The Peak Shape of the Pair Distribution Function

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Significant progress in X-ray and neutron diffraction experiments on powder samples has been achieved in recent years. High-resolution data nowadays make the comparison of theoretical calculations with experimental measurements to a higher degree of accuracy. Because of this, small systematic errors that were ignored before can lead to the noticeable disagreement that can now be observed.

It was shown [1] that in measurements of Pair Distribution Function (PDF) from powder samples, the positions of the peaks shifted and that the measured atomic distances are bigger then the actual one. It was also shown that the shape of the peaks is not gaussian as it often assumed. It was also pointed out that effect is relatively small.

Here we present further developments of the work [1]. We have derived an approximate expression for the non-gaussian peak shape. It is the most probable to see this effect in highly anisotropic materials. Estimates for the relative size of the effect were made. In some special cases this is a significant correction, but usually it is not.

1

We calculated the Radial Distribution Function (RDF) for buckyball and benzene molecules using the Gaussian98 [2] program with AM1 and SNDO semi-empirical methods. Due to the highly anisotropic structure of those molecules one could expect that it will be possible to see in their RDF non-Gaussian behavior of the peaks. However it was shown that effect is very small for buckyballs. For the benzene molecule, the effect is quite large for one peak.

Using the calculated results for the radial distribution function we calculated pair distribution function of the fullerite crystal, and a comparison with the experiment resulta of Billinge, Petkov and Yavas was made. The role of the finite resolution measurements of experiment is discussed. It is shown that correction to the theoretical calculations due to the finite resolution of the measurements significantly improves the agreement with experiment.

Non-Gaussian Peak Shape of Pair Distribution Function

Let suppose that we consider a crystal and the equilibrium position of an atom i is $\vec{r}_i = (x_i, y_i, z_i)$ with respect to the "center" atom. Atoms vibrate near their equilibrium positions. The probability that the atom i will be found at position $\vec{r} = (x, y, z)$ is given by

$$P(x, y, z) = \frac{1}{\sqrt{(2\pi)^3 \sigma_x^2 \sigma_y^2 \sigma_z^2}} \exp\left(-\frac{(x - x_i)^2}{2\sigma_x^2} - \frac{(y - y_i)^2}{2\sigma_y^2} - \frac{(z - z_i)^2}{2\sigma_z^2}\right)$$

Coordinates $\vec{r}_i = (x_i, y_i, z_i)$ and $\vec{r} = (x, y, z)$ are given in the frame of principal axes, where the matrix of displacements $\langle u_\alpha u_\beta \rangle$ is diagonal ($\vec{r} = \vec{r}_i + \vec{u}$).

We want to find the $P(r)$ for a highly anisotropic

($\sigma_x \neq \sigma_y \neq \sigma_z$) powder materials.

Earlier, when PDF was calculated, it was assumed that $\sigma_x = \sigma_y = \sigma_z = \sigma$ and that

$$P_{gauss}(r) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(r - r_i)^2}{2\sigma^2}\right)$$

Nowadays when experimental techniques for PDF measurement was improved significantly one can expect to see the difference between measured PDF and the PDF $P_{ngauss}(r)$ calculated under assumption above.
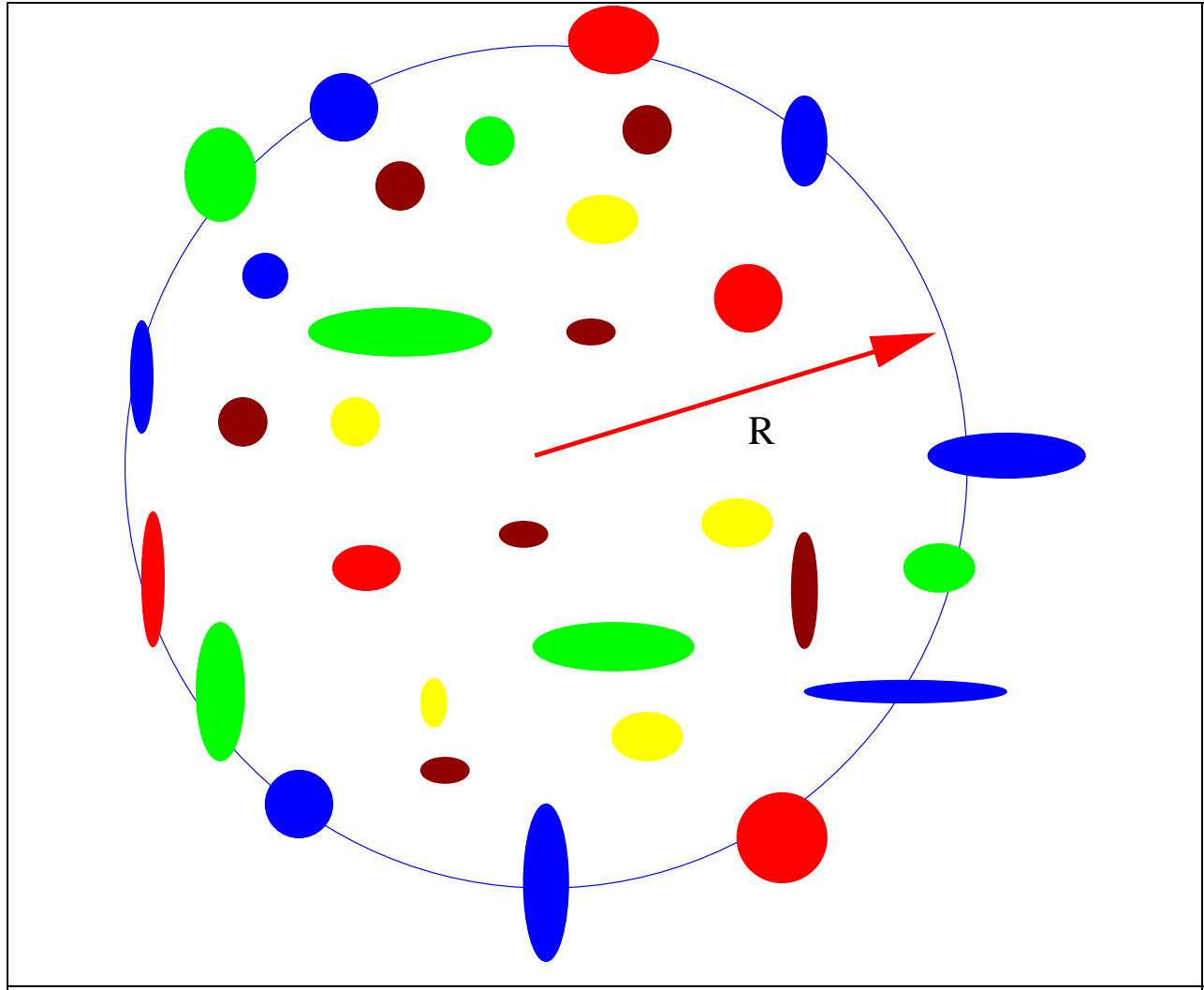
Performing of angular average is equivalent to the finding the mass that is lying on the sphere of radius R. On average due to vibrations the mass of every atom is distributed with some probability over its own ellipse. It was shown that the mass distribution in every ellipse is the product of the three gaussians in Cartesian coordinates. The sphere of radius R cuts the ellipses in a way that depends on the ellipse position and orientation.

To find PDF of higly anisitropic powder meterials one should perform the angular average:

1)

$$P(r) = r^2 \int \frac{1}{\sqrt{(2\pi)^3 \sigma_x^2 \sigma_y^2 \sigma_z^2}} \exp\left(-\frac{(x-x_i)^2}{2\sigma_x^2} - \frac{(y-y_i)^2}{2\sigma_y^2} - \frac{(z-z_i)^2}{2\sigma_z^2}\right) d\Omega$$

It is easy to show that in isotropic case when ($\sigma_x = \sigma_y = \sigma_z = \sigma$) this average leads to (exact result):

$$P_{iso}(r) = \frac{1}{\sqrt{2\pi\sigma^2}}\left(\frac{r}{r_i}\right)\left\{\exp\left(-\frac{(r-r_i)^2}{2\sigma^2}\right) - \exp\left(-\frac{(r+r_i)^2}{2\sigma^2}\right)\right\} \cong \frac{1}{\sqrt{2\pi\sigma^2}}\left(\frac{r}{r_i}\right)\exp\left(-\frac{(r-r_i)^2}{2\sigma^2}\right)$$

This result can be rewritten as:

$$P_{iso}(r) \cong \frac{1}{\sqrt{2\pi\sigma^2}}\exp\left(-\frac{(r-r_i)^2}{2\sigma^2}\right)\left(1 + \frac{r-r_i}{r_i}\right).$$

(D.A.Dimitrov et al. [1]).

If the peaks are narrow the difference between $P_{gauss}(r)$ and $P_{ngauss}(r)$ is small. But there is a possibility that in high quality measurements this difference can be seen and $P_{ngauss}(r)$ can give better agreement between theory and experiment then $P_{gauss}(r)$.

In anisotropic case ($\sigma_x \neq \sigma_y \neq \sigma_z$) difference between real peak shape and its gaussian approximation can be even bigger. We derived approximate expression (expansion) for the peak shape in anisotropic

case. In many cases this expression gives significantly better agreement with real shape then former gaussian approximation.
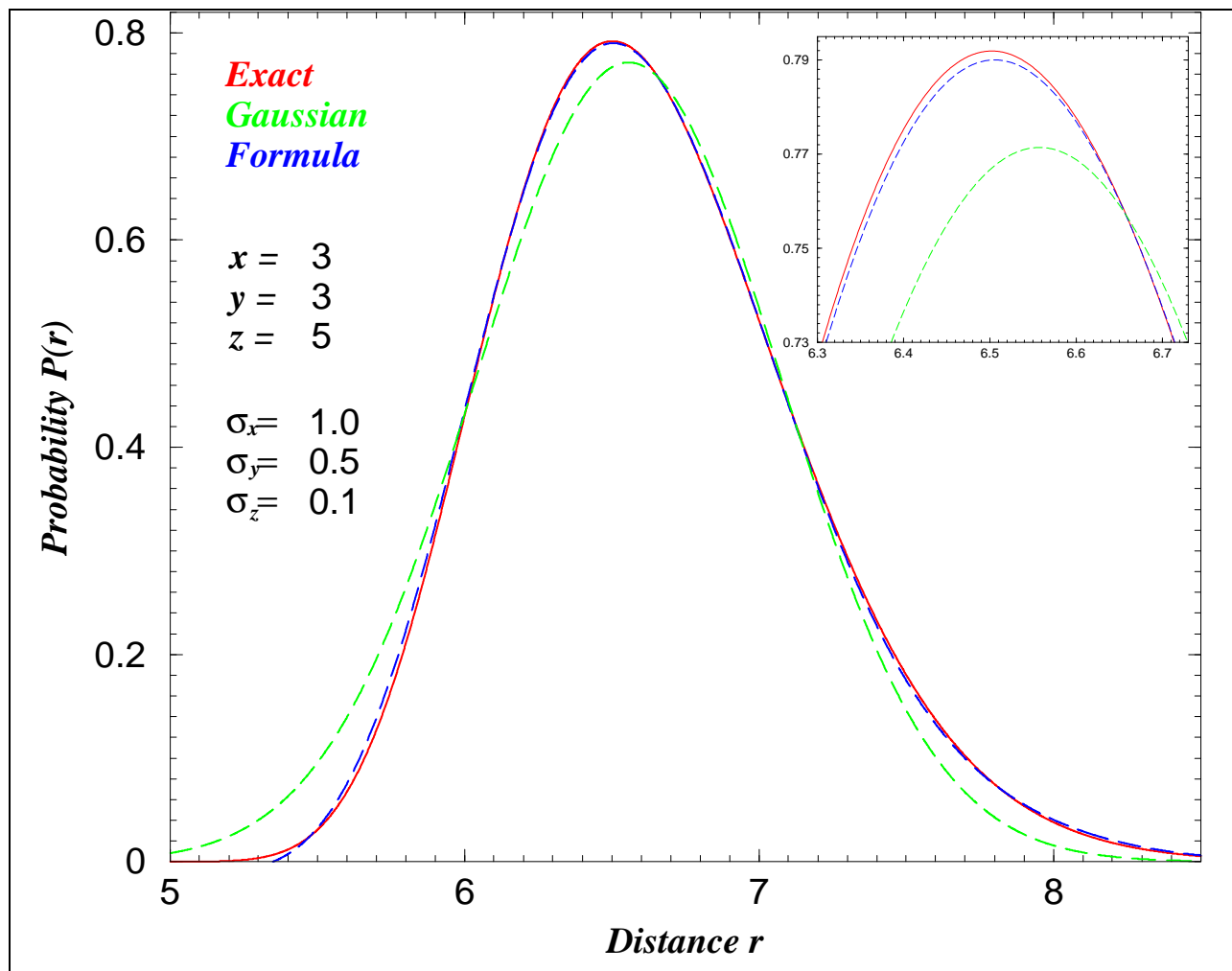
Summary of derived formulas

2) $P^i_{ngauss}(r) = \dfrac{1}{\sqrt{2\pi\Sigma^2}} \exp\left(-\dfrac{(r-r_i)^2}{2\Sigma^2}\right)\left[1 + \left(\dfrac{\Sigma}{r_i}\right)\Psi(r)_1 + \left(\dfrac{\Sigma}{r_i}\right)^2 \Psi_2(r)\right]$

$\Psi_1(r) = a_1 f_1(r) + a_3 f_3(r)$ $\qquad \Psi_2(r) = a_2 f_2(r) + a_4 f_4(r) + a_6 f(r)$

$f_n(r) = 2^{-\frac{n}{2}} H_n\left(\dfrac{r}{\sqrt{2}\Sigma}\right)$ $\qquad \Sigma^2 = \dfrac{x^2\sigma_x^2 + y^2\sigma_y^2 + z^2\sigma_z^2}{x^2 + y^2 + z^2}$

$a_i = a_i\left(x, y, x, \sigma_x, \sigma_y, \sigma_z\right)$

It follows from the formulas above that the biggest deviations from the gaussian peak shape should occur in case of strong anisotropic materials. The further is the peak from the origin the better our approximation works. On another hand the best resolution is usually achieved on the first peak that is the closest to the origin.

Examples

Exact curve is obtained by direct numerical integration of (1).

Gaussian curve is the curve that represents the exponential part of the derived formula without correction terms in brackets. This corresponds to the approximation that was used before.

Formula curve shows the approximation of exact curve given by (2).
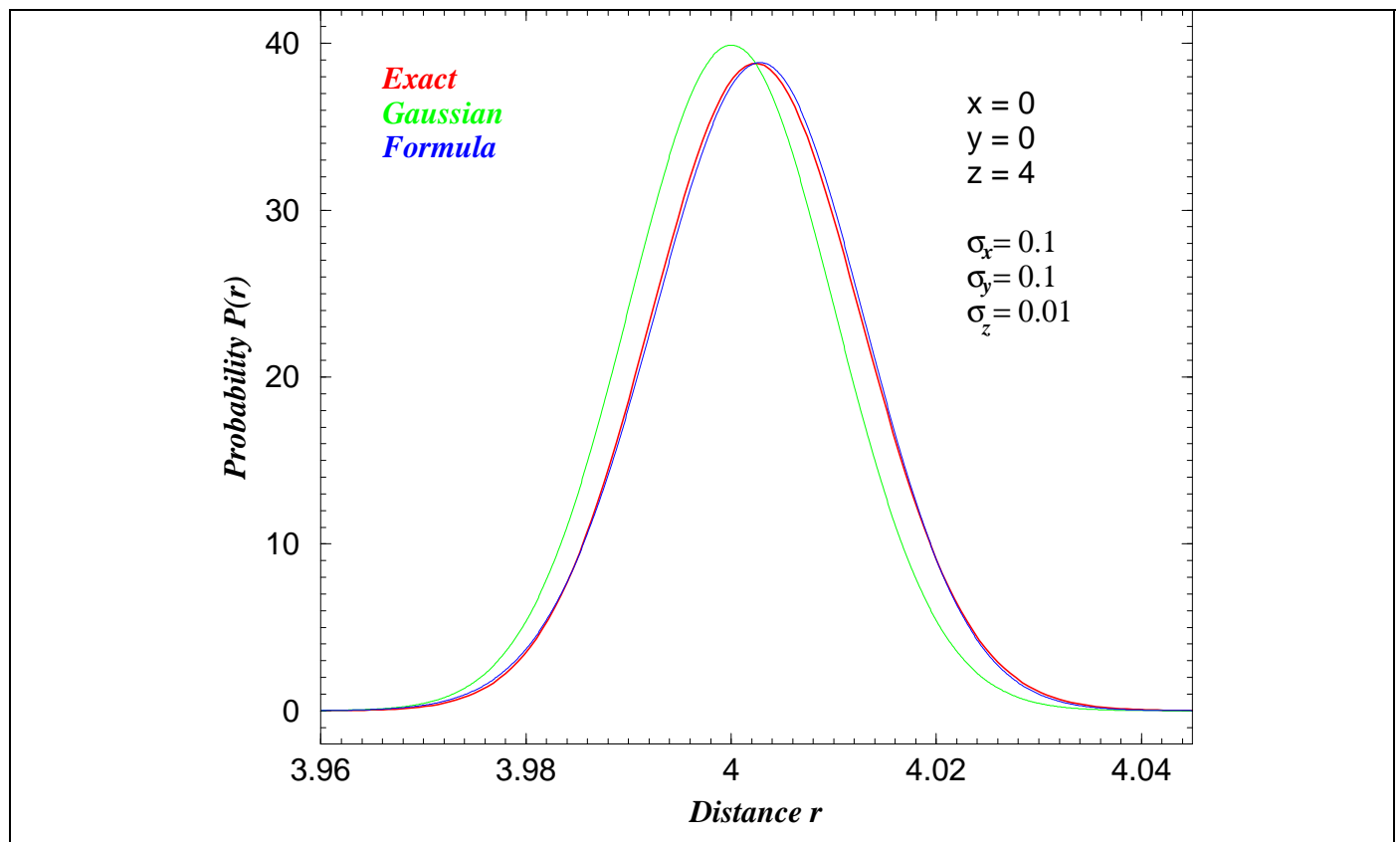
Non-Gaussian Peak Shape of Anisotropic Molecules

Simple way to check how important the corrections to the previously used gaussian line shape are is to calculate Radial Distribution Function (RDF) and PDF of anisotropic molecules. In fact all molecules are anisotropic and that difference between molecules and crystalline solids is very important for our case. We consider molecules of fullerene and benzene.
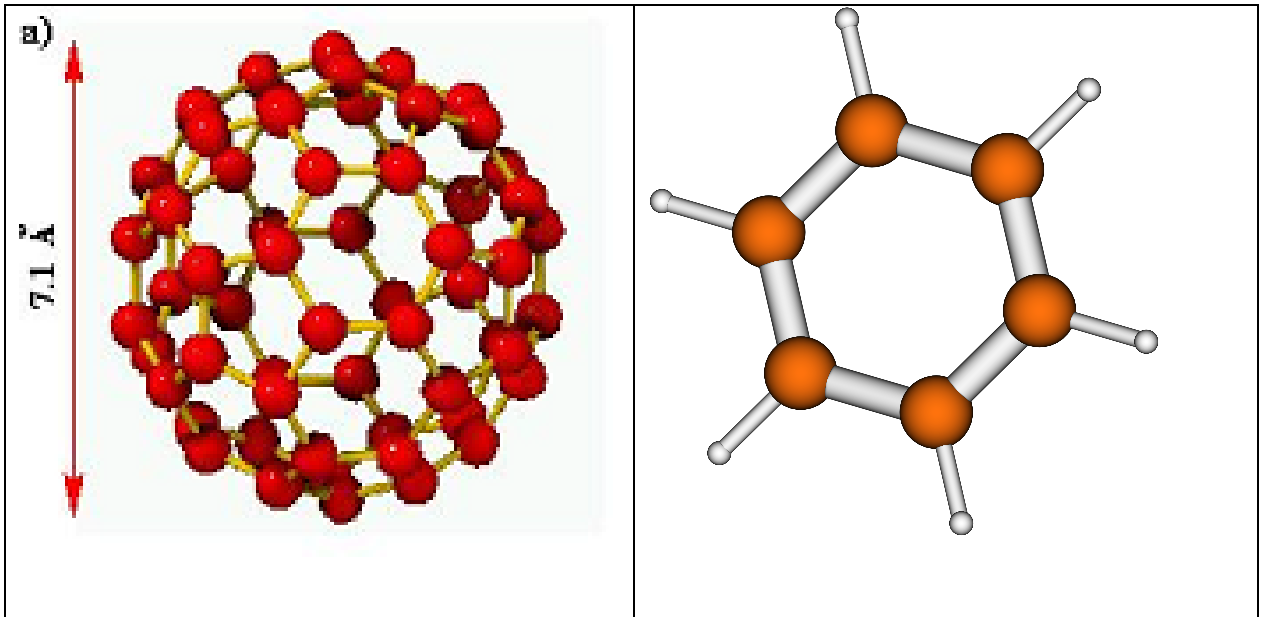
One can expect that in fullerene the vibrations of the carbon atoms in direction parallel and perpendicular to the surface have significantly different amplitudes. The same can be true for in plane and out of plane atomic vibrations in benzene.

In order to calculate the RDF of the molecules we have to calculate average (relative) displacements of the atoms ($\sigma_x, \sigma_y, \sigma_z$) due to their vibrations. The matrix of (relative) average displacements U_{xy} can be calculated if the eigenfrequencies and eigenvectors of molecular vibrations are known. Our derivation shows that:

$$\left\langle \left(u_i - u_j\right)_\alpha \left(u_i - u_j\right)_\beta \right\rangle = \sum_\lambda \frac{\hbar}{\omega_\lambda}\left(n_\lambda + \frac{1}{2}\right)\left(\frac{e_{i\alpha}^\lambda e_{i\beta}^\lambda}{m_i} + \frac{e_{j\alpha}^\lambda e_{j\beta}^\lambda}{m_j} - \frac{e_{i\alpha}^\lambda e_{j\beta}^\lambda}{\sqrt{m_i m_j}} - \frac{e_{j\alpha}^\lambda e_{i\beta}^\lambda}{\sqrt{m_i m_j}}\right)$$

Where $\langle(u_i - u_j)_\alpha (u_i - u_j)_\beta \rangle$ is the matrix of relative atomic displacements.

ω_λ are the frequencies of molecular vibrations. $e_{i\alpha}^\lambda$ are orthogonal and normalized Cartesian (α) components of the atomic i displacements that correspond to the eigenfrequncy ω_λ. m_i is the mass of atom i and Bose-Einstein distribution function.

The matrix of atomic displacements can be diagonalized and its eigenvalues are the squares of $\sigma_x, \sigma_y, \sigma_z$. Then the coordinates of the atoms in the frame where U_{xy} is diagonal can be found. After that the application of out formulas is straightforward.
In order to calculates eigenfrequencies and eigenvectors of molecules vibrations we used Gaussian98 program and two semi empirical methods: AM1 and CNDO.

In the tables below we show the values of coordinates and average atomic displacements for the several nearest atoms for the molecules of fullerene and benzene.

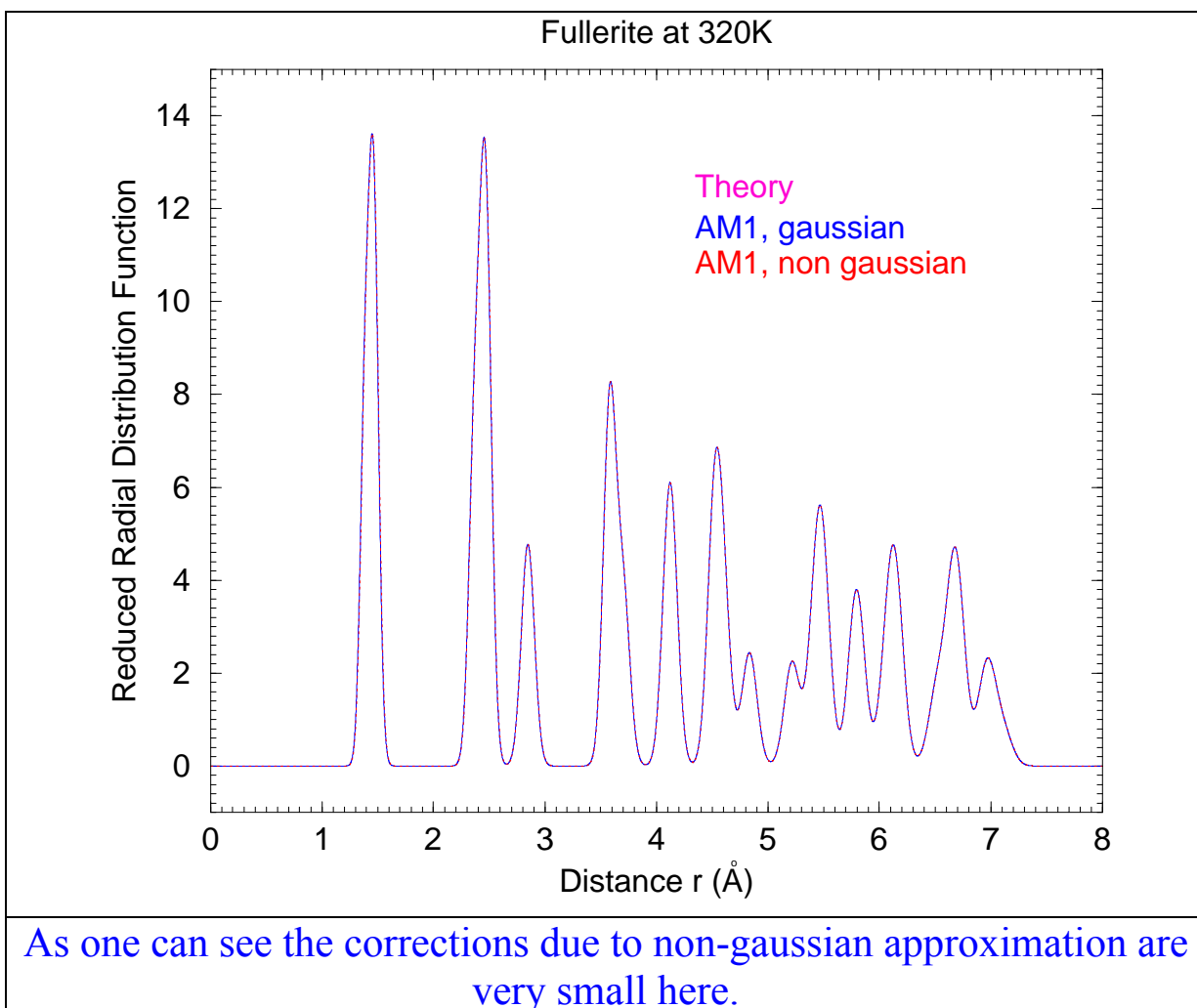Fullerene at 320K. All distances are in angstroms.

R	1.384646		
x, y, z	2.5638377E-03	6.5836781E-03	1.384628
$\sigma_x, \sigma_y, \sigma_z$	5.2550513E-02	6.6601180E-02	4.1193563E-02
R	1.464106		
x, y, z	-1.464053	-1.0683392E-02	6.3597430E-03
$\sigma_x, \sigma_y, \sigma_z$	4.4662178E-02	5.0684605E-02	6.5412231E-02
R	1.464106		
x, y, z	-1.3223997E-03	1.464032	1.4654270E-02
$\sigma_x, \sigma_y, \sigma_z$	5.0589468E-02	4.4681683E-02	6.5730289E-02

Benzene at 300K. All distances are in angstroms (From Carbon)

R to H	1.099661		
x, y, z	-7.4287732E-07	1.099661	0.0000000E+00
$\sigma_x, \sigma_y, \sigma_z$	0.1419376	9.4040588E-02	0.1980861

R to C	1.395030		
x, y, z	-3.0353773E-05	1.395030	0.0000000E+00
$\sigma_x, \sigma_y, \sigma_z$	3.6183592E-02	3.1343620E-02	3.0343700E-02
R to H	2.165508		
x, y, z	-1.901419	1.036354	0.0000000E+00
$\sigma_x, \sigma_y, \sigma_z$	0.1136719	0.1418967	0.2111952
R to C	2.416264		
x, y, z	-2.416264	3.0265868E-05	0.0000000E+00
$\sigma_x, \sigma_y, \sigma_z$	3.6252398E-02	2.9739901E-02	2.7127609E-02

One can see that it is the most probable to see the first peak in benzene since it is close to the origin and it is caused by the most anisotropic vibrations of the nearest hydrogen atom.

Fullerite at 320K

Theory
AM1, gaussian
AM1, non gaussian

As one can see the corrections due to non-gaussian approximation are very small here.

Pair Distribution Function Of Fullerite Crystal

In order to make the comparison with experiment one should calculate the Pair Distribution Function (PDF) defined as:

$$G(r) = 4\pi r \left[\rho(r) - \rho_o \right]$$

ρ_o is the average density of the material it is equal to zero for the case of a single isolated molecule. The $\rho(r)$ obeys normalization condition:

$$N(R) = \int_0^R 4\pi r^2 \rho(r) dr$$

Where $N(R)$ is the number of atoms inside the sphere of radius R. Thus for the single molecule we have:

$$G(r) = 4\pi r \left[\frac{1}{4\pi r^2} \sum_i P_{new}^i(r) \right] = \frac{1}{r} \sum_i Z_o Z_i P_{new}^i(r)$$

P_{new}^i is the new derived function that should substitute old gaussian approximation. In case of X-ray scattering Z_o and Z_i stand for the number of electrons in the cental atom and atom i. The same function can be plotted for the old gaussian approximation in assumption that $\sigma = \Sigma$.

Next two pictures show the calculated $G(r)$ for the case of fulleren and benzen.

One can see that the role of the corrections in case of C_{60} is very small.

In case of benzene there is significant effect that corresponds to the Carbon-Hydrogen peak. Unfortunately the intensity is smaller then intensity of Carbon-Carbon Peaks.

Benzene C$_6$H$_6$, T=300K
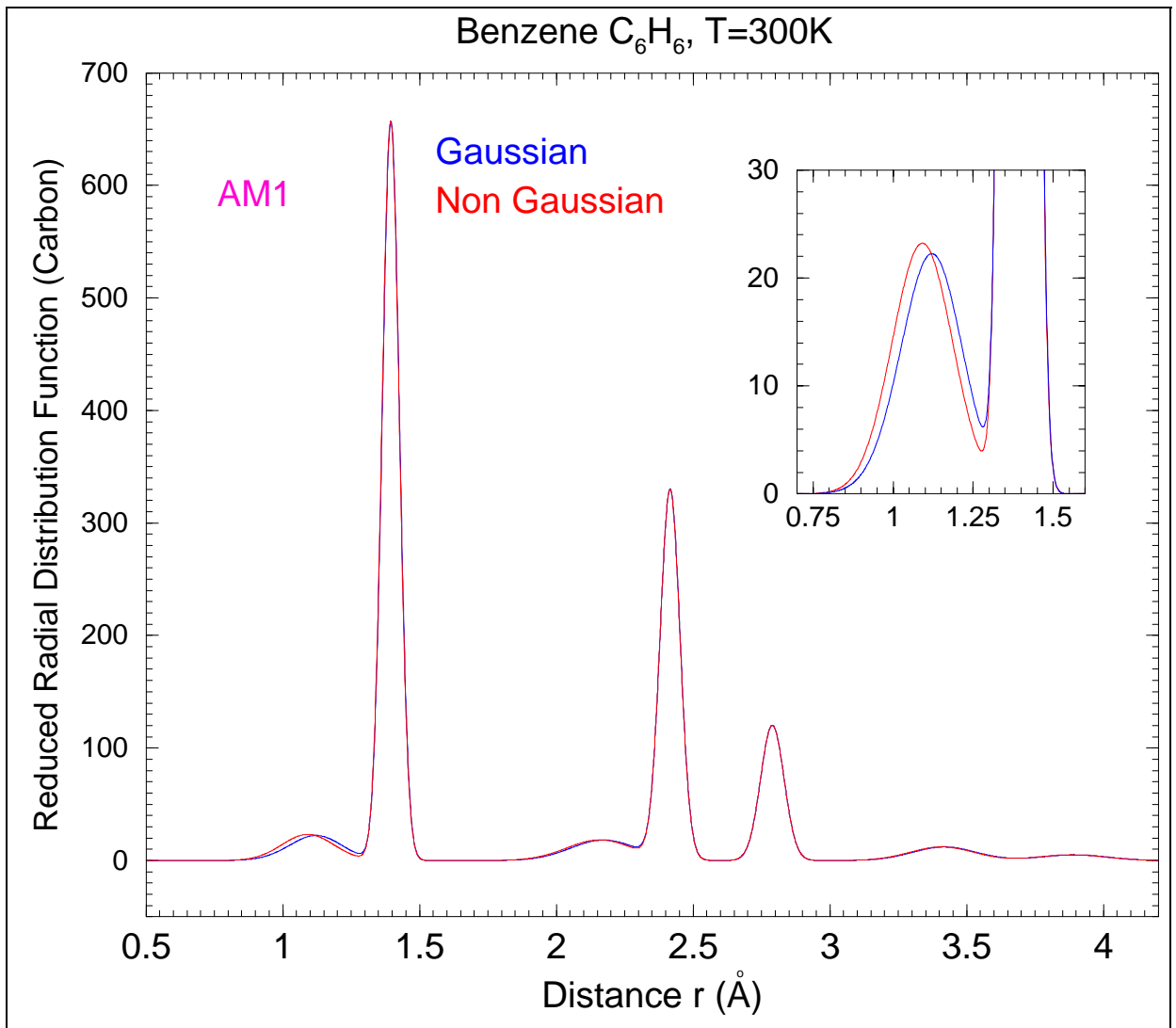
Here the corrections due to non-gaussain approximation are bigger, but they are related to the small first peak. Hydrogen is one of the atoms that cause the first peak. That is why it should be hard to measure in the X-ray diffraction experiments.

Pair Distribution Function of the Fullerite Crystall.

The molecules of fulleren form fcc crystal. At 320 K molecules rotales around there centers.
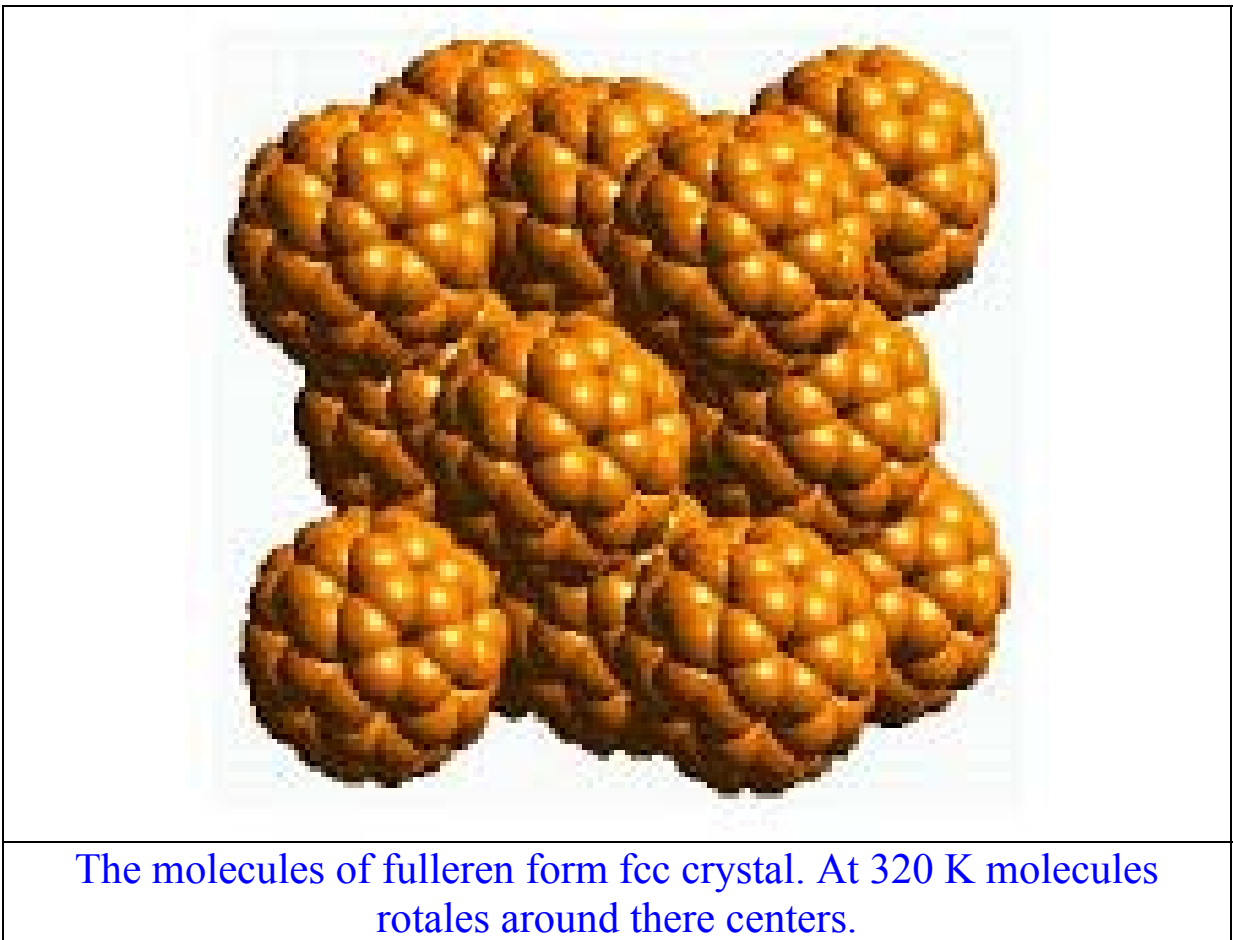
It is important to compare the results of out calculations with the experimental measurements [3].

Let suppose that we sit on a particular atom that belongs to some of the fullerene molecules. Then we can see that atoms that belong to the same molecule as the atom on which we are sitting are in more or less fixed positions with respect to us. On another hand due to the rotations of fullerene molecule we see the smooth distribution of the atoms mass over the surfaces of the others molecule.

Thus the contribution to $\rho(r)$ from the other molecules can be modeled as the RDF of two spherical shells with continuous distribution of mass.
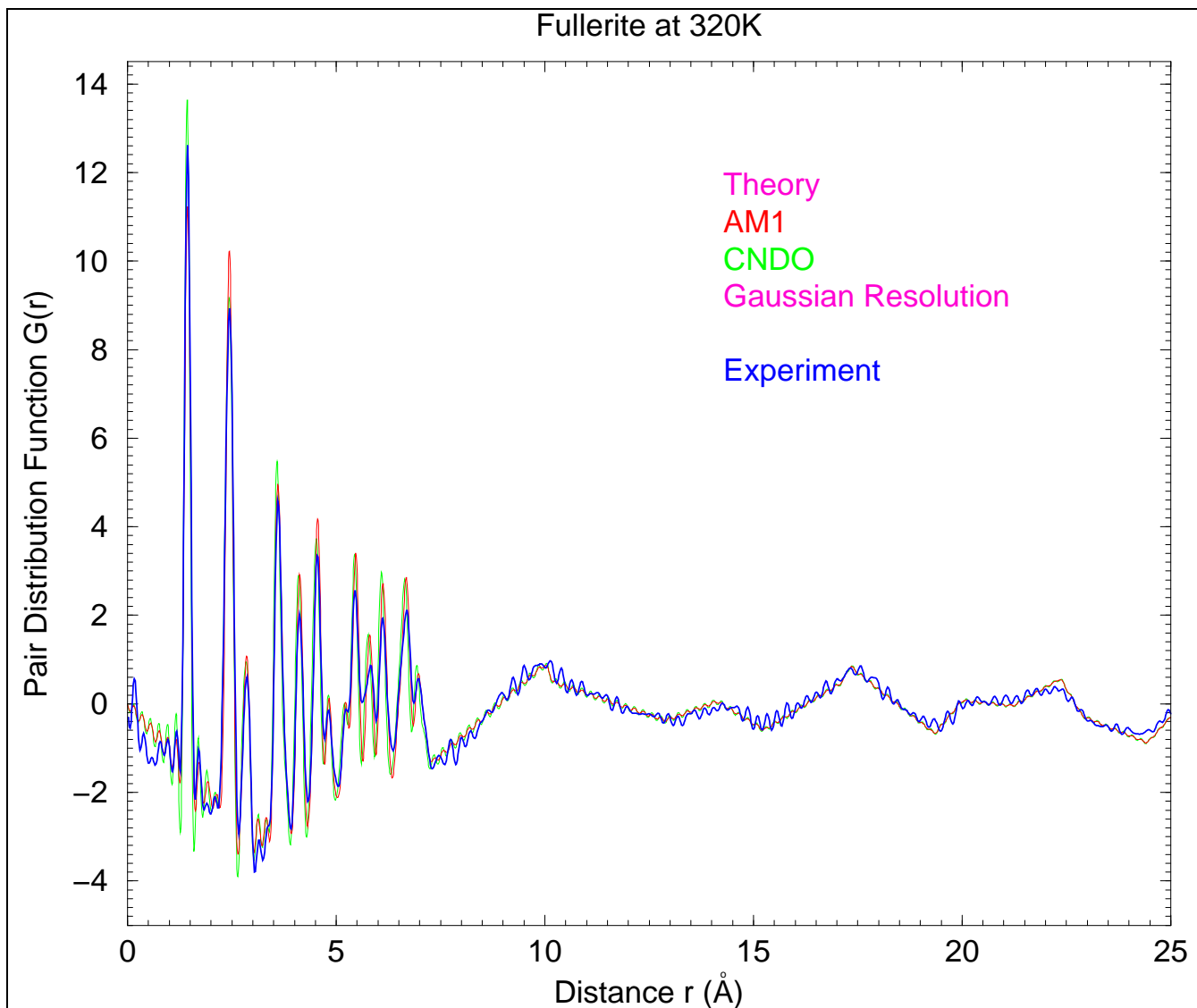
Thus $\rho(r)$ consist of two parts contribution from the atoms in the same molecule $\rho_{mol}(r)$ and contribution from the others molecules (correlations) $\rho_{corr}(r)$.

$$\rho(r) = \rho_{mol}(r) + \rho_{corr}(r)$$

I discussed above only the first contribution. For the details of second contribution you can to the M.Lei's poster.
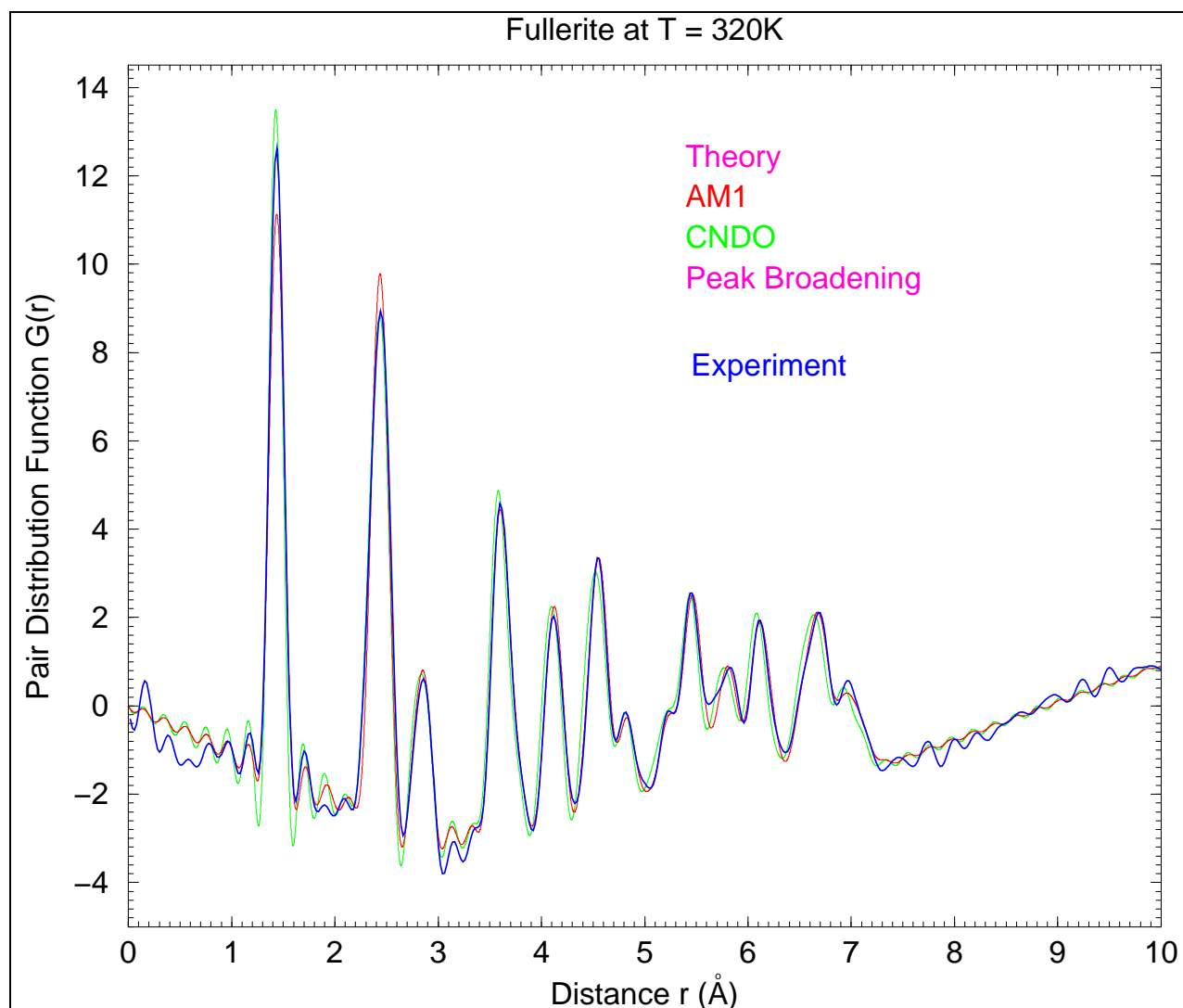
PDF of the fullerite.

Fullerite at 320K

Fullerite at 320K
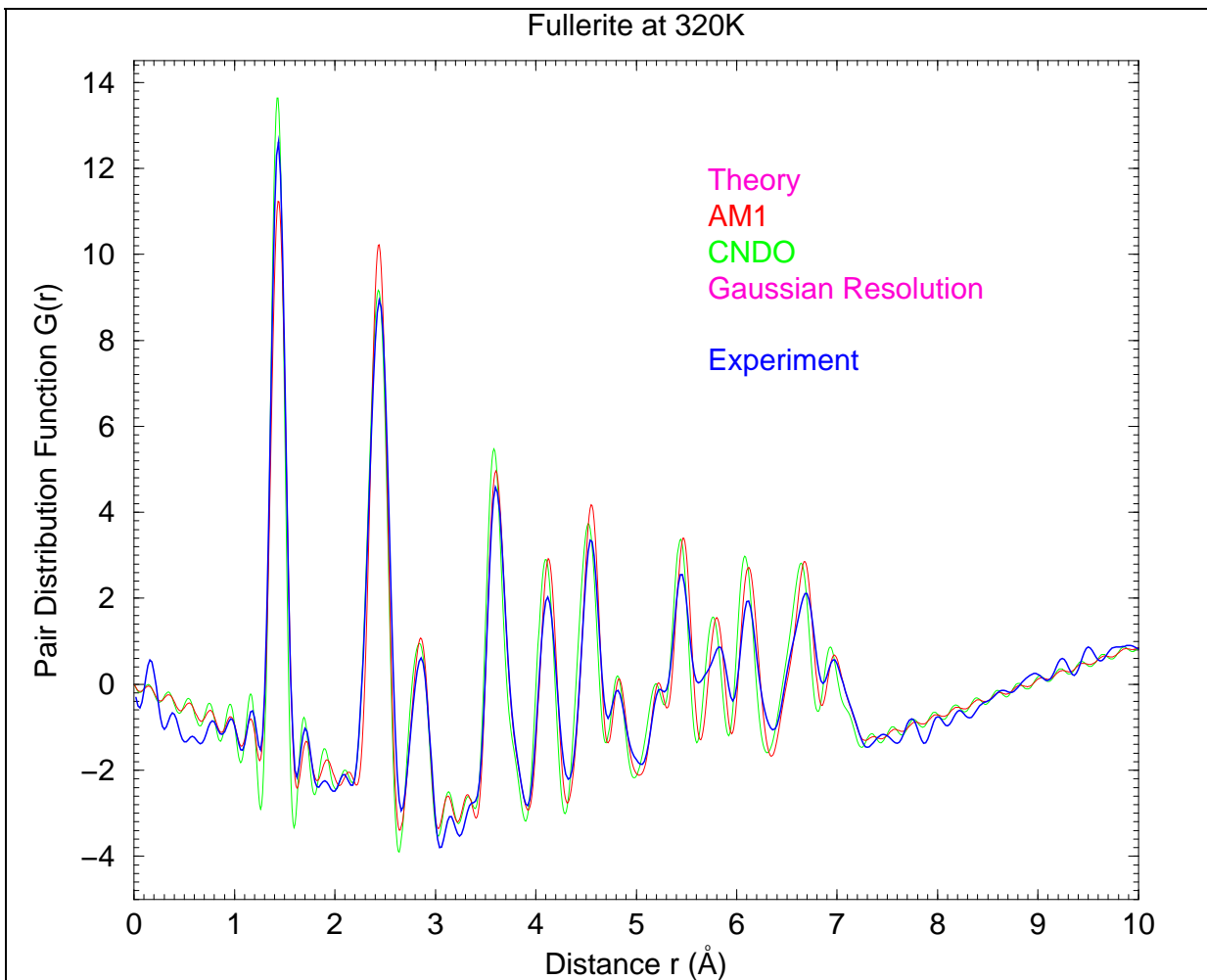
The agreement on the pictures above can be improved if one will take into account the finite resolution in experimental measurements of the scattering intensity.

The Pair Distribution Function of Fullerite with correction to the finite resolution in the measurements of scattering intensity.

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