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2. TPS

Many Pathways

Find a saddle point, drop from each side
Approach
→ Postulate q
→ Compute probability distribution
→ If successful, compute $D^f$
→ If not, go back to postulating a new q
Pick any pathway that connects A to B in time $\tau$.
Pick another via a monte carlo pathway in space.
→ Shooting - Take a point along the path and perturb the momentum.
\[ p_i \rightarrow \delta p_i + p_{io} \]
Run it forward and backward to A and B within time $\tau$

$\rightarrow$ Shifting - Take a path and shift it by $\Delta x$ and run again.

Stochastic $\rightarrow$ MD to create phase space.

$Z_A\rightarrow = K + AB\tau$

How does one choose $\tau$? It’s determined by the method you use, and it’s usually $\sim 1$ ps.

It generally needs to be greater than the relaxation time.

3. Chandler-Bennett Formalism

$x(t)$ is a point in phase space $(r,p)$ along a trajectory $x$ at time $t$

$h_a(x(t)) = 1$ if system is in A, 0 if it’s not in A

$h_b(x(t)) = 1$ if system is in B, 0 if it’s not in B

$k(t) = \langle h_a(x(0))h_b(x(t)) \rangle$

Related to the rate at which system goes to B

$\approx K_A \rightarrow e^{\frac{\text{trxn}}{K}}$

$\tau_r^{-1, xn} = K_{A \rightarrow B} + K_{B \rightarrow A}$

Since system is almost always in A or always in B, $\langle h_a \rangle + \langle h_b \rangle \approx 1$

For barriers $< K_b T$, $k(t)$ reaches a plateau because $e^{\frac{\text{trxn}}{K}} \sim 1$

$K_{A \rightarrow B} = \langle h_a(x(0))h_b(x(t)) \rangle$

$K(t) = \nu(t)P(x(\tau)) = \nu(t)P(L)$ Where L is the length, $P(L)$ is the probability

$v(t) = \langle h_b(x(\tau)) \rangle_{AB}$

$P(L) = e^{-\frac{\Delta G^*}{K}}$

Recall from TST

$K^{TST} = K_b T e^{\frac{\Delta G^*}{K_b T}}$

$K = \kappa \frac{k_b T e^{\frac{\Delta G^*}{K_b T}}}{h}$

If $\Delta G^* \leftrightarrow \Delta G^*_q$

then $\kappa = \frac{h}{k_b T} v(t)$

so, can pick any $q$, and if you calculate $v(t)$, can back out real reaction rate.

Compute $v(t)$ from harvesting TP trajectories

$\langle h_a \rangle_{AB}$ go from A to B

So, need to (in practice) get to a constant slope very quickly