# Thermodynamic Monte Carlo simulations

- in statistical physics, we usually work with various types of ensembles of states and to determine the mean value of some quantity of interest (such as internal energy, pressure etc.)

  we use the ergodic hypothesis and replace the averaging over time with averaging over possible configurations i.e. we have to evaluate many-dimensional integrals of the type

$$\langle X \rangle = \int_{\text{phase space}} X(r^N, p^N)\, \wp(r^N, p^N)\, dr^N dp^N$$

  where $X$ is the quantity of interest and $\wp(r^N, p^N)$ is the propability density function of finding a certain configuration $(r^N, p^N)$ of the studied system under given conditions and with $N$ particles

  - the most common ensemble is the canonical ensemble characterized by the number of particles $N$, volume $V$ and temperature $T$ (NVT ensemble),

    in this case $\wp(r^N, p^N; N, V, T) = \dfrac{K\, e^{-\beta H(r^N, p^N)}}{Z}$

    where $\beta = \dfrac{1}{k_B T}$ with $k_B$ being the Boltzmann constant

    $H(r^N, p^N)$ is the Hamiltonian of the system

    and $Z = K \int_{\text{phase space}} e^{-\beta H(r^N, p^N)}\, dr^N dp^N$

    is the partition function with the normalization factor $K = \dfrac{1}{N!\,(2\pi\hbar)^{3N}}$

- if we have a system of identical classical particles (generalization to mixture of various particles is straightforward) and the Hamiltonian is of the form

$$H = K(p^N) + V(r^N)$$

($K(p^N)$: kinetic energy; $V(r^N)$: potential energy)

then we can integrate over impulses and get

$$Z_{NVT} = \frac{Q_{NVT}}{N!\,\Lambda^{3N}}, \quad \Lambda = \sqrt{\frac{2\pi\hbar^2}{m k_B T}}$$

where

$$Q_{NVT} = \int_{\text{config. space}} e^{-\beta V(r^N)}\, dr^N$$

and the mean value of $X(r^N)$ which does not depend on impulses is

$$\langle X \rangle_{NVT} = \frac{1}{Q_{NVT}} \int_{\text{config. space}} X(r^N)\, e^{-\beta V(r^N)}\, dr^N$$

(there are similar expressions for other ensembles, see any textbook of statistical mechanics)

- in the MC method we approximate in general the mean value of the quantity $X$ as

$$\langle X \rangle_{MC} = \frac{1}{N_c} \sum_{\text{config.}} X(\text{config.})$$

where the sum runs over $N_c$ random configurations generated according to the probability distribution given by $\rho(r^N, p^N)$ which is usually proportional to $e^{-\beta H(r^N, p^N)}$ or for the canonical ensemble

$$\rho(r^N) \sim e^{-\beta V(r^N)}$$

- here we use with an advantage the Metropolis-Hastings algorithm to generate only configurations which contribute mostly to $\langle X \rangle$

- when using the Metropolis-Hastings algorithm to generate a sequence of configurations $\{\sigma_k\}$ we need only ratios

$$\frac{\varrho(\sigma_{try})}{\varrho(\sigma_k)} = \frac{\frac{1}{Z} e^{-\beta H(\sigma_{try})}}{\frac{1}{Z} e^{-\beta H(\sigma_k)}} = e^{-\beta(H(\sigma_{try}) - H(\sigma_j))}$$

or for the canonical ensemble

$$\frac{\varrho(\sigma_{try})}{\varrho(\sigma_j)} = e^{-\beta[V(\sigma_{try}) - V(\sigma_k)]}$$

- thus we do not need the partition function
- moreover, we need to calculate only the energy difference of two (mostly close) configurations

$$\Delta E = H(\sigma_{try}) - H(\sigma_j)$$

which can be done often effectively (especially if we change positions (or states) of only a few particles when generating a new configuration)

- the algorithm usually proceeds in the following way:
  a) initialize the system (ideally with a configuration the energy of which is reasonable)
  b) thermalize the system by performing sufficient number of steps of the M-H algorithm
  c) continue the M-H algorithm with „measurements"
     - calculate all quantities of interest in each step
  d) average all obtained quantities to get approximations of mean values

- one step of the Metropolis-Hastings algorithm consists of:

1) choose one (or a few) particles (sites in a lattice) (either systematically or randomly)

2) change a little bit the current configuration $\sigma_k$ into a new one $\sigma_{try}$ (by changing randomly the position(s) or state(s) of the site(s) in the lattice)

3) calculate $\Delta E = H(\sigma_{try}) - H(\sigma_k)$

4) if $\Delta E < 0$ or if $e^{-\beta \Delta E} \geq \xi_{\langle 0,1 \rangle}$ (a random number on $\langle 0,1 \rangle$ uniformly distributed)

then $\sigma_{k+1} = \sigma_{try}$

otherwise $\sigma_{k+1} = \sigma_k$

5) go back to 1)

Notes:

1) Thermalization is necessary (especially if we consider low temperatures and we generate the initial configuration randomly (see examples in Mathematica for the Ising model)

2) We usually do „measurements" after a certain number of steps of the M-H algorithm due to correlations (e.g. if we are changing states of all particles (sites) systematically, we do „measurements" after one or a few „sweeps" over all particales, or we can set $N_{measure}$, so we do „measurements" whenever $N_c \bmod N_{measure} = 0$ or similarly)

3) For discrete systems, the integrals are replaced by very large sums over all possible configurations, again we use the M-H algorithm to approximate such sums by sums over configurations which are important