INTERFACE DYNAMICS OF MODEL SYSTEMS:
FROM LOCAL PROPERTIES TO BOUNDARY CONDITIONS

Guillaume Galliero, LFCR, Pau University, France

Collaborators :
H. Hoang, H. Si Hadj Mohand, LFCR, Pau Univ.
D. Legendre, IMFT, Toulouse Univ.

Workshop on Modeling and Simulation of Interface Dynamics
IMS - Singapore

16th May 2018
Quantifying accurately **Multiphase Fluid Dynamics** in porous medium is crucial for the Petroleum Engineering.

Various tools are available for that purpose but most of them are limited when employed to deal with “new” systems:

- **Complex resources**: Sour/Acid Gases, Shales gas/oil ...
- **Complex conditions**: Extreme HP/HT, Tight reservoirs ...
- **Complex recovery methods**: Smart Water, Polymer Flooding ...

Data and more physically based models are required.

*But experiments are hard to achieve (HSE, HP ...)*
METHODODOLOGY
**FROM NANO TO GIGA-SCALE: DIFFERENT TOOLS**

The choice is guided by time/length scales

*Direct or Indirect Coupling between scales/tools is possible*

Adapted from Gubbins & Moore, IECR (2010)
Our Group Strategy

Develop/use molecular simulations codes to study/quantify finely fluid behavior at interfaces at the nanoscale

Thermophysical properties
Tension, Diffusion ...

Physical mechanisms
Transport, Osmosis ...

Direct/indirect upscaling
Boundary conditions ...
INTERFACE DYNAMICS: ISSUES IN A SIMPLE SYSTEM
INTERFACE DYNAMICS AT THE NANOSCALE

E.g.: A nanodroplet of a simple fluid moved by body forces on a perfectly flat and rigid surface

Fluid Inhomogeneities?
(Local density/viscosity ?)

Viscous stress
(Slip ?)

Uncompensated Young Tension
(Dynamic microscopic angle?)

Viscous stress
(Boundary Conditions)

\~5 \text{ nm}
Fluid Inhomogeneities?
(Local density/viscosity ?)
LOCAL FLUID TRANSPORT PROPERTIES IN INHOMOGENEOUS FLUIDS

H. HOANG, G. PIJAUDIER-CABOT (LFCR) AND F. MONTEL (TOTAL)

**Fluid Inhomogeneities Issues**

At solid interfaces, fluids are strongly inhomogeneous (SFA, DFT ...)

⇒ Spatially variable viscosity?

Couette like simulations of a simple fluid (LJ) in a nanoslit

Density of a “oil” drop in a nanopore

Density profiles

~5 nm
The local viscosity computed by MD cannot be deduced from the local thermodynamic variables alone ($T$ and $\rho$)

There are non local effects

---

Hoang & Galliero, PRE (2012)
Using the microscopic formulation of the momentum flux, shear viscosity is decomposed in two parts: $\eta = \eta_t + \eta_c$

Translation  Collisions

To introduce non-local effects, $\eta_c$ is assumed to be a function of the density averaged over a typical length.

$\eta(x) = \eta_0 \left( \frac{\rho(x)}{\rho_{\text{bulk}}} \right)^\alpha + \eta_c \left( \overline{\rho(x)} \right)$

with e.g. $\overline{\rho(x)} = \frac{1}{\sigma} \int_{-\sigma/2}^{\sigma/2} \rho(x+s) \, ds$

This method can be more accurate using more evolved weight functions and a perturbation scheme.

Non local viscosity is well modeled by the simplest DFT

Effective viscosity can multiplied by an order of magnitude relatively to the bulk

Can be combined with DGT/DFT to introduce fluid inhomogeneities...

Hoang & Galliero, PRE (2012)
TO SHEAR AT FLUID-FLUID INTERFACES ...

Viscous stress
(Slip ?)
VELOCITY SLIP AT FLUID-FLUID INTERFACES

M. BUGEL, J.P. CALTAGIRONE (I2M, BORDEAUX, FRANCE)

The partial slip (Navier B.C.) at fluid-solid interfaces is well known, but what about Fluid-Fluid interfaces?

Slip is known to occur at polymer-polymer interfaces.

Hybrid and MD simulations of Fluid-fluid interfaces under shear.
Hybrid MD-CFD simulations

Coupling on primary variables ($v$, $T$)

Schwartz alternating method

At the liquid-gas interface a partial slip seems to occur!
Phase I & II have the same properties but are weakly miscible ($\varepsilon_{12} = k_{ij}\varepsilon$, with $k_{ij} < 1$)

The velocity profile exhibits a “jump” at the interface

Galliero, PRE (2010)
The partial slip increases with the interfacial tension

The interfacial viscosity is lower than the one deduced from ρ profile (DGT?)

In a water wet nanopore (10 nm) the theoretical oil relative permeability is roughly two times higher when the partial slip is taken into account

Interfacial self-diffusion is probably inversely proportionally increased ...
Young tension at the contact line ...

Uncompensated Young tension
(Dynamic microscopic angle?)
CONTACT LINE DYNAMICS: (NANO?) DROPLETS SPECIFICITIES

H. HOANG (LFCR), S. DELAGE-SANTACREU (LMAP, PAU, FRANCE)

R. LEDESMA, D. LEGENDRE (IMFT, TOULOUSE, FRANCE)

Hoang et al., in preparation
**Young Stress Issues**

Young stress occurs at the Contact Line but is it valid at the nanoscale?

MD simulations of nanodroplets on a perfectly flat and rigid surface.

**Equilibrium**

**Dynamic (external force)**

Lennard-Jones 2D droplets on LJ CFC solid surface for $0.4\pi < \theta < 0.85\pi$
EQUILIBRIUM: YOUNG TENSION (1/2)

At the contact line the (integrated) shear stress is macroscopically equal to the Young tension i.e. $\gamma \cos(\theta(z))$

$$\sum_{Int}(z) = \int_{x_{Int}^L}^{x_{Int}^R} \tau_{zx}(x, z) dx$$

Irving-Kirwood/Method of Plane

At equilibrium, shear stress is localized at the Liquid Vapor interface and decreases when $z$ increases (consistent with Young tension)
**EQUILIBRIUM: YOUNG TENSION (2/2)**

How shear tension $\sum_{Int}(z) = \int_{x_{Int}}^{x_{R}} \tau_{zx}(x,z)dx$ compares to Young tension?

Shear minus Young tensions ($\theta \approx 0.85\pi$)

Shear minus Young tensions ($\theta \approx 0.4\pi$)

But Young stress = shear stress at liq/vap interface above $z_\gamma \sim$ some molecular sizes ($z_\gamma$ scales with $\theta^{-1}$)

Shear tension at the contact line differs from $\gamma\cos(\theta)$!
DYNAMICS: SHEAR/YOUNG TENSION ($\theta_{Eq} = \pi/2$)

Young tension is compared with shear tension at different $z$ and different $Ca$ ...

Even out of equilibrium
Shear tension=Young tension above $z \approx 5$!

The influence of $Ca$ on shear tension is not negligible

CL dynamics (at $z>5$) driven by
$\gamma[\cos (\theta_{NE})-\cos(\theta_{Eq})] + \text{viscous stress } (\propto Ca)$

Consistent with Qian et al. PRE 2003, Ren and E, PF 2007
The problem becomes more complex when an adsorbed layer (macromolecules) occurs ...

How upscaling MD results when dealing with wetting case (thin films ...)?
To Boundary Conditions
LIQUID-LIQUID NANOÇOUETTE FLOW: WHICH BOUNDARY CONDITIONS?

H. HOANG H. SI HADJ MOHAND (LFCR)

D. LEGENDRE (IMFT, TOULOUSE, FRANCE)
There exists many CL boundary conditions options but which one is the most appropriate when all scales are solved?

Seminal works of Robbins, Koplik, Qian, Ren ...

Comparison between CFD and MD simulation on a liq-liq Couette flow

Phase I & II (Lennard-Jones fluids) have the same properties but are non miscible
Navier-Stokes (NS) Equations + Volume Of Fluids (VOF, interface) 

Equilibrium angle: $\theta_Y = \pi/2$

---

**CFD MODELS (JADIM)**


Used slip length model (Navier): $U_w \cdot V = \left. \frac{U}{n_w} \right|_{\text{w}}$ where $\lambda = 1.63 \sigma$

**Tested dynamic angle models:**

Static: $\theta_d = \theta_Y$

Generalized Navier BC (GNBC*): $\cos \theta_Y \cos \theta_d = \frac{U_{cl}}{B_{cl}}$

Molecular Kinetic Theory (MKT**): $\cos \theta_Y \cos \theta_d = \frac{U_{cl}}{\frac{v}{3} \exp \left( \frac{(1+\cos \theta_Y)}{nk_B T} \right)}$

Mesh size < Slip length

---

*Qian et al. PRE (2003), Ren and E, PF (2007), **Blake and co-workers*
NS Simulation – GNBC model
with normalized friction $B_{cl}=3.02$

NS Simulation – MKT model
with normalized friction $f=14.3$

Unstable case: the MKT “friction” is too large
VOF-NS VERSUS MD: PREDICTIONS

No Contact Line model seems to be fully predictive when combined with VOF-NS.

Too much slip

Slip is modified by friction

<table>
<thead>
<tr>
<th>NS - Static model</th>
<th>NS – GNBC model (friction $B_{cl}=3.02$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Graph 1" /></td>
<td><img src="image2.png" alt="Graph 2" /></td>
</tr>
<tr>
<td><img src="image3.png" alt="Graph 3" /></td>
<td><img src="image4.png" alt="Graph 4" /></td>
</tr>
</tbody>
</table>
NS+VOF describes well this nanoflow when all scales are solved

If adjusted, all CL models yield reasonable results!
OUTCOMES
OUTCOMES

✓ Shear viscosity can be variable in space at the Contact Line
  o Non locals effects on viscosity occur close to a solid surface
  o Interfacial region may lead to apparent fluid-fluid slip

✓ Macroscopic laws are very robust in liquids if all scales are solved
  o Uncompensated Young tension dominant at the CL (but at z>0)
  o For Liq-Liq Couette flow, CL models works well when fitted

And for future works ...

Include non local density/viscosity .... introduce upscaling ...
Acknowledgments
Pau University
CNRS
And TOTAL
All colleagues collaborating

THANK YOU FOR YOUR ATTENTION!
EXTRAS
MOLECULAR SIMULATIONS: WHAT FOR?

Molecular Model
Force Fields

Molecular Simulations
MC,MD

“Exact” emerging properties/fields
$\gamma$, $\theta$, $P_c$, $k$, $\eta$, $D$, $V$ ...

Test/Development of Theories
✓ Boundary conditions
✓ Confinement effects
✓ Wettability ...

Pseudo-experimental Data
✓ Contact angles
✓ Diffusion coefficients
✓ Slip length ...

Boundary conditions
Confinement effects
Wettability
Contact angles
Diffusion coefficients
Slip length
Molecular Simulations: How It Works?

A set of $N$ interacting particles

Molecular Dynamics (Temporal evolution)

10$^5$-10$^7$ timesteps ($\Delta t \approx 1$ ns)

Monte Carlo (Statistical evolution)

$n (\approx 10^6$-10$^8$) configurations

$X$ a physical property

Average over configurations

$\langle X \rangle_{MC} = \frac{1}{n} \sum_{i=1}^{n} X_i$

Average over time

$\langle X \rangle_{MD} = \frac{1}{\Delta t} \int X(t) dt$

Ergodic Theorem

$\langle X \rangle_{MC} = \langle X \rangle_{MD}$

No assumption concerning the physical phenomena that may emerge!
At a time step $t$ each centre of forces (atom or molecule) is characterised by its position $r(t)$, its velocity $v(t)$ and its acceleration $a(t)$.

**Newton’s Equation + Effective interaction potentials ($V$)**

$$ \sum_j F_{ij} = m_i \frac{dv_i}{dt} $$

$$ F_{ij} = - \frac{\partial V}{\partial r_{ij}} \hat{r}_{ij} $$

**New position at $t + \Delta t$ (various integrator)**

$$ p_i(t + \Delta t) = p_i(t) + (\Delta t)v_i(t) + \frac{1}{2}(\Delta t)^2 \frac{P_i(t)}{m_i} $$

**Explicit Scheme, “easily” parallelised (domain decomposition)**

Computation time $\propto N^2$ (can be reduced to $N \log N$)

**Quasi-experimental process (data with error bars ...)**
FORCE FIELDS: THE CORE OF THE PROBLEM

From hard-sphere representation to a full atom (ab initio) description, but no ideal model

The choice is guided by the goal (pseudo-experimental vs understanding)

Dispersive/repulsive interactions: usually a Lennard-Jones pot. but Mie/Exp pot. are used

\[ U_{LJ} = 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right) \]

Polar interactions: isotropic or point charges

Internal degrees of freedom: Bonding, Flexion ...

Mixtures: Combining rules (Lorentz-Berthelot ...)
**How computing macroscopic quantities?**

All physical properties are “mesurable” *in the ad hoc ensemble*

---

**Equilibrium/Thermodynamic properties**

\[
P = \frac{1}{3V_c} \left( 2E_c + \left\langle \sum_{i=1}^{N} \sum_{j>i}^{N} F_{ij} \cdot r_{ij} \right\rangle \right)
\]

\[
\gamma = \int_{x_1}^{x_2} \left( P_N(x) - P_T(x) \right) dx
\]

*Sound velocity, ...*

**Dynamic properties**

The property is deduced from the fluctuations (*Equilibrium*)

A flux is imposed (heat, momentum, ...) and the response is measured (*Non-Equilibrium*)

---

**Field properties**

The strain, velocity, temperature, pressure, concentration ... fields are deduced from averages (over time or ensemble)
Extensive Molecular Dynamics simulations on well controlled Vapor/Liquid/Solid systems

Sessile Lennard-Jones droplets on a CFC flat rigid LJ solid

Variable wetting properties
Lennard-Jones interactions

\[ U = 4C \varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \]

Fluid-Fluid: C=1; Fluid-Solid: C =0.25-0.55

Static and migration under external force configurations

Static nanodroplet

Moving nanodroplet
The Contact angle is determined by a circle fit
(using Gibbs dividing surface and extrapolated at z=0.5)

The contact angle is proportional to fluid-solid interactions
Consistent with literature

The contact angle is weakly size dependent (here R ~ 5nm)
**EQUILIBRIUM: YOUNG-LAPLACE EQUATION (1/2)**

When a **curved fluid-fluid interface** is present a **pressure (capillary) difference** between the fluids exist.

\[ P_{\text{Liq}} - P_{\text{Vap}} = \frac{\gamma_{LV}}{R} \]

Young-Laplace Eq.

But what occurs at the nanometer scale?

As well known \( P_z = \text{cst} \) everywhere but not \( P_x \) (cf. \( \gamma = \int (P_z - P_x) \, dz \))

---

Vapor pressure profile (\( \theta \approx \pi/2 \))

Liquid pressure profile (\( \theta \approx \pi/2 \))
From *liquid/vapor interfaces simulations* one can *compute surface tension* $\gamma$

$$\gamma_{LV} \approx 0.6$$

And from the *droplet normal pressure* $\Rightarrow R \left( P_{z,Liq} - P_{z,Vap} \right) \approx 0.6$

Young-Laplace equation, $\gamma_{LV} = R \Delta P$, is well respected for such nano-droplets *(using normal pressure)*

$\Rightarrow$ *The curvature correction to $\gamma_{LV}$ (Tolman’s length) is negligible!*

In 3D droplets, line tension is negligible as well ... *(works of Bresme ...)*
**EQUILIBRIUM: YOUNG-DUPRÉ LAW (1/2)**

At the **contact line** the three (Sol/Vap, Sol/Liq and Liq/Vap) tensions compensate each others

From the computation of all three $\gamma$, the Young angle can be estimated

$$\theta_Y = \cos^{-1}\left(\frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}\right)$$

Young angle, $\theta_Y$, is not equal to the measured angle at $z=0.5$!
**EQUILIBRIUM: YOUNG-DUPRÉ LAW (2/2)**

Is there a distance from the solid surface at which $\theta_{YD} = \theta$, i.e. macro angle = micro angle?

Distance at which $\theta_Y = \theta$, noted $z_Y$, Scales $1/\theta_Y$

*Why so:*

$P_x$ (and so $\gamma$) is affected by the surface over long-range (cf. vdW forces)

Finite size effects on the result when $\theta \rightarrow 0$ ($z_Y > h$)

Macroscopically described by disjoining pressure (when $h < z_Y$)
DYNAMICS: DROPLET ($\theta_{\text{Eq}} = \pi/2$) UNDER AN EXTERNAL FIELD

Droplet under a « gravity » field

Flow field (Ca=0.2)

Droplet velocity vs external force

Slip length at Liq/Sol~1

By varying $F_{\text{ext}}$, the capillary number is changed

$Ca=\eta V/\gamma \sim 0.05-0.35$

A friction coefficient can be deduced (here $\xi=F/V \approx 0.07$)

Non linear response occurs for smaller $\theta$ and high $V$
At both contact lines **advancing** and **receding angles** can be measured. Hydrodynamics model predict that $\theta^3 \propto Ca$.

A hydrodynamic behavior holds for both angles at $z = 5$!

Even with nano-droplets (but not too low $\theta$), hydrodynamics seem to be well respected above $z \gamma_s$!