Stochastic interacting particles with strongly singular repulsion and killing coupled to a continuum environment

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joint work with

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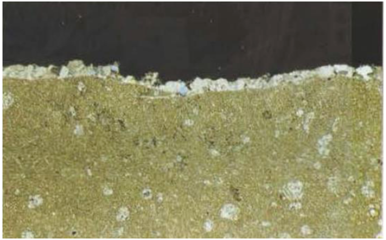
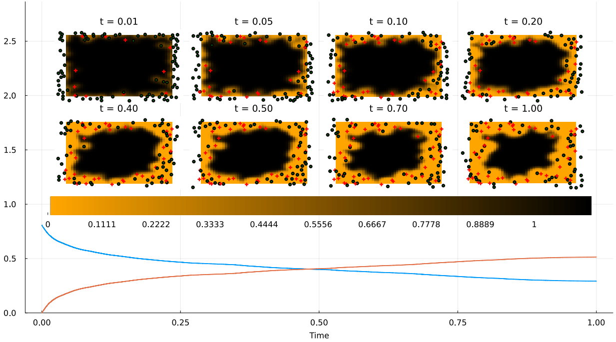
The chemical reaction

1 The problem

calcium carbonate, sulfuric acid, gypsum

$$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2$$





The model

The acid particles state: $(X_t^i, H_t^i)_{i=1,\cdots,N}$ $\quad X_t^i : \quad \mathbb{R}_+ \to D \subset \mathbb{R}^d$

$H_t^i : \quad \mathbb{R}_+ \to \{0 = \text{"alive"},\ 1 = \text{"dead"}\}$

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

Let $t \in [0,T], x \in D \subseteq \mathbb{R}^d$.

$$\begin{cases} dX_t^i &= 1_0(H_t^i)\ \left(F_{\text{part}}^i(X_t, H_t)dt + F_{\text{env}}^i(X_t^i, c, g)dt + \sigma dW_t^i\right), \\ H_t^i &= H_0^i + \int_0^t d\Pi^i(s), \qquad \Pi^i \text{ Poisson with intensity } \Lambda(X_s^i, H_s^i, c) \\ \frac{\partial}{\partial t} c(t,x) &= -\lambda\, c(t,x)\, K * \nu_t^N(x), \qquad K \textit{ Smooth kernel} \\ \frac{\partial}{\partial t} g(t,x) &= +\lambda\, c(t,x)\, K * \nu_t^N(x). \end{cases}$$

A hybrid model of sulphation reactions: stochastic particles in a random continuum environment
N. Jävergård, D. Morale, G. Rui, A. Muntean, S. Ugolini, arXiv:2503.01856, 2025

The model

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

Particle interaction: $F^i_{\text{part}}(X_t, H_t) = -\sum_{j\neq i} \nabla\Phi\left(|X_t^i - X_t^j|\right)\, 1_0(H_t^j)$

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

Lennard-Jones type potential

Environment interaction:

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

F. Flandoli, M. Leocata (2019)

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

Well Posedness of Lennard-Jones stochastic interacting particles

The system

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

$$\Phi(r) := \frac{A}{r^\alpha} - \frac{B}{r^\beta}, \qquad \alpha > \beta \geq 0$$

admits a unique, global, strong solution provided that the initial data satisfies:

$$\mathbb{E}\left[|X_0^i|^2\right] < \infty, \qquad \mathbb{E}\Big[\sum_{i\neq j} \Big|\nabla\Phi(X_0^i - X_0^j)\Big|\Big] < \infty.$$

The hypotheses ensuring the second condition depend on the singularity exponent α. When $\alpha < d$, it holds under i.i.d. initial data with $\rho \in L^p$, where $p = \frac{2d}{d-\alpha}$, by the Hardy–Littlewood–Sobolev inequality. For $\alpha \geq d$, structured initial laws (e.g., Gibbs or hard-core) are required.

The aim of the proof: Non collision among particles

J.G. Liu and R. Yang. (2016)
Repulsive potential of order $\alpha = d - 2$.

Idea of the proof:

- construct a regularized problem, modifying the potential in a small interval $[0, \epsilon]$
- define *collision times*

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

- prove that given any finite time horizon T the probability of collision in finite times vanishes in the limit

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

The main step

We apply Itô formula to the total interaction among particles

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

and obtain estimates on the *sup*, *inf* of the martingale $M_{t\wedge\tau_\epsilon}$:

$$\sup_{t\in[0,T]} M_{t\wedge\tau_\epsilon} \geq \sup_{t\in[0,T]} \Phi_t^\epsilon - \Phi_0 - 2TC_N,$$

$$\inf_{t\in[0,T]} M_{t\wedge\tau_\epsilon} \geq -N^2\eta - \Phi_0 - 2TC_N.$$

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

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

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.

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

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

$$\mathbb{P}(\tau_\epsilon \le T) \overset{Markov,Doob}{\le} \frac{C_{\Phi_0}}{R} + \frac{R + \overline{C}_N}{\Phi(\epsilon)} \underset{\epsilon\to 0^+}{\longrightarrow} 0, \qquad \text{choosing } R = \sqrt{\Phi(\epsilon)}$$

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

Let us introduce the solution to the regularized problem:

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

Convergence to a solution of the original system

Let us introduce the solution to the regularized problem:

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

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:

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

□

Let $\rho_N(t)$ be the joint law of N particles, and $\rho(t)$ the one-particle law. We say that *propagation of chaos* holds if:

$$\forall\, k \in \mathbb{N}, \quad \rho_N^{(k)}(t, x_1, h_1, \dots, x_k, h_k) \xrightarrow[N\to\infty]{} \prod_{i=1}^{k} \rho(t, x_i, h_i)$$

The *relative entropy*

$$\mathcal{H}_N(t) := \frac{1}{N} \int_{\Pi^N} \rho_N(t) \log\left(\frac{\rho_N(t)}{\rho^{\otimes N}(t)}\right)$$

quantifies the deviation of ρ_N from the product law $\rho^{\otimes N}$.

Goal: Show that for suitable initial data and under regularity conditions on $\rho_N(t), \rho(t)$,

$$\lim_{N\to\infty} \mathcal{H}_N(t) = 0 \quad \forall\, t \in [0, T],$$

which implies propagation of chaos in the strong sense.

Why use relative entropy?

- Robust to random type changes,

T.S. Lim, Y. Lu and J.H. Nolen (2020)
"Quantitative Propagation of Chaos in the bimolecular chemical reaction-diffusion model."

- Compatible with the nonlinear Fokker–Planck structure of the limit equation,
- Provides strong convergence in law (e.g., via Csiszár–Kullback–Pinsker inequality).

Limitations of the method:

- Requires regularity and positivity of both ρ_N and ρ, meaning we must work on compact domains (e.g., $\mathbb{T}^d$) or add confining potentials.
- The interaction potential Φ must be sufficiently smooth.
- Not robust to history-dependent dynamics or delay terms.

In this analysis, we treat $c(t,x)$ and $g(t,x)$ as given to avoid feedback complications.

Context and related work

This work contributes to an active research direction aiming to introduce stochasticity into the modeling of sulphation reactions, extending classical PDE models.

Previous work:

- Deterministic PDE model for marble sulphation via porous media diffusion

  Natalini et al. (2001-2023)

- Introduction of stochastic boundary conditions for random pollutant input

  M. Maurelli, D. Morale and S. Ugolini, SPA (2025)
  "Well-posedness of a reaction–diffusion model with stochastic dynamical boundary conditions"
  F. Arceci, D. Morale, and S. Ugolini, (2024)
  "A numerical study of a PDE-ODE system with a stochastic dynamical boundary condition: a nonlinear model for sulphation phenomenon"

- A fully stochastic microscopic model

  D. Morale, G. Rui, and S. Ugolini (2025)
  "A stochastic interacting particle model for the marble sulphation process"

- Probabilistic interpretation of the deterministic PDEs

  Morale, D. and Tarquini, L. and Ugolini, S. (2024)
  "A probabilistic interpretation of a non-conservative and path-dependent nonlinear reaction-diffusion system for the marble sulphation in Cultural Heritage"

Thank you!

Essential Bibliography

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[2] F. Flandoli and M. Leocata. “A particle system approach to aggregation phenomena”. In: *Journal of Applied Probability* (2019).

[3] F.R. Guarguaglini and R. Natalini. “Global existence of solutions to a nonlinear model of sulphation phenomena in calcium carbonate stones”. In: *Nonlinear Analysis: Real World Applications* (2005).

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Strategy and Main Result

Step 1: Derive entropy production estimate

$$\partial_t \mathcal{H}_N(t) \le C(t)\, \mathcal{H}_N(t) + \frac{C(t)}{N}$$

where $C(t)$ depends on norms of $\rho(t)$, $\nabla \log \rho$, and coefficients.

Step 2: Grönwall inequality yields

$$\mathcal{H}_N(t) \le \left(\mathcal{H}_N(0) + \frac{1}{N} \right) \exp\left(\int_0^t C(s)\, ds \right)$$

Conclusion:

$$\mathcal{H}_N(0) \to 0 \quad \Rightarrow \quad \mathcal{H}_N(t) \to 0 \quad \Rightarrow \quad \text{Propagation of Chaos holds.}$$

This provides a quantitative, non-asymptotic route to chaos.