Foundations of Multiscale Modelling: Kinetics
(Seminars/Labs)
Lesson 1

Feb, 2022

Langevin Equation and Brownian Dynamics (5 points)

Stochastic differential equation

$$M\frac{dv}{dt} = -\gamma v + F(t),$$

where $F(t)$ is the random force (Gaussian noise):

$$\langle F(t)\rangle = 0, \quad \left\langle F(t)F(t')\right\rangle = \Gamma\delta(t-t'), \quad \Gamma = 2k_BT\gamma.$$

(a) Find an analytic expression for the VACF:

$$K_v(t) = \frac{\langle v(0)v(t)\rangle}{\langle v^2(0)\rangle}.$$

- An ensemble of different realizations E of $v(t,E)$ with $F(t,E)$;
- the average $\langle \dots \rangle$ is carried out over all realizations E.

Box-Muller transform

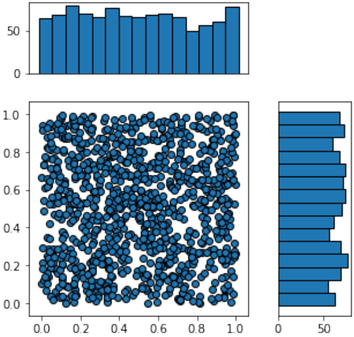
(b)–(c) Produce $\xi \sim \mathcal{N}(0,1)$ from a uniform distribution.

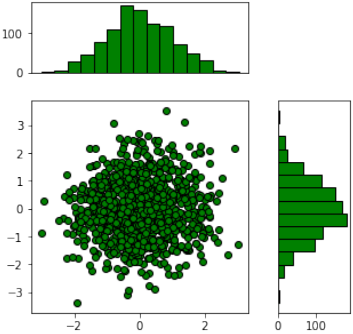
Lemma

If $U_1, U_2 \sim \mathcal{U}(0,1)$ are independent, then

$$Y_1 = \sqrt{(-2\ln U_1)}\cos(2\pi U_2), \qquad Y_2 = \sqrt{(-2\ln U_1)}\sin(2\pi U_2)$$

are independent and $Y_1, Y_2 \sim \mathcal{N}(0,1)$.





Finite-difference scheme for the Langevin equation

(d) Write a program that simulates the Langevin equation using

$$v_{n+1} - v_n = -\frac{\gamma}{M} v_n \Delta t + \frac{1}{M} \left(\Gamma \Delta t\right)^{1/2} \xi_n.$$

(e) Calculate the VACF and compare it with the analytic result (a) by putting them on one plot.

- For simplicity, assume $\gamma = 1$, $M = 1$ and $k_B T = 1$;
- in python, for ξ_n use *random.normal* from *numpy*;
- you should gain a good agreement for the VACF $K_v(t)$ in (e).

Generalized Langevin Equation* (2 points)

Assuming that the friction depends on the history, we have

$$M\frac{dv}{dt} = -\int_0^t G(t-\tau)v(\tau)d\tau + F(t),$$

where the random force $F(t)$ **is not** a Gaussian white noise:

$$\langle F(t)\rangle = 0, \qquad \left\langle F(t)F(t')\right\rangle = 2k_BTG(t-t').$$

(a) Program the finite difference scheme for the equation and calculate the VACF. Consider two cases,

$$G(t) = \mathrm{e}^{-a|t|}, \qquad G(t) = \mathrm{e}^{-b|t|^2}.$$

- choose $M = 1$, $k_BT = 0.5$, and a and b from your own choice;
- the convolution integral can be represented as a sum over already obtained history of the system.

Colored noise

How to simulate the colored noise $\xi(t) \equiv F(t)$ properly?

An exponentially correlated noise,

$$\langle \xi(t)\xi(t') \rangle = \mathrm{e}^{-a|t-t'|},$$

can be obtained from the following equation

$$\frac{\mathrm{d}\xi}{\mathrm{d}t} = -a\xi + \sqrt{2a}\,\eta(t).$$

Here, $\eta(t)$ is a Gaussian white noise,

$$\langle \eta(t)\eta(t') \rangle = \delta(t-t').$$

- program the finite-difference scheme for the system of two equations (generate ξ_n from the colored noise equation);
- this equation does not depend on the velocity $v(t)$.

Colored noise: general approach

The colored noise $\xi(t)$,

$$\langle \xi(t) \rangle = 0, \qquad \langle \xi(t)\xi(t') \rangle = G(t-t'),$$

can be discretized to $\boldsymbol{\xi} = (\xi_1, \ldots, \xi_n)^T$, where

$$\xi_i = \xi(t_i), \qquad \langle \xi_i \rangle = 0, \qquad \langle \xi_i \xi_j \rangle = G_{ij}.$$

Multivariate normal distribution with the covariance matrix

$$\Sigma = (G_{ij})_{i,j=1}^{n} \in \mathbb{R}^{n\times n}, \qquad \Sigma \equiv \langle \boldsymbol{\xi}\boldsymbol{\xi}^T \rangle, \qquad \Sigma^T = \Sigma > 0.$$

To generate $\boldsymbol{\xi}$, apply the following method:

1. find the Cholesky decomposition: $C^T C = \Sigma$;
2. generate $\mathbf{x} = (x_1, \ldots, x_n)$, $x_i \sim \mathcal{N}(0,1)$ are i.i.d.;
3. make linear transformation: $\boldsymbol{\xi} = C^T \mathbf{x}$.

(b) For the case $G(t) = \mathrm{e}^{-a|t|}$ find an analytic solution for the VACF:

$$M\frac{d}{dt}K_v(t) = -\int_0^t G(t-\tau)K_v(\tau)d\tau.$$

Compare the VACF with the simulations result (a) by putting them on one plot.

- Use the Laplace transform

  $$\mathcal{L}\left\{f\right\}(s) = \int_0^\infty f(t)\mathrm{e}^{-st}\,\mathrm{d}t$$

  to reduce the equation to an algebraic form;
- use the inverse Laplace transform to get the result in real time;

Fluctuation-Dissipation Theorem (2 points)

Assume that the quantities A and B are correlated as

$$\langle A(0)B(t)\rangle = C\mathrm{e}^{-|t|/\tau}.$$

Find the imaginary part of the linear response function $\chi_{AB}(\omega)$.

How would you describe the physical meaning of this function?

- Use lecture notes.

Homework upload

Upload here:

`https://skoltech.instructure.com/login/canvas`

`https://jupyter.org`

Jupyter advantages:

- code can be divided into severals problems within *one* file (cells);
- *your* runs results are presented above the code (graphs, etc.);
- scans of analytics can be attached in ipynb as jpg/png files;
- analytic expressions can by written directly using LaTeX.

Telegram chat for the course (to be in touch):