HybridMD

Coupling atomistic molecular dynamics and fluctuating hydrodynamics: shear and sound.

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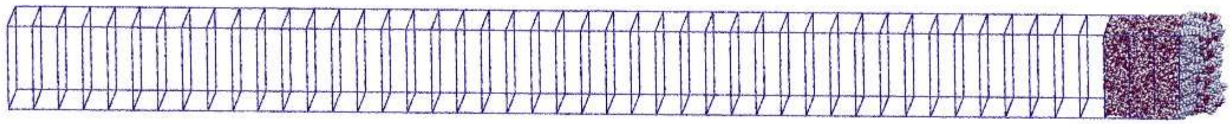
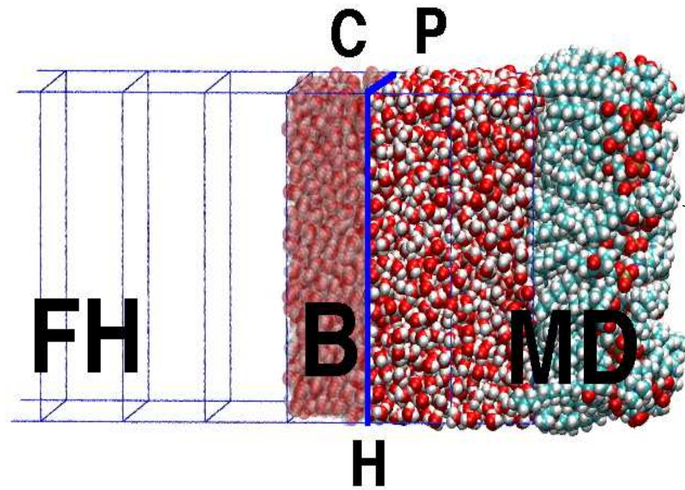
Hybrid particule-continuum models
Forewords and applications

- Multiscale modeling: predicted as a scientific milestone in near future by the 2020 Science Group. [*Nature* **440** (7083): 383 (2006)]
- Phenomena involving a fine interplay between molecular and hydrodynamic scales.
  - Complex fluids near interfaces: microfluidics, slip of liquid flow past surfaces
  - Fluid-fluid or soft interfaces (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,
  - Constant chemical potential simulations for confined systems: osmosis driven flows through membranes, thin films, water in clays,
  - etc...

Multiscale modelling
Embedding molecular dynamics within fluctuating hydrodynamics

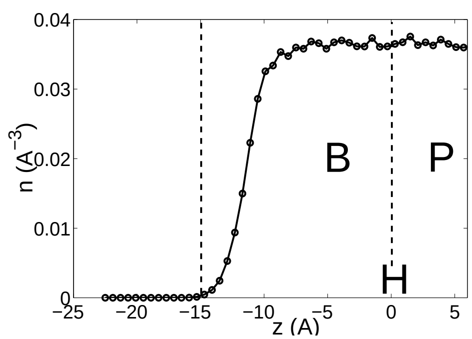


Hybrid MD-FH setup



DMPC
(lipid layer)

water density profile



PRL, 97, 134501 (2006)

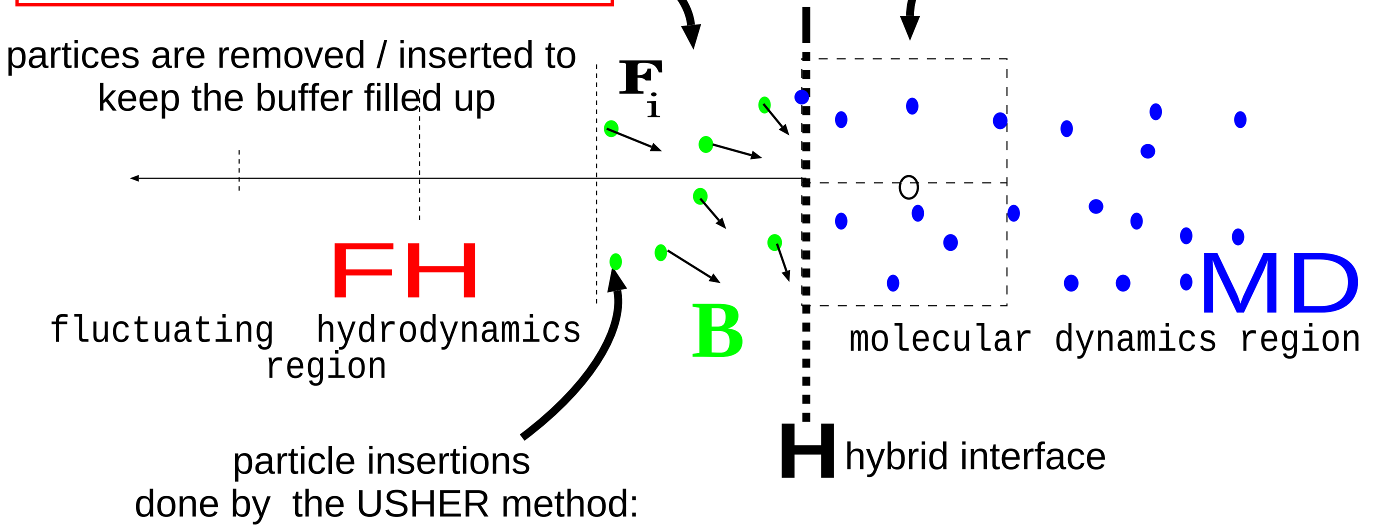
PRE, 76, 036709 (2007)

Flux coupling enables to solve unsteady flows

Spatial Coupling

At the particle buffer **B** the FH local fluxes are transfered to the particle system by imposing non-conservative forces $\mathbf{F}_i$ to the buffer particles

Local stress tensor at **P cell** is obtained from molecular dynamics and used as boundary condition for FH.



USHER: J. Chem. Phys., 119, 978 (2003)

USHER for water: J.Chem.Phys.121, 12139 (2004)

General flux boundary conditions for MD

PRE **72**, 026703 (2005)

- Introduce external forces $\mathbf{F_i}$ at the particle buffer
- **Objective:** impose the desired energy flux J_e and momentum flux $\mathbf{J_p}$ into MD.

- Momentum and energy input over Δt (A is the area of the interfase H)

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

- External forces: $\mathbf{F}_i = \mathbf{F} + \mathbf{F}'_i$ (particle $i \in B$)
- Mean force $\langle \boldsymbol{F}_i \rangle = \mathbf{F}$ provides the desired **input of momentum**

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

- Fluctuating part $\mathbf{F}'_i$ provides **energy input** via dissipative work, (it gives no momentum $\sum_{i=1}^{N_B} \mathbf{F}'_i = 0$).

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

Molecular dynamics at various ensembles PRE, **72**, 026703 (2005)

The amount of heat and work into the MD system is exactly controlled

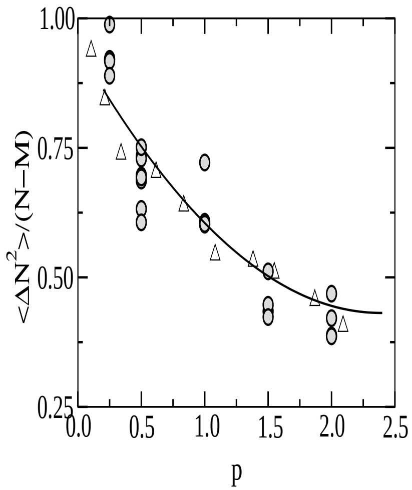
- This fact enables to work in:
  - Grand-canonical ensemble. μVT, with $\mu = \mu(p^C, T^C)$ chemical potential at the reservoir B.
  - Isobaric ensemble NPT. $\mathbf{J_p} = p\hat{\mathbf{n}}$.
  - Constant enthalpy HPT. $\mathbf{J}_e^H = M\langle \mathbf{v} \rangle \cdot F$ and $\Delta N = 0$. $\Delta E + p\Delta V = \Delta H = 0$. (Joule-Thompson)
  - Constant heat flux. $\mathbf{J}_e = cte.$ (growth of solid phase -ice-, heat exchange at complex surfaces.)

- Further benefits
  - The system comunicates with the exterior at its boundaries (B), as a real system does.
  - *Dynamic properties* are measurable. Inside the interest region, MD is not altered by any artifact (thermostat, manostat, etc...).

Flux particle BC´s are thermodynamically consistent

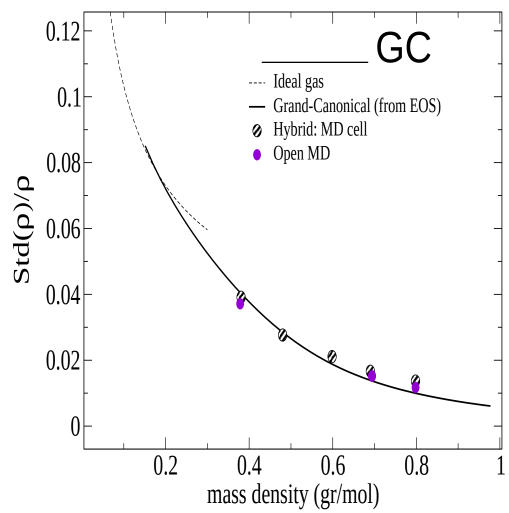
with the Grand Canonical ensemble

Soft-particles
DPD-like



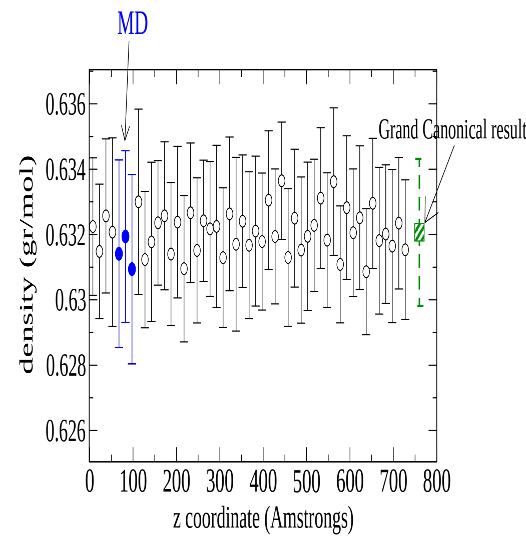
pressure

Liquid argon



density

Water (T=300 K)

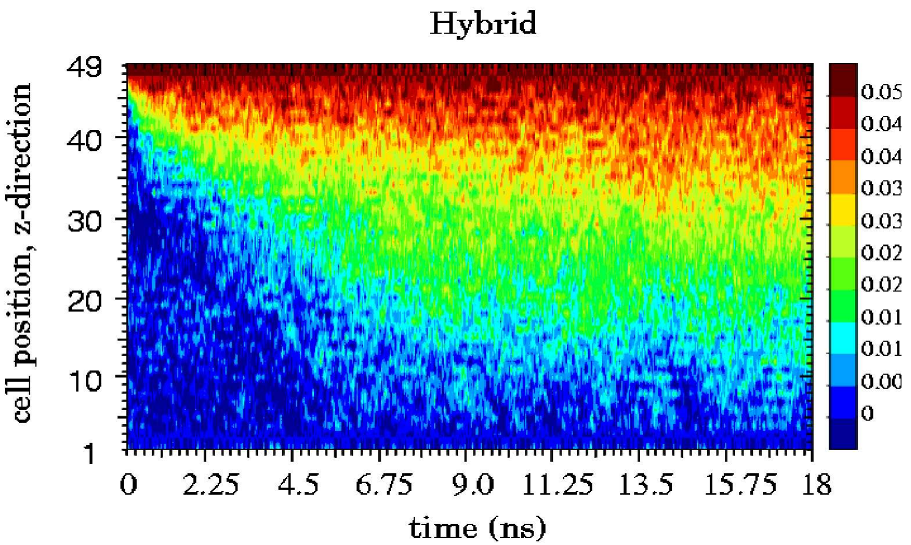


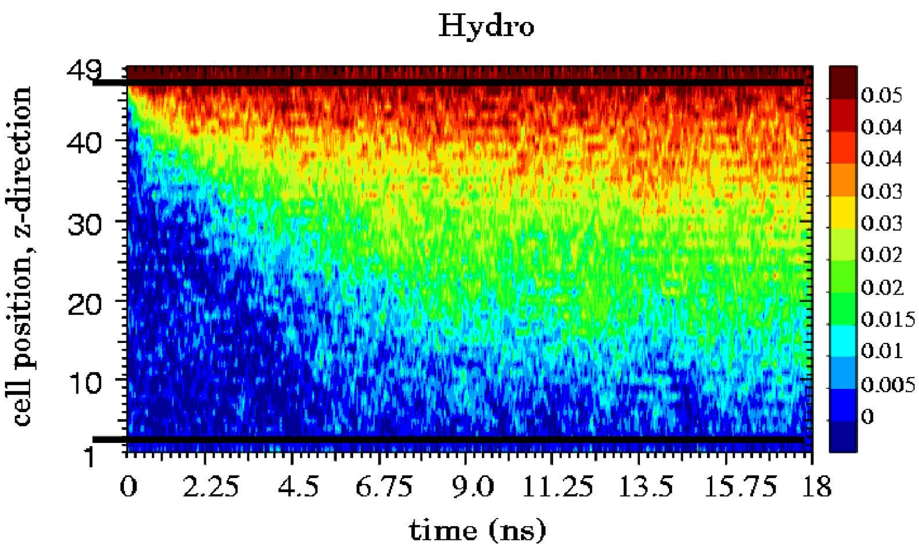
cell-coordinate

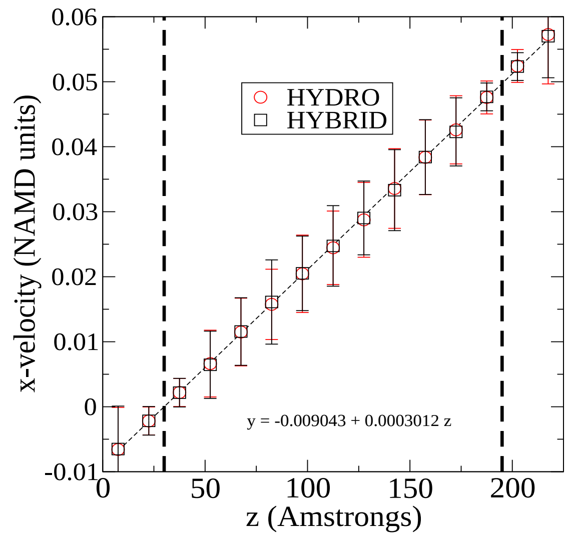
Grand Canonical ensemble:

$\mathrm{Std}[\rho] = [\rho k_b T/(V c_T^2)]^{1/2}$, where $c_T^2 = (\partial P/\partial \rho)_T$ is the squared sound velocity.

Non-equilibrium: unsteady shear flow

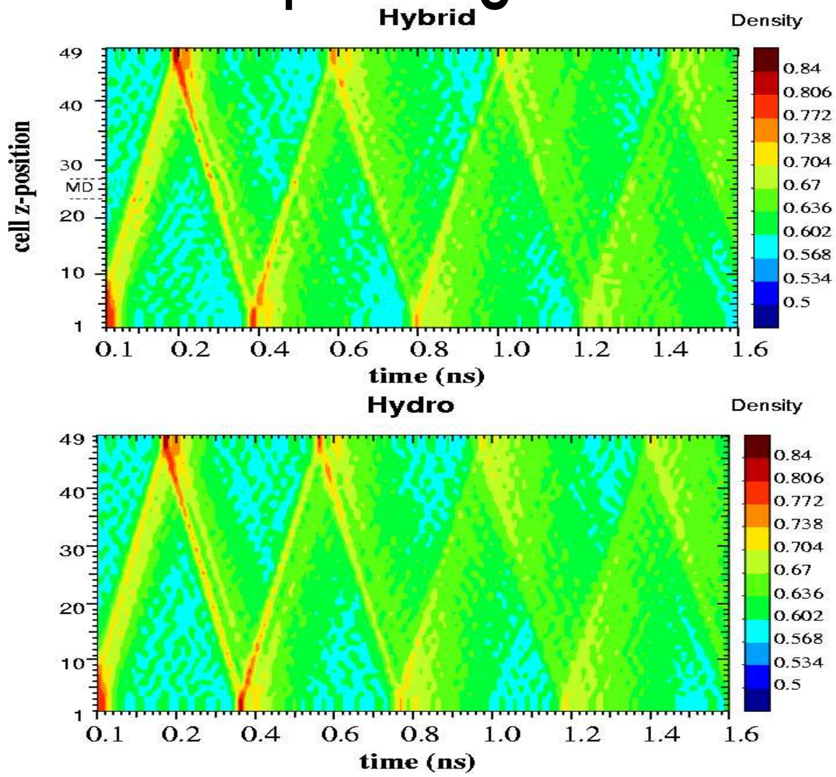




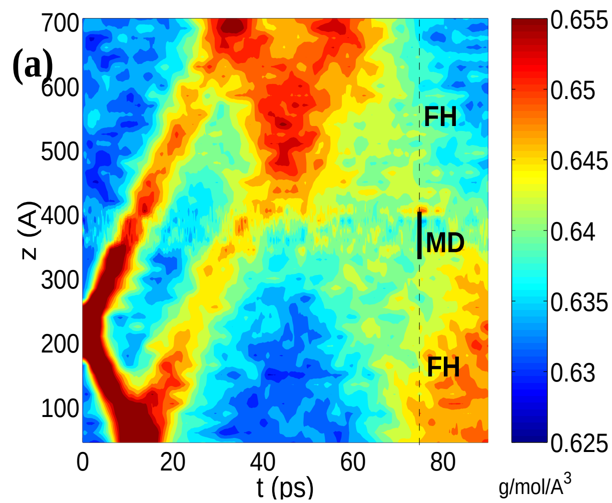


Non-equilibrium: sound waves

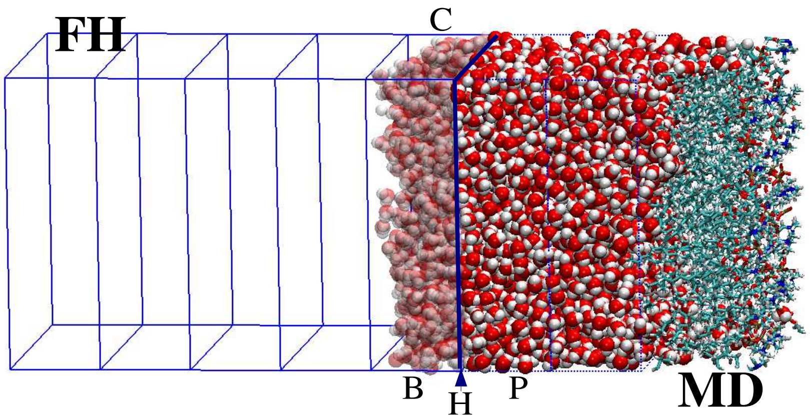
liquid argon



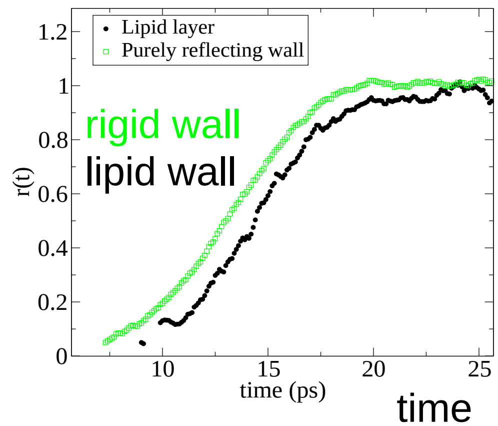
water



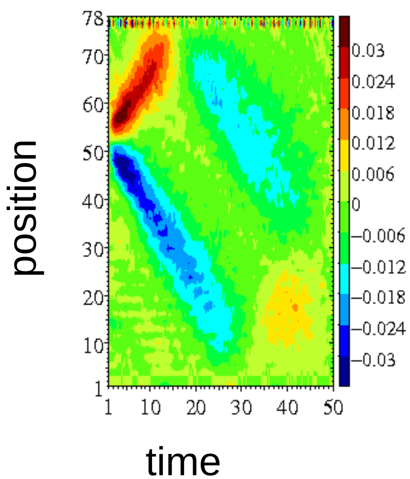
Collision of a water wave against a lipid monolayer (DMPC)



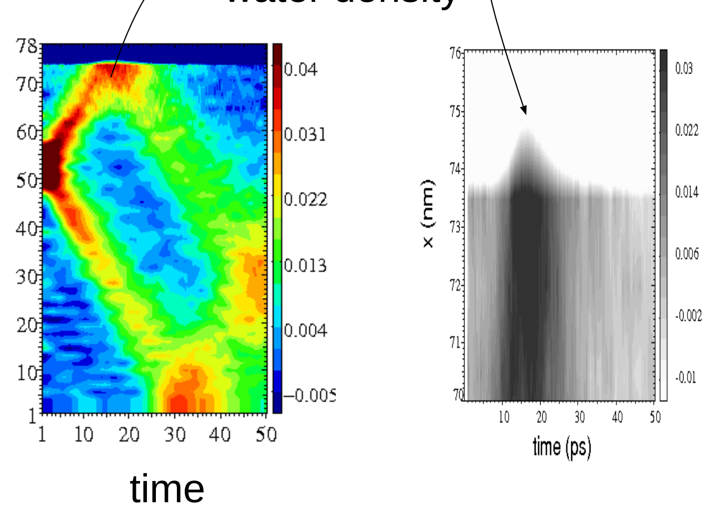
Reflection coefficient



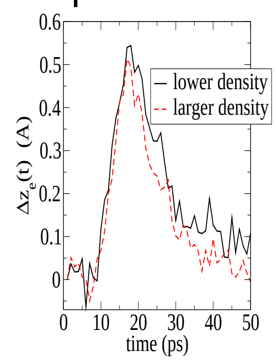
velocity



water density



lipids' tail displacement



Conclusions

- Hybrid scheme coupling molecular dynamics and fluctuating hydrodynamics.
- Chemical specificity (water solvating complex molecules), CHARMM27 force field.
- Shear and **sound** and **heat**.

The model

- Respects conservation laws by construction (flux-exchange).
- MD is an open system and its mass fluctuation is consistent with the **grand canonical ensemble**.
- MD velocity and pressure fluctuations are consitent with FH.