Random walk methods for reactive transport in porous media

Nicolae Suciu
Tiberiu Popoviciu Institute of Numerical Analysis
Romanian Academy, Cluj-Napoca, România

8 February 2023 - Karlstad Applied Analysis Seminar

TIBERIU POPOVICIU
INSTITUTE OF NUMERICAL ANALYSIS
ROMANIAN ACADEMY

A selective history

[Einstein, 1905] introduces the Brownian motion as model of the irregular movement of particles suspended in a fluid: increasing the coordinates of the particle at successive times by mutually independent increments results in a trajectory of the diffusion process.
$\rightarrow$ *Itô integral*

[Chorin, 1973, Chorin, 1978] introduces a random vortex method to solve the Navier-Stokes equation: the diffusive part of the equation is solved by decomposing the vorticity into a sum of blobs moving along trajectories of diffusion processes.
$\rightarrow$ *particle tracking (PT)*

[Pope, 1981] solves equations for the probability density functions used in combustion theory by a Monte Carlo method: the solution is represented by ensembles of "elements" at each grid point which are redistributed according to the coefficients of the the equation, e.g., half to the right and half to the left (in the mean) to simulate one-dimensional diffusion.
$\leftrightarrow$ *random walk (RW)*

- solutions for advection-diffusion problems based on the equivalence

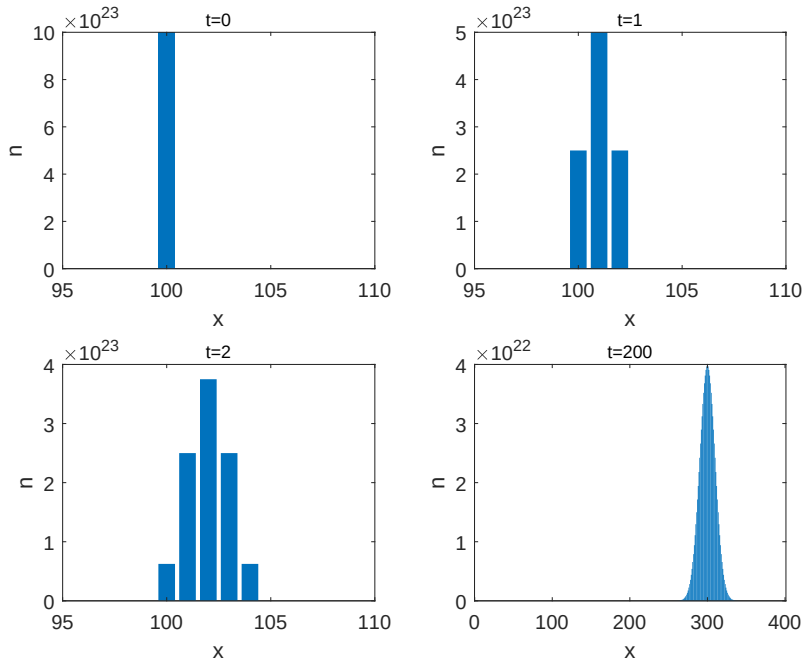
  $\partial_t p + V\partial_x(p) = D\partial_{xx}p$ (Fokker-Planck Eq.) $\Leftrightarrow dX = Vdt + \sqrt{2D}dW$ (Itô Eq.)

  where $p(x,t)$ is the probability density of the Itô process $X(t)$,
- weak solutions as RW on lattices: $X_{t+\Delta t} - X_t = (v + \xi d)\Delta x$
  - $P(\xi = \pm 1) = \frac{r}{2}$, $P(\xi = 0) = (1 - r)$
  - integer d and $v = \lfloor \frac{V\Delta t}{\Delta x} \rfloor$ (= integer Courant number $Cr \geq 1$)
  - $r = \frac{2D\Delta t}{(d\Delta x)^2}$ (= dimensionless diffusion coefficient)
  - $\Rightarrow p(i\Delta x, k\Delta t) \sim n_{i,k}$
  - $n_{i,k} = \delta n_{i+v|i,k} + \delta n_{i+v-d|i,k} + \delta n_{i+v+d|i,k}$
- counting the number of particles at lattice sites (binomially distributed random variable $n_{i,k}$) $\Rightarrow$ global random walk (GRW) - sequential computation of individual PT trajectories is no longer necessary
- weak solutions as biased RW on lattices: $X_{t+\Delta t} - X_t = \xi\Delta x$
  - $P(\xi = \pm 1) = \frac{1}{2}(r \pm v)$, $P(\xi = 0) = (1 - r)$; $r = \frac{2D\Delta t}{\Delta x^2}$, $v = \frac{V\Delta t}{\Delta x}$
  - $n_{i,k} = \delta n_{i|i,k} + \delta n_{i-1|i,k} + \delta n_{i+1|i,k}$
  - $\Rightarrow$ biased global random walk (BGRW)

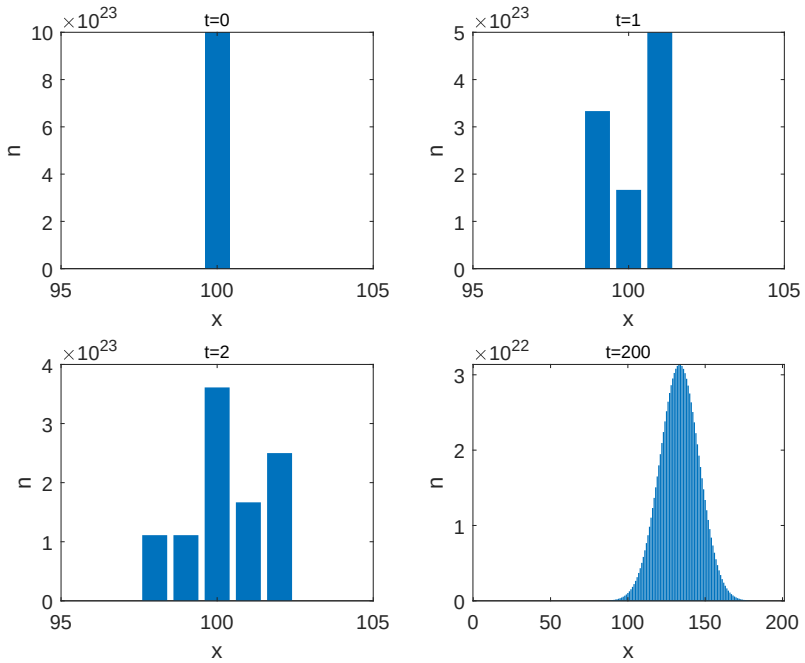
GRW simulations of Gaussian diffusion

- $\overline{\delta n_{i+v|i,k}} = (1-r)\overline{n_{i,k}}$, $\overline{\delta n_{i+v\pm d|i,k}} = \frac{1}{2} r\ \overline{n_{i,k}}$ $\Rightarrow$ unbiased GRW
- $\overline{\delta n_{i|i,k}} = (1-r)\overline{n_{i,k}}$, $\overline{\delta n_{i\pm 1|i,k}} = \frac{1}{2}(r \pm v)\ \overline{n_{i,k}}$ $\Rightarrow$ biased GRW (BGRW)

unbiased GRW:



BGRW:



Note: $v \leq r$ implies Pé $= V\Delta x/D \leq 2$ in BGRW codes.

GRW approximations of continuous diffusion process

A diffusion process is defined if the following limits exist for all $\epsilon > 0$ [Kloeden and Platen, 1992, Sect. 4.6],

$$i) \lim_{\Delta t \to 0} \text{Prob}\{|X_{t+\Delta t} - X_t| > 0\} = 0 \text{ (continity with probability 1)}$$

$$ii) \lim_{\Delta t \to 0} \frac{1}{\Delta t} E\{X_{t+\Delta t} - X_t\} = V \text{ (drift coefficient)}$$

$$iii) \frac{1}{2} \lim_{\Delta t \to 0} \frac{1}{\Delta t} E\{(X_{t+\Delta t} - X_t)^2\} = D \text{ (diffusion coefficient)}$$

GRW:

- *i)* $\max |X_{t+\Delta t} - X_t| = (|v| + d)\Delta x \leq \epsilon$ holds with probability 1 if

  $\Delta t = \frac{r(d\Delta x)^2}{2D} \leq \frac{r(d\epsilon)^2}{2D(|v|+d)^2} = \Delta t^* \Rightarrow$

  if $\Delta t \leq \Delta t^*$

  $\text{Prob}\{|X_{t+\Delta t} - X_t| > \epsilon\} = 1 - \text{Prob}\{|X_{t+\Delta t} - X_t| \leq \epsilon\} = 0.$

GRW approximations of continuous diffusion process

- *ii)* for all $\epsilon > 0$ and $\Delta t \leq \Delta t^*$,

$$\lim_{\Delta t \to 0} \frac{1}{\Delta t} E\{X_{t+\Delta t} - X_t\} = \lim_{\Delta t \to 0} \frac{1}{\Delta t} E\{V\Delta t + \Delta v \Delta x + \xi d \Delta x\}$$
$$= V + \lim_{\Delta t \to 0} \frac{1}{\Delta t} \Delta v \Delta x,$$

  where $\Delta v = v - V\frac{\Delta t}{\Delta x}$ is the truncation error of the advective displacement.

- *iii)* for all $\epsilon > 0$ and $\Delta t \leq \Delta t^*$,

$$\frac{1}{2} \lim_{\Delta t \to 0} \frac{1}{\Delta t} E\{(X_{t+\Delta t} - X_t)^2\} = \frac{1}{2} \lim_{\Delta t \to 0} \frac{1}{\Delta t} E\{(V\Delta t + \Delta v \Delta x + \xi d \Delta x)^2\}$$
$$= D + \frac{D}{rd^2} \lim_{\Delta t \to 0} (\Delta v)^2$$

$\Rightarrow X_t$ approximates, up to truncation errors, a continuous diffusion process and the distribution of the computational particles on the GRW lattice approximates the solution of the Fokker-Planck equation.

GRW approximations of continuous diffusion process

BGRW:

- *i)* Since in BRGW algorithms only jumps to neighbor lattice sites are allowed, the continuity condition is verified for all $\epsilon = \Delta x > 0$.
- *ii)*

$$\lim_{\Delta t \to 0} \frac{1}{\Delta t} E\{\hat{X}_{k+1} - \hat{X}_k\} = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \left[\frac{1}{2}(r+v)\Delta x + \frac{1}{2}(r-v)(-\Delta x)\right]$$

$$= \lim_{\Delta t \to 0} \frac{1}{\Delta t} v \Delta x = V,$$

- *iii)*

$$\frac{1}{2} \lim_{\Delta t \to 0} \frac{1}{\Delta t} E\{(\hat{X}_{k+1} - \hat{X}_k)^2\} = \frac{1}{2} \lim_{\Delta t \to 0} \frac{1}{\Delta t} \left[\frac{1}{2}(r+v)\Delta x^2 + \frac{1}{2}(r-v)\Delta x^2\right]$$

$$= \lim_{\Delta t \to 0} r \frac{\Delta x^2}{2\Delta t} = D.$$

$\Rightarrow$ BGRW fulfils exactly the conditions *ii)* and *iii)*.

Numerical diffusion

$c(x,t) = (4\pi Dt)^{-1/2} \exp\left[-(x-Vt)^2/(4Dt)\right]$ (Gaussian diffusion)

$\mu(t) = \int xc(x,t)dx = Vt, \quad s(t) = \int [x-\mu(t)]^2 c(x,t)dx = 2Dt \Rightarrow D = s(t)/(2t)$

- straightforward quantification of numerical diffusion: $\varepsilon_D = |D^{num} - D|/D$, with D^{num} computed from the solution c^{num} of the numerical scheme.
- GRW: $Y_{t+\Delta t} = X_{t+\Delta t} - X_t = (v + \xi d)\Delta x, \quad E\{\xi\} = 0, \quad E\{\xi^2\} = r$

  $\mu(t+\Delta t) = E\{Y_{t+\Delta t}\} = v\Delta x + (d\Delta x)E\{\xi\} = v\Delta x$

  $s(t+\Delta t) = E\{(Y_{t+\Delta t} - v\Delta x)^2\} = (d\Delta x)^2 E\{\xi^2\} = r(d\Delta x)^2$

  $\Rightarrow \quad s(t+\Delta t)/(2\Delta t) = r(d\Delta x)^2/(2\Delta t) = D$
- BGRW: $Y_{t+\Delta t} = X_{t+\Delta t} - X_t = \xi\Delta x, \quad E\{\xi\} = v, \quad E\{\xi^2\} = r$

  $\mu(t+\Delta t) = E\{Y_{t+\Delta t}\} = \Delta x E\{\xi\} = v\Delta x$

  $s(t+\Delta t) = E\{(Y_{t+\Delta t} - v\Delta x)^2\} = \Delta x^2 E\{\xi^2 - 2v\xi + v^2\} = (r - v^2)(\Delta x)^2$

  $\Rightarrow \quad [s(t+\Delta t) + (V\Delta t)^2]/(2\Delta t) = r(\Delta x)^2/(2\Delta t) = D$

Numerical diffusion

Numerical diffusion quantified by $\varepsilon_{D_x} = |D_x - D|/D$ and $\varepsilon_{D_z} = |D_z - D|/D$, with D_x and D_z computed from numerical solutions (2-dim. advection-diffusion with constant D and velocity $(0, V)$, unbounded domain and final time $t = T$):

	$\Delta x = \Delta z$	$T/\Delta t$	Pé	ε_{D_x}	ε_{D_z}
BGRW	0.1	2	3.31	7.55e-02	2.60e-01
	0.05	9	1.65	1.90e-16	1.48e-15
	0.01	239	0.33	4.16e-16	1.02e-15
	0.005	960	0.17	2.93e-15	3.63e-15
GRW	0.1	4	3.31	1.94e-16	6.14e-16
	0.05	4	1.65	6.60e-17	8.05e-16
	0.01	19	0.33	1.94e-16	4.79e-16
	0.005	39	0.17	2.10e-15	8.92e-16
TPFA-Finite Volume	0.1	5	3.31	9.16e-03	1.99e-01
	0.05	10	1.65	4.69e-03	9.94e-02
	0.01	50	0.33	9.58e-04	1.99e-02
	0.005	100	0.17	5.38e-04	9.89e-03

$$\frac{\partial}{\partial t}\theta(\psi, c) - \nabla \cdot [K(\theta(\psi, c)\nabla(\psi + z)] = 0, \quad \mathbf{q} = -K(\theta(\psi, c)\nabla(\psi + z)$$

$$\frac{\partial}{\partial t}[\theta(\psi, c)c] - \nabla \cdot [D\nabla c - \mathbf{q}c] = R(c)$$

- Richards and transport Eqs. fully coupled through $\theta(\psi, c)$ and $\theta(\psi, c)c$
- degenerate parabolic-elliptic Richards Eq.($\theta = f(\psi, c) \leftrightarrow \theta(\psi > 0) = const$)
- strongly nonlinear $K(\theta(\psi, c)$ (e.g., van Genuchten-Mualem model)
- Solution approach:
  - FD schemes + $L(\psi^{s+1}_{i,j,k} - \psi^{s}_{i,j,k})$, iterations until $\|\psi^{s+1} - \psi^{s}\| \leq \varepsilon$
  - ψ & $c \approx n^{s}_{i,j,k}/\mathcal{N}$, $\mathcal{N} = 10^{24}$ random walkers $\equiv$ GRW
  - jump probabilities $r_\psi(K) \leq 1/(2d)$, $r_c(D, \mathbf{q}) \leq 1/(2d)$, $d = 1, 2$

$\Rightarrow$ GRW algorithms for both flow and transport are free of numerical diffusion

[S, Iliano, Prechtel, Radu, 2021]
[S, Radu, 2022]

https://github.com/PMFlow/RichardsEquation (Matlab codes)

Explicit schemes for one-dimensional Richards equation: finite difference L-scheme

$$\frac{\partial \theta(\psi)}{\partial t} - \frac{\partial}{\partial z}\left[K(\theta(\psi))\frac{\partial}{\partial z}(\psi + z)\right] = 0$$

- staggered finite difference scheme with backward discretization in time

$$\begin{aligned}
&\theta(\psi_{i,k}) - \theta(\psi_{i,k-1}) \\
&= \tfrac{\Delta t}{\Delta z^2}\{[K(\psi_{i+1/2,k})(\psi_{i+1,k} - \psi_{i,k}) - K(\psi_{i-1/2,k})(\psi_{i,k} - \psi_{i-1,k})] \\
&+ \left(K(\psi_{i+1/2,k}) - K(\psi_{i-1/2,k})\right)\Delta z\}
\end{aligned}$$

- addition of a stabilization term $L(\psi_{i,k}^{s+1} - \psi_{i,k}^{s})$, $L = const$

$$\begin{aligned}
\psi_{i,k}^{s+1} = [1 - (r_{i+1/2,k}^{s} + r_{i-1/2,k}^{s})]\psi_{i,k}^{s} + r_{i+1/2,k}^{s}\psi_{i+1,k}^{s} + r_{i-1/2,k}^{s}\psi_{i-1,k}^{s} \\
+(r_{i+1/2,k}^{s} - r_{i-1/2,k}^{s})\Delta z - (\theta(\psi_{i,k}^{s}) - \theta(\psi_{i,k-1}))/L
\end{aligned}$$

where $r_{i\pm1/2,k}^{s} = K(\psi_{i\pm1/2,k}^{s})\Delta t/(L\Delta z^2)$

- iterations $s = 1, 2, \ldots$ of the L-scheme until $\|\psi_k^s - \psi_k^{s-1}\| \leq \varepsilon_a + \varepsilon_r\|\psi_k^s\|$

Explicit schemes for one-dimensional Richards equation: GRW *L*-scheme

- $\psi^s_{i,,k}$ is represented by $\mathcal{N}$ particles at distributed over lattice sites, $\psi^s_{i,k} \approx n^s_{i,k} a/\mathcal{N}$, where a is unit length

$$n^{s+1}_{i,k} = [1-(r^s_{i+1/2,k} + r^s_{i-1/2,k})]n^s_{i,k} + r^s_{i+1/2,k} n^s_{i+1,k} + r^s_{i-1/2,k} n^s_{i-1,k} + \lfloor \mathcal{N} f^s \rfloor$$

where $f^s = (r^s_{i+1/2,k} - r^s_{i-1/2,k})\Delta z - [\theta(n^s_{i,k}) - \theta(n_{i,k-1})]/L$

- imposing $r^s_{i\pm 1/2,k} \leq 1/2 \Rightarrow n^s_{j,k} = \delta n^s_{j|j,k} + \delta n^s_{j-1|j,k} + \delta n^s_{j+1|j,k}$ BGRW with

$$\overline{\delta n^s_{j|j,k}} = [1-(r^s_{j-1/2,k} + r^s_{j+1/2,k})]\overline{n^s_{j,k}}, \quad \overline{\delta n^s_{j\mp 1/2|j,k}} = r^s_{j\mp 1/2,k}\overline{n^s_{j,k}}$$

- in particular, for saturated regime, $\theta = const$, with space-variable hydraulic conductivity K and a given source term f, after setting $L = 1/a$ and disregarding the time index $k \Rightarrow$ a transient scheme to solve the equation for the hydraulic head $h = \psi + z$

$$\frac{1}{a}\frac{\partial h}{\partial s} - \frac{\partial}{\partial z}[K\frac{\partial h}{\partial z}] = f$$

Explicit BGRW scheme for reactive transport

$$\frac{\partial}{\partial t}[\theta(\psi, c)c] - \frac{\partial}{\partial z}[D\frac{\partial}{\partial z}c - qc] = R(c),$$

- finite difference scheme with backward time discretization

$$\theta(\psi_{i,k}, c_{i,k})c_{i,k} - \theta(\psi_{i,k-1}, c_{i,k-1})c_{i,k-1}$$
$$= -\frac{\Delta t}{2\Delta z}(q_{i+1,k}c_{i+1,k} - q_{i-1,k}c_{i-1,k}) + \frac{D\Delta t}{\Delta z^2}(c_{i+1,k} - 2c_{i,k} + c_{i-1,k}) + R(c_{i,k})$$
$$= -\frac{2D\Delta t}{\Delta z^2}c_{i,k} + (\frac{D\Delta t}{\Delta x^2} - \frac{\Delta t}{2\Delta x}q_{i+1,k})c_{i+1,k} + (\frac{D\Delta t}{\Delta x^2} + \frac{\Delta t}{2\Delta x}q_{i-1,k})c_{i-1,k} + R(c_{i,k})$$

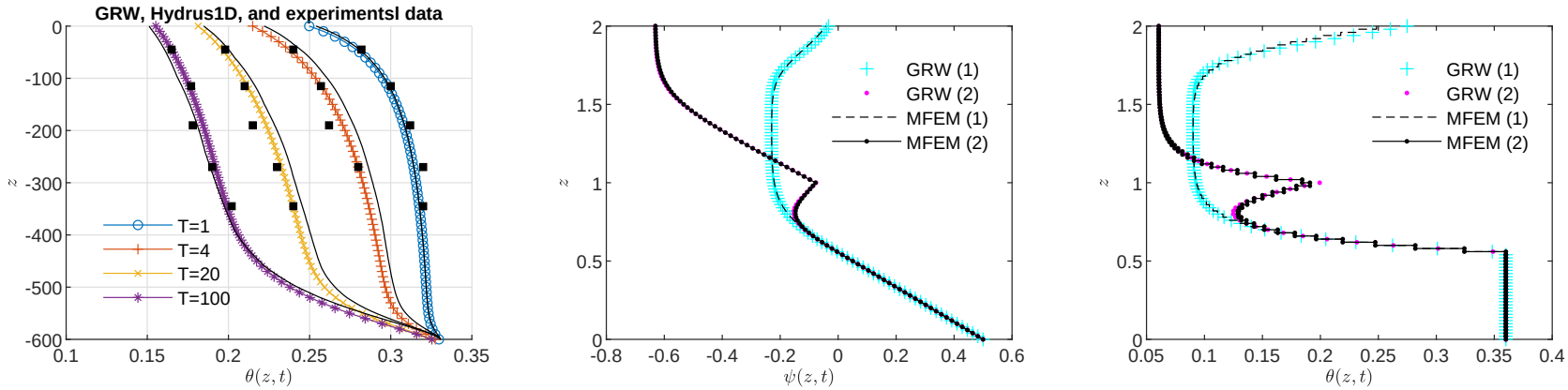
- with $L(c_{i,k}^{s+1} - c_{i,k}^{s})$, $r = \frac{2D\Delta t}{L\Delta z^2}$, $v_{i\pm1,k}^{s} = \frac{\Delta t}{L\Delta z}q_{i\pm1,k}^{s}$ and $c_{i,k}^{s} \approx n_{i,k}^{s}/\mathcal{N} \Rightarrow$

$$n_{i,k}^{s+1} = (1-r)n_{i,k}^{s} + \frac{1}{2}(r - v_{i+1,k}^{s})n_{i+1,k}^{s} + \frac{1}{2}(r_x + v_{i-1,k}^{s})n_{i-1,k}^{s}\lfloor \mathcal{N}g^{s}\Delta t \rfloor,$$
$$\text{where } g^{s} = R(n_{i,k}^{s})/L - [\theta(\psi_{i,k}^{s}, n_{i,k}^{s})n_{i,k}^{s} - \theta(\psi_{i,k-1}, n_{i,k-1})n_{i,k-1}]/L$$

- imposing $r \leq 1$, $|v_{l,k}^{s}| \leq r$, the contributions to $n_{i,k}^{s+1} \Leftarrow$ BGRW algorithm

$$n_{l,k}^{s} = \delta n_{l|l,k}^{s} + \delta n_{l-1|l,k}^{s} + \delta n_{l+1|l,k}^{s}$$
$$\overline{\delta n_{l|l,k}^{s}} = (1-r)\,\overline{n_{i,k}^{s}}, \quad \overline{\delta n_{l\pm1|l,k}^{s}} = \frac{1}{2}(r \mp v_{l,k}^{s})\overline{n_{l,k}^{s}}$$

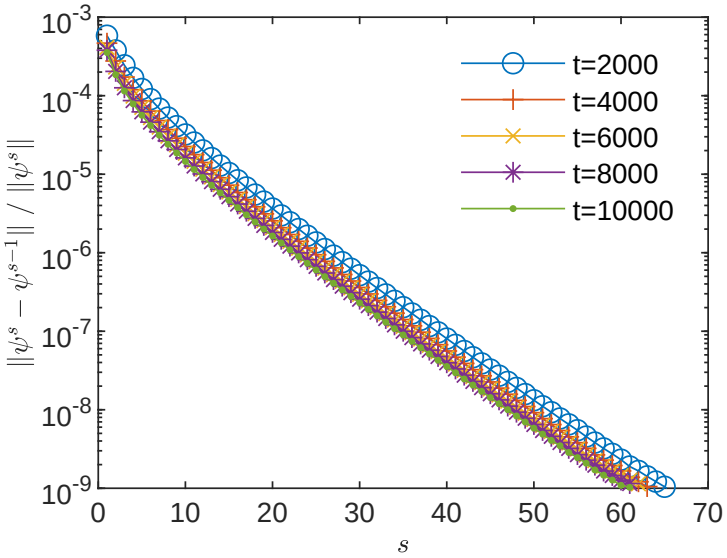
- unsaturated 1-dim flows (Richards equation in pressure formulation):



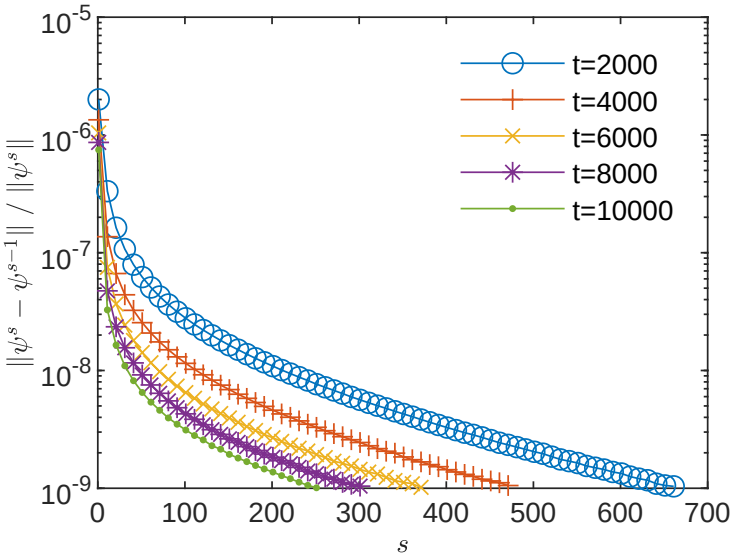
Left panel: comparison between measured water content in a free drainage experiment, Hydrus 1D solutions, and GRW solutions.
Middle panel: pressure profiles computed with the GRW solver and Richy MFEM for saturated/unsaturated flow in a soil column with constant pressure at the bottom and variable flux at the top, for constant $K = K_{saturated}$ (scenario 1) and $K = K_{saturated}(z)$ with finite jump at the half height of the domain (scenario 2).
Right panel: water content for the same scenarios as in the middle panel.

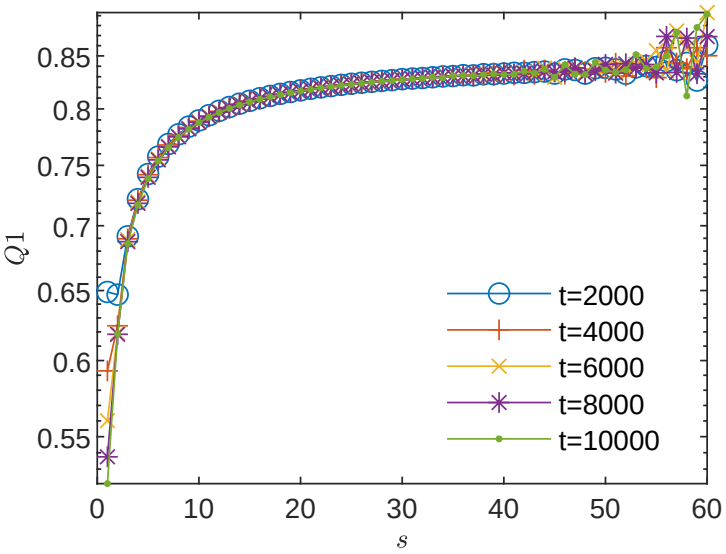
- solutions $z(\theta, t)$ and $\theta(z, t)$ (obtained with a BGRW for the diffusion-like Richards equation in θ-formulation) are close to analytical solutions within a relative precision $\sim 10^{-2}$ [S, Iliano, Prechtel, Radu, 2021, Tables 2 and 3].

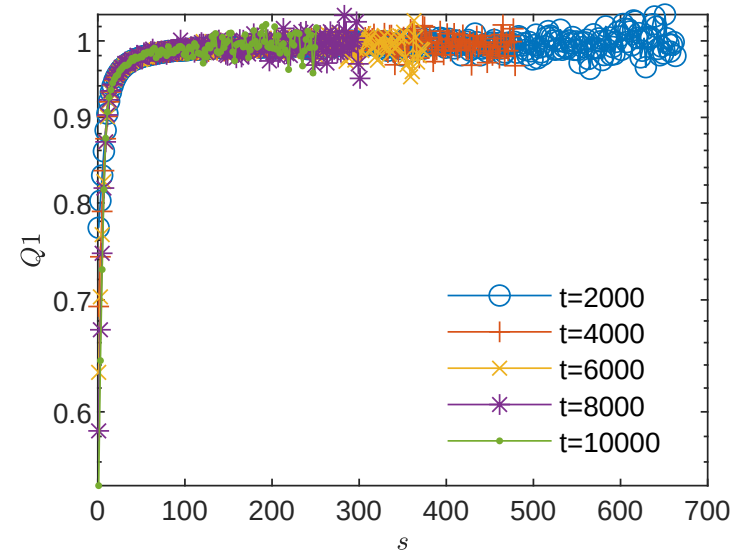
scenario (1)



scenario (2)







testing linear convergence [Cătinaș, 2021]: $Q_1 = \lim_{s\to\infty} \|\psi^{s+1} - \psi^s\| / \|\psi^s - \psi^{s-1}\| < 1$

Transition from unsaturated to saturated regime:

- manufactured solutions of the 1-dimensional problem,

$$\psi_m(z,t) = -tz(z-1) + z/4, \quad c_m(z,t) = tz(z-1) + 1$$

- degenerate parabolic-elliptic Richards equation, **van Genuchten-Mualem** parameterizations $\theta(\psi)$ and $K(\Theta(\psi))$ for a loam-soil model,

$$\Theta(\psi) = \begin{cases} (1+(-\alpha\psi)^n)^{-m} \\ 1, \end{cases} \quad K(\Theta(\psi)) = \begin{cases} K_{sat}\Theta(\psi)^{\frac{1}{2}}\left[1-\left(1-\Theta(\psi)^{\frac{1}{m}}\right)^m\right]^2 & \psi < 0 \\ K_{sat} & \psi \geq 0, \end{cases}$$

where $\Theta = (\theta - \theta_{residual})/(\theta_{saturated} - \theta_{residual})$

- L-schemes converge with $L_\psi = 10$, $L_c = 1$, $\varepsilon = 10^{-9}$ after $\sim 10^4$ iterations
- by successively refining the mesh $\Rightarrow$ estimated orders of convergence (EOC) of the numerical solution twoards the analytical solution:

Δz	$\|\psi - \psi_m\|$	EOC	$\|q - q_m\|$	EOC	$\|c - c_m\|$	EOC
1.00e-1	5.85e-02	–	3.60e-03	–	1.72e-02	–
5.00e-2	1.42e-02	2.05	1.09e-03	1.73	5.05e-03	1.77
2.50e-2	3.27e-03	2.11	2.92e-04	1.90	1.34e-03	1.92
1.25e-2	3.27e-03	2.01	1.07e-04	1.45	3.45e-04	1.95

unsaturated flow:
$\psi_m(x,z,t) = -tx(x-1)z(z-1) - 1,\ \theta(\psi) = 1/(1-\psi),\ K(\theta(\psi)) = \psi^2$:

	BGRW		TPFA	
Δz	$\|\psi - \psi_m\|$	EOC	$\|\psi - \psi_m\|$	EOC
1.00e-1	3.71e-03	–	8.14e-03	–
5.00e-2	9.18e-04	2.02	4.27e-03	0.93
2.50e-2	2.40e-04	1.94	2.20e-03	0.95
1.25e-2	8.78e-05	1.45	1.12e-03	0.97

explicit BGRW - higher EOC and one order of magnitude faster than implicit TPFA

saturated flow: random $K(x,z)$ with Gaussian correlated $\ln K$ of variance 0.1:

	BGRW		TPFA	
Δz	$\|\psi - \psi_m\|$	EOC	$\|\psi - \psi_m\|$	EOC
1.00e-1	7.37e-02	–	9.22e-02	–
5.00e-2	1.87e-02	1.98	2.30e-02	2.00
2.50e-2	6.03e-03	1.63	5.75e-03	2.00
1.25e-2	2.73e-03	1.14	1.44e-03	2.00

explicit BGRW - lower EOC and up to two orders of magnitude slower than implicit TPFA

The water flow and the fate of electron donor, electron acceptor, and biomass concentrations, c_1, c_2, c_3, are governed by the system of coupled equations

$$\frac{\partial}{\partial t}\theta(\psi) - \nabla \cdot [K(\theta(\psi))\nabla(\psi + z)] = 0, \quad \mathbf{q} = (U, V) = -K(\theta(\psi))\nabla(\psi + z)$$

$$\frac{\partial}{\partial t}(\theta c_\nu) - \nabla \cdot (D_\nu \nabla c_\nu - \mathbf{q} c_\nu) = R_\nu, \quad \nu = 1, 2$$

$$\frac{\partial}{\partial t} c_3 = R_3 \left(1 - \gamma \frac{c_3}{c_{3_{max}}}\right) - k_d c_3$$

$$\mu = \mu_{max} \frac{c_1}{M_1 + c_1} \frac{c_2}{M_2 + c_2} c_3$$

$R_1 = -\theta\alpha_1\mu$, $R_2 = -\theta\alpha_2\mu$, $R_3 = Y\mu$, α_1, α_2 are stoichiometric constants, μ_{max} is the maximum growth rate, M_1, M_2 are Monod constants, Y is the microbial yield coefficient, k_d is the decay rate, and the factor of R_3 with $\gamma = 1$ accounts for the growth limitation of the biomass.

- flow & transport solved with BGRW/GRW algorithms
- reaction step performed deterministically with each moll of reactant represented by $\mathcal{N} = 10^{24} \approx$ Avogadro's number

Code verification and convergence tests - constant transport parameters

- $U = 0,\ V = -1,\ D_1 = D_2 = D = 0.1,\ \theta = 1$
- nonlinear reaction terms $R_1 = -c_1 c_2^2$ and $R_2 = -2c_1 c_2^2$
- domain $\Omega = (0,2) \times (0,3)$ and final simulation time $T = 1$.
- manufactured analytical solutions

$$c_{1m}(x,z,t) = x(2-x)z^3 \exp(-0.1t)/27$$
$$c_{2m}(x,z,t) = (x-1)^2 z^2 \exp(-0.1t)/9$$

$\Delta x = \Delta z$	$\|c_1 - c_{1m}\|$	EOC	$\|c_2 - c_{2m}\|$	EOC
2.00e-1	3.53e-03	–	4.91e-03	–
1.00e-1	8.64e-04	2.03	1.12e-03	2.13
5.00e-2	2.12e-04	2.02	2.67e-04	2.07
2.50e-2	5.30e-05	2.00	6.50e-05	2.04
1.25e-2	1.32e-05	2.00	1.60e-05	2.02
6.25e-2	3.30e-06	2.00	3.99e-06	2.01

Code verification and convergence tests - coupled flow and transport (with Monod)

- manufactured solution of parabolic-elliptic degenerate Richards equation

$$\psi_m(x,z,t) = -tx(2-x)z(3-z) + x/4 + z/4$$

- with nontrivial parameterizations $\theta(\psi)$ and $K(\theta(\psi))$

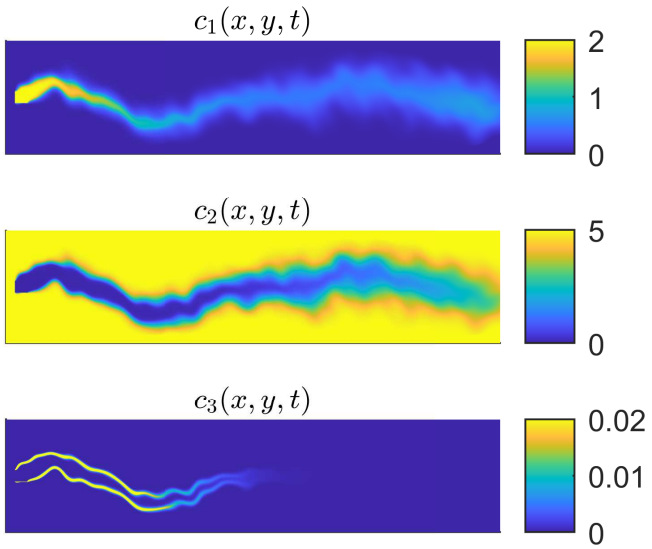
$$\theta(\psi) = \begin{cases} 1/(3.3333-\psi) \\ 0.3 \end{cases} \qquad K(\Theta(\psi)) = \begin{cases} 0.05[1-(0.3-\theta(\psi))] & \psi < 0 \\ 0.05 & \psi \geq 0 \end{cases}$$

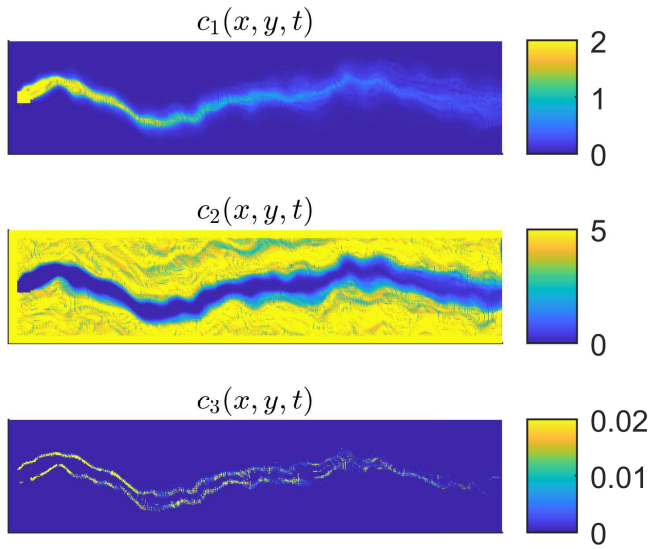
Δx	$\|\psi - \psi_m\|$	EOC	$\|V_x - V_{xm}\|$	EOC	$\|V_z - V_{zm}\|$	EOC
2.00e-1	6.62e-01	–	1.85e-02	–	9.17e-03	–
1.00e-1	1.69e-01	1.97	6.87e-03	1.43	2.86e-03	1.68
5.00e-2	4.22e-02	2.00	2.40e-03	1.52	9.36e-04	1.61
2.50e-2	1.06e-02	2.00	8.15e-04	1.56	3.06e-04	1.61

Δx	$\|c_1 - c_{1m}\|$	EOC	$\|c_2 - c_{2m}\|$	EOC
2.00e-1	3.14e-02	–	5.84e-02	–
1.00e-1	1.02e-02	1.62	1.88e-02	1.64
5.00e-2	2.86e-03	1.83	5.23e-03	1.84
2.50e-2	7.32e-04	1.97	1.34e-03	1.97

Biodegradation in heterogeneous saturated aquifers

- random K (Gaussian correlation and variance 0.1), continuous injection of benzene (c_1) at the inflow boundary, uniform initial concentrations of oxygen (c_2) and biomass ($c_3 = 1$) in $\Omega = (0, 80) \times (0.20)$:

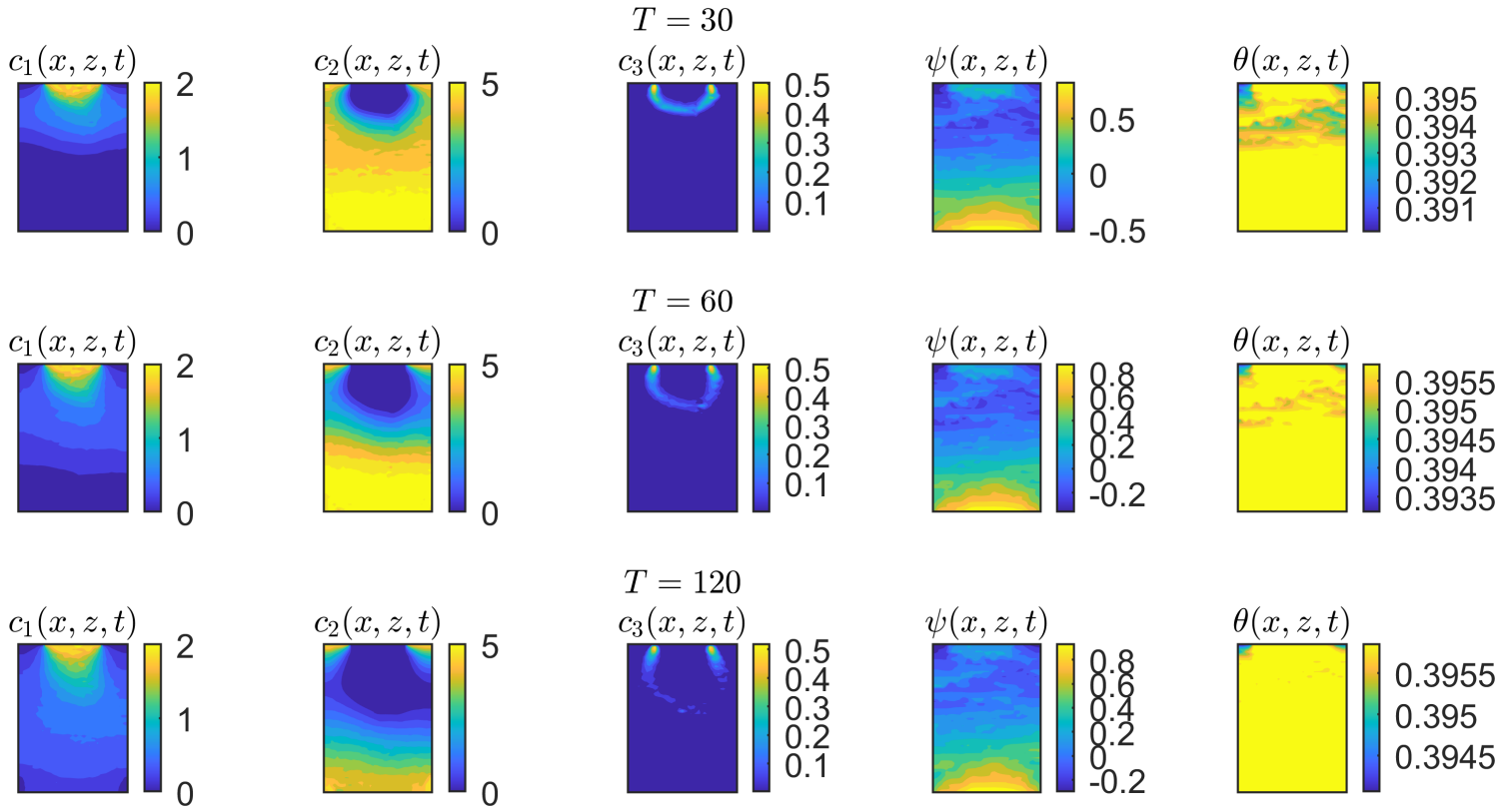




Reference BGRW solutions: good agreement with results of [Cirpka et al., 1999; Bause & Knabner, 2004].

Unbiased GRW solutions: reproduce the shape of the reference solutions but are affected by overshooting.

Biodegradation in variably saturates soils



Concentrations of the electron donor (c_1), electron acceptor (c_2), and biomass (c_3), pressure head (ψ), and water content (θ) computed by the BGRW L-scheme coupled with the GRW flow solver for loam soil parameters in $\Omega = (0, 2) \times (0, 3)$.

[Vamoș, Georgescu, S, Turcu, 1996]: coarse-grained space-time (CGST) aver.
[S, Radu, Pop, 2022]: CGST averaging over RW microscopical descriptions

If a microscopic description of a system of $\mathcal{N}$ particles is given by piecewise analytic time functions $\varphi_i(t) : [0, T] \longmapsto \mathbb{R}$, then

1) there exists a macroscopic description given by a.e. continuous fields

$$\langle\varphi\rangle(x, t; a, \tau) = \frac{1}{2\tau(2a)^d} \sum_{i=1}^{\mathcal{N}} \int_{t-\tau}^{t+\tau} \varphi_i(t') \prod_{\alpha=1}^{d} \chi_\alpha(r_{\alpha i}(t'))dt',$$

where $\mathbf{r}_i(t)$ is the trajectory of the ith particle, and $\prod_{\alpha=1}^{d} \chi_\alpha(r_{\alpha i}(t))$ is the characteristic function of the cube $C_x = \{y \in \mathbb{R}^d \mid |y_\alpha - r_\alpha| < a, \alpha = 1, \ldots, d\}$,
2) $\langle\varphi\rangle$ has continuous partial derivatives a.e. in $\mathbb{R}^3 \times (\tau, T - \tau)$ and satisfies the identity

$$\partial_t\langle\varphi\rangle + \partial_\alpha\langle\varphi\xi_\alpha\rangle = \langle\frac{d}{dt}\varphi\rangle + \delta\varphi,$$

where $\xi_{i\alpha} = dr_{\alpha i}/dt$, are the velocity components of the ith particle and $\delta\varphi$ accounts for discontinuous variations of φ produced when a particle is created or consumed in chemical reactions.

The continuous concentration field $c^*(\mathbf{x}, t)$ at the scale of the mathematical continuum (fine-grained concentration) is an average M over the ensemble of realizations $\mathbf{X}_i(t, \omega)$ of the transport process,

$$c^*(\mathbf{x}, t) := M\left[\sum_{i=1}^{\mathcal{N}} \delta(\mathbf{X}_i(t, \omega) - \mathbf{x})\right].$$

Writing the characteristic function of the cube as a Dirac functional,

$$\prod_{\alpha=1}^{d} \chi_\alpha(X_{\alpha i}(t)) = \chi_{C(\mathbf{x},a)}(\mathbf{X}_i, t) = \int_{\mathbb{R}^d} \chi_{C(\mathbf{x},a)}(x')\delta(\mathbf{X}_i(t, \omega) - \mathbf{x}')d\mathbf{x}',$$

$\Rightarrow$ the stochastic average of the CGST average for $\varphi_i \equiv 1$ is a space-time average of the fine-grained concentration,

$$M[\langle 1\rangle](\mathbf{x}, t; a, \tau) = \frac{1}{2\tau(2a)^d} \int_{t-\tau}^{t+\tau} dt' \int_{C(\mathbf{x},a)} c^*(\mathbf{x}', t')d\mathbf{x}'.$$

$M[\langle 1\rangle](\mathbf{x}, t; a, \tau) = c(\mathbf{x}, t)$ defines the continuous concentration field observed at the spatio-temporal scale (a, τ) --→ ST averaging local balance equations and T-averaged homogenization solutions.

Verification of the averaging procedure (1-dim. case)

- - $\varphi = 1$: $\langle 1 \rangle(x,t) = c(x,t) =$ concentration field
  - $\frac{1}{c}\langle \xi \rangle(x,t) = u(x,t) =$ velocity defined as hydrodynamic mean
  - $\delta\varphi = 0 \Rightarrow$ continuity equation, $\partial_t c + \partial_x(cu) = 0$
- $cu = \langle \xi \rangle = \langle \frac{dr}{dt} \rangle = \partial_t \langle r \rangle + \partial_x \langle r\xi \rangle \Rightarrow \partial_t c + \partial_x \partial_t \langle r \rangle = \partial_x^2(-\langle r\xi \rangle)$
- assuming steady-state conditions, $\partial_t c = 0$, $\partial_t \langle r \rangle = 0$,
  $\Rightarrow \partial_x^2(Dc) = 0$ (stationary diffusion with diffusion coefficient $D = -\langle r\xi \rangle / c$)

BGRW & GRW simulations of advection-diffusion with $D = 10^{-4}$, $u = 1$ and CGST averages with $a = 0.05$, $\tau = 0.1$:

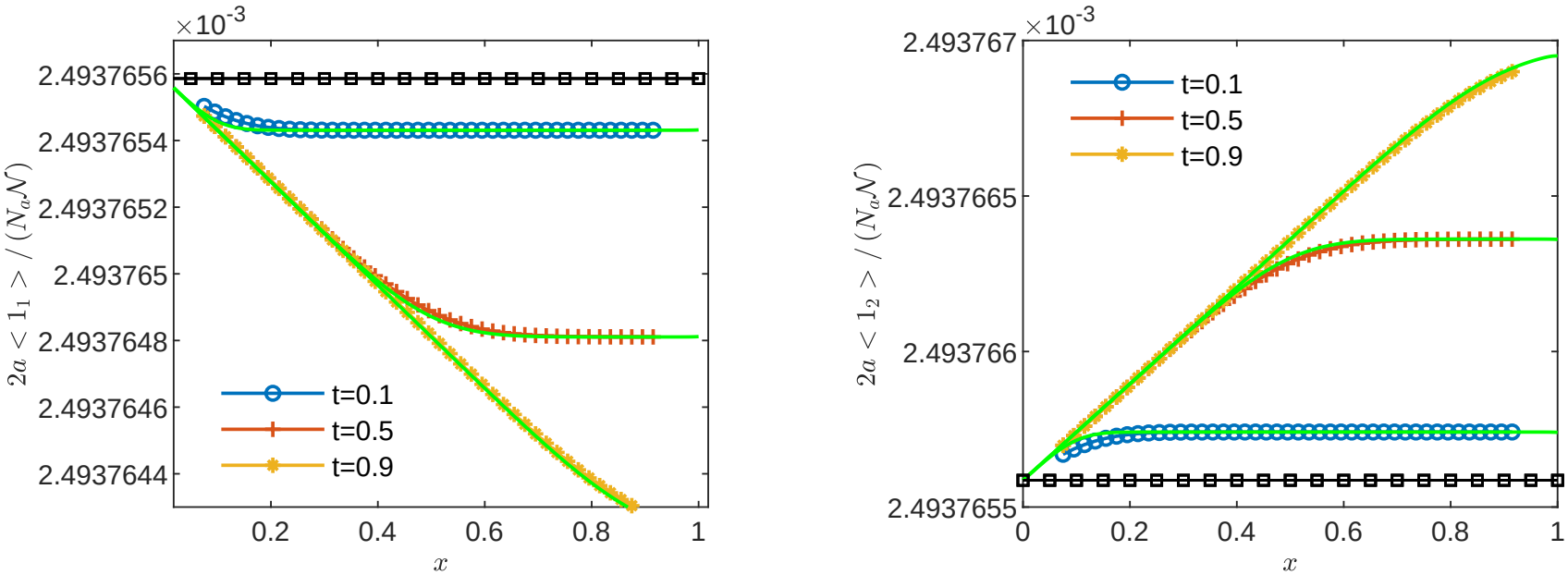
	$\overline{D}$		$\overline{u}$	
Δx	BGRW	GRW	BGRW	GRW
5.00e-03	1e-04± 2.25e-19	1e-04± 2.51e-19	1± 0.00	1± 0.00
2.50e-03	1e-04± 5.07e-19	1e-04± 6.21e-19	1± 0.00	1± 0.00
1.25e-03	1e-04± 1.16e-18	1e-04± 1.30e-18	1± 2.36e-16	1± 0.00
6.25e-04	1e-04± 1.42e-18	1e-04± 1.78e-18	1± 2.36e-16	1± 0.00

Bimolecular reaction with conservation of the total mass (1-dim. case)

- one species is consumed and another is augmented at the same rate

$$\partial_t c_\nu^* + u\partial_x(c_\nu^*) - D\partial_x^2 c_\nu^* = R_\nu(c_1^*, c_2^*),\ \nu = 1, 2$$

- $R_1 = -K_r c_1^* c_2^{*2}$, $R_2 = -R_1$ $\Rightarrow$ the total mass is conserved



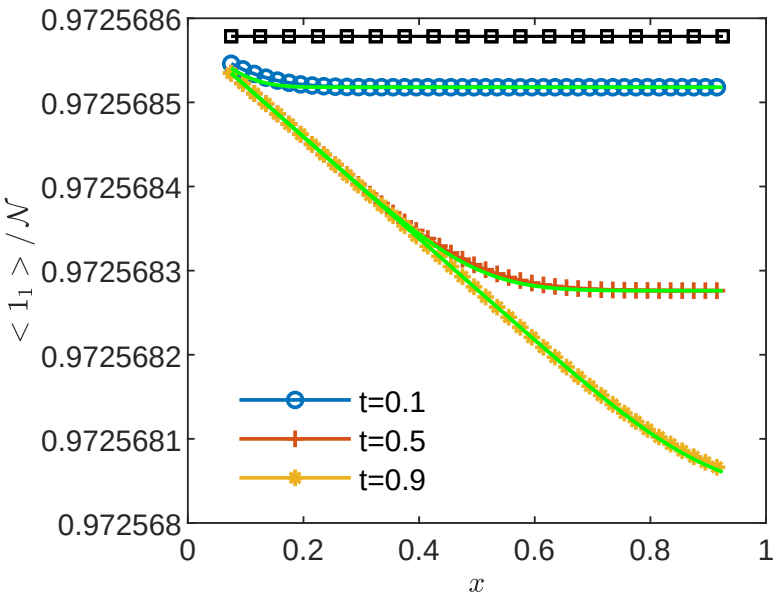
Moving averages over points in $(-a, a)$ and the time interval $(-\tau, \tau)$, fine-grained concentrations (full lines) and half total concentration $(c_1^* + c_2^*)/2$ (squares).

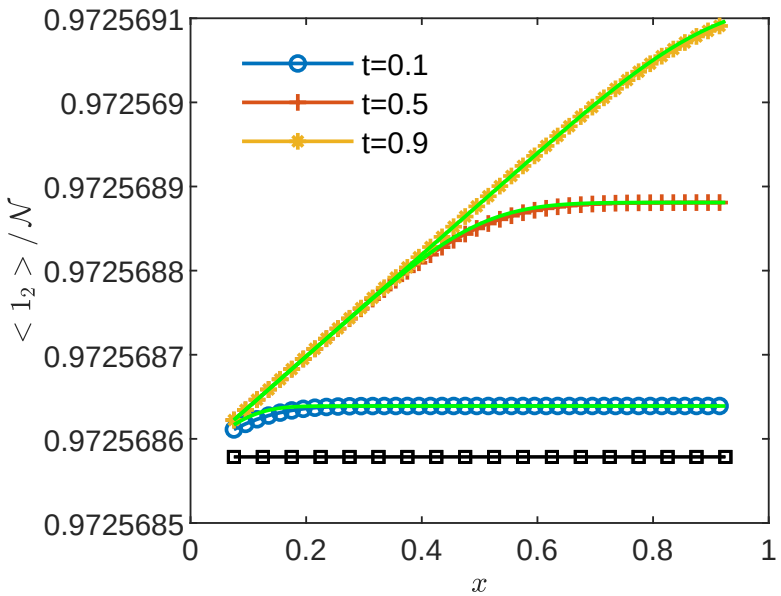
Bimolecular reaction with conservation of the total mass (1-dim. case)

- CGST averages of the two molecular species satisfy a.e. identities having the general form the advection-diffusion equation

$$\partial_t \langle 1_\nu \rangle + \partial_x \langle 1_\nu \xi \rangle = \delta 1_\nu, \ \nu = 1, 2$$

- $\delta 1_1 + \delta 1_2 = 0$ and the sum $(\langle 1_1 \rangle + \langle 1_2 \rangle)$ is conserved

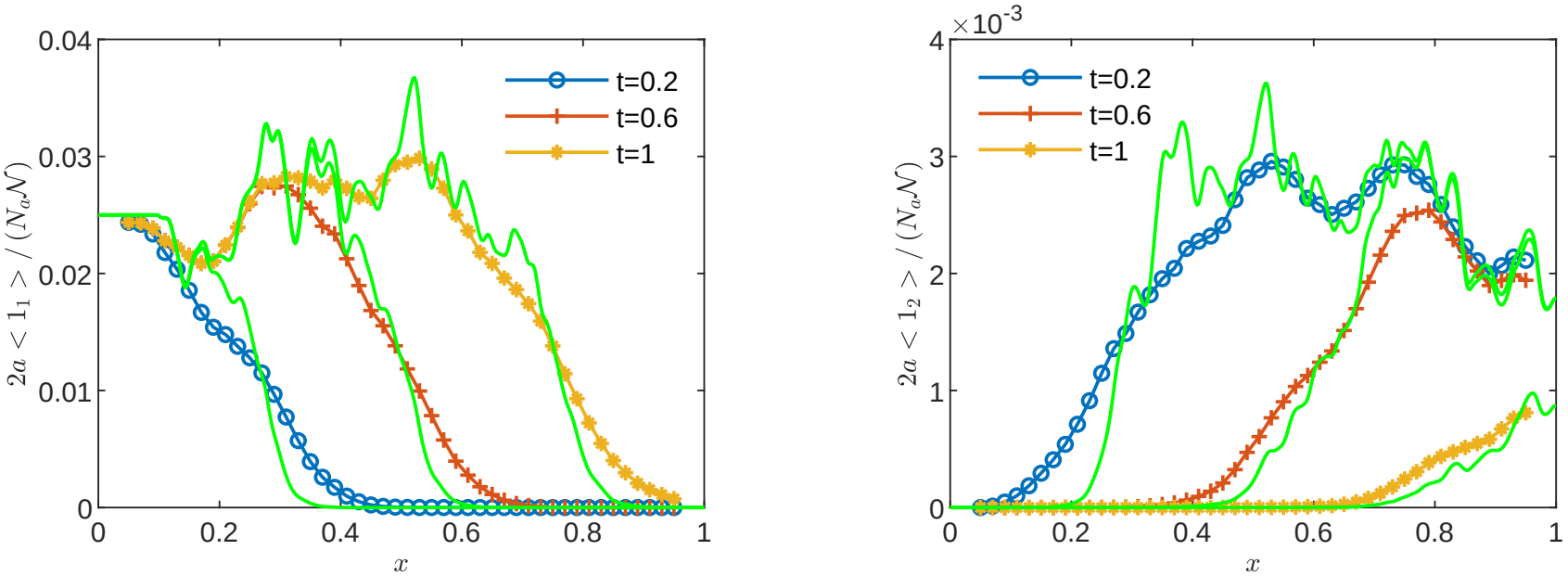




CGST average concentrations ($a = 0.05$, $\tau = 0.1$) compared to volume averages (full lines) and half total concentration $(\langle 1_1 \rangle + \langle 1_2 \rangle)/2$ (squares).

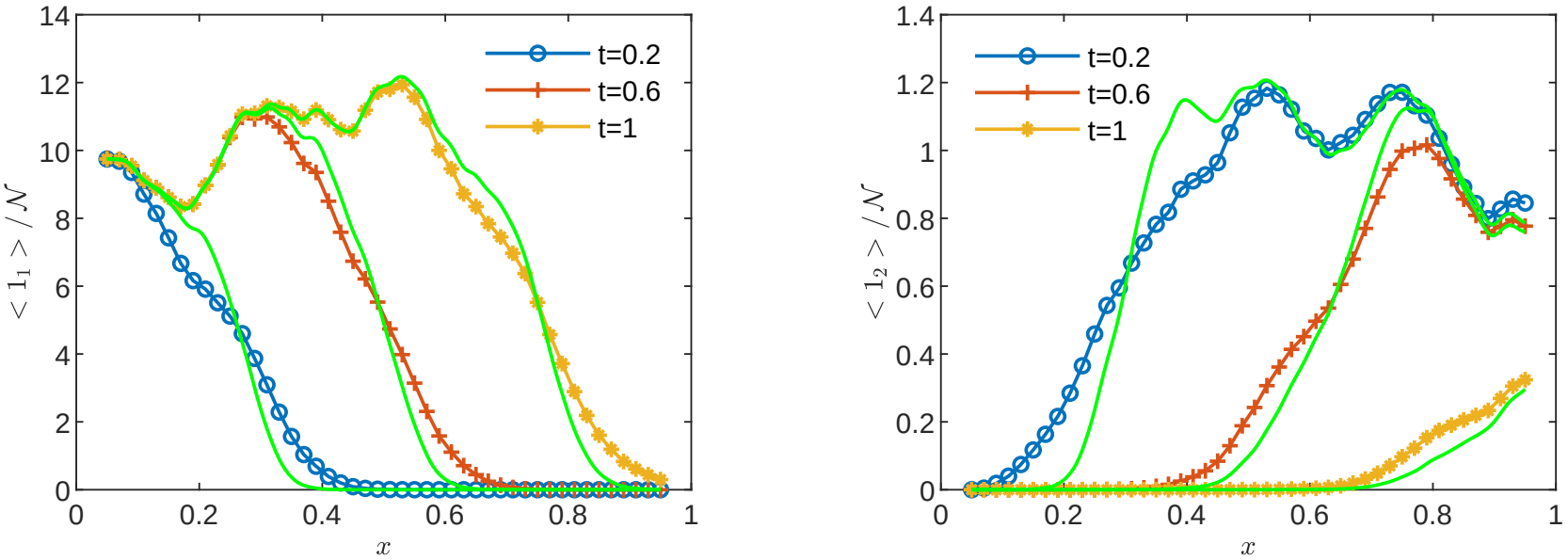
Biodegradation in aquifers (1-dim. case)

- aerobic biodegradation processes: electron donor contaminant (e.g., benzene) with concentration c_1, electron acceptor (oxygen) with concentration c_2, biomass with $c_3 = 1$ uniformly distributed in $\Omega = (0, 1)$,
- mobile species are transported by dispersion in realizations of a random velocity field modeling heterogeneous aquifers (BGRW simulation):



Moving averages and fine-grained concentrations (full lines).

Biodegradation in aquifers (1-dim. case)



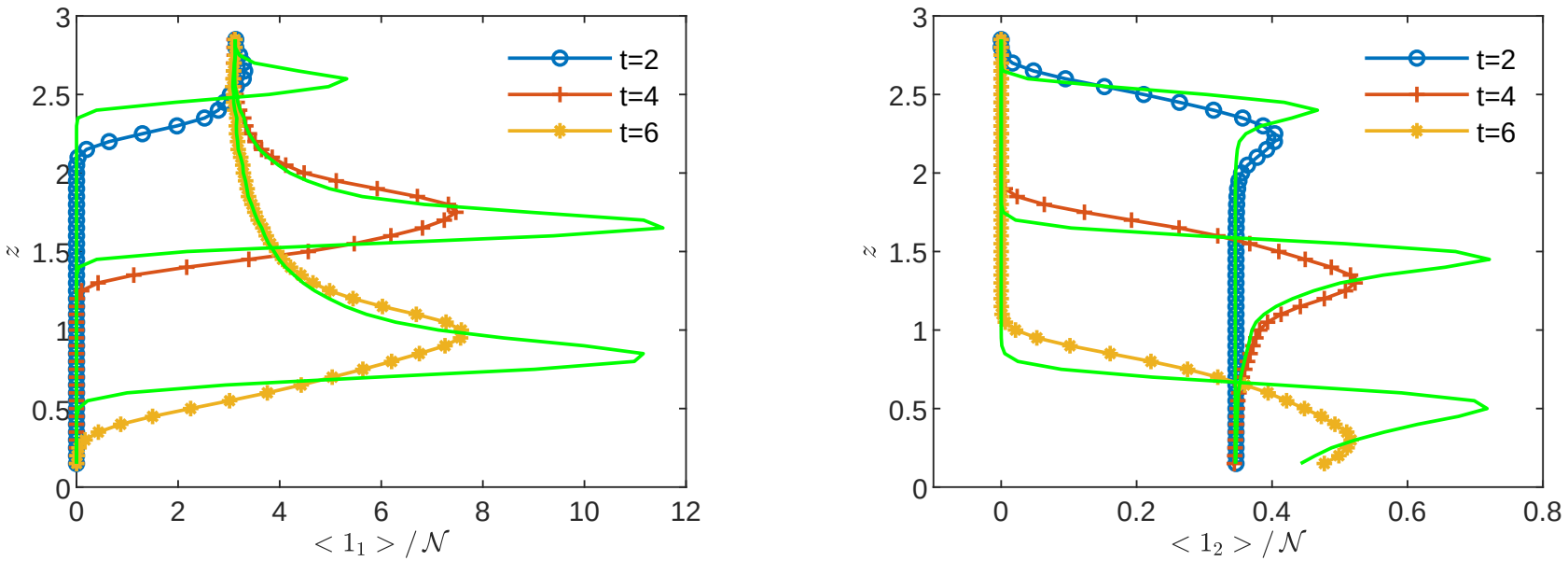
CGST concentrations ($a = 0.05,\ \tau = 0.2$) and volume averages $\overline{c_\nu^*}$ (full lines).

$$\varepsilon_{c_\nu} = \max(|\langle 1_\nu \rangle - \overline{c_\nu^*}|)/\langle 1_\nu \rangle (\arg(\max(|\langle 1_\nu \rangle - \overline{c_\nu^*}|))),\ \nu = 1, 2.$$

	realization		ensemble	
t	ε_{c_1}	ε_{c_2}	ε_{c_1}	ε_{c_2}
0.2	0.2561	0.2976	0.2155	0.6988
0.6	0.5112	0.4264	0.5898	0.4449
1.0	0.5400	0.4706	0.4926	0.3529

Biodegradation in variably saturated soils (1-dim. case)

- aerobic biodegradation process in $\Omega = (0, 3)$, driven by a continuous injection of the contaminant on the top of the column in conditions of free drainage at the bottom, modeled by an iterative BGRW scheme:

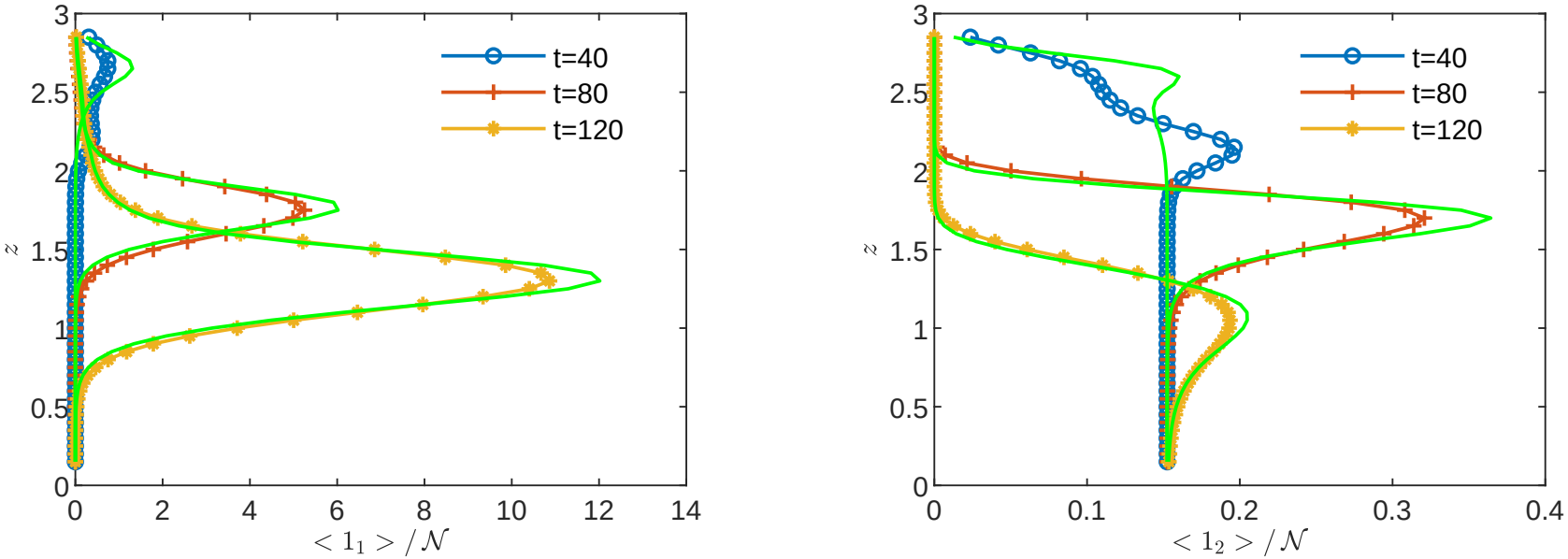


CGST concentrations ($a = 0.05$, $\tau = 0.6$) and volume averages (full lines).

t	ε_{c_1}	ε_{c_2}
2	0.9895	0.5867
4	0.6950	0.6057
6	0.7702	0.6576

Biodegradation in variably saturated soils (2-dim. case)

- similar aerobic biodegradation process in $\Omega = (0,2) \times (0,3)$:



CGST averaged concentrations ($a = 0.05$, $\tau = 12$) compared to volume averaged concentrations (full lines), sampled on a vertical line at $x = 1.75$.

	centered		decentered	
t	ε_{c_1}	ε_{c_2}	ε_{c_1}	ε_{c_2}
40	0.8041	0.1389	0.7670	0.5471
80	0.1636	0.3479	0.1737	0.1354
120	0.0880	0.0462	0.1062	0.2204

Particle tracking versus random walk

- both PT and RW can be used to solve parabolic and elliptic PDEs
- unlike PT, RW avoid the computation of individual trajectories: counting the number of particles at lattice sites $\Rightarrow$ GRW
- GRW schemes $\Leftarrow$ either equivalence of Itô and Fokker-Planck descriptions of diffusion or by randomization of explicit finite difference schemes

GRW versus BGRW

- GRW is faster than BGRW but prone of discretization and overshooting errors
- BGRW is slower (restricted by Pé≤ 2) but more accurate: it is a better approximation of the diffusion process and is free of overshooting errors

Are computational particles always necessary?

- not for flow schemes: they are basically explicit finite difference L-schemes, randomization does not bring any improvement
- important in transport schemes: reactive transport represented by the actual number of molecules involved in reactions provides a "microscopic description"

Measurements and space-time upscaling

- CGST averages over microscopic descriptions simulate measurements
- In conditions of non-stationary reactive transport processes, volume averages alone may significantly differ from space-time averages.

Einstein, A., 1905. On the movement of small particles suspended in stationary liquids required by the molecularkinetic theory of heat. Annalen der Physik, 17, 549–560 (in German). https://doi.org/10.1002/andp.2005517S112

https://www.maths.usyd.edu.au/u/UG/SM/MATH3075/r/Einstein_1905.pdf (English translation)

Chorin, A.J., 1973. Numerical study of slightly viscous flow. Journal of Fluid Mechanics 57(4), 785–796. https://doi.org/10.1017/S002211207300201 6

Chorin, A.J., 1978. Vortex sheet approximation of boundary layers. Journal of Computational Physics, 27(3), 428-442. https://doi.org/10.1016/0021-9991(78)90019-0

Pope, S.B., 1981. A Monte Carlo method for the PDF equations of turbulent reactive flow. Combustion Science and Technology, 25:5-6, 159-174. https://doi.org/10.1080/00102208108547500

Kloeden, P. E., and E. Platen (1992), Numerical Solutions of Stochastic Differential Equations, Springer, Berlin. https://doi.org/10.1007/978-3-662-12616-5_4


Cătinaș, E., 2021. How many steps still left to x*? SIAM Rev., 63(3), 585–624. https://doi.org/10.1137/19M1244858


Suciu, N., Illiano, D., Prechtel, A., Radu, F.A., 2021. Global random walk solvers for fully coupled flow and transport in saturated/unsaturated porous media. Adv. Water Resour. 152, 103935. https://doi.org/10.1016/j.advwatres.2021.103935


Suciu, N., Radu, F.A., 2022. Global random walk solvers for reactive transport and biodegradation processes in heterogeneous porous media. Adv. Water Resour. 166, 104268. http://dx.doi.org/10.1016/j.advwatres.2022.104268


Suciu, N., Radu, F.A., Pop, I.S., 2022. Space-time upscaling of reactive transport in porous media. arXiv:2112.10692v4. https://doi.org/10.48550/arXiv.2112.10692


Vamoș C., Georgescu A., Suciu N., Turcu I., 1996. Balance equations for physical systems with corpuscular structure. Phys. Stat. Mech. Appl., 227(1), 81–92. http://dx.doi.org/10.1016/0378-4371(95)00373-8.

Work supported by the Deutsche Forschungsgemeinschaft (German Research Foundation – DFG) under Grant SU 415/4-1 – 405338726 *"Integrated global random walk model for reactive transport in groundwater adapted to measurement spatio-temporal scales"*

Thank you for your attention!