Dynamic Monte Carlo as a Markov process

In Markov-chain theory the emphasis is on P which determines the equilibrium distribution π.
In our Monte Carlo applications we work in the opposite way.

The equilibrium distribution π is known: π should be identified with the statistical-mechanics measure.
In this setting the state point x is, for instance, the set of the coordinates of the particles $x = \{\mathbf{r}_1, \ldots \mathbf{r}_N\}$. In the canonical ensemble, $\pi_x = \exp(-\beta U)/Z$

Then, we devise a transition matrix P such that π satisfies the stationarity condition for P.

The uniqueness theorem guarantees that π is the equilibrium distribution of the process.

Ensemble averages can be computed as averages over the Markov process (ergodic theorem).

IMPORTANT: The probability distribution depends on the partition function and we do not know it (as we shall partition functions cannot be computed with MC methods)
However, Z is **NOT** needed to devise the transition matrix P.
The stationarity condition can be written as

$$\sum_x \pi_x P_{xy} = \pi_y \Rightarrow \sum_x \frac{e^{-\beta H(x)}}{Z} P_{xy} = \frac{e^{-\beta H(y)}}{Z} \Rightarrow \sum_x e^{-\beta H(x)} P_{xy} = e^{-\beta H(y)}.$$

The partition function Z drops out!

Detailed balance

There is an infinite number of matrices P that satisfy the stationarity condition. It is often easier to look for a matrix P which satisfies the stronger condition

$$\pi_x P_{xy} = \pi_y P_{yx}$$

for any x, y. This condition is called **reversibility condition** or **detailed-balance condition**.

Let us prove that if P is reversible, then it satisfies the stationarity condition. Summing over x the detailed-balance condition and using the fact that $\sum_x P_{yx} = 1$ we have

$$\sum_x \pi_x P_{xy} = \sum_x \pi_y P_{yx} \qquad \Rightarrow \qquad \sum_x \pi_x P_{xy} = \pi_y .$$