WETTABILITY PHENOMENA THROUGH SCALES: Tutorial on LBM

Caetano R. Miranda

Dept. of Materials Physics and Mechanics

Institute of Physics

University of Sao Paulo (USP)

São Paulo - Brazil

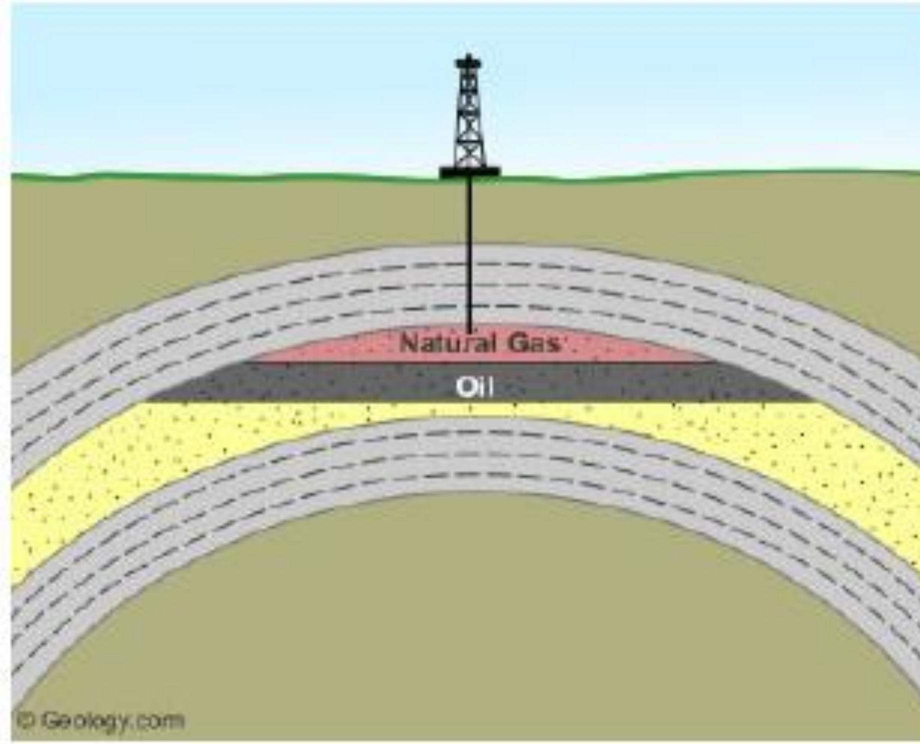
cmiranda@if.usp.br

Files and lecture notes

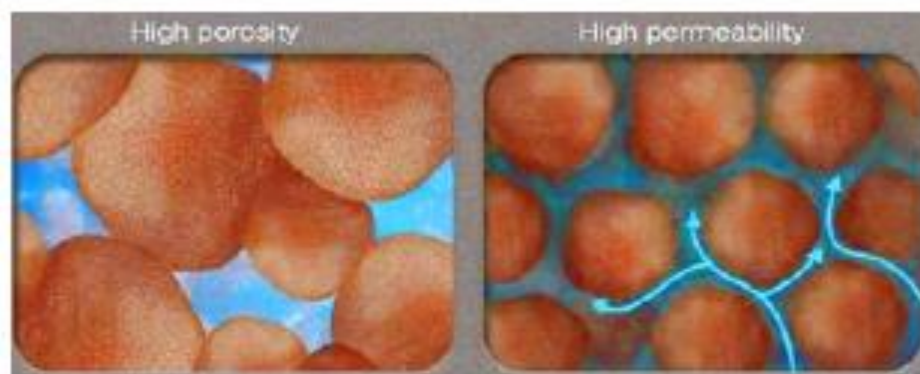
http://sites.google.com/site/cae2016ictp/files

Outline

- *Wettability phenomena*
- *Lattice Boltzmann method (LBM)*
- *Wettability phenomena in heterogenous surface through LBM*

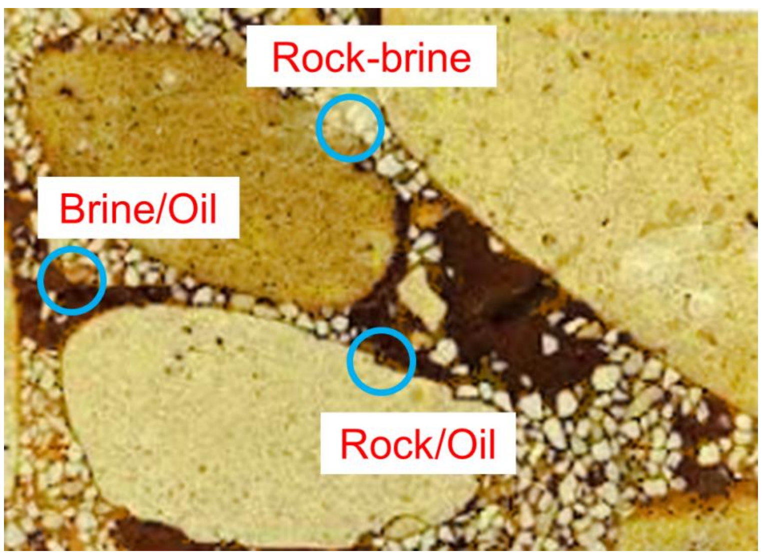


WETTABILITY PHENOMENA

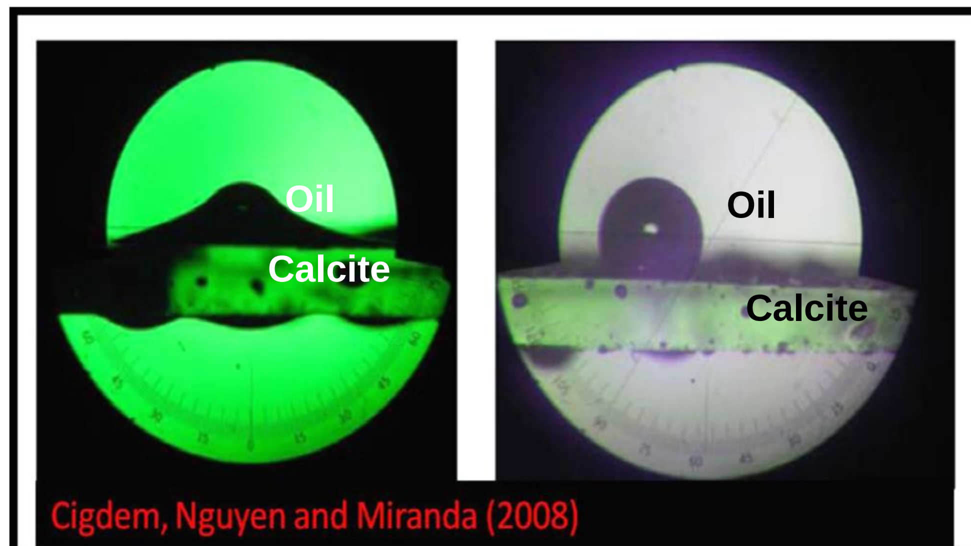


IOR & EOR

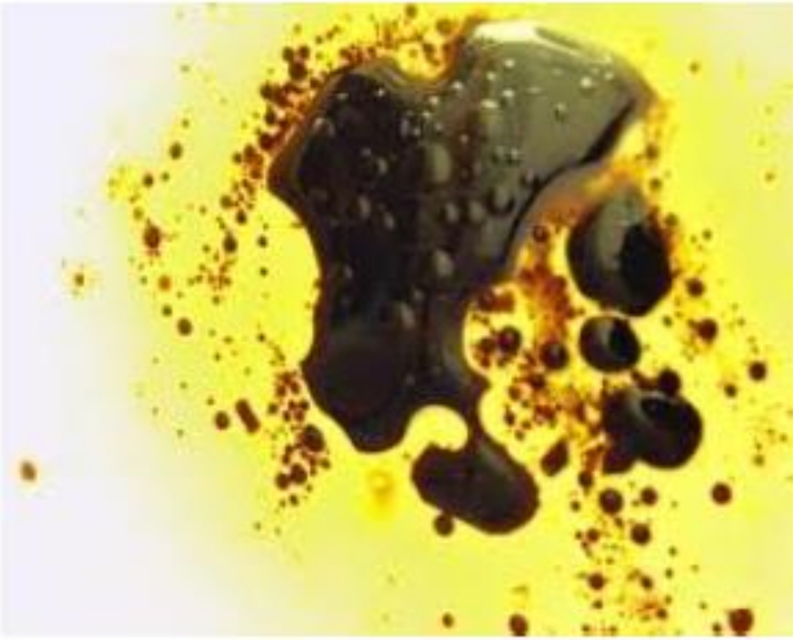
The main strategy is to reduce the interfacial tension (IFT) or the viscosity of crude oil by molecular additives, which can be adsorbed on the oil-fluid interface, or migrate to the crude oil through the interface.

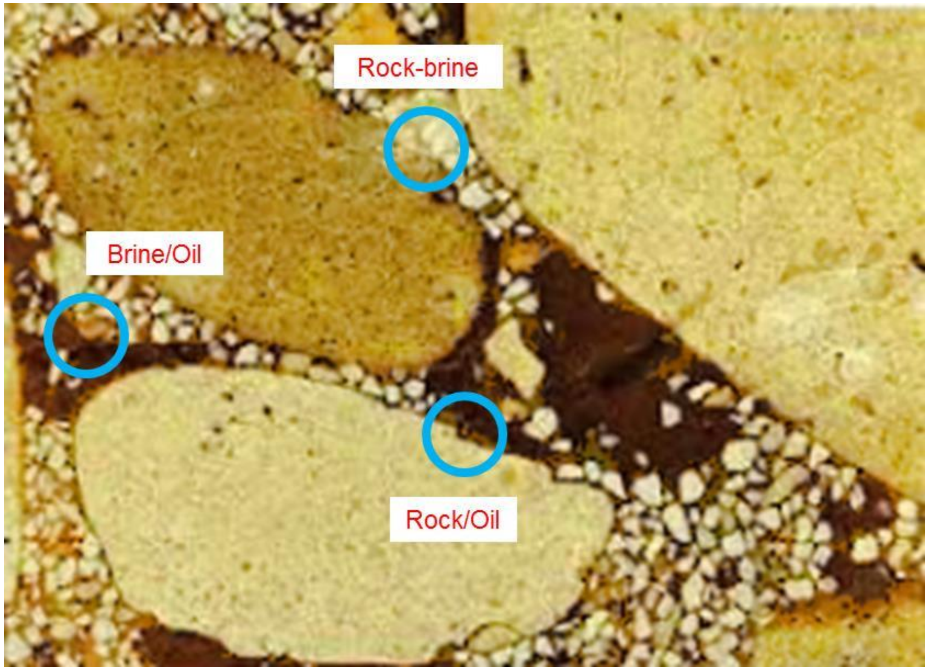


H_2O + SiO_2 nanoparticle



Wettability





Case 1 - Low spreading coefficient interaction brine - crude oil

Accumulation, fractionation and release of oil

$$S = \gamma_{wv} - (\gamma_{ov} + \gamma_{wo})$$

Case 2 - High spreading coefficient

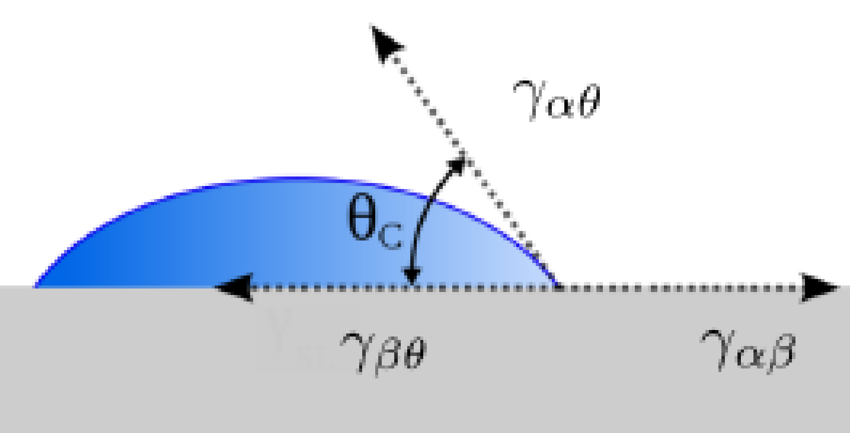
Oil thin film interacting at three-phase interfaces (gas-brine-rock)

Residual-Oil Recovery :

S > 0 → high recovery
S < 0 → low recovery

Three coexisting phases

The Young's relation:



$$\gamma_{\alpha\beta} = \gamma_{\beta\theta} + \gamma_{\theta\alpha} cos\theta_c$$

where α, β and θ are phases of the system.

How QM can help the O&G upstream industry ?

Multi-scale approach

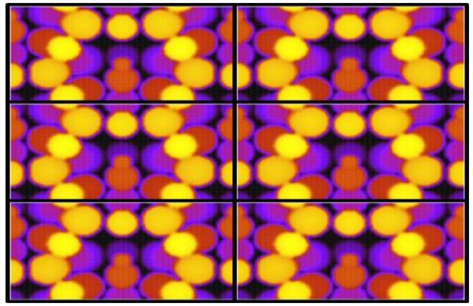
Quantum Mechanics
First principles methods

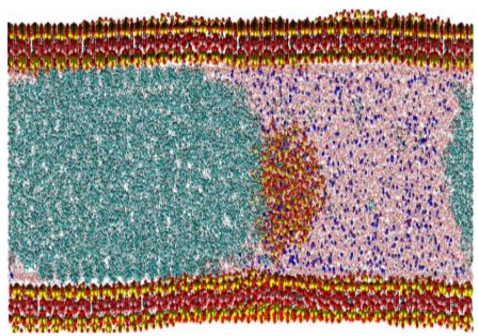
DFT + vdW
NMR,
AFM,XAS

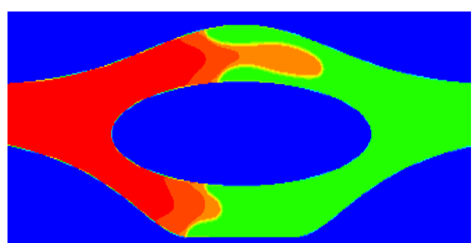
Thermodynamics & Kinetics
Molecular Dynamics

Fed for Mesoscale modeling
& experimental comparison

Lattice Boltzmann







MD (atomistic):
Nanoparticles < 20 nm

DLVO theory:
Nanoparticles > 20 nm
Incorrect predictions for high level of salt % and low pH.

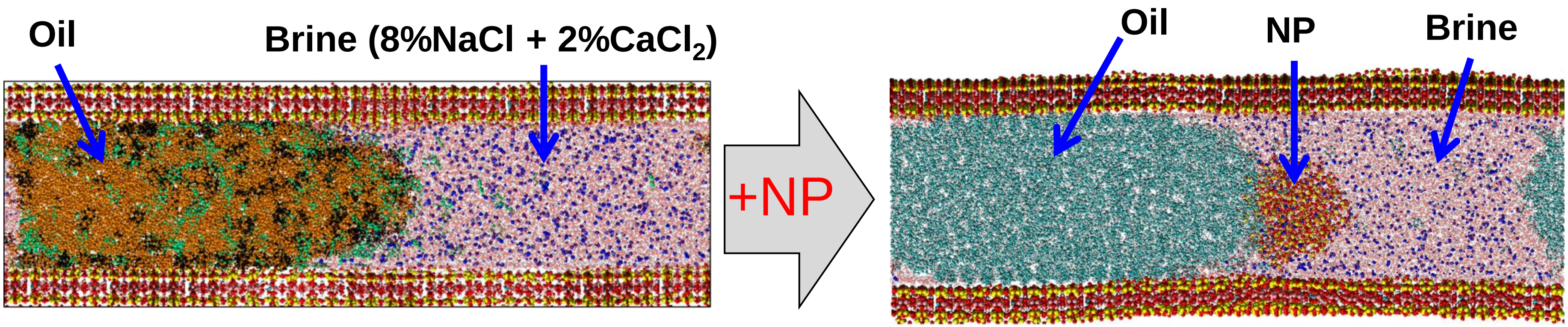
Development of polarazible ab initio based interatomic potentials
Interfacial and transport properties

Stability
Diffusion
Surface tension
Viscosity
Adsorption energies and Resident time

Case study: Brine+NP/Oil/MMT System

MD : nm ns
LBM : µm/mm µs/ms

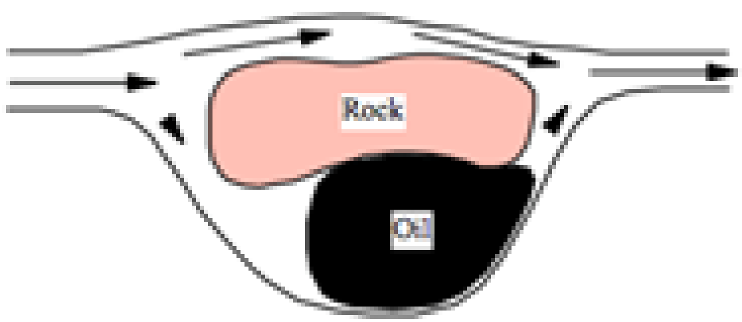
T=300K – 400K
P=1 to 200atm



MD Physical properties
ρ_o=0.81 g/cm^3; ρ_b=0.96 g/cm^3;
η_o=3.62 mPa-s; η_b=0.79 mPa-s;
γ_{ob}=43 mN/m; θ_w= 28^o

ρ_o=0.81 g/cm^3; ρ_b=0.96 g/cm^3;
η_o=3.60 mPa-s; η_b=0.88 mPa-s;
γ_{ob}=38 mN/m; θ_w= 21^o

LBM parameters:
$G = 0.14$; G_w =-0.015;
τ_{oil} = 1.50; τ_{brine}= 0.70



$G = 0.15$; G_w =-0.02;
τ_{oil} = 1.50; τ_{brine} = 0.75

USP

Nanopetro

Interfacial tension from MD

$$\gamma = \left(\frac{\partial F}{\partial A}\right)_{N,V,T} = \left(\frac{\partial G}{\partial A}\right)_{N,P,T}$$

$$\gamma_{ij} = \int [p_B - p_{tt}]dn$$

$$\gamma_{ij} = \int [p_{nn} - p_{tt}]dn$$

$$\gamma_{ij} = \int \Delta p dz$$

where

$$\Delta p = p_{zz} - \frac{p_{xx} + p_{yy}}{2}$$

$$\gamma = \frac{L_z}{2}\left[p_{zz} - \frac{p_{xx} + p_{yy}}{2}\right]$$

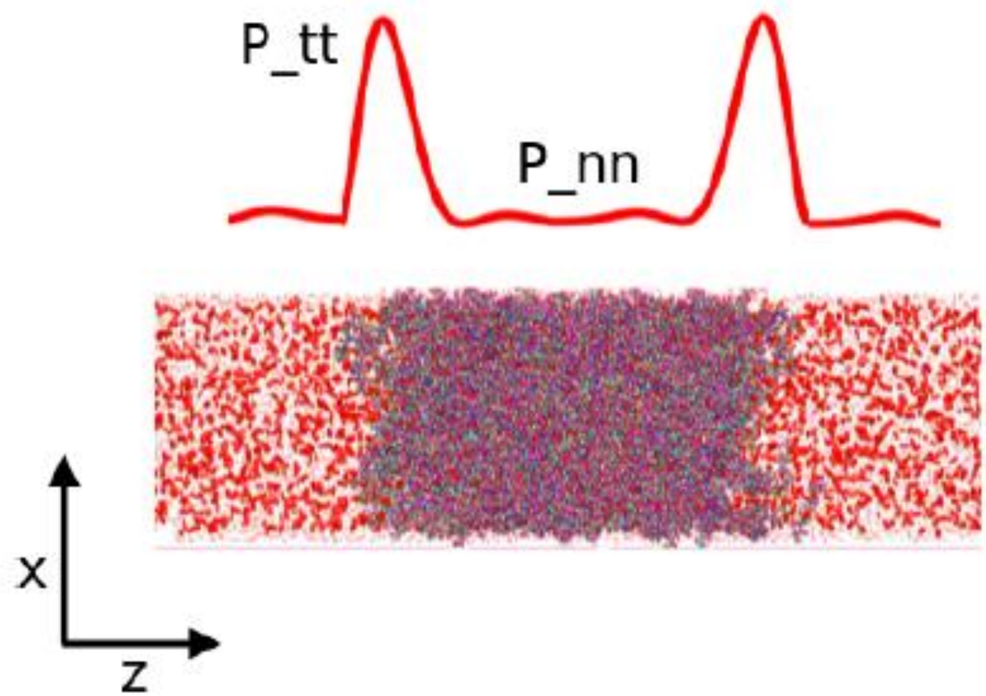
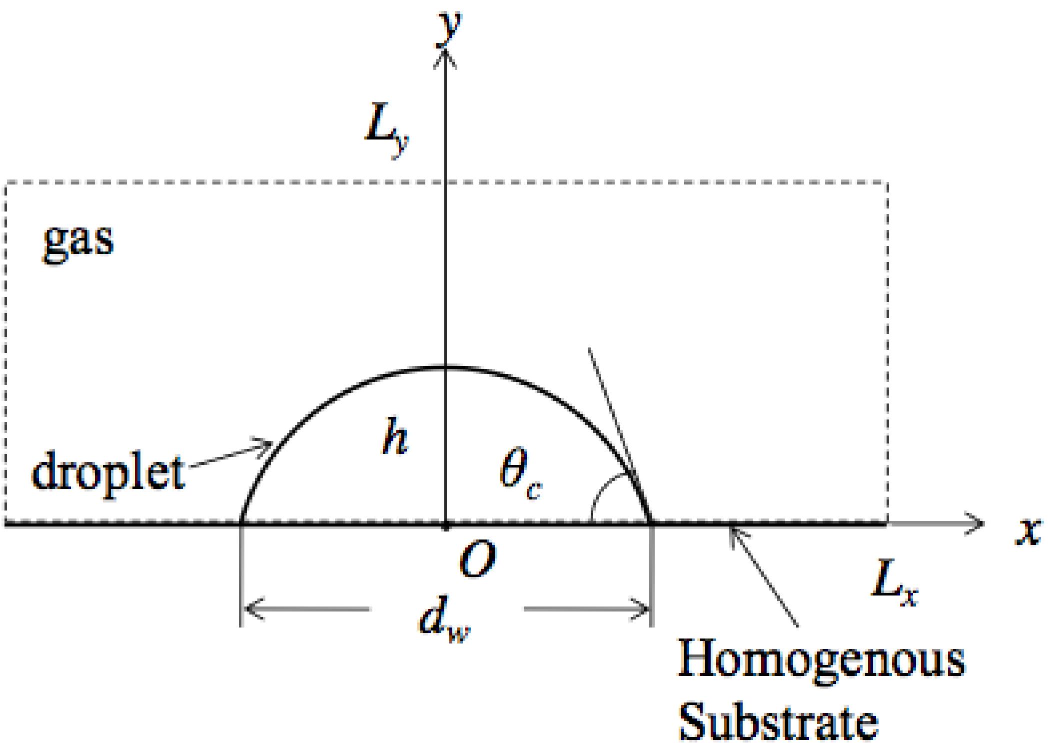


Figure: Application of the Pressure Profile

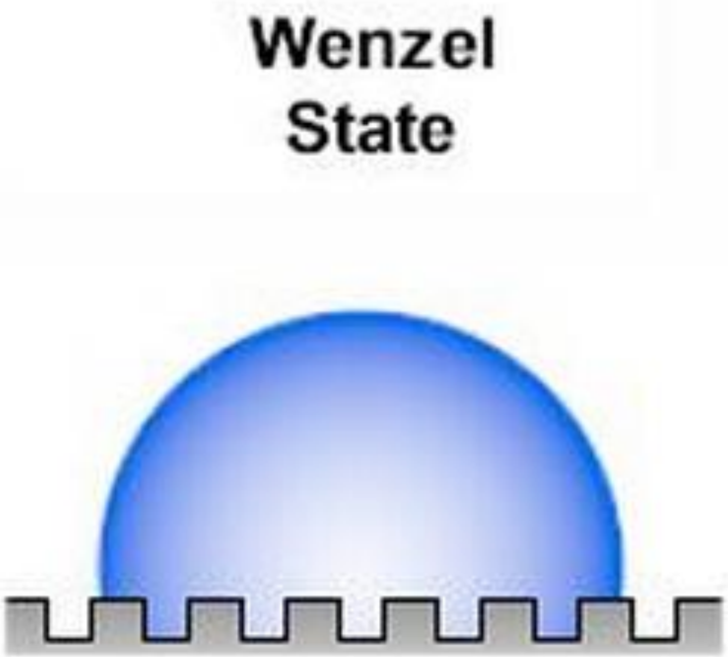
Homogeneous surface - wet

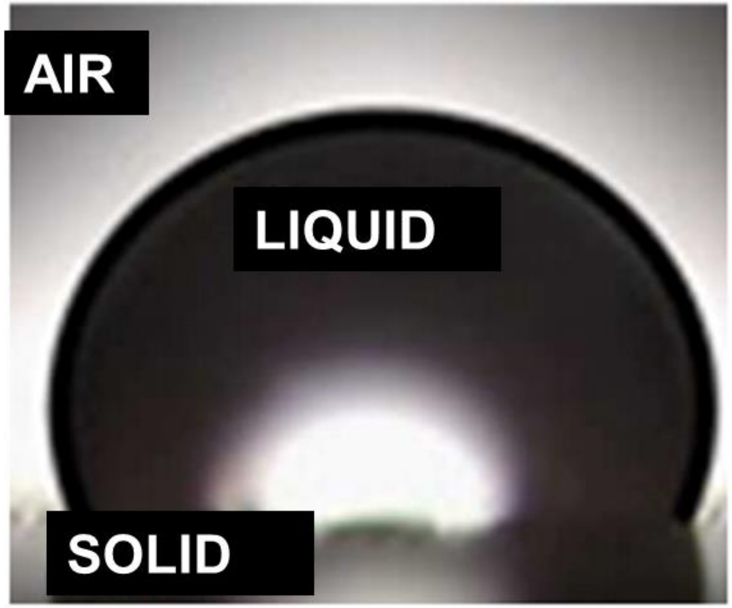
Geometric method: determination of the contact angle



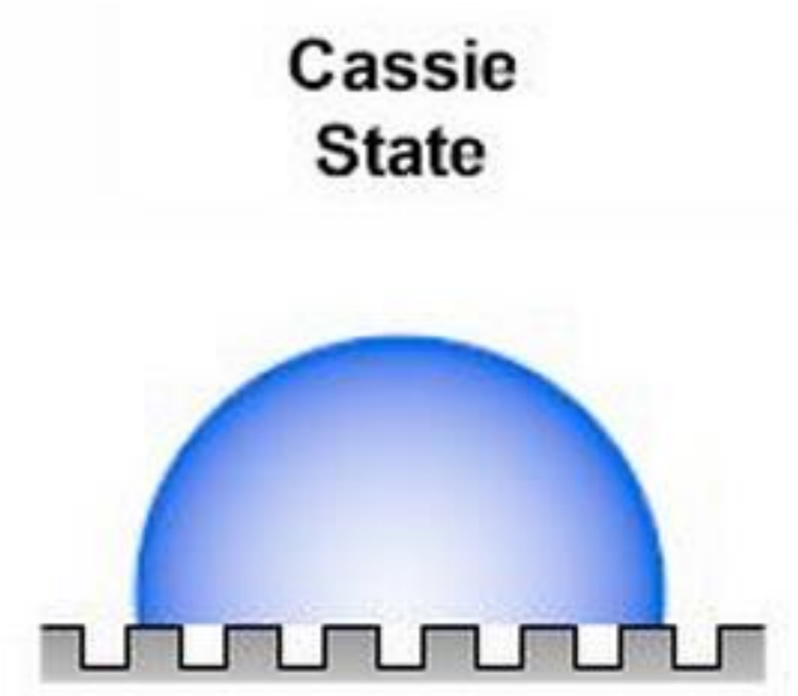
$$\theta_c = \arcsin\left(\frac{d_w h}{(d_w/2)^2 + h^2}\right)$$

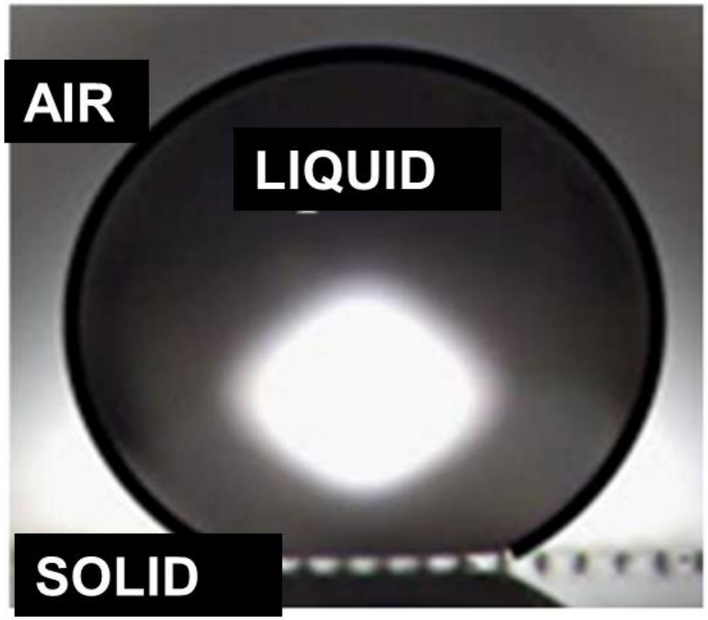
Homogeneous surface - wet



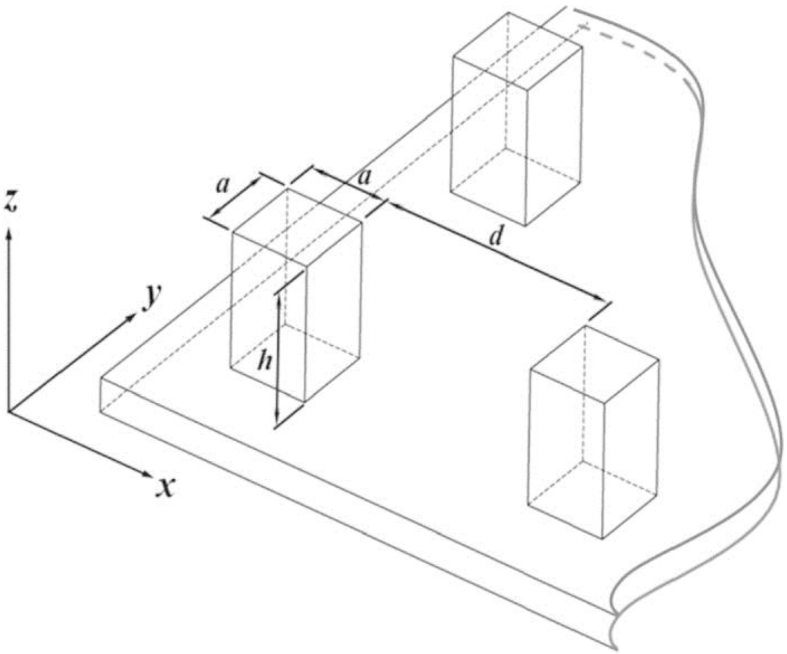


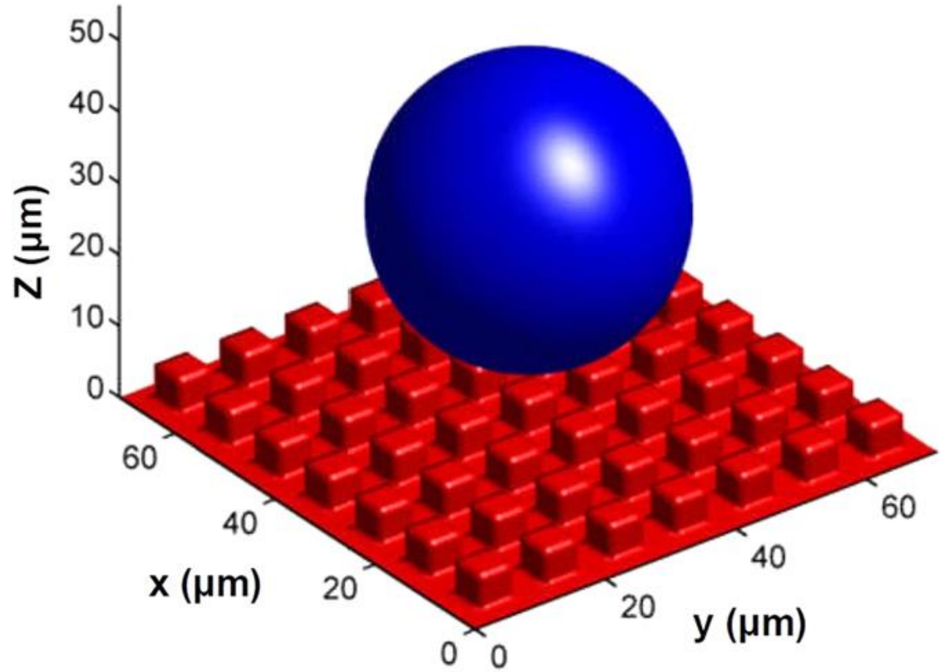
Homogeneous surface - no wet surface





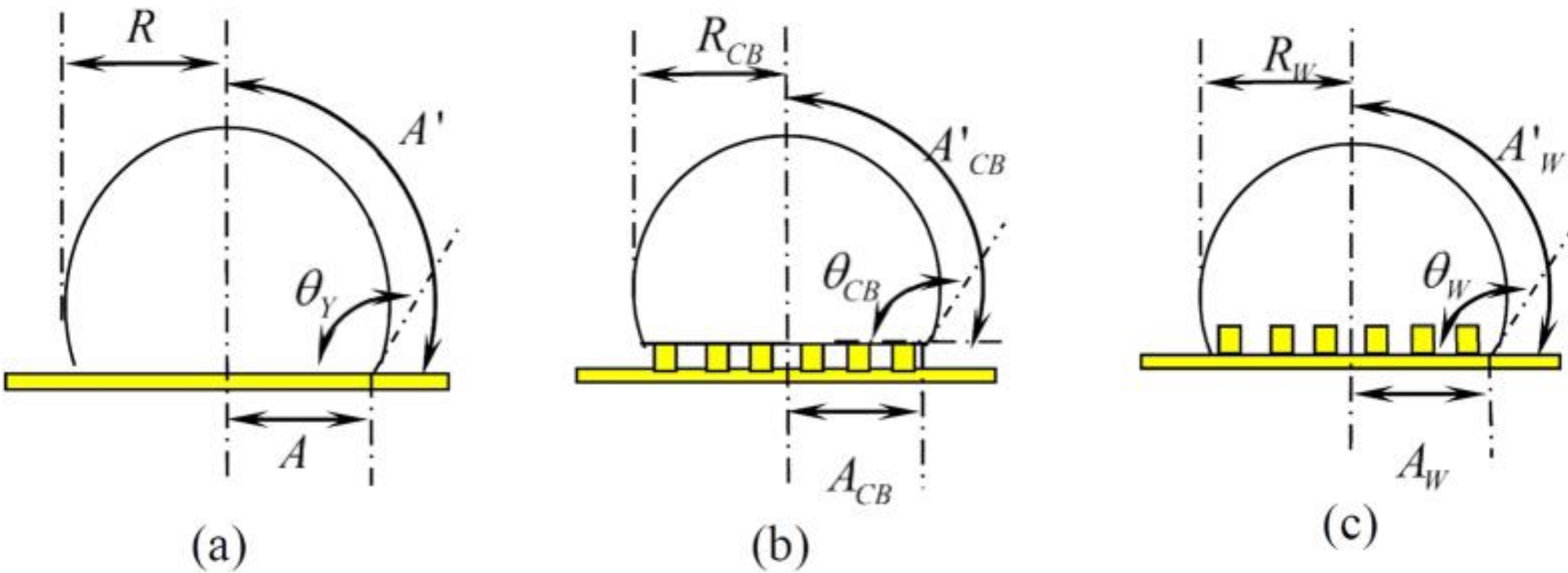
Single Droplet on Micro Square-Post Patterned Surfaces





Y. Q. Zu and Y. Y. Yan, Sci Rep. 2016; 6: 1928

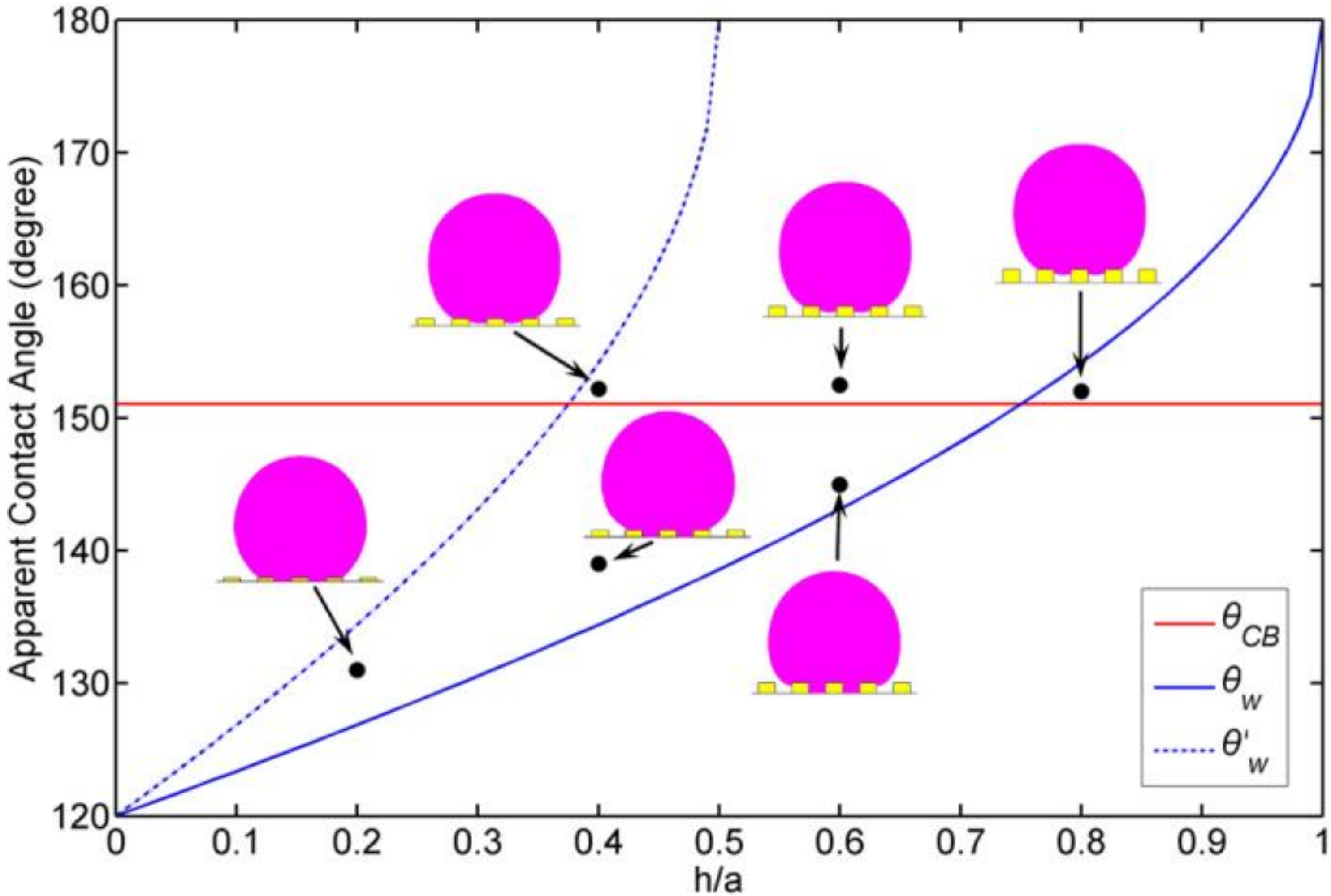
Single Droplet on Micro Square-Post Patterned Surfaces



Cross-section view of the droplet on the surface:(a) droplet on flat surface (**b**) droplet in Cassie state (c) droplet in Wenzel state.

Y. Q. Zu and Y. Y. Yan, Sci Rep. 2016; 6: 1928

Single Droplet on Micro Square-Post Patterned Surfaces



Y. Q. Zu and Y. Y. Yan, Sci Rep. 2016; 6: 1928

Outline

- *Wettability phenomena*
- *Lattice Boltzmann method (LBM)*
- *Wettability phenomena in heterogenous surface through LBM*

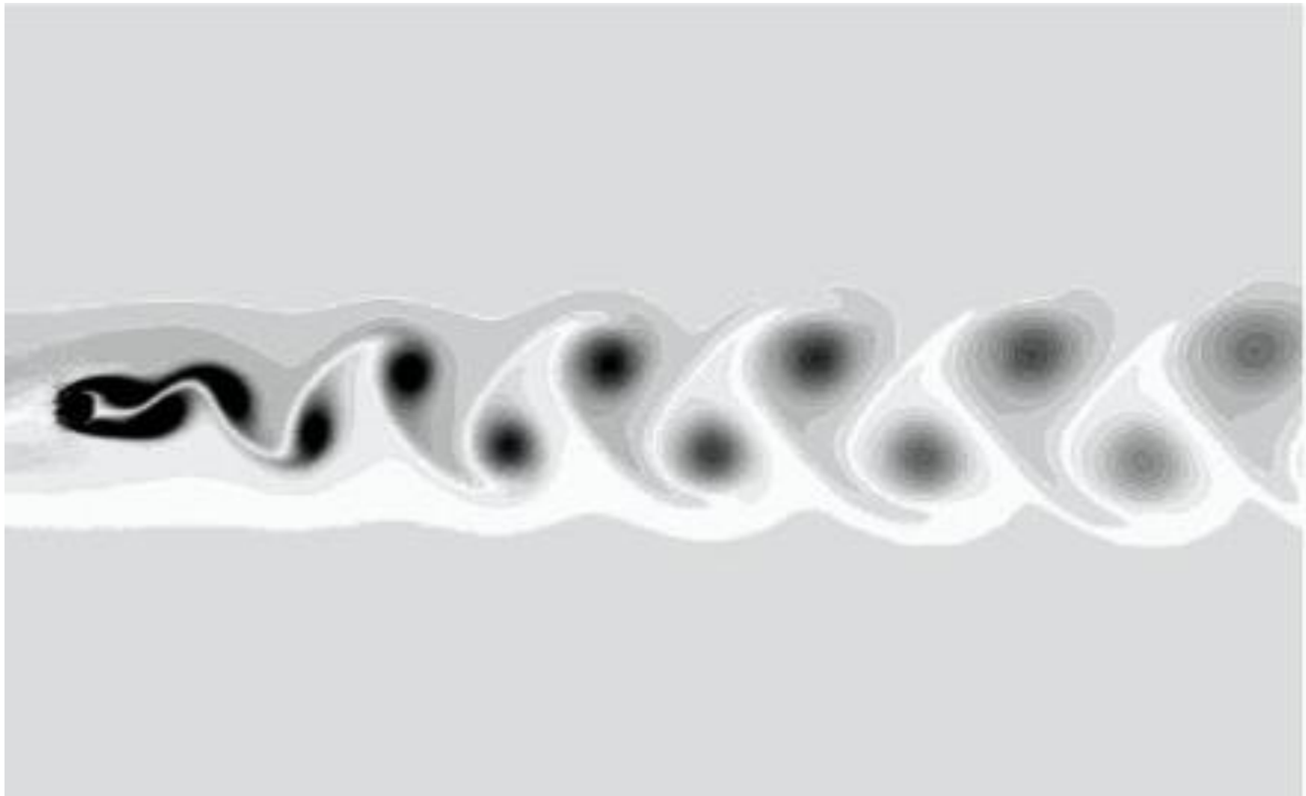
Lattice Boltzmann method (LBM)

- To simulate the fluid hydrodynamics of one or more phases in distinct media.

- It can capture satisfactory phenomena like:

  - Turbulence
  - Phase separation
  - Heat and solute transport
  - Metastable states
  - Evaporation
  - Condensation
  - Interactions between fluids and solids
  - ...

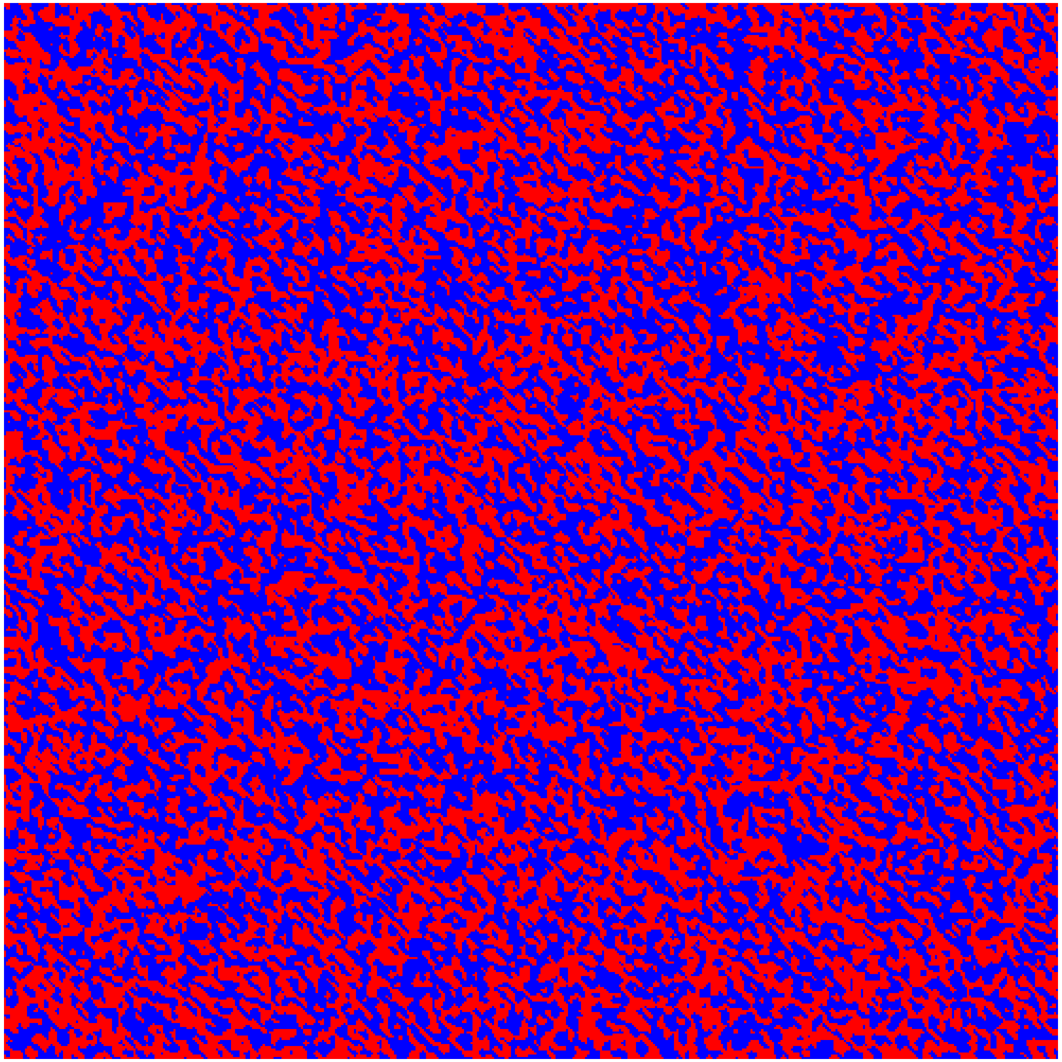
Turbulence



Large Reynolds numbers:

$$Re = \frac{uL}{\nu}$$

Phase separation



Lattice Boltzmann method (LBM)

- It has been used with success over several fields: :
  - Enhanced Oil Recovery (EOR)
  - Carbon capture and sequestration
  - Blood dynamics
  - Infrastructure (Civil Engineering)
  - ...

Lattice Boltzmann method (LBM)

Basic Idea

- Gas/fluids are composed by interacting particles that can be described as "classical particles"

- Given the large amount of particles, a statistical treatment is considered.

- The most simple way to describe the system dynamics is considering: 1) flux and 2) collision between particles.

Molecular Dynamics X LBM :
a Soccer perspective

- **Random**
- **Collisions**
- **Interactions between players result in a goal**

foosball
Simple way to describe the movement of players during a game

Lattice Boltzmann Method X Soccer Game

foosball

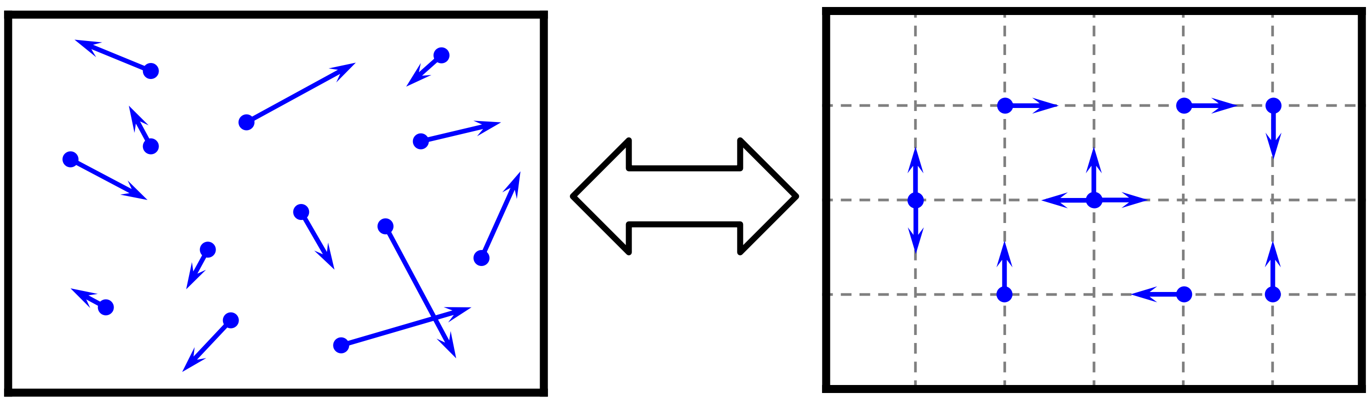
- **Players are confined**
- **Interactions between players is maintained to attain a goal**

Lattice Boltzmann Method X Soccer Game

LBM is very similar to the foosball idea

Microscopic particles inside fluids

Collection of virtual particles with a finite amount of the fluid velocity moving along the lattice links

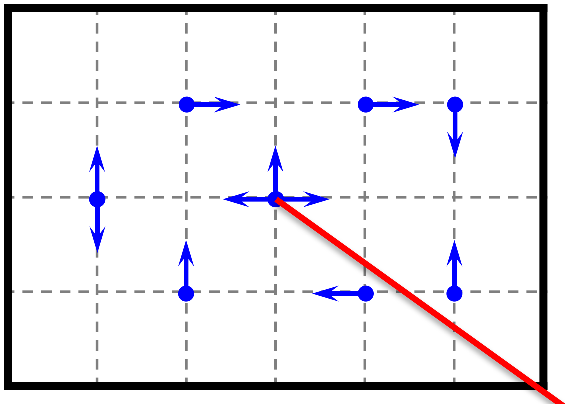


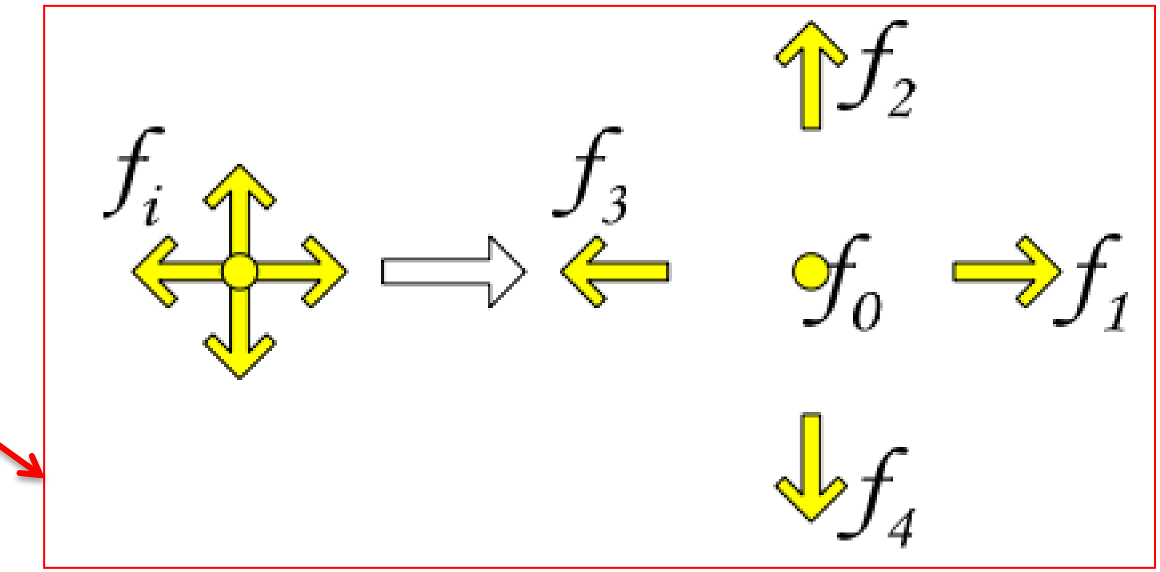
Interaction between particles is through the streaming and collision steps

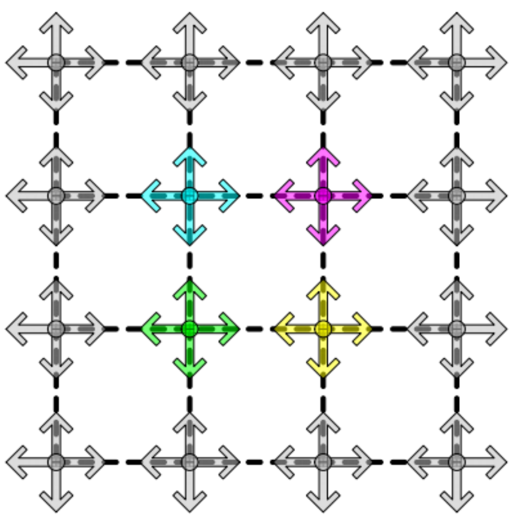
DYNAMICS

Lattice Boltzmann Method

Physical properties are described by a set of distribution functions defined on each direction of the lattice







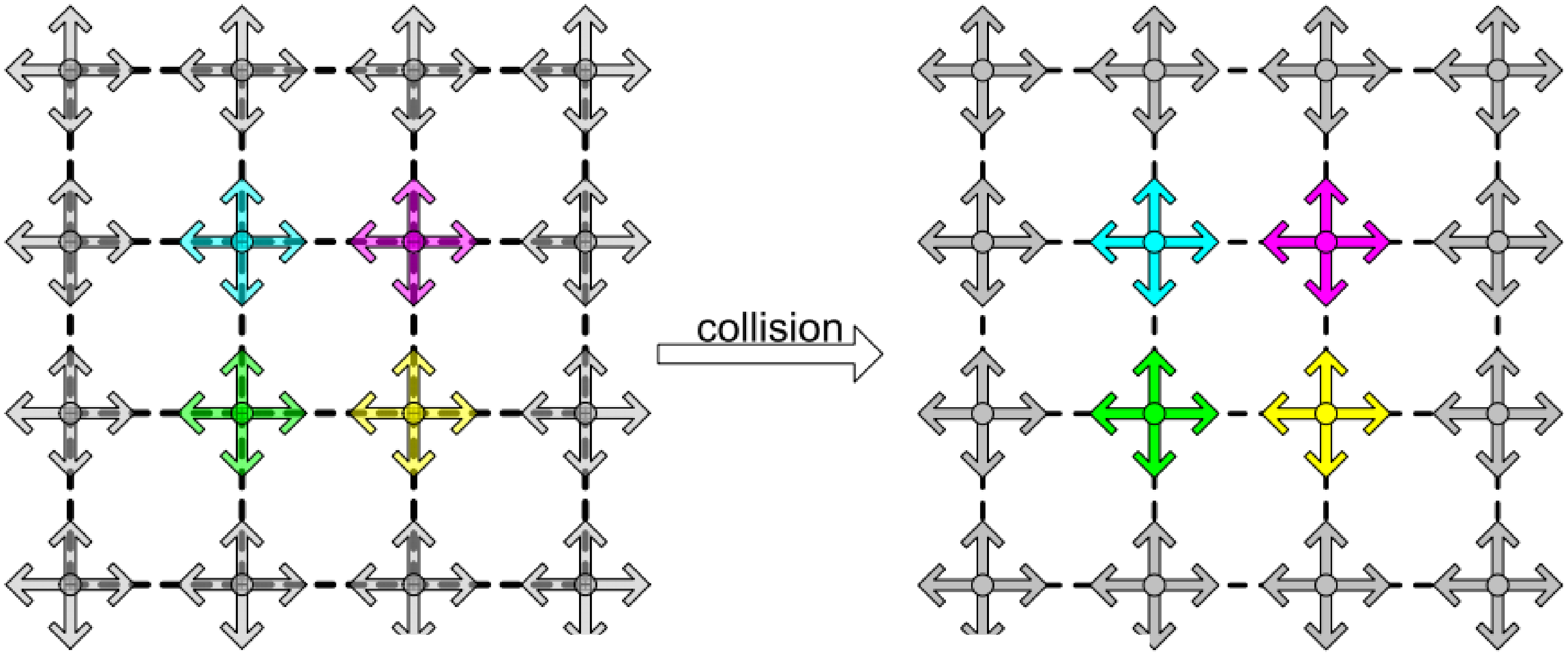
Probability of the amount of fluid in each lattice direction

Lattice Boltzmann Method

Dynamics is described by 2 steps:

$$f_i(r + \Delta t \cdot e_i, t + \Delta t) = f_i(r,t) + \Omega_i(f)$$

Collision Step



$$\Omega(f_i) = -\frac{1}{\tau}(f_i - f_i^{eq})$$

Ensure the correct description of equilibrium properties

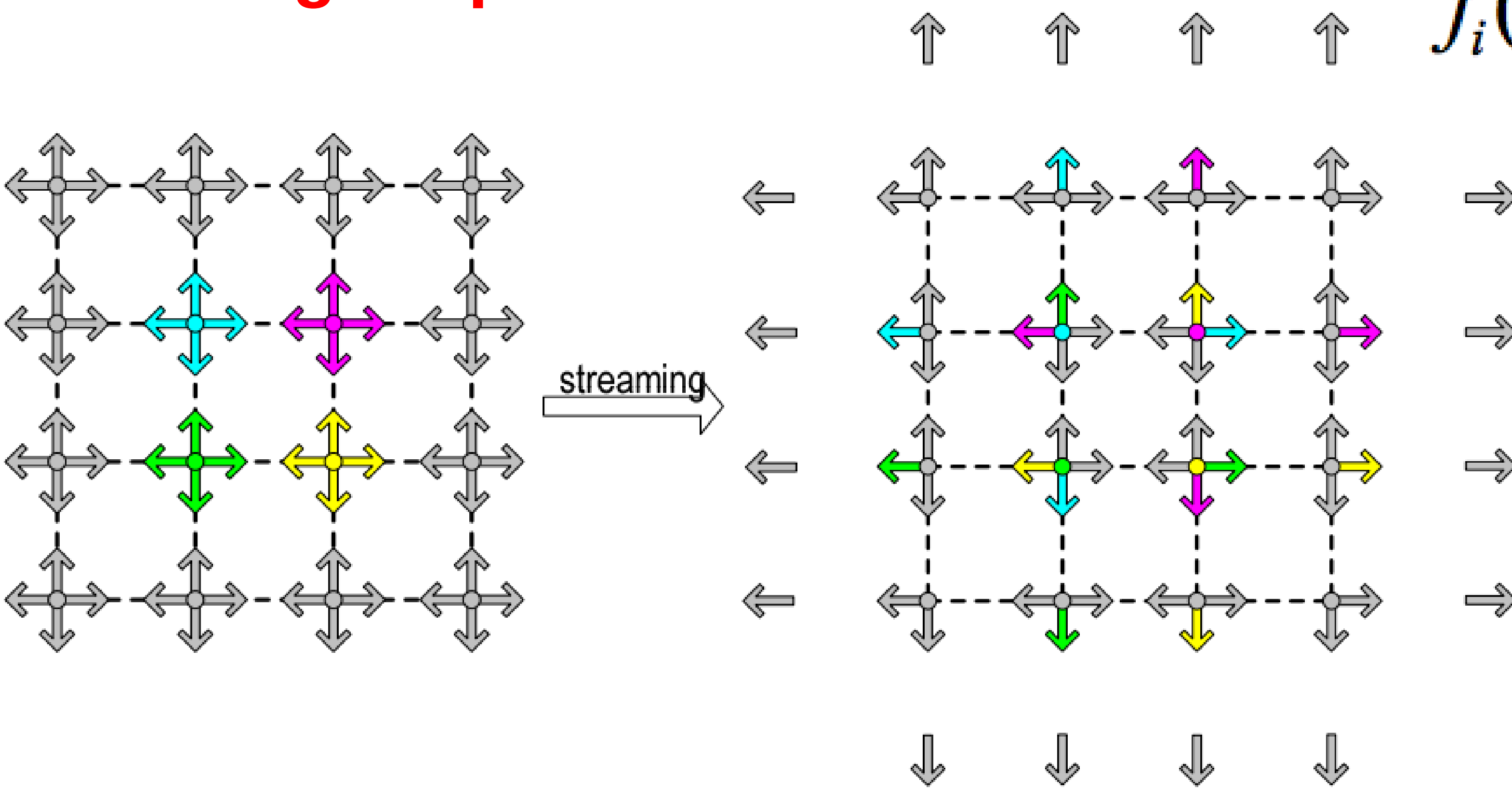
Lattice Boltzmann Method

Dynamics is described by 2 steps:

$$f_i(r + \Delta t \cdot e_i, t + \Delta t) = \underline{f_i(r,t) + \Omega_i(f)}$$

Streaming Step

$$f_i(r,t^*)$$



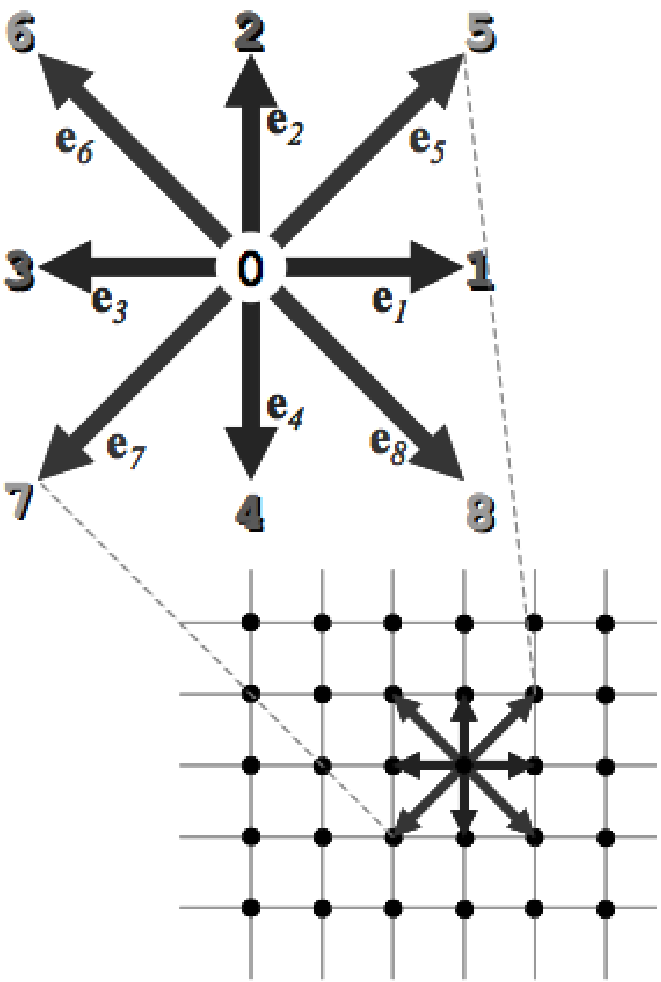
Time evolution

$$f_i(r+e_i,t+1) = f_i(r,t^*)$$

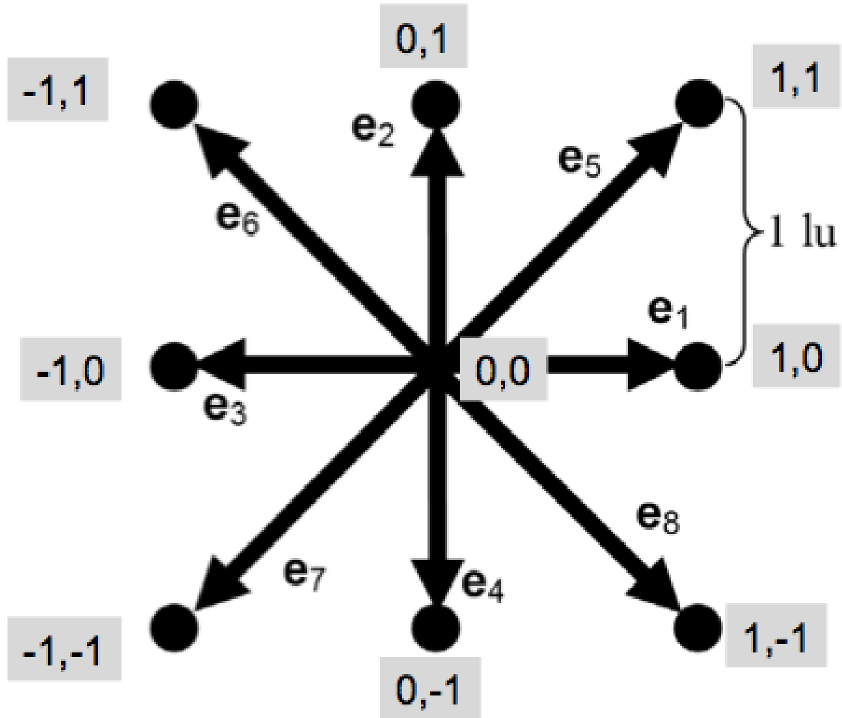
LBM: Shan-Chen model

D2Q9

Phys. Rev. E **47, 1815-1819 (1993)**



Lattice velocity components:



LBM: Shan-Chen model

***Phys. Rev. E* 47, 1815-1819 (1993)**

Equations of motion: Boltzmann equation

$$\underbrace{f_a(\mathbf{x}+\mathbf{e}_a\Delta t, t+\Delta t) = f_a(\mathbf{x},t)}_{\text{Streaming}} - \underbrace{\frac{\left[f_a(\mathbf{x},t) - f_a^{eq}(\mathbf{x},t)\right]}{\tau}}_{\text{Collision}}$$

Equilibrium distribution function:

$$f_a^{eq}(\mathbf{x}) = w_a \rho(\mathbf{x}) \left[1 + 3\frac{\mathbf{e}_a \cdot \mathbf{u}}{c^2} + \frac{9}{2}\frac{(\mathbf{e}_a \cdot \mathbf{u})^2}{c^4} - \frac{3}{2}\frac{\mathbf{u}^2}{c^2}\right]$$

Macroscopic properties:

Visosity

$$\nu = \tfrac{1}{3}(\tau - \tfrac{1}{2})$$

$$\rho = \sum_{a=0}^{8} f_a$$

Density

Velocities

$$\mathbf{u} = \frac{1}{\rho}\sum_{a=0}^{8} f_a \mathbf{e}_a$$

Equation of state (EOS): $P = \dfrac{\rho}{3} + \dfrac{G}{6}\Psi^2(\rho)$

LBM: Shan-Chen model

Phys. Rev. E **47, 1815-1819 (1993)**

The interactions:

-Fluid-fluid (two-phase systems)
-Fluid-solid (wettability)
-External forces: gravity

These interactions can be introduced as variations of the momentum :

$$\mathbf{F} = m\mathbf{a} = m\frac{d\mathbf{u}}{dt} \Rightarrow \Delta\mathbf{u} = \frac{\tau\mathbf{F}}{\rho} \Rightarrow \mathbf{u}^{eq} = \mathbf{u} + \Delta\mathbf{u} = \mathbf{u} + \frac{\tau\mathbf{F}}{\rho}$$

Solid-fluid interaction

$$\mathbf{F}_{ads}(\mathbf{x},t) = -G_{ads}\psi(\mathbf{x},t)\sum_{a} w_a s(\mathbf{x}+\mathbf{e}_a\Delta t)\mathbf{e}_a$$

S=0: No Solid
S=1: Solid phase

G_{ads}: defines wettability

LBM: Shan-Chen model

***Phys. Rev. E* 47, 1815-1819 (1993)**

Ingredients:

- Density
- Viscosity (through the relaxation time τ)
- Surface and interfacial tension (through G)
- wettability (through G_{ad})
- Gravity
- Other external fields (Temperature gradient, electric and magnetic fields, ...)

Explicit Forcing Lattice Boltzmann Method

Porter et al., *Phys. Rev. E* 86, 036701 (2012)

- **Multicomponent interparticle-potential LBM**
- **External forces are incorporated into the discrete Boltzmann equation for each component**
- **Viscosity-independent equilibrium densities**
- **Kinematic viscosity ratios greater than 1000**

Streaming

$$f_i^k(\mathbf{x}+\mathbf{e}_i\Delta t, t+\Delta t) - f_i^k(\mathbf{x},t) = \frac{1}{\tau_k}\left[f_i^{eq,k}(\mathbf{x},t) - f_i^k(\mathbf{x},t) - \frac{\Delta t}{2} f_i^{F,k}\right] + \Delta t f_i^{F,k}$$

Collision

Forcing terms

Outline

- *Wettability phenomena*
- *Lattice Boltzmann method (LBM)*
- *Wettability phenomena in heterogenous surface through LBM*

Simulation: homogenous surface

Compile the codes:

```
MANDY:LAB_LBM aopereira$ gfortran -o shanchen.x ShanChen-D2Q9.f90
MANDY:LAB_LBM aopereira$ gcc -o bmp2top.x converter.c
```

Parameters:

- t = 1
- G_{ad} = -120.0
- G_{w} = -250.0
- Gravity = 0.0
- Droplet density= 500
- Density (out of the droplet)= 100
- Lattice size: 128x80
- Time: Nt = 3000
- Interval in time to print the results: Ntdis = 100
- Droplet radiius= 15 lu
- Position of the droplet´s center (x,y) in l.u.: 64 9

Simulation: homogenous surface

LBM simulation:
Step 1: Define the surface´s topology from an input file
Convert a bmp file in to text file

Copy the file with the name ´topology.bmp´

```
MANDY:LAB_LBM aopereira$ cp topology_homogeneo.bmp topology.bmp
```

To generate the topology surface input file:

Let us use the **bmp2top.x** to convert the topology.bmp to be used in the **shanchen.x** code.

Simulation: homogenous surface

LBM simulation:

Step 1: Define the surface´s topology from an input file

Convert a bmp file into text file

Execute the bmp2top.x file

- It will create an text file (BC.top) with 128x80 dimension.
- Modify the name of the BC.top to keep this specific topology (homogenous)
- bmp2top.x overwrites the BC.top in each run.

```
MANDY:LAB_LBM aopereira$ ./bmp2top.x

128
80
MANDY:LAB_LBM aopereira$ ls
BC.top                  converter.c             topology_hetero_2.bmp
BC.txt                  shanchen.x              topology_hetero_3.bmp
ShanChen-D2Q9.f90       topology.bmp            topology_homogeneo.bmp
bmp2top.x               topology_hetero_1.bmp
MANDY:LAB_LBM aopereira$ mv BC.top BC_homogeneo.top
```

Simulation: homogenous surface

Code running:

```
MANDY:LAB_LBM aopereira$ ./shanchen.x

 Entrer size of grid (Nx,Ny):
128 80
 Enter time for silumation: Nt
10000
 Enter time interval to display results: Ntdis
500
 Enter relaxation time: Tau
1.0
 Poiseuille Simulation (1), Phase Separation (2), Droplet Spreading (3):
3

 !!!!! Spreading of a Droplet !!!!!

 Enter Radius of the droplet:
15
 Density inside the droplet:
500
 Density outside the droplet:
100
 Enter coordinates of the center of the droplet (Xcen,Ycen):
64 9
 Enter gravity acceleration in lattice units:
0.0
 Enter Interaction Strength between fluid phases (Gad):
-120.0
 Enter Interaction Strength between fluid and solid phases (Gw):
-250.0
 Enter Input file for topology (BC):
BC_homogeneo.top

 Grid Size          128          80
 Number of time interactions     =      10000
 How often results are displayed =        500
 TauF =    1.0000000000000000
 !&& TIME =           500
```

Simulation: homogenous surface

Results: FILE PRESSURE000100.dat

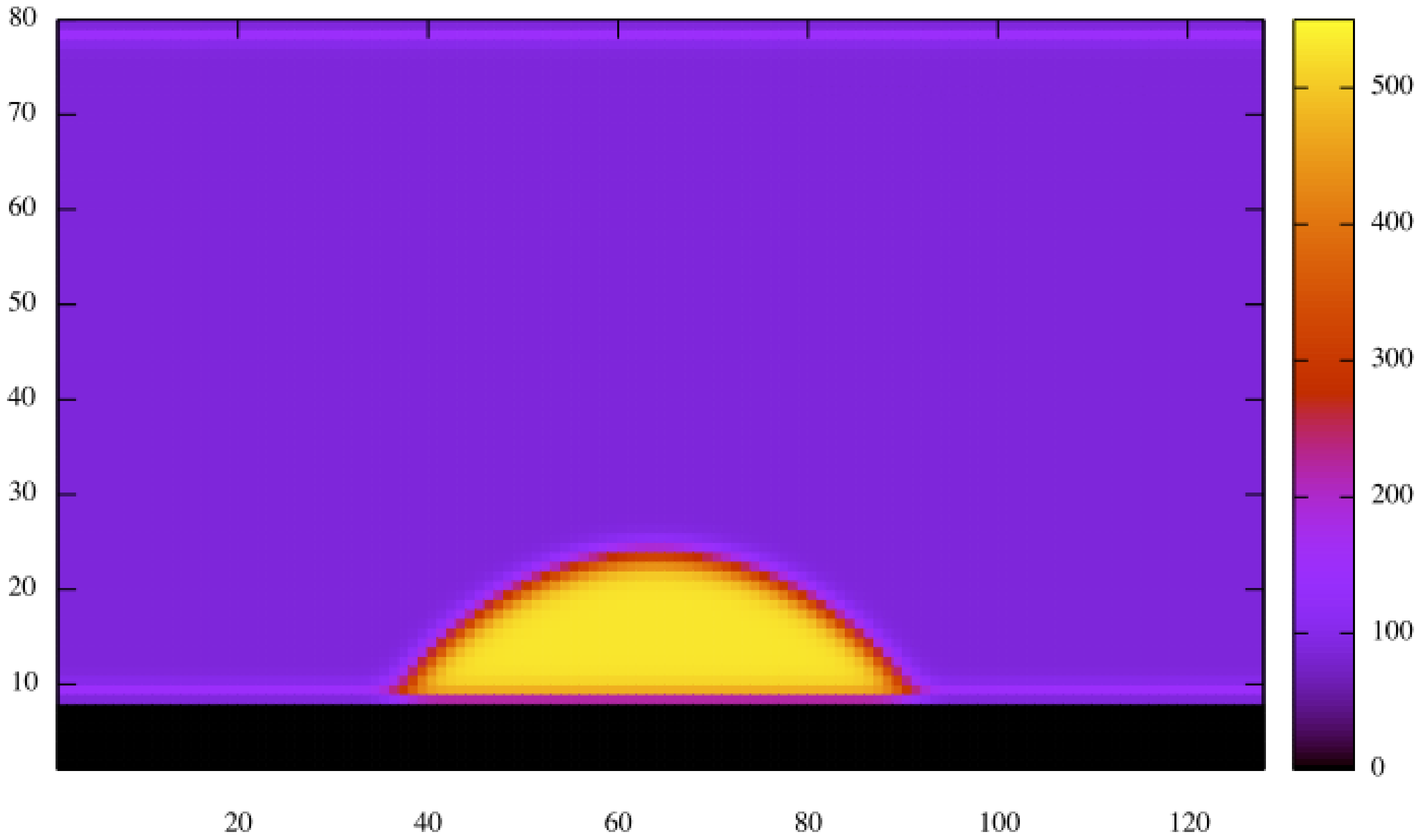
```
# x,y,Pr(x,y),ueq(1,x,y),ueq(2,x,y)
           1           1   0.0000000000000000        0.0000000000000000        0.0000000000000000
           1           2   0.0000000000000000        0.0000000000000000        0.0000000000000000
           1           3   0.0000000000000000        0.0000000000000000        0.0000000000000000
           1           4   0.0000000000000000        0.0000000000000000        0.0000000000000000
           1           5   0.0000000000000000        0.0000000000000000        0.0000000000000000
           1           6   0.0000000000000000        0.0000000000000000        0.0000000000000000
           1           7   0.0000000000000000        0.0000000000000000        0.0000000000000000
           1           8   0.0000000000000000        0.0000000000000000        0.0000000000000000
           1           9   0.0000000000000000        0.0000000000000000        0.0000000000000000
           1          10   0.0000000000000000        0.0000000000000000        0.0000000000000000
           1          11   0.0000000000000000        0.0000000000000000        0.0000000000000000
           1          12   0.0000000000000000        0.0000000000000000        0.0000000000000000
           1          13   0.0000000000000000        0.0000000000000000        0.0000000000000000
```

X   Y   Pressure   Velocities-X   Velocities-Y

Simulation: homogenous surface

Results: Density profile

```
gnuplot>
gnuplot> set pm3d map; set size ratio -1; set cbrange[0:550]
gnuplot> splot [1:128][1:80]'DENSITY003500.dat' u 1:2:3
gnuplot>
```



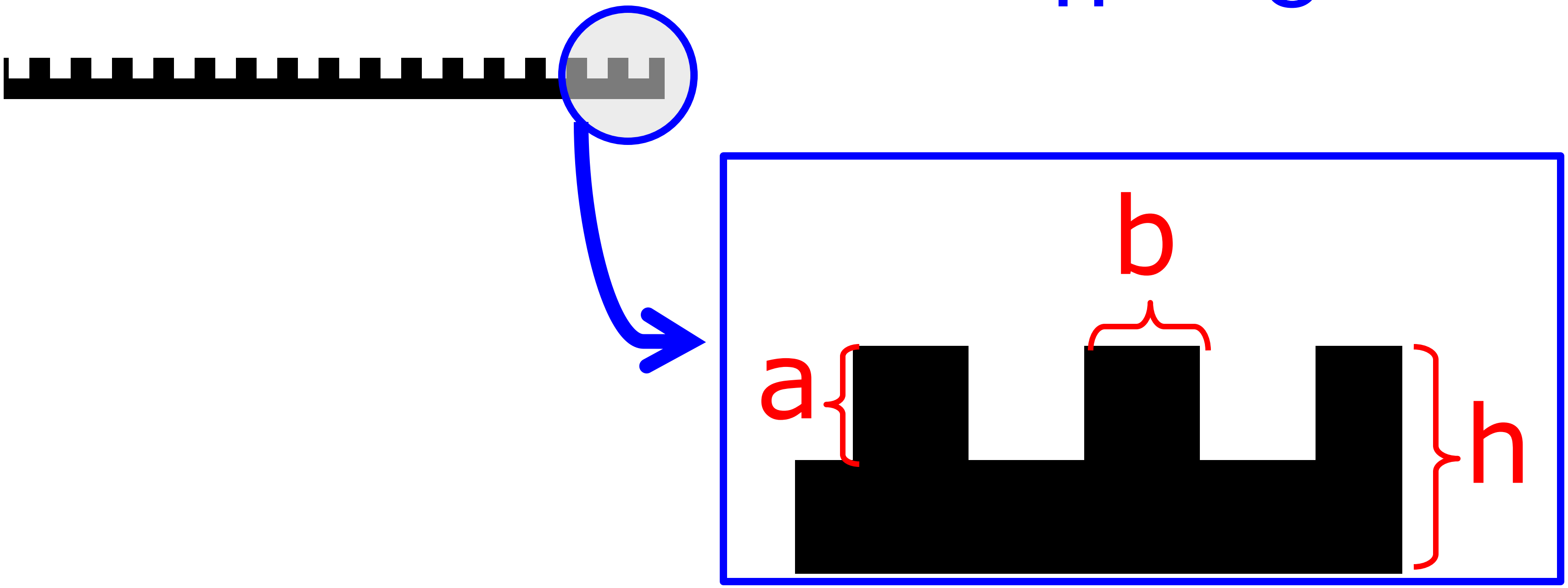
Simulation: heterogenous surface

Surface TYPE I

$a = 4$

$b = 4$

$h = 8$



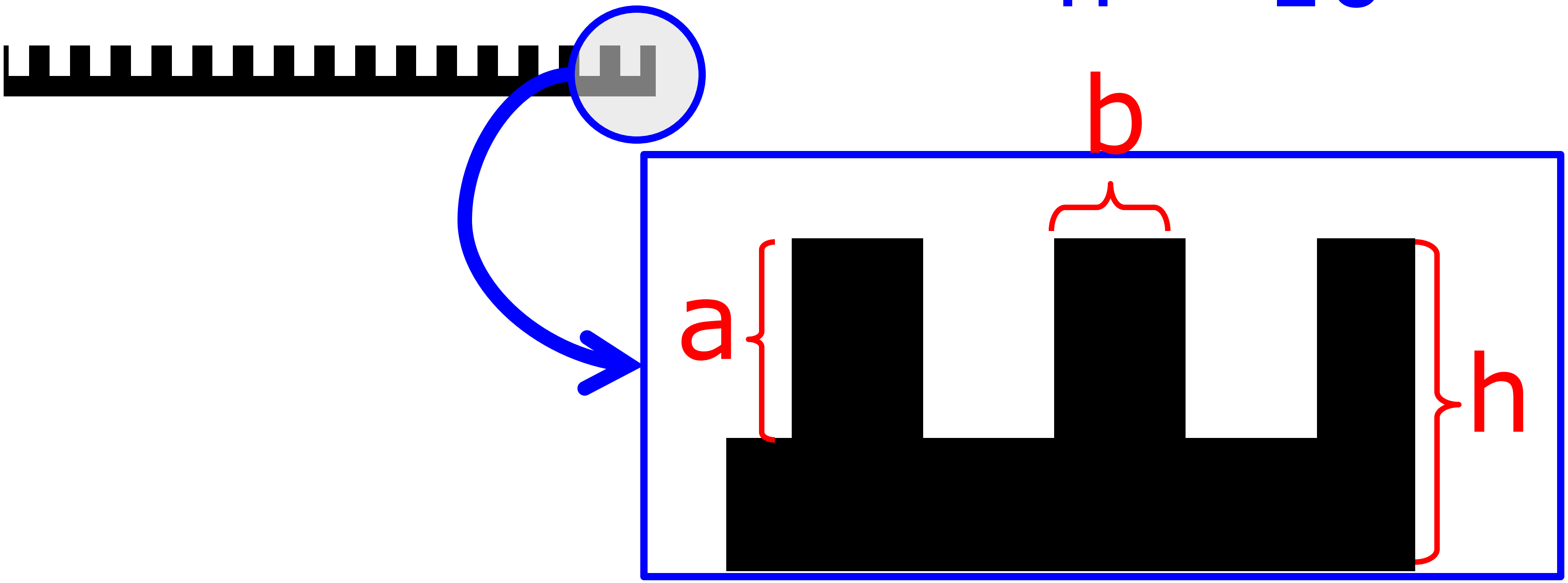
Simulation: heterogenous surface

Surface TYPE I

$a = 6$

$b = 4$

$h = 10$



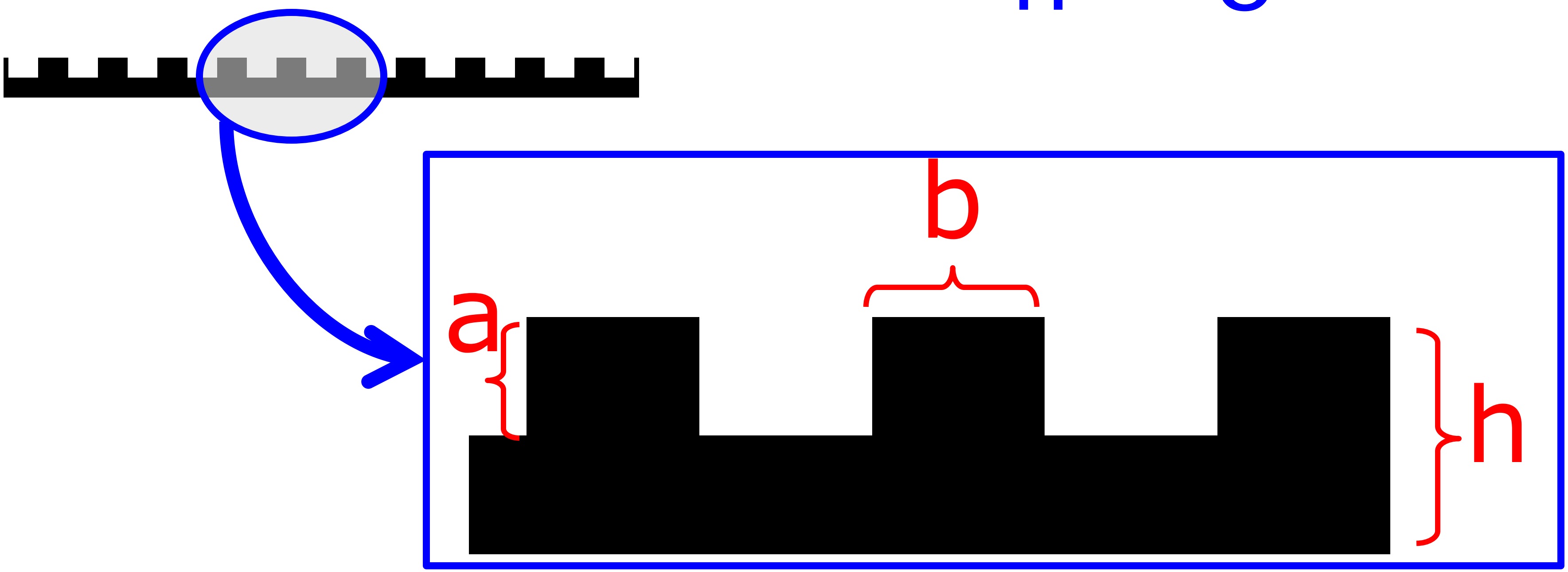
Simulation: heterogenous surface

Surface TYPE I

$a = 4$

$b = 6$

$h = 8$



Computer experiments – part 1

- Vary the Gw values within the interval (-327, -46).
- Verify how the contact angle is affected by this quantity.
- Generate a curve (Contact angle versus Gw)

Computer experiments – part 2

- Simulate the Cassie and Wenzel states for different surfaces:

  a = 4 e b = 4 (topology_hetero_1.bmp);
  a = 6 e b = 4 (topology_hetero_2.bmp);
  a = 4 e b = 6 (topology_hetero_3.bmp).

Computer experiments - Challenge

- Verify the effects of gravity over the Cassie and Wenzel´s states.

- Use values of the order of **10^{-5}.**