# Efficient Sampling of Large Rare Event Networks using Multiple State Transition Interface Sampling

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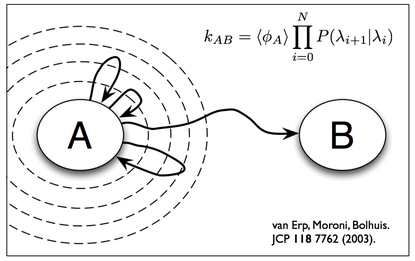
## Transition Interface Sampling (TIS)



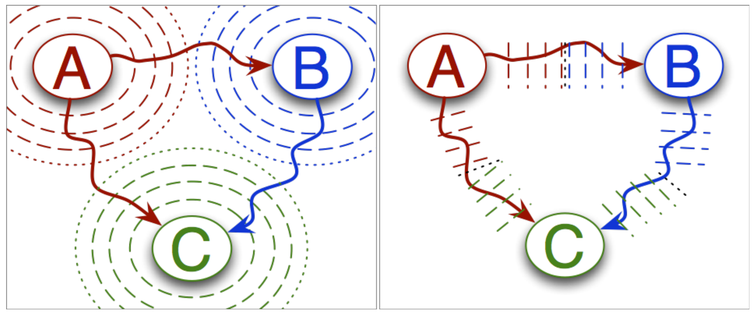

Transition interface sampling (TIS) is a path-sampling based approach to studying rare events. TIS includes several interfaces, each with its own path ensemble. Paths for each interface must begin in a state, cross the interface, and end in either the initial state or a target state.

TIS makes it very easy to calculate the rate for a transition. With the extension of replica exchange between interfaces, it can also sample different transition channels, and it can efficiently relax the environment between successive transitions.

## Multiple State and Multiple Interface Set TIS

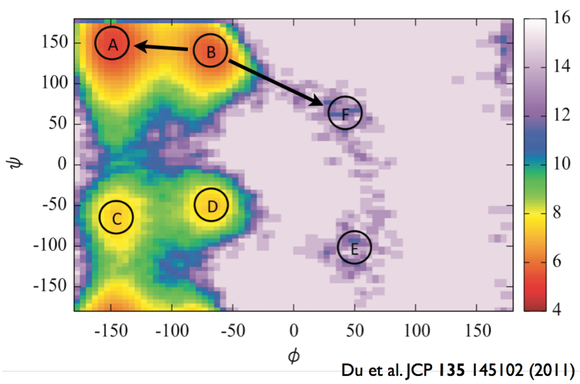
Recent work has extended TIS and TPS to cases with more than two states. When there are more than two states, there is a transition network. Studying these networks requires the development of new and specialized tools.

Multiple State TIS has been developed based on the idea of using a single interface for each state. Here, we extend multiple state TIS to allow more than one interface set per state. This multiple interface set approach allows us to choose the best order parameter for each transition, instead of the older one-size-fits-all approach.




## "Rarer" Events

One situation where the multiple interface set approach can be useful is in the case of "rarer" events, where two transitions starting in the same state have very different probabilities. By selecting a different order parameter for each transition, we can more efficiently sample both types of transitions.

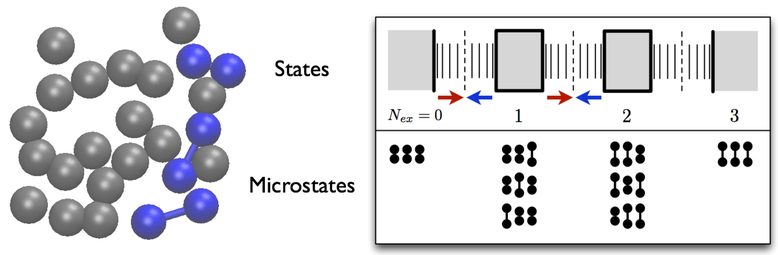



Du et al. JCP 135 145102 (2011)

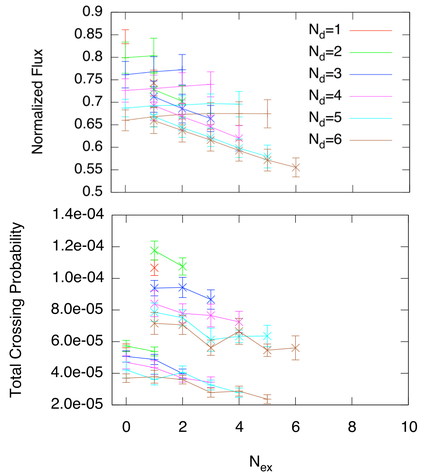
## Multiple Dimer Model System

To study how the existence of multiple possible rare events in a system can lead to environmental effects which are dependent on the global state of the system, we turn to a simple model of dimers in a bath of WCA particles. Each dimer is subject to a double-well potential such that it can be either condensed or extended. We study all the condensing and extending transitions in the system.

The total transition network therefore becomes very large, since from any state each dimer can make a transition. We simplify the network by considering states defined by the number of extended dimers, and grouping all possible microstates (which specific dimers are extended) into that. We also only consider transitions in which only one dimer is condensed or extended (the state changes by one).




## Effect of Global State on Local Transitions

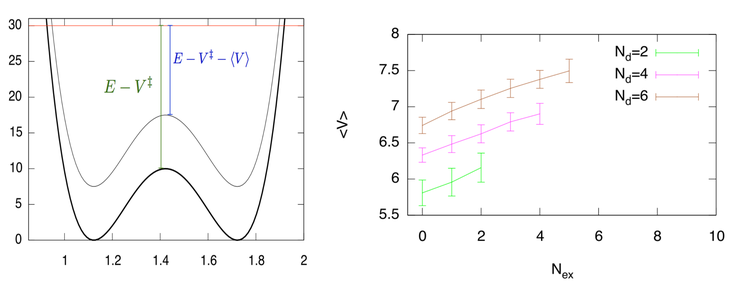



Each individual transition in this model (isolated from its environment) is identical, so the question becomes how the global environment affects these local transitions. Since TIS splits the rate calculation into the calculation of a flux and of a crossing probability, we consider trends in each of these separately.

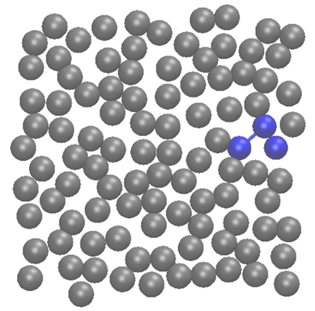
As we increase the number of initially extended dimers, the flux per extending transition increases, whereas the flux per condensing transition decreases. This is what would be expected from an excluded volume explanation.

However, in the rates, these trends are overwhelmed by the trends in the total crossing probability. The total crossing probability decreases with initially extended dimers regardless of whether the transition is extending or condensing.

To explain this, we consider the fact that our model is not a hard-sphere system. No matter how which direction the transition is going, having more dimers extended means that those extended dimers are having more (repulsive) interactions, increases the average potential energy. Since our dynamics are *NVE*, this in turn means that the average excess energy at the barrier is lower, decreasing the crossing probability. We confirm this by calculating the average potential energy in each state.

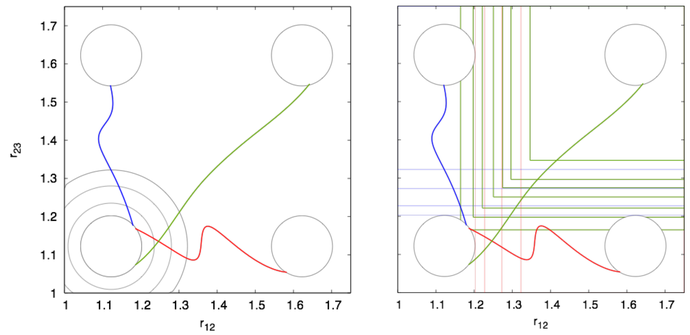



## "Rarer" Events Model System

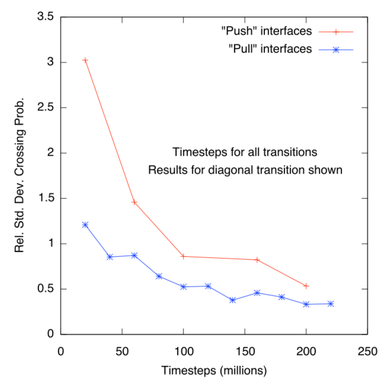


To explore the efficiency of the multiple interface approach for "rarer" events, we use a system which was initially used to introduce multiple state TIS. This system is similar to the multiple dimer system, except it includes two double wells which share a common atom, making a trimer with four possible states. Unlike in the dimer case, in this example we do not group equivalent microstates together.

The "diagonal" transition from all-condensed to all-extended is a rarer event than the transitions from all-condensed to one-extended. We compare the results from a single interface set with those from a multiple interface set approach.




## Multiple Interface Sets are More Efficient




The multiple interface set approach (labelled "pull") leads to significantly less error in the diagonal transition crossing probability than the single interface set approach (labelled "push"). The results are plotted for the *total* number of time steps, which includes calculated all the transitions.

These results only allow replica exchange between within a given interface set; replica exchange between different sets of the "pull" approach may improve them. Furthermore, a hybrid approach that begins with a single interface set and then forks into different sets is also possible, and may be even more efficient.

## Additional References

Replica Exchange TIS: T.S. van Erp, *Phys. Rev Lett.* **98**, 268301 (2007).

Multiple State TIS: J. Rogal and P.G. Bolhuis, *J. Chem. Phys.* **129**, 224107 (2008).

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