

# Recent simulation methods for resolving molecular details in thermodynamics and kinetics

---

Cameron F. Abrams

October 10, 2019

Drexel University, Department of Chemical and Biological Engineering

# Making Milestoning Practical: Transition-Path Theory and Markovian Milestoning in Voronoi Tessellations

E. Vanden-Eijnden et al. *J Chem Phys* **130**:194101 (2009).

Estimate  $q_{ik,ij}$  using MD confined to Voronoi cells in feature-space

In each cell  $i$ , use confined MD of duration  $T_i$  to tally:

1.  $N_{ik,ij}^i$ ,
2.  $R_{ij}^i$ , and,
3.  $N_{i \rightarrow j}^i$ : # of transition attempts from  $i$  to any neighbor  $j$ .

Compute apparent transition rate constants:

$$k_{i \rightarrow j} = \frac{N_{i \rightarrow j}^i}{T_i}$$

And enforce equilibrium among all  $\Lambda$  cells, so

$$\sum_{j=1, j \neq i}^{\Lambda} \pi_j k_{j \rightarrow i} = \pi_i \sum_{j=1, j \neq i}^{\Lambda} k_{i \rightarrow j} \quad \sum_i \pi_i = 1$$

providing equilibrium probabilities to be in cell  $i$ ,  $\pi_i$ . This allows construction of  $q_{ik,ij}$ :

$$q_{ik,ij} = \frac{\pi_i N_{ik,ij}^i / T_i}{\pi_i R_{ij}^i / T_i + \pi_j R_{ij}^j / T_j}.$$

