A multiscale link between atomistic and continuum hydrodynamics via adaptive coarse-graining.

Rafael Delgado-Buscalioni
Departamento de Fisica Teorica de la Materia Condensada Universidad Autonoma de Madrid Cantoblanco, Madrid E-28049, Spain
rafael.delgado@uam.es
Coworkers

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

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

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

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

Can a better link between atomistic modeling and continuum modeling be made via DPD, thus creating a multiscale modeling protocol?

The general frame

- **Dissipative**: random forces and friction replaced the integrated effect of removed degrees of freedom (entropy)

- **Particle**: conservative forces, fluid structure (enthalpy)

- **Dynamics**:
  - A formulation for proper particle diffusion?.
  - Local momentum conservation upon binary collisions: **Hydrodynamics**.
Scales and models
with hydrodynamics

MODELS
Continuum
Particles

fluctuating hydrodynamics
deterministic hydrodynamics

length

time

degrees of freedom (DoF)

mind the gap

Scales and models
with hydrodynamics

Continuum
Particles

fluctuating hydrodynamics
deterministic hydrodynamics

length

time

degrees of freedom (DoF)

mind the gap

- Complex fluids near interfaces: microfluidics, slip of liquid flow past surfaces.
- Fluid-fluid or soft interfaces (e.g., Rayleigh-Taylor instability, membrane’s dynamics)
- Macromolecules-sound interaction (proteins) [Science, 309:1096, 2005.]
- Crystal growth from liquid phase.
- Wetting phenomena: microscopic treatment of the wetting front. Lubrication
- Confined systems: driven to chemical equilibrium, osmosis driven flows through membranes, thin films, water between membranes, clays,
- etc...
Domain decomposition

Interfacing models with different degrees of freedom

OPEN B.C.

continuum models

particle models

degrees of freedom

Open boundary conditions:
OUTSIDE WORLD
steady state,
thermodynamic reservoir

continuum models

particle models

MD

DPD

FH

CFD
Domain decomposition
some recent works

- E. Flekkoy, RDB, P. Coveney, PRE (2005)
  - MD
  - or
  - DPD

- G. De Fabritiis, RDB, P. Coveney, PRL (2006)
  - MD
  - FH

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

- RDB, M. Praprotnik, K. Kremer JCP (2008)
  - MD
  - DPD
  - CFD

- RDB, Anne Dejoan, PRE (to appear, 2008)
  - FH
  - CFD
  - open fluctuating hydrodynamics
  - OPEN BOUNDARY
Coupling two fluid models

- exchanged conserved quantities
- hydrodynamic modes
- momentum
- mass
- energy
- shear
- sound
- heat

Interfase
Overlapping region
Matching conditions

Particle-Particle coupling

• Fluid structure: radial distribution function (RDF), angular distribution functions...

• Thermodynamics
  – Equation of state (pressure-density relation).
  – Fluctuations (mass \(\rightarrow\) grand canonical ensemble)

• Dynamics
  – Self diffusion coefficient
  – Viscosity, etc...
Matching conditions

Particle-Continuum coupling

- Fluid structure (near the interface region)

- Thermodynamics
  - Equation of state: pressure-density relation $\rightarrow$ sound.
  - Fluctuations (MD-FH)
    * Momentum $\rightarrow$ Temperature
    * Stress tensor $\rightarrow$ Consistency in Green Kubo relations
    * Mass $\rightarrow$ Grand canonical

- Dynamics
  - Viscosity, thermal diffusivity.
**Matching conditions**

**Open Boundaries**

**Objective:** Couple a finite, non-periodic simulation box to the thermodynamic and mechanical state at the outer world (*reservoir*).

- Avoid finite size effects present in periodic boundary conditions (e.g. sound loops)

- Evacuate waves out of the system (sound, heat, vortex).

- Introduce the desired amount of heat and/or work into the system \(\Rightarrow\) **generalized thermodynamic ensembles**, including thermal and velocity gradients, Joule -Thompson expansion, etc...

**References:**

- **Particle model:** Flux boundary conditions for particle simulations, E. Flekkoy, RDB, P. Coveney, *Phys. Rev. E*

- **Fluctuating hydrodynamics:** Open boundaries for fluctuating hydrodynamics, RDB, A. Dejoan, *Phys. Rev. E* (accepted)
Particle models

Dissipative particle dynamics

\[ m_i \frac{dv_i}{dt} = \sum_{i \neq j} F_{C_{ij}} + F_{D_{ij}} + F_{R_{ij}} \]

\[ F_{D_{ij}} dt = -m_i \gamma \omega^2 (r_{ij}) \hat{r}_{ij} \cdot \hat{v}_{ij} \hat{r}_{ij} dt \quad (1) \]

\[ F_{R_{ij}} dt = m_i \sigma \omega (r_{ij}) \hat{r}_{ij} dW_{ij} \]

\[ m \sigma^2 = 2 \gamma kT \]

Molecular dynamics

\[ m_i \frac{dv_i}{dt} = \sum_{i \neq j} F_{C_{ij}} + \text{(thermostats)} \]

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

MD $\rightarrow$ DPD
Coupling MD to DPD

Adaptive Resolution Scheme (AdResS)

Coupling MD to “DPD”
Adaptive Resolution Scheme for liquid water
Coupling MD to “DPD”

Adaptive Resolution Scheme

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

\[
F_{\text{atom}}^i_{\alpha j \beta} = -\frac{\partial U_{\text{atom}}}{\partial r_{i\alpha j \beta}} \quad \text{Atomistic}
\]

\[
F_{\text{c.m.}}^\alpha\beta = -\frac{\partial U_{\text{c.m.}}}{\partial R_{\alpha\beta}} \quad \text{Coarse – Grained}
\]
Coupling MD to DPD

Effective potential for c.m. interaction

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

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

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

• Small correction $\Delta U^{cm} = U_0(1 - r/r_c)$ to equilibribrate pressures.
Coupling MD and DPD
Matching liquid structure and pressure

Tetraedral fluid
\( kT = 1 \); \( \rho = 0.175 \)
Coupng MD and DPD

Dynamics: self-diffusion across interface

Position dependent Langevin thermostat

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

\[ \langle W_i(x, 0) \rangle = 0 \]

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

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

Dynamics: self-diffusion across interface

[Graph showing probability distribution with labels for coarse-grain, transition, and all-atom phases at different times.]
Coupling MD and DPD

AdResS

pros

• Reduction of degrees of freedom for the liquid outside the region of interest.

• Conserves momentum (3rd Newton Law by construction)

• Recovers the fluid structure and pressure in the coarse-grained domain

• Self-diffusion of atomistic and coarse-grained domains can be somehow matched (a first-principles theory is lacking in the literature).
Coupling MD and DPD

AdResS

cons

• It does not conserve energy $\Rightarrow$ heat transfer is not described.

• Requires substantial pre-evaluation of the effective potential $U^{cm}$ using iterative Boltzmann inversion for each fluid and thermodynamic state considered

  – Restricted to homogenous, or near equilibrium states
  – Pressure corrections using iterative Boltzmann inversion within the hybrid region might be required to obtain seamless density profiles.

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

MD / FH
General issues concerning particle-continuum coupling

Information exchanged
variables / fluxes

Time dependence
Steady / Unsteady

Fluctuations
Deterministic CFD or
Fluctuating Hydrodynamics (FH)

End of particles box
open / closed

Particle buffer B
Maxwell daemons or
External forces

Continuity at interface H
- imposed to P / imposed to C
- continuity in fluctuations
MD-CFD: **Hybrid schemes depending upon the exchanged information**

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

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

REFS: Hadjiconstantinou, Koumoutsakos

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

loop

1) Solve $P$ imposing $\phi_C$ at $\delta(P)$

2) Solve $C$ imposing $\langle \phi_P \rangle$ at $\delta(C)$

Check for convergence within $\text{PNC}$

Maxwell Daemon for velocity
Dirichlet B.C.
# Constrained dynamics .vs. velocity continuity

<table>
<thead>
<tr>
<th>Authors</th>
<th>Nie et al (MD-CFD)</th>
<th>RDB (MD-FH); Garcia (DSMC-CFD)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>velocity</strong></td>
<td>Constrained particle dynamics</td>
<td>Relaxation BC for C</td>
</tr>
<tr>
<td><strong>mass flux</strong></td>
<td>Imposed to P</td>
<td>Measured from P</td>
</tr>
</tbody>
</table>

## Constrained particle dynamics:

\[
\frac{dx^2_i}{dt} = F_i/m + \frac{1}{\tau_r} \left( v^C_B - \langle v \rangle^P_B \right)
\]

## Continuum velocity relaxation:

\[
\frac{[\Delta \rho \mathbf{v}]^C_H}{\Delta t} = [\text{Navier – Stokes}] + \frac{1}{\tau_r} \left( \langle [\rho \mathbf{v}]^P \rangle_H - [\rho \mathbf{v}]^C_H \right)
\]

**Note:** Constraining the particle dynamics affects the particle collective properties. It also destroys energy balance. Relaxation of C is simple and efficient, \( \tau_r << \tau_{\text{hydro}} \).
**MD-CFD Flux exchange**


Continuum subdomain: \( C \)
Particle subdomain: \( P \)
Particle buffer: \( B \)

Total system: \( C + P \)
Extended system: \( C + P + B \)

Conservation

\[
\Delta \phi_C = A \mathbf{J}_\phi^H \cdot \mathbf{n} \Delta t \\
\Delta \phi_P = -A \mathbf{J}_\phi^H \cdot \mathbf{n} \Delta t
\]

Conservation laws apply for the total system: \( P + C \)

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

- **Conservation law** conserved quantity per unit volume $\Phi$

\[
\frac{\partial \Phi}{\partial t} = -\nabla \cdot J^\Phi
\]

<table>
<thead>
<tr>
<th>mass</th>
<th>$\Phi = \rho$</th>
<th>$J^\rho = \rho u$</th>
</tr>
</thead>
<tbody>
<tr>
<td>momentum</td>
<td>$\Phi = g \equiv \rho u(r, t)$</td>
<td>$J^g = \rho uu + P$</td>
</tr>
<tr>
<td>energy</td>
<td>$\rho e$</td>
<td>$J^e = \rho ue + P : u + Q$</td>
</tr>
</tbody>
</table>

- **Closure relations**

  **Equation of state**

  $p = p(\rho)$

  **Constitutive relations**

  **Pressure tensor**

  $P = p1 + \Pi + \tilde{\Pi}$

  **Viscous tensor**

  $\Pi = -\eta (\nabla u + \nabla u^T) + (2\eta/3 - \xi) \nabla \cdot u$

  **Conduction heat flux**

  $Q = -\kappa \nabla T + \tilde{Q}$

  **Fluctuating heat and stress a la Landau**

  **Stress fluctuations**

  $\langle \tilde{\Pi}(r_1, t)\tilde{\Pi}(r_2, 0) \rangle = 2k_B T C_{\alpha\beta\gamma\delta}(r_2 - r_1) \delta(t)$

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

  **Heat flux fluctuations**

  $\tilde{Q}$
The finite volume scheme
Finite volume schemes for fluctuating hydrodynamics

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

\[
\int_{V_c} \frac{\partial \Phi}{\partial t} = - \int_{S_\alpha} \mathbf{J} \cdot \mathbf{d}s \\
V_c \frac{\Delta \Phi_c}{\Delta t} = - \sum_{f=\text{faces}} A_f \mathbf{J}^\phi_f \cdot \mathbf{e}_f \quad \text{(explicit Euler scheme)}
\]

| \text{mass} | \Phi = \rho | \mathbf{J}^\rho = \rho \mathbf{u} |
| \text{momentum} | \Phi = \mathbf{g} \equiv \rho \mathbf{u}(\mathbf{r}, t) | \mathbf{J}^g = \rho \mathbf{uu} + \mathbf{P} |
| \text{energy} | \rho \mathbf{e} | \mathbf{J}^e = \rho \mathbf{ue} + \mathbf{P} : \mathbf{u} + \mathbf{Q} |
Finite volume scheme

\[ J^\phi_f = \frac{J^\phi_c + J^\phi_{c+1}}{2} \]
MD-FH: \textit{hybridMD scheme}

\[ J_H^\phi = \left( \frac{J_C^\phi + J_P^\phi}{2} \right) \]

\[ \Phi_C, \Phi_P \]

\[ \text{FH} \quad \text{f-1} \quad \text{H} \quad \text{f+1} \quad \text{MD} \]
MD-FH: Local P variables

\[ J_H^\Phi = \left( \frac{J_C^\Phi + J_P^\Phi}{2} \right) \]

\[ \frac{1}{V_P} \sum_{i \in P} m_i \phi_i \]
MD-FH: Local P fluxes

\[ J_H^\phi = \frac{J_C^\phi + J_P^\phi}{2} \]

Irving-Kirwood (micro)
or
Const. relation (meso)

\[ C^{-1} \quad \phi_C \quad C \quad \phi_P \quad P \quad (P+1) \]

FH f^{-1} H f^{+1} MD
MD-FH: Imposing fluxes into MD

\[ J_H^\Phi = \frac{1}{2} \left( J_C^\Phi + J_P^\Phi \right) \]

only momentum and energy flux are imposed to \( P \)

flux correction
MD-FH: flux balance

\[ \Phi_H^f = \left( \Phi_C^f + \Phi_P^f \right) / 2 \]
MD-FH: flux balance: conservative scheme

\[ J_H^\phi = \left( \frac{J_C^\phi + J_P^\phi}{2} \right) \]

\[ \Phi C \quad -\Delta \Phi_P \quad \Delta \Phi_P \quad \Phi_P \quad \Phi_P \]

FH \quad f-1 \quad H \quad f+1

imposed (via relaxation)

measured

conservative scheme
open molecular dynamics
MD-FH **Flux boundary conditions for open MD**
Flekkoy, RDB, Coveney, PRE 72, 026703 (2005)

Energy flux $J_e$ and momentum flux $J_p$ imposed into MD across $H$

**Momentum over $\Delta t$**

$$J_p A \Delta t = \sum_{i \in B} F_{ext}^i \Delta t + \sum_{i'} \Delta (m v_{i'})$$

**Energy over $\Delta t$**

$$J_e A \Delta t = \sum_{i \in B} F_{ext}^i \cdot v_i \Delta t + \sum_{i'} \Delta \epsilon_{i'}$$

*Total input*  
*External force*  
*Particle insertion/removal*

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

**Momentum:** introduced by the mean external force $\langle F_i \rangle$

$$\langle F_{ext} \rangle = \frac{A}{N_B} \tilde{j}_p \quad \text{where} \quad \tilde{j}_p \equiv J_p - \frac{\sum_{i'} \Delta (m v_{i'})}{A \Delta t}.$$  

**Energy:** introduced by the fluctuating force $\tilde{F}_{ext}^i$ via dissipative work.

$$\tilde{F}_{ext}^i = \frac{A v_{i'}^i}{\sum_{i=1}^{N_B} v_i^2} \left[ \tilde{j}_e - \tilde{j}_p \cdot \langle v \rangle \right] \quad \text{with} \quad \tilde{j}_e \equiv J_e - \frac{\sum_{i'} \Delta \epsilon_{i'}}{A \Delta t}.$$
Molecular dynamics at various ensembles

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

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

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

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

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

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

- **Constant heat flux.** $J_e = cte$. (*melting dynamics*, growth of solid phase -ice-, heat exchange at complex surfaces...
Mass fluctuations: grand canonical ensemble

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

Flux particle BC’s are thermodynamically consistent with the Grand Canonical ensemble
MD-FH Time coupling

\[ \delta t_s \text{ sampling time} \]

\[ \Delta t_c = n_{FH} \Delta t \]

\[ \Delta t_c = n_{MD} \delta t \]

\[ \text{coupling time} \]
MD-FH Coupling time and stress fluctuations

Green-Kubo relations

• **Molecular dynamics:** decorrelation time $\tau_c \sim 100\text{fs}$ (simple liquids)

$$\langle J_{MD}^2 \rangle = \frac{\eta k_B T}{V \tau_c} \quad \text{with, } \tau_c \equiv \frac{\int_0^\infty \langle J(t)J(0) \rangle dt}{\langle J(0)^2 \rangle}$$

• **Fluctuating hydrodynamics:** decorrelation time $\Delta t/2$,

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

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

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

In general,

$$\Delta t_c = n_{FH} \Delta t = 2N_s \tau_c$$
The buffer’s tasks

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

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

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

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

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

At $B$ the FH local fluxes are transferred to the MD domain by imposing non-conservative forces $F_i$ to those particles at the buffer.

Local stress tensor at $P$ cell is obtained from MD and used as boundary condition for FH.

Fluctuating hydrodynamics region $FH$

Molecular dynamics region $MD$

Hybrid interface $H$

Particles are removed / inserted to keep the buffer filled up.

Particle insertions using the **USHER** method:
MD-CFD **Force distribution at the buffer**

Momentum flux across $H$: $\mathbf{J}_H \cdot \mathbf{e}_H$

$A_H$ is the area of the interface $H$

$$F^{ext}_i = \frac{g(x_i)}{\sum_{i \in B} g(x_i)} A_H \mathbf{J}_H \cdot \mathbf{e}_H$$

---

**Density profile**

- $\rho(x)/\rho_0$
- $x$ (normal to interface)
- Buffer
- Bulk
- $g(x)$
- $g(x_i)$
- $F^{ext}_i$

**References**

- RDB and P. Coveney, PRE (2002)
- Flekkoy et al. EPL, (2000)
- RDB et al., PRE (2007)
**USHER energy controlled molecule insertion**


- **Objective:** Insert a new molecule at target potential energy \( E_T \).

- **Method:** Newton-Raphson-like search in the potential energy landscape.
  
  Successful insertion \(|\Delta E/E_T| < 0.01\) where \( \Delta E = E_T - E_i^{(n)} \)

  \[
  \begin{align*}
  r_{cm}^{n+1} &= r_{cm}^n + \frac{F_{cm}^n}{F_{cm}^n} \delta r \\
  r_{cm,i}^{n+1} &= R_{\delta \theta}^{(n)} r_{cm,i}^n \\
  \delta r &= \min(\Delta E/F, \Delta R_{max}); \\
  \Delta R_{max} &\sim \text{half distance of first peak of radial distribution} \\
  \delta \theta &= \min(\Delta E/\tau, \Delta \Theta_{max}) \\
  \text{the maximum rotation allowed is } \Delta \Theta_{max} &\sim 45^\circ
  \end{align*}
  \]

  **Translation** of the centre of mass along force direction \( F \)

  **Rotation** around the torque axis: (water)

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

  **Negligible insertion cost:**
  
  - LJ particles \((\rho < 0.85)\) \(< 1\% \text{ total CPU}\)
  - Water into water \(\sim 3\% \text{ total CPU}\)

  Insertions done at the mean energy/molecule contribution \( E_T = 2U_{eos} \)
**USHER:** fast and controlled particle insertion


Applications: Constant chemical potential simulations, unfolding of proteins via water insertion (Goodfellow), water insertion in confined systems (e.g. proteins).
MD-FH Setup for tests

Water against a lipid layer at $T = 300K$
[G.Fabritiis, RDB, Coveney PRL, 97 (2006)].
Equation of state $p = p(\rho)$ for argon and water TIP3P, $T = 300K$ [G.Fabritiis et al. PRE, 76 (2007)].

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

**argon (LJ) water (TIP3P)**
MD-FH Velocity and stress fluctuations

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

STD Stress tensor components

STD velocity

position

STD velocity

position
MD-FH Density fluctuations

Standard deviation of density argon at several densities, $T = 300K$

RDB and G. Fabritiis et al. PRE, 76 (2007)
**MD-FH Shear flow**

viscosity calibration
hybridMD as a rheometer

\[ \gamma_{MD} \eta_{MD} = \gamma_{FH} \eta_{FH}^{(guess)} \]

Couette flow
steady solution

- \( y = -0.00810 + 0.004649 z \)
- \( y = -0.18874 + 0.006546 z \)
- \( y = -0.27141 + 0.006607 z \)
MD-FH Unsteady shear

Start-up Couette

Oscillatory shear

Stokes flow

Lennard-Jones fluid

Finite Volume method

Oscillatory wall

P CP

C

Hybrid

Hydro

Cell position, z-direction

time (ns)

y velocity (σ/τ)

x (σ)

Stokes flow

P

PC CP

C

Finite Volume method

Oscillatory wall

P CP

C

Stokes flow

Lennard-Jones fluid

Finite Volume method

Oscillatory wall

P CP

C

Finite Volume method

Oscillatory wall
MD-FH Sound waves

liquid argon

water

(a)
MD-FH Sound waves: time resolution $\sim 0.02 \text{ ns}$
MD-FH Sound - (soft) matter interaction

particle - particle-continuum

MD DPD CFD
MD-DPD-CFD

Triple scale coupling


General motivation

Complex molecules

• Technical issues
  – Generalize the (MD-DPD) AdResS scheme to include hydrodynamics
  – Solve the insertion of larger molecules in hybridMD

• Applications
  – Phenomena involving flow-matter interaction at multiple length scales
    complex fluids near surfaces, lubrication, macromolecules in flow,...
  – Grand canonical molecular dynamics involving complex molecules
    confined systems
MD-DPD-CFD Two possible setups


Homogeneous (CG) buffer

Heterogeneous model buffer
MD-DPD-CFD: Two possible setups


• **Homogeneous buffer**
  - **con:** Requires fine tuning of CG model
    - *Viscosity* or molecular diffusion coefficient
    - *Equation of state*
  - **pro:** Requires smaller buffer size
  - **pro:** Permits to introduce CG molecular information into the MD (explicit) region (structure, diffusion rates, etc...)

• **Heterogeneous buffer**
  - **con:** Larger buffer size
  - **pro:** The P-cell is fully atomistic (correct viscosity, EOS, fluctuations)
  - **pro:** Does not requires fine tuning of CG model and hyb models
MD-DPD-CFD: **Shear flow**

**Heterogeneous buffer**

high density tetraedral liquid under shear
density and velocity profiles
MD-DPD-CFD: **Shear flow**

*Homogeneous buffer*

High density tetraedral liquid under shear density and velocity profiles

![Graph showing velocity profiles](image)
MD-DPD-CFD: Equilibrium

liquid structure around the hybrid interface

Radial distribution function
high density tetraedral liquid
MD-DPD-CFD: **Equilibrium: grand canonical**

**Mass fluctuations**

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

<table>
<thead>
<tr>
<th>( \rho )</th>
<th>simulation</th>
<th>Grand canonical</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.2</td>
<td>0.17</td>
</tr>
<tr>
<td>0.175</td>
<td>0.1</td>
<td>0.07</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Coarse Grained</th>
<th>hyb</th>
<th>atomistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.9</td>
<td>14.2</td>
<td>14.5</td>
</tr>
</tbody>
</table>
MD-DPD-CFD: Unsteady flows

Start Couette flow

(a) 

(b)
MD-DPD-CFD: **Unsteady flows**

**Stokes flow (oscillatory shear)**

\[ \begin{align*}
\text{cell #5} & \quad \text{cell #6} \\
\text{cell #8} & \quad \text{cell #10}
\end{align*} \]
MD-DPD-CFD: **Unsteady flows**

**Diffusive delay in long buffers**

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

• Multiscale modeling based on domain decomposition

• Coupling across scales:
  - MD-DPD
    * Proper coarse-grained structure and pressure
    * Diffusive (mass) transport at mesoscale can be (to some extent) matched
  - MD-continuum hydrodynamics; MD-Fluctuating hydrodynamics.
    * Sound, heat and energy transfer
    * Open molecular dynamics (grand canonical \( \mu VT \) and other ensembles)
  - Triple scale model: MD-DPD-continuum
    * Coarse-grained (DPD like) intermediate model
    * Proper hydrodynamics on shear and isothermal sound transport (not heat)
    * Solves insertion of complex molecules in hybrid schemes
Some key authors on the subject

- **MD-DPD**
  - M. Praprotnik, L. Delle Site, K. Kremer

- **MD-continuum hydrodynamics**
  - DSMC-CFD: A. Garcia, F. Alexander, B. Alder (AMAR)
  - MD-CFD: E. Flekkoy, Koumoutsakos, Hadjiconstantinou, M. Robbins, Nie, S. Yip
  - MD-FH: G. De Fabritiis, P. Coveney, Delgado-Buscalioni

- **Triple scale model: MD-DPD-continuum**
  - Delgado-Buscalioni, M. Praprotnik, K. Kremer