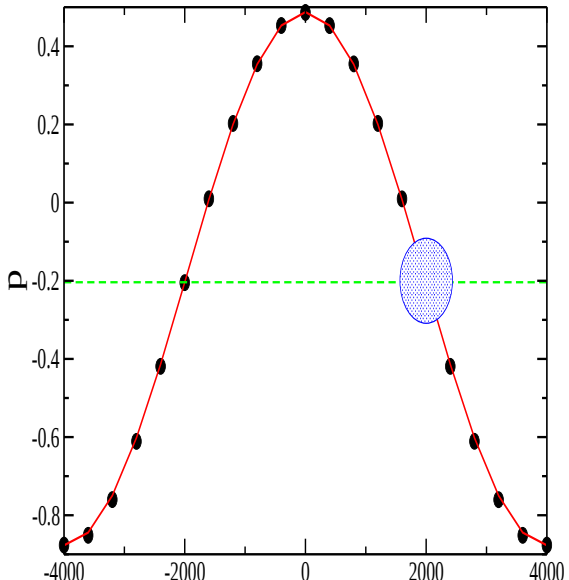
Particle radius: R_{NS}

Simulation

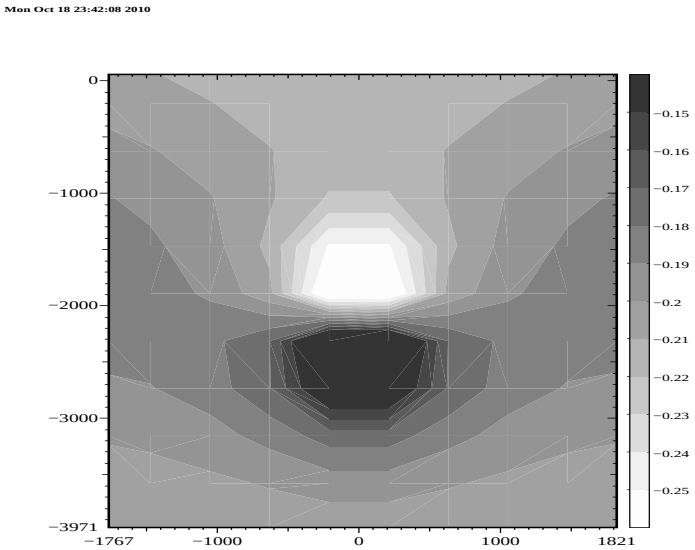
$R_{NS}/\lambda \simeq 0.06$.

Viscous effects: $\delta/R_{NS} \simeq 0.2$

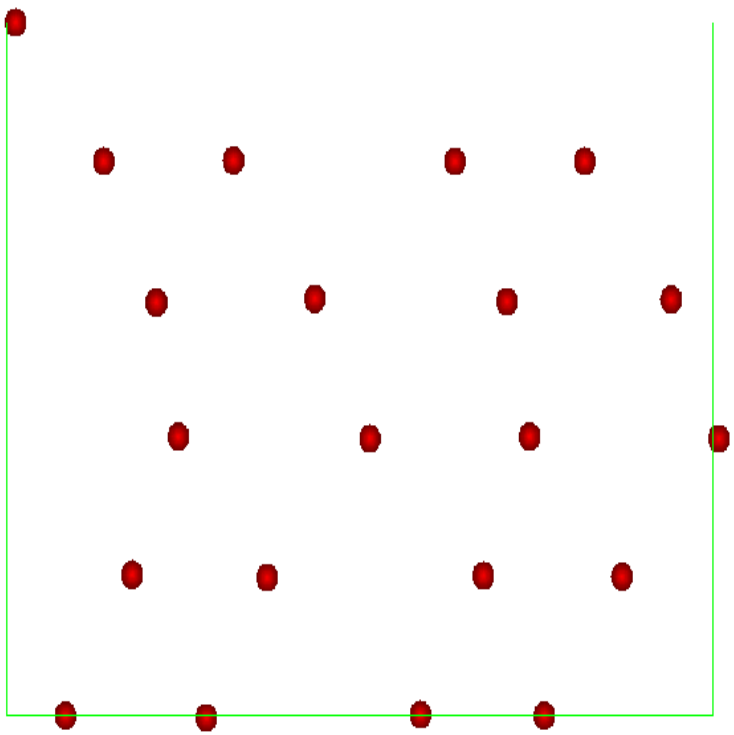
(Stokes limit $\delta/R_H >> 1$ is **not** valid)



Direct forcing: pressure perturbation around particle

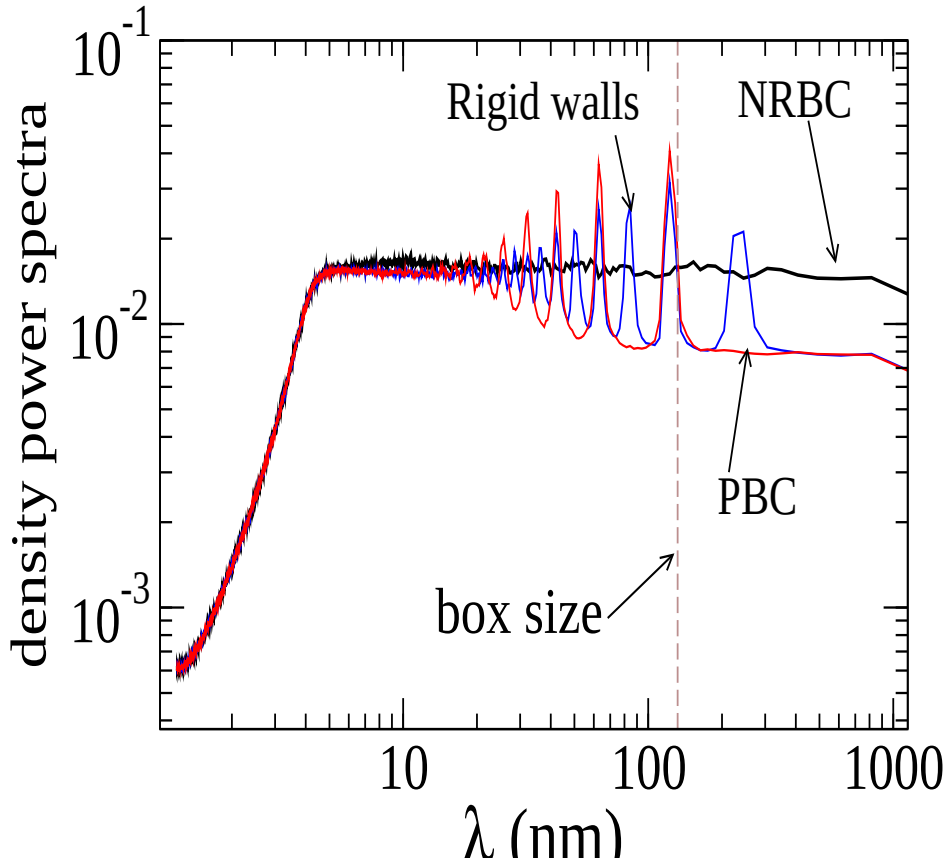


Direct forcing: sound-particle interaction



Open Fluctuating hydrodynamics

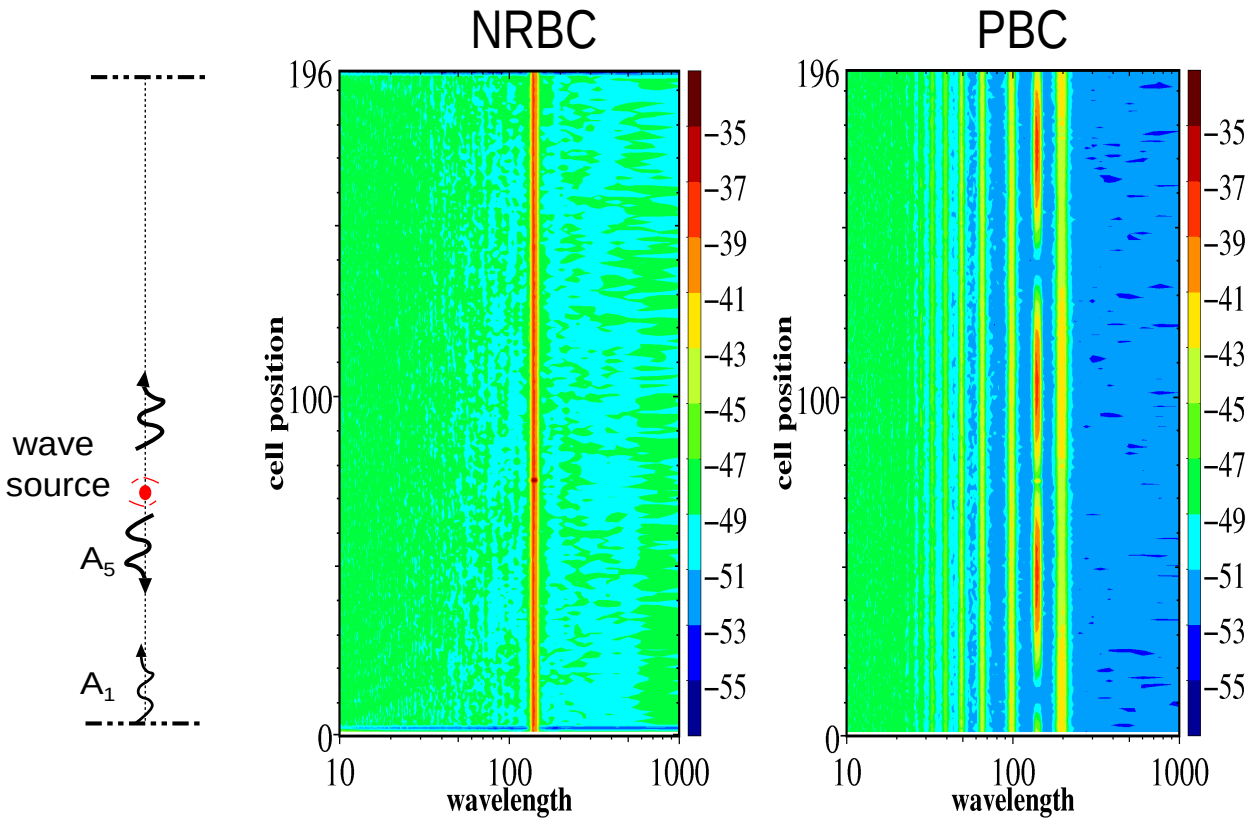
RDB & Dejoan, Phys. Rev. E **78**, 046708 (2008)
Power spectra of density fluctuations: liquid argon @ equilibrium
NRBC=Non-Reflecting boundary conditions



Open Fluctuating hydrodynamics

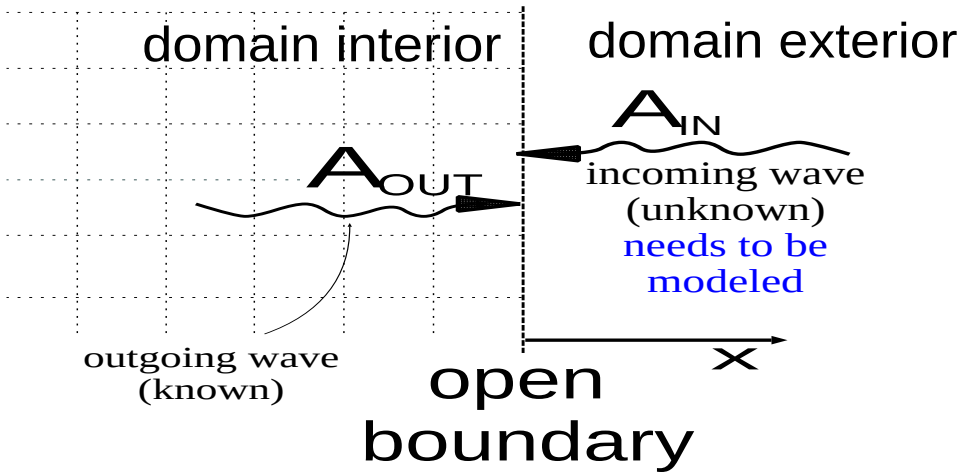
Evacuation of sound waves using non-reflecting boundaries

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,

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

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,

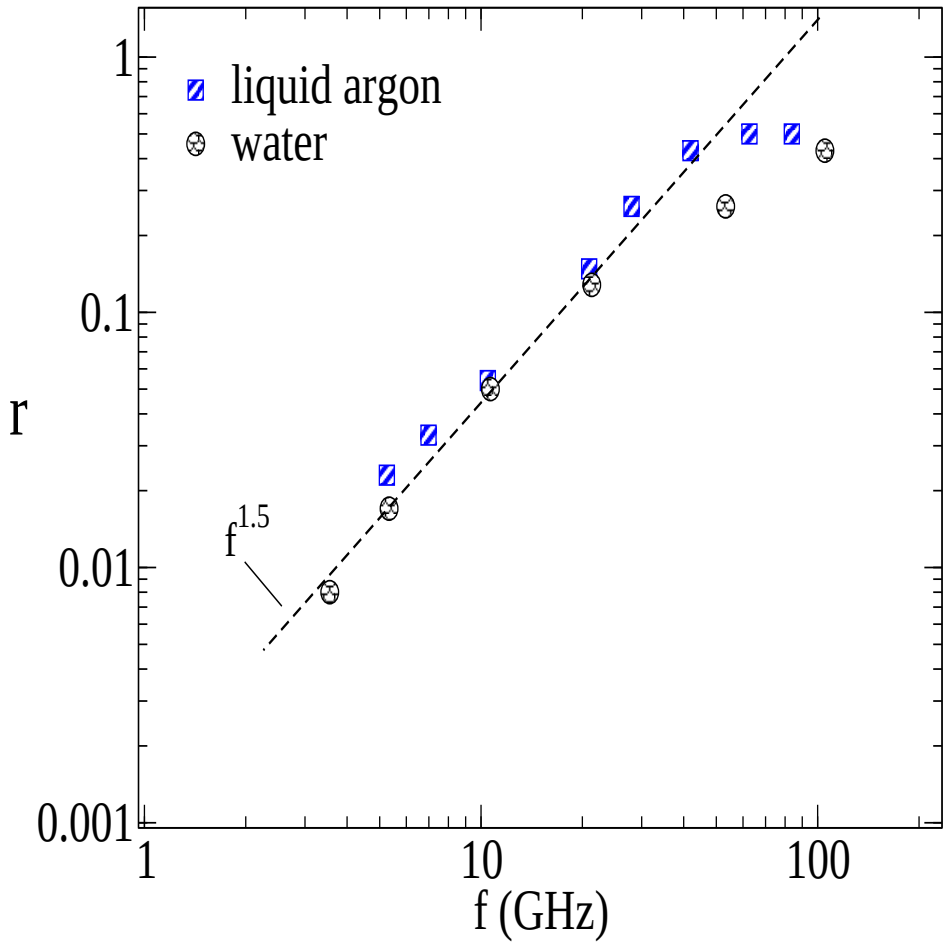
$$\begin{aligned} L_{OUT} &= (u-c)\frac{\partial A_{OUT}}{\partial x} \text{ Measured within domain} \\ L_{IN} &= K(\rho c A_{IN}) \quad \text{Modelled} \\ K &= \frac{\nu_L}{(0.4\Delta x)^2} \text{ Satisfies FD balance} \end{aligned}$$

NRBC Eqs. for boundary cells,

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

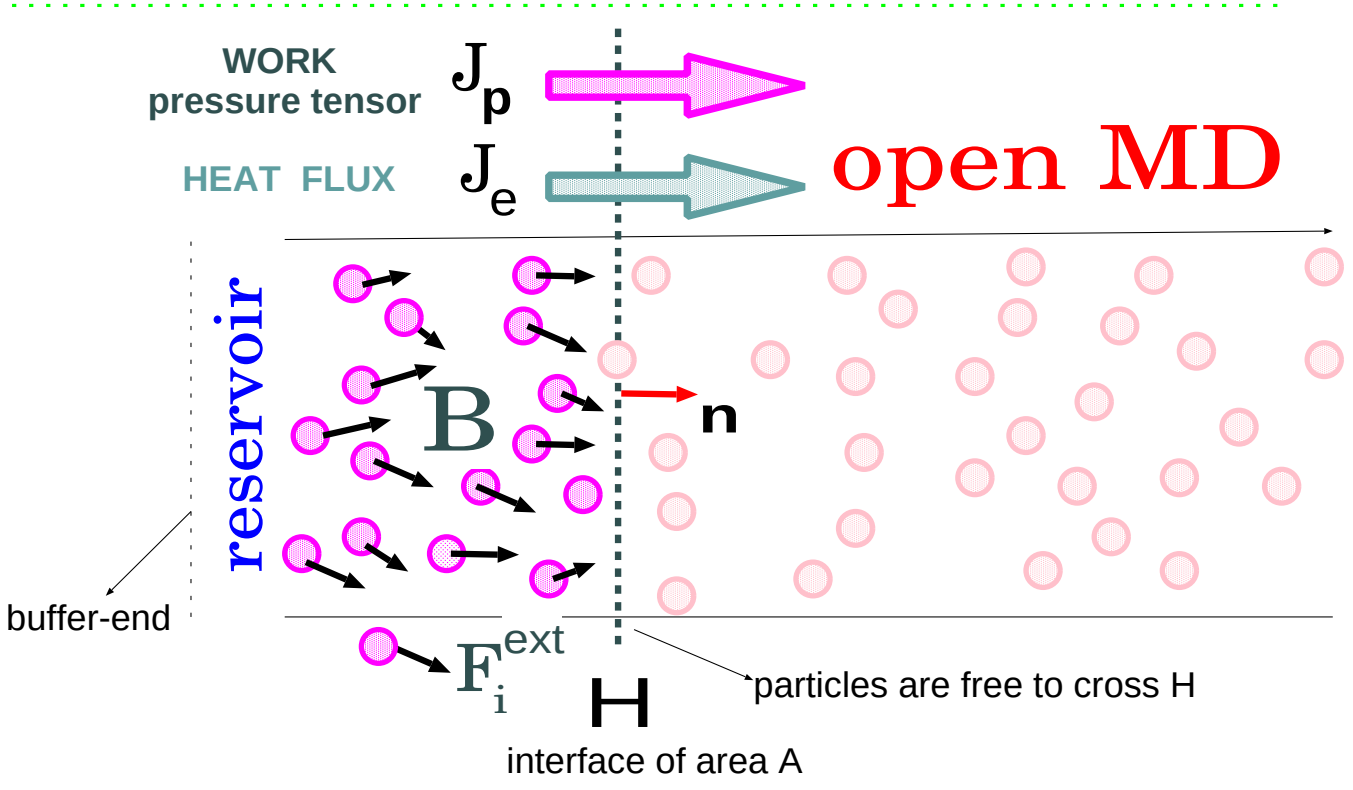
Open Fluctuating hydrodynamics

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:

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:

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

Exponential freezing (very fast, $\xi/m >> \xi/M = \gamma$).
Thermostatting is required (DPD better than 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 Δt

$$\begin{aligned}
\Delta E &= \sum_{i \in B} \mathbf{f}_i^{\text{ext}} \cdot \mathbf{v}_i \Delta t + \sum_k e_k \\
\mathbf{f}_i^{\text{ext}} &= A\mathbf{P}_n/N + \frac{\mathbf{v}_i}{\sum_{i \in B} v_i^2} \dot{Q}_e \\
\Delta E &= A\mathbf{P}_n \cdot \bar{\mathbf{v}} \Delta t + \dot{Q}_e \Delta t + \sum_k e_k
\end{aligned}$$

Thermodynamics of Flux-Coupling

Energy input over Δt

$$\begin{aligned}
\Delta E &= \sum_{i \in B} \mathbf{f}_i^{\text{ext}} \cdot \mathbf{v}_i \Delta t + \sum_k e_k \\
\mathbf{f}_i^{\text{ext}} &= A\mathbf{P}_n/N + \frac{\mathbf{v}_i}{\sum_{i \in B} v_i^2} \dot{Q}_e \\
\Delta E &= A\mathbf{P}_n \cdot \bar{\mathbf{v}} \Delta t + \dot{Q}_e \Delta t + \sum_k e_k
\end{aligned}$$

Entropy change (quasi-statiorary, $\dot{Q}_e$ not so large)

$$\begin{aligned}
T\Delta S' &= \sum_k e_k - \mu \Delta N \text{ Particle insertions} \\
T\Delta S &= \dot{Q}_e \Delta t + T\Delta S' \text{ Total}
\end{aligned}$$

Thermodynamics of Flux-Coupling

Energy input over Δt

$$\begin{aligned}
\Delta E &= \sum_{i\in B} \mathbf{f}_i^{\text{ext}} \cdot \mathbf{v}_i \Delta t + \sum_k e_k \\
\mathbf{f}_i^{\text{ext}} &= A\mathbf{P}_n/N + \frac{\mathbf{v}_i}{\sum_{i\in B} v_i^2} \dot{Q}_e \\
\Delta E &= A\mathbf{P}_n \cdot \bar{\mathbf{v}} \Delta t + \dot{Q}_e \Delta t + \sum_k e_k
\end{aligned}$$

Entropy change (quasi-statiorary, $\dot{Q}_e$ not so large)

$$\begin{aligned}
T\Delta S' &= \sum_k e_k - \mu \Delta N \text{ Particle insertions} \\
T\Delta S &= \dot{Q}_e \Delta t + T\Delta S' \text{ Total}
\end{aligned}$$

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

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

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

Flux-coupling: OPEN MD in generalized 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.

Flux-coupling: OPEN MD in generalized 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.

Flux-coupling: OPEN MD in generalized 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.

Grand canonical μ_BVT

Dynamics of confined systems

Flux-coupling: OPEN MD in generalized 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.

Grand canonical μ_BVT

Dynamics of confined systems

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

Outlet B.C., Hybrids

Flux-coupling: OPEN MD in generalized 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.

Grand canonical μ_BVT	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

Flux-coupling: OPEN MD in generalized ensembles

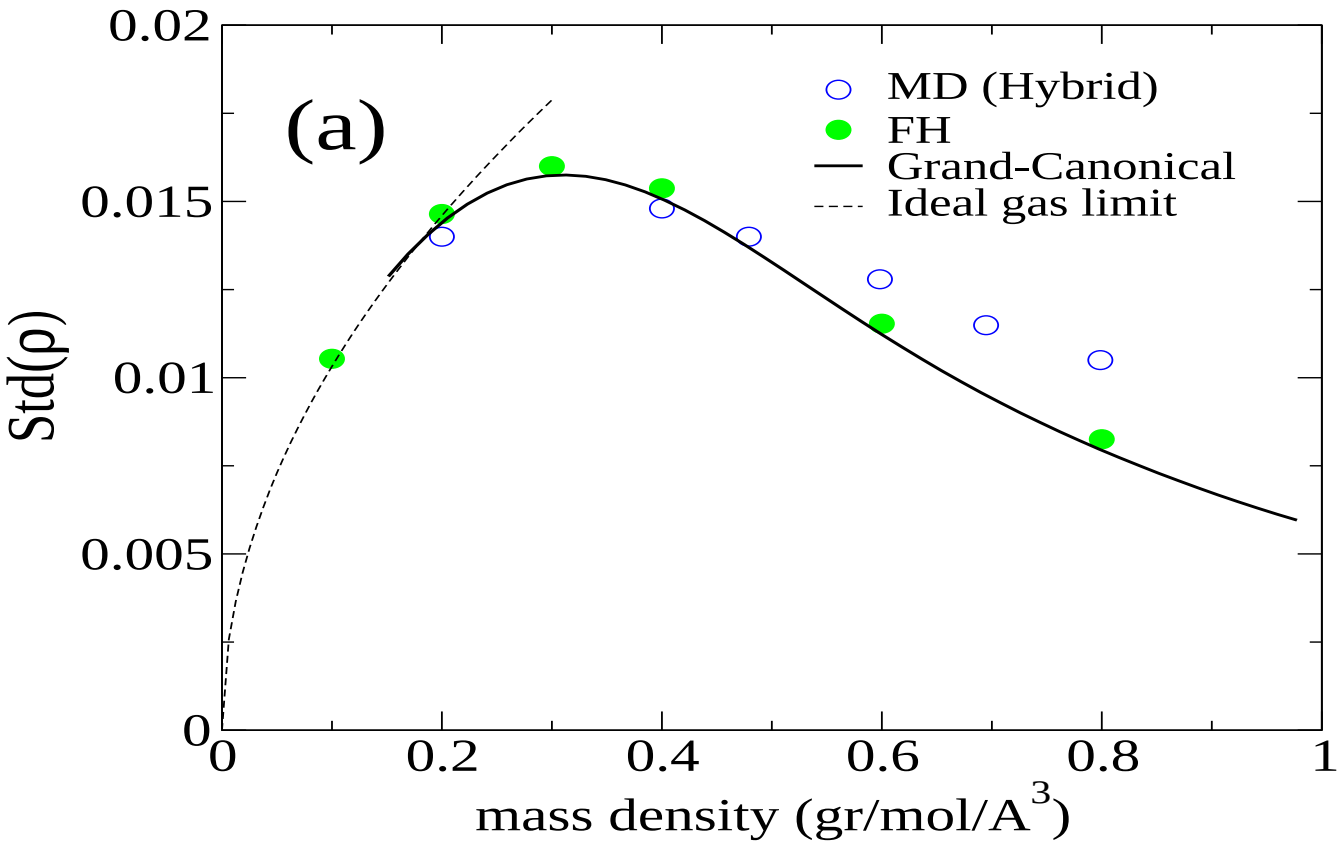
- The amount of HEAT and WORK done into the MD system is exactly controlled
- The system comunicates with the exterior at its boundaries, like a real system.

Grand canonical μ_BVT	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, $T = 300K$

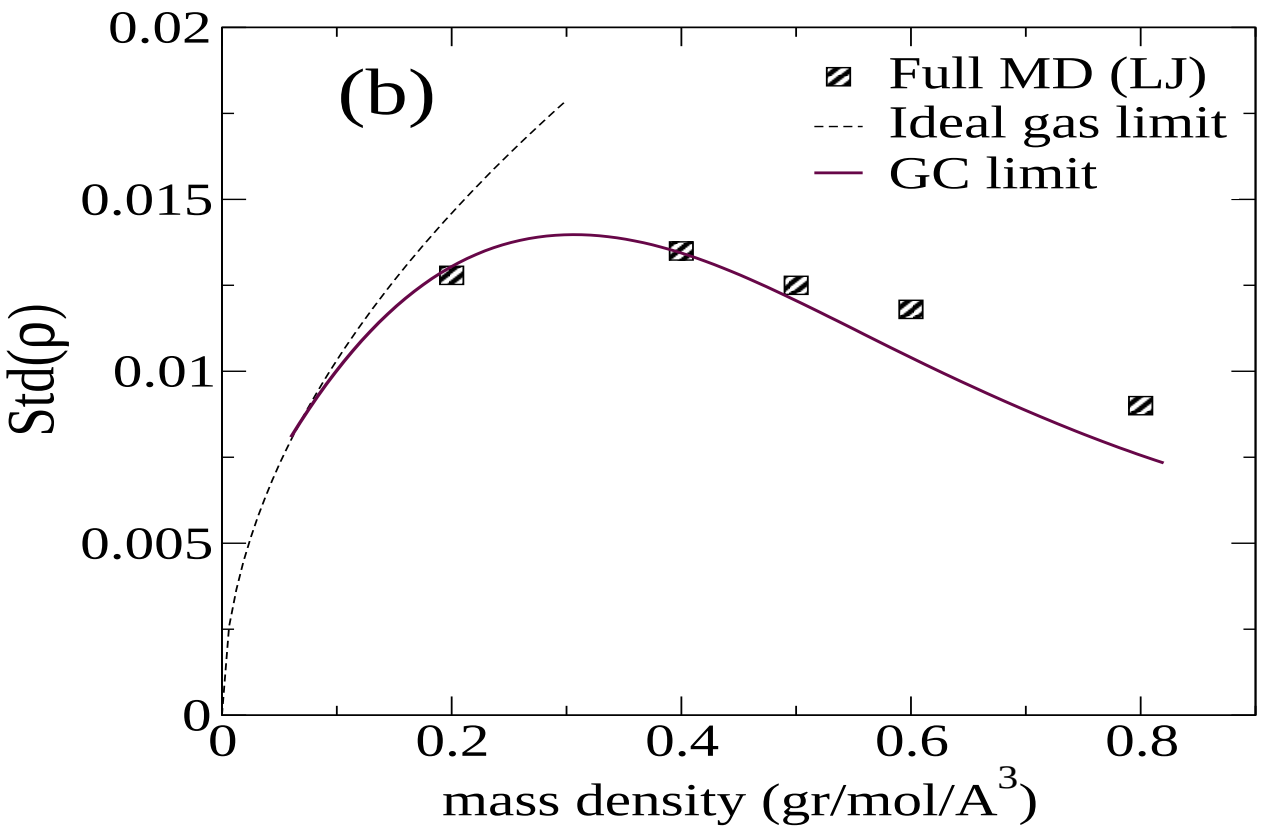
RDB and G.Fabritiis et al. PRE, **76** (2007)



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:

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

Open MD
Density profile at the buffer

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

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

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

Open MD
Density profile at the buffer

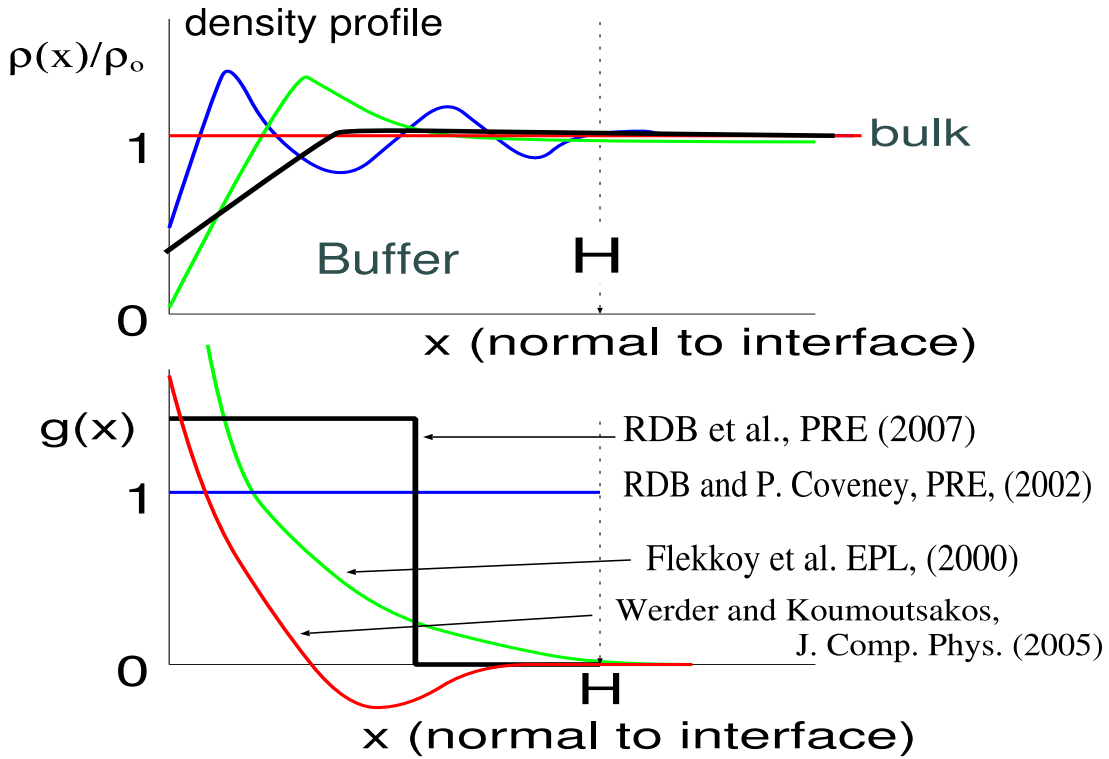
- The external force on a molecule i in the buffer:

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

- 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.

Open MD
Density profile at the buffer

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



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)

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)
- 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) 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)
- 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) 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)
- 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) 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)
- 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)

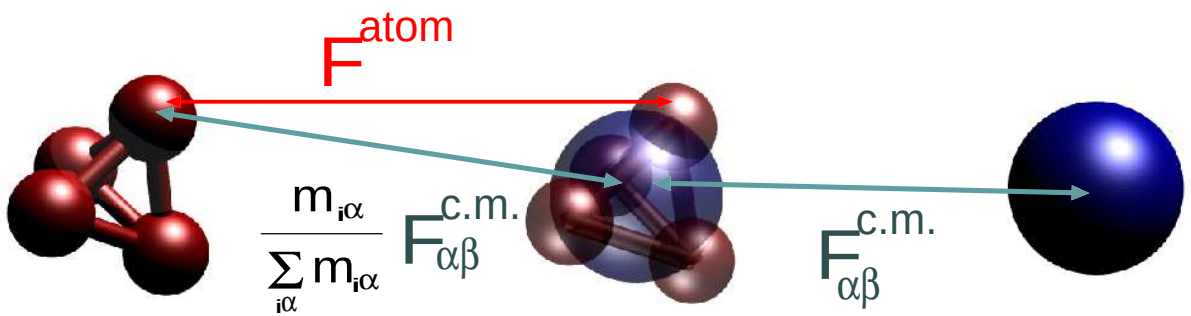
Adaptive Resolution Scheme

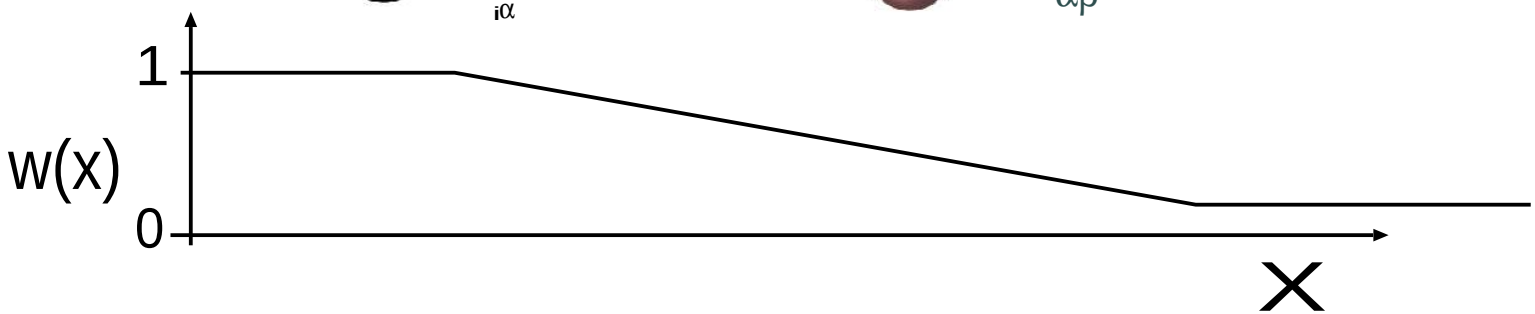
Praprotnik, Delle Site, Kremer, Annu. Rev. Phys. Chem. 59, 545 (2008)

center of mass

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

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



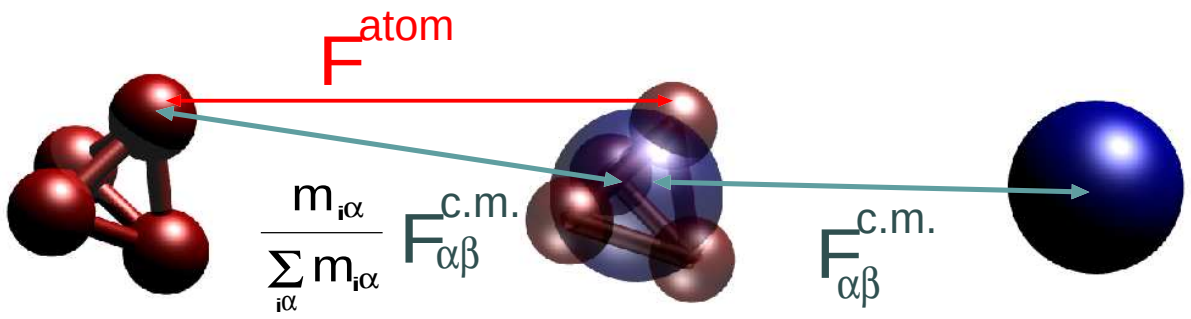


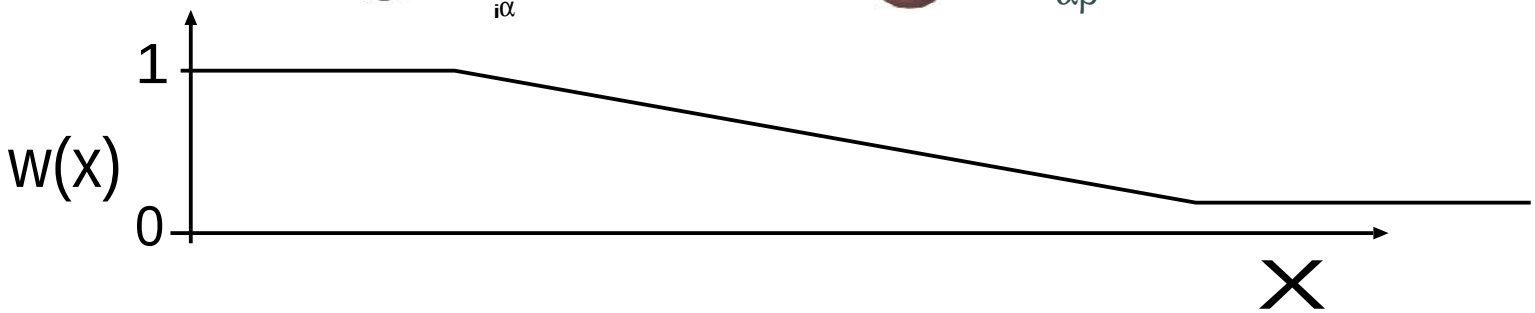
Adaptive Resolution Scheme

center of mass

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

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





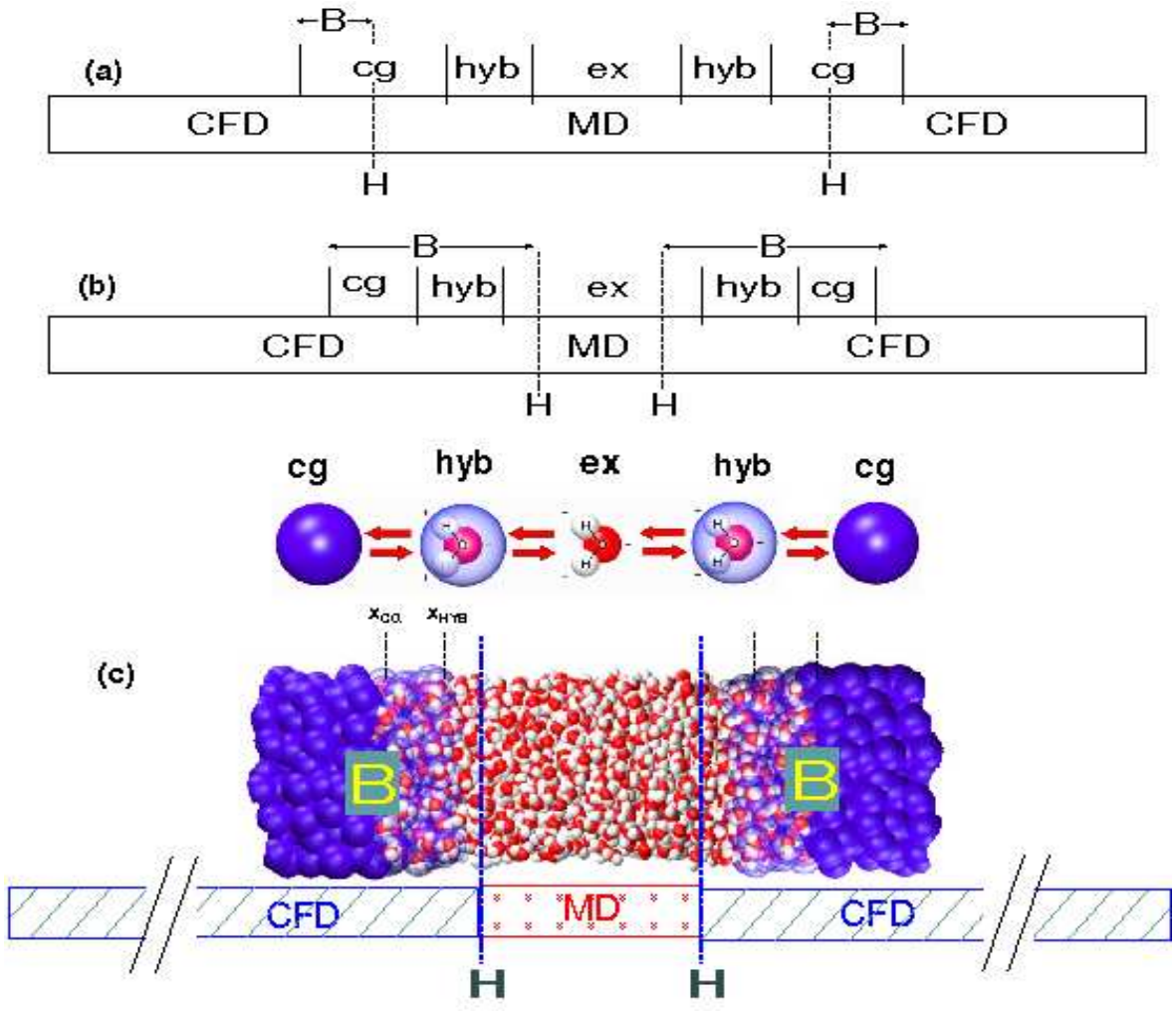
$$\mathbf{F}_{\alpha\beta} = w(x_\alpha)w(x_\beta)\sum_{i\alpha j\beta}\mathbf{F}^{\text{atom}}_{i\alpha j\beta} + [1 - w(x_\alpha)w(x_\beta)]\mathbf{F}^{\text{c.m.}}_{\alpha\beta}$$

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

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

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

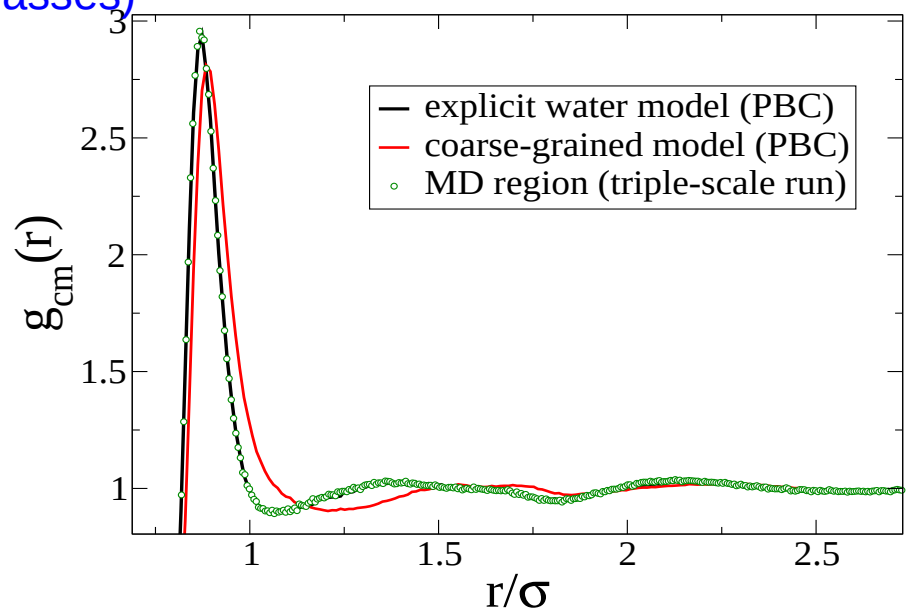
RDB, Kremer, Praprotnik, J.Chem.Phys. **131**, 244107 (2009)

Viscosities (oxigen-LJ units)

CG η=20

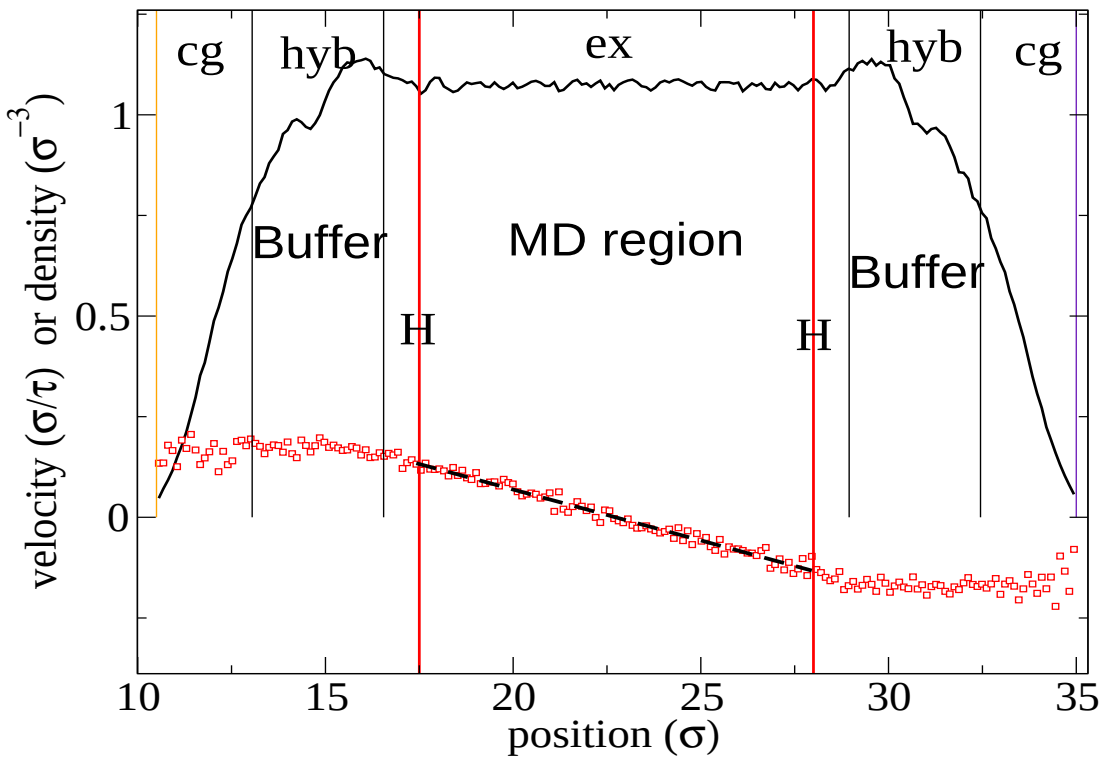
EX η=45 —— **Flexible TIP3P water model**

Radial distribution funcions (center of masses)



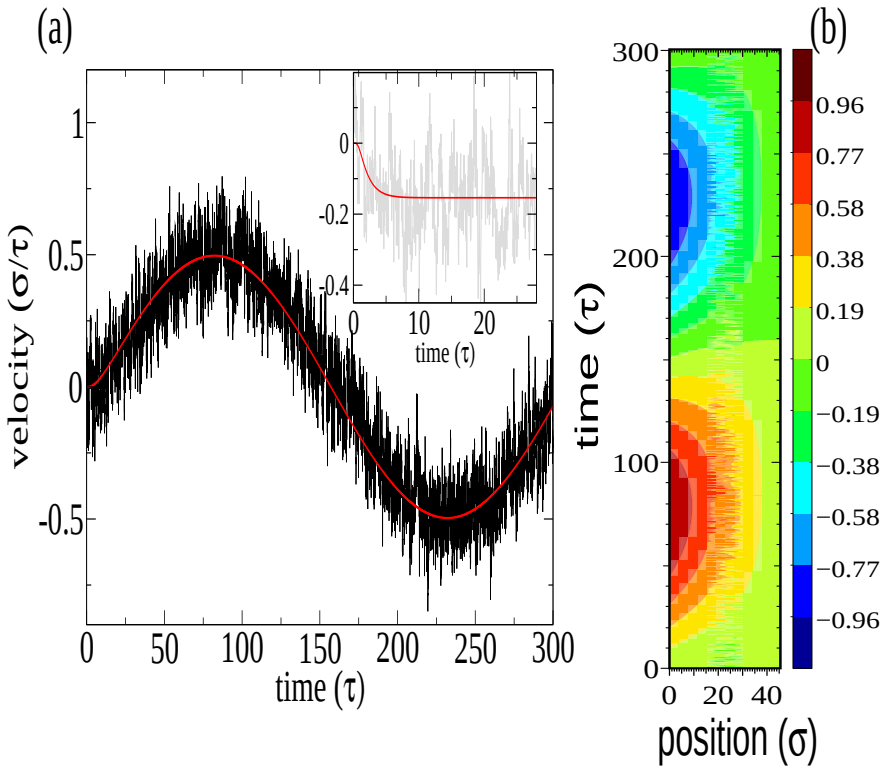
HybridMD-AdResS triple scale

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

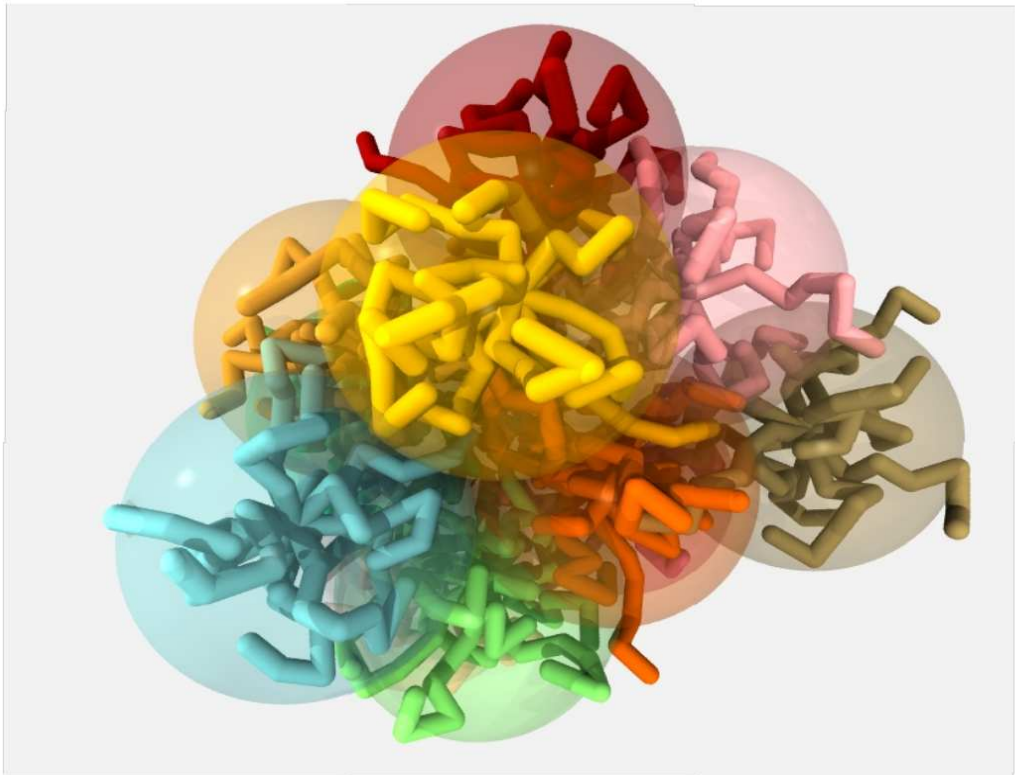


HybridMD-AdResS triple scale

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

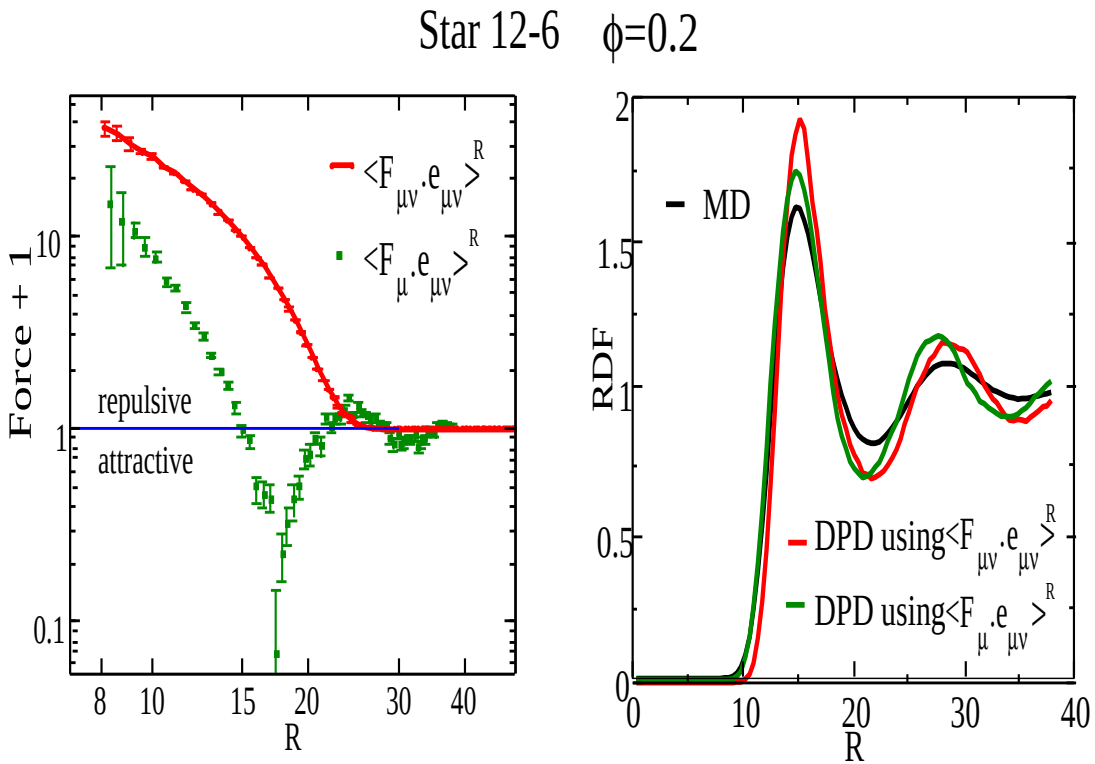


Melts of star polymers via Open MD-AdResS



Melts of star polymers via OPEN MD-AdResS

[R.D-B and Praprotnik, in preparation]

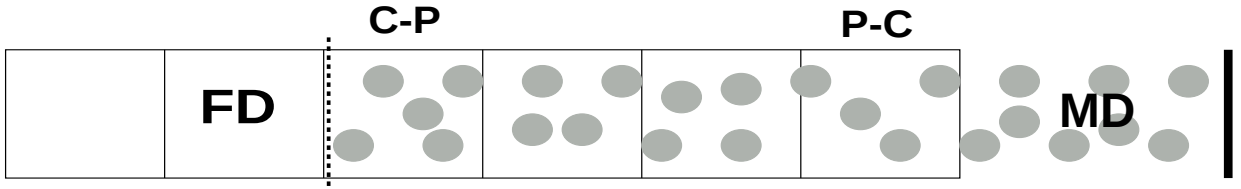


Hybrid particle-continuum schemes: alternatives

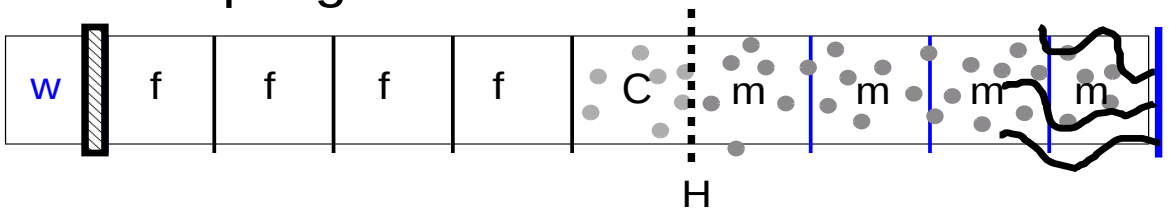
- **State scheme:** Non-conservative, no fluctuations (requires averaging), incompressible.
- **Flux scheme:** Conservative, fluctuations, compressible.

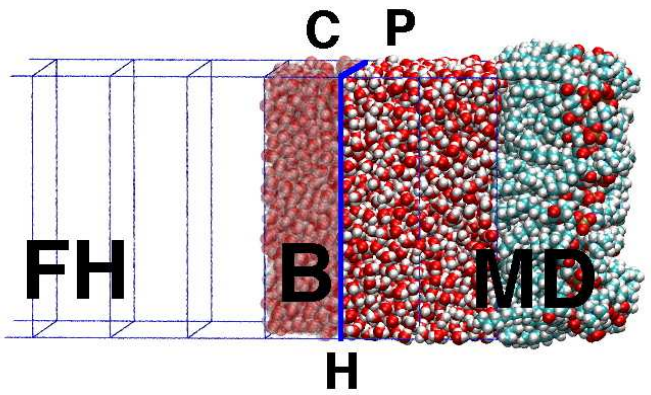
Hybrid particle-continuum schemes: set-up

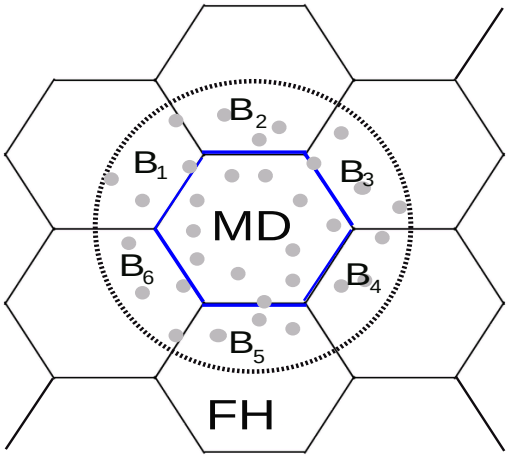
State-coupling



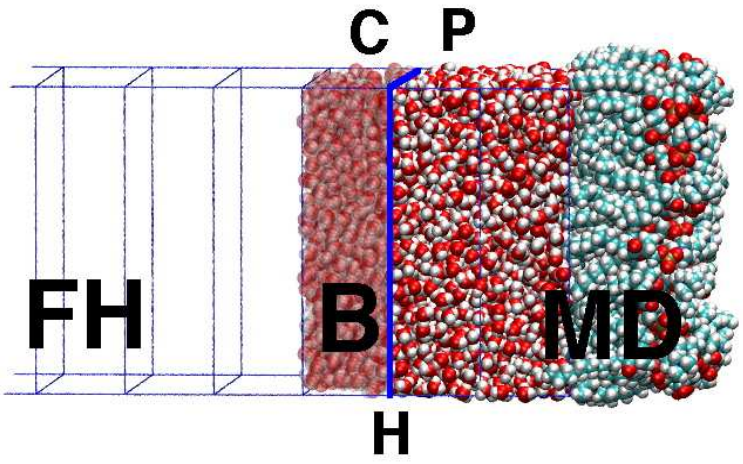
Flux-coupling







Continuity in flux schemes



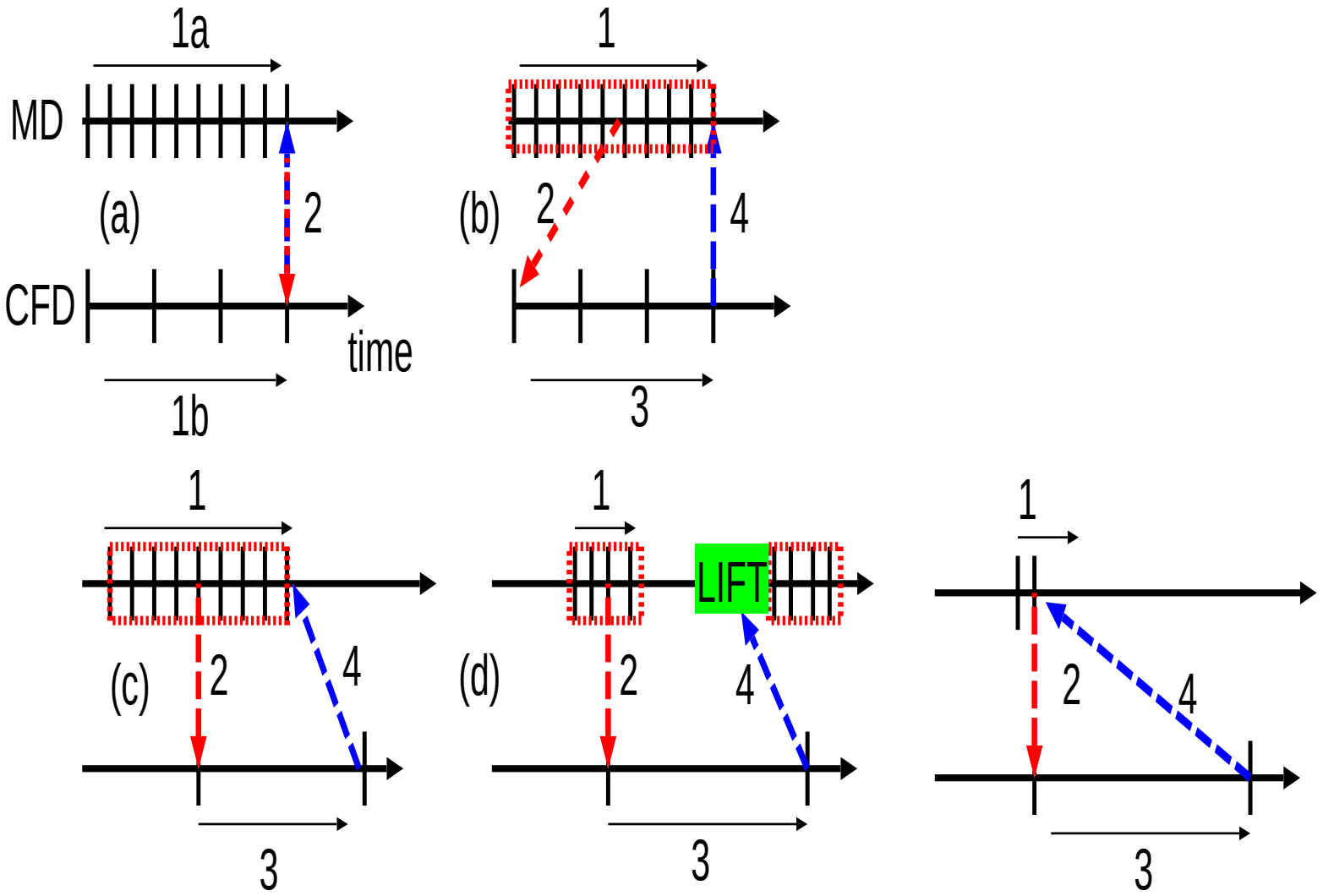
The continuum solver, schematically

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

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, $\boxed{\langle J^2_{MD} \rangle = \langle J^2_{FH} \rangle}$:

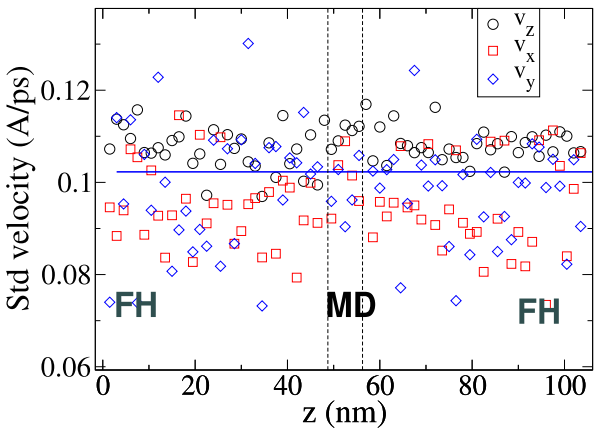
$\Delta t_{FH} = 2\tau_c = \delta t_S$ Sampling time = twice MD decorrelation time

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

Hybrid MD-Fluctuating Hydrodynamics: equilibrium state

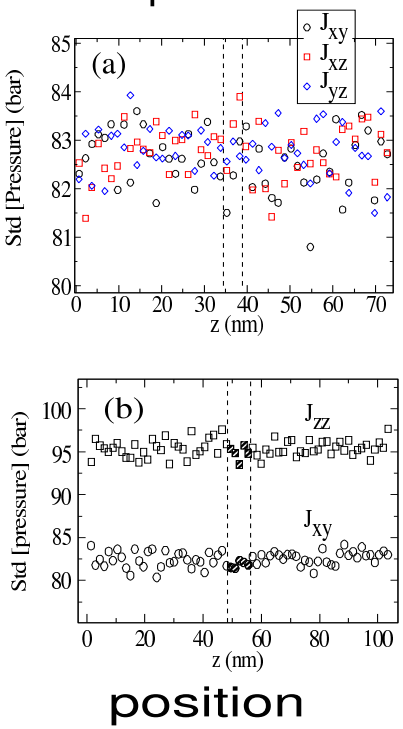
`Standard deviation of velocity` (kinetic temperature)
liquid argon @ $T = 300K$
RDB and G.Fabritiis et al. PRE, **76** (2007)

STD velocity



position

STD Stress tensor components



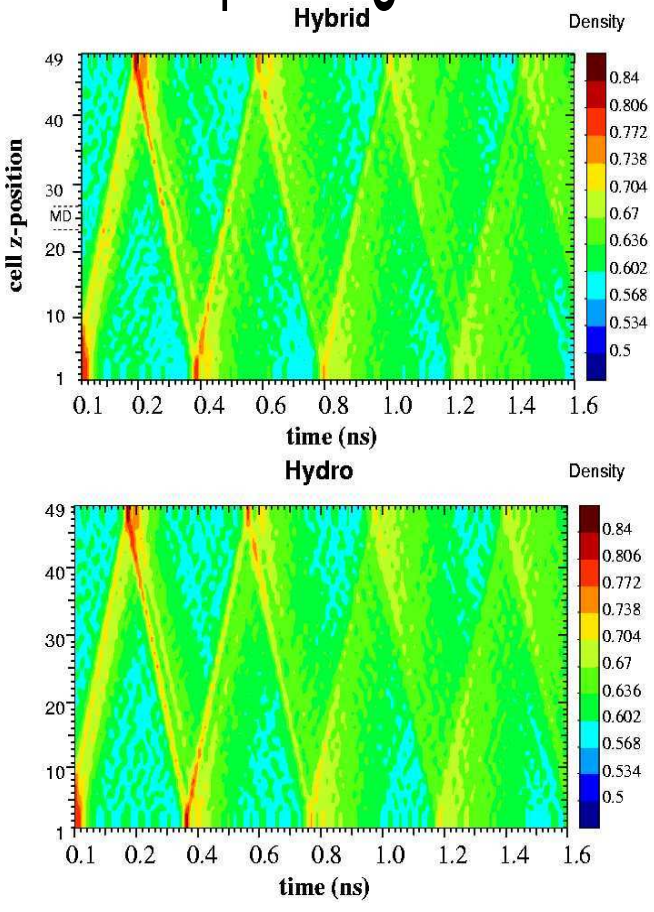
position

Hybrid MD-Fluctuating Hydrodynamics

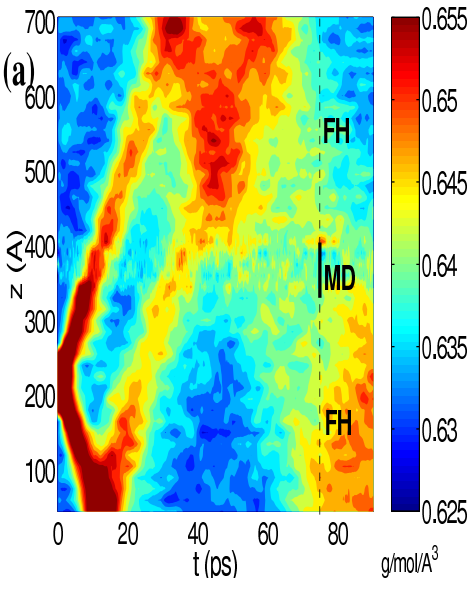
Some test cases: sound

De Fabritiis, R.D-B and P. Coveney, PRL, 97 (2006)

liquid argon



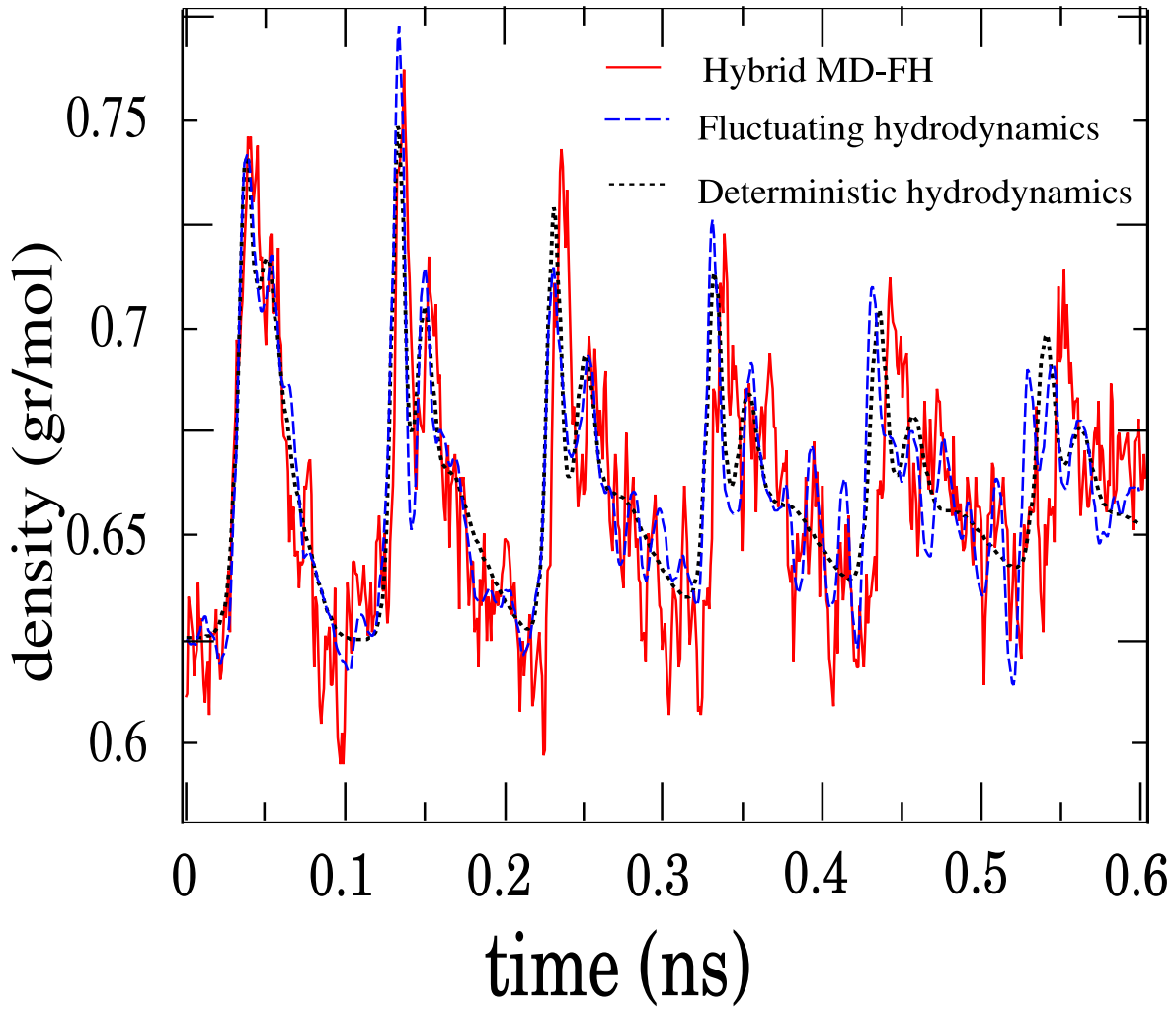
water



Hybrid MD-Fluctuating Hydrodynamics

Some test cases: sound

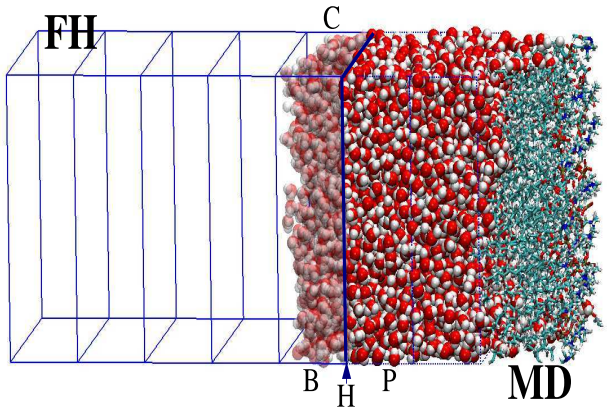
De Fabritiis, R.D-B and P. Coveney, PRL, 97 (2006)

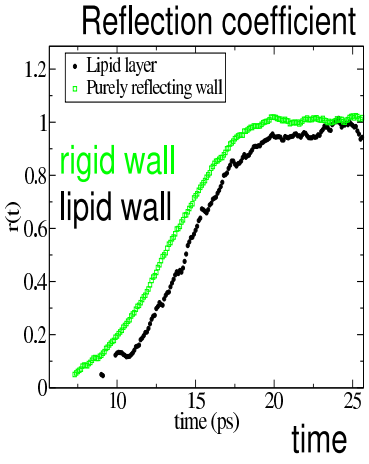


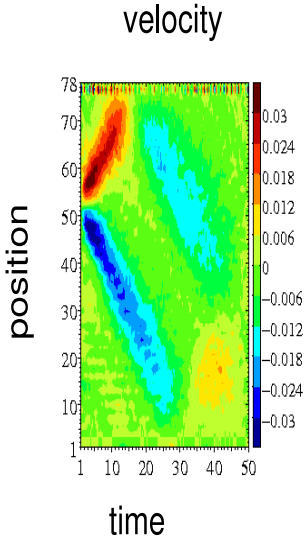
Hybrid MD-Fluctuating Hydrodynamics
Collision of sound waves against DMPC lipid layer

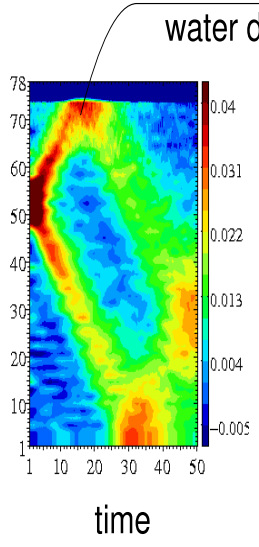
De Fabritiis, R.D-B and P. Coveney, PRL, 97 (2006)

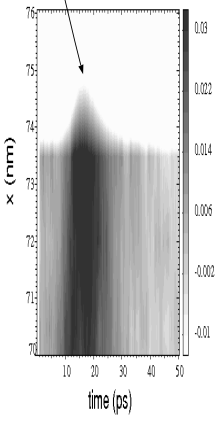
RDB et al, Proc IMechE, Part C: J Mech. Eng. Sci. **222** (2008)

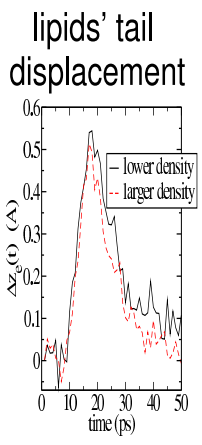












Conclusions

- New tools are required to study the effects of sound in soft matter.
- Molecular information about effective friction, draining and slip boundary conditions is required to feed micron-scale simulations.
- Sound simulations require **open systems**: OPEN MD, OPEN FH possibly used in combination with AdResS
- Sound at micron and submicron scales: Direct Forcing in compressible flow.
- Sound at nano-scale: Hybrid MD