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   - Nanotubes@zeolite: structural characteristics of nanotubes from diffuse scattering analysis
   - DIPSΦ₄(I₃)₀.₇₄: a one-dimensional liquid
   - DNA:  ● B-DNA structure from diffuse scattering pattern
     ● coexistence of A- and B-form of DNA

5. Diffuse scattering in powder patterns
1. INTRODUCTION - General expression for diffuse scattering

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

\[ I(\vec{s}) \propto \left| \sum_{n,m} F_n e^{-i2\pi\vec{s}\cdot\vec{R}_n} F^*_n e^{i2\pi\vec{s}\cdot(\vec{R}_n + \vec{R}_m)} \right| \propto \sum_m \left< F_n F^*_{n+m} \right>_{n,t} e^{i2\pi\vec{s}\cdot\vec{R}_m} \]

- Average long range order: first-kind disorder

\[ I(\vec{s}) \propto \frac{1}{V} \left| \left< F_n (\vec{s}) \right>_n \right|^2 \sum_{h,k,l} \delta(\vec{s} - \vec{G}_{h,k,l}) + \sum_m \left( \left< F_n F^*_{n+m} \right>_n - \left| \left< F_n (\vec{s}) \right>_n \right|^2 \right) \cdot e^{i2\pi\vec{s}\cdot\vec{R}_m} \]

- No long range order: second-kind disorder

<table>
<thead>
<tr>
<th>ORDER</th>
<th>DISORDER</th>
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<td>Average structure</td>
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<td>\textbf{ORDER}</td>
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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

Same site occupancy (50%)
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).

  ![Substitution disorder diagram]

  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).

  ![Displacement disorder diagram]

  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.

Max Intensity: 170.875369
Probability: 0.75
Displacement: -0.07
2. 1D CHAIN LATTICE – 1st kind of disorder-simulations

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

ANSWERS:

- Random: \( p = 1/2 \)
  
  *Substitution disorder, \( p = 1/2 \)*

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

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

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

\[
\begin{align*}
\text{Substitution, } p &= 0.6 \\
\text{Substitution, } p &= 0.75 \\
\text{Displacements, } p &= 0.75
\end{align*}
\]
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

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

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

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

A atoms: red, B: purple
\( c_A = c_B = 1/2 \)
\( p = \) probability to have a ‘A(red)-B(purple)’ pair
2. 1D CHAIN LATTICE – 1st kind of disorder-calculations

Demonstration

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

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

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

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

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

\[
= \frac{|f_A - f_B|^2}{4} \left[ 1 + 2 \sum_{m>0} \alpha_m \cos(2\pi ma) \right]
\]
2. 1D CHAIN LATTICE – 1st kind of disorder - calculations

Interactions between nearest neighbors only:

\[ p_m = \text{prob}_{AB}^{m-1} \text{prob}_{BB}^1 + \text{prob}_{AA}^{m-1} \text{prob}_{AB}^1 = p_{m-1}(1 - p) + (1 - p_{m-1})p \]

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

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

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

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

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

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

*Formula used in Diff1D*

\( p=1/2 : \alpha_1=0 : I_D \propto \frac{\left| f_A - f_B \right|^2}{4} \) \quad \text{Laue formula}

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

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

\( A=B : \text{no disorder} : \text{no diffuse scattering} \)
b. Displacement disorder

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

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

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

Formula used in Diff1D

\( I_D(s=0) = 0 \)

\( u=0 : \) no disorder : no diffuse scattering
3. Size effect
Combination of correlated displacement and substitution disorder

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

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

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

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

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

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

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

\[
\begin{align*}
\{ f_B > f_A, \varepsilon_{BB} > 0, \varepsilon_{AA} < 0 \} & \implies \beta_1 > 0 \\
\implies -\beta_1 \sin(2\pi sa) > 0 \text{ for } s < na, < 0 \text{ for } s > na
\end{align*}
\]

Formula used in Diff1D : \( m=1 \)
2. 1D CHAIN LATTICE – 2nd kind of disorder

Second-kind disorder

No long range order

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

\[ a = \frac{(r_A + r_B)}{2} \]

Cumulative fluctuations in distance ⇒ Peak widths increase with s

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

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: $S(z) = \delta(z) + \sum_{m \geq 0} (h_m(z) + h_{-m}(z))$
⇒ 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: $h_1(z) \sim \exp(-(z-d)^2/2\sigma^2)$ : $H(s) \sim \exp(-2\pi^2s^2\sigma^2)\exp(i2\pi sd)$
⇒ $I(s) \sim \sinh(4\pi^2s^2\sigma^2/2)/(\cosh(4\pi^2s^2\sigma^2/2) - \cos(2\pi sd))$

3. DIFFUSE SCATTERING ANALYSIS

A few properties of the diffuse scattering

• WIDTH

- 1st kind disorder : width \( \propto \frac{1}{\text{correlation length}} \)
  
  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

⇒ 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 ⇒ displacement directions...
  \( I \sim f(s.u) : s \perp u \Rightarrow I=0 \)
3. DIFFUSE SCATTERING ANALYSIS

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.
4. EXAMPLES - Barium IV


Synchrotron radiation Source, Daresbury Lab. and laboratory source

Tetragonal symmetry
Diffuse planes $l/3.4\text{Å}$

Diffuse planes in reciprocal space $\Rightarrow$ in direct space?

No diffuse scattering in the plane $l=0 \Rightarrow$ 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

$$I_D(s) = f(s \cdot u)$$

No contribution for $s \perp \vec{u}$
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


(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 $\Rightarrow$ 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: \[ I_D \propto \frac{|f_A - f_B|^2}{4} \]

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

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  -  DIPS\Phi_4(I_3)_{0.75}

- No intensity for $l=0 \Rightarrow$ displacement disorder along the chain axes

- Widths of the diffuse planes increase with $l$
  $\Rightarrow$ second-type disorder
  $\Rightarrow$ 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 - DIPS$\Phi_4(I_3)_{0.75}$

3D ordered state below 182K
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

![Diagram of B-DNA structure with molecular dimensions and extinction points.]
4. EXAMPLES - A- and B-form DNA coexist in a single crystal lattice

4. EXAMPLES - A- and B-form DNA coexist in a single crystal lattice

3.4Å: reinforcement of the molecular structure factor by the base stacking in B-DNA

DC: streaks at 
$(n+1/2)2\pi/c$
$c=41.7\text{Å}$

DC: streaks at 
$2\pi/P$
$P=34\text{Å}$
$(28-34\text{Å})$

What disorder for B-DNA octamers in the channels?
4. EXAMPLES - A- and B-form DNA coexist in a single crystal lattice

Diffuse peaks at \((n+1/2)2\pi/c\)

\(2c\)
\[\bullet + \bullet + \bullet + \bullet + \]

B-DNA octamer length \(\sim 2c/3\)

\(\bullet = \text{one octamer, } + = \text{nothing}

or \(\bullet = 2 \text{ octamers, } + = \text{nothing}\)

Substitutional disorder between \(\bullet\) and +
5. DIFFUSE SCATTERING in POWDER PATTERNS

$C_{60}$ fullerenes

Single crystal


Powder

5. DIFFUSE SCATTERING in POWDER PATTERNS

Turbostratic carbon

Random stacking of graphene layers

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

![Graphene layers diagram with 3.45 Å label]
The scattering angle decreases. The smallest scattering angle. The scattering angle increases again.

Sawtooth peak:

![Diagram of sawtooth peak with scattering angles and intensity graph](image)

\[
I \propto \frac{1}{2\theta_{Min}}
\]
- Diffraction peaks (00l)
- Diffuse lines (hk)
- Symmetric (00l) peaks
- Sawtooth shaped (hk) reflections

Powder average

- Graphite diffraction pattern
- Turbostratic carbon diffraction pattern
For other examples, see e.g. the review articles:

- *Interpretation of Diffuse X-ray Scattering via Models of Disorder*,

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

- *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