Fluctuating Hydrodynamics Approach Toward Realistic Simulation of Reactive Microfluids

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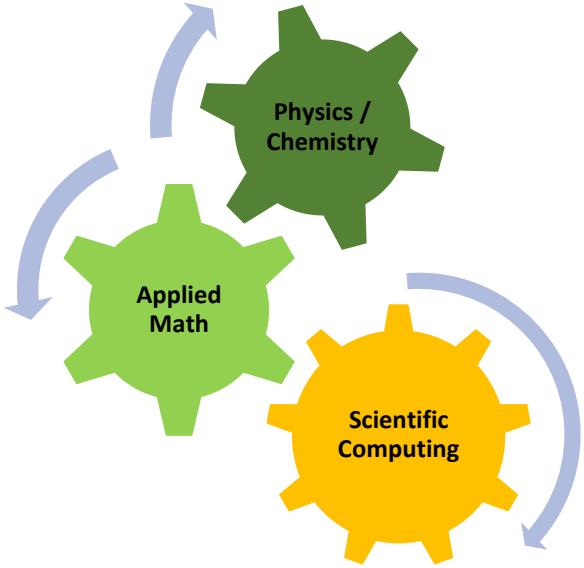


Dynamics of Fluids at Small Scales

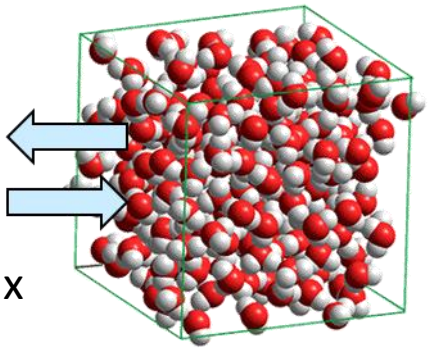
Fluid equation

$$\rho \frac{\partial \boldsymbol{v}}{\partial t} + \nabla \pi = -\rho \nabla \cdot (\boldsymbol{v}\boldsymbol{v}^T) + \nabla \cdot (\eta \overline{\nabla} \boldsymbol{v} + \boldsymbol{\Sigma}) + \boldsymbol{f}$$

$$\nabla \cdot \boldsymbol{v} = 0$$

Stochastic momentum flux

Dissipative momentum flux



Species equation

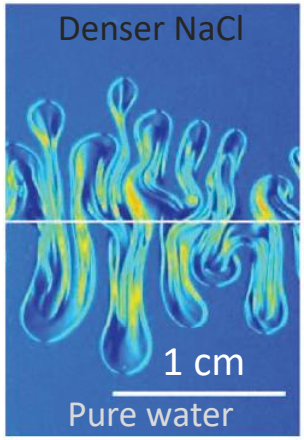
$$\frac{\partial \rho_s}{\partial t} = -\nabla \cdot (\rho_s \boldsymbol{v}) - \nabla \cdot \overline{\boldsymbol{F}}_s + m_s \overline{\Omega}_s$$

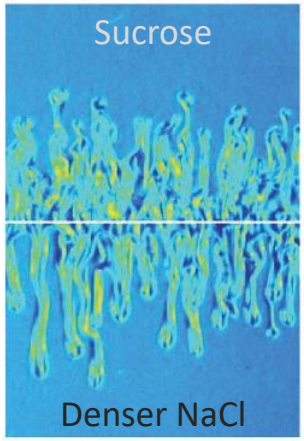
advection diffusion reaction

Fluctuating Hydrodynamics (FHD) approach

- $\overline{\boldsymbol{F}} = \{\overline{\boldsymbol{F}}_s\}$ is replaced by $\boldsymbol{F} = \overline{\boldsymbol{F}}$ (dissipative mass fluxes) + $\widetilde{\boldsymbol{F}}$ (stochastic mass fluxes).
- $\overline{\Omega} = \{\overline{\Omega}_s\}$ (described by the law of mass action) is replaced by stochastic chemistry Ω.

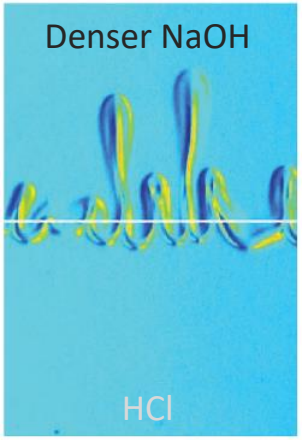
Buoyancy-Driven Mixing Instabilities

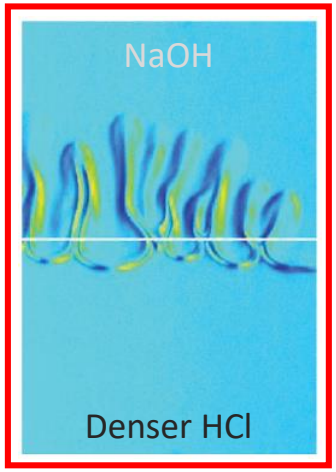




- ❖ Experiments in a vertically oriented Hele-Shaw cell
- ❖ Colors correspond to refractive index changes.

- ➢ Unstable configuration → Rayleigh-Taylor instability
- ➢ Stable configuration with fast diffusing bottom species → Double-diffusion instability





$$HCl + NaOH \rightarrow H_2O + NaCl$$

Fingers grow only upwards.

Our simulation studies are the first to use a three-dimensional model and include thermal fluctuations.

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Effects of Thermal Fluctuations

What is known:

- Instability phenomena are extremely sensitive to initial conditions.
- Once an uneven interface appears, the dynamic instability dominates and thermal fluctuations play a secondary role in subsequent pattern formation.

What we expect:

- For a perfectly flat initial interface, thermal fluctuations play an essential role in perturbing the interface at early times.

What we do:

- Our simulations are initialized with natural mass and momentum fluctuations without any artificial perturbation. → an *ideal* experiment

What we want to know:

Which stochastic component is most influential?

- Initial equilibrium momentum fluctuations
- Initial equilibrium concentration fluctuations
- Stochastic momentum fluxes
- Stochastic mass fluxes
- Stochastic chemistry

Effects of Charged Species

In a dilute binary electrolyte solution, two ions A^{+V_+} and B^{-V_-} tend to diffuse together.

The salt can be modeled as an uncharged substance with an effective diffusion coefficient:

$$D^{\mathrm{amb}} = \frac{(V_+ + V_-)D_+D_-}{V_+D_+ + V_-D_-}$$

However, this **ambipolar approximation** may not be valid with multiple ion species.

$D_{\mathrm{Na}^+} = 1.33 \cdot 10^{-5}$

$D_{\mathrm{Cl}^-} = 2.03 \cdot 10^{-5}$

$D_{\mathrm{H}^+} = 9.35 \cdot 10^{-5}$

$D_{\mathrm{OH}^-} = 5.33 \cdot 10^{-5}$

Ambipolar approximation

$D_{\mathrm{HCl}} = 3.34 \cdot 10^{-5}$

$D_{\mathrm{NaOH}} = 2.13 \cdot 10^{-5}$

$D_{\mathrm{NaCl}} = 1.61 \cdot 10^{-5}$

- Part 2: simulation with ions
- Part 1: simulation with molecules

Part 1

Fluctuating Hydrodynamics Simulations with Uncharged Species

Governing Equations

Fluid equation

$$\rho \frac{\partial \boldsymbol{v}}{\partial t} + \boldsymbol{\nabla}\pi = -\rho \boldsymbol{\nabla}\cdot(\boldsymbol{v}\boldsymbol{v}^T) + \boldsymbol{\nabla}\cdot(\eta\overline{\boldsymbol{\nabla}}\boldsymbol{v} + \boldsymbol{\Sigma}) + \boldsymbol{f}$$

$$\boldsymbol{\nabla}\cdot\boldsymbol{v} = 0$$

Buoyancy force

$$\boldsymbol{f} = -\left(\sum_{\text{solute } s} \beta_s \rho_s\right) g \boldsymbol{e}_y$$

Stochastic momentum flux modeled by GWN

$$\boldsymbol{\Sigma} = \sqrt{\eta k_B T}[\boldsymbol{\mathcal{Z}}^{\text{mom}} + (\boldsymbol{\mathcal{Z}}^{\text{mom}})^T]$$

$$\left\langle \mathcal{Z}_i^{\text{mom}}(\boldsymbol{r},t)\mathcal{Z}_j^{\text{mom}}(\boldsymbol{r}',t')\right\rangle = \delta_{ij}\delta(\boldsymbol{r}-\boldsymbol{r}')\delta(t-t')$$

Species equation

$$\frac{\partial \rho_s}{\partial t} = -\boldsymbol{\nabla}\cdot(\rho_s \boldsymbol{v}) - \boldsymbol{\nabla}\cdot\boldsymbol{F}_s + m_s\Omega_s$$

Maxwell-Stefan formulation (for general mixtures)

$$\boldsymbol{F} = \{\boldsymbol{F}_s\} = \overline{\boldsymbol{F}} + \widetilde{\boldsymbol{F}}$$

$$\overline{\boldsymbol{F}} = -\rho \boldsymbol{W}\boldsymbol{\chi}\boldsymbol{\Gamma}\boldsymbol{\nabla}\boldsymbol{x}$$

$$\widetilde{\boldsymbol{F}} = \sqrt{2\overline{m}\rho}\boldsymbol{W}\boldsymbol{\chi}^{1/2}\boldsymbol{\mathcal{Z}}^{\text{mass}}$$

$\Rightarrow$

In a dilute solution

$$\overline{\boldsymbol{F}}_s \approx -D_s\boldsymbol{\nabla}\rho_s$$

$$\widetilde{\boldsymbol{F}}_s \approx \sqrt{2D_s m_s \rho_s}\boldsymbol{\mathcal{Z}}_s^{\text{mass}}$$

Stochastic Reaction (near Macroscopic Limit)

$$\mathrm{HCl} + \mathrm{NaOH} \rightarrow \mathrm{H_2O} + \mathrm{NaCl}$$

Law of mass action (deterministic description)

$$\text{reaction rate } \; a = k n_{\mathrm{HCl}} n_{\mathrm{NaOH}}$$

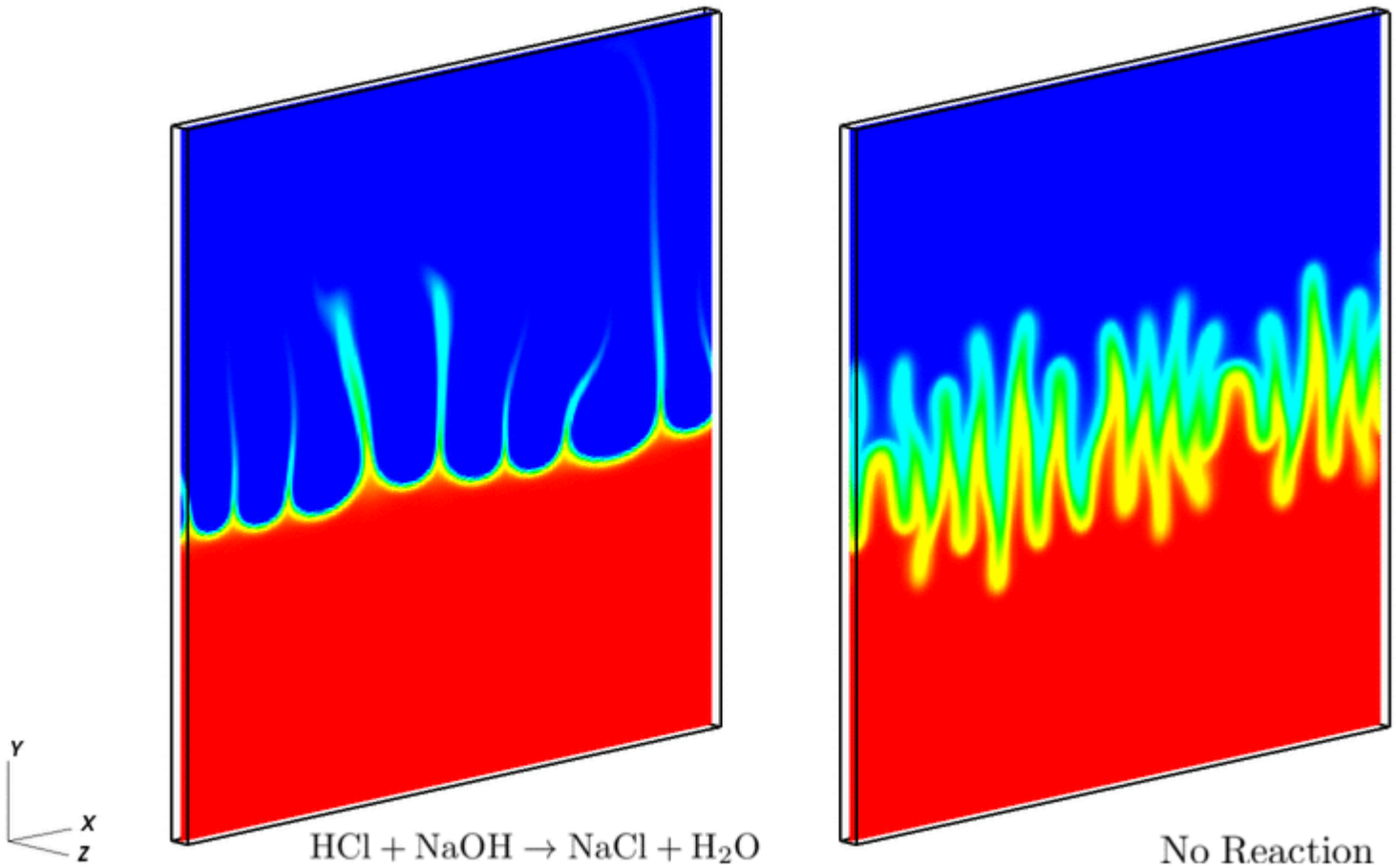
We use an accurate stochastic chemistry model based on Poisson statistics.

Near the macroscopic limit (i.e. weak fluctuations), its **Gaussian approximation** becomes the Langevin description.

Chemical Langevin equation (CLE) description

$$\Omega^{\mathrm{CLE}}_{\mathrm{H_2O}} = \Omega^{\mathrm{CLE}}_{\mathrm{NaCl}} = -\Omega^{\mathrm{CLE}}_{\mathrm{HCl}} = -\Omega^{\mathrm{CLE}}_{\mathrm{NaOH}} = a + \sqrt{a} Z^{\mathrm{react}}$$

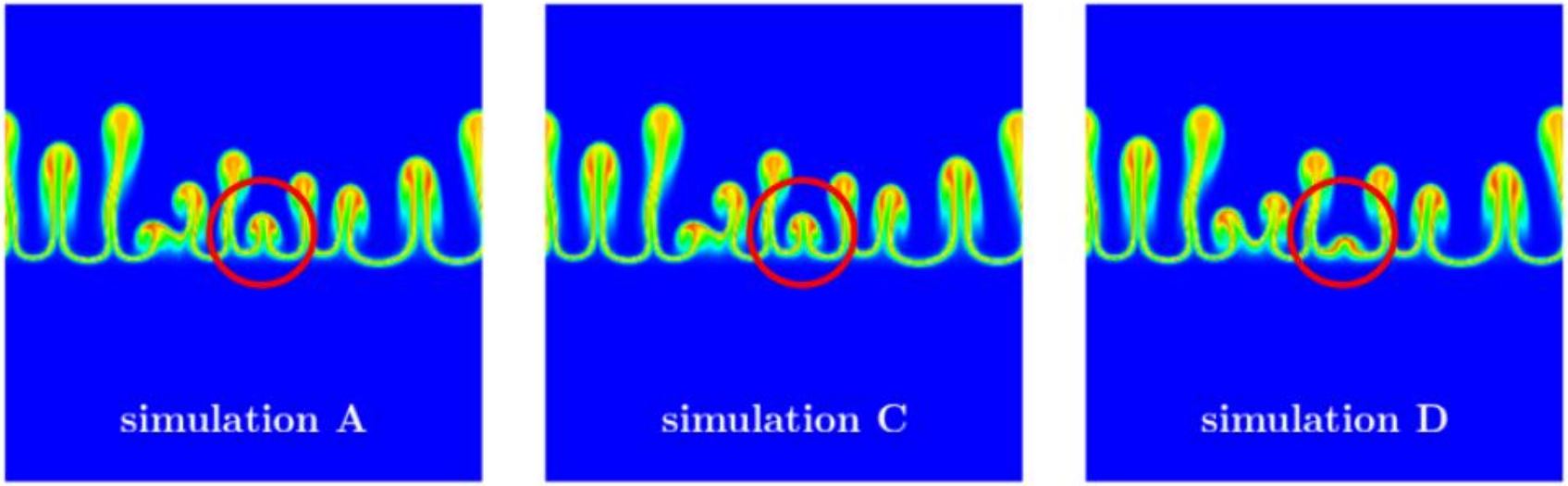
Simulation Result: ρ_{HCl}



Most Influential Stochastic Component

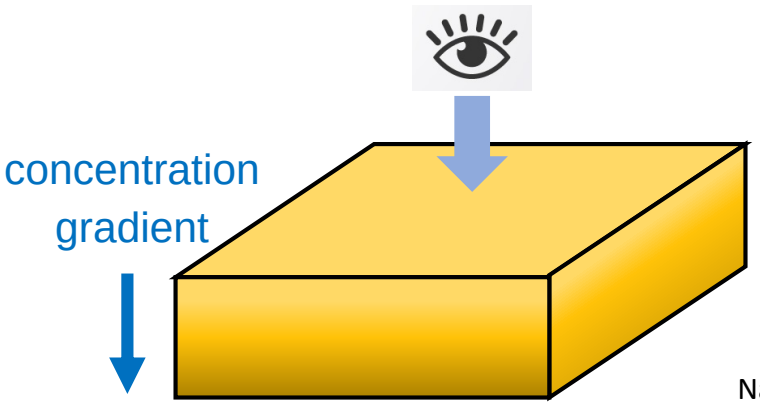
	Chemistry	Initial fluctuations		Stochastic fluxes	
		Mass	Momentum	Mass	Momentum
Simulation A	Stochastic	On	On	On	**On**
Simulation C	Deterministic	Off	On	Off	**On**
Simulation D	deterministic	Off	Off	Off	**On**

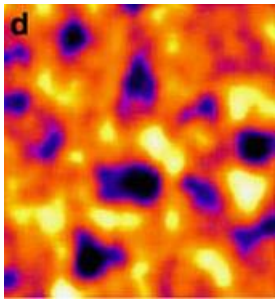
ρ_{NaCl} at $t = 30$



❖ The same random numbers for each stochastic component were used.

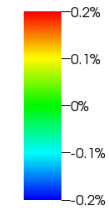
Giant Fluctuations



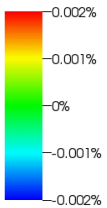


Nat. Commun. 2, 290 (2011)
Microgravity experiment
in space

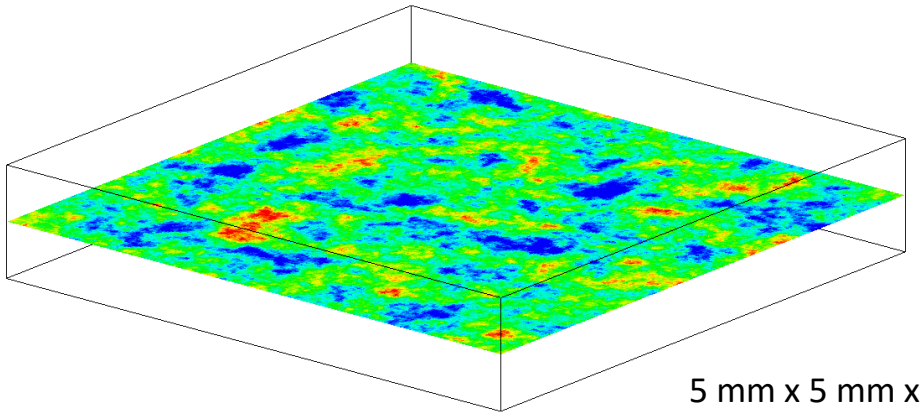
random advection (by thermal velocity fluctuations) coupled with a constant concentration gradient leads to (long-ranged) giant concentration fluctuations

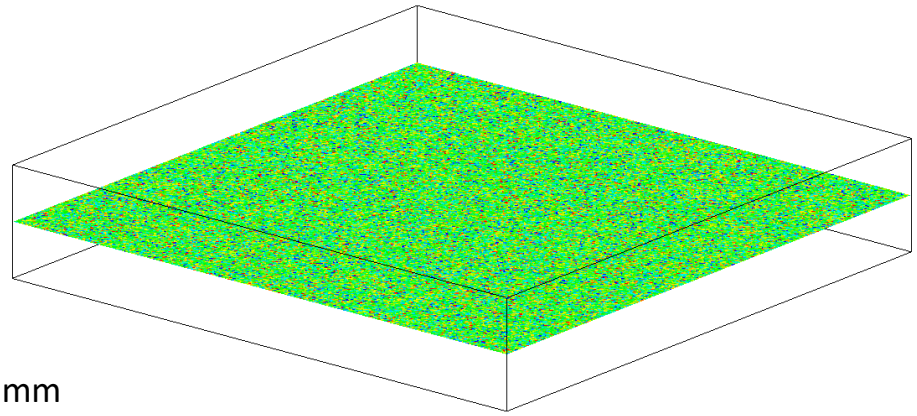


FHD simulation
Under concentration gradient



Corresponding equilibrium case
(no concentration gradient)





5 mm x 5 mm x 1 mm

Part 2

Fluctuating Hydrodynamics Simulations with Charged Species (Ions)

(Original) Governing Equations

Fluid equation

$$\rho \frac{\partial \boldsymbol{v}}{\partial t} + \nabla \pi = -\rho \nabla \cdot (\boldsymbol{v}\boldsymbol{v}^T) + \nabla \cdot (\eta \bar{\nabla} \boldsymbol{v} + \boldsymbol{\Sigma}) + \underbrace{\nabla \cdot (\epsilon \nabla \Phi) \nabla \Phi}_{\boldsymbol{f}_E} + \boldsymbol{f}$$

$$\nabla \cdot \boldsymbol{v} = 0$$

Poisson equation

$$-\nabla \cdot (\epsilon \nabla \Phi) = \underbrace{\sum_s z_s \rho_s}_{q}$$

$$\boldsymbol{f}_E = q\boldsymbol{E}$$

$$\nabla \cdot (\epsilon \boldsymbol{E}) = q$$

$$\boldsymbol{E} = -\nabla \Phi$$

Electric potential

Species equation

$$\frac{\partial \rho_s}{\partial t} = -\nabla \cdot (\rho_s \boldsymbol{v}) - \nabla \cdot \boldsymbol{F}_s + m_s \Omega_s$$

$$\bar{\boldsymbol{F}} = -\rho \boldsymbol{W} \boldsymbol{\chi} \left(\boldsymbol{\Gamma} \nabla \boldsymbol{x} + \frac{\bar{m} \boldsymbol{W} \boldsymbol{z}}{k_B T} \nabla \Phi \right) \qquad \tilde{\boldsymbol{F}} = \sqrt{2\bar{m}\rho} \boldsymbol{W} \boldsymbol{\chi}^{1/2} \boldsymbol{\mathcal{Z}}^{\text{mass}}$$

Electro-diffusion

Electroneutral Approximation

The original formulation resolves the Debye length scale $\boldsymbol{\lambda_{\mathrm{D}}}$.
As a result, **the time step size is limited** by $\tau_{\mathrm{D}} = \lambda_{\mathrm{D}}^2/D$.

At length/time scales larger than the Debye scales, electrolytes are effectively electroneutral.

$$Z = \sum_s z_s \rho_s = 0$$

Enforced electroneutrality

$$\frac{\partial Z}{\partial t} = \sum_s z_s \left(-\boldsymbol{\nabla} \cdot (\rho_s \boldsymbol{v}) - \boldsymbol{\nabla} \cdot \boldsymbol{F}_s + m_s \Omega_s\right) = \boldsymbol{\nabla} \cdot (\boldsymbol{z}^T \boldsymbol{F}) = 0$$

$$\boldsymbol{\nabla} \cdot \left[\left(\frac{\bar{m}\rho}{k_B T} \boldsymbol{z}^T \boldsymbol{W} \boldsymbol{\chi} \boldsymbol{W} \boldsymbol{z}\right) \boldsymbol{\nabla} \Phi\right] = \boldsymbol{\nabla} \cdot (\boldsymbol{z}^T \boldsymbol{F}_{\mathrm{d}})$$

Resulting elliptic equation

In the electroneutral limit, the **electric potential Φ becomes a Lagrange multiplier** that enforces the electroneutrality condition. **cf. Pressure in the incompressible formulation.**

Electroneutral Formulation

Fluid equation

$$\rho \frac{\partial \boldsymbol{v}}{\partial t} + \boldsymbol{\nabla}\pi = -\rho \boldsymbol{\nabla} \cdot (\boldsymbol{v}\boldsymbol{v}^T) + \boldsymbol{\nabla} \cdot (\eta \overline{\boldsymbol{\nabla}}\boldsymbol{v} + \boldsymbol{\Sigma}) + \boldsymbol{\nabla} \cdot (\epsilon \boldsymbol{\nabla}\Phi)\boldsymbol{\nabla}\Phi + \boldsymbol{f}$$

$$\boldsymbol{\nabla} \cdot \boldsymbol{v} = 0$$

Electroneutral Poisson equation

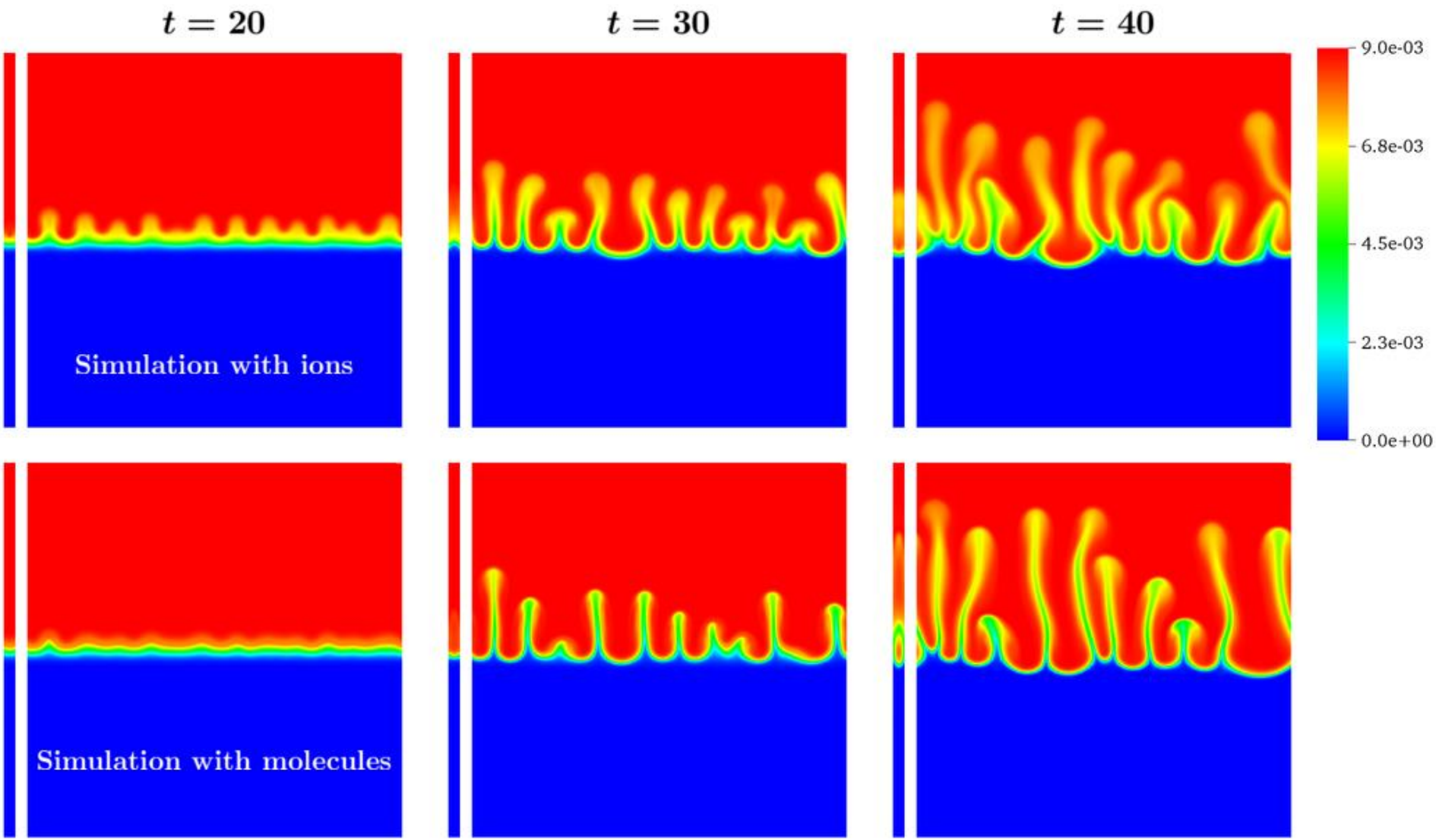
$$\boldsymbol{\nabla} \cdot \left[\left(\frac{\overline{m}\rho}{k_B T} \boldsymbol{z}^T \boldsymbol{W} \boldsymbol{\chi} \boldsymbol{W} \boldsymbol{z} \right) \boldsymbol{\nabla}\Phi \right] = \boldsymbol{\nabla} \cdot (\boldsymbol{z}^T \boldsymbol{F}_{\mathrm{d}})$$

Species equation

$$\frac{\partial \rho_s}{\partial t} = -\boldsymbol{\nabla} \cdot (\rho_s \boldsymbol{v}) - \boldsymbol{\nabla} \cdot \boldsymbol{F}_s + m_s \Omega_s$$

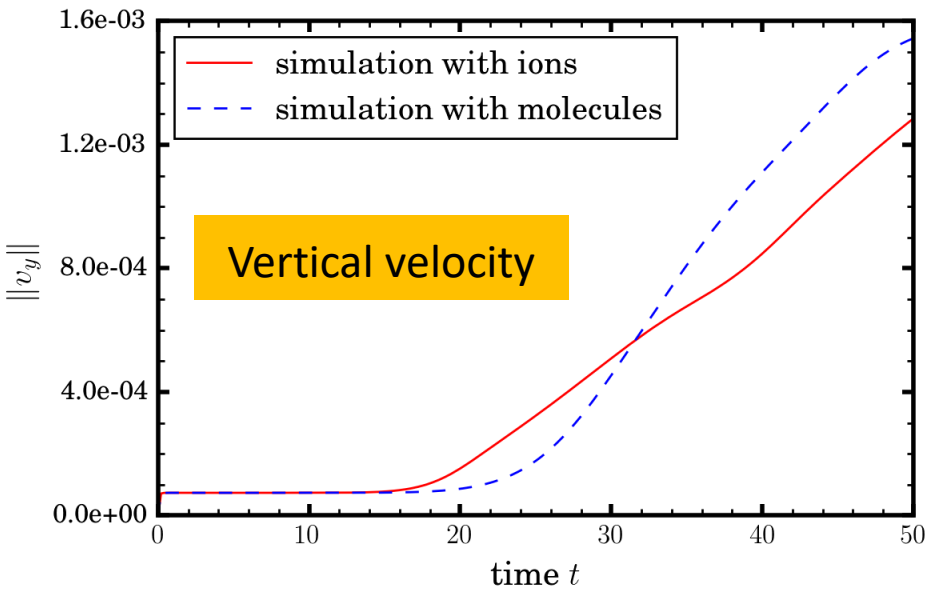
$$\overline{\boldsymbol{F}} = -\rho \boldsymbol{W} \boldsymbol{\chi} \left(\boldsymbol{\Gamma} \boldsymbol{\nabla} \boldsymbol{x} + \frac{\overline{m} \boldsymbol{W} \boldsymbol{z}}{k_B T} \boldsymbol{\nabla}\Phi \right) \qquad \widetilde{\boldsymbol{F}} = \sqrt{2\overline{m}\rho} \boldsymbol{W} \boldsymbol{\chi}^{1/2} \boldsymbol{\mathcal{Z}}^{\mathrm{mass}}$$

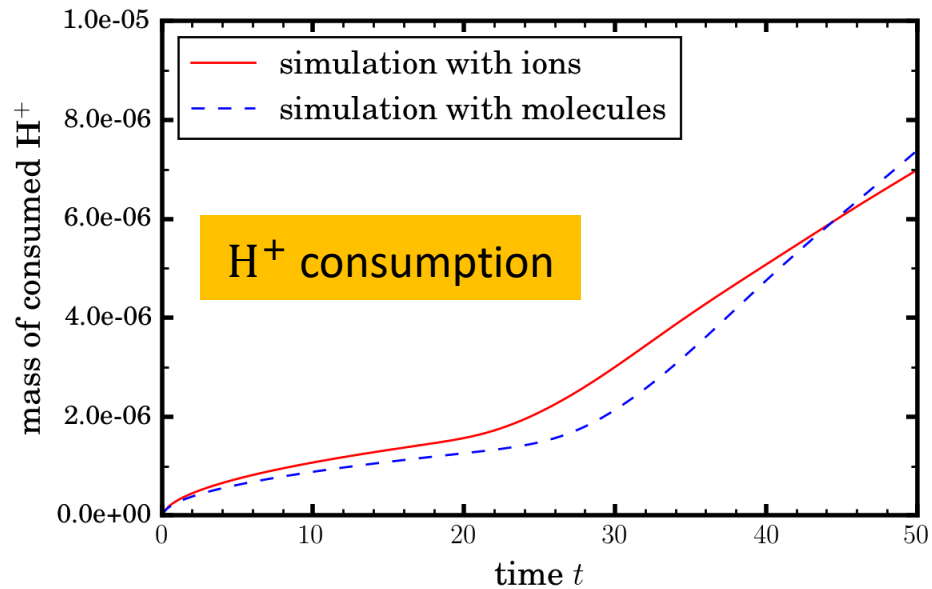
Comparison (ρ_{Na^+})



❖ The same random numbers for $\mathcal{Z}^{\mathrm{mom}}$ (stochastic mass fluxes) were used.

Quantitative Comparison





Conclusions

1. Using fluctuating hydrodynamics, we performed simulation studies for a mixing instability phenomenon with a neutralization reaction initiated with a perfectly flat interface.

2. Thermal fluctuations play an important role in the onset of mixing instability and the contribution of the stochastic momentum flux is most influential.

3. Modeling the acid, base, and salt as neutral species diffusing with ambipolar diffusion coefficients may lead to *quantitatively-wrong* results unless the diffusion coefficients of the ions are very similar.

Thank You!!!

References

1. C. Kim, A. Nonaka, J.B. Bell, A.L. Garcia, A. Donev, "**Fluctuating hydrodynamics of reactive liquid mixtures**", *J. Chem. Phys.* 149, 084113 (2018).
2. A. Donev, A. Nonaka, C. Kim, A.L. Garcia, J.B. Bell, "**Fluctuating hydrodynamics of electrolytes at electroneutral scales**", to be submitted for publication in *Phys. Fluids*.