The Shape of the
Pair Distribution Function.

Valentin Levashov and M.F. Thorpe
Department of Physics & Astronomy and
Center for Fundamental Materials Research
Michigan State University

Significant progress in high-resolution diffraction experiments on powder samples has been achieved in recent years. We present some new developments of theoretical methods for the calculation of the pair distribution function that gives improved agreement with experiment.

The role of the experimental resolution function in pair distribution calculations will be discussed; together with a comparison with high-quality measurement on lead.

An approximate expression for the non-Gaussian peak shape that should be observed in the pair distribution function in highly anisotropic powder materials is derived.
Finally we discuss the importance of including all multi-phonon processes in the comparison of theoretical models with experimental results.

The role of the experimental resolution function in pair distribution calculations

Experimental PDF:

$$G(r) = \frac{2}{\pi} \int_0^\infty q[S(q)-1]\sin(qr)dq \qquad q[S(q)-1] = \int_0^\infty G(r)\sin(qr)dr$$

$$S(q) = \frac{I(q)}{Nf^2}, \quad I(q) = \left| \sum_i^N f(q)e^{i\vec{q}\vec{r}_i} \right| \quad \text{Scattering intensity, } f(q) \text{ atomic form factor.}$$

$G(r)$ is not an exact Fourier transformation of $q[S(q)-1]$ since the data in experiment can be collected only over a finite scattering momentum range $[0, Q_{max}]$.

There is finite resolution in experimental measurements of $I(q)$.

Theoretical PDF:

$$G(r) = 4\pi r \left[\frac{1}{4\pi r^2} \sum_i \left\{ \frac{\exp\left(-\frac{(r-r_i)^2}{2\sigma_i^2}\right)}{\sqrt{2\pi\sigma_i^2}} \right\} - \rho_o \right]$$	This form does not take into account finite resolution and finite scattering momentum range in experimental measurements. The correction to the theoretical PDF due to finite range can be made through convolution function (was made before).

Two peaks in experimental $S(q)$ can be resolved as separate peaks if the distance between them is bigger then $\sigma(q)$. The proposed form for experimental resolution function is:

$$F(q,q') = \frac{1}{\sqrt{2\pi\sigma_{q'}^2}}\exp\left(-\frac{(q-q')^2}{2\sigma_{q'}^2}\right) \qquad \sigma_{q'} = \delta q'$$

Then:

$$S_c(q) = \int S(q')F(q,q')dq'$$

It is assumed here that $S(q')$ is pure theoretical intensity and $S_c(q')$ is intensity that can be compared with experimental measurements.
Let:

$$S_c(q) = \int F_c(r) e^{iqr} dr \qquad\qquad S(q') = \int F(r) e^{iq'r} dr$$

Then it can be shown that:

$$F_c(r) = \int F(r') C(r,r') dr' \qquad\qquad C(r,r') = \frac{1}{\sqrt{2\pi r^2 \delta^2}} e^{-\frac{(r-r')}{2r^2\delta^2}}$$

Now if we assume that every atom brings its own gaussian into the $G(r)$ then this gaussian should be transformed according to:

$$F(r) = \frac{1}{\sqrt{2\pi\sigma_i^2}} \exp\left(-\frac{(r-r_i)^2}{2\sigma_i^2}\right) \;\rightarrow\; F_c(r) = \int F(r') C(r,r') dr' = \frac{1}{\sqrt{2\pi(\sigma_i^2 + \delta^2 r^2)}} \exp\left(-\frac{(r-r_i)^2}{2(\sigma_i^2 + \delta^2 r^2)}\right)$$

Thus the wideness of the peaks in $F_c(r)$ is increases with r compare with the case of $F(r)$. But since peaks are narrow one can substitute $\sigma_i^2 + \delta^2 r^2$ with $\sigma_i^2 + \delta^2 r_i^2$.

The final expression for pair distribution function has the form:

$$G_c(r) = 4\pi r\left[\frac{1}{4\pi r^2} \sum_i \left\{\frac{\exp\left(-\frac{(r-r_i)^2}{2(\sigma_i^2 + \delta^2 r_i^2)}\right)}{\sqrt{2\pi(\sigma_i^2 + \delta^2 r_i^2)}}\right\} - \rho_o\right]$$

In order to take into account the finite range of momentum over which scattering intensity $I(q)$ was measured it is also necessary to convolute this expression with convolution function.

Finally:

$$G_{exp}(r) = \frac{1}{\pi} \int_0^\infty G_c(r')\left[\frac{\sin\{q_{max}(r-r')\}}{r-r'} - \frac{\sin\{q_{max}(r+r')\}}{r+r'}\right] dr'$$

We compare the results of our calculations with results of high quality measurements on lead. In order to obtain theoretical PDF at a particular temperature it is necessary to calculate σ_i. Calculations were performed in the frame of Kirkwood model. The method of calculation was discussed earlier (1).

Comparison with Experiment.

The parameters were chosen in order to obtain the best agreement on the forth figure.

Thus first three figures shows how the agreement increases when the effects of finite range and finite resolutions are included separately and when they are included together.

The red curve on all figures represents the results of experiment. This curve is the same on all four figures.
The blue dotted curves shows the results of calculations when different effects like finite range of interaction or finite resolution or both are taken into account.

Yes-means: were taken into account
No-means: were not taken into account

	Fig. 1	Fig. 2	Fig. 3	Fig. 4
Finite range	No	Yes	No	Yes
Finite resolution	No	No	Yes	Yes

Fig. 3

Fig. 4
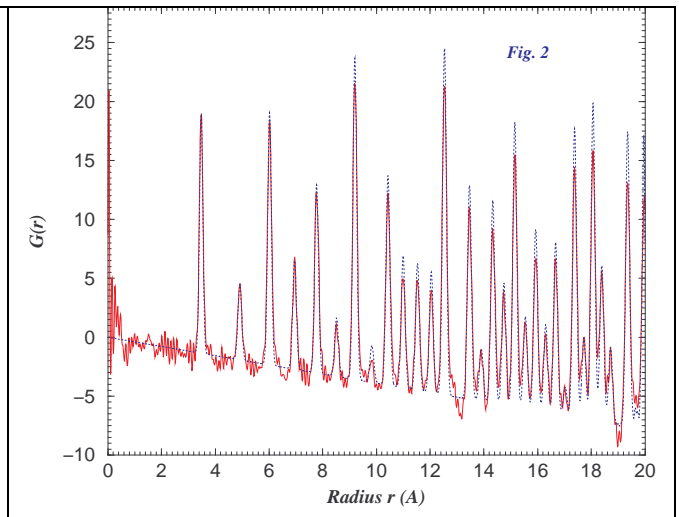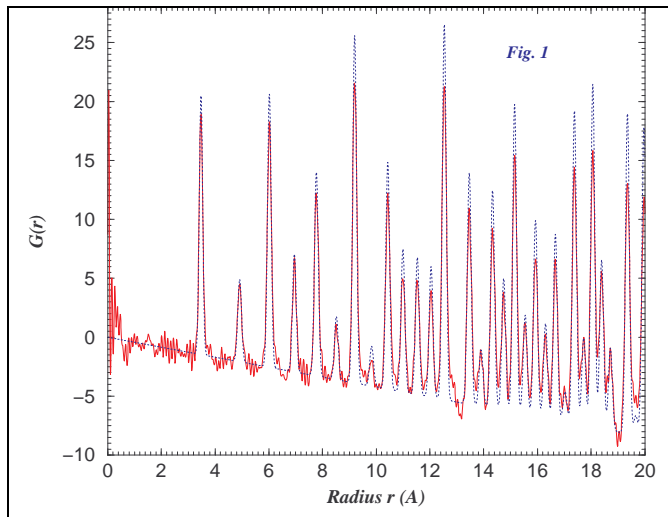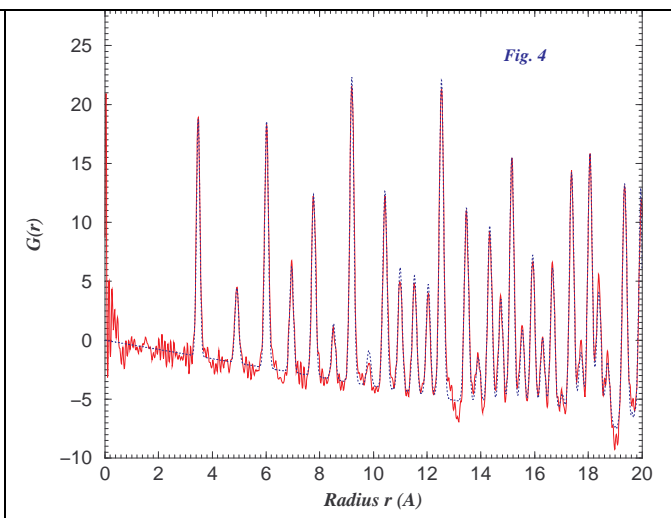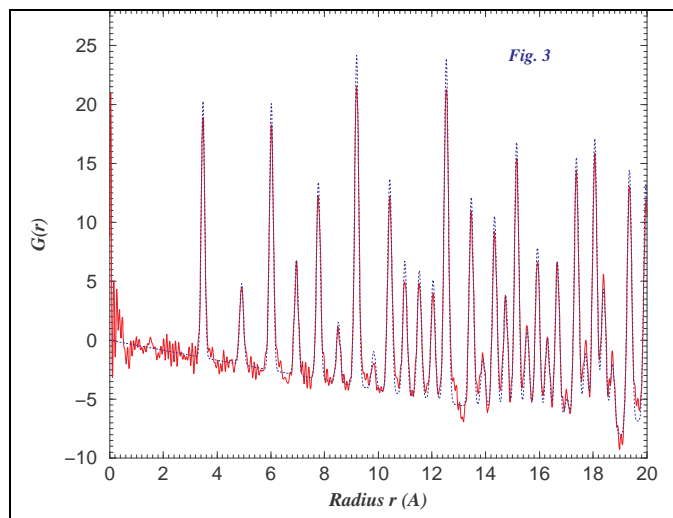
Non-Gaussian Peak Shape of Pair Distribution Function

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 in the point $\vec{r} = (x, y, z)$ is given by

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

Where 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 PDF (e.g. $P(r)$) of 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

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

Nowadays when experimental techniques for PDF measurement was improved significantly one can expect to see the difference between measured PDF and the PDF $P_{old}(r)$ calculated under assumption above.

In order to find PDF of higly anisitropic meterials one should perform the angular average:

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

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

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

This result can be rewritten as:

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

Thus one can see that if peaks are very narrow then the difference between $P_{old}(r)$ and $P_{new}(r)$ is small. But there is a possibility that in high quality measurements this difference can be seen and $P_{new}(r)$ can give better agreement between theory and experiment then $P_{old}(r)$.

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

$$P(r) = \frac{\exp\left(-\dfrac{(r - r_i)^2}{2\Sigma^2}\right)}{\sqrt{2\pi\Sigma^2}}\left[1 + \left(\frac{\Sigma}{r_i}\right)\Psi_1 + \left(\frac{\Sigma}{r_i}\right)^2\Psi_2\right]$$

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

$$f_n(r') = 2^{-\frac{n}{2}} H_n\left(\frac{r'}{\sqrt{2\Sigma}}\right)$$

$$a_1 = \left(\frac{R}{\Sigma}\right)\alpha \qquad a_2 = \left(\frac{R}{\Sigma}\right)^2\tau \qquad a_3 = \left(\frac{R}{\Sigma}\right)\beta \qquad a_4 = \left(\frac{R}{\Sigma}\right)^2\gamma \qquad a_6 = \left(\frac{R}{\Sigma}\right)^2\varepsilon$$

$$\alpha = \frac{M_1}{\Sigma} \qquad \tau = \frac{1}{2!}\left[\frac{M_2}{\Sigma^2} - 1\right] \qquad \beta = \frac{1}{3!}\left[\frac{M_3}{\Sigma^3} - 3\frac{M_1}{\Sigma}\right]$$

$$\gamma = \frac{1}{4!}\left[\frac{M_4}{\Sigma^4} - 6\frac{M_2}{\Sigma^2} + 3\right] \qquad \varepsilon = \frac{1}{6!}\left[\frac{M_6}{\Sigma^6} - 15\frac{M_4}{\Sigma^4} + 45\frac{M_2}{\Sigma^2} - 15\right]$$

$$M_1 = \frac{A_2 - B_2}{2r_i} \qquad M_2 = B_2 + \frac{A_4 - 6A_2 B_2 + 5B_4}{4r_i^2} \qquad M_3 = \frac{3}{2}\left(\frac{A_2 B_2 - B_4}{r_i}\right)$$

$$M_4 = B_4 + \frac{3A_4B_2 - 10A_2B_4 + 7B_6}{2r_i^2} \qquad M_5 = \frac{5}{2}\left(\frac{A_2B_4 - B_6}{r_i}\right) \qquad M_6 = B_6 + \frac{3}{4}\left(\frac{5A_4B_4 - 14A_2B_6 + 9B_8}{r_i^2}\right)$$

$$A_2 = \sigma_x^2 + \sigma_y^2 + \sigma_z^2 \qquad A_4 = 2\left(\sigma_x^4 + \sigma_y^4 + \sigma_z^4\right) + \left(\sigma_x^2 + \sigma_y^2 + \sigma_z^2\right)^2$$

$$A_6 = 6\left(\sigma_x^6 + \sigma_y^6 + \sigma_z^6\right) + 9\left(\sigma_x^4 + \sigma_y^4 + \sigma_z^4\right)\left(\sigma_x^2 + \sigma_y^2 + \sigma_z^2\right) + 6\sigma_x^2\sigma_y^2\sigma_z^2$$

$$B_2 = \Sigma^2 \qquad B_4 = 3\Sigma^4 \qquad B_6 = 15\Sigma^6 \qquad B_8 = 105\Sigma^8$$

$$A_2B_2 = \left(\sigma_x^2 + \sigma_y^2 + \sigma_z^2\right)\left(\frac{x^2\sigma_x^2 + y^2\sigma_y^2 + z^2\sigma_z^2}{r_i^2}\right) + 2\left(\frac{x^2\sigma_x^4 + y^2\sigma_y^4 + z^2\sigma_z^4}{r_i^2}\right)$$

$$A_4B_2 = 6\left(\frac{x^2\sigma_x^6 + y^2\sigma_y^6 + z^2\sigma_z^6}{r_i^2}\right) + 6\left(\frac{\sigma_x^2 + \sigma_y^2 + \sigma_z^2}{r_i^2}\right)\left(\frac{x^2\sigma_x^4 + y^2\sigma_y^4 + z^2\sigma_z^4}{r_i^2}\right) +$$

$$3\left(\frac{x^2\sigma_x^2 + y^2\sigma_y^2 + z^2\sigma_z^2}{r_i^2}\right)\left(\sigma_x^4 + \sigma_y^4 + \sigma_z^4\right) + 2\sigma_x^2\sigma_y^2\sigma_z^2$$
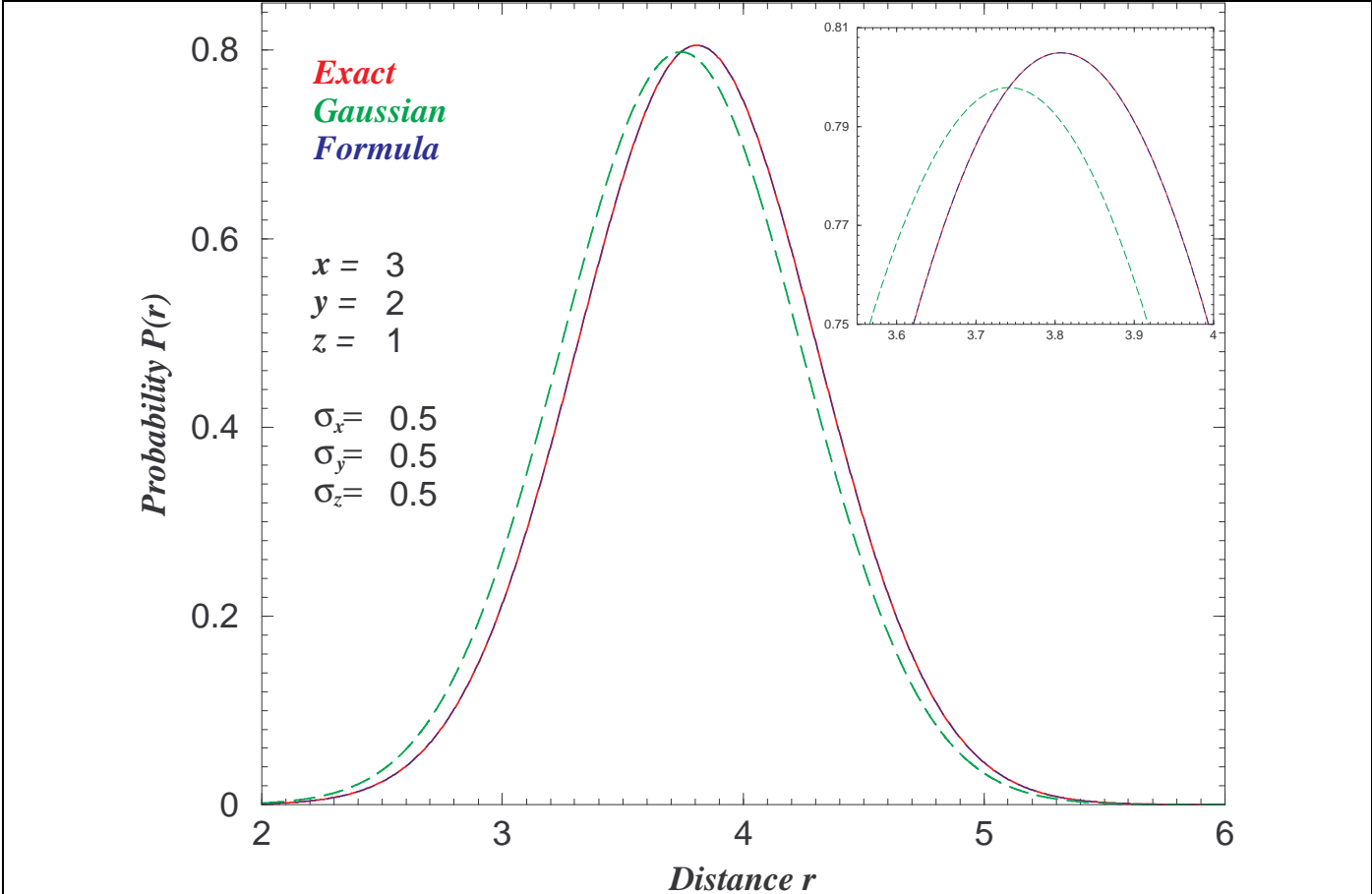
$$A_2B_4 = 12\left(\frac{x^4\sigma_x^6 + y^4\sigma_y^6 + z^4\sigma_z^6}{r_i^4}\right) - 6\left(\sigma_x^2 + \sigma_y^2 + \sigma_z^2\right)\left(\frac{x^4\sigma_x^4 + y^4\sigma_y^4 + z^4\sigma_z^4}{r_i^4}\right) +$$
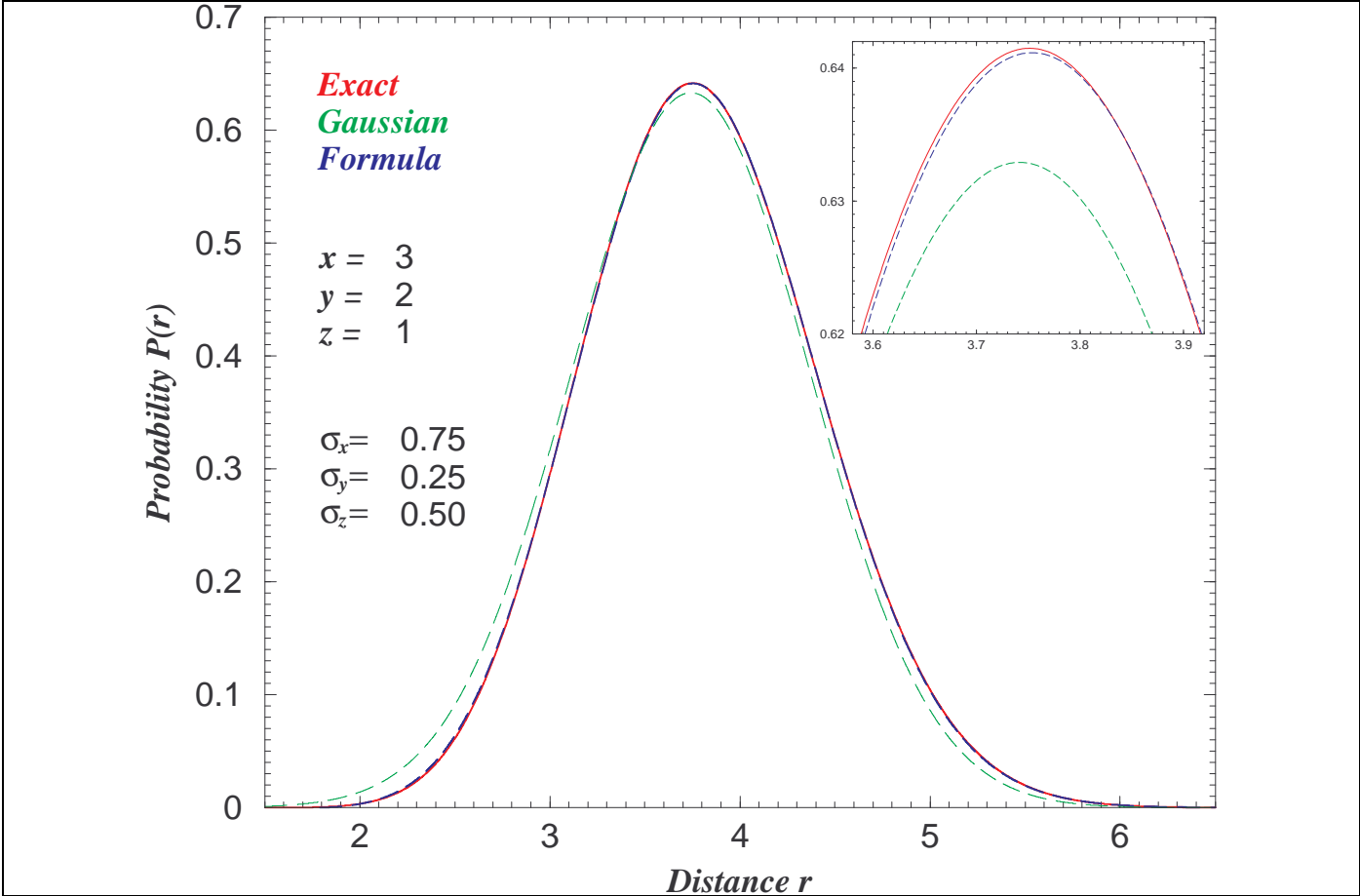
$$9\left(\sigma_x^2 + \sigma_y^2 + \sigma_z^2\right)\left(\frac{x^2\sigma_x^2 + y^2\sigma_y^2 + z^2\sigma_z^2}{r_i^2}\right)^2 - 6\left(1 - \frac{x^4 + y^4 + z^4}{r_i^4}\right)\sigma_x^2\sigma_y^2\sigma_z^2$$
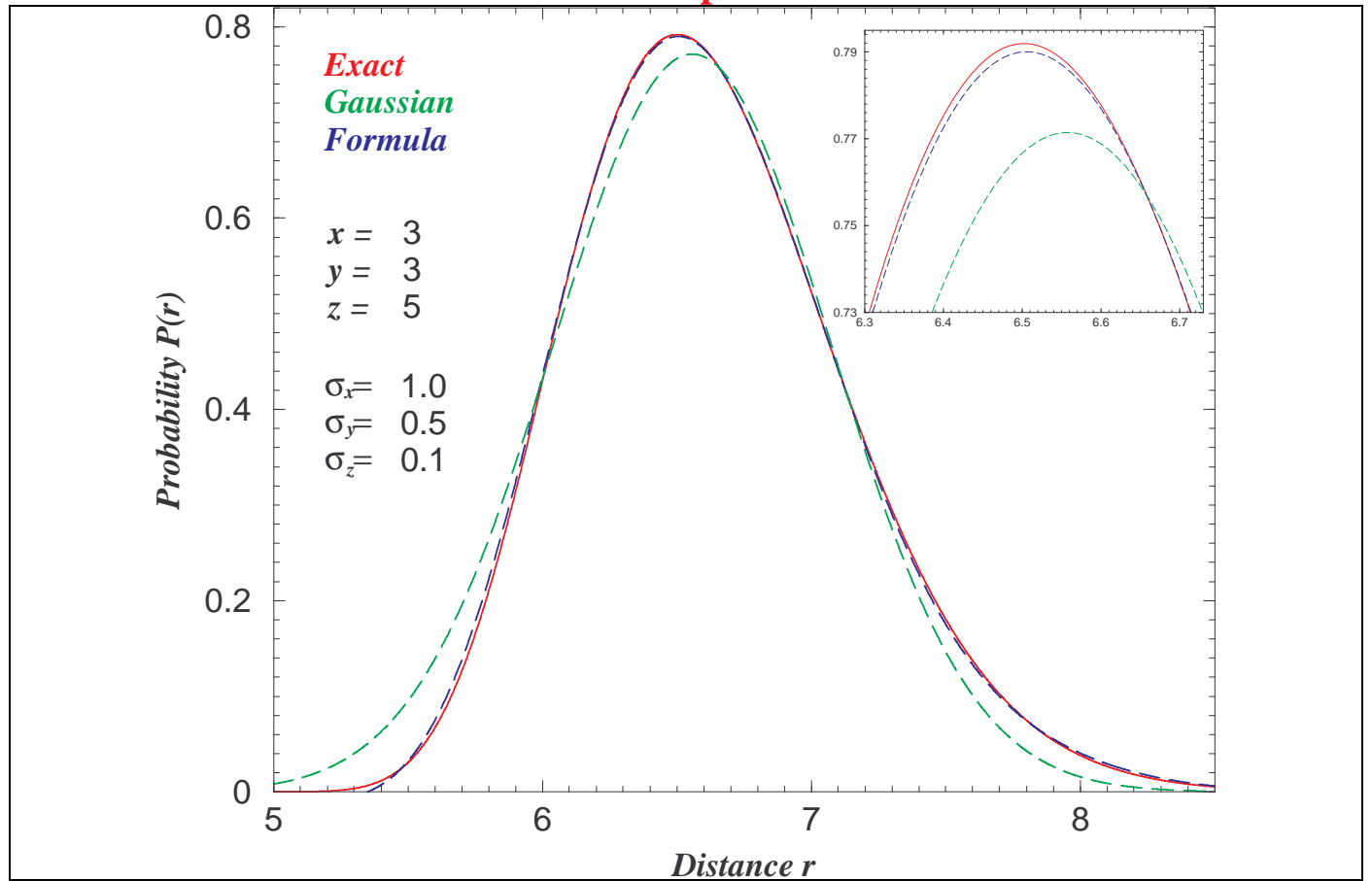
$$A_2B_6 = 15(A_2B_2)(B_4) - 2(A_2)(B_6)$$

$$A_4B_4 = -(A_4)(B_4) + 6(A_4B_2)(B_2) + 6(A_2B_2)^2 + 2(A_2)^2(B_4) - 12(A_2B_2)(A_2)(B_2)$$
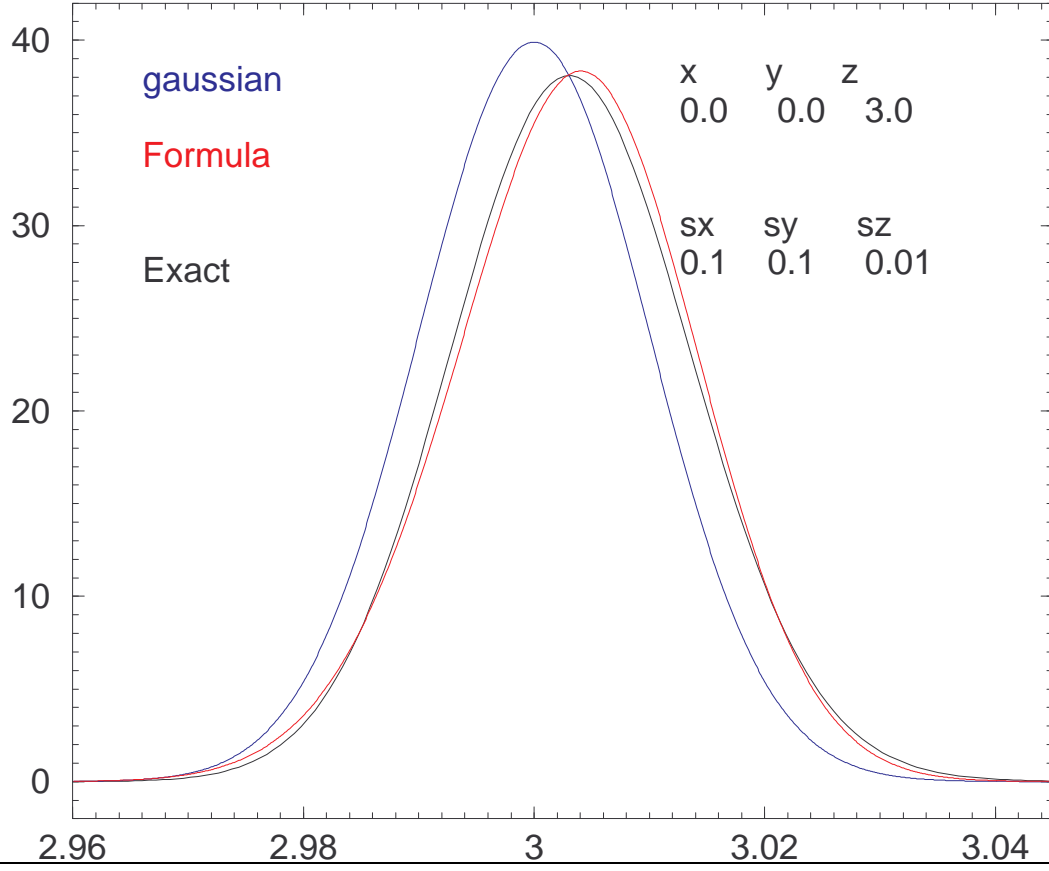
Some Examples

Exact
Gaussian
Formula

$x = 3$
$y = 2$
$z = 1$

$\sigma_x = 0.5$
$\sigma_y = 0.5$
$\sigma_z = 0.5$

Probability $P(r)$

Distance r

Exact
Gaussian
Formula

$x = 3$
$y = 2$
$z = 1$

$\sigma_x = 0.75$
$\sigma_y = 0.25$
$\sigma_z = 0.50$

Probability $P(r)$

Distance r

Some Examples

Exact
Gaussian
Formula

$x = 3$
$y = 3$
$z = 5$

$\sigma_x = 1.0$
$\sigma_y = 0.5$
$\sigma_z = 0.1$

Probability P(r)

Distance r

Multiphonon contributions to peaks in the PDF.

If the atoms in a crystal would not vibrate then the PDF of the crystal should consist of a set of δ -functions. Peak broadening occurs due to the atoms/lattice vibrations.

Here we discuss the role of different multiphonon contributions to the peak broadening.

The width of the PDF peak is can be calculated exactly within the harmonic approximation by the expression

$$\rho_{ij}(r) = \frac{1}{2\pi}\int dq e^{-iq\left(r-r_{ij}^{0}\right)} C_{ij}(q)$$

where

$$C_{ij}(q) = \left\langle e^{iq u_{ij} \cdot r_{ij}} \right\rangle = e^{-(1/2)q^2 \left\langle \left(u_{ij} \cdot r_{ij} \right)^2 \right\rangle} = e^{-q^2\sigma^2} e^{-(1/2)\lambda q^2 \left(\sigma_{ij}^2 - 2\sigma^2\right)} = e^{-2W} e^{-(1/2)\lambda q^2 \left(\sigma_{ij}^2 - 2\sigma^2\right)}$$

$W = -\frac{1}{2}q^2\sigma^2$ is Debye-Waller, $\sigma_{ij}^2 = \left\langle \left(\vec{r}_{ij} \vec{u}_{ij} \right) \right\rangle$, $\vec{r}_{ij} = \vec{r}_j - \vec{r}_i$, $\vec{u}_{ij} = \vec{u}_j - \vec{u}_i$ and λ is expansion

parameter. It can be shown that $\rho_{ij}(r)$ is equal to

$$\frac{1}{\sqrt{4\pi\sigma^2(1-\mu)}} e^{-x^2/2(1-\mu)}$$

$$= \frac{1}{\sqrt{4\pi\sigma^2}} e^{-x^2/2} \left[\begin{array}{c} 1 + \mu\left(1-x^2\right)/2 + \mu^2\left(3-6x^2+x^4\right)/8 \\ + \mu^3\left(15-45x^2+15x^4-x^6\right)/48 \\ + \mu^4\left(105-420x^2+210x^4-28x^6+x^8\right)/384 + ... \end{array} \right]$$

Where: $x_{ij}^2 = \left(r-r_{ij}^0\right)^2 / 2\sigma^2$, $\mu_{ij} = \lambda\left(2\sigma^2 - \sigma_{ij}^2\right)/2\sigma^2$

Where the first term is the Gaussian from the Bragg scattering
(with its associated Debye –Waller factor). The term linear in μ is the one phonon contribution, the term in μ^2 is the two phonon contribution etc..
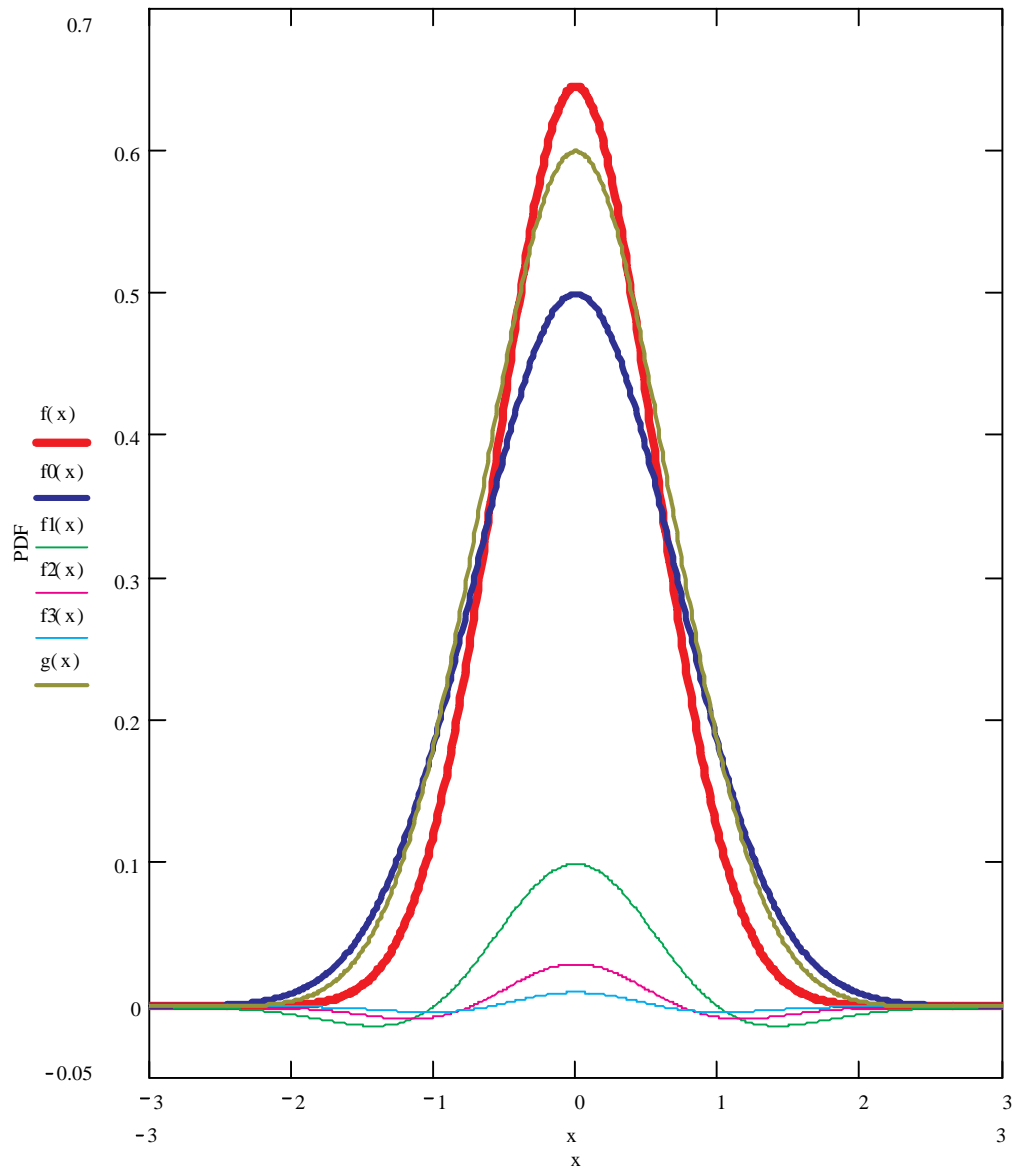
Figure 1. Plot of different multiphonon contributions is shown shown using a parameter $\mu = \left(2\sigma^2 - \sigma_{ij}^2\right)/2\sigma^2 = 0.4$ which is a reasonable value.. The total peak is in red, the Bragg contribution in blue, the sum of the Bragg and one-phonon contribution in green, and the one phonon contribution in green, the two phonon contribution in purple, and the three phonon contribution in blue.

The peak is Gaussian if only the Bragg contribution is counted or if all the contributions are counted. Otherwise the shape is more complex.

Figure 2 Showing how the peak in the PDF can go negative with only
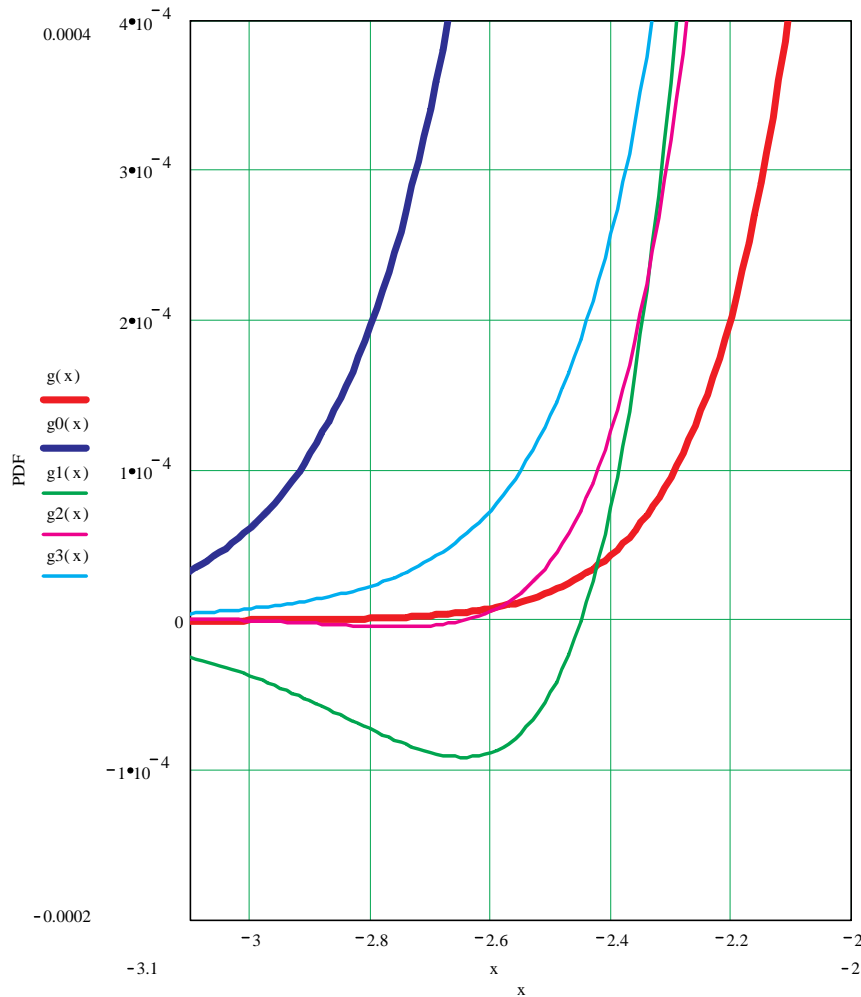
the one and two phonon pieces added. We have also checked that summing up to the 3 phonon part also goes negative so it is likely that all terms are needed for convergence.

Figures above show that all multiphonon contributions can be important for the determination of peak shape in pair distribution function.