
MATH0488 – Elements of stochastic processes

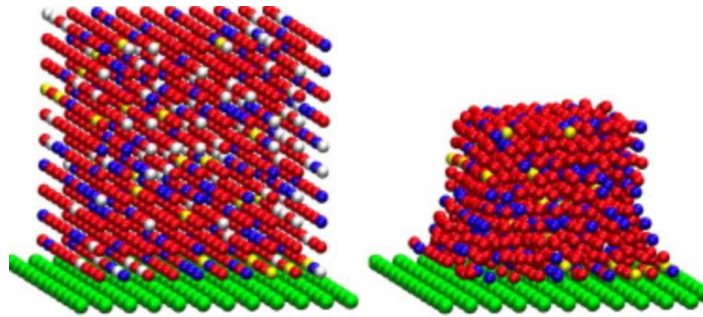
Molecular dynamics: Brownian motion and Wiener process

Maarten Arnst

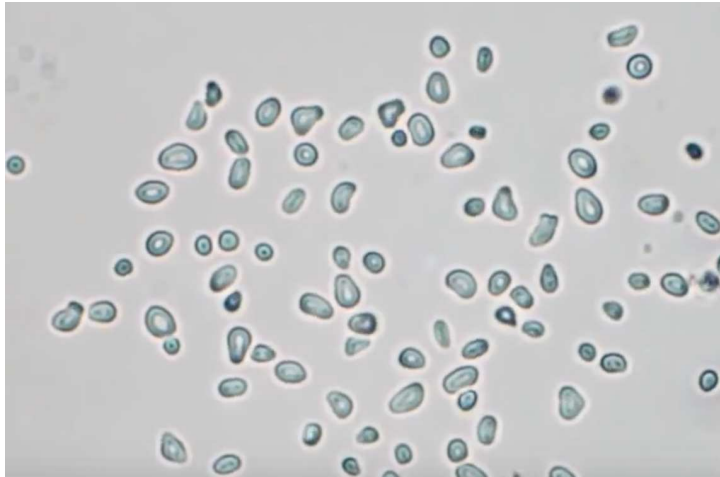
Marco Lucio Cerquaglia, Adrien Crovato, Joffrey Coheur, Thomas Lambert, and Cédric Laruelle

March 13, 2018

- Introduction.
- Foundational discoveries of Brown and Einstein.
 - ◆ Overview.
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- Background on stochastic processes.
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- Matter is made out of a great many interacting atoms, or elementary parts. Thus, macroscale behavior (mechanical, electrical, . . .) of matter should be explainable in terms of the microscopic behavior and motion of the atoms, or the elementary parts.
- Realistic physical bodies are composed of a huge number of atoms; for example, 1 mm^3 of bulk metal contains about 10^{19} atoms. We are not going to be able or want to know how every atom is actually behaving or where it is actually moving. A deterministic approach is not feasible.
- Systems of vast numbers of atoms are governed by principles that call for a probabilistic description. We are going to want to know about average behavior and what the odds are for different effects occurring. We are going to want to describe the motion of atoms as a random motion.
- A probabilistic description can also be motivated by the behavior of atoms being not according to classical mechanics, but rather quantum mechanics, but this is beyond the scope of this course.



Macroscale behavior: little particles of plant pollens jiggle around in a liquid.

Robert Brown.
(botanist, experimentalist).

Microscale origin: effect of collisions with smaller liquid molecules in thermal motion.

Albert Einstein.
(theoretical physicist).

We will look at foundational discoveries of Brown and Einstein.

Foundational discoveries of Brown and Einstein

INVESTIGATIONS ON THE THEORY OF THE BROWNIAN MOVEMENT

I

ON THE MOVEMENT OF SMALL PARTICLES
SUSPENDED IN A STATIONARY LIQUID
DEMANDED BY THE MOLECULAR-
KINETIC THEORY OF HEAT



IN this paper it will be shown that according to the molecular-kinetic theory of heat, bodies of microscopically-visible size suspended in a liquid will perform movements of such magnitude that they can be easily observed in a microscope, on account of the molecular motions of heat. It is possible that the movements to be discussed here are identical with the so-called “Brownian molecular motion”; however, the information available to me regarding the latter is so lacking in precision, that I can form no judgment in the matter (I).

If the movement discussed here can actually be observed (together with the laws relating to

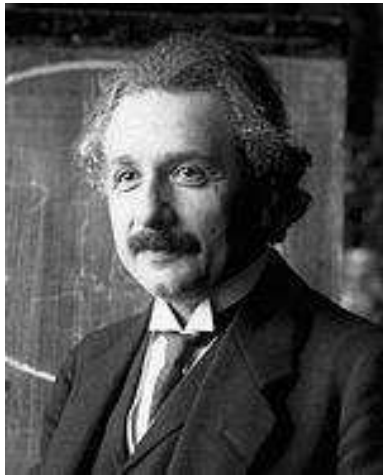
A. Einstein. Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen. Annalen der Physik, 17:549-..., 1905.

www.rpgroup.caltech.edu/courses/aph161/Handouts/Einstein1905A.pdf.

- The Brownian motion was discovered in 1827 by Robert Brown, a botanist. While he was studying microscopic life, he noticed little particles of **plant pollens jiggling around in the liquid** he was looking at in the microscope.
- “In this paper it will be shown that according to the molecular-kinetic theory of heat, bodies of microscopically-visible size suspended in a liquid will perform movements of such magnitude that they can be easily observed in a microscope, **on account of the molecular motions of heat**. It is possible that the movements to be discussed here are identical with the so-called “Brownian molecular motion”; however, the information available to me regarding the latter is so lacking in precision, that I can form no judgment in the matter (I).”
- “**If the movement discussed here can actually be observed** (together with the laws relating to it that one would expect to find), then classical thermodynamics can no longer be looked upon as applicable with precision to bodies even of dimensions distinguishable in a microscope: an exact determination of actual atomic dimensions is then possible. On the other hand, had the prediction of this movement proved to be incorrect, a weighty argument would be provided against the molecular-kinetic conception of heat.”

- There are two main lines of thought in Einstein's paper:
 1. The first line of thought consists in **explaining the movement of the particles as the effect of molecular collisions**. As part of this line of thought, Einstein also establishes that the evolution of the probability density function of each component of the position of a particle relative to its initial position obeys a diffusion equation whose diffusion coefficient is related to the second moment of the particle movement.
 2. The second line of thought consists in **establishing relationships between the theory and experimentally observable behavior**, thus paving the way for validating the theory through experiments and, in this way, providing evidence for the atomic nature of matter. Such experiments were later carried out by J. B. Perrin.

- Please note that in this section, we use (mostly) Einstein's notations. Thus, uppercase letters referring to random quantities and lowercase letters to deterministic quantities does not apply.



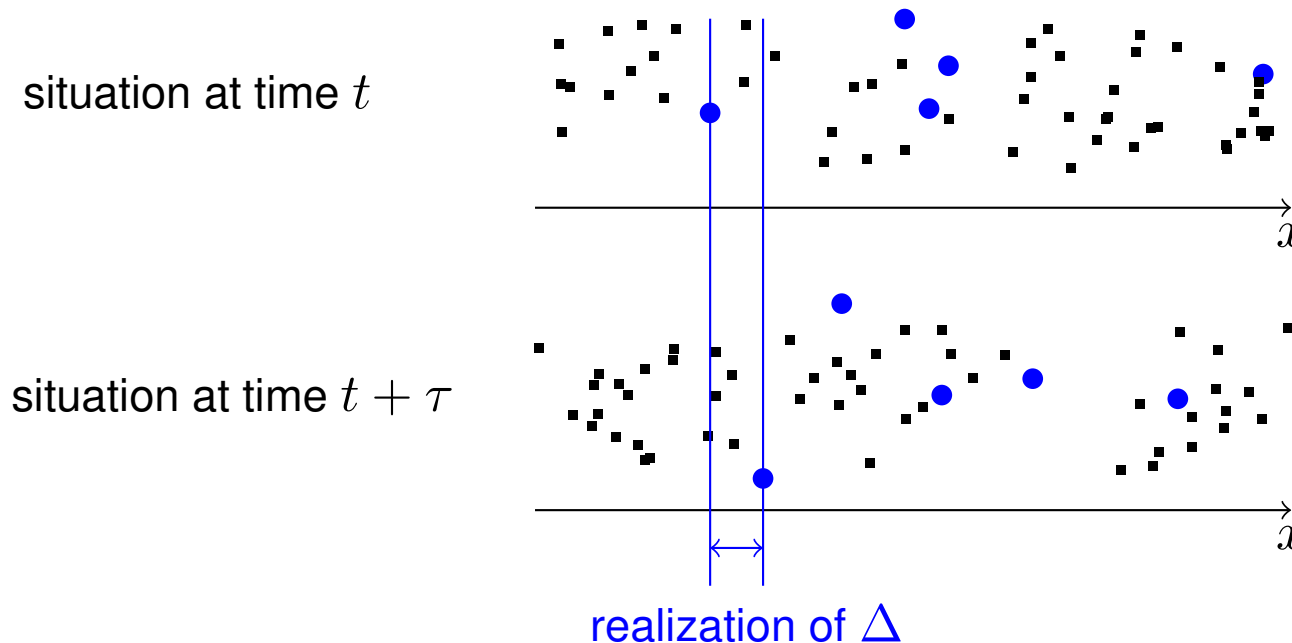
A. Einstein.
Nobel laureate in Physics, 1921.



J. B. Perrin.
Nobel laureate in Physics, 1926.

Molecular diffusion

- Einstein considers the horizontal component of motion (x -direction) in an unbounded domain involving particles (large blue dots in the sketch) suspended in a liquid (small black dots):



and Einstein denotes by $\nu(x, t)$ the number density of particles in a volume element (of unit area in the $y - z$ -plane) centered on spatial coordinate x at time t (assumed to depend only on x and t).

- “Evidently it must be assumed that each single particle executes a movement which is independent of the movement of all other particles.”
- “the movements of one and the same particle after different intervals of time must be considered as mutually independent processes, so long as [...] these intervals of time [are] not too small.”

- “We will introduce a time-interval τ in our discussion, which is to be very small compared with the observed interval of time, but, nevertheless, of such a magnitude that the movements executed by a particle in two consecutive intervals of time τ are to be considered as mutually independent [. . .].”
- “In an interval of time τ the x -co-ordinates of the single particles will increase by Δ , where Δ has a different value (positive or negative) for each particle. **For the value of Δ a certain probability [density function] will hold** [denoted by ϕ , which] fulfils the condition $\phi(\Delta) = \phi(-\Delta)$. We get

$$\nu(x, t + \tau) = \int_{-\infty}^{+\infty} \nu(x + \Delta, t) \phi(\Delta) d\Delta.”$$

- Einstein then constructs the Taylor series

$$\begin{aligned} \nu(x, t + \tau) &= \nu(x, t) + \tau \frac{\partial \nu}{\partial t} + \dots \\ \nu(x + \Delta, t) &= \nu(x, t) + \Delta \frac{\partial \nu}{\partial x}(x, t) + \frac{\Delta^2}{2!} \frac{\partial^2 \nu}{\partial x^2}(x, t) + \dots \end{aligned}$$

- “We can bring [these expansions] under the integral sign [. . .]. We obtain

$$\nu(x, t) + \tau \frac{\partial \nu}{\partial t} = \int_{-\infty}^{+\infty} \nu(x, t) \phi(\Delta) d\Delta + \int_{-\infty}^{+\infty} \Delta \frac{\partial \nu}{\partial x}(x, t) \phi(\Delta) d\Delta + \int_{-\infty}^{+\infty} \frac{\Delta^2}{2!} \frac{\partial^2 \nu}{\partial x^2}(x, t) \phi(\Delta) d\Delta [+ \dots].”$$

- “On the right-hand side the second, fourth, etc., terms vanish since $[\phi(\Delta) = \phi(-\Delta)]$; whilst of the first, third, fifth, etc., terms, every succeeding term is very small compared with the preceding. [...]

Bearing in mind that $\int_{-\infty}^{+\infty} \phi(\Delta)d\Delta = 1$, and putting

$$D = \frac{1}{\tau} \int_{-\infty}^{+\infty} \frac{\Delta^2}{2} \phi(\Delta)d\Delta,$$

[...] we get [...]

$$\frac{\partial v}{\partial t} = D \frac{\partial^2 v}{\partial x^2}.$$

This is the well-known **[partial] differential equation for diffusion**, and we recognise that D is the coefficient of diffusion.”

- Einstein finds that the second moment of the displacement over a time interval of length τ is related to the diffusion coefficient D as

$$\int_{-\infty}^{+\infty} \Delta^2 \phi(\Delta)d\Delta = 2D\tau.$$

Relationships with experiments

- To establish relationships with experiments, on the one hand, Einstein considers the problem of "diffusion outwards from a point," in which 1 particle starts from the origin $x = 0$ at time $t = 0$:

$$\begin{cases} \frac{\partial \rho}{\partial t}(x, t) - D \frac{\partial^2 \rho}{\partial x^2}(x, t) = 0, \\ \rho(x, 0) = \delta(x). \end{cases}$$

Einstein interprets this **diffusion equation** as describing the **evolution of the probability density function** for (the x -component of) the position of a particle (relative to its initial position).

- This problem has the solution

$$\rho(x, t) = \frac{1}{\sqrt{2\pi}\sqrt{2Dt}} \exp\left(-\frac{1}{2}\left(\frac{x}{\sqrt{2Dt}}\right)^2\right).$$

At any given time t , the probability density function $x \mapsto \rho(x, t)$ for the x -component of the position of the particle given that this particle was at the origin $x = 0$ at time 0 is the Gaussian probability density function with mean 0 and second moment $2Dt$. This expresses Einstein's famous finding that the **second moment** of (the x -component of) the position of a particle (relative to its initial position) is **proportional to the elapsed time**:

$$\overline{x^2} = 2Dt.$$

Relationships with experiments

- To establish relationships with experiments, on the other hand, Einstein elaborates a thought experiment in which he assumes that on each particle is exerted a force K that just balances the diffusion in the sense that there is no net flow of particles. For example, if the particles were charged, this force could be exerted by an electric field.
- “If the suspended particles have spherical form (radius a), and if the liquid has viscosity k , then [by **Stokes’s law**] the force K imparts to the single particles a velocity $\frac{K}{6\pi k a}$ and there will pass [...] per unit of time $\nu \frac{K}{6\pi k a}$ particles. [By **Fick’s law**] as the result of diffusion there will pass in a unit of time $-D \frac{\partial \nu}{\partial x}$ particles. Since there must be dynamic equilibrium [**conservation of mass**]:

$$\nu \frac{K}{6\pi k a} - D \frac{\partial \nu}{\partial x} = 0.”$$

- “Equilibrium with the force K is brought about by pressure [...]: $K\nu - \frac{\partial p}{\partial x} = 0$. [By **Van ’t Hoff’s law**] if there are ν particles in a unit volume [...] [in an equilibrium condition], there will be a corresponding osmotic pressure $p = \frac{RT}{N} \nu$, where N [Avogadro’s number] signifies the number of molecules contained in [1 mole, R is the ideal gas constant, and T is the absolute temperature]. The required condition of equilibrium [**conservation of momentum**]:

$$-K\nu + \frac{RT}{N} \frac{\partial \nu}{\partial x} = 0.”$$

Relationships with experiments

- “We can [eliminate the force K and] calculate the coefficient of diffusion from the two conditions [...]. We get

$$D = \frac{RT}{N} \frac{1}{6\pi k a}.”$$

- “Formula for the [**root-mean-square**] **displacement** of suspended particles:

$$\sqrt{\overline{x^2}} = \sqrt{t} \sqrt{\frac{RT}{N} \frac{1}{3\pi k a}.”$$

- “It is to be hoped that some enquirer may succeed shortly in solving the problem suggested here which is so important in connection with the theory of heat.”

Background on stochastic processes

Notations and conventions

- Let $f : \mathbb{R} \rightarrow \mathbb{R}$ be an **integrable function**, that is, $\int_{\mathbb{R}} |f(t)| dt < +\infty$. Then, the **Fourier transform** \hat{f} of f is the bounded, continuous function \hat{f} from \mathbb{R} into \mathbb{C} such that

$$\hat{f}(\omega) = \mathcal{F}f(\omega) = \int_{\mathbb{R}} \exp(-i\omega t) f(t) dt.$$

The Fourier transform of an integrable function is not necessarily integrable itself.

- Let $f : \mathbb{R} \rightarrow \mathbb{R}$ be a **square-integrable function**, that is, $\int_{\mathbb{R}} |f(t)|^2 dt < +\infty$. Then, the **Fourier transform** \hat{f} of f is the square-integrable function \hat{f} from \mathbb{R} into \mathbb{C} such that

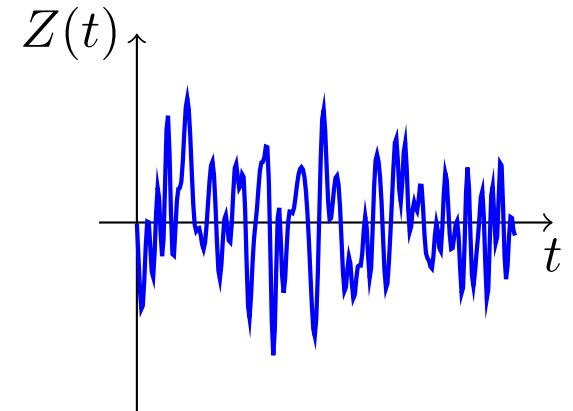
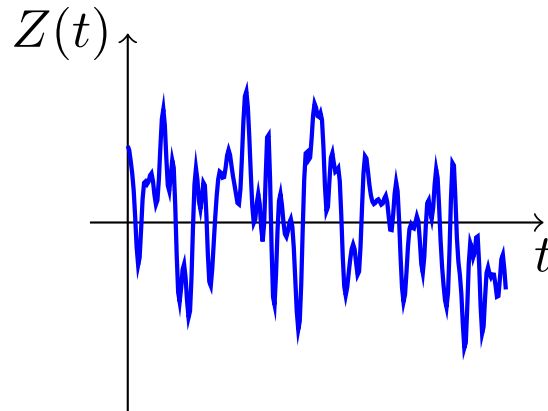
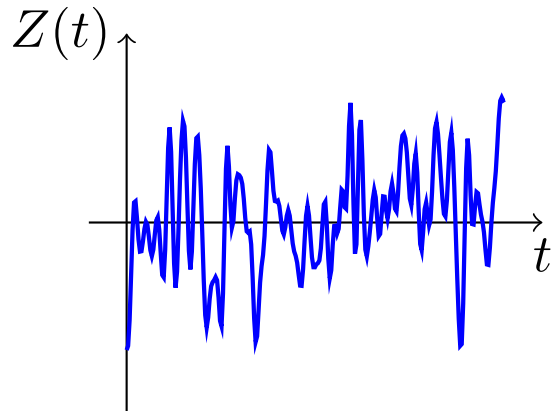
$$\begin{cases} \hat{f}(\omega) = \mathcal{F}f(\omega) = \int_{\mathbb{R}} \exp(-i\omega t) f(t) dt, \\ f(t) = \mathcal{F}^{-1}\hat{f}(t) = \frac{1}{2\pi} \int_{\mathbb{R}} \exp(i\omega t) \hat{f}(\omega) d\omega. \end{cases}$$

- These definitions indicate that one cannot take the Fourier transform of any function: these definitions provide the Fourier transform only for integrable and square-integrable functions.
- We include the minus sign in the forward transform and the factor $\frac{1}{2\pi}$ in the inverse transform.

- **Random variables** (samples are scalars, vectors, matrices,...):



- **Stochastic processes** (“samples are functions of one variable”):



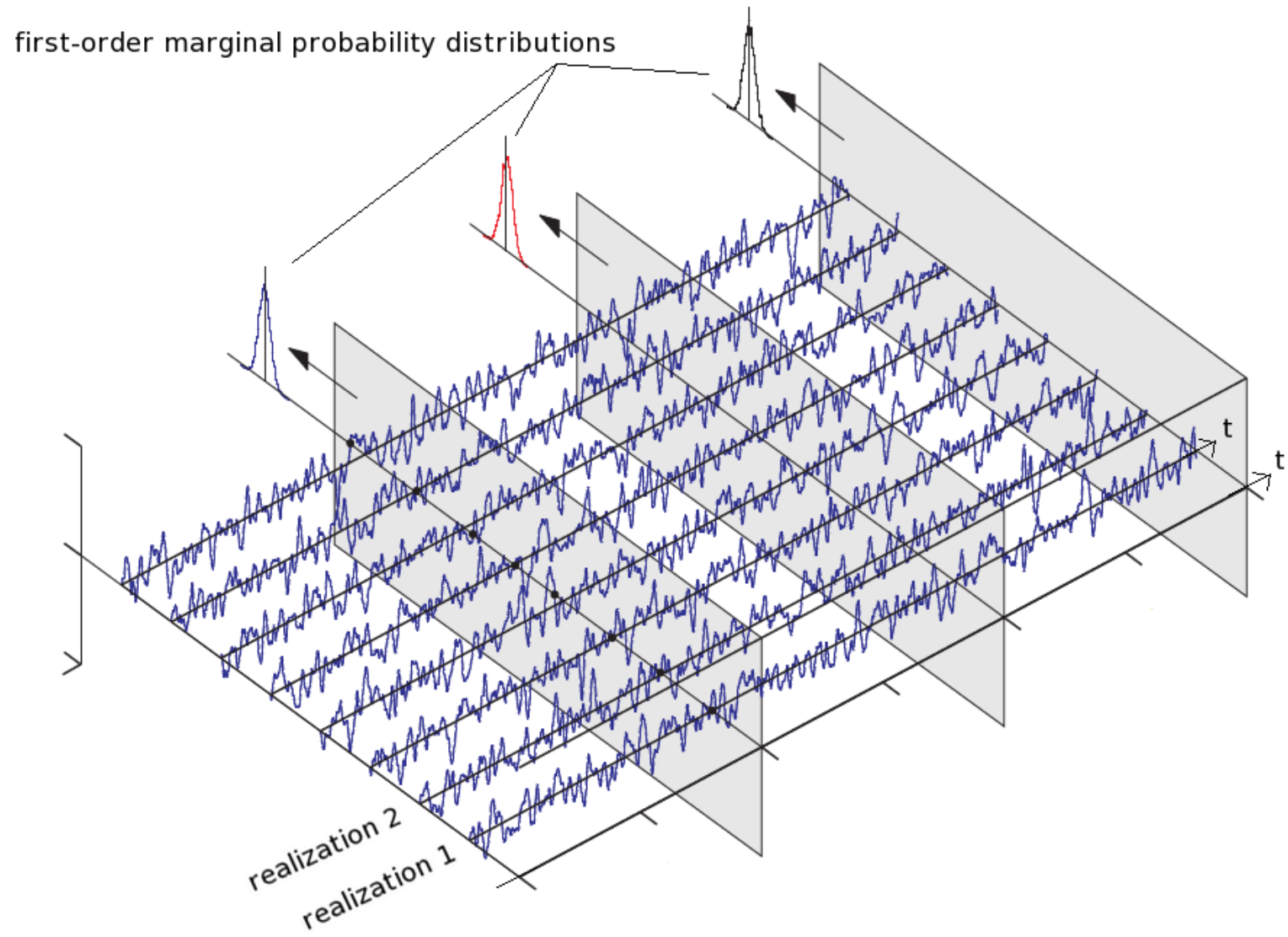
Second-order stochastic processes

- A **stochastic process** $\{Z(t), t \in \mathcal{T}\}$ indexed by a subset \mathcal{T} of \mathbb{R} and with values in \mathbb{R} is a collection of random variables $Z(t)$ with values in \mathbb{R} indexed by t in \mathcal{T} .
- For any nonempty finite subset $\{t_1, \dots, t_m\}$ of \mathcal{T} , where m denotes the number of elements in this subset, the joint probability density function $\rho_{(Z(t_1), \dots, Z(t_m))}$ of $(Z(t_1), \dots, Z(t_m))$ (provided that it exists) is called a **(m -th order) marginal probability density function** of the stochastic process $\{Z(t), t \in \mathcal{T}\}$.

The collection of all the marginal probability density functions (provided that they exist) of a stochastic process is called the **system of marginal probability density functions**.

- A stochastic process $\{Z(t), t \in \mathcal{T}\}$ indexed by \mathcal{T} and with values in \mathbb{R} is **Gaussian** if each probability density function in its system of marginal probability density functions is Gaussian.

Second-order stochastic processes



Second-order stochastic processes

- A stochastic process $\{Z(t), t \in \mathcal{T}\}$ indexed by \mathcal{T} with values in \mathbb{R} is of the **second order** if

$$E\{Z(t)^2\} = \int_{\mathbb{R}} z^2 \rho_{Z(t)}(z) dz < +\infty, \quad \forall t \in \mathcal{T}.$$

- The **mean function** of a second-order stochastic process $\{Z(t), t \in \mathcal{T}\}$ indexed by \mathcal{T} with values in \mathbb{R} is the function \bar{z} from \mathcal{T} into \mathbb{R} such that

$$\bar{z}(t) = E\{Z(t)\} = \int_{\mathbb{R}} z \rho_{Z(t)}(z) dz.$$

- The **autocorrelation function** of a second-order stochastic process $\{Z(t), t \in \mathcal{T}\}$ indexed by \mathcal{T} with values in \mathbb{R} is the function r_Z from $\mathcal{T} \times \mathcal{T}$ into \mathbb{R} such that

$$r_Z(t, \tilde{t}) = E\{Z(t)Z(\tilde{t})\} = \int_{\mathbb{R} \times \mathbb{R}} z \tilde{z} \rho_{(Z(t), Z(\tilde{t}))}(z, \tilde{z}) dz d\tilde{z}.$$

- The **covariance function** of a second-order stochastic process $\{Z(t), t \in \mathcal{T}\}$ indexed by \mathcal{T} with values in \mathbb{R} is the function c_Z from $\mathcal{T} \times \mathcal{T}$ into \mathbb{R} such that

$$c_Z(t, \tilde{t}) = E\left\{ (Z(t) - \bar{z}(t)) (Z(\tilde{t}) - \bar{z}(\tilde{t})) \right\} = \int_{\mathbb{R} \times \mathbb{R}} (z - \bar{z}(t)) (\tilde{z} - \bar{z}(\tilde{t})) \rho_{(Z(t), Z(\tilde{t}))}(z, \tilde{z}) dz d\tilde{z}.$$

- Please note that $c_Z(t, \tilde{t}) = E\left\{ (Z(t) - \bar{z}(t)) (Z(\tilde{t}) - \bar{z}(\tilde{t})) \right\} = r_Z(t, \tilde{t}) - \bar{z}(t)\bar{z}(\tilde{t})$.

Second-order stochastic processes

- A second-order stochastic process $\{Z(t), t \in \mathbb{R}\}$ indexed by \mathbb{R} with values in \mathbb{R} is **mean-square stationary** if $\bar{z}(t) = \bar{z}$ is independent of t and $r_Z(t, \tilde{t}) = r_Z(t - \tilde{t})$ depends on only $t - \tilde{t}$.
- The **power spectral density function** of a zero-mean, mean-square stationary, second-order stochastic process $\{Z(t), t \in \mathbb{R}\}$ indexed by \mathbb{R} with values in \mathbb{R} , if it exists, is the function s_Z from \mathbb{R} into \mathbb{R}^+ such that

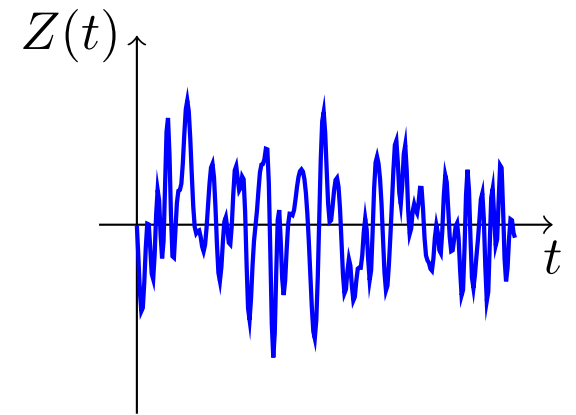
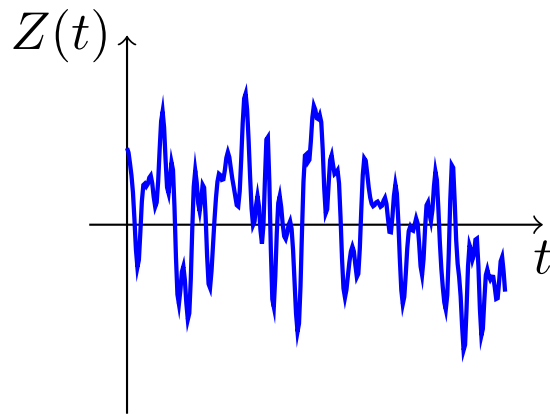
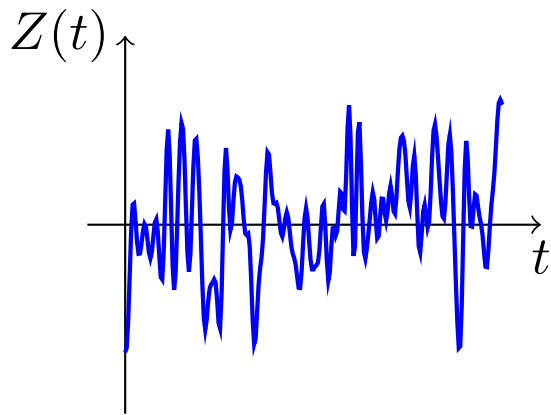
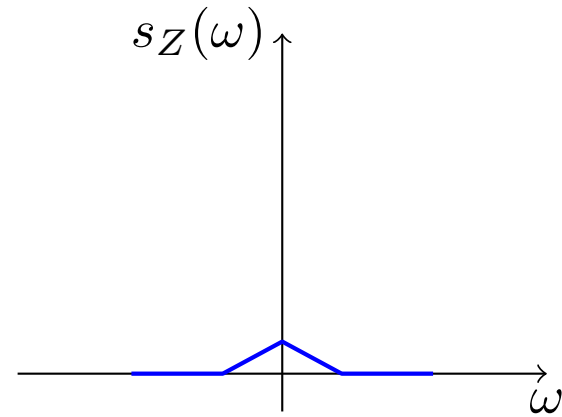
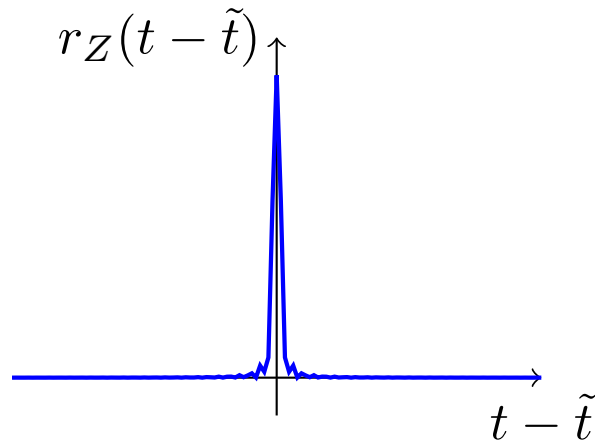
$$r_Z(t - \tilde{t}) = \frac{1}{2\pi} \int_{\mathbb{R}} s_Z(\omega) \exp(i\omega(t - \tilde{t})) d\omega.$$

The power spectral density function s_Z has the following properties:

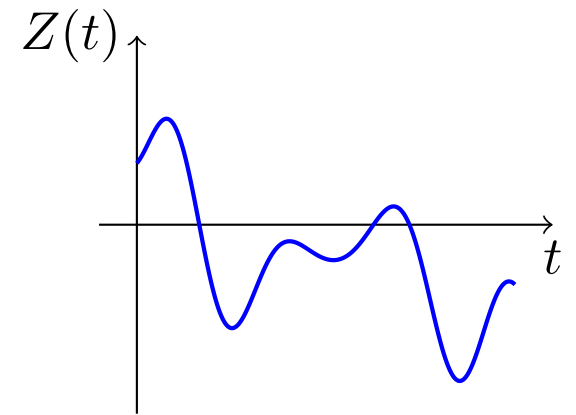
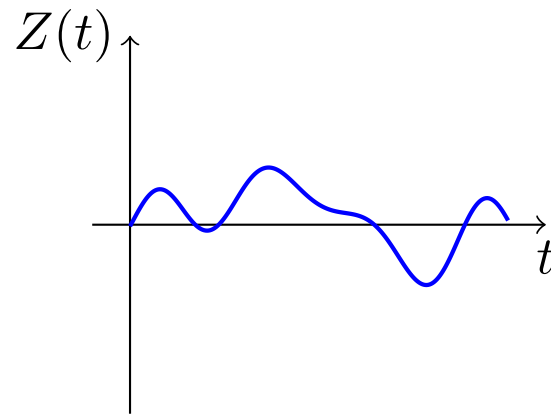
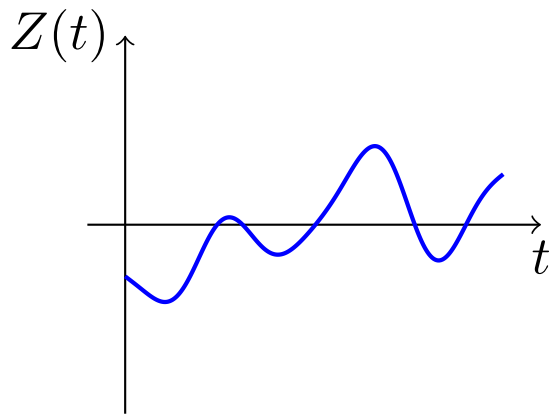
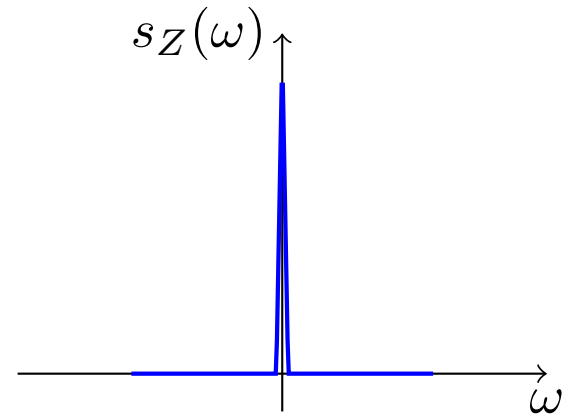
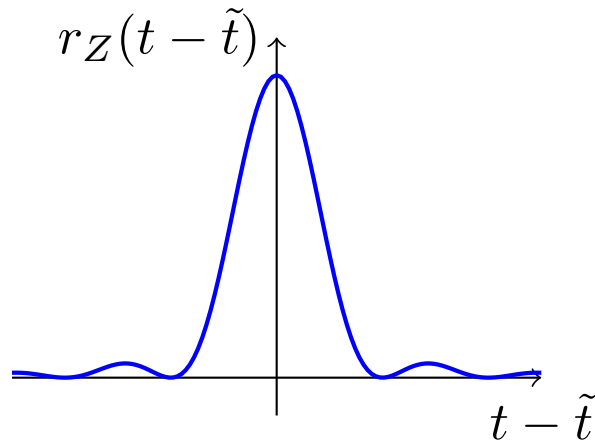
- ◆ it is even because of the evenness of r_Z ,
 - ◆ it is positive owing to Bochner's theorem,
 - ◆ it is integrable because $E\{Z(t)^2\} = r_Z(0) = \frac{1}{2\pi} \int_{\mathbb{R}} s_Z(\omega) d\omega < +\infty$.
- If α is an integer, the **spectral moment of order α** , denoted by m_α , if it exists, is the integral

$$m_\alpha = \frac{1}{2\pi} \int_{\mathbb{R}} \omega^\alpha s_Z(\omega) d\omega.$$

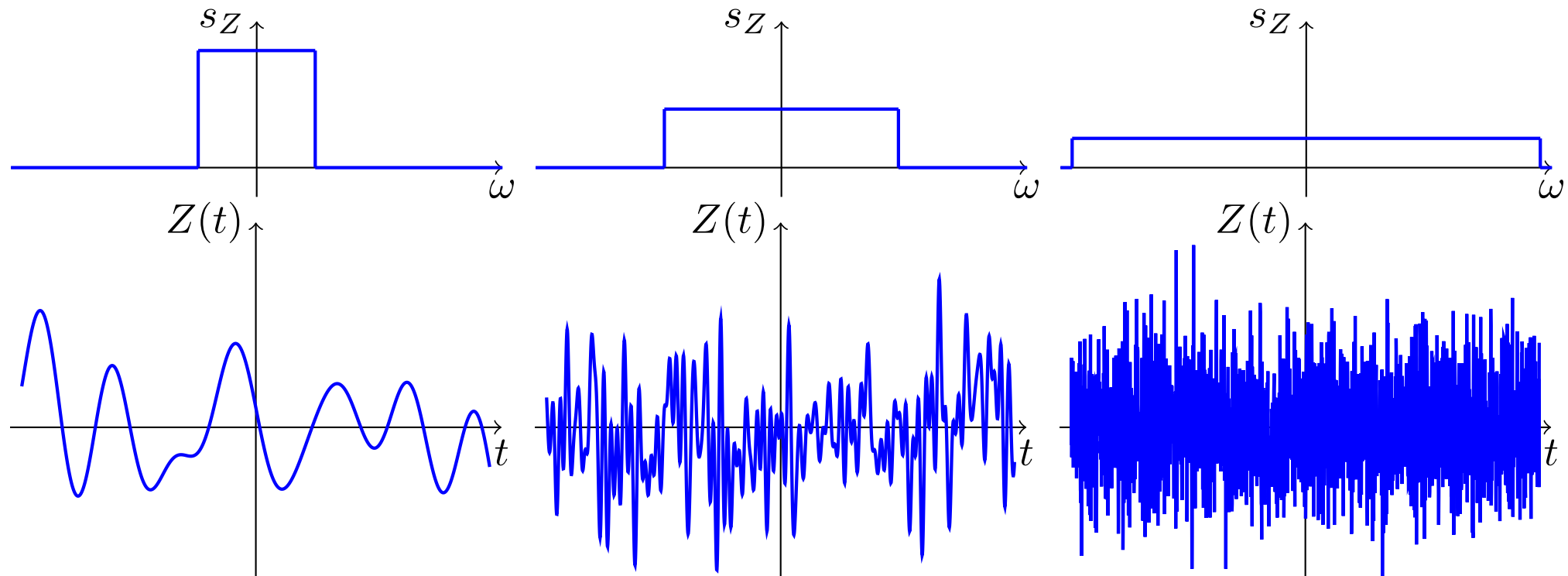
Second-order stochastic processes



Second-order stochastic processes



- In the engineering literature, a **white noise** is intuitively construed as a stochastic process with **constant power spectral density function** and **delta autocorrelation function**. However, such a white noise cannot be defined within the context of second-order stochastic processes because its variance is infinite. In fact, a Gaussian white noise can be defined as a mathematical construct within the theory of generalized stochastic processes, but this is beyond the scope of this course.
- We can visualize sample paths of band-limited flat-spectrum stochastic processes:

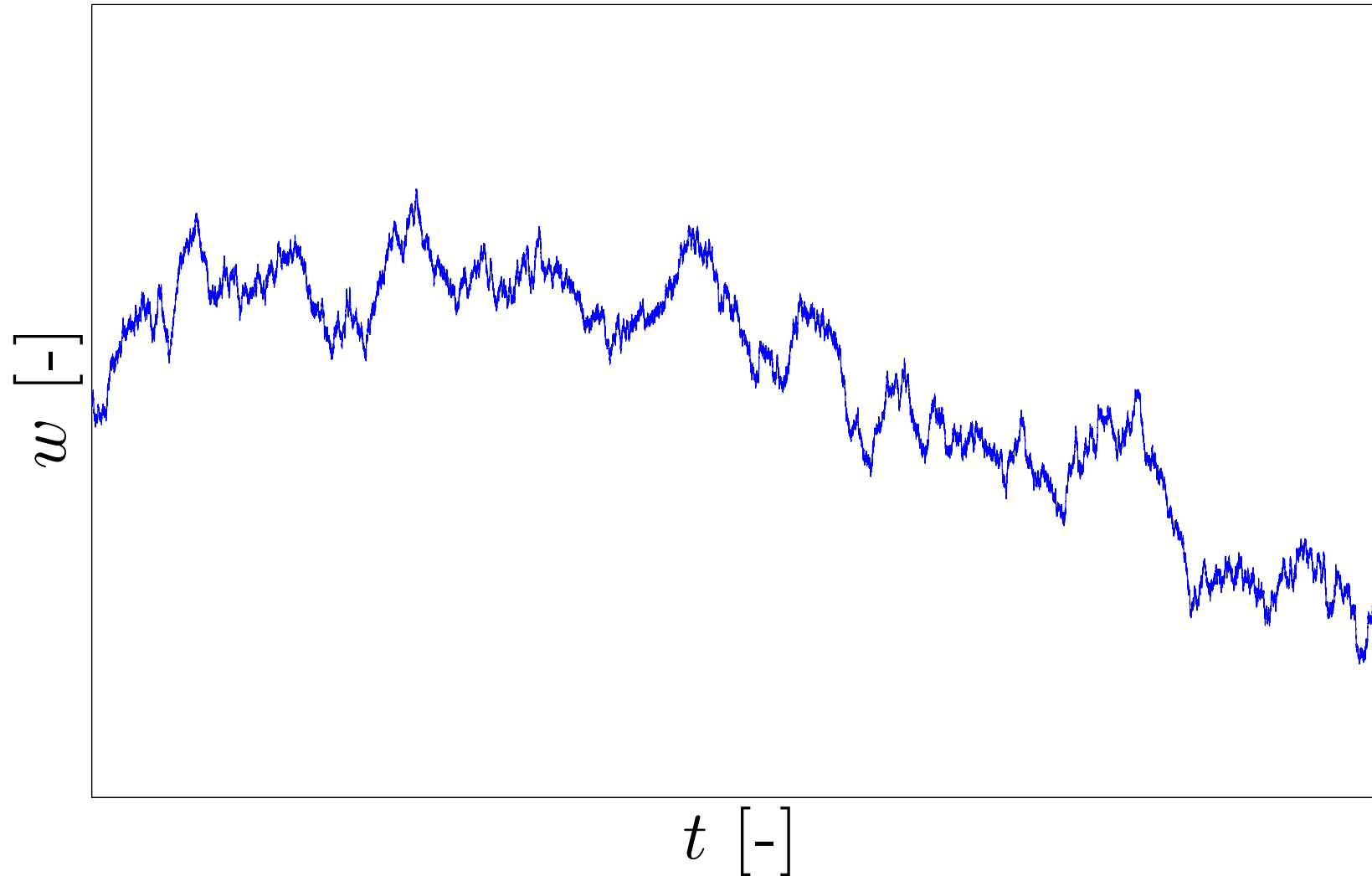


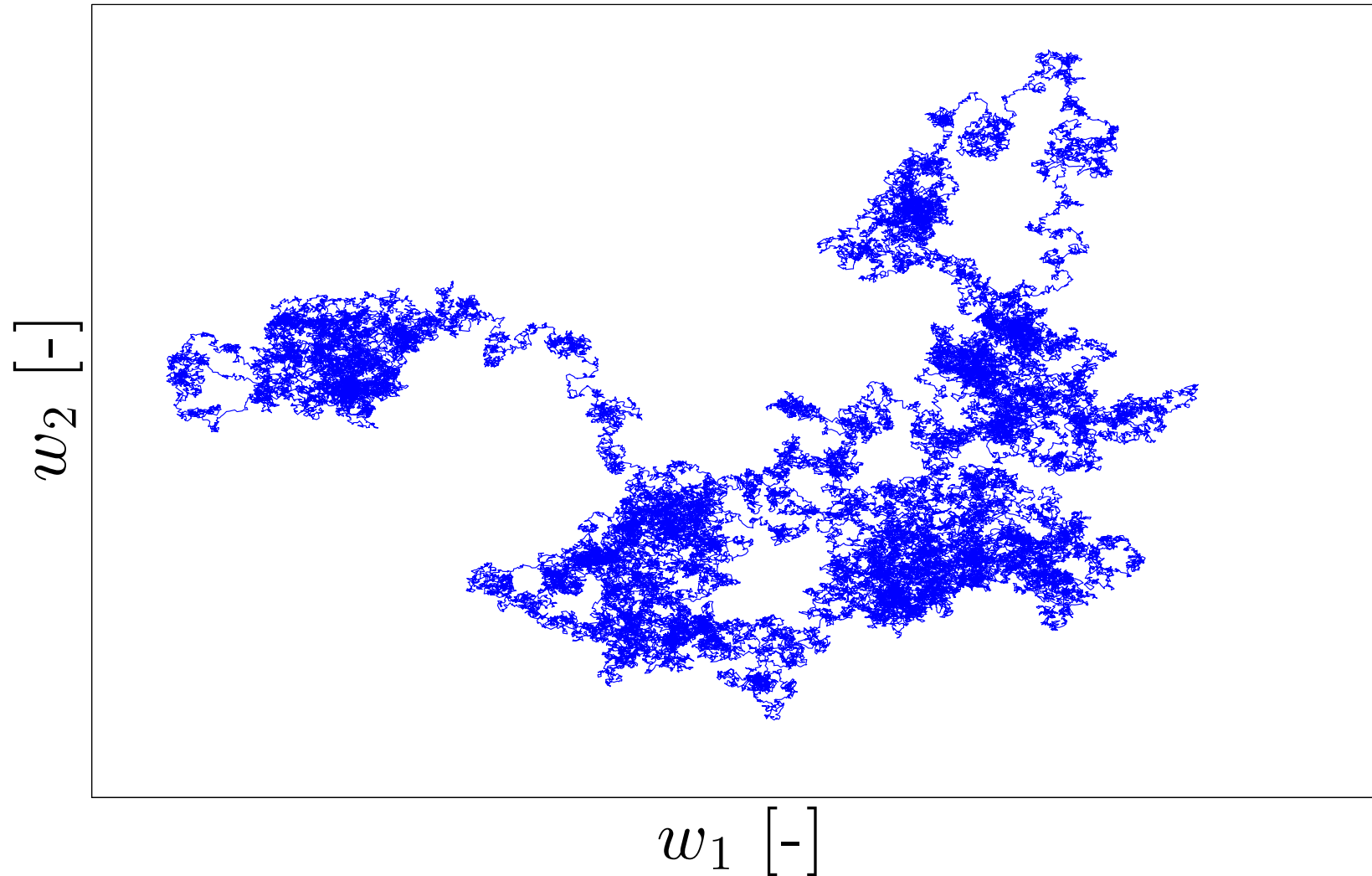
However, sample paths of a white noise, a flat-spectrum stochastic process of infinite bandwidth, cannot be visualized. We can only think of sample paths of white noise as a sort of limit of sample paths of band-limited flat-spectrum stochastic processes as the bandwidth increases to infinity.

Wiener process

- The Wiener process is a stochastic process that draws from Einstein's study the idea of independent increments and the idea of the second moment increasing proportionally with elapsed time.
- A (scalar-valued) **Wiener process** is a stochastic process $\{W(t), t \in \mathbb{R}^+\}$ indexed by the positive real line \mathbb{R}^+ with values in \mathbb{R} such that
 1. $W(0) = 0$,
 2. for $0 \leq s < t < u < v$, the increments $W(t) - W(s)$ and $W(v) - W(u)$ are statistically independent,
 3. for $0 \leq s < t$, the increment $W(t) - W(s)$ is a Gaussian random variable with mean zero and variance $t - s$.
- A (vector-valued) **Wiener process** is a stochastic process $\{\mathbf{W}(t), t \in \mathbb{R}^+\}$ indexed by the positive real line \mathbb{R}^+ with values in \mathbb{R}^n such that
 1. $\mathbf{W}(0) = \mathbf{0}$,
 2. for $0 \leq s < t < u < v$, the increments $\mathbf{W}(t) - \mathbf{W}(s)$ and $\mathbf{W}(v) - \mathbf{W}(u)$ are statistically independent,
 3. for $0 \leq s < t$, the increment $\mathbf{W}(t) - \mathbf{W}(s)$ is a Gaussian random variable with mean zero and covariance matrix $(t - s)[I]$, where $[I]$ is the $(n \times n)$ -dimensional identity matrix.

- Simulating sample paths of the Wiener process $\{W(t), t \in \mathbb{R}^+\}$ indexed by \mathbb{R}^+ with values in \mathbb{R} typically entails seeking to simulate its values at discrete time instants. We thus set $t_n = n \Delta t$, with n the index of the time instant and Δt the time step.
- We let W_n denote $W(t_n)$. Then, condition 1 indicates that $W_0 = 0$, and conditions 2 and 3 indicate that $W_{j+1} = W_j + \Delta W_j$ with $j = 0, 1, 2, \dots$, where each ΔW_j is a statistically independent Gaussian random variable with mean zero and variance Δt .
- Thus, to simulate a sample path $\{w_0, w_1, w_2, \dots\}$ of the values taken by the Wiener process at the discrete time instants t_0, t_1, t_2, \dots , one begins with setting $w_0 = 0$; then, for $j = 0, 1, 2, \dots$, one recursively generates a realization Δw_j of a statistically independent Gaussian random variable with mean zero and variance Δt and sets $w_{j+1} = w_j + \Delta w_j$.
- The Matlab functions `randn` and `cumsum` can be useful.





- Since the Wiener process has statistically independent increments, its time derivative can be intuitively construed as a stochastic process whose values at different time instants are statistically independent, that is, **the time derivative of the Wiener process is a white noise**. In fact, the time derivative of the Wiener process being a Gaussian white noise can be made rigorous within the theory of generalized stochastic processes, but this is beyond the scope of this course.
- To make this property more explicit, albeit still intuitive and not rigorous, consider the finite-difference approximation

$$f_{\Delta t}(t) = \frac{W(t + \Delta t) - W(t)}{\Delta t}.$$

Then, it can be shown (see the assignment) that the covariance function of $\{f_{\Delta t}(t), t \in \mathbb{R}^+\}$ is

$$E\{f_{\Delta t}(t)f_{\Delta t}(s)\} = \begin{cases} \frac{1}{\Delta t} \left(1 - \frac{|t-s|}{\Delta t}\right) & \text{if } |t-s| \leq \Delta t, \\ 0 & \text{otherwise.} \end{cases}$$

Thus, as $\Delta \rightarrow 0$ and the finite-difference approximation thus tends to the time derivative, the covariance function tends to a Dirac delta.

Assignment

- Please read the papers written by Einstein and Perrin. Describe in a few lines the experiment that Einstein suggests that “some enquirer” carry out, and briefly point out its historical significance.
- Please determine the total variation of the Wiener process over a time interval $[0, \tau]$, that is, the limit

$$\lim_{n \rightarrow +\infty} \sum_{j=1}^n \sqrt{E \left\{ \left| W \left(\frac{j\tau}{n} \right) - W \left(\frac{(j-1)\tau}{n} \right) \right|^2 \right\}};$$

Interpret your result.

- Please determine the quadratic variation of the Wiener process over a time interval $[0, \tau]$, that is,

$$\lim_{n \rightarrow +\infty} \sum_{j=1}^n E \left\{ \left| W \left(\frac{j\tau}{n} \right) - W \left(\frac{(j-1)\tau}{n} \right) \right|^2 \right\};$$

- Please show that the covariance function of the Wiener process is $E\{W(t)W(s)\} = \min(t, s)$. Deduce the expression for the covariance function of $\{f_{\Delta t}(t), t \in \mathbb{R}^+\}$ stated on Slide 31/34.
- Implement the algorithm stated on Slide 28/34, and plot a few sample paths of the scalar-valued and vector-valued Wiener processes. Carry out a few tests to verify that your sample paths can indeed be considered sample paths of the scalar-valued and vector-valued Wiener processes.

Suggested reading material

- V. Denoel. *Eléments de processus stochastiques*. ULg, 2014–2015.
- A. Einstein. *Investigations on the theory of the Brownian movement*. www.bnpublishing.com, 2011. www.rpgroup.caltech.edu/courses/aph161/Handouts/Einstein1905A.pdf.
- J. B. Perrin. *Mouvement Brownien et réalité moléculaire*. *Annales de Chimie et de Physique*, 19:5–104, 1909. Secs. 27–31. http://hermes.ffn.ub.es/luisnavarro/nuevo_maletin/Perrin_1909.pdf.

Additional references also consulted to prepare this lecture

- F. Comets and T. Meyre. *Calcul stochastique et modèles de diffusions*. Dunod, 2006.
- R. Feynman. *The Feynman lectures on physics*. Volume 1: *Mainly mechanics, radiation, and heat*. Basic Books, 2010.
- D. Higham. *An algorithmic introduction to numerical simulation of stochastic differential equations*. *SIAM Review*, 43:525–546, 2001.
- W. Liu, E. Karpov, and H. Park. *Nano mechanics and materials*. Wiley, 2006.
- C. Soize. *The Fokker–Planck equation for stochastic dynamical systems and its explicit steady state solutions*. World Scientific Publishing, 1994.