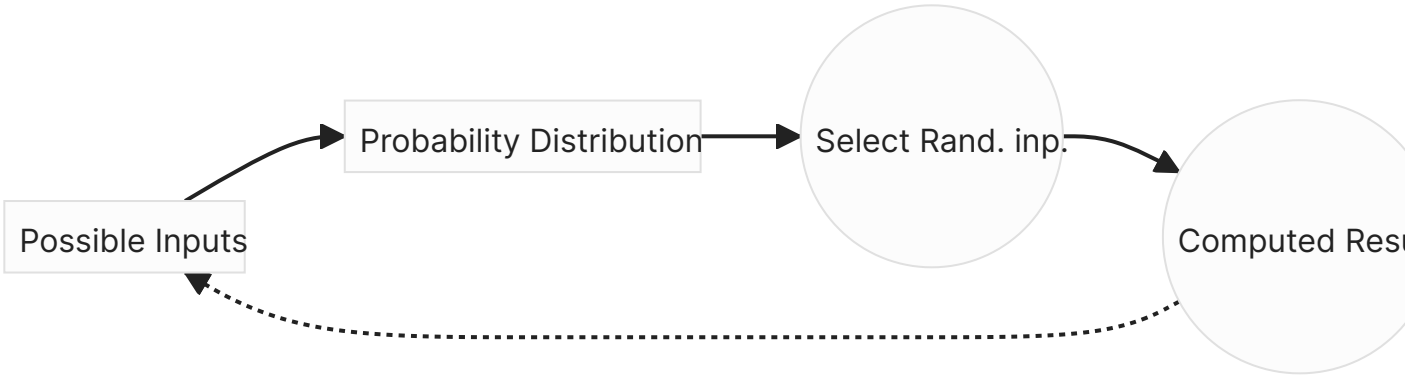
Kinetic Monte Carlo

What is Monte Carlo?

Solves a probem using random input.



Kinetic Monte Carlo

> When we use Monte Carlo to study Kinematics of a system

Time Scale Problems

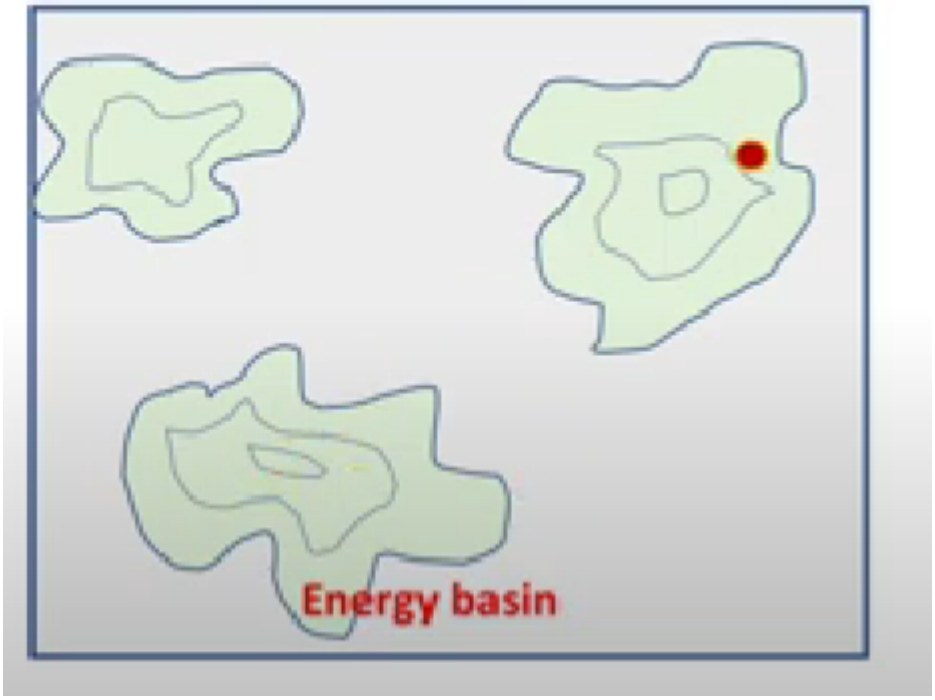
MD approach

- Use differential equations that are modelled classically.
- Do this by choosing appropriate interatomic potentials

Issues with MD apprach

- Chosen Interatomic potentials might not be adequate.
- Boundary conditions
- Quantum dynamical effects

- Time scale might be very slow (instead of the fs to ns range, it might be μs).



KMC solution

- Only consider state-state transition, i.e. from one energy basin to another.
- Ignore vibrational d.o.f.

Issues with KMC

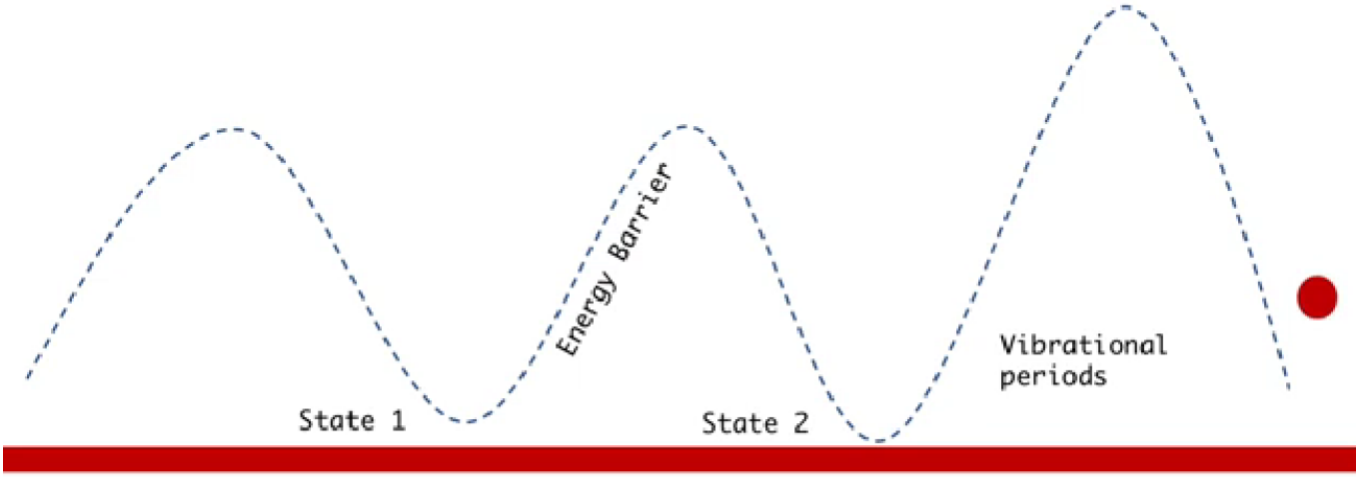
- **Highly rate dependent:** Might lead to the faster process getting a higher probability of occuring as the random event in each run.

Improving KMC solutions

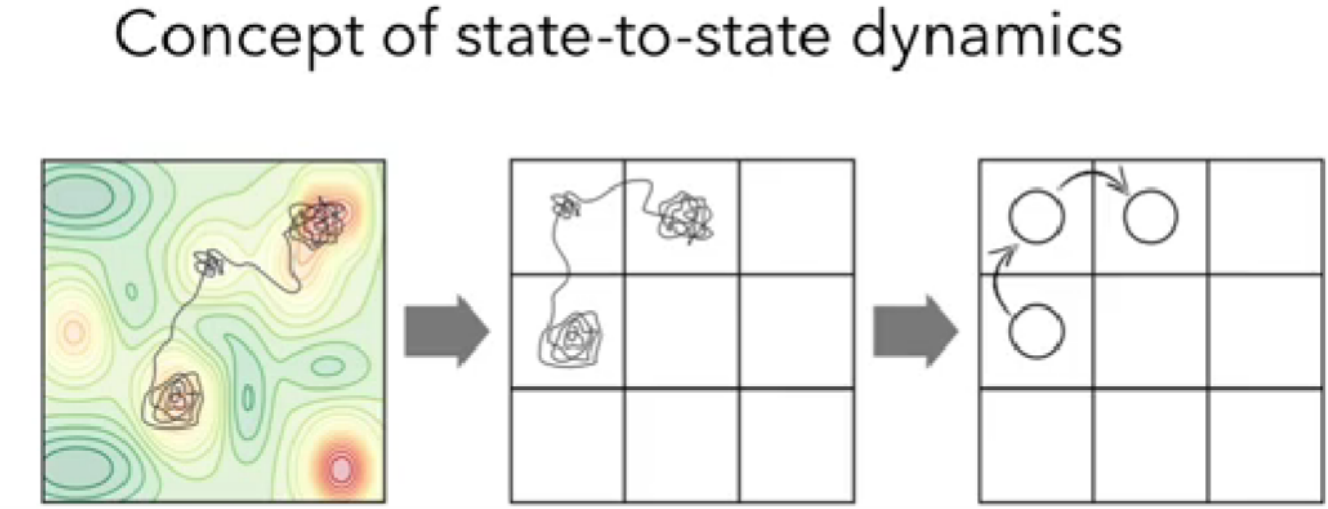
- τ**-Leap method**: Fire off multiple processes at once. When time population does not change dramatically.

- **Separation of 'slow' and 'fast' processes**: User has to deparately define time scales.
- Limiting number of executions of the fast process via **Quasi equilibriation**
- Decrease rate of fast process and scale later manually.

Rare events in KMC



The atom will remain in each basin for some time before gaining enough energy to cross the barrier, such an event of crossing the barrier is called a `rare event`.



Thus, the system goes from a state i, and tries to get to the

bottom of the energy basin of that state until it jumps to another state. Since the system spends a long time in vibrational mode, it has no memory of how it got there.

Markov Chains and KMC

> Future events are independent of the preceding events of history.

Thus, the probability of transition of system from state i to any other state is dependent upon the rate constants for these events.

$$p_{i \to j} \propto e^{\frac{-E_b}{k_{ij} \cdot T}}$$

When the system is in state i, we will have an array of choices of the final state to go in : $\{p_{ij_1}, p_{ij_2}, p_{ij_3} \ldots\}$.
Thus, when a random state is picked, a higher probability event is more likely to be picked.

Absorption-Desorption using KMC

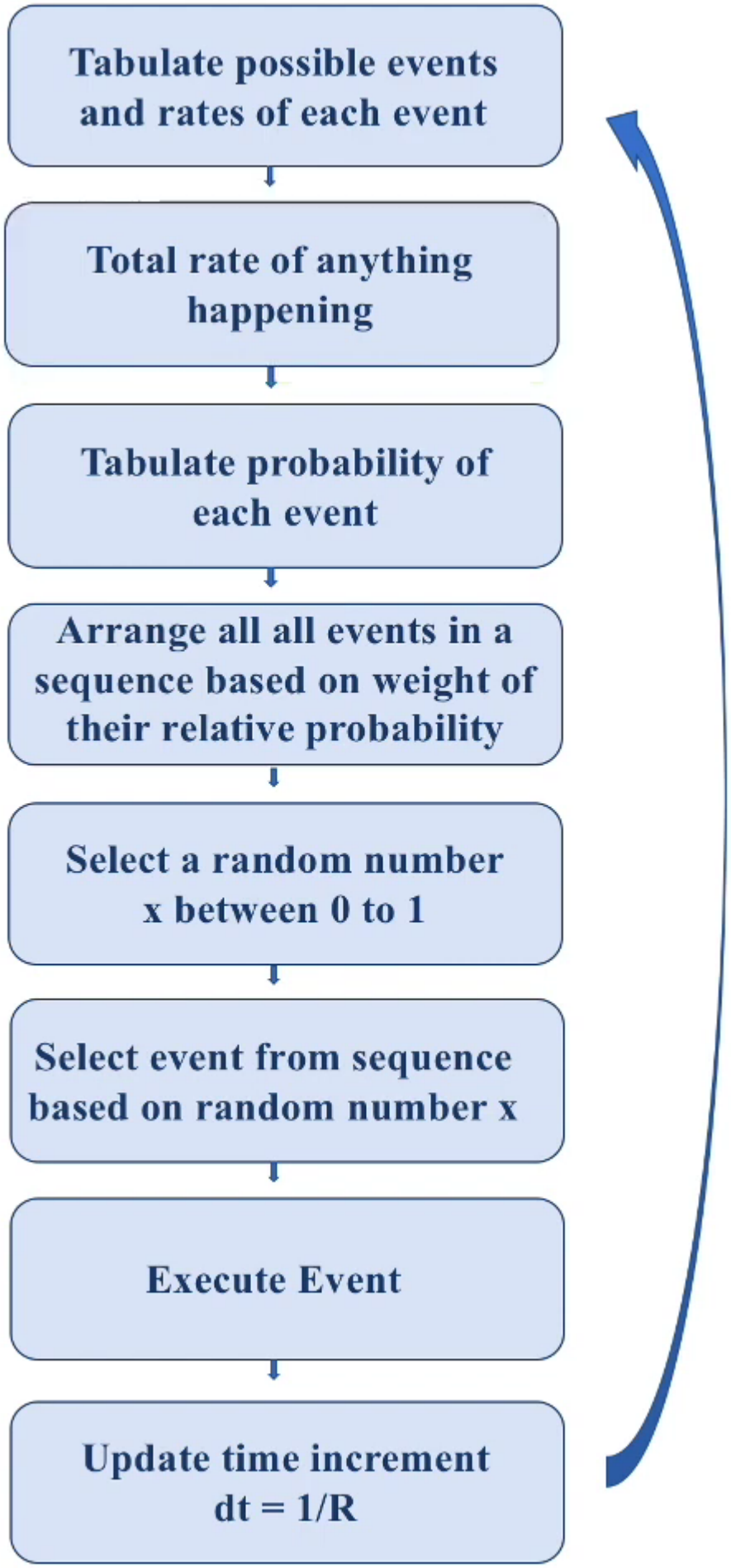
> Langmuir adsorption assumes that the adsorbate is an ideal gas

Assumptions

- Adsorption $\longleftrightarrow$ Desorption is reversible.
- All sites are equal.

- Adsorbed atoms are immobile. (Diffusion)
- No interaction between two adjacent adsorbed atoms.
- Monolayer coverage.

KMC Algorithm


Tabulate possible events and rates of each event
Total rate of anything happening
Tabulate probability of each event
Arrange all all events in a sequence based on weight of their relative probability
Select a random number x between 0 to 1
Select event from sequence based on random number x
Execute Event
Update time increment dt = 1/R

Model Graphene Lattice in Kinetic Monte Carlo simulation

> To use KMC for modelling Graphene Lattice