Stochastic Processes — Tutorial 5

10 May 2018 — Brownian Motion

Universität Leipzig
Institut für Theoretische Physik
Jürgen Vollmer

Exercise 1 *Brownian motion as a Markov process*

For reference in this exercise the cumulants for Brownian motion are given in the Appendix to this exercise sheet. In another exercise we will show that Brownian motion is a Gaussian process, i.e., the probability distribution for Brownian motion is completely specified by the first two cumulants.

(a) Show that the probabiltiy distribution $P(v, t|v_0, 0)$ to find a velocity v at time t when it was v_0 at time 0 takes the form

$$P(v, t|v_0, 0) = N(t)\ \exp\left[-\frac{\left(v - v_0\ \mathrm{e}^{-\lambda t}\right)^2}{\frac{2\,d}{\lambda}\left(1 - \mathrm{e}^{-2\lambda t}\right)}\right] ,$$

where $N(t)$ is an appropriate normalization of this conditional probability.
What is the appropriate normalization $N(t)$?
Hint: This expression assumes $\mathcal{C}_0(v, v) = 0$ and $\langle v_0 \rangle = v_0$. Why is this justified?

(b) Under which condition on λ will Brownian motion become a Markov process for the velocities? What is special about the resulting conditional probability?

(c) Adopt the limit $\lambda \to \infty$ at a fixed diffusion coefficient $D = d/\lambda^2$. Show that in this limit the probabiltiy distribution $P(x, t|x_0, 0)$ to find the Brownian particle at position x at time t when it was at x_0 at time 0 takes the form

$$P(x, t|x_0, 0) = (4\pi D t)^{-1/2}\ \exp\left[-\frac{(x - x_0)^2}{4\,D\,t}\right] . \tag{1}$$

(d) Brownian motion is Markovian iff Eq. (1) satisfies the Chapman-Kolmogorov-criterion that for any set of times $t_1 < t_2 < t_3$ and positions x_1, x_2, x_3 one must have

$$P(x_3, t_3|x_1, t_1) = \int \mathrm{d}x_2\ P(x_3, t_3|x_2, t_2)\ P(x_2, t_2|x_1, t_1)$$

Verify that it holds!

Exercise 2 *Variance of positions*

In this exercise we derive the expression for $\mathcal{C}_t(x,x)$ that is given in the appendix. We start from

$$x(t) = x_0 + \frac{v_0}{\lambda}\ \left(1 - \mathrm{e}^{-\lambda\, t}\right) + \int_0^t \mathrm{d}s_1\ \mathrm{e}^{-\lambda\, s_1}\ \int_0^{s_1} \mathrm{d}s_2\ A(s_2)\ \mathrm{e}^{\lambda\, s_2}$$

(a) Introduce the function $W(s_1) = \int_0^{s_1} \mathrm{d}s_2\ A(s_2)\ \mathrm{e}^{\lambda\, s_2}$ and use integration by parts to show that

$$x(t) = x_0 + \frac{v_0}{\lambda}\ \left(1 - \mathrm{e}^{-\lambda\, t}\right) + \lambda^{-1}\ \int_0^t \mathrm{d}s\ \left(1 - \mathrm{e}^{(s-t)}\right)\ A(s)\,. \tag{2a}$$

(b) Use Eq. (2a) to evaluate

$$\mathcal{C}_t(x,x) = \left\langle \left(x(t) - \langle x(t)\rangle\right)^2 \right\rangle\,.$$

(c) Show that in the limit of long times the resulting expression reduces to

$$\mathcal{C}_t(x,x) \simeq \left(\mathcal{C}_0(x,x) - \frac{D}{\lambda}\right) + \lambda^{-2}\ \left(\mathcal{C}_0(v,v) - \frac{d}{\lambda}\right) + 2\,D\,t \tag{2b}$$

where we introduced the diffusion coefficient $D = d/\lambda^2$.
Provide an interpretation for the three contributions to this expression.

(d) The result Eq. (2b) suggests that $\mathcal{C}_t(x,x)$ may take negetive values when $\mathcal{C}_0(x,x) = \mathcal{C}_0(v,v) = 0$ and small t.
What is wrong about this argument?
Find the expression that should rather be considered to discuss this special case of $\mathcal{C}_t(x,x)$.

Exercise 3 *Covariance of position and velocity*

(a) Determine the covariance

$$\mathcal{C}_t(x,v) = \left\langle \left(x(t) - \langle x(t)\rangle\right)\ \left(v(t) - \langle v(t)\rangle\right) \right\rangle\,.$$

(b) Compare the result to the variance $\mathcal{C}_t(v,v)$. What do you observe?

(c) For an equilibrated velocity ensemble, where $\mathcal{C}_0(v,v) = 0$, the asymptotics for large and small times becomes

$$\mathcal{C}_t(x,v) \simeq \begin{cases} d t/\lambda & \text{for} \quad \lambda\, t \ll 1\,, \\ d/\lambda^2 & \text{for} \quad \lambda\, t \gg 1\,. \end{cases}$$

What does this mean physically?
Which interpretation does this suggest for the diffusion coefficient $D = d/\lambda^2$?

Exercise 4 *Estimating the diffusive displacement*

In the lecture I indicated that Nageli[1] dismissed the role of molecular collisions as origin of Brownian motion. In this exercise we revisit his argument that is based on his estimate of the speed, $U_B \simeq 1\mu\text{m/s}$, of a Brownian particles with a diameter of about $R_B \simeq 2\mu\text{m}$.

(a) According to Stoke's law the friction force on a solid spherical particle is

$$F_S = 6\pi\, R_B\, \rho_s\, \nu_s\, U_B$$

where ρ_s and ν_s are the density and the kinematic viscosity of the surrounding fluid, respectively. For water they take the values $\rho_s \simeq 10^3\text{kg/m}^3$ and $\nu_s \simeq 10^{-6}\text{m}^2/\text{s}$. Show that for these parameters the damping takes the value $\lambda \simeq 10^6/\text{s}$.
Bonus: Note that smaller particles have a larger damping. Which radius will result in the damping $\lambda \simeq 10^7/\text{s}$ that was quoted in the lecture?

(b) When the particle is at thermal equilibrium it should have a velocity U_E

$$\frac{1}{2}\,\frac{4\pi\rho_B R_B^3}{3}\,U_E^2 = \frac{3}{2}\,k_B\,T$$

Estimate U_E for a particle that has roughly the same density as water.

(c) Assume that water molecules have an effective radius of about $R_w \simeq 4 \times 10^{-10} m$. What would the momentum balance

$$M_B U_B \simeq M_w U_w$$

imply about typical verlocity U_B for our Brownian particle when it collides with water molecules in thermal equilibrium?

(d) Show that the diffusion coefficient takes a value of the order to $D \simeq 10^{-13}\text{m}^2/\text{s}$, and calculate the diffusive displacement $\Delta X(t) = 2\,D\,t$ for time intervals $t = 0.1, 1.0, 10, 100\text{s}$.

(e) Compare now Nageli's estimate of $U = 10^{-6}\text{m/s}$ to the velocity $U_t = \Delta X(t)/t$.
What does this imply about the time and space resolution of Nageli's observation?
Observe also that $U_E > U_t > U_P$. Why would one expect this relation?

[1]K. von Nageli, Sitzungsberichte der Königlich Bayrischen Akademie der Wissenschaften München, Mathematisch-physikalische Klasse **9** (1879) 389–453.

Appendix: Derivation of the Cumulants

Velocity

$$v(t) = v_0\ \mathrm{e}^{-\lambda\, t} + \int_0^t \mathrm{d}s\ A(s)\ \mathrm{e}^{\lambda\,(s-t)}$$

$$\begin{aligned} \text{with velocity}\quad & v(t) \quad \text{at time } t \\ & v_0 \quad \text{at initial time } 0 \\ \text{relaxation rate}\quad & \lambda \\ \text{random forces}\quad & A(t) \\ \text{where}\quad & \langle A(t)\rangle = 0 \\ \text{where}\quad & \langle A(t_1)\, A(t_2)\rangle = 2\, d\, \delta(t_1 - t_2) \end{aligned}$$

Expectation

$$\mathcal{C}_t(v) = \langle v(t)\rangle = \langle v_0\rangle\ \mathrm{e}^{-\lambda\, t} + \int_0^t \mathrm{d}s\ \langle A(s)\rangle\ \mathrm{e}^{\lambda\,(s-t)} = \langle v_0\rangle\ \mathrm{e}^{-\lambda\, t}$$

Starting from its initial value $\langle v_0\rangle$ the expectation decays exponentially to zero.

Variance

$$\begin{aligned} \mathcal{C}_t(v,v) = \left\langle (v(t) - \langle v(t)\rangle)^2 \right\rangle &= \left\langle \left((v_0 - \langle v_0\rangle)\ \mathrm{e}^{-\lambda t} + \int_0^t \mathrm{d}s\ A(s)\ \mathrm{e}^{\lambda\,(s-t)} \right)^2 \right\rangle \\ &= \left\langle (v_0 - \langle v_0\rangle)^2 \right\rangle\ \mathrm{e}^{-2\lambda t} + 2\,\mathrm{e}^{-\lambda t} \int_0^t \mathrm{d}s\ \left\langle (v_0 - \langle v_0\rangle) A(s)\right\rangle\ \mathrm{e}^{\lambda\,(s-t)} + \left\langle \left(\int_0^t \mathrm{d}s\ A(s)\ \mathrm{e}^{\lambda\,(s-t)} \right)^2 \right\rangle \\ &= \mathcal{C}_0(v,v)\ \mathrm{e}^{-2\lambda t} + \int_0^t \mathrm{d}s_1\ \mathrm{e}^{\lambda\,(s_1-t)} \int_0^t \mathrm{d}s_2\ \mathrm{e}^{\lambda\,(s_2-t)}\ \langle A(s_1)\ A(s_2)\rangle \\ &= \mathcal{C}_0(v,v)\ \mathrm{e}^{-2\lambda t} + 2\, d \int_0^t \mathrm{d}s_2\ \mathrm{e}^{2\,\lambda\,(s_2-t)} \\ &= \left(\mathcal{C}_0(v,v) - \frac{d}{\lambda} \right)\ \mathrm{e}^{-2\lambda t} + \frac{d}{\lambda} \end{aligned}$$

Starting from ints initial value $\mathcal{C}_0(v,v)$ the variance decays exponentially to the value d/λ.

Position

$$x(t) = x_0 + \int_0^t \mathrm{d}s\ v(s) = x_0 + \frac{v_0}{\lambda}\ \left(1 - \mathrm{e}^{-\lambda\, t}\right) + \int_0^t \mathrm{d}s_1 \int_0^{s_1} \mathrm{d}s_2\ A(s_2)\ \mathrm{e}^{\lambda\,(s_2-s_1)}$$

Expectation

$$\mathcal{C}_t(x) = \langle x(t) \rangle = \langle x_0 \rangle + \frac{\langle v_0 \rangle}{\lambda}\ \left(1 - \mathrm{e}^{-\lambda\,t}\right)$$

When the expectation of the velocity in the initial ensemble vanishes, $\langle v_0 \rangle = 0$, the expectation of the position remains constant at $\langle x_0 \rangle$. Otherwise, it decays exponentially to its asymptotic value $\langle x_0 \rangle + \langle v_0 \rangle / \lambda$.

Variance

$$\begin{aligned}
\mathcal{C}_t(x,x) &= \left\langle \left(x(t) - \langle x(t) \rangle\right)^2 \right\rangle \\
&= \mathcal{C}_0(x,x) + \frac{\left(1 - \mathrm{e}^{-\lambda\,t}\right)^2}{\lambda^2}\ \left(\mathcal{C}_0(v,v) - \frac{d}{\lambda}\right) + \frac{2\,d}{\lambda^3}\left(\lambda\,t - \left(1 - \mathrm{e}^{-\lambda\,t}\right)\right)
\end{aligned}$$

The derivation and interpretation is given as an exercise.