Flows of molecular fluids in nano-structured channels

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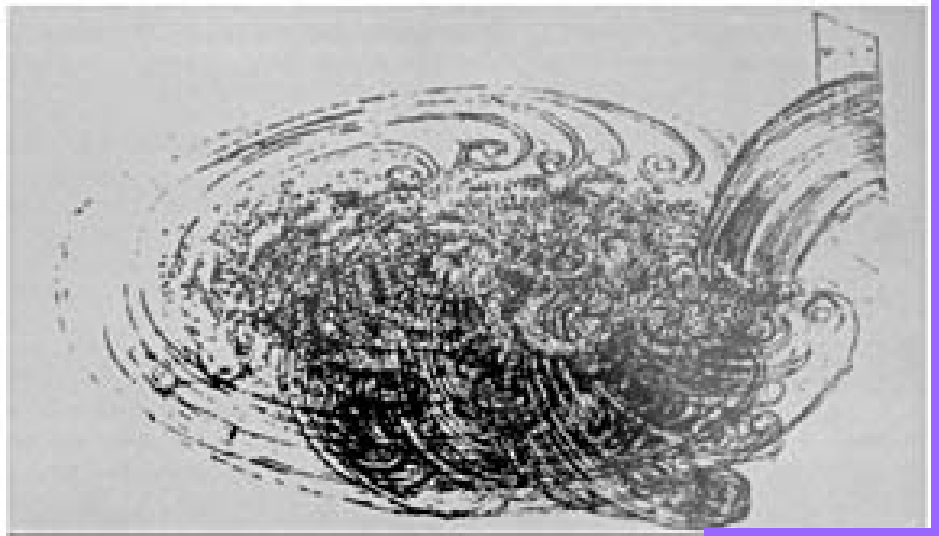
1998-2001,

Phys. Rev. Lett. **86**, 803 (2001)

European NaPa Project

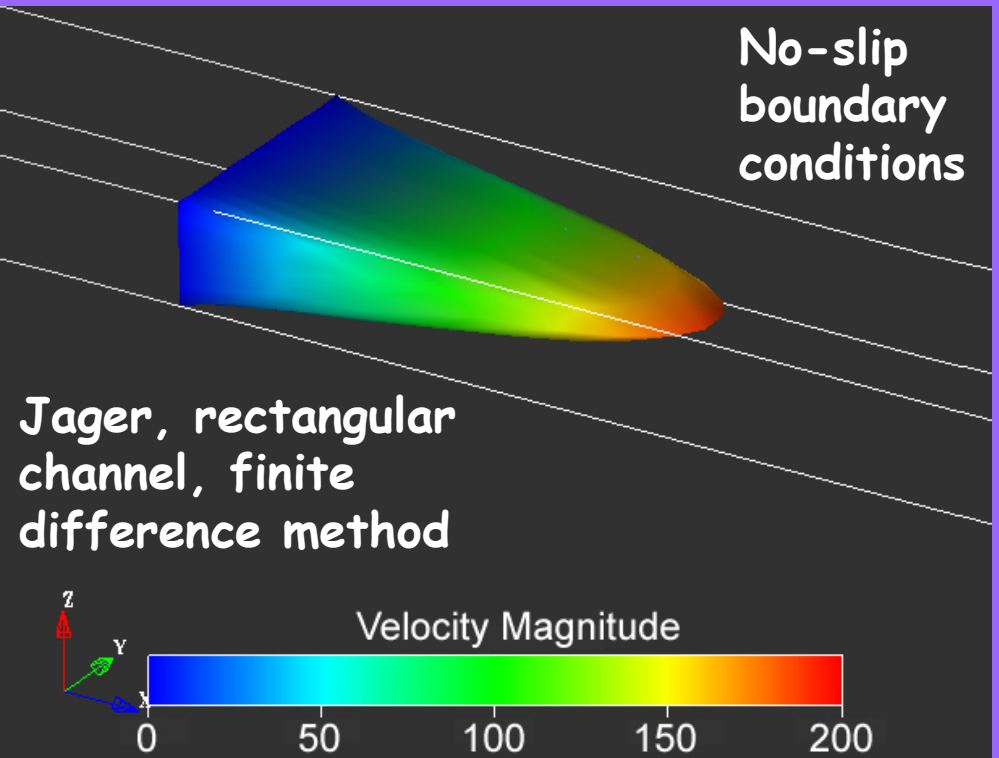
(Emerging Nano-Patterning Methods)

Phys. Rev. Lett. (2006)



Fluid Dynamics from 1500

Da Vinci

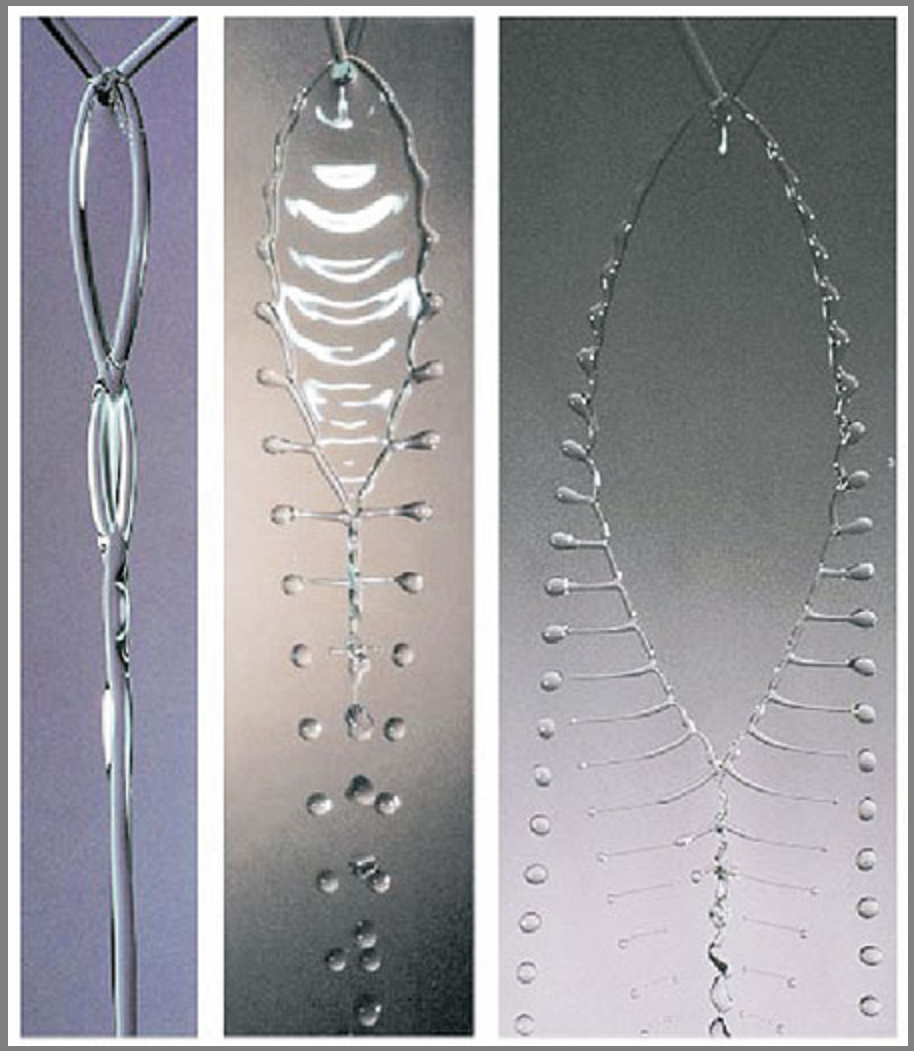


Poiseuille (1799-1869) – measured circulation in arteries

$$Q = \frac{\pi P r^4}{8 \eta l}$$

Flow rate; the velocity profile - parabolic

Situations that require molecular-level description



Hasha & Bush MIT 2004 collision of laminar glycerol-water jets: fluid chains and fishbones

With a continuum theory

Molecular Dynamics:

Moving contact lines

Interfacial instabilities (coalescence of drops, rupture of liquid threads, splashes)

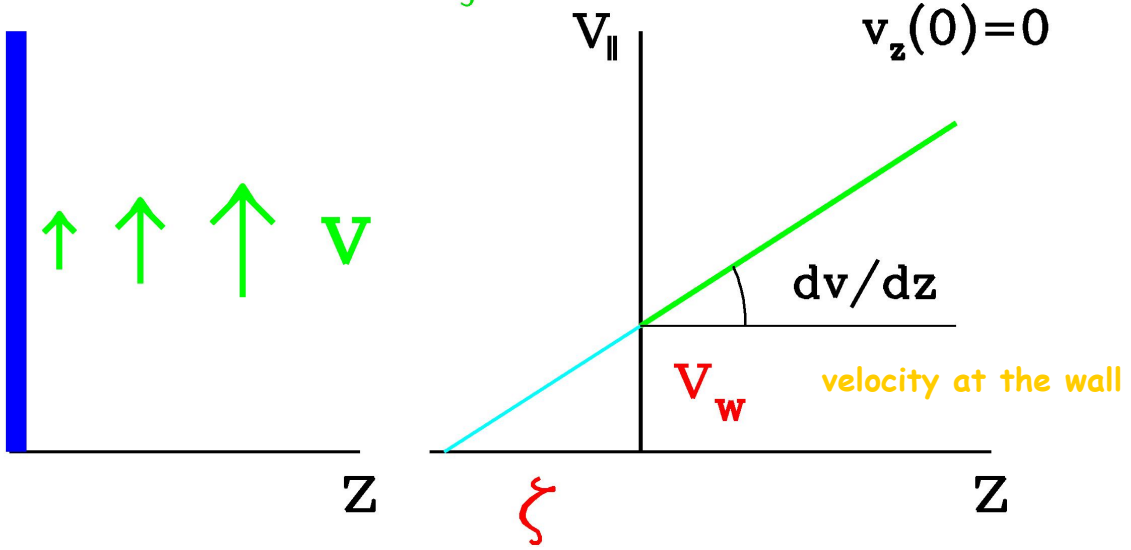
Non-Newtonian fluids (conformation affects the flow)

Sliding friction of atomic monolayers

FLUID–SOLID INTERFACE

Nature of the boundary conditions requires atomic-level understanding

SLIP LENGTH ζ



$$\zeta = \frac{v_w}{dv/dz} \sim \lambda \frac{2-f}{f} \qquad Maxwell$$

$$\lambda = \frac{1}{\sqrt{2}\pi\rho\sigma^2} \qquad mean\ free\ path$$

commonly used boundary conditions

DENSE FLUIDS + THERMAL WALLS: NO-SLIP

Millikan 1923:

f=1 for air on mercury, machined brass, old shellac

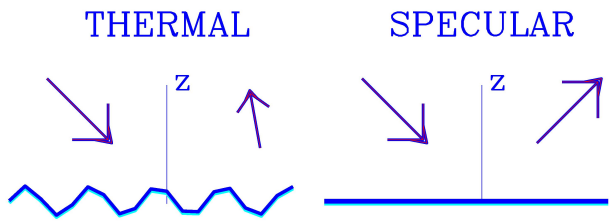
f=0.89 for air on glass

Maxwell's hypothesis (1879)

Is it valid?

a wall reemits incident atoms with the velocity distribution:

$$P(v_\alpha) = f\phi_\alpha(v_\alpha) + (1-f)\delta(v_\alpha - v_\alpha^{sp})$$



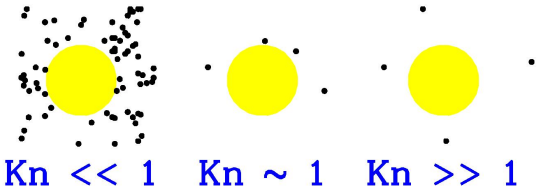
$$\phi_x(v_x) = \sqrt{\frac{m}{2\pi k_B T}}\, exp(-\frac{mv_x^2}{2k_B T})$$

$$\phi_z(v_z) = \frac{m}{k_B T}\, v_z\, exp(-\frac{mv_z^2}{2k_B T})$$

Important for miniature systems in which surface related phenomena dominate the physics

KNUDSEN FLOWS $Kn=\lambda/L$

DILUTE GAS LARGE SLIP SUBCONTINUUM

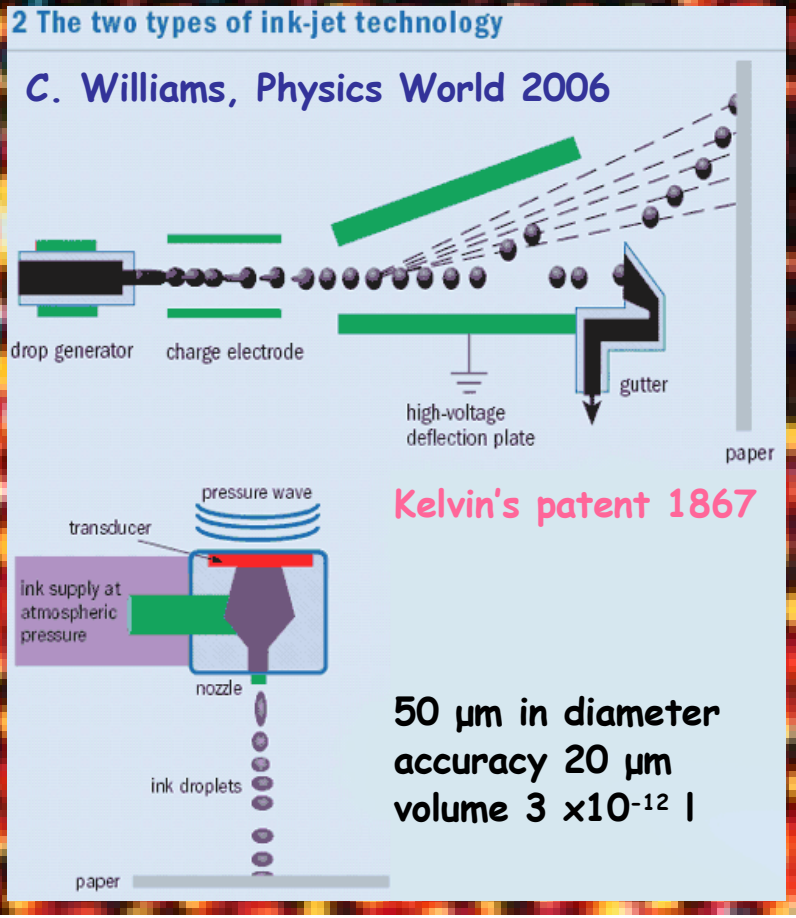


Huge slip length

How does the slip length depend on density?

New frontier: microfluidics and nanofluidics

Started with inkjet printers. Control tiny amounts of fluids



Kelvin's patent 1867

50 μm in diameter
accuracy 20 μm
volume 3 x10^{-12} l

1994: Epson, Canon, HP

microfluidics and nanofluidics

microreactor

capillary electrophoresis

micromixer

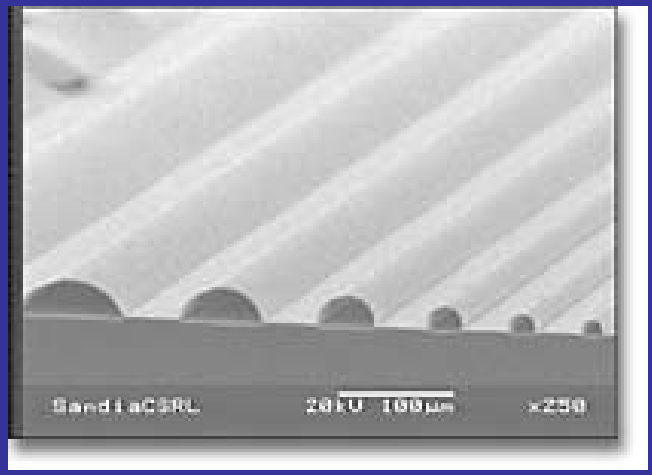
in glass

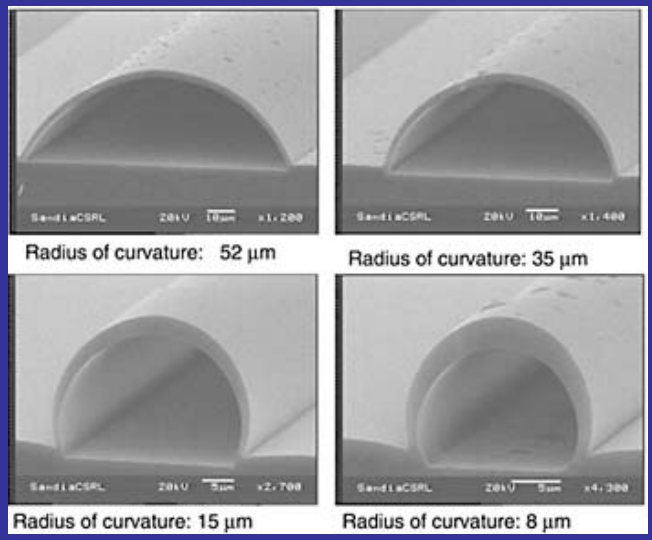
"lab on a chip"

10 µm

Matzke

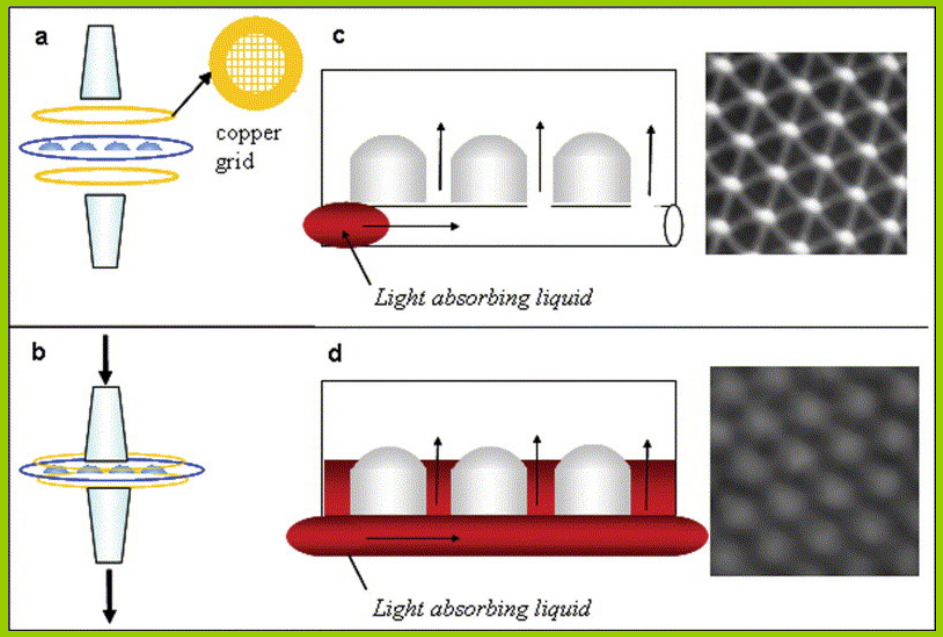
Troian – T gradients





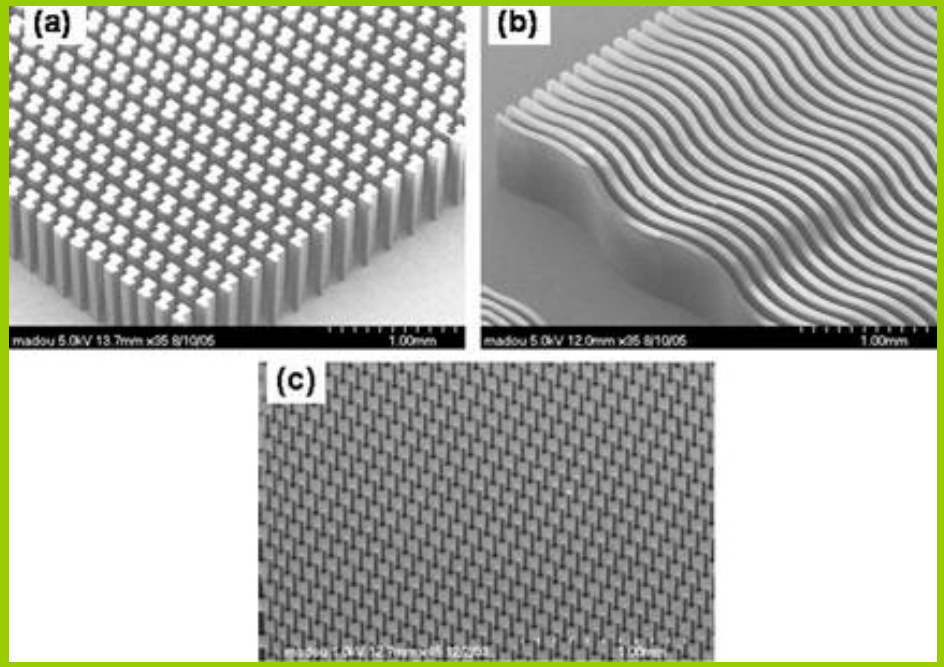
Breuer (Brown): 'bacteria carpet'

Harnessing Serratia mercescens to push particles through rubber channels with 12 µm long flagellae (at 25 µm/s; controlled by glucose)



Controlled microlenses

Yang (UPenn) &
Aizenberg (Lucent)



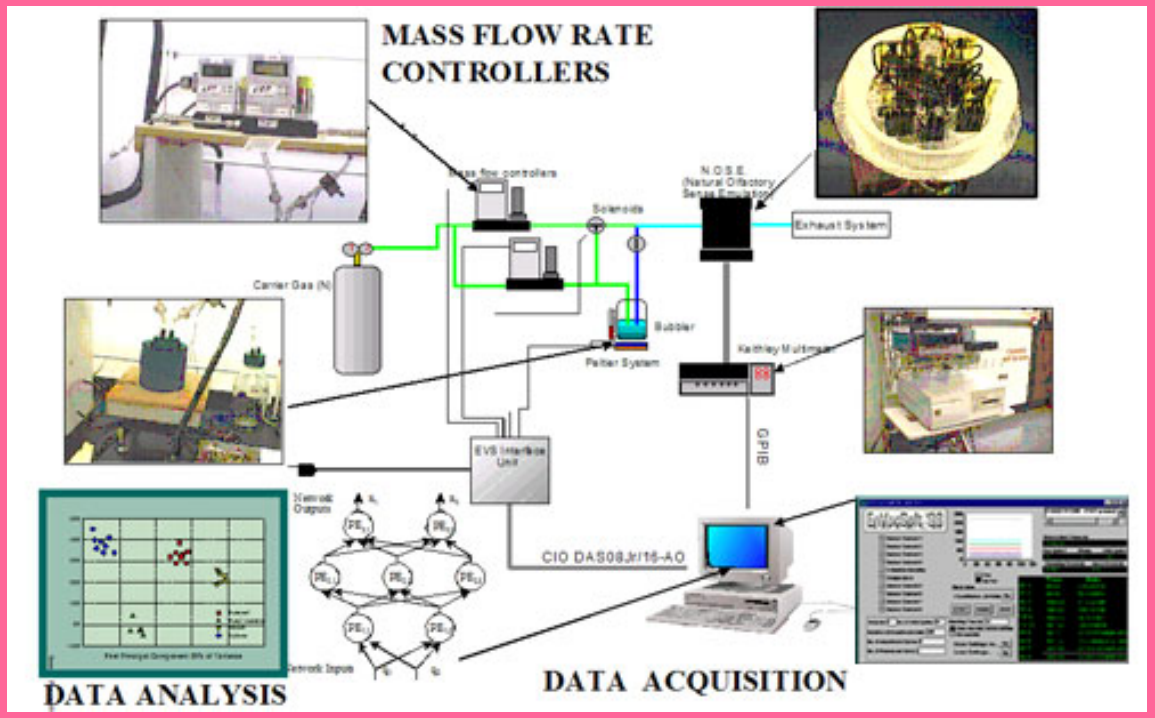
Carbon microbatteries

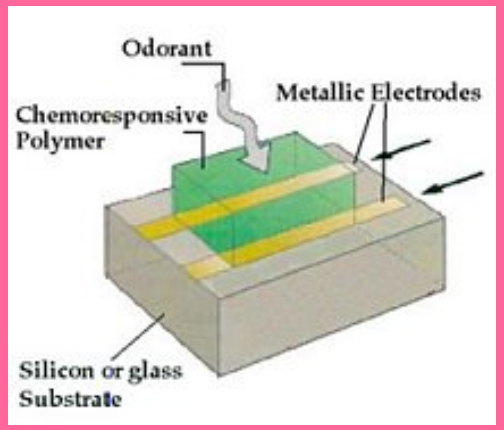
Madou (UC Irvine)

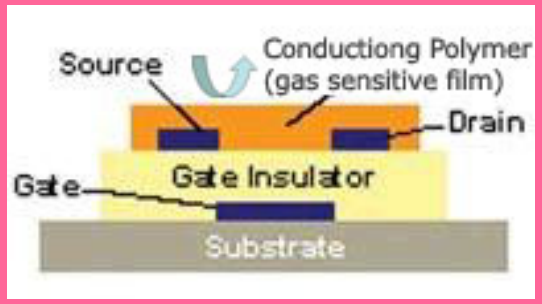
C-MEMS with $LiMn_2O_4$

3 V micro-power

E-NOSE





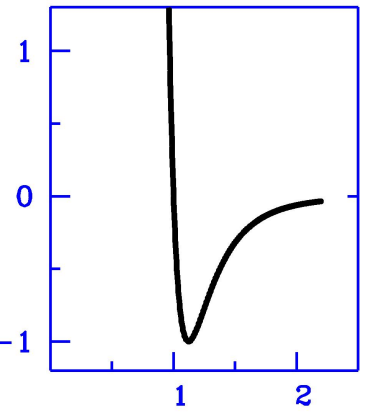


Detection and monitoring of gases and vapors

Conductive polymers (polyaniline, polypyrrole, filled nano-tube) change work function on adsorption.

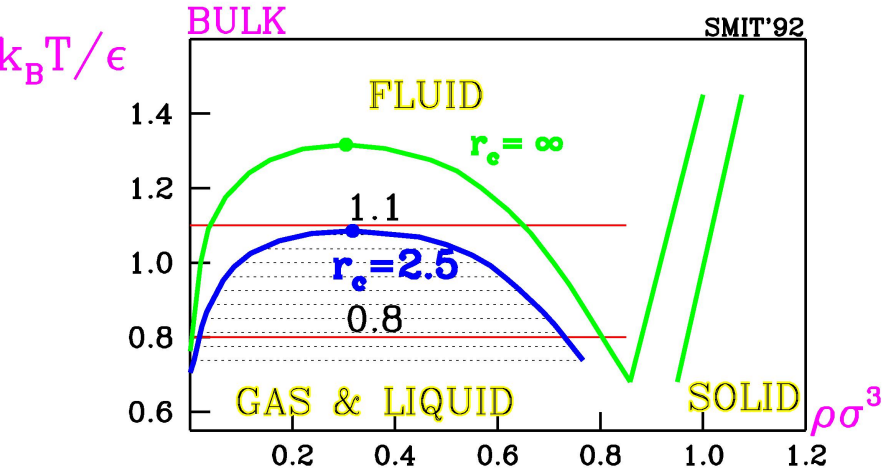
Train for odors

C3B @ Clemson



$V_{LJ}=4\epsilon\ [(r/\sigma)^{-12} - (r/\sigma)^{-6}]$

$\tau_0=(m\sigma^2/\epsilon)^{1/2}$



r_c - cutoff in the potential

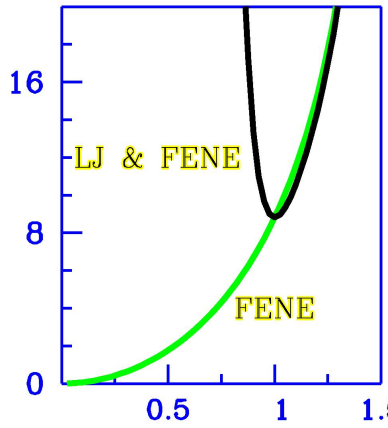
$r_c=2.2\sigma$

Lennard-Jones fluids

ARGON:

$\varepsilon/k_B=120$ K $\sigma = 3.405$ A $\tau = 10$ fs

POLYMERS



finitely extensible nonlinear elastic
Kroeger, Loose, Hess '93

$V_{FENE}=-\kappa/2\ \log[1 - (r/r_0)^2]$

$\kappa=30\epsilon$ $r_0=1.5\sigma$

n=10 monomers

Interactions with the wall atoms controlled by *A*

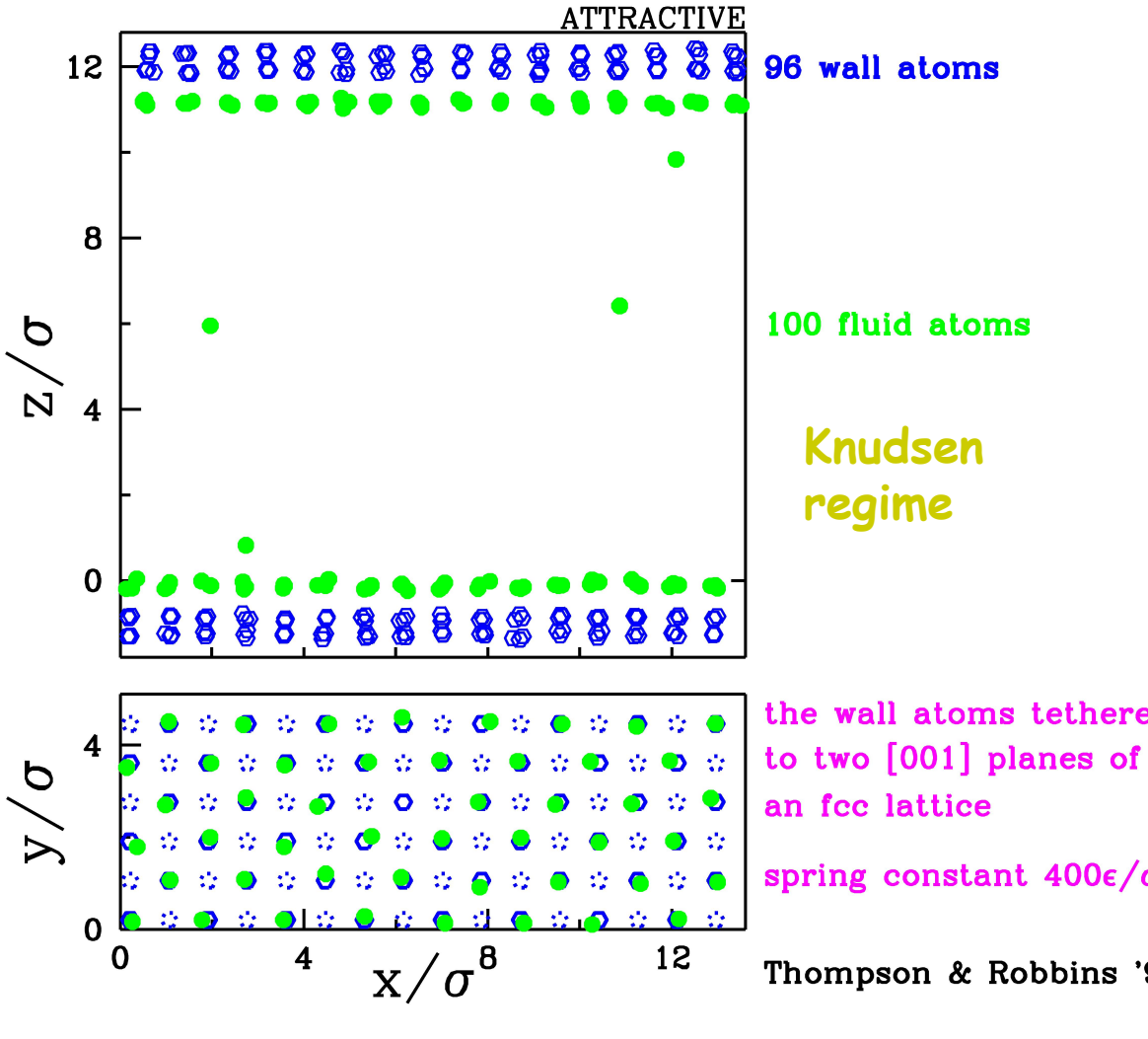
$$V_{wf} = 16\epsilon \left[(r/\sigma)^{-12} - A(r/\sigma)^{-6} \right]$$

A=1 strongly attractive or strongly wetting

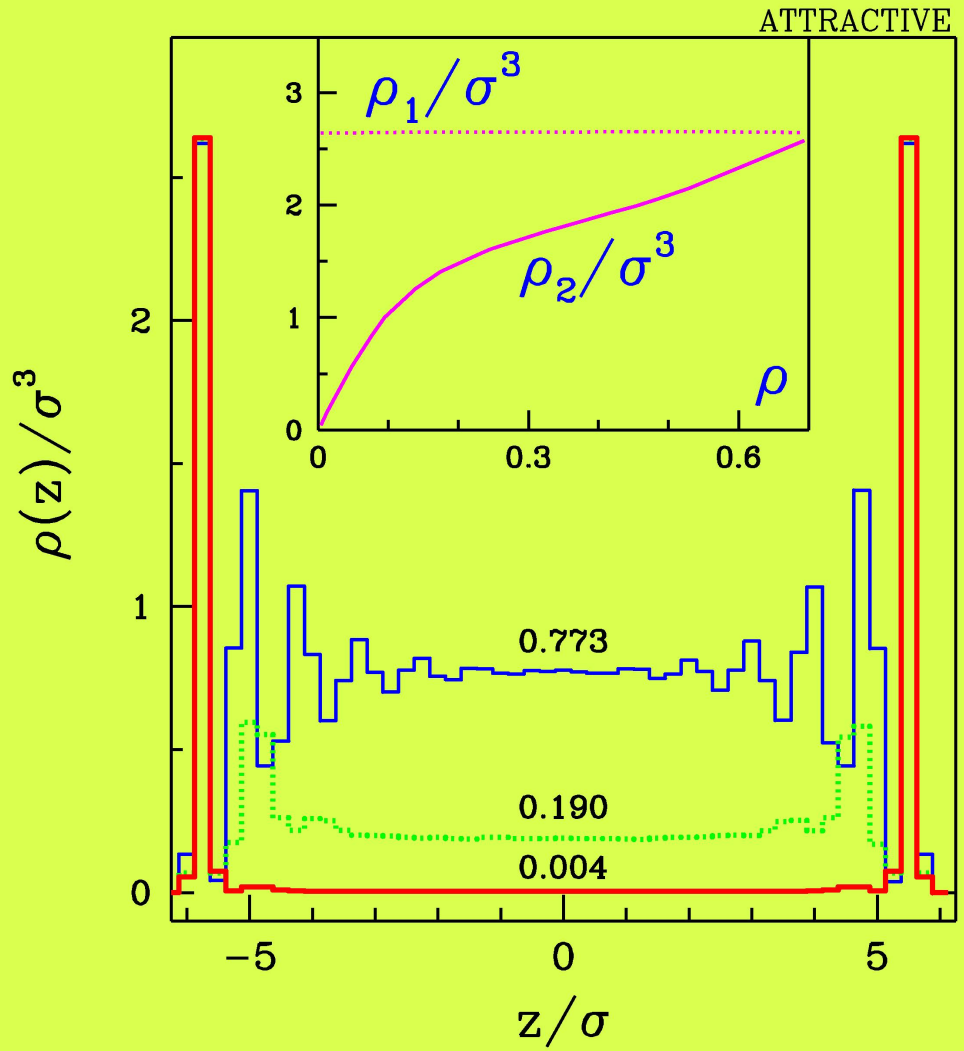
A=0 purely repulsive or non-wetting

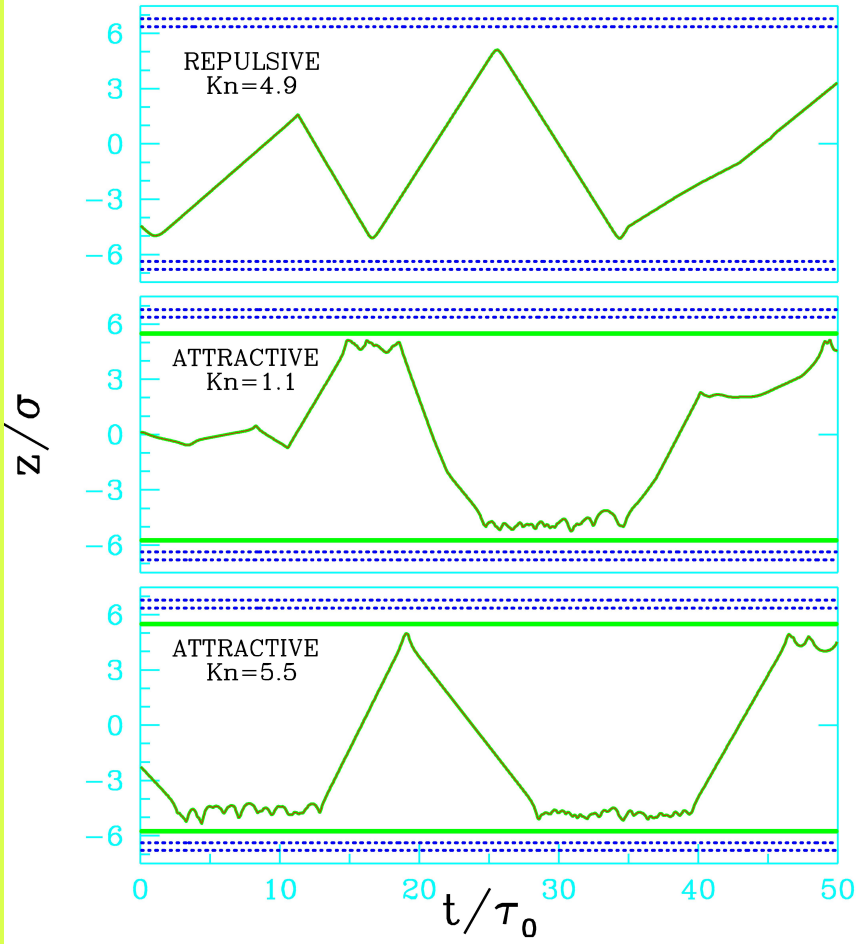
Discuss first homogeneous, then patterned walls

The channel geometry



The density profile for A=1



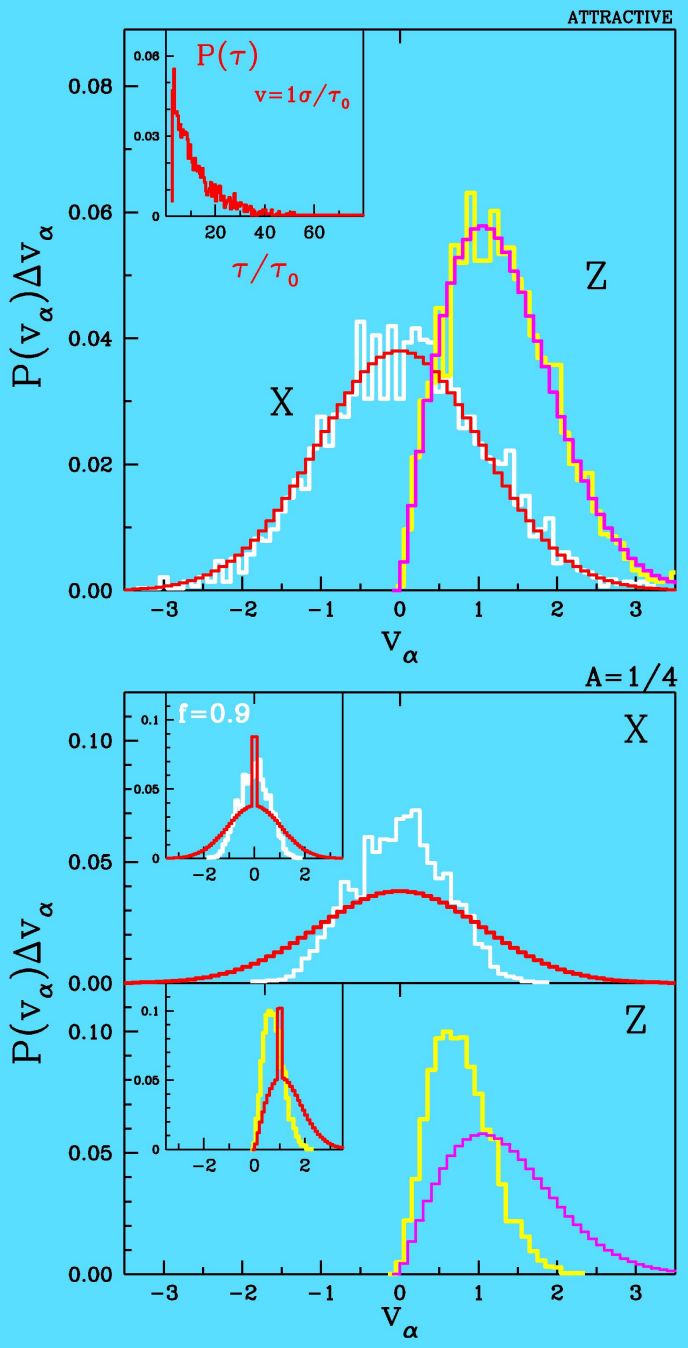


Ballistic motion between the walls at low density

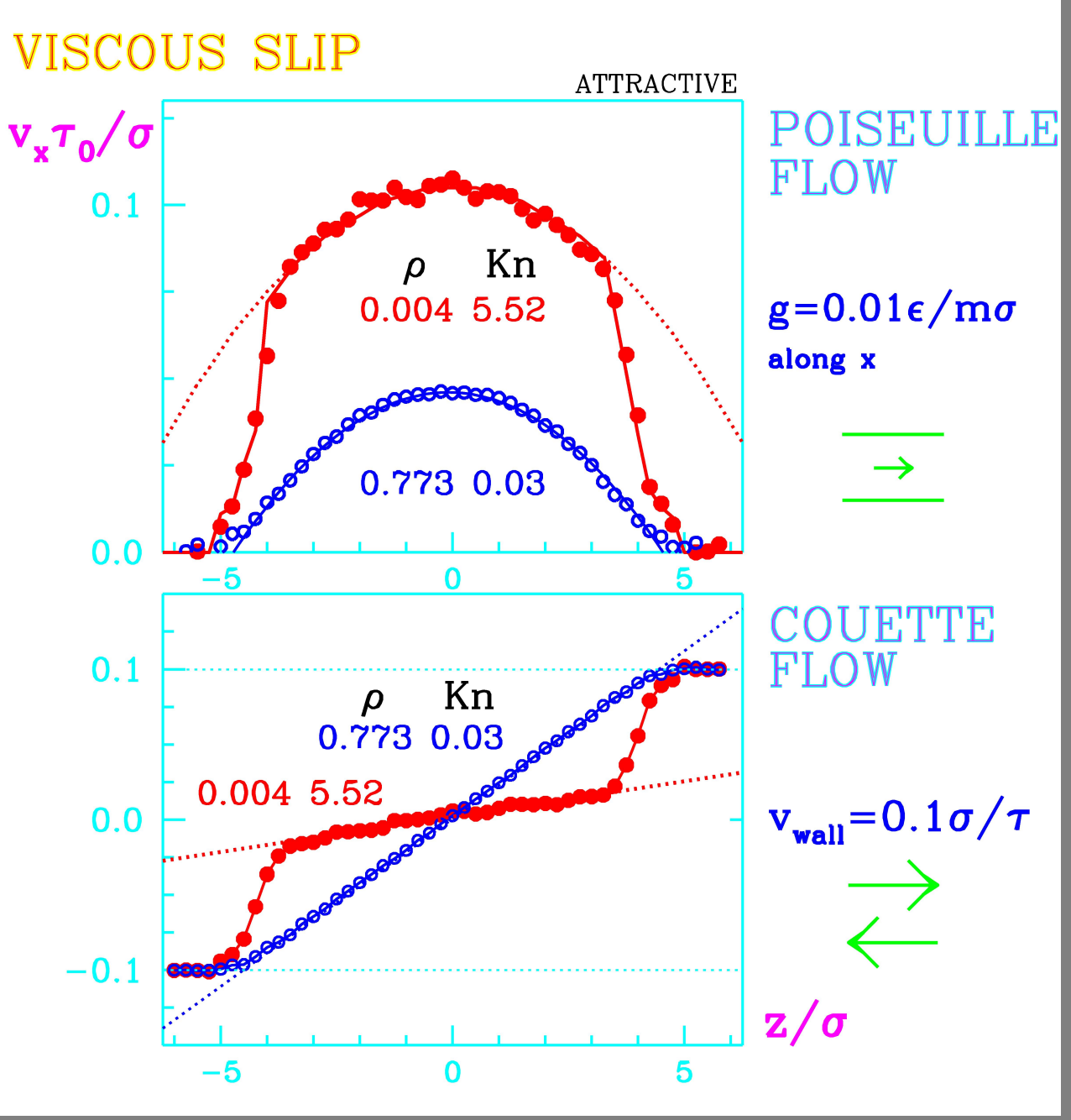
Atoms sent normally towards to wall with a unit velocity – distribution of velocities of the reemerging atoms

Maxwell's hypothesis valid at $A=1$ and $A=0$ but not in-between

ζ needs to be determined at the molecular level



Monatomic fluid



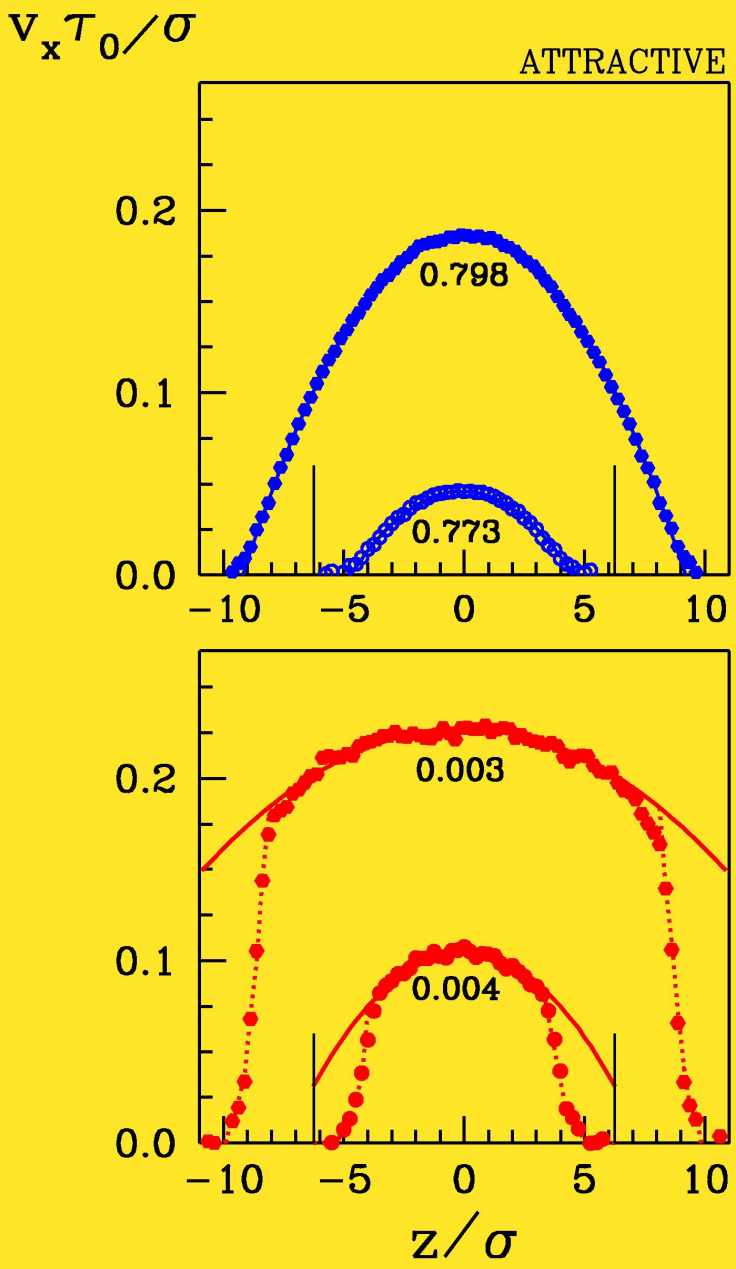
Thermal slip also studied

Double the width of the channel

$v_x(z)=$

$\rho g/2\eta\,(L/2+z)(L/2-z)$

ballistic



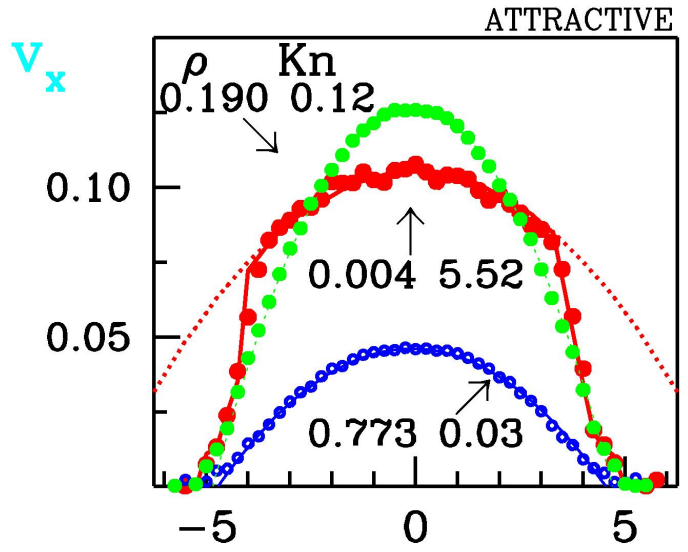
DENSE

$v_{max} \sim L^2$

DILUTE

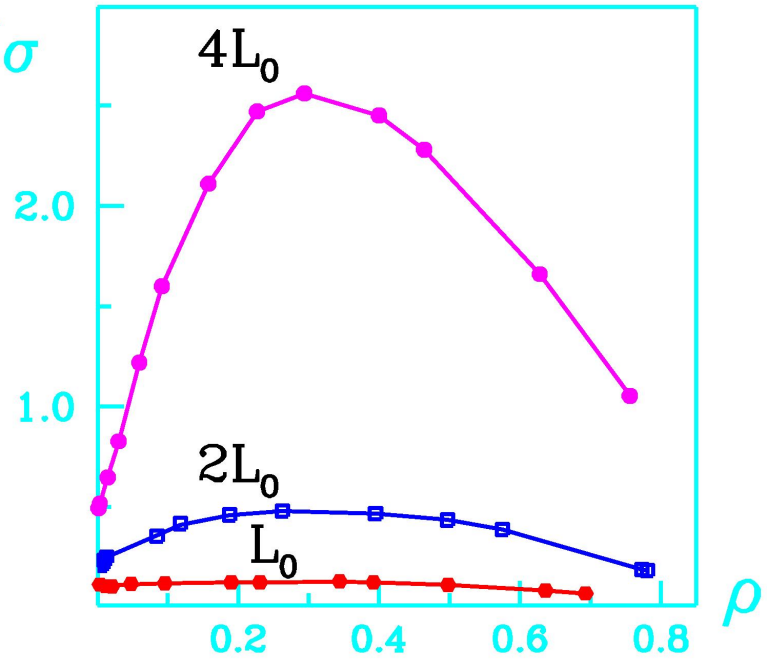
$v_{max} \sim L$

Knudsen 1909
Smoluchowski 1910
(flowrate in cylinders)



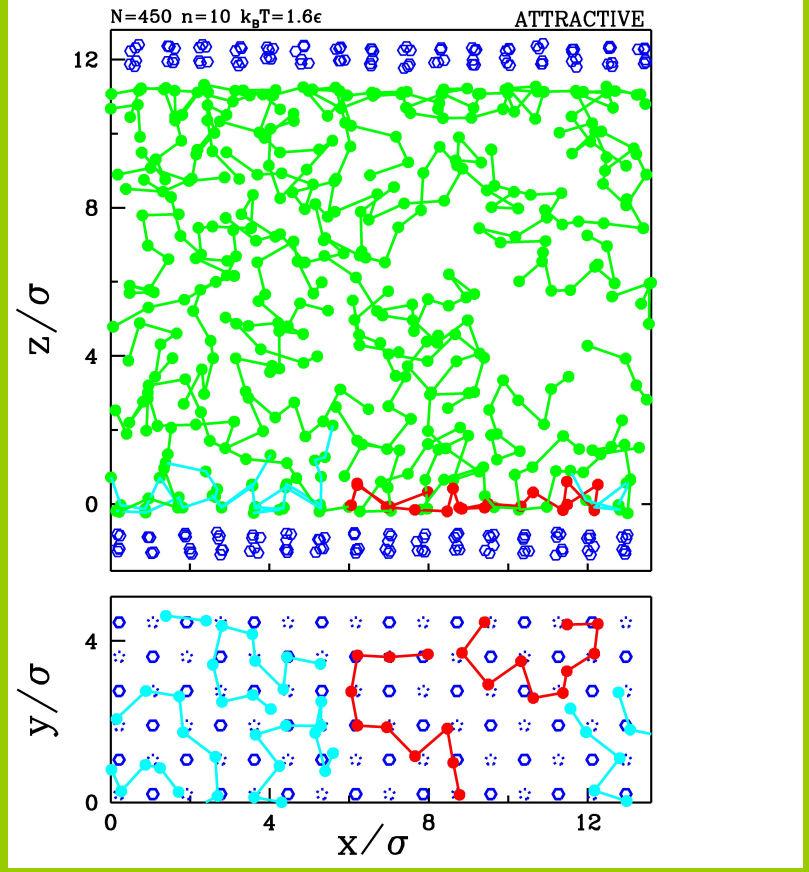
MONATOMIC

$v_{max}\tau_0/\sigma$

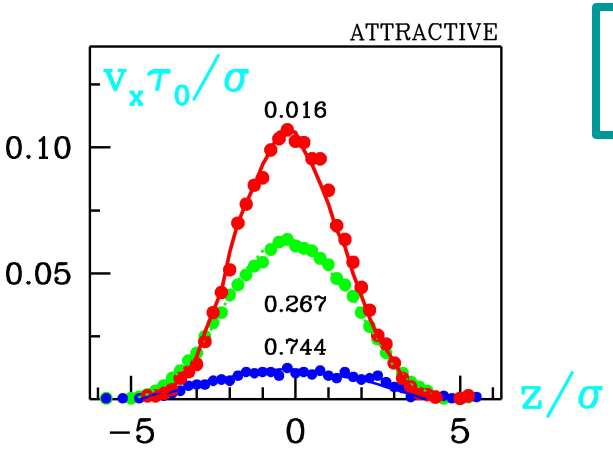


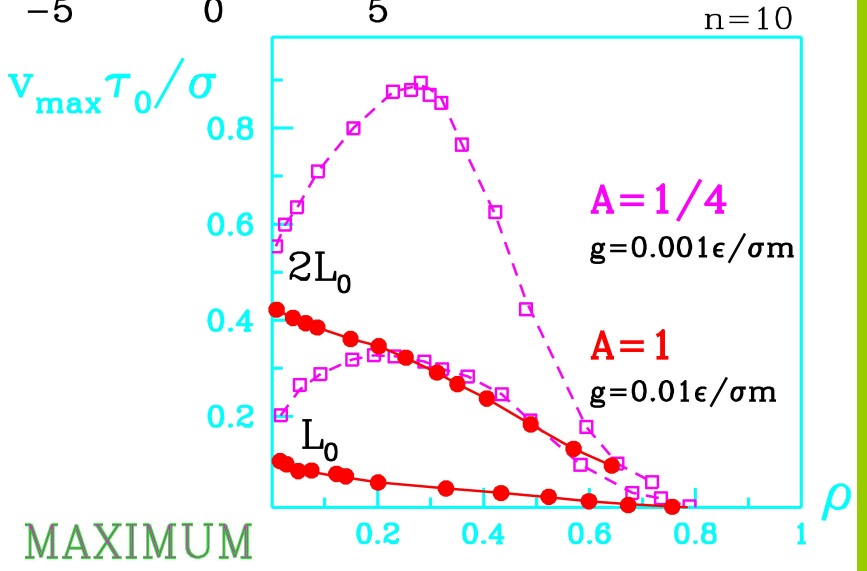
ρ_K

MAXIMUM

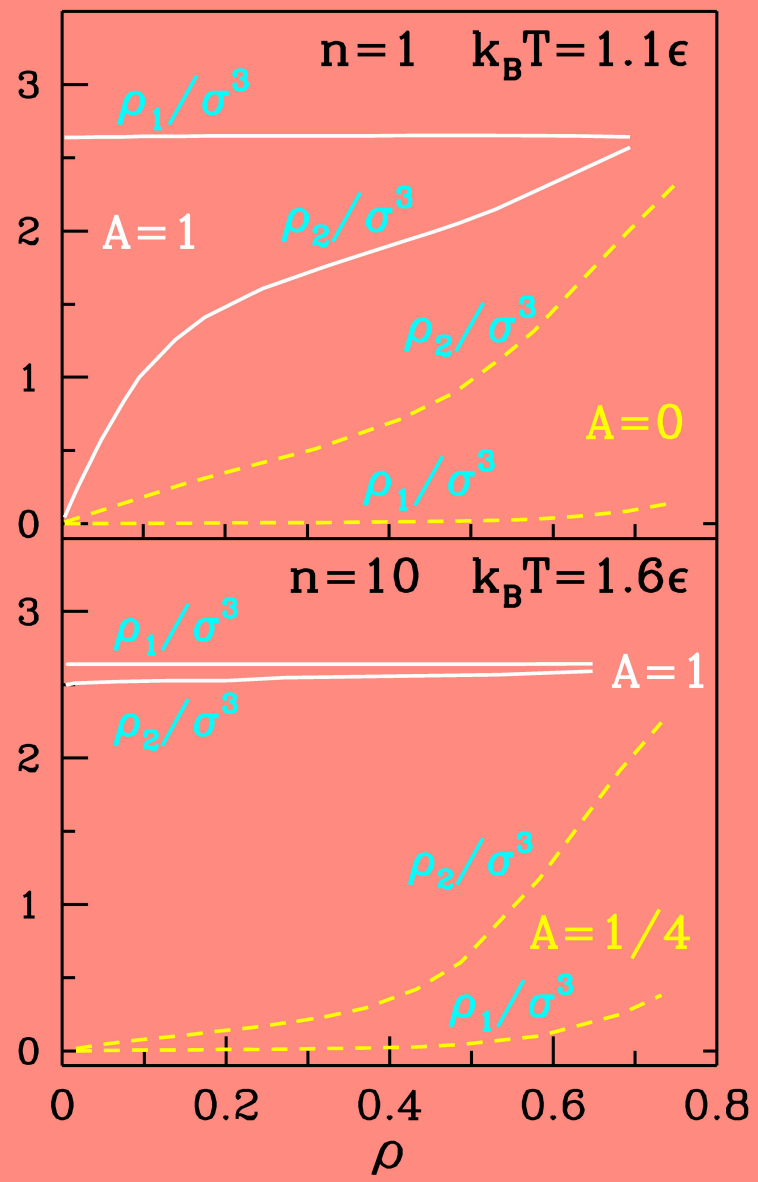


POLYMERS





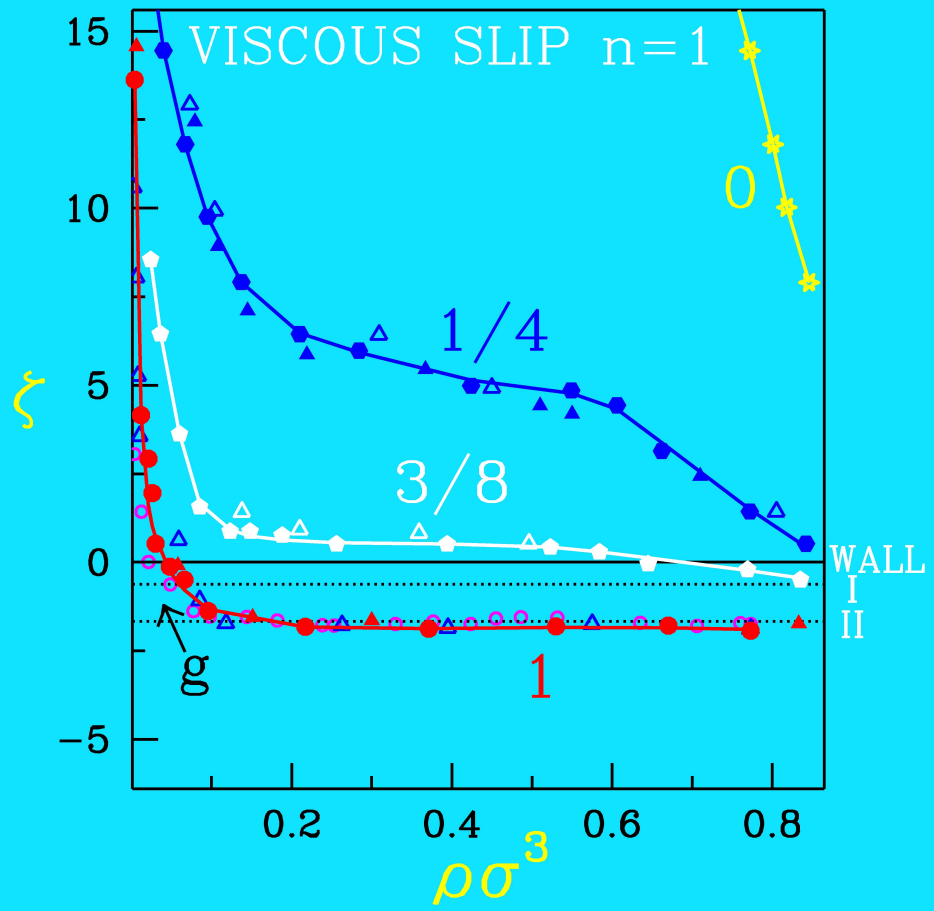
NO MAXIMUM

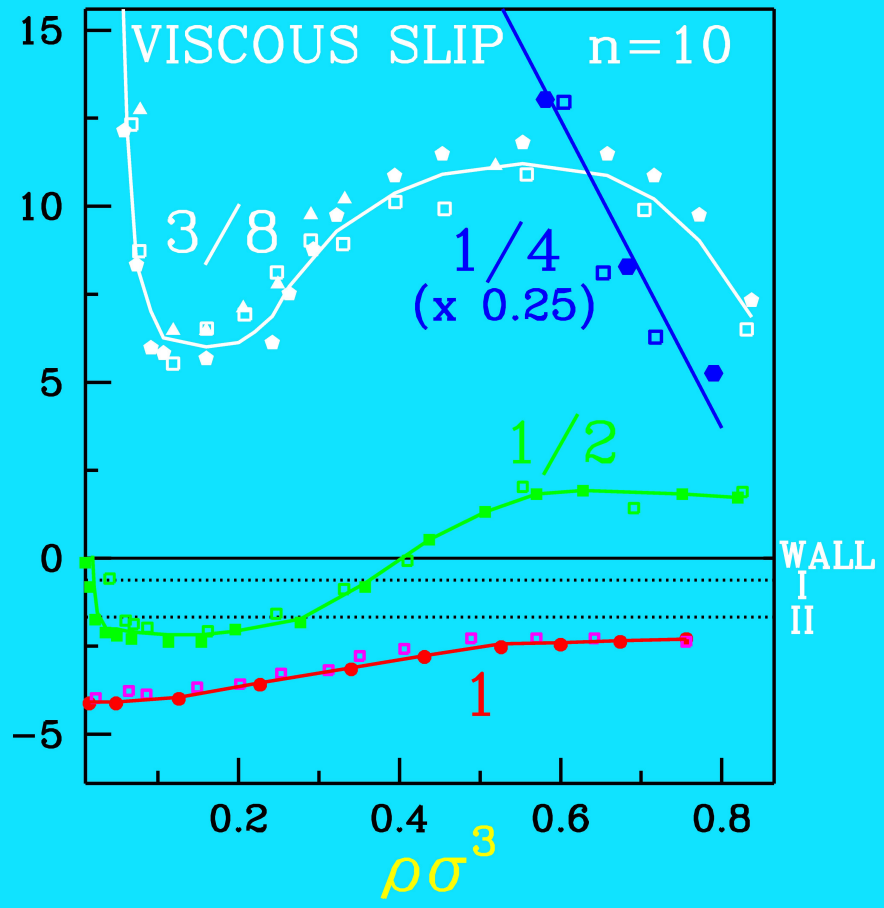


The build-up in the second layer makes the effective flow-width narrower

A rigid near-wall structure in the polymeric case

The slip length for various values of A





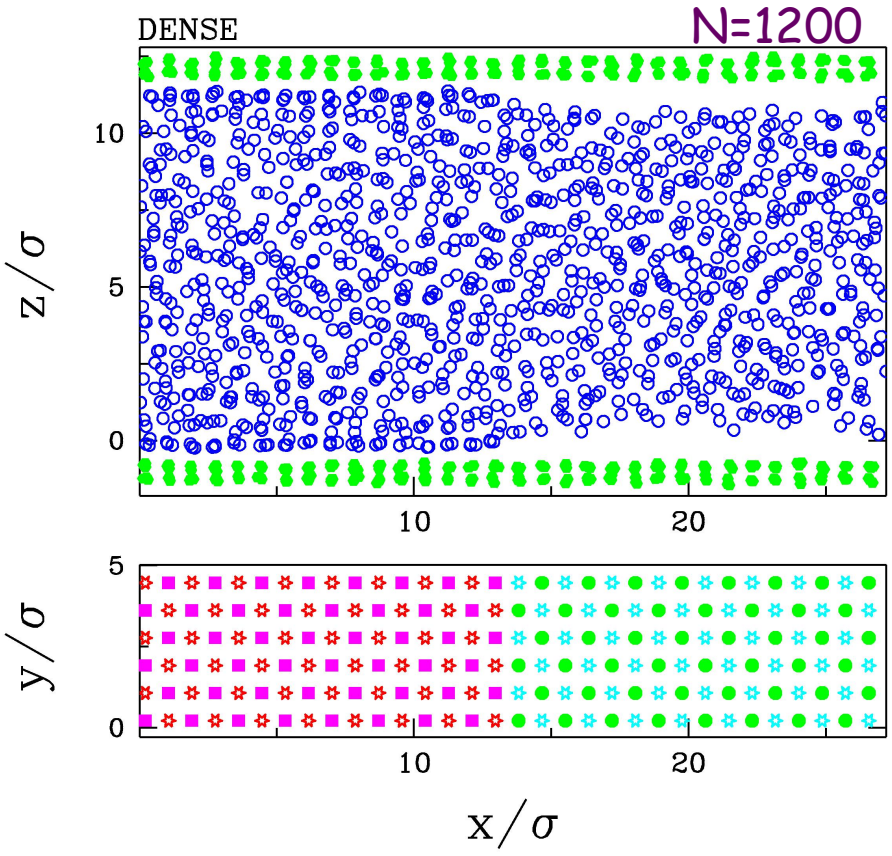
An accelerating flow for A=0

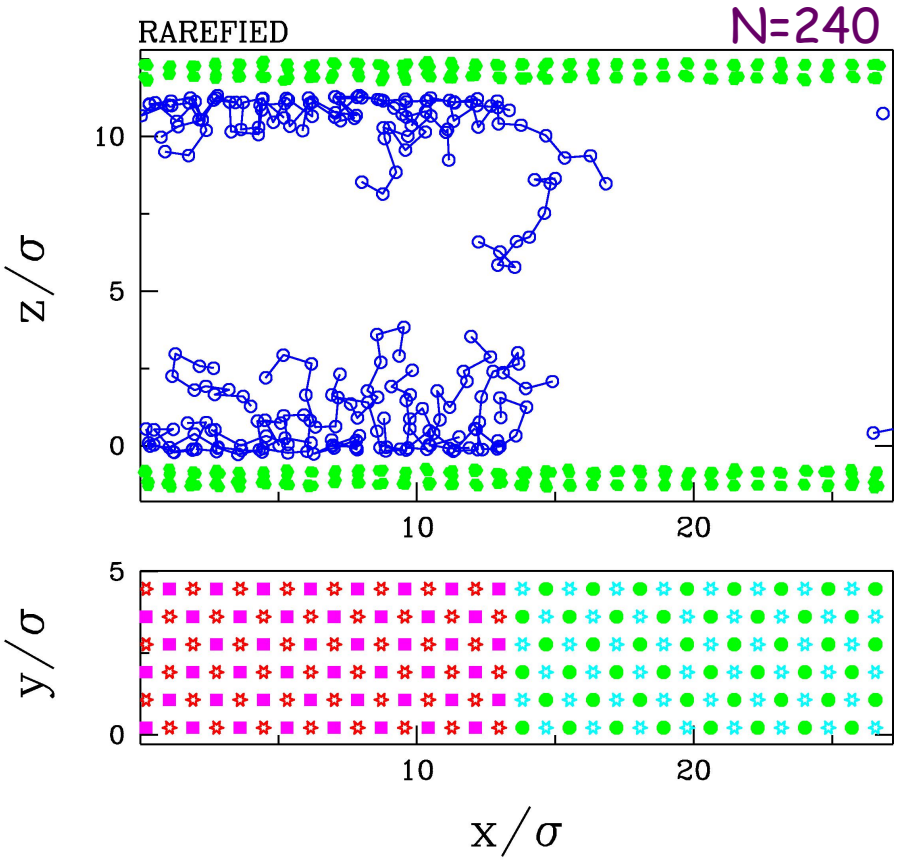
Couette and Poisseuille results combined

Poisseuille flows in mixed wettability channels

Polymeric n=10

(the length doubled)





A=1 A=0

wetting non-wetting

Profiles at A B C

(glass)

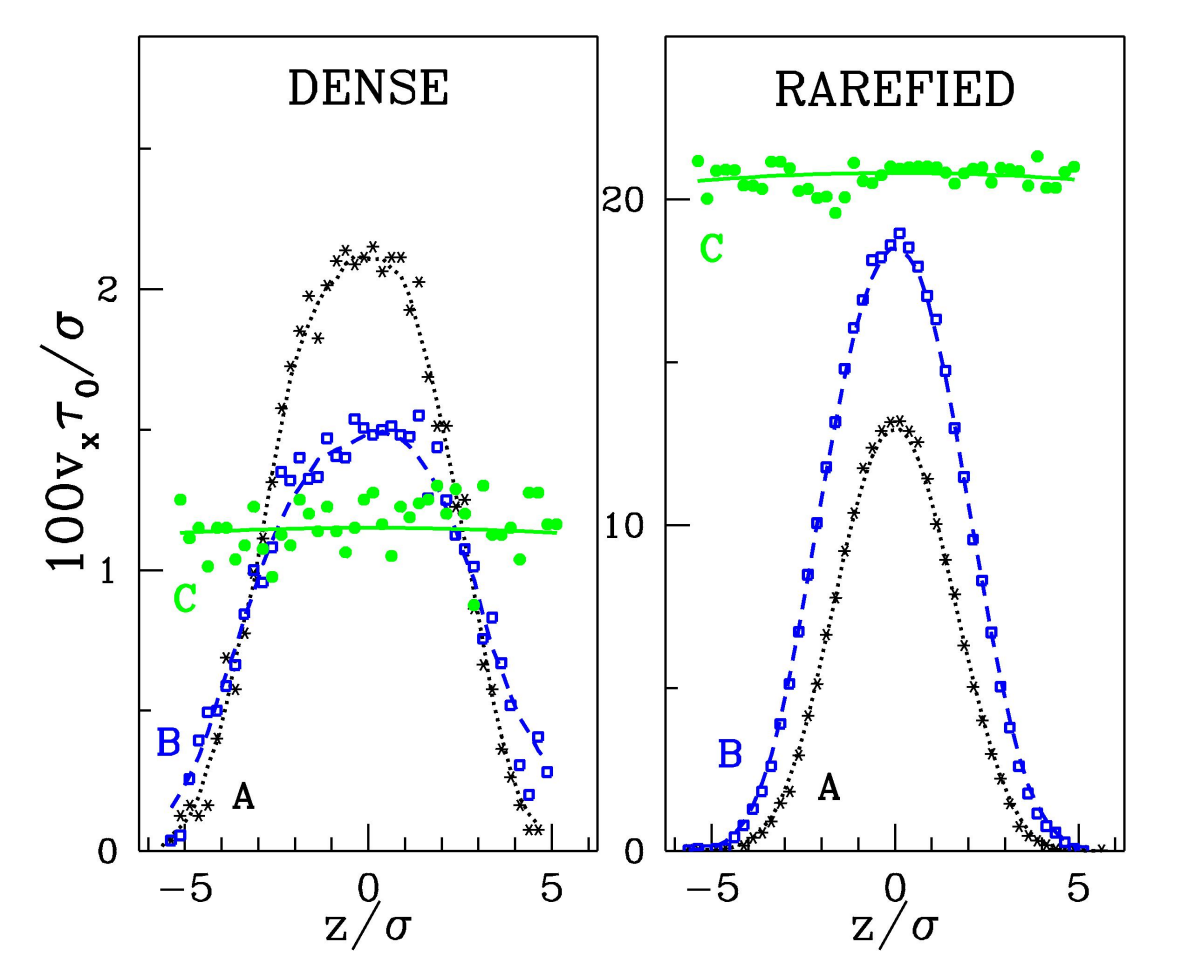
Variations in the velocity profile along the channel

A: wetting

B: at the switch

C: non-wetting

Stationary plug flow at c



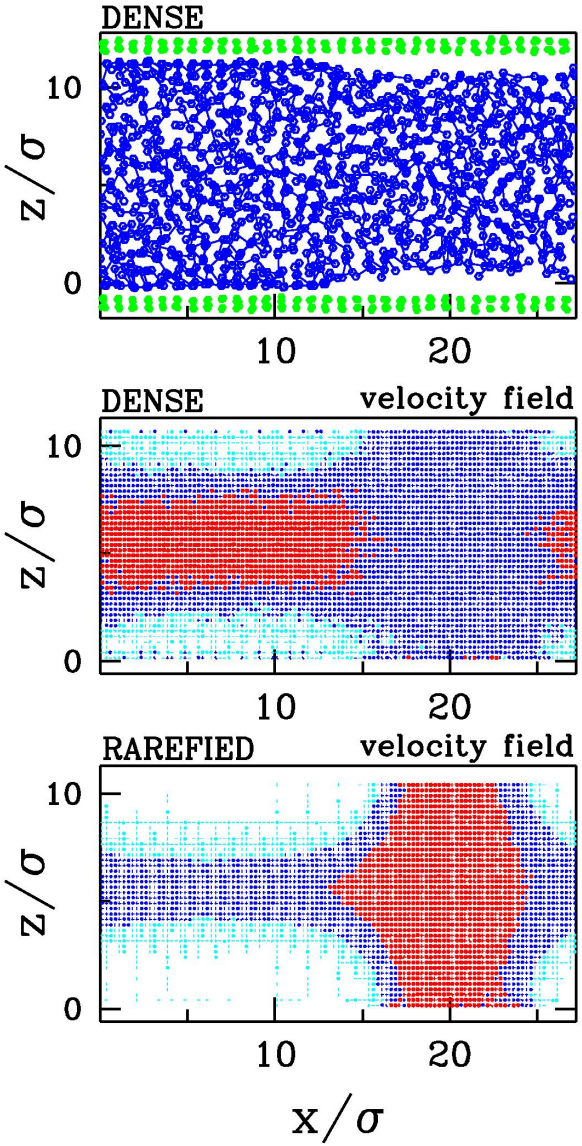
Chemical patterning yields novel stationary flows that are spatially structured

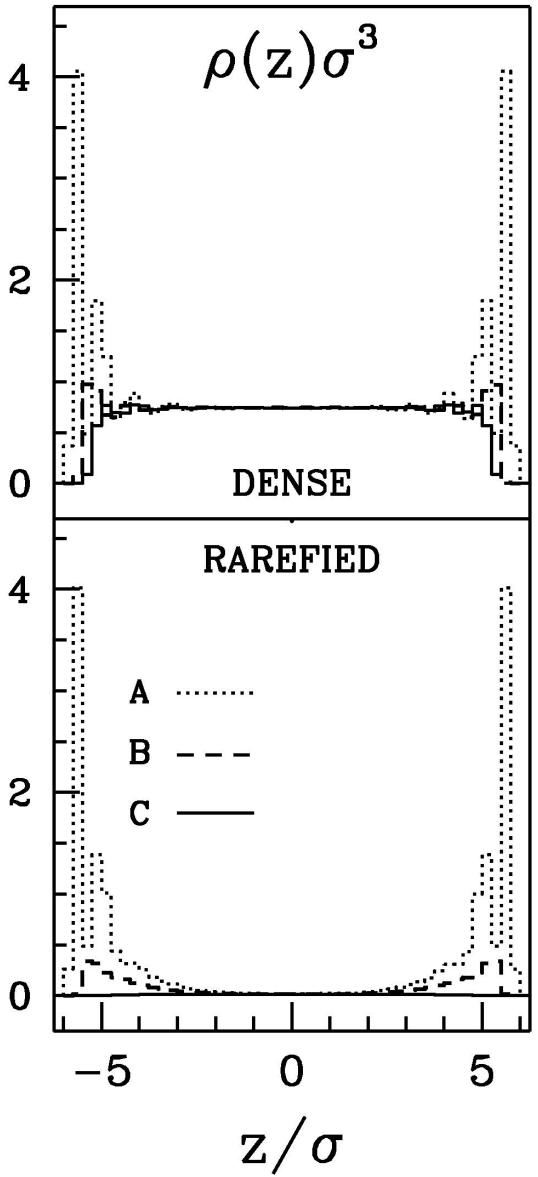
red – fast

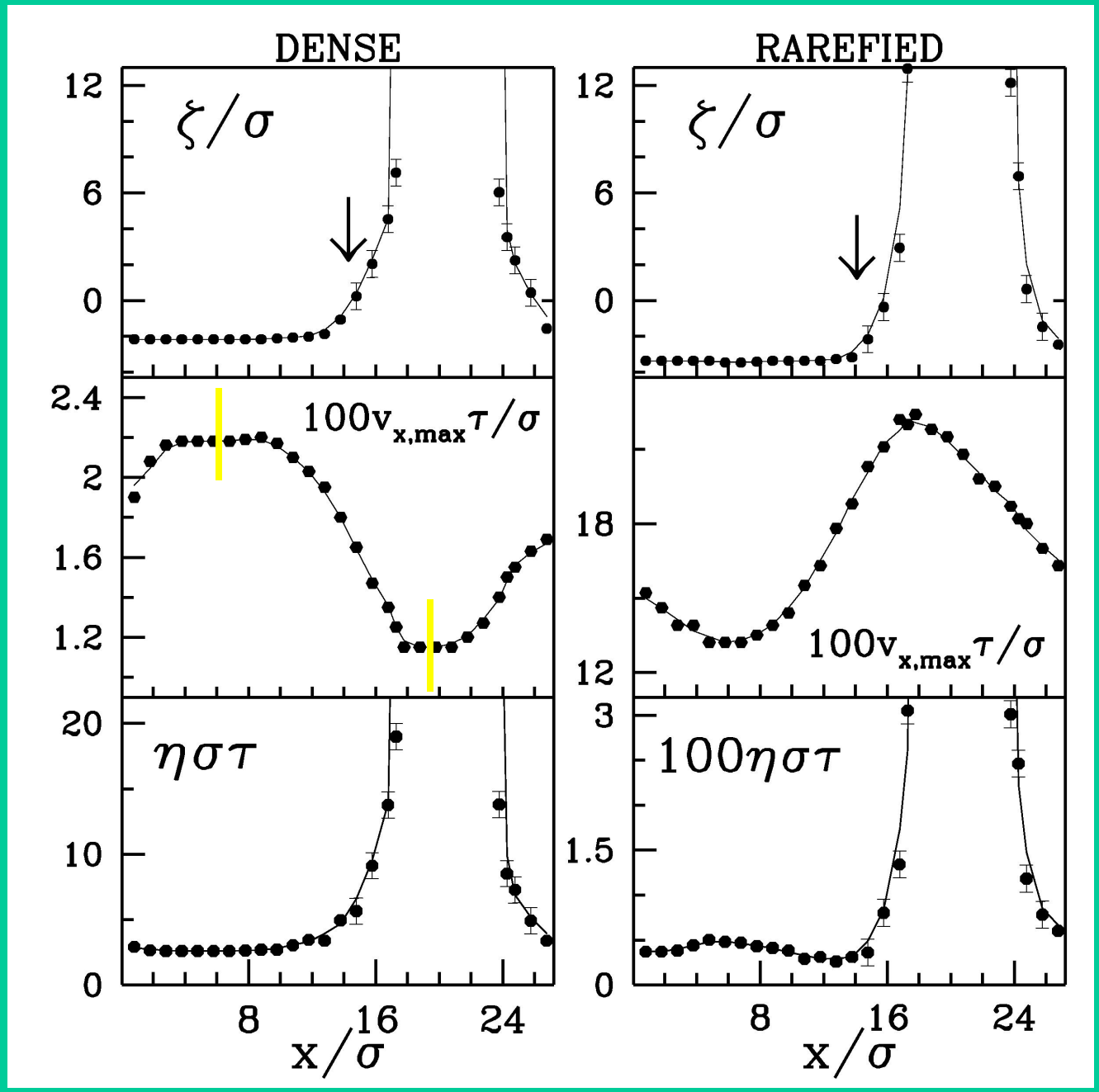
turquoise - slow

Dense- moving to an effectively wider channel

Rarefied – moving to a substantially lower density (no dissipation at non-wetting walls)






DENSE
RAREFIED
ζ/σ
$100v_{x,max}\tau/\sigma$
$\eta\sigma\tau$
$100\eta\sigma\tau$
12
6
0
2.4
2
1.6
1.2
20
10
18
3
1.5
8
16
24
x/σ

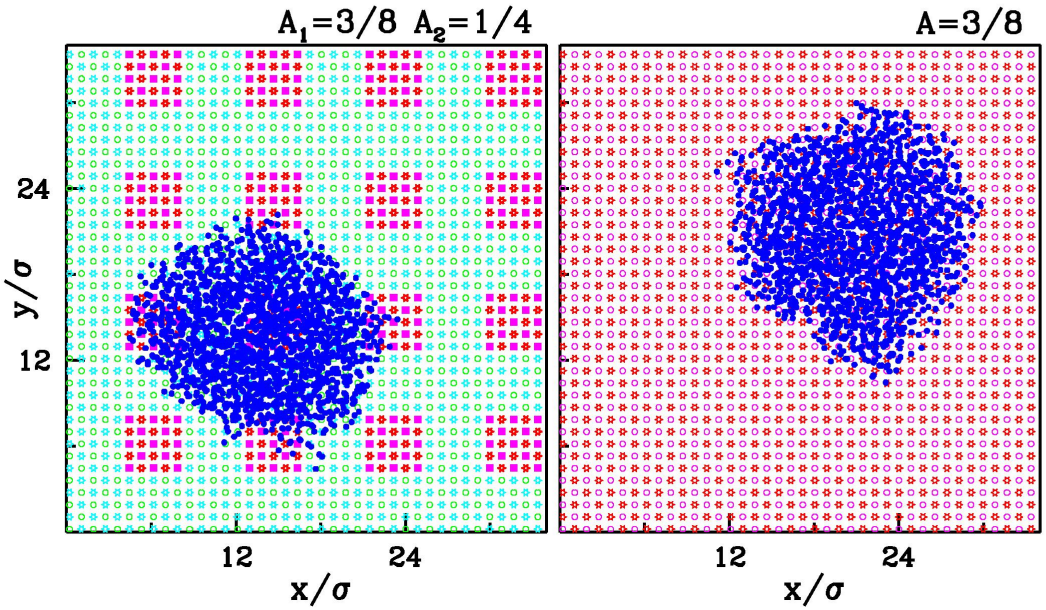
A non-wetting droplet at T/ε=0.8

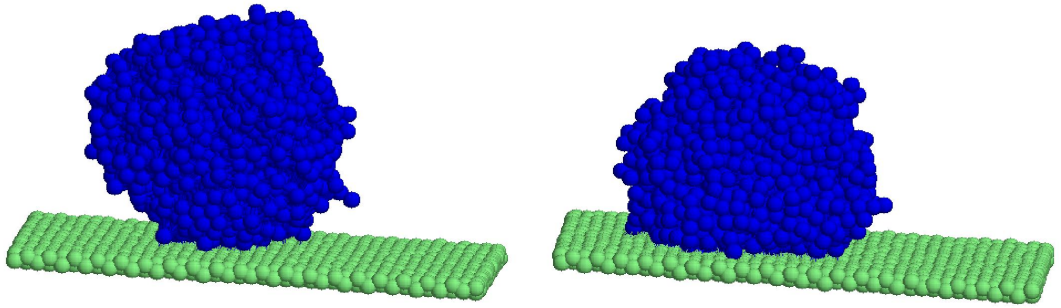
180 polymeric molecules of n=10

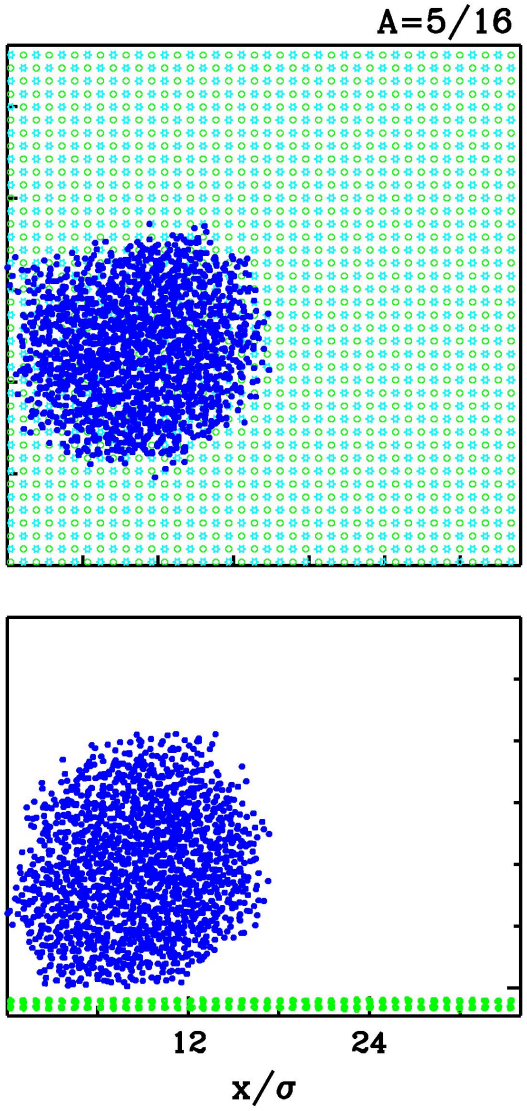
Green- A_2:

less attractive

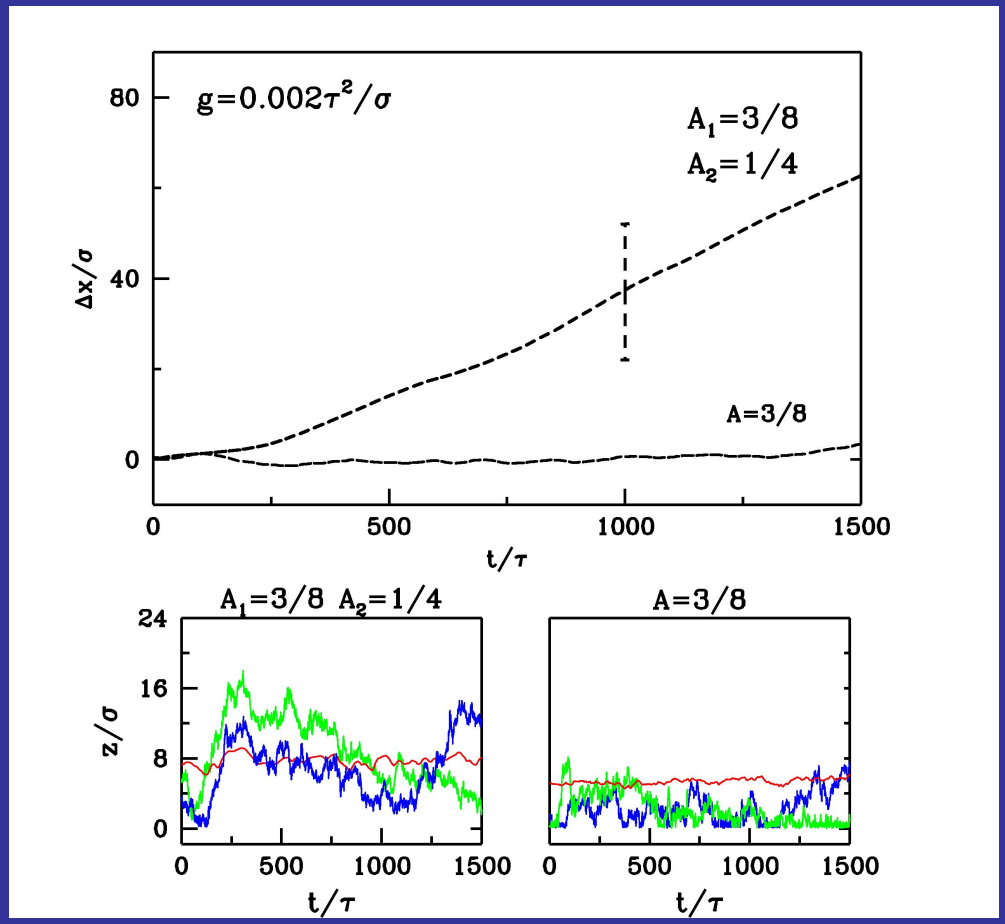
Chemical patterning: patches







x-displacement of the center of mass



The droplet moves faster on the patterned surface – the lotus effect

Selected 2 particles - rolling

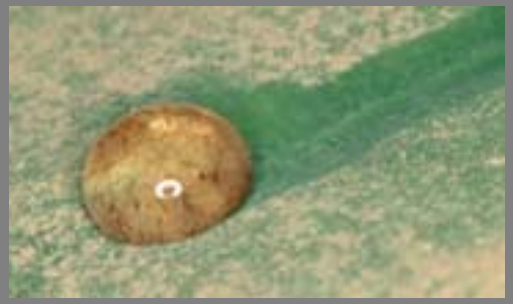
Barthlott & Nienhuis 1997: 'Purity of the sacred lotus, or escape from contamination in biological surfaces'

Querre 2002

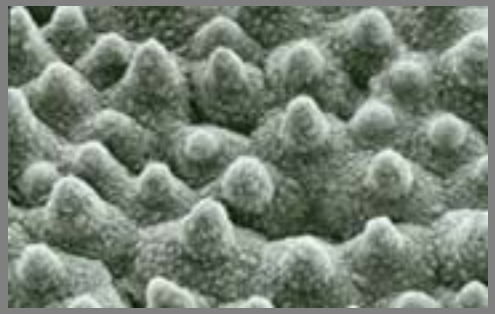
Super-hydrophobic

Contact angles > 90°

The surface of a lotus leaf is always clean

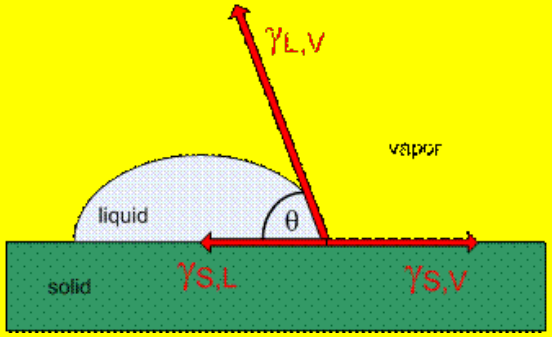


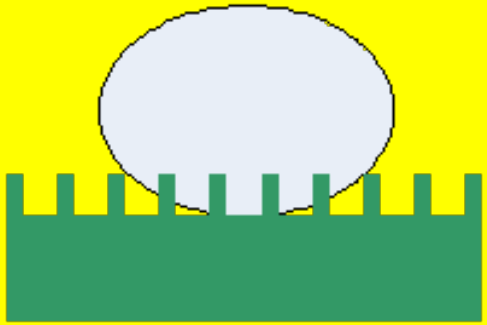
Droplets collect hydrophilic dirt



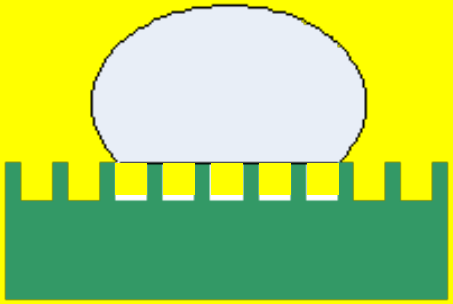
nano- and micro structures

SEM image



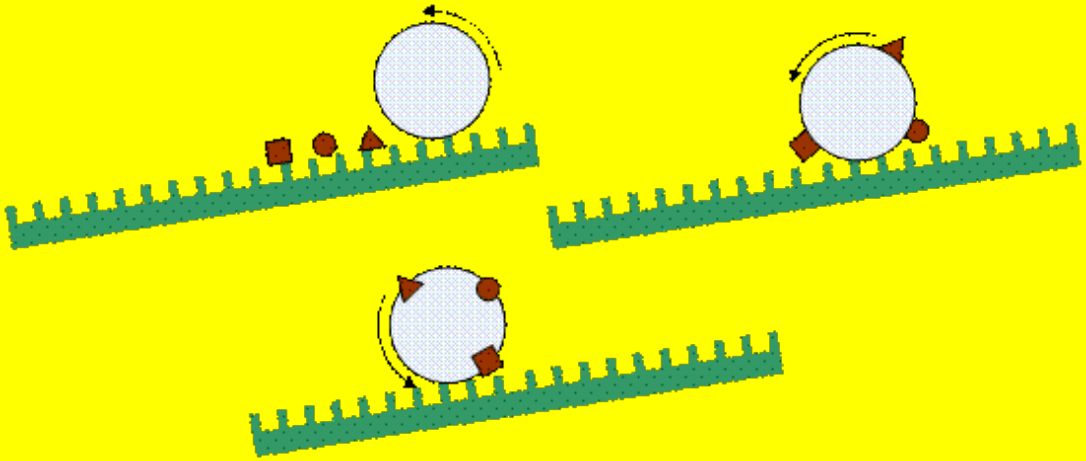


A droplet on a hydrophilic rough surface (Θ < 90°) sinks into the gaps



On a rough hydrophobic surface - sits on the spikes

Droplets do not slide down but roll off and capture impurities



Gecko hair (setae) is tiny and facilitates formation of van der Waals bonds both with hydrophobic and hydrophylic surfaces

The role of water-based forces: disputed

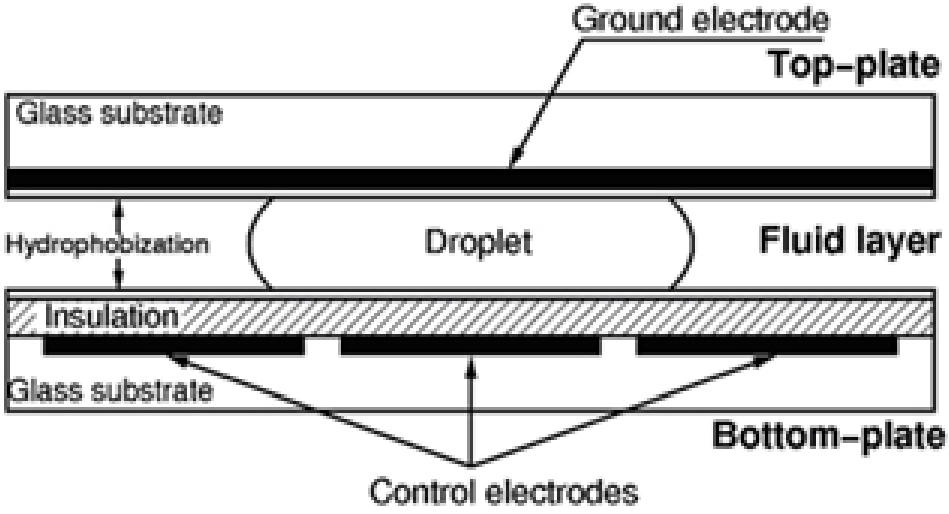
Hang off any surfaces at any angle

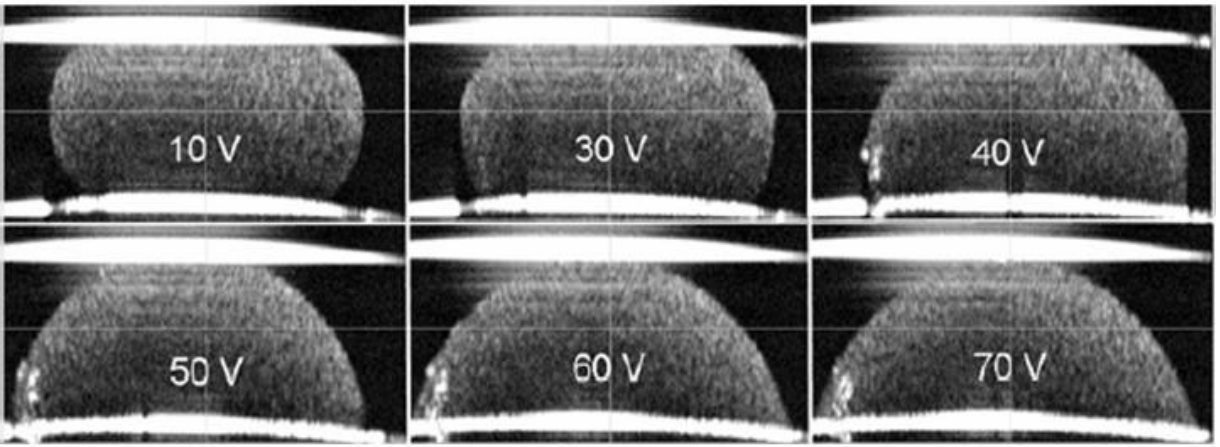
Synthetic gecko tape. Flexible plastic hairs 2 μ high

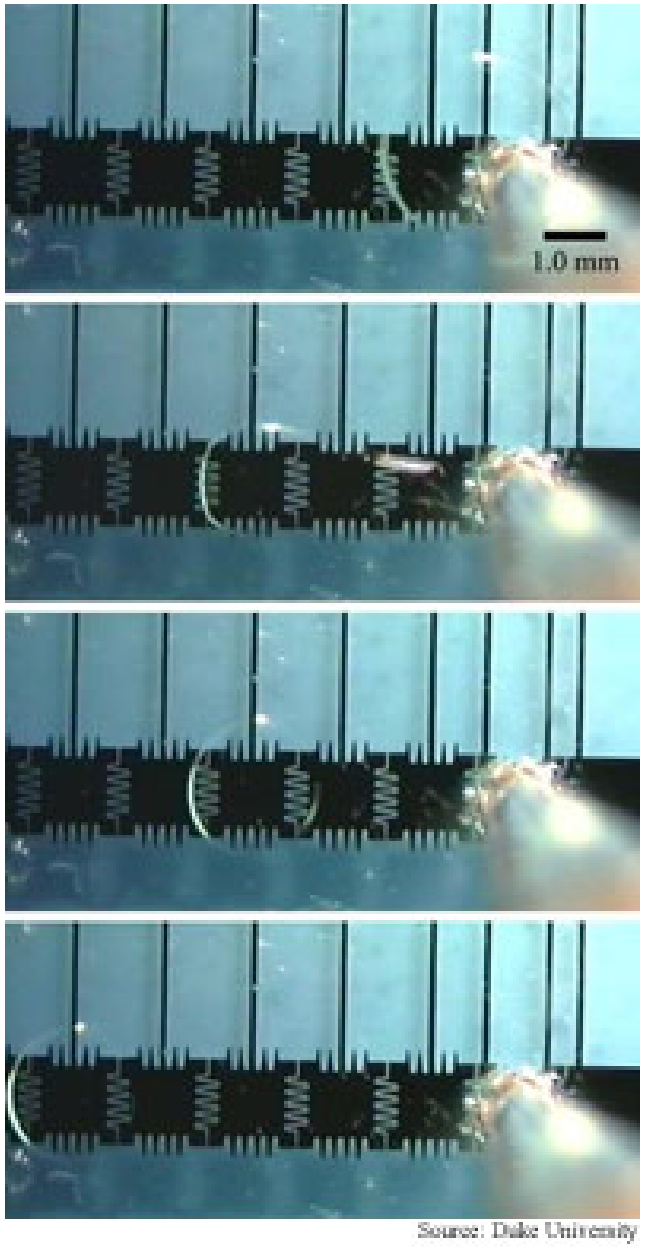
Electrowetting – control of surface tension through electric field

Fair & Pollack (Duke); KCl droplet

0.15mm diameter → 1.5 m/s







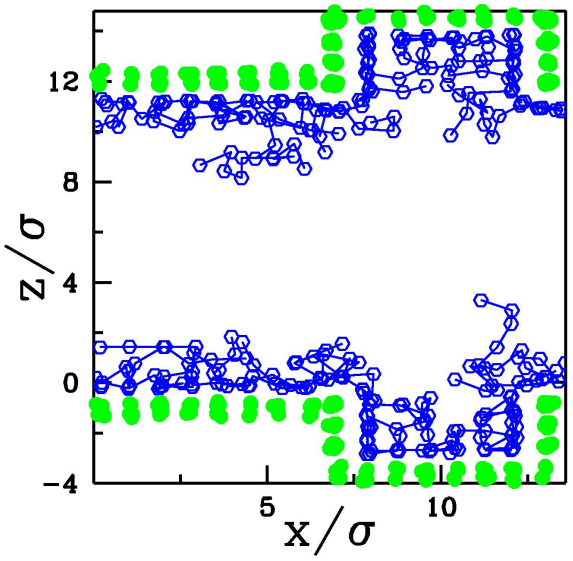
Source: Duke University

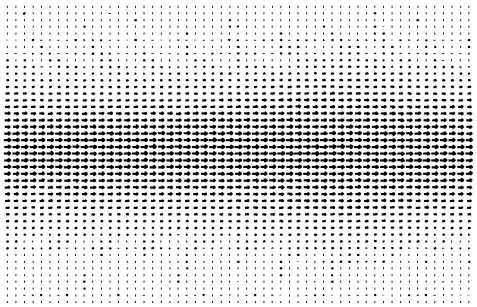
These four frames show a drop's progress as electric fields pull it across a surface.

GEOMETRICAL PATTERNING

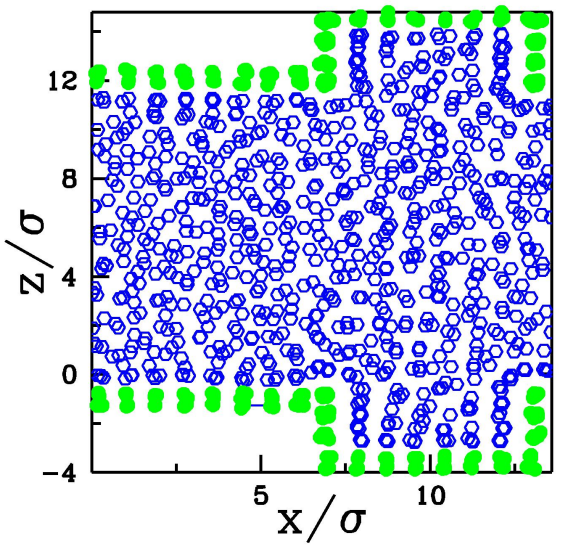
very different – as though there were no wall corrugation

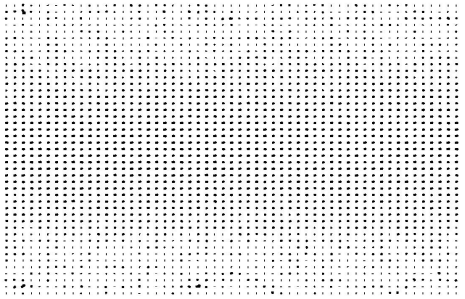
Knudsen



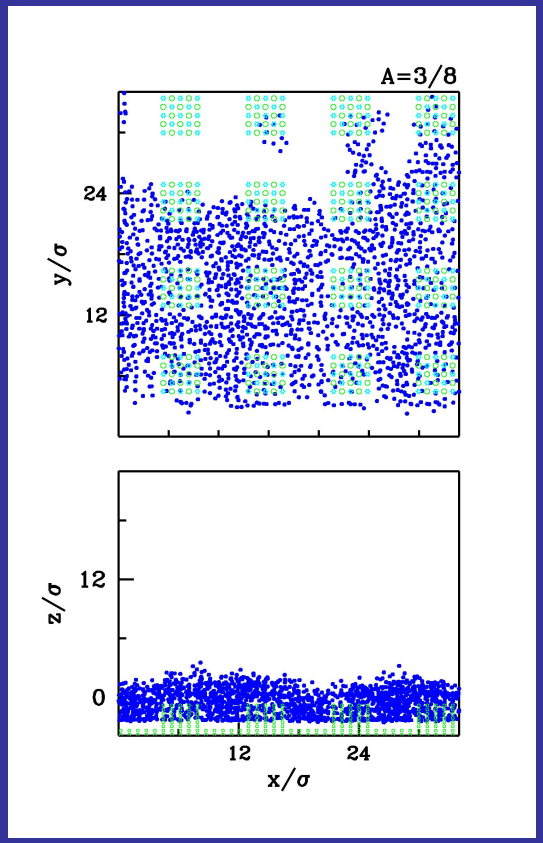


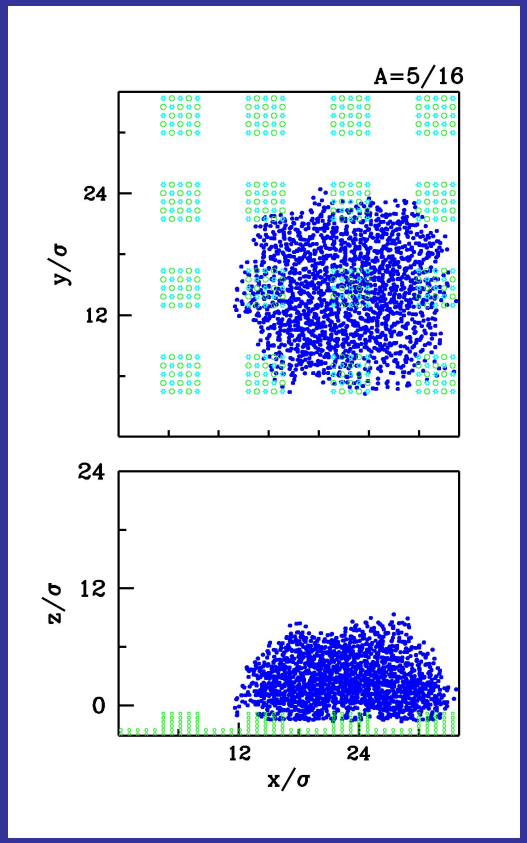
Dense fluid

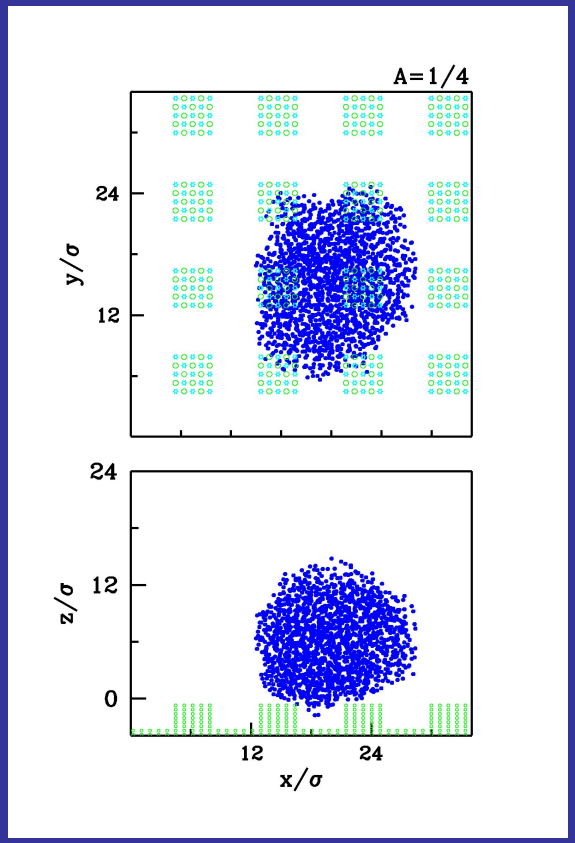




Droplet on pillars – geometrical patterning

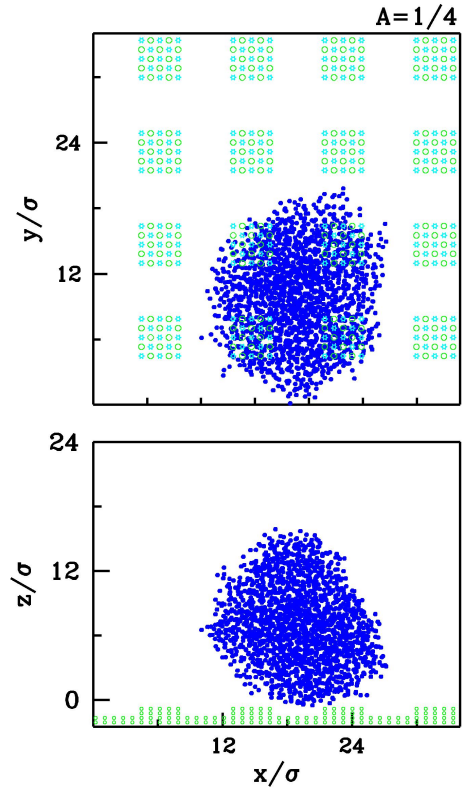


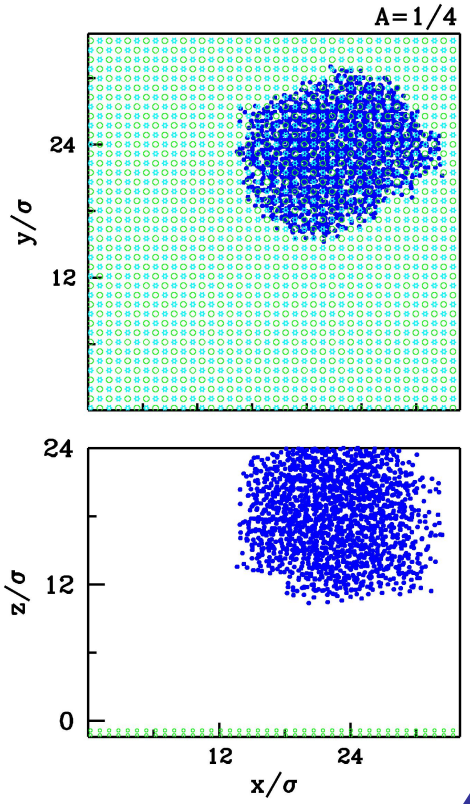




Very sensitive to the value of A – variations by 1/16

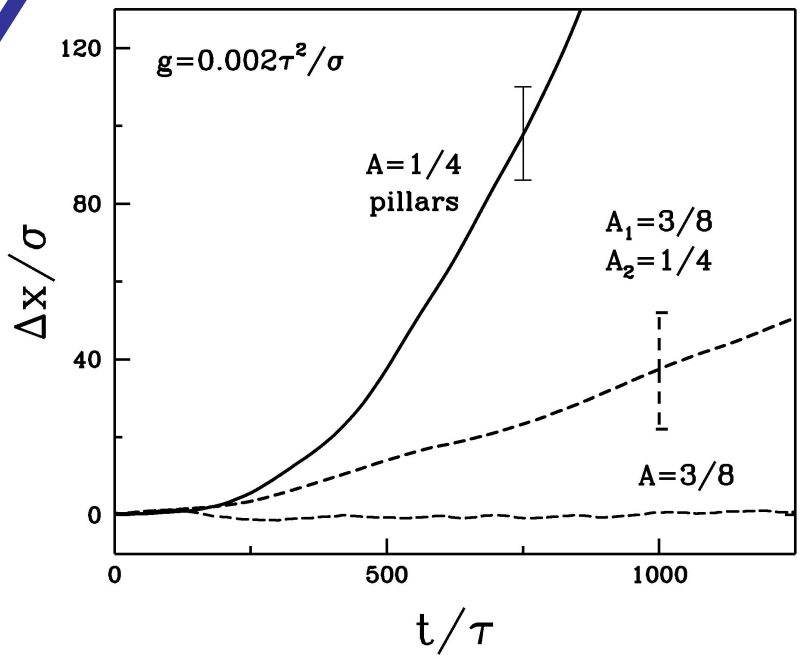
Marginality moved to a lower value of A compared to chemical patterning



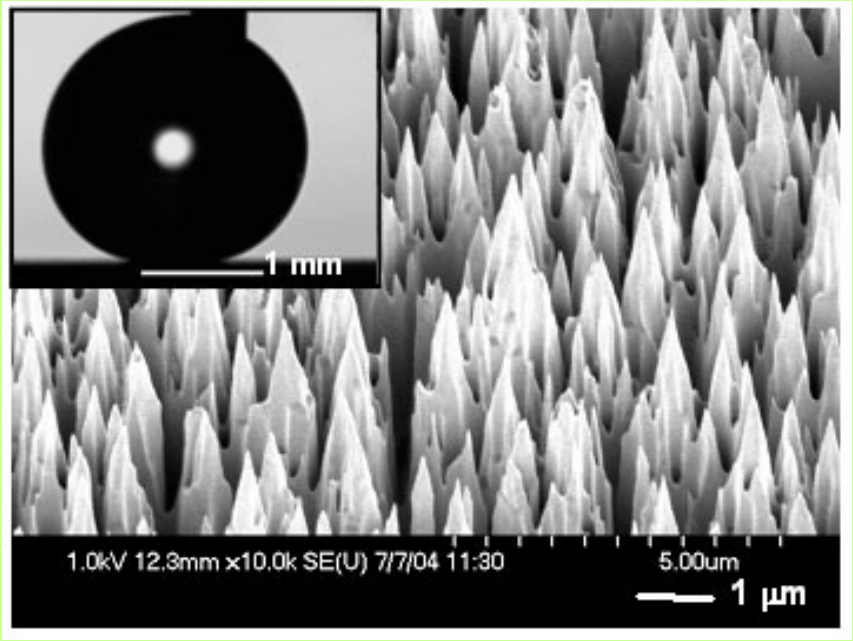


Detachment if no steps

Faster motion at the marginal value of *A*



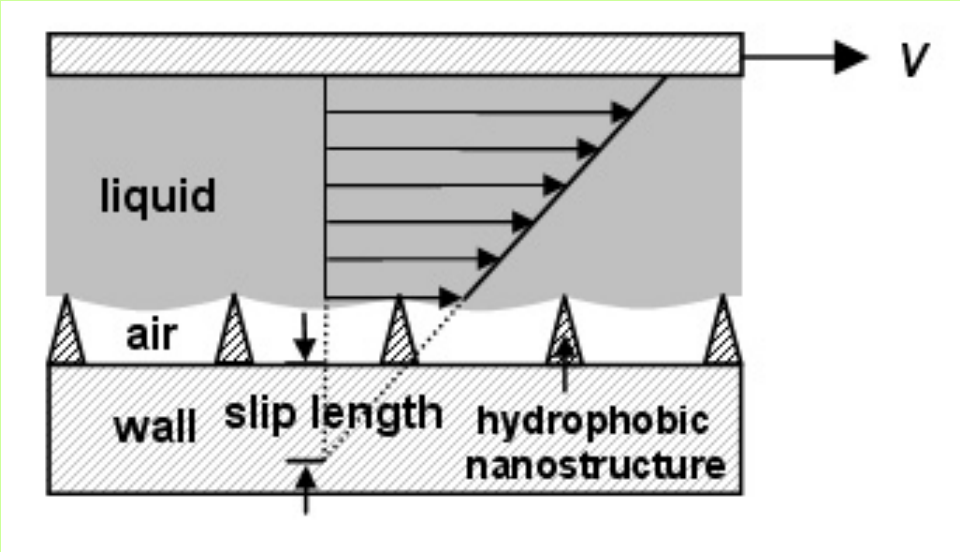
Choi & Kim UCLA 2006



Slip length of order 20 µm for water on teflon-coated silicon "nanoturf"

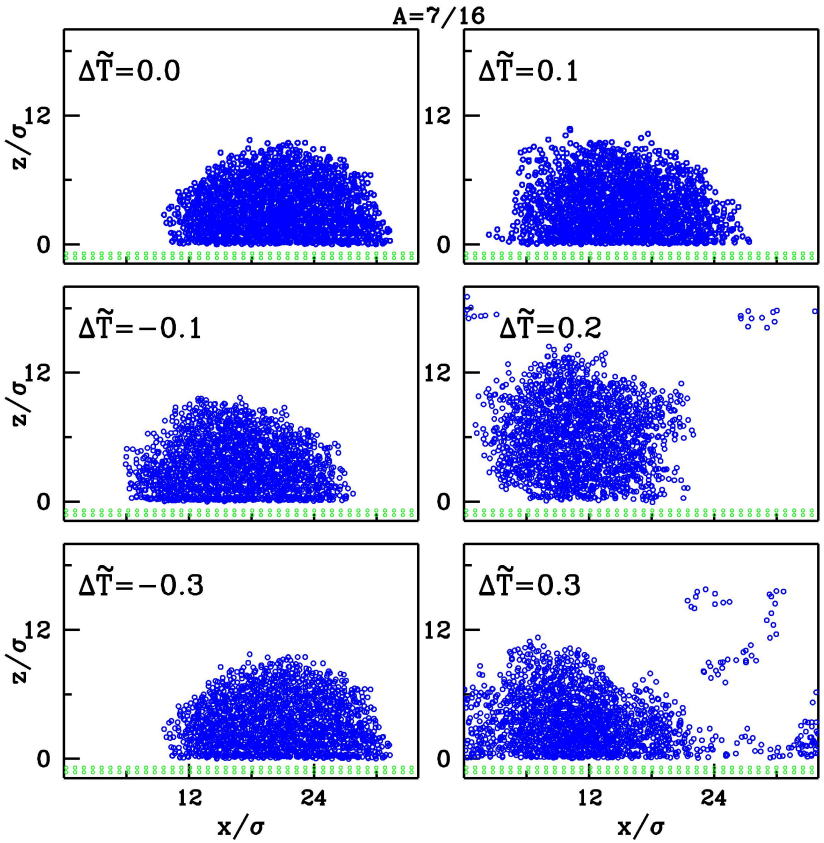
Smooth surface – contact angle 120°

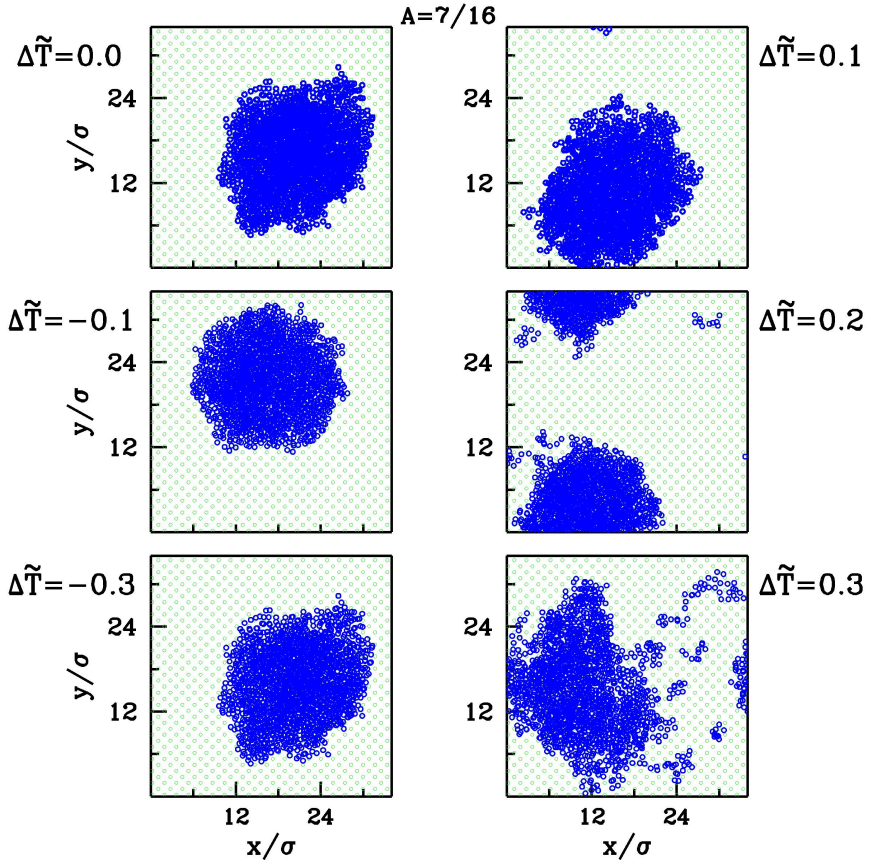
On nanoturf: 175°



(hydrophilic: use O_2 plasma)

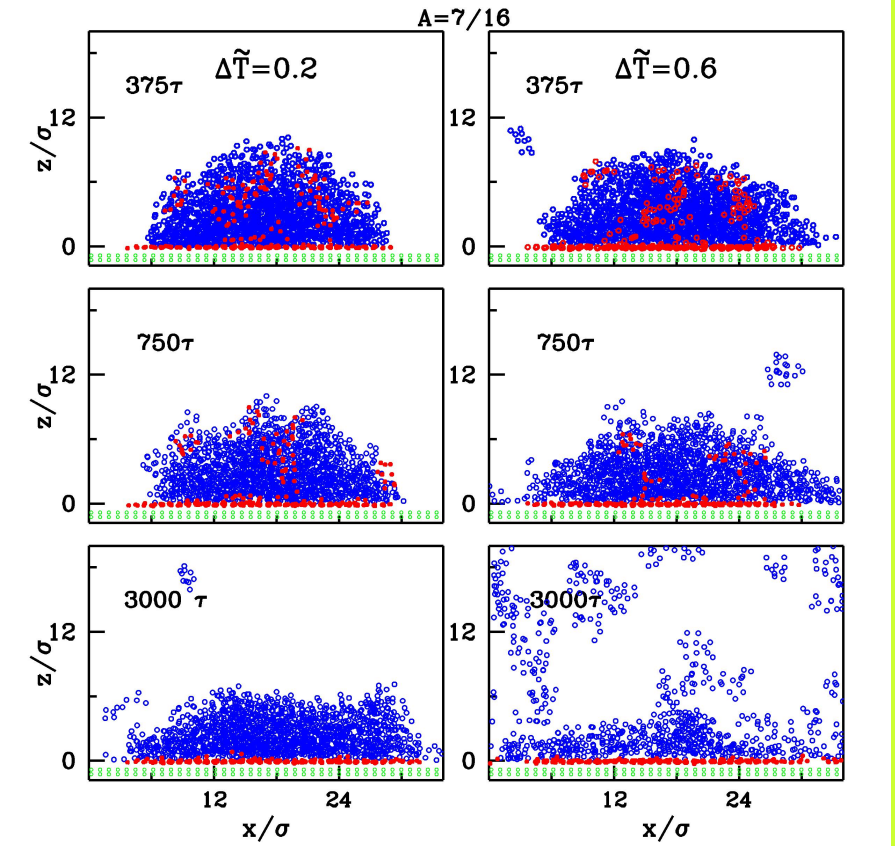
Evaporation of a droplet on a temperature controlled surface





ZX

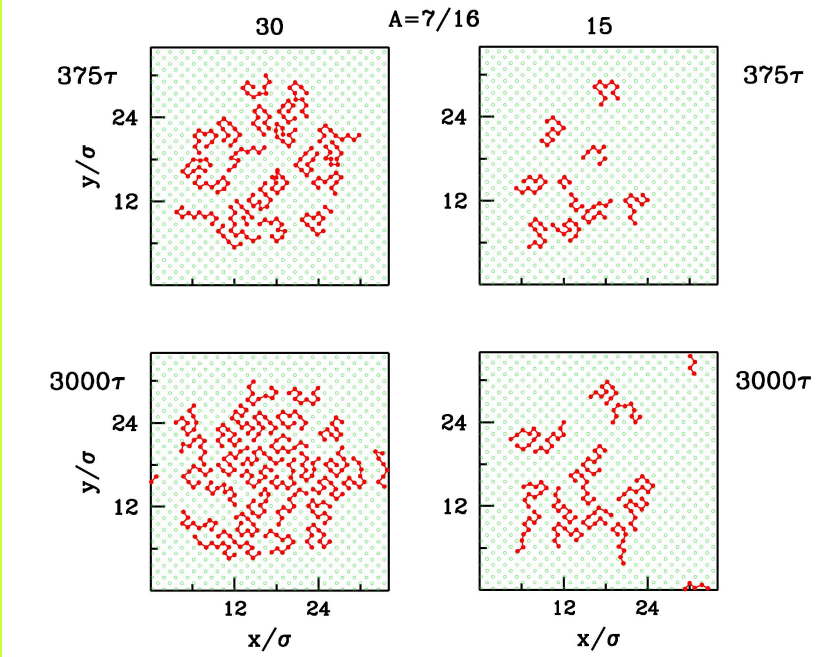
XY



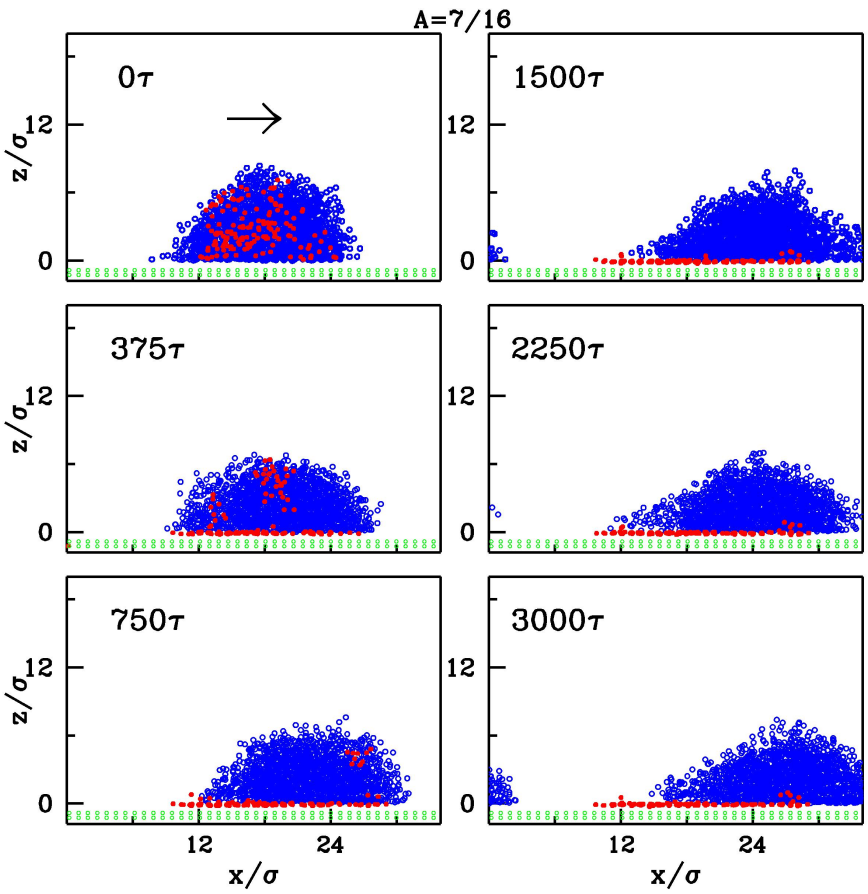
Two kinds of miscible chains – the red molecules stick to the surface once near it

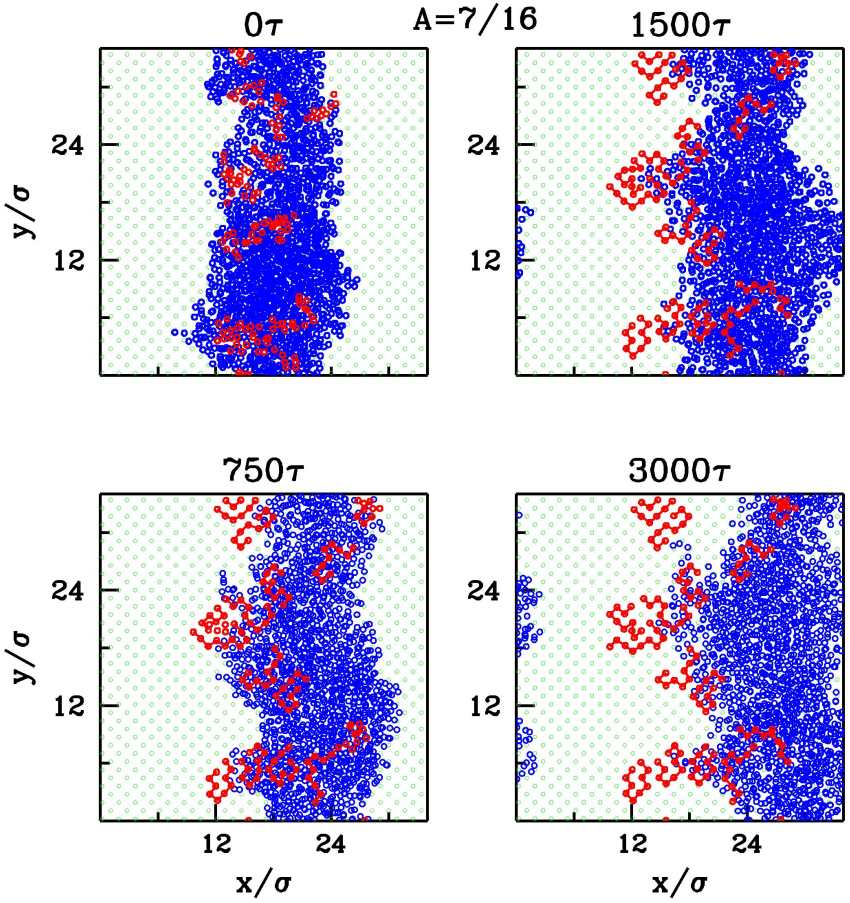
Soft lithography

The resulting pattern on the surface



A moving droplet - molecular combing

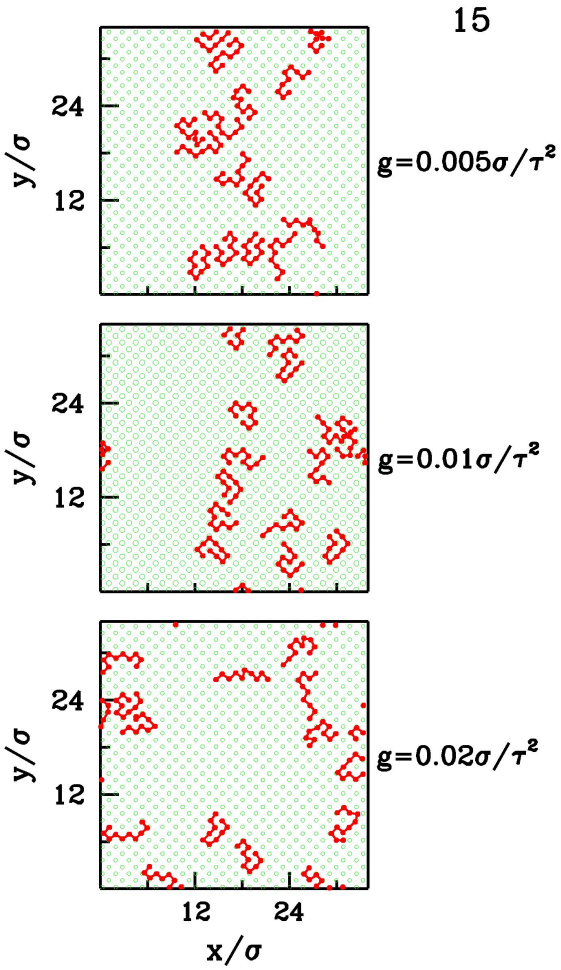


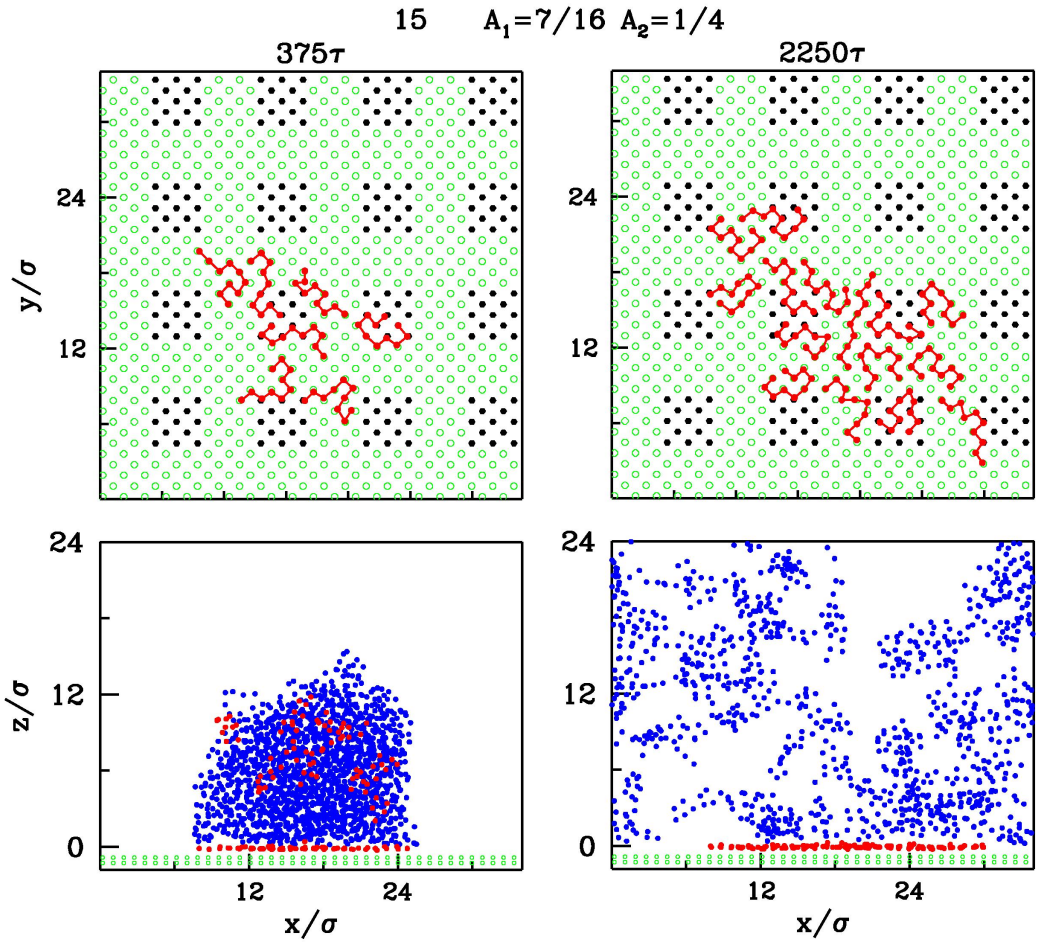


XZ

XY

EVAPORATION ON A PATTERNED SURFACE





CONCLUSIONS

Molecular dynamics studies elucidate the nature of the boundary conditions and the slip length at solid-fluid interfaces.

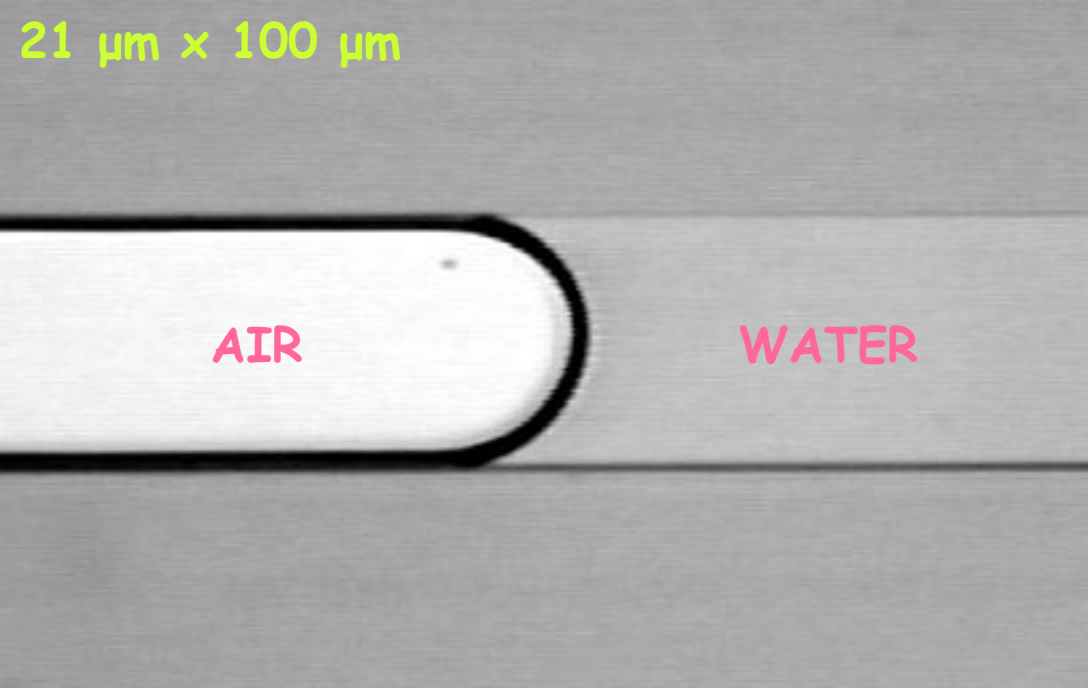
Maxwell's scenarios of behavior near the wall realized only in the limiting cases – crossover complicated

The slip length (also in thermal slip) is a sensitive function of the wall-fluid interactions and of the density

Reconstruction in the density profile near the wall leads to a maximum in the flow velocity as a function of density

Mixed wetability channels generate stationary plug flows in the non-wetting regions. Different crossovers from wetting to non-wetting regions for the dense and Knudsen cases.

Hydrophobic patterned surfaces give rise to the lotus-like behavior



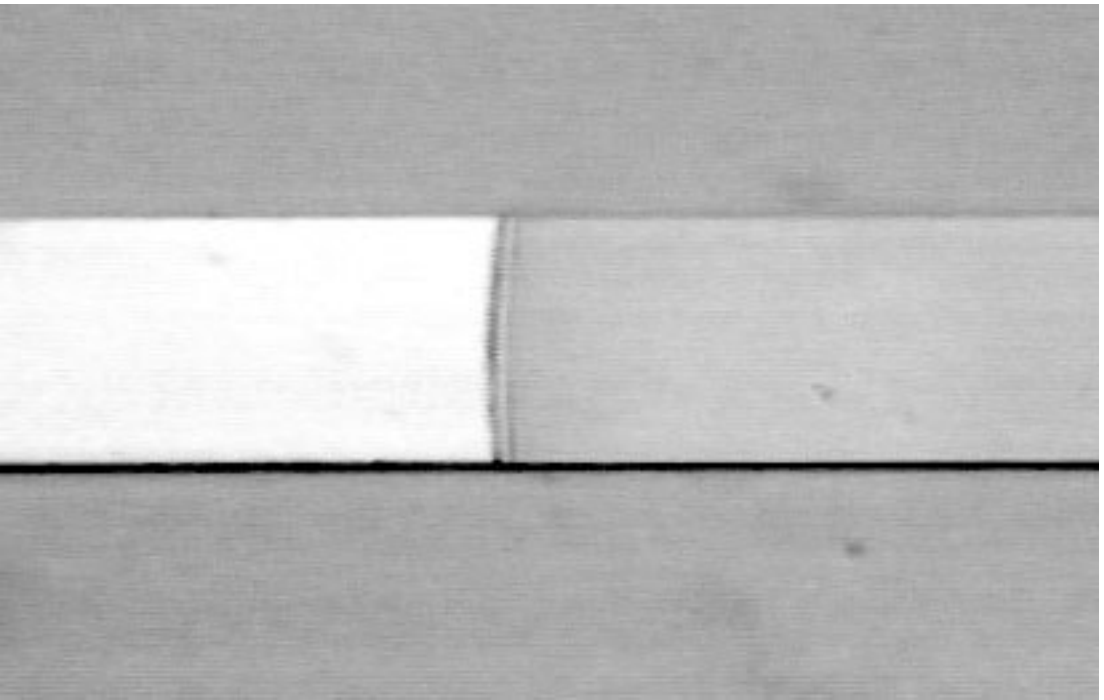
K. Breuer 2003

Stationary meniscus

The two – fluid case

Hydrophilic

(glass)



Hydrophobic

(glass coated by OTS)

Molecular Dynamics: fixed volume V and fixed energy – the simplest case

N particles, mass m: N vectorial Newton equations. For the x-component of the i'th particle: $F_{ix} = ma_{ix}$ $\qquad F_{ix} = -\partial_x U(r_1, r_2, \ldots, r_N)$

Start from an initial state, e.g. atoms on a lattice.

Time averages of quantities after transient effects die out

Simple difference formulae Verlet, Phys. Rev. 159, 98 (1967)

Runge-Kutta methods Berne et al. Adv. Chem. Phys. 17, 63 (1970)

Williamson, J. Comput. Phys. 35, 48 (1980)

Predictor-corrector schemes Rahman, Phys. Rev. A 136, 405 (1964)

Fifth-order predictor-corrector method due to C. W. Gear

Numerical Initial Value Problems in Ordinary Differential Equations, Prentice-Hall, 1971

PREDICTOR-CORRECTOR

Prediction: molecular positions $\mathbf{r}_i$ and their first five time-derivatives at time $(t+\Delta t)$ are predicted by Taylor's expansion from their values at time t

Evaluation: force on each molecule $\mathbf{F}_i$ at time $(t+\Delta t)$ is calculated using the predicted positions

Correction: an error term in the acceleration Δa_i is obtained from the difference between the predicted acceleration and that given by the force $\mathbf{F}_i$. This error is used to correct the predicted positions and their time-derivatives

Characteristic time $\tau=\sigma\sqrt{m/\varepsilon}$

ARGON: τ = 10 fs

Divide into small time intervals $\Delta t = \tau/200$

A box with the periodic boundary conditions - if possible

$X = x_i$ $Xm = x^{(m)}_i (\Delta t)^m / m!$ The m'th derivative m=0,1,2,3,4,5

$X^P(t+\Delta t)=X(t)+X1(t)+X2(t)+X3(t)+X4(t)+X5(t)$

$X1^P(t+\Delta t)=X1(t)+2X2(t)+3X3(t)+4X4(t)+5X5(t)$

$X2^P(t+\Delta t)=X2(t)+3X3(t)+6X4(t)+10X5(t)$

$X3^P(t+\Delta t)=X3(t)+4X4(t)+10X5(t)$

$X4^P(t+\Delta t)=X4(t)+5X5(t)$

$X5^P(t+\Delta t)=X5(t)$

Error: $\Delta X2=X2(t+\Delta t)-X2(t+\Delta t)$

$X(t+\Delta t)= X^P(t+\Delta t) + a_0\Delta X2$

$X1(t+\Delta t)=X1^P(t+\Delta t) + a_1\Delta X2$

$X2(t+\Delta t)=X2^P(t+\Delta t) + a_2\Delta X2$

$X3(t+\Delta t)=X3^P(t+\Delta t) + a_3\Delta X2$

$X4(t+\Delta t)=X4^P(t+\Delta t) + a_4\Delta X2$

$X5(t+\Delta t)=X5^P(t+\Delta t) + a_5\Delta X2$

a_m depend on the degree of the differential equations and on the order of the Taylor series used: to ensure numerical stability

5'th order:

3/16, 251/360, 1, 11/18, 1/6, 1/60

3'rd order:

1/6, 5/6, 1, 1/3

Calculation of the forces: the most time-consuming part of an MD simulation

N(N-1)/2 pairs of atoms

Cutoff r_c: $r_{ij} > r_c$ then F=0 $r_c = 2.5\sigma$ or 2.2σ

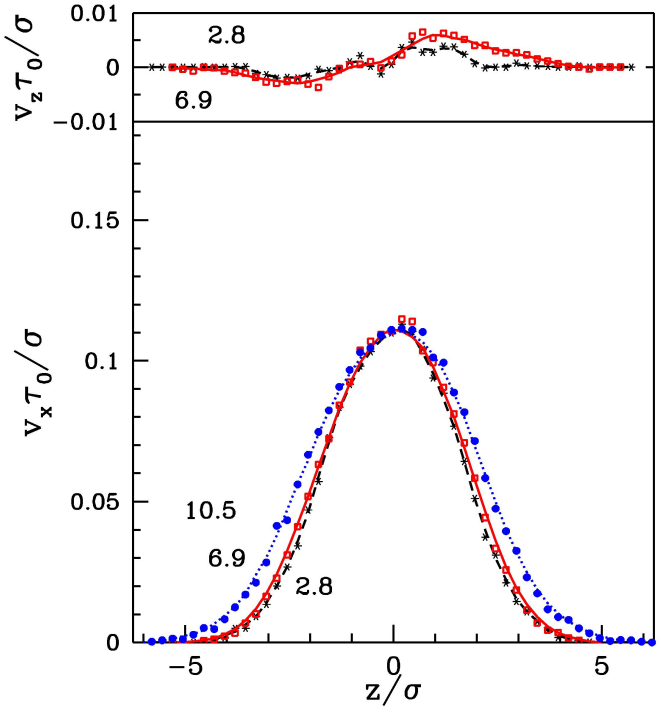
Verlet list: for each particle keep a list of neighboring atoms that lie within a distance r_L of i, where $r_L > r_c$ (slightly)

Update the list periodically, say, every 10 steps.
$r_L = r_c + 0.3\sigma$ - typically 40 neighbors

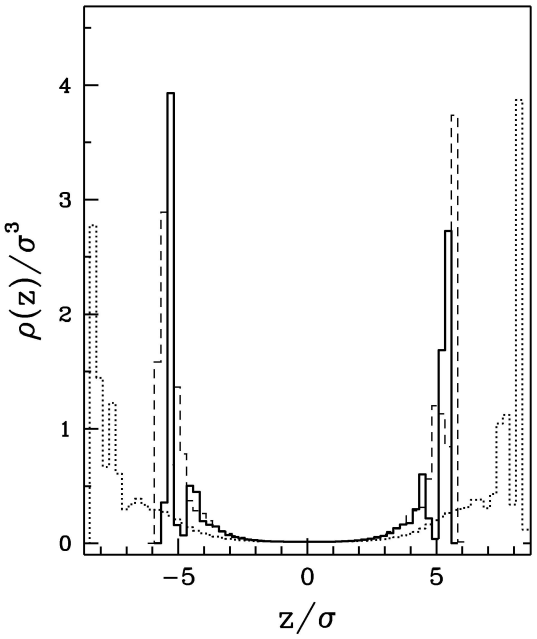
Study diffusion of one atom to distinguish between liquid and solid

Temperature, energy, correlations, pressure form the virial theorem

Velocity profiles change little along the channel



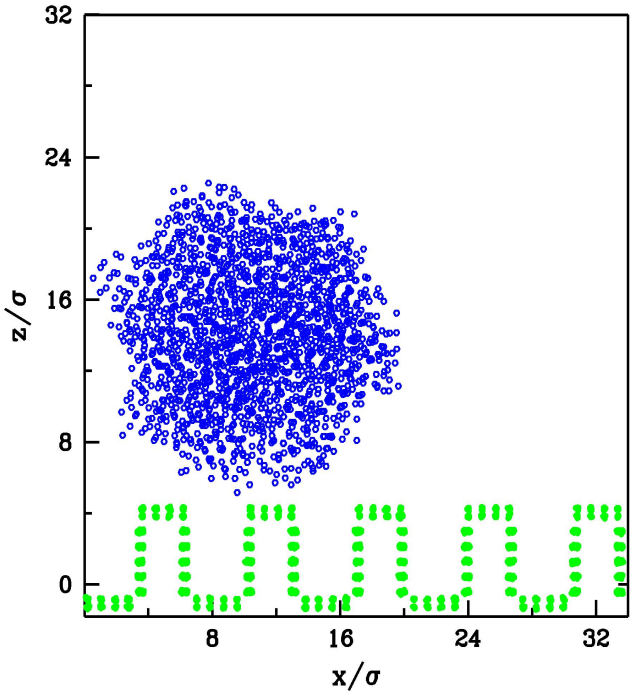
Density profiles do change: coating of the walls

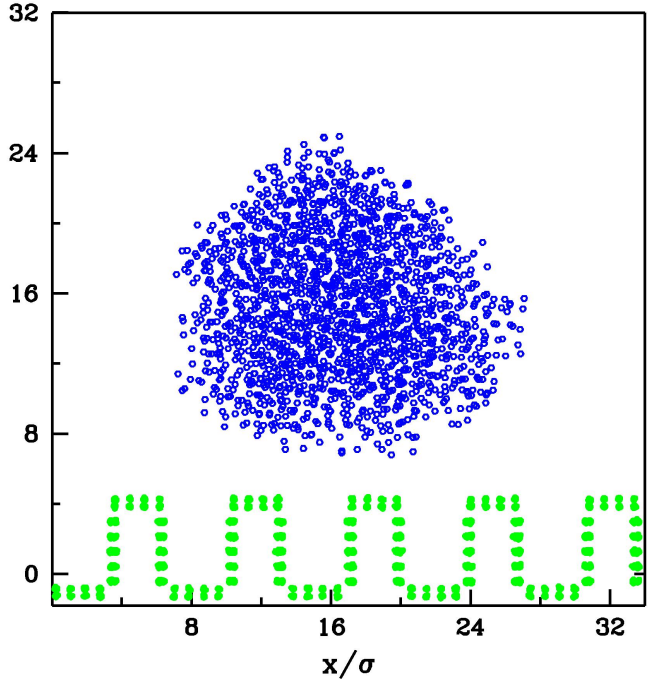


A non-wetting fluid droplet moving along a nanocomb

A horizontal pressure gradient

Acceleration of the center of mass goes down on making the 'canyons' deeper



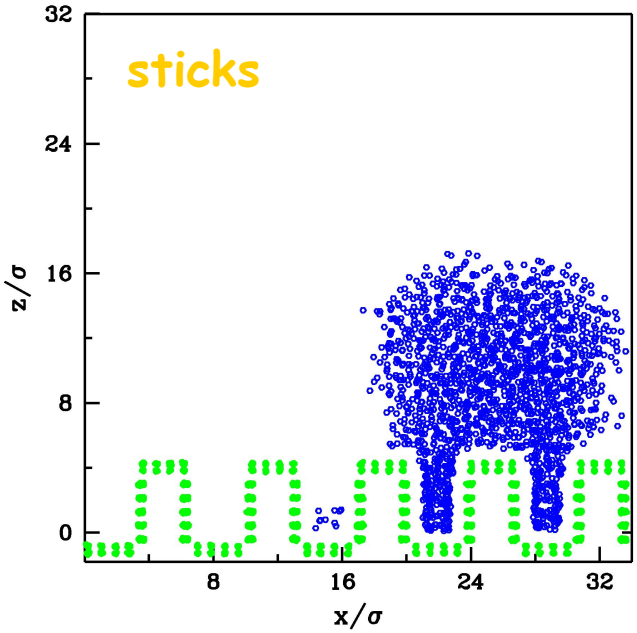


movement

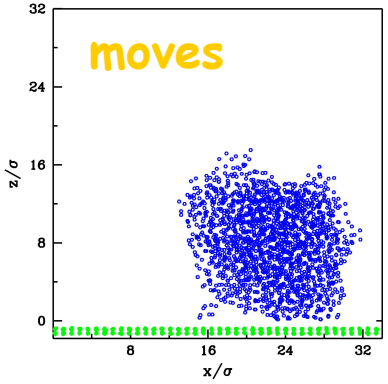
A=3/16
T=0.8

1800 fluid molecules;
atomic wall (vibrating)

A=1/4

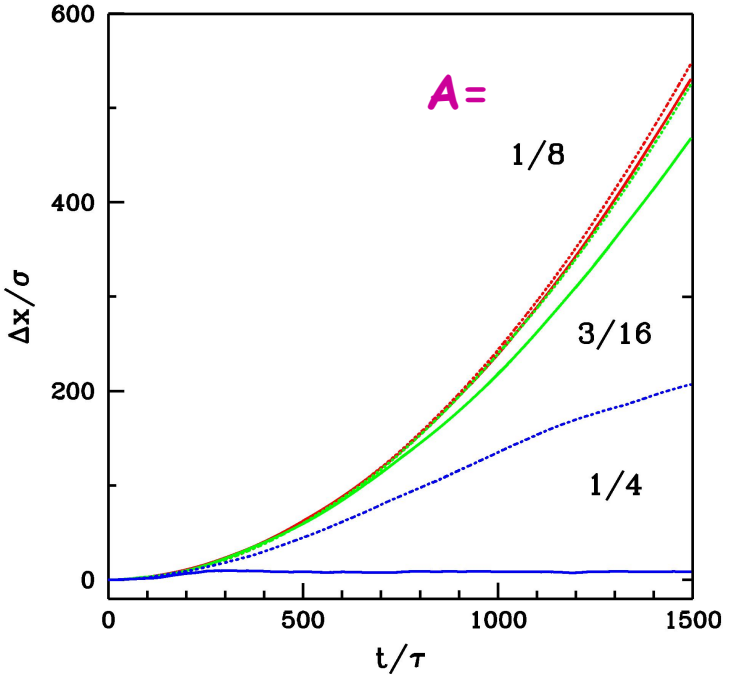


flat



Location of the center of mass as a function of time – parabolic except for A=1

Strongly non-wetting: corrugation does not affect the motion



Solid line: the corrugated wall

Dotted line – flat wall

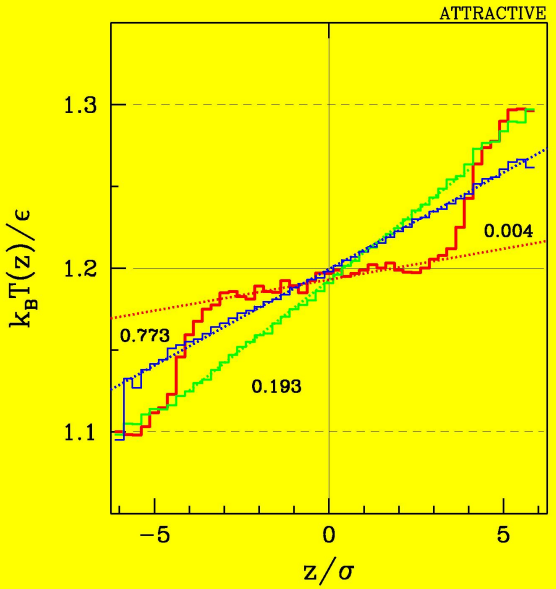
Other studies:

Work on evaporation of binary droplets – self organization of particles that attach to the surface – with Toulouse

Preparatory work on particles falling on a comb-like surface (Toulouse): where do they deposit

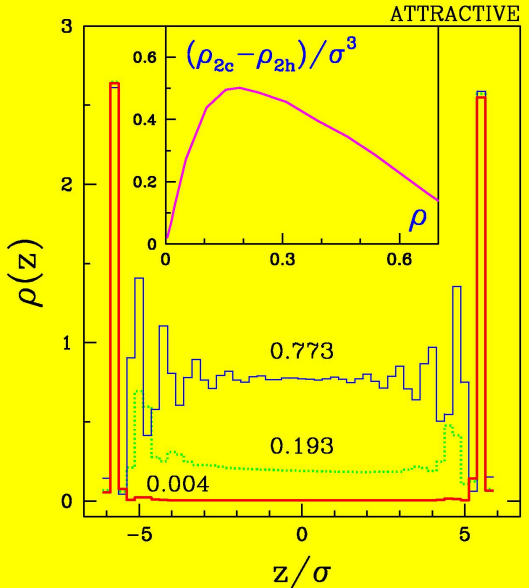
Hydrodynamic and entropic effects

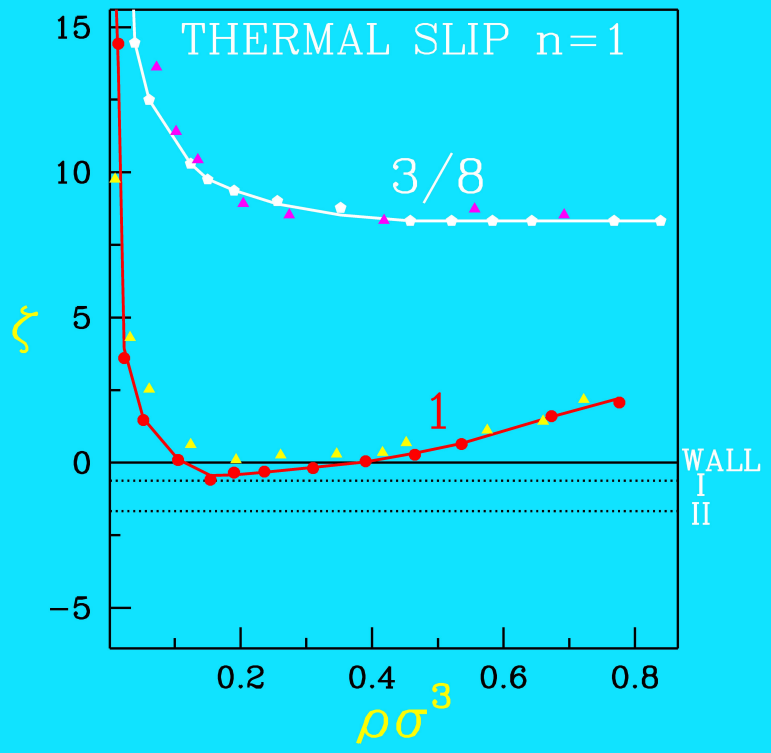
THERMAL SLIP



HOT

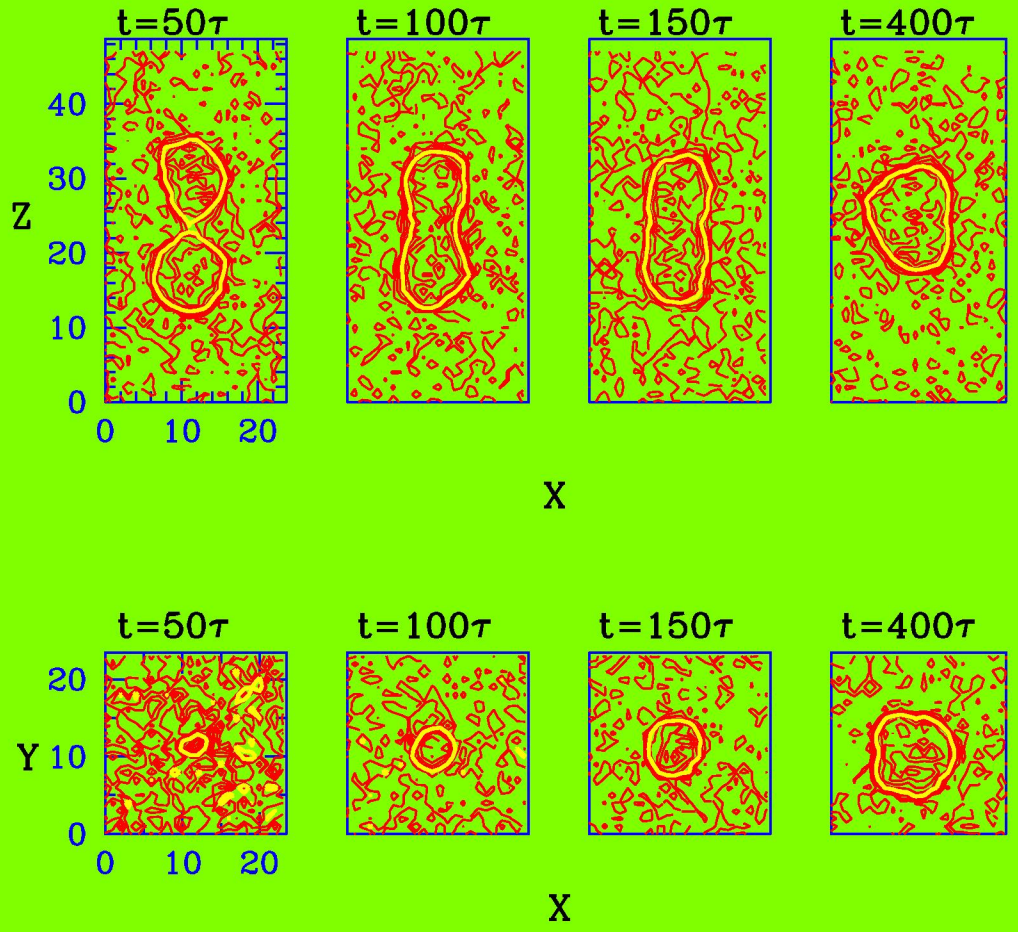
COLD

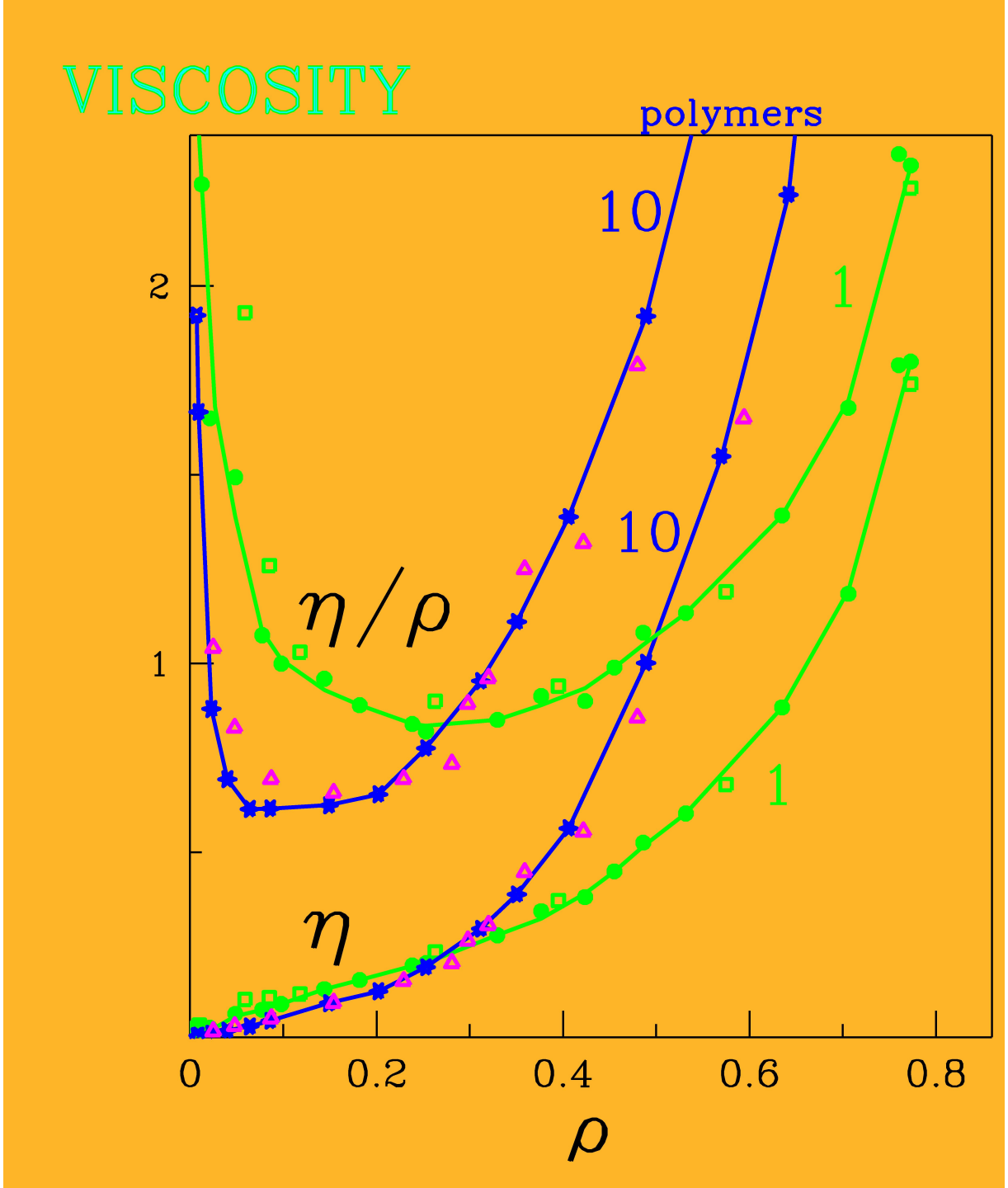




Droplet coalescence

MD appropriate when molecular effects are important




VISCOSITY
polymers
10
1
10
1
η/ρ
η
2
1
0
0.2
0.4
0.6
0.8
ρ