“I think you have to be a bit more explicit here in step two”

Pair Distribution Function Analysis

Chris Benmore
X-ray Science Division, Argonne National Lab.
Pioneers in the history of PDF

Fig. 1.—Vacuum camera with monochromator for making X-ray diffraction patterns of glass.

X-ray determination of the Structure of Glass

The partial structure factors of liquid Cu-Sn
Enderby JE, North DM and Egelstaff PA.
Types of Disorder

Temperature

Pressure

Orientational Disorder

Critical point

Dense fluid

Liquid

Solid

Vapour

Triple point

Translational Disorder

Plastic Crystals

Defects

Nanoparticles

Perfect Crystals

Quasicrystals

Dense fluid

Liquids

Glasses

Perfect Crystals

Dense fluid

Triple point

Critical point

Dense fluid
Each diver has a simple set of rules for bonding to the next, but there is sufficient flexibility for different patterns of ordering to be created on the scale of a few body lengths.

A formation of skydivers illustrates order on an intermediate length scale.


“Each diver has a simple set of rules for bonding to the next, but there is sufficient flexibility for different patterns of ordering to be created on the scale of a few body lengths.”

Faber-Ziman formalism – element specific

\[
S_{\text{Red-Red}}(Q) \\
S_{\text{Red-Green}}(Q) \\
S_{\text{Green-Green}}(Q)
\]

Bhatia-Thornton formalism

\[
S_{\text{Number-Number}}(Q) - \text{topology} \\
S_{\text{Concentration-Concentration}}(Q) - \text{chemical ordering} \\
S_{\text{Number-Concentration}}(Q)
\]
## PDF in context with other common methods

<table>
<thead>
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<th>Experiment</th>
<th>Simulation</th>
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<tr>
<td><strong>Neutrons/X-ray PDF</strong></td>
<td><strong>Inverse Methods:</strong></td>
</tr>
<tr>
<td>Good AVERAGE overview of structure</td>
<td>Perfect fits to PDF data</td>
</tr>
<tr>
<td>Short range order (SRO)</td>
<td>Reverse Monte Carlo (RMC)</td>
</tr>
<tr>
<td>Medium range order (MRO)</td>
<td>Empirical Potential</td>
</tr>
<tr>
<td>Neutron Diffraction Isotope Substitution</td>
<td>Structure Refinement (EPSR)</td>
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<td>Crystallography</td>
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<tr>
<td>Long Range Order (LRO)</td>
<td>Molecular Dynamics</td>
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<tr>
<td><strong>EXAFS, XANES</strong></td>
<td></td>
</tr>
<tr>
<td>SRO, Element Specific, Small concs.</td>
<td><strong>Ab initio simulations</strong></td>
</tr>
<tr>
<td>Anomalous x-ray</td>
<td>Density Functional Theory (DFT)</td>
</tr>
<tr>
<td>SRO, MRO. Element specific,</td>
<td></td>
</tr>
<tr>
<td>Difficult to do accurately</td>
<td></td>
</tr>
<tr>
<td><strong>Vibrational Spectroscopy</strong></td>
<td></td>
</tr>
<tr>
<td>Inelastic N and X, Raman and Infrared.</td>
<td></td>
</tr>
<tr>
<td>SRO, MRO. Need good structural model.</td>
<td></td>
</tr>
<tr>
<td><strong>NMR</strong></td>
<td></td>
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<tr>
<td>Isotope Specific. Speciation Q_n.</td>
<td></td>
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</table>
Monochromatic PDF versus time-of-flight PDF

$S(Q,\omega)$ cuts along a liquid structure factor

Introduction to the Liquid State.
Neutron and X-ray differential cross sections

**Neutron**

\[
\frac{d\sigma}{d\Omega} = \frac{d\sigma}{d\Omega}_{\text{self}} + \frac{d\sigma}{d\Omega}_{\text{Inelastic}} + \frac{d\sigma}{d\Omega}_{\text{distinct}}
\]

\[= \sum_\alpha c_\alpha b_\alpha^2 + P(\theta) + F_N(Q)\]

Self scattering

Distinct scattering

Inelastic scattering

“Plazeck”

**X-ray**

\[
\frac{d\sigma}{d\Omega} = \frac{d\sigma}{d\Omega}_{\text{self}} + \frac{d\sigma}{d\Omega}_{\text{Compton}} + \frac{d\sigma}{d\Omega}_{\text{distinct}}
\]

\[= \sum_\alpha c_\alpha f_\alpha^2(Q) + C_X(Q) + I_X(Q)\]

Self scattering

Distinct scattering

Compton scattering
Neutron and X-ray Static Structure Factors

**Neutron Nuclear function**

\[
S_N(Q) - 1 = \frac{F_N(Q)}{\left(\sum_\alpha c_\alpha b_\alpha\right)^2} = \frac{1}{\left(\sum_\alpha c_\alpha b_\alpha\right)^2} \sum_{\alpha,\beta} c_\alpha b_\alpha c_\beta b_\beta (S_{\alpha\beta}(Q) - 1)
\]

Coherent neutron scattering length

**Distinct scattering**

**X-ray pseudo-nuclear function**

\[
S_X(Q) - 1 = \frac{I_X(Q)}{\left(\sum_\alpha c_\alpha f_\alpha(Q)\right)^2} = \frac{1}{\left(\sum_\alpha c_\alpha f_\alpha(Q)\right)^2} \sum_{\alpha,\beta} c_\alpha f_\alpha(Q) c_\beta f_\beta(Q) (S_{\alpha\beta}(Q) - 1)
\]

X-ray form factor

De-convolute electron cloud
Neutron and X-ray differential cross sections

\[
\frac{d\sigma_N}{d\Omega} = \sum_\alpha c_\alpha b_\alpha^2 + P(\theta) - F_N(Q)
\]

\[
\frac{d\sigma_X}{d\Omega} = \sum_\alpha c_\alpha f_\alpha^2(Q) + C_X(Q) - I_X(Q)
\]

Related to isothermal compressibility for a liquid:

\[
\frac{d\sigma}{d\Omega}(Q = 0) = \rho K_B T \chi T \sum_\alpha c_\alpha b_\alpha^2
\]
Outline of time-of-flight neutron analysis procedure

- Sample
- Container
- Background
- Vanadium

Calculate **Attenuation (A)** and **Multiple Scattering (MS)** corrections

Calculate neutron Differential Cross Section (DCS)

\[
DCS = \frac{\text{Sample} - \text{Container}}{\text{Smoothed Vanadium x density}}
\]

with A and MS corrections applied at each angle

Group corrected DCS spectra at each angle.
Apply Placzek correction

**Neutron Structure Factor S(Q)**

Fourier transform to obtain radial distribution function g(r)
Neutron diffraction corrections

Placzek correction

\[ P(Q, \theta) = -\frac{2ym}{M} X + \frac{m k_B T Y}{M 2E_0} \]

Paalman and Pings attenuation factors

\[ F_s(Q) = K \left( \frac{I_0^{sc} - B}{A_{s,sc}} - \frac{A_{c,sc} (I_0^{c} - B)}{A_{s,sc} A_{c,c}} \right) \frac{\sigma_{sc}}{4\pi b^2} M_{sc} \]

Ideal neutron PDF experiment designed so that attenuation and multiple scattering effects are \(~10\%\)
How do the corrections effect the measured data?

**CCl₄**

- Uncorrected I(Q)
- Relative intensity
- Placzek graph
- Absorption coefficient $A_{s,s}$ graph
- Multiple scattering graph
- $F(Q) \times 10^2$ barns graph

**D₂O**

- Uncorrected I(Q)
- Relative intensity
- Placzek graph
- Absorption coefficient $A_{s,s}$ graph
- Multiple scattering graph
- $F(Q) \times 10^2$ barns graph

---

*Time-of-Flight Neutron Total Scattering Data Analysis implemented in the software suite ISAW.*

Proton recoil and Vanadium normalization

Chebyshev polynomial

Vanadium rods
same geometry as sample

Hydrogen Placzek Correction
Check: cross-sections at all angles overlap

A.K. Soper
Interpreting Structure Factors

Tetrahedral glasses

$r_1$ = first peak position in real space

FSDP – First Sharp Diffraction Peak: Intermediate Range Order

SSDP – Second Sharp Diffraction Peak: Extended Range Order

**Weighted Partial Structure Factors**

Total Structure Factor, $S(Q)$ = Weighting factors, $W_{\alpha\beta}(Q)$ \times Partial Structure Factors, $S_{\alpha\beta}(Q)$

**Neutron**
- $S_N(Q)$
  - $Q$ (Å$^{-1}$)
  - $S_N(Q)$

**X-ray**
- $S_X(Q)$
  - $Q$ (Å$^{-1}$)
  - $S_X(Q)$

**Vitreous Germania**
- $S_{GeGe}(Q)$
  - $Q$ (Å$^{-1}$)
  - $S_{GeGe}(Q)$

- $S_{GeO}(Q)$
  - $Q$ (Å$^{-1}$)
  - $S_{GeO}(Q)$

- $S_{OO}(Q)$
  - $Q$ (Å$^{-1}$)
  - $S_{OO}(Q)$
The Miracle step

\[ g(r) = 1 + \frac{1}{2\pi^2 \rho r} \int Q \, i(Q) \sin(Qr) \, dQ \]

- \( g(r) \to 0 \) as \( r \to 0 \)
- \( g(r) \to 1 \) as \( r \to \infty \)

Radial distribution function

\( T(r) = 4\pi \rho r \cdot g(r) \)
Total distribution function

\( D(r) = 4\pi \rho r \cdot [g(r) - 1] \)
Differential distribution function

\[ \sin \left( \frac{\pi Q}{Q_{\text{max}}} \right) \left( \frac{\pi Q}{Q_{\text{max}}} \right)^{-1} \]
Lorch modification function

Truncate at a positive node to minimize Fourier artifacts
A question of resolution – the effect of Q_max

As₄O₆ molecule

**Inversion of data to real space**

‘First sharp diffraction peak’

**Sine Fourier Transformation**

\[
S(Q) \rightarrow T(r) = 4\pi pr\cdot g(r)
\]
Flaw of Averages

PDF measures the AVERAGE structure i.e. coordination number
Naturally occurring nuclides for NDIS

Identified by feasibility of Neutron Diffraction Isotopic Substitution experiment

\[ \Delta b = 0.10 \text{ fm} \]

**NOT** 0.46 fm

Scratched!


Second order difference $\Delta b > 10$ fm
First order difference $\Delta b > 1$ fm
Feasible using NOMAD at SNS
Other

Isotopic Substitution and Partial Structure Factors
Partial Structure Factors for glassy SiO₂

Matrix for extracting partial structure factors from two neutron $^{29}\text{Si}$ and $^{28}\text{Si}$ and one high energy x-ray experiment.

$$
\begin{bmatrix}
    I_N(Q)^	ext{Nat} \\
    I_N(Q)^	ext{29Si} \\
    I_X(Q)
\end{bmatrix} = 
\begin{bmatrix}
    c_{\text{Si-Nat}}^2 b_{\text{Si}}^2 & 2c_{\text{Si}} c_{\text{O-Nat}} b_{\text{Si}} b_{\text{O}} & c_{\text{O}}^2 b_{\text{O}}^2 \\
    c_{\text{Si-29Si}}^2 b_{\text{Si}}^2 & 2c_{\text{Si}} c_{\text{O-29Si}} b_{\text{Si}} b_{\text{O}} & c_{\text{O}}^2 b_{\text{O}}^2 \\
    c_{\text{Si}}^2 f_{\text{Si}}^2(Q) & 2c_{\text{Si}} c_{\text{O}} f_{\text{Si}}(Q) f_{\text{O}}(Q) & c_{\text{O}}^2 f_{\text{O}}^2(Q)
\end{bmatrix} \cdot 
\begin{bmatrix}
    S_{\text{SSi}}(Q) - 1 \\
    S_{\text{SiO}}(Q) - 1 \\
    S_{\text{Oo}}(Q) - 1
\end{bmatrix}
$$

$$I_X(Q) = \langle F^2 \rangle . S_X(Q) = S_X(Q) \sum_{i,j=\text{Si, O}} c_i c_j f_i(Q) f_j(Q)$$

$$I_N(Q) = 4\pi b^2 . S_N(Q)$$

$b^{\text{NatSi}} = 4.1491(10)$ fm and $b^{28\text{Si}} = 4.80(5)$ fm

$\Delta b = 0.65$ fm

Partial Pair Distribution Functions of vitreous Silica

Courtesy of Shinji Kohara
H/D substitution: Partial Structure Factors for water

Neutron data

$g_{\text{D}_2\text{O}}(r)$

$g_{\text{HDO}}(r)$

(50%H$_2$O + 50%D$_2$O)

$g_{\text{H}_2\text{O}}(r)$

Extracted partials

$g_{\text{OH}}(r)$

$g_{\text{OO}}(r)$ (~ $g_{\text{xray}}(r)$)

$g_{\text{HH}}(r)$

$b_H = -3.74$ fm
Solving the Nanoprobe

![Graphs and images showing molecular distances and correlations with variances](image)

High energy x-ray beamlines at APS

II-ID-C

II-ID-B

I-ID

Large area detector

~20 Å⁻¹

Diffracted beam

2θ

Beam stop

High energy incident x-ray beam $E_i = 100$ KeV

Monitor diode

Incident beam slit

Incident wavelength $\lambda \sim 0.1$ Å

Scattering angle $2\theta \sim 20^\circ$

Q-range ~0.5 to 20 Å⁻¹
State of the art neutron instrumentation.
Nanoscale Ordered MAterials Diffractometer

Online in 2011

<table>
<thead>
<tr>
<th></th>
<th>D4c (ILL)</th>
<th>GEM (ISIS)</th>
<th>DRACULA (ILL Project)</th>
<th>NOMAD Project</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time averaged flux ($10^8$ n/cm$^2$)</td>
<td>0.4</td>
<td>~0.02</td>
<td>~1</td>
<td>~1.7 (1.4MW)</td>
</tr>
<tr>
<td>Detector coverage (strad)</td>
<td>0.11</td>
<td>4.0</td>
<td>1.5</td>
<td>~10</td>
</tr>
<tr>
<td>Product ($10^6$)</td>
<td>4.4</td>
<td>8</td>
<td>150</td>
<td>1700</td>
</tr>
</tbody>
</table>
Anomalous neutron diffraction - new possibilities at SNS

Anomalous Neutron Diffraction of Disordered Materials

Argonne National Laboratory

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Reverse Monte Carlo Modeling of Neutron and X-ray data

Best (essential ?) to use more than one structure factor plus chemical constraints
Empirical Potential Structure Refinement

Quantum isotope effects in water

H$_2$O-D$_2$O

Molecular dynamics Simulations

Y₂O₃-Al₂O₃ Black lines = MD

X-ray

30%Al₂O₃
27%Al₂O₃
30%Al₂O₃
27%Al₂O₃

Neutron

S(Q)

0 5 10 15 20 25
Q (Å⁻¹)

Tetrahedral oxygen triclusters in Yttria-Alumina glasses

Specialized Sample Environments: Levitator

T_{\text{max}} = 300^\circ \text{C.}
Supercool liquids several hundreded degrees.

Specialized Sample Environments: High Pressure

Time Resolved Measurements: Chemical Reactions

Courtesy of Eugene Bychkov

$P_4$, $P_4S_3$, $P_4S_7$, $P_4S_{10}$
Last slide

Chris’s PDF guidelines
Real space peak position = bond length
Peak area $\propto$ coordination number
Model disagrees with data = it’s wrong!
No peaks = no atoms