Atomic pair distribution function (PDF) analysis: What, When, Why, How?

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Department of Physics and Astronomy, Michigan State University

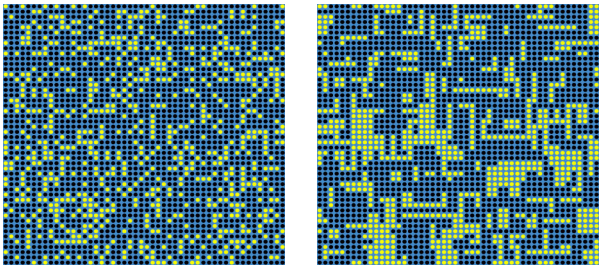
Goals of the Talk

- PDF: what, when, why, how
- Software Projects and Software Engineering
  - DANSE project
- Some provocative remarks

PDF: why?

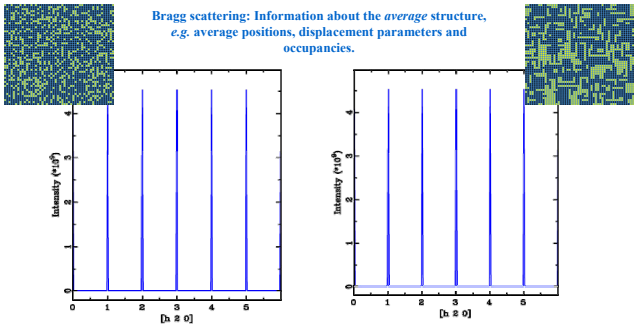
- When your crystals have defects that you care about
  - "Crystals are like people, it is their defects that make them interesting" (attributed to F. C. Franck)
  - Defects can be static, dynamic (phonons), chemical disorder, displacive disorder…
- When your crystals aren't crystals at all
  - Short-range order only (glasses, liquids)
  - Intermediate range order (nanoparticles, nanocrystallinity)
- Extracting this information is
  - Important
  - Difficult
  - Not crystallography (by definition, defects break periodicity), though MANY crystallographic concepts are fundamentally useful
  - "The nanostructure problem"

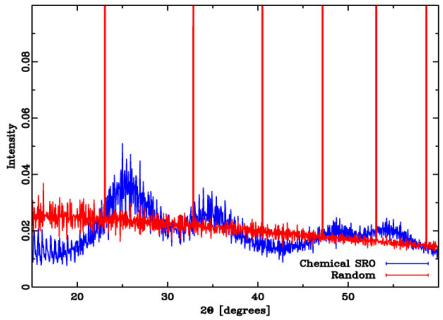
PDF: what



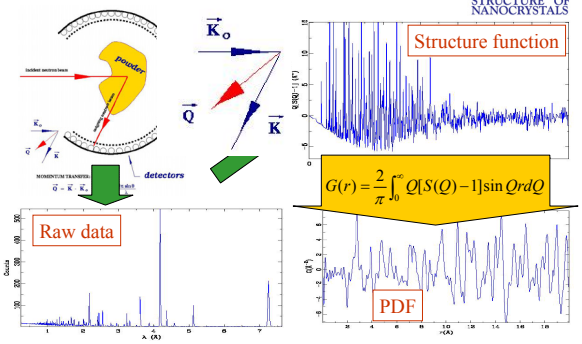
Cross section of 50x50x50 unit cell model crystal with 70% black atoms and 30% *vacancies* ! Thanks to Thomas Proffen for the simulations!

Bragg peaks are blind ..



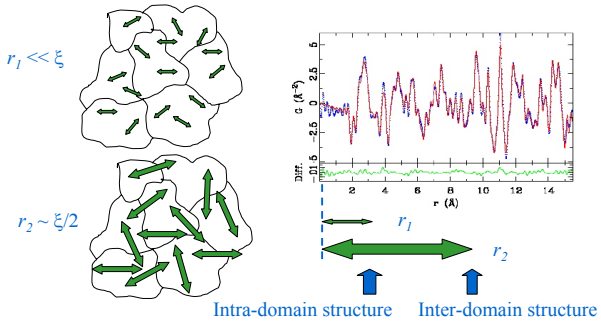


Obtaining the PDF



http://nirt.pa.msu.edu/

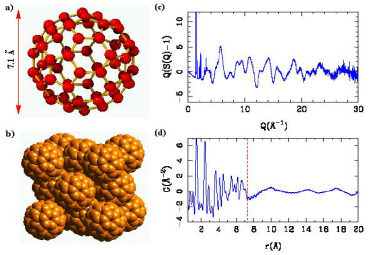
Observing Domains in the PDF



http://nirt.pa.msu.edu/

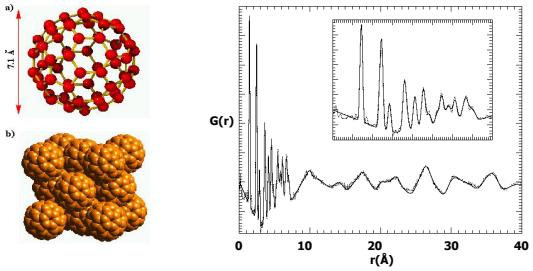
What is the PDF?

- Sit on an atom and look at your neighborhood
- *G(r)* gives the probability of finding a neighbor at a distance *r*
- PDF is experimentally accessible



http://nirt.pa.msu.edu/

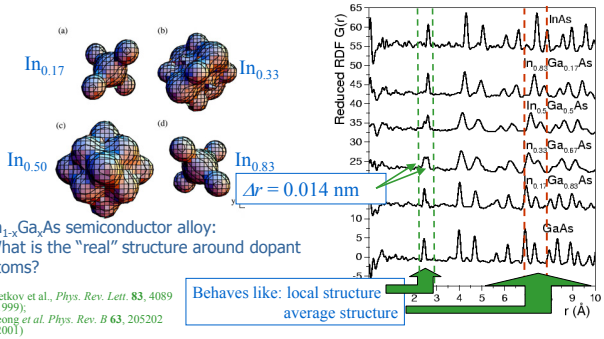
Quantitative modeling



- Refinement of local structure using least-squares methods
- Excellent *quantitative* agreement for intra- and inter- particle order
- Quantitative fits by Ming Lei and Mike Thorpe

http://nirt.pa.msu.edu/

PDF: when? Defects in crystals



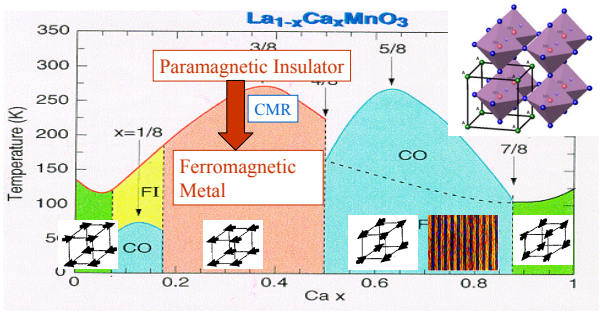
$In_{1-x}Ga_xAs$ semiconductor alloy: What is the "real" structure around dopant atoms?

Petkov et al., *Phys. Rev. Lett.* **83**, 4089 (1999); Jeong *et al. Phys. Rev. B* **63**, 205202 (2001)

Behaves like: local structure / average structure

http://nirt.pa.msu.edu/

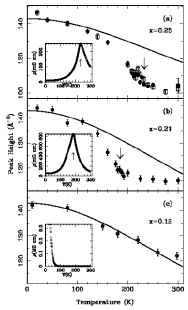
Charge localization in the lattice: polarons in $La_{1-x}Ca_xMnO_3$



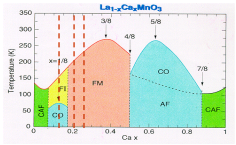
Phase diagram: S-K.Cheong et al.

http://nirt.pa.msu.edu/

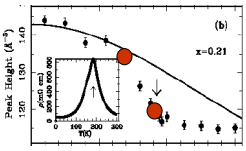
MI(T) transition is polaronic localization-delocalization transition



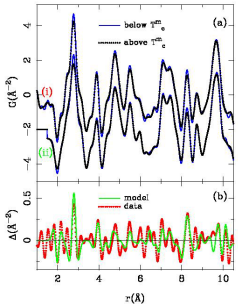
- PDF peaks are broad and low when polarons are present
- PDF peaks are narrow and sharp when polarons are absent
- SJLB *et al*, *Phys. Rev. Lett.* 77, 715 (1996).



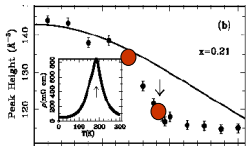
What do the polarons look like?



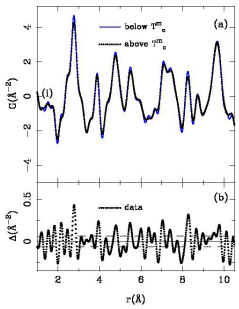
- How does the local structure change on going through the MI transition?



What do the polarons look like?

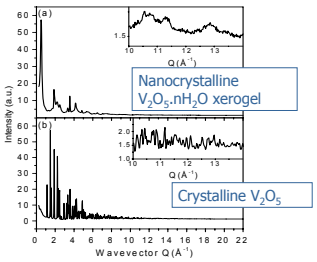


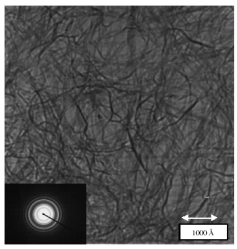
- How does the local structure change on going through the MI transition?
- Software for Data Transformations: corollary to Kevin Cowtan's talk yesterday



PDF when?
When your chemistry colleagues give you muck like this:

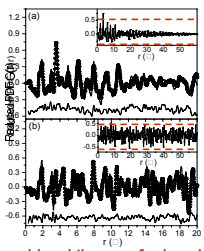
- Nanocrystalline materials:

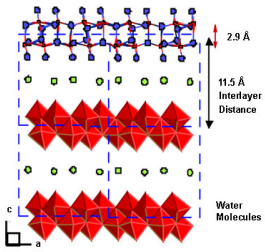




- Samples from the group of Mercouri Kanatzidis, MSU Chemistry

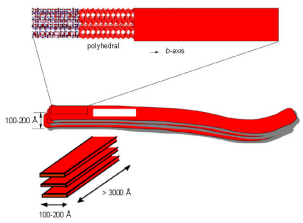
Structure of xerogel

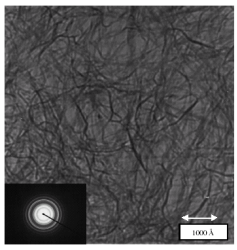




- Xerogel has bilayers of edge-shared VO_6 octahedra separated by water molecules
- Notice loss in peak amplitude above 11.5 Å => turbostratic disorder

"Nanostructure" in the xerogel

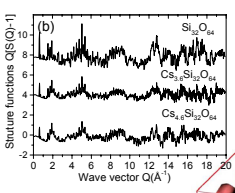


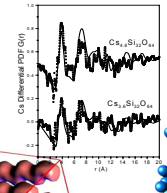


- Turbostratic disorder seen in the PDF consistent with bent and tangle fibres

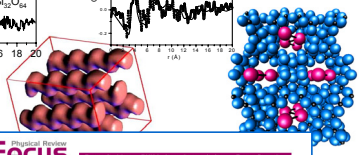
V. Petkov, et. al., *J. Am. Chem. Soc.* **121**, 10157 (2002).

Structure of intercalants: inorganic electride





•Cs forms Cs^+ in zig-zag pattern
•Electrons are counter-ions



- With Valeri Petkov, Tom Vogt and Dye group
- Zeolite ITQ-4 has 1D char… of ~7Å diameter
- Cs is intercalated
- X-ray data from NSLS-X7A


Physical Review Focus
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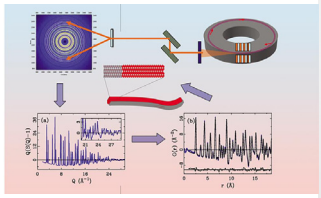
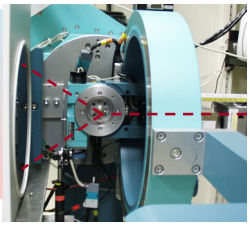
Previous Story / Next Story / January - June 2002 Archive
Phys. Rev. Lett. 89, 075502
(print issue of 12 August 2002)
Title and Authors
29 July 2002
Close-Up of Atomic Cave-Dwellers

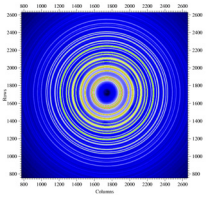
RAPDF Geometry

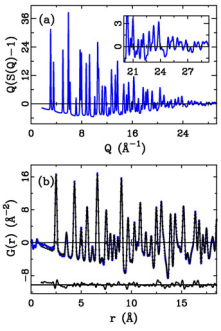




Rapid Acquisition PDFs

Fast x-ray PDFs
- Four orders of magnitude decrease in data collection time!
- Nickel data, 1s collection time, Q_{max} 28 Å^{-1}
- Developed in collaboration with Xiangyun Qiu, Pete Chupas, Jon Hanson, Peter Lee and Clare Grey





Computational issues: A Brief History of PDF

- Pieter Debye, 1912:

$$I = \sum_n \sum_m f_m f_n^* \frac{\sin qr_{mn}}{qr_{mn}}$$

- Fritz Zernike and Jon Prins, 1927:

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_a + \frac{2r}{\pi} \int_0^\infty qi(q) \sin qr dq$$

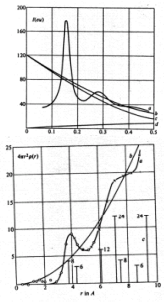
History

Debye and Menke, Z. Phys. (1930)

PDFs of mercury

Tarasov, L. P., and Warren, B. E., (1936) *J. Chem. Phys.*, **4**, 236.

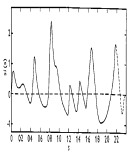
X-ray PDFs of molten sodium

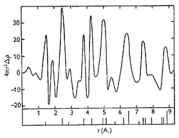


History of PDF

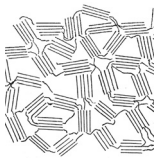
- Early 1930's
  - Computer: slide rule
  - Time to Fourier transform: few days
  - Time to paper: 6 months

History





Disordered Carbon



Warren, B. E., (1934) *J. Chem. Phys.* **2**, 551.

Franklin R. E. (1950) *Acta Crystallogr.* **3**, 107

Franklin R. E. (1951) *Proc. R. Soc. London A,*. **209**, 196

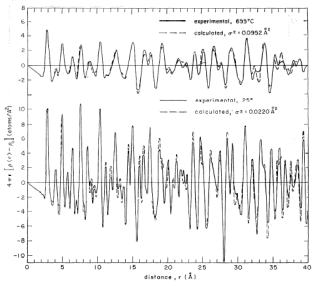
History of PDF

- 1930's
  - Computer: slide rule
  - Time to Fourier transform: few days
  - Time to paper: 6 months
- 1950's
  - Computer: Beevers Lipson strips + pen + paper
  - Time to Fourier transform: "The whole procedure is very simple and it is readily performed in three or four hours"-B.E. Warren
  - Time to paper: 6 months

Beevers Lipson strips

Gould BCA newsletter

History



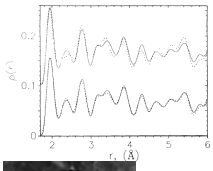
PDFs from crystalline Aluminum

R. R. Fessler, Roy Kaplow and B. L. Averbach, *Phys. Rev.* **150**, 34 (1966).

First use of Reverse-Monte-Carlo refinement

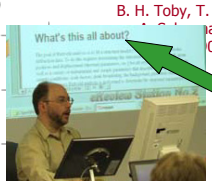
Kaplow R, Rowe, T. A. and Averbach, B. L. (1968), *Phys. Rev.* **168**, 1068.

20 years later…



Combine Monte-Carlo modelling with crystalline PDFs to get real, quantitative, local structural information: the first such paper was on Tl high-Tc superconductors

B. H. Toby, T. Egami, J. D. Jorgensen, and M. [illegible]anian, *Phys. Rev. Lett.* **64**, 2414-[illegible]0)



And yet 10 years on Brian's still confused about the subject

History of PDF

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- 1950's
  - Computer: Beevers Lipson strips + pen + paper
  - Time to Fourier transform: "The whole procedure is very simple and it is readily performed in three or four hours"-B.E. Warren
  - Time to paper: 6 months
- 1980's
  - Computer: DEC microvax
  - Time to Fourier transform: ~15 mins.
  - Time to paper: 6 months

PDF of crystals: the early days

- Microvax: 16Mb memory, 100Mb hard drive
- PDFvax: 6 students, 2 postdocs, no crashes
- Picture credit: Tom Carlson
  Location: Williamsburg, VA
- Well, my employer was re-modeling the basement and they were going to **throw it out**! Look at it! Would you let them just toss it! I think not. (And to think, they kept the AS/400! What were they thinking?) So I somehow wedged both towers into my Volkswagen and went to pick up my wife at her work. I could tell you what she said, but I like schools to be able to link to here.

History of PDF

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  - Computer: slide rule
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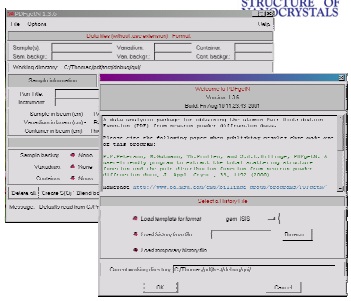
- 1950's
  - Computer: Beevers Lipson strips + pen + paper
  - Time to Fourier transform: "The whole procedure is very simple and it is readily performed in three or four hours"-B.E. Warren
  - Time to paper: 6 months
- 1980's
  - Computer: DEC microvax
  - Time to Fourier transform: ~15 mins.
  - Time to paper: 6 months
- 2000's
  - Computer: 1.5GHz Pentium PC
  - Time to Fourier transform: <1 second
  - Time to paper: 6 months

PDF how: Data Analysis software

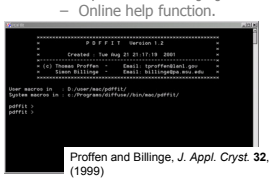
- E.g., PDFgetN, PDFgetX2. Available from ccp14 and:
  - http://www.totalscattering.org
  - **http://nirt.pa.msu.edu/**
- Graphical user interface & integrated plotting.
- Supports most TOF neutron powder file formats.
- Records all processing parameters as part of output files G(r) and S(Q).
- Runs on Windows 95/98/NT/2000 and UNIX
- Legacy code, wrapped by Pete Peterson and Thomas Proffen



Peterson et al., *J. Appl. Cryst.* **33**, 1192 (2000)

Modelling software, e.g., PDFFIT – real space Rietveld ..

- Program features
  - Controlled by FORTRAN style command language including loops and IF statements.
  - User defined relation between parameters and refinement variables.
  - Multiple structural phases supported.
  - Multiple data sets (neutron and X-ray) supported.
  - Interfaces with DISCUS, KUPLOT and ATOMS.
  - Available from ccp14 and:
  - **http://www.totalscattering.org**
  - Online help function.

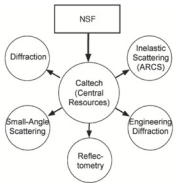


Proffen and Billinge, *J. Appl. Cryst.* **32**, 572 (1999)

- Technical information
  - UNIX or Windows operating system.
  - Binary or source code distribution.
  - Written in FORTRAN-77 (and some C).
  - Written by Thomas Proffen after an earlier effort by Simon Billinge

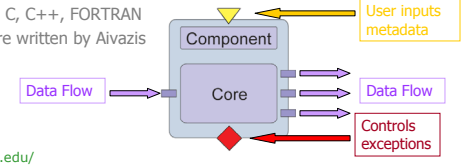
What is DANSE?

- It stands for Distributed Data analysis for neutron scattering experiments
- It is a software proposal for $13M to the NSF
- It has received one year of design funding (~$1M)
- There will be a funding decision for construction funding in November
- Lead PI's Michael Aivasis and Brent Fultz (Caltech)

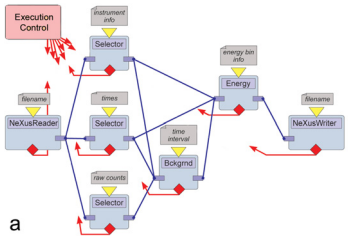


DANSE basic philosophy

- Software Component architecture design
  - Maintainable, extensible, reusable code
- Framework is Pyre, python based wrappers that will support distributed computing and data-streaming
  - Combines speed of compiled languages (component cores) with flexibility of scripting languages (python)
  - Component cores will include legacy code and new code
    - C, C++, FORTRAN
  - Pyre written by Aivazis

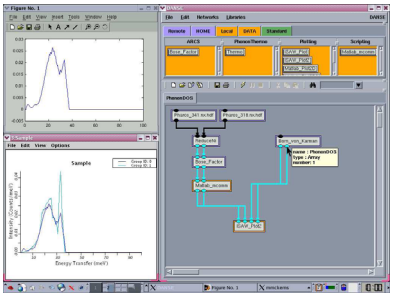


Applications are networks of components



- Schematic of an application to produce an energy spectrum from inelastic scattering tof neutron data
- Components themselves can be nested
- Framework handles things such as exceptions and validation of inputs

Cobra/Viper GUI



- GUI is obsolete, but gives an idea of how this can work
- Directories reside on different computers, componenents are dragged and dropped onto the desktop and wired together
- Users interact with the software on different levels: novice, senior scientist, component developer, framework maintainer/developer
- Cobra/Viper and independent development

Provocative remark 1: Inheritance, code design and UML

- Scientific Programs are algocentric
  - Start with the algorithm, build out
- Commercial software is usercentric
  - Need to sell the software
  - Need to figure out what the people will buy
  - Need to build that
- Determining "Use Cases" is the business of finding out what people want and how they will use the code
- Once you have that, you build the code to deliver what is wanted
- UML diagrams can help

Provocative remark 2: Inheritance, code design and UML

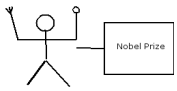
```
Class Science()
    def __init__()
    def getData()
    def analyzeData()
    def writePaper()
    def giveTalk()
Class rewards(science)
    def __init__()
    def payRaise()
Class Prize(rewards)
    def __init__()
    def thesis()
    def nobel()
    def knighthood()
```

```
If __name__=='__main__'
…
greatData1=science.getdata(student1)
greatResults1=science.analyzeData(student1,
greatData1)
Nature=science.writePaper(student1,greatRes
ults1)
…
Science=science.writePaper(student1,greatRe
sults3)

greatData4=science.getdata(student2)
greatResults4=science.analyzeData(student2,
greatData4)
PRL=science.writePaper(student2,
greatResults4)

simonRich=rewards.payraise(simon)
simonFamous=prize.nobel(simon)
```

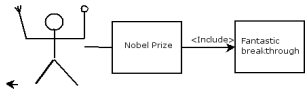

Inheritance, code design and UML

```
Class Science()
    def __init__()
    def getData()
    def analyzeData()
    def writePaper()
    def giveTalk()
Class rewards(science)
    def __init__()
    def payRaise()
Class Prize(rewards)
    def __init__()
    def thesis()
    def nobel()
    def knighthood()
```

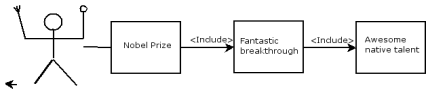

What can UML do for us?



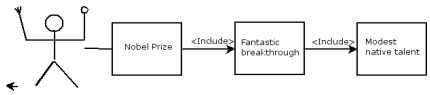
What can UML do for us?



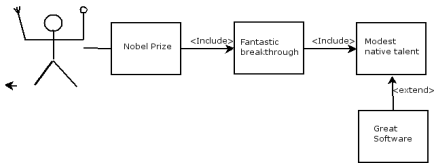
What can UML do for us?



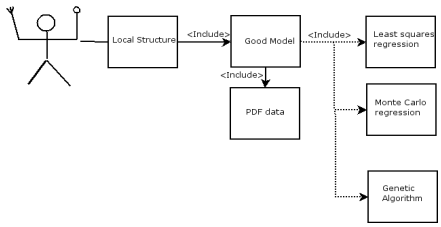
What can UML do for us?



What can UML do for us?



What can UML do for us?



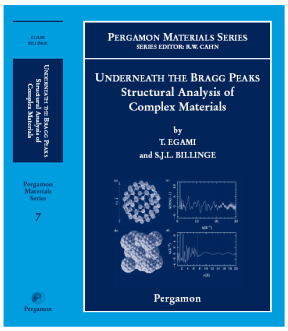
Summary

- PDF: what, when, why, how
  - Disorder in crystals
  - Nanocrystals, nanoparticles and nanostructured materials
- Software Projects and Software Engineering
  - Component architectures
  - DANSE project
- Some provocative remarks

Useful introductory paper:

S. J. L. Billinge and M. G. Kanatzidis **Beyond crystallography: the study of disorder nanocrystallinity and crystallographically challenged materials**, *Chem. commun.* , 749-760 (2004).

Useful book



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