ε-Machine Spectral Reconstruction Theory Applied to Discovering Planar Disorder in Close-Packed Structures

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Readings for this lecture:

BTFM1 and BTFM2 articles in CMR and Lecture Notes
Phenomenology of Polytypism

• Definition: Polytypism is the phenomenon of a substance that can assume two or more layer-like structures each having the same stoichiometry but differing in the manner of the stacking of layers. (Called Modular Layers)

• One-Dimensional: The *intra*-layer bonding is much stronger than the *inter*-layer bonding, creating effectively one-dimensional materials.

• Wide Spread: Occurs in SiC, ZnS, CdI₂; micas such as muscovite and manganite; III-VI compounds like GaS, GaSe and InSe; metals and alloys like Co, Li and ZrCr₂; oxides like Ba₅Nb₄O₁₅ and BaRuO₃; sulfides like BaTaS₃.

• Variety of Materials: Many have widely varying properties: metals & insulators, covalent & ionic bonding.

• Plethora of Structures: In some compounds, there can be 100’s of different crystalline structures.

• Long Range Order: Some of these structures can exist over 100 modular layers.

• Disordered: Many of these structures have considerable planar disorder.
Stacking Faults in SiC

Previous Descriptions of Planar Disorder

- Jagodzinski's Disorder Theory (Jagodzinski, 1949)
- The Fault Model (Sebastian & Krishna, 1980 and many others)
- Reverse Monte Carlo (McGreevy & Pusztai, 1988)
Close-Packed Structures
Hexagonal Close-Packed Structures (2H)

Hexagonal Close-Packed Structure
as seen from above

Hexagonal Close-Packed Structure
as seen from the side
Cubic Close-Packed Structures (3C)

Cubic Close-Packed Structure as seen from above

Cubic Close-Packed Structure as seen from the side
The Structure of Zinc Sulphide

• Consider the ‘basic unit’ to be a zinc-sulphur pair stacked vertically. (A green-brown pair in the figure to the left.)

• Then, Modular Layers are formed from a hexagonal net of these units.

• It turns out that there are only three possible orientations any modular layer can occupy. Call them A, B, and C.

• A sample is specified by giving the sequence of modular layers.

• The stacking constraints can be expressed as no two adjacent layers can have the same orientation.

• We can take advantage of this by using an alternate labeling scheme:

  \[ A \rightarrow B \rightarrow C \rightarrow A : '1' \]
  \[ A \rightarrow C \rightarrow B \rightarrow A : '0' \]

• So the sequence to left (reading from bottom to top) would be \textbf{ABABCA} which could be written in as \textbf{10111}.

Thus, a crystal is completely specified by a sequence of \textbf{1}'s and \textbf{0}'s
Some Common Stacking Structures in CPSs

3C⁺: ...ABCABCABCABC... or ...11111111111... or (1)*
3C⁻: ...ACBACBACBACB... or ...00000000000... or (0)*  (Not shown)
2H: .....ABABABABABAB... or ...10101010101... or (01)*
4H: .....ABCBCBACBABC... or ...11001100110... or (1100)*
6H₁: .....ABCACBABCACB... or ...11100111100... or (111000)*
6H₂: .....ABCABCBCBABC... or ...11001100110... or (110010)*
9R⁺: ...ACABABCBCACA... or ...01101101101... or (011)*  (Not shown)
9R⁻: ....ABACACBCBABA... or ...10010010010... or (100)*

Notice that the period in the two notations need not be the same!
“Figure 9a illustrates the stacking fault existed in a single nanobelt, which is parallel to the axis and runs through out the nanobelt. Figure 9b shows two types of structure zone existed in a leg of tetrapod ZnS. One consists of the wurtzite structure (hcp, hexagonal close-packed) in zone a and the other is sphalerite structure (fcc, face centered cubic) in zone b, and the two different structures were formed by changing the stacking sequence of the closed-packed planes of the ZnS crystal and resulted from the crystallogenesis of ZnS. It should be noted that some properties, such as the photoluminescence, gas sensing property of obtained products are closely related to the intrinsic defects in crystals (Jiang et al., 2003).”

Polytypes in Bulk Zn$_{1-x}$Mg$_x$Se crystals

“HRTEM images of plate B5: (a) 2H domain with a defect consisting of additional planes with cubic stacking indicated by the dashed lines. On the right side of the picture the stacking sequence is explained. (b) Direct 8H/4H interface; a stacking fault in 8H domain is indicated by the vertical arrow, (c) An 8H/4H interface; at the interface, a strip built of 17 planes stacked according to the 3C structure is observed.” From: W Paszkowicz, P Dluewski and ZM Spolnik and F Firszt and H Meczynska (1999) Journal of Alloys and Compounds 286, pp. 224-235.
Experiment measures the intensity $I$ scattered into an angle $\theta$. Sometimes, though, the intensity is reported as a function of the component of the reciprocal lattice vector perpendicular to the modular layers ($l$). Without going through the kinematics, it is sufficient to know that $l$ indexes the angle $\theta$. Thus, instead of $I(\theta)$ we often have $I(l)$. 
Four Circle Diffractometer

Four Circle Diffractometer

Diffraction Spectra from Close-Packed Structures

\[
I(l) = \psi^2(l) \left( \frac{\sin^2(\pi N l)}{\sin^2(\pi l)} - 2\sqrt{3} \sum_{n=1}^{N} (N - n) [Q_c(n) \cos(2\pi nl + \frac{\pi}{6}) + Q_a(n) \cos(2\pi nl - \frac{\pi}{6})] \right),
\]

- \(I(l)\) is the diffracted intensity along the direction perpendicular to the stacking,
- \(l\) indexes the magnitude of the perpendicular component of the diffracted wave,
- \(\psi^2(l)\) accounts for scattering factors,
- \(N\) is the number of modular layers,
- \(Q_c(n)\) and \(Q_a(n)\) are the Correlation Functions, i.e., the probability any two modular layers at separation cyclically or anti-cyclically related. \(Q_s(n)\) is probability that two layers at separation \(n\) have the same orientation. Note that \(Q_c(n) + Q_a(n) + Q_s(n) = 1\).

We can expand the cosine terms and integrate over a unit interval and find,

\[
X(n) = \int I(l) \cos(2\pi nl) \, dl \quad \text{and} \quad Y(n) = \int I(l) \sin(2\pi nl) \, dl
\]

Thus the correlation functions can be written as:

\[
Q_c(n) = \frac{1}{3} - \frac{1}{3} \left[ X(n) - \sqrt{3}Y(n) \right] \quad \text{and} \quad Q_a(n) = \frac{1}{3} - \frac{1}{3} \left[ X(n) + \sqrt{3}Y(n) \right]
\]

Thus, the correlation functions can be found by Fourier Analysis of the Diffraction Spectrum.
Figures-of-Merit for Diffraction Spectra

It can be shown that the diffraction spectrum must obey two equalities when integrated over a unit interval in \( l \). We can use this to evaluate the quality of data over candidate unit intervals.

\[
\gamma = \int 1(l) \cos(2\pi l) \, dl = -1/2
\]

\[
\beta = 2Q_c(1) + Q_c(2) - Q_a(2) = 1
\]

Quick Derivations:

\[
Q_c(1) + Q_a(1) = 1
\]

\[
X(1) = -1/2
\]

\[
\gamma = \int 1(l) \cos(2\pi l) \, dl = -1/2
\]

\[
\beta = 2Q_c(1) + Q_c(2) - Q_a(2) = 1
\]

\[
\Pr(00) + 2\Pr(01) + \Pr(11) = 1
\]

\[
\Pr(01) = \Pr(1) - \Pr(11)
\]

\[
\Pr(00) + 2\Pr(1) - \Pr(11) = 1
\]

\[
2Q_c(1) + Q_c(2) - Q_a(2) = 1
\]

\[
\beta = 2Q_c(1) + Q_c(2) - Q_a(2) = 1
\]
Some Diffraction Spectra for Periodic CPSs

Diffraction Pattern for a FOC Lattice

<table>
<thead>
<tr>
<th>Intensity in arb. units</th>
<th>0</th>
<th>2000</th>
<th>4000</th>
<th>6000</th>
<th>8000</th>
<th>10000</th>
<th>12000</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l$</td>
<td>0</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
<td>1</td>
</tr>
</tbody>
</table>

$3C^+$

$(1)^*$

Diffraction Pattern for a HCP Lattice

<table>
<thead>
<tr>
<th>Intensity in arb. units</th>
<th>0</th>
<th>2000</th>
<th>4000</th>
<th>6000</th>
<th>8000</th>
<th>10000</th>
<th>12000</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l$</td>
<td>0</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
<td>1</td>
</tr>
</tbody>
</table>

$2H$

$(01)^*$

Diffraction Pattern for the 4H Process

<table>
<thead>
<tr>
<th>Intensity in arb. units</th>
<th>0</th>
<th>2000</th>
<th>4000</th>
<th>6000</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l$</td>
<td>0</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
</tr>
</tbody>
</table>

$4H$

$(1100)^*$

Diffraction Pattern for the 6H Process

<table>
<thead>
<tr>
<th>Intensity in arb. units</th>
<th>0</th>
<th>500</th>
<th>1000</th>
<th>1500</th>
<th>2000</th>
<th>2500</th>
<th>3000</th>
<th>3500</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l$</td>
<td>0</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
<td>0.6</td>
<td>0.7</td>
</tr>
</tbody>
</table>

$6H_1$

$(111000)^*$
The \( r = 3 \) Spectral Equations for CPSs

\[
\begin{align*}
\Pr(0000) + \Pr(0001) + \Pr(0010) + \Pr(0011) + \Pr(0100) + \Pr(0101) + \Pr(0110) + \Pr(0111) + \Pr(1000) + \Pr(1001) + \Pr(1010) + \Pr(1011) + \Pr(1100) + \Pr(1101) + \Pr(1110)\Pr(1111) &= 1
\end{align*}
\]

\[
\begin{align*}
Q_c(2) &= \Pr(0000) + \Pr(0001) + \Pr(0010) + \Pr(0011), \\
Q_r(2) &= \Pr(1100) + \Pr(1101) + \Pr(1110) + \Pr(1111), \\
Q_c(3) &= \Pr(0110) + \Pr(0111) + \Pr(1010) + \Pr(1011) + \Pr(1000) + \Pr(1001), \\
Q_r(3) &= \Pr(0001) + \Pr(1011) + \Pr(0111), \\
Q_c(4) &= \Pr(0010) + \Pr(0100) + \Pr(0010) + \Pr(0010) + \Pr(0001), \\
Q_r(4) &= \Pr(0000) + \Pr(0111) + \Pr(0110) + \Pr(1011) + \Pr(1110), \\
Q_c(5) &= \frac{\Pr^2(0000)}{\Pr(0000) + \Pr(0001)} + \frac{\Pr(0111)\Pr(1110)}{\Pr(1110) + \Pr(1111)} + \frac{\Pr(0011)\Pr(0110)}{\Pr(0111) + \Pr(0110)} + \frac{\Pr(0101)\Pr(1011)}{\Pr(1011) + \Pr(1010)} + \frac{\Pr(0100)\Pr(1011)}{\Pr(1110) + \Pr(1111)}, \\
Q_r(5) &= \frac{\Pr^2(1111)}{\Pr(1111) + \Pr(1110)} + \frac{\Pr(1001)\Pr(0001)}{\Pr(1000) + \Pr(0010)} + \frac{\Pr(1010)\Pr(1001)}{\Pr(1001) + \Pr(1010)} + \frac{\Pr(0101)\Pr(0100)}{\Pr(0100) + \Pr(0101)}.
\end{align*}
\]

All of the equations are linear except for the last two. We solve them for sequence probabilities \( \Pr(s_{1234}) \) given the correlation functions.

Lecture 36: Natural Computation & Self-Organization, Physics 256B (Spring 2013); Jim Crutchfield
The $\varepsilon$MSR Algorithm

1. Experimental Diffraction Pattern

2. Experimental Correlation Functions

3. Solve the Spectral Eqs for $P(\omega')$

4. Construct the candidate $\varepsilon$-M

5. Calculate Theoretical Correlation Functions

6. Calculate Theoretical Diffraction Pattern

7. Compare Experimental and Theory Diffraction Patterns

8. Good Agreement

9. Quit

10. Bad Agreement: $r \to r + 1$


Lecture 36: Natural Computation & Self-Organization, Physics 256B (Spring 2013); Jim Crutchfield
The most general $r=3$ $\varepsilon$-Machine. We show only the recurrent portion of the $\varepsilon$-machine as the transient part is not physically relevant. The causal states are labeled by the last three spins seen, i.e, $S_5$ means that 101 were the last three spins seen. The edge label $s|p$ indicates a transition on spin $s$ with probability $p$. By ‘most general’ we mean that all pasts at $r=3$ are distinguished, and all possible transitions between causal states exist. This is a 3$^{rd}$ order Markov Process.
Definition: Causal State Cycles

Causal State Cycle: A non-self intersecting, closed, symbol-specific path on an $\varepsilon$-machine.
The causal state cycles that correspond to the 3C structure on an $r=3$ $\varepsilon$-machine. Recall, $3C^+$ is just \ldots 1111111\ldots, and $3C^-$ is just \ldots 0000000\ldots.
The causal state cycle that correspond to the 2H structure on an $r=3$ ε-machine. Recall, 2H is just $...010101...$. 

Lecture 36: Natural Computation & Self-Organization, Physics 256B (Spring 2013); Jim Crutchfield
The causal state cycle that correspond to the 4H structure on an $r=3$ ε-machine. Recall, 4H is just ...11001100...
6H Crystal Structure on an $r = 3$ $\varepsilon$-Machine

The causal state cycle that correspond to the 6H structure on an $r=3$ $\varepsilon$-machine. Recall, 6H is just ...111000111000....

Diffraction Pattern for the 6H Process

(...000111000111...)

Lecture 36: Natural Computation & Self-Organization, Physics 256B (Spring 2013); Jim Crutchfield
Completely Random Stacking of Layers

Diffraction Pattern for a RNG

For contrast, here is the diffraction spectrum for a completely random stacking structure. The spectrum is entirely diffuse.
Causal State Cycles: A non-self intersecting, closed, symbol specific path on an \( \varepsilon \)-machine. They can lead to crystal structures: \( 3C \) (green), \( 2H \) (blue), \( 6H \) (red), and \( 4H \) (cyan). These are four of the possible 19 causal state cycles on an \( r=3 \) \( \varepsilon \)-machine. They can also lead to faulting structures, as seen on the next slide.
Faulting Structures for 3C

**Growth Fault:** The stacking rule is broken for a layer, such that the next layer added isn’t different from the previous two. This leads to a twinned crystal:

```
...000000000... → ...0000|1111...
```

**Deformation Fault:** A spin is flipped. This can’t lead to a twinned crystal:

```
...111111111... → ...11011111...
```

**Layer Displacement Fault:** Two adjacent layers switch orientation. This is equivalent to flipping three adjacent spins. This can’t lead to a twinned crystal:

```
...111111111... → ...10011111...
```
Faulting Structures for 2H

**Growth Fault:** Insertion of spin: \( \ldots101010\ldots \rightarrow \ldots1010010\ldots \)

**Deformation Fault:** Flip a spin: \( \ldots010101\ldots \rightarrow \ldots011101\ldots \)

**Layer Displacement Fault:** Exchange adjacent spins: \( \ldots010101\ldots \rightarrow \ldots011001\ldots \)
Polytypism in Zinc Sulphide

- Discovered by Frondel and Palache in 1948.
- Over 185 observed crystalline structures that can be formed and co-exist under virtually identical thermodynamic conditions.
- Longest period observed is 114 modular layers.
- Many disordered structures exist.
- Found in both mineral and synthetic ZnS crystals.
- Only two stable structures in ZnS are thought to exist: The hexagonal close-packed (HCP, aka 2H and wurtzite) above 1024 C, and the face-centered cubic (FCC, aka cubic close-packed, 3C and zinc-blende) below 1024 C. All others are believed to be metastable.
- ZnS can undergo solid-state transformations upon annealing.
The experimental spectrum for zinc sulphide. This spectrum should be periodic in $l$ with period one but clearly it is not. This illustrates the need to choose a unit interval in $l$ that is relatively error free.
The experimental spectrum for zinc sulphide. This spectrum should be periodic in $l$ with period one but clearly it is not. This illustrates the need to choose a unit interval in $l$ that is relatively error free.

The figures-of-merit calculated over various intervals $l_0$ to $l_0 + 1$. We see that near $l_0 = 0$, the figures-of-merit are roughly near their theoretical values.
The $r = 3$ Reconstructed $\varepsilon$-Machine for SK134

![Diagram of the $r = 3$ Reconstructed $\varepsilon$-Machine for SK134]
Experimental Spectrum SK134

- Left graph: Plot of $Q_s(n)$ against $n$.
- Right graph: Intensity in arb. units vs. $l$.

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Lecture 36: Natural Computation & Self-Organization, Physics 256B (Spring 2013); Jim Crutchfield

Wednesday, May 22, 13
Experimental Spectrum SK134

<table>
<thead>
<tr>
<th>Structure</th>
<th>$\varepsilon$-M</th>
<th>FM</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H</td>
<td>64%</td>
<td>83%</td>
</tr>
<tr>
<td>3C</td>
<td>8%</td>
<td>0%</td>
</tr>
<tr>
<td>Deformation</td>
<td>16%</td>
<td>17%</td>
</tr>
<tr>
<td>Growth</td>
<td>6%</td>
<td>0%</td>
</tr>
<tr>
<td>Layer - Displacement</td>
<td>6%</td>
<td>0%</td>
</tr>
</tbody>
</table>
Experimental Spectrum SK135

\[ Q_s(n) \]

\[ \text{Intensity in arb. units} \]

Lecture 36: Natural Computation & Self-Organization, Physics 256B (Spring 2013); Jim Crutchfield
Experimental Spectrum SK135

\[ Q_s(n) \]

\[ n \]

\[ \text{Intensity in arb. units} \]

\[ l \]

\[ S_7 \]
\[ (0.31) \]

\[ S_6 \]
\[ (0.08) \]

\[ S_4 \]
\[ (0.05) \]

\[ S_2 \]
\[ (0.01) \]

\[ S_0 \]
\[ (0.33) \]

\[ S_3 \]
\[ (0.08) \]

\[ S_1 \]
\[ (0.05) \]
Experimental Spectrum SK135

No sensible fault model analysis is possible here.
Computational, informational, and physical quantities calculated for the two samples, as well as the three crystalline structures we considered. $E$ is configurational energy per Zn-S pair associated with the stacking. $\alpha$ is the hexagonality of each sample. (The hexagonality is defined as that fraction of modular layers which are hexagonally related to their neighbors.)

<table>
<thead>
<tr>
<th>System</th>
<th>$P$</th>
<th>$r_1$</th>
<th>$h_\mu$(bits/ML)</th>
<th>$C_\mu$(bits)</th>
<th>$E$ (meV)</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>1.0</td>
<td>1.95</td>
<td>1.00</td>
</tr>
<tr>
<td>3C</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0.0</td>
<td>-1.79</td>
<td>0.00</td>
</tr>
<tr>
<td>6H</td>
<td>6</td>
<td>3</td>
<td>0</td>
<td>2.6</td>
<td>-0.65</td>
<td>0.33</td>
</tr>
<tr>
<td>SK134</td>
<td>4.8</td>
<td>3</td>
<td>0.50</td>
<td>2.3</td>
<td>1.13</td>
<td>0.80</td>
</tr>
<tr>
<td>SK135</td>
<td>5.6</td>
<td>3</td>
<td>0.59</td>
<td>2.5</td>
<td>-1.02</td>
<td>0.24</td>
</tr>
</tbody>
</table>
Advantages over Other Methods

Table 1: A comparison between $\epsilon$-machine spectral reconstruction ($\epsilon$MSR), the fault model (FM) and Jagodzinski’s disorder model (JDM). We see that $\epsilon$MSR has many advantages over previous analyses.

<table>
<thead>
<tr>
<th></th>
<th>$\epsilon$MSR</th>
<th>FM</th>
<th>JDM</th>
<th>RMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Description of Disorder</td>
<td>$\epsilon$-Machine</td>
<td>Fault Probabilities</td>
<td>Conditional Probabilities</td>
<td>Stacking Sequence</td>
</tr>
<tr>
<td>2. Method of Analysis</td>
<td>Fourier Analysis</td>
<td>Peak Analysis</td>
<td>Fit Diffraction Spectrum or Correlation Functions</td>
<td></td>
</tr>
<tr>
<td>3. Treats any amount of Disorder?</td>
<td>yes</td>
<td>no</td>
<td>yes (?)</td>
<td>yes</td>
</tr>
<tr>
<td>4. Unique Description?</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>5. Assumes a Markov Process?</td>
<td>yes, $r = 3$</td>
<td>yes, $r = 3$</td>
<td>yes, $r = 2$</td>
<td>yes (?)</td>
</tr>
<tr>
<td></td>
<td>(can go higher)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. Simultaneously Allows more than one Crystal Structure?</td>
<td>yes</td>
<td>no</td>
<td>yes (limited)</td>
<td>yes</td>
</tr>
<tr>
<td>7. Treats Crystal/Fault Structure the Same?</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>8. Uses all the Information in the Diffraction Pattern?</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>9. Allows Calculation of Physical Parameters</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>yes</td>
</tr>
</tbody>
</table>
So, Summing Up:

• $\varepsilon$MSR provides the most general description possible of disorder in one dimension.

• No assumption about the crystal structure or fault structure need be made.

• Any kind or amount of planar disorder can be treated.

• There may be more than one crystal structure present.

• Treats fault and crystal structure on an equal footing.

• All the information in the spectrum---both Bragg like and diffuse scattering---is used to generate the model.

• Parameters of physical interest are amenable to calculation from the $\varepsilon$-machine.

• $\varepsilon$MSR can evaluate the quality of experimental data before beginning reconstruction.
Open Research Questions

1. Impose symmetry conditions on the sequence probabilities, and develop symmetric \( \varepsilon \)-machine spectral reconstruction theory (S\( \varepsilon \)MSR).
2. Extend \( \varepsilon \)MSR and S\( \varepsilon \)MSR to the \( r = 4 \) case.
3. Use Reverse Monte Carlo Modeling to find sample, disordered crystals, and then use standard reconstruction techniques to find the \( \varepsilon \)-machine.
4. Simulate layer displacement faulting to model the 2H to 3C transformation, and both deformation and layer displacement faulting to simulate the 3C to 2H transformation.
5. Examine other close-packed structures, like SiC or perhaps graphene. Or more complicated polytypes for that matter.
6. Consider the implications of various kinds of disorder on various phenomena in condensed matter systems, such as Anderson Localization.
7. Consider the interpretations/applications of new computational measures in the polytype setting.
8. Suppose that one had some phase information, how could one incorporate that into the Spectral Equations?
9. It is claimed that from the analysis of peak profiles one can extract correlation information--\( Q_s(n) \)--from powder diffraction data, assuming spin inversion symmetry. When one combines this with S\( \varepsilon \)MSR, how good is the reconstructed \( \varepsilon \)-machine?
10. Explore how \( \varepsilon \)MSR handles noisy diffraction spectra.
11. Two Dimensions, Anyone?
References


