Course 11/2

Monte Carlo simulation of Lennard-Jones liquid

- Ensemble average for a classical liquid
- Trial move
- Application of Metropolis algorithm
- Trial move and computational effort

Ensemble average for a classical liquid

NVT ensemble

T – contact with a heat bath of fixed temperature *T* , canonical ensemble.

V – Fixed volume *V* (here: periodic boundary conditions, simple cubic).

N – Fixed number of particles *N.*

Ensemble average

We are interested in the ensemble average of a physical quantity *A* that depends on the coordinates of all the particles $\vec{X}$.

$$\langle A \rangle = \frac{\int d\vec{X} \; A(\vec{X}) \exp [- \beta U(\vec{X})]}{\int d\vec{X} \; \exp [- \beta U(\vec{X})]}$$

For example: potential energy, bond length, bond angles.

Importance sampling through correlated sampling

$$\langle A \rangle = \frac{\int d\vec{X} \; A(\vec{X}) \exp[-\beta U(\vec{X})]}{\int d\vec{X} \; \exp[-\beta U(\vec{X})]} \cong \frac{1}{N} \sum_{i=1}^{N} A(\vec{X}_i)$$

provided the configurations $\vec{X}_i$ in phase space are sampled according to the weight function

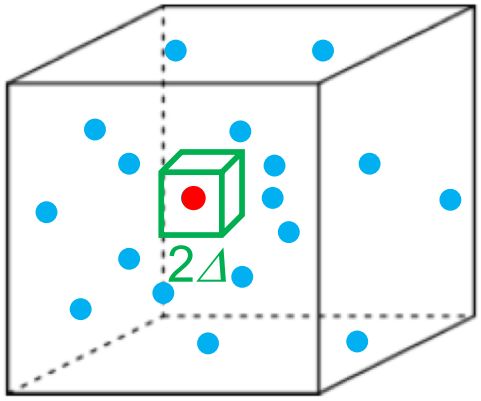
$$\omega(\vec{X}) = \frac{\exp[-\beta U(\vec{X})]}{\int d\vec{X} \; \exp[-\beta U(\vec{X})]}$$

We want to achieve this by correlated sampling using the Metropolis algorithm.

Trial move

We need to define the trial configuration $\vec{X}_t$ in phase space.

This implies specifying the coordinates of all the particles of the system.



1. Select one particle *i*.

2. Make a trial move : uniform choice within a cubic box of side 2Δ centered at the position of particle *i*.

$$x_i^t = x_i^n + \Delta\,(2\alpha - 1)$$

$$y_i^t = y_i^n + \Delta\,(2\beta - 1)$$

$$z_i^t = z_i^n + \Delta\,(2\gamma - 1)$$

where α, β and γ are random numbers $\in (0,1)$

3. All other particles do not move.

NB Δ determines the size of the move

Application of Metropolis algorithm

We calculate:

$$r = \frac{\omega(\vec{X}_t)}{\omega(\vec{X}_n)} = \frac{\exp[-\beta U(\vec{X}_t)]}{\exp[-\beta U(\vec{X}_n)]}$$

1

$r \geq 1$  Accepted $\vec{X}_{n+1} = \vec{X}_t$

$r < 1$ A random number $\eta \in (0,1)$ is extracted.

2

$\eta \leq r$  Accepted $\vec{X}_{n+1} = \vec{X}_t$

$\eta > r$  Rejected $\vec{X}_{n+1} = \vec{X}_n$

NB Δ should be chosen such that:
accepted moves ≅ # rejected moves

Trial move and computational effort

$$r = \frac{\exp\left[-\beta U(\vec{X}_t)\right]}{\exp\left[-\beta U(\vec{X}_n)\right]} = \exp\left\{-\beta\left[U(\vec{X}_t) - U(\vec{X}_n)\right]\right\}$$

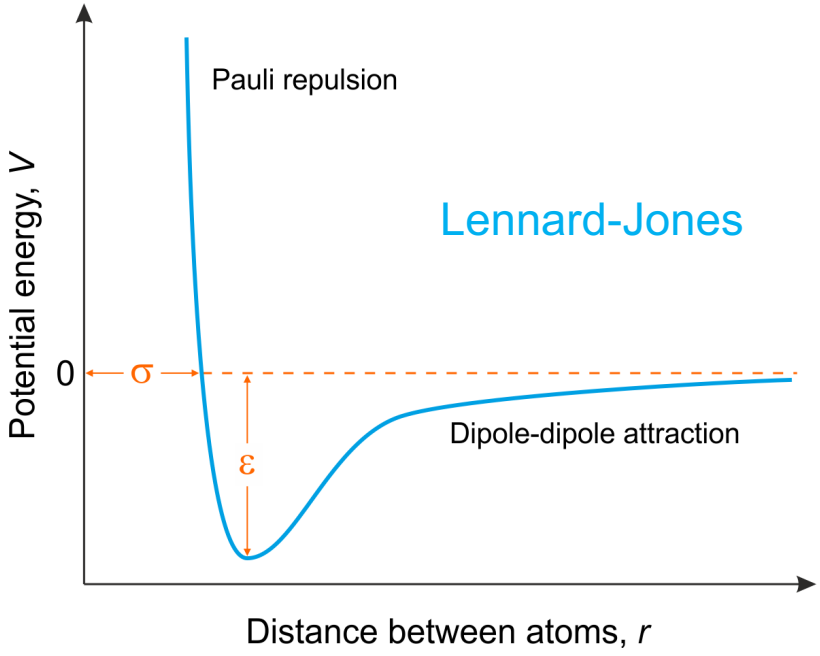
$$r = \exp\left(-\beta \Delta U\right) \qquad \text{where} \qquad \Delta U = U(\vec{X}_t) - U(\vec{X}_n)$$

Example: liquid argon, with pair interactions

$$U(\vec{X}) = \sum_{\substack{j,\,k=1 \\ j>k}}^{N} V(r_{jk})$$

$$= \sum_{\substack{j,\,k=1 \\ j>k}}^{N} V\left(\left|\vec{r}_j - \vec{r}_k\right|\right)$$

position of particle j



Trial move and computational effort

$$\Delta U = U(\vec{X}_t) - U(\vec{X}_n)$$

$$= \sum_{\substack{j,\,k=1 \\ j>k}}^{N} V(|\vec{r}_j^{\,t} - \vec{r}_k^{\,t}|) - \sum_{\substack{j,\,k=1 \\ j>k}}^{N} V(|\vec{r}_j^{\,n} - \vec{r}_k^{\,n}|)$$

The trial step involves only particle *i* :

$$\begin{cases} \vec{r}_i^{\,t} \neq \vec{r}_i^{\,n} & \text{for } k = i \\ \vec{r}_k^{\,t} = \vec{r}_k^{\,n} & \text{when } k \neq i \end{cases}$$

$$= \sum_{\substack{j=1 \\ j \neq i}}^{N} [\, V(|\vec{r}_j^{\,t} - \vec{r}_i^{\,t}|) - V(|\vec{r}_j^{\,n} - \vec{r}_i^{\,n}|) \,]$$

double sum is reduced to a single sum !

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