Let us consider a Markov process whose transition matrix is $P(x, y)$ (i.e. the matrix that identifies the probability to move from state x to state y). Initially let us consider discrete cases only.
Let us denote by $\pi(x)$ a generical probability distribution function (i.e. a function that tells the probability of finding the system in the state x).
If we initially prepare the system in a state x_0 our initial distibution is

$$\pi^0(x) = \begin{cases} 1 & \text{if } x = x_0 \\ 0 & \text{otherwise} \end{cases}$$

If we think of π^0 as a row vector that gives a probability of beeing in the state x_i at the step 0 then it would be something like

$$\pi^0 = (0, 0, 0, \dots, 1, \dots, 0, 0, 0)$$

We can then let the probability distibution evolve by multiplying it to the right by the transition matrix. We then expect to find a new probability distribution given by the row-matrix product

$$\pi^1 = \pi^0 P = \sum_i \pi_i^0 P_{ij} = \sum_i \pi^0(x_i) P(x_i, y_j)$$

After N steps the probability distribution becomes

$$\pi^N = \pi^{N-1} P = \pi^{N-2} P^2 = \pi^0 P^N$$

If after some N_0 one has that

$$\pi^{N+1} = \pi^N P \qquad \forall N > N_0$$

the probability distribution function is said to be stationary. This means that the probability of being in a state x has become independent of the step number but depends only on the state, hence we can call this distribution $\pi(x)$. The last equation can be rewritten by dropping the step number as

$$\pi = \pi P$$

or

$$\pi_j = \sum_i \pi_i P_{ij} \tag{1}$$

The existence of such distibution can be guaranteed by the following two sufficient (but not necessary) conditions

1. Detailed balance holds (which is equivalent to ask for reversibility of the chain), that is

$$\pi(x_i) P(x_i, x_j) = \pi(x_j) P(x_j, x_i) \qquad \forall x_i x_j \tag{2}$$

2. The stationary distribution must be unique. This is guaranteed by ergodicity (or irreducibility which means that the chain does not "lose" pieces and it is always possibile to reach every state in a finite number of steps) and aperiodicity (the chain does not have a regular pattern, this is the generalisation of the -1 eigenvalue case for which the period is 1).

The reason why detailed balance is a sufficient condition can be seen by taking the sum over i of equation 2

$$\begin{gathered} \sum_i \pi_i P_{ij} = \sum_i \pi_j P_{ji} \\ (\pi P)_j = \pi_j \\ \pi P = \pi \end{gathered}$$

where from line 1 to 2 I used the fact that the sum extended to all x_j of probabilities to move from x_i to x_j is 1 (we have to end up somewhere).
Now suppose that one wants to extract some samples from a distribution $\pi(x)$. One way to do so is to use the Metropolis-Hasting algorithm. The algorithm simply consists in constructing a transition matrix of the form $P(x_i, x_j) = g(x_i, x_j) A(x_i, x_j)$ where $g(x_i, x_j)$ is another transition matrix that can be arbitrarilly chosen (or cleverly chosen, depends on the point of view) and $A(x_i, x_j)$ is defined as

$$A(x_i, x_j) = min\left(1, \frac{\pi(x_j) g(x_j, x_i)}{\pi(x_i) g(x_i, x_j)}\right)$$

Why this procedure leads to a stationary distribution that is exactly π? Practically one assumes condition 2 valid :) For condition 1, we have to prove that

$$\pi(x_i)P(x_i, x_j) = \pi(x_j)P(x_j, x_i)$$

via the given definitions, hence convergence to π is guaranteed by what previously said.
We first note by looking at the definition of A that if

$$\pi(x_i)g(x_i, x_j) < \pi(x_j)g(x_j, x_i)$$

then $A(x_i, x_j) = 1$ and $A(x_j, x_i) < 1$.
Instead, if

$$\pi(x_i)g(x_i, x_j) > \pi(x_j)g(x_j, x_i)$$

then $A(x_i, x_j) < 1$ and $A(x_j, x_i) = 1$ or, in other words, either $A(x_i, x_j)$ or $A(x_j, x_i)$ are different from one. This allows us to write

$$\frac{A(x_i, x_j)}{A(x_j, x_i)} = \frac{\pi(x_j)g(x_j, x_i)}{\pi(x_i)g(x_i, x_j)}$$

which is always true. Rearranging therms

$$\frac{\pi(x_i)}{\pi(x_j)} = \frac{A(x_j, x_i)g(x_j, x_i)}{A(x_i, x_j)g(x_i, x_j)} = \frac{P(x_j, x_i)}{P(x_i, x_j)}$$

where I used th definition of P, and finally

$$\pi(x_i)P(x_i, x_j) = \pi(x_j) = P(x_j, x_i)$$

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