Monte Carlo simulations

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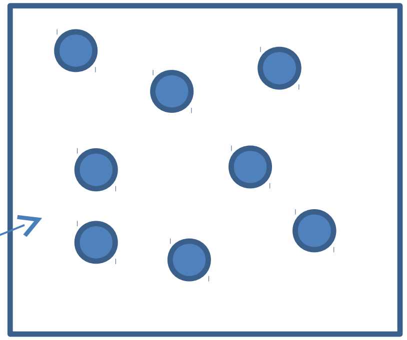
Thermodynamic averages

From statistical mechanics

$$\langle A \rangle = \frac{\int d\mathbf{p}^N d\mathbf{r}^N A(\mathbf{p}^N, \mathbf{r}^N) \exp(-\beta H(\mathbf{p}^N, \mathbf{r}^N))}{\int d\mathbf{p}^N d\mathbf{r}^N \exp(-\beta H(\mathbf{p}^N, \mathbf{r}^N))}$$

2dN dimensional integral

NVT ensemble



Thermodynamic averages

Suppose the property depends only on the position of the particles

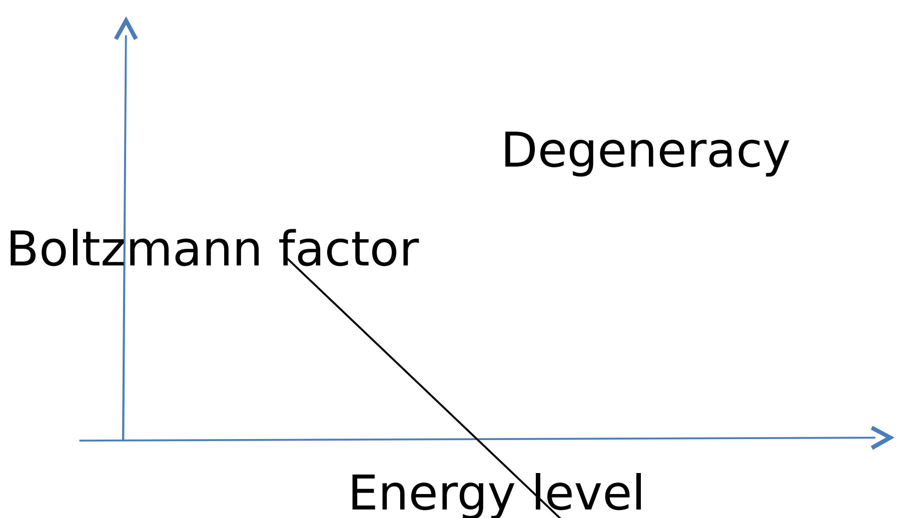
$$\langle A \rangle = \frac{\int d\mathbf{r}^N A(\mathbf{r}^N) \exp(-\beta U(\mathbf{r}^N))}{\int d\mathbf{r}^N \exp(-\beta U(\mathbf{r}^N))}$$

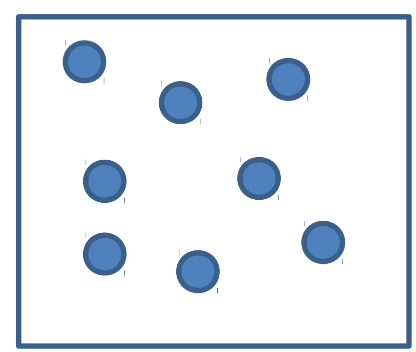
dN dimensional integral

Standard integration techniques - prohibitively expensive

Thermodynamic averages

$$\langle A \rangle = \frac{\int d\mathbf{r}^N A(\mathbf{r}^N)\exp(-\beta U(\mathbf{r}^N))}{\int d\mathbf{r}^N \exp(-\beta U(\mathbf{r}^N))} = \frac{\sum_i A(\zeta_i)\exp(-\beta U(\zeta_i))}{\sum_i \exp(-\beta U(\zeta_i))}$$





Evaluating thermodynamic averages

Suppose the property depends only on the position of the particles

$$\langle A \rangle = \frac{\int d\mathbf{r}^N A(\mathbf{r}^N) \exp(-\beta U(\mathbf{r}^N))}{\int d\mathbf{r}^N \exp(-\beta U(\mathbf{r}^N))}$$

Monte Carlo can be used to sample the most probable states of the system

What is Monte Carlo?

A class of techniques that employ random numbers

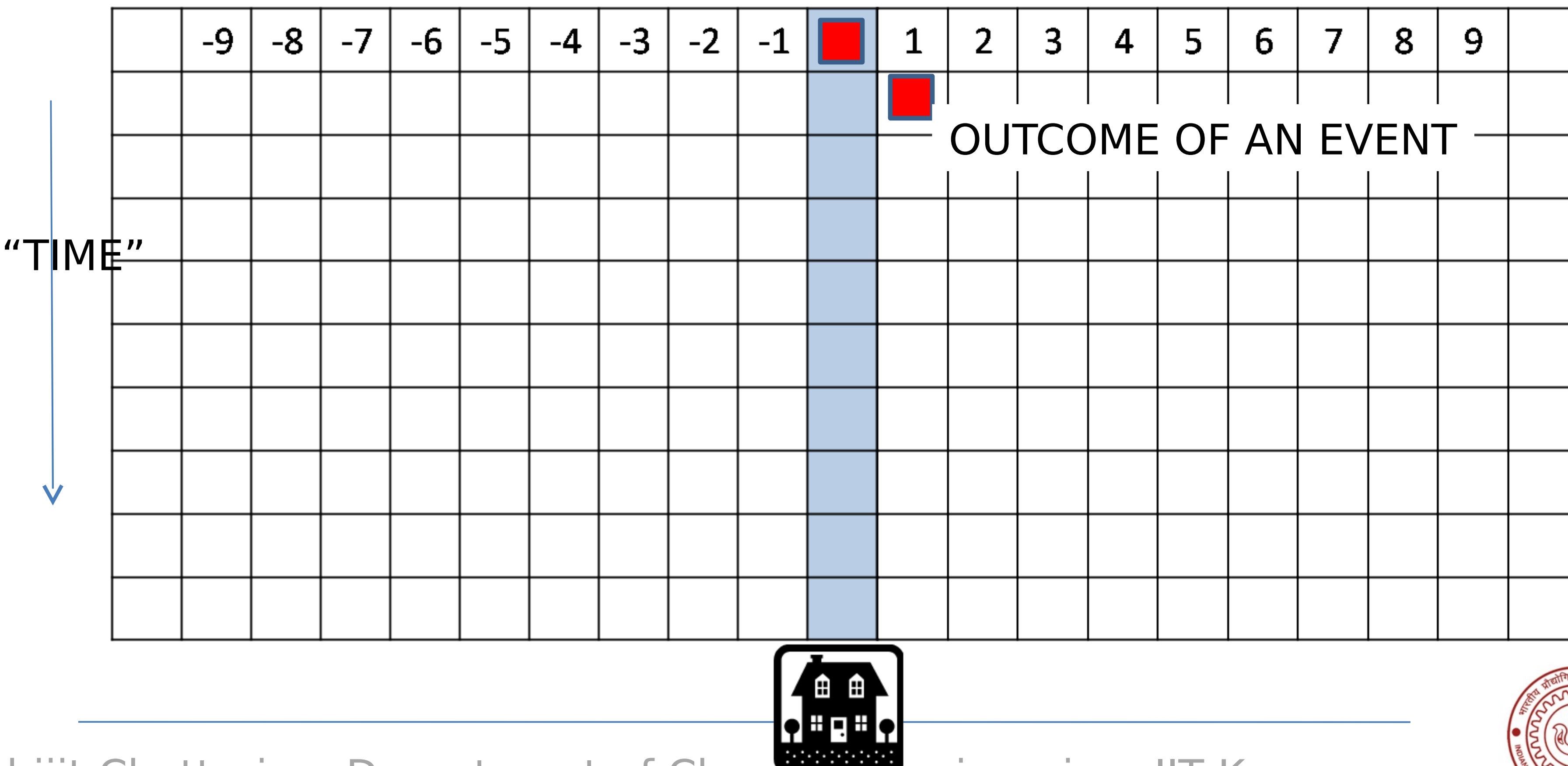
Can be used to solve deterministic problems

Convert deterministic problem to probabilistic analog

Perform stochastic sampling experiment

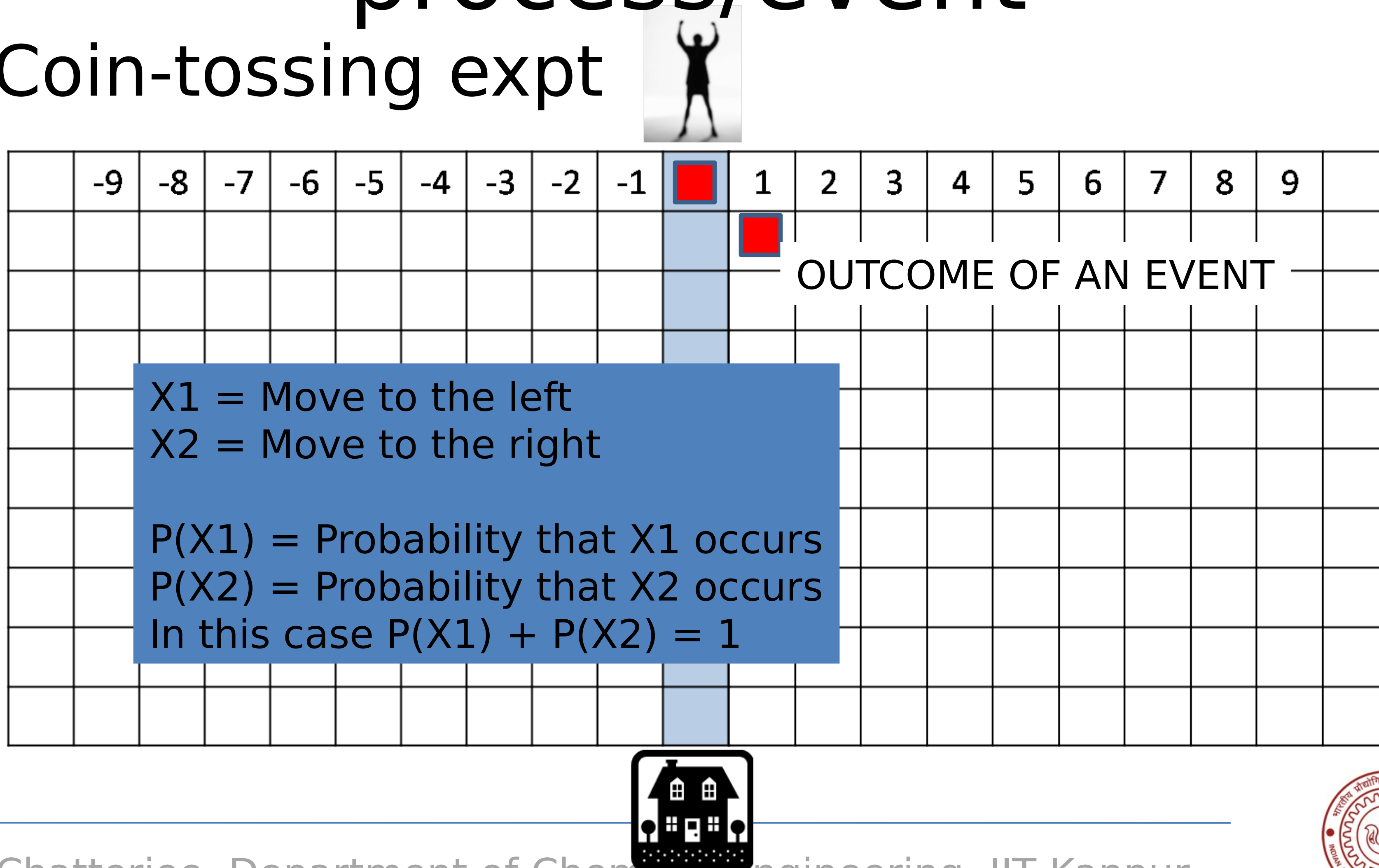
Concept of a random process/event

Coin-tossing expt



Concept of a random process/event

Coin-tossing expt



X1 = Move to the left
X2 = Move to the right

P(X1) = Probability that X1 occurs
P(X2) = Probability that X2 occurs
In this case P(X1) + P(X2) = 1

Probability of an event

Probability that the discrete random variable X assumes the value xj is denoted by p(j)

Probability mass function

$$P(X = x_j) = \lim_{n \to \infty} \frac{n_j}{n} = P(j)$$

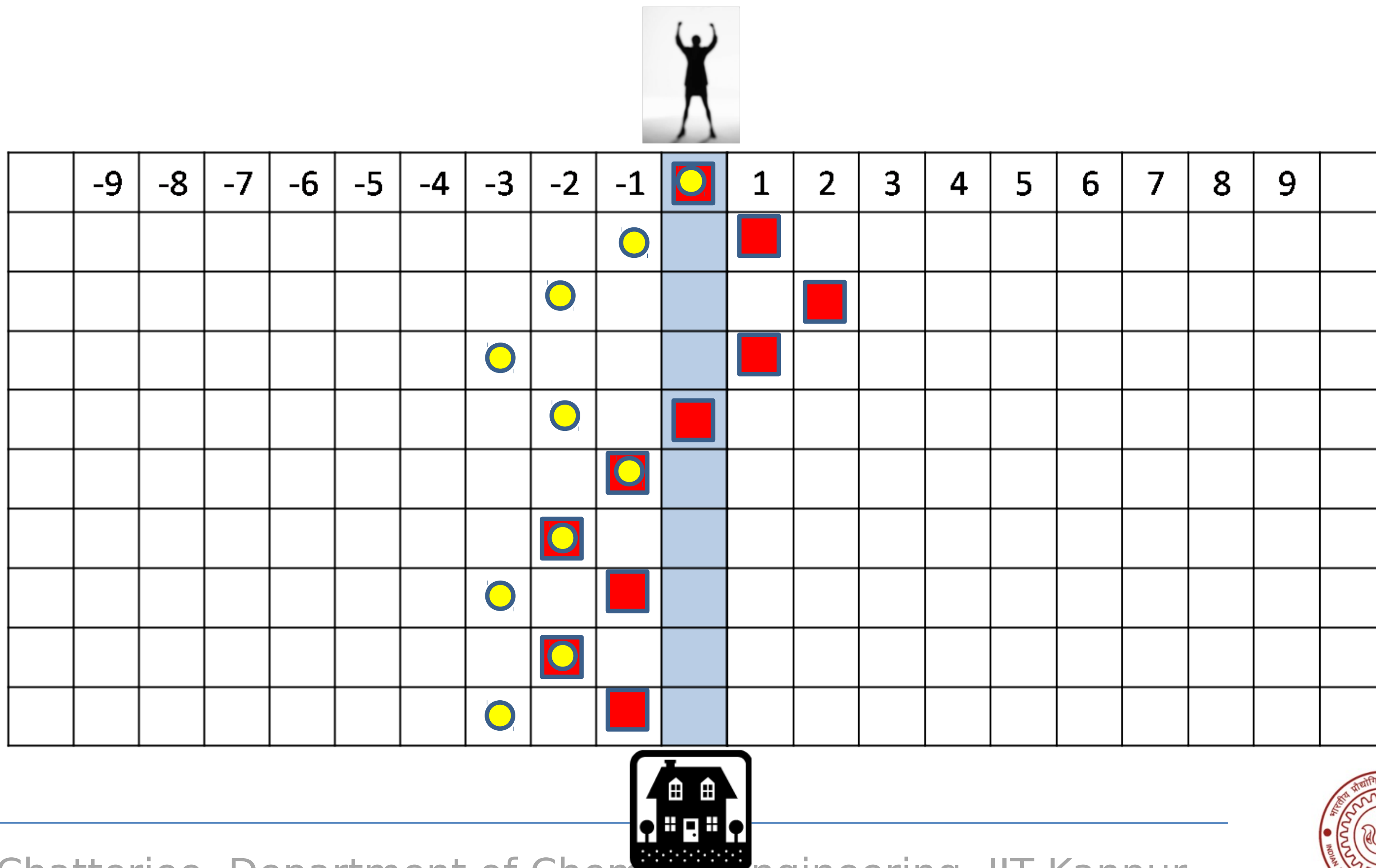
$$\sum_j P(j) = 1$$

Similarly, for continuous random variable X the probability density function is given by

$$p(x)dx = \Pr ob\{x < X \le x + dx\}$$

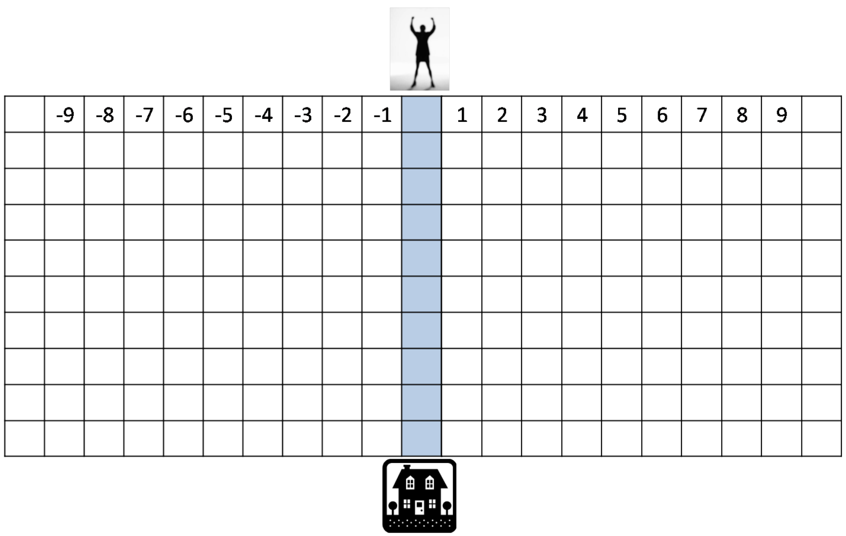
$$\int_{volume} p(x)dx = 1$$

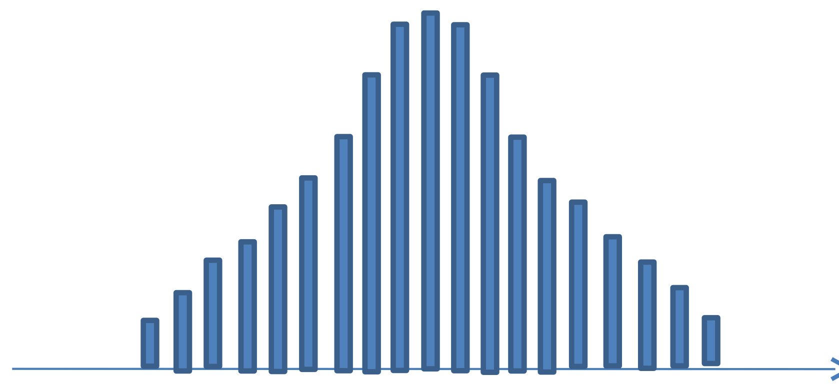
Random walk



Random walk

Probability of each outcome after 10 steps





Binomial distribution

$$p(m, N) = \frac{N!}{\left(\frac{N+m}{2}\right)!\left(\frac{N-m}{2}\right)!}\left(\frac{1}{2}\right)^N$$

Standard distributions available

Uniform distribution

Binomial distribution

Poisson distribution

Normal distribution

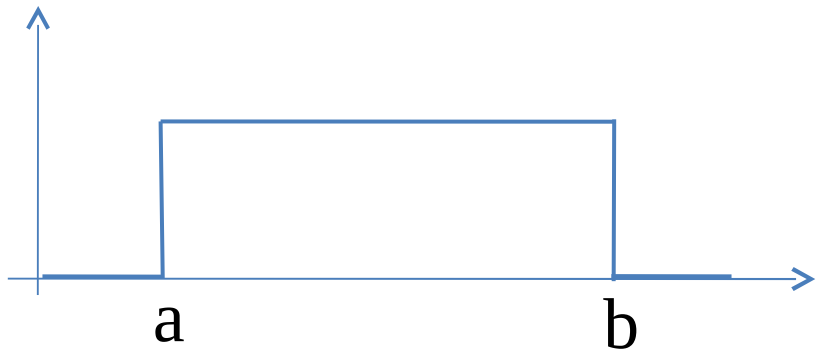
…

Example of sources: C, Fortran, MATLAB, Numerical recipes, …

Uniform distribution

Continuous random variable

$$p(x)\Delta x = \frac{\Delta x}{b-a}$$



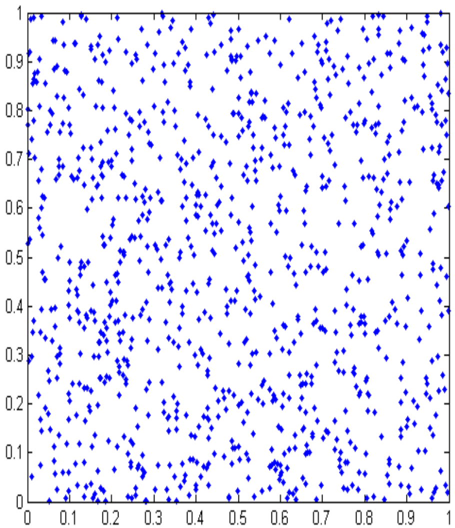
Uniform random numbers (URN) are built into C and Fortran languages

$$0 \le x < 1$$

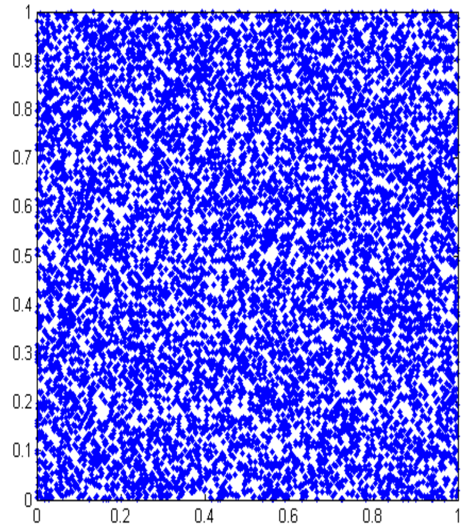
In Fortran

```
CALL random_number(h)    h=0.898456
CALL random_number(h)    h=0.125385
```

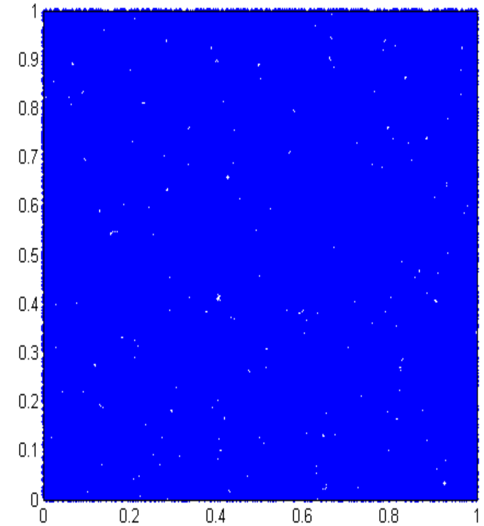
URNs for two dimensions



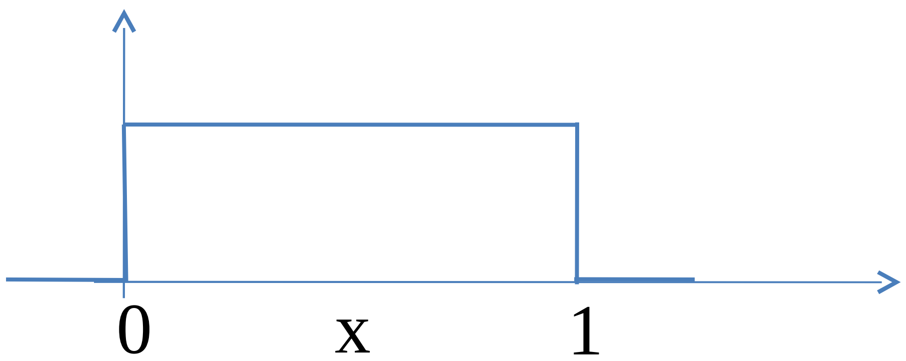
1000 URN

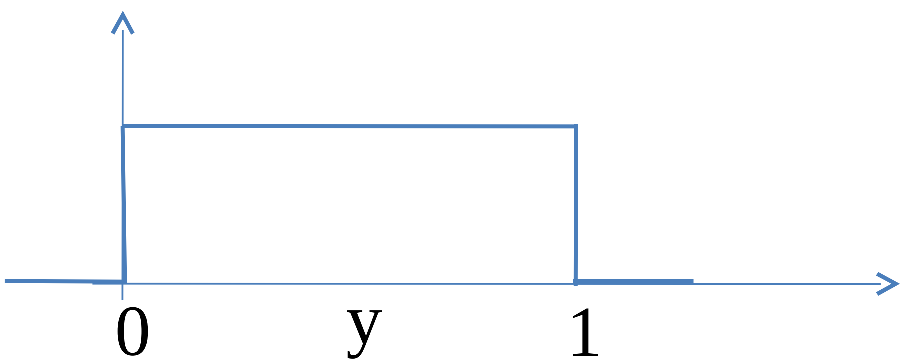


10000 URN



20000 URN

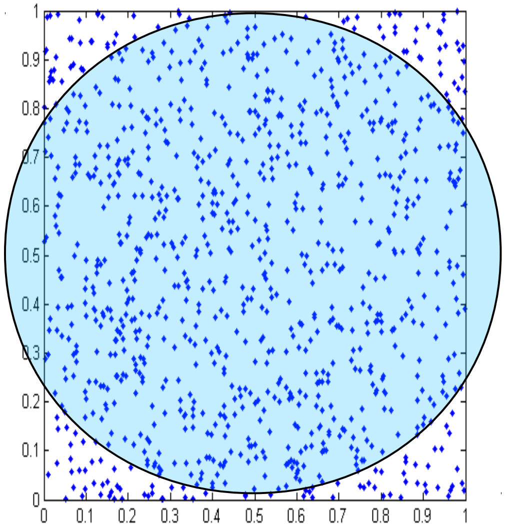




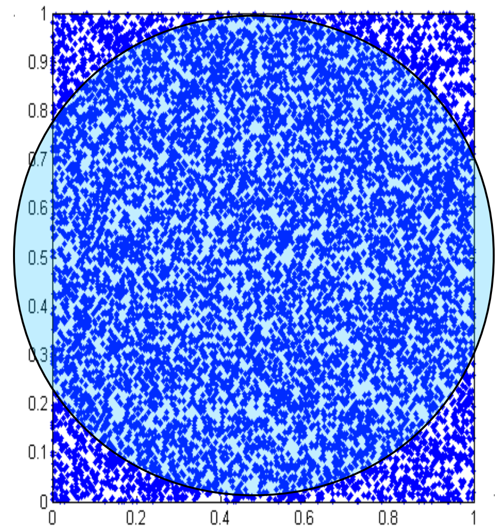
Application of URN: Example 1

Example: Calculation of value of pi

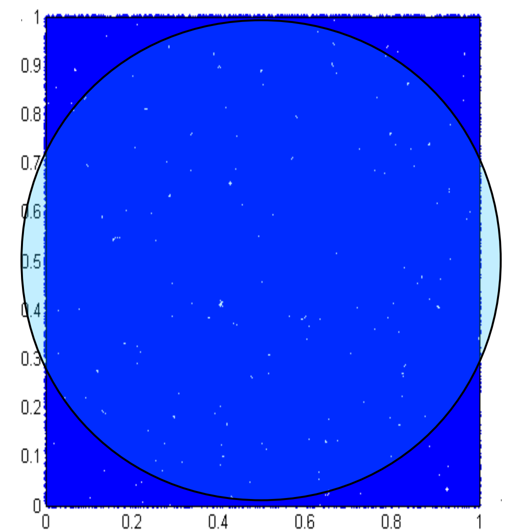
What is the fraction of dots lying in the



1000 URN



10000 URN

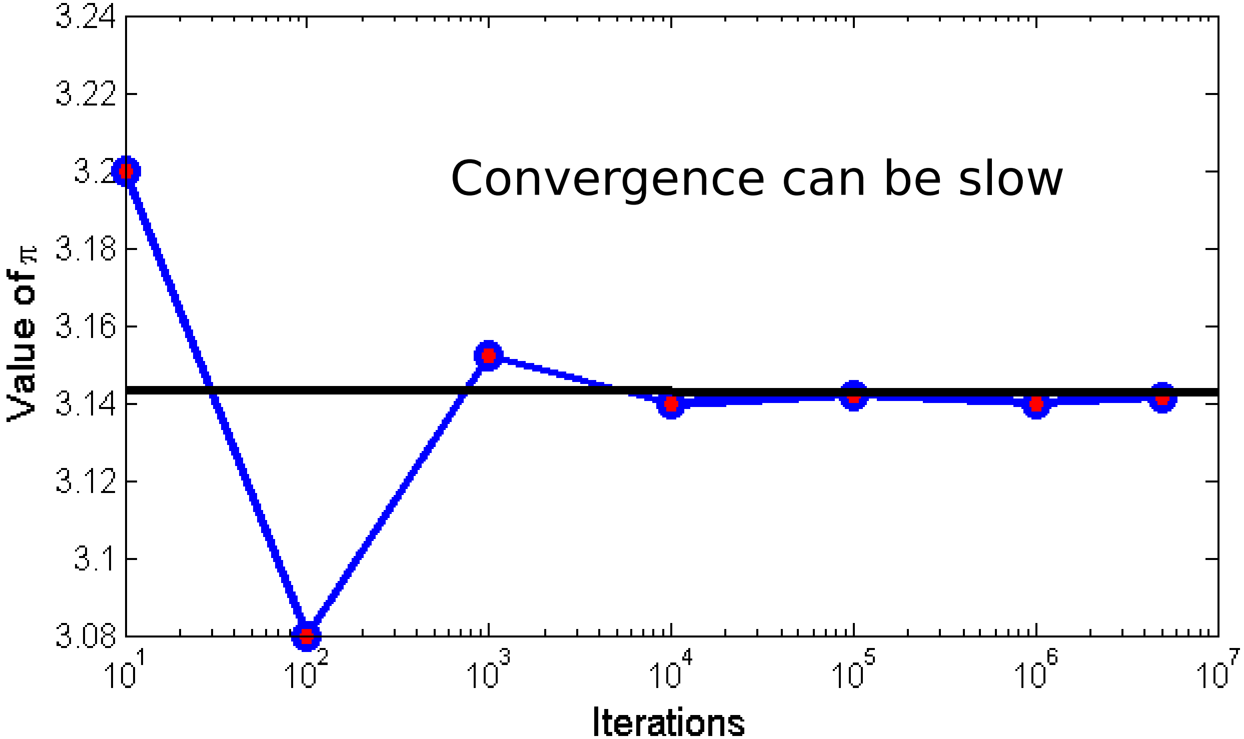


20000 URN

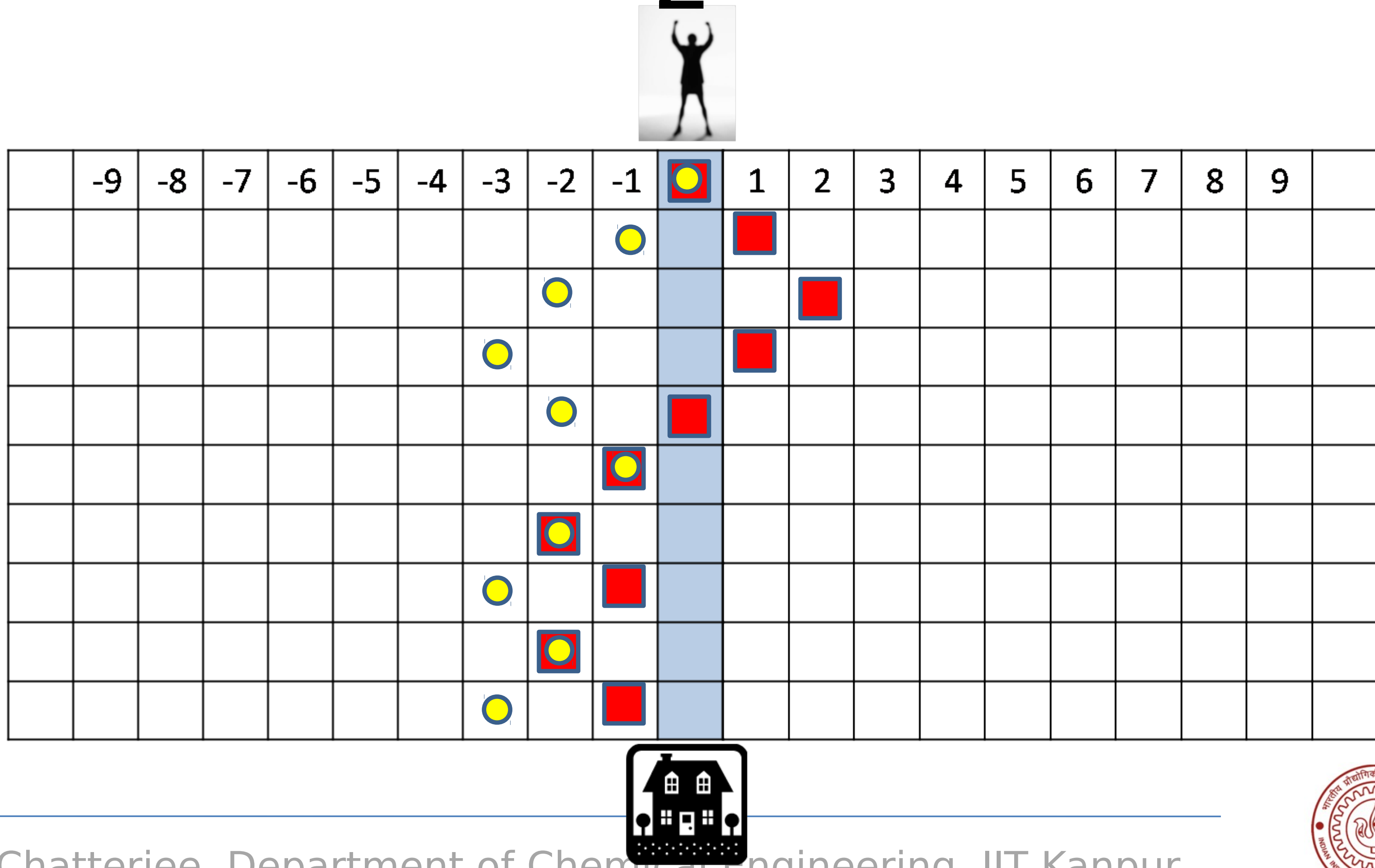
Application of URN: Example 1

Example: Calculation of value of pi

What is the fraction of dots lying in the circl



Application of URN: Example 2



Generating a random walk using a computer

Let perform the random walk, but now on a computer

ALGORITHM FOR THE "COIN-TOSSING EXPERIMENT"

1. Obtain the initial condition
2. Generate a uniform random number and store the value in p
3. If $p<0.5$ then jump to the left, otherwise jump to the right
4. If total number of jumps is equal to the desired number of jumps then stop. Otherwise go to step 2

Application of URN: Simple integration

Simple integration based on sampling

Find the average "height" of the function

$$\xi = (b-a)x$$

↑ URN

$$\int_a^b f(\xi)d\xi = \langle f(\xi) \rangle (b-a)$$

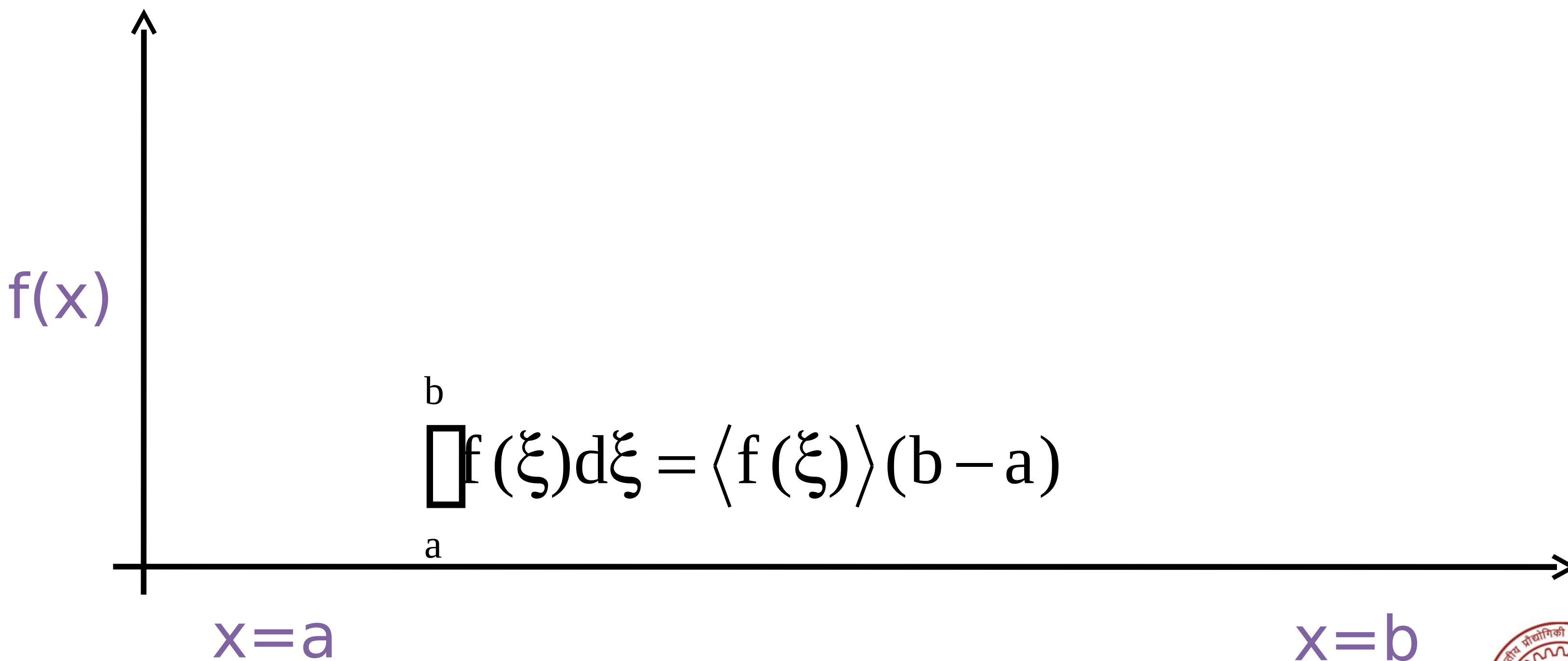
f(x)

x=a

x=b

Application of URN: Simple integration

Can this be used for obtaining thermodynamic averages?



$$\int_a^b f(\xi)\,d\xi = \langle f(\xi)\rangle (b-a)$$

Normal/Gaussian distribution

μ ισ τηε μεαν ανδ μ ισ τηε στανδαρδ δεϖιατιον

$$P(x;\mu,\sigma)=\frac{1}{\sqrt{2\pi\sigma}}\exp\left[\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^{2}\right]$$

Importance sampling

Sample only the terms that are important to the integral

$$\int_a^b f(x)\,dx = \int_a^b \left(\frac{f(x)}{p(x)}\right) p(x)\,dx$$

In our case

$$\langle A \rangle = \int d\mathbf{r}^N \left(\frac{A(\mathbf{r}^N)\,\rho_{NVT}(\mathbf{r}^N)}{p(\mathbf{r}^N)}\right) p(\mathbf{r}^N)$$

Multivariate (joint) distributions

For continuous random variables, the joint probability density function is given by

$$p(x_1, x_2, \dots, x_N)dx_1 dx_2 \dots dx_N =$$

$$\Pr ob\{x_1 < X_1 \leq x_1 + dx_1, \dots, x_N < X_N \leq x_N + dx_N\}$$

For independent RV

$$p(x_1, x_2, \dots, x_N) = p(x_1) \dots p(x_N)$$

Marginal probability density function

$$p(x_1)dx_1 = \Pr ob\{x_1 < X_1 \leq x_1 + dx_1\}$$

$$= dx_1 \int p(x_1, x_2, \dots, x_N)dx_2 \dots dx_N$$

Markov process

Generate a random walk $\mathbf{r}_0, \mathbf{r}_1, .., \mathbf{r}_t, ...$

In terms of conditional probability

$$\mathrm{P}(\mathbf{r}_n) = \mathrm{P}(\mathbf{r}_n \mid \mathbf{r}_0, \mathbf{r}_1, .., \mathbf{r}_{n-1})\mathrm{P}(\mathbf{r}_{n-1})$$

Markov process

$$\mathrm{P}(\mathbf{r}_n) = \mathrm{P}(\mathbf{r}_n \mid \mathbf{r}_{n-1})\mathrm{P}(\mathbf{r}_{n-1})$$

Conditional probabilities

For two RVs,

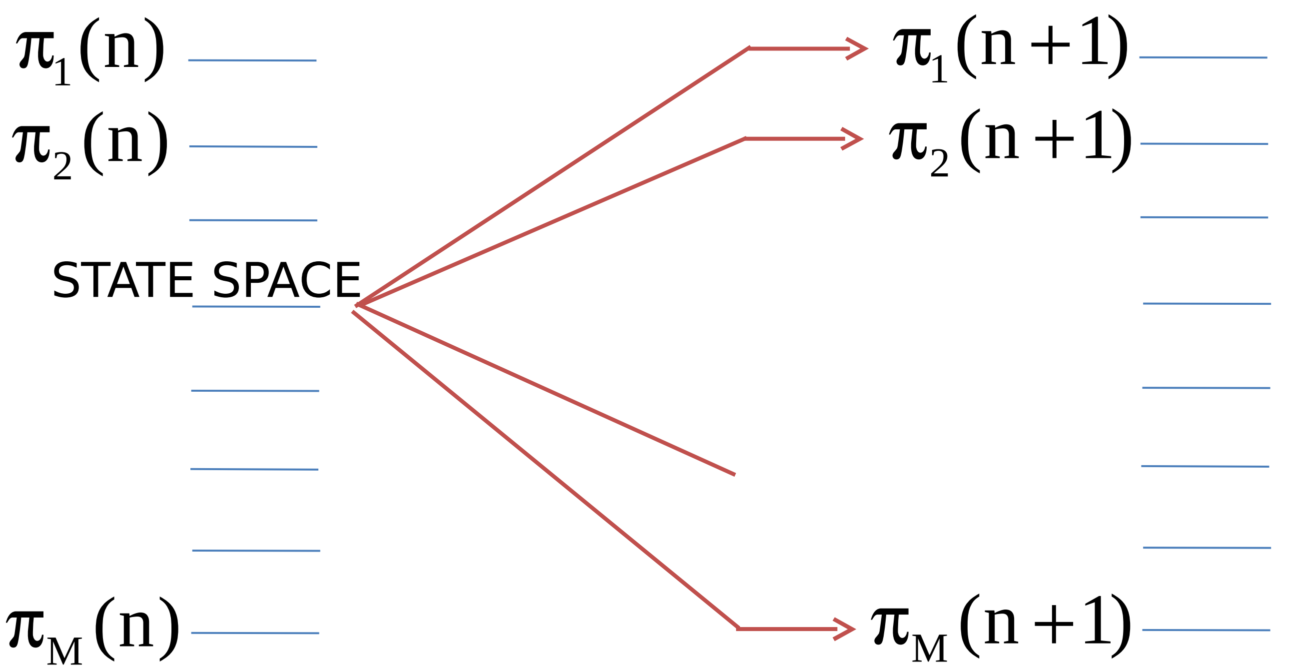
$$p(x_1 \mid x_2)dx_1 = \Pr ob\{x_1 < X_1 \leq x_1 + dx_1 \ \text{ if } \ X_2 = x_2\}$$

From Bayes' rule one obtains

$$p(x_1, x_2) = p(x_1 \mid x_2)p(x_2) = p(x_2 \mid x_1)p(x_1)$$

Markov process

Lets look at simple example with discrete number of states



Transition probability matrix

For the discrete M-state example

$$\pi_j(1) = \sum_i p_{ij}(1)\pi_i(0) = \sum_i p_{ij}\pi_i(0)$$

Similarly,

$$\pi_j(2) = \sum_i p_{ij}(2)\pi_i(0) = \sum_i \left[\sum_k p_{ik}p_{kj}\right]\pi_i(0)$$

In general,

$$\boldsymbol{\pi}(n) = \boldsymbol{\pi}(0).\mathbf{P}^n$$

Detailed balance

We obtain

$$\pi_j(n+1) - \pi_j(n) = \sum_{\substack{i \\ i \ne j}} p_{ij}\pi_i(n) - \sum_{\substack{i \\ i \ne j}} p_{ji}\pi_j(n)$$

At "equilibrium" the pdf is time-invariant

$$\pi_j(n+1) - \pi_j(n) = 0 = \sum_{\substack{i \\ i \ne j}} p_{ij}\pi_i(n) - \sum_{\substack{i \\ i \ne j}} p_{ji}\pi_j(n)$$

Hence,

$$\sum_{\substack{i \\ i \ne j}} p_{ij}\pi_i(n) = \sum_{\substack{i \\ i \ne j}} p_{ji}\pi_i(n)$$

$$p_{ij}\pi_i = p_{ji}\pi_j$$

Metropolis algorithm

Generate a random walk the underlying probability distribution

$$p(\mathbf{r}^N) = \frac{\exp(-\beta U(\mathbf{r}^N))}{Q_{NVT}}$$

The detailed balance condition requires

$$\pi(\text{old})p(\text{old} \rightarrow \text{new}) = \pi(\text{new})p(\text{new} \rightarrow \text{old})$$

$$\frac{p(\text{old} \rightarrow \text{new})}{p(\text{new} \rightarrow \text{old})} = \exp\left\{-\beta(U_{new} - U_{old})\right\}$$

Metropolis algorithm

$$\pi(\text{old})\,p(\text{old} \rightarrow \text{new}) = \pi(\text{new})\,p(\text{new} \rightarrow \text{old})$$

$$\frac{p(\text{old} \rightarrow \text{new})}{p(\text{new} \rightarrow \text{old})} = \exp\left\{-\beta(U_{new} - U_{old})\right\}$$

$$p(i \rightarrow j) = \begin{cases} \exp\left\{-\beta(U_i - U_j)\right\}, & \rho_i < \rho_j \\ 1, & \rho_i \geq \rho_j \end{cases}$$

Others transition probabilities can be devised, e.g., Baker sampling

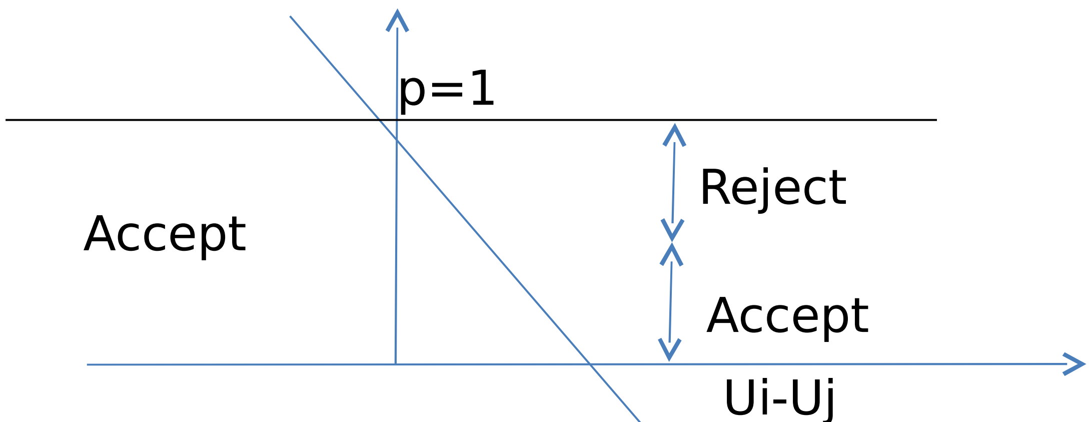
Baker sampling

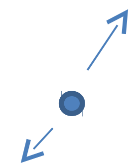
$$p(m \rightarrow n) = \frac{\alpha_{mn}\pi_n}{\pi_n + \pi_m}$$

$$p(m \rightarrow m) = 1 - \sum_{n \neq m} p(m \rightarrow n)$$

Metropolis algorithm

$$p(i \to j) = \begin{cases} \exp\{-\beta(U_i - U_j)\}, & \rho_i < \rho_j \\ 1, & \rho_i \geq \rho_j \end{cases}$$





Metropolis algorithm

Pseudocode

Step 1. Obtain initial condition, find U_{old}

Step 2. Generate a new configuration

Step 3. Evaluate $p = \min(1, \exp(-\beta(U_{new} - U_{old}))$

Step 4. Generate a URN ξ

Step 5. Accept the new configuration provided $\xi < p$

Step 6. If the new configuration is accepted, $U_{old} \leftarrow U_{new}$

Step 7. Go to step 2