Multiscale simulation of complex fluid flow using coupled models

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

- Complex fluids near interfaces: microfluidics, slip of liquid flow past surfaces.
- Fluid-fluid or soft interfaces (e.g., Rayleigh-Taylor instability, membrane’s dynamics)
- 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
Scherzzo
Zaubern

τεχνασμα = technasma
Multiscale modelling
for different states of matter

<table>
<thead>
<tr>
<th>SOLIDS</th>
<th>QM-MD</th>
<th>PRL 93, 175503 (2004)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MD-FD</td>
<td>PRL 87(8),086104 (2001)</td>
</tr>
<tr>
<td></td>
<td>QM-MD-FD</td>
<td>Abraham</td>
</tr>
<tr>
<td>GASES</td>
<td>DSMC-CFD</td>
<td>AMAR [A. Garcia]</td>
</tr>
<tr>
<td></td>
<td>MC-CFD</td>
<td>Deposition (crystal growth from vapour phase) PRB, 64 035401.(2001)</td>
</tr>
</tbody>
</table>

LIQUIDS
- Domain decomposition: MD-CFD, MD-FH
- Eulerian-Lagrangian: MD-LB, MD-FH
- Velocity-Stress coupling: MD-SMFD, MD-FD

Acronyms

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


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.

<table>
<thead>
<tr>
<th>Molecular region</th>
<th>localized</th>
<th>in bulk</th>
<th>concentrated solution or melt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Best method</td>
<td>Domain decomposition</td>
<td>Eulerian-Lagrangian hybrid: Stokes force coupling</td>
<td>Velocity-Stress mesh coupling</td>
</tr>
<tr>
<td>applications</td>
<td>interfaces, surfaces, single macromole-fluid interaction</td>
<td>hydrodynamics of semidilute solutions</td>
<td>Highly non-Newtonian fluid flow</td>
</tr>
</tbody>
</table>

- **Continuum fluid dynamics**
- **Explicit solvent-solute interaction**
- **Particles: MD**
- **Continuum: LB or FH.**
- **Fluctuations in C model needed.**

**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.
Mulsticale models based on domain decompositon.

General issues concerning hybrid models

continuum fluid dynamics

C boundary condition

Information exchanged between domains? variables or fluxes of variables?

How to treat the end of the particle system P open or closed?

How to impose BC to the particle system. Continuity across P and C (mean variables, fluxes, fluctuations)

How to deal with fluctuations from P to C Local spatio-temporal particle averages. C model: deterministic or stochastic?

Steady or unsteady flow?
## Hybrids based on domain decomposition

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

*(Note: ...via relaxation)*
**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: only valid for incompressible flow with **no** mass exchange across the interface.

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

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

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

Check for convergence within PNC.
The Flux coupling scheme

Previous flux based schemes

Continuum subdomain: C
Overlapping region: ?
Particle subdomain: P

Flux continuity

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

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

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 $\Delta t$.
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**

At the **PC** cell the coarse-grained particles local fluxes are transferred to the C-boundary cell. At the buffer **B** the continuum local fluxes are transferred to the particle system imposing non-conservative forces $F_i$ to the buffer particles.

- **P**: molecular dynamics region
- **C**: continuum hydrodynamics region
- **H**: hybrid interface

13
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.

\[
\frac{dN_B}{dt} = \frac{1}{\tau_B} (\alpha N_C P - N_B)
\]

with \( \tau_B \simeq [10 - 100] \text{fs} \) (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


(water)

![Graph showing the number of insertion trials versus potential energy](image)

**Number of insertion trials (or iterations) required to insert a water molecule in water, at a potential energy E**

- **Random insertion**
- **USHER algorithm for water**

**Insertion process at constant energy per particle**

---

- **Dashed line thermodynamic analytical solution (Lennard-Jones fluid)**
- **Average potential energy per molecule at 300K**
- **Water chemical potential at 300K**

**Density increases with time, dρ/dt = 0.01 σ⁻³ s⁻¹**
**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.


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 \( H \):

\[
J^H_\phi = \left( J^{CP}_\phi + J^{PC}_\phi \right) / 2
\]

**Objective.** Evaluate \( J^{PC}_\phi \) (with \( \phi = \{p, e\} \) average flux at the PC cell over \( \Delta t \)).

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

\[
\langle J^P_p \rangle = \langle m_i v_i v_i - \frac{1}{2} \sum_j^N r_{ij} F_{ij} \rangle \\
\langle J^P_e \rangle = \langle m_i \epsilon_i v_i - \frac{1}{2} \sum_j^N r_{ij} v_i F_{ij} \rangle
\]

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

Using the averaged variables \( \Phi_P = \sum_i \chi_P(r_i) \phi_i \) (total \( \phi \) at PC cell) where \( \chi_P \) is the characteristic function of the cell \( P \), i.e. \( \chi_P(r) = 1 \) if \( r \in P \) and 0 otherwise.
On how macro talks to micro:

\[ C \rightarrow P \]


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

**Method:** By adding an external force \( F_i \) to the particles at the \( B \) reservoir.

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

\[
\begin{align*}
\text{Momentum} & : \quad J_p A \Delta t = \sum_{i \in CP} F_i \Delta t + \sum_{i'} \Delta (m v_{i'}) \\
\text{Energy} & : \quad J_e A \Delta t = \sum_{i \in B} F_i \cdot v_i \Delta t + \sum_{i'} \Delta \epsilon_{i'}
\end{align*}
\]

where \( A \) is the \( H \)-interface area and the index \( i' \) runs only over added/removed particles during \( \Delta t \).
On how macro talks to micro: $C \rightarrow P$ (cont.)

**Decomposition of the external particle force:** $F_i = F + F'_i$

The mean value $\langle F_i \rangle = F$ provides the desired input of momentum

$$F = \frac{A}{N_B} \tilde{j}_p \quad \text{where} \quad \tilde{j}_p \equiv J_p - \sum_{i'} \frac{\Delta (m v_{i'})}{A \ dt}.$$  \hspace{1cm} (1)

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

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


**Amount of heat and work into the MD system is exactly controlled.**

**Enabling**

- **Grand-canonical ensemble.** $\mu VT$. Where $\mu = \mu(p^C, T^C)$ is the chemical potential at the reservoir B.
- **Isobaric ensemble** NPT. $J_p = pn$.
- **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)
- **Constant heat flux.** $J_e = cte$. (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: \(\text{Grand-Canonical ensemble}\)

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

\[
\text{Grand Canonical ensemble: } \text{Std}[\rho] = \left[ \rho k_b T / (V c_T^2) \right]^{1/2}, \text{ where } c_T^2 = (\partial P / \partial \rho)_T
\]
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?

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

(a) Constrained dynamics: \[ \frac{dx_i^2}{dt} = \frac{F_i}{m} + \frac{1}{\tau_r} \left( v_C^{CP} - \langle v \rangle_P^{CP} \right) \]

(b) Relaxation of first C cell: \[ \frac{[\rho v]_C^{CP}}{dt} = NS + \frac{1}{\tau_r} \left( \langle [\rho v]^P \rangle_{CP} - [\rho v]_C^{CP} \right) \]

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.**

<table>
<thead>
<tr>
<th>Fluid</th>
<th>$V_{PC}$</th>
<th>$T$</th>
<th>$\eta$</th>
<th>$\text{Var}[j_{xy}^P]$</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>WCA</td>
<td>81</td>
<td>1</td>
<td>1.75</td>
<td>0.51</td>
<td>0.60</td>
</tr>
<tr>
<td>WCA</td>
<td>173</td>
<td>1</td>
<td>1.75</td>
<td>0.40</td>
<td>0.41</td>
</tr>
<tr>
<td>WCA</td>
<td>138</td>
<td>1</td>
<td>1.75</td>
<td>0.33</td>
<td>0.38</td>
</tr>
<tr>
<td>WCA</td>
<td>338</td>
<td>1</td>
<td>1.75</td>
<td>0.25</td>
<td>0.24</td>
</tr>
<tr>
<td>WCA</td>
<td>2778</td>
<td>1</td>
<td>1.75</td>
<td>0.08</td>
<td>0.06</td>
</tr>
<tr>
<td>WCA</td>
<td>2778</td>
<td>1</td>
<td>1.75</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>LJ</td>
<td>121.5</td>
<td>4.0</td>
<td>2.12</td>
<td>1.09</td>
<td>1.08 (1.19)</td>
</tr>
<tr>
<td>LJ</td>
<td>121.5</td>
<td>2.0</td>
<td>1.90</td>
<td>0.66</td>
<td>0.72 (0.71)</td>
</tr>
<tr>
<td>LJ</td>
<td>121.5</td>
<td>1.0</td>
<td>1.75</td>
<td>0.39</td>
<td>0.49 (0.43)</td>
</tr>
</tbody>
</table>

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).

\[ \frac{\partial}{\partial t} \begin{pmatrix} \text{Variables, } \Phi \\ \rho \\ \rho u \\ \rho e \end{pmatrix} = -\nabla \begin{pmatrix} \text{Fluxes, } J \\ \rho u \\ \rho \alpha u + \Pi \\ \rho \alpha e + \Pi : u + Q \end{pmatrix} - \nabla \begin{pmatrix} \text{Fluctuations, } \tilde{J} \\ 0 \\ \tilde{\Pi} \\ \tilde{Q} \end{pmatrix} \]

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

\[ \frac{d}{dt} \int_{V_k} \phi(x, t) \, dx = \sum_l A_{kl} J_{ kl}^\phi \cdot e_{kl}, \]
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,

$$dM^t_k = \sum_l g_{kl} \cdot e_{kl} A_{kl} dt,$$

$$dP^t_k = \sum_l \left[ \frac{\Pi_l}{2} \cdot e_{kl} + g_{kl} \cdot e_{kl} v_{kl} \right] A_{kl} dt + d\tilde{P}^t_k,$$

where $g_{kl} = \frac{1}{2}(\rho_k + \rho_l) \frac{1}{2}(v_k + v_l)$.

Discretization of the gradients satisfying the fluctuation-dissipation theorem.

$$\Pi^{\alpha\beta}_k = \eta_k V_k \sum_l \left[ \frac{1}{2} A_{kl} (e_{kl}^{\alpha} v_l^{\beta} + e_{kl}^{\beta} v_l^{\alpha}) - \frac{\delta^{\alpha\beta}}{D} A_{kl} e_{kl}^{\gamma} v_l^{\gamma} \right],$$

$$\pi_k = \frac{\zeta_k}{V_k} \sum_l \frac{1}{2} A_{kl} e_{kl}^{\beta} v_l^{\beta}.$$

The fluctuating component of the momentum is

$$d\tilde{P}^t_k = \sum_l \frac{1}{2} A_{kl} \left( 4 k_b T_l \eta_l V_l \right)^{1/2} d\tilde{W}_{l}^S \cdot e_{kl} + \sum_l \frac{1}{2} A_{kl} \left( 2 D k_b T_l \zeta_l V_l \right)^{1/2} \frac{tr[dW_l]}{D} e_{kl},$$

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

27
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

![Diagram showing the x-velocity over time for Hybrid and Hydro simulations.](image)

The plots display the x-velocity over time for different simulations. The equation $y = -0.009043 + 0.0003012 z$ is also provided, indicating a trend in the data.
Hybrid MD-FH under non-equilibrium: sound waves of argon and water within a closed box
Water wave reflecting against a DMPC monolayer
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).