

Absence of Decay in the Amplitude of Pair Distribution Functions at Large Distances

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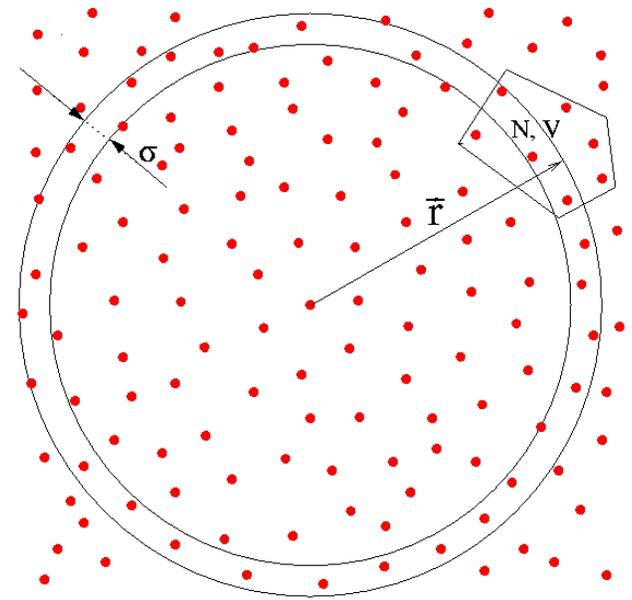
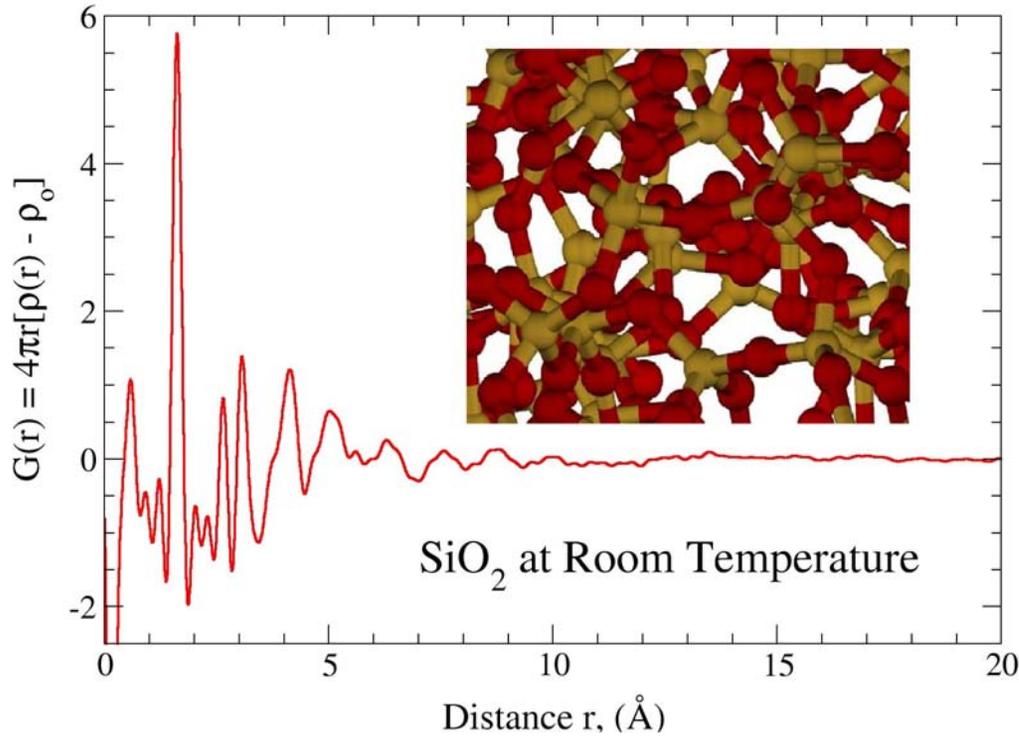
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Motivation:

We found that **Pair Distribution Function (PDF)** calculated for the crystals in assumption of **the infinite instrumental resolution** does not exhibit decay at large distances.

The goal is to understand this surprising behavior.

Glasses and Liquids: PDF quickly decays



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

$$G(r) = \frac{2}{\pi} \int_0^\infty F(q) \sin(qr) dq$$

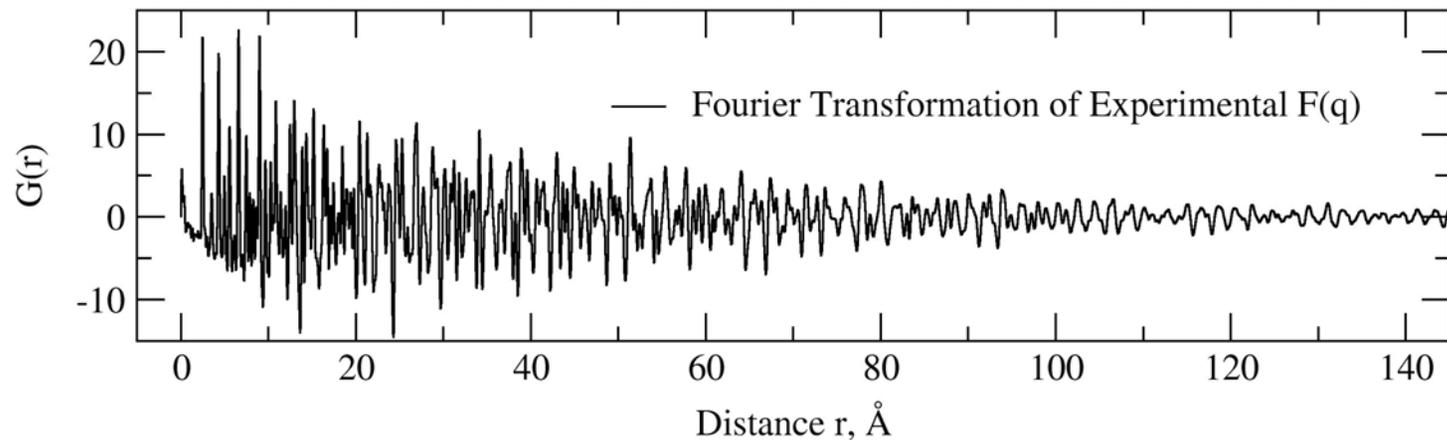
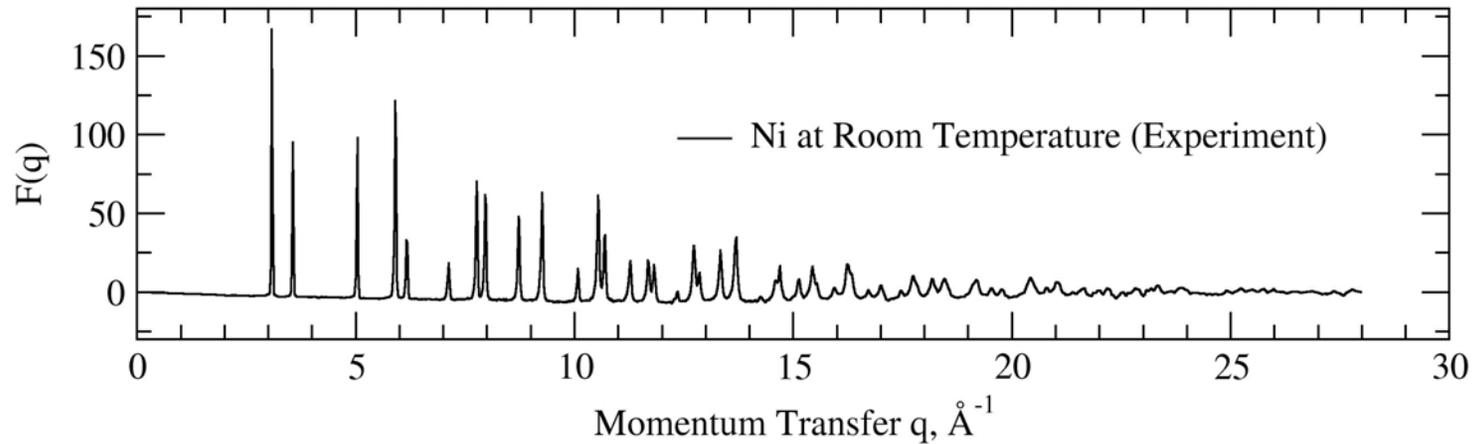
$$\rho_i(r) = \frac{N_i(r)}{4\pi r^2 \sigma} \quad \rho_i(r) \xrightarrow{r \rightarrow \infty} \rho_o$$

$$F(q) = q[S(q) - 1] \quad S(q) = \frac{I(q)}{Nf^2}$$

$$\rho(r) = \frac{1}{N} \sum_{i=1}^N \rho_i(r)$$

Pair Distribution Function for the Crystal of Ni

In the last 20 years PDF was also used to extract information about atomic interactions in crystals.

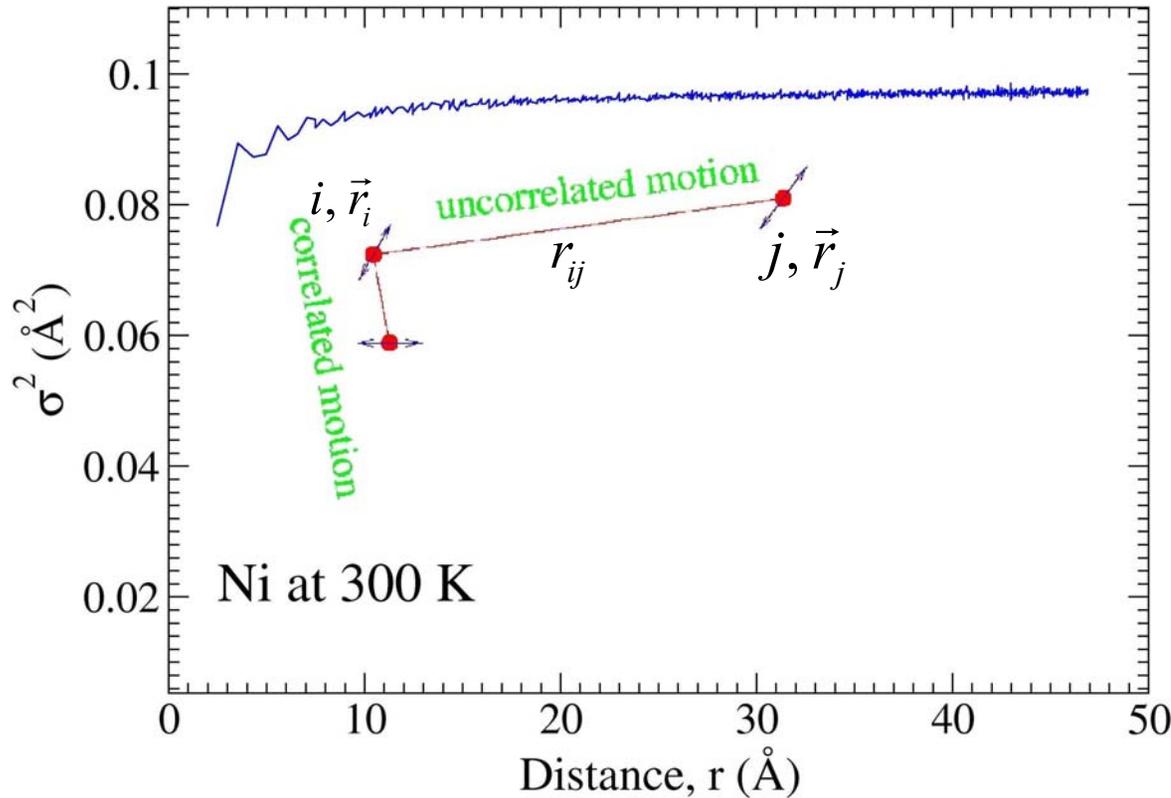


What is the origin of decay at large distances?

Is it “Natural decay” or is decay due to Finite Instrumental Resolution?

Do both effects lead to the decay?

Calculation of Pair Distribution Function



$$\sigma_{ij}^2 = \langle (r_{ij} - \bar{r}_{ij})^2 \rangle$$

$$\sigma_{ij}^2 \xrightarrow{r_{ij} \rightarrow \infty} \sigma^2$$

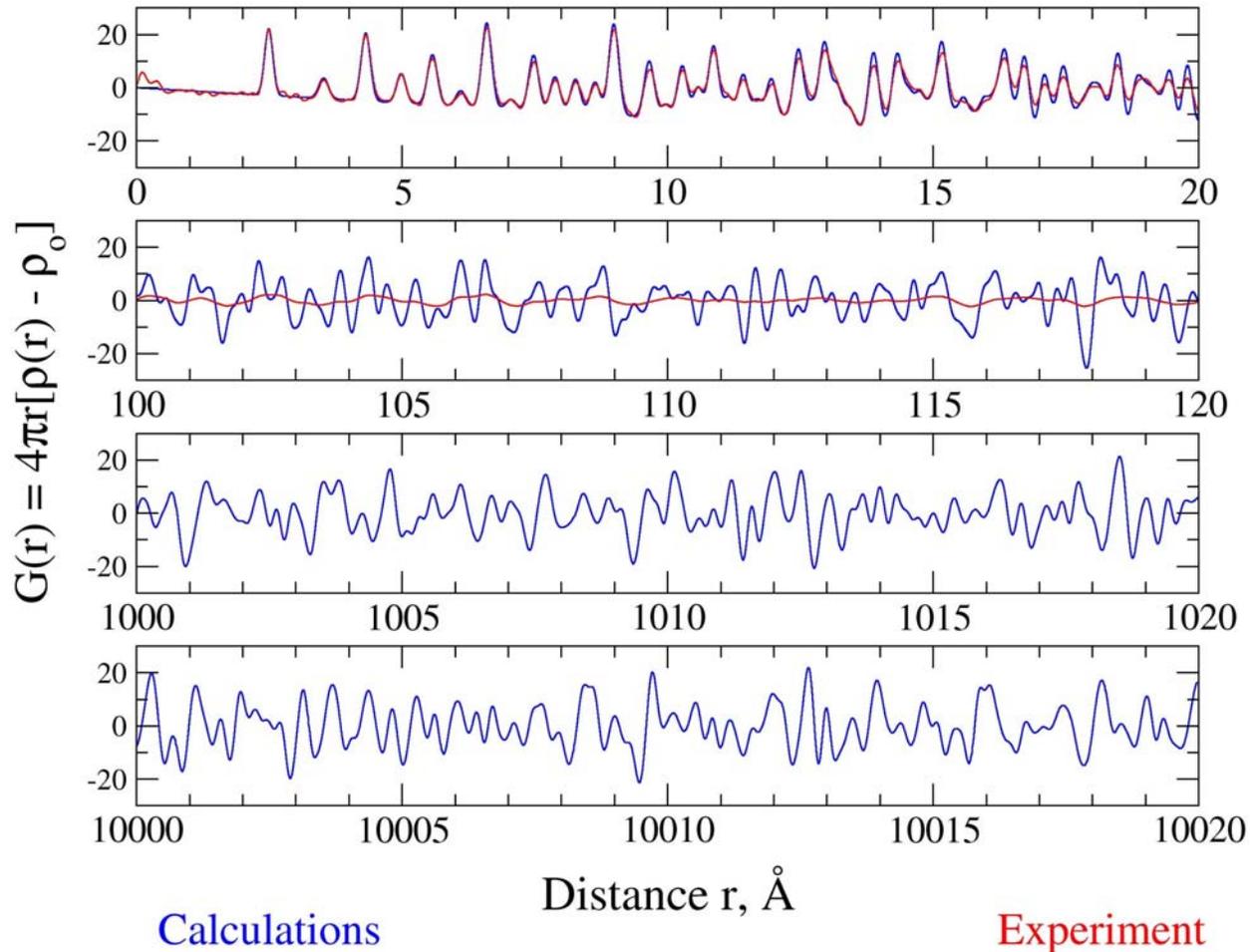
$$G(r) = 4\pi r [\rho(r) - \rho_o]$$

$$\rho(r) = \frac{1}{N} \sum_{i=1}^N \rho_i(r)$$

$$\rho_{ij}(r) = \frac{1}{4\pi r^2} \frac{1}{\sqrt{2\pi\sigma_{ij}^2}} \exp\left[-\frac{(r - \bar{r}_{ij})^2}{2\sigma_{ij}^2}\right]$$

$$\rho_i(r) = \sum_{j \neq i} \rho_{ij}(r)$$

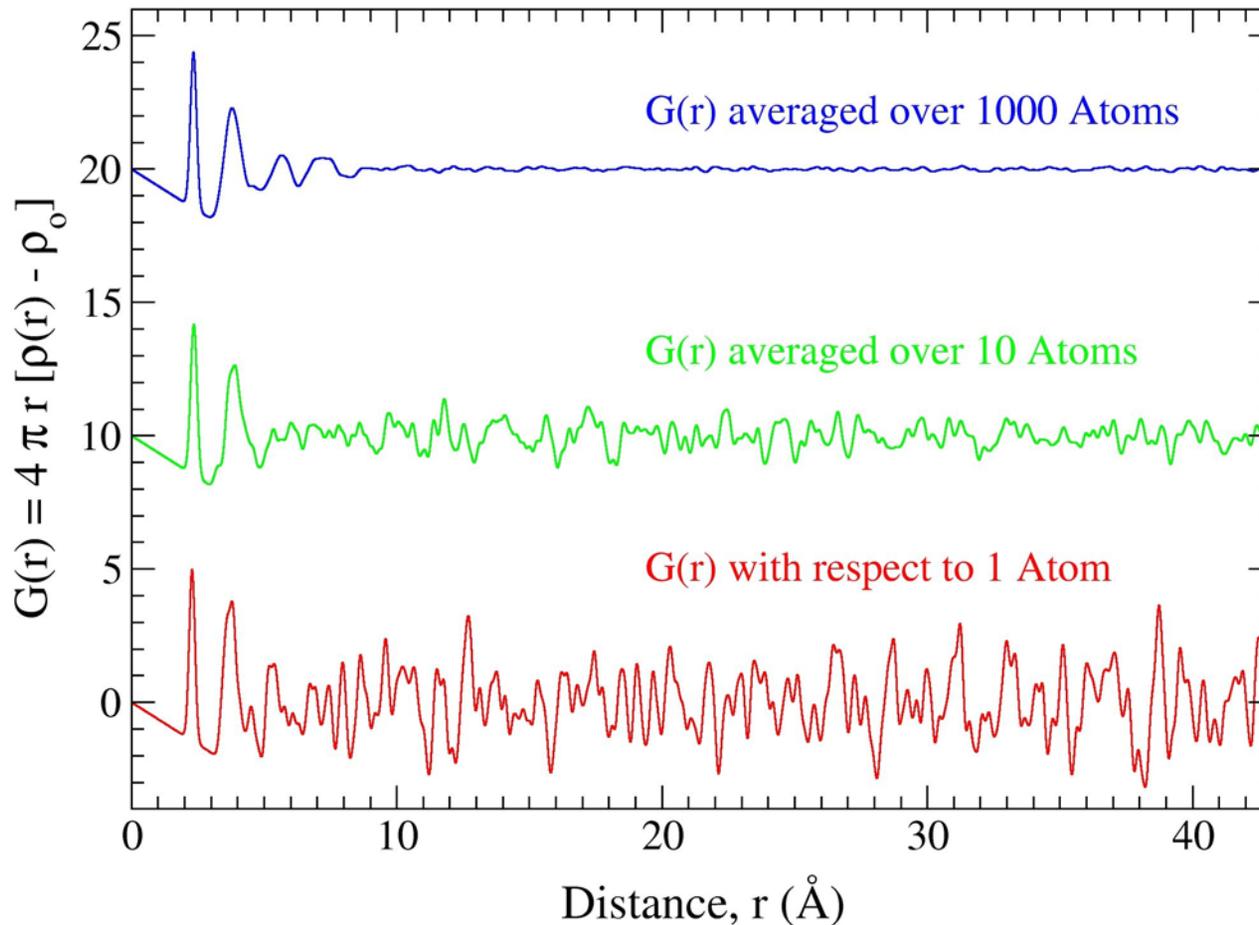
Pair Distribution Function of Ni at Large Distances



Thus experimental PDF of crystals decay only due to finite experimental resolution

How about Glasses?

Amorphous Si at Room Temperature. $\sigma = 0.098$ (Å)



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

$$\rho(r) = \frac{1}{N} \sum_{i=1}^N \rho_i(r)$$

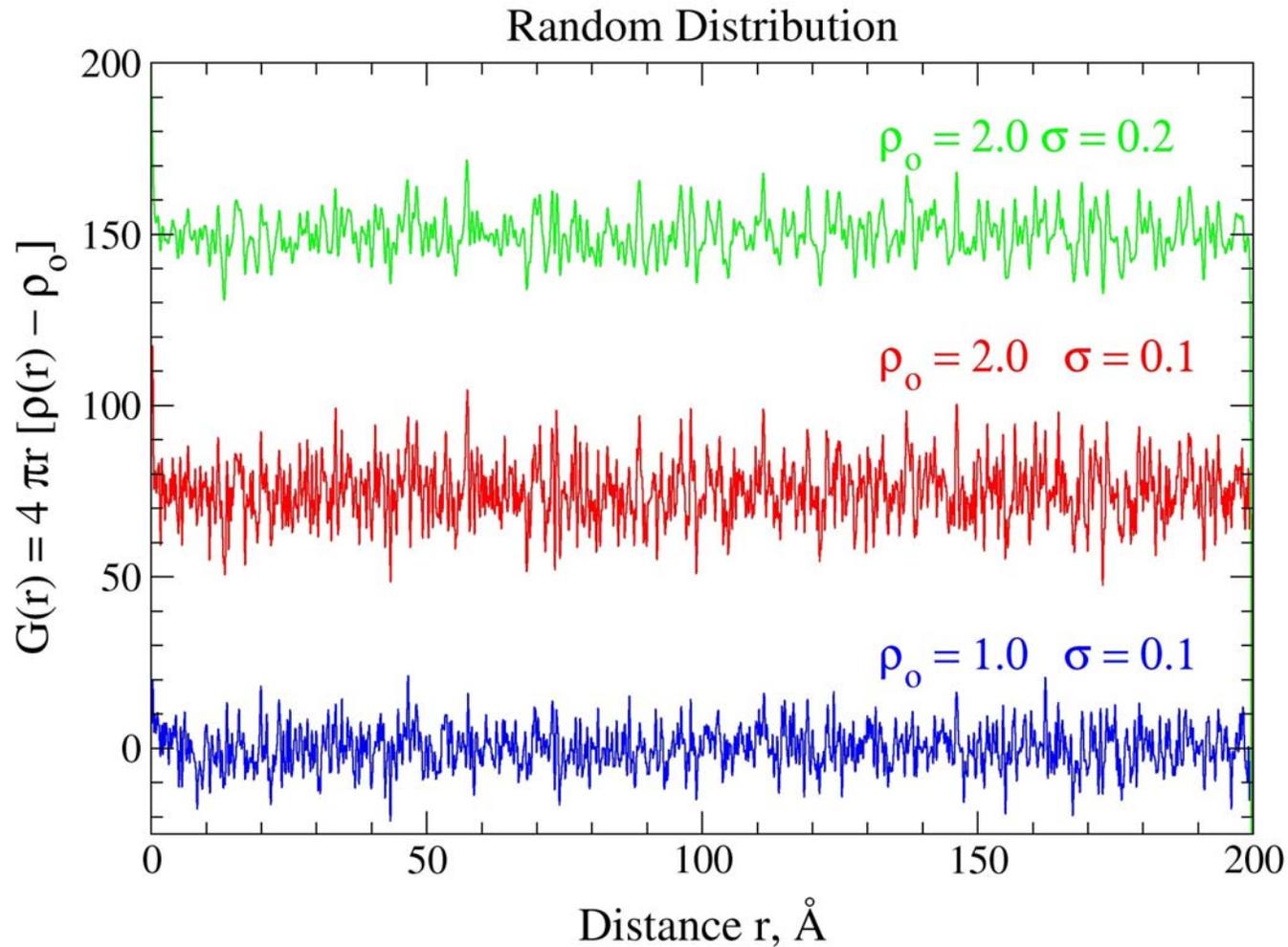
$$G_i(r) = 4\pi r [\rho_i(r) - \rho_o]$$

Thus PDF in glasses decays because at large distances every atom has different random environment.

What will happen if sites distributed randomly?

(e.g. atoms can sit on top of each other)

Pair Distribution Function with respect to one particular site.



The absence of decay is due to the fluctuations in the number of particles

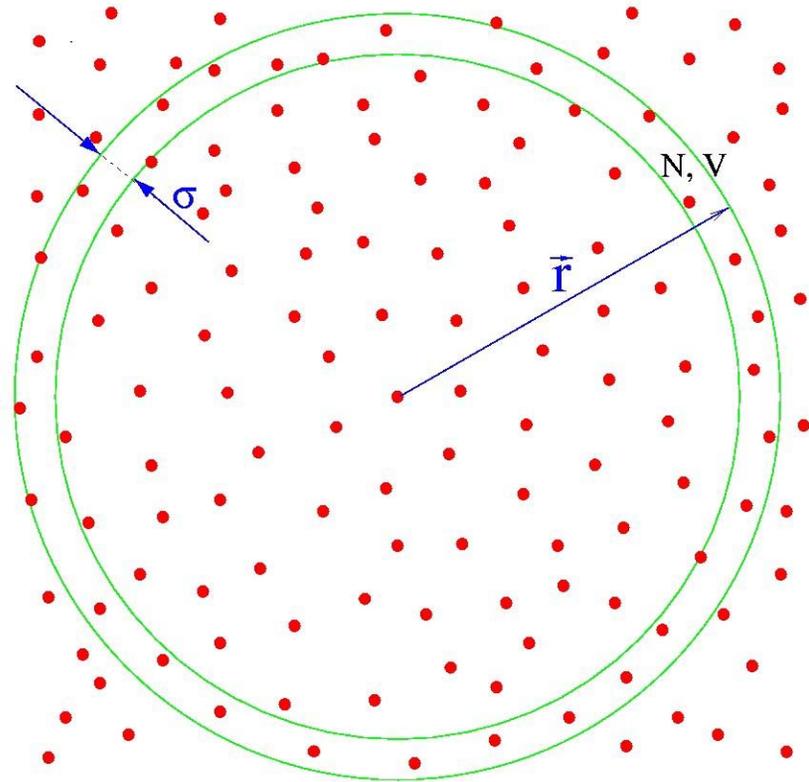
$$G_i(r) = 4\pi r [\rho_i(r) - \rho_o]$$

Non measurable for glasses

$$\langle G_i^2(r) \rangle \cong \frac{\langle [4\pi r^2 \sigma \rho_i(r) - 4\pi r^2 \sigma \rho_o]^2 \rangle}{r^2 \sigma^2}$$

$$\langle G_i^2(r) \rangle \cong \frac{\langle [N_i(r, \sigma) - \bar{N}(r, \sigma)]^2 \rangle}{r^2 \sigma^2}$$

$$\langle G_i^2(r) \rangle \cong \frac{\bar{N}(r, \sigma)}{r^2 \sigma^2} = \frac{4\pi r^2 \sigma \rho_o}{r^2 \sigma^2} = 4\pi \frac{\rho_o}{\sigma}$$



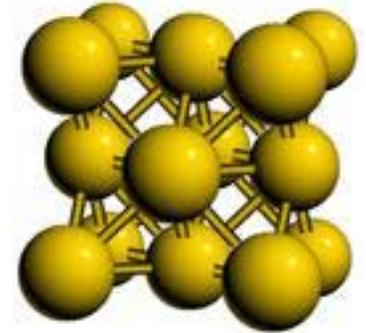
The exact result for the random case:

$$N(r, \sigma) = 4\pi r^2 \sigma \rho_o$$

$$\langle G_i^2(r) \rangle \frac{\sigma}{\rho_o} = 2\sqrt{\pi}$$

How to proceed in single component crystals?

In crystals we can not do averaging over different configurations, because all atoms/sites in crystals are equivalent. But it also means that: is measurable.

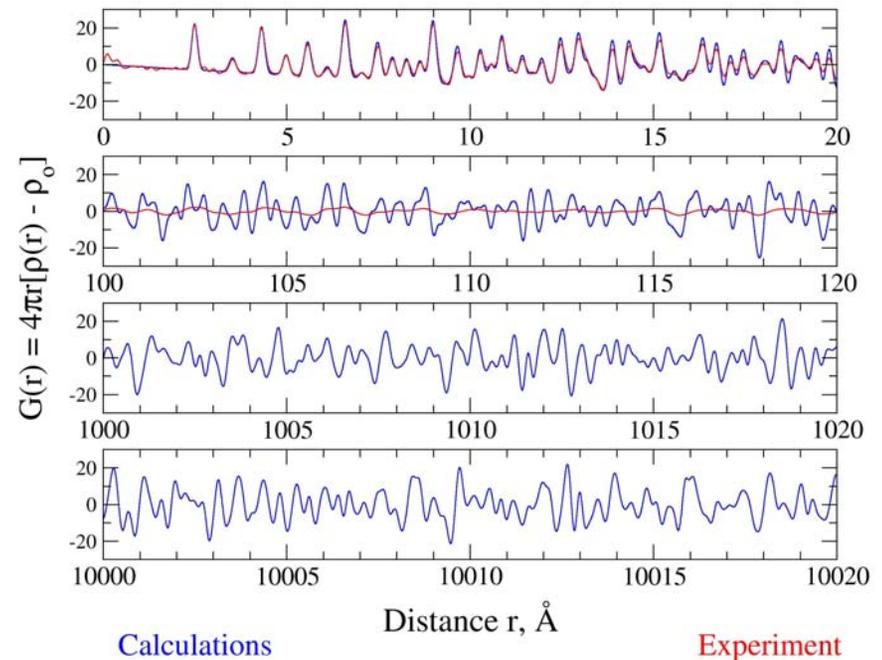


$$G_i(r) = G(r)$$

Integral Approach

$$\overline{G^2(r)} = \int_{R_1}^{R_2} G^2(r) dr$$

For the random case both methods: averaging over different configurations and integral approach give the same result as they should.



Dimensional Analysis

$$G(r) = 4\pi r [\rho(r) - \rho_o] \Rightarrow [G(r)] = \frac{1}{L^2}$$

$$\left[\overline{G^2(r)} \frac{\sigma}{\rho_o} \right] = 1$$

For the random distribution

$$\overline{G^2(r)} = 2\sqrt{\pi} \frac{\rho_o}{\sigma}$$

$$\overline{G^2(r)} \frac{\sigma}{\rho_o} = 2\sqrt{\pi} \cong 3.55$$

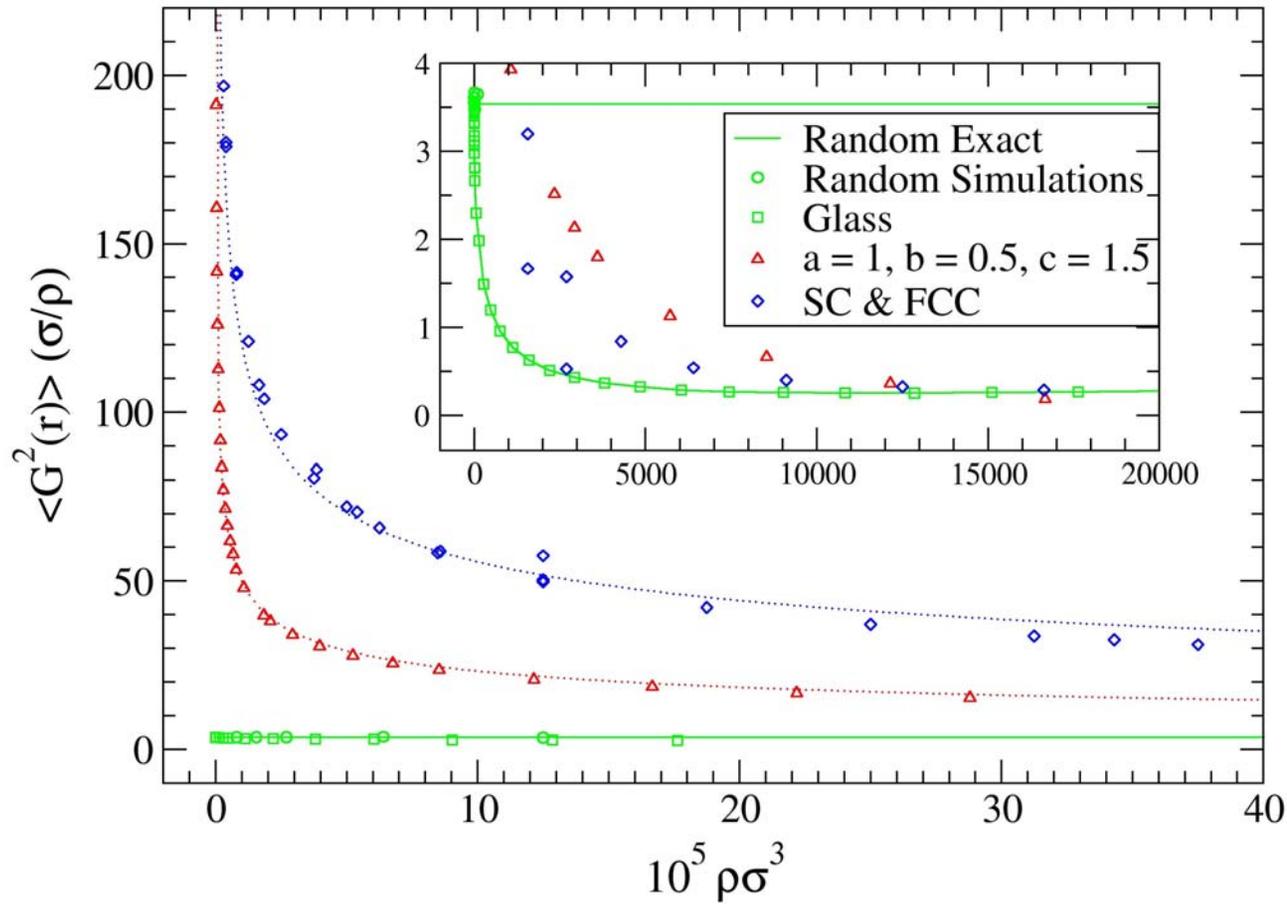
For the given type of lattice

$$\overline{G^2(r)} \frac{\sigma}{\rho_o}$$

can depend only on

$$\rho\sigma^3$$

Crystals vs. Glasses vs. Random Distributions



Why in case of crystals there is dependence on $\rho \sigma^3$?
We do not know.

Note: PDF for d-dimensional space

$$G_d(r) \propto r^{\frac{d}{2}} [\rho(r) - \rho_o]$$

Conclusions:

- 1) PDFs in glasses and liquids decay **not because** there is no **long range atomic ordering**, but because **every atom has its own surrounding disorder**.
- 2) PDFs in crystals decay only due to the Finite Instrumental Resolution.
- 3) Single component crystals provide natural and simple way to test instrumental resolution.