Dynamics

INTRODUCTION

Dynamics characterizes two dynamical properties of confined water from a Gromacs molecular dynamics simulation. This is a useful routine to perform when you are interested in characterizing the dynamics of water inside of a nanopore, created by a protein active site. The output from Dynamics, when fit with a bi-exponential decay equation can be used to acquire either the 1) average residency times, or 2) the orientational correlation times.

1) The average residency times describe the average duration of time any given water molecule spends inside of a nanopore, and is obtained from lifetime correlation function. The relative strength of the interactions compared to bulk solvent, are assessed from the average residency times. Average residency times are calculated from bi-exponential fits of the lifetime correlation function. Longer residency times compared to bulk are associated to stronger interactions. Fast residency times are assumed to be associated with exchange with bulk at the pore boundary. For analysis intepretation examples, see the Examples section.

The lifetime correlation function, is calculated by averaging autocorrelation functions of pore water. The algortihm uses a spherical approximatation to describe pore geometry. The user is required to submit a max radius for the pore; this requires the calculation of the radial distribution function using Structure, to determine a definition for the pore radius of your system.

2) Orientational correlation times describes rotational freedom of water, and are acquired from the dipole correlation function. Nanopore water can experience different rotational processes, dependening on it's orientation relative to the pore axis. The pore axis is defined by a normal vector calculated from a user specified set of vectors, and is described in detail in the manual for the Orientation program (not needed for this program).

For the output from Dynamics, orientational correlation times can be obtained with a bi-exponential fit to the dipole correlation function. The dipole correlation function is obtained by averaging single autocorrelation functions of water dipole moments, for nanopore water.

ALGORITHMS

The algorithm for the lifetime correlation fucntion is given by

$$\mathrm{C}(\tau) = \langle\; \mathrm{A(t)} \cdot \mathrm{A(t}+\tau)\; \rangle = \frac{1}{(\tau_{max}-i)} \sum_{i=1}^{\tau_{max}} \sum_{j=1}^{Nwat} c_j.$$

c_j is equal to 1 if a specific water molecule j is inside the pore at time t and t+τ, equal to 0 when this condition is not satisfied. This algorithm has a complexity of $\mathcal{O}(n^2)$, which is repeated for a number of user specified timesteps by τ_{max}. n is the number water molecules in the MD simulation. $\langle\; \mathrm{A(t)} \cdot \mathrm{A(t}+\tau)\; \rangle$ is the time-averged autocorrelation function for lag time τ. For all-atom MD simulations of protein+water systems on the nanosecond timescale, the time required to calculate correlations for all possible lag times is expensive. For confined water, we are generally interested in correlations between fluctuations in the femtosecond to sub-nanosecond timescale. The correlations at long lag times τ are random, not interesting, therefore you need to calculate correlations only up to a specified max lag times τ_{max}. You will need to experiment with this.

The algorithm for the dipole correlation function, is obtained just as the lifetime correlation function, with the excpetion that the autocorrelation function is described as

$$C(\tau) = \langle \, \vec{\mu}(t) \cdot \vec{\mu}(t+\tau) \, \rangle = \sum_{i=1}^{\tau_{max}} \sum_{j=1}^{Nwat} |\vec{\mu}(t)||\vec{\mu}(t+\tau)|cos(\theta).$$

$\langle \, \vec{\mu}(t) \cdot \vec{\mu}(t+\tau) \, \rangle$ is computed from the average of single water dipole autocorrelation functions, of nanopore water. $|\vec{\mu}(t)|, |\vec{\mu}(t+\tau)|$ are the magnitudes of the dipole vectors at time t and t+τ. θ is the angle between the two vectors.

REQUIRMENTS

- Both algroithms in Dynamics requires a distance index file just like Structure. To generate the distance file, perform the same procedure discussed in the Structure manual for each algorithm seperately.

- Dynamics requires maximum lag time τ_{max} in the input. Both algorithms scale as $\mathcal{O}(n^2)$, in order to minimize computational time, correlations are only computed up to certain time cutoff.

- Only the distance file is required to calculate the lifetime correlation function. The dipole correlation function will need an additional input, a ***.gro** file that contains the absolute positions of each water atom, at each simulation timestep, to 9 decimal precsion.

USING DYNAMICS

Dynamics is in development. However, we have developed the routines to calculate both the lifetime and dipole correlation functions. At the moment you will have to independently compile these using gcc, or clang, as follows.

gcc dipoleCor/lifetime.c -o executableName

or

clang dipoleCor/lifetime.c -o executableName

For instructions on what to input into the routines, hit enter with the executable on your terminal as follows
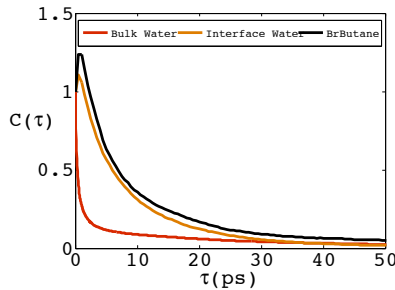
./executableName

ANALYSIS EXAMPLES

Figure 1. Lifetime correlation function for water in the β-cyclodextrin pore. Calculations made for water and 1-bromobutane, from simulations of β-cyclodexrin in bulk and biphasic simulations. These plots qualitatively show that at a liquid-liquid interface, confined solvent resides in the pore for longer periods of time. Using a bi-exponential fit, we determined there to be a fast and slow component to the decay. The fast component is associated with solvent exhange at the barier of the pore, and the slow component represents exchange of inner pore water.
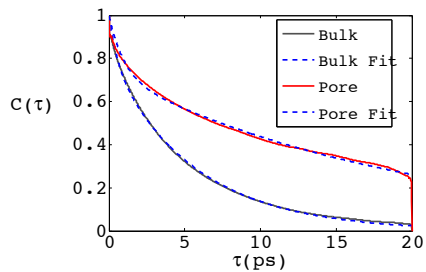

Figure 2. Dipole correlation functions for bulk and pore water from simulation of β-cyclodextrin in water. The correlation function for the pore water relative to bulk, is slower to decay, indicative of restricted rotation inside of the pore. Code tested on simulations of rigid tip3p water model.