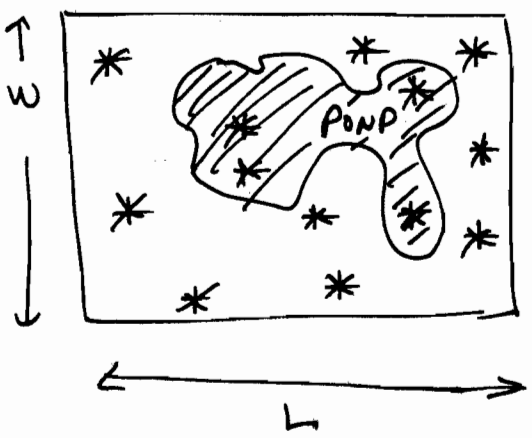
History

von Neumann, Ulam + Metropolis (1947) → Studies of diffusion of neutrons in fissionable matter. Coined the term "Monte Carlo".

Metropolis, Rosenbluth[2], Teller[2] (1953) → first MC simulation for equilibrium stat. mech. properties.

Monte Carlo Integration

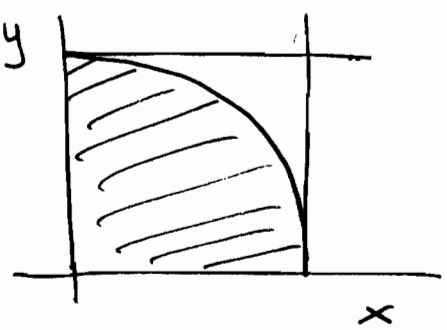


Consider a pond of arbitrary shape. Possible way: throw rocks at random, in area bounded by W×L rectangle

$$\text{Area of pond} = W \times L \times \frac{\text{hits in pond}}{\text{total hits}}$$

Finding an area is an integration problem, so that "Monte Carlo" is a way to perform multidimensional integrals.

E.g.



Find area of quarter circle (or value of π) by above method:

After 10^7 trials $\pi \simeq 3.1417$ (4 sig. figures)

The gain in accuracy is only 1 decimal point per 10x in the number of trials.

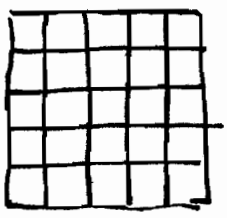
For a system of low dimensionality, analytical or direct numerical methods (e.g. Simpson's rule) work much better than Monte Carlo. E.g. for 10^4 function evaluations (intervals) Simpson's rule integration gives $\pi \simeq 3.141593$ (6 sig. figures)

Multidimensional Integrals

Canonical Partition function for $N \simeq 20$ particles

$$Q = \sum_{\text{pos } 1} \sum_{\text{pos } 2} \sum_{\text{pos } 3} \cdots \sum_{\text{pos } N} \exp(-\beta \mathcal{U})$$

Even if each particle only has 25 possible positions, one needs $25^{20} \simeq 10^{28}$ function evaluations for a direct integration. Moreover, most of the configurations contribute very little to Q:



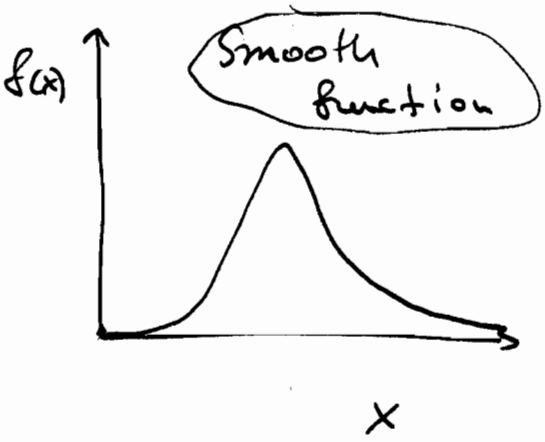
← 25 positions

① ② ③ ④ ⑤ ⑥ ⑦ ⑧ ⑨ ⑩ ... ⑳

Throw 20 particles at random

Assume no two particles can occupy same position in space. What fraction of configurations generated this way are allowable?

Things are better for less dense systems, but most of the systems of interest in stat. mechanics have this problem → function to be integrated has non-zero values only in small regions of phase space



Importance Sampling (also called Metropolis MC)

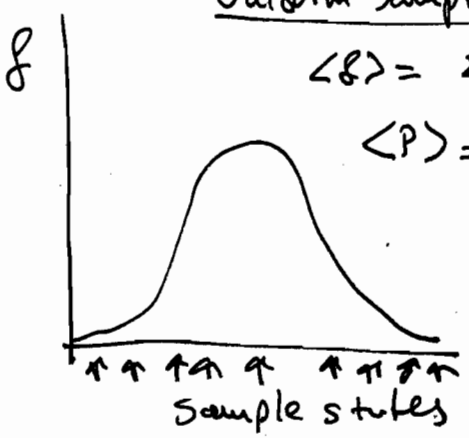
Overcomes sampling problem by generating states with a desired probability distribution, rather than uniformly.

This does not work for getting $\int f(x)dx$, but does work for getting properties that depend on $f(x)$:

Uniform Sampling

$\langle f \rangle = \Sigma f_i / n$

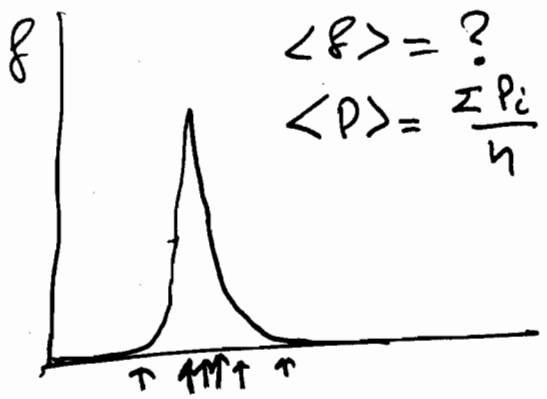
$\langle P \rangle = \frac{\Sigma f_i P_i}{\Sigma f_i}$



Importance Sampling

$\langle f \rangle = ?$

$\langle P \rangle = \frac{\Sigma P_i}{n}$



How do we generate states with the correct probability?

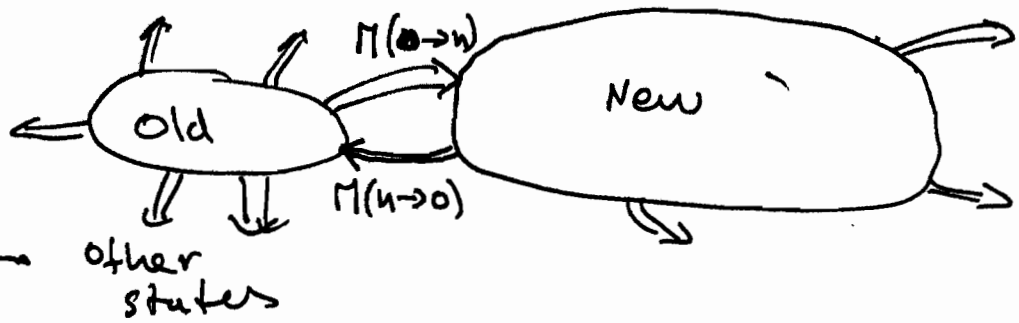
Consider the system of 5 particles in 10 positions - the number of possible states (for distinguishable particles) is $10^5 = 100{,}000$ states

Now consider two configurations Old (o) and New (n)

In a thought experiment, we can perform a mc simulation with a number of samples much greater than the number of states (samples $\gg 10^5$). In this simulation, we generate ~~random~~ uniform configurations. In the large sample, there are $N(o)$ and $N(n)$ realizations for the "old" and "New" configurations, with

$$\frac{N(o)}{N(n)} = \frac{\exp(-\beta U(o))}{\exp(-\beta U(n))} = \exp(-\beta \Delta U)$$ [in the NVT ensemble!]

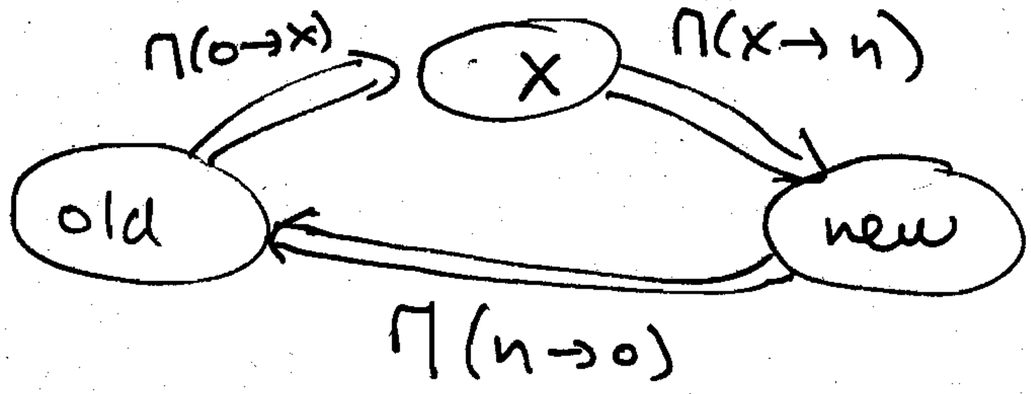
Now consider the case of non-uniform sampling. To ensure that configurations appear with the correct probability, one possible way is to require that in the evolution of configurations,



Detailed Balance Condition: $N(o)\cdot\Pi(o\to n) = N(n)\cdot\Pi(n\to o)$

In other words, we must have that the probabilities of going from $o \to n$ and $n \to o$ must be inversely proportional to the desired probability of finding each state.

Why is this only one possible way? → One could have this:



See Manousiouthakis + Deem, J. Chem. Phys. 110: 2753 (1999) for proof Detailed Balance is not necessary

But, in practice, it is very hard to make sure that this type of simulation (that violates detailed balance) is correct

The probability of going from state o to state n has two parts:

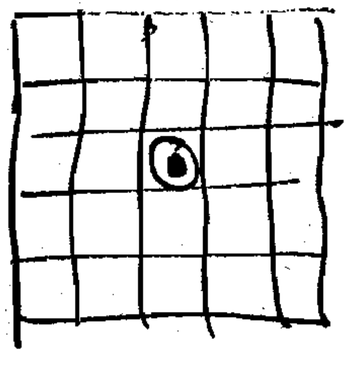
$$\Pi(o\to n) = \alpha(o\to n) \times \text{accept}(o\to n)$$

↑ probability of selecting State n from state o

↑ to be determined

$\alpha(o\to n)$ contains the rules of the simulation –

e.g.



{ try to move particle to a new position to the left, right, top, or bottom of the old position }

The best choice for $\alpha(o \to n)$ is one that satisfies

<u>microscopic reversibility</u> $\quad \alpha(o \to n) = \alpha(n \to o)$

so that the probability of trying state n from o is the same as the probability of trying o from n.

E.g. <u>attempted move</u> ① select random particle, attempt to move it to the left or top position
↳ violates microscopic reversibility

② select random particle, attempt to move to a randomly selected position → OK

③ select random particle, attempt to move it to a randomly selected <u>unoccupied</u> position → is this ok? [class problem]

Now we can derive the acceptance condition:

$$N(o) \cdot \Pi(o \to n) = N(n) \cdot \Pi(n \to o) \Rightarrow$$

$$N(o) \cdot \alpha(o \to n) \cdot \text{accept}(o \to n) = N(n) \cdot \alpha(n \to o) \cdot \text{accept}(n \to o)$$

$$\Rightarrow \boxed{\frac{\text{acc}(o \to n)}{\text{acc}(n \to o)} = \frac{N(n)}{N(o)} = \exp\left(-\beta\left[u(n) - u(o)\right]\right)}$$

There are many possibilities for $\text{acc}(o \to n)$ that satisfy this equation – for example:

Metropolis Rule:

$$acc(o \to n) = 1 \quad \text{if } U(n) < U(o)$$

$$acc(o \to n) = \exp(-\beta[U(n) - U(o)]) \quad \text{if } U(n) \geq U(o)$$

Symmetrical (Barker) Rule:

$$acc(o \to n) = \frac{\exp(-\beta U(n))}{\exp(-\beta U(o)) + \exp(-\beta U(n))}$$

Example of appliation of these rules:

Consider a system with exactly 10 states, numbered j:

j	1	2	3	4	5	6	7	8	9	10
$\exp(-\beta U(j))$	1	2	3	4	5	6	7	8	9	10

} probability is equal to index

What is the partition function? (Class Problem)
What is the equilibrium probability of state 1?

Now, let's make an importance sampling simulation.

Transition rule? $\alpha(o \to n) = 1/10$ for any pair of states o and n (including $o = n$)

$\Pi(o \to n)$ Metropolis

$o \downarrow$ / $\to n$	1	2	3	...	10
1	1/10	1/10	1/10	...	1/10
2	1/20	3/20	1/10	...	1/10
3	1/30	2/30	...		1/10
⋮					
10	1/100	2/100	...		11/20

$\Pi(o \to n)$ Barker

$o \downarrow$ / $\to n$	1	2	3	...	10
1	0.252	$\frac{2}{30}$	$\frac{3}{40}$	...	$\frac{10}{110}$
2	1/30	0.371	$\frac{3}{50}$	...	$\frac{10}{120}$
3	1/40				
⋮					
10	1/110		...		0.719

Barker's probability of remaining in the same state is higher than for Metropolis acceptance. In general, convergence from an arbitrary starting state to equilibrium is faster with Metropolis acceptance.

Example of flow of probabilities with the system with 10 states – The starting state is state 3, which we represent as [0 0 1 0 0 0 0 0 0 0]

Metropolis

Trial										
0	0	0	1	0	0	0	0	0	0	0
1	0.033	0.067	0.200	0.100	0.100	0.100	0.100	0.100	0.100	0.100
2	0.024	0.049	0.083	0.089	0.102	0.114	0.124	0.132	0.139	0.145
3	0.02	0.04	0.062	0.079	0.097	0.113	0.128	0.142	0.154	0.165
4	0.019	0.038	0.057	0.075	0.093	0.111	0.128	0.145	0.16	0.174
5	0.018	0.037	0.055	0.074	0.092	0.11	0.128	0.145	0.162	0.178
6	0.018	0.037	0.055	0.073	0.091	0.109	0.128	0.145	0.163	0.18
7	0.018	0.036	0.055	0.073	0.091	0.109	0.127	0.146	0.163	0.181
8	0.018	0.036	0.055	0.073	0.091	0.109	0.127	0.145	0.164	0.182
OO	0.018	0.036	0.055	0.073	0.091	0.109	0.127	0.145	0.164	0.182

Barker

0	0	0	1	0	0	0	0	0	0	0
1	0.025	0.040	0.454	0.057	0.063	0.067	0.070	0.073	0.075	0.077
2	0.025	0.046	0.225	0.075	0.086	0.095	0.103	0.109	0.115	0.12
3	0.023	0.044	0.128	0.079	0.093	0.106	0.118	0.128	0.137	0.145
4	0.021	0.041	0.087	0.078	0.095	0.11	0.124	0.137	0.149	0.16
5	0.019	0.039	0.069	0.077	0.094	0.111	0.127	0.141	0.155	0.168
6	0.019	0.038	0.061	0.075	0.093	0.111	0.128	0.144	0.159	0.173
7	0.019	0.037	0.057	0.074	0.093	0.11	0.128	0.145	0.161	0.176
8	0.018	0.037	0.056	0.074	0.092	0.11	0.128	0.145	0.162	0.178
9	0.018	0.037	0.055	0.073	0.092	0.11	0.128	0.145	0.163	0.18
10	0.018	0.036	0.055	0.073	0.091	0.11	0.128	0.145	0.163	0.18
11	0.018	0.036	0.055	0.073	0.091	0.109	0.127	0.145	0.163	0.181
12	0.018	0.036	0.055	0.073	0.091	0.109	0.127	0.146	0.163	0.181
13	0.018	0.036	0.055	0.073	0.091	0.109	0.127	0.145	0.164	0.181
14	0.018	0.036	0.055	0.073	0.091	0.109	0.127	0.145	0.164	0.182
OO	0.018	0.036	0.055	0.073	0.091	0.109	0.127	0.145	0.164	0.182