How to calculate a three-dimensional $g(r)$ under periodic boundary conditions

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If under simple periodic boundary conditions one wants to compute the pair distribution function $g(r)$ beyond half the simple cubic box length, minimum image issues require an extension of the standard procedure. These notes summarize the required modifications.

The pair correlation function $g(r)$ may be defined as the probability density of finding a particle a distance r away from another particle, divided by the probability density for the same event in a noninteracting system. Equivalently, we can take the number $N(r)$ of particles within a distance range between r and $r + \mathrm{d}r$ and divide it by the number $N_{\mathrm{id}}(r)$ within the same interval in an ideal system. If ρ is the average particle density, we evidently have

$$N_{\mathrm{id}}(r) \ = \ \rho \times 4\pi r^2 \ \mathrm{d}r \ . \tag{1}$$

In other words, apart from a trivial prefactor ρ, we essentially divide $N(r)$ by the surface area of a sphere of radius r. This of course takes care of the fact that the farther away we go from the central particle, the more possibilities one has to put another particle at a distance r.

However, this simple reasoning does not work under periodic boundary conditions. Or, more precisely, it only works provided that $r \le \frac{1}{2}L$ – where we assume that we have a cubic box with box length L. The reason is quite obvious: Once r becomes bigger than $\frac{1}{2}L$, there are certain directions along which the minimum image distance between two particles is shorter than r. Or, in other words, even for an ideal system the number of particles at a distance r does not keep increasing like $4\pi r^2$.

There are two solutions to this problem: A plain one and a clever one. The plain one is: don't plot $g(r)$ beyond $r = \frac{1}{2}L$. This is acceptable, but may be a waste of information.

The clever solution is to find out, what the actual number of particles at a given *minimum image distance* r is. This basically can be reduced to the following problem:

> *Given a cubic simulation box of side length 1, what is the probability density $p(r)$ for having a particular minimum image distance r?*

The answer to this question is

$$p(r) = \begin{cases} 4\pi r^2 & , \quad 0 < 2r \le 1 \\ 2\pi r(3-4r) & , \quad 1 < 2r \le \sqrt{2} \\ 2r\big[3\pi - 12 f_1(r) + f_2(r)\big] & , \quad \sqrt{2} < 2r \le \sqrt{3} \end{cases} , \tag{2}$$

where we used the abbreviations

$$f_1(r) \ = \ \arctan\sqrt{4r^2-2} \tag{3a}$$

$$f_2(r) \ = \ 8r \ \arctan\frac{2r(4r^2-3)}{\sqrt{4r^2-2}\ (4r^2+1)} \tag{3b}$$

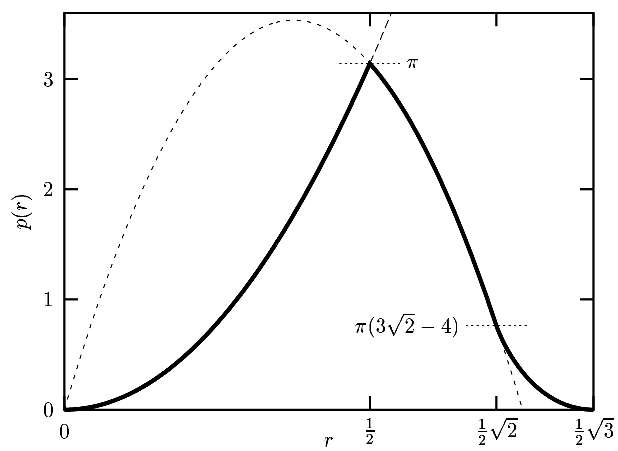

FIG. 1: Probability density $p(r)$ for the minimum image distance between two points randomly picked from the unit cube—Eqn. (2).

The graph of $p(r)$ is sketched in Fig. 1. The required modification now is simply to divide the number of particles $N(r)$ within a certain *minimum image distance* between r and $r+\mathrm{d}r$ by the following modified normalization number:

$$\tilde{N}_{\mathrm{id}}(r) \ = \ \rho \times p(r/L)\ L^2 \ \mathrm{d}r \ . \tag{4}$$

Sometimes it is useful to also know the integrated probability density, i.e., the probability distribution

$$D(r) \ := \ \int_0^r \mathrm{d}\bar{r}\ p(\bar{r}) \ , \tag{5}$$

for instance if bins are wide and one needs a better expression for their volume $V = D(r+\Delta r) - D(r) = p(r)\Delta r + \mathcal{O}(\Delta r^2)$. Luckily, the integration can be done analytically:

$$D(r) = \begin{cases} \frac{4\pi}{3} r^3 & , \quad 0 < 2r \le 1 \\ -\frac{\pi}{12}(3 - 36r^2 + 32r^3) & , \quad 1 < 2r \le \sqrt{2} \\ -\frac{\pi}{4} + 3\pi r^2 + \sqrt{4r^2-2} + \\ (1-12r^2) f_1(r) + \frac{2}{3} r^2 f_2(r) & , \quad \sqrt{2} < 2r \le \sqrt{3} \end{cases} \tag{6}$$

After these modifications $g(r)$ can be plotted up to $\frac{1}{2}\sqrt{3}\,L$, respectable 73% farther than the trivial range. Beyond this value it finally ceases to exist, because there simply is no larger minimum image separation available in a cubic box.