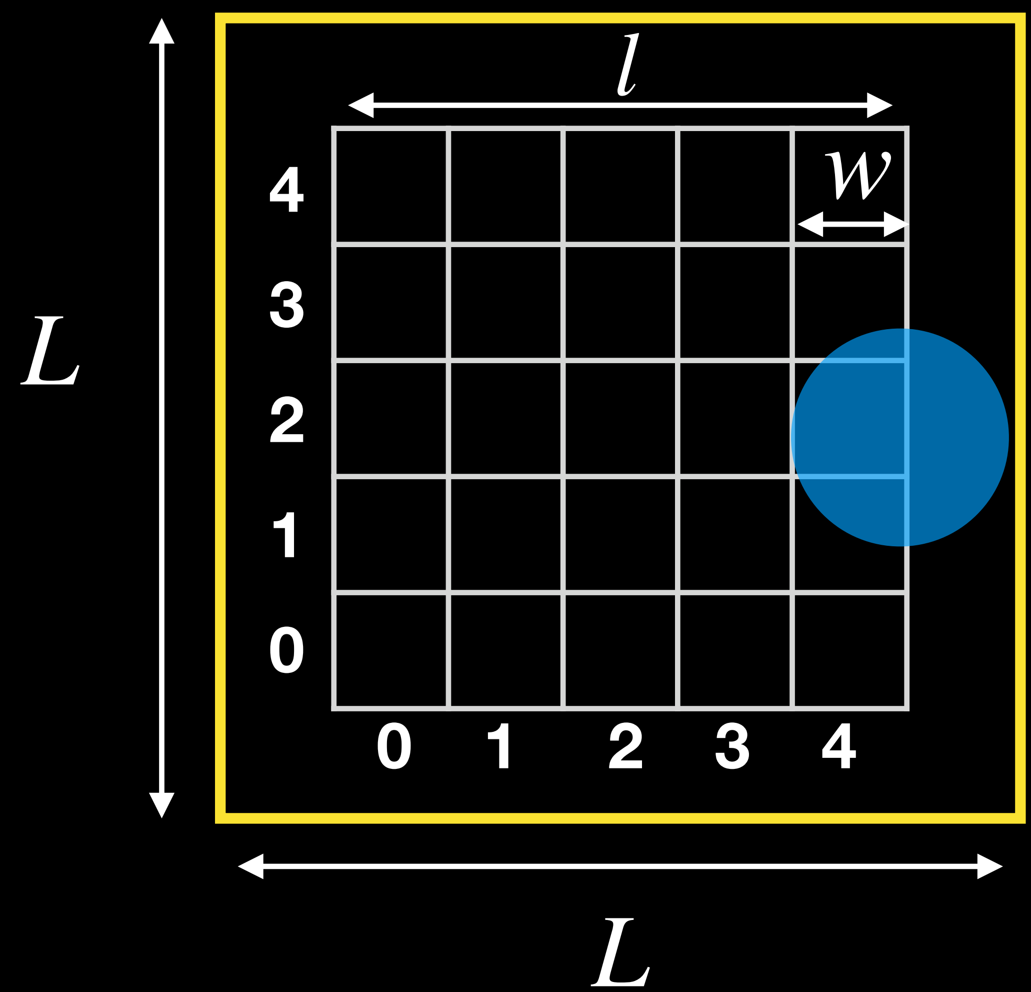
Project 4) Depletion interactions

It is a simple question with a surprising result: Do the confining walls attract particles? In particular, what is with the corners of the box?

To answer this question, you must create a two-dimensional histogram of the distribution of the particle positions. This means you must discretise the continuous space. (See also the material of lab session 2, central limit theorem, of the python course last year.)



The accessible area must be covered by a 2D grid, i.e. a two-dimensional array $H[X_i, Y_i]$.

The accessible area is $l \times l$, with $l = L - 2R$ (note the gap of the radius between the wall and the histogram).

If the dimension of the array is $N \times N$, then the width of one histogram bin is $w = l/N$.

A particle position (x_i, y_i) is associated to the indices $X_i = x_i//w$ and $Y_i = y_i//w$ of the two-dimensional histogram. Here $a//b$ is the floor division operation of python.

Does the result depend on the density ?

What happens, if you put a hand full of big particles in a bath of small particles? Are the big particles attracting each other?

Literature: http://blancopeck.net/Statistics.pdf chapter 6.1.2 The Asakura–Oosawa depletion interaction (p. 273)

Note: It is not necessary, that one and the same code does everything. You can write several codes, which do one specific measurement.

Additional insights - explanation of what we see

0) The definition of free energy is
F = -k_B T log Z,
where k_B is the Boltzmann constant, T the temperature, and Z is the partition function. You know that physical systems want to **minimise** their free energy.

1) You are in the micro canonical ensemble, i.e. total Energy = const = E_kin, number of particles N = constant, and the volume (are of the box) V = constant.
In this NVE ensemble the partition function
Z = W,
where W is simply the total number of accessible configurations.
Furthermore, entropy is given by
S = k_B log W.
This means that in the micro canonical ensemble the free energy is simply
F = - T S = - k_b T log W
Here you see that the system **minimises** its free energy if it **maximised** its entropy, which it does if it **maximises the total number of accessible states**.
(In general systems try to maximise their Entropy - maximum Entropy principle).

So what your system does is that it "finds tricks" to maximise the total number of accessible states. This trick is called depletion interaction.

What do I mean with trick?
Consider a one-dimensional system as in the attached PDF (next page).
W_1 is the number of accessible configurations in case 1, where particle 1 and 2 are **not** close to the wall.
W_2 is the number of accessible configurations in case 2, where particle 1 and 2 are **in contact with** the wall.
You see clearly that W_1 < W_2.
With other words, if particles are close to the wall, the system is able to maximise its total number of accessible configurations.
The trick the system uses is therefore to place particles close to the walls, such that additional space is created in the center of the system, i.e. the walls become effectively attractive to deplete the bulk density.

Question: When is the attraction measurable? Only at high densities!
Make sure you understand yourself that if N = const, but large:
-> W_1 ~ W_2 at low densities, i.e. when the box is large.
-> W_1 << W_2 at high densities, i.e. when the box is small.

Only when W_1 << W_2 the depletion becomes a measurable effect. In words it simply means that the number of configurations where particles are **not close to the walls** is **much smaller** than the number of configurations **where particles are very close to the walls.**

If you need more detailed references, you may want to check the literature indicated in the project description.

From this explanation you should understand that you need **many particles and high densities** in order to see the effect of the depletion interactions.

3) Concerning the discretisation of the space for your histogram: The histogram bins should have a width and hight which is comparable to the radius of the particles. You can try what happens if your bins have a with and hight equal to the radius, or twice the radius, or triple the radius etc.

You should make sure that your histogram covers the area which is accessible to the particles. Consider the image in the project description. For example the histogram does NOT cover the x positions from L_min to L_min+radius, because the particle cannot be closer to the wall than L_min+radius.

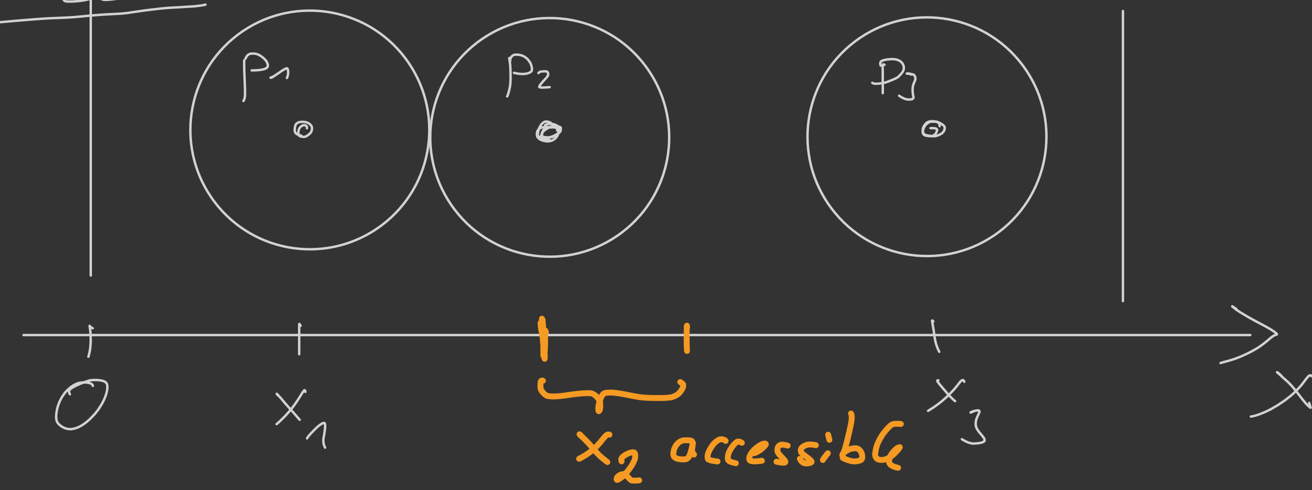
Finally you need to average your histogram over a long time (i.e. you should declare it as a global variable inside MolecularDynamicsLoop). So you should just keep adding to your histogram and normalise it only in the end of your simulation.

4) A check if your histogram is correct? At low densities it should be uniform, i.e. it should have only one colour At high densities you should have a higher probability to see the particles close to the walls and especially in the corners the probability should be high.

5) If you want to initialise your particles at very high densities, you may want to place the positions of the particles on a perfect lattice. But you don't need to do this. Even with the random initial positions, you should be able access densities high enough to see the depletion interactions.

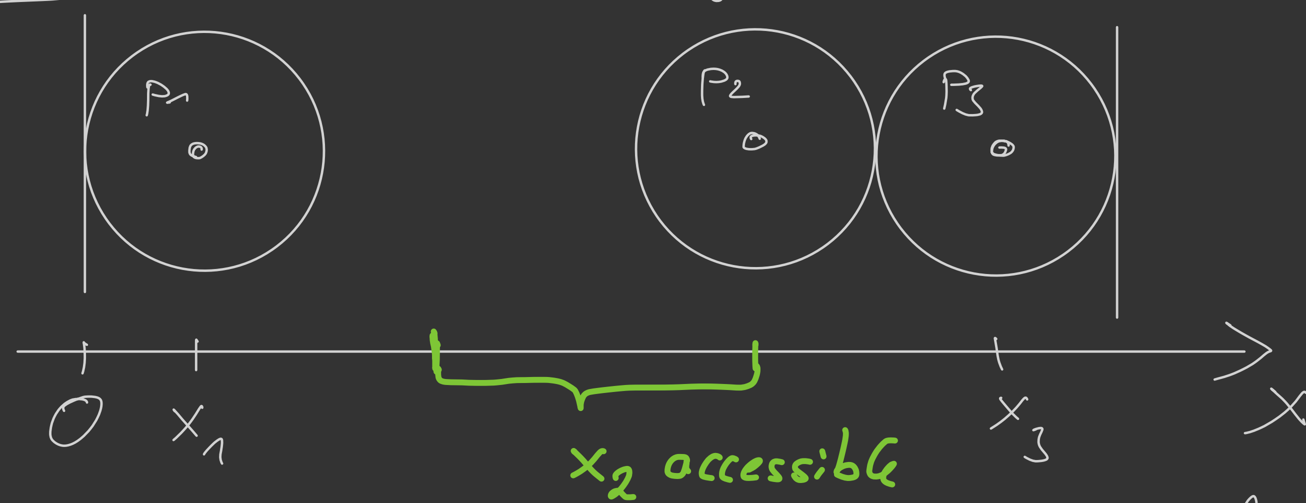
You may also try a log scale in the color: https://colab.research.google.com/drive/1YM0F2KHUA_2Uizk4IwB72YBEWiJiP2bU?usp=sharing

Case 1:



fix x_1 & x_3: available positions for x_2 is only the orange interval

Case 2:



fix x_1 & x_3: available positions for x_2 is the whole green interval

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W_1: total numbes of accesible configurations in case 1

W_2: total numbes of accesible configurations in case 2