Stochastic modeling of sulphation-induced marble degradation:

A strongly repulsive particle system chemically interacting with the environment.

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joint work with

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UNIVERSITÀ DEGLI STUDI DI MILANO

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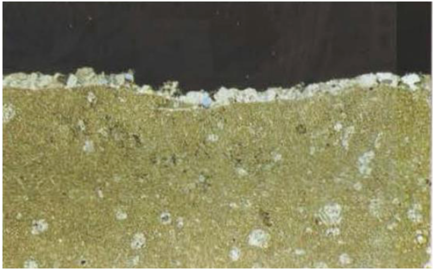
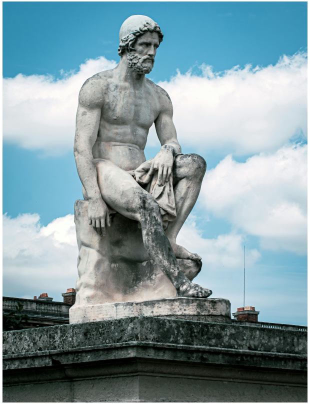
The chemical reaction

1 The problem

$$\underbrace{CaCO_3}_{\text{calcium carbonate}} + \underbrace{H_2SO_4}_{\text{sulfuric acid}} + H_2O \rightarrow \underbrace{CaSO_4 \cdot 2H_2O}_{\text{gypsum}} + CO_2$$





Challenges in Modeling Corrosion

Developing a flexible and accurate corrosion model is challenging due to its strong dependence on various environmental factors, including:

- Material composition,
- Variability in atmospheric pollutants,
- Temperature variations,
- Relative humidity levels,
- Atmospheric metal pollutants, and more.

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A continuous deterministic model

$$\begin{cases} \partial_t\left(\varphi(c)s\right) & = \nabla\cdot\left(\varphi(c)\nabla s\right) - \lambda\varphi(c)sc \\ \partial_t c & = -\lambda\varphi(c)sc \end{cases} \qquad \begin{aligned} s(0,x) &= s_0 \\ c(0,x) &= c_0 \end{aligned}$$

Porosity: $\varphi(c) = A + Bc$

R. Guarguaglini and R. Natalini (2005)

Stochastic boundary conditions:

$$
\begin{aligned}
s(t,0) &= \psi(t) \\
d\psi(t) &= \alpha\left(\gamma - \psi(t)\right)dt + \sigma\sqrt{\psi(t)\left(\eta - \psi(t)\right)}dW_t.
\end{aligned}
$$

F. Arceci, M. Maurelli, D. Morale, and S. Ugolini (2023)

A fully stochastic particle model:

$$
\begin{cases}
dX_t^i &= \beta_{H_t^i}\left(\underline{M}_t\right)dt + \epsilon_{H_t^i} dW_t^i, \\
H_t^i &\in \{C, S, G, D\}
\end{cases}
$$

D. Morale, G. Rui, and S. Ugolini (to appear)

The acid particles state:

$$(X_t^i, H_t^i)\ i = 1, \ldots, N \qquad \begin{aligned} X_t^i &: \quad \mathbb{R}_+ \to D \subset \mathbb{R}^d \\ H_t^i &: \quad \mathbb{R}_+ \to \{0 = \text{"alive"}, 1 = \text{"dead"}\} \end{aligned}$$

The empirical measure and density of the active particles:

$$\begin{aligned} \nu_t^N(dx) &:= \frac{1}{N} \sum_{i=1}^{N} \varepsilon_{(X_t^i, H_t^i)} (dx \times \{0\}) \\ u_N(t,x) &:= \left(K * \nu_t^N\right)(x) \qquad K \in L^\infty(D) \text{ Estimating kernel} \end{aligned}$$

Carbonate and Gypsum densities:

$$c(t,x), g(t,x) : \mathbb{R}_+ \times D \to \mathbb{R}_+$$

Stochastic particles in a random continuum environment

$$
\begin{cases}
dX_t^i & = F^i_{\text{part}}(X_t, H_t)dt + F^i_{\text{env}}(X_t^i, c, g)dt + \sigma dW_t^i, \qquad & t \in [0, T_i],\ i \in \{1, \ldots, N\} \\
H_t^i & = H_0^i + \Pi^i \left(\int_0^t \Lambda(X_s^i, H_s^i, c) ds \right), & t \in [0, T] \\
\dfrac{\partial}{\partial t} c(t, x) & = -\lambda\, c(t, x)\, u_N(t, x), & (t, x) \in [0, T] \times D, \\
\dfrac{\partial}{\partial t} g(t, x) & = +\lambda\, c(t, x)\, u_N(t, x), & (t, x) \in [0, T] \times D.
\end{cases}
$$

The reaction counter: a non homogeneous Poisson process

$$\Pi^i(t) \quad = \quad \overline{N}^i \left(\int_0^t \Lambda^i \left(X_s^i, H_s^i, c \right) ds \right)$$

$$\Lambda^i \left(X_t^i, H_t^i, c \right) \quad := \quad \lambda \, c(t, X_t^i) \, 1_0(H_t^i)$$

The reaction time T_i: the first (and only) jump time of $\Pi^i(t)$, or equivalently given a random variable $Z \sim \exp(1)$:

$$T_i = \inf_t \left\{ Z \leq \int_0^t \Lambda^i \left(X_s^i, H_s^i, c \right) ds \right\} .$$

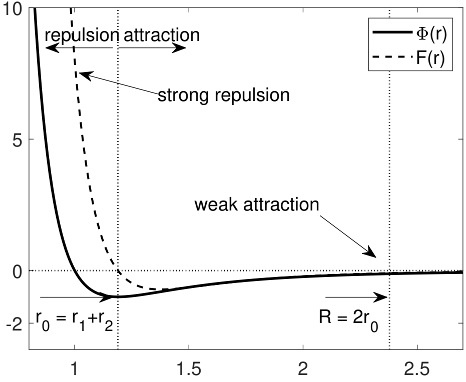
Particle-particle interaction

The Lennard-Jones potential

$$F^i_{\text{part}}(X_t, H_t) = -\sum_{\substack{j:H^j_t=0\\ j\neq i}} \nabla\Phi\left(\left|X^i_t - X^j_t\right|\right)$$

The Lennard Jones potential is strongly repulsive and weakly attractive at close range:

$$\Phi(r) = 4\,\eta\left[\left(\frac{\varsigma}{r}\right)^{4d} - \left(\frac{\varsigma}{r}\right)^{2d}\right]$$



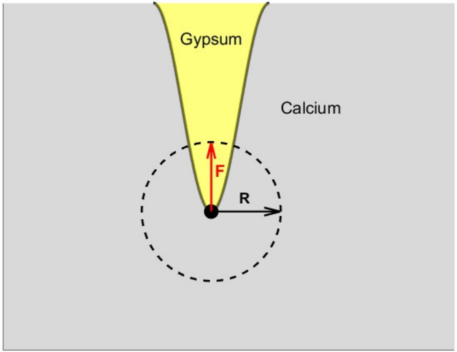
Particle-field interaction

A non local effect of porosity

$$F^i_{\text{env}}(X^i_t, c, g) := \gamma \int_D \frac{y - X^i_t}{|y - X^i_t|} f(|y - X^i_t|,\ c(t,y),\ g(t,y))\, dy\, dt$$

Interaction directed towards a higher concentration of gypsum:

$$f(r, c, g) := \frac{g}{c+g}\, e^{-r}\, 1_{(0,\infty)}(g)\, 1_{(0,R]}(r)$$



Stochastic particles in a random continuum environment

$$
\begin{cases}
dX_t^i & = F^i_{\text{part}}(X_t, H_t)dt + F^i_{\text{env}}(X_t^i, c, g)dt + \sigma dW_t^i, \qquad t \in [0, T_i],\ i \in \{1, \dots, N\} \\
H_t^i & = H_0^i + \Pi^i \left(\int_0^t \Lambda(X_s^i, H_s^i, c) ds \right), \qquad t \in [0, T] \\
\dfrac{\partial}{\partial t} c(t,x) & = -\lambda\, c(t,x)\, u_N(t,x), \qquad (t,x) \in [0,T] \times D, \\
\dfrac{\partial}{\partial t} g(t,x) & = +\lambda\, c(t,x)\, u_N(t,x), \qquad (t,x) \in [0,T] \times D.
\end{cases}
$$

Pairwise interaction - singular drifts

For a wide class of singular drifts well posedness has been proven. Despite that, the regularity required is much higher than the one we have.

The Coulomb potential

J.G. Liu and R. Yang. (2016)

$$\Phi(r) := \frac{C}{r^{d-2}}$$

The Lennard Jones potential

$$\Phi(r) := \frac{A}{r^{4d}} - \frac{B}{r^{2d}}$$

Well Posedness of Lennard-Jones stochastic interacting particles

The system

$$\begin{cases} dX_t^i = \sum_{j\neq i} \nabla\Phi(X_t^i - X_t^j)dt + \sigma dW_t^i & X_t^i \in \Pi^d, t \in [0,T] \\ (X_t^i)_{|t=0} = X_0^i & i = 1, ..., N \end{cases} \tag{1}$$

admits a unique, global, strong solution provided that the initial data are independent and identically distributed, $\mathbb{E}\left[|X_0|^2\right] < \infty$ and almost certainly $|X_0^i - X_0^j| \geq \epsilon > 0 \; \forall i \neq j$. In particular almost surely $X_t^i \neq X_t^j$ for all $t \in [0,T], i \neq j$.

The aim of the proof: Non collision among particles

If there exists two particles X_t^i, X_t^j colliding with each other for some time $t < \infty$, then $F(X_t^i - X_t^j) = \infty$ and the solution to (1) breaks up. We prove that this almost surely does not happen in a finite time.

This is equivalent of asking that given a time horizon $T > 0$

$$\lim_{\epsilon \to 0} \mathbb{P}(\tau_\epsilon \leq T) = 0$$

where

$$\tau_\epsilon := \inf \left\{ t \in [0, 2T] : \min_{i \neq j} |X_t^{i\epsilon} - X_t^{j\epsilon}| < \epsilon \right\}.$$

A regularized problem

$$
\begin{cases}
dX_t^{i\epsilon} = \sum_{j\neq i} F_\epsilon(X_t^{i\epsilon} - X_t^{j\epsilon})dt + \sigma dW_t^i \\
X_0^{i\epsilon} = X_0^i
\end{cases}
$$

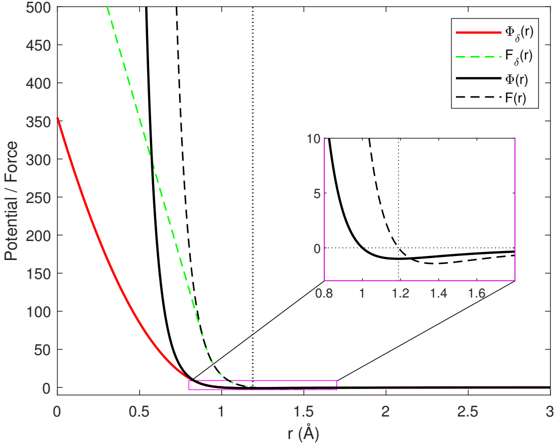
Properties:

1. $F_\epsilon \in \mathcal{C}^1(\mathbb{R}^d)$
2. $F_\epsilon(x) = F(x) \quad \forall |x| \geq \epsilon,$
3. $|F_\epsilon(x)| \leq \min\{\frac{c|x|}{\epsilon^{4d+2}}, |F(x)|\}$
4. $|\nabla \cdot F_\epsilon(x)| \leq \frac{c}{\epsilon^{4d+3}}$
5. $\Phi_\epsilon(x) \underset{\epsilon\to 0^+}{\longrightarrow} +\infty.$

We approximate with the Taylor polinomial at the first order in $[0, \epsilon]$

$$F_\epsilon(r) := \begin{cases} \frac{16\eta d}{\varsigma}\left[\left(\frac{\varsigma}{\epsilon}\right)^{4d+1} - \frac{1}{2}\left(\frac{\varsigma}{\epsilon}\right)^{2d+1}\right]\vec{r} \\ \qquad -\frac{16\eta d}{\varsigma^2}\left[(4d+1)\left(\frac{\varsigma}{\epsilon}\right)^{4d+2} - \frac{2d+1}{2}\left(\frac{\varsigma}{\epsilon}\right)^{2d+2}\right](r-\epsilon)\vec{r}, & r \in [0, \epsilon] \\ \frac{16\eta d}{\varsigma}\left[\left(\frac{\varsigma}{r}\right)^{4d+1} - \frac{1}{2}\left(\frac{\varsigma}{r}\right)^{2d+1}\right]\vec{r}, & r \geq \epsilon. \end{cases}$$

A regularized problem



A more compact notation

We choose a more compact notation for the interactions:

$$
\begin{aligned}
\Phi^{i,j}_{\epsilon,t} &:= \Phi_\epsilon\left(X^{i,\epsilon}_t - X^{j,\epsilon}_t\right) \\
F^{i,j}_{\epsilon,t} &:= F_\epsilon\left(X^{i,\epsilon}_t - X^{j,\epsilon}_t\right) \\
\Phi^{\epsilon}_t &:= \sum_{\substack{i,j=1 \\ i\neq j}}^{N} \Phi^{i,j}_{\epsilon,t\wedge\tau_\epsilon}
\end{aligned}
$$

Applying the Itô formula to the overall interaction Φ_t^ϵ we obtain

$$\Phi_t^\epsilon = \Phi_0 + M_{t\wedge\tau_\epsilon} - 2\int_0^{t\wedge\tau_\epsilon} \sum_{i=1}^{N} \left(\sum_{\substack{j=1 \\ j\neq i}}^{N} F_{\epsilon,s}^{i,j} \right)^2 ds + \frac{\sigma^2}{2} \int_0^{t\wedge\tau_\epsilon} \sum_{\substack{i,j=1 \\ i\neq j}}^{N} \Delta\Phi_{\epsilon,s}^{i,j}\, ds$$

where $M_{t\wedge\tau_\epsilon}$ is the martingale

$$M_{t\wedge\tau_\epsilon} = -\sigma \sum_{\substack{i,j=1 \\ i\neq j}}^{N} \int_0^{t\wedge\tau_\epsilon} F_{\epsilon_s}^{i,j}\,(dW_s^i - dW_s^j).$$

Step 2: some estimates

Lemma 1

Given the Lennard Jones force F defined above, for any triplets of particles i, j, k we have

$$\vec{F}^{\,i,j} \cdot \left(\vec{F}^{\,i,k} - \vec{F}^{\,j,k} \right) \quad \geq \quad -G(i,j,k)$$

where

$$\begin{aligned} G(i,j,k) &= H^2 + \left(F\left(\frac{r_0}{2}\right) + 2H \right) \max\left\{ |\vec{F}^{\,i,j}|, |\vec{F}^{\,i,k}|, |\vec{F}^{\,j,k}| \right\}, \\ F(r_0) &= 0, \\ -H &:= \min_{r>0} F(r). \end{aligned}$$

Lemma 2

Given the Lennard Jones force F defined above, for any $N \geq 2$

$$\sum_{i=1}^{N} \left(\sum_{\substack{j=1 \\ j \neq i}}^{N} F^{\,i,j} \right)^2 \geq \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \left(F^{i,j}\right)^2 - 2 \sum_{1 \leq i < j < k \leq N} G(i,j,k)$$

with $G(i,j,k)$ obtained in Lemma 2.

$$2\sum_i \left(\sum_{j\neq i} F^{i,j}_{\epsilon,t}\right)^2 - \frac{\sigma^2}{2}\sum_{i,j\neq i}\Delta\Phi^{i,j}_{\epsilon,t} \geq -C_N \qquad \forall t \in [0,\tau_\epsilon]$$

where:

$$C_N = 2\binom{N}{2}\left[-I - 2(N-2)\left(F\left(\frac{r_0}{2}\right) + 3H\right)F(r_N)\right],$$

$$F^2(r_N) \geq \frac{\sigma^2}{2}\Delta\Phi(r_N) + 2(N-2)\left[H^2 + \left(2H + F\left(\frac{r_0}{2}\right)\right)F(r_N)\right].$$

Recalling

$$\Phi_t^\epsilon = \Phi_0 + M_{t\wedge\tau_\epsilon} - 2\int_0^{t\wedge\tau_\epsilon} \sum_{i=1}^N \left(\sum_{\substack{j=1 \\ j\neq i}}^N F_{\epsilon,s}^{i,j} \right)^2 ds + \frac{\sigma^2}{2}\int_0^{t\wedge\tau_\epsilon} \sum_{\substack{i,j=1 \\ i\neq j}}^N \Delta\Phi_{\epsilon,s}^{i,j}\, ds,$$

since the minimum of $\Phi(r)$ is $-\epsilon$ we have $\Phi_t^\epsilon \geq -N^2\epsilon$ and obtain the estimates

$$\begin{aligned} \sup_{t\in[0,T]} M_{t\wedge\tau_\epsilon} &\geq \sup_{t\in[0,T]} \Phi_t^\epsilon - \Phi_0 - 2TC_N, \\ \inf_{t\in[0,T]} M_{t\wedge\tau_\epsilon} &\geq -N^2\eta - \Phi_0 - 2C_N T. \end{aligned}$$

$$
\begin{aligned}
\{\tau_\epsilon \le T\} &\subseteq \left\{ \sup_{t\in[0,T]} \Phi^\epsilon_t \ge \Phi^\epsilon_{\tau_\epsilon} \right\} \\
&\subseteq \left\{ \sup_{t\in[0,T]} M_{t\wedge\tau_\epsilon} \ge \Phi^\epsilon_{\tau_\epsilon} - \Phi_0 - 2TC_N \right\} \\
&\subseteq \left\{ \sup_{t\in[0,T]} M_{t\wedge\tau_\epsilon} \ge \Phi(\epsilon) - N^2\eta - \Phi_0 - \overline{C}_N \right\} \\
&\subseteq \left\{ \sup_{t\in[0,T]} M_{t\wedge\tau_\epsilon} \ge \Phi(\epsilon) - \Phi_0 - \overline{C}_N,\ \inf_{t\in[0,T]} M_{t\wedge\tau_\epsilon} \ge -\Phi_0 - \overline{C}_N \right\}.
\end{aligned}
$$

Given $R > 0$ arbitrary,

$$\begin{aligned}
\mathbb{P}\left(\tau_\epsilon \le T\right) &\le \mathbb{P}\left(\sup_{t\in[0,T]} M_{t\wedge\tau_\epsilon} \ge \Phi(\epsilon) - R - \overline{C}_N, \inf_{t\in[0,T]} M_{t\wedge\tau_\epsilon} \ge -R - \overline{C}_N, -R \ge -\Phi_0\right) \\
&\le \mathbb{P}\left(\Phi_0 \ge R\right) + \mathbb{P}\left(\sup_{t\in[0,T]} M_{t\wedge\tau_\epsilon} \ge \Phi(\epsilon) - R - \overline{C}_N, \inf_{t\in[0,T]} M_{t\wedge\tau_\epsilon} \ge -R - \overline{C}_N\right)
\end{aligned}$$

Using Markov inequality:

$$\mathbb{P}\left(\Phi_0 \ge R\right) \le \frac{\mathbb{E}[|\Phi_0|]}{R} \le \frac{C_{\Phi_0}}{R}$$

Step 3: Non collision in finite times

Defining the first hitting times of the martingale $T_\alpha := \inf\{t \geq 0 : M_{t\wedge\tau_\epsilon} = \alpha\}$ the second term in the inequality becomes

$$\begin{aligned} \mathbb{P}\left(\sup_{t\in[0,T]} M_{t\wedge\tau_\epsilon} \geq b-a, \inf_{t\in[0,T]} M_{t\wedge\tau_\epsilon} > -a\right) &\leq \mathbb{P}\left(T_{b-a} \leq T \leq T_{-a}\right) \leq \\ &\leq \mathbb{P}\left(T_{b-a} \leq T_{-a}\right) \end{aligned}$$

Doobs Optional sampling theorem for zero mean martingales tells us that for any $a, b > 0$

$$\mathbb{P}\left(T_{b-a} \leq T_{-a}\right) = \frac{a}{b}$$

Step 3: Non collision in finite times

As a consequence, given $R > 0$ arbitrary,

$$\mathbb{P}(\tau_\epsilon \leq T) \quad \leq \quad \frac{c_{\Phi_0}}{R} + \mathbb{P}\left(\inf_{t\in[0,T]} M_{t\wedge\tau_\epsilon} > -R - \overline{C}_N, \sup_{t\in[0,T]} M_{t\wedge\tau_\epsilon} \geq \Phi_\epsilon(\epsilon) - R - \overline{C}_N \right)$$

$$\downarrow$$

$$\mathbb{P}(\tau_\epsilon \leq T) \overset{Doob}{\leq} \frac{C_{\Phi_0}}{R} + \frac{R + \overline{C}_N}{\Phi(\epsilon)} \xrightarrow[\epsilon\to 0^+]{} 0, \qquad \text{if we choose } R = \sqrt{\Phi(\epsilon)}$$

$$\boxed{\Longrightarrow \exists \epsilon_0 > 0 : \quad \forall \epsilon < \epsilon_0 \quad \tau_\epsilon > T \quad \text{a.s.}}$$

The solution to the regularized problem:

$$X_t^{i\epsilon}(\omega) = X_0^i(\omega) + \sum_{j\neq i} \int_0^t F_\epsilon\left(X_s^{i\epsilon} - X_s^{j\epsilon}\right) ds + \sigma W_t^i \qquad \forall t \in [0,T].$$

Step 4: convergence to a solution of the original system

The solution to the regularized problem:

$$X_t^{i\epsilon}(\omega) = X_0^i(\omega) + \sum_{j\neq i} \int_0^t F_{\cancel{\epsilon}}\left(X_s^{i\epsilon} - X_s^{j\epsilon}\right) ds + \sigma W_t^i \qquad \forall t \in [0, T].$$

The solution is unique, thus:

$$X_t^{i,\epsilon}(\omega) \equiv X_t^{i,\epsilon_0}(\omega) \quad \forall \epsilon \leq \epsilon_0$$

and the limit is well defined:

$$X_t^i := \lim_{\epsilon \to 0} X_t^{i,\epsilon}$$

Theorem (Well posedness under more general singular drifts.)

The system

$$\begin{cases} dX_t^i = \sum_{j\neq i} \nabla\Phi(X_t^i - X_t^j)dt + \mu(X_t^i)dt + \sigma dW_t^i \\ (X_t^i)_{|t=0} = X_0^i \end{cases} \tag{2}$$

admits a unique global strong solution and in particular almost surely $X_t^i \neq X_t^j$ *for all* $t \in [0, T], i \neq j$ *for any* $\Phi(r) = \frac{A}{r^\alpha} - \frac{B}{r^\beta}$, $\alpha > \beta \geq 0$ *and* $\mu : \mathbb{R}^d \to \mathbb{R}^d$ *is bounded, and regular enough that the regularized system*

$$\begin{cases} dX_t^{i,\epsilon} = \sum_{j\neq i} F_{\epsilon,t}^{i,j} dt + \mu(X_t^{\epsilon,i})dt + \sigma dW_t^i \\ (X_t^{\epsilon,i})_{|t=0} = X_0^i \end{cases} \tag{3}$$

admits a unique global strong solution, provided that the initial data is i.i.d. with finite second moment $\mathbb{E}\left[|X_0|^2\right] < \infty$ *and such that* $|X_0^i - X_0^j| \geq \delta > 0 \; \forall i \neq j$ *a.s..*

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5 Numerical experiments

Evolution of the total mass of calcium and gypsum

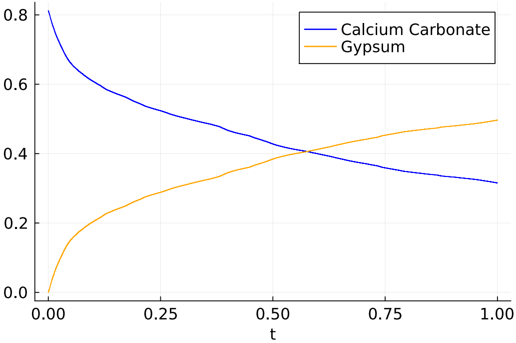


Figure: The total mass of calcium carbonate and gypsum, computed as the spatial integral on the domain. The relative unevenness of the curves comes from the coupling with the stochastic concentration of the acid.

Case study 1

5 Numerical experiments

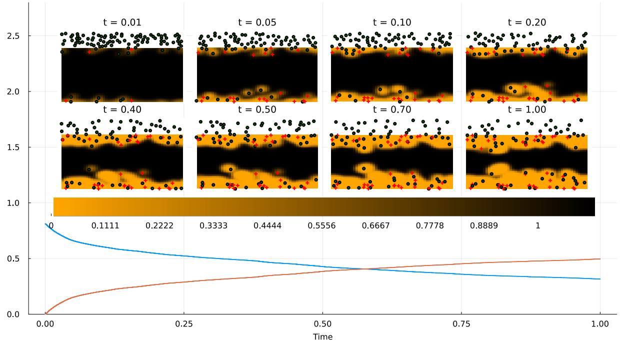
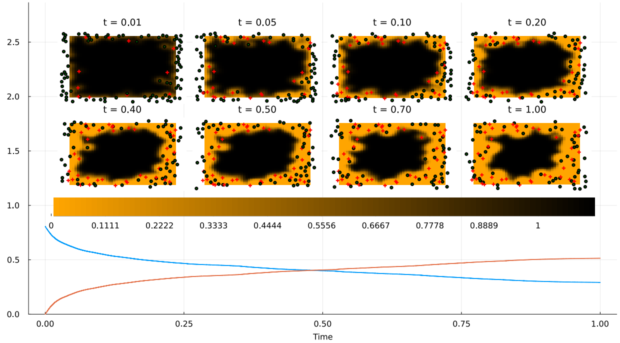


Figure: (Top) Evolution of the system at specific times: spatial gypsum (orange) and calcium (black) densities; active (green circle) and reacted (red cross) sulfuric acid particles locations. (Bottom) Temporal evolution of the total mass mass of gypsum and calcium carbonate.

Case study 2

5 Numerical experiments



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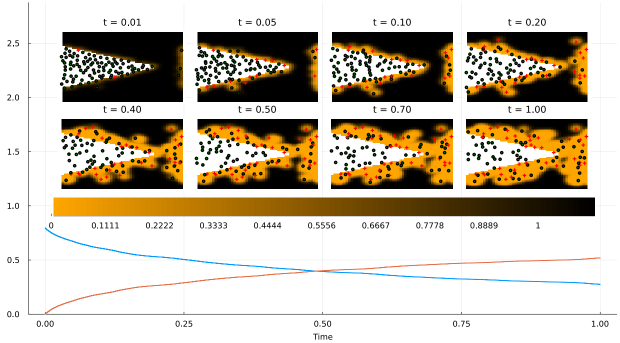

Figure: (Top) Evolution of the system at specific times: spatial gypsum (orange) and calcium (black) densities; active (green circle) and reacted (red cross) sulfuric acid particles locations. (Bottom) Temporal evolution of the total mass mass of gypsum and calcium carbonate.

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6 Future Research

- Exploring the mean-field limit as $N \to \infty$,
- Investigating a possible homogenization of the system,
- Studying the application to more general reactions.

Thank you!

Essential Bibliography

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