

Multiscale simulation of complex fluid flow using coupled models

Rafael Delgado Buscalioni

**Universidad de Educación a Distancia
Madrid**

collaboration with:

Gianni De Fabritiis (University College London)

Jens Harting (Stuttgart University). **HPC-Europa funding @ HLRS**

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.
- Constant chemical potential simulations for confined systems: osmosis driven flows through membranes, thin films, water in clays,
- etc...

Multiscale techniques

the art of inventing a wise...

Trick

Astuce

Truco

Scherzozzo

Zaubern

τεχνασμα = technasma

Multiscale modelling

for different states of matter

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

LIQUIDS

Domain decomposition: MD-CFD, MD-FH
 Eulerian-Lagrangian: MD-LB, MD-FH
 Velocity-Stress coupling: MD-SMFD, MD-FD
 Particle-particle: MD-SRD; new method: JChemPhys, **123** 224106 (2005)

Acronyms

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

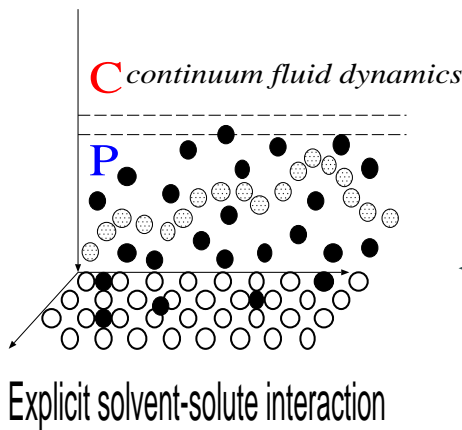
Multiscale modelling: Complications with liquids

- Large intermolecular potential energy, cohesion.
- Large mobility. Open systems, particle insertion, etc...
- Fluctuations are important at molecular scales:
 - Fluctuating-deterministic coupling (how to reduce effect of particle fluctuations in the continuum region).
 - Use of stochastic fluid models: fluctuating hydrodynamics
- Soft matter: self-assembly process (eg,. water+surfactants)
- Wide gap between time-scales: time decoupling. Coarse-grained models with specific molecular properties.

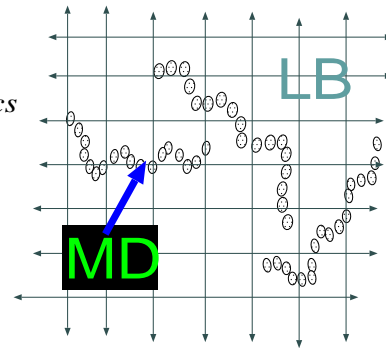
Multiscale modelling of liquids: different scenarios.

Molecular region	localized	in bulk	concentrated solution or melt
Best method	Domain decomposition	Eulerian-Lagrangian hybrid: Stokes force coupling	Velocity-Stress mesh coupling

applications interfacial, surfaces, single macromole-fluid interaction

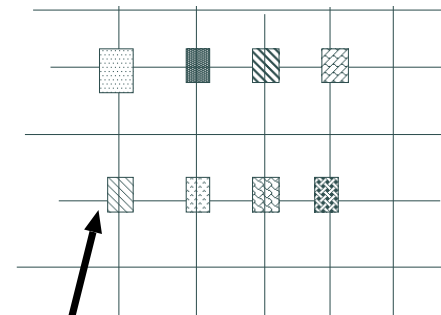


hydrodynamics of semidilute solutions



Particles: MD
Continuum: LB or FH.
Fluctuations in C model needed.

Highly non-Newtonian fluid flow

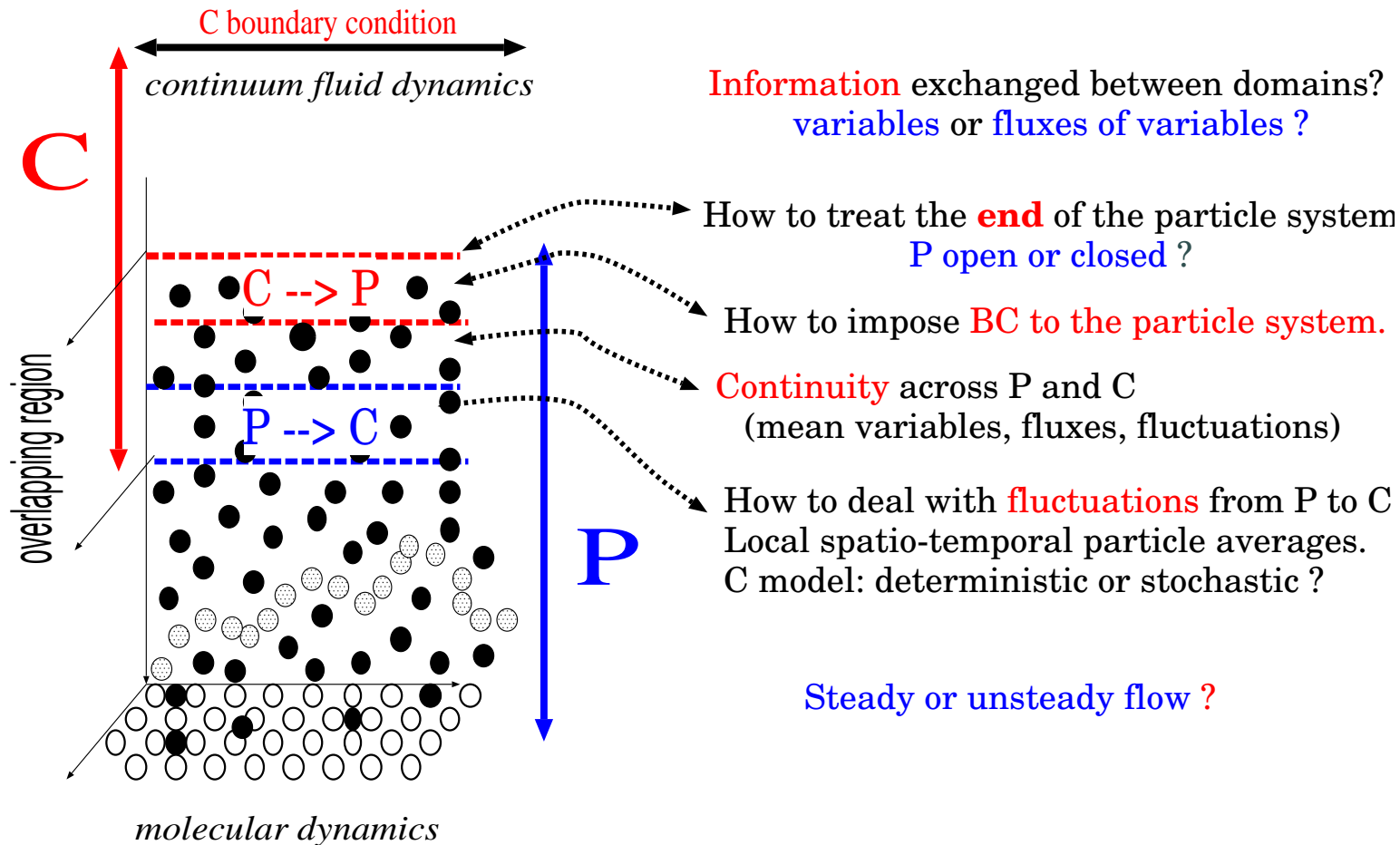


MD simulations in periodic boxes (MD nodes) evaluate the **local stress** for the Continuum solver.

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

Multiscale models based on domain decomposition.

General issues concerning hybrid models



Hybrids based on domain decomposition

Model	Information exchanged	P: open or closed	Boundary conditions imposed to P	Continuity	C Deterministic or Stochastic	Steady or Unsteady
Schwartz coupling	Variables: transversal velocity (shear)	closed: shear, incompressible fluids)	Maxwell daemon to velocity	Variable (YES), Fluxes (NO), Fluctuations (NO)	Deterministic	Steady
Flux coupling	Fluxes of conserved quantities (mass, momentum, energy)	open: sound+energy	External forces	Variables (YES) ... <i>(via relaxation)</i> Fluxes (YES) Fluctuations (YES)	Stochastic or Deterministic	Unsteady

The Schwartz algorithm

Pros

Fast convergence to steady state.

Continuity of variable ensured by construction

Reduces fluctuations at the Continuum region

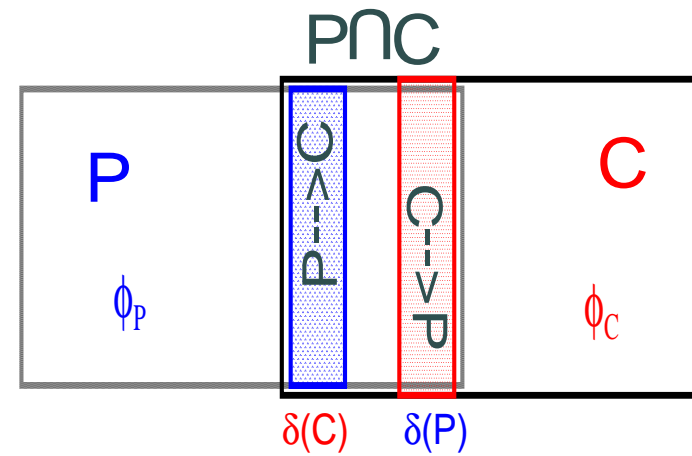
Cons

Conservation laws are not respected.

Is not thermodynamically consistent.

Maxwell daemon alters particle's collective behaviour (diffusion, transport coef..).

Particle domain is closed: **no** mass exchange across the interface.



0) Solve **C** using an initial guess for ϕ_C at $\delta(C)$

loop

1) Solve **P** imposing ϕ_C at $\delta(P)$ Maxwell Daemon for velocity

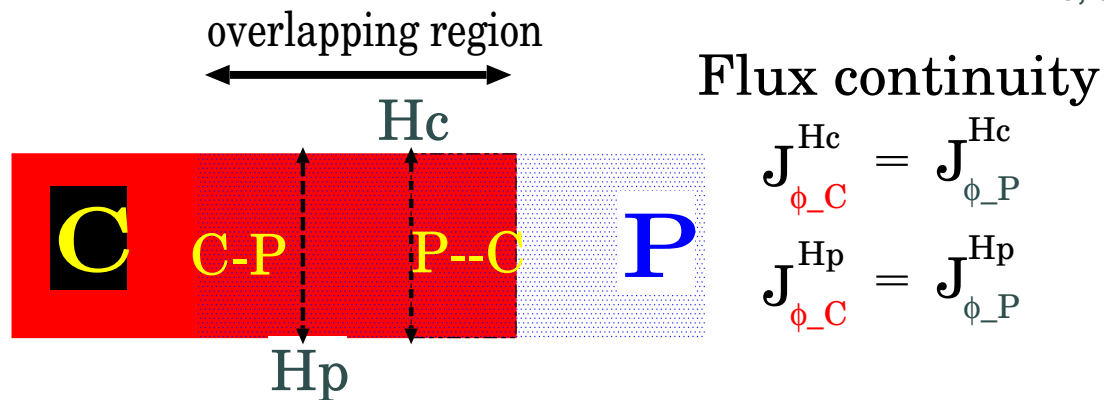
2) Solve **C** imposing $\langle \phi_P \rangle$ at $\delta(C)$ Dirichlet B.C.

Check for convergence within **PnC**

The Flux coupling scheme

Previous flux based schemes

Flekkoy et al.
RDB & P. Coveney
Nie, et al.



Continuum subdomain: **C**

Overlapping region: ?

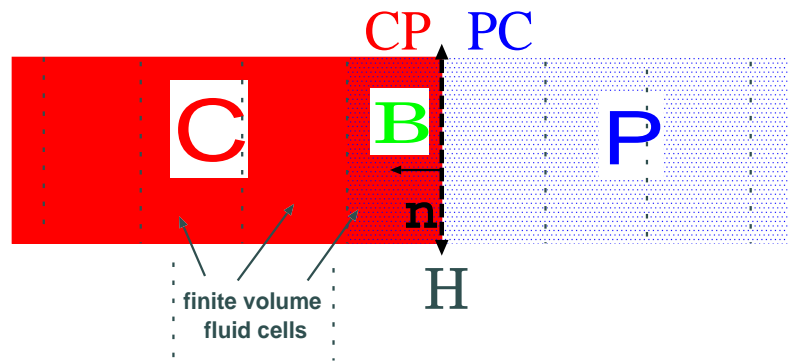
Particle subdomain: **P**

Total system : ??

The total system was not well defined

The Flux coupling scheme

Present scheme (conceptually simpler)



Continuum subdomain: C

Particle subdomain: P

Particle buffer: B

Total system : C+P

Extended system: C+P+B

Flux of ϕ across
hybrid interface H

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

Conservation

$$\Delta\phi_{CP} = A J_{\phi}^H \cdot \mathbf{n} \Delta t$$

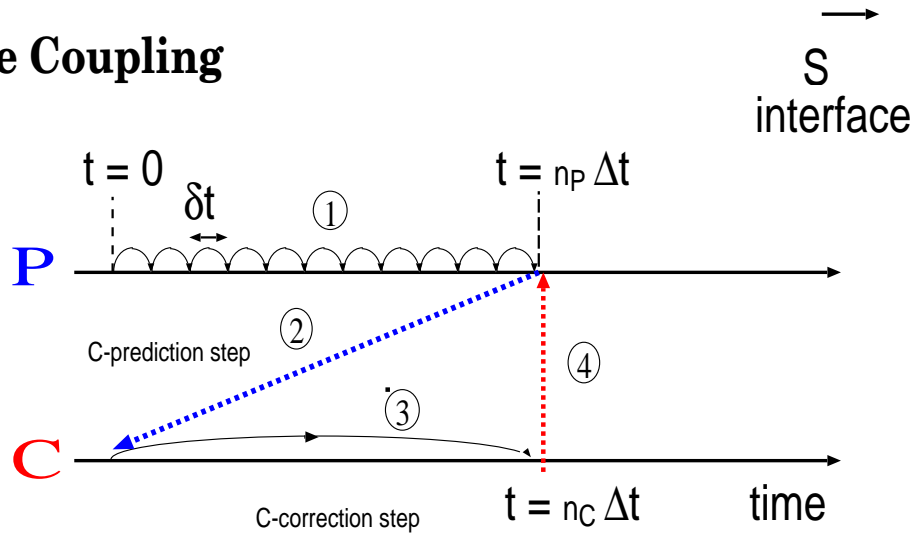
$$\Delta\phi_{PC} = -A J_{\phi}^H \cdot \mathbf{n} \Delta t$$

Conservation laws apply for the total system: P+C

G. De Fabritiis, RDB, P. Coveney; PRL 97, 134501 (2006)

Flux coupling for unsteady flows.

Time Coupling

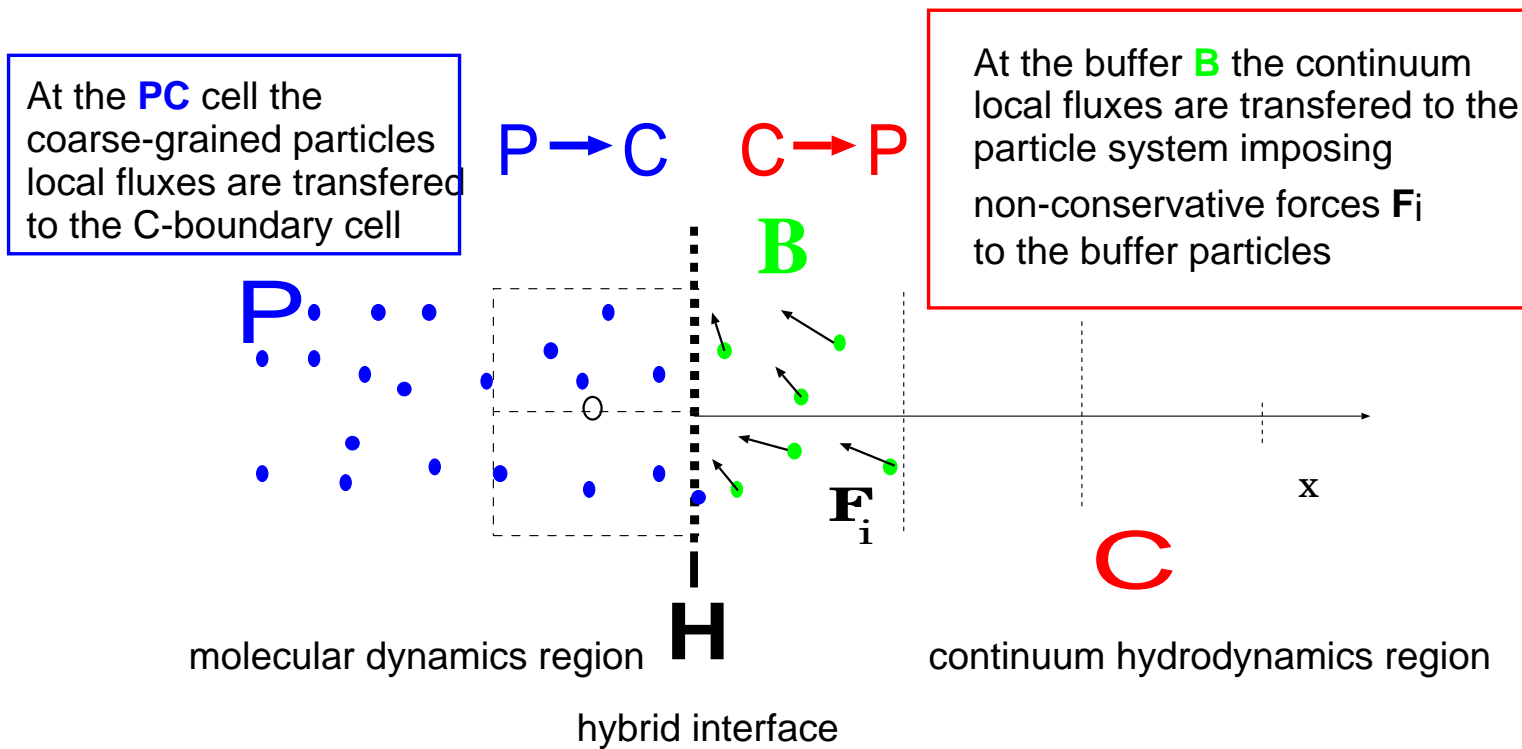


Loop

- ① Advance the n_p particle time steps towards $t = n_p \delta t$.
- ② Send average particle information to C. Send particle mass across interface H during Δt
- ③ Advance n_c continuum time steps towards $t = n_c \Delta t = n_p \delta t$
- ④ Impose the continuum stress and heat rate at CP to the buffer particles B.

Flux coupling for unsteady flows.

Spatial Coupling



The particle buffer **B**

- **Objective:** Impose momentum and energy ($C \rightarrow P$)
- **Requirement:** Control the buffer's mass $M_B = m N_B$
- **Method:** The buffer is always filled with particles via a simple relaxation algorithm.

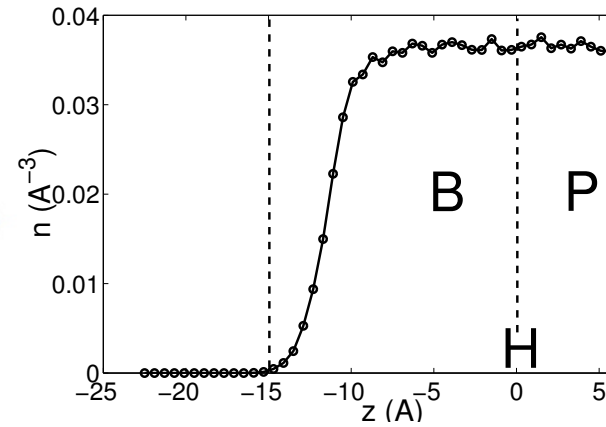
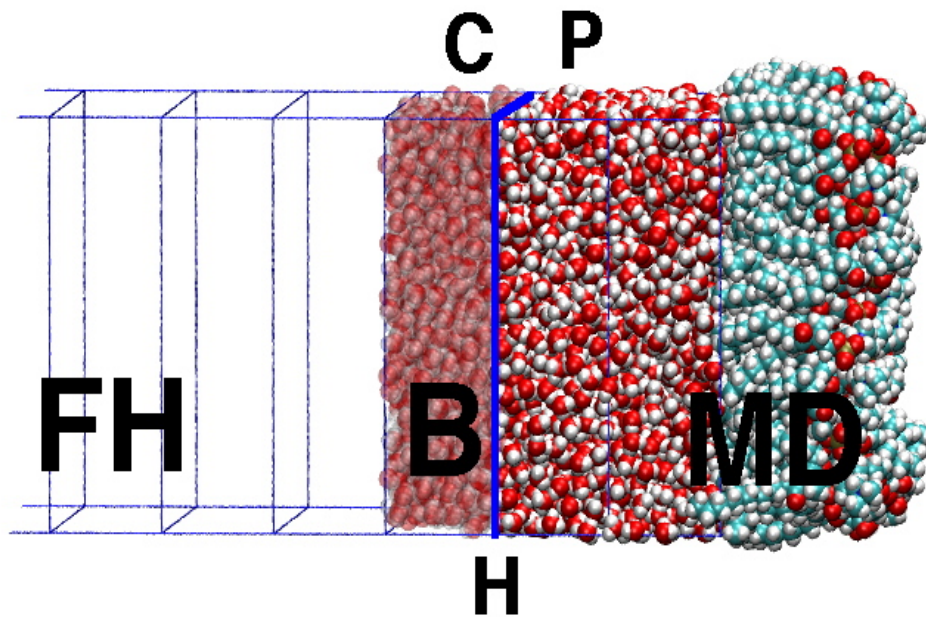
$$\frac{dN_B}{dt} = \frac{1}{\tau_B} (\alpha N_{CP} - N_B)$$

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

- Particle evaporating out of the buffer **B** are removed. If $\Delta N_B > 0$, particles are inserted using the **USHER algorithm** (insertion energy equal to the mean energy/particle)

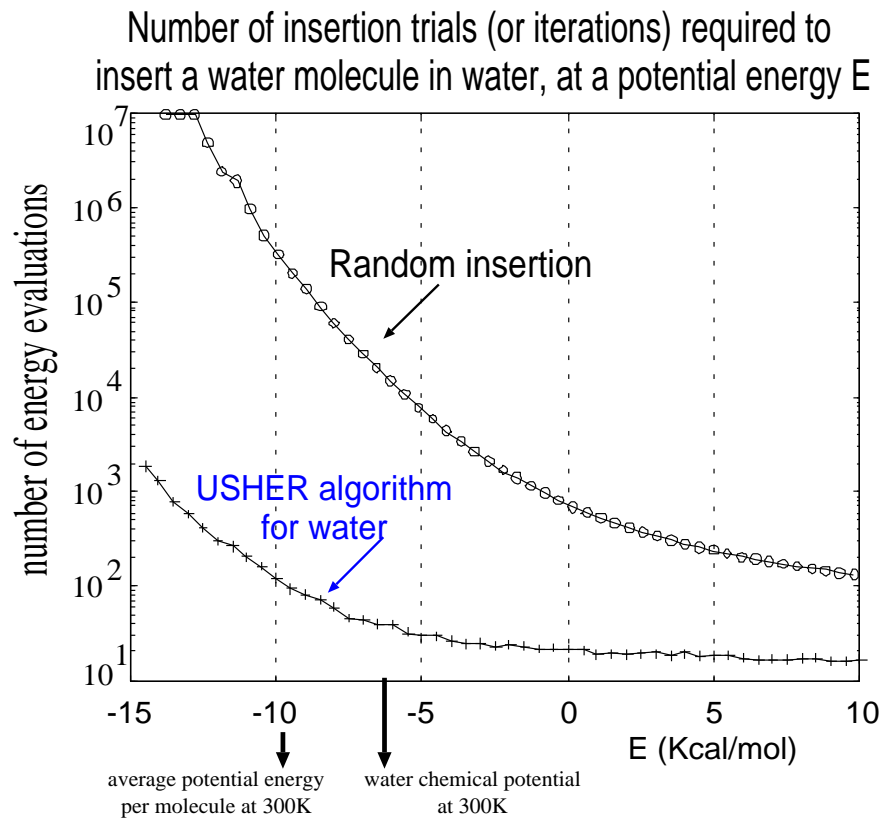
A simulation with water.

Buffer density profile



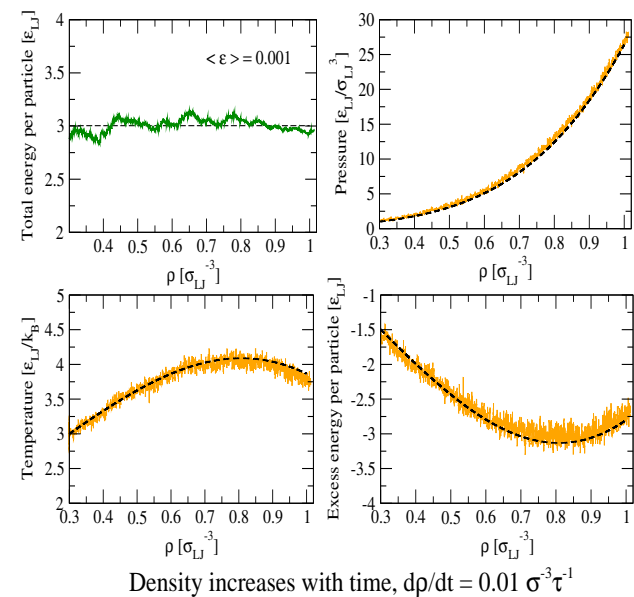
Fast particle insertion with controlled release of potential energy

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



Insertion process at constant energy per particle

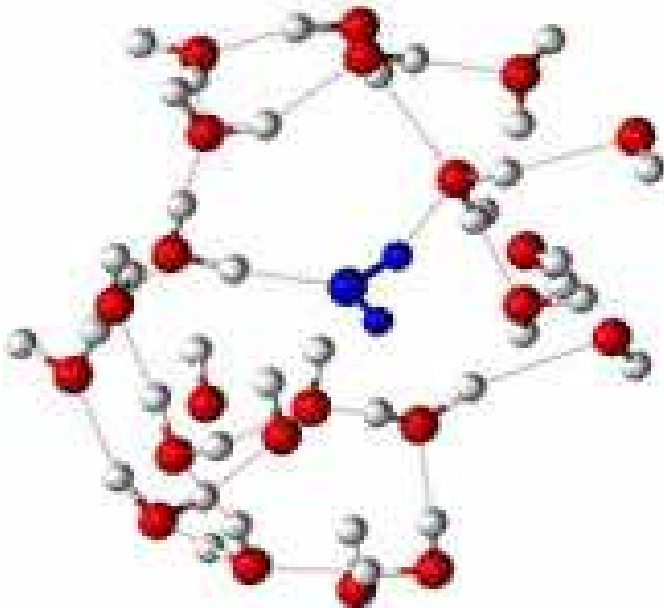
..... dashed line thermodynamic analytical solution (Lennard-Jones)



USHER: New particles are placed at locations where the release of potential energy to the system takes the desired specified value. The USHER uses a variant of Newton-Raphson method to locate low-energy regions in the complex energy landscape.

G. De Fabritiis, RDB, P. Coveney, Energy controlled insertion of polar molecules in dense fluids, *J. Chem. Phys.* **121**, 12139 (2004)

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



On how *micro* talks to *macro*

$$P \rightarrow C$$

Recall that all we need the flux across the hybrid interface H:

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

Objective. Evaluate J_{ϕ}^{PC} (with $\phi = \{\mathbf{p}, e\}$ average flux at the PC cell over Δt).

(1) Via **Kinetic Theory formulae** for pressure tensor and energy flux:

$$\begin{aligned} \langle \mathbf{J}_{\mathbf{p}}^P \rangle &= \langle m_i \mathbf{v}_i \mathbf{v}_i - \frac{1}{2} \sum_j^N \mathbf{r}_{ij} \mathbf{F}_{ij} \rangle \\ \langle \mathbf{J}_e^P \rangle &= \langle m_i \epsilon_i \mathbf{v}_i - \frac{1}{2} \sum_j^N \mathbf{r}_{ij} \mathbf{v}_i \mathbf{F}_{ij} \rangle \end{aligned}$$

(2) Via the **constitutive relations**: Newtonian fluid and Fourier law.

Using the averaged variables $\Phi_P = \sum_i \chi_P(\mathbf{r}_i) \phi_i$ (total ϕ at PC cell) where χ_P is the characteristic function of the cell P, i.e. $\chi_P(\mathbf{r}) = 1$ if $\mathbf{r} \in P$ and 0 otherwise.

On how *macro* talks to *micro*:

$$C \rightarrow P$$

[Flekkoy, RDB, Coveney, *Phys. Rev. E*, **72**, 026703 (2005)]

Objective: To impose into the **P** system the desired (exact) energy and momentum flux across the interface H: that is J_e^H and J_p^H , respectively.

Method: By adding an external force \mathbf{F}_i to the particles at the **B** reservoir.

Momentum and energy added to **P+ **B** over one (long) time step $dt = \Delta t$**

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

where A is the H-interface area and the index i' runs only over added/removed particles during Δt .

On how *macro* talks to *micro*: $C \rightarrow P$ (cont.)

Decomposition of the external particle force: $\mathbf{F}_i = \mathbf{F} + \mathbf{F}'_i$

The mean value $\langle \mathbf{F}_i \rangle = \mathbf{F}$ provides the desired **input of momentum**

$$\mathbf{F} = \frac{A}{N_B} \tilde{\mathbf{j}}_p \quad \text{where } \tilde{\mathbf{j}}_p \equiv \mathbf{J}_p - \frac{\sum_{i'} \Delta(m\mathbf{v}_{i'})}{A dt}. \quad (1)$$

The fluctuating part \mathbf{F}'_i provides the desired **energy input** via dissipative work (note that \mathbf{F}'_i gives no net momentum input because $\sum_{i=1}^{N_B} \mathbf{F}'_i = 0$).

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

Under equilibrium, the second law of thermodynamics is respected and the particle system behaves like an open system at constant chemical potential, $\mu = \mu(P^C, T^C)$, given by the pressure P^C and temperature T^C imposed at the B reservoir.

Molecular dynamics at various ensembles

[Flekkoy, RDB, Coveney, *Phys. Rev. E*, **72**, 026703 (2005)]

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

Enabling

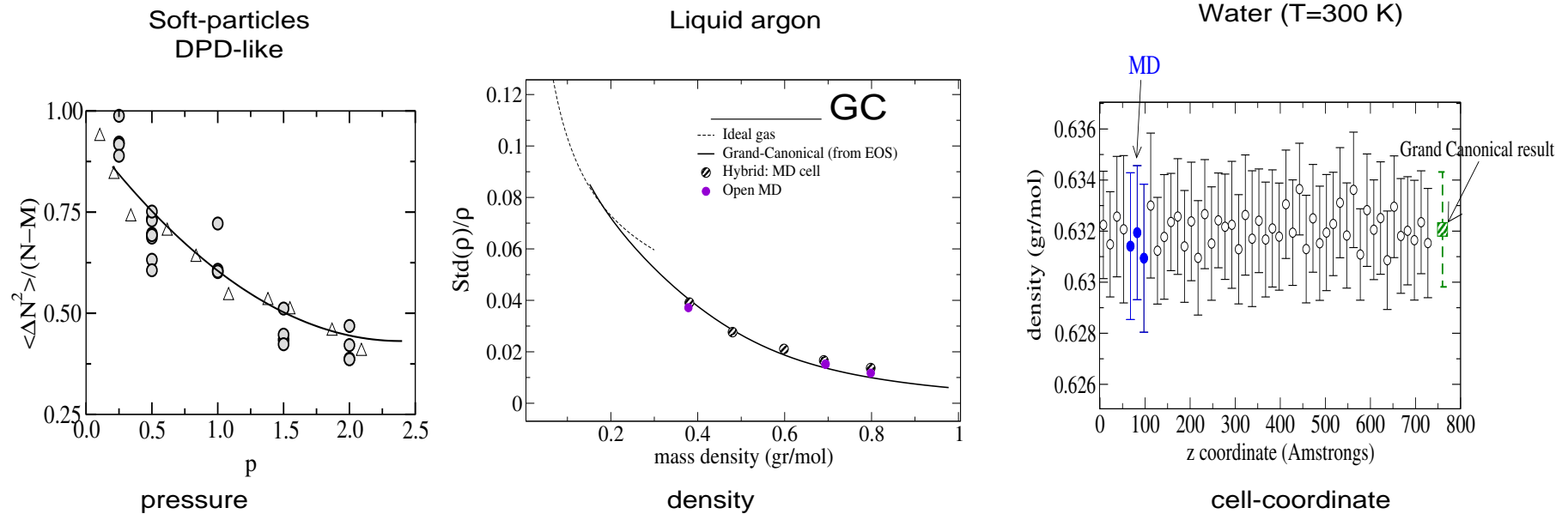
- **Grand-canonical ensemble.** μVT . Where $\mu = \mu(p^C, T^C)$ is the chemical potential at the reservoir B.
- **Isobaric ensemble** NPT. $\mathbf{J}_p = p\mathbf{n}$.
- **Constant enthalpy** HPT. $\mathbf{J}_e^H = M\langle\mathbf{v}\rangle \cdot \mathbf{F}$ and $\Delta N = 0$. $\Delta E + p\Delta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

with further benefits

- The system communicates 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...).

Thermodynamic consistency: *Grand-Canonical ensemble*

Flux particle BC's are thermodynamically consistent
with the Grand Canonical ensemble



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

Variable continuity: On how *macro* and *micro* finally agree.

Important question: In case of disagreement, who is right, **P** or **C**?

	C is right	P is right
Authors	Nie <i>et al</i>	Present work (and Garcia DSMC-CFD)
<i>velocity continuity:</i>	(a) Constraint particle dynamics	(b) Relaxation term in NS eqs. for CP cell
<i>mass flux</i>	imposed by C to P	Given by the particle flux across H (ruled by pressure)

(a) Constrained dynamics: [Thompson and O'Connell, PRE, (1995); Nie *et al.* J. Fluid Mech. (2004)].

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

(b) Relaxation of first C cell: [RDB, Flekkoy, P.Coveney, EuroPhys. Lett. (2005)]

$$\frac{[\rho \mathbf{v}]_{CP}^C}{dt} = NS + \frac{1}{\tau_r} \left(\langle [\rho \mathbf{v}]^P \rangle_{CP} - [\rho \mathbf{v}]_{CP}^C \right)$$

Note: Constraining the particle dynamics affects the particle collective properties. It also destroys energy balance. Relaxation of the Continuum cell (CP) is simple and efficient, $\tau_r \ll \tau_{hydro}$.

Fluctuations are important at the nanometer and micron scales

MD Stress fluctuations are consistent with
Landau Theory for fluctuating hydrodynamics.

Fluid	V_{PC}	T	η	Numerical $\text{Var}[j_{xy}^P]$	Theoretical Landau theory or (Zwanzig and Mountain, 1965)
WCA	81	1	1.75	0.51	0.60
WCA	173	1	1.75	0.40	0.41
WCA	138	1	1.75	0.33	0.38
WCA	338	1	1.75	0.25	0.24
WCA	2778	1	1.75	0.08	0.06
WCA	2778	1	1.75	0.04	0.03
LJ	121.5	4.0	2.12	1.09	1.08 (1.19)
LJ	121.5	2.0	1.90	0.66	0.72 (0.71)
LJ	121.5	1.0	1.75	0.39	0.49 (0.43)

Density $\rho = 0.8$ (all in LJ units)

Fluctuations are important at the nanometer and micron scales

Thus it is possible to couple
molecular dynamics with fluctuating hydrodynamics

MD-FH hybrid

For liquid phase: water, argon...

Fluctuating hydrodynamics solver based on *Landau Theory*

Conservative stochastic equations, solved using an Eulerian **Finite Volume method** with an explicit time integration scheme (Euler).

$$\frac{\partial}{\partial t} \begin{pmatrix} \text{Variables, } \Phi \\ \rho \\ \rho \mathbf{u} \\ \rho e \end{pmatrix} = -\nabla \begin{pmatrix} \text{Fluxes, } \mathbf{J} \\ \rho \mathbf{u} \\ \rho \mathbf{u} \mathbf{u} + \mathbf{\Pi} \\ \rho \mathbf{u} e + \mathbf{\Pi} : \mathbf{u} + \mathbf{Q} \end{pmatrix} - \nabla \begin{pmatrix} \text{Fluctuations, } \tilde{\mathbf{J}} \\ 0 \\ \tilde{\mathbf{\Pi}} \\ \tilde{\mathbf{Q}} \end{pmatrix} \quad \begin{matrix} \text{mass} \\ \text{momentum} \\ \text{energy} \end{matrix} \quad (3)$$

Finite Volume: space is discretized using control cells of volume V_c

$$\frac{d}{dt} \int_{V_k} \phi(x, t) dx = \sum_l A_{kl} \mathbf{J}_{kl}^\phi \cdot \mathbf{e}_{kl},$$

[G. De Fabritiis, RDB, preprint, 2006; GDF, Mar Serrano, RDB, preprint, 2006] The value of any quantity at the surface kl is approximated as $\phi_{kl} = (\phi_l + \phi_k)/2$. We then obtain the following formal stochastic equations,

$$dM_k^t = \sum_l \mathbf{g}_{kl} \cdot \mathbf{e}_{kl} A_{kl} dt, \quad (4)$$

$$d\mathbf{P}_k^t = \sum_l \left[\frac{\mathbf{\Pi}_l}{2} \cdot \mathbf{e}_{kl} + \mathbf{g}_{kl} \cdot \mathbf{e}_{kl} \mathbf{v}_{kl} \right] A_{kl} dt + d\tilde{\mathbf{P}}_k^t, \quad (5)$$

where $\mathbf{g}_{kl} = \frac{1}{2}(\rho_k + \rho_l) \frac{1}{2}(\mathbf{v}_k + \mathbf{v}_l)$.

Discretization of the gradients satisfying the fluctuation-dissipation theorem.

$$\begin{aligned} \mathbf{\Pi}_k^{\alpha\beta} &= \frac{\eta_k}{V_k} \sum_l \left[\frac{1}{2} A_{kl} (e_{kl}^\alpha v_l^\beta + e_{kl}^\beta v_l^\alpha) - \frac{\delta^{\alpha\beta}}{D} A_{kl} e_{kl}^\gamma v_l^\gamma \right], \\ \pi_k &= \frac{\zeta_k}{V_k} \sum_l \frac{1}{2} A_{kl} e_{kl}^\beta v_l^\beta. \end{aligned} \quad (6)$$

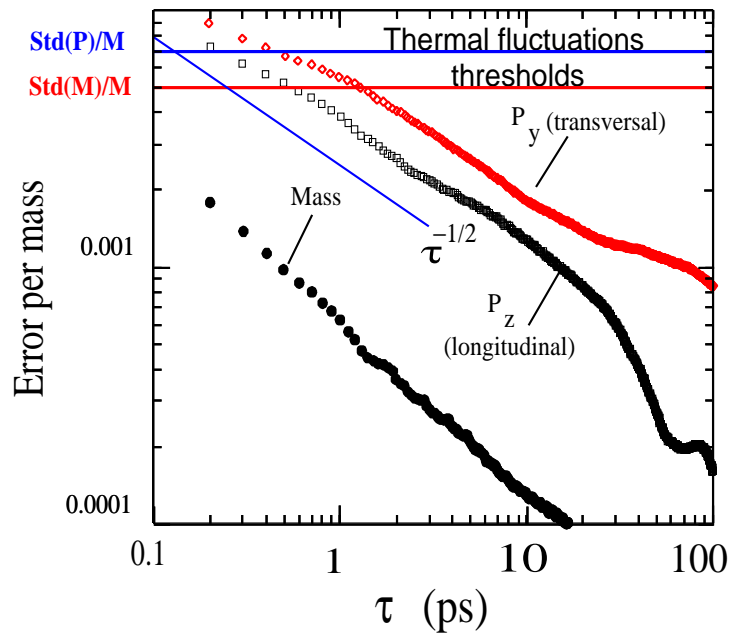
The fluctuating component of the momentum is

$$d\tilde{\mathbf{P}}_k^t = \sum_l \frac{1}{2} A_{kl} \left(4k_b T_l \frac{\eta_l}{V_l} \right)^{1/2} d\bar{\mathbf{W}}_l^S \cdot \mathbf{e}_{kl} + \sum_l \frac{1}{2} A_{kl} \left(2Dk_b T_l \frac{\zeta_l}{V_l} \right)^{1/2} \frac{tr[d\mathbf{W}_l]}{D} \mathbf{e}_{kl}, \quad (7)$$

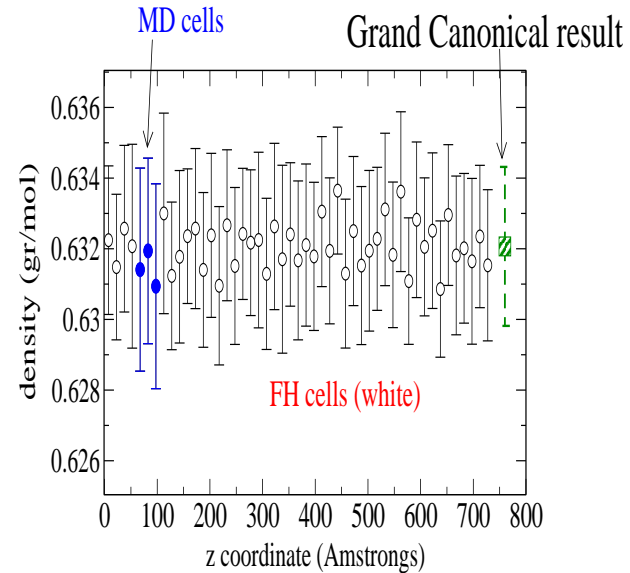
where $d\bar{\mathbf{W}}_l^S = (d\mathbf{W}_l + d\mathbf{W}_l^T)/2 - tr[d\mathbf{W}_l]/D \mathbf{1}$ is a traceless symmetric random matrix and $d\mathbf{W}_l$ is a $D \times D$ matrix ($D = 3$ in three dimensions) of independent Wiener increments satisfying $\langle d\mathbf{W}_k^{\alpha,\beta} d\mathbf{W}_l^{\gamma,\delta} \rangle = \delta_{k,l} \delta_{\alpha,\gamma} \delta_{\beta,\delta} \delta t$.

Hybrid MD-FH at equilibrium

Global mass & momentum conservation
(isothermal case, water, T=300 K)

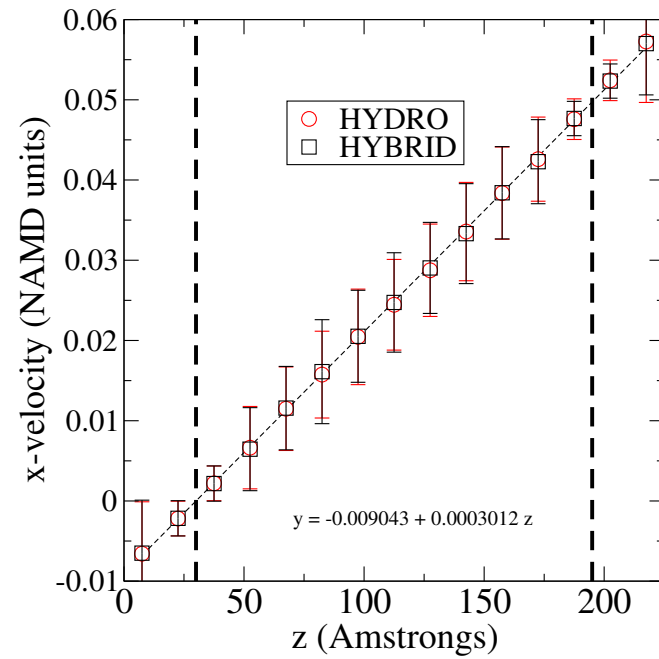
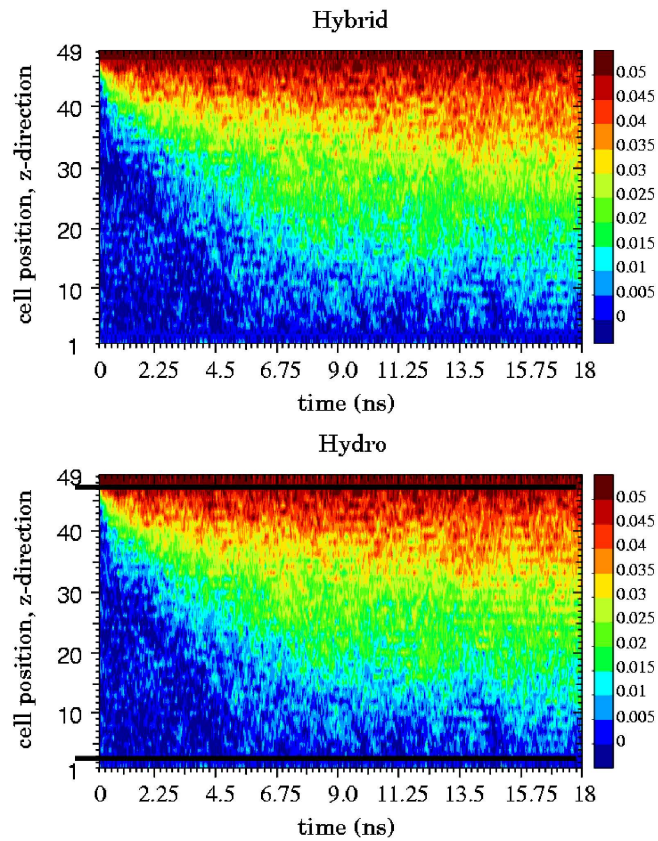


Density-pressure consistency
(isothermal case, water, T=300 K)

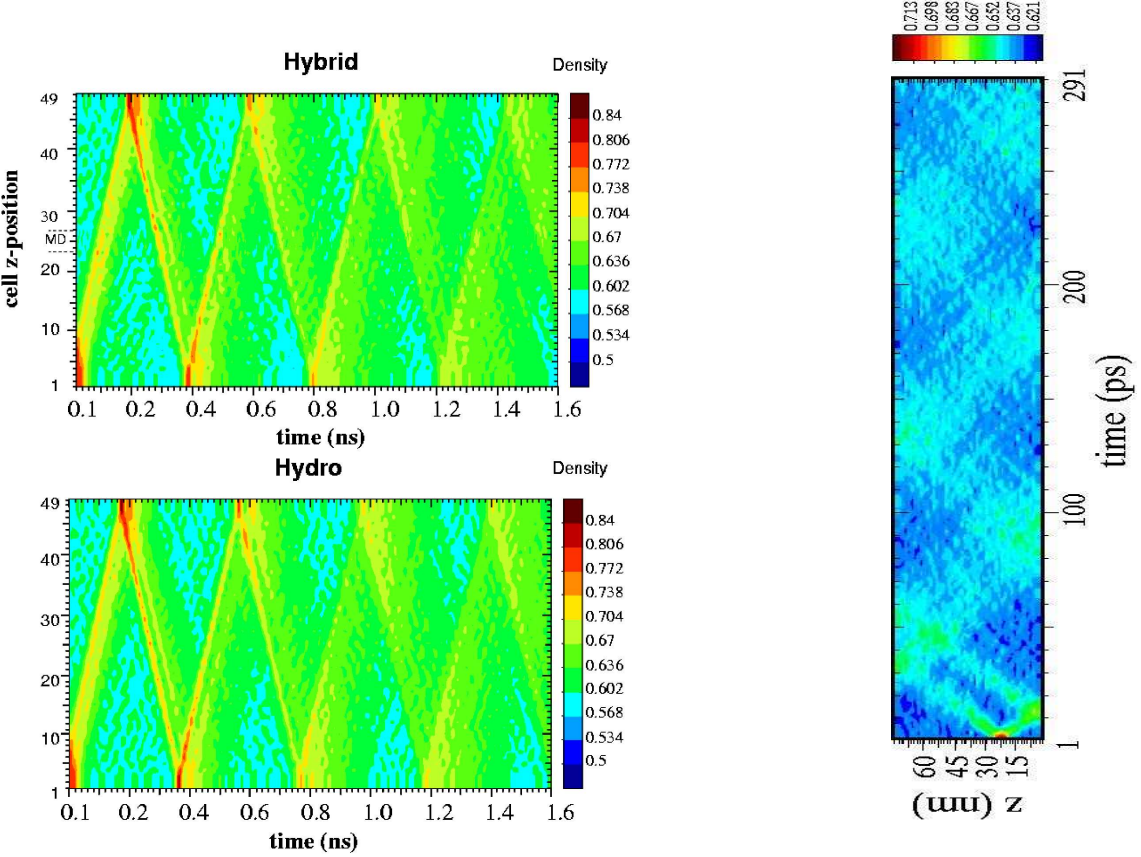


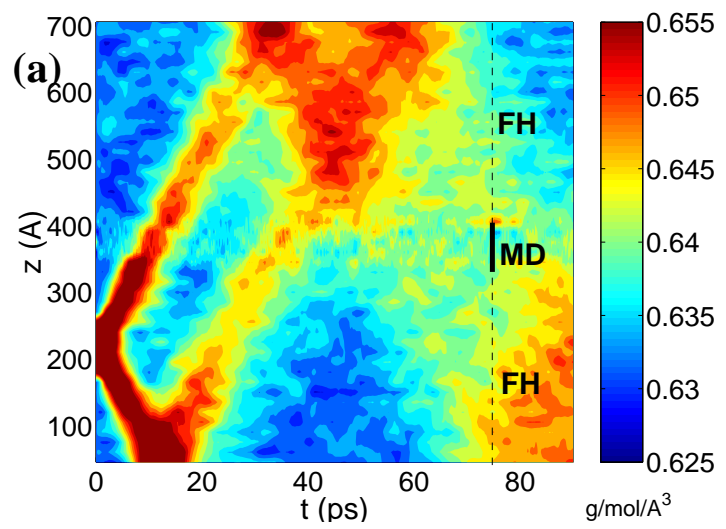
isothermal simulations: **DPD thermostat for MD** [(Dünweg et al.)]

Hybrid MD-FH under non-equilibrium: unsteady shear flow



Hybrid MD-FH under non-equilibrium: sound waves of argon and water within a closed box





Water wave reflecting against a DMPC monolayer

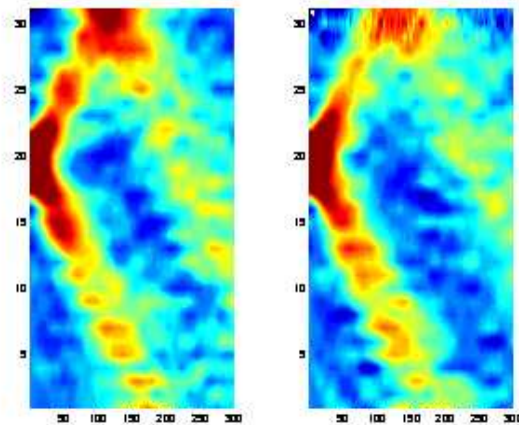
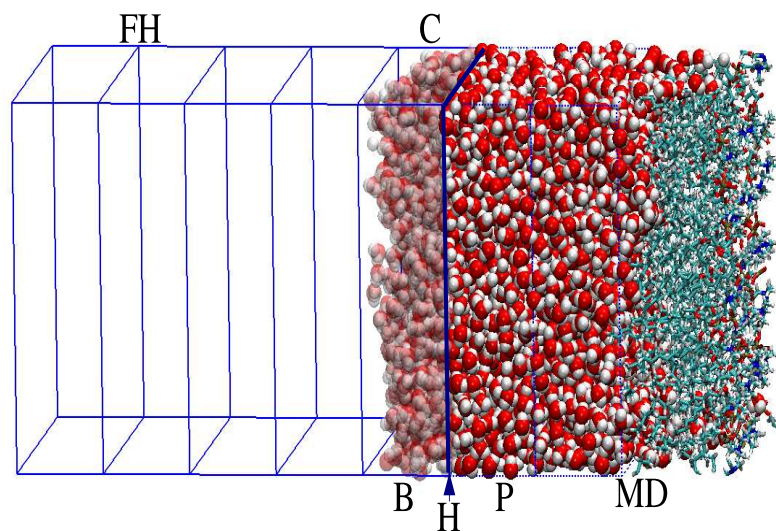


FIG. 2: Water wave.

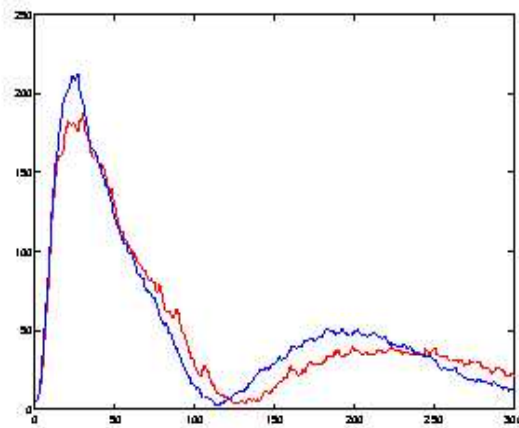


FIG. 3: Water wave.

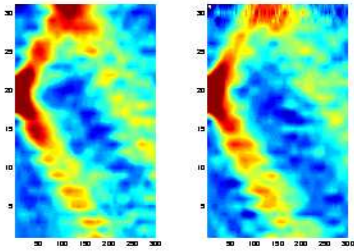
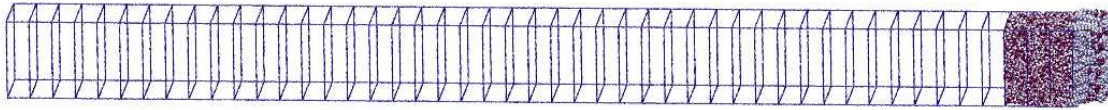


FIG. 2: Weber wave.

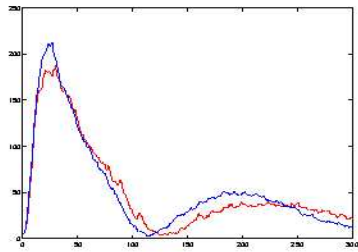
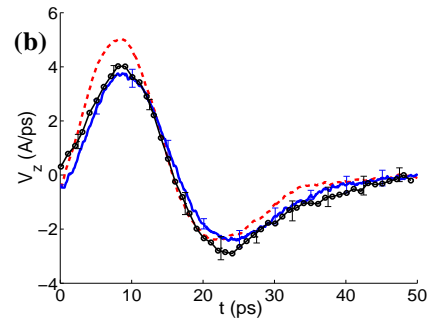


FIG. 3: Weber wave.



Conclusions

- Overview of the multiscale methods for liquid phase.
- Previous hybrid models for liquid phase were not mature enough for many problems: restricted to shear flow, deterministic continuum and Lennard Jones atoms:
- In this work we generalize the hybrid scheme for liquids and include:
 - Sound and energy (mass transport)
 - fluctuating hydrodynamics (FH)
 - Realistic MD potentials: water as solvent, complex molecules as solutes (using MINDY).

The model

- Respect 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 consistent with FH.
- **Applied problem (1):** Slippage of water over hydrophobic surfaces (DMPC monolayer); effect of including small amount of dissolved argon.
- **Applied problem (2):** Macromolecule sound interaction (resonance under high-frequency perturbation).