

Correlation: An Analyzing Tool for Liquids and for Amorphous Solids

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Summary

For almost a century, since Bernal's attempts at a molecular theory of liquid structure ([Bernal, 1937](#)), correlation functions have been the bridge to compare theoretical calculations with experimental measurements in the study of disordered materials.

Pair Distribution Functions ($g(r)$), Radial Distribution Functions ($J(r)$), Plane Angle Distributions ($g(\theta)$) and Coordination Numbers (n_c) have been widely used to characterize amorphous and liquid materials ([Elliott, 1986](#); [Valladares et al., 2011](#); [Waseda, 1980](#)) and, in particular Bulk Metallic Glasses ([Galván-Colín et al., 2015](#); [Miller & Liaw, 2007](#)).

Correlation is an Open-Source software designed to analyze liquid structures and amorphous solids; the software is user-friendly, the modular design makes it easy to integrate in High-Throughput Computing (HTC) to process structures with a large number of constituents in a standardized fashion. **Correlation** is ready to be used in Windows, Linux and Mac. Currently, we support DMol3 (CAR), CASTEP (CELL), ONETEP (DAT) and VASP (POSCAR) structure files. The code can handle up to 25,000 atoms, so it can be used to analyze both classical and first-principles simulations. At the end, the output of every single correlation function is exported to the corresponding comma-separated value file (CSV), to further analyze the results.

Statement of Need

As time goes by, the number of atoms in theoretical calculations has grown from a few dozens to hundreds of thousands of atoms, and with this increment the complexity to calculate the correlation functions that represent the structure of materials has steadily increased. To answer this need, there have been several tools developed to calculate some of the most used correlation functions like: pair distribution functions, radial distribution functions and plane angle distributions. However, the use of these tools has been limited, either by a prohibiting cost, or has been restricted to private academic groups, or geopolitical limitations introduced by the licensing, or by being specially designed to an specific software for material simulation.

With these limitations in mind, we decided to create a software that could calculate several correlation functions of materials, as well as the more interesting properties derived from these functions. While making the software accessible to as many people as possible.

Mathematical Background

Pair Distribution Functions

The structure factor is one of the most useful tools in analyzing the scattering patterns obtained from X-ray, electron and neutron diffraction experiments of crystalline, disordered and amorphous materials. The Fourier transform of the scattering intensity given by the structure factor $S(Q)$, yields the pair distribution function (PDF) $g(r)$ defined by:

$$G(r) = 4\pi\rho_0(g(r) - 1) = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1]\sin(Qr)dQ, \quad (1)$$

where $G(r)$ is the reduced pair distribution function (rPDF) which will be discussed next.

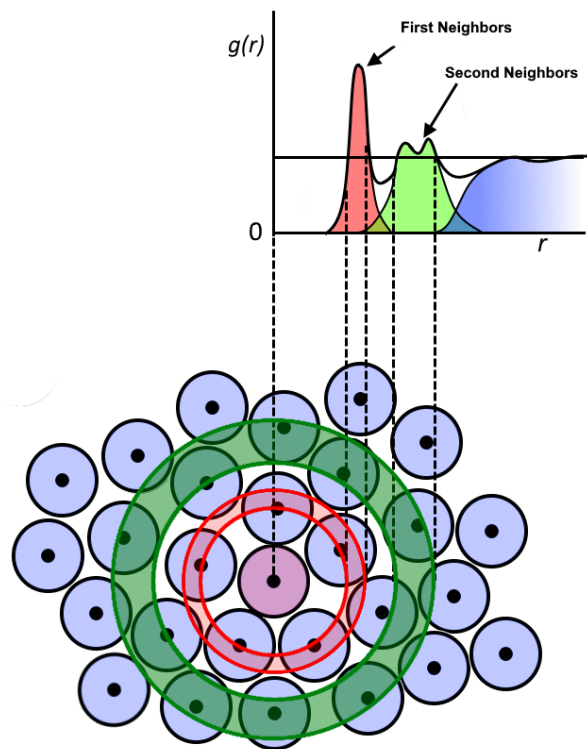


Figure 1: Schematic depiction of the first and second neighbor's coordination spheres for an amorphous metallic alloy and the corresponding pair distribution function. Design inspired by J. M. Ziman, *Models of disorder* (Cambridge University Press, 1979).

The pair distribution function could also be seen like a distance map inside the material, the $g(r)$ function gives how feasible is finding two atoms separated by the distance (r) as can be seen in Figure 1 (Ziman, 1979).

The PDF is normalized so that, as $r \rightarrow \infty$, $g(r) \rightarrow 1$. Also, as $r \rightarrow 0$ (for r shorter than the distance of the closest approach of pair of atoms), $g(r)$ becomes zero. The main advantage of the PDF and the related functions, is that they emphasize the short-range order of a material.

50 Reduced pair distribution function $G(r)$

51 One of the most widely used pair correlation function is the reduced pair distribution function.
 52 This is defined as $G(r) = 4\pi\rho_0(g(r) - 1)$. From this definition, and the previously discussed
 53 tendency at large r of the PDF, it's clear that the reduced pair distribution function (rPDF)
 54 oscillates around zero as $r \rightarrow \infty$. It also becomes evident that as $r \rightarrow 0$ (for r smaller than
 55 the closest pair of atoms), the rPDF behaves like $-4\pi\rho_0$.

56 While the PDF ($g(r)$) has an intuitive geometric definition, the rPDF ($G(r)$) can be directly
 57 obtained by a Fourier transform of the structure factor ($S(Q)$) as can be seen in [Equation 1](#);
 58 this close relation with the experimental data explains the popularity that this function has.
 59 Also, it has another advantage over other correlation functions [like PDF ($g(r)$)] as the nu-
 60 merical density $\rho_0 = N/V$ needs to be estimated in order to normalize the functions. This
 61 is not necessary in rPDF ($G(r)$); where this information is already contained in $G(r)$ as the
 62 slope of the function when $r \rightarrow 0$.

63 Radial distribution function $J(r)$

64 The last correlation function we shall discuss is also one of the most physically intuitive, the
 65 RDF, $J(r)$, which is related to the Pair Distribution Function (PDF) by:

$$J(r) = 4\pi r^2 \rho_0 g(r). \quad (2)$$

66 The RDF has the useful property that the quantity $J(r)dr$ gives the number of atoms in a
 67 spherical shell with inner radius r and thickness dr around every atom as depicted in [Figure 1](#).
 68 For example, the coordination number, or the number of neighbors (n_c), is given by:

$$n_c = \int_{r_1}^{r_2} J(r)dr, \quad (3)$$

69 where r_1 and r_2 define the RDF peak corresponding to the coordination shells in question.

70 Plane Angle Distribution

71 The use of higher order correlation functions to analyze the structure of liquids and amorphous
 72 solids has been proposed in the literature ([Galvan-Colin et al., 2016](#); [Hafner, 1982](#)), trying to
 73 reproduce the success obtained by Bernal in the analysis of the structure of liquids ([Bernal,](#)
 74 [1964](#)).

75 In particular, the Plane Angle Distribution, also known as the Bond Angle Distribution $f(\theta)$ has
 76 been used to characterize the short-range order of amorphous and liquid structures ([Galvan-](#)
 77 [Colin et al., 2016](#); [Galván-Colín et al., 2015](#); [Mata-Pinzón et al., 2016](#)). Here we propose to
 78 substitute the term "Bond Angle Distribution" (BAD), by the term "Plane Angle Distribution"
 79 (PAD), also frequently used, since in condensed matter, proximity does not necessarily imply
 80 bonding.

Benchmarks

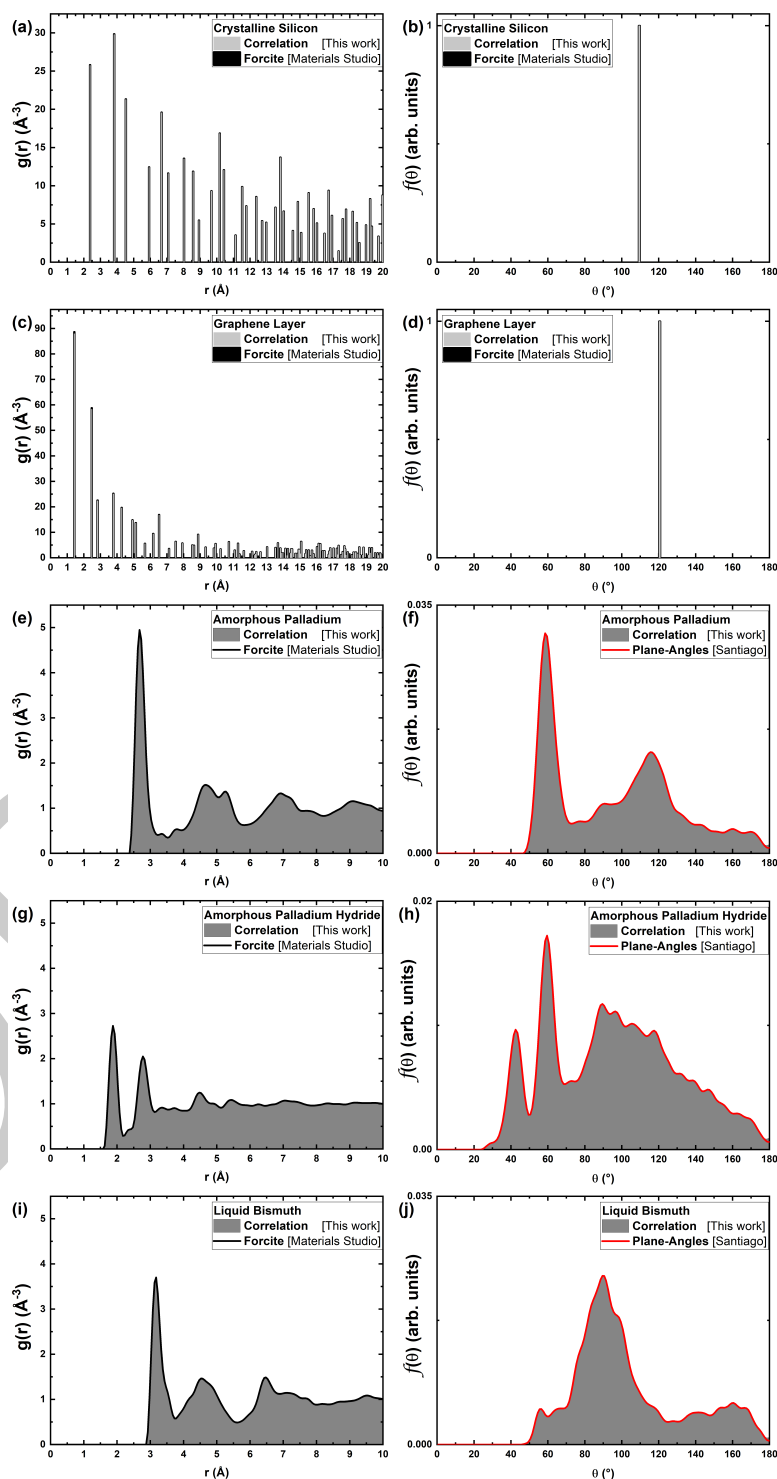


Figure 2: Pair Distribution Functions $g(r)$ on the left, Plane Angle Distributions on the right for: crystalline silicon, graphene Layer, amorphous palladium, amorphous palladium hydride and liquid bismuth. Correlation in gray, Forcite in black, Plane Angles in red. Similarity is remarkable between **Correlation** and Forcite as can be seen in all PDFs. Figures (a) to (d) indicate that the coincidence in the two results overlap completely.

In order to assess the performance of **Correlation**, we calculated the PDF and PAD for two well known structures (Crystalline Silicon and a Graphene Layer), and compared the results with the commercially available software Forcite included in the Materials Studio suite ([Materials Studio 2016](#), 2016); to test **Correlation** in amorphous and liquid materials we selected amorphous palladium ([Rodríguez et al.](#), 2019), amorphous palladium hydride ([Rodríguez](#), 2019) and liquid bismuth. Because of the complexity to calculate PAD of amorphous and liquids in Forcite, we chose to compare them with the code developed by U. Santiago within our group. ([Santiago](#), 2011).

The results of these benchmarks are shown in [Figure 2](#), and the structures used to calculate these figures are included in the code as tests 1 to 5. The last structure included as test 6 is a 2x2x2 supercell of amorphous palladium hydride included in test 4, to benchmark memory and CPU performance in a structure with thousands of atoms.

Conclusion & Perspective

Correlation is a lightweight, modular software that can be used in HPC and adapted to analyze the main correlation functions used to characterize: crystalline, amorphous solids and liquids.

Correlation software has been used in previously published work ([Galvan-Colin et al.](#), 2016; [Galván-Colín et al.](#), 2015; [Mata-Pinzón et al.](#), 2016) as well as several PhD Theses ([Galvan-Colin](#), 2016; [Mata-Pinzón](#), 2016; [Mejía-Mendoza](#), 2014; [Rodríguez](#), 2019; [Romero-Rangel](#), 2014; [Santiago](#), 2011) developed in our group. We will continue to support and enrich the software in the foreseeable future. We are open to receive suggestions that would further improve the functionality of the software. Address all comments and observations to the first author, I.R: isurwars@ciencias.unam.mx

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