Electric Current Estimation

Basics

For a given network of nanoparticles (NPs) with an evolving charge distribution $\vec{q}(t)$ and potential landscape $\vec{\phi}(t)$ at time t, we want to estimate the average electric current I for a particular NP-to-NP or NP-to-Electrode junction (node-to-node in general). For this we consider fixed batches with N_{batch} kinetic Monte Carlo Steps. For each of those batches we then calculate the electric current $I_{batch,n}$ using one of these two methods:

1. **Counting-Method:** Within batch n, we define two counters J_+ and J_-. If an elementary charge e jumps from node i to node j we increase J_+ by an e. If a charge jumps from j to i, we increase J_- by an e. After N_{batch} jumps, we calculate

   $$I_{batch,n} = \frac{J_+ - J_-}{t_n}$$

   with t_n as the time passed in batch n. The issue in this method is the strong dependence of I_{batch} from N_{batch} as small values in N_{batch} might even lead to zero jumps at all for the consider node-to-node junction. Additionaly, if N_{batch} is large we might average over changes in $\vec{q}(t)$ or $\vec{\phi}(t)$ occuring on smaller time frames. Therefore this mehod is only suited for estimating I of the steady network state at large N_{batch} values.
2. Γ**-Method:** For a given time t the electric current in between node i and node j can be defined as $I(t) = e \cdot (\Gamma_+(t) - \Gamma_-(t))$ with $\Gamma_+(t)$ as the rate for a charge jumping event from i to j and $\Gamma_-(t)$ as the rate for a charge jumping event from j to i. The average electric current for a batch, can then be calculated as \begin{equation}

   $$I_{batch,n} = \frac{e}{t_n} \sum_{m=0}^{N_{batch}} (\Gamma_+(t_m) - \Gamma_-(t_m)) \cdot t_m$$

   with t_n as the total time passed in batch n and t_m as the time passed for single jump m. Here we have the major advantage compared to **Counting-Method** that there is an electric

current $I(t_m)$ in each time step t_m. This allows us to also cover smaller N_{batch} values, especially suited for time dependent simulations or whenever the network states $\vec{q}(t)$ or $\vec{\phi}(t)$ are non steady on small time frames.

Eventually, as soon as one of those two methods calculated a couple of batched electric currents, for a steady state the final average electric current estimate is given as \begin{equation}

$$I = \frac{1}{N} \sum_{n=0}^{N} I_{batch,n}$$

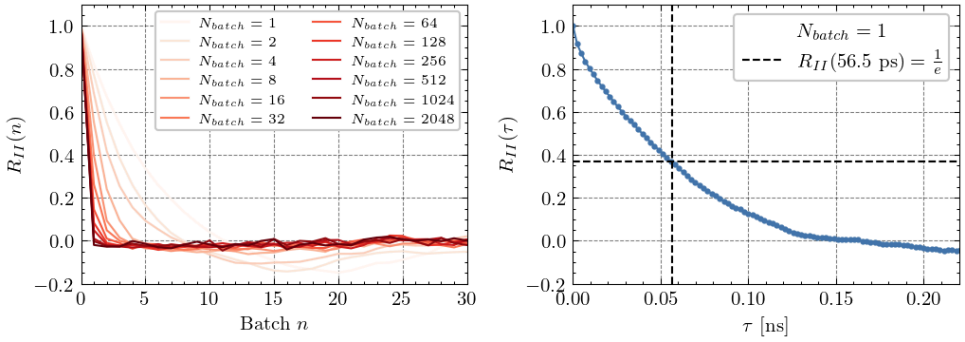
with N as the number of batches. Here we assume that in all batches about the same time $t_1 \approx t_2 \approx ... \approx t_n$ passed. Otherwise we would use \begin{equation}

$$I = \frac{1}{T} \sum_{n=0}^{N} I_{batch,n} \cdot t_n$$

The error of our estimated mean is given as

$$e_I = \frac{\sigma}{\sqrt{N}}$$

in case the $I_{batch,n}$ are non-correlated. The Figure below shows the autocorrelation R of the electric currents $I_{batch,n}$ (here just denoted as I) calculated using the Γ**-Method**. Each R is based on 300 different electrode voltage combinations. I is associated to the current between a NP and an electrode. The system was firstly equilibrated.

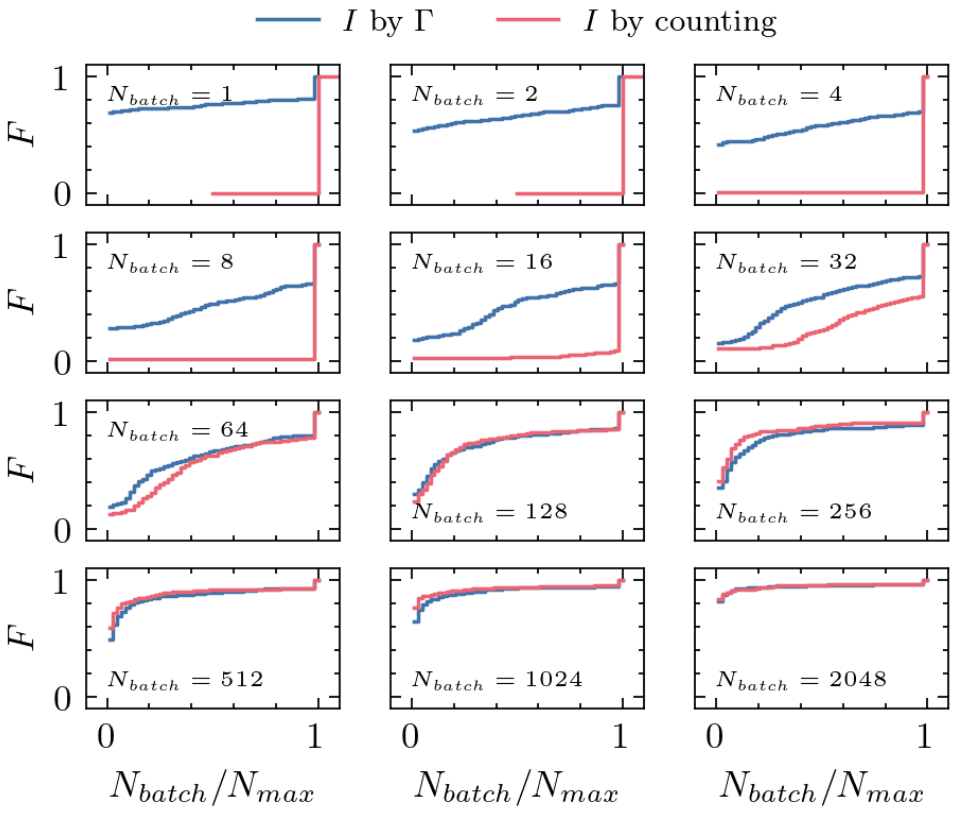


The left plot argues that batched electric currents decorrelate for about $N_{batch} > 100$. The right plot shows a correlation length / response time of the electric current of about 56.5 ps (here defined as the τ value for which $R = 1/e$). The correlation length might

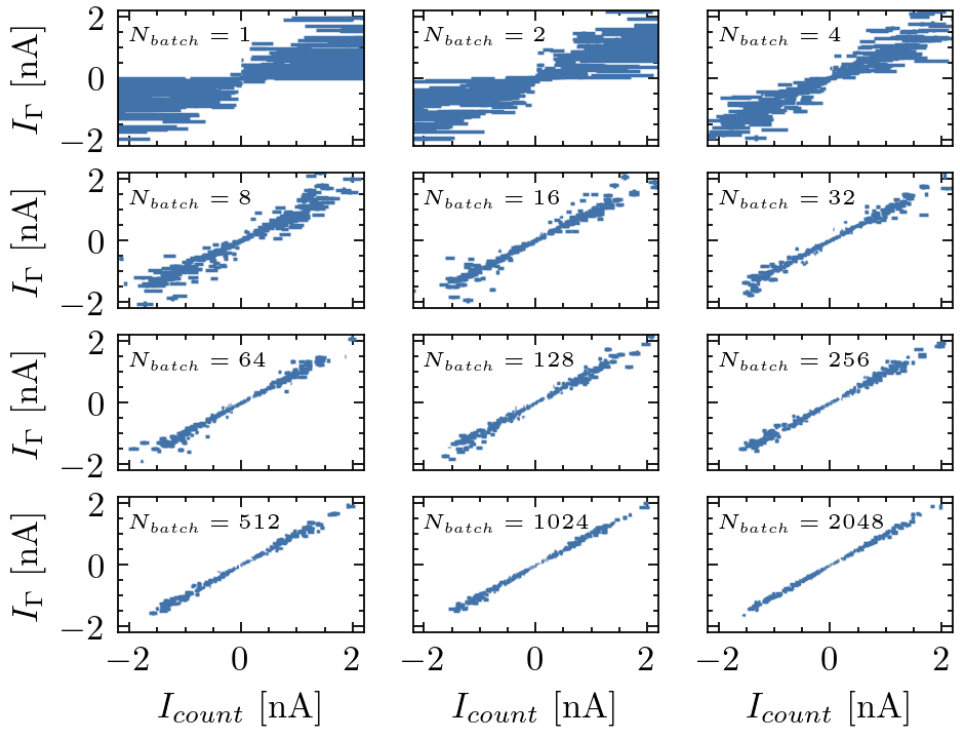
vary for different system sizes. Here we used a $7x7$ network of NPs and 8 electrodes.

Counting vs. Γ

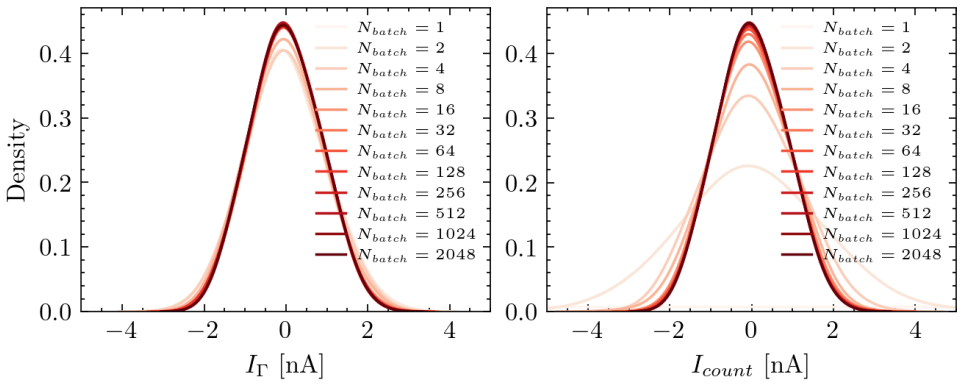
The average electric current I is calculated based on N_{batch} batches. The amount of batches needed is determined by the relative standard error $\frac{e_I}{I}$. If the relative standard error falls below 5% the simulation stops. However, some voltage configurations might not reach 5% (trivial example all voltages equals zero). For these cases we also define a maximum amount of batches N_{max} so that the simulation duration doesn't explode. The Figure below shows the cimulative distribution function F of the N_{batch}/N_{max} based on 300 voltage configurations in a $7x7$ system, i.e. the amount of runs reaching the limit or not convergig.



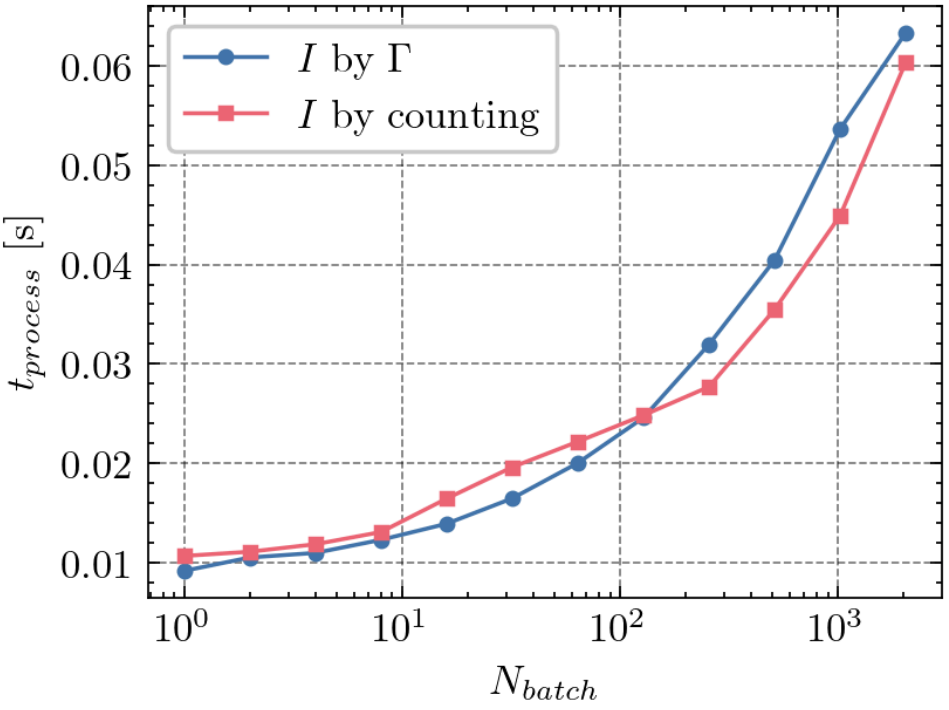
We see that for $N_{batch} > 100$ there is no difference between the **counting** and Γ algorithm. For small values of N_{batch}, the counting algorithmn does not converge most cases. Correspondingly, when the batch size is small, the actual average electric current when counting I_{count} is widely spreaded across the x-axis. For large values of N_{batch} both algorithms produce the same electric currents.



Accordingly, looking at the probability density of I_Γ and I_{count} we see the wrong estimations in I_{count} for small N_{batch} values as a broad distribution. I_Γ already resamples a decent distribution at $N_{batch} = 4$.



Finally, the lower figure compares the simulation duration per voltage configuration. Counting takes less as we increase N_{batch} above 100, while Γ is faster below this threshold.


I by Γ
I by counting
0.06
0.05
0.04
0.03
0.02
0.01
$t_{process}$ [s]
10^0
10^1
10^2
10^3
N_{batch}