Hibrid kinetic schemes for modeling complex fluids

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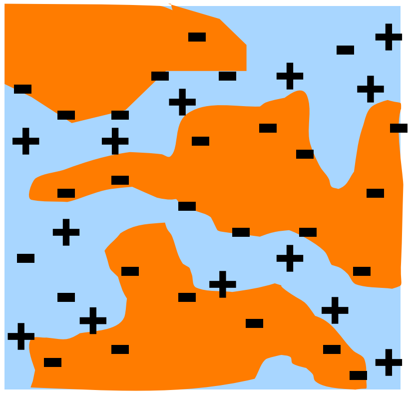
1. Introduction

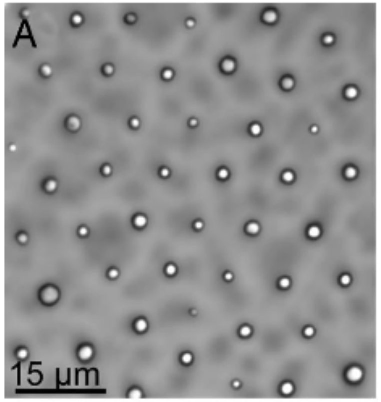
Complex fluids: Interfaces, fluctuations, instabilities

Porous media



Rocks, membranes

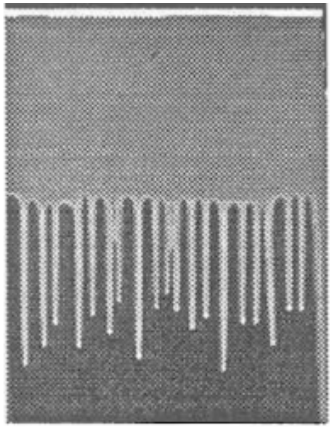
Colloidal systems



Surfactant free w/o emulsions

Leunissen et al., PNAS, 104, 2585 (2007)

Capillary flows



Dynamic wetting instabilities

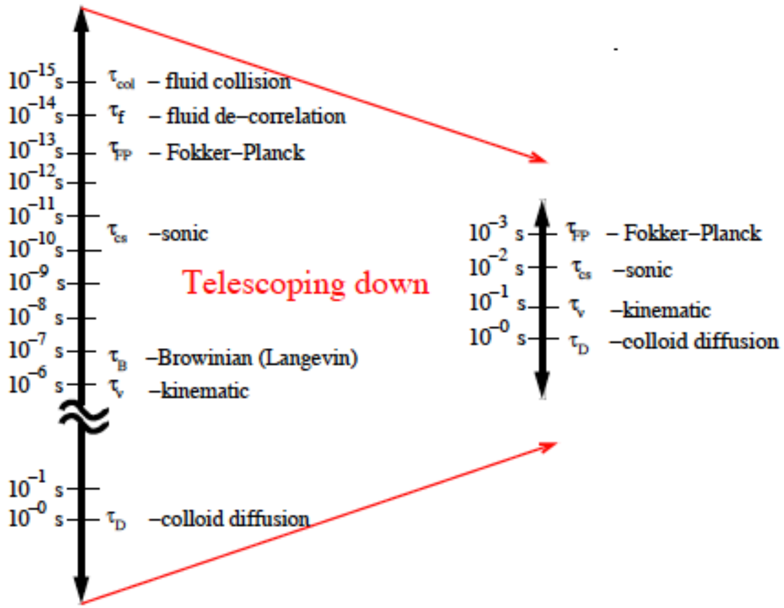
Fluid charged over Debye screening length

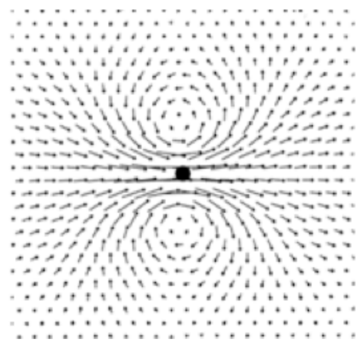
k^{-1} ~ 1-10 nm in water

Fluid/solid interactions for generic fluids

➡ Coupling between ionic and solvent flows

1. Introduction



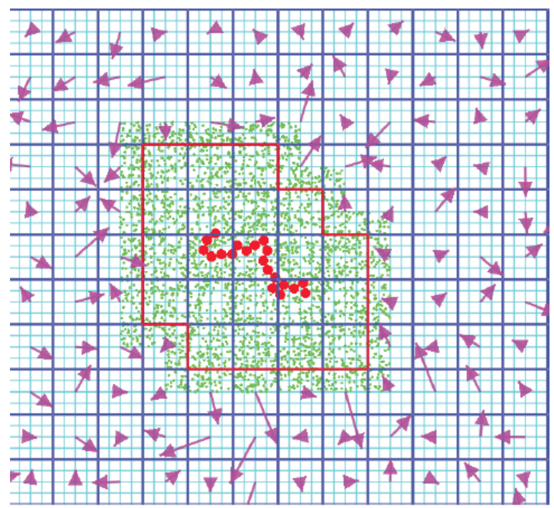


Kinetic theory
    Systematic approach

    Identify conserved variables

Particle based methods
Kinetic approaches
Fluctuating hydrodynamics +
    embedded particles

Hybrid approaches
    systematic?



1. Introduction

Why coarse-grained?

MODEL

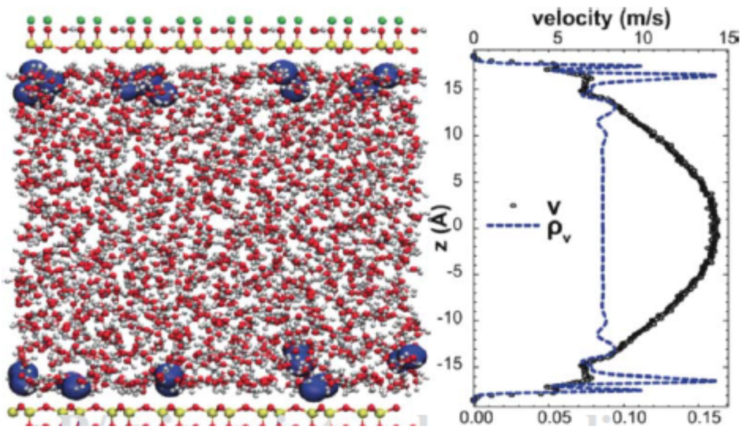
- No molecular structure : Local fields (densities, fluxes, …)
- Evolution : Principle

  Composition = (simple) DDFT
  Hydrodynamic description of the solvent

- Evolution : Numerics

  Lattice-based algorithms

  Strict charge conservation



LIMITATIONS

- No correlations

1. Introduction

Simulating coupled solvent and ionic dynamics

Goals

Describe correctly

- ➡ Advection, diffusion and migration of ions
- ➡ Oil / Water interface, solvation of ions
- ➡ Forces acting on the fluid
- ➡ Boundary conditions

Compute observables

- ➡ Collective properties : $\rho(r)$, $\rho_{\pm}(r)$, $v(r)$, κ, σ, …
- ➡ Individual trajectories ? $D(t)$, D_e

Tools

Lattice Boltzmann, Link flux and Moment Propagation

2. Kinetic models

Models motivated from kinetic theory:

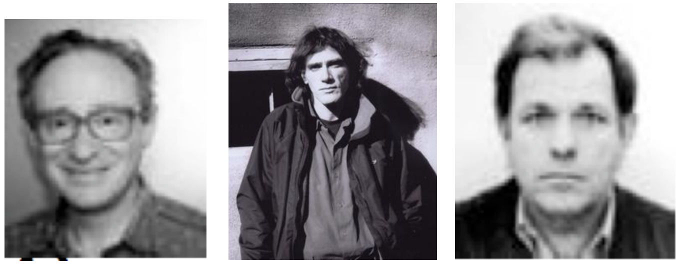
Statistical description of exact dynamical evolution of a system
Long tradition back to Boltzmann: solid starting point
Fokker-Planck / diffusion equations as a limit

Why is such an approach useful for complex fluids?

-systematic procedure to integrate out degrees of freedom in an operational/systematic way
-underlying solid theoretical treatments

2. Lattice Gases

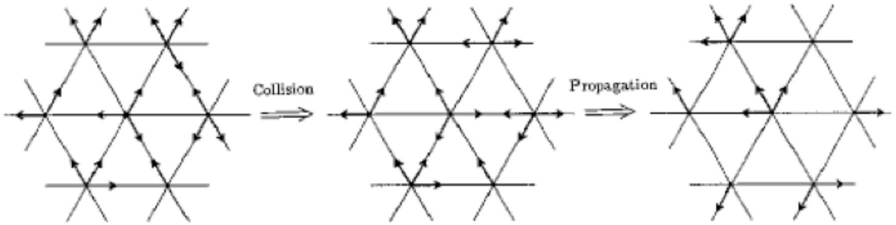
1986: Lattice Gas Cellular Automaton
(LGCA)



Frisch/Hasslacher/Pomeau

Individual particles in lattice nodes

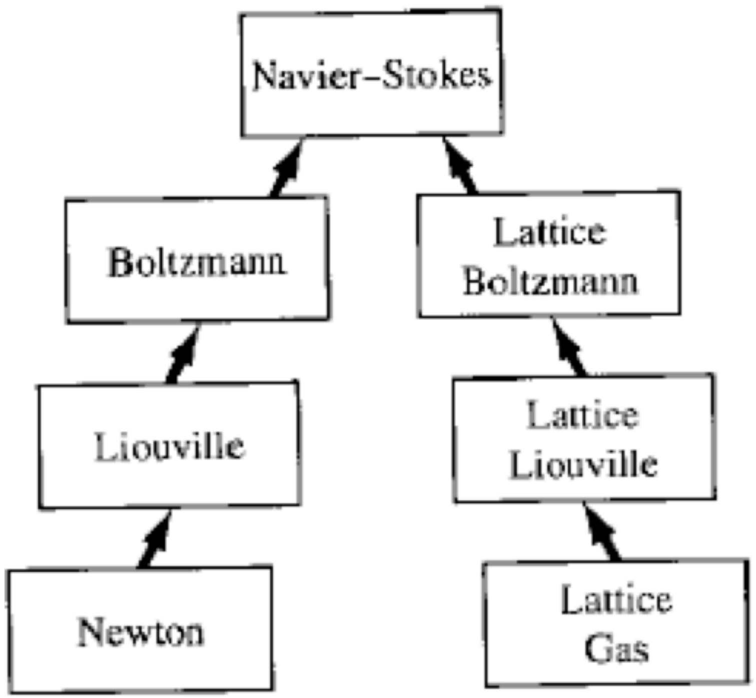
Discrete positions/velocities
Each time step: local collision
advection to nearest neighbours
completely local dynamics



Large expectations: High Re -> turbulence

Drawbacks: No Galilean invariance (for all lattices)
Pressure dependence on velocity
Difficult to reach low viscosities
Need of large statistics (noise)

2. Lattice Gases



Solid theoretical basis

Parallel to basic statistical physics

"Lattice kinetic theory"

From Fermi to Boltzmann

2. Lattice Boltzmann

$$f_i(\vec{r}+\vec{c}_i, t+1) = f_i(\vec{r},t)^* = f_i(\vec{r},t) + \Sigma_j L_{ij}[f_j(\vec{r},t) - f_j^{eq}(\vec{r},t)] + \boldsymbol{F}_i$$

Lattice occupation density

No Boolean variables

Euler (explicit) update

Simplest rule

Improved integrators

Velocity averages
Hydrodynamic variables

$$\Sigma_i f_i(\vec{r},t) = \rho(\vec{r},t)$$

$$\Sigma_i f_i(\vec{r},t)\vec{c}_i = \rho\vec{u}(\vec{r},t) = \vec{j}$$

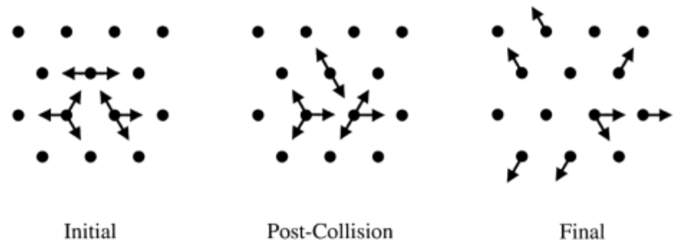
$$\Sigma_i f_i(\vec{r},t)\vec{c}_i\vec{c}_i = \rho\vec{u}\vec{u}(\vec{r},t) + \overleftrightarrow{P}(\vec{r},t)$$

Lattice geometry DnQm

Symmetry requirements to avoid lattice anisotropies

3. Lattice Boltzmann Model

Lattice kinetic model: "microscopic" dynamics



$$f_i(r + c_i, t + 1) = f_i(r,t) - \omega[f_i(r,t) - f_i^{eq}(r,t)]$$

$$\sum f_i = \rho$$

$$\sum f_i c_i = \rho v$$

$$\sum f_i c_i c_i = \rho v v + P$$

Conserved variables
Proper symmetries

Hydrodynamic equations

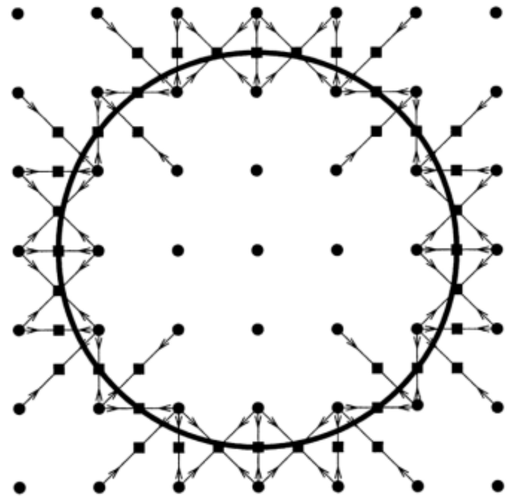
Colloid

rigid hollow surface

collision

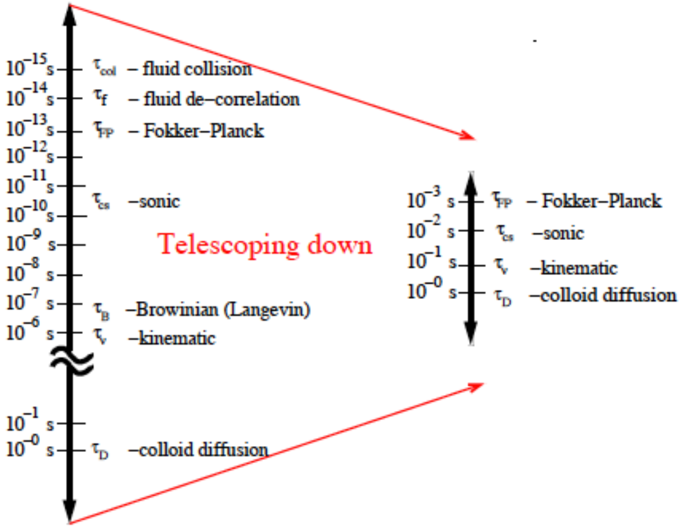
bounce-back

molecular dynamics



Hybrid scheme:
Pre-selection of relevant degrees of freedom

3. Lattice Boltzmann Model



How to bridge scales?

reduce separation

$$\tau=\sigma/c_s << \tau=\sigma^2/\nu << \tau=\sigma^2/D$$

Importance to keep proper hierarchy

length

time scales

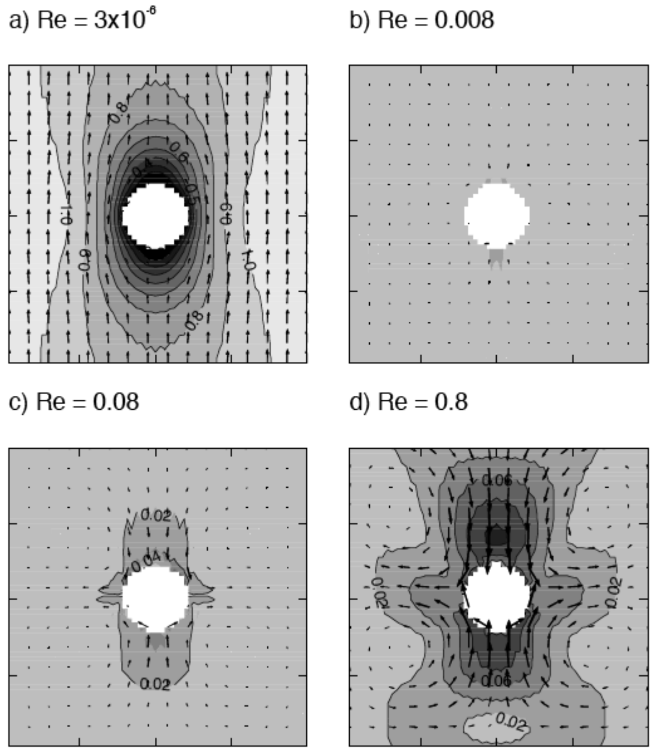
Impossibility to capture real parameters

how far can we take it?

slow speed of sound

wide interfaces

finite Reynolds numbers



Effect of finite Re

$$Re=U\sigma/\nu<<1 \quad Pe=U\sigma/D<1$$

Sedimenting sphere

3. Lattice Boltzmann Model

Thermodynamics of non ideal mixtures

Free energy

$$\beta f = \sum_{k=s,\pm} \rho_k \left(\ln \Lambda^3 \rho_k - 1\right) + \beta f^{ex}$$

Mean-field excess term

$$\beta f^{ex} = \frac{1}{2}\beta e\psi \sum_k \rho_k z_k$$

$$\beta f^{ex} = -\frac{1}{2}B\phi^2 + \frac{1}{4}B\phi^4 + \frac{\kappa}{2}(\nabla\phi)^2$$

Other possibilities, e.g. Landau-Ginzburg (oil/water, polymers)

Chemical potential and pressure

$$\beta\mu_k = \frac{\delta(\beta f)}{\delta\rho_k} = \ln\rho_k + \beta\mu_k^{ex} \quad \Rightarrow \quad \beta\mu_k = \ln\rho_k + \beta z_k e\psi$$

$$\beta\nabla p = \sum_k \rho_k \beta\nabla\mu_k = \beta\nabla p^{id} + \sum_k \rho_k \beta\nabla\mu_k^{ex}$$ Gibbs-Duhem

3. Lattice Boltzmann Model

Link flux method for solutes

Principle

Integrated conservation law $$\partial_t \int_{V_0} \rho_k \, \mathrm{d}V = -\oint_{A_0} \mathbf{j_k} \cdot \mathbf{n} \, \mathrm{d}A$$

Algorithm $$n_k(\mathbf{r}, t + \Delta t) - n_k(\mathbf{r}) = -A_0 \sum_i j_{ki}(\mathbf{r})$$

Link fluxes

Discretized $$\mathbf{j_k} = -D_k e^{-\beta\mu_k^{ex}} \nabla \left[\rho_k e^{+\beta\mu_k^{ex}} \right]$$

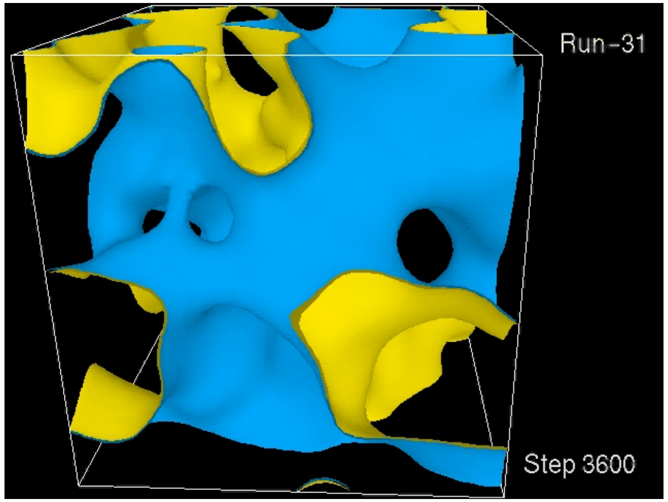
$$j_{ki}(\mathbf{r}) = -d_k \frac{e^{-\beta\mu_k(\mathbf{r})} + e^{-\beta\mu_k(\mathbf{r}+\mathbf{c_i}\Delta t)}}{2} \times \left[\frac{n_k(\mathbf{r}+\mathbf{c_i}\Delta t) e^{\beta\mu_k(\mathbf{r}+\mathbf{c_i}\Delta t)} - n_k(\mathbf{r}) e^{\beta\mu_k(\mathbf{r})}}{||\mathbf{c_i}\Delta t||} \right]$$

➡ $j_{ki}(\mathbf{r}) = -j_{ki'}(\mathbf{r} + \mathbf{c_i}\Delta t)$

➡ Boltzmann distribution in equilibrium

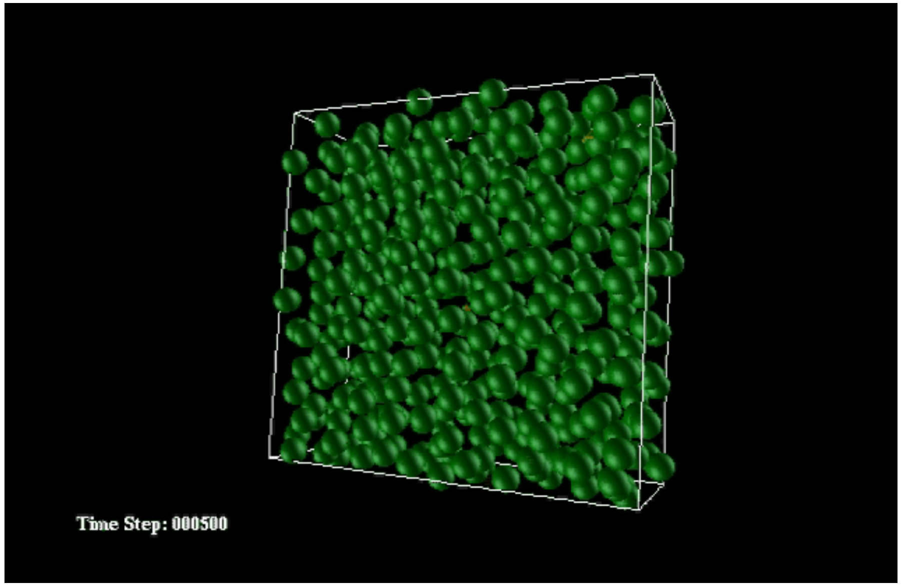
4. Dynamics of complex fluids

Controlling materials through external fields
shearing
gravity
electric/magnetic fields



Use internal capabilities of materials

Temperature quench
internal structure
length/time scale competition
emerging structures



Spontaneous internal motion
actuated/internal propulsion
interaction with actuating fields

K. Stratford et al. Science (2005)

4. Dynamics of complex fluids

$$L_0 = \eta^2 / (\rho\sigma)$$

$$T_0 = \eta^3 / (\rho\sigma^2)$$

material parameters

Universal scaling

Viscous regime

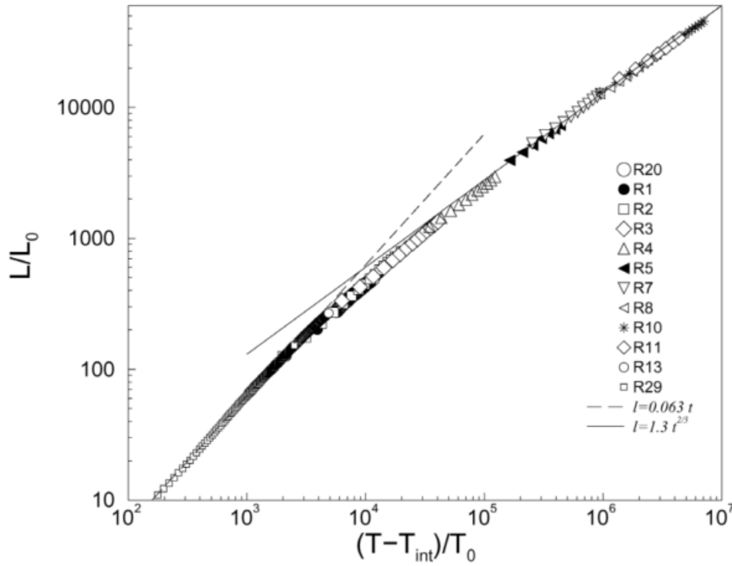
$$L / L_0 \sim A(T / T_0)^1$$

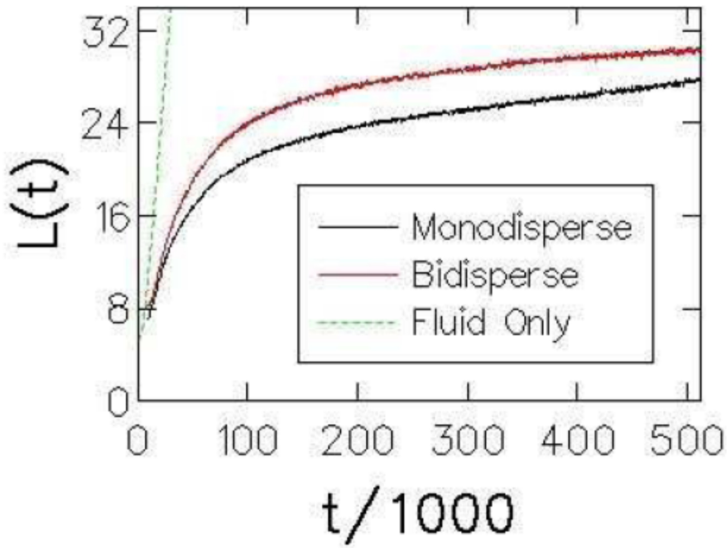
Inertial regime

$$L / L_0 \sim B(T / T_0)^{2/3}$$

Crossover regime

Colloids arrest phase separation
gel formation





5. Mixtures of oil, water and ions

Free energy model

$$F[\phi, \rho_+, \rho_-] = \int d\mathbf{r} \left[-\frac{1}{2} B\phi^2 + \frac{1}{4} B\phi^4 + \frac{\kappa}{2} (\nabla\phi)^2 \right]$$

$$+ \sum_{\alpha=\pm} \int d\mathbf{r}\ \rho_\alpha(\mathbf{r}) \left[k_B T \left(\ln \frac{\rho_\alpha(\mathbf{r})}{\rho_s} - 1 \right) + f_\alpha(\mathbf{r}) + \frac{z_\alpha e}{2} \psi(\mathbf{r}) \right]$$

and parametrize ε and f_α as a function of composition

Contains

Immiscibility of solvents

Solvation of ions $\quad f_\pm \propto \Delta\mu_\pm = \mu_\pm^o - \mu_\pm^w$

Electrostatics, including without ions (dielectrophoresis)

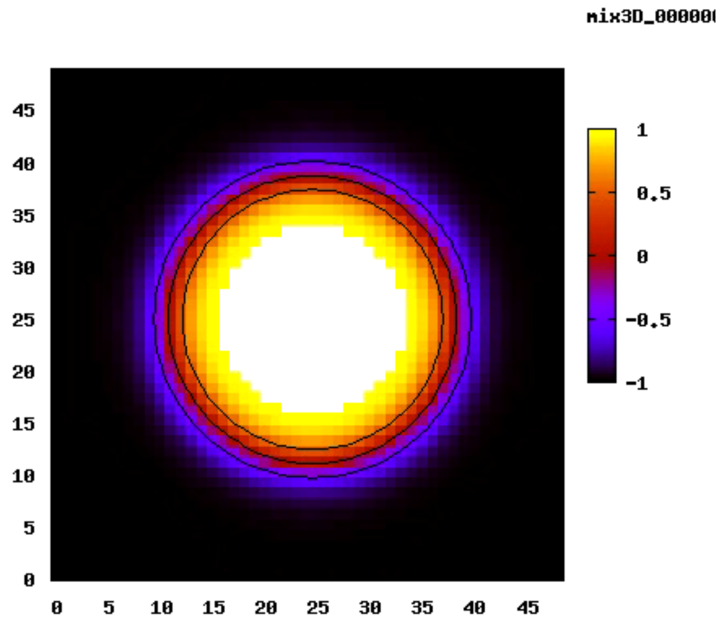
Dynamics of composition parameter = Cahn-Hilliard

5. Mixtures of oil, water and ions

Uncharged oil/water mixtures

Differential permitivity

Applied E field

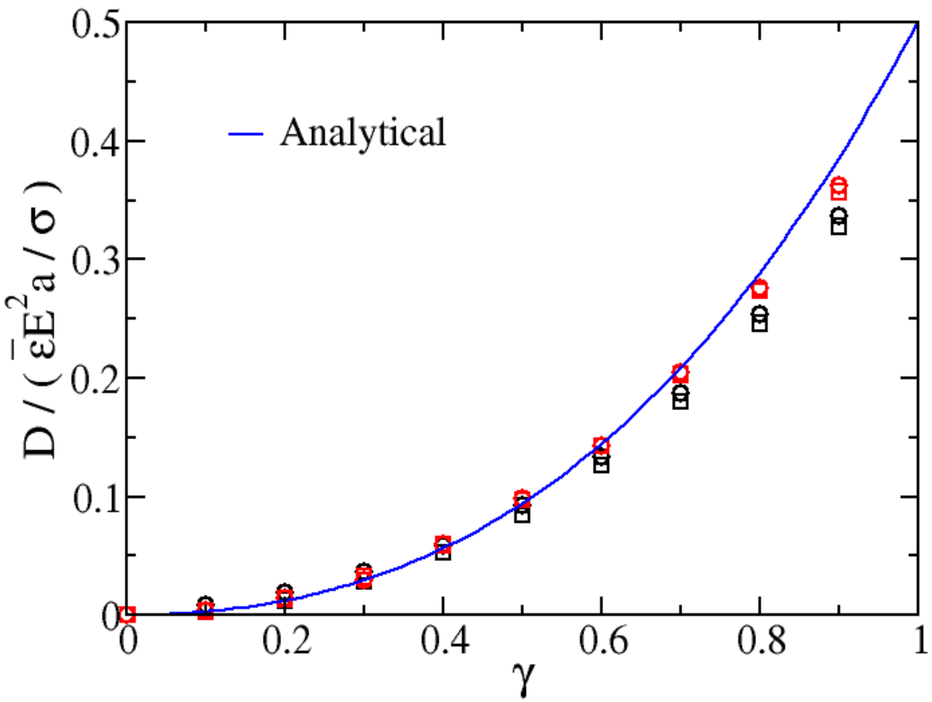


Oil in water droplet deformation

Transient hydrodynamic flow

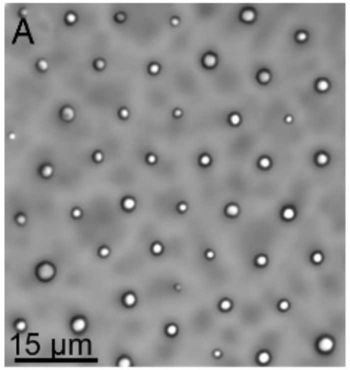
Small deformations

$$D = \frac{\bar{\epsilon} E^2 a}{4\sigma} \times \gamma^2(1+\gamma)$$



with $\gamma = \frac{\epsilon_w - \epsilon_o}{\epsilon_w + \epsilon_o}$

5. Mixtures of oil, water and ions

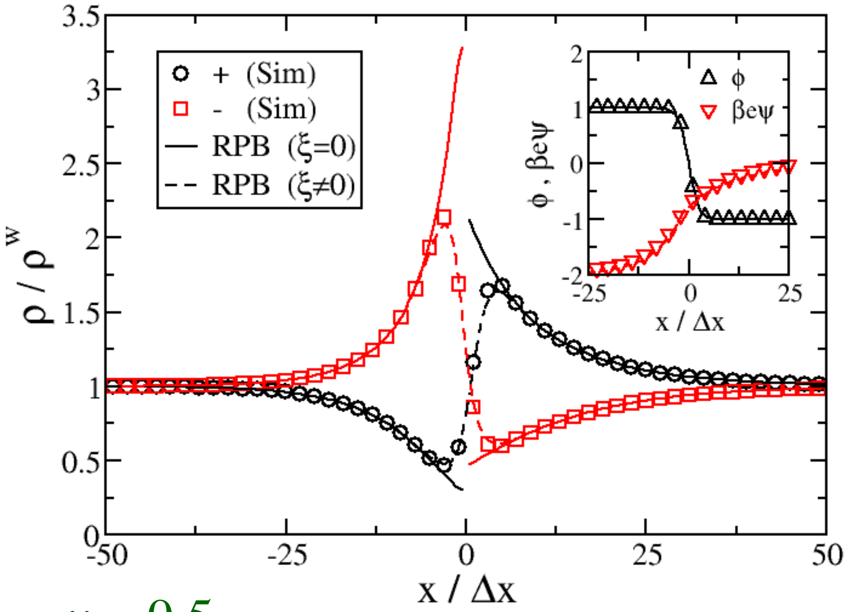


Anions and cations with different solubility

➡ Spontaneous charge separation

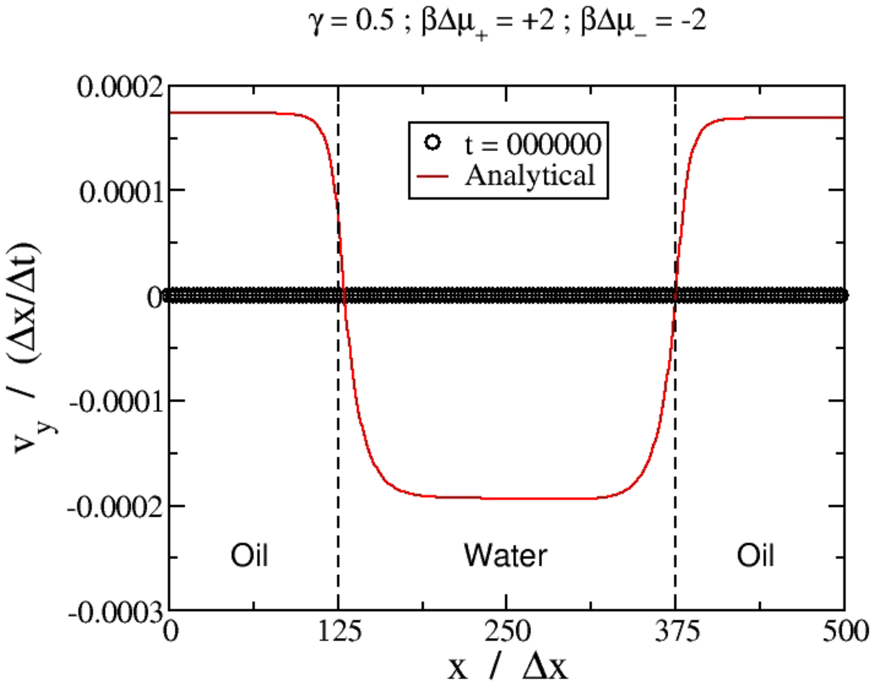
Leunissen et al., PNAS, 104, 2585 (2007)

Ionic profiles



$\gamma = 0.5$

Electroosmotic flow

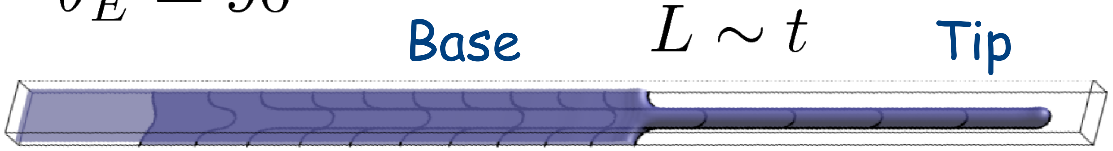


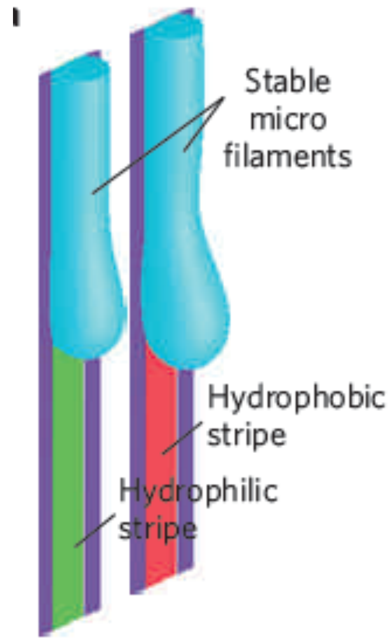
$\Delta\mu_{\pm} = \pm 2\ k_B T$: hydrophilic cation & hydrophobic anions

6. Dynamic wetting instability

Non linear regime

$\theta_E = 90^\circ$

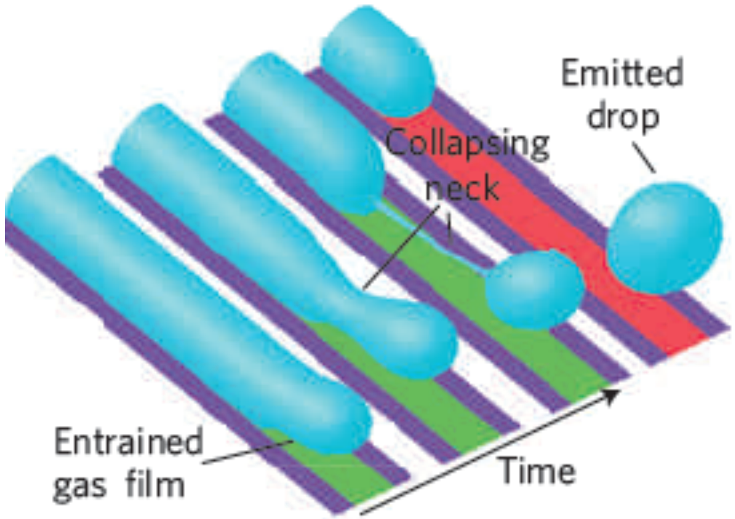




Forced thin film or rivulet

Stabilized by incoming flow

Localized by wetting missmatch



Due to substrate hydrophobicity/hydrophilicity

Different from Rayleigh-Plateau

6. Dynamic wetting instability

Non linear regime

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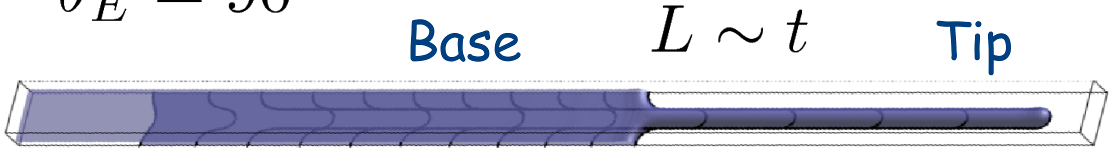

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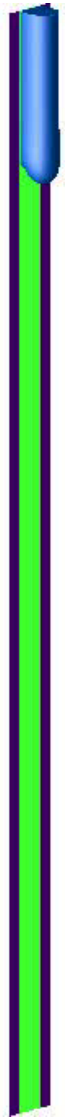
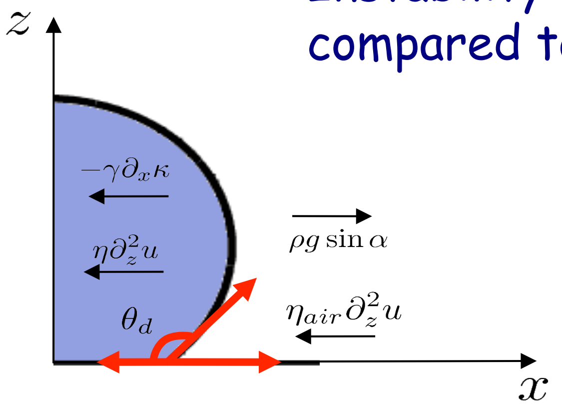


6. Dynamic wetting instability

Instability induced when forcing on protusion too large compared to friction at contact line



Capillary pressure

Gravity

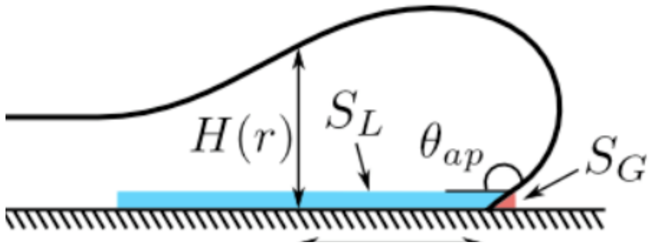
\+ Dissipation in the film

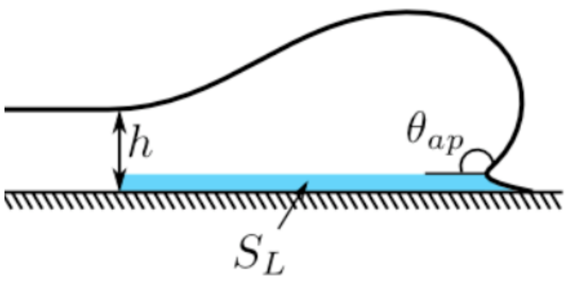
Dissipation in the air

Contact line force

$$\theta_d = f(Ca)$$

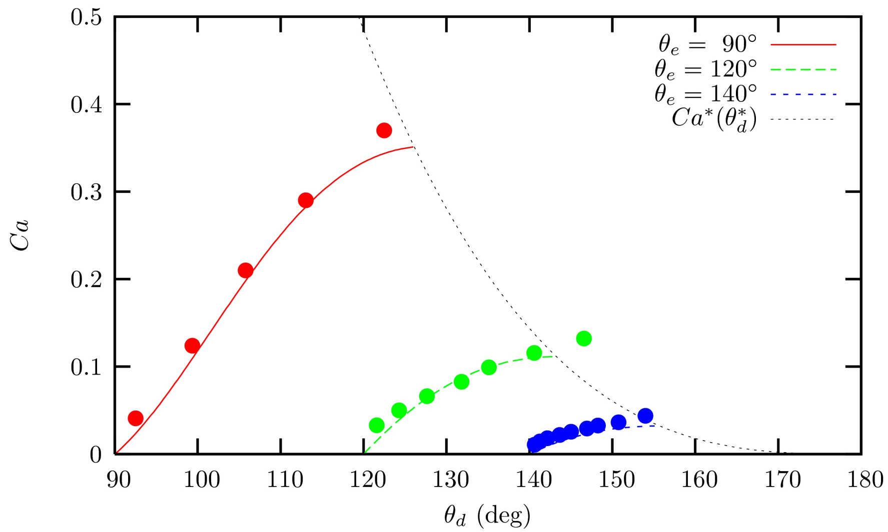
$$Ca = \frac{\eta U}{\gamma}$$

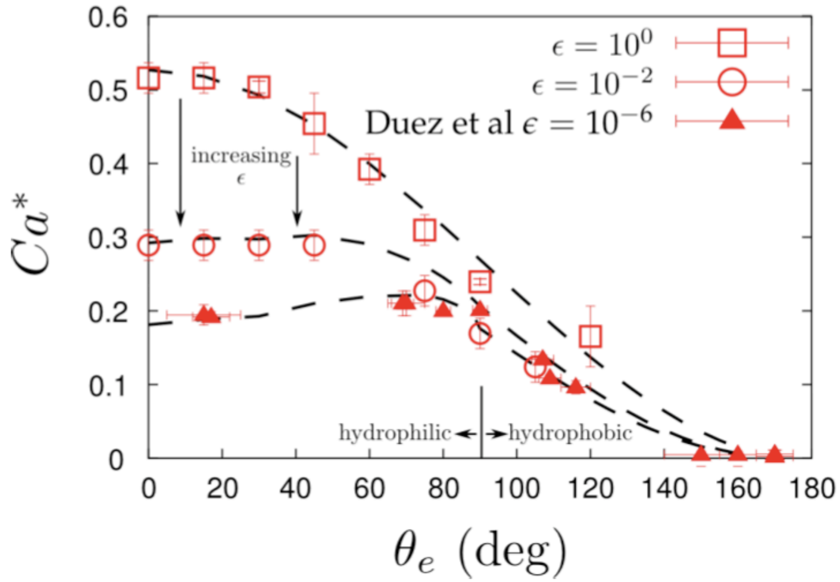




Shape of contact line
changes with attraction to solid substrate

6. Dynamic wetting instability





Identify critical Ca

Compares with lubrication theory

Larger angle requires less forcing

Drop emission

Periodic process

Hydrophobic substrate

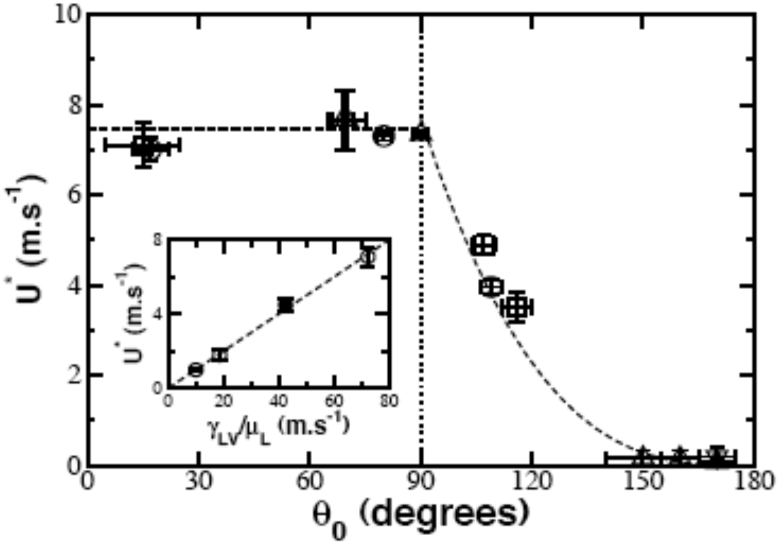
Controlled by gas wedge

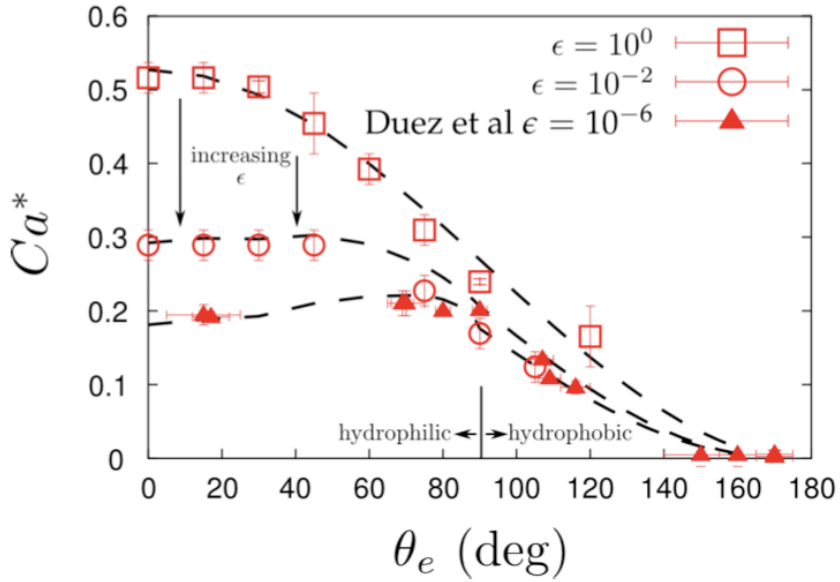
Hydrophilic substrate

Foot explains plateau

6. Dynamic wetting instability

Bocquet et al. (2007)





Identify critical Ca

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7. Moment propagation

Principle

Probabilistic interpretation LB

In addition to $f_i(r,c_i,t)$ for the fluid (~solvent), scalar $P(r,t)$ e.g. ρ_k

$$P(\mathbf{r},t+1) = \sum_i P(\mathbf{r}-\mathbf{c_i}\Delta t,t)p_i(\mathbf{r}-\mathbf{c_i}\Delta t,t) + P(\mathbf{r},t)\left(1-\sum_i p_i(\mathbf{r},t)\right)$$

$p_i(r,t)$ = probability to jump from r to $r+c_i\,\Delta t$

$$p_i(\mathbf{r},t) = \boxed{\frac{f_i(\mathbf{r},t)}{\rho_f(\mathbf{r},t)} - w_i} + \boxed{\lambda w_i\left\{\frac{1}{4}\beta q\mathbf{E}\cdot\mathbf{c}_i\Delta t + \frac{1}{1+e^{-\beta[V(\mathbf{r})-V(\mathbf{r}+\mathbf{c_i}\Delta t)]}}\right\}}$$

Includes interactions + sensitivity to applied external fields

Ensures detailed balance

7. Moment propagation

Based on transition probabilities

Propagate other quantities using same scheme

Correlation functions

Propagate P(r,t) = probability to arrive in r at t, weighted by v(0)

$$\langle v_\alpha(t) v_\alpha(0) \rangle = \sum_{\mathbf{r}} P(\mathbf{r}, t) \times \left(\sum_i p_i(\mathbf{r}, t) c_{i\alpha} \right)$$

Average over all possible trajectories done at once

Choose equilibrium initial condition

$$P(\mathbf{r}, 1) = \sum_i \frac{e^{-\beta V(\mathbf{r} - \mathbf{c_i} \Delta t)}}{Q} p_i(\mathbf{r} - \mathbf{c_i} \Delta t) c_{i\alpha}$$

$$Z_\alpha(0) = \sum_{\mathbf{r}, i} \frac{e^{-\beta V(\mathbf{r})}}{Q} p_i(\mathbf{r}) c_{i\alpha} c_{i\alpha}$$

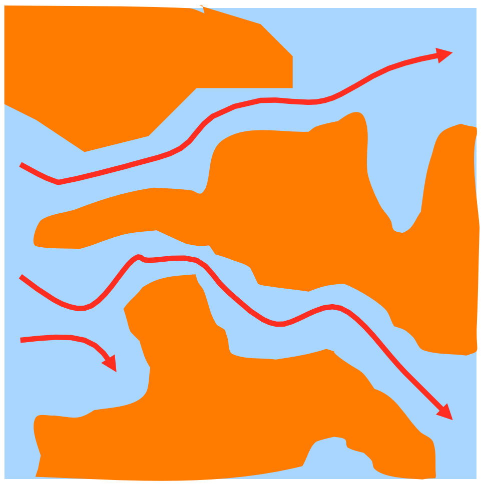
8. Diffusion in porous medium

Charged Tracer diffusion in a clay

$$\frac{D_e^-}{D_0^-} < \frac{D_e^w}{D_0^w} < \frac{D_e^+}{D_0^+}$$

slower faster

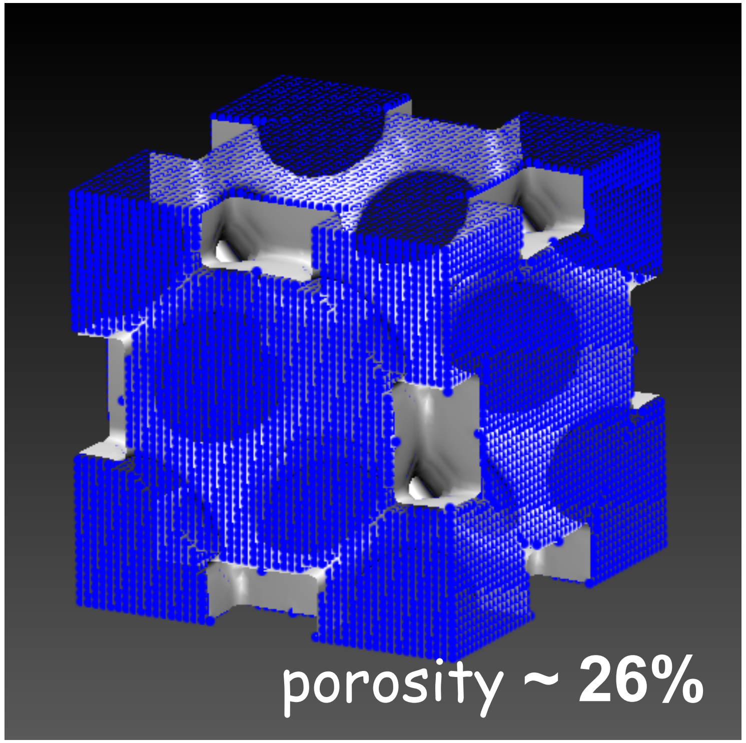
Effect decreases with ionic strength



Insight looking at pore scale?

8. Diffusion in porous medium

Model porous medium



FCC lattice. Spheres Z<0

Counterions + salt (controls κ)

Large pores connected by small ones

Continuous double layer

Tracer of charge $z \in \{ -1, 0, +1 \}$
same D_0

Effective diffusion coefficient?

Relation to explored porosity?

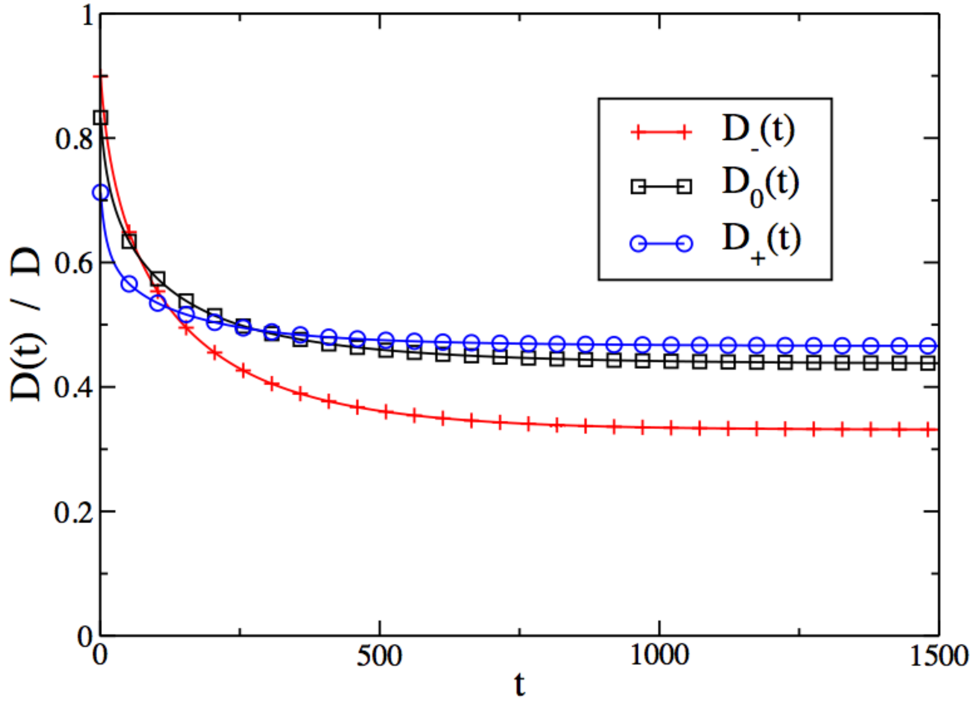
Time dependent diffusion, D(t)

8. Diffusion in porous medium

D(t) and D_e

$$D_e = \lim_{t \to \infty} D(t)$$

$D_+ > D_0 > D_-$

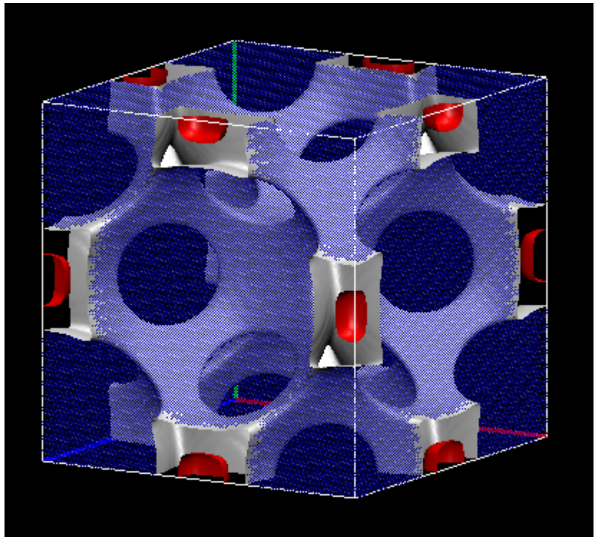


Characteristic time

To explore the porosity accessible to each tracer

$$\tau = \int_0^\infty \frac{D(t) - D_e}{D - D_e}\,\mathrm{d}t \quad \Rightarrow \quad \tau_+ < \tau_0 < \tau_-$$

4. Diffusion in porous medium



Observations

1) $D_+ > D_0 > D_-$

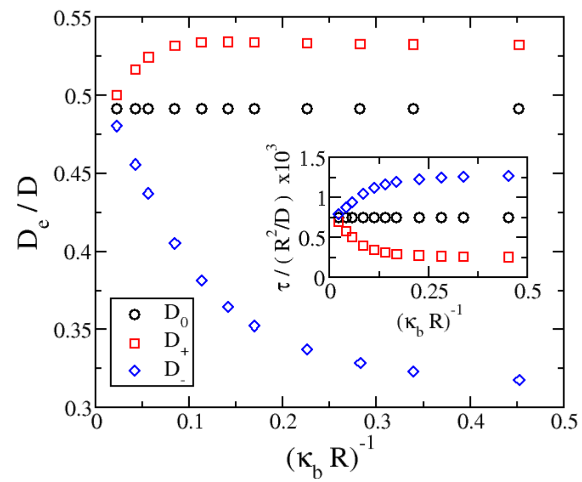
2) $\tau_+ < \tau_0 < \tau_-$

Cations

Close to surfaces

Double-layer = « highway »

small, connected volume (small t, large D)



Anions

Far from surfaces

« Electrostatic bottlenecks » = barrier to jump from one cavity to the next (larger t, smaller D)

8. Diffusion in porous medium

Couple localized species at liquid/solid boundary

Surface diffusion
+ Local Langmuir kinetics

$$\partial_t \Gamma(\mathbf{r},t) = -k_d \Gamma(\mathbf{r},t) + k_a \rho(\mathbf{r},t)$$

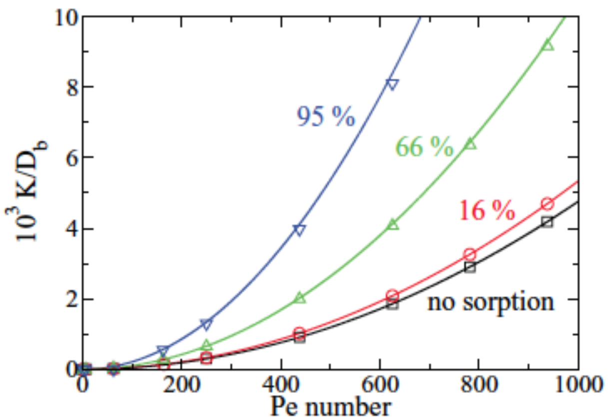
Local kinetic rules
efficient performance

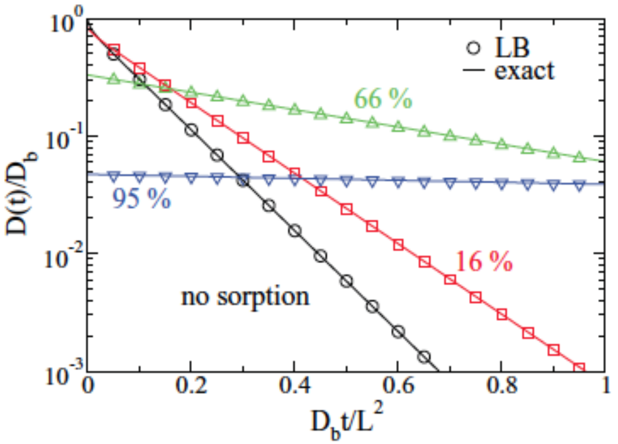
$$P_{\text{ads}}(\mathbf{r},t+\Delta t) = P(\mathbf{r},t)p_a + P_{\text{ads}}(\mathbf{r},t)(1-p_d),$$

$$P(\mathbf{r},t+\Delta t) = P^{\star}(\mathbf{r},t+\Delta t) + P_{\text{ads}}(\mathbf{r},t)p_d$$

Bulk vs Surface transport in porous medium?

New modes of transport?
Resonances in oscillatory driving?
Enhanced Taylor dispersion?





9. Fluctuating Lattice Boltzmann

Thermal fluctuations absent in LB

From Boltzmann equation recover Navier-Stokes

Need effect of other particles on single particle distribution function

Zwanzig-Bixon
recover fluctuating hydrodynamics
random distribution: conserves mass/momentum
stress satisfies FDT

Thermal noise added as an additional external force

$$f_i(\vec{r} + \vec{c}_i, t+1) = f_i(\vec{r}, t) + \Sigma_j L_{ij}[f_j(\vec{r}, t) - f_j^{eq}(\vec{r}, t)] + \xi_i$$

9. Fluctuating hybrid schemes

Need to satisfy FDT at lattice

Diffusion model for order parameter

$$F(\psi) = \int [f(\psi) + \frac{K}{2} (\nabla \psi)^2] \, d\mathbf{r}$$

$$f(\psi) = -\frac{A}{2}\psi^2 + \frac{B}{4}\psi^4$$

Equilibrium spectrum

$$P[\psi(\mathbf{q})] = \frac{e^{\beta F_q}}{Z}$$

Discretize on lattice?

$$\frac{\partial \psi}{\partial t} = M \nabla^2 \frac{\delta F}{\delta \psi} + \nabla \cdot \hat{\xi}$$

$$\langle \psi^2 \rangle = \frac{kT}{A}$$

$$\langle |\widetilde{\psi}_q|^2 \rangle = \frac{kT}{A + K\mathbf{q}^2}$$

9. Fluctuating hybrid schemes

How do we implement this scheme on previous link flux?

$$\partial_t \psi = \sum_i w_i \mathbf{c}_i \cdot \mathbf{j}^{\mu}(\mathbf{r} + \frac{1}{2}\mathbf{c}_i) + \sum_i w_i \mathbf{c}_i \cdot \hat{\boldsymbol{\xi}}(\mathbf{r} + \frac{1}{2}\mathbf{c}_i)$$

Link fluxes (deterministic/random)

$$\mathbf{j}^{\mu}(\mathbf{r} + \frac{1}{2}\mathbf{c}_i) = M\frac{1}{2}\left[\nabla\mu(\mathbf{r}) + \nabla\mu(\mathbf{r} + \mathbf{c}_i)\right]$$

$$\nabla \cdot \mathbf{j}^{\mu}(\mathbf{r} + \frac{1}{2}\mathbf{c}_i) = \frac{1}{c_s^4}\sum_j w_j \mathbf{c}_j \left[M \sum_k w_k \mathbf{c}_k \mu(\mathbf{r} + \mathbf{c}_j + \mathbf{c}_k)\right]$$

$$\hat{\boldsymbol{\xi}}(\mathbf{r} + \frac{1}{2}\mathbf{c}_i) = \frac{1}{2}\left[\hat{\boldsymbol{\xi}}(\mathbf{r}) + \hat{\boldsymbol{\xi}}(\mathbf{r} + \mathbf{c}_i)\right]$$

In Fourier they show proper symmerty on lattice

$$\partial_t \psi_{\mathbf{q}} = \boldsymbol{\Gamma}_{\mathbf{q}} \cdot (M \boldsymbol{\Gamma}_{\mathbf{q}} \mu_{\mathbf{q}}) + \boldsymbol{\Gamma}_{\mathbf{q}} \cdot \boldsymbol{\xi}_q \qquad \boldsymbol{\Gamma}_{\mathbf{q}} \equiv \sum_i w_i \mathbf{c}_i \exp(i\mathbf{q} \cdot \mathbf{c}_i)$$

9. Fluctuating hybrid schemes

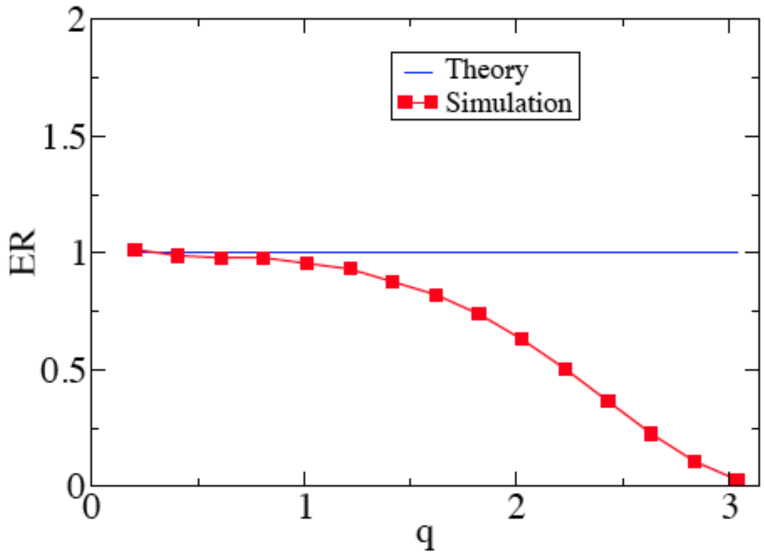
$$[\nabla^2 \psi](\mathbf{r}) = \sum_i \widehat{\omega}_i \psi(\mathbf{r} + \mathbf{c}_i) \quad \Rightarrow \quad [\nabla^2 \psi](\mathbf{q}) = \sum_i \widehat{\omega}_i e^{i\mathbf{q}\cdot\mathbf{c}_i} \widetilde{\psi}(\mathbf{q}) = L(\mathbf{q}) \widetilde{\psi}(\mathbf{q})$$

$$\left[\nabla \cdot \hat{\xi}\right](\mathbf{r}) = \sum_i \omega_i \mathbf{c}_i \cdot \hat{\xi}(\mathbf{r} + \mathbf{c}_i) \quad \Rightarrow \quad \left[\nabla \cdot \hat{\xi}\right](\mathbf{q}) = \sum_i \omega_i \mathbf{c}_i e^{i\mathbf{q}\cdot\mathbf{c}_i} \cdot \widetilde{\xi}(\mathbf{q}) = \Gamma(\mathbf{q}) \cdot \widetilde{\xi}(\mathbf{q})$$

$$\partial_t \widetilde{\psi}(\mathbf{q}) = M L(\mathbf{q}) \widetilde{\psi}(\mathbf{q}) + \Gamma(\mathbf{q}) \cdot \widetilde{\xi}(\mathbf{q}).$$

FDT on lattice requires

$$L(\mathbf{q}) = \Gamma(\mathbf{q}) \cdot \Gamma(\mathbf{q}).$$

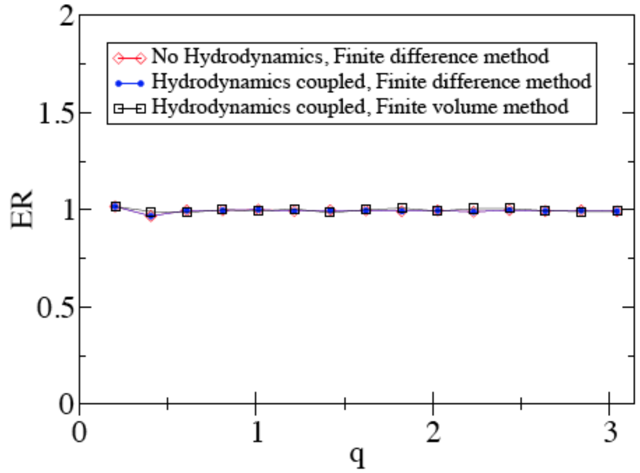


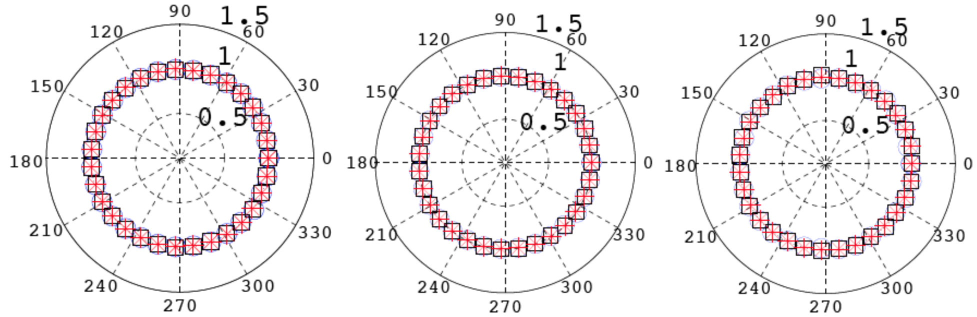
Standard approach to
Discretized Model B dynamics

9. Fluctuating hybrid schemes

Proper fluctuation spectrum at all wave numbers

$$\langle \psi^2 \rangle = \frac{kT}{A}$$

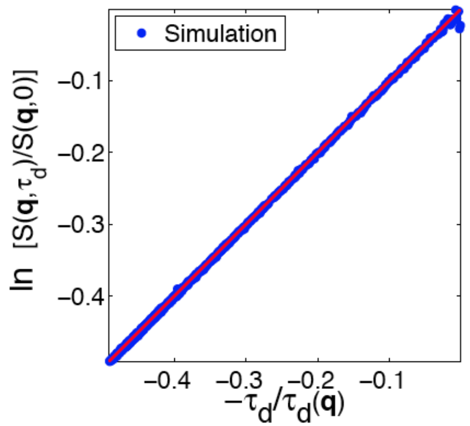




No lattice anisotropies

Diffusive decay of correlations

$$\langle |\widetilde{\psi}_q|^2 \rangle = \frac{kT}{A + K\mathbf{q}^2}$$

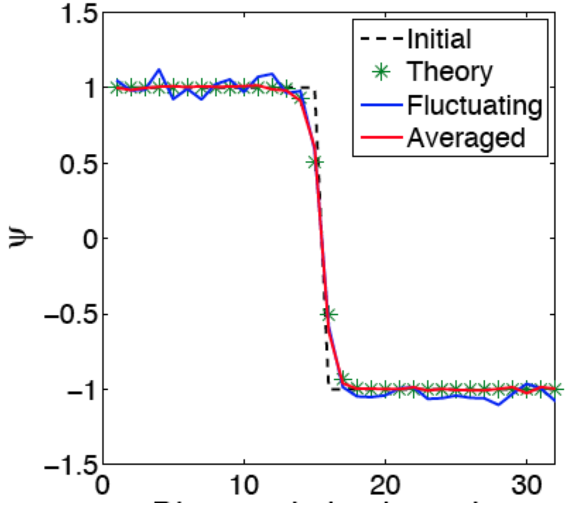


$$\langle \widetilde{\psi}_q(t)\widetilde{\psi}_q(t+\tau_d) \rangle = \frac{kT}{A + K\mathbf{q}^2} e^{-M\mathbf{q}^2(A+K\mathbf{q}^2)\tau_d}.$$

9. Fluctuating hybrid schemes

Fluid/fluid coexistence

Average profile



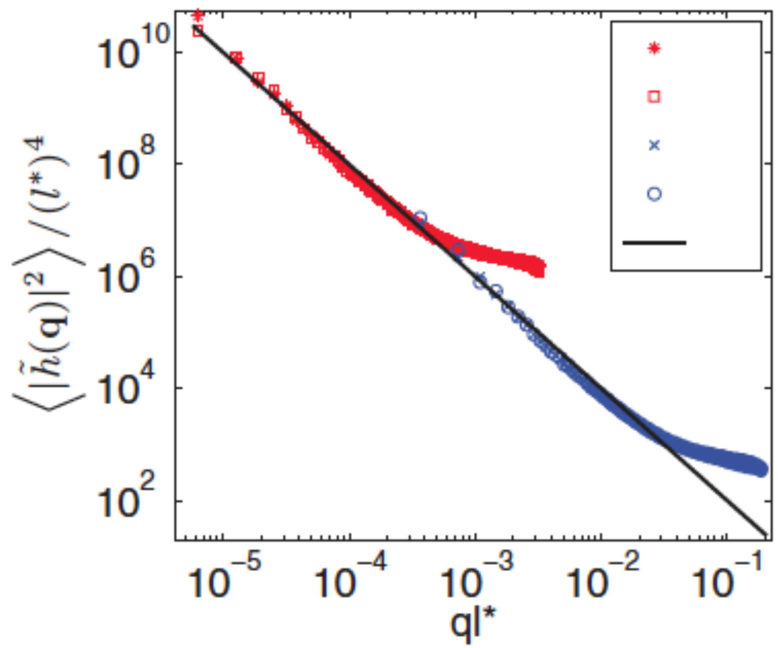
Interface fluctuation spectrum

Capillary waves

$$\Delta F_s = \frac{1}{2}\gamma \int dxdy(h_x^2 + h_y^2)$$

$$\Delta F_s = \frac{\gamma}{2}\sum_{\mathbf{q}} \mathbf{q}^2 |h(\mathbf{q})|^2$$

$$\langle |h(\mathbf{q})|^2 \rangle = \frac{kT}{\gamma \mathbf{q}^2}$$



10. Conclusions

Hybrid lattice scheme

Lattice-Boltzmann for momentum conservation

Evolution of composition by link-flux

Consistent thermal fluctuations in general complex fluid mixtures

Moment propagation in general complex fluid mixtures

An efficient tool for charged, heterogeneous systems

Porous media (solid/liquid)

Immiscible solvents (liquid/liquid)

Charged oil/water mixture

Electrokinetic mobility of surfactant free emulsion

Emulsion electrokinetics

With solid surfaces

Capillary instabilities: role of dynamic wetting...