22.3: Representations of Dynamics

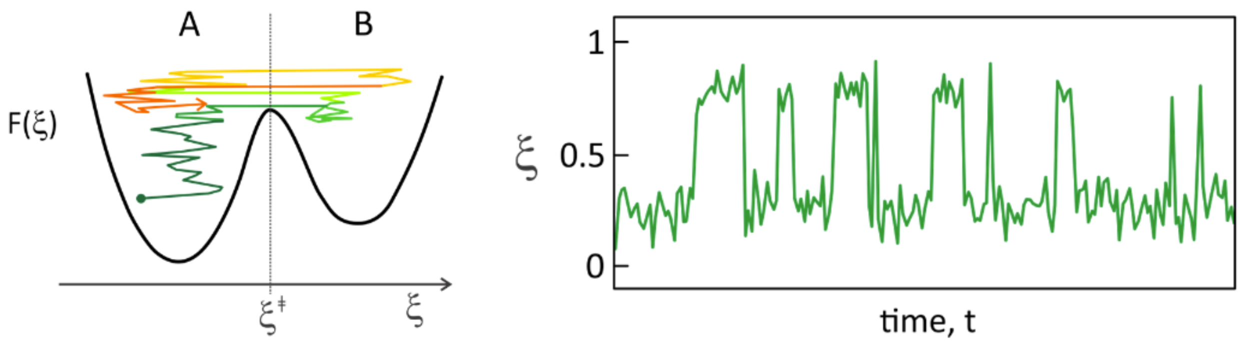
We will survey different representation of time-dependent processes using examples from one-dimension.

Trajectories

Watch the continuous time-dependent behavior of one or more particles/molecules in the system.

Time-dependent structural configurations

A molecular dynamics trajectory will give you the position of all atoms as a function of time $\{\mathbf{r}^N, t\}$. Although there is an enormous amount of information in such a trajectory, the raw data is often overwhelming and not of particularly high value itself. However, it is possible to project this high dimensional information in structural coordinates onto one or more collective variables ξ that forms a more meaningful representation of the dynamics, ξ(t). Alternatively, single molecule experiments can provide a chronological sequence of the states visited by molecule.

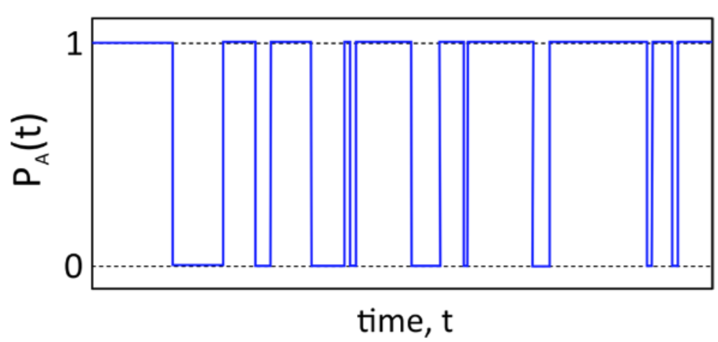


State trajectories: Time-dependent occupation of states

A discretized representation of which state of the system the particle occupies. Requires that you define the boundaries of a state.

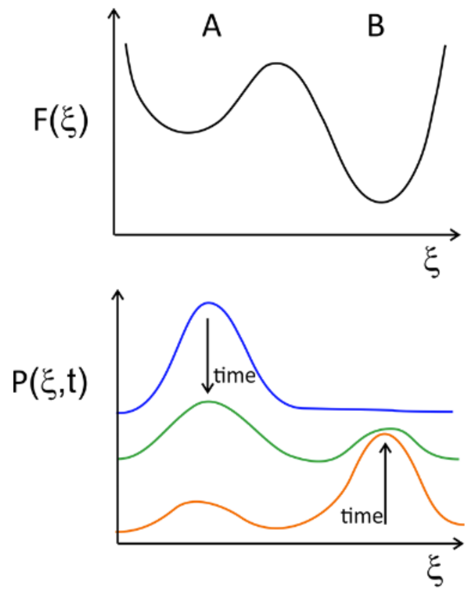
Example: A two state trajectory for an equilibrium $A \rightleftharpoons B$, where the time-dependent probability of being in state A is:

$$P_A(t) = \begin{cases} 1 \text{ if } \xi(t) < \xi^{\ddagger} \\ 0 \text{ if } \xi(t) > \xi^{\ddagger} \end{cases} \tag{22.3.1}$$



Time-Dependent Probability Distributions and Fluxes

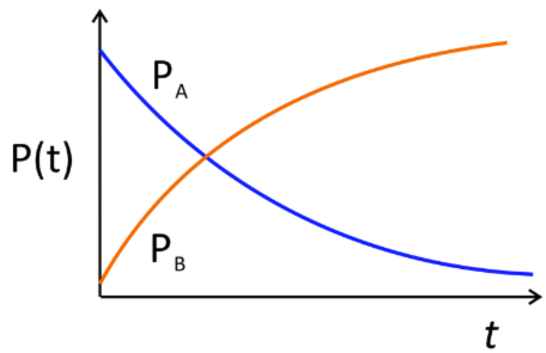
With sufficient sampling, one can average over trajectories in order to develop a time-dependent probability distribution $P(\xi, t)$ for the non-equilibrium evolution of an initial state.



State Populations: Kinetics

- Average over states to get time-dependent populations of those states.

$$\int_{\text{state A}} P(\xi, t) d\xi = P_A(t) \tag{22.3.2}$$



- Alternatively, one can obtain the same information by analyzing waiting time distributions from state trajectories, as described below.
- The kinetics can be modeled with rate equations/master equation: P=**k**P.

Time-Correlation Functions

Time-correlation functions are commonly used to characterize trajectories of a fluctuating observable. These are described next