CHEMISTRY

Why do the peaks in a radial distribution function graph have a probability >1

Asked 4 months ago Active 4 months ago Viewed 641 times

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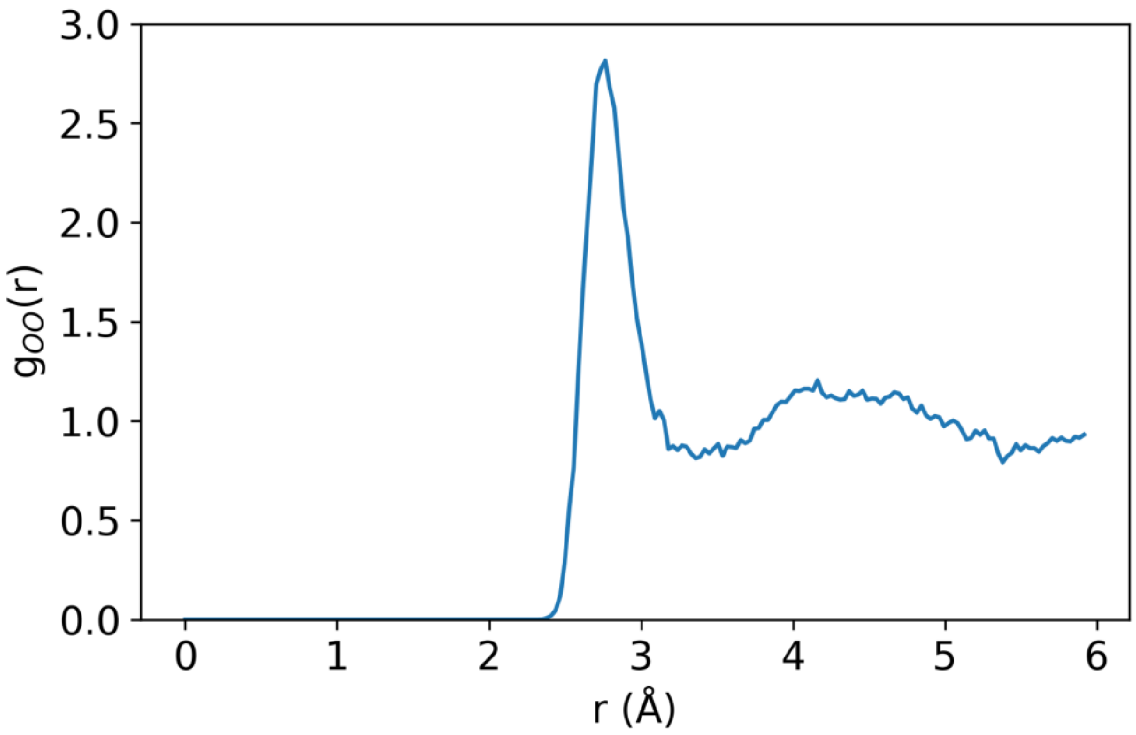
Why do RDF plots have the probability at a particular distance >1. How can probability be more than one?

I am asking this because I want to understand what do the peaks of different length but at the same position on the x axis mean

The below is an example of a RDF plot:



molecular-dynamics

edited Jul 13 at 13:01
Ian Bush
1,637 1 9 17

asked Jul 12 at 8:05
fireball.1
460 3 14

7 This is not probability. – Ivan Neretin Jul 12 at 8:20

1 Answer

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The radial distribution function isn't a probability or a probability density. The usual definition is

$$g(r) = \frac{\rho(r)}{\rho_0}$$

where $\rho(r)$ is the number density at a particular distance r away from some specified atom and ρ_0 is the bulk density of the material.

It can be larger than one if the local density is greater than the bulk (which you see in the first peak of your graph), so it can't be a probability. It also can't be a probability density, as the local density should eventually converge to bulk at long distance, so $g(r)$ converges to 1 (as you start to see on the right-hand side of your graph) so the integral would continue to increase as you increase the range of integration.

So what does the RDF tell you? Well if you integrate it over a spherical shell and multiply by the bulk density, you obtain the number of atoms in that shell. One particular shell we are often interested in is the first coordination sphere. Using the RDF, we can define the number of particles in the first coordination sphere as

$$n(r') = 4\pi\rho_0 \int_0^{r'} g(r) r^2 dr$$

where r' is the location of the first minimum of the RDF. We can similarly determine the number of atoms in the n^{th} coordination sphere by integrating from the $(n-1)^{\text{th}}$ minimum to the n^{th} minimum.

answered Jul 13 at 1:54

Tyberius
9,915 3 30 76

chem.libretexts.org/Bookshelves/… defines RDF for bound electrons. – Karsten Theis Jul 13 at 10:13

This is not about electrons – Ian Bush Jul 14 at 9:03