EXERCISE 1 - FREE ENERGY

Consider two particles in a 3-dimensional space, of coordinates $\vec{r}_1$ and $\vec{r}_2$, evolving at temperature $T = 1$ under the action of a potential

$$V(\vec{r}_1, \vec{r}_2) = \exp(-|\vec{r}_1 - \vec{r}_2|)\,\chi(R - |\vec{r}_1|) \tag{1.1}$$

where $R > 0$ and $\chi(x) = 1$ if $x > 0$ and $\chi(x) = \infty$ otherwise. Compute the free energy as a function of $S(\vec{r}_1, \vec{r}_2) = |\vec{r}_1 - \vec{r}_2|$.

The free energy as a function of the collective variabile $s = S(r_1, r_2)$ is

$$\begin{aligned}
F(s) &= -k_B T \log \int_{\mathbb{R}^3} d\vec{r}_1 \int_{\mathbb{R}^3} d\vec{r}_2 \exp\Big(-\frac{V(\vec{r}_1, \vec{r}_2)}{k_B T}\Big)\delta(s - S(\vec{r}_1, \vec{r}_2)) \\
&= -\log \int_{|\vec{r}_1|<R} d\vec{r}_1 \int_{\mathbb{R}^3} d\vec{r}_2 \exp(-e^{-|\vec{r}_1 - \vec{r}_2|})\delta(s - |\vec{r}_1 - \vec{r}_2|) \\
&= e^{-s} - \log \int_{|\vec{r}_1|<R} d\vec{r}_1 \int_{\mathbb{R}^3} d\vec{r}_2\, \delta(s - |\vec{r}_1 - \vec{r}_2|) \\
&= e^{-s} - \log \int_{|\vec{r}_1|<R} d\vec{r}_1 \int_{\mathbb{R}^3} d(\vec{r}_2 - \vec{r}_1)\, \delta(s - |\vec{r}_1 - \vec{r}_2|) \\
&= e^{-s} - \log \int_{|\vec{r}_1|<R} d\vec{r}_1 4\pi s^2 = e^{-s} - \log\Big(\frac{4}{3}\pi R^3 \cdot 4\pi s^2\Big) \\
&= e^{-s} - 2\log s + const.
\end{aligned} \tag{1.2}$$

The free energy $F(s)$ as a function of the distance between the two particles is monotonically decreasing, consistently with the given potential $V(\vec{r}_1, \vec{r}_2)$. Note that the probability distribution $P(\vec{r}_1, \vec{r}_2)d\vec{r}_1 d\vec{r}_2 = P(s)ds$ (with $s = S(\vec{r}_1, \vec{r}_2)$ cannot be normalized.

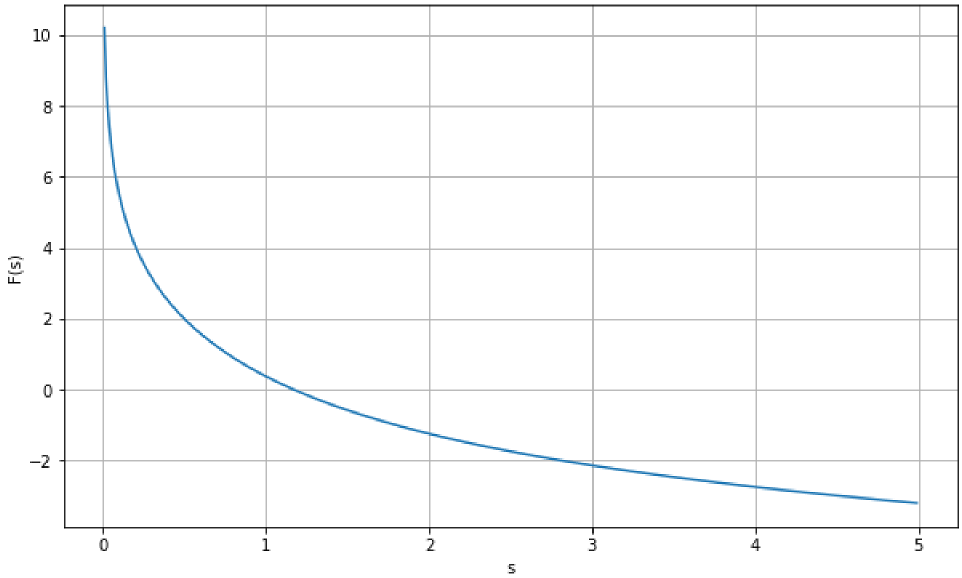

Figure 1.1: Free energy $F(s)$ as a function of the collective variable $S(\vec{r}_1, \vec{r}_2)$.

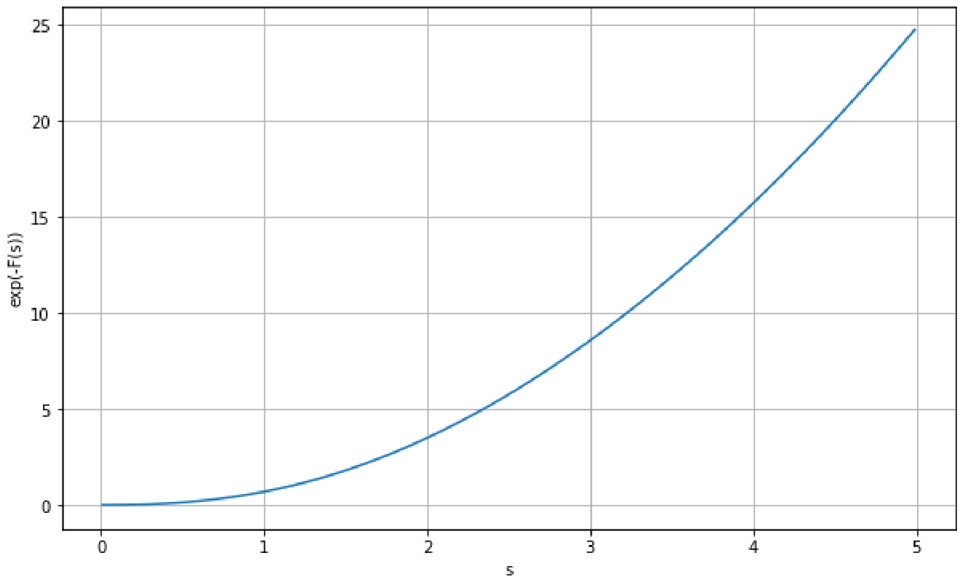

Figure 1.2: Non-normalized probabilty density $e^{-F(s)}$ as a function of the collective variable $S(\vec{r}_1, \vec{r}_2)$.

EXERCISE 2 - FREE ENERGY AND ARRHENIUS EQUATION

Consider a system evolving under the action of a 2-dimensional potential

$$V(x,y) = -\log\Big(6\exp\Big(-2x^2 - \frac{1}{4}y^2\Big) + 4\exp\Big(-\Big(x-\frac{3}{2}\Big)^2 - \Big(y-\frac{5}{2}\Big)^2\Big)\Big) \tag{2.1}$$

at a temperature $T = 1$. Compute the probabilities $P(x)$, $P(y)$ and the free energies $F(x)$ and $F(y)$. Then, by using the Arrhenius formula estimate the mean first passage time from the potential energy minimum in (approximatively) $(0,0)$ and the potential energy minimum in (approx.) $\left(\frac{3}{2},\frac{5}{2}\right)$. Assume $\tau_{ex} = 1\,ps$.

The free energy as a function of x is

$$\begin{aligned} F(x) &= -k_BT\log\int_{\mathbb{R}} dy\exp\Big(-\frac{V(x,y)}{k_BT}\Big) \\ &= -\log\int_{\mathbb{R}} dy\Big[6\exp\Big(-2x^2-\frac{1}{4}y^2\Big) + 4\exp\Big(-\Big(x-\frac{3}{2}\Big)^2 - \Big(y-\frac{5}{2}\Big)^2\Big] \\ &= -\log\Big[6e^{-2x^2}\cdot 2\sqrt{\pi} + 4e^{-(x-3/2)^2}\cdot\sqrt{\pi}\Big] \\ &= -\log\Big(3e^{-2x^2} + e^{-(x-3/2)^2}\Big) + const, \end{aligned} \tag{2.2}$$

so the marginal probability density $P(x)$ is

$$P(x) = \frac{e^{-F(x)}}{\int_{\mathbb{R}} dx\, e^{-F(x)}} = \frac{3e^{-2x^2} + e^{-(x-3/2)^2}}{(3\sqrt{2}/2+1)\sqrt{\pi}}. \tag{2.3}$$

The free energy as a function of y is

$$\begin{aligned} F(y) &= -k_BT\log\int_{\mathbb{R}} dx\exp\Big(-\frac{V(x,y)}{k_BT}\Big) \\ &= -\log\Big(3\sqrt{2}e^{-y^2/4} + 4e^{-(y-5/2)^2}\Big) + const, \end{aligned} \tag{2.4}$$

so the marginal probability density $P(y)$ is

$$P(y) = \frac{e^{-F(y)}}{\int_{\mathbb{R}} dy\, e^{-F(y)}} = \frac{3e^{-y^2/4} + 2\sqrt{2}e^{-(y-5/2)^2}}{2(3+\sqrt{2})\sqrt{\pi}}. \tag{2.5}$$

The probability density $P(x, y)$ is the sum of two gaussians localized quite far from each other (being the distance from their centers $\sqrt{34}/2 \simeq 2.9$ and their standard deviations $\sigma_x = 1/2$, $\sigma_y = \sqrt{2}$ and $\sigma_x = \sigma_y = 1/\sqrt{2}$), so its maxima are approximatively the maxima of each of the two gaussians (and the same for the minima of the free energy). The Arrhenius formula estimate the first passage time from the minimum A to the minimum B as

$$\bar{\tau}_{AB} = \tau_{ex} \exp\Big(-\frac{F_A - F_{ex}}{k_B T}\Big) = \tau_{ex} \frac{P_A}{P_{ex}} \tag{2.6}$$

with F_{ex} the free energy in the saddle point between the two minima and P_{ex} the corresponding probability. The (non-normalized) probability density $e^{-V(x,y)}$ in A is $\exp(-V_A) = 6+4\exp(-34/4) \simeq 6.00$, the one in B is $\exp(-V_B) = 6\exp(-43/4)+4 \simeq 4.01$, the one in the saddle point $(x, y) \simeq (0.547, 2.053)$ is $exp(-V_{ex}) \simeq 2.47$. Hence, the estimated first passage time from A to B is

$$\bar{\tau}_{AB} \simeq 1\,ps \cdot \frac{6.00}{2.47} \simeq 2.43\,ps. \tag{2.7}$$

The estimated first passage time from B to A is

$$\bar{\tau}_{BA} = \tau_{ex} \frac{P_B}{P_{ex}} = \bar{\tau}_{AB} \frac{P_B}{P_A} \simeq 2.43\,ps \cdot \frac{4.01}{6.00} \simeq 1.62\,ps. \tag{2.8}$$

Since it is $P_B < P_A$, the two first passage times are $\bar{\tau}_{BA} < \bar{\tau}_{AB}$ (the system needs more time to go from the lower minimum of the free energy A to the higher one B).

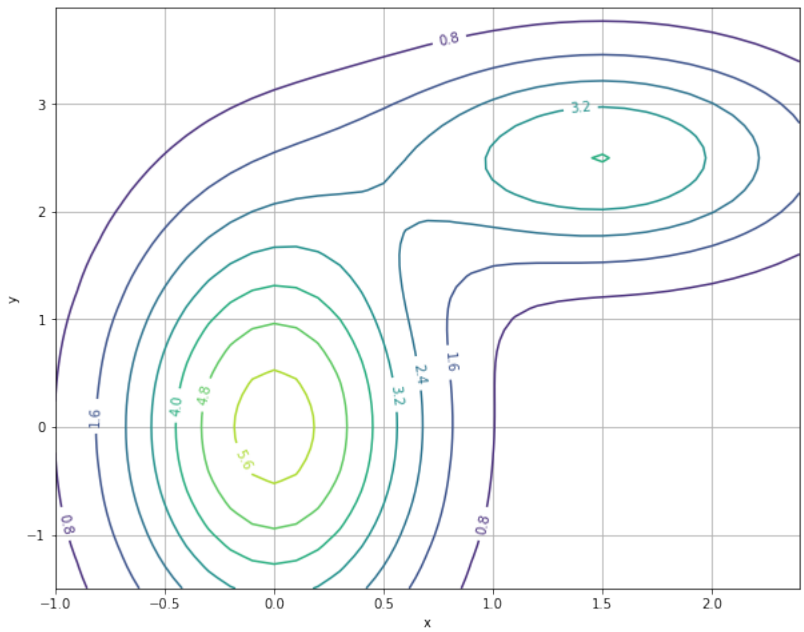

Figure 2.1: Non-normalized probabilty density $e^{-V(x,y)}$ (contour lines).

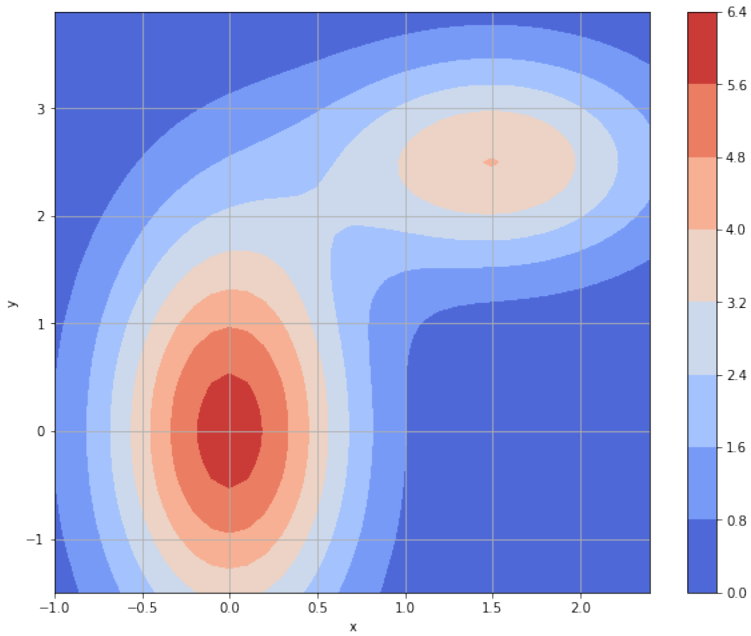

Figure 2.2: Non-normalized probabilty density $e^{-V(x,y)}$.

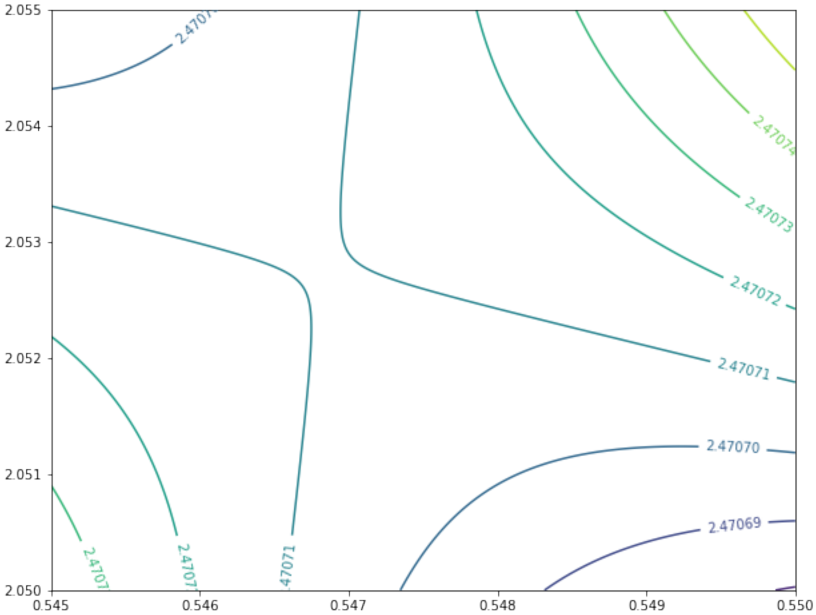

Figure 2.3: Saddle point for the (non-normalized) probabilty density $e^{-V(x,y)}$.

EXERCISE 3 - BLOCK ANALYSIS

For each of the three trajectories shown in the figures below, I compute their average $\bar{x}$ and standard deviation on the average $\sigma_{\bar{x}} = \frac{\sigma}{\sqrt{N}}$, being N the n. of data points. Due to correlations in the trajectory, this estimate of the error $\sigma_{\bar{x}}$ is distorted downwards, so a better estimate is done through block analysis, getting the errors ϵ (shown in the table). This value is computed by taking the plateau value of the plot $\epsilon_{N_b}(N_b)$ (average over the values ϵ_{N_b} up to N_b^*, where the plateau extends), being

$$\epsilon_{N_b}^2 = \frac{var(\bar{O}_b; N_b)}{N_b}, \tag{3.1}$$

with $var(\bar{O}_b; N_b)$ the variance of the averaged values O_b of each block. The plot $\epsilon_{N_b}(N_b)$ can also be used to estimate the autocorrelation time $\tau \sim N/N_b^*$.

The results are the following. For trajectory n.1, a plateau is clearly visible up to $N_b^* \simeq 500$, corresponding to a typical autocorrelation time $\tau \sim 20$ and an error $\epsilon = 0.006$, larger than the standard deviation $\sigma_{\bar{x}} = 0.002$. For trajectory n.2, the correlations are very high, as you can see from the plot. Hence, the plateau is very short, up to $N_b^* \sim 15$ blocks, resulting in an autocorrelation time of about $\tau \sim 10^3$, in agreement with the plot of the trajectory. The appropriate error for this average is $\epsilon = 0.2$, much higher than the standard deviation $\sigma_{\bar{x}} = 0.006$. Finally, in trajectory n.3 it is not clearly visible when the plateau stops, meaning that the points are poorly correlated, indeed the standard deviation $\sigma_{\bar{x}} = 0.005$ is of the same order of the estimated error (plateau value) $\epsilon = 0.006$.

dataset	N	$\bar{x}$	$\sigma_{\bar{x}}$	ϵ	N_b^*	τ
$n.1$	10^4	-0.0012	0.0023	0.0064	~ 500	~ 20
$n.2$	$2 \cdot 10^4$	0.7452	0.0055	0.18	~ 15	$\sim 10^3$
$n.3$	$2 \cdot 10^3$	0.9960	0.0050	0.0064	–	–

Table 3.1: For each of the three datasets: size N (n. of values), average $\bar{x}$, standard deviation on the average $\sigma_{\bar{x}}$, error ϵ estimated through block analysis, number of blocks N_b up to which the plateau extends, approximative estimate of the autocorrelation time τ.

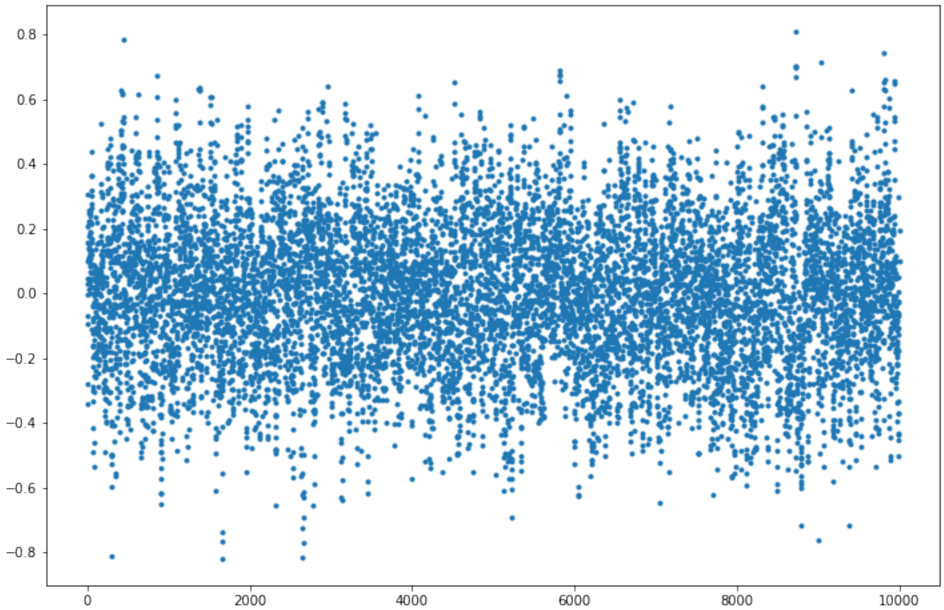

Figure 3.1: Trajectory n. 1.

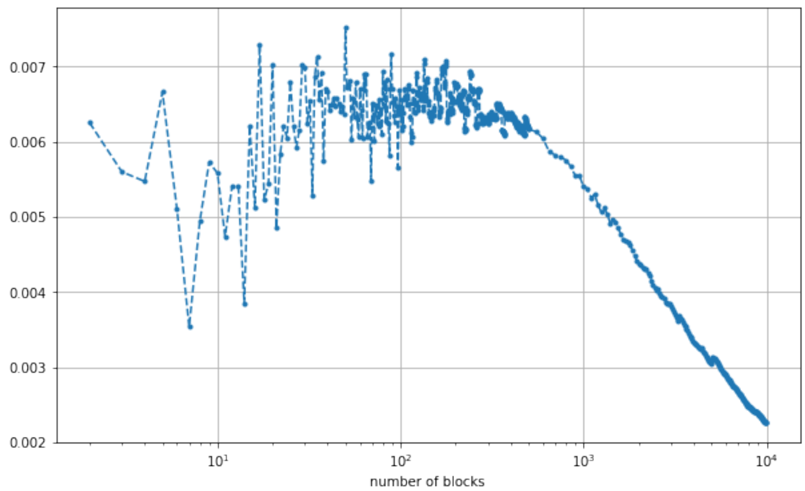

Figure 3.2: Block analysis for trajectory n. 1: error ϵ as a function of the number of blocks N_B.

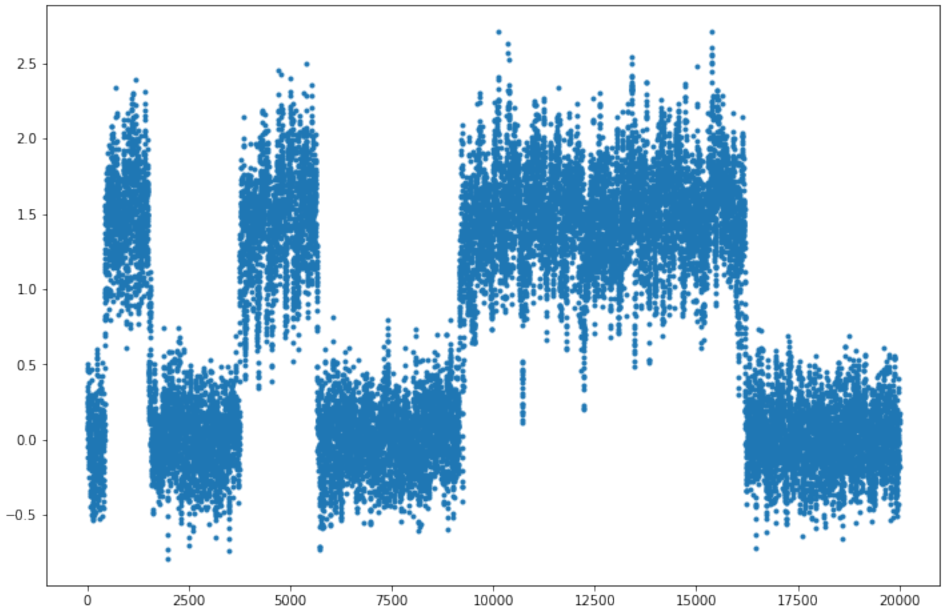

Figure 3.3: Trajectory n. 2.

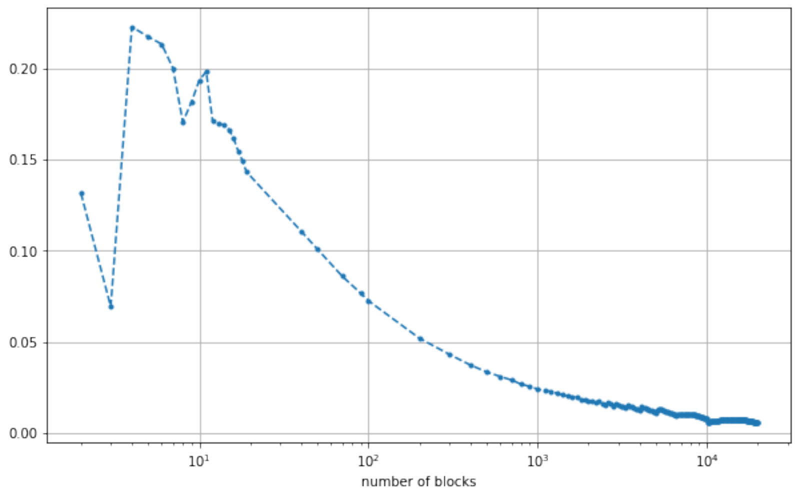

Figure 3.4: Block analysis for trajectory n. 2: error ϵ as a function of the number of blocks N_B.

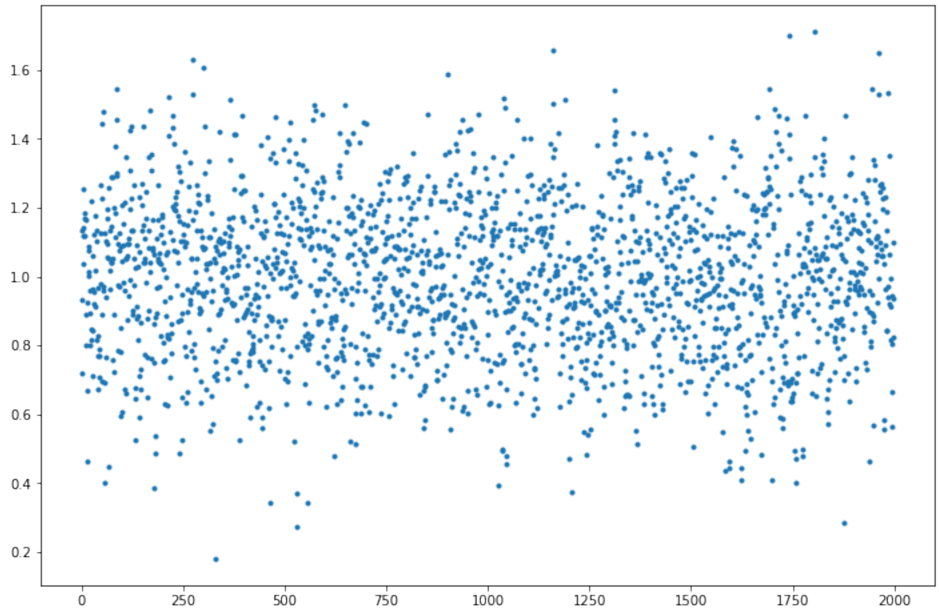

Figure 3.5: Trajectory n. 3.

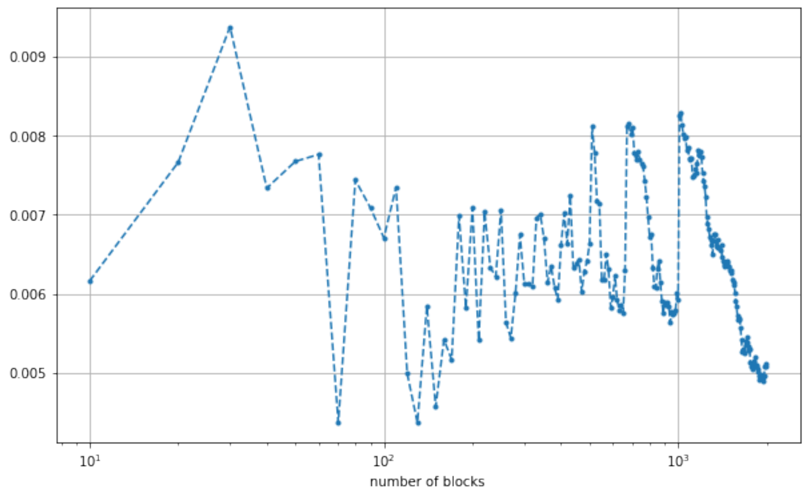

Figure 3.6: Block analysis for trajectory n. 3: error ϵ as a function of the number of blocks N_B.