Simulating SoftFlowMat

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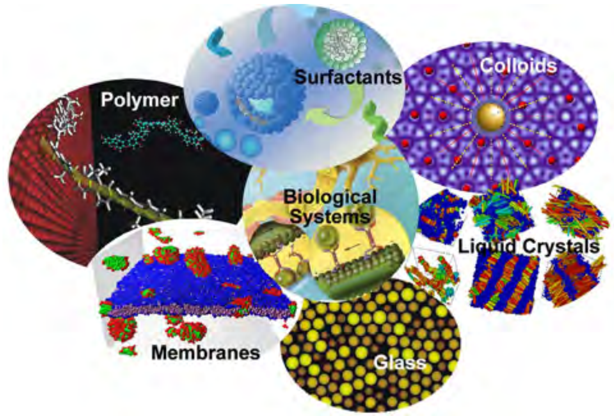


European Research Council
Established by the European Commission

S. Succi,
IIT Rome&Harvard Phys

Nanofluidics at the crossroads

You are here

COLLÈGE DE FRANCE
1530

CdF Paris, May 25 2023

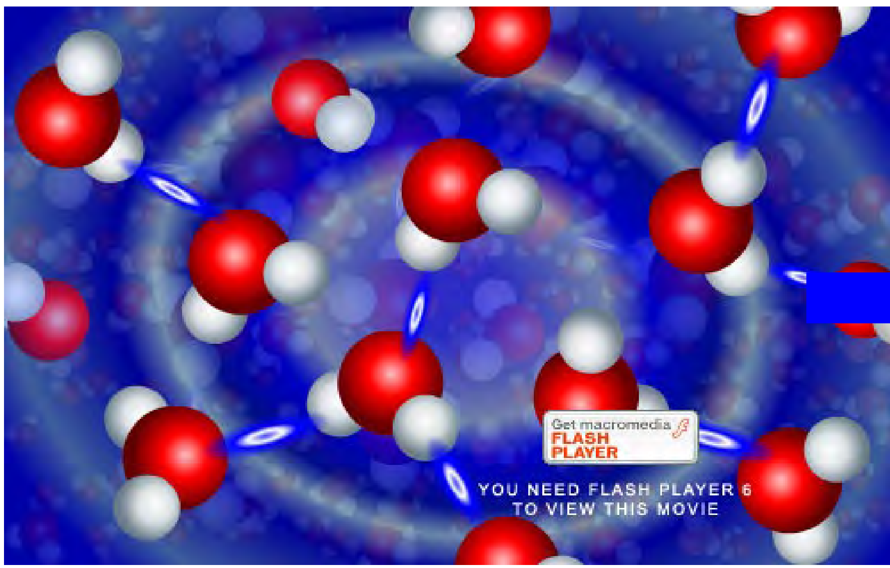
Plan

1. Soft Flowing Matter
2. Computational Methods
3. Droplet-based soft materials
4. From passive to active droplets
5. Meso coupling to quantum-nano fluidics

From Condmat to DropMat

What if molecules would be replaced by droplets?
What kind of dropled-based materials can we envisage?
How do we simulate, design and realize them in the lab?

Molecules (~ nm)

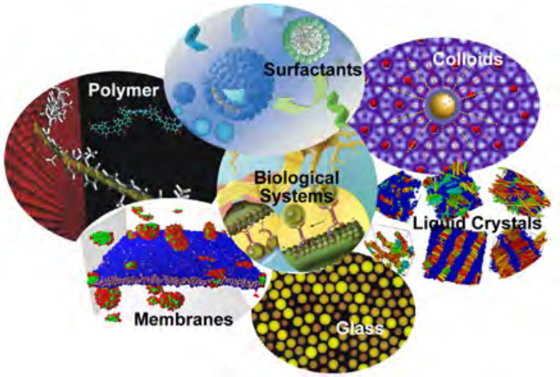


Meso-molecules (10-100 microns)

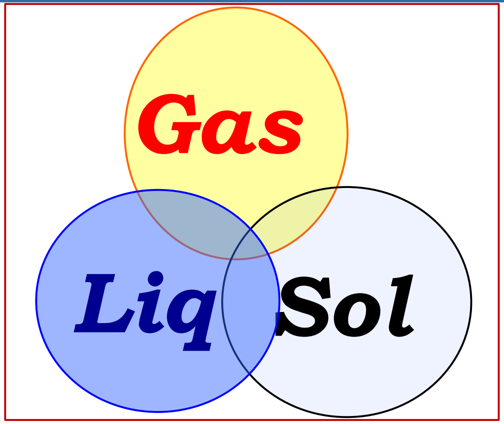
Explore the non-equil pattern formation properties of multi-droplet configurations under strongly confined flow.

(No chemical specificity, sorry ...)

Soft Flowing Matter



Entangled "kT physics"



Phys: Non-equil pattern formation under flow

Num: Multiscale/physics problem

Mat: Novel mesoscale porous materials

Eng: New microfluidic experiments

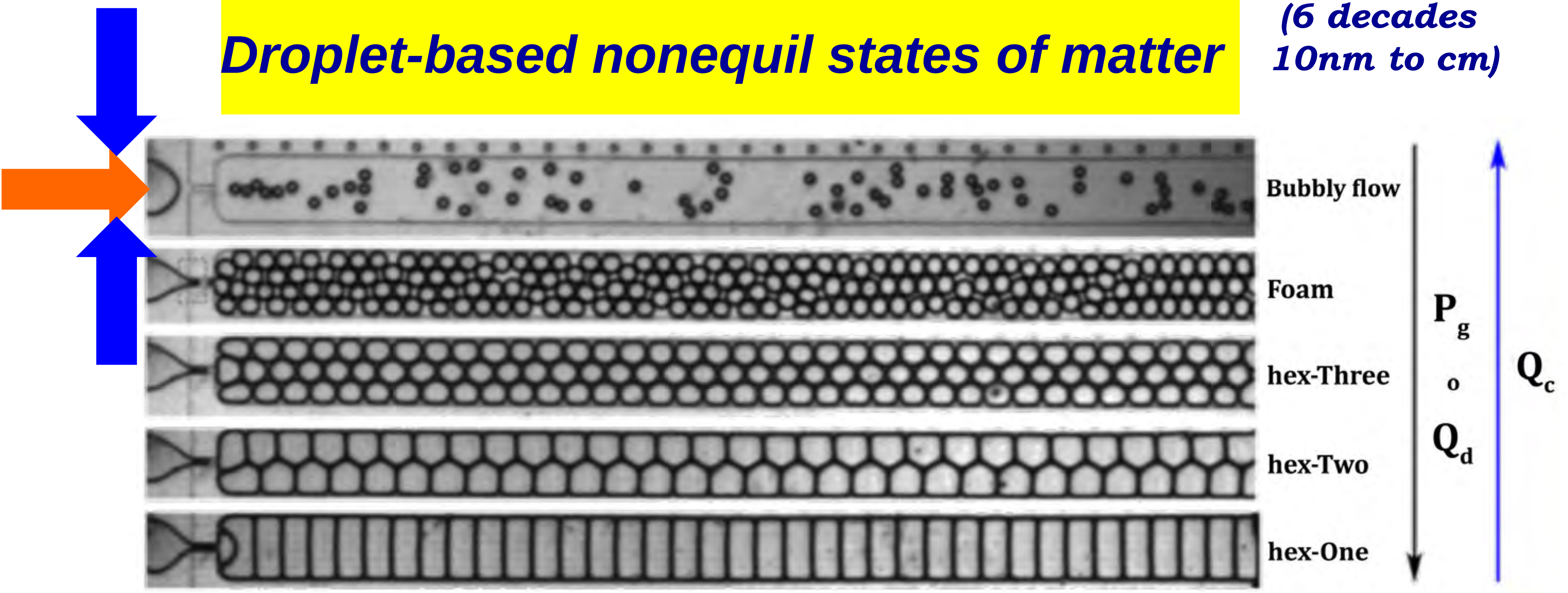
App: Biomed devices, catalysis, cell motion

SFM: nonlin «entanglement» of G+L+S with genuinely new properties NOT shared by any of G,L,S!
Configurational DOF: nonlin&nonloc multi-body effects

Microfluidics

Droplet-based nonequil states of matter

(6 decades 10nm to cm)



(Raven and Marmottant, PRL 2009)

By regulating the flow rate of the dispersed phase Q_d (or gas pressure Pg in the case of foams) and of the continuous phase Q_c, different pore sizes (different configurations/arrangements can be obtained).

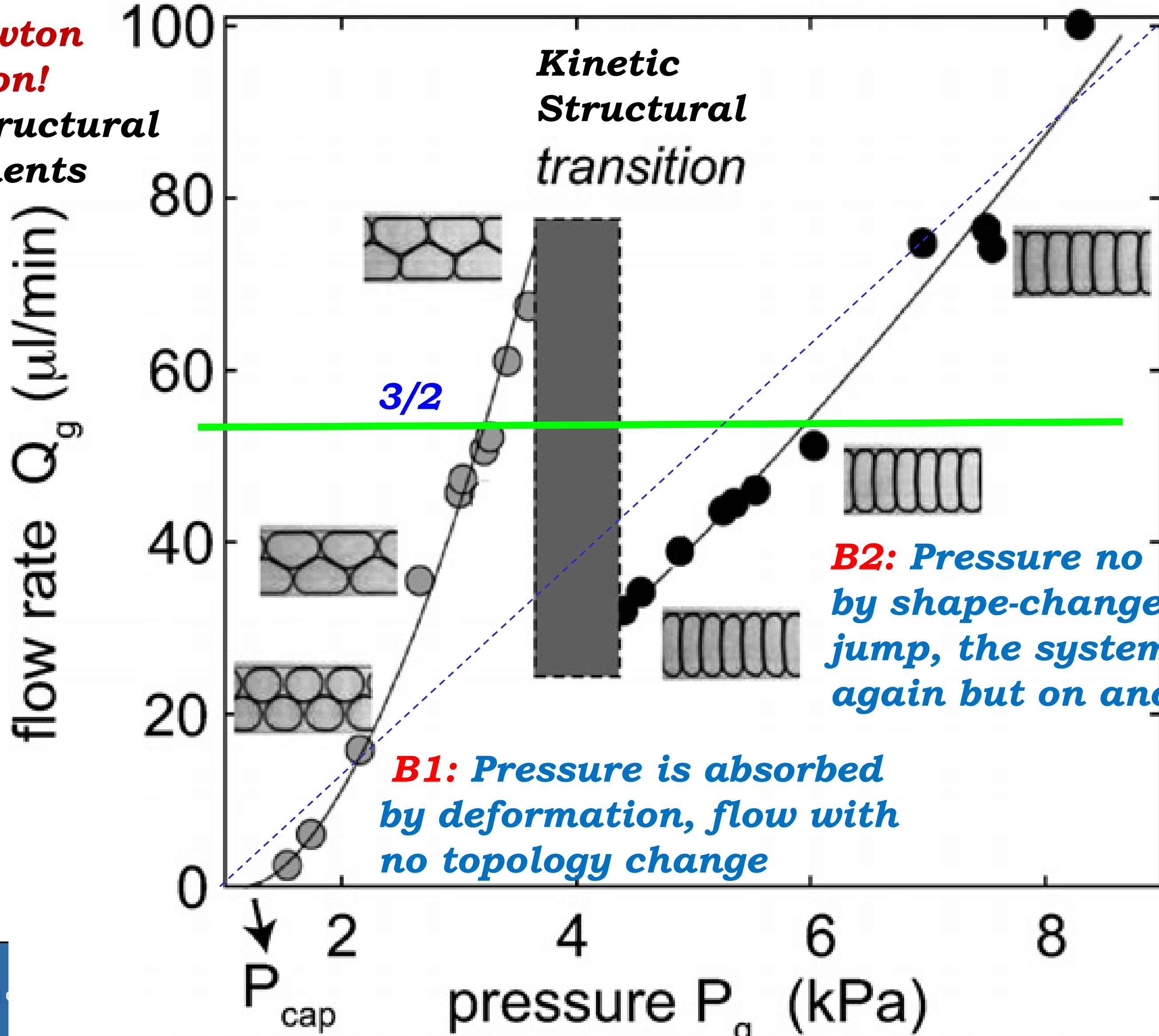
EASY AND ACCURATE CONTROL

Goal: rheological properties

Nonlinear rheology

Marmottant-Raven experiment, PRL 2009

Newton+Newton = Non-Newton!
Dynamic structural rearrangements
Internal Dissipation

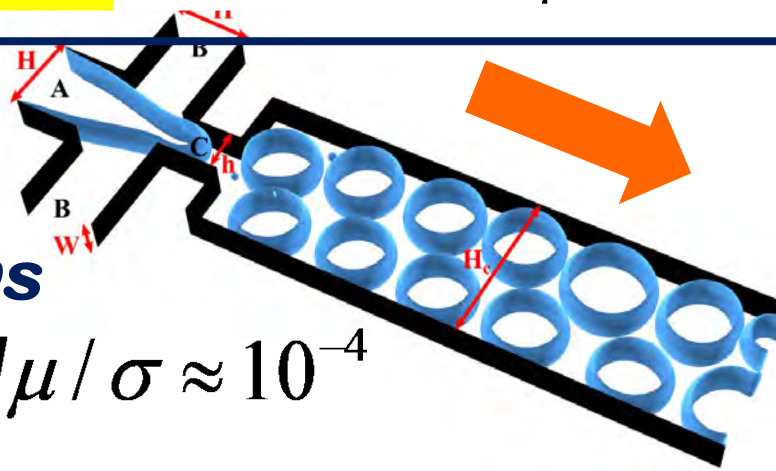


Microfluidic interactions

$$g = \nabla p / \rho$$

$$F_{vis} = \mu U / D^2 \qquad F_{ine} = \rho U^2 / D$$

$$F_{nc} = A\,kT / h^4 \qquad F_{cap} = \sigma / D^2$$



Very slow flows

$$Ca \equiv F_{vis} / F_{cap} = U\mu / \sigma \approx 10^{-4}$$

$$Re \equiv F_{ine} / F_{vis} = Uw / \nu \approx 10^{-3}$$

$$Mo \equiv g\nu / V_{cap}^3 = g\mu^4 / \rho\sigma^3 << 1$$

Soft particles

$U \approx 10^{-3}$ *m/s*

$D \approx 10^{-4}$ *m*

$$D / H \approx 0.2 - 1$$

NON LOCAL EFFECTS: confinement is key!

(L. Bocquet et al, fluidity models)

Open questions

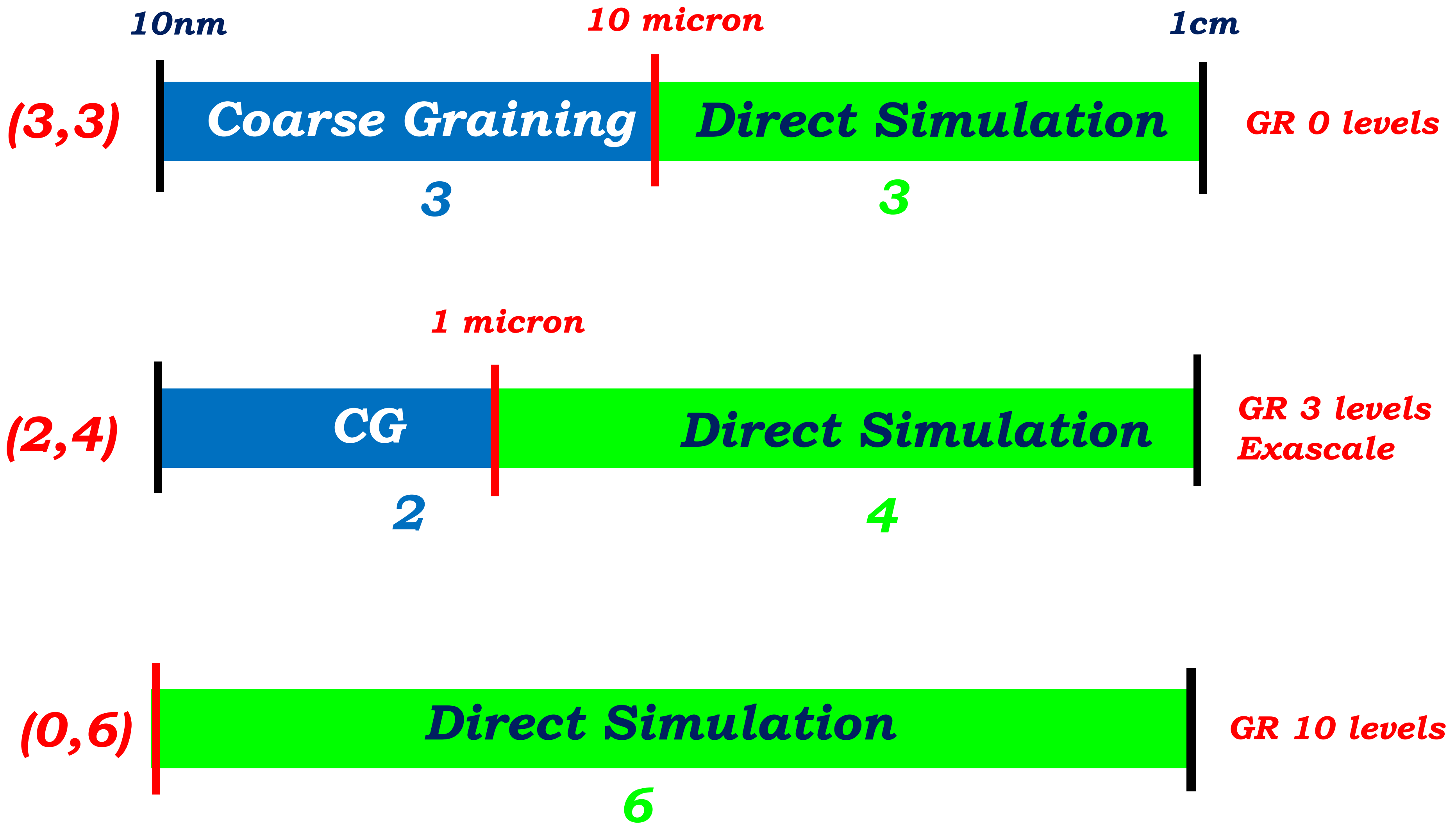
Continuum methods are very hard (high S/V)
Atomistic methods are short in space and time)

Can we meso-simulate SFM rheology?
Multiscale physics: 6 spatial decades
(like airliner turbulence)
No Exascale can take it, it's 10^18 DOF

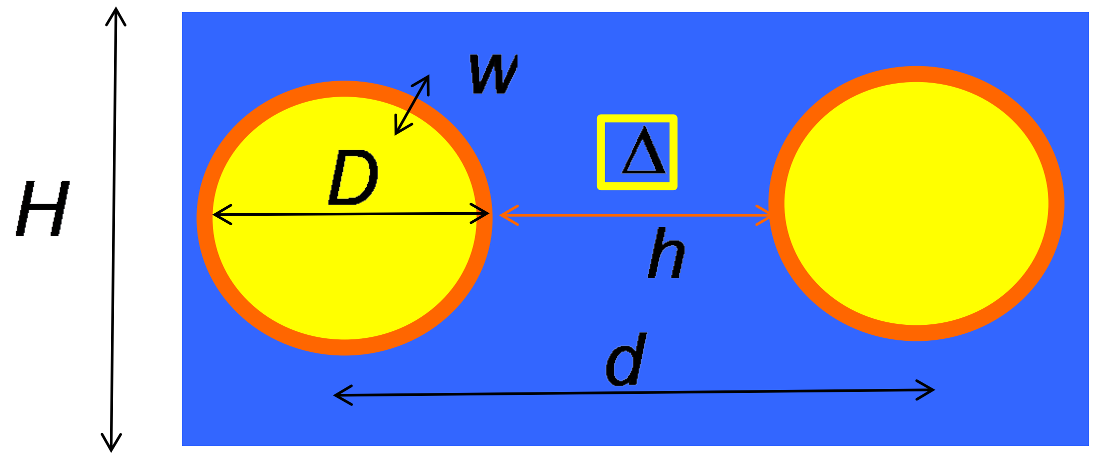
Keys: Dense, Confined, Deformable

Rheo is very rich and largely uncharted

Multiscale CG-DS strategies



Micro-Meso-Macro connection (6 decades)



$H = 1\,mm$

$D = 10 - 100\,\mu$

$h = d - D$

$\Delta = D/100;\ 1\mu$

$w = 1\,nm$

Dilute regime:

$$\varphi_d \sim \frac{V_d}{V_d + V_c} << 1$$

$$h > D$$

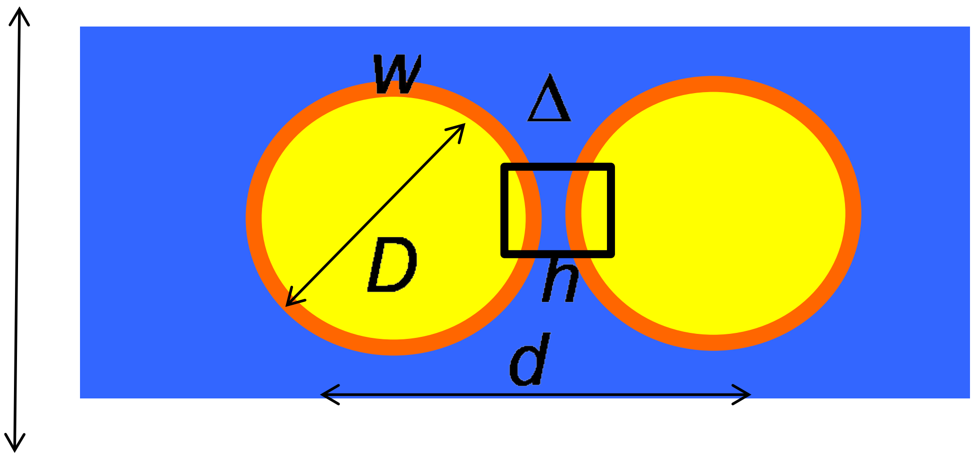
NCI's are silent

$$w << \Delta < h \sim D < H$$

Numerics is ok

Length-scales

H



$H = 1\,mm$

$D = 10 - 100\,\mu$

$\leftarrow \Delta$

$h = 10\,nm$

Δ = 1nm

$w = 1\,nm$

Standard

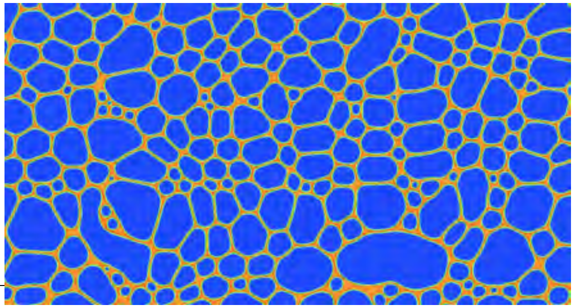
$$\frac{\Delta}{h} \approx 10^2$$

Dense regime: NCI's take stage!

$$F(h) = A / h^n \ldots$$

$A < 0$ ***Coalescence***

$A > 0$ ***Long-lived states***



Low density regime, OK $w \ll \Delta < h \ll D$

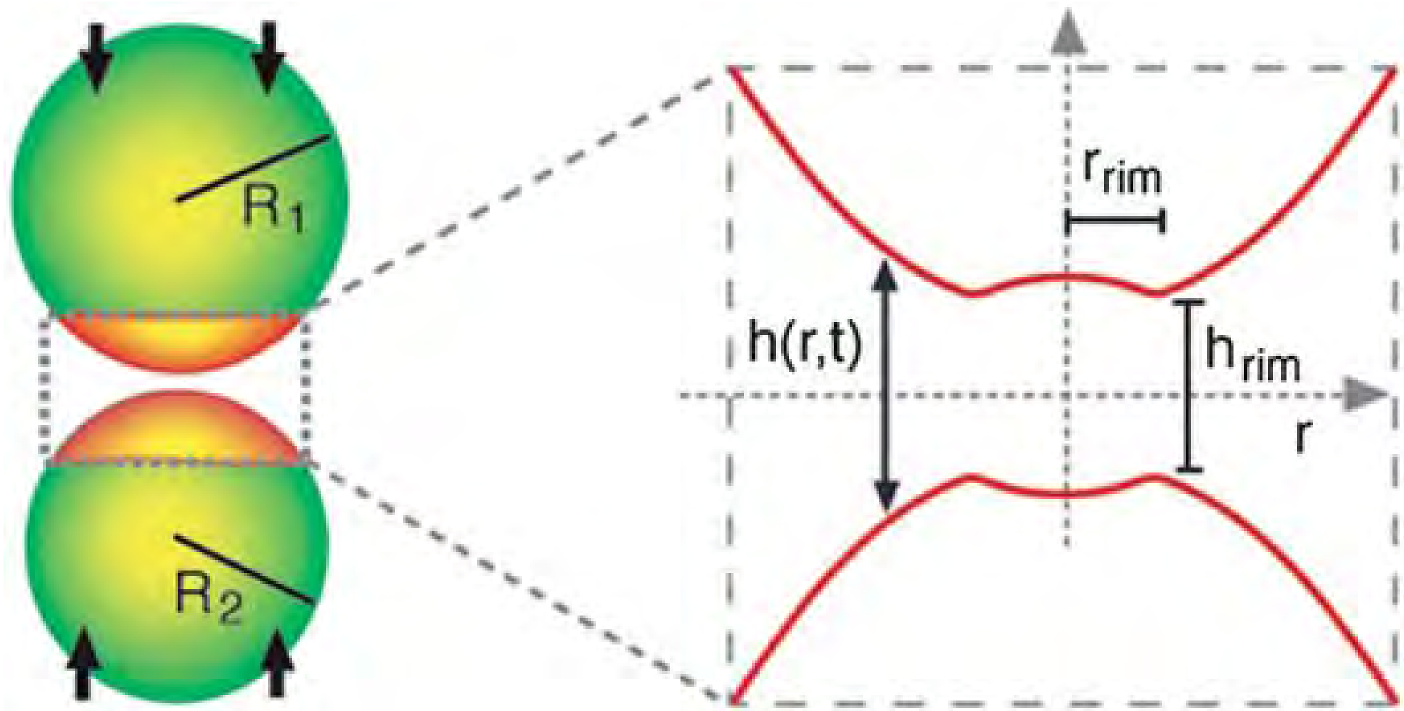
High density regime:

$w < h < \Delta \ll D$ ***Subgrid LB, tough***

$\Delta < w \approx h \ll D$ ***Molecular, resolve interface***

Soft droplets

Dimples, Wimples, Pimples: interface waves
Do they affect the large-scale structure of the flow?



$$\varepsilon = \delta / D$$

$$\partial_t h + \frac{\tau}{\mu} h \partial_x h = \frac{\sigma}{\mu} \partial_x (h^3 \partial_x^3 h);$$

$$h > 0$$
$$h = 0$$
$$h < 0$$

Thin film theory: Non linear waves

New many-body metastable states (Theory?)

Methods

Lattice Boltzmann: crystal hydrodynamics

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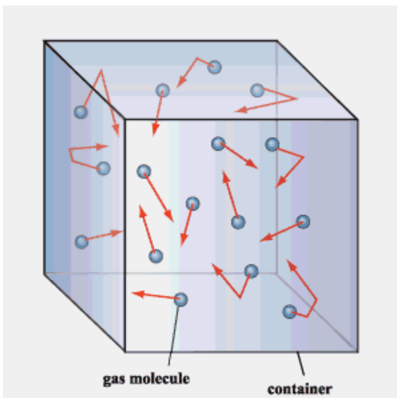
$$f(\vec{x},\vec{v};t) = \sum_{i=0}^{b} f_i(\vec{x},t)\delta(\vec{v}-\vec{c}_i) \qquad i = 0, b$$

Triple infinity to just 18!

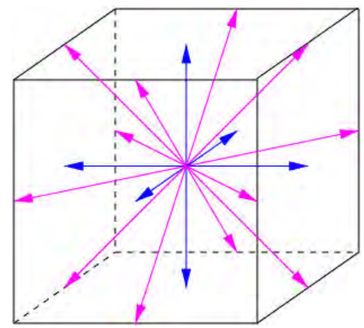
Quasiparticles: magic speeds!

Exact sampling of frequent events



Universality

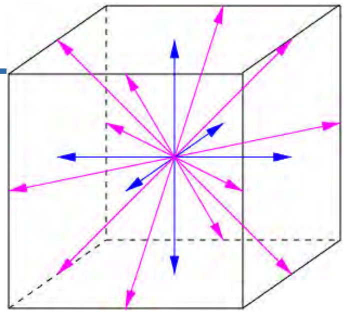
Individuality



$$\rho(\vec{x};t)\bar{a}(\vec{x};t) = \int a(\vec{v}) f(\vec{x},\vec{v};t)\, d\vec{v} = \sum_{i=0}^{b} a_i f_i(\vec{x};t)$$

Gauss-like quadrature: low order moments are EXACT

LBE: Stream&Collide



Math paradigm for complex flowing systems:

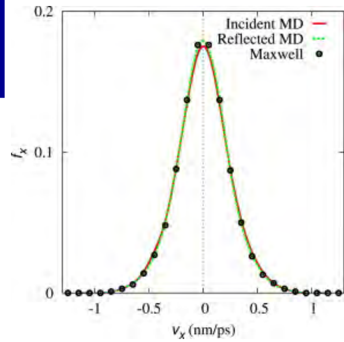
Free-streaming **Collisions** **Sources**

$$f_i(\vec{r}+\vec{c}_i,t+1)-f_i(\vec{r},t)=-\Omega_{ij}\left(f_j-f_j^{eq}\right)+S_i$$

$$f_i^{eq}=\rho w_i\{1+\beta\vec{u}\cdot\vec{c}_i+\frac{1}{2}[(\beta\vec{u}\cdot\vec{c}_i)^2-\beta u^2]\}+\ldots$$

$\beta=1/kT$

(EoS)



$$\{\rho,\rho\vec{u},\overleftrightarrow{P},\ldots\}=\sum_{i=0}^{b}\{1,\vec{c}_i,\vec{c}_i\vec{c}_i,\ldots\}f_i$$

Conservative (zero modes)
Mass-Mom-MomFlux

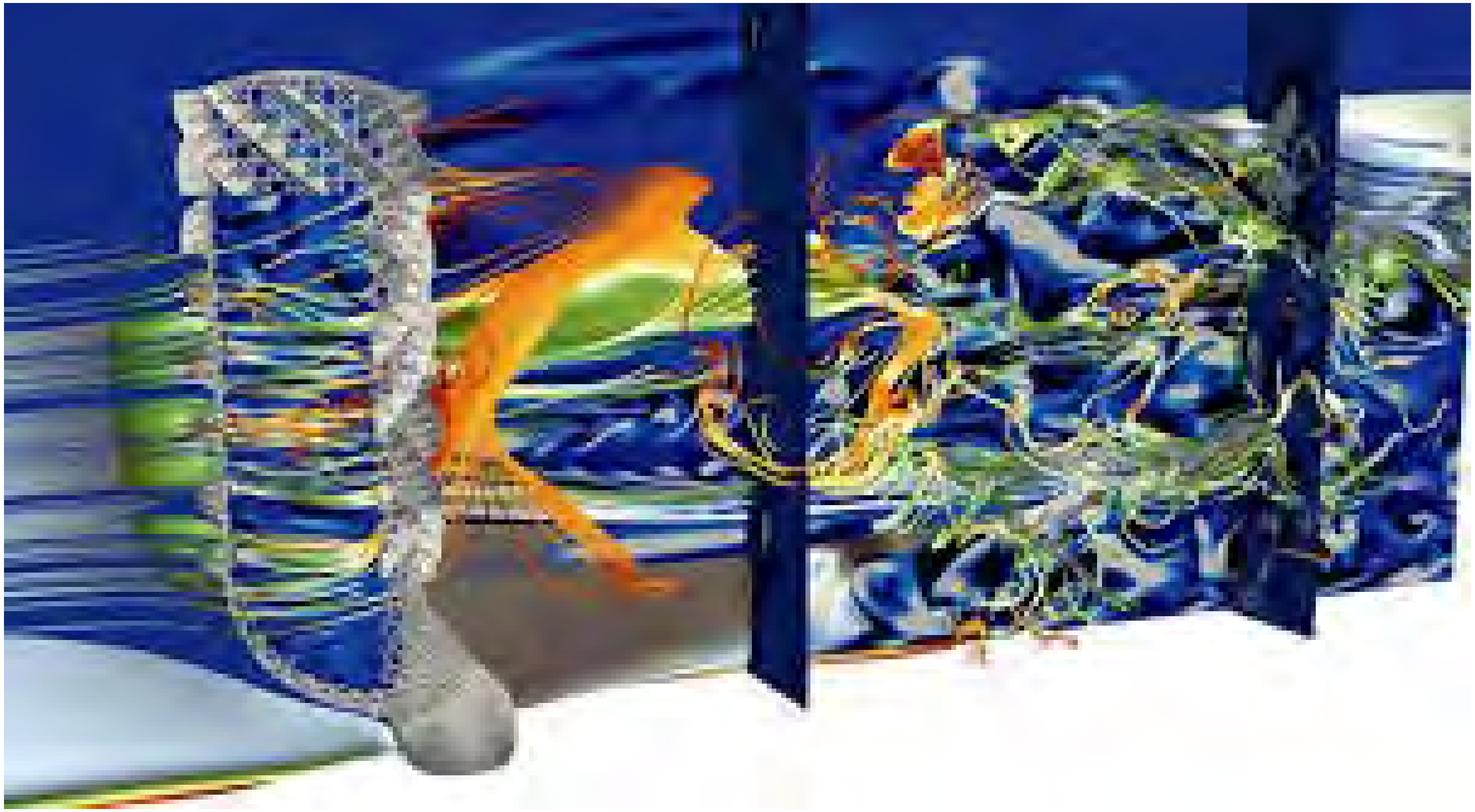
$$\Omega_{ij}=\Omega(\vec{c}_i\cdot\vec{c}_j)$$

Transport/Dissipation

S_i **External/Internal drives = Soft Collisions**

NOT LIMITED TO DILUTE GAS !

Petascale LB



50 Billions sites, 5Pflops on Marconi 100 (Top 9)

G. Falcucci, G. Amati, M. Porfiri, P. Fanelli, Polverino,
V. Krastev & SS, Nature, July 2021

Droplet-based microfluidics

Density Functional Kinetic Theory

1. *Free-Energy Functional:*

$$\mathcal{F}[\varrho] = \int [\varphi(\varrho) + \chi(\nabla\rho)^2] dx$$

2. *Non-ideal Pressor (Korteweg):*

$$K_{ab} = \frac{\delta^2\mathcal{F}}{\delta\nabla_a\rho\,\delta\nabla_b\rho}$$

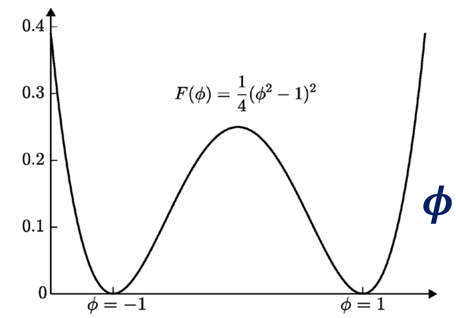
3. *Non-ideal capillary force:*

$$F_a = -\partial_b\, K_{ab}$$

4. *Streaming in velocity space = Soft Collisions:*

$$S = F_a \partial_{v_a} f$$

Cahn-Hilliard potential



$$\phi = \frac{\varrho_A - \varrho_B}{\varrho_A + \varrho_B}$$

Non Ideal EoS

Surface Tension

Disjoining pressure

The force is non-local (third order in space)

Rothman-Keller (1988) Shan-Chen (1993), Orlandini et al (1996),

Color Gradient LB+NCI: Montessori et al, JFM 2019

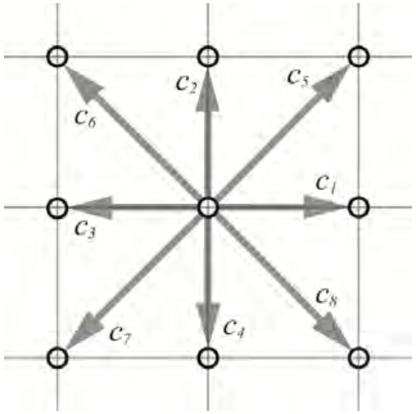
Lattice pseudo-potentials

Continuum Kinetic Theory

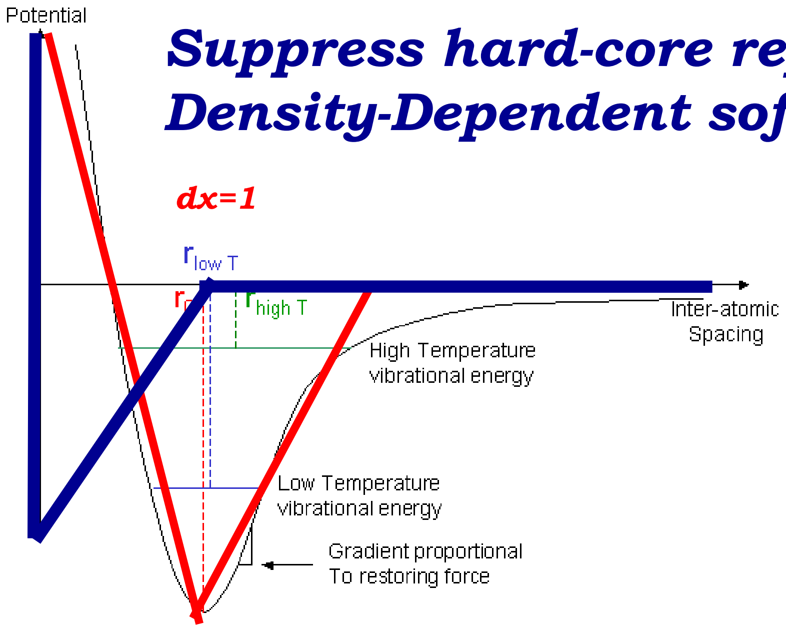
$$\frac{df}{dt} \equiv \frac{\partial f}{\partial t} + \vec{v} \bullet \frac{\partial f}{\partial \vec{r}} + \frac{\vec{F}(\vec{x},t)}{m} \bullet \frac{\partial f}{\partial \vec{v}}$$

Lattice Pseudo Force

$$-G\psi(\boldsymbol{x})\sum_i w_i \psi(\boldsymbol{x}+\boldsymbol{c_i})\boldsymbol{c_i},$$



Suppress hard-core repulsion
Density-Dependent soft-core attraction



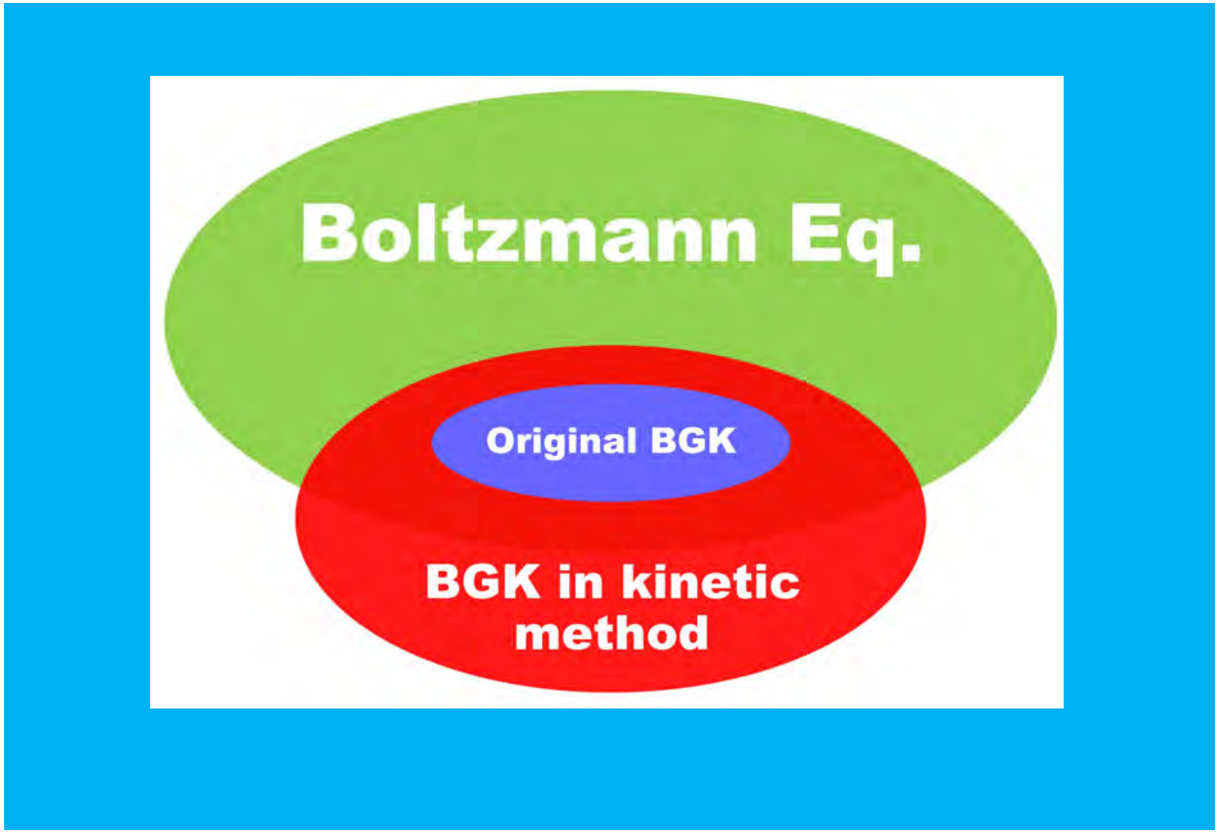
Handy, but high surftens: coalescence

Shan-Chen PRE 1993

SCUOLA NORMALE SUPERIORE

Density Functional Kinetic Theory

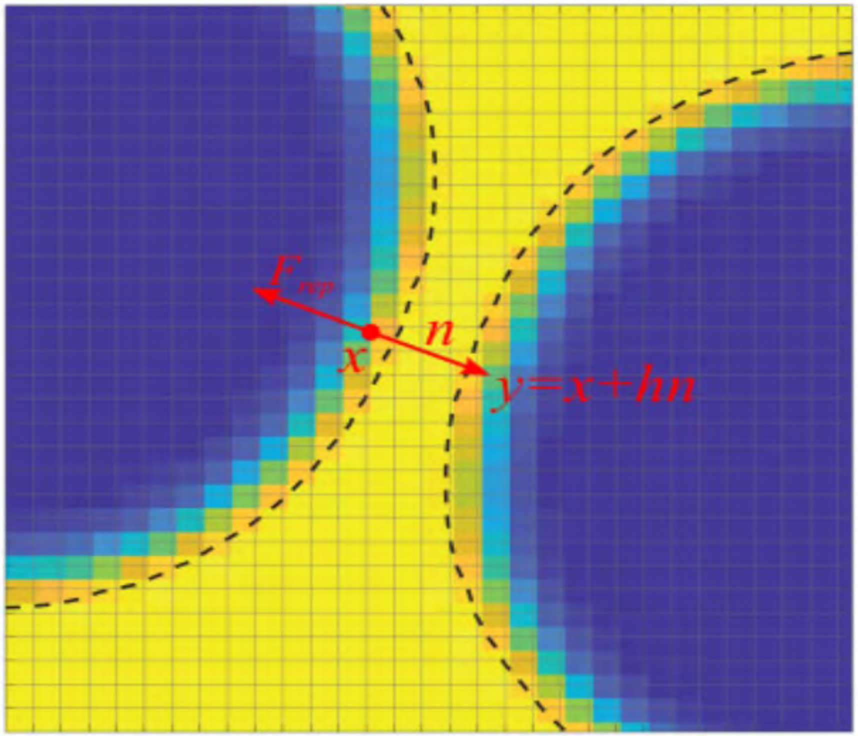
By using generalized equilibria and relaxation operators the BGK approximation delivers «analytic continuations» of Boltzmann's kinetic theory, and extend it to dense&confined non-equilibrium fluids without losing lattice realizability



Near-Contact Interactions

$$F_{nc} = A\, kT / h^4$$

$$N = A \left(\frac{kT}{\sigma h^2}\right) \left(\frac{D^2}{h^2}\right) \qquad A = \left(\frac{\epsilon}{kT}\right)$$



Soft potential << 1
D/h ~ 10^4

LB-NCI scheme

1. Move along the interface normal, up to 4 lattice units

2. If another interface is met, apply FNC.

3. Else: No action

Hand-shaking to Nano!

Montessori et al, JFM 2019

Sample App's

«Exotic» soft «materials»

Computer Experiments

- *Soft flowing crystals*
- *Dense confined emulsions*
- *Multicore emulsions*
- *Pickering emulsions, Bijels*
- *Soft Granular Media*
- *Silica Sponges*
- *Electrospun fibers*
- *Functional amyloids*

Stability of the SFC phase

$$N = A\left(\frac{kT}{\sigma h^2}\right)\left(\frac{D^2}{h^2}\right)$$

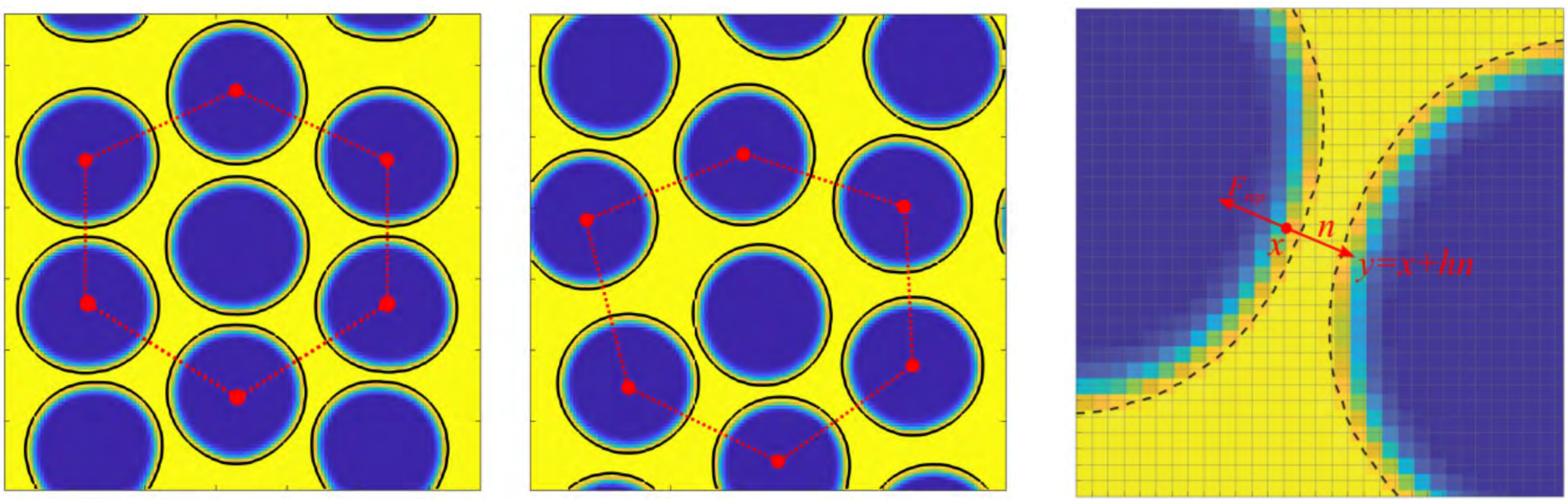
$N \to 0$ **Coalescence**

$N \sim 0.1$ **Soft flowing crystal**

$N > 1$ **Disordered emulsion**

- *Bi-disperse dense emulsion*
- *in a microfluidic channel*
- *under an external constant*
- *body force.*

- *Substantial near-contact*
- *interactions perturb the hexagonal crystal-like configuration.*

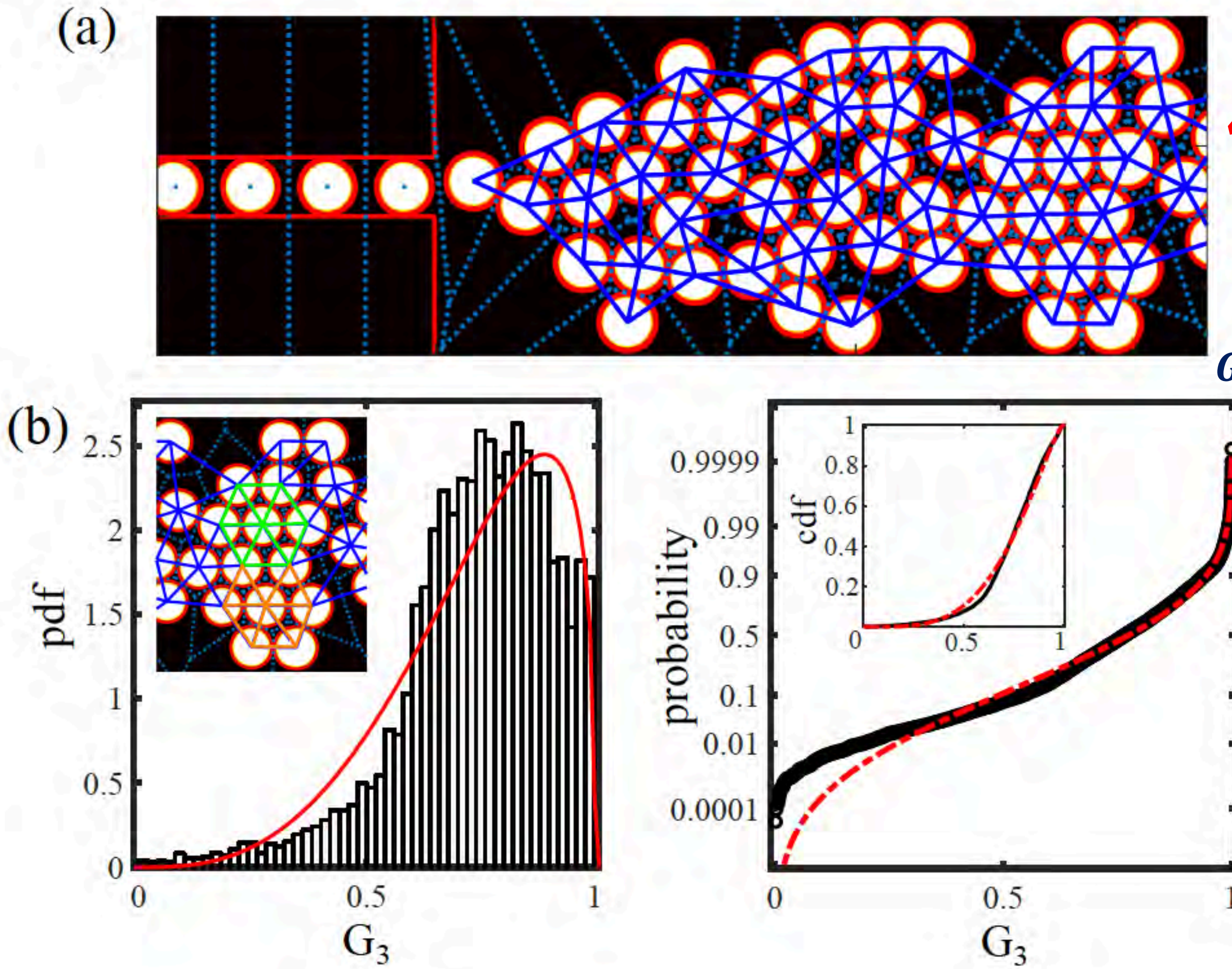


Soft Flowing Crystal

Montessori et al, JFM 2019

Dense emulsions

Functional gradient materials, Select connectivity by tuning the flow rate and the aperture angle



«Melting» the 1d SFC

$$G_3(n) = \frac{1}{n}\sum_{j=1}^{n} cos(3\theta_j)$$

Orientational Order Parameters (SF Quasi-Crystals)

Dense Confined Emulsions

Slow: new type of collective order (soft spacetime crystals)

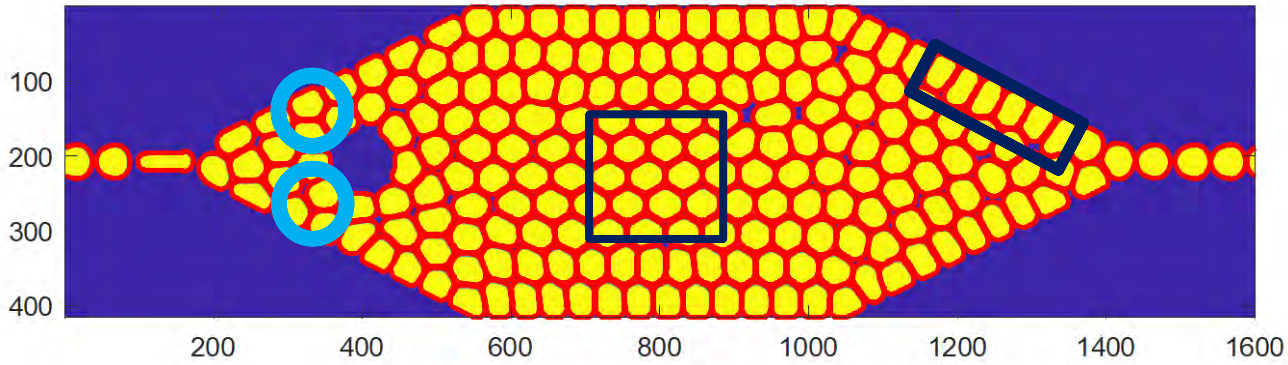
Fast: «solid» to «liquid» transition:
2d bulk slow SFC ,1d peripheral SFC «fast lane»

Long range dissipative effects
Plastic rearrangements (defects) propagate like
non-linear waves across the elastic granular «solid»

Fluidity is a non-local field, frictionless dissipation!

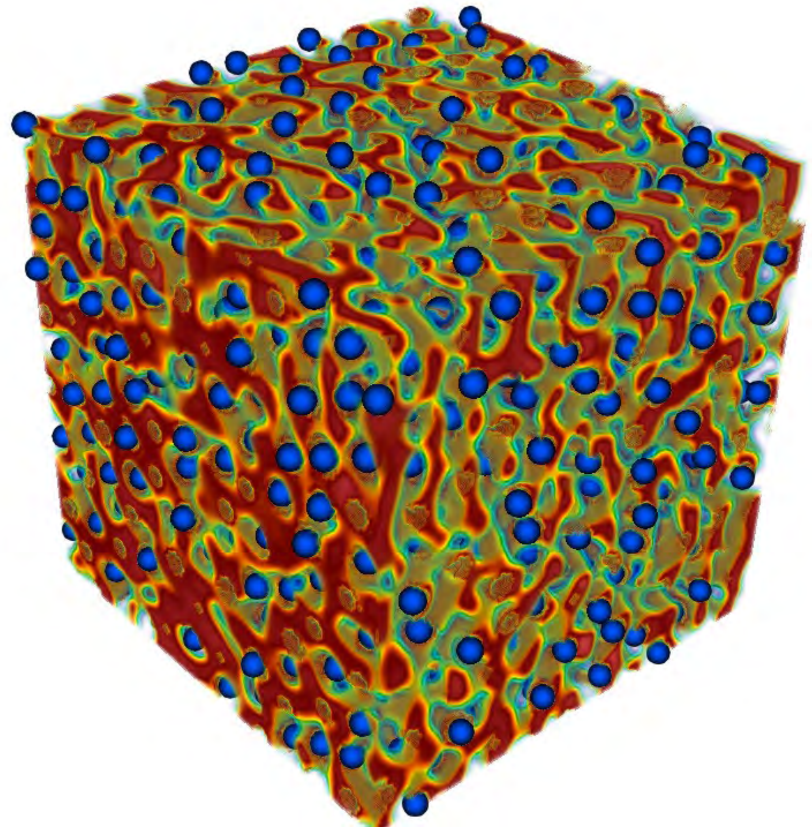
«Altruistic droplets»: stuck to facilitate other droplets motion

$$f = \dot{\gamma}/\sigma$$ ***(L. Bocquet et al)***



(Y. Gai, A.Montessori, S. Succi, S. Tang, PoF 2022)

Colloidal Bijels



Two fluids with dispersed colloids

Colloids slow down and arrest the coarsening

New porous materials with tunable mechanical and rheological properties

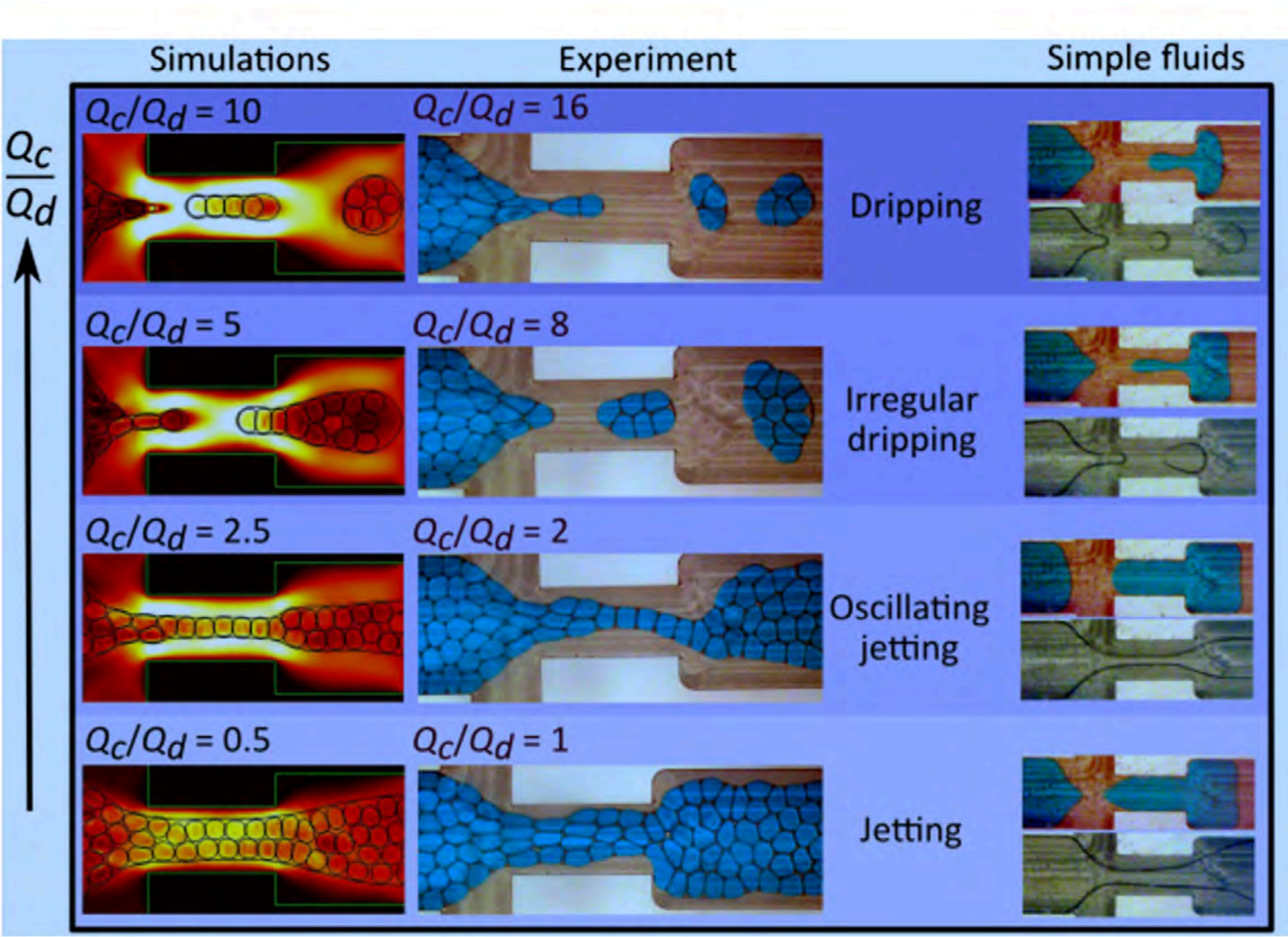
First found in-silico (Stratford et al, Science 2005)

LBCUDA: >100 GLUPS: 200 updates/s 1 billion sites

Cell screen-covers, food processing, oil recovery…--------→ Smart Materials?

F. Bonaccorso and COPMAT team, CPC, 2022

Soft granular materials

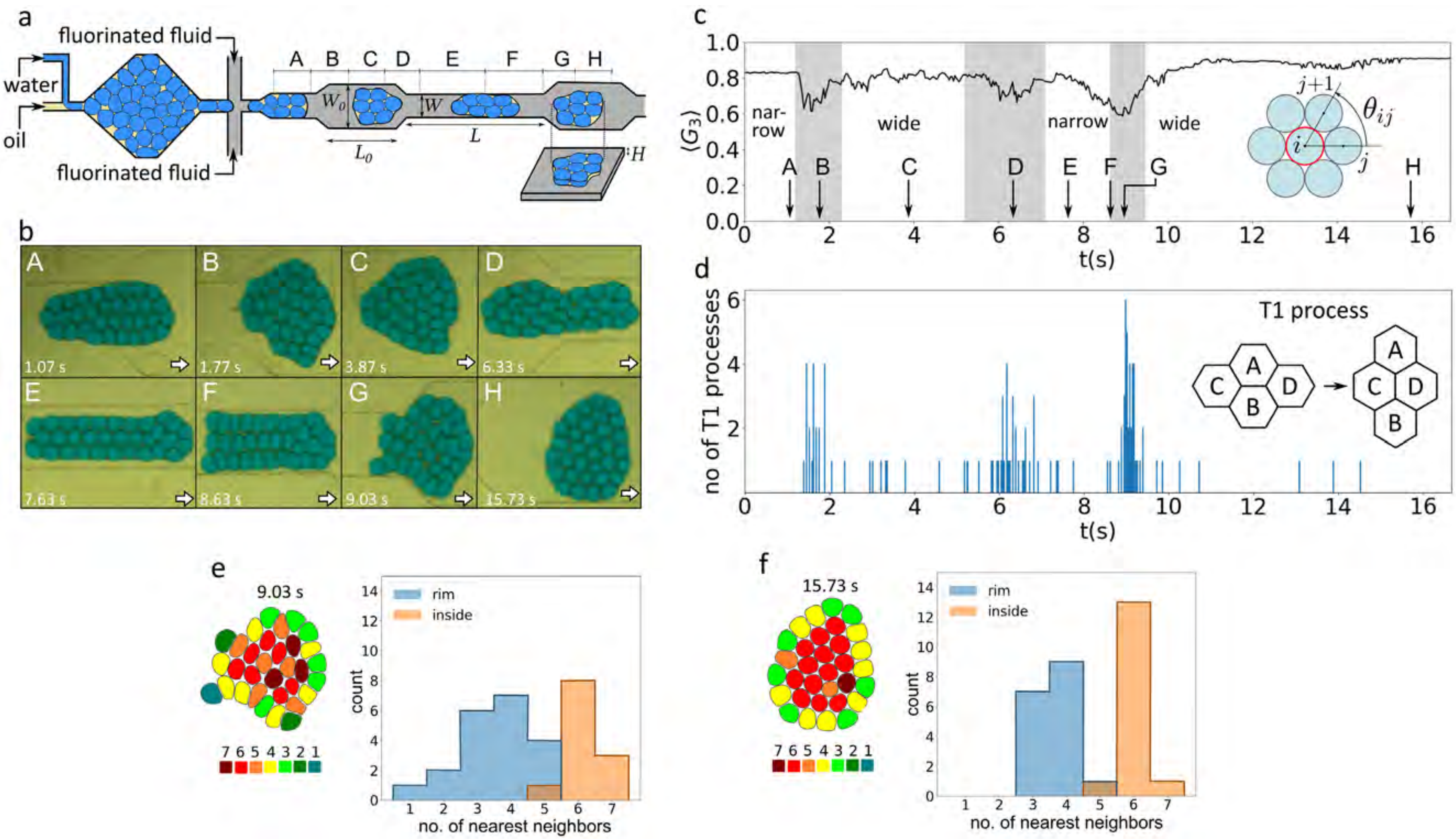


Interplay of Individual and Collective dynamics

(M. Bogdan, J. Guzowski and COPMAT, PRL 2022)

Cluster dynamics in microchannels

Topological microfluidics

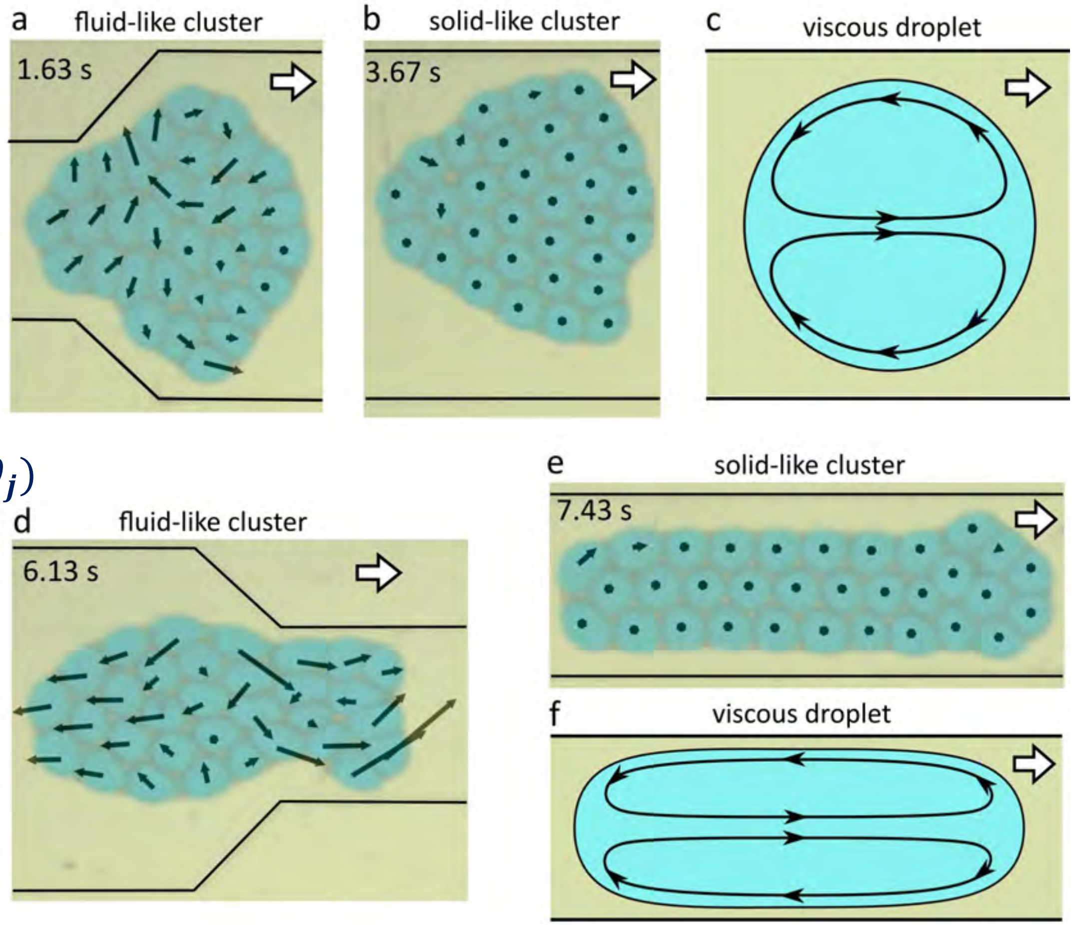


M. Bogdan, J. Guzowski, M. Durve, Leon, SS, 2023

«Solidification/Melting»

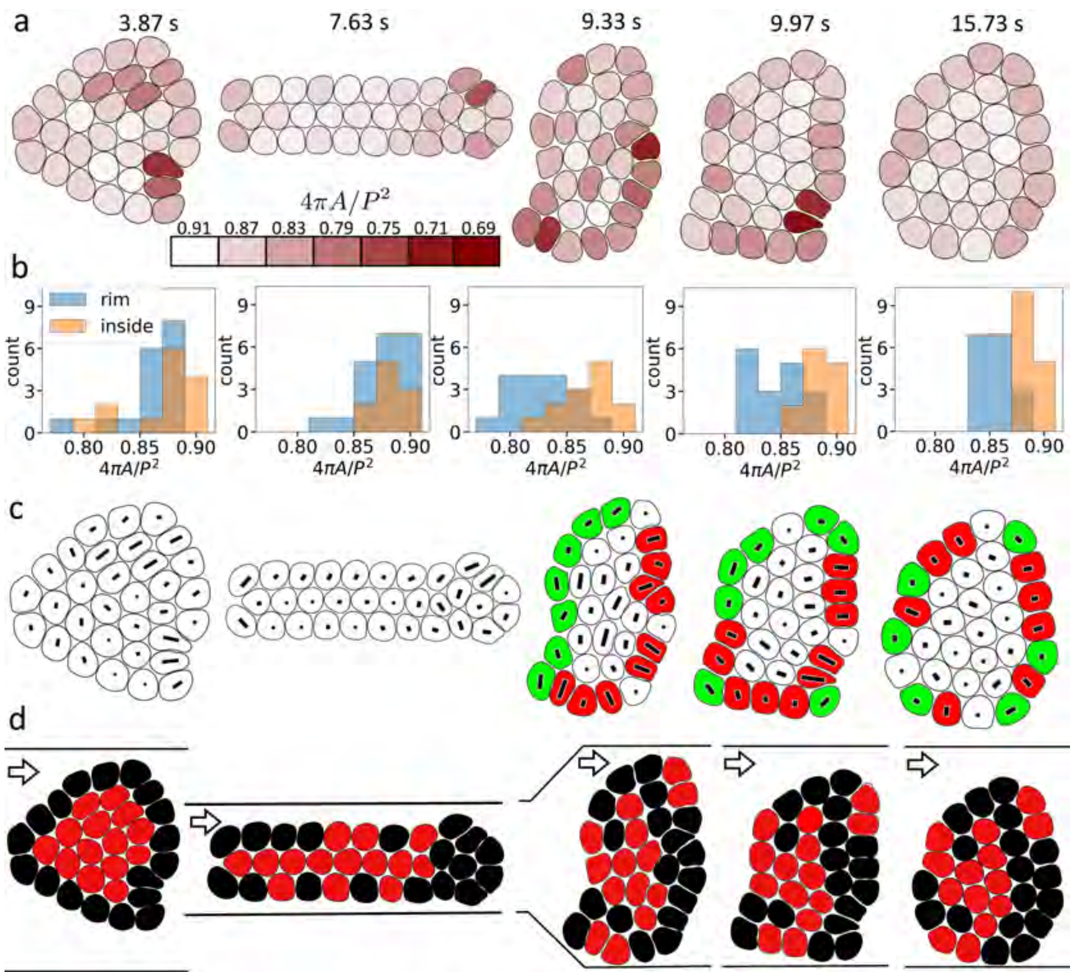
Quasi-crystal Order Parameter

$$G_3(n,R) = \frac{1}{n}\sum_{j=1}^{n} R_j cos(3\theta_j)$$



M. Bogdan, J. Guzowski, M. Durve, Leon, SS, 2023

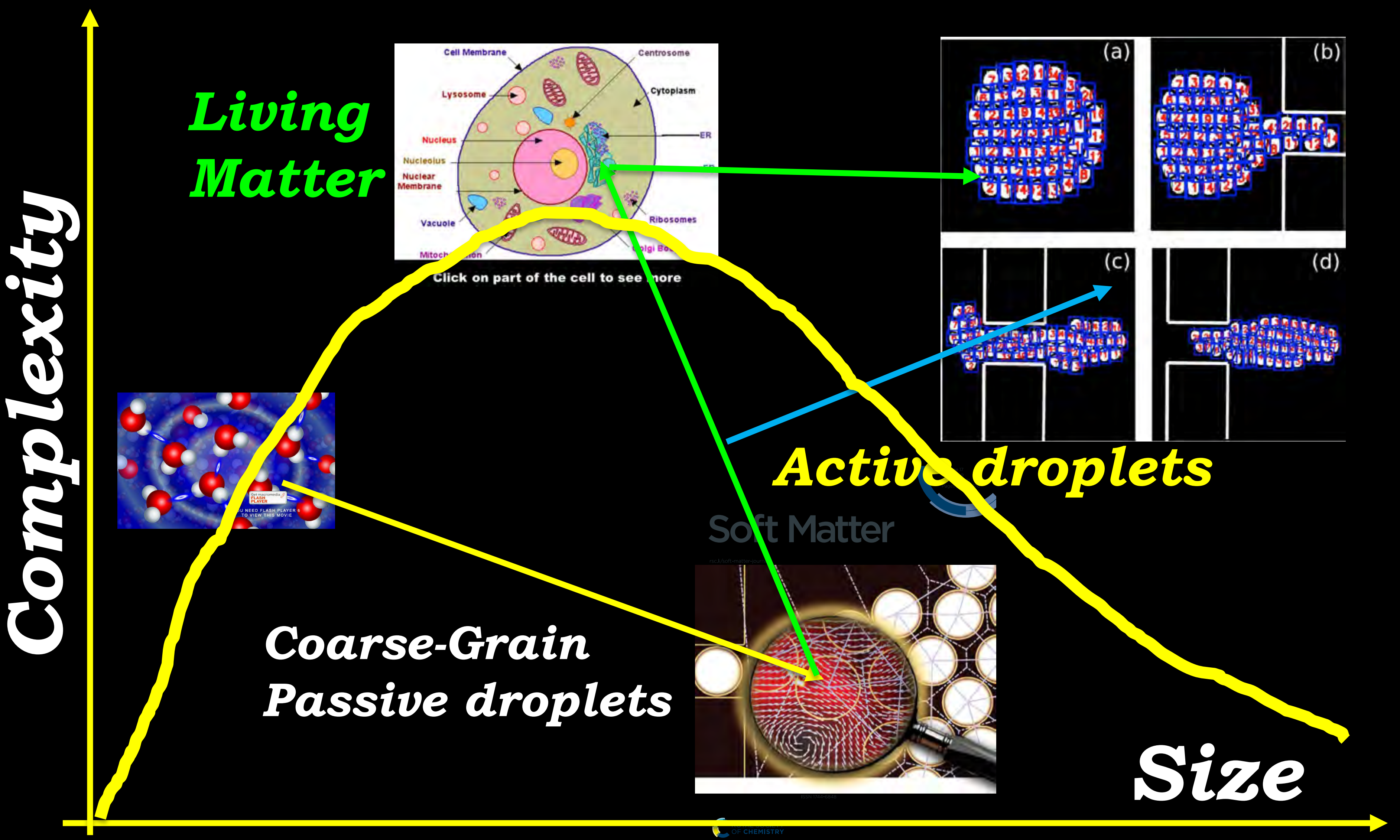
Topologically induced dynamic heterogeneities



M. Bogdan, J. Guzowski, M. Durve, Leon, SS, 2023

Active Matter

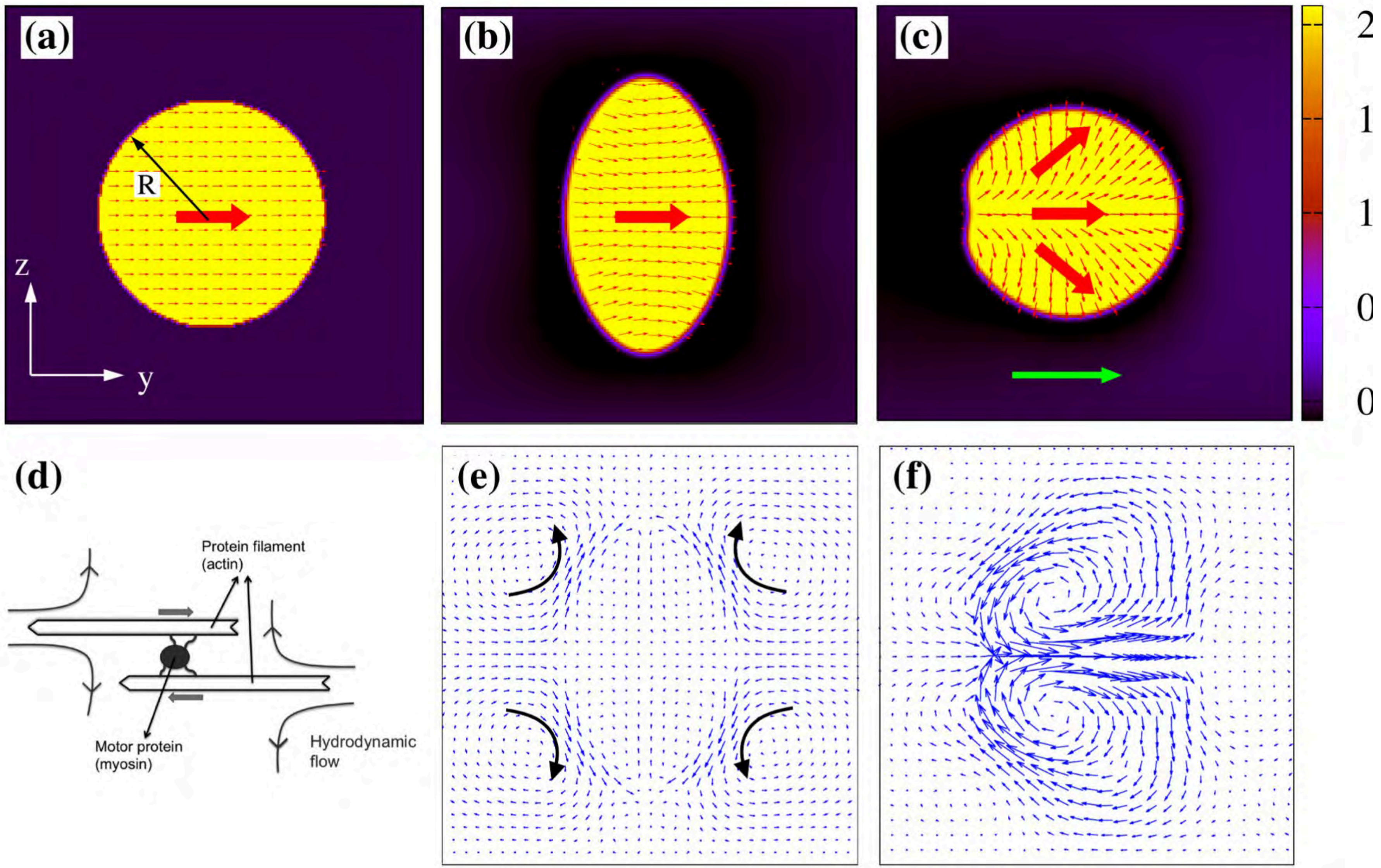
From drops to cells: micro-physiology



Inject specificity: synergy with biologists

Active Droplets

Parity breaking term: $\sigma_{ab} = -\zeta\varphi\, P_a P_b$



(Tjhung, Marenduzzo, Cates, PNAS 2012)

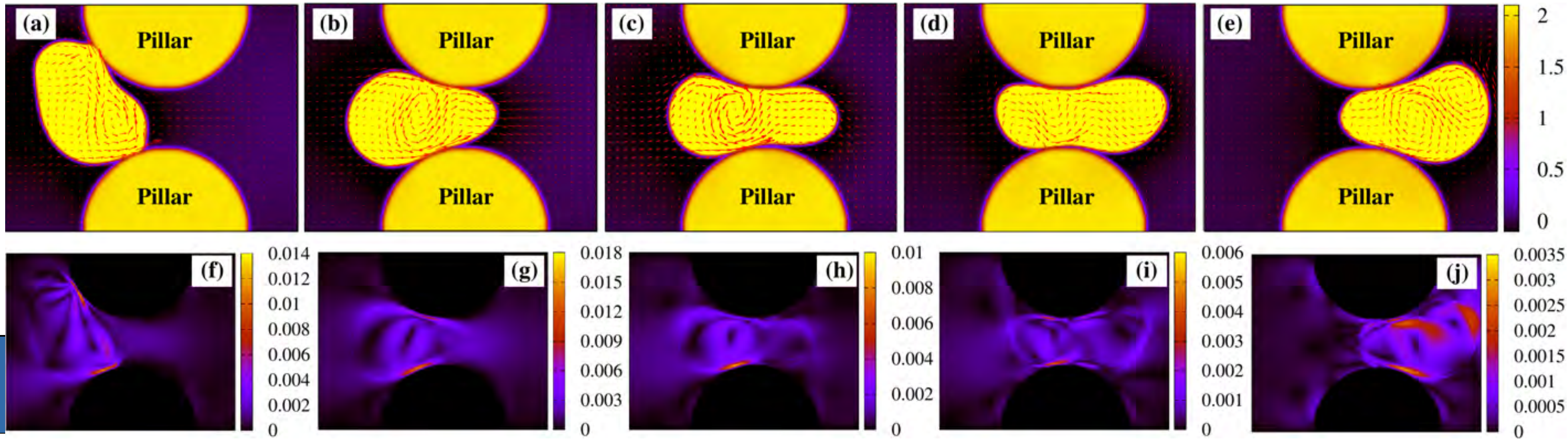
The role of adhesion

The camel thru the needle-eye:
D>h transmigration: Mission Impossible for rigid spheres!

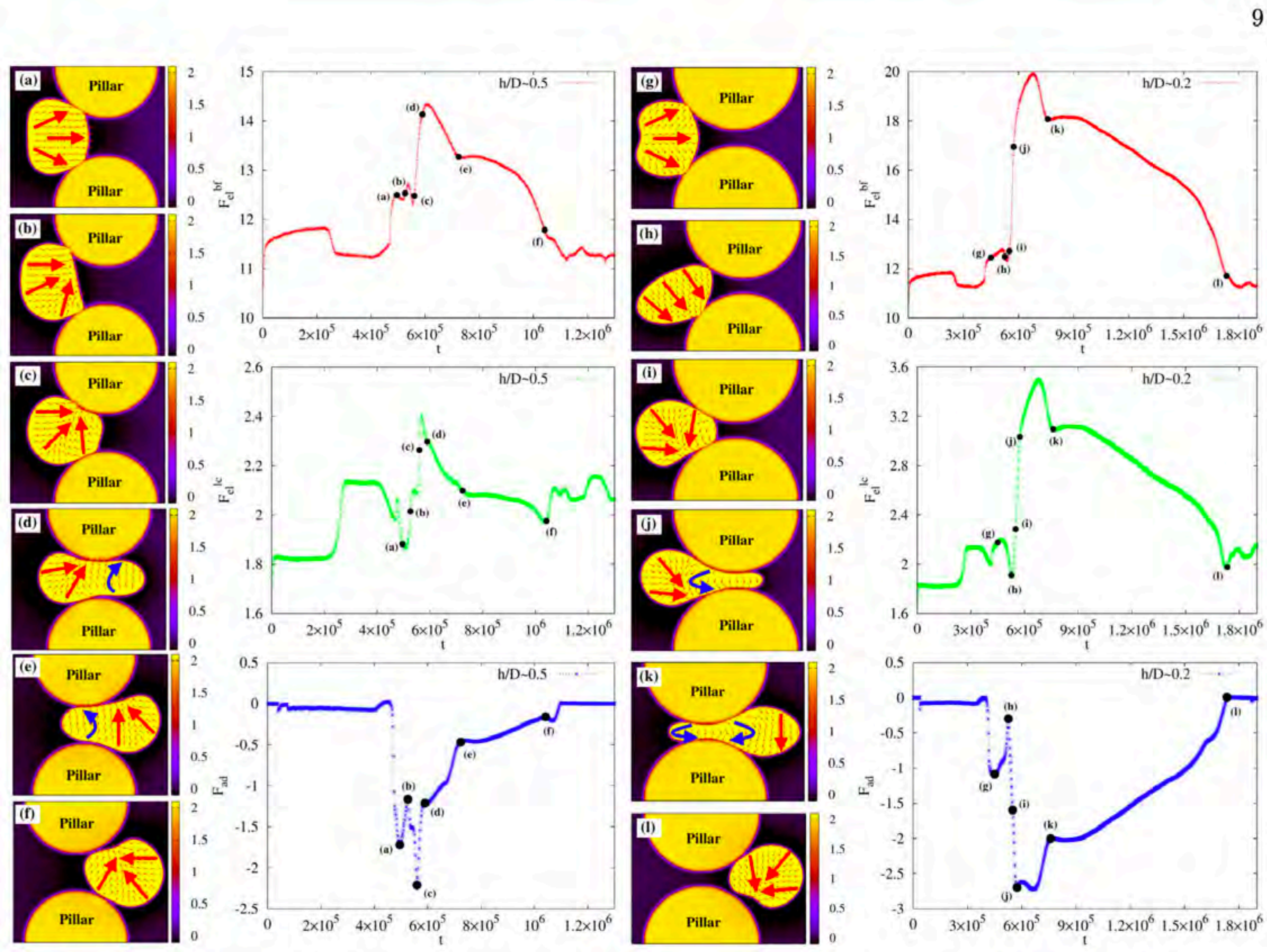
Rigid body:
h/D<1: clogging
h/D>1: unidirectional motion

$$\mathcal{F}[\boldsymbol{\varphi}] = \int [\boldsymbol{f}(\boldsymbol{\varphi}) + \cdots \boldsymbol{\chi}\boldsymbol{\partial}_{\boldsymbol{a}}(\boldsymbol{\varphi})\boldsymbol{\partial}_{\boldsymbol{b}}(\boldsymbol{\varphi}) + \cdots .]\boldsymbol{dr}$$

Unsymmetric adhesion is key

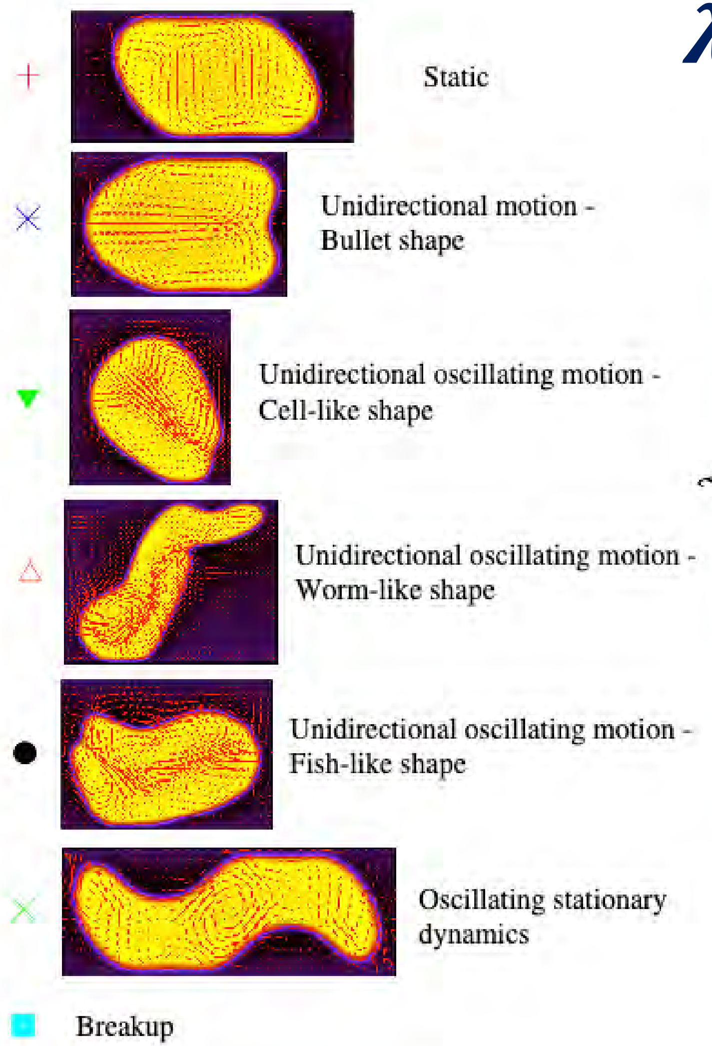


Translocation Energetics

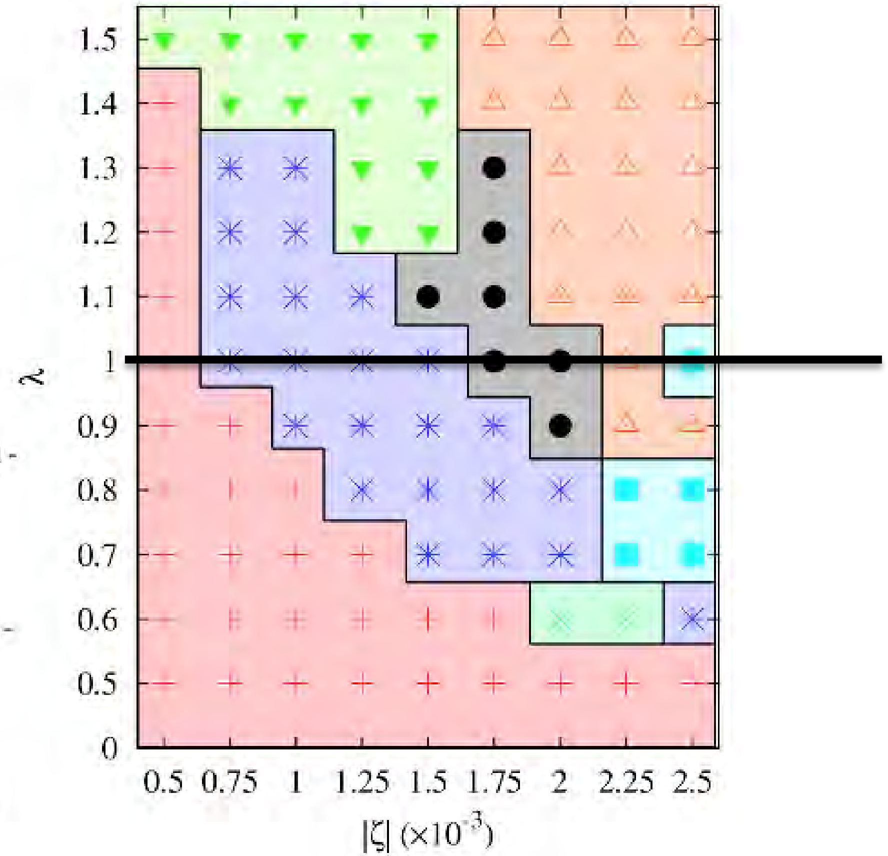


Tiribocchi and COPMAT team, Nature Comm., 2023

Motility Phase Diagram



$\lambda = h/D$



Each morphology has its own rheology: multi-rheological behaviour

Soft Active Layers

Polarization waves in the active layer drive the passive particle[10]

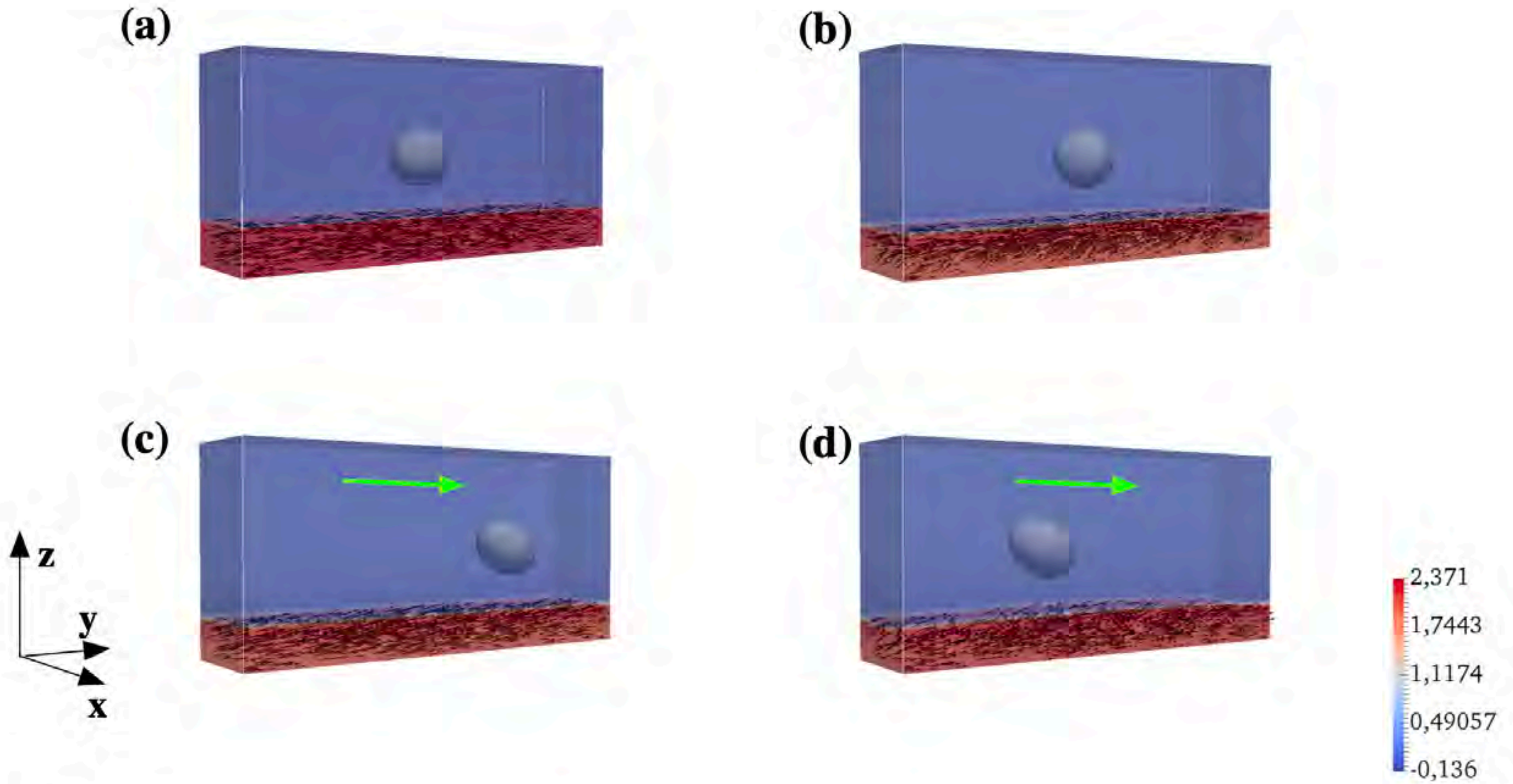


Figure 10. Three dimensional simulation of a passive fluid droplet moving within an active microchannel for $\zeta = 4 \times 10^{-3}$. (a) The droplet is initially surrounded by a passive fluid (blue) in the middle of the channel and a liquid crystal layer (red) covers the bottom wall. (b) Once the activity is turned on, a spontaneous flow triggers the motion of the passive droplet. (c)-(d) At the steady state, the droplet acquires a permanent ellipsoidal shape moving along a rectilinear trajectory.

Meso coupling to QN

«The emerging interface between hydrodynamics, electro- dynamics, condensed matter physics, and quantum mechanics is an uncharted territory that begs for further exploration».

(Coquinot,Bocquet,Kavokine, PRX 2023)

How can we contribute?

Quantum Friction

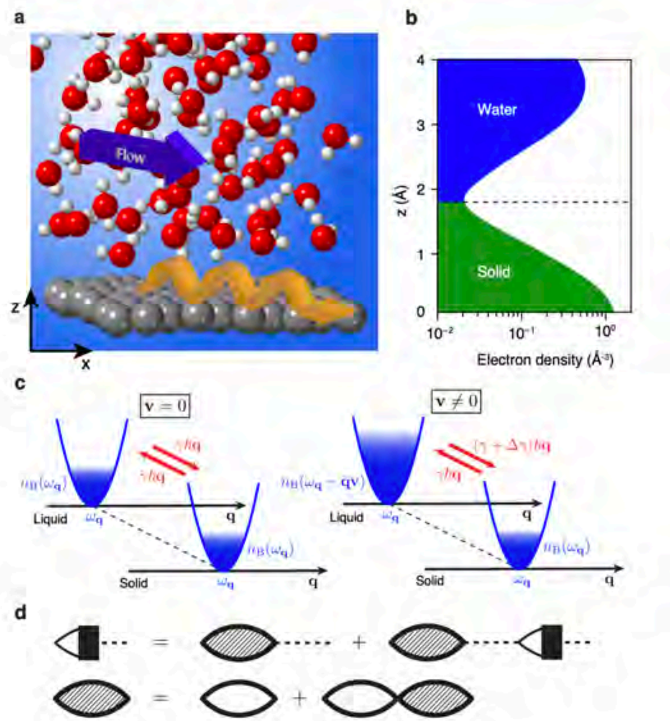
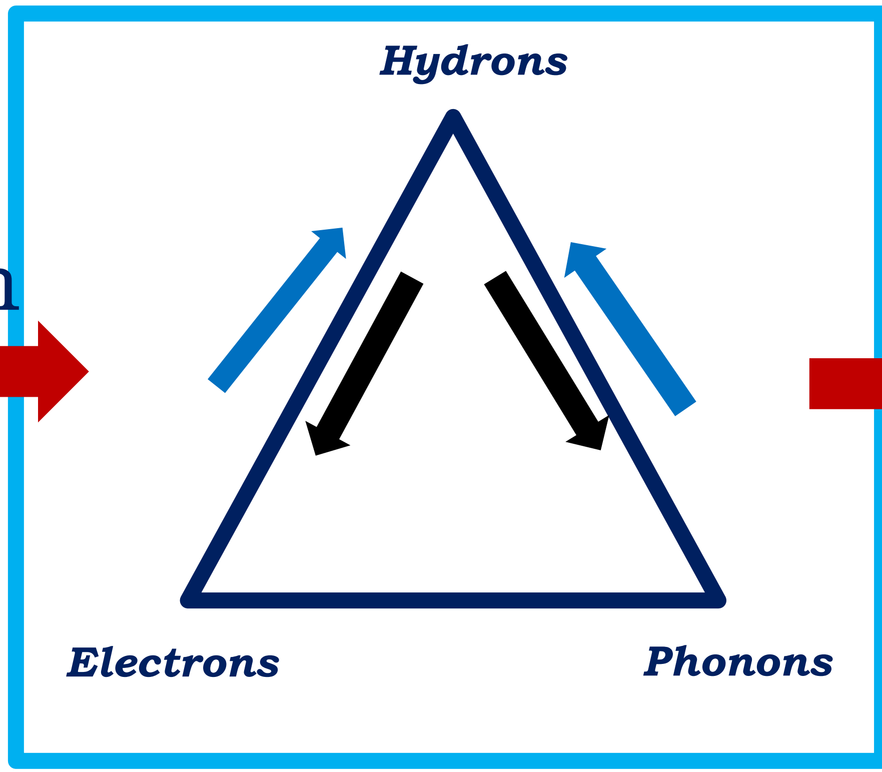


FIG. 1. **Quantum friction at the solid-liquid interface.** **a.** Artist's view of the quantum friction phenomenon: water charge fluctuations couple to electronic excitations within the solid surface, represented by the orange arrow. **b.** Average electronic density, as obtained from density functional calculations (SI, section 7), at the water-graphene interface. **c.** Schematic of the quantum friction mechanism, showing quasiparticle tunnelling between two surface modes at wavevector $\mathbf{q}$ and frequency $\omega_{\mathbf{q}}$. The filling of the blue parabolas represents the occupation of each mode, according to the Bose-Einstein distribution n_{B}. The back and forth tunnelling rates γ are different in the presence of flow, resulting in net momentum transfer from the liquid to the solid. Further details are given in the SI, section 2.8. **d.** Feynman diagram representation of the Dyson equation for the electron-water density correlation function. Full lines are electron propagators, and dashed lines are water propagators. The equation expresses that electron-water correlations are mediated by all possible coupled fluctuations of the water and electron densities.

The HEP fluid and qfriction

Keldysh HEP box

Quantum
Many
Body



$$\vec{F} = -\gamma q(y)\rho\vec{v}$$

Momentum may flow from Solid to Liquid: Negative Friction!

Meso-forces

$$f_i\left(\vec{r}+\vec{c}_i,t+1\right)-f_i\left(\vec{r},t\right)=-\Omega_{ij}\left(f_j-f_j^{eq}\right)+S_i$$

$$S_i \sim \vec{F}\cdot\vec{c_i} \;\; + h.o.t.$$

The «magic touch»
EMERGENT COMPLEXITY
in O(10) lines of code

$$\vec{F} = \rho\vec{g}$$

$$\vec{F} = -\mathrm{div}\,\overleftrightarrow{P}(\rho,\nabla\rho,\Delta\rho)$$

Korteweg tensor
(surftens, disjoining pressure)

$$\vec{F} = -\gamma(y)\rho\vec{v}$$

«Molecular» friction»

The mesoforces import micro(nano) physics and scale it up to the device dimensions (cm), including heterogeneities. Success heavily hinges on EXTENDED UNIVERSALITY

Graphene-Oxide Layers

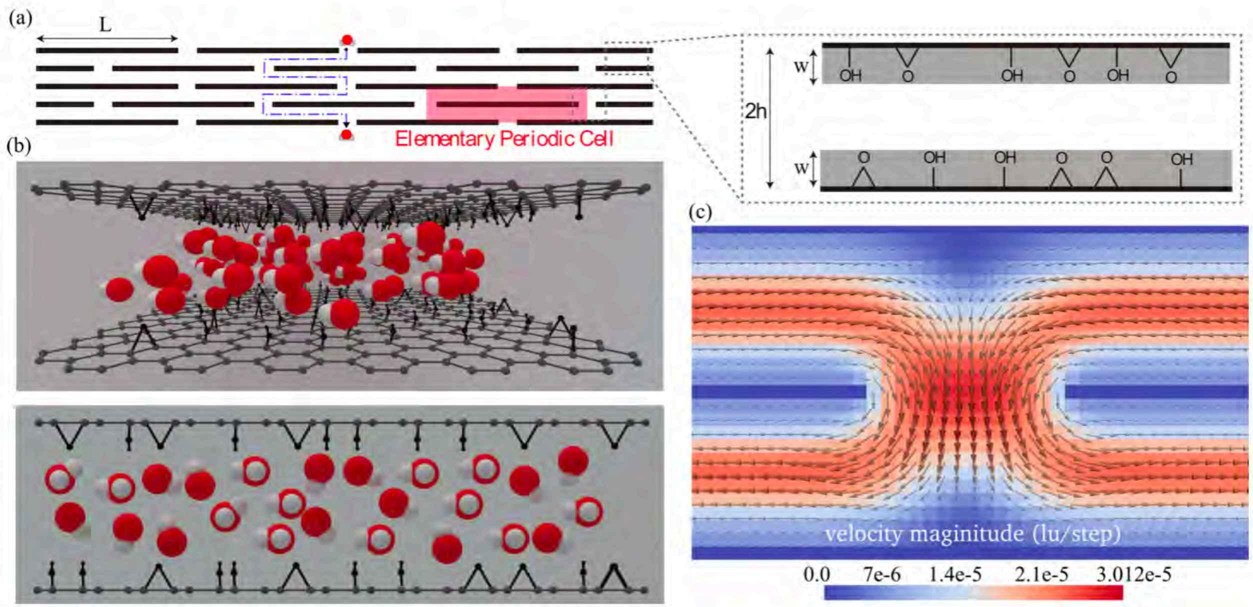


FIG. 1. Sketch of the GOL structure with a zoom of the GO nanochannel decorated with oxygen functionalities (panel (a)). In the sketch, L is the GO flake's length, $2h$ is the spacing between two GO layers and w is the spatial extent of the Langevin-like frictional force. The red area in the GOL structure identifies the elementary periodic cell used in the simulation. As shown in panel (b), hydroxide abd epoxide groups interact with the water molecules slowing down their motion inside the GO nanochannels. In panel (c), the water molecules flow from the inlet port (top) to the outlet port (bottom), under the effect of applied pressure. The vertical motion is hindered by a series of horizontal staggered plates (GO flakes), which force the water molecules to follow a tortuous path from inlet to outlet ports.

(Montessori, Amadei, SS, Vecitis, EPL 2016)

LB versus NEMD

Exponential decay gamma(y) out of the wall (y=0) may generate inverted curvature

$$u''(y) + \gamma(y)u(y) = g$$

Space-dep friction acts as a sort of potential

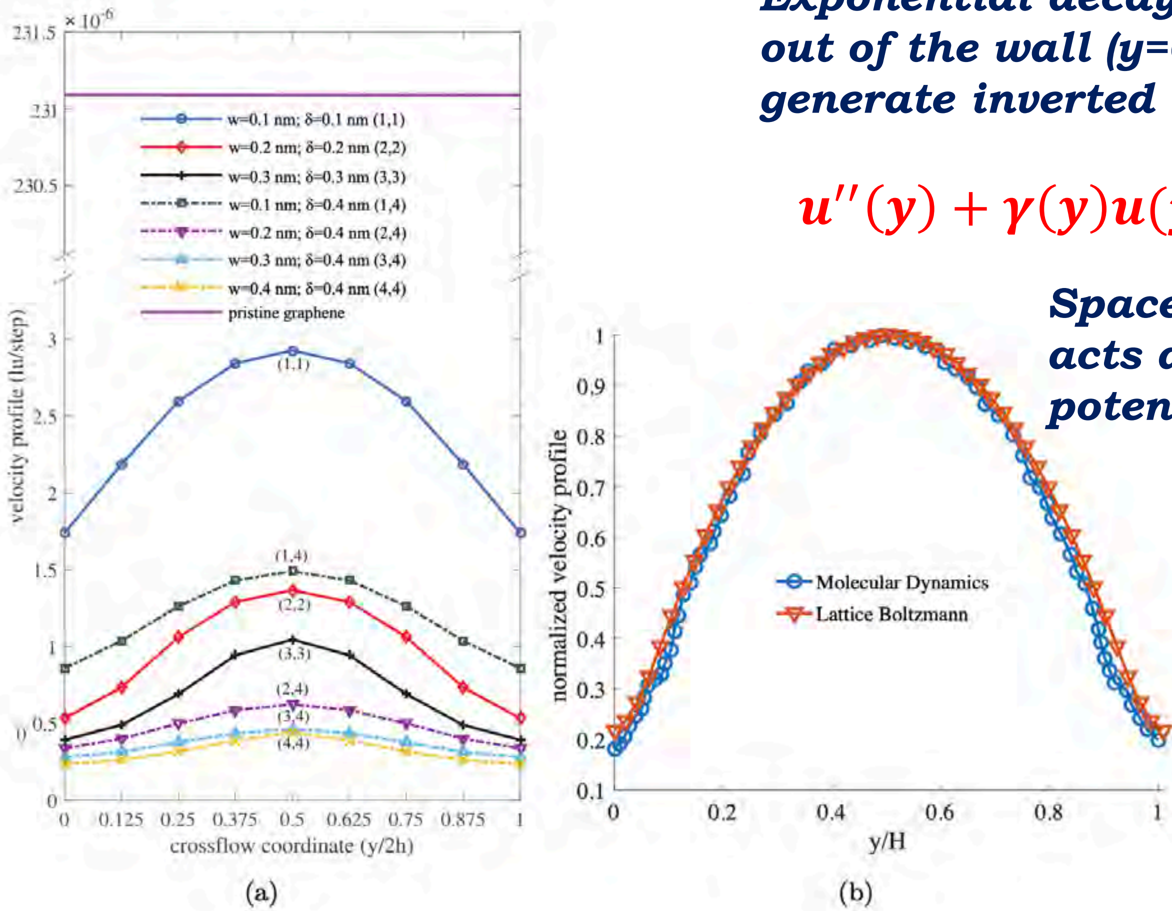
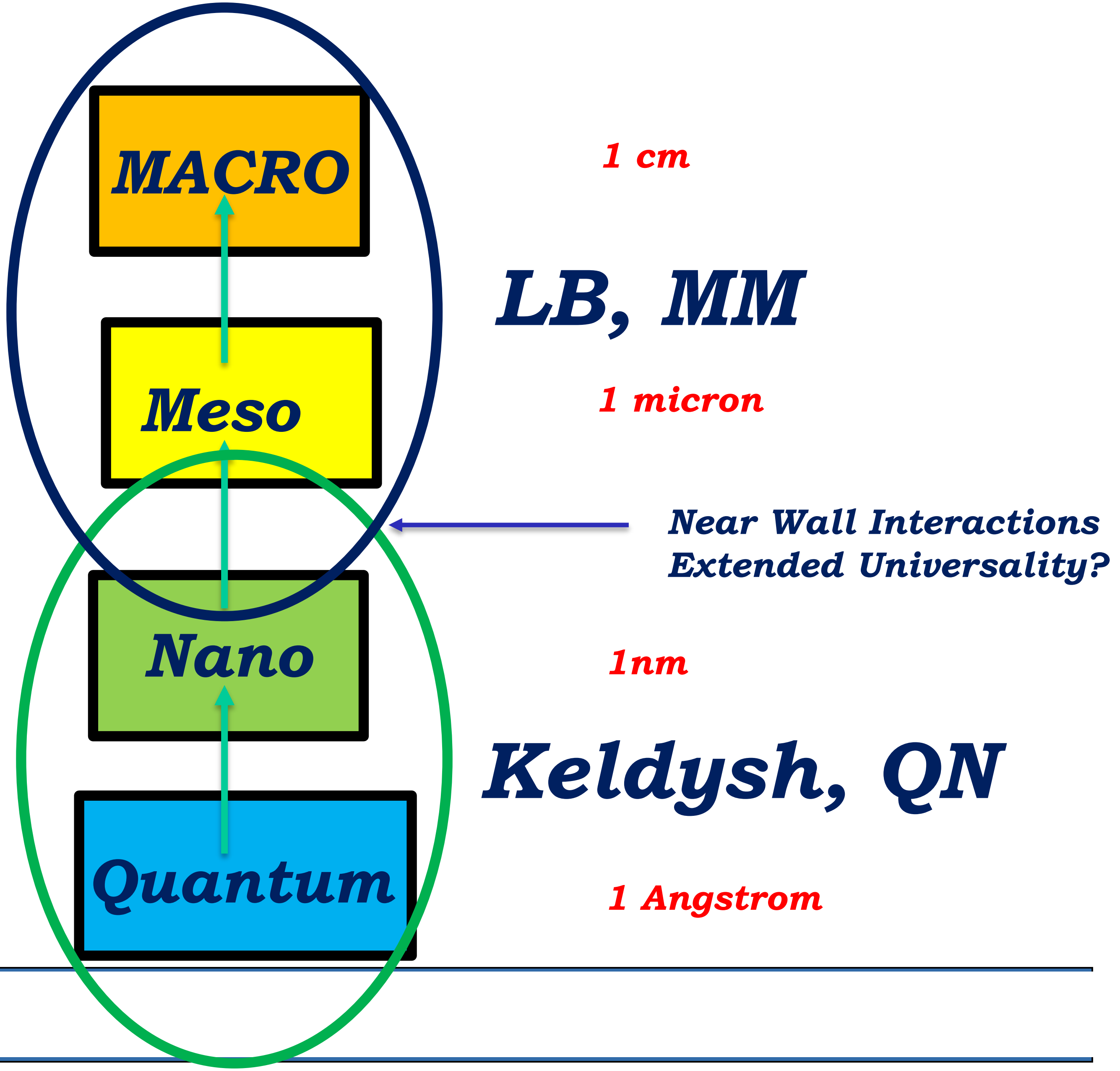


FIG. 4. (a) Flow profiles $u_x(y)$ for different values of the friction length w and cutoff length δ, (w, δ). The horizontal line refers to the free-slip flow in the absence of Langevin friction. The two numbers within parenthesis denote the values of w and δ. Friction and cutoff lengths are made dimensionless by dividing them by half of the channel spacing $h = 0.4\ nm$. In panel (b) we report the velocity profile obtained by the Langevin-LB on a 3 nm wide channel flow using 50 lattice point compared to the MD profile taken from [13].On the x-axis the non-dimensional channel width (y/2h) is reported. The profiles are rescaled by the peak value of the velocity.

QN/MM coupling



Future Directions

New LBs for soft flowing matter

Link to experiments for new materials

Nano-Meso-Macro Multiscale

Topological microfluidics

Cluster materials, microphysiology

From passive to active droplets

Meso/Macro effects of QN fluidics

Incorporate the quantum effects into effective boundary friction/forces. Rheological effects of heterogeneity, obstacles, coatings…

THANKS!

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