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

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Workshop on Modeling and Simulation of Interface Dynamics
IMS - Singapore

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MOTIVATIONS

OIL AND GAS ISSUES

Quantifying accurately Multiphasic 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:

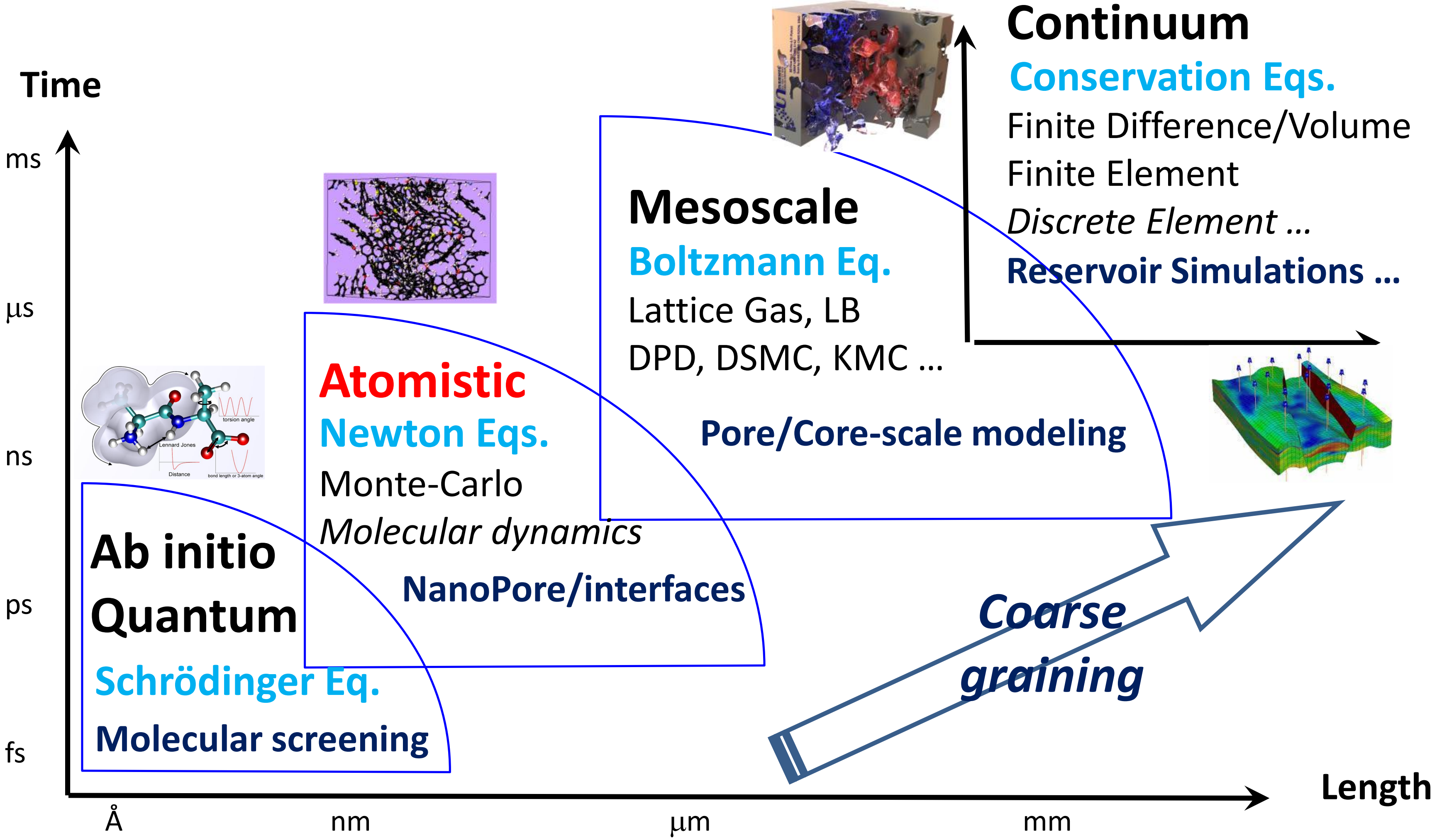
- ***Complex resources : Sour/Acid Gases, Shales gas/oil …***
- ***Complex conditions : Extreme HP/HT, Tight reservoirs …***
- ***Complex recovery methods: Smart Water, Polymer Flooding …***

Data and more physically based models are required

But experiments are hard to achieve (HSE, HP …)

METHODOLOGY

FROM NANO TO GIGA-SCALE: DIFFERENT TOOLS



Continuum
Conservation Eqs.
Finite Difference/Volume
Finite Element
Discrete Element …
Reservoir Simulations …

Mesoscale
Boltzmann Eq.
Lattice Gas, LB
DPD, DSMC, KMC …

Pore/Core-scale modeling

Atomistic
Newton Eqs.
Monte-Carlo
Molecular dynamics

NanoPore/interfaces

Ab initio
Quantum
Schrödinger Eq.
Molecular screening

Coarse graining

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

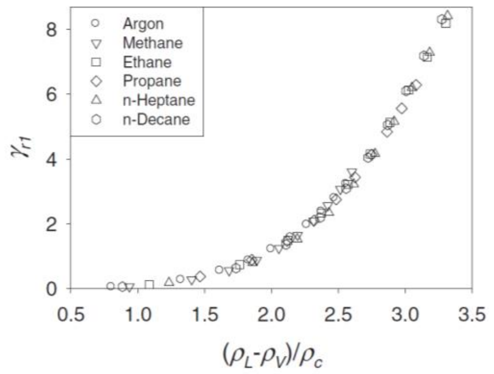
Tension, Diffusion …

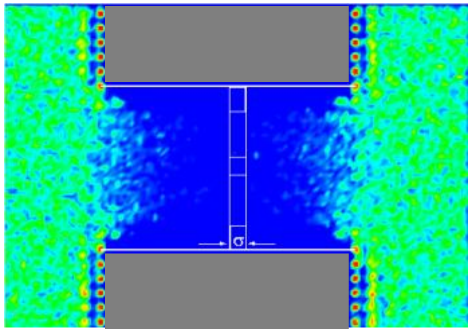
Physical mechanisms

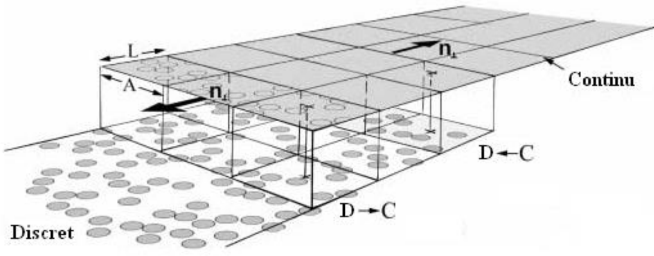
Transport, Osmosis …

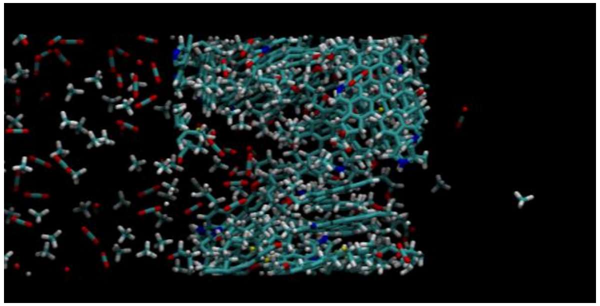
Direct/indirect upscaling

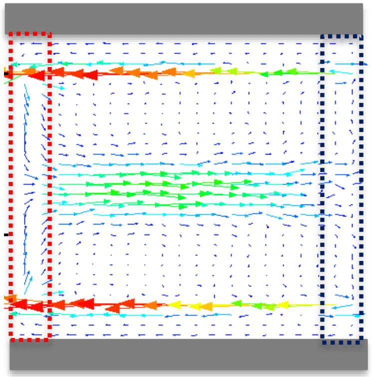
Boundary conditions …

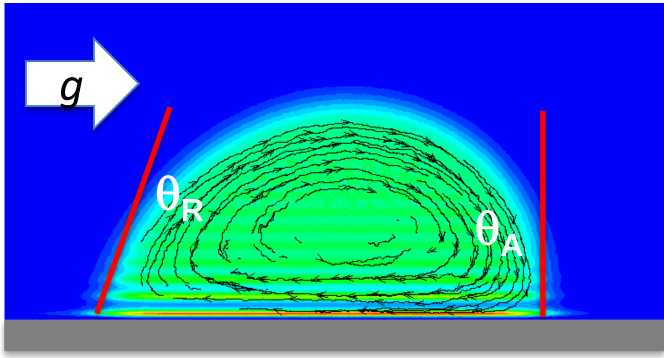








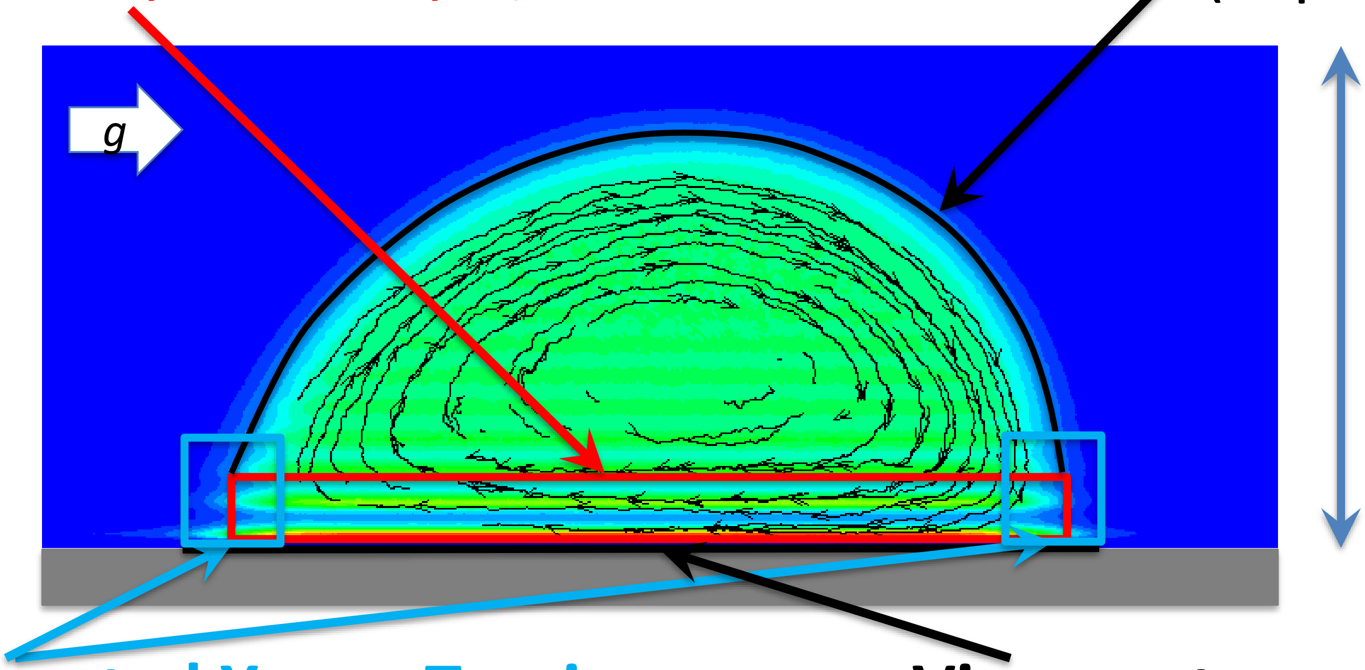




INTERFACE DYNAMICS:
ISSUES IN A SIMPLE SYSTEM

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 ?)

~5 nm

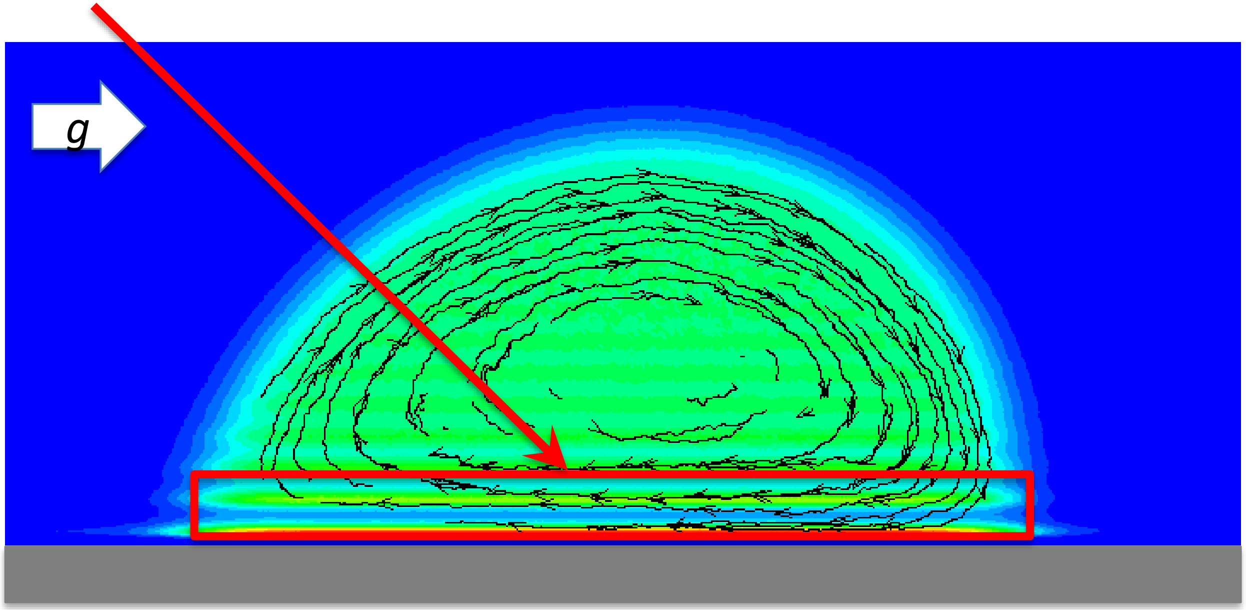
Uncompensated Young Tension
(Dynamic microscopic angle?)

Viscous stress
(Boundary Conditions)

FROM LOCAL PROPERTIES ...

Fluid Inhomogeneities?

(Local density/viscosity ?)



LOCAL FLUID TRANSPORT PROPERTIES IN INHOMOGENOUS FLUIDS

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

Hoang and Galliero, PRE (2012), JCP (2013), JPCM (2014), PRE (2015)

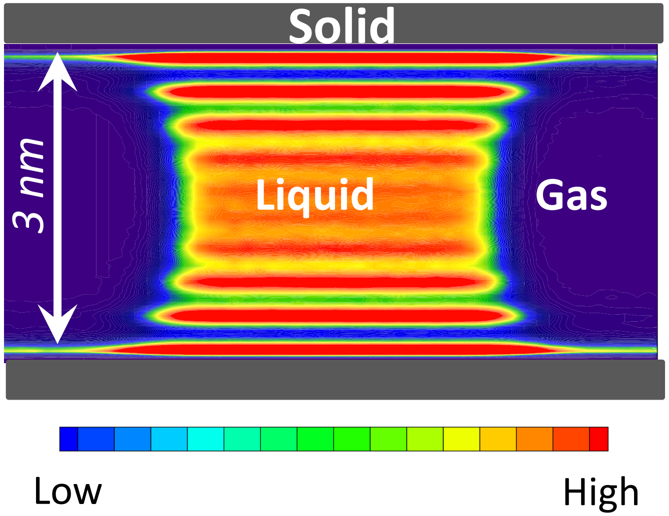
FLUID INHOMOGENEITIES ISSUES

At solid interfaces, fluids are strongly inhomogeneous

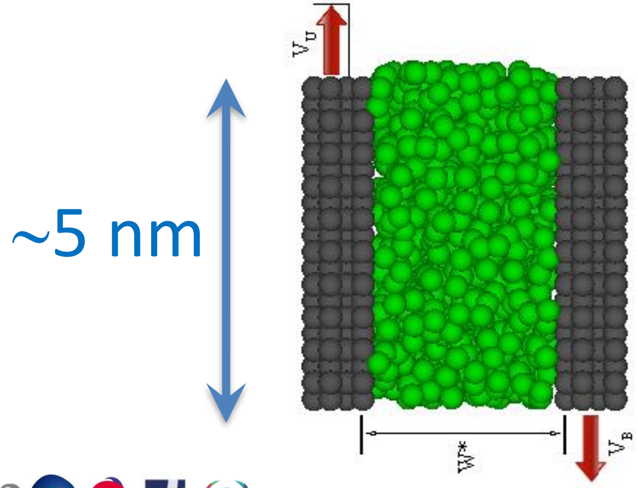
(SFA, DFT …)

⇨ ***Spatialy variable viscosity ?***

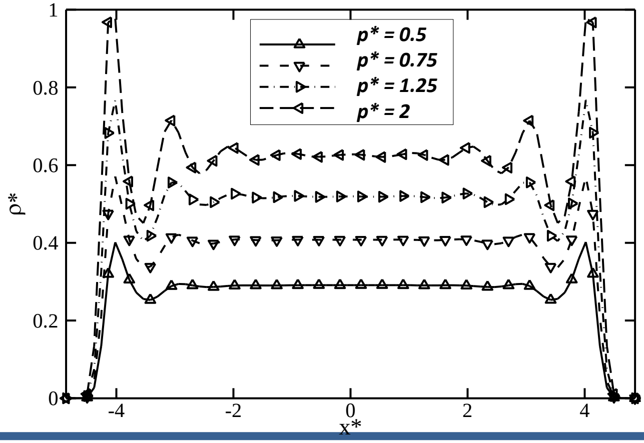
Density of a “oil” drop in a *nanopore*



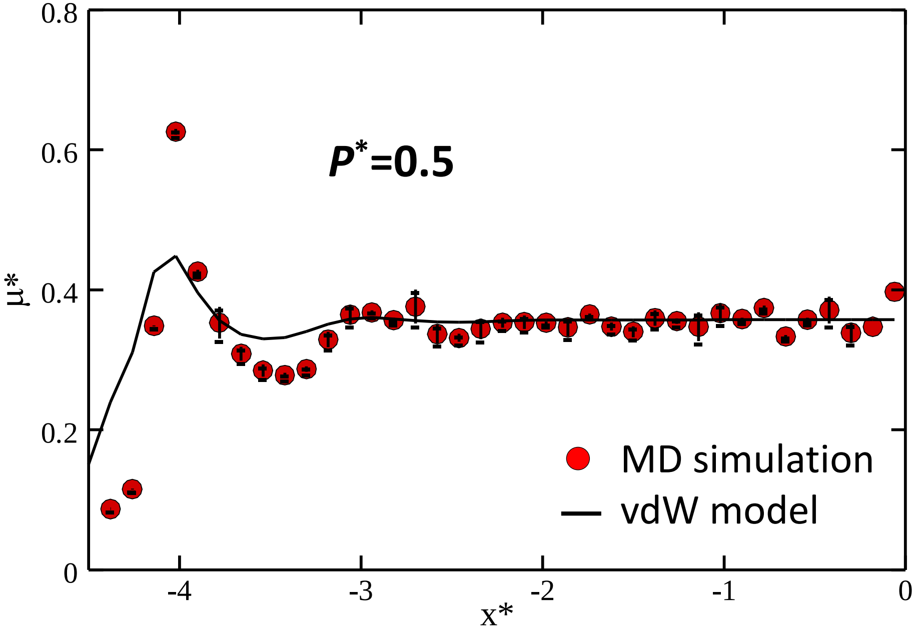
Couette like simulations of a simple fluid (LJ) in a nanoslit



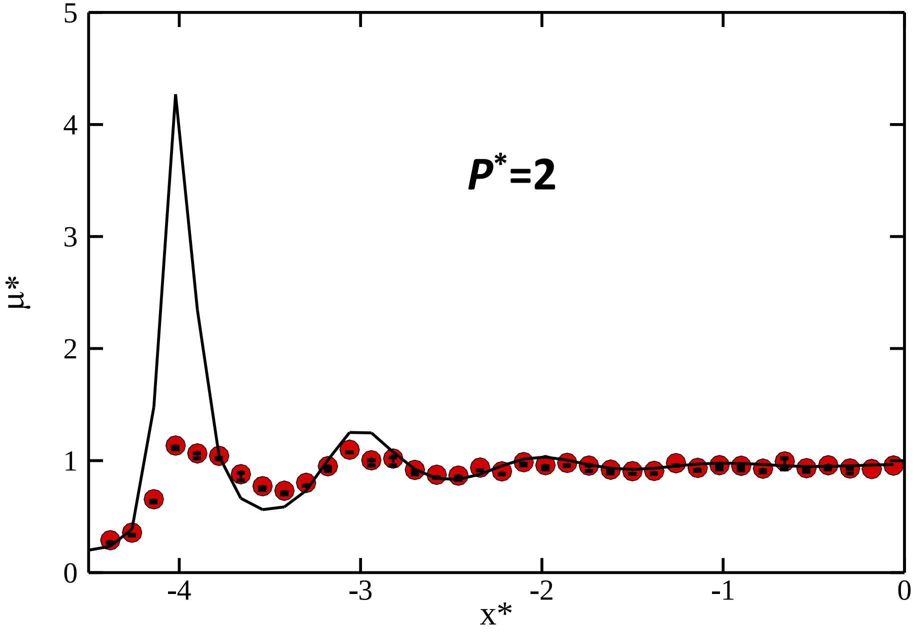
Density profiles



A VARIABLE VISCOSITY ?



Local Viscosity profile



Local Viscosity profile

The fluid viscosity is variable in space !

The local viscosity computed by MD cannot be deduced from the local thermodynamic variables alone (T and ρ)

There are non local effects

Hoang & Galliero, PRE (2012)

INTRODUCING NON LOCAL EFFECTS

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, η_c is assumed to be a function of the density averaged over a typical length

Similar to Bitsanis et al. J. Chem. Phys. 1987

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

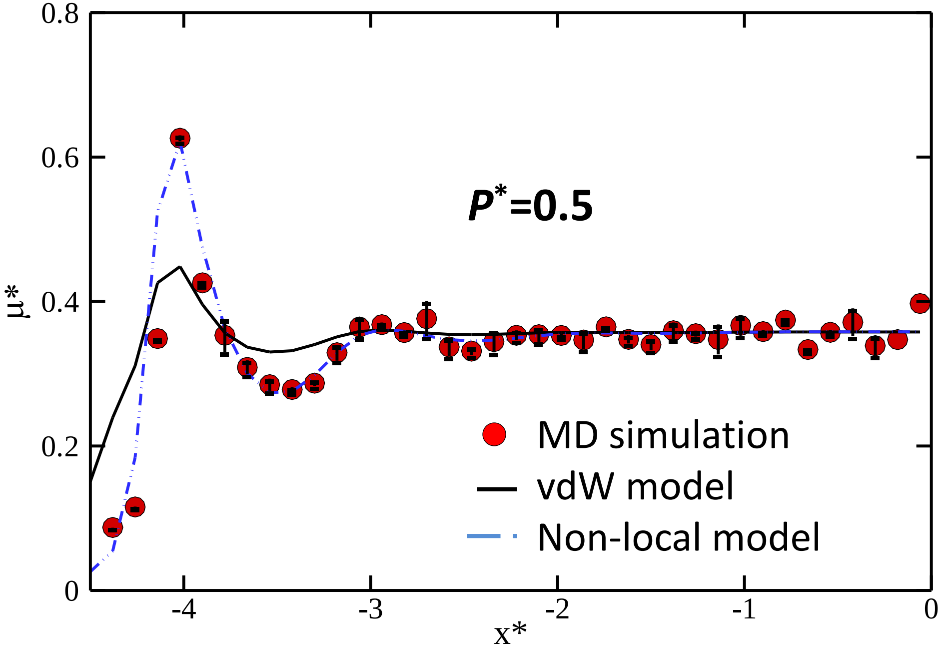
with e.g. $\bar{\rho}(x) = \frac{1}{\sigma} \int_{-\sigma/2}^{\sigma/2} \rho(x+s)\,ds$

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

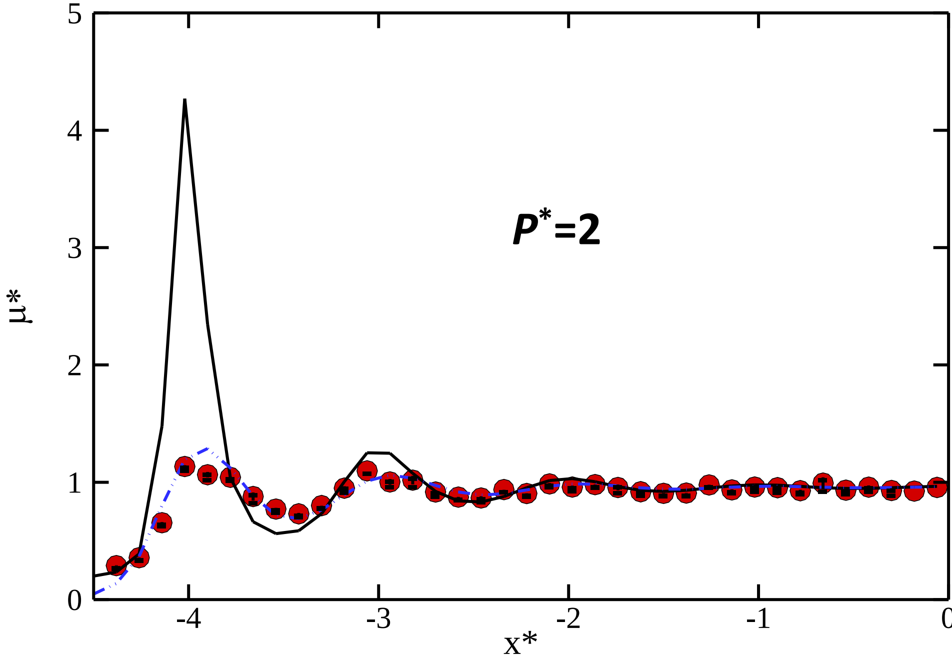
Hoang & Galliero, JCP (2013), JPCM (2014)

NON LOCAL VISCOSITY ?

Local Viscosity profiles



Local Viscosity profiles



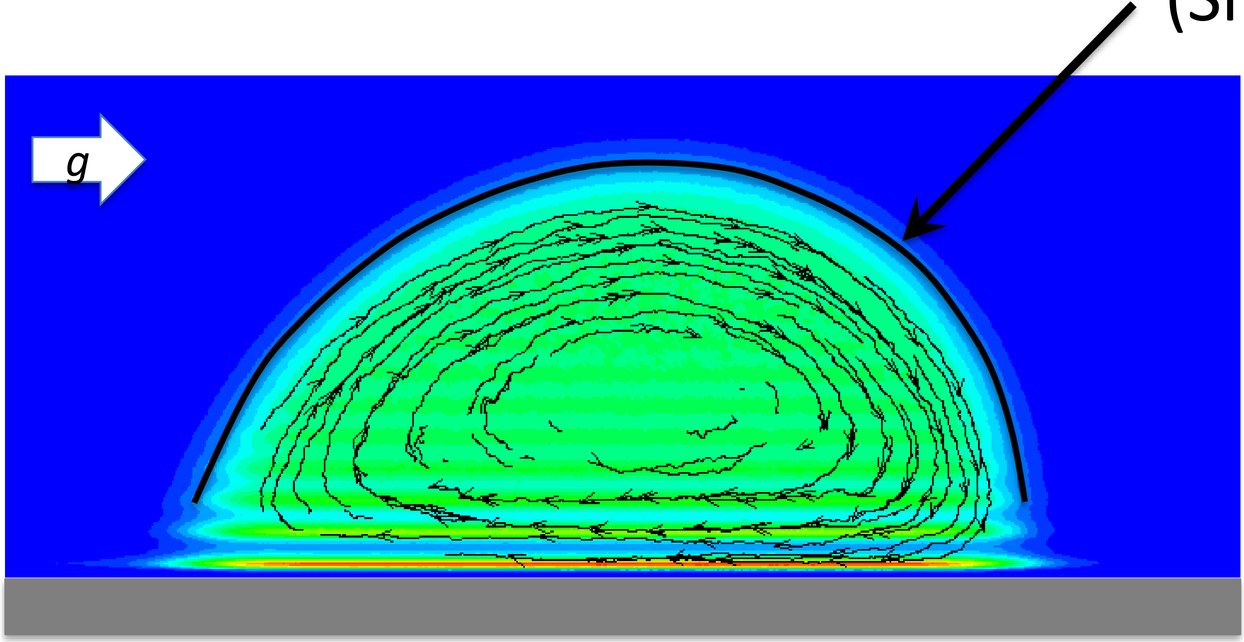
Non local viscosity is well modeled by the simplest DFT

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)

Galliero, PRE (2010), Bugel et al. Micro&Nanofluid. (2011)

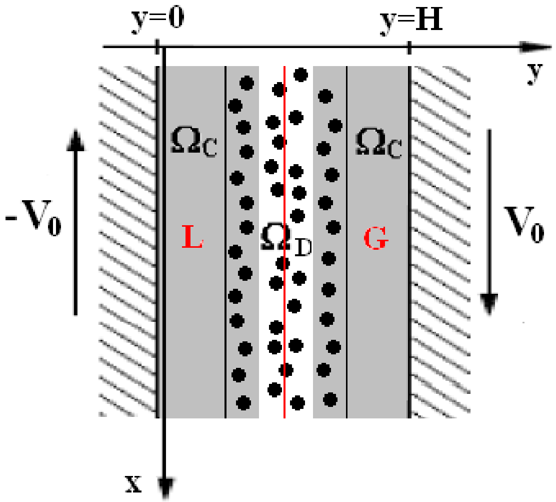
FLUID-FLUID SHEAR STRESS ISSUES

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

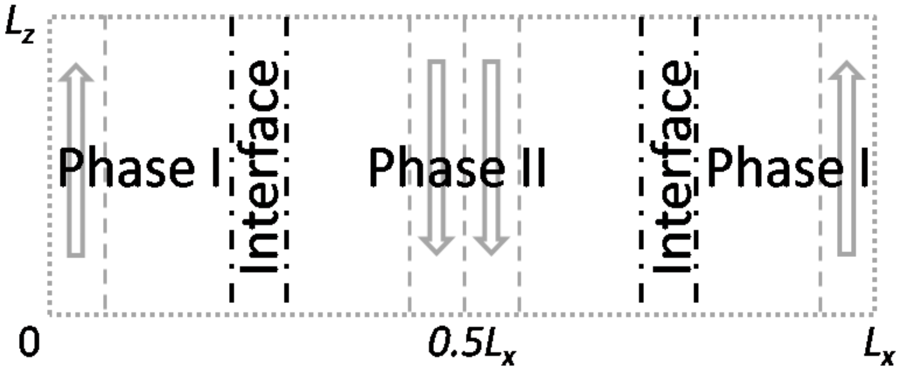
Slip s known to occur at polymer-polymer interfaces

Hybrid and MD simulations of Fluid-fluid interfaces under shear

Liquid-Gas



Liquid-Liquid

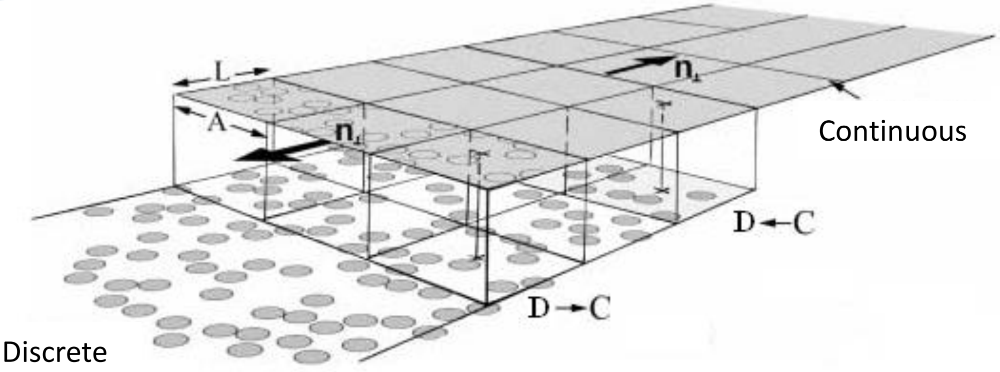


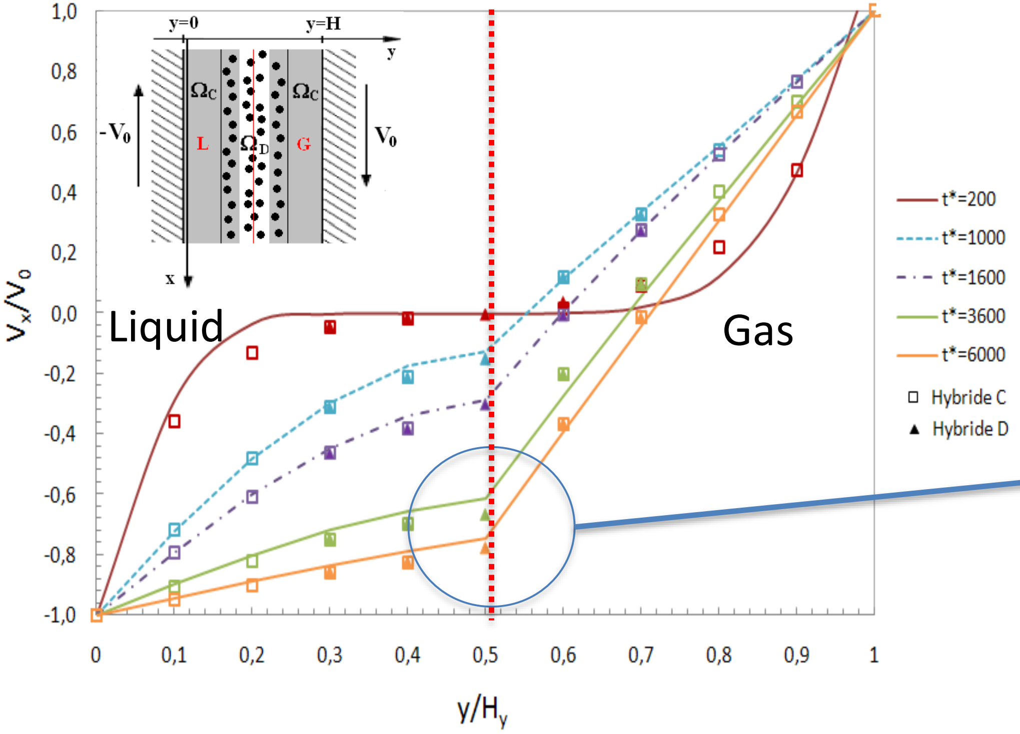
HYBRID SIMULATIONS OF A DIPHASIC COUETTE FLOW

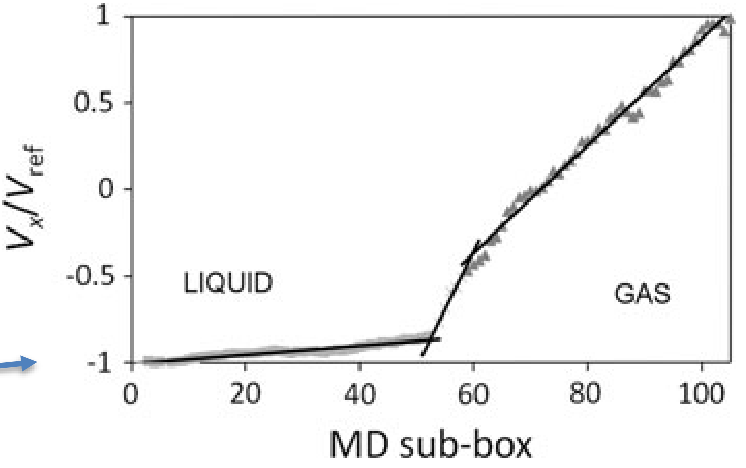
Hybrid MD-CFD simulations

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

Schwartz alternating method





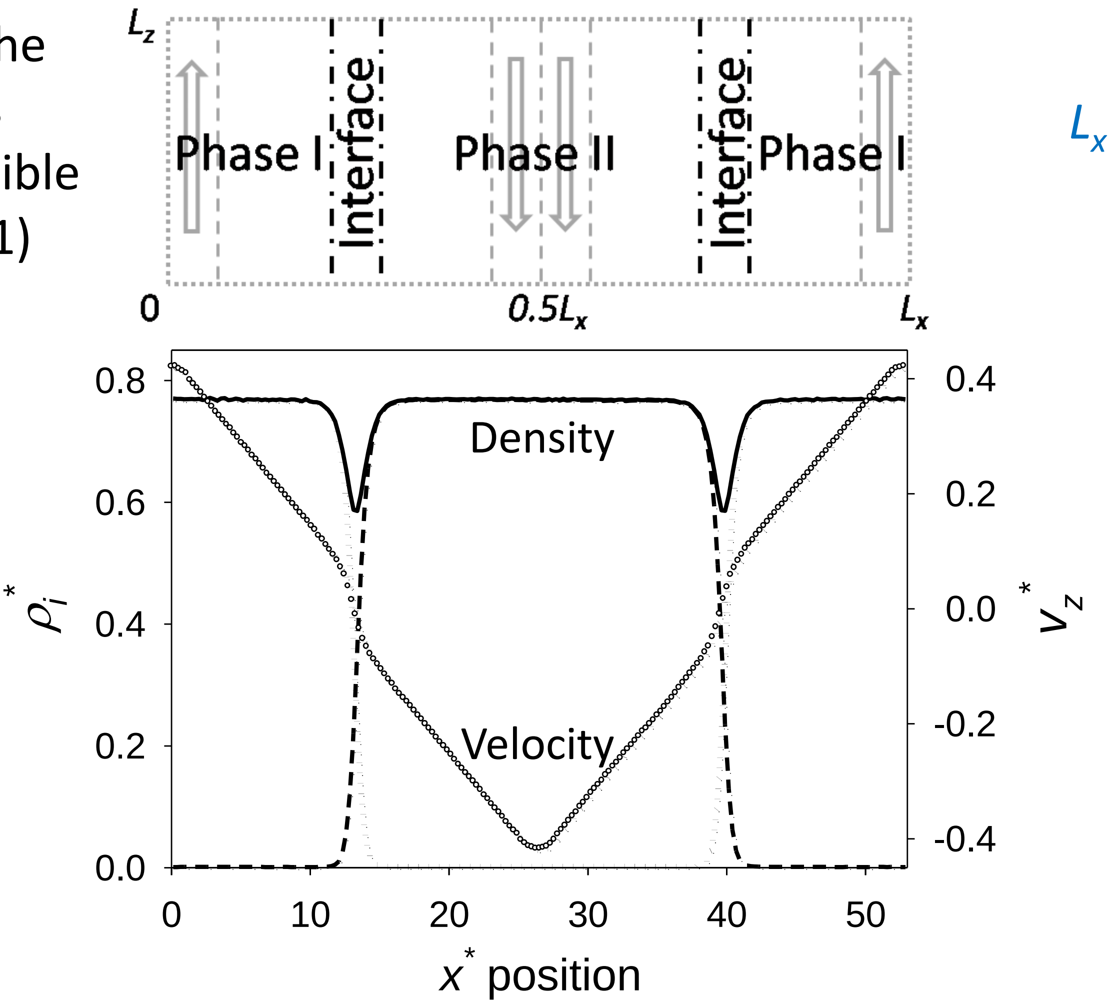


At the liquid-gas interface a partial slip seems to occur !

Bugel et al., M&N (2011)

VELOCITY JUMP AT A LIQUID-LIQUID INTERFACE

Phase I & II have the same properties but are weakly miscible ($\varepsilon_{12}=k_{ij}\varepsilon$, with $k_{ij}<1$)

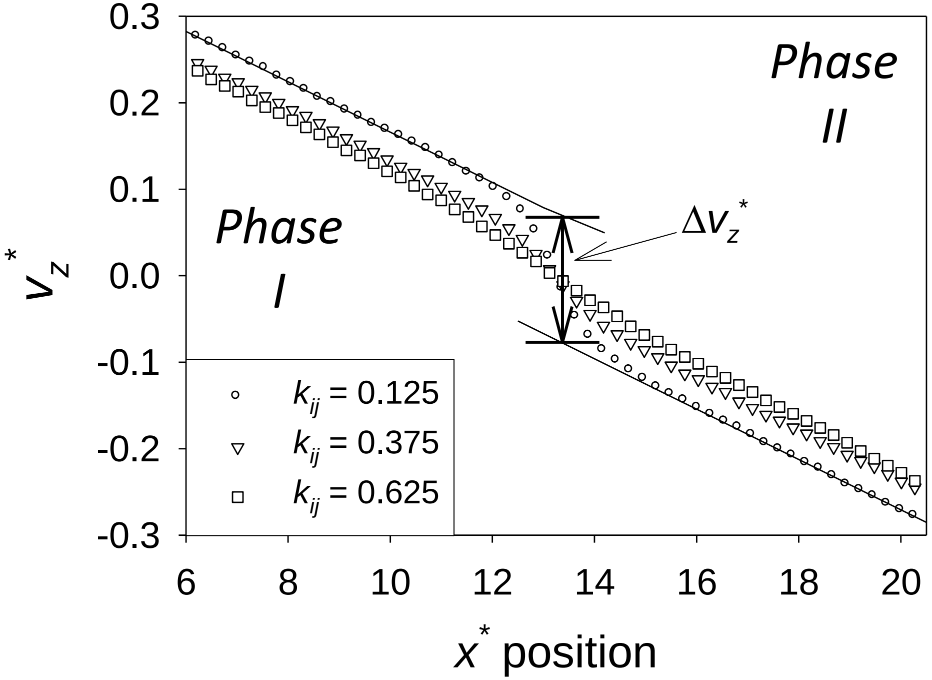


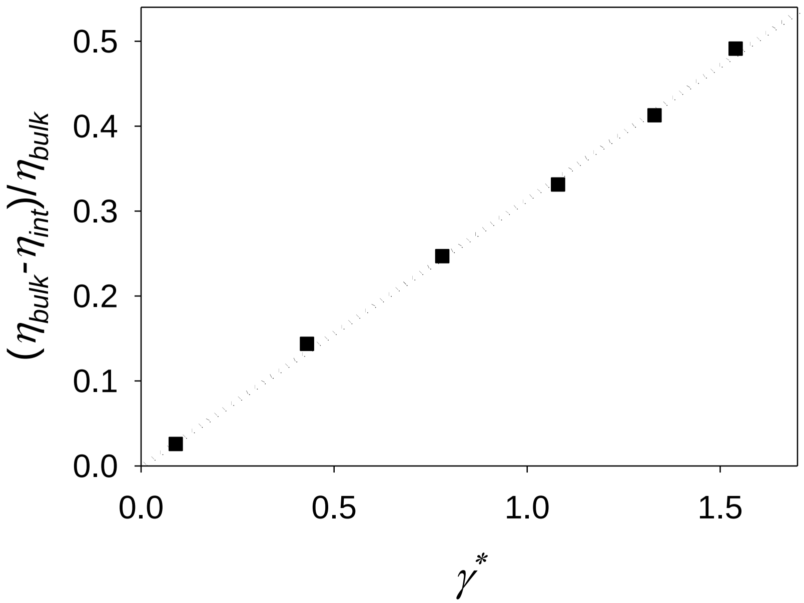
L_x ~30 nm

The velocity profile exhibits a "jump" at the interface

Galliero, PRE (2010)

INTERFACIAL VISCOSITY IN SIMPLE FLUIDS ?


Velocity jump for various miscibility


Interfacial viscosity

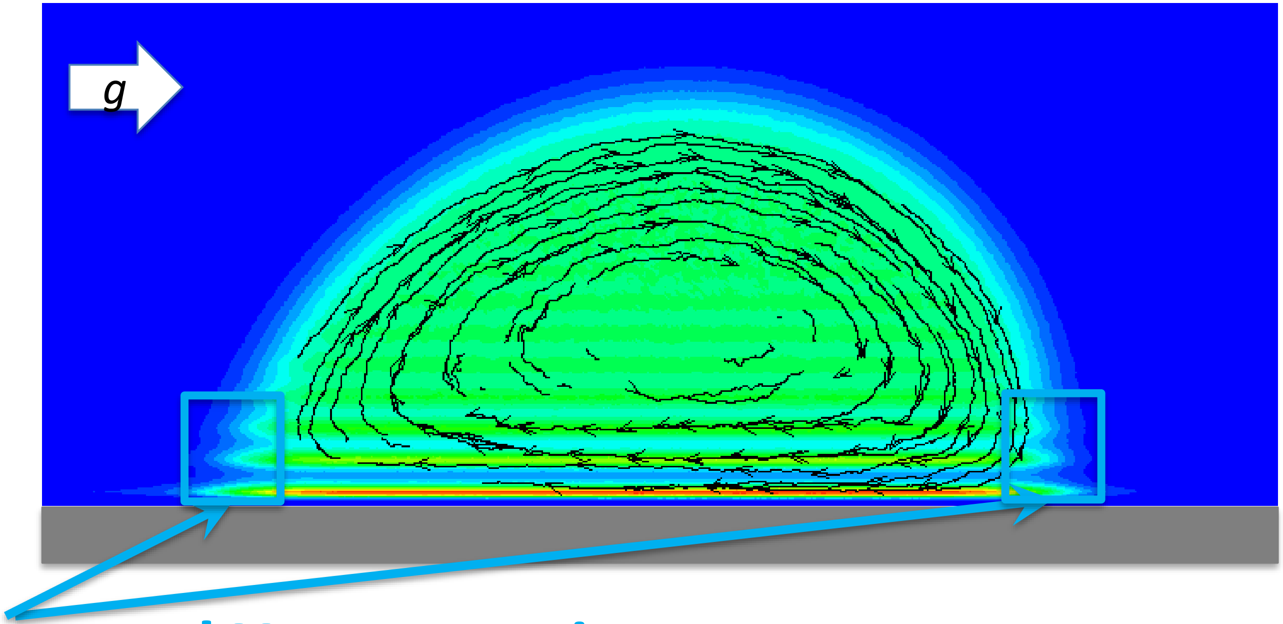
The partial slip increases with the interfacial tension

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

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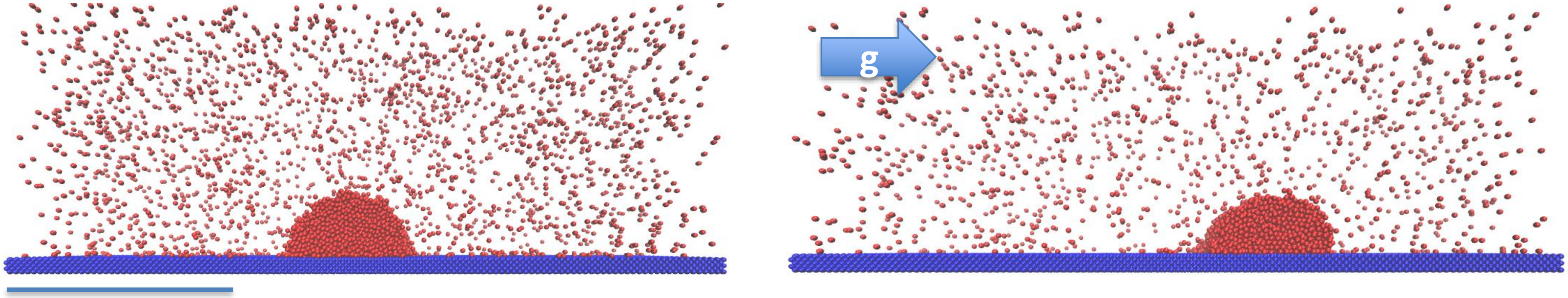
YOUNG STRESS ISSUES

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)

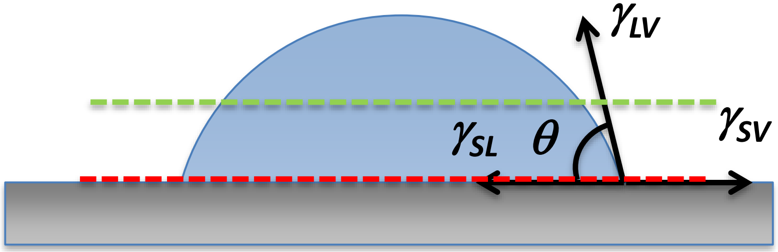


~10 nm

Lennard-Jones 2D droplets on LJ CFC solid surface for $0.4\pi < \theta < 0.85\pi$

EQUILIBRIUM: YOUNG TENSION (1/2)

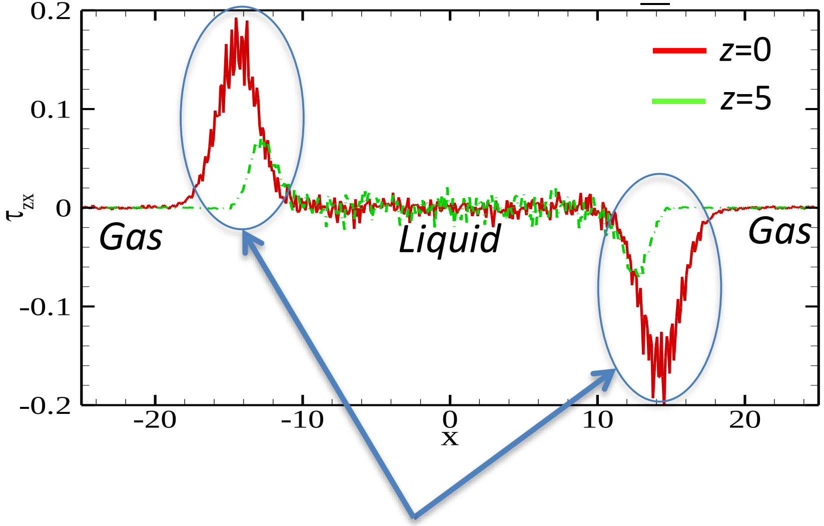
At the ***contact line*** *the (integrated)* ***shear stress*** *is* ***macroscopically*** *equal to the* ***Young tension*** *i.e.* $\gamma\cos\left(\theta(z)\right)$



$$\sum\nolimits_{Int}(z) = \int_{x_{Int}^L}^{x_{Int}^R} \tau_{zx}(x,z)\mathrm{d}x$$

Irving-Kirwood/Method of Plane

Local shear stress (τ_{zx})



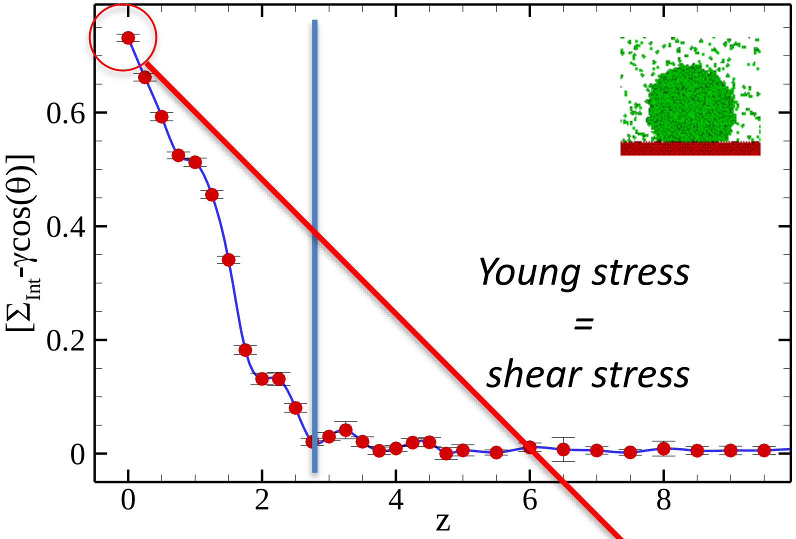
Young tension ?

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*** $\sum_{Int}(z) = \int_{x_{Int}^{L}}^{x_{Int}^{R}} \tau_{zx}(x,z)\mathrm{d}x$ *compares to* ***Young tension*** *?*

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

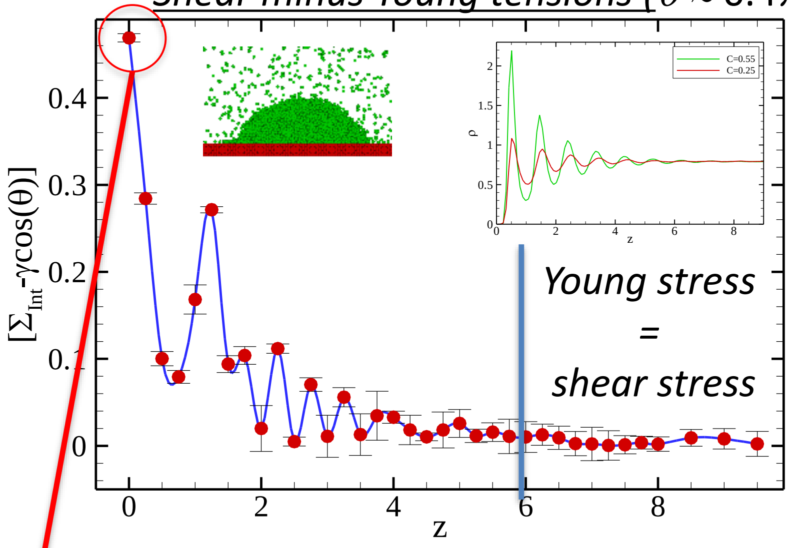


Young stress

=

shear stress

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



Young stress

=

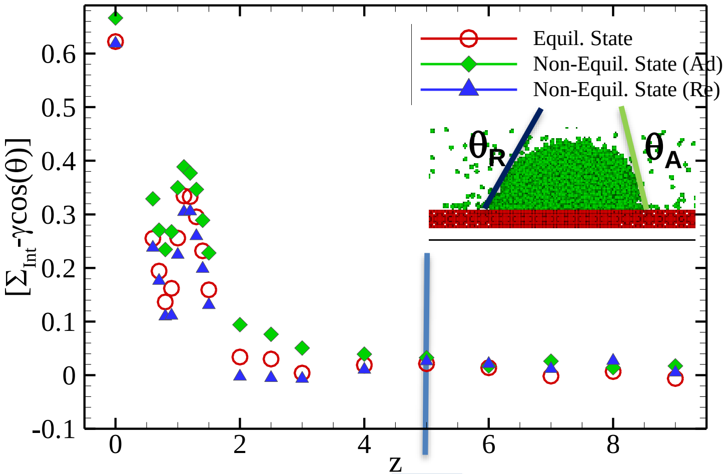
shear stress

Shear tension at the contact line differs from γcos(θ)!

But Young stress = shear stress at liq/vap interface above z_Y ~ some molecular sizes (z_y scales with θ^{-1})

DYNAMICS: SHEAR/YOUNG TENSION ($\theta_{Eq} = \pi/2$)

Shear minus Young tension (Ca=0.2)



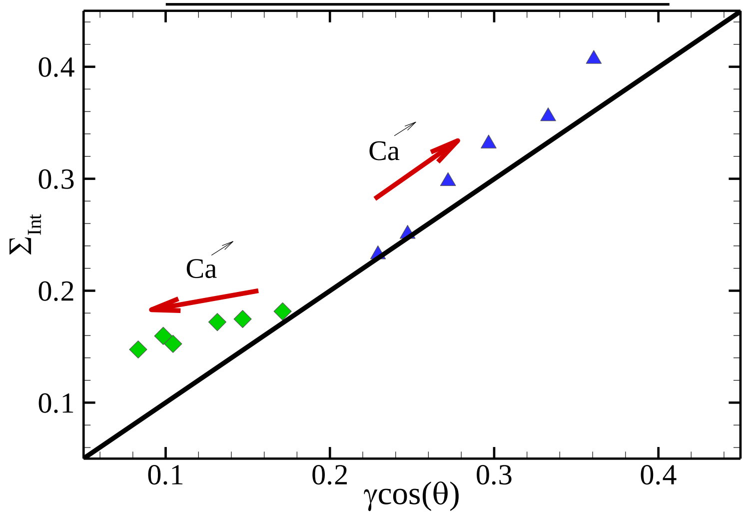
***Young tension** is **compared with shear tension** at different z and different Ca …*

Even out of equilibrium

Shear tension=Young tension

above z ≈ 5 !

Shear tension at z=5 vs Ca

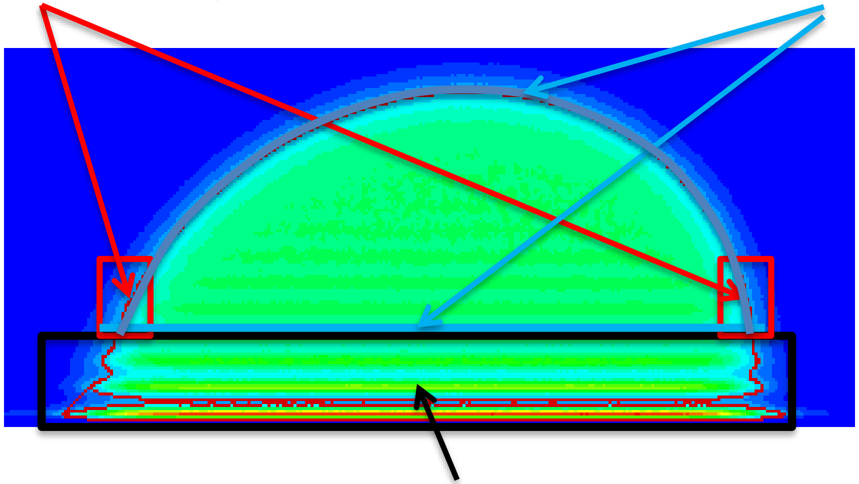


The influence of Ca on shear tension is not negligible

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

Consistent with Qian et al. PRE 2003, Ren and E, PF 2007

A SPECIFIC MICROSCOPIC PICTURE ?



Uncompensated Young Stress

$\gamma[\cos(\theta_{NE})-\cos(\theta_{Eq})]$

Viscous stress

(Navier BC)

Classical (homogeneous) continuum breaks down ($\propto\theta^{-1}$)

In not too wetting cases, classical laws are really robust !

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 NANOCOUETTE FLOW: WHICH BOUNDARY CONDITIONS ?

H. HOANG H. SI HADJ MOHAND (LFCR)

D. LEGENDRE (IMFT, TOULOUSE, FRANCE)

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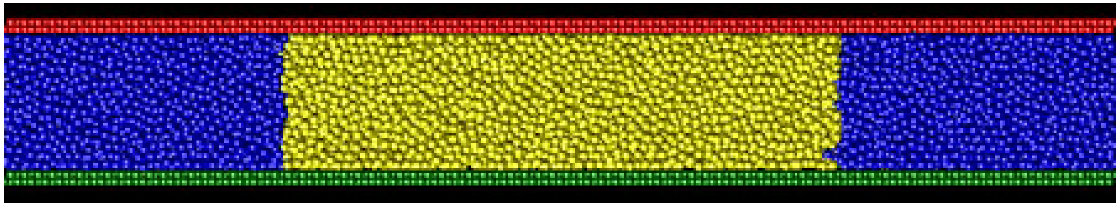
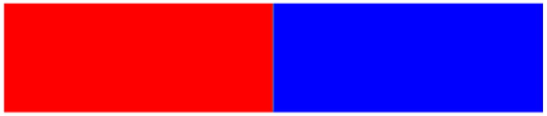
BOUNDARY CONDITIONS ISSUES

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

CFD MODELS (JADIM)

Navier-Stokes (NS) Equations

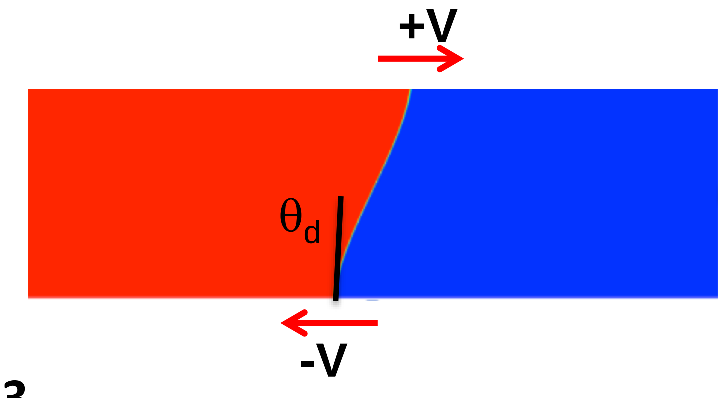
+

Volume Of Fluids (VOF, interface)

Imposed Slip length + Dynamic angle

Mesh size < Slip length

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



Reference case : MD of Qian et al., Phys. Fluids, 2003

Used slip length model (Navier): $U_W - V = \lambda \left.\frac{\partial U}{\partial n}\right|_W$ where $\lambda = 1.63\,\sigma$

Tested dynamic angle models :

Static : $\theta_d = \theta_Y$

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

$B_{cl} = 3.02\,(\varepsilon m)^{1/2}/\sigma^3$

Molecular Kinetic Theory (MKT**) : $\cos\theta_Y - \cos\theta_d = \frac{U_{cl}}{\gamma} \frac{\mu v}{\lambda^3} \exp\left(\frac{\sigma(1+\cos\theta_Y)}{n k_B T}\right)$

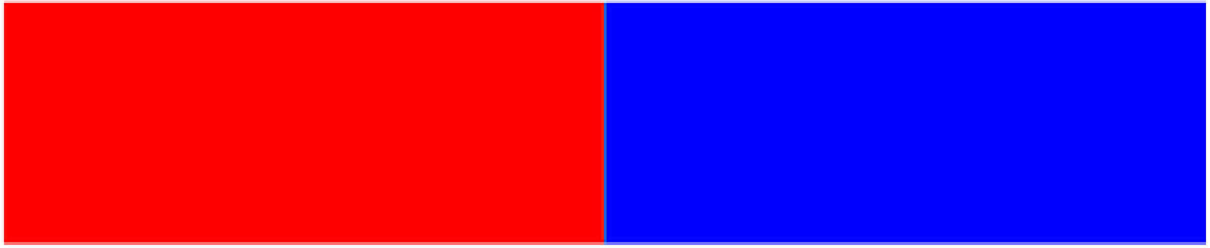
$f = 14.3\,(\varepsilon m)^{1/2}/\sigma^3$

**Qian et al. PRE (2003), Ren and E, PF (2007), **Blake and co-workers*

CONTACT ANGLE FRICTION CONTROLS THE STABILITY

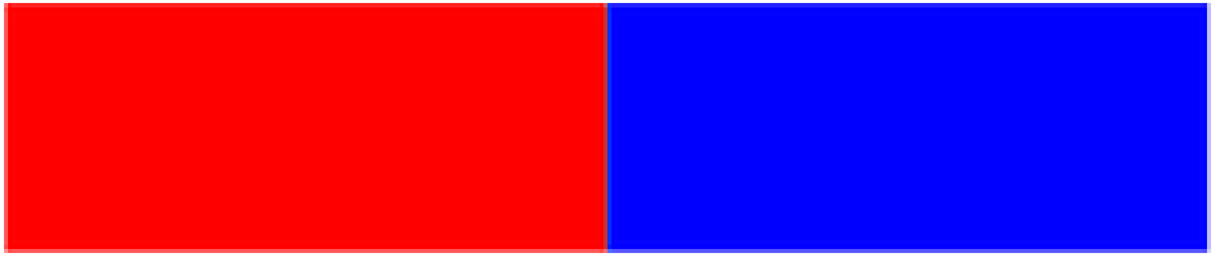
NS Simulation – GNBC model

with normalized friction $B_{cl}=3.02$



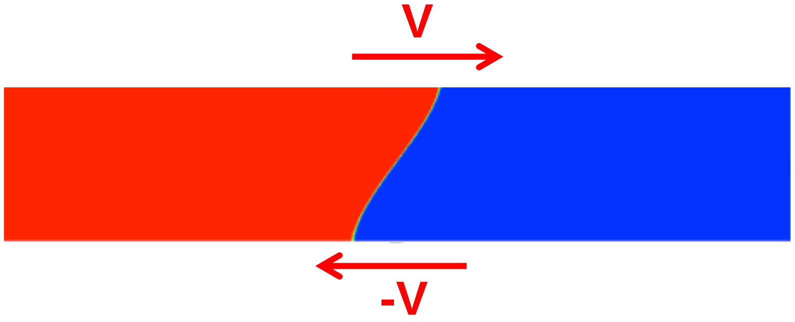
NS Simulation – MKT model

with normalized friction $f=14.3$

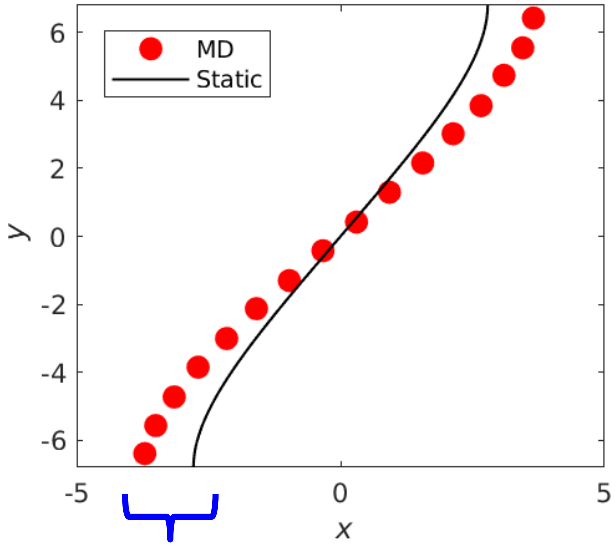


Unstable case : the MKT “friction” is too large

VOF-NS VERSUS MD: PREDICTIONS

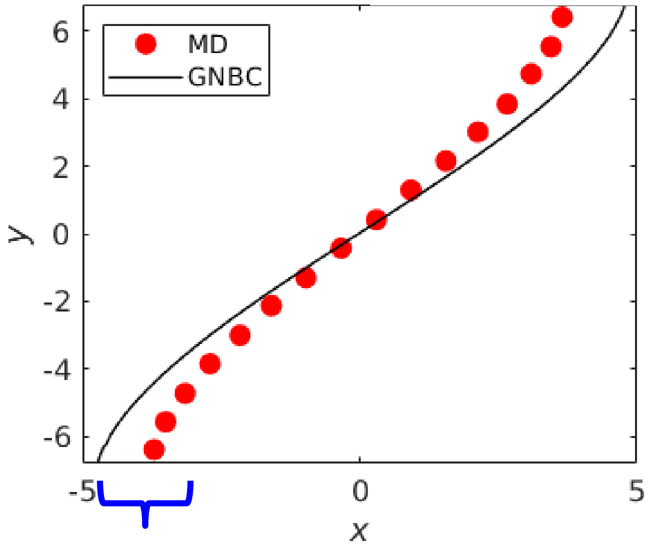


NS - Static model



Too much slip

NS – GNBC model (friction $B_{cl}=3.02$)



Slip is modified by friction

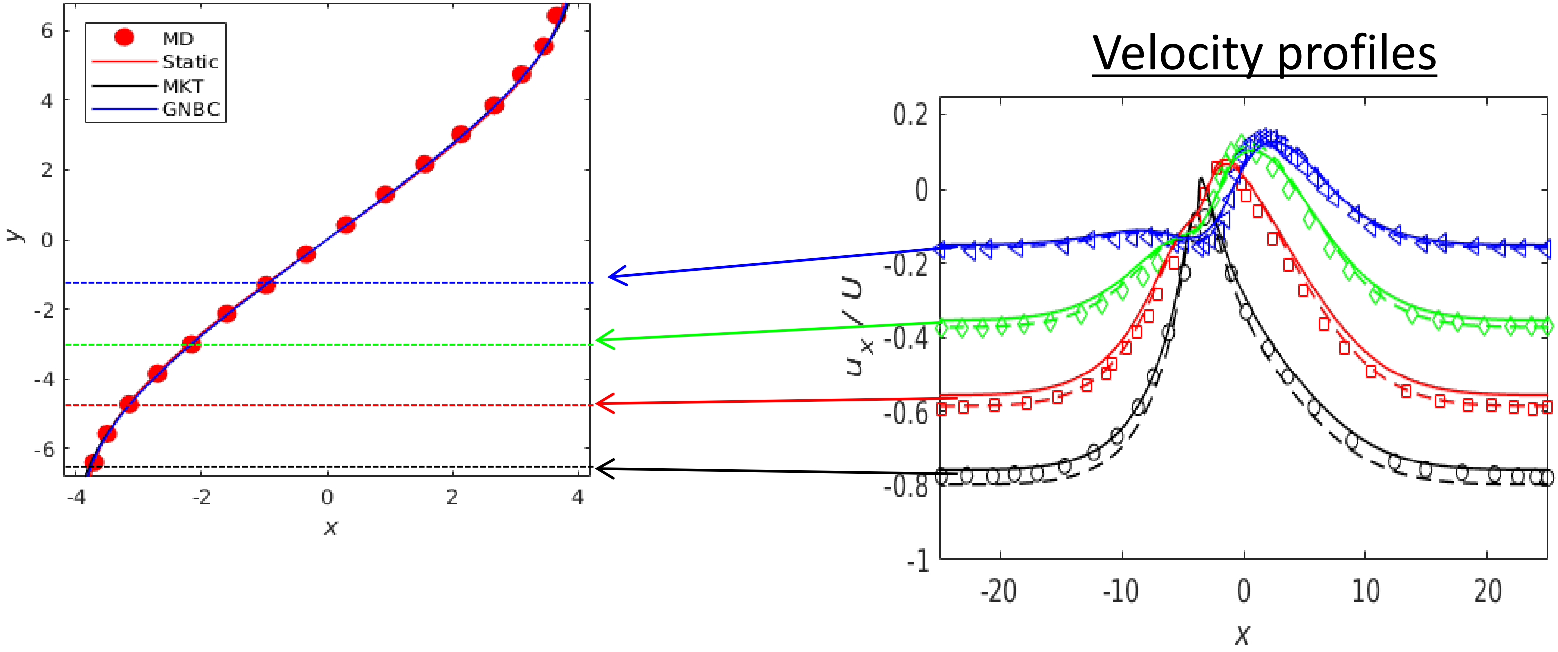
No Contact Line model seems to be fully predictive when combined with VOF-NS

VOF-NS VERSUS MD: ADJUSTED MODELS

Static: λ=1.63 => λ=1.2

GNBC: B_{cl}=3.01 => B_{cl}=1.7

MKT: f=14.3 => f=1.7



Velocity profiles

NS+VOF describes well this nanoflow when all scales are solved

If adjusted, all CL models yield reasonable results !

OUTCOMES

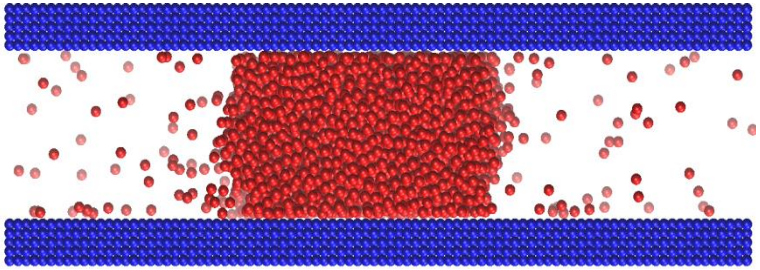
OUTCOMES

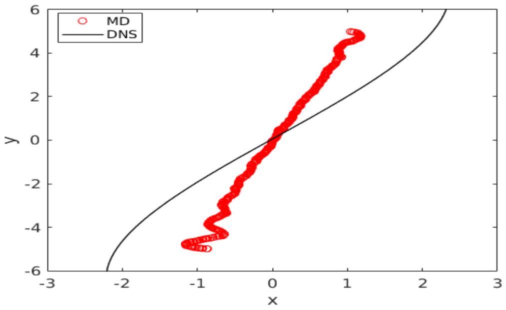
- ✓ **Shear viscosity can be variable in space at the Contact Line**
  - ○ **Non locals effects on viscosity occur close to a solid surface**
  - ○ **Interfacial region may lead to apparent fluid-fluid slip**

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

And for future works …

Sheared Liq-Gas





Include non local density/viscosity …. introduce upscaling …

Acknowledgments

Pau University

CNRS

And TOTAL

All colleagues collaborating

THANK YOU FOR YOUR ATTENTION !

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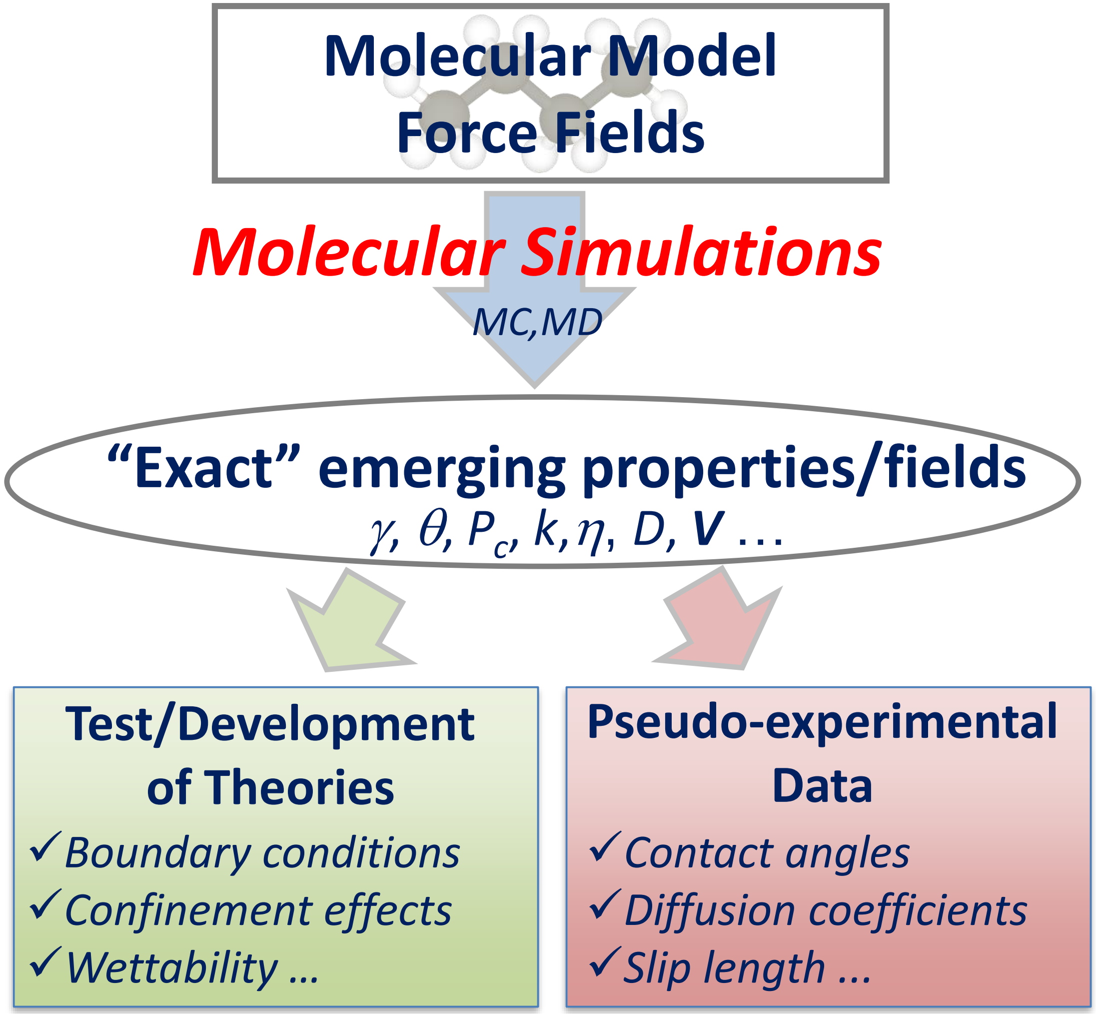
EXTRAS

MOLECULAR SIMULATIONS: WHAT FOR ?



Molecular Model
Force Fields

Molecular Simulations

MC,MD

“Exact” emerging properties/fields

γ, θ, P_c, k, η, D, $\mathbf{V}$ …

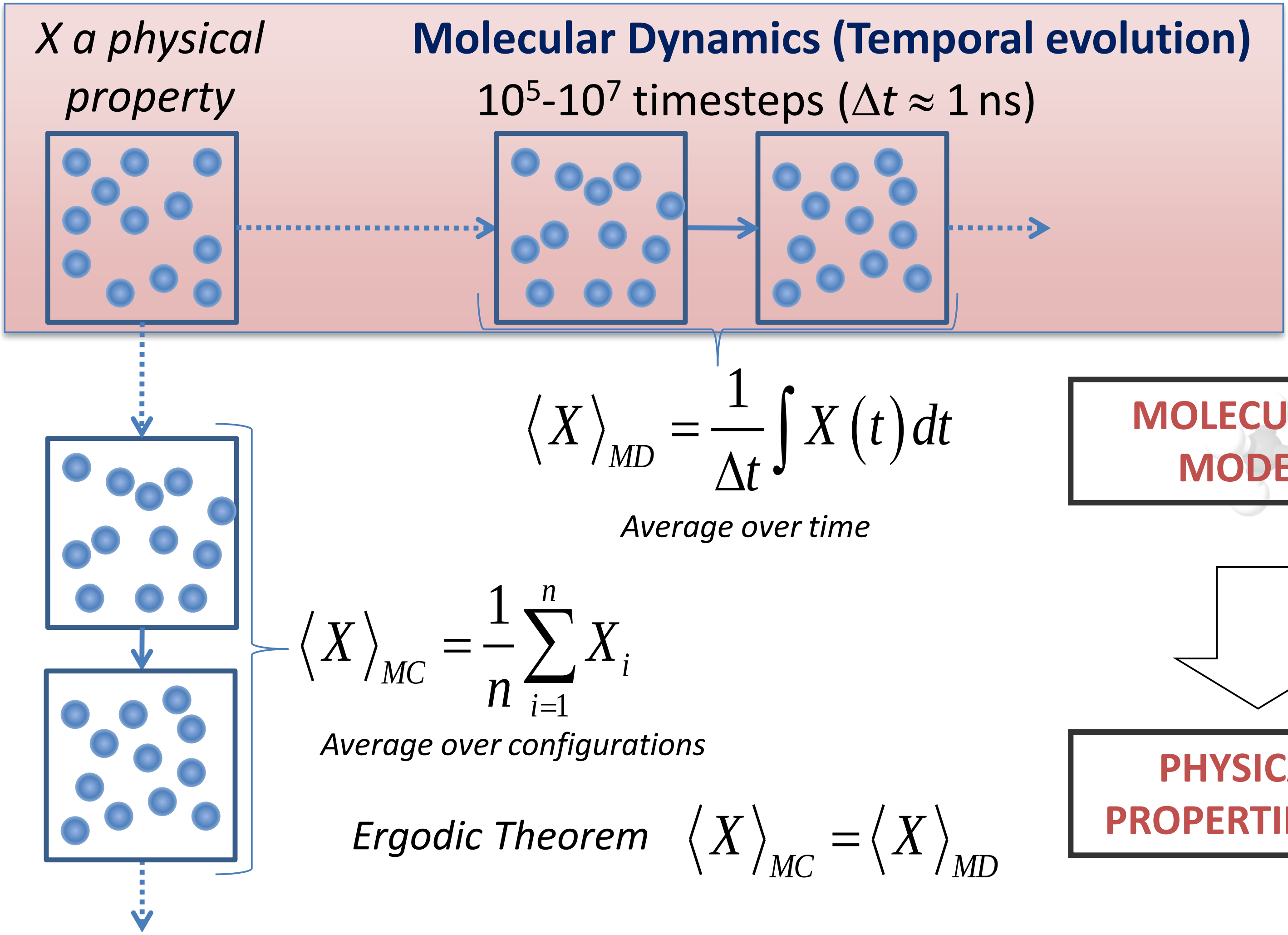
Test/Development of Theories

✓*Boundary conditions*
✓*Confinement effects*
✓*Wettability …*

Pseudo-experimental Data

✓*Contact angles*
✓*Diffusion coefficients*
✓*Slip length …*

MOLECULAR SIMULATIONS: HOW IT WORKS ?



X a physical property

Molecular Dynamics (Temporal evolution)

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

A set of N interacting particles

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

Average over time

MOLECULAR MODEL

PHYSICAL PROPERTIES (*X*)

Monte Carlo (Statistical evolution)

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

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

Average over configurations

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

No assumption concerning the physical phenomena that may emerge!

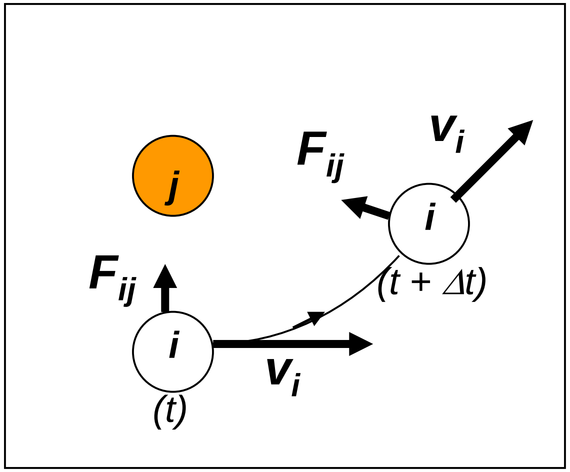
MOLECULAR DYNAMICS: HOW IT WORKS ?

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*)

$$\sum_j \vec{F}_{ij} = m_i \frac{d\vec{v}_i}{dt}$$

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



New position at *t* + Δ*t* *(various integrator)*

$$\vec{r}_i(t+\Delta t) = \vec{r}_i(t) + (\Delta t)\vec{v}_i(t) + \frac{1}{2}(\Delta t)^2 \frac{\vec{F}_i(t)}{m_i}$$

Explicit Scheme, "easily" parallelised (domain decomposition)

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

***Quasi-experimental* process (data with error bars ...)**

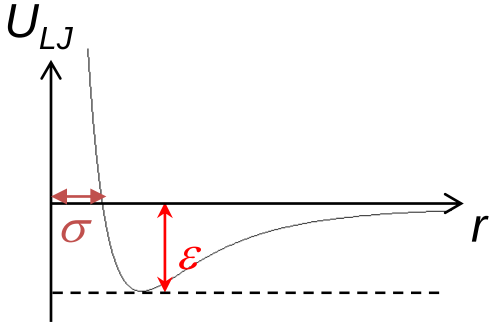
FORCE FIELDS: THE CORE OF THE PROBLEM

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

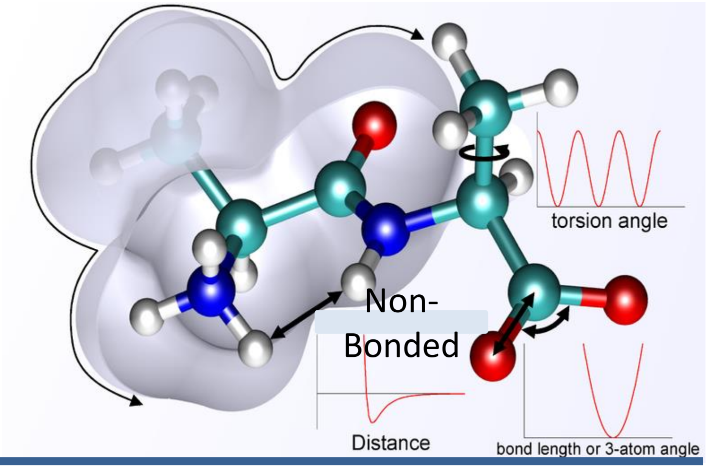
$$U_{LJ} = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$$



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

$$P = \frac{1}{3V_c}\left(2E_c + \left\langle \sum_{i=1}^{N}\sum_{j>i}^{N} \mathbf{F}_{ij}\cdot\mathbf{r}_{ij} \right\rangle\right)$$

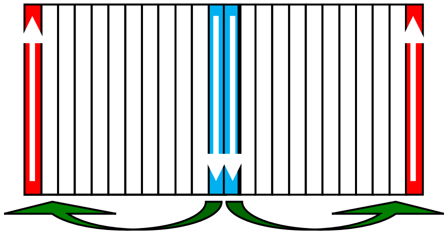
$$\gamma = \int_{x_1}^{x_2} \left(P_N(x) - P_T(x)\right) dx$$

Sound velocity, …

Dynamic properties

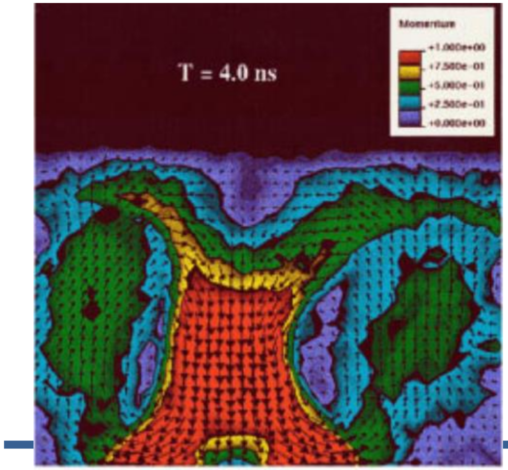
The property is deduced from the fluctuations (*Equilibrium*)

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



Momentum/Energy Exchange

Field properties



The strain, velocity, temperature, pressure, concentration … fields are deduced from averages (over time or ensemble)

METHODOLOGY

Extensive Molecular Dynamics simulations on well controlled Vapor/Liquid/Solid systems

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

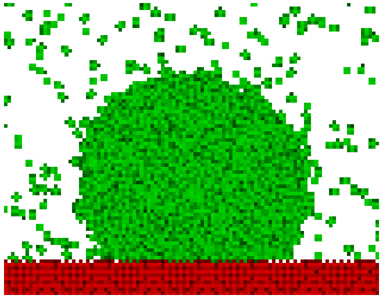
- **Variable wetting properties**

Lennard-Jones interactions

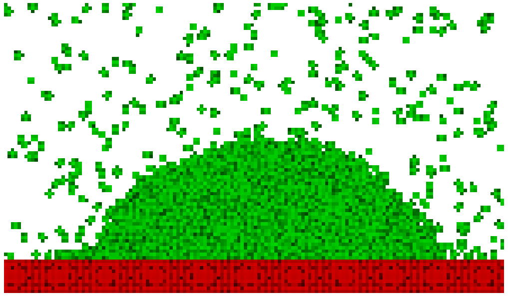
$$U = 4C\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

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

$C=0.25\ (\theta \sim 0.85\pi)$

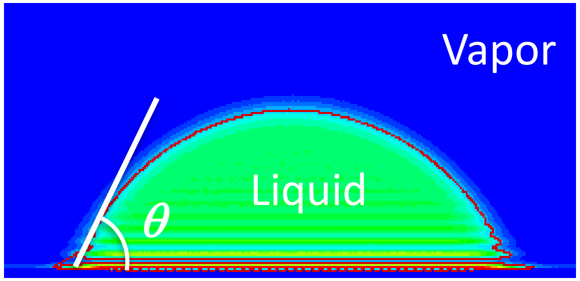


$C=0.55\ (\theta \sim 0.4\ \pi)$

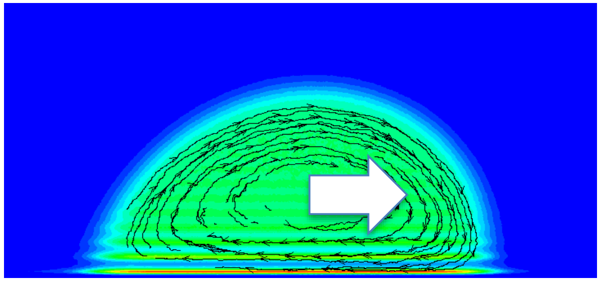


- **Static and migration under external force configurations**

Static nanodroplet



Moving nanodroplet

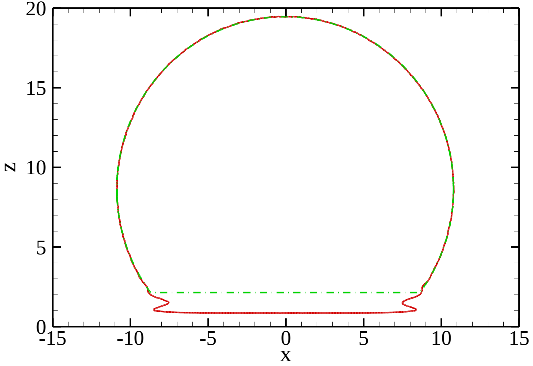


EQUILIBRIUM : CONTACT ANGLE

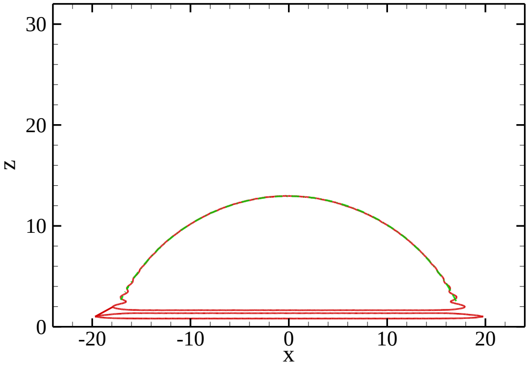
*The **Contact angle** is **determined** by a **circle fit***

(using Gibbs dividing surface and extrapolated at z=0.5)

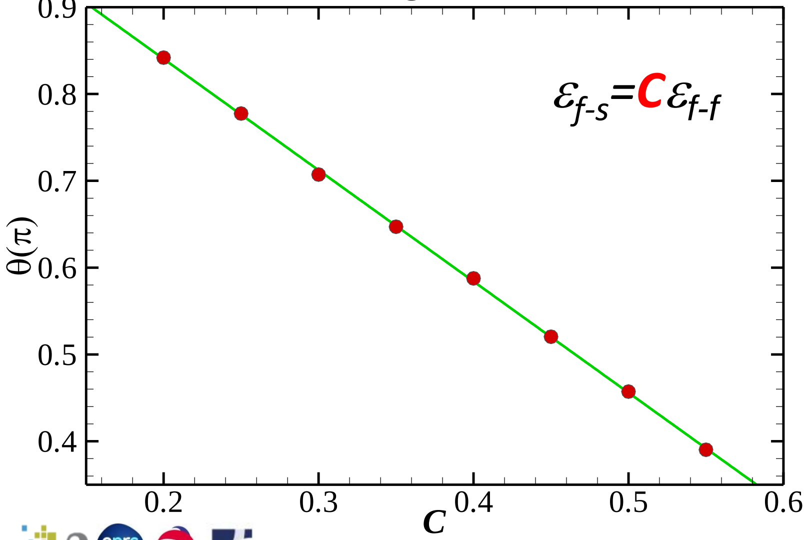
C=0.25 ($\theta \sim 0.4\pi$)



C=0.55 ($\theta \sim 0.85\pi$)



Contact Angle at z=0.5



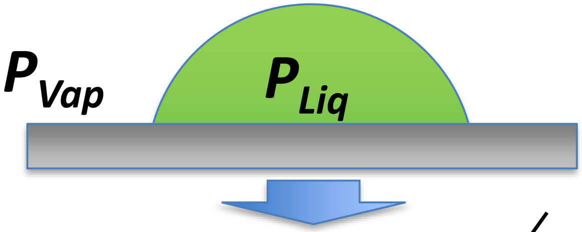
The contact angle is proportional to fluid-solid interactions

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*



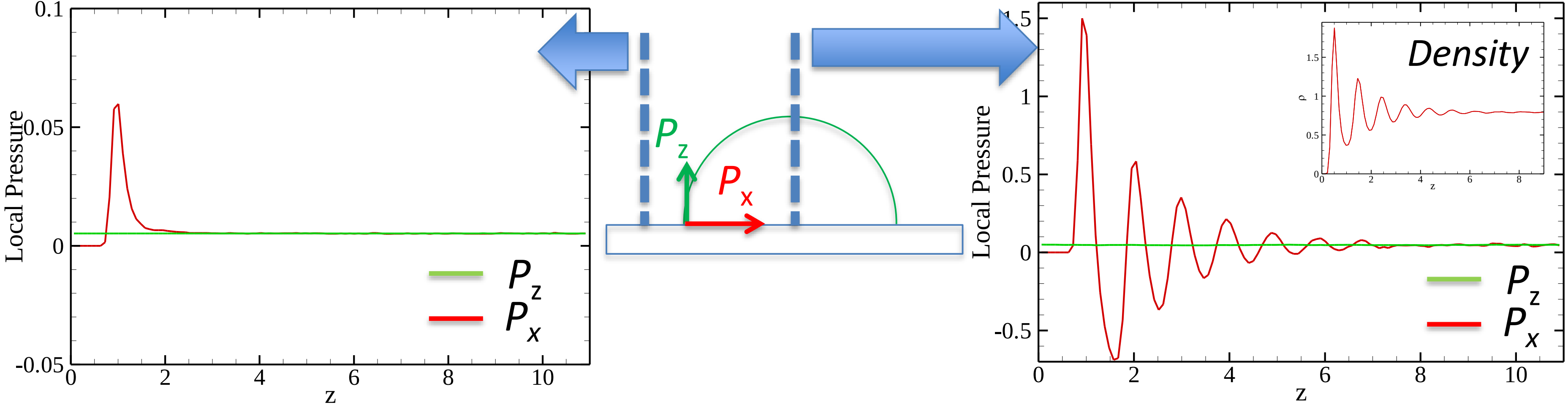
$$P_{Liq} - P_{Vap} = {}^{\gamma_{LV}}\!/_{R}$$

Young-Laplace Eq.

But what occurs at the nanometer scale ?

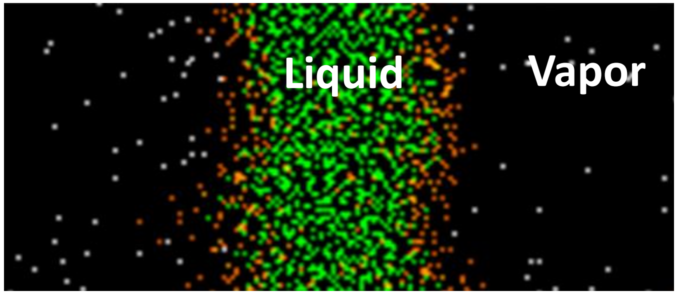
Vapor pressure profile ($\theta \approx \pi/2$)

Liquid pressure profile ($\theta \approx \pi/2$)



As well known P_z= cst everywhere but not P_x (cf. $\gamma = \int (P_z - P_x)dz$)

EQUILIBRIUM: YOUNG-LAPLACE EQUATION (2/2)



From ***liquid/vapor interfaces simulations*** *one can* ***compute surface tension*** γ

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

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

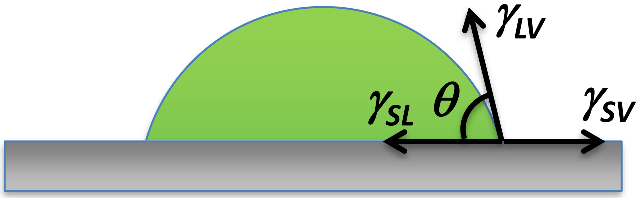
Young-Laplace equation, $\gamma_{LV} = R\Delta P$, is well respected for such nano-droplets *(using normal pressure)*

⇨The curvature correction to γ_{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***



$$\gamma_{LV}\cos\theta_Y = \gamma_{SV} - \gamma_{SL}$$

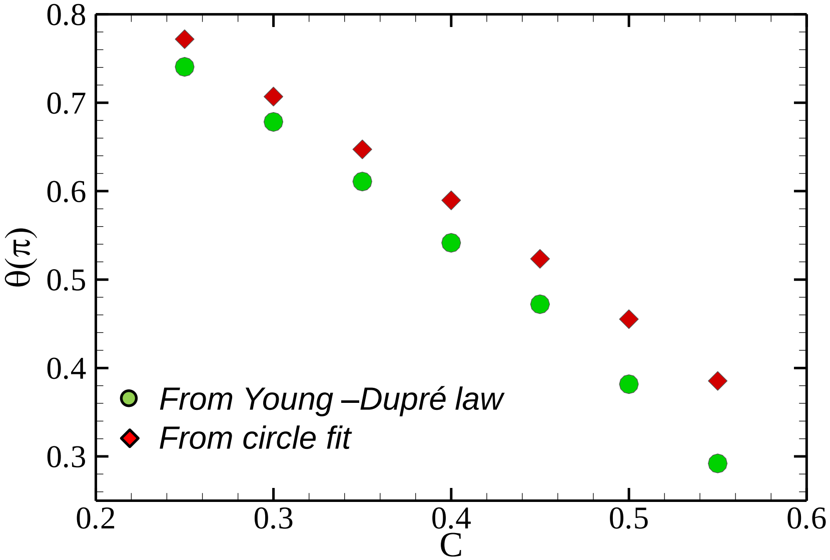
Young-Dupré law

From the computation of all three γ, the Young angle can be estimated

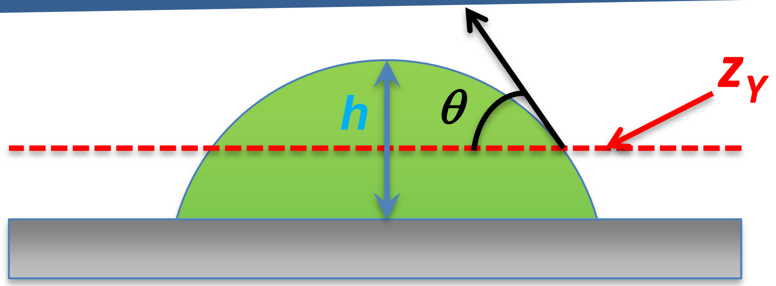
$$\theta_Y = \cos^{-1}\left(\frac{\gamma_{SV}-\gamma_{SL}}{\gamma_{LV}}\right)$$

Young angle, θ_Y, is not equal to the measured angle at *z*=0.5 !

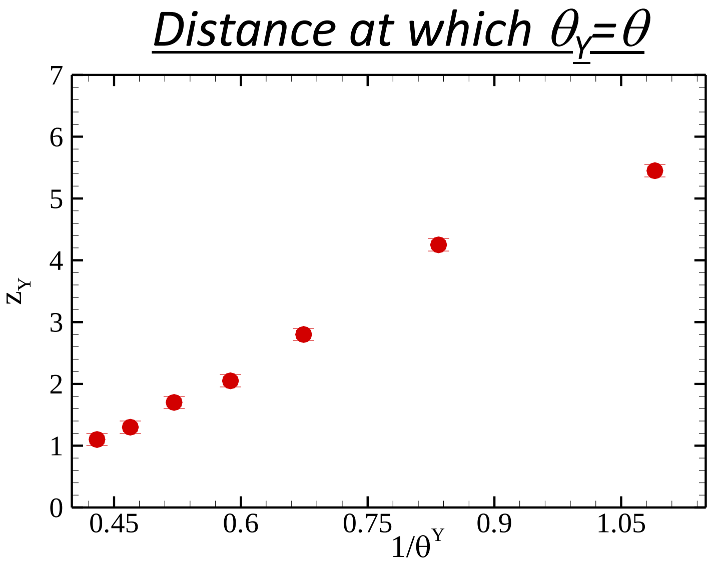
Contact angles vs C



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 $\theta_Y=\theta$

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

Why so:

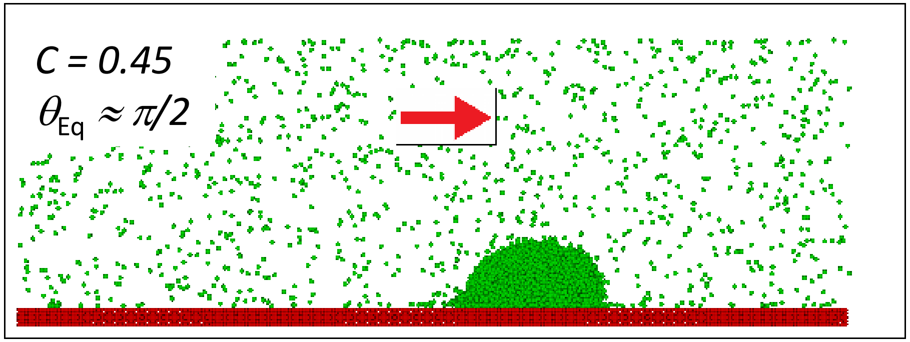
P_x (and so γ) is affected by the surface over long-range (cf. vdW forces)

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

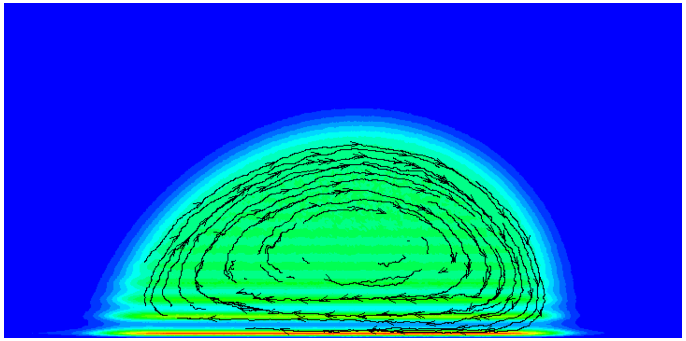
Macroscopically described by disjoining pressure (when $h < z_Y$)

DYNAMICS: DROPLET ($\theta_{Eq} = \pi/2$) UNDER AN EXTERNAL FIELD

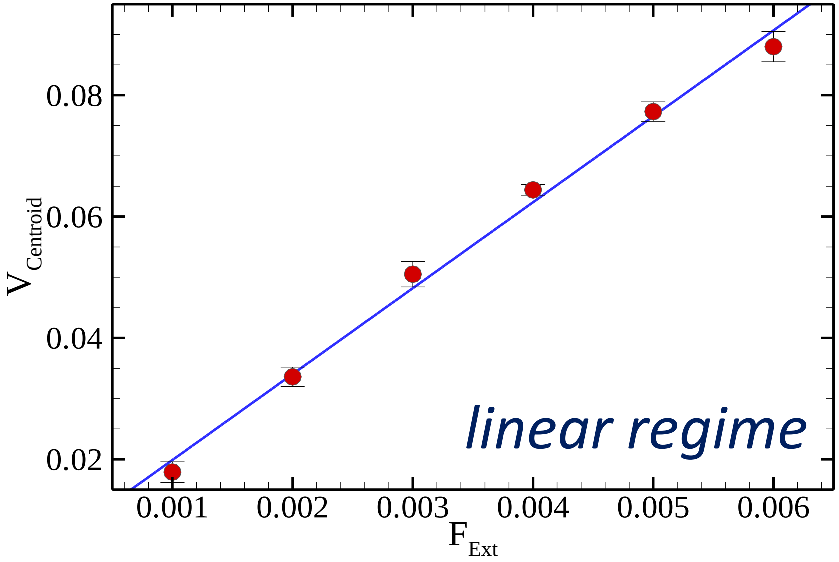
Droplet under a « gravity » field



Flow field (Ca=0.2)



Droplet velocity vs external force



Slip length at Liq/Sol~1

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

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

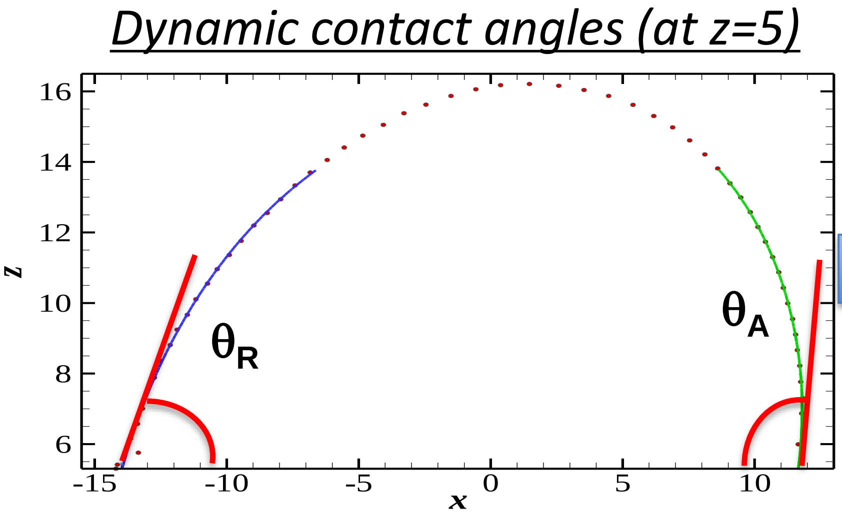
A friction coefficient can be deduced (here $\xi=F/V \approx 0.07$)

Non linear response occurs for smaller θ and high V

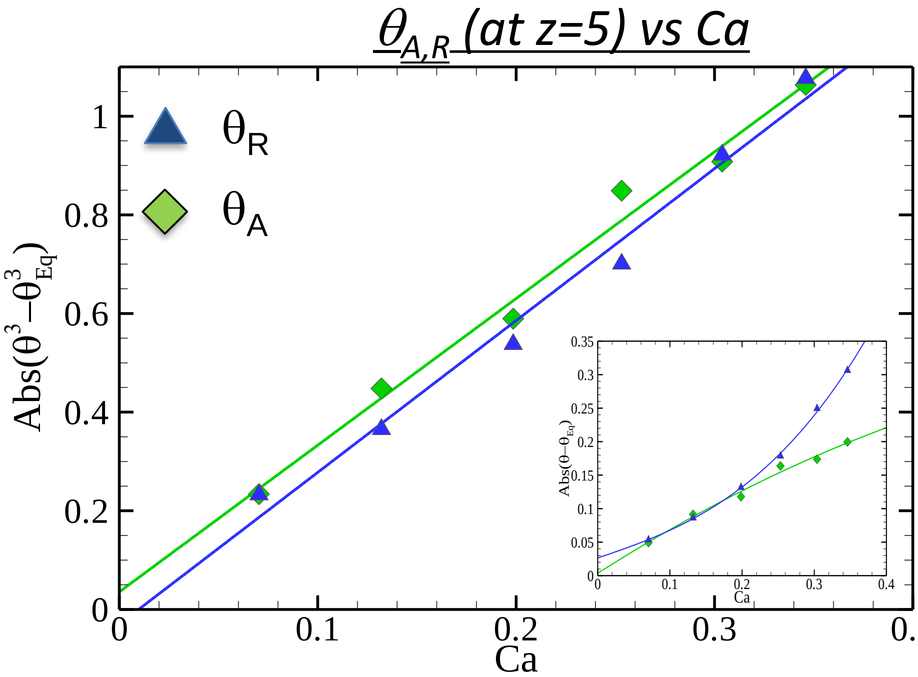
DYNAMICS: ADVANCING/RECEDING CONTACT ANGLES ($\theta_{Eq} = \pi/2$)

*At both contact lines **advancing** and **receding angles** can be measured*

Hydrodynamics model predict that $\theta^3 \propto$ **Ca**


Dynamic contact angles (at z=5)

Circle fit is stil valid


$\theta_{A,R}$ (at z=5) vs Ca

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

Even with nano-droplets (but not too low θ),
hydrodynamics seem to be well respected above z_{YS}!