10.2: Correlation Function from a Discrete Trajectory

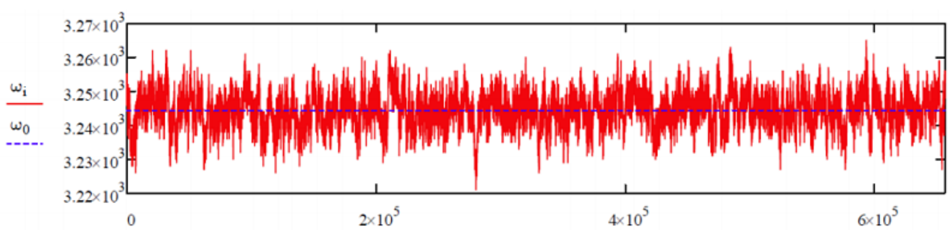
In practice classical correlation functions in molecular dynamics simulations or single molecule experiments are determined from a time-average over a long trajectory at discretely sampled data points. Let's evaluate C_{AA} for a discrete and finite trajectory in which we are given a series of N observations of the dynamical variable A at equally separated time points ti. The separation between time points is $t_{i+1} - t_i = \Delta t$, and the length of the trajectory is $T = N\Delta t$. Then we have ,

$$C_{AA} = \frac{1}{T} \sum_{i,j=1}^{N} \Delta t A(t_i) A(t_j) = \frac{1}{N} \sum_{i,j=1}^{N} A_i A_j \tag{10.2.1}$$

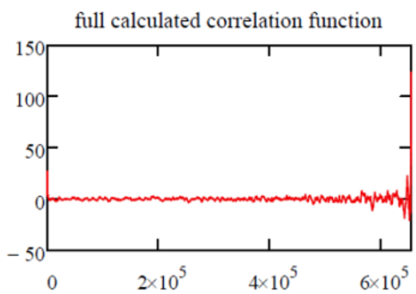
where $A_i = A(t_i)$. To make this more useful we want to express it as the time interval between points $\tau = t_j - t_i = (j-i)\Delta t$, and average over all possible pairwise products of A separated by τ. Defining a new count integer $n = j - i$, we can express the delay as $\tau = n\Delta t$. For a finite data set there are a different number of observations to average over at each time interval (n). We have the most pairwise products—N to be precise—when the time points are equal (ti=tj). We only have one data pair for the maximum delay $\tau = T$. Therefore, the number of pairwise products for a given delay τ is $N - n$. So we can write Equation 10.2.1 as

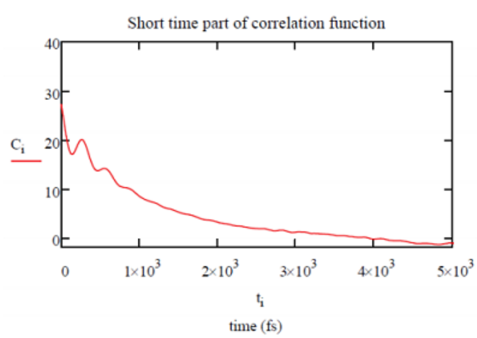
$$C_{AA}(\tau) = C(n) = \frac{1}{N-n} \sum_{i=1}^{N-n} A_{i+n} A_i \tag{10.2.2}$$

Note that this expression will only be calculated for positive values of n, for which $t_j \geq t_i$. As an example consider the following calculation for fluctuations in a vibrational frequency $\omega(t)$, which consists of 32000 consecutive frequencies in units of cm^{-1} for points separated by 10 femtoseconds, and has a mean value of $\omega_0 = 3244\text{cm}^{-1}$. This trajectory illustrates that there are fast fluctuations on femtosecond time scales, but the behavior is seemingly random on 100 picosecond time scales



After determining the variation from the mean $\delta\omega(t_i) = \omega(t_i) - \omega 0$, the frequency correlation function is determined from Equation 10.2.2, with the substitution $\delta\omega(t_i) \rightarrow A_i$.





We can see that the correlation function reveals no frequency correlation on the time scale of 10^4 –10^5 fs, however a decay of the correlation function is observed for short delays signifying the loss of memory in the fluctuating frequency on the 10^3 fs time scale. From Equation ???, we find that the correlation time is $\tau_C = 785\ fs$.