Foundations of Multiscale Modelling: Kinetics
(Seminars/Labs)

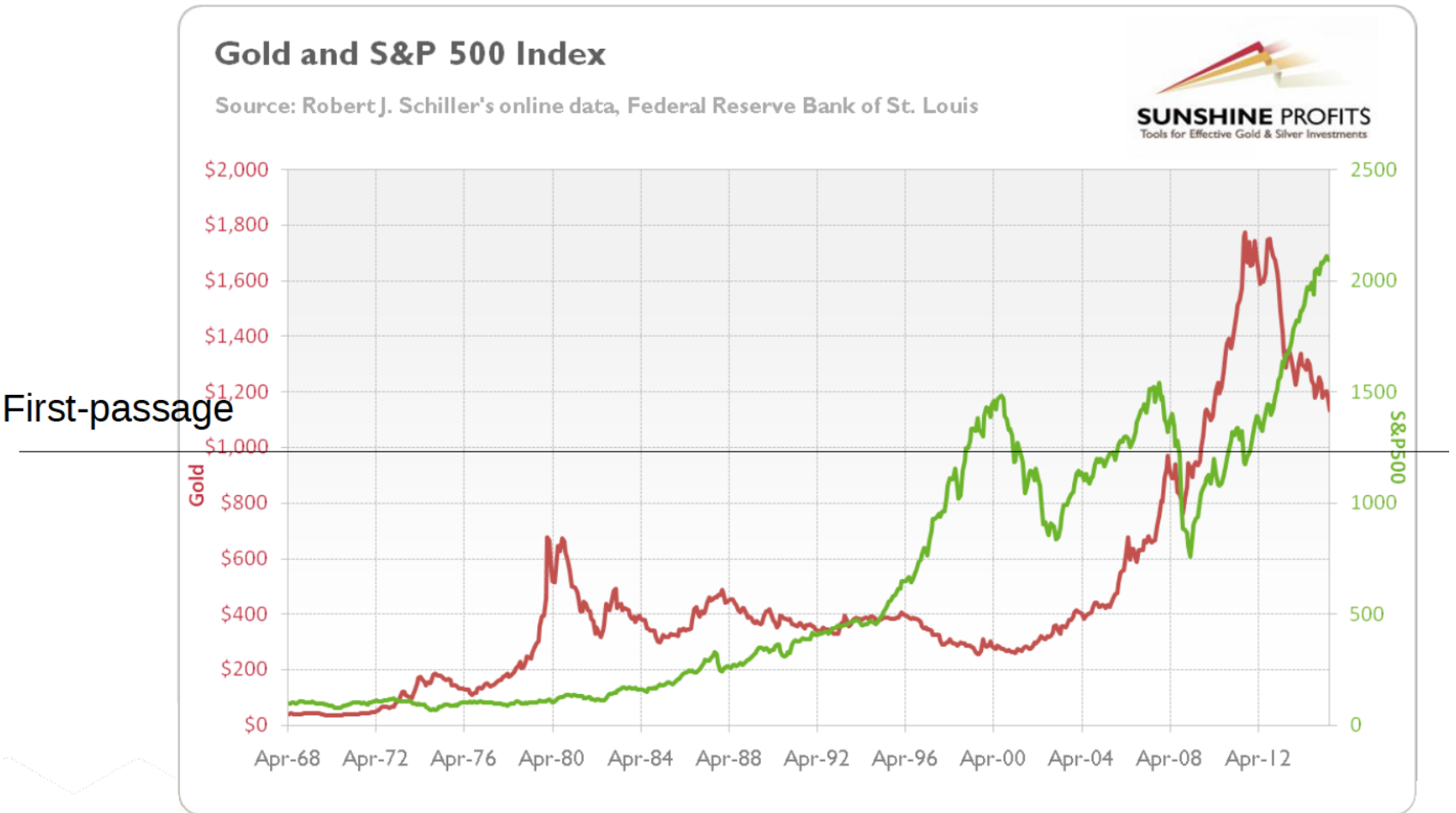
Lesson 2

Diffusion and the first passage

February, 2022

First-passage problem

When do we expect to cross a boundary for the first time?



Diffusion on a semi-infinite interval

Fokker-Planck equation with $U(x) = ux$ and $D(x) \equiv D$:

$$\frac{\partial}{\partial t}P(x,t) = \frac{u}{\gamma}\frac{\partial}{\partial x}P(x,t) + D\frac{\partial^2}{\partial x^2}P(x,t), \qquad x \geq 0.$$

Initial condition:

$$P(x, t = 0) = \delta(x - x_0).$$

Boundary conditions:

- $P(x = \infty, t) = 0$ — natural;
- $P(x = 0, t) = 0$ — absorbing.

The absorbing condition can be satisfied by the **method of images**.

First-passage characteristics

The survival probability

$$S(t) = \int_0^\infty P(t, x)\,\mathrm{d}x.$$

The absorption probability

$$A(t) = 1 - S(t).$$

The first-passage density

$$\varphi_{\mathrm{FP}}(t) = -\frac{\mathrm{d}S(t)}{\mathrm{d}t}.$$

The mean first-passage time

$$\langle T \rangle = \int_0^\infty t\varphi_{\mathrm{FP}}(t)\,\mathrm{d}t.$$

Overdamped Langevin equation

Write a program to simulate

$$\frac{dx}{dt} = -\frac{1}{\gamma}u + \frac{1}{\gamma}F(t),$$

where $F(t)$ is a Gaussian white noise,

$$\langle F(t)F(t')\rangle = 2k_{\mathrm{B}}T\gamma\delta(t-t').$$

For simulations, set $k_{\mathrm{B}}T = 1$ and $\gamma = 1$ and start from $x_0 = 1$.

Apply the **absorbing condition**: once $x(t)$ reaches 0 first time during a simulation run (say, at $t = t^*$), update: $\varphi_{\mathrm{FP}}(t^*) = \varphi_{\mathrm{FP}}(t^*) + 1$.

Finally, normalize the calculated $\varphi_{\mathrm{FP}}(t)$ to unity and get the first passage time density.

Kramers formula

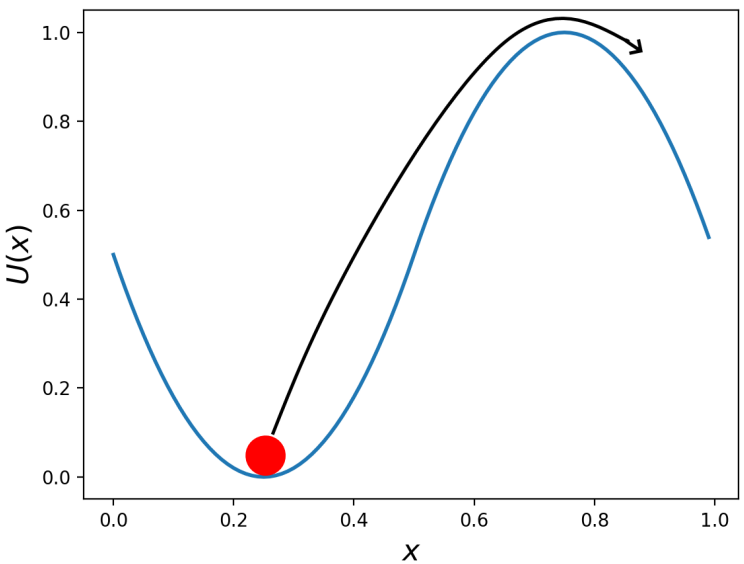
(a) The potential is given by

$$U(x) = \begin{cases} \omega(x-0.25)^2, & x \in [0, 0.5]. \\ \omega/8 - \omega(x-0.75)^2, & x \in (0.5, 1]. \end{cases}$$

The mean first passage time T_{MFPT} can be estimated as

$$T_{\mathrm{MFPT}} = \frac{2\pi\gamma \mathrm{e}^{\Delta U/k_{\mathrm{B}}T}}{|U''(x_{\mathrm{min}})U''(x_{\mathrm{max}})|^{1/2}},$$

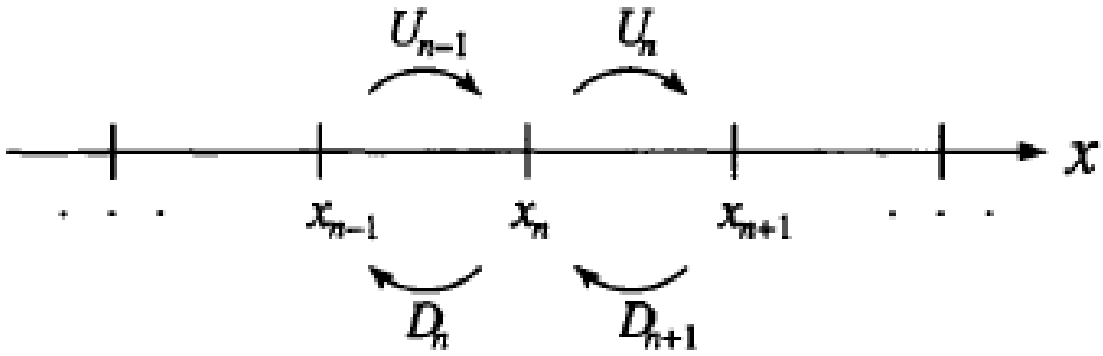
where $\Delta U = U(x_{\mathrm{max}}) - U(x_{\mathrm{min}})$.



Random walks on a lattice simulation

(b) Consider $x \in [0, 1]$ and $x_0 = 0.25$ as a starting point.

Boundaries: left — reflective, right — absorbing.



The transition rates are

$$U_n = \frac{k_B T}{\Delta x^2} \mathrm{e}^{-\Delta U_{n+1}/2k_B T}, \qquad \Delta U_{n+1} = U(x_{n+1}) - U(x_n),$$

and

$$D_n = \frac{k_B T}{\Delta x^2} \mathrm{e}^{-\Delta U_n/2k_B T}, \qquad \Delta U_n = U(x_n) - U(x_{n-1}).$$

Hint. For more details, see Doering.pdf

Monte Carlo algorithm

Set $t_{\mathrm{tot}} = 0$. Starting from x_0 with step Δx:

1. Calculate the transitions rates U_n and D_n.
2. Calculate the amount of time the particle waits at site x_n:

$$t = -(U_n + D_n)^{-1} \ln(X_1), \qquad X_1 \sim \mathcal{U}(0,1), \qquad t_{\mathrm{tot}} = t_{\mathrm{tot}} + t.$$

3. Generate $X_2 \sim \mathcal{U}(0,1)$ and compare with the jump probabilities:

$$P(x_n \to x_{n+1}) = \frac{U_n}{U_n + D_n}, \qquad P(x_n \to x_{n-1}) = \frac{D_n}{U_n + D_n}.$$

4. Make a jump $x_n \to x_{n+1}$ or $x_n \to x_{n-1}$ according to comparison.

Repeat until the absorption happens.

After N runs we calculate $T_{\mathrm{MFPT}} = \langle t_{\mathrm{tot}} \rangle$.

Numerical methods for Fokker-Planck equation*

Implement a finite-difference scheme to solve

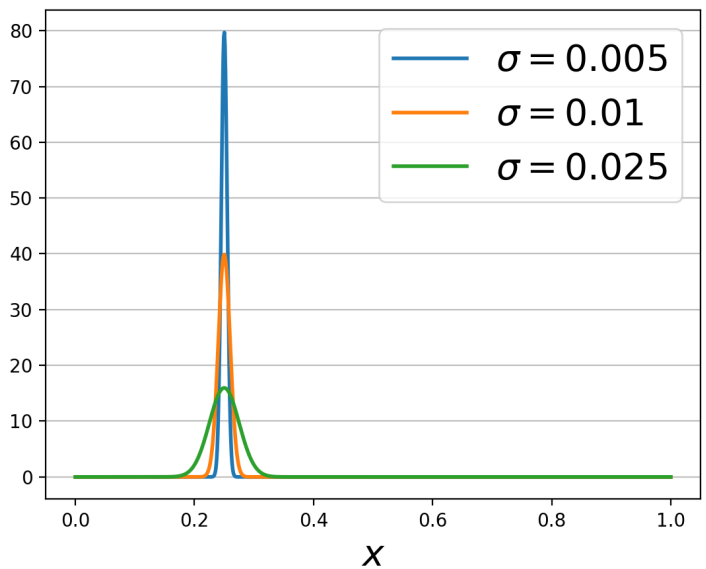
$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(\frac{\partial U(x)}{\partial x}P(x,t)\right) + \frac{\partial^2}{\partial x^2}P(x,t), \qquad x \in [0,1],$$

with the harmonic potential $U(x) = a(x-0.5)^2$.

Absorbing boundary conditions:
$P(0,t) = P(1,t) = 0.$

Initial condition:
$P(x,0) = \delta(x-0.25).$

Smooth approximation of $\delta(x-x_0)$ is the Gaussian PDF with $\mu = x_0$ and small variance $\sigma \ll 1$.



Hint. The solution should tend to the stationary: $P_{st}(x) = Ce^{-U(x)}$.

Forward Time Centered Space method (FTCS)

We take into account

$$\frac{\partial U(x)}{\partial x} = V(x), \qquad \frac{\partial^2 U(x)}{\partial x^2} = 2a,$$

and rewrite the Fokker-Planck equation as

$$\frac{\partial P(x,t)}{\partial t} = 2aP(x,t) + V(x)\frac{\partial P(x,t)}{\partial x} + \frac{\partial^2 P(x,t)}{\partial x^2}.$$

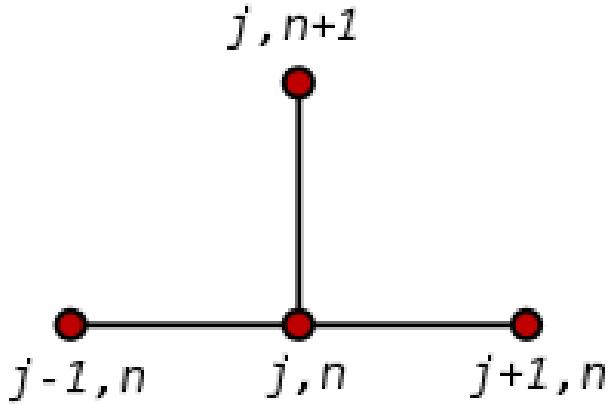
The finite-difference scheme reads,

$$\frac{P_j^{n+1} - P_j^n}{\Delta t} = 2aP_j^n + V_j \frac{P_{j+1}^n - P_{j-1}^n}{2\Delta x} + \frac{P_{j+1}^n - 2P_j^n + P_{j-1}^n}{\Delta x^2},$$

where $j = 1, 2, \ldots, N_x - 1$.

For the boundaries,

$$P_0^{n+1} = P_0^n = P_{N_x}^{n+1} = P_{N_x}^n \equiv 0.$$



Vectorized form of FTCS

Rearranging, we write the finite-difference scheme as

$$P_j^{n+1} = (-v_j + \gamma)P_{j-1}^n + \beta P_j^n + (v_j + \gamma)P_{j+1}^n,$$

where $v_j = V_j \Delta t/(2\Delta x)$, $\beta = 1 + 2a\Delta t - 2\gamma$ and $\gamma = \Delta t/\Delta x^2$.

Introducing $\mathbf{P}^n = (P_0^n, P_1^n, \ldots, P_{N_x}^n)^T$, we can write the scheme as

$$\mathbf{P}^{n+1} = M\mathbf{P}^n,$$

where M is the $(N_x + 1) \times (N_x + 1)$ matrix of the form

$$M = \begin{pmatrix} 1 & 0 & 0 & 0 & \ldots & 0 \\ -v_1 + \gamma & \beta & v_1 + \gamma & 0 & \ldots & 0 \\ 0 & -v_2 + \gamma & \beta & v_2 + \gamma & \ldots & 0 \\ \vdots & \vdots & \ddots & \ddots & \ddots & \vdots \\ 0 & 0 & \ldots & -v_{N_x-1} + \gamma & \beta & v_{N_x-1} + \gamma \\ 0 & 0 & \ldots & 0 & 0 & 1 \end{pmatrix}$$

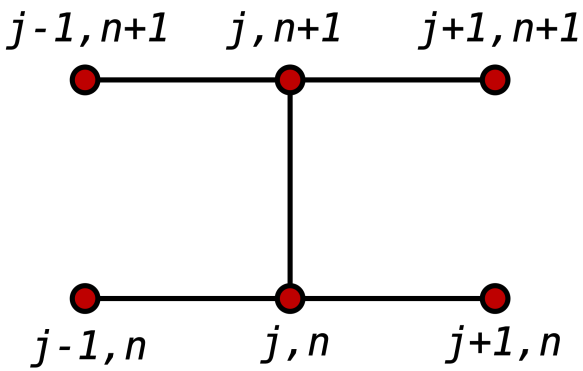
Cranck-Nicolson method

The finite-difference scheme reads,

$$\frac{P_j^{n+1}-P_j^n}{\Delta t}=\frac{1}{2}\left[2aP_j^{n+1}+V_j\frac{P_{j+1}^{n+1}-P_{j-1}^{n+1}}{2\Delta x}+\frac{P_{j+1}^{n+1}-2P_j^{n+1}+P_{j-1}^{n+1}}{\Delta x^2}\right.$$
$$\left.+2aP_j^n+V_j\frac{P_{j+1}^n-P_{j-1}^n}{2\Delta x}+\frac{P_{j+1}^n-2P_j^n+P_{j-1}^n}{\Delta x^2}\right],$$

Rearranging, we come to

$$(v_j-\gamma)P_{j-1}^{n+1}+\alpha P_j^{n+1}+(-v_j-\gamma)P_{j+1}^{n+1}$$
$$=(-v_j+\gamma)P_{j-1}^n+\beta P_j^n+(v_j+\gamma)P_{j+1}^n,$$



where $v_j=V_j\Delta t/(4\Delta x)$, $\gamma=\Delta t/(2\Delta x^2)$,
$\alpha=1-a\Delta t+\gamma$ and $\beta=1+a\Delta t-\gamma$.

Vectorized form of Cranck-Nicolson method

At each time step we need to solve the linear system of equations,

$$M_1 \mathbf{P}^{n+1} = M_2 \mathbf{P}^n \equiv \mathbf{f}^n,$$

$$M_1 = \begin{pmatrix} 1 & 0 & 0 & 0 & \dots & 0 \\ v_1 - \gamma & \alpha & -v_1 - \gamma & 0 & \dots & 0 \\ 0 & v_2 - \gamma & \alpha & -v_2 - \gamma & \dots & 0 \\ \vdots & \vdots & \ddots & \ddots & \ddots & \vdots \\ 0 & 0 & \dots & v_{N_x-1} - \gamma & \alpha & -v_{N_x-1} - \gamma \\ 0 & 0 & \dots & 0 & 0 & 1 \end{pmatrix}$$

and

$$M_2 = \begin{pmatrix} 1 & 0 & 0 & 0 & \dots & 0 \\ -v_1 + \gamma & \beta & v_1 + \gamma & 0 & \dots & 0 \\ 0 & -v_2 + \gamma & \beta & v_2 + \gamma & \dots & 0 \\ \vdots & \vdots & \ddots & \ddots & \ddots & \vdots \\ 0 & 0 & \dots & -v_{N_x-1} + \gamma & \beta & v_{N_x-1} + \gamma \\ 0 & 0 & \dots & 0 & 0 & 1 \end{pmatrix}$$

Thank you for attention!