Novel Visualization of Crystal Structure and Energetics

Robert M. Hanson
St. Olaf College, Northfield, MN
http://www.stolaf.edu/people/hansonr

1st International Conference on Computational & Applied Physics (ICCAP 2021)
Bilda, Algeria (virtual)
Sep 26-28, 2021
Land Acknowledgment

In southeastern Minnesota, we stand on the homelands of the Wahpekute Band of the Dakota Nation. We honor with gratitude the people who have stewarded this land throughout the generations and their ongoing contributions to this region. We acknowledge the ongoing injustices that we have committed against the Dakota Nation, and we wish to interrupt this legacy, beginning with acts of healing and honest storytelling about this place.
Research Acknowledgment

It has been an honor to work with so many exceptional collaborators over the past 15 years. To name just a few…

- **Past principal developers of Jmol** – Dan Gezelter, Egon Willighagen, Michael “Miguel” Howard
- **Current and past developers of Jmol** – Nicolas Vervelle, René Kanters, Robert Lancashire, Angel Herráez, Jonathan Gutow, Paul Pillot, Pieremanuele Canepa, Simone Sturniolo
- **Power users** – Joel Sussman, Jaime Prilusky, Eric Martz, Karsten Theis, Dean Johnston, Rick Spinney, Rolf Huene, James Stewart, Xiang-Jun Lu, many more
- **Java2Script** – Zhou Renjian, Udo Borkowski
- **International collaborators, specifically in crystallography** – Mois Aroyo, Juan Manuel “Manu” Perez-Mato, Gotzon Madariaga, Václav Petříček, Stefano Curtarolo, Roberto Dovesi, Piero Ugliengo, Silvia Casassa, Bartolomeo “Mimmo” Civalleri
- **Undergraduate, graduate, and postdoc collaborators** – David Hicks, José Plata, Cormac Toher, Corey Oses, Eric Gossett, Pieremanuele Canepa, Ben Hinke, Matt Van Koevering, Hai Nguyen, Sasha Schrandt, Amanda Leone, Kellan Passow, Brigette Honaker, Patrik Stefek, Elizabeth New, Jacob LaNasa, Ben Hinke, Nadia el Mouldi, Matt van Koevering Andreas Raduege, My Nguyen, Jacob Packard, Minghzi Zhao, Andrew Lee, Tahir Ahsan, Nikesh Yadav, Sophia Musacchio, Marianne Peterson, Andrew Salij, Geoffrey van Dover, Lucia Wagner, Sydney O’Dell
Alternative Title
Visualization:
Connecting Disciplines
Connecting Communities

Caveats

• I am not a physicist (though I have many physicist friends)
• I don’t speak French (apologies!)
• I tend to speak rather fast, especially when I am excited (which I am)
• It turns out that “jet lag” has nothing to do with jets (I woke up for this at 2 AM my time)
• I have 71 slides (oh, oh!)
Presentation Objectives

• Emphasize the benefit of cross-disciplinary discussion and collaboration.

• Suggest that visualization is more than a pretty picture, sometimes allowing us to think about our research in novel ways that we have not previously considered.

• Argue that having the right tool does not just make the job easier. Sometimes it makes the job possible. And sometimes it creates all new jobs.

• Highlight the advantage of thinking “outside the box” – read unit cell.
Background: Jmol

Mission: The high-quality, real-time visualization of molecular structure, dynamics, and energetics on all platforms.

Jmol is:
- open-source Java+JavaScript
- cross-disciplinary
- community-driven

Jmol is not:
- a commercial enterprise
- a quantum computational package
Embedding Jmol in a web page allows the telling of a story interactively, with context.
Influenza is a contagious disease caused by a virus. Influenza A\(^1\) (one of several genera and species of influenza) is the most virulent form infecting humans. Largely by facilitating secondary bacterial pneumonias, influenza kills 500,000 people worldwide annually (including about 36,000 in the USA), mostly during seasonal epidemics\(^2\) each year. Most people killed in the annual influenza epidemics are people whose immune defenses are weak, including the very young and the old. Influenza also kills large numbers of animals and birds, both domestic and wild\(^2\). The influenza virus includes only eight proteins. Sequences of these proteins as obtained from numerous strains are available in the NCBI Influenza Virus Resource. For more about the structure and biology, including references for the points made here, please see Influenza at Wikipedia.
Point group symmetry for inorganic chemistry

Symmetry Resources at Otterbein University

Welcome to the world of symmetry! The resources contained within this web site are designed to help students learn concepts of molecular symmetry and to help faculty teach concepts of molecular symmetry. The materials are designed for a variety of levels, so look around and see what we have to offer. Choose from the following pages:

- **Symmetry Tutorial** - An interactive point group symmetry tutorial. Guides students through all of the symmetry elements and operations, with interactive displays and animations.

- **The Symmetry Gallery** - A collection of nearly 70 unique molecules with interactive display of all symmetry elements and animation of all operations. The molecules are organized by point group, so you can select examples to demonstrate particular symmetry elements. Includes links to the chemical literature when available.

- **The Symmetry Challenge** - Using the same set of molecules from the Gallery, the Challenge includes a flow chart that details the process of determining the point group of each molecule. A great way to practice the point group determination process.

Dean Johnston, Otterbein College  http://faculty.otterbein.edu/djohnston/sym/
Space group symmetry for crystallography

https://journals.iucr.org/j/issues/2010/05/02/kk5066/index.html
Space group symmetry for crystallography

https://chemapps.stolaf.edu/jmol/jsmol/jcse
Today -- Visualization Challenges

1. Beyond the unit cell -- Seeing the “bigger picture”
2. Comparing structures
3. Conceptualizing phase transitions
4. Visualizing incommensurate modulation
5. To be continued -- Your ideas!
Today -- Visualization Challenges

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1. Beyond the unit cell

The problem: Primitive cells are terrific for calculation, but horrible for visualization!

AFLOW (Stefano Curtorolo, Duke Univ.)  http://aflowlib.org/
1. Beyond the unit cell

The problem: Primitive cells are terrific for calculation, but horrible for visualization!

294 binary Ag-Au alloy prototypes

What to make of this?

AFLOW (Stefano Curtorolo, Duke Univ.)  http://aflowlib.org/
1. Beyond the unit cell

One solution: instead of just showing the primitive cell, fill a volume with atoms

294 binary Ag-Au alloy prototypes

Patterns emerge when we take a broader view.

AFLOW (Stefano Curtorolo, Duke Univ.)  http://aflowlib.org/
1. Beyond the unit cell

Conclusion #1:

Sometimes a simple change in perspective can completely change the way we see a structure.

Unit cells do not tell the whole story – sometimes very little of it, actually.
Today -- Visualization Challenges

1. Beyond the unit cell -- Seeing the “bigger picture”
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5. To be continued -- Your ideas!
2. Comparing Structures

Say we have two structures from two different databases. Q: Are they the same? How similar are they?

Omeprazole from PubChem (top) and NCI/CADD (bottom)
2. Comparing Structures

LOAD FILES
“$omeprazole”":omeprazole“
FRAME *

Ouch!
2. Comparing Structures

compare {2.1} {1.1}
rotate translate

\[ \text{RMSD} = 6.86 \text{ Ang} \]

Ouch again!
2. Comparing Structures

A classic question in cheminformatics is “Are these two structures the same?” Solution: SMILES strings

*Simplified Molecular Input Line Entry System* strings are used extensively in cheminformatics.
2. Comparing Structures

Say we have two structures from two different databases. Q: Are they the same? How similar are they?

Omeprazole from PubChem (top) and NCI/CADD (bottom)

Q: How could we use SMILES to answer this question?
2. Comparing Structures

print {2.1}.find("SMILES")

print {1.1}.find("SMILES")
2. Comparing Structures

They are the same structure.
2. Comparing Structures

compare \{2.1\} \{1.1\}

**SMILES** rotate
translate

\[ \text{RMSD} = 1.68 \text{ Ang} \]

*Better!*
2. Comparing Structures

compare {2.1} {1.1}

BOND SMILES
rotate translate

\[ \text{RMSD} = 0.13 \text{ Ang} \]

Better!
2. Comparing Structures

compare {2.1} {1.1}
BOND SMILES
HYDROGEN rotate translate

\[ RMSD = 0.12 \text{ Ang} \]

Excellent!
2. Comparing Structures

compare \{2.1\} \{1.1\}
BOND SMILES
HYDROGEN rotate
translate

coloring by distance

Excellent!
2. Comparing Structures

The Problem: What if it is not a molecule?

ErFe$_2$
ICSD 169364
ICSD 630450

Fig 6: Primitive unit cells for two independent crystallographic determinations of the structure ErFe$_2$

Jacob LaNasa, Brigette Honaker, Elizabeth New, Patrik Štefek, Robert M. Hanson, Stefano Curtarolo APS March Meeting 2016
2. Comparing Structures

A general solution – Bilbao COMPSTRU

https://www.cryst.ehu.es/cryst/compstru.html
2. Comparing Structures

Comparison of crystal structures of the same symmetry C2/c (No. 15) [unique axis b]

Structure #1

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>13.800</td>
<td>5.691</td>
<td>9.420</td>
</tr>
<tr>
<td></td>
<td>90.0</td>
<td>102.3</td>
<td>90.0</td>
</tr>
</tbody>
</table>

Pb | 1 | 4e | 0.000000 | 0.291000 | 0.250000 |
Pb | 2 | 8f | 0.317000 | 0.309000 | 0.352000 |
P | 1 | 8f | 0.599000 | 0.241000 | 0.447000 |
O | 1 | 8f | 0.643000 | 0.030000 | 0.392000 |
O | 2 | 8f | 0.634000 | 0.464000 | 0.374000 |
O | 3 | 8f | 0.642000 | 0.280000 | 0.612000 |
O | 4 | 8f | 0.491000 | 0.222000 | 0.450000 |

Structure #2

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>13.967</td>
<td>5.560</td>
<td>104.778</td>
</tr>
<tr>
<td></td>
<td>90.0</td>
<td>166.713</td>
<td>90.0</td>
</tr>
</tbody>
</table>

Pb | 1 | 4e | 0.000000 | 0.000000 | 0.750000 |
Pb | 2 | 8f | 0.000000 | 0.000000 | 0.856300 |
P | 1 | 8f | 0.000000 | 0.000000 | 0.951000 |
O | 1 | 8f | 0.000000 | 0.000000 | 0.914500 |
O | 2 | 8f | 0.271500 | 0.728500 | 0.888500 |
O | 3 | 8f | 0.957000 | 0.500000 | 0.117000 |
O | 4 | 8f | 0.728500 | 0.271500 | 0.611500 |

2. Comparing Structures

Our Solution: Jmol “polySMILES”

Jacob LaNasa, Brigette Honaker, Elizabeth New, Patrik Štefek, Robert M. Hanson, Stefano Curtarolo APS March Meeting 2016
2. Comparing Structures

Our Solution: Jmol “polySMILES”

[Er@PH16/r=6.0/]
[Fe]12345.[Fe]26789
[Fe]61%10%11%12.[Fe]4%13%14%15%16
[Fe]%11%17%18%19%20.[Fe]8%21%22%23%24
[Fe]%13%25%26%27%28.[Fe]%15%25%29%30%31
[Fe]%17%30%32%33%34.[Fe]%19%33%35%36%37
[Fe]%21%27%38%39%40.[Fe]%23%36%41%39%42
[Er]%26%29%34%35%40%42.[Er]3%10%16%18%31%32
[Er]%57%14%22%38%28.[Er]9%12%20%24%37%41

 vertex connectivity
and winding order

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2. Comparing Structures

Our Solution: Jmol “polySMILES”

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2. Comparing Structures

Our Solution: Jmol “polySMILES”

SMILES are comparable and mappable: `smiles1.find("SMILES",smiles2, "map")`

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2. Comparing Structures

Our Solution: Jmol “polySMILES”

compare frames polyhedra

\[ \text{RMSD} = 0.00537 \text{ Å} \]

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2. Comparing Structures

Our Solution: Jmol “polySMILES”

Conclusion #2:

*Extension of the highly successful small-molecule SMILES idea to polyhedra allows for automated quantitative crystal structure comparison*

Jacob LaNasa, Brigette Honaker, Elizabeth New, Patrik Štefek, Robert M. Hanson, Stefano Curtarolo *APS March Meeting 2016*
Today -- Visualization Challenges

1. Beyond the unit cell -- Seeing the “bigger picture”
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4. Visualizing incommensurate modulation
5. To be continued -- Your ideas!
3. Conceptualizing Phase Transitions

Phase transitions occur in solids subjected to changes in temperature and pressure.

Q: How does that work?

https://www.researchgate.net/publication/233010160
3. Conceptualizing Phase Transitions

Phase transitions occur in solids subjected to changes in temperature and pressure. Two structures of BaTiO$_3$:

- **low temperature structure (Amm2)**
- **high-temperature structure (Pm-3m)**
3. Conceptualizing Phase Transitions

Landau (1969) hypothesized that phase transitions in solids are associated with the loss (or gain) of symmetry involving a single irreducible representation of the symmetry operations of a space group.

\[ \text{BaTiO}_3 \text{ ITA 221 Pm-3m} \]

3. Conceptualizing Phase Transitions

Landau (1969) hypothesized that phase transitions in solids are associated with the loss (or gain) of symmetry involving a single irreducible representation of the symmetry operations of a space group.


**BaTiO₃** ITA 221 Pm-3m
3. Conceptualizing Phase Transitions

Landau (1969) hypothesized that phase transitions in solids are associated with the loss (or gain) of symmetry involving a single irreducible representation of the symmetry operations of a space group.

Some of this symmetry will be lost during the phase transition. But which ones?

BaTiO$_3$ ITA 221 Pm-3m

See https://en.wikipedia.org/wiki/Landau_theory
3. Conceptualizing Phase Transitions

Landau (1969) hypothesized that phase transitions in solids are associated with the loss (or gain) of symmetry involving a single irreducible representation of the symmetry operations of a space group.

Phase changes involve (generally small) changes in atom position.

3. Conceptualizing Phase Transitions

Landau (1969) hypothesized that phase transitions in solids are associated with the loss (or gain) of symmetry involving a single irreducible representation of the symmetry operations of a space group.

switching to Amm2, but still high symmetry

See https://en.wikipedia.org/wiki/Landau_theory
3. Conceptualizing Phase Transitions

Landau (1969) hypothesized that phase transitions in solids are associated with the loss (or gain) of symmetry involving a single irreducible representation of the symmetry operations of a space group.

See https://en.wikipedia.org/wiki/Landau_theory

**BaTiO$_3$** high symmetry phase (high temp)
3. Conceptualizing Phase Transitions

Landau (1969) hypothesized that phase transitions in solids are associated with the loss (or gain) of symmetry involving a single irreducible representation of the symmetry operations of a space group.

$\text{BaTiO}_3$ low symmetry phase (low temp)

See https://en.wikipedia.org/wiki/Landau_theory
3. Conceptualizing Phase Transitions

The situation is similar to vibrational normal modes, where symmetry “allows” only certain transitions to be observed.

Each mode is associated with a specific irreducible representation of the $C_{2v}$ point group.

- **O-H symmetric stretching** ($a_1$)
  - 3585 cm$^{-1}$
  - (IR intensity = 0.17)
  - (Raman active)

- **O-H asymmetric stretching** ($b_2$)
  - 3506 cm$^{-1}$
  - (IR intensity = 1.0)
  - (Raman active)

- **H-O-H bending** ($a_1$)
  - 1885 cm$^{-1}$
  - (IR intensity = 0.15)
  - (Raman active)
3. Conceptualizing Phase Transitions

The situation is similar to vibrational normal modes, where symmetry “allows” only certain transitions to be observed.

Each mode is has its own amplitude, reflected in the IR or Raman intensity.

https://www.chem.purdue.edu/jmol/vibs/h2o.html
3. Conceptualizing Phase Transitions

The Bilbao Crystallographic Server AMPLIMODES program carries out the analysis.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>WP</th>
<th>Modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>3c</td>
<td>GM4-(2) GM5-(1)</td>
</tr>
<tr>
<td>Ti1</td>
<td>1b</td>
<td>GM4-(1)</td>
</tr>
<tr>
<td>Ba1</td>
<td>1a</td>
<td>GM4-(1)</td>
</tr>
</tbody>
</table>

Note: The primary mode is written in bold letters.

### Summary of Amplitudes

<table>
<thead>
<tr>
<th>K-vector</th>
<th>Irrep</th>
<th>Direction</th>
<th>Isotropy Subgroup</th>
<th>Dimension</th>
<th>Amplitude (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0,0,0)</td>
<td>GM4-</td>
<td>(a,a,0)</td>
<td>Amm2 (38)</td>
<td>4</td>
<td>0.1649</td>
</tr>
<tr>
<td>(0,0,0)</td>
<td>GM5-</td>
<td>(0,a,-a)</td>
<td>Amm2 (38)</td>
<td>1</td>
<td>0.0056</td>
</tr>
</tbody>
</table>

Global distortion: 0.1650 Å

Mois Aroyo, Juan Manuel Perez Mato, [https://www.cryst.ehu.es/cryst/amplimodes.html](https://www.cryst.ehu.es/cryst/amplimodes.html)
3. Conceptualizing Phase Transitions

Jmol represents the irrep principal components as “vibrations” either normalized (for inspection) or unnormalized (for comparing significance).
3. Conceptualizing Phase Transitions

Jmol represents the irrep principal components as “vibrations” either normalized (for inspection) or unnormalized (for comparing significance).
3. Conceptualizing Phase Transitions

Conclusion #3:

Visualizations can be adapted for use in ways that were not initially imagined.
Today -- Visualization Challenges

1. Beyond the unit cell -- Seeing the “bigger picture”
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4. Visualizing incommensurate modulation
5. To be continued -- Your ideas!
4. Visualizing Incommensurate Modulation

Incommensurate modulations are periodic perturbations of a “perfect” crystal that are not the wavelength of the lattice.
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Incommensurate modulations are periodic perturbations of a “perfect” crystal that are not the wavelength of the lattice.
4. Visualizing Incommensurate Modulation

Modulations, being periodic themselves, can be represented as wave functions operating in reciprocal space.

\[ q = \sigma_1 \mathbf{a}_1^* + \sigma_2 \mathbf{a}_2^* + \sigma_3 \mathbf{a}_3^* \]
4. Visualizing Incommensurate Modulation

There can be more than one cell wave vector, and more than one unit cell.

\[ q_1 = \sigma_{11} a_1^* + \sigma_{12} a_2^* + \sigma_{13} a_3^* \]
\[ q_2 = \sigma_{21} a_1^* + \sigma_{22} a_2^* + \sigma_{23} a_3^* \]
4. Visualizing Incommensurate Modulation

An elegant representation of modulation is via superspace groups, where we have augmented real 3d space by $n$ additional orthogonal dimensions.

This is not easily represented on a 2D slide!

Sander van Smaalen
*Incommensurate Crystallography*
IUCr/Oxford Science, 2007
4. Visualizing Incommensurate Modulation

An elegant representation of modulation is via superspace groups, where we have augmented real 3d space by $n$ additional orthogonal dimensions.

One can think of a atom as being a $3d+n$-dimensional string that is being projected into real space.
4. Visualizing Incommensurate Modulation

An example of a CIF file for an incommensurately modulated structure.

_symmetry_cell_setting
orthorhombic
_space_group_ssg_name
'Xm2m(\a00)00s'

loop_
_space_group_symop_ssg_id
_space_group_symop_ssg_operation_algebraic
1  x1,x2,x3,x4
2  x1,x2,-x3,x4+1/2
3  -x1,x2,x3,-x4
4  -x1,x2,-x3,-x4+1/2
5  x1+1/2,x2,x3+1/2,x4
6  x1+1/2,x2,-x3+1/2,x4+1/2
7  -x1+1/2,x2,x3+1/2,-x4
8  -x1+1/2,x2,-x3+1/2,-x4+1/2
9  x1+1/2,x2+1/2,x3,x4+1/2
10 x1+1/2,x2+1/2,-x3,x4
11 -x1+1/2,x2+1/2,x3,-x4+1/2
12 -x1+1/2,x2+1/2,-x3,-x4
13 x1,x2+1/2,x3+1/2,x4+1/2
14 x1,x2+1/2,-x3+1/2,x4
15 -x1,x2+1/2,x3+1/2,-x4+1/2
16 -x1,x2+1/2,-x3+1/2,-x4

_loop_
_cell_modulation_dimension 1
loop_
_cell_wave_vector_seq_id
_cell_wave_vector_x
_cell_wave_vector_y
_cell_wave_vector_z
1 0.566740 0.000000 0.000000
4. Visualizing Incommensurate Modulation

(magnified) incommensurate modulation as “vibration” showing strong correlations
4. Visualizing Incommensurate Modulation

Incommensurately modulated magnetic structures

4. Visualizing Incommensurate Modulation

Incommensurately modulated magnetic structures

4. Visualizing Incommensurate Modulation

Incommensurately modulated magnetic structures

In summary...

...visualization is **more than a pretty picture**!
...**having the right tool** helps!
...**thinking “outside the box”** is fun!
...**cross-disciplinary collaborations** are the best!
Today -- Visualization Challenges

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Ideas? I would love to hear from you!
Thank You!

hansonr@stolaf.edu