# TAMMBER:
## *Temperature Accelerated construction of Markov Models with Bayesian Estimation of Rates*

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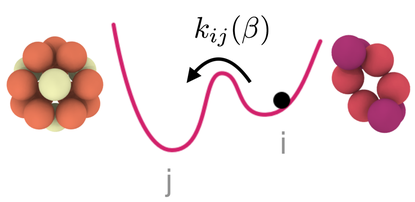
## Introduction

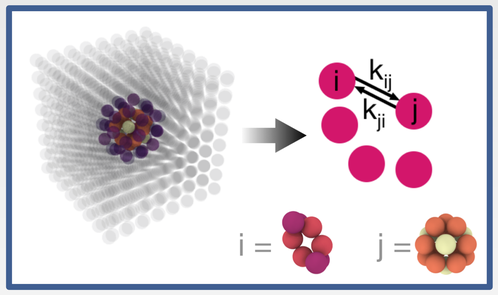
Transport in solids such as Fe and $UO_2$ is dictated by the potential energy landscape experienced by defects – the valleys and mountain passes that separate those valleys. The astronomical vastness, complexity, and roughness of the potential energy landscape of materials make the investigation of their long-time dynamical evolution extremely difficult.




One dimensional illustration of the rare event problem. The expected escape time is the inverse rate, which due to the Arrhenius relation can be extremely large at temperatures of practical relevance.

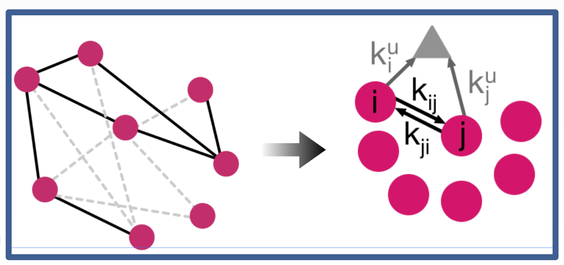
Due to significant free energy barriers between different metastable basins of configuration space, direct simulation methods are typically unfeasible. Indeed, molecular dynamics (MD) simulations of materials are typically restricted to sub-microsecond timescales, which is often much too short for a trajectory to cross the barriers that determine the long-time behavior.

A bulk crystal containing a defect can have multiple metastable basins in configuration space, corresponding to different defect structures. We identify states through structural analysis of the basin energy minimum. A Markov model of the state-to-state dynamics can in principle access long timescales, but without a complete set of possible transitions the model can produce erroneous predictions.




A common goal of multi-scale materials simulation is to build kinetic Monte Carlo models (or more generally Markov models) from the transitions between metastable basins observed during molecular dynamics trajectories. Identifying basins as states, after calculating interstate transition rates, the Markov model can efficiently simulate long state-to-state trajectories, providing access to the long timescale dynamics.

However, constructing such mesoscale models from atomistic simulations is fraught with danger - if all possible transformation pathways are not observed, the predicted behavior over long time scales can become uncontrollably erroneous.




The unknown rate. Any real state network will have unobserved states and connections after a finite amount of sampling (left). We represent this incompleteness by assigning an 'unknown rate' to each state, which leads to an absorbing state (right). Importantly, if the unknown rate is larger then the unobserved rate, the dynamics of the right network are statistically identical to those of the left before absorption occurs.

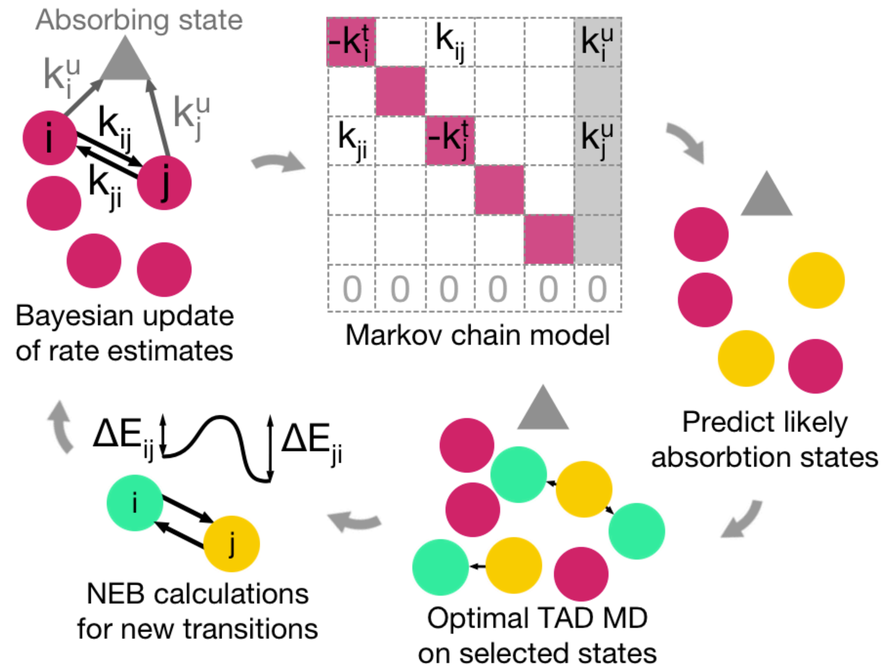
## Reference

TD Swinburne and D Perez. "Self-optimized construction of transition rate matrices from accelerated atomistic simulations with Bayesian uncertainty quantification." Physical Review Materials 2.5 (2018): 053802.

## TAMMBER

The challenge addressed by TAMMBER is to efficiently leverage massively parallel computational resources to construct mesoscale Markov models from MD, whilst controlling (or at least quantifying) the error induced due by incomplete sampling. The central conceptual tool which we use to do this is the 'unknown rate.' TAMMBER assigns an 'unknown' rate to each state, which is an estimate of the remaining (unobserved) rate and leads to an absorbing 'unknown' state. The validity time of the model network is then the expected time to absorption given an initial state distribution. The validity time is used by TAMMBER as a key measure of the model quality.

As shown on the right, TAMMBER distributes thousands of accelerated MD simulations across massively parallel computational resources. Bayesian uncertainty estimators are used to determine in which set of metastable states additional computational effort is most profitable, allowing TAMMBER to autonomously allocate computational work to optimally increase the model quality. This poster outlines each stage of the process and provides some example applications.

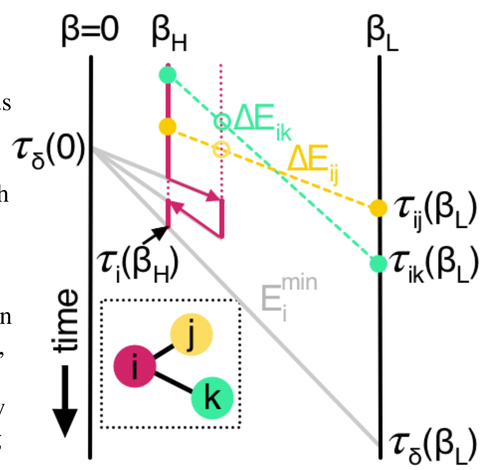



The TAMMBER workflow. Temperature accelerated MD produces interstate transition trajectories which are analyzed by Bayesian rate estimators and static calculation. An absorbing Markov chain then gives the expected validity time of the model and optimally allocates resources and the degree of temperature acceleration to grow this time as fast as possible.

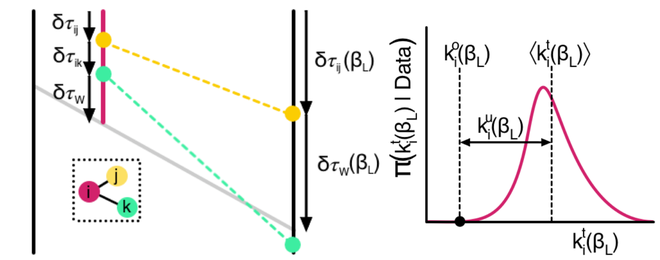
## Elements of TAMMBER

### *Temperature Accelerated Dynamics*

To efficiently find high barrier processes we use the temperature accelerated dynamics method (TAD). TAD relies on the Arrhenius behavior of harmonic transition state theory to infer low temperature escape times from high temperature escape times. To do this, one must calculate the energy barrier for an observed process. In addition, the Poissonian distribution of escape times allows one to infer, with a controlled uncertainty, the effective total sampling time at low temperature from a given sampling time at high temperature.



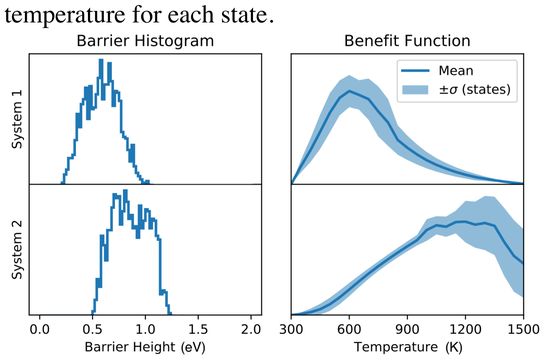

### *Unknown rate estimation*




After a period of TAD on a single state, TAMMBER will have found a set of escape pathways with associated rates and first passage times in a total sampling time (*left*). TAMMBER then exploits the Poisson distribution to derive the likelihood of the observed data for a given total rate. Using Bayes' rule with a minimum information prior, we then have a posterior distribution for the total escape rate (*right*), from which moments of the unknown rate can be obtained.

### *Optimal TAD temperature*

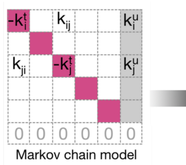
A TAD simulation expends computational work performing MD, barrier calculations, and energy minimization. For a given low temperature, there is an optimal high acceleration temperature; too high, and either repeated transitions or very large barrier events of negligible low-temperature influence will dominate. Too low, and all the effort will be spent in MD without any transitions. Our estimate of the unknown rate leads to a cost function for TAD yielding, autonomously, the optimal acceleration temperature for each state.




Local self-optimization. Left: For a given spectrum of escape barriers, TAMMBER's TAD cost function finds the optimal acceleration temperature. Right: With a systematically higher barrier distribution, the cost function autonomously realizes the optimal acceleration temperature for this state should be higher.

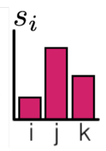
### *Optimal Allocation of Computational Work*

Using the calculated rates to build an absorbing Markov Chain, we can derive an expression for the expected residence time of the network and the gradient of this time with additional computational work in each state. We then allocate computational work proportionally to this gradient in order to maximize the residence time.




$$\langle \tau^{res} \rangle = -\mathbf{P}_{\mathcal{K}}(0) \cdot \mathbf{Q}_{\mathcal{K}}^{-1} \cdot \mathbf{1}_{\mathcal{K}}$$

$$\frac{\delta \langle \tau^{res} \rangle}{\delta c} = \sum_{i \in \mathcal{K}} s_i \frac{\delta \langle \tau^{res} \rangle}{\delta c_i}$$




$$s_i = \eta \frac{\delta k_i^{un}(\beta_L)}{\delta c_i} \left[\mathbf{P}_{\mathcal{K}}(0) \cdot \mathbf{Q}_{\mathcal{K}}^{-1}\right]_i \left[\mathbf{Q}_{\mathcal{K}}^{-1} \cdot \mathbf{1}_{\mathcal{K}}\right]_i$$

Change in unknown rate with more computation — Time in state *i* — Time | start on *i*



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