BOUNDARY CONDITIONS

Typical liquid densities : 10-100 molecules/nm^3

Typical simulation boxes: size up to 10 nm

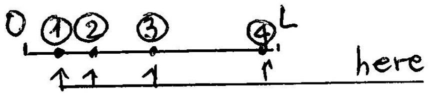
Boxes are so small that boundaries are important!

WAY OUT: periodic boundary conditions (p.b.c.)

$\Downarrow$

We add images

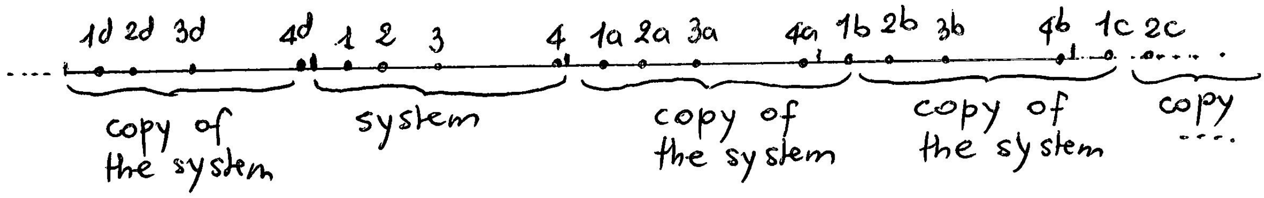
EXAMPLE: ONE DIMENSION (4 particles)



here are the four particles

length L

$\downarrow$ p.b.c



Of course $|r_1 - r_{1a}| = L \quad |r_1 - r_{1b}| = 2L \quad |r_1 - r_{1c}| = 3L$

$|r_2 - r_{2a}| = L \quad |r_2 - r_{2b}| = 2L$ and so on

<u>Define</u>: $U \equiv$ potential energy for each system

$$U = \sum_{i<j} V(|r_i - r_j|) = \frac{1}{2} \sum_{i \neq j} V(|r_i - r_j|)$$

$\downarrow$ becomes

$$U = \frac{1}{2} \sum_{i \neq j} V(|r_i - r_j|) + \frac{1}{2} \sum_{\substack{m=-\infty \\ m \neq 0}}^{+\infty} \sum_{ij} V(|r_i - r_j - mL|)$$

NOTE : the second sum is over all images including the image of the particle under consideration (we consider $i=j$ in the second sum)

In our example we include

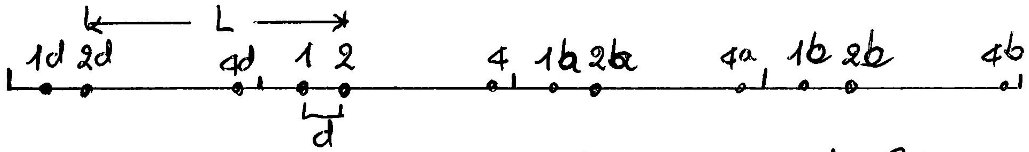
$$V(|\bar{r}_1-\bar{r}_{1a}|)+V(|\bar{r}_1-\bar{r}_{1b}|)+\dots$$

The use of p.b.c. reduces size effects

PRICE TO PAY : an infinite sum over all images

WAY OUT : we use a cutoff such that $r_c \leq L/2$

CONSEQUENCES FOR ONE DIMENSIONAL SYSTEMS



Interactions between particle 1 and 2 + images of 2

$$|r_1-r_2|=d \quad |r_1-r_{2a}|=d+L \quad |r_1-r_{2d}|=L-d$$

With the chosen cutoff r_1 can only interact with particle $\vec{r}_2$ or $\vec{r}_{2d}$

If $d<\frac{L}{2}$ (this is what it appears in the picture)

- $L-d>\frac{L}{2}$ there is no interaction between $\vec{r}_1$ and r_{2d}
- The only interaction is between r_1 and r_2

If instead we consider $\bar{r}_1$ and $\bar{r}_4$
again we should ~~not~~ consider only $\bar{r}_4$ and $\bar{r}_{4d}$
But now $|\bar{r}_1 - \bar{r}_4| = d > \frac{L}{2}$, therefore there is no interaction between $\bar{r}_1$ and $\bar{r}_4$.
On the contrary $|r_1 - r_{4d}| = L - d < \frac{L}{2}$ so that $\bar{r}_1$ and $\bar{r}_{4d}$ interact.

CONCLUSION: Consider particle i in $\bar{r}_i$.
Given j, particle i interacts with particle in r_i
OR with one image
(and only one)

In practice, the contribution of the interactions (i,j)

$$\sum_m V(|\bar{r}_i - \bar{r}_{j,m}|) = V(d_{ij}) \qquad d_{ij} = \min(d, L-d)$$

$$d = |\bar{r}_1 - \bar{r}_j|$$

$\uparrow$
somma su tutte
le immagini +
particella originale in r_j

A Useful formula

Define ANINT(x) the function that gives the closest integer.

$$\begin{cases} \text{ANINT}(3.7) = 4 & \text{ANINT}(4.2) = 4 \\ \text{ANINT}(-3.7) = -4 & \text{ANINT}(-5.1) = -5 \end{cases}$$

We prove that

$$d_{ij} = \min(d, L-d) = \left| r_i - r_j - L * \text{ANINT}\left(\frac{r_i - r_j}{L}\right)\right|$$

note that $-L < r_1 - r_j < L$. Thus, we distinguish three cases

(a) $-L < r_1 - r_j < -\frac{L}{2} \Rightarrow \text{ANINT}\left(\frac{r_1 - r_j}{L}\right) = -1$

$$\left| r_1 - r_j - L * \text{ANINT}\left(\frac{r_1 - r_j}{L}\right)\right| = |-d + L| = |d - L|$$
$$= \min(d, L-d)$$

(b) $-\frac{L}{2} < r_1 - r_j < \frac{L}{2} \Rightarrow \text{ANINT}(\ ) = 0$

$$|r_1 - r_j| = d = \min(d, L-d)$$

(c) $\frac{L}{2} < r_1 - r_j < L \Rightarrow \text{ANINT}(\ ) = +1$

$$\left| r_1 - r_j - L * \text{ANINT}\left(\frac{r_1 - r_j}{L}\right)\right| = |d - L| = L - d$$
$$= \min(d, L-d).$$

The formula has an advantage.

If $r_i' = r_i + nL$ n integer

$$r_1' - r_j - L * ANINT\left(\frac{r_1' - r_j}{L}\right) =$$

$$= \bar{r}_i' - \bar{r}_j - L * ANINT\left(n + \frac{r_1 - r_j}{L}\right) =$$

$$= r_1 + \cancel{nL} - r_j - \cancel{nL} - L * ANINT\left(\frac{r_1 - r_j}{L}\right) =$$

$$= r_1 - r_j - L * ANINT\left(\frac{r_1 - r_j}{L}\right)$$

THE RESULT DOES NOT REQUIRE $0 < r_i < L$.

Practical advantage: in the Metropolis update there is no need to "keep the particle in the box"

$$r_i' = r_i + \Delta(RAN - 0.5)$$

THERE IS NO NEED TO CHECK THAT

<u>$0 < r_i' < L$</u>

THREE-DIMENSIONAL VERSION

The strategy can be generalized to 3D

To compute the potential energy

$$U = \sum_{i<j} V(\hat{r}_{ij})$$

where $\hat{r}_{ij}$ is computed as follows

$$\vec{r}_i = (x_i, y_i, z_i) \qquad \vec{r}_j = (x_j, y_j, z_j)$$

$$\left\{\begin{array}{l} x_{ij} = x_i - x_j - L * ANINT\left(\frac{x_i - x_j}{L}\right) \\ y_{ij} = y_i - y_j - L * ANINT\left(\frac{y_i - y_j}{L}\right) \\ z_{ij} = z_i - z_j - L * ANINT\left(\frac{z_i - z_j}{L}\right) \end{array}\right. \Rightarrow \hat{r}_{ij} = \left[x_{ij}^2 + y_{ij}^2 + z_{ij}^2\right]^{1/2}$$

THIS APROACH WORKS <u>ONLY</u> FOR $r_c \leq \frac{L}{2}$

$\hat{r}_{ij}$ is CALLED DISTANCE COMPUTED USING THE "MINIMUM IMAGE CONVENTION"