ICFP M2 Internship Defence

Probabilistic Approach to Diffusion-Mediated Surface Phenomena

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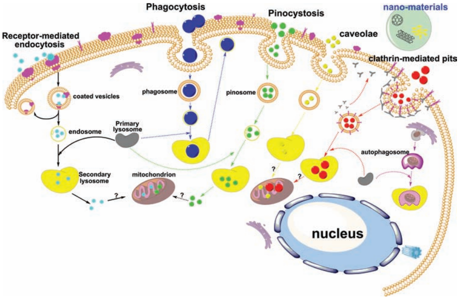
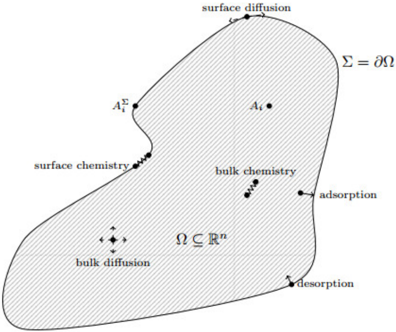
July 5, 2023

Motivation





B. Augner, and D. Bothe. arXiv:1911.13030, **2019**
F. Zhao, et al. *Small*, **2011**, *7*(10), 1322-1337

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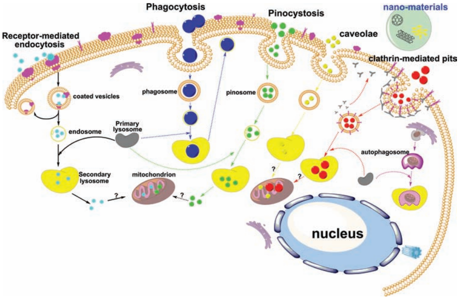
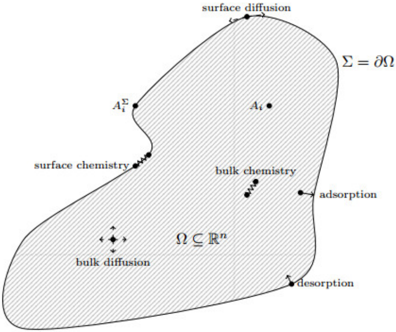
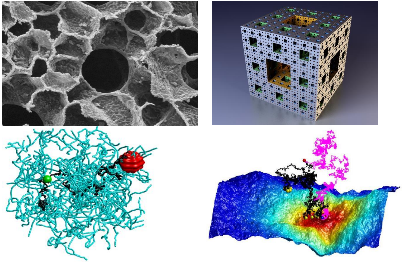




How does the complicated environment affect diffusion-mediated surface phenomena?

B. Augner, and D. Bothe. arXiv:1911.13030, **2019**
F. Zhao, et al. *Small*, **2011**, *7*(10), 1322-1337

Aims



- ⋆ **Efficient numerical implementation of the "encounter-based approach" in complex media**.
- ◦ Understanding of respective roles of complex environment and various surface reaction mechanisms.
- ◦ Identifying experimental settings for comparisons.
- ◦ New applications of this approach in chemistry and biology.

Content

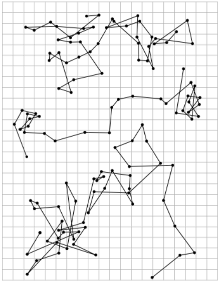
- **Introduction**
- **Theoretical Background**
  $\rightarrow$ Diffusion, Complex environment, Boundary local time
- **Numerical Simulations**
  $\rightarrow$ Harmonic measure, Spread harmonic measure
- **Conclusion & Perspectives**

Diffusion process

Consider the random trajectory $\mathbf{x}_t$ of a particle with external force $\mathbf{F}(\mathbf{x})$ at temperature T:

$$\mathrm{d}\mathbf{x}_t = \frac{D}{k_\mathrm{B} T}\mathbf{F}(\mathbf{x}_t)\mathrm{d}t + \sqrt{2D}\mathrm{d}\mathbf{W}_t \tag{1}$$

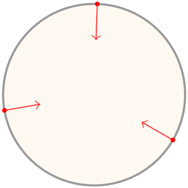
where $\mathbf{W}_t$ is a standard Brownian motion, D is the diffusion coefficient, and $k_\mathrm{B} T$ represents thermal energy of the bath.



$\mathbf{F}(\mathbf{x})$ should be non-zero only near the boundary, forcing the particle to move away from the boundary back to the interior, like

$$\frac{\mathbf{F}(\mathbf{x})}{k_\mathrm{B} T} = \frac{1}{\varepsilon}\mathbf{n}(\mathbf{x})\mathbb{I}_{\partial\Omega_\varepsilon}(\mathbf{x}) \tag{2}$$

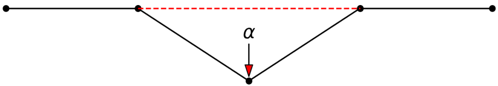
where $\mathbf{n}(\mathbf{x})$ is the normal vector to the boundary $\partial\Omega$, and $\partial\Omega_\varepsilon$ refers to the boundary layer of width ε, inside which the force $\mathbf{F}(\mathbf{x})$ acts.



J. Perrin, in *Atoms*, London: Constable **1914**, pp. 115.

Koch snowflakes

Given a segment with length L, we insert three points with angle $\alpha \in (0, \pi)$:



Parameters:
Polygon shape _ Angle α, Direction (concave $+$, convex $-$), Level of generation g.

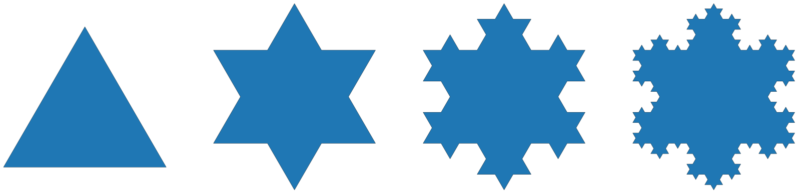
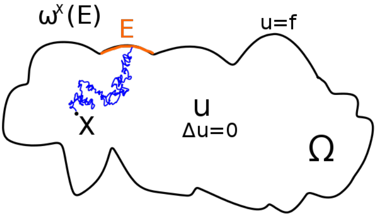


Figure: Koch snowflakes $3\_\pi/3 - g$

Harmonic measure

Let Ω be a bounded open domain in n-dimensional Euclidean space $\mathbb{R}^n$, $n \geq 2$, and let $\partial\Omega$ denote the boundary of Ω. Any continuous function $f : \partial\Omega \to \mathbb{R}$ determines a unique harmonic function u that solves the Dirichlet problem:

$$\begin{cases} \Delta u(x) = 0, & x \in \Omega \\ u(x) = f(x), & x \in \partial\Omega \end{cases}$$

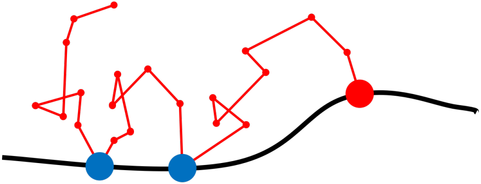


If a point $x \in \Omega$ is fixed, $u(x)$ determines a measure $\omega^x(E)$ on $\partial\Omega$ by

$$\begin{cases} \Delta \omega^x(E) = 0, & x \in \Omega \\ \omega^x(E) = \mathbb{I}_E(x), & x \in \partial\Omega \end{cases} \qquad \mathbb{I}_E(x) = \begin{cases} 1, & x \in E \\ 0, & 0 \notin E \end{cases}$$

The measure $\omega^x(E)$ is called the **harmonic measure**.

Reactivity & Boundary local time



- **Local time** ℓ_t characterizes the number of encounters with the boundary.
- Surface reaction occurs when ℓ_t exceeds a random threshold $\hat{\ell}$ characterized by $\Psi(\ell) = \mathbb{P}\left\{\ell < \hat{\ell}\right\}$:
  - ⋆ standard surface reactions with constant reactivity q: $\Psi(\ell) = e^{-q\ell}$;
  - ⋆ various surface reactions (activation, passivation, etc): **arbitrary** $\Psi(\ell)$;
- This approach was only applied in simple confinements like sphere.

D. S. Grebenkov, *Phys. Rev. Lett.*, **2020**, *125*, 078102

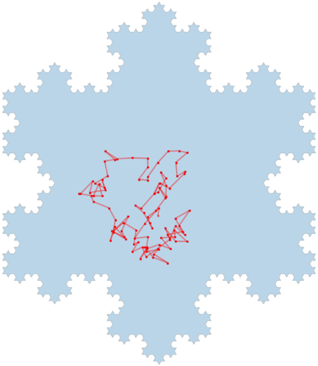
Brownian motion as Markov-chain Monte Carlo

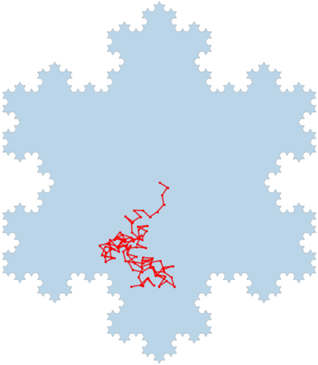
$$\delta = 2D\Delta t = \text{constant}$$

$$\Delta x_i,\ \Delta y_i = \mathcal{N}(0,\delta)$$

$$r = \text{constant},\ \theta_i = \text{ran}(0, 2\pi)$$

$$\Delta x_i = r\cos\theta_i, \qquad \Delta y_i = r\sin\theta_i$$

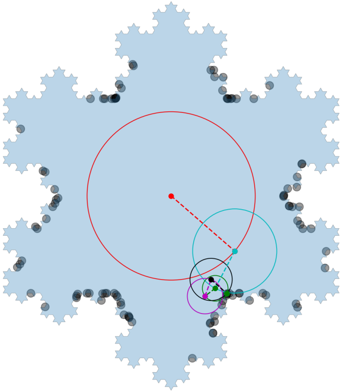




NOT efficient for precise results if $r \ll l_g = L/3^g$.

Geometry-adapted fast random walk (GAFRW)

$$r_i \neq \text{constant}, \qquad \theta_i = \text{ran}(0, 2\pi)$$

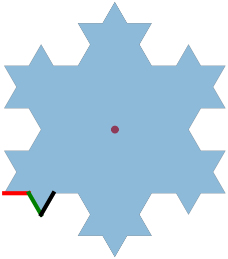


- Calculate distances between the particle and boundary segments at each step.
- Determine the radius as the minimum one of all distances.
- Jump uniformly towards a new position.
- Repeat this process until the particle is attached on the boundary.

⋆ Improvement:
Only search among relevant intervals.

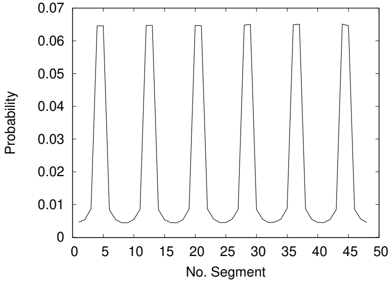
M. E. Muller, *Ann. Math. Statist.*, **1956**, *27*, 569-589
D. S. Grebenkov, et al. *Phys. Rev. E*, **2005**, *71*(5), 056121

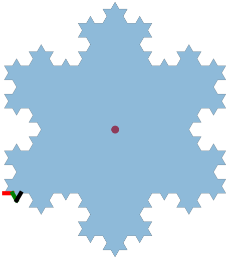
Hitting probability distribution

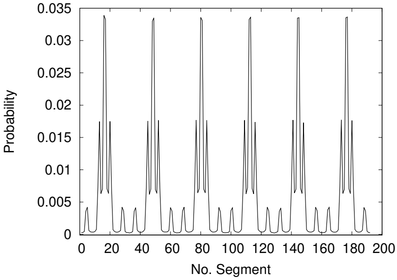


No. Segment

- 1st: Red
- 2nd: Green
- 3rd: Black
- ⋆ Anti-clockwise







After the first arrival ...

There are three relevant choices to stop our numerical simulations:

- Stop the simulation after a given time T.
- Stop the simulation after a random time δ, such that $\mathbb{P}(\delta > t) = e^{-pt}$, where t is time passed for diffusion.
- Stop the simulation when the boundary local time ℓ_t exceeds a random threshold $\hat{\ell}$.

After the first arrival ...

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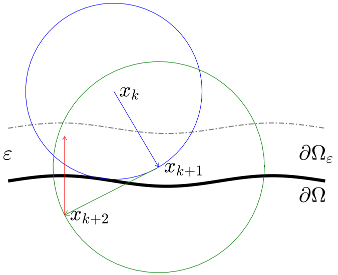
- Stop the simulation when the boundary local time ℓ_t exceeds a random threshold $\hat{\ell}$.

We focus on the third choice and take the threshold $\hat{\ell}$ with the probability:

$$\mathbb{P}\{\ell < \hat{\ell}\} = e^{-q\ell}$$

where q is the reactivity parameter. In practice, we can generate the threshold $\hat{\ell}$ as $\hat{\ell} = -\ln[\mathrm{ran}(0,1)]/q$.

Encounter-based reflection



$$\vec{x}_{k+1} = \vec{x}_k + \rho_k(\cos\theta_k, \sin\theta_k)$$

$$\langle\tau_k\rangle = \frac{\rho_k^2}{4D}$$

$$t_{k+1} = t_k + \langle\tau_k\rangle$$

$$\ell_{t_{k+1}} = \ell_{t_k} + \sqrt{\frac{\pi}{2}\cdot D\cdot\langle\tau_k\rangle}\cdot\mathbb{I}_{\partial\Omega_\varepsilon}\cdot\mathbb{I}_{N_{\mathrm{touch}}>0}$$

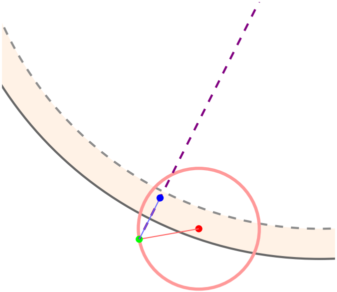
- Fix a radius ρ_k to be a constant ρ, e.g. a value proportional to the boundary layer thickness ε.
- Execute a uniform jump on the circle with this given radius ρ towards a new position.
- Once the new position is out of the domain, we **reflect** this position with boundary $\partial\Omega$ for another location inside the domain.
- Repeat this procedure until the particle exit the boundary layer $\partial\Omega$, then we take standard GAFRW.

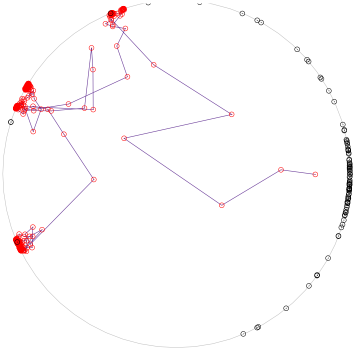
Y. Zhou, et al. *Commun. Math. Sci.*, **2017**, *15*(1), 237-259

Verification on circle

We take a simple domain, a circle with radius $R = 1$, and we put each particle at $(r_0, 0)$ initially. For a disk, the spread harmonic measure density is known explicitly, and one can compute the hitting probability of any arc.

$$p_k = \frac{1}{N} + \sum_{j=1}^{\infty} \frac{2qr_0^j}{\pi j(j+q)} \sin\left(\frac{\pi j}{N}\right) \cos\left(\frac{2\pi j}{N}(k - \frac{1}{2})\right) \tag{15}$$

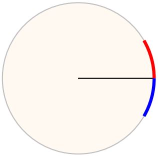




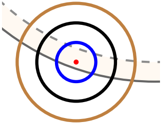
D. S. Grebenkov, *Phys. Rev. E*, **2015**, *91*(5), 052108

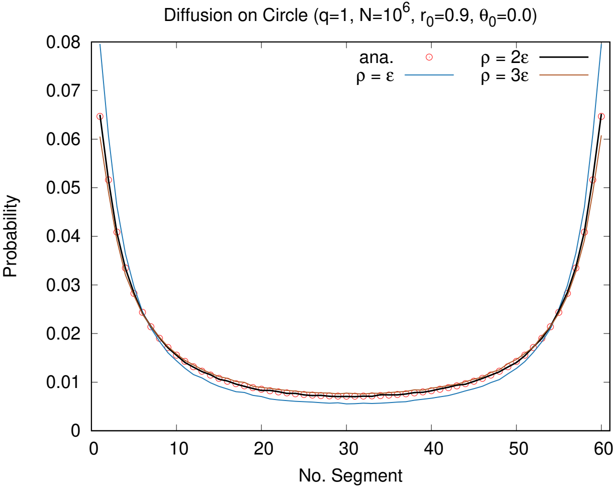
Choice of $\rho \propto \varepsilon$

Anti-clockwise
k-th segment
$\in \frac{2\pi}{N}(k-1, k)$

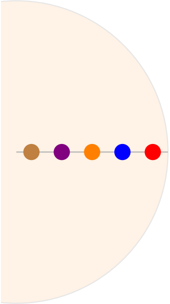


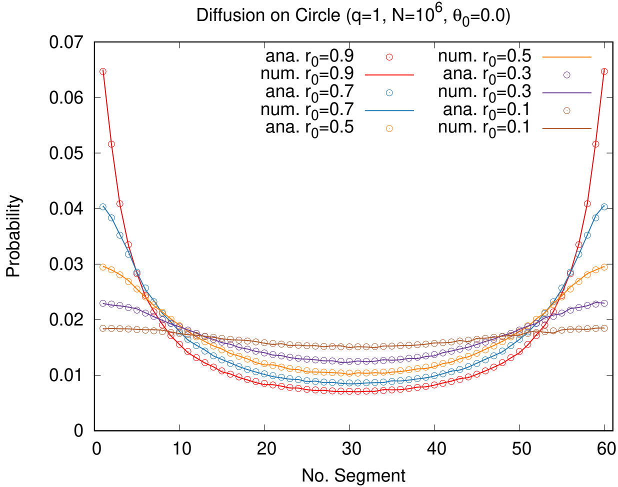
We should
select $\rho = 2\varepsilon$!



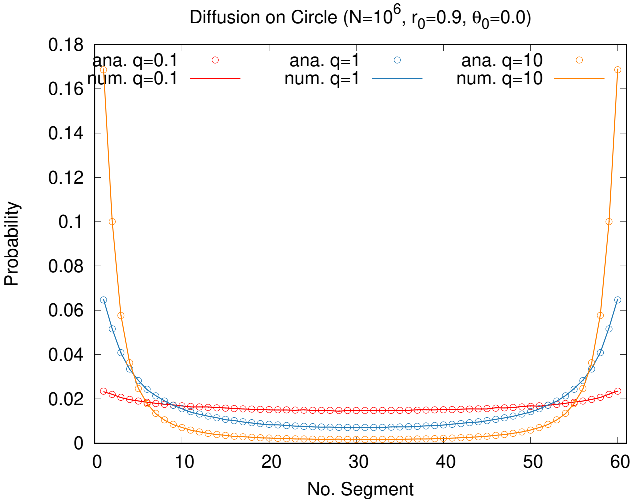


Effects of initial positions r_0





Effects of reactivity parameter q



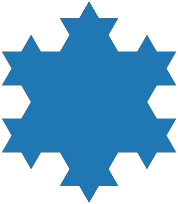
Practice on Koch snowflake

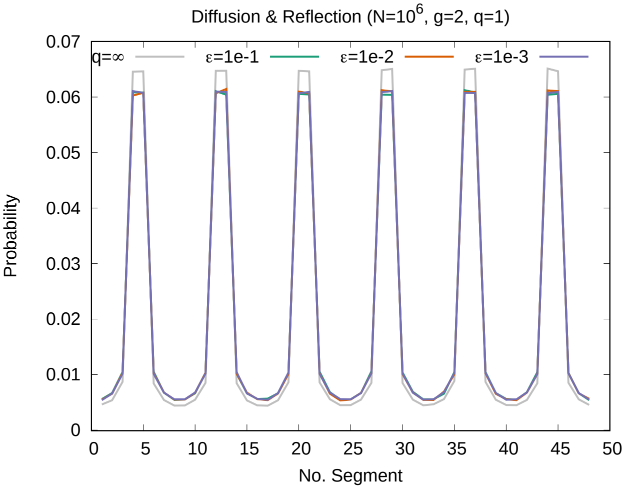
Large domain

$3\_\pi/3 - 2$

$L = 10^3$

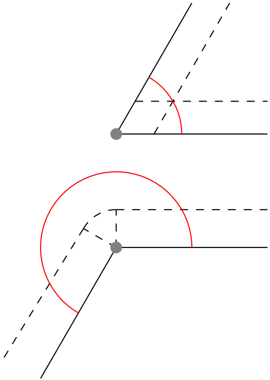
$q = 1$



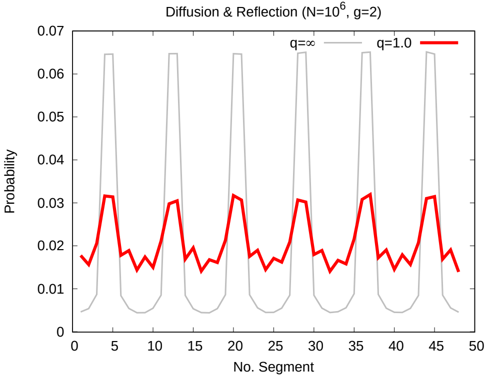


Practice on Koch snowflake

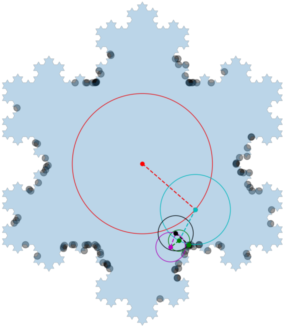
Probably **trapped** in the corner?
Jump uniformly from the corner.

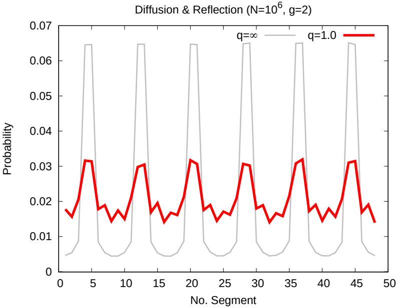


Small domain, $L = 2$.
$3\_\pi/3 - g$, $q = 1$



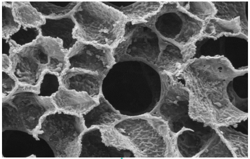
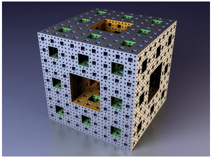
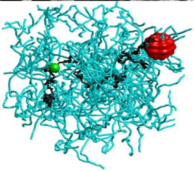
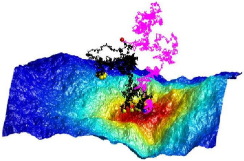
Conclusion & Perspectives





- Realize GAFRW in Koch snowflakes ($3\_\pi/3 - g$) for harmonic measure.
- Realize "Encounter-based reflection" for spread harmonic measure.
- ◦ Step further towards other complex boundaries, like $\alpha \neq \pi/3$, or even in 3D.
- ◦ Look forward to comparisons with experiment.

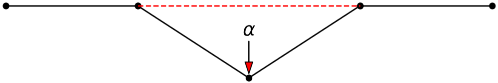
Probabilistic Approach to Diffusion-Mediated Surface Phenomena

Thanks for your attention!

Complex boundary - Koch snowflakes

Given a segment with length L, we insert three points with angle $\alpha \in (0, \pi)$:



Four black segments have the same length l, red dashed line for d, we have

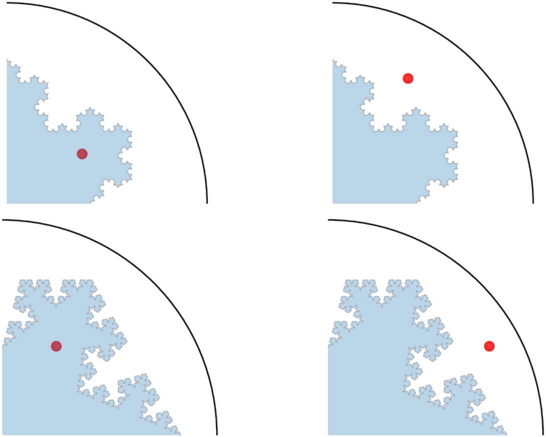
$$\begin{cases} d^2 = l^2 + l^2 - 2l^2 \cos \alpha \\ d + 2l = L \end{cases} \tag{3}$$

and thus the solution reads:

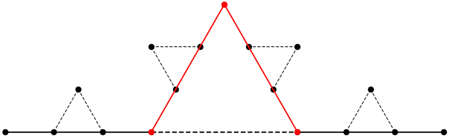
$$\begin{cases} l = \dfrac{L}{\sqrt{2(1 - \cos \alpha)} + 2} \\ d = \dfrac{\sqrt{2(1 - \cos \alpha)}L}{\sqrt{2(1 - \cos \alpha)} + 2} \end{cases} \tag{4}$$

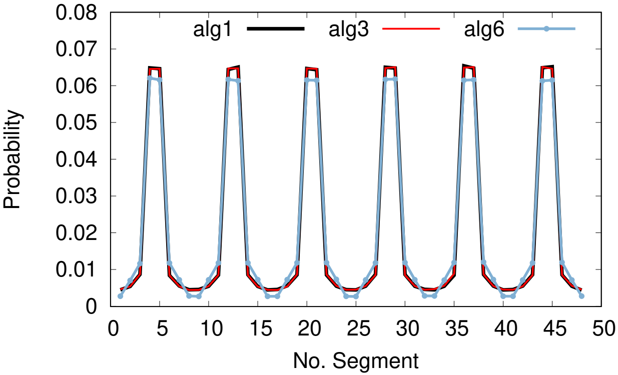
Diffusion region

We only consider the first case: particles inside the convex boundary.



Comparison of different algorithms





- Alg 1.
  Whole space searching.
- Alg 3.
  Partial space searching.
- Alg 6.
  Generation-wise diffusion.

Dirichlet problem

In mathematics, a Dirichlet problem is the problem of finding a function which solves a specified partial differential equation (PDE) in the interior of a given region that takes prescribed values on the boundary of the region.

The Dirichlet problem can be solved for many PDEs, although originally it was posed for Laplace's equation. In that case the problem can be stated as follows:

> *Given a function f that has values everywhere on the boundary of a region in $\mathbb{R}^n$, is there a unique continuous function u twice continuously differentiable in the interior and continuous on the boundary, such that u is harmonic in the interior and $u = f$ on the boundary?*

This requirement is called the Dirichlet boundary condition. The main issue is to prove the existence of a solution; uniqueness can be proved using the maximum principle.

Harmonic function

In mathematics, mathematical physics and the theory of stochastic processes, a **harmonic function** is a twice continuously differentiable function $f : U \to \mathbb{R}$, where U is an open subset of $\mathbb{R}^n$, that satisfies Laplace's equation, that is,

$$\frac{\partial^2 f}{\partial x_1^2} + \frac{\partial^2 f}{\partial x_2^2} + \cdots \frac{\partial^2 f}{\partial x_n^2} = 0$$

everywhere on U. This is usually written as

$$\nabla^2 f = 0 \qquad \text{or} \qquad \Delta f = 0$$

Boundary local time

$$\mathrm{d}\mathbf{X}_t = \frac{D}{k_\mathrm{B} T}\mathbf{F}(\mathbf{X}_t)\mathrm{d}t + \sqrt{2D}\mathrm{d}\mathbf{W}_t$$

$\mathbf{F}(\mathbf{X})$ should be zero inside Ω, except for a very thin boundary layer of width a, in which $\mathbf{F}(\mathbf{X})$ should force the particle to move away from the boundary back to the interior.

$$\frac{\mathbf{F}(\mathbf{X})}{k_\mathrm{B} T} = \frac{1}{a}\mathbf{n}(\mathbf{X})\mathbb{I}_{\partial\Omega_a}(\mathbf{X})$$

$$\ell_t^a = \frac{D}{a}\int_0^t \mathrm{d}t' \mathbb{I}_{\partial\Omega_a}(\mathbf{X}_{t'})$$

Langevin equation takes the form

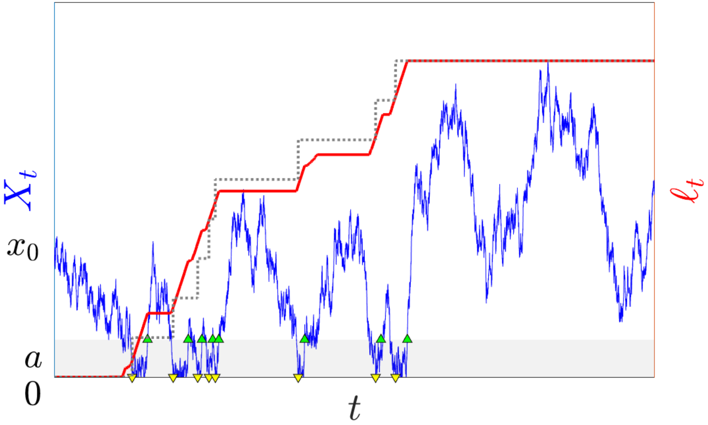
$$\mathrm{d}\mathbf{X}_t = \mathbf{n}(\mathbf{X})\mathrm{d}\ell_t^a + \sqrt{2D}\mathrm{d}\mathbf{W}_t$$

$\frac{a}{D}\ell_t^a$ is the residence time inside the boundary layer $\partial\Omega_a$ up to time t.

$$\ell_t = \lim_{a\to 0} \ell_t^a$$

The boundary local time ℓ_t can also be related to the number $\mathcal{N}_t^a$ of crossings of the boundary layer $\partial\Omega_a$.

$$\ell_t = \lim_{a\to 0} a\mathcal{N}_t^a$$



D. S. Grebenkov, *Phys. Rev. Lett.*, **2020**, *125*, 078102

Reactivity q

On the partially reactive region $\partial\Omega_R$

$$-D\partial_n c(\mathbf{x}, t) = \kappa_0 c(\mathbf{x}, t)$$

where D is the diffusion coefficient of particles, ∂_n is the normal derivative on the boundary oriented outwards the confining domain, and κ_0 is the reactivity of the region.
If the particle attempts to react independently on each encounter with probability

$$p \simeq a\kappa_0/D \ll 1$$

the probability of no surface reaction up to the n-th encounter is

$$1 - \sum_{k=1}^{n} p(1-p)^{k-1} = (1-p)^n \simeq e^{-pn} \simeq e^{-q\ell}$$

where $q = \kappa_0/D$, $\ell = na$; a is a small width of the reactive layer. Thus we write

$$\Psi(\ell) = \mathbb{P}\left\{\ell < \hat{\ell}\right\} = \int_{\ell}^{\infty} \mathrm{d}\ell' \psi(\ell') = e^{-q\ell}$$

D. S. Grebenkov, *J. Chem. Phys.*, **2023**, *158*(21), 214111

Random threshold $\hat{\ell}$

For the continuous distribution $\pi(x)$, we have the cumulative distribution as:

$$\Pi(x) = \Pi(x - \mathrm{d}x) + \pi(x)\mathrm{d}x = \int_{-\infty}^{x} \pi(x)\mathrm{d}x \tag{A1}$$

Working with normalized $\pi(x)$, the possible value of Π, which we call Υ, is a uniform distribution on (0,1). Let Π^{-1} be the inverse function of Π, then the random number $x = \Pi^{-1}(\Upsilon)$ is distributed as $\pi(x)$. The tricky step is usually to find Π^{-1}.

In our case, the local time threshold is a function of reactivity q, with the distribution as $\psi(\ell) = qe^{-q\ell}$, then we compute the cumulative distribution

$$\Pi(\ell) = \int_{0}^{\ell} \psi(x)\mathrm{d}x = 1 - e^{-q\ell} = \Upsilon = \mathrm{ran}(0,1) \tag{A2}$$

Then $\ell = \Pi^{-1}(\Upsilon) = -\ln(1-\Upsilon)/q$. Since both Υ and $1-\Upsilon$ are ran(0,1), we have the random threshold as

$$\hat{\ell} = -q \ln\left[\mathrm{ran}(0,1)\right] \tag{A3}$$

Spread harmonic measure on circle

Inside a disk of radius R and center at origin, we consider a particle with initial position (r_0, θ_0) and its diffusion. Define the probability density ω_q such that a particle is attached on the circle (R, θ) finally:

$$\omega_q(\theta|r_0,\theta_0) = \frac{1}{2\pi R} \times \left\{ 1 + 2\sum_{j=1}^{\infty} \left(\frac{r_0}{R}\right)^j \frac{\cos\left[j(\theta-\theta_0)\right]}{1+\frac{j}{qR}} \right\} \tag{A4}$$

There is no segment for continuous θ, so we divide the circle into N arcs in numerical practice, such that $\theta \in [k-1, k] \times \frac{2\pi}{N}$, with $k = 1, 2, 3, ..., N$. The hitting probability p_k on k-th segment is thus expressed as the integration of density ω_q:

$$\begin{aligned} p_k &= R \times \int_{\frac{2\pi}{N}(k-1)}^{\frac{2\pi}{N}k} \omega_q(\theta|r_0,\theta_0)\mathrm{d}\theta \\ &= N + \sum_{j=1}^{\infty} \frac{2qR}{\pi j(j+qR)} \left(\frac{r_0}{R}\right)^j \sin\left(\frac{\pi j}{N}\right) \cos\left[j\left(\frac{2\pi}{N}(k-\frac{1}{2}) - \theta_0\right)\right] \end{aligned} \tag{A5}$$

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