Reweighting simulations in and out of equilibrium

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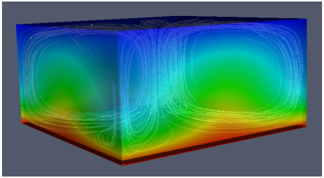
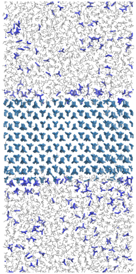
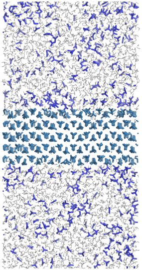
Motivation and Contents

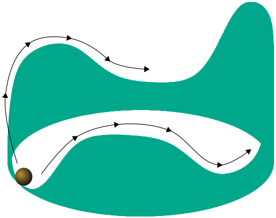
- Simulation of complex systems in non-equilibrium steady state
- Explore relation between equilibrium and non-equilibrium systems
- *Markov State Modelling (MSM)*: Construct long trajectories
- *Maximum Caliber (MaxCal)* provides microscopic relations beyond detailed balance
  - MSM construction protocol in off-equilibrium
  - Ensemble reweighting in off-equilibrium







Toy Model



- 1d ring potential
- Single Particle
- Driven by external force
- Overdamped Dynamics

$$0 = \frac{\partial U(x)}{\partial x} - \gamma \dot{x} + \sqrt{2\gamma k_B T} R(t) + f_{ext}$$

$R(t)$ - Gaussian noise
f_{ext} - Nonconservative external force

Jayne's Maximum Caliber

- Off-equilibrium extension of Gibbs' Maximum Entropy

Maximum Entropy

Microstate i with p_i
$S = -\sum_i p_i \log p_i$
Impose constraints in form of averages $\langle A_k \rangle$

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Maximum Caliber

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$$\mathcal{J}[p(x)] = \int_\Omega p(x) \log\left(\frac{p(x)}{q(x)}\right) dx + \nu\left(\int_\Omega p(x)dx - 1\right) + \beta\left(\int_\Omega p(x)A(x) - \langle A\rangle\right)$$

$$\frac{\delta \mathcal{J}[p(x)]}{\delta p(x)} = 0 \quad \rightarrow p(x) = Z^{-1} q(x) \exp\left(-\beta A(x)\right)$$

Markov Chain Maximum Caliber

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Following Assumptions

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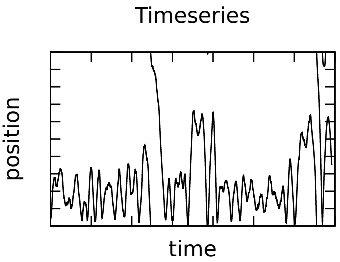
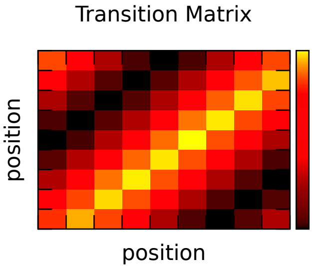
$\to \pi(\mathbf{F}, \mathbf{q}, \langle F_{new} \rangle) \qquad \mathbf{p}(\mathbf{F}, \mathbf{q}, \langle F_{new} \rangle)$

Markov State Modelling





Perform:

- Space discretisation
- Time discretisation
- Dimensional reduction

s.th. Markov property is fulfilled

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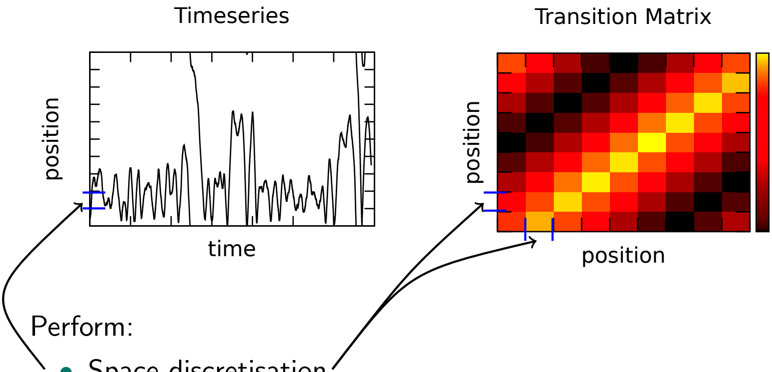

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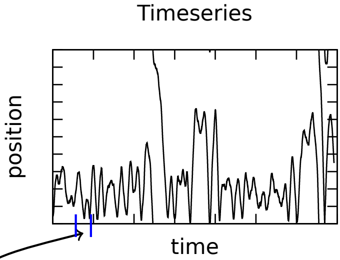

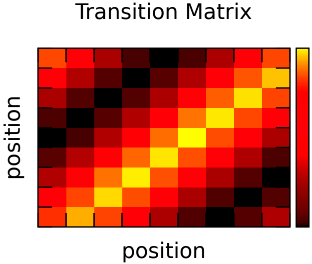

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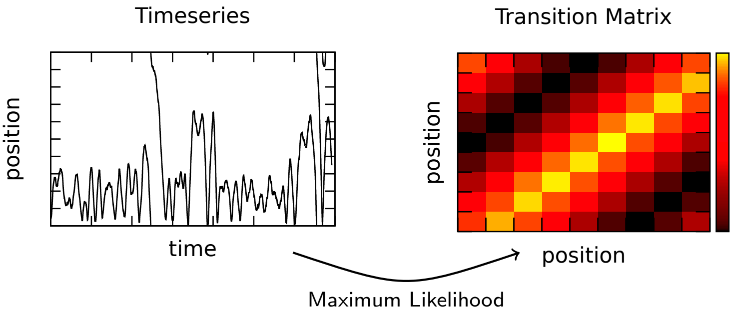

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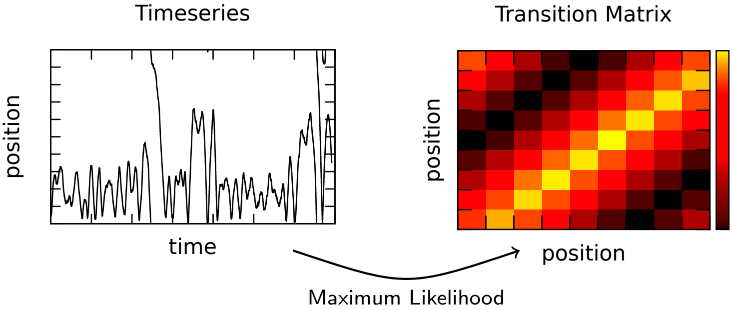

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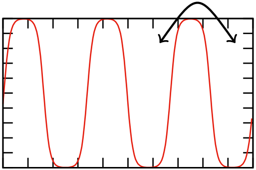
In Equilibrium:

- Enforce detailed balance
- Analyse form and timescale of processes

Results - Simulation vs Reweighting



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- Compare Simulation and Reweighted Model
  - by entropy production S_{prod}
  - by first passage time distribution

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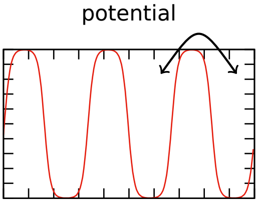

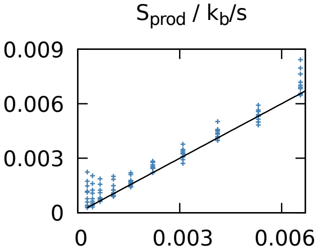

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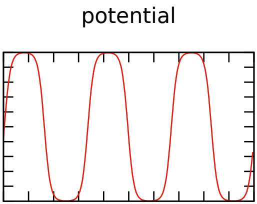

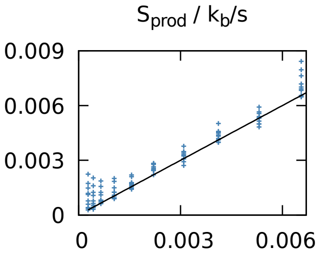

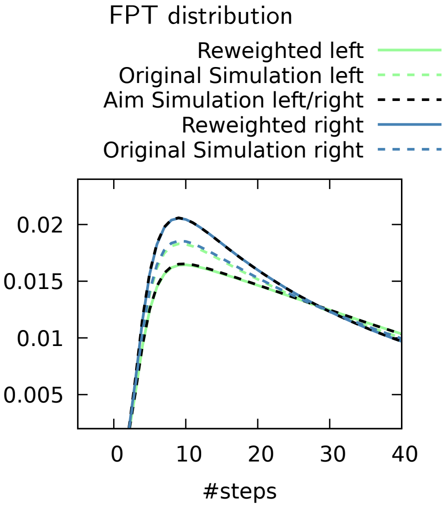

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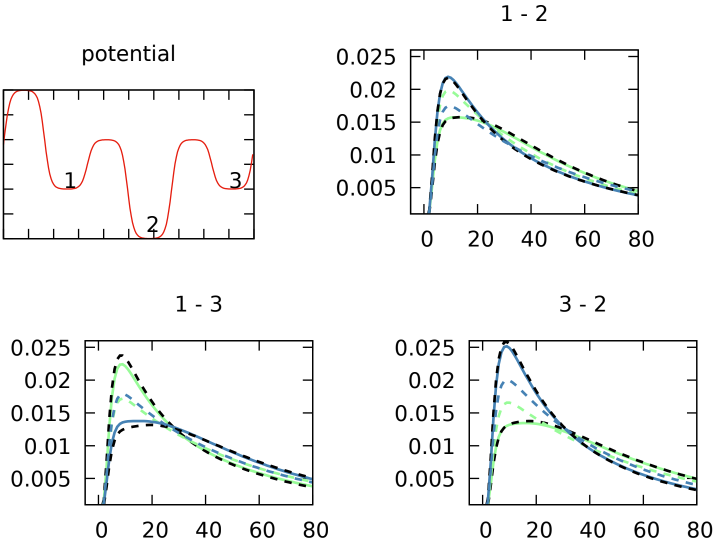

Summary

- Trajectory Space can be controlled by Markov State Models
- Maximum Caliber connects macroscopic quantities to microscopic trajectories
- Dynamics of system can be reweighted. It requires:
  - Generating reference Markov Model
  - Microscopic description of constraint(s): F_{ij}

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Next Steps:

- Extend to complex system
- Systematically deduce F_{ij}

Acknowledgments

Biomolecular
simulations
MPIP

MATERIALS IN MAINZ SCIENCE

Minimisation

$$\mathcal{C} = \underbrace{-\sum_{i,j} p_i p_{ij} \log \frac{p_{ij}}{q_{ij}}}_{\text{Relative Path Entropy (Markov)}} \underbrace{+ \sum_i \nu_i \left(\sum_j p_{ij} - 1 \right) + \zeta \sum_i (p_i - 1)}_{\text{Normalisation}} + \underbrace{\sum_j \mu_j \left(\sum_i p_i p_{ij} - p_j \right)}_{\text{Global Balance}} + \underbrace{\gamma \left(\sum_{i,j} p_i p_{ij} F_{ij} - \langle F \rangle \right)}_{\text{Flux Constraint}}$$

solved by

$W_{ij} = qij \exp(-\gamma F_{ij})$

$\sum_j W_{ij} \Phi_j = \nu \Phi_i$

$p_{ij} = \frac{\Phi_j}{\nu * \Phi_i}$