

Recent simulation methods for resolving molecular details in thermodynamics and kinetics

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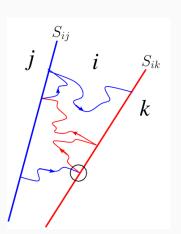
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Making Milestoning Practical: Transition-Path Theory and Markovian Milestoning in Voronoi Tesselations

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. $N_{i o j}^i$: # of transition attemps from i to any neighbor j.

Compute apparent transition rate constants:

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

And enforce equilibrium among all Λ 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, π_i . This allows construction of $q_{ik,ij}$:

$$q_{ik,ij} = \frac{\pi_i N^i_{ik,ij}/T_i}{\pi_i R^i_{ij}/T_i + \pi_j R^j_{ij}/T_j}.$$