DIFFUSE SCATTERING

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1. **Introduction**
   General expression for diffuse scattering
   Diffuse scattering/properties
   A brief history

2. **1D chain**
   - First kind disorder
     Simulations of diffuse scattering/local order
     Analytical calculations
   - Second kind disorder

3. **Diffuse scattering analysis**
   General rules
   To go further
   Note: static or dynamic origin…

4. **Examples**
   - **Crystals**
     - Barium IV: self-hosting incommensurate structure
     - Nanotubes@zeolite: structural characteristics of nanotubes from diffuse scattering analysis
     - DIPS\(\Phi_4(I_3)_{0.74}\): a one-dimensional liquid
     - Graphene
   - **Fibers**
     - DNA: structure from diffuse scattering pattern
   - **Powders**
     - \(C_{60}\) fullerenes
     - Turbostratic graphite
     - Peapods \(C_{60}\)@single walled carbon nanotube
1. INTRODUCTION - General expression for diffuse scattering

\[ F_n = \text{FT(electronic density within a unit cell ‘n’) } \]

\[ I(\vec{s}) \propto \left\langle \sum_{n,m} F_n e^{-i2\pi s \vec{R}_n} F_n^* e^{i2\pi s (\vec{R}_n+\vec{R}_m)} \right\rangle_t \propto \sum_{m} \left\langle F_n F_{n+m}^* \right\rangle_{n,t} e^{i2\pi s \vec{R}_m} \]

• Average long range order : first-kind disorder

\[ I(\vec{s}) \propto \frac{1}{V} \left| \left\langle F_n(\vec{s}) \right\rangle_n \right|^2 \sum_{h,k,l} \delta(\vec{s} - \vec{G}_{h,k,l}) + \sum_{m} \left( \left\langle F_n F_{n+m}^* \right\rangle_n - \left| \left\langle F_n(\vec{s}) \right\rangle_n \right|^2 \right) \cdot e^{2i\pi s \vec{R}_m} \]

Average structure
ORDER
Bragg peaks

2-body correlations
DISORDER
Diffuse scattering

• No long range order : second-kind disorder
1. INTRODUCTION - General expression for diffuse scattering

- Diffuse scattering: not negligible with respect to Bragg peaks
- Conservation law:
  \[ \int (\text{Diffuse} + \text{Bragg}) (s) = \int \rho(r)^2 \]
1. INTRODUCTION - General expression for diffuse scattering

From Welberry and Butler, J. Appl. Cryst. 27 (1994) 205

(a) Same site occupancy (50%)
(b) Same two-site correlations (0)
(a): completely disordered;
(b): large three-site correlations

Same scattering patterns!

Scattering experiments: probe 2-body correlations

Ambiguities can exist
=> Use chemical-physical constraints
1. INTRODUCTION - Diffuse scattering vs properties

Diffuse scattering ↔ defects, disorder, local order, dynamics

- **Physical properties**
  
  Lasers
  Semiconductor properties (doping)
  Hardness of alloys (Guinier-Preston zones)
  Plastic deformation of crystals (defect motions)
  Ionic conductivity (migration of charged lattice defects)

- **Geosciences** ↔ Related to growth conditions

- **Biology**
  
  biological activity of proteins: intramolecular activity...
1. INTRODUCTION - A brief history

A few dates ...

• 1918: calculation of diffuse scattering for a disordered binary alloy (von Laue)
• 1928: calculation of scattering due to thermal motions (Waller)
• 1936: first experimental results for stacking faults (Sykes and Jones)
• 1939: measurement of scattering due to thermal motion

Diffuse scattering measurements and analysis: no routine methods

Many recent progresses:

- power of the sources (synchrotron...)
  - improvements of detectors
  - computer simulations
2. 1D CHAIN LATTICE – 1st kind of disorder-simulations

Program ‘Diff1D’
to simulate diffuse scattering for a 1D chain:

➢ **Substitution disorder**
Atoms and vacancies on an infinite 1D periodic lattice (concentrations=1/2).

\[ \bullet + + + + \bullet + \bullet \bullet + \bullet + \bullet \bullet \bullet \]

The local order parameter \(p\) is the probability of ‘atom-vacancy’ nearest-neighbors pairs.

➢ **Displacement disorder**
Atoms on an infinite 1D periodic lattice, with displacements (+u) or (-u) (same concentration of atoms shifted right and left).

\[ + \bullet + + + + + \bullet + \bullet + \bullet + \bullet \bullet \bullet \]

The local order parameter \(p\) is the probability of ‘(+u)/(-u)’ nearest-neighbors pairs.

➢ **Size effect**
Atoms and vacancies: local order + size effects (interatomic distance \(d\Rightarrow d+\varepsilon\)).
2. 1D CHAIN LATTICE – 1st kind of disorder-simulations

DIFF1D (program: D. Petermann, P. Launois, LPS)

Case of atoms displaced of [+u] or [-u] on an infinite 1D periodic lattice (same concentration of atoms shifted right and left). The local order parameter $p$ is the probability of "[+u]/[-u]" pairs.

Probability: 0.75
Displacement: -0.07
Max Intensity: 170.875369
QUESTIONS:

- What parameter $p$ would create a random vacancy distribution?

- Describe and explain the effect of correlations (diffuse peak positions and widths).

- What is the main difference between substitution and displacement disorder for the diffuse scattering intensity?

- Size effect: compare diffuse scattering patterns with substitutional disorder and with displacement disorder correlated with substitutional disorder. Discuss the cases $\varepsilon > 0$ and $\varepsilon < 0$.

- Simulate the diffuse scattering above a second order phase transition, when lowering temperature.
ANSWERS:

- Random: \( p = \frac{1}{2} \)

  *Substitution disorder, \( p = \frac{1}{2} \)*

- \( p > \frac{1}{2} \) : positions of maxima \( = (2n+1) \frac{a^*}{2} \), \( n \) integer (ABAB: doubling of the period)

- \( p < \frac{1}{2} \) : positions of maxima \( = n \frac{a^*}{2} \) (small domains: AAAA, BBBBB)

Width \( \propto (\text{correlation length})^{-1} \)

- Substitution, \( p = 0.6 \)

- Substitution, \( p = 0.75 \)

- Displacements, \( p = 0.75 \)


2. 1D CHAIN LATTICE – 1st kind of disorder - simulations
2. 1D CHAIN LATTICE – 1st kind of disorder-simulations

- Substitution disorder: intensity at low s.

Displacement disorder: no intensity around s=0.

- Size effect : intensity asymmetry around s=na* (n integer).

For $\varepsilon > 0$: atom-atom distance larger than vacancy-vacancy distance, atom scattering factor > that of a vacancy (0) => positive contribution just before na*, negative contribution just after na*.
2. 1D CHAIN LATTICE – 1st kind of disorder-calculations

Analytical calculations

a. Substitution disorder

A atoms: red, B: purple

\[ c_A = c_B = \frac{1}{2} \]

\[ p = \text{probability to have a ‘A(red)-B(purple)’ pair} \]

\[
I(s) \propto \frac{1}{a} \left| \langle F_n(s) \rangle_n \right|^2 \sum_h \delta(s - h/a) + \sum_m \left( \langle F_n F_{n+m} \rangle_n - \left| \langle F_n(s) \rangle_n \right|^2 \right) e^{2i\pi sma}
\]

\[
|f_A + f_B|^2 \left/ 4 \right.
\]

\[
I_D \propto \frac{|f_A - f_B|^2}{4} \left[ 1 + 2 \sum_{m>0} \alpha_m \cos(2\pi sma) \right]
\]

With \( \alpha_m = 1 - 2p_m \), \( p_m \) being the probability to have a pair AB at distance (ma); \( p_0 = 0 \), \( p_1 = p \).

\( \alpha_m \) : Warren-Cowley coefficients
2. 1D CHAIN LATTICE –1st kind of disorder-calculations

Demonstration

\[ \langle F_n F_{n+m}^* \rangle_n - \langle F_n(s) \rangle_n^2 = \langle (F_n - \langle F_n \rangle)(F_{n+m}^* - \langle F_{n+m}^* \rangle) \rangle \]

\[ n = A : F_n - \langle F \rangle = \Rightarrow f_A - \frac{f_A + f_B}{2} = \frac{f_A - f_B}{2} \]

\[ \Rightarrow \langle F_n F_{n+m}^* \rangle_n - \langle F_n(s) \rangle_n^2 = \frac{|f_A - f_B|^2}{4} \left[ \frac{1}{2} (1 - p_m) + \frac{1}{2} (1 - p_m) - \frac{1}{2} p_m - \frac{1}{2} p_m \right] \]

\[ \Rightarrow \langle F_n F_{n+m}^* \rangle_n - \langle F_n(s) \rangle_n^2 = \frac{|f_A - f_B|^2}{4} \alpha_m \]

\[ \sum_m \left( \langle F_n F_{n+m}^* \rangle_n - \langle F_n(s) \rangle_n^2 \right) \cdot e^{2i\pi sma} = \frac{|f_A - f_B|^2}{4} \sum_{m=-\infty}^{\infty} \alpha_m \exp(i2\pi sma) \]

\[ = \frac{|f_A - f_B|^2}{4} \left[ 1 + 2 \sum_{m>0} \alpha_m \cos(2\pi sma) \right] \]

\[ \alpha_m = 1 - 2p_m \]
\[ \alpha_0 = 1; m \neq 0, \alpha_m = \alpha_{-m} \]
2. 1D CHAIN LATTICE – 1st kind of disorder – calculations

Interactions between nearest neighbors only:

\[ p_m = \text{prob}_A^m \text{prob}_B^{m-1} + \text{prob}_A^{m-1} \text{prob}_B^1 = p_{m-1} (1-p) + (1-p_{m-1}) p \]

\[ \Rightarrow \alpha_m = (1-2p)^m = \alpha_1^m \]

\[ \sum_{m=0}^{\infty} \alpha_m \exp(2i \pi s ma) = \sum_{m=0}^{\infty} [\alpha_1 \exp(2i \pi sa)]^m = \frac{1}{1-\alpha_1 \exp (2i \pi sa)} \]

\[ \sum_{m=-\infty}^{-1} \alpha_m \exp(2i \pi s ma) = \sum_{m=1}^{\infty} [\alpha_1 \exp(-2i \pi sa)]^m = \frac{1}{1-\alpha_1 \exp (-2i \pi sa)} - 1 \]

\[ I_D \propto \frac{\left| f_A - f_B \right|^2}{4} \frac{1-\alpha_1^2}{1-2\alpha_1 \cos(2\pi sa) + \alpha_1^2} \]

X-Ray Diffraction in Crystals, Imperfect Crystals and Amorphous Bodies, A. Guinier, Dover publications.
2. 1D CHAIN LATTICE – 1st kind of disorder calculations

\[ I_D \propto \frac{|f_A - f_B|^2}{4} \frac{1 - \alpha_1^2}{1 - 2\alpha_1 \cos(2\pi sa) + \alpha_1^2} \]

Formula used in Diff1D

\[ p = \frac{1}{2} : \alpha_1 = 0 : I_D \propto \frac{|f_A - f_B|^2}{4} \]

Laue formula

\[ p > \frac{1}{2} : \alpha_1 < 0 : \text{positions of maxima} = (2n+1) a^*/2, \text{ n integer} \]

\[ P < \frac{1}{2} : \alpha_1 > 0 : \text{positions of maxima} = n a^* \]

A=B : no disorder : no diffuse scattering
2. 1D CHAIN LATTICE – 1st kind of disorder - calculations

b. Displacement disorder

\[
I_D = \frac{|f_A - f_B|^2}{4} \frac{1 - \alpha_1^2}{1 - 2\alpha_1 \cos(2\pi s a) + \alpha_1^2}
\]

with \( f_A \rightarrow f_A e^{i2\pi su} \) and \( f_B \rightarrow f_A e^{-i2\pi su} \)

\[
\Rightarrow I_D = |f_A|^2 \sin^2(2\pi su) \frac{1 - \alpha_1^2}{1 - 2\alpha_1 \cos(2\pi s a) + \alpha_1^2}
\]

*Formula used in Diff1D*

\[I_D(s=0) = 0\]

\( u=0 \): no disorder: no diffuse scattering
2. 1D CHAIN LATTICE –1st kind of disorder-calculation

3. Size effect
Combination of correlated displacement and substitution disorder

\[ I_D(s) \propto \sum_m \left( \langle F_n F_{n+m}^* \rangle_n - \langle F_n(s) \rangle_n \right)^2 \cdot e^{2i\pi s d_m} \]

m\textsuperscript{th} neighbors:
\[ d_{AA}^m = m(1+\varepsilon_{AA}^m), d_{BB}^m = m(1+\varepsilon_{BB}^m), d_{AB}^m = m(1+\varepsilon_{AB}^m) \]

Mean-distance=ma ⇒ \[ \varepsilon_{AB}^m = \frac{(1-p_{AB}^m)(\varepsilon_{AA}^m+\varepsilon_{BB}^m)}{2p_{AB}^m} \]

\[ \exp(i2\pi s m a(1+\varepsilon_{AA}^m)) = (1+i2\pi s m a\varepsilon_{AA}^m) \exp(i2\pi s m a) \ldots \]

\[ I_D = \frac{|f_A - f_B|^2}{4} \left[ 1 + 2 \sum_{m>0} \alpha_m \cos(2\pi s m a) - 2 \sum_{m>0} \beta_m 2\pi s m a \sin(2\pi s m a) \right] \]

\[ \beta_1 = \frac{f_B}{f_B - f_A} (1 + \alpha_1) \varepsilon_{BB} - \frac{f_A}{f_B - f_A} (1 + \alpha_1) \varepsilon_{AA} \]

Warren, X-Ray Diffraction, Addison-Wesley pub.
2. 1D CHAIN LATTICE – 1st kind of disorder-calculations

\[ \begin{align*} 
  f_B &> f_A \\
  \varepsilon_{BB} &> 0 \\
  \varepsilon_{AA} &< 0 \\
\end{align*} \]
\[ \Rightarrow \beta_1 > 0 \]

*Formula used in Diff1D: m=1*

\[ \Rightarrow -\beta_1 \sin(2\pi sa) > 0 \text{ for } s \sim <na, <0 \text{ for } s \sim >na \]

$I_D$ vs $a^*$

- $\varepsilon_{ij} = 0$
- Red: Size effect

Guinier-Preston zones

1938

Alliage Al-Cu après un revenu de 22 h à 100°C.
2. 1D CHAIN LATTICE – 2nd kind of disorder

Second-kind disorder
No long range order

Cumulative fluctuations in distance \( \Rightarrow \) Peak widths increase with \( s \)

\[ c_A = c_B = 1/2, \ p = 1/2 \]

\[ a = (r_A + r_B)/2 \]
1D liquid:
* distribution function $h_1(z)$ of the first neighbors of an arbitrary reference unit
  * $h_m(z) = h_1(z) * h_1(z) * ... * h_1(z)$
∴ Total distribution function: $S(z) = \delta(z) + \sum_{m>0} (h_m(z) + h_{-m}(z))$
∴ Fourier transform: $1 + 2 \sum_{m>0} (H^m(s) + H^*m(s)) = 1 + 2 \text{Re}(H(s)/(1-H(s)))$
  where $H(s) = \text{FT}(h_1)$

Gaussian liquid: $h_1(z) \sim \exp\left(-\frac{(z-d)^2}{2\sigma^2}\right)$: $H(s) \sim \exp\left(-2\pi^2 s^2 \sigma^2\right) \exp(i2\pi sd)$
∴ $I(s) \sim \frac{\sinh(4\pi^2 s^2 \sigma^2/2)}{(\cosh(4\pi^2 s^2 \sigma^2/2) - \cos(2\pi sd))}$

3. DIFFUSE SCATTERING ANALYSIS

- A few properties of the diffuse scattering

  • WIDTH
  - 1st kind disorder: width $\propto 1/(\text{correlation length})$
    
    modulations larger than Brillouin Zone: no correlations;
    diffuse planes: 1D ordered structures with no correlations;
    diffuse lines: disorder between ordered planes

  - Width increases with $s$: 2nd kind of disorder

  • POSITION

    $\Rightarrow$ local ordering in direct space (AAAA, ABABAB...)

  • INTENSITY

    Scattering at small $s$: contrast in electronic density (substitution disorder...)

    No scattering close to $s=0$: displacements involved

    Extinctions $\Rightarrow$ displacement directions... $I \sim f(\mathbf{s} \cdot \mathbf{u}): s \perp \mathbf{u} \Rightarrow I=0$
To go further and understand/evaluate microscopic interactions ...

calculations.

- **Analytical.**
  Modulation wave analysis (for narrow diffuse peaks),
  Correlation coefficients analysis (for broad peaks).

- **Numerical.**
  Model of interactions (with chemical and physical constraints)
  
  Direct space from Monte-Carlo or molecular dynamics simulations;
  Or use of mean field theories ...

  Scattering pattern.
3. DIFFUSE SCATTERING ANALYSIS

- Diffuse scattering origin can be static or dynamic

4. EXAMPLES - Barium IV

Tetragonal symmetry

Diffuse planes in reciprocal space ⇒ in direct space?

No diffuse scattering in the plane l=0 ⇒ in direct space?
4. EXAMPLES - Barium IV

Diffuse planes in reciprocal space $\Rightarrow$ Disorder between chains in direct space

No diffuse scattering in the plane $l=0$ $\Rightarrow$ displacements along the chain axes

$$I_D(s) = f(s \cdot \vec{u})$$

No contribution for $\overrightarrow{s} \perp \vec{u}$
Tetragonal ‘host’, with ‘guest’ chains in channels along the c axis of the host. These chains form 2 different structures, one well crystallized and the other highly disordered and giving rise to strong diffuse scattering. The guest structures are incommensurate with the host.

An incommensurate host-guest structure in an element!
4. EXAMPLES - Nanotubes inside zeolite


Diffuse Scattering zeolite

DS nanotubes

(a) Standard source CuKα, LPS
(b) ID1, ESRF

Diffuse scattering in the plane l=0 close to the origin => ?
4. EXAMPLES - Nanotubes inside zeolite

Zeolite AlPO_4-5 (AFI)                 Nanotubes inside the zeolite channels

Intensity at small s ⇒ Contrast in electronic density :
partial occupation of the channel - different between channels

Schematic drawing of the nanotubes electronic density projected in the z=0 plane
4. EXAMPLES - Nanotubes inside zeolite

Laue formula: \( I_D \propto \frac{|f_A - f_B|}{4} \)

Small s, l=0: \( I_D(s) \propto f_C^2 \cdot (J_0(2\pi s\Phi/2))^2 \)

Nanotubes with \( \Phi \approx 4\text{Å} \). The smallest nanotubes. Vs superconductivity?

Tang et al., Science 292, 2462 (2001)
4. EXAMPLES - DIPSΦ₄(I₃)₀.75

Tetraphenyldithiapyranylidene iodine C₃₄H₂₄I₂.2⁸S₂


FIG. 1. (001) projection of the DIPSΦ₄(I₃)₀.76 structure. Heavy dots point to the position of the triiodide chains in the channels.
4. EXAMPLES - DIPSΦ₄(I₃)₀.₇₅

LURE (synchrotron)
c axis= horizontal

Diffuse scattering in planes l/(9.79Å)

- Extinctions?
- Intensity distribution between the different diffuse planes?
- Widths of the diffuse planes?
4. EXAMPLES - DIPSΦ₄(I₃)₀.₇₅

- No intensity for \( l=0 \) ⇒ displacement disorder along the chain axes

- Widths of the diffuse planes increase with \( l \)
  ⇒ second-type disorder
  ⇒ One-dimensional liquid at Room Temperature

- The most intense planes: \( l=3,4, 6 \) and \( 7 \): due to the molecular structure factor of the triiodide anions.
4. EXAMPLES - DIPSΦ₄(I₃)₀.₇₅

3D ordered state below 182K
4. EXAMPLES - Graphene
Electron scattering

4. EXAMPLES - Structure of B-DNA

The structure of DNA
R. Franklin + J.D. Watson and F.H.C. Crick (1953)

B form of DNA in fiber
4. EXAMPLES - Structure of B-DNA

Angle inversely related to helix radius

Spacing proportional to $1/P$

Pitch = $P$

Spacing corresponds to $1/p$

meridian
4. EXAMPLES - Structure of B-DNA

\[ t_0 = \frac{3P}{8} \]

\[ p = 3.4 \text{Å} \]

\[ P = 34 \text{Å} \]
4. EXAMPLES – $C_{60}$ powder

Fullerenes $C_{60}$

Single crystal


Powder

4. EXAMPLES – Turbostratic carbon

Turbostratic carbon
Random stacking of graphene layers

- Diffraction peaks (00l)
- Diffuse lines (hk)

![Graph showing diffraction peaks and lines]

[Diagram showing random stacking of layers with a labeled height of 3.45 Å]

[Graph showing Q vs. intensity with labeled average]

? Powder average
Sawtooth peak:

The scattering angle decreases

The smallest scattering angle

The scattering angle increases again

\[ I \]

\[ 2\theta_{\text{Min}} \]

\[ 2\theta \]
- Diffraction peaks (00l)
- Symmetric (00l) peaks
- Diffuse lines (hk)
- Sawtooth shaped (hk) reflections

**Powder average**
4. EXAMPLES – Peapods

\[ \delta(Q_z) \]

\[ 4\pi/L \]
\[ 2\pi/L \]
\[ Q_z=0 \]
\[ 2\pi/L \]
\[ 4\pi/L \]

K. Hirahara et al.,

2\pi/L

Intensity

0,60 0,65 0,70 0,75 0,80

Q(Å⁻¹)

1D crystal after powder average

Pink arrow labeled L

Powder average → sawtooth peak
• 1D liquid

• Quantification of the increase of liquid fluctuations with increasing T

PHYSICAL REVIEW B 86, 045446 (2012)

Progressive melting in confined one-dimensional C_{60} chains

Colin Bousige, Stéphane Rols, Erwan Paineau, Stéphan Rouzière, Cristian Mocuta, Bart Verberck, Jonathan P. Wright, Hiromichi Kataura, and Pascale Launois
For other examples, see e.g. the review articles:

- *Diffuse X-ray Scattering from Disordered Crystals*,

- *The interpretation and analysis of diffuse scattering using Monte Carlo simulation methods*

- *Diffuse scattering in protein crystallography*,

- *Diffuse scattering from disordered crystals (minerals)*,

- *Special issue of Z. Cryst. on ‘Diffuse scattering’*
  Free access: http://www.extenza-eps.com/OLD/loi/zkri