

Monte Carlo

the algorithm

in conventional Monte Carlo simulation → canonical (NVT) ensemble.

The choice of ensembles for Monte Carlo simulations is wider: isobaric-isothermal, constant-stress-isothermal, grand canonical (i.e., constant μ), and even microcanonical

Simulation in different ensembles → observable differences in the statistical averages.

Most of these differences disappear in the thermodynamic limit and are already relatively small for systems of a few hundred particles.


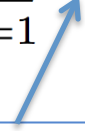
However, the choice of ensemble does make a difference when fluctuations in thermodynamic quantities.

Application to the NVT MC simulation of a system of N particles

we wish to know the ratio of two integrals. What Metropolis showed is that it is possible to devise an efficient Monte Carlo scheme to sample such a ratio.

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

$$\langle A \rangle \approx \frac{1}{L} \sum_{i=1}^L n_i A(\mathbf{r}_i^N)$$

Z  Probability density \rightarrow
 $\mathcal{N}(\mathbf{r}^N) \equiv \frac{\exp[-\beta\mathcal{U}(\mathbf{r}^N)]}{Z}$
 

we don't know Z

we know \rightarrow $\exp[-\beta\mathcal{U}(\mathbf{r}^N)]$

relative probability
of state n / state o \rightarrow $\exp\{-\beta [U_n - U_o]\}$

Application to the NVT MC simulation of a system of N particles

we wish to know the ratio of two integrals. What Metropolis showed is that it is possible to devise an efficient Monte Carlo scheme to sample such a ratio.

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

$$\langle A \rangle \approx \frac{1}{L} \sum_{i=1}^L n_i A(\mathbf{r}_i^N)$$

“Brute” MC \rightarrow sampling ALL configuration space (mostly with zero n_i)

Metropolis MC \rightarrow “important” sampling (non-zero n_i)

The principal idea of **importance sampling** is to use a Monte Carlo procedure to generate a random walk in those regions of phase space that have an important contribution to the ensemble averages. (high $n_i = \text{high } \exp\{-\beta U\} / Z$)

The principal idea of **importance sampling** is to use a Monte Carlo procedure to generate a random walk in those regions of phase space that have an important contribution to the ensemble averages.

The steps in the random walk are accepted or rejected with a given probability (acceptance rules)

The acceptance rules have to be chosen such that these configurations occur with a frequency prescribed by the desired probability distribution.

if **detailed balance** is obeyed we are guaranteed to have a correct sampling scheme. (although DB is not necessary)

1. Decide which distribution we want to sample, in which ensemble.
2. Impose the condition of detailed balance (DB)

$$W_{ji}P_{eq}(S_j) = W_{ij}P(S_i).$$

probability of change $j \rightarrow i$ = probability of change $i \rightarrow j$

$j = \text{old } (o)$

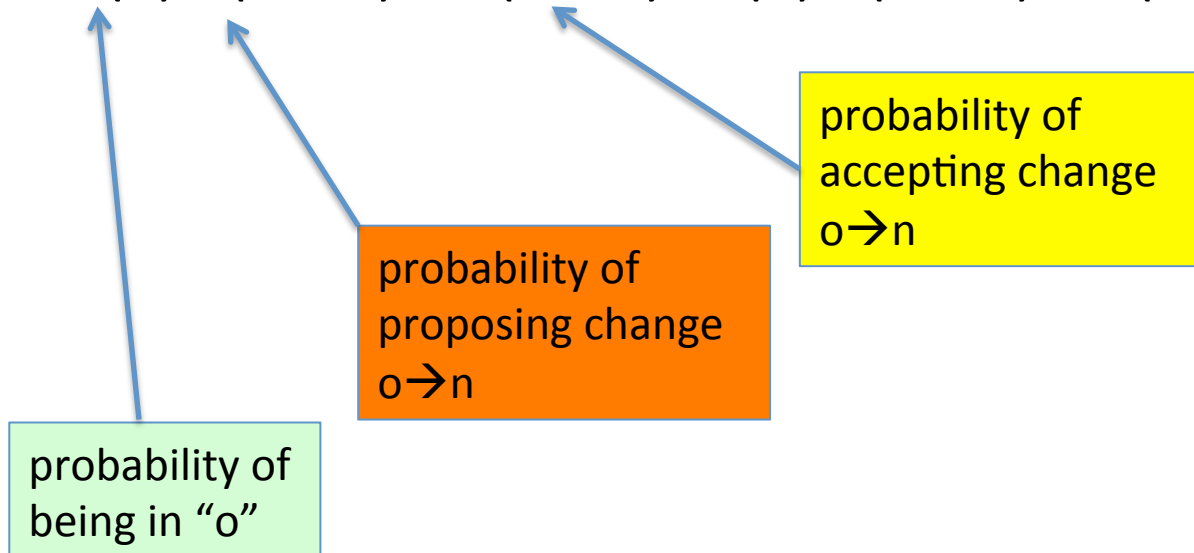
$i = \text{new } (n)$

$$K(o \rightarrow n) = K(n \rightarrow o)$$

1. Decide which distribution we want to sample, in which ensemble.
2. Impose the condition of detailed balance (DB)

$$K(o \rightarrow n) = K(n \rightarrow o)$$

$$N(o) \alpha(o \rightarrow n) \text{acc}(o \rightarrow n) = N(n) \alpha(n \rightarrow o) \text{acc}(n \rightarrow o)$$



1. Decide which distribution we want to sample, in which ensemble.
2. Impose the condition of detailed balance (DB)

$$K(o \rightarrow n) = K(n \rightarrow o)$$

$$N(o) \alpha(o \rightarrow n) \text{acc}(o \rightarrow n) = N(n) \alpha(n \rightarrow o) \text{acc}(n \rightarrow o)$$

$$N(o) \text{acc}(o \rightarrow n) = N(n) \text{acc}(n \rightarrow o) \quad (\text{for symmetric } \alpha)$$

3. Define probability $\text{acc}(o \rightarrow n) = \min\{1, N(n)/N(o)\}$

1. Decide which distribution we want to sample, in which ensemble.
2. Impose the condition of detailed balance (DB)

$$K(o \rightarrow n) = K(n \rightarrow o)$$

$$N(o) \alpha(o \rightarrow n) \text{acc}(o \rightarrow n) = N(n) \alpha(n \rightarrow o) \text{acc}(n \rightarrow o)$$

$$N(o) \text{acc}(o \rightarrow n) = N(n) \text{acc}(n \rightarrow o) \quad (\text{for symmetric } \alpha)$$

3. Define probability $\text{acc}(o \rightarrow n) = \min\{1, N(n)/N(o)\}$

Proof that complies DB:

suppose $N(n) < N(o) \rightarrow \text{acc}(o \rightarrow n) = N(n)/N(o)$

and $\text{acc}(n \rightarrow o) = 1$

then $\text{acc}(o \rightarrow n)/\text{acc}(n \rightarrow o) = N(n)/N(o) \quad \checkmark$

for example in the canonical ensemble, the partition function is:

$$Q(N, V, T) = \frac{1}{\Lambda^{3N} N!} \int dr^N \underbrace{\exp[-\beta U]}_{N(U)}$$

the probability of a configuration is:

$$N = \exp\{-\beta U\}$$

MC move: $r_o \rightarrow r_n$

$$\text{acc}(o \rightarrow n) = \min(1, \exp\{-\beta(U_n - U_o)\})$$

Heart of MC: Basic Metropolis Scheme

Application to the NVT MC simulation of a system of N particles

- Select randomly a particle
- Give a random displacement to the particle selected
- Accept the move with probability :

$$\text{acc}(o \rightarrow n) = \text{Min}[1, \exp\{-\beta [U_n - U_o]\}]$$

If the new energy is lower $\rightarrow U_n < U_o \rightarrow U_n - U_o < 0 \rightarrow \exp\{-\beta [U_n - U_o]\} > 1$
 $\text{acc} = 1$

i.e. a move that lowers the total energy is accepted right away.

If the new energy is higher we don't accept it nor reject it right away.
Those moves will be accepted "sometimes"

Sometimes means with probability $p = \text{acc} = \exp\{-\beta [U_n - U_o]\} < 1$

How to accept something with probability p ?

We choose randomly a number (rn) between $[0,1]$

if the $rn < p$ we accept, otherwise reject

The probability that a random number is less than p is p

For example

$p=1$, probability is 1 (all rn in $[0,1]$ are less than 1)

$p=0$, probability is 0

$p=0.4$, probability is 0.4 (40% are less than 0.4)

We use the RNG many times!
RNG is an important component of a MC simulation.

If RNG is not good: ☹️

- we may not sample the phase space as in a “Markov chain”
- Ergodicity is lost
- we may have a bias toward over (under) acceptance

Today there are good RNG in the market

In the old times, the RN came in tables !!!

Initial set up

- The goal of the simulations is (not always but most of the times) to study a “macroscopic” system. However we can simulate only 1000s of particles, not 10^{23}
- At the start the particles are set in positions in a “simulation cell”
- Never start from a random distribution since particles may “overlap” and result in infinitely large energy or force.
- Although ideally the results do not depend on the initial configuration, a bad choice can result in computing instabilities.
- The MC algorithm is applied millions of times before we start doing the ensemble averages. The first millions of runs are discarded, in that way we know the system has:
 - reached equilibrium
 - forgotten the initial condition
- The initial positions are usually a lattice or a previous run.

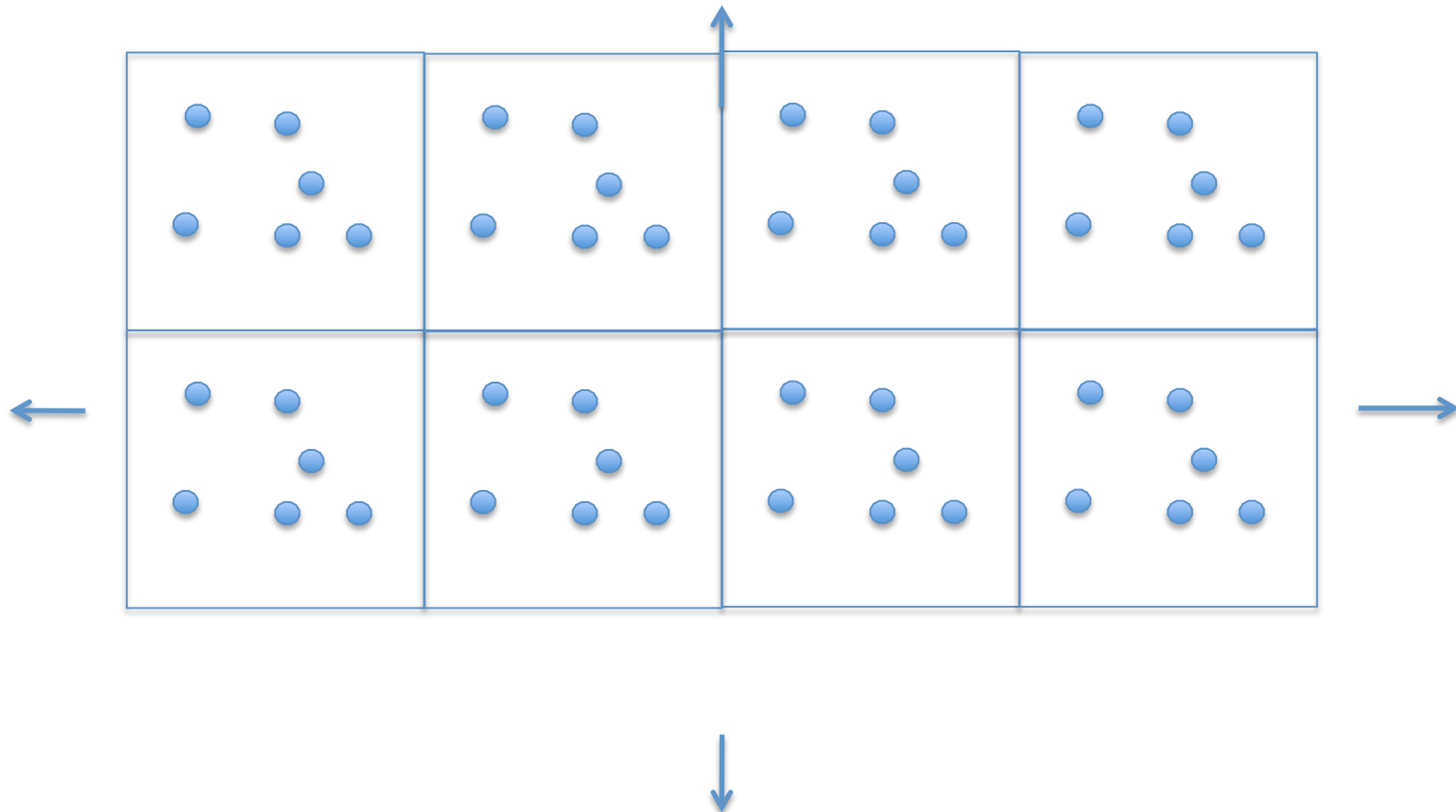
The Simulation cell

- The simulation cell is usually a cube or rectangular, but not necessarily.
- The size of the simulation cell can not be too small or too large.
- If it is too small, the simulation will have “size effects” , i.e. the results will depend on the size of the cell. Always check that the results are not size dependent. If they are, the cell is too small.
- If the cell is too big, it would take too long to sample the phase space

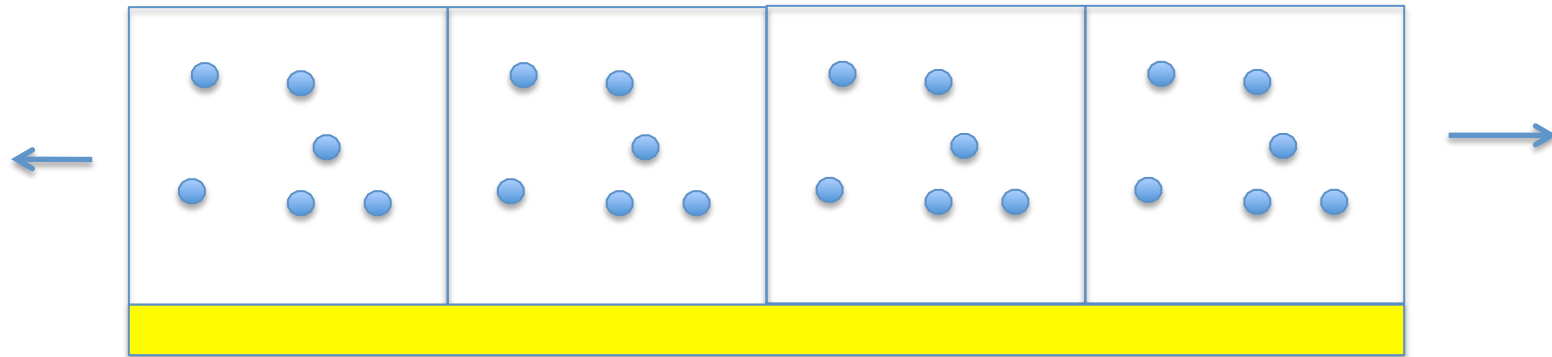
Boundary Conditions

To “mimic” a macroscopic system we repeat the simulation cell periodically in all directions.

The simulation cell is a primitive cell of an infinite periodic lattice of identical cells



In some cases periodic BC can not be used, for example if there is a wall containing the system.



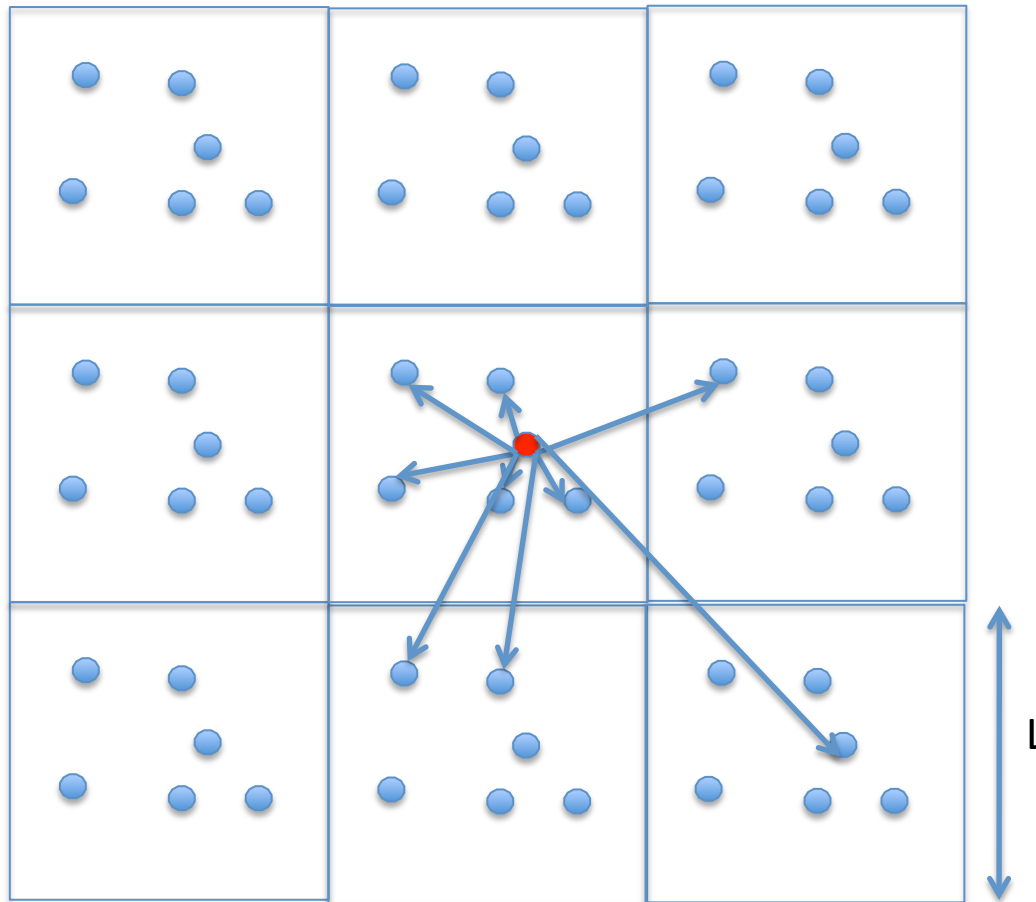
In this case we use “reflective” BC.

The choice of BC is important and has to represent the model.

The BC can affect the results.

For example, an artificial periodicity is introduced.

The actual MC is done on the primitive cell, but the atoms interact with ALL the atoms in all cells around



$$U_{\text{tot}} = \sum U(r_{ij} + n L)$$

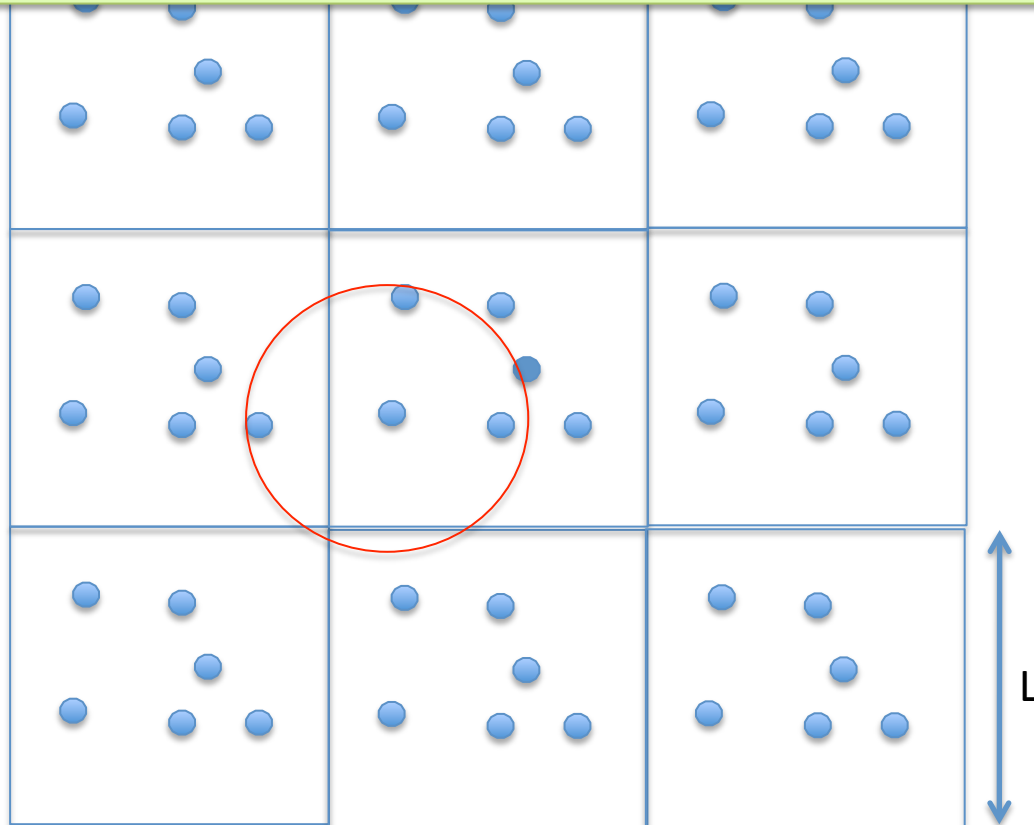
where n is a vector of 3 integer numbers denoting the cell around

The sum has infinite terms!

Truncation of interactions

Case where the interactions in the system are short-range (like Lennard Jones)

We define a cut-off distance (r_c) and neglect the interaction between particles that are at a distance $r > r_c$



This is an approximation → we have to estimate the error introduced.

We can always choose a value of r_c that makes the error small enough.

The truncation of interactions results in a SYSTEMATIC error in the energy U_{tot}

Estimation of error as the “tail contribution”:

$$U^{total}(r) = \sum_{i < j} U(r_{ij}) + \frac{N\rho}{2} \int_{r_c}^{\infty} dr U(r) 4\pi r^2$$

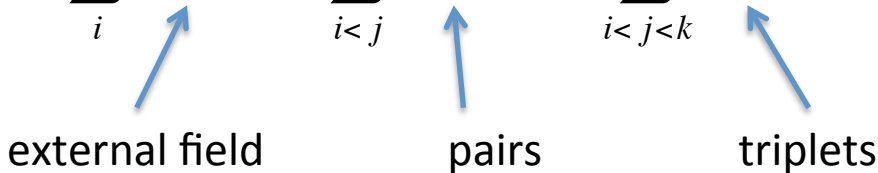
If U does NOT decay faster than r^{-3} the tail correction is infinite!

For dispersion forces $U \sim r^{-6}$ OK

For Coulomb and dipolar interaction is not OK But IT IS OK in 2D (Adsorbates)

Inter-atomic potentials

The potential energy of a system of many atoms can be written as:

$$U = \sum_i u_1(r_i) + \sum_{i < j} u_2(r_i, r_j) + \sum_{i < j < k} u_3(r_i, r_j, r_k) + \dots$$


external field pairs triplets

u_2 usually depends on the distance r_{ij}

u_3 is rarely included in simulations, however can be important for liquids.

Higher order terms, four-body, etc are expected to be small.

Lennard-Jones: simplest, most commonly used

$$U^{lj}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$$

the second (negative) term represents the attractive dispersion force, or van der Waals

The first term ϵ, σ

The constants are parameters for each atom, with values selected to fit experimental properties

Trial Moves

Let's assume that:

- we have an atomic or molecular model system in a suitable starting configuration
- we have specified all intermolecular interactions.

We must now set up the underlying Markov chain, that is, the matrix α .

→ we must decide how we are going to generate trial moves.

2 possible moves:

1. moves that involve only the molecular centers of mass
2. moves that change the orientation or possibly even the conformation of a molecule.

Translational Moves

The position of the CM of the molecule changes as:

$$x'_i = x_i + \Delta (rn - 0.5)$$

$$y'_i = y_i + \Delta (rn - 0.5)$$

$$z'_i = z_i + \Delta (rn - 0.5)$$

where rn are random numbers $[0,1]$

the reverse trial move is equally probable (hence, α is symmetric)