Welcome to
CHE 384T: Computational Methods in Materials Science

Introduction to Computational Materials Science

Programming Day 4

The University of Texas at Austin
McKetta Department
of Chemical Engineering
Cockrell School of Engineering

Programming Day Agenda

Some numerical aspects:

- Numerical Derivatives
- Checking your structure
- Convergence
- Fluctuations in MD simulations

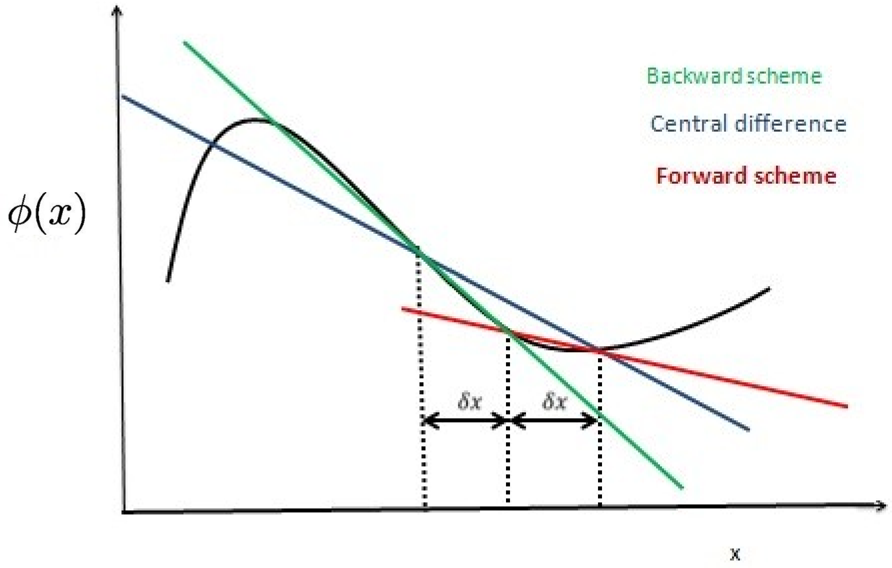
Time for HW4 questions or final project proposal questions

Visualizing your Results

Numerical Derivatives

Central Difference Derivative

$$\frac{d\phi_i}{dx} = \frac{\phi_{i+1} - \phi_{i-1}}{2a}$$



Numerical Derivatives

Central Difference Derivative
(non-compact form)

$$\frac{d^2\phi_i}{dx^2} = \frac{\frac{d\phi_{i+1}}{dx} - \frac{d\phi_{i-1}}{dx}}{2a}$$

$$= \frac{\frac{\phi_{i+2}-\phi_i}{2a} - \frac{\phi_i-\phi_{i-2}}{2a}}{2a}$$

$$= \frac{\phi_{i+2} + \phi_{i-2} - 2\phi_i}{4a^2}$$

Central Difference Derivative
(compact form)

$$\frac{d^2\phi_i}{dx^2} = \frac{\frac{d\phi_{i+1/2}}{dx} - \frac{d\phi_{i-1/2}}{dx}}{a}$$

$$= \frac{\frac{\phi_{i+1}-\phi_i}{a} - \frac{\phi_i-\phi_{i-1}}{a}}{a}$$

$$= \frac{\phi_{i+1} + \phi_{i-1} - 2\phi_i}{a^2}$$

Numerical Derivatives

First-order

Second-order
(non-compact & compact)

Fourth-order
(compact)

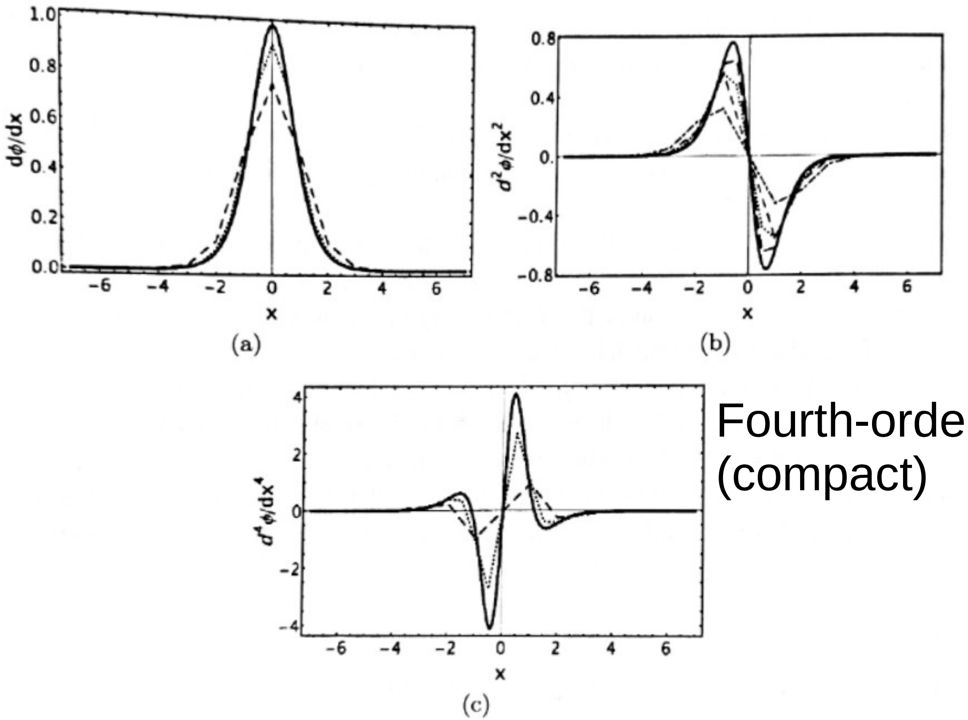


Figure I.5 Comparison of discrete and exact derivatives of $\phi = \tanh(\gamma x)$, shown as the solid black lines. (a) $d\phi/dx$ from Eq. (I.10): dashed line with a grid size of 1 and dotted line with a grid size of 1/2. (b) $d^2\phi/dx^2$ from the non-compact form in Eq. (I.11): dot-dashed line with a grid size of 1 and dotted line with a grid size of 1/2; $d^2\phi/dx^2$ from the compact form in Eq. (I.12): small-dashed line with a grid size of 1 and large-dashed line with a grid size of 1/2. (c) $d^4\phi/dx^4$ from Eq. (I.13): dashed line with a grid size of 1 and dotted line with a grid size of 1/2.

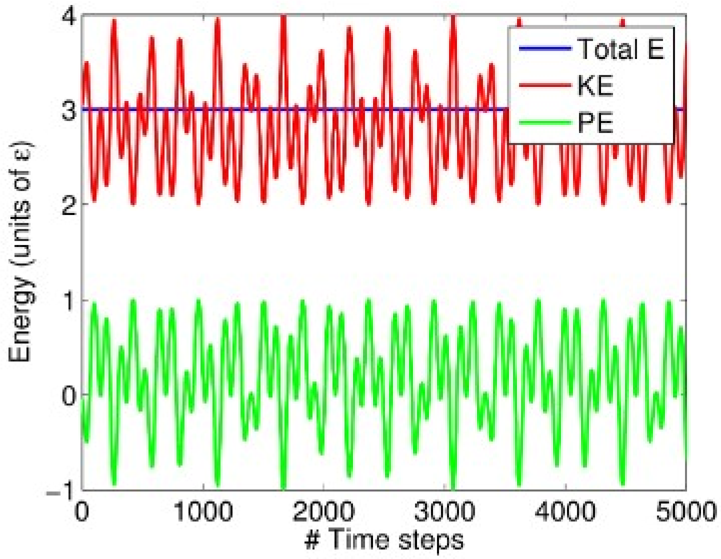
Exact
Grid size = $1/\gamma$
Grid size = $1/2\gamma$

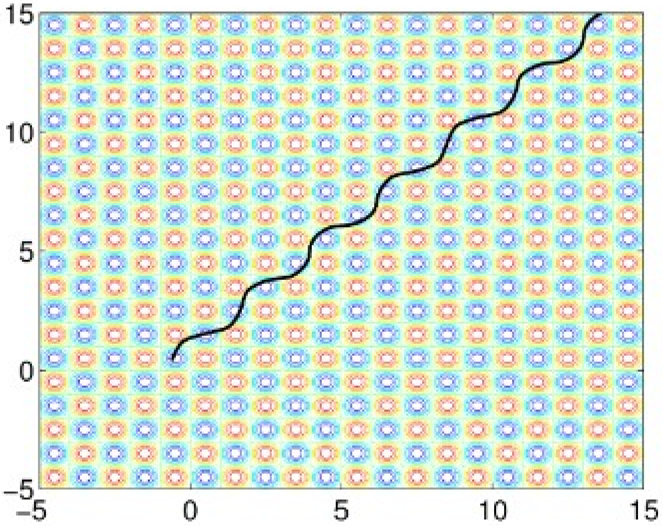
$$\phi(x) = \tanh(\gamma x)$$

Inspecting your calculation

Monitor the energies **and** the structure

Look at intermediate quantities, e.g., initial positions, velocities





Inspecting your calculation

Reduced units

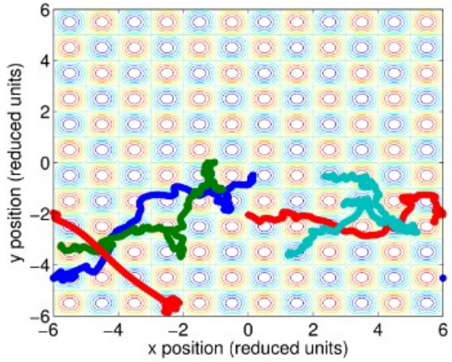
$$\phi^*(r^*) = 4\left[\left(\frac{1}{r^*}\right)^{12} - \left(\frac{1}{r^*}\right)^{6}\right]$$

$$\phi^* = \phi/\epsilon$$
$$r^* = r/\sigma$$

Table 6.1 Reduced units in Lennard-Jones systems

Value	In reduced units
Potential energy	$U^* = U/\epsilon$
Temperature	$T^* = k_B T/\epsilon$
Density	$\rho^* = \rho\sigma^3$
Pressure	$P^* = P\sigma^3/\epsilon$
Time	$t^* = t/t_o$, where $t_o = \sigma\sqrt{m/\epsilon}$

ϵ and σ are defined in Eq. (6.21). All energies are in units of ϵ, e.g., $E^* = E/\epsilon$, $K^* = K/\epsilon$.



A note on convergence

When is the calculation converged enough?

Numerical errors are a few orders of magnitude smaller
than the quantity of interest

structural accuracy (e.g., bond length)
~ 0.01 -0.001 Angstroms

chemical accuracy
(e.g., diffusion barriers, formation energies, free energies)
~ 1 kcal/mol ~ 0.043 eV ~ 0.0016 Hartree

Energies converge relatively quickly
Forces and stresses are generally a more stringent criteria for convergence

Basics: Ensembles

Thermodynamic ensembles[17]

	Microcanonical	Canonical	Grand canonical
Fixed variables	E, N, V	T, N, V	T, μ, V
Microscopic features	Number of microstates	Canonical partition function	Grand partition function
	W	$Z = \sum_k e^{-E_k/k_BT}$	$\mathcal{Z} = \sum_k e^{-(E_k-\mu N_k)/k_BT}$
Macroscopic function	Boltzmann entropy	Helmholtz free energy	Grand potential
	$S = k_B \log W$	$F = -k_BT \log Z$	$\Omega = -k_BT \log \mathcal{Z}$

Wikipedia

NVE: maximize entropy *S* at equilibrium
NVT: minimize Helmholtz free energy *F* at equilibrium

Basics: Stat Mech

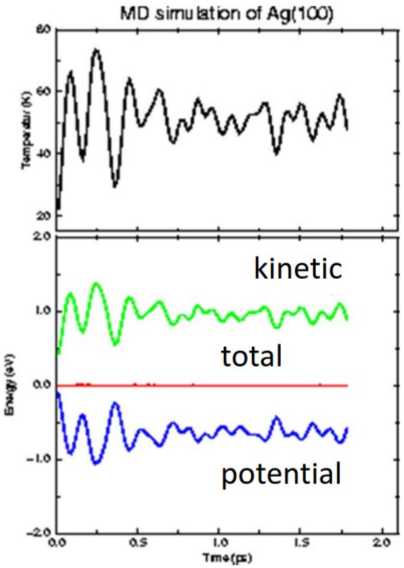
Temperature fluctuations, e.g., in NVE ensemble

Total energy is fixed while kinetic energy (and *T*) fluctuate by equal and opposite values

(Fluctuations in total energy will happen practically due to finite timestep in integration but should be small relative to the fluctuations in *K*)

$$\langle \sigma_T^2 \rangle = \langle T^2 \rangle - \langle T \rangle^2 = \frac{k_B T^2}{N C_V}$$

For large systems, fluctuations in *T* is negligible



B. Kozinsky, APCOMP 275

Basics: Stat Mech

Energy fluctuations, e.g., in NVT ensemble

Temperature is fixed while total energy is allowed to fluctuate

$$\langle E \rangle = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} \qquad \langle E^m \rangle = \frac{1}{\mathcal{Z}} \sum_j E_j^m e^{-\beta E_j}$$

Can show that:

$$\langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 = \sigma_E^2 = \frac{\partial^2 \ln \mathcal{Z}}{\partial \beta^2}$$

Basics: Ensembles

Equivalence of ensembles for the thermodynamic limit

Integrating Newton's equations with MD naturally corresponds to NVE ensemble

But other ensembles such as NVT are more convenient
(e.g., better correspondence with experimental conditions)

Is there still valid dynamical information from these other ensembles?

Yes, up to a point, but practically always dealing with finite sized systems

e.g., NVT approaches NVE in thermodynmic limit (fluctuations in *E* vanish)

$$\frac{\sigma_E}{\langle E \rangle} = \frac{\sqrt{\langle E^2 \rangle - \langle E \rangle^2}}{\langle E \rangle} \sim \frac{\sqrt{N}}{N} \to 0 \quad \mathrm{for} N \to \infty$$

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STARTING TIPS: MAKING FIGURES AND IMAGES

Wang Materials Group Meeting Tutorials

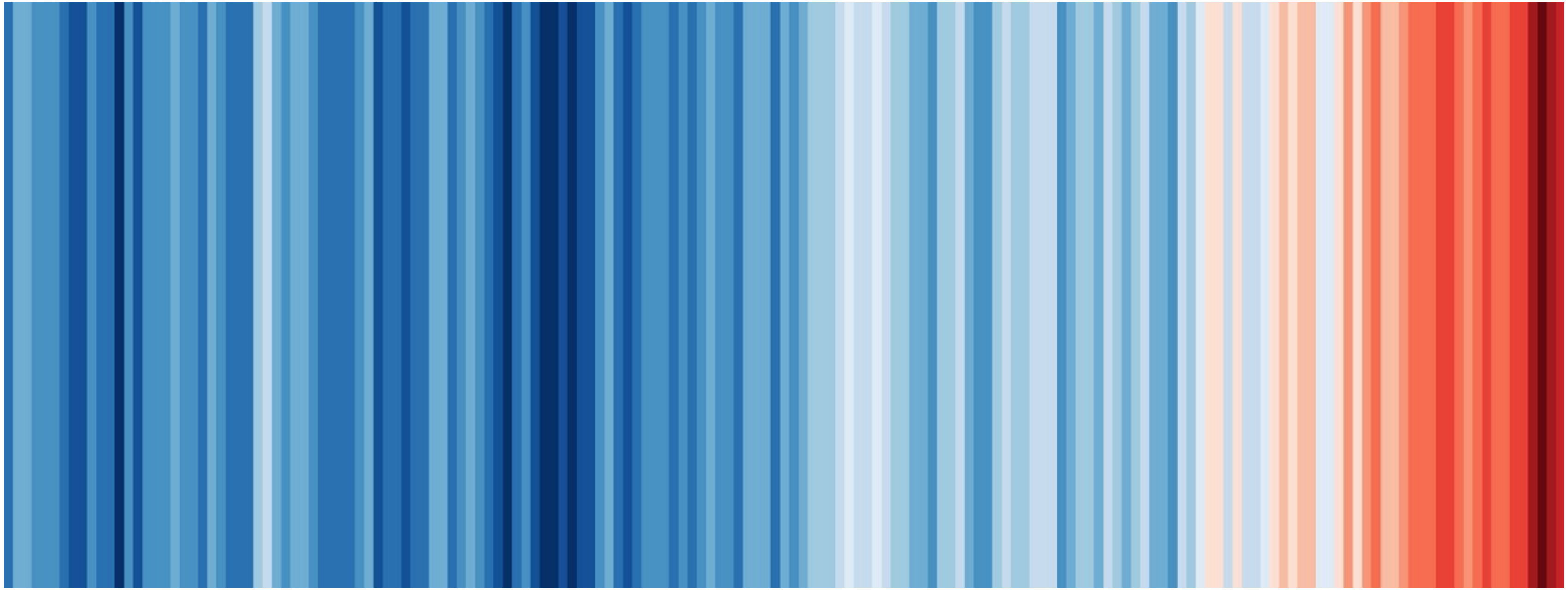
Wennie Wang
Wang Materials Group (https://wangmaterialsgroup.com)
The University of Texas at Austin, McKetta Department of Chemical Engineering

Why bother making a nice figure?

- A figure is worth a thousand words
- It is often the first impression you make to the reader
- Visual communication is just as powerful a form of communication as written!

Good design is memorable

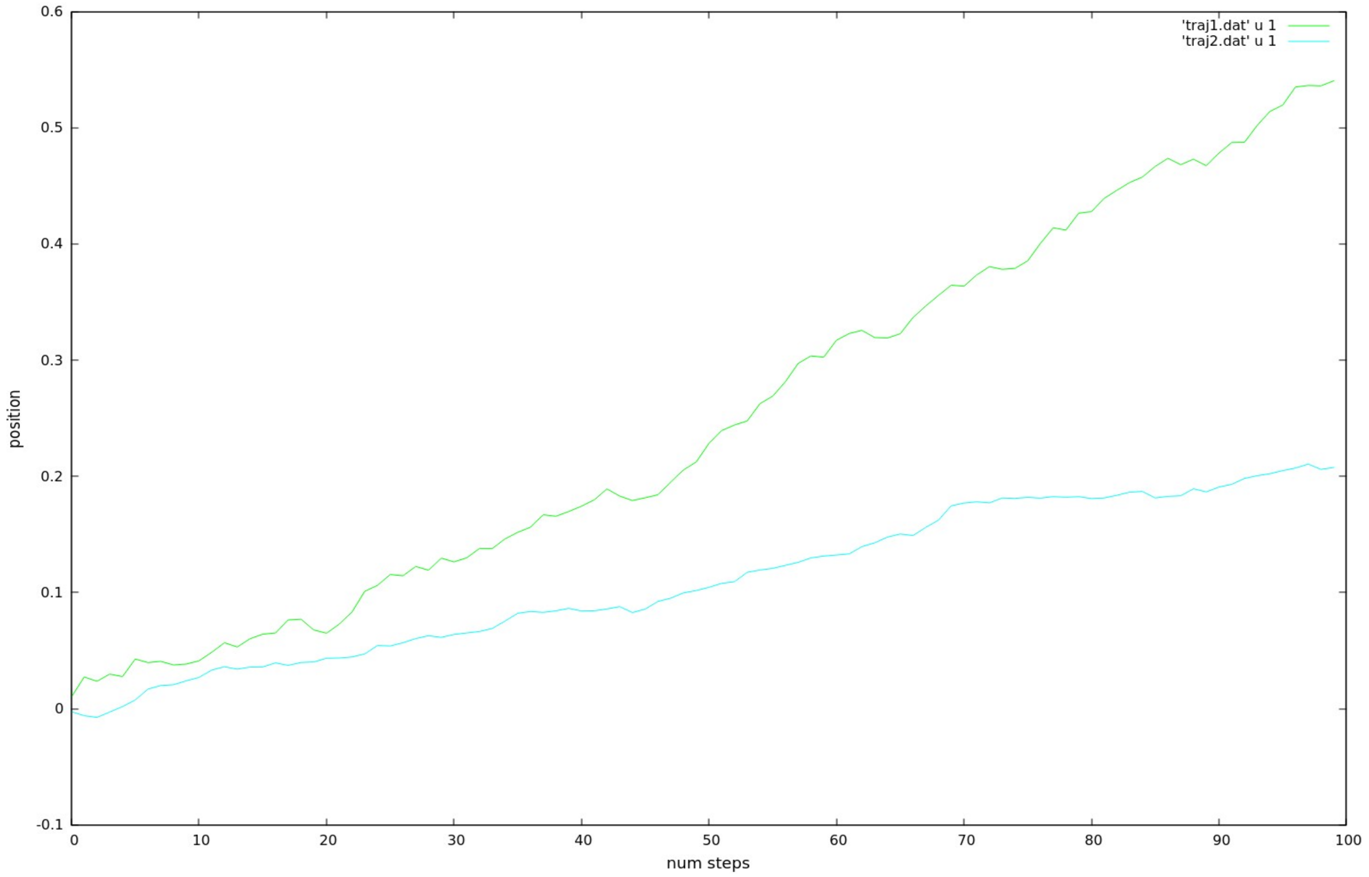
Example: Warming stripes, Ed Hawkins
Annual average global temperature 1850-2010



Figures are a form of visual design

- Design with intent
- Do not just directly copy a figure in a paper into a presentation
- The visual design will not always translate
  - adjust the relative scale of axes labels, tick marks, etc.
  - break down a complex or information dense figure

A bad figure



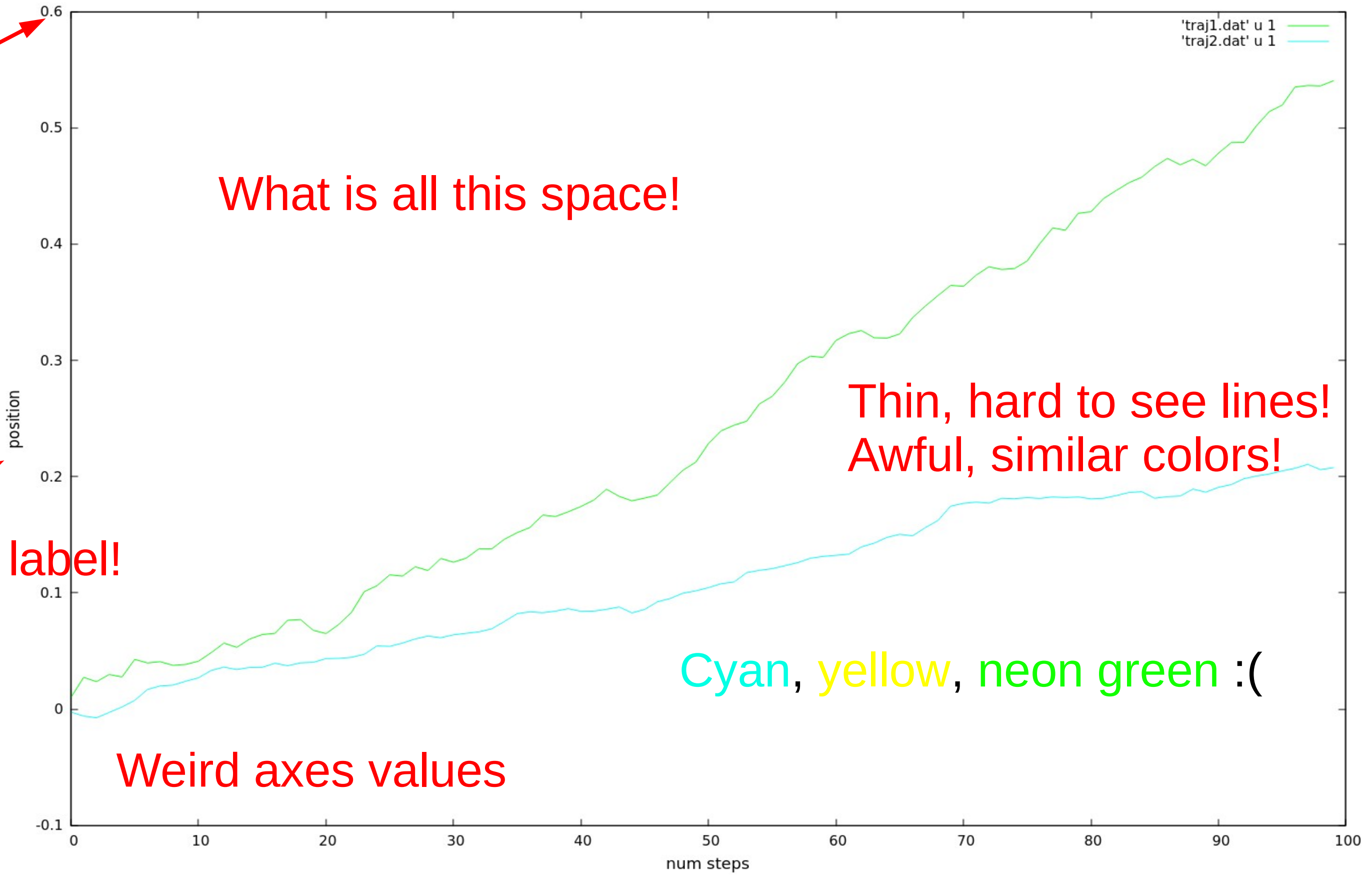
'traj1.dat' u 1
'traj2.dat' u 1
position
num steps
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
0
10
20
30
40
50
60
70
80
90
100

Ok for quick visualization
Not ok for paper figure

A bad figure

Meaningless key!

Tiny font!



What is all this space!

Thin, hard to see lines!
Awful, similar colors!

Informal axes label!
No units!

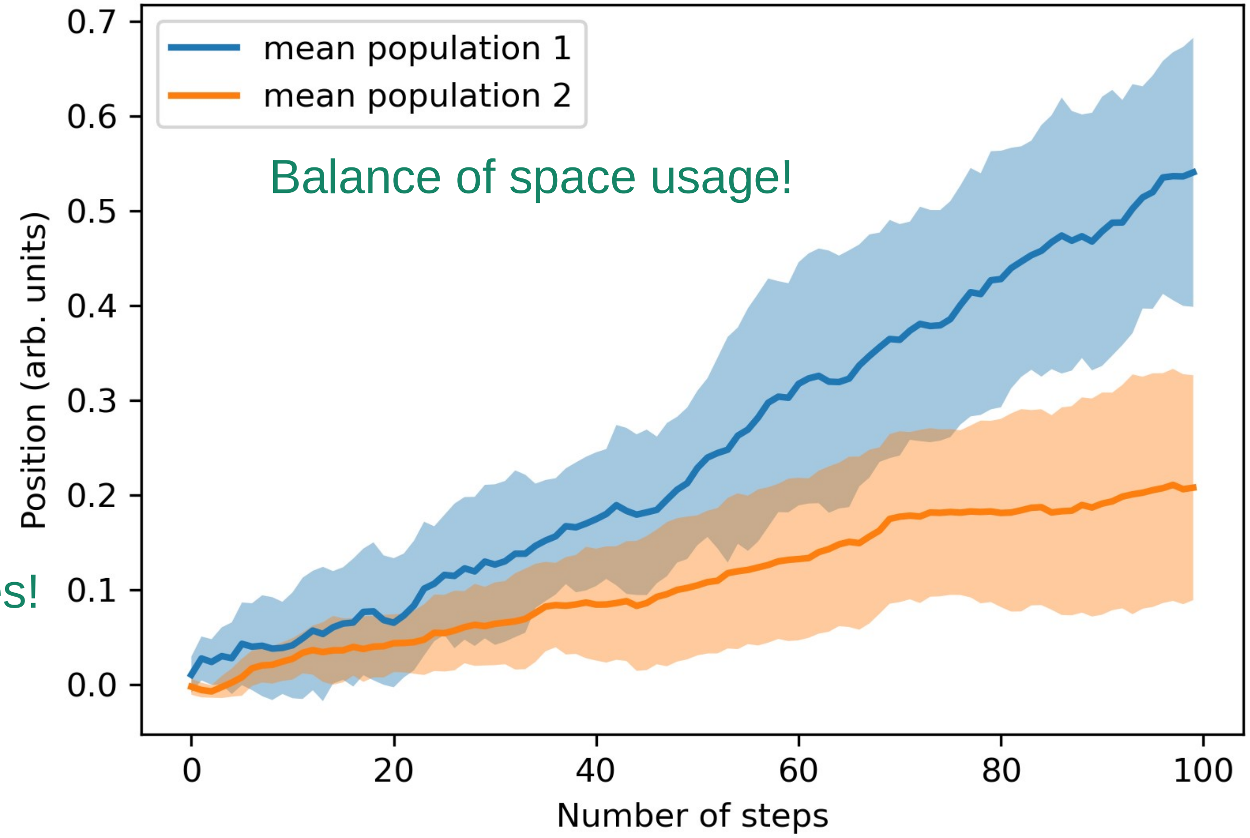
Cyan, yellow, neon green :(

Weird axes values

A better figure

Clear lines
with contrasting,
complementary colors!

Legible font!



Balance of space usage!

Descriptive axes!

Inclusion of statistics!
(If relevant)

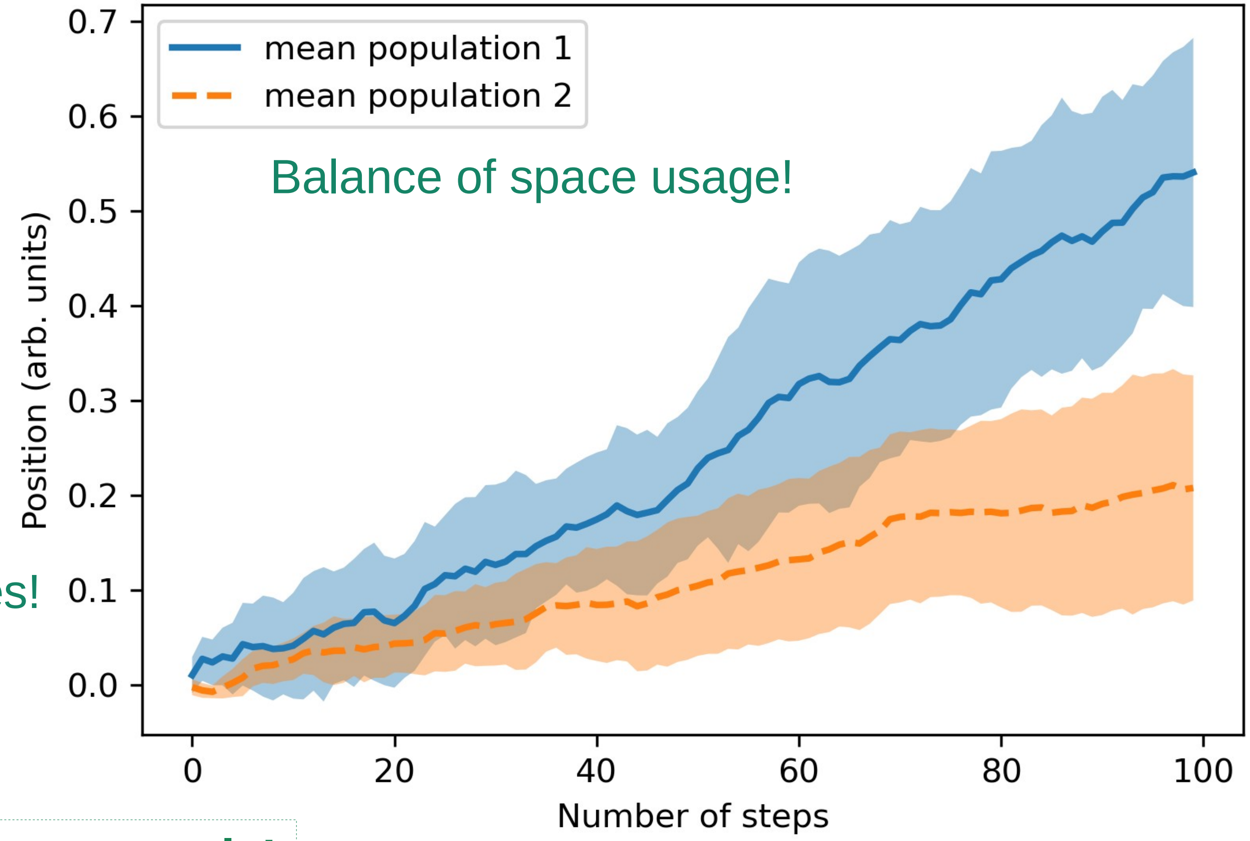
Crisp resolution!

Displacement of 10 random walkers

A better figure

Clear lines
with contrasting,
complementary colors!

Legible font!



Balance of space usage!

Inclusion of statistics!
(If relevant)

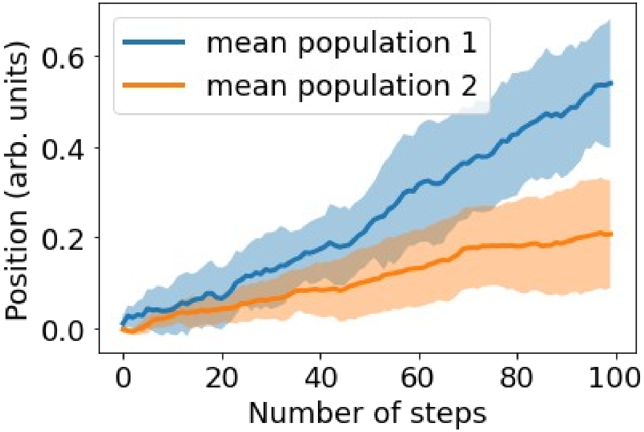
Descriptive axes!

Crisp resolution!

Redundancy in greyscale!

Displacement of 10 random walkers

Make it scalable

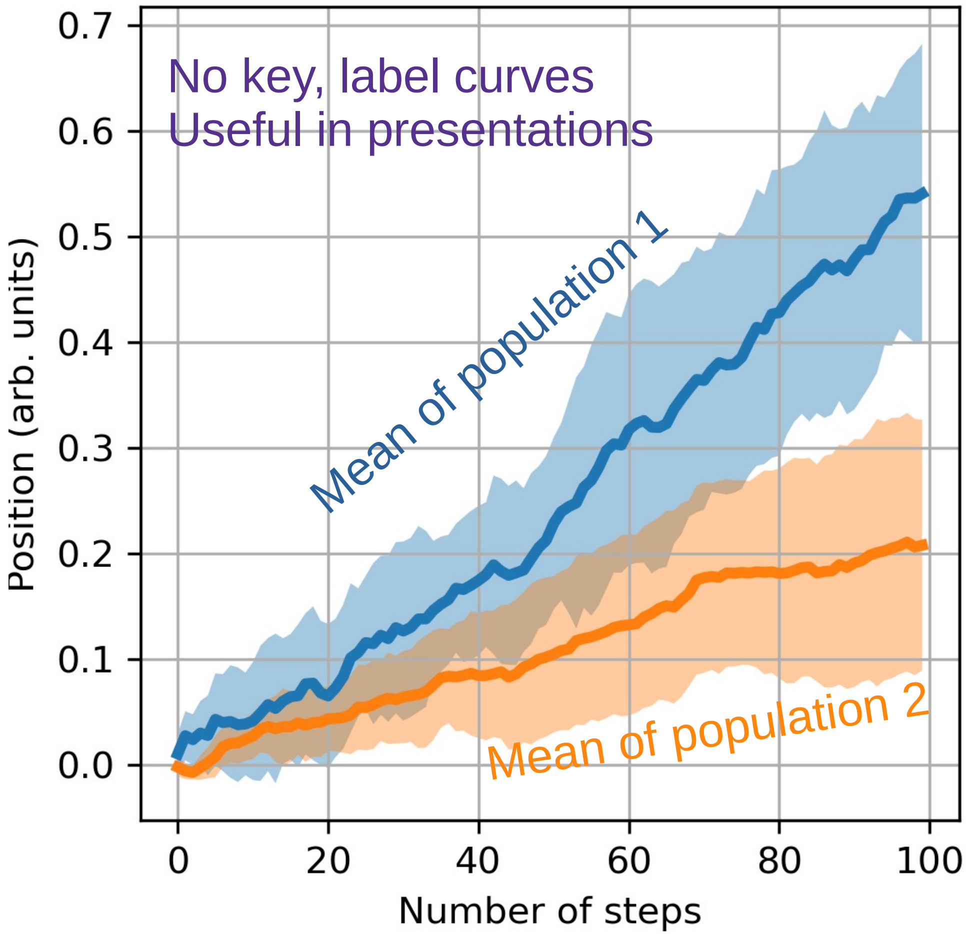


The font size is scaled to match the scaling of the figure

You can save space without compromising on the readability of the figure!

Some things of personal choice

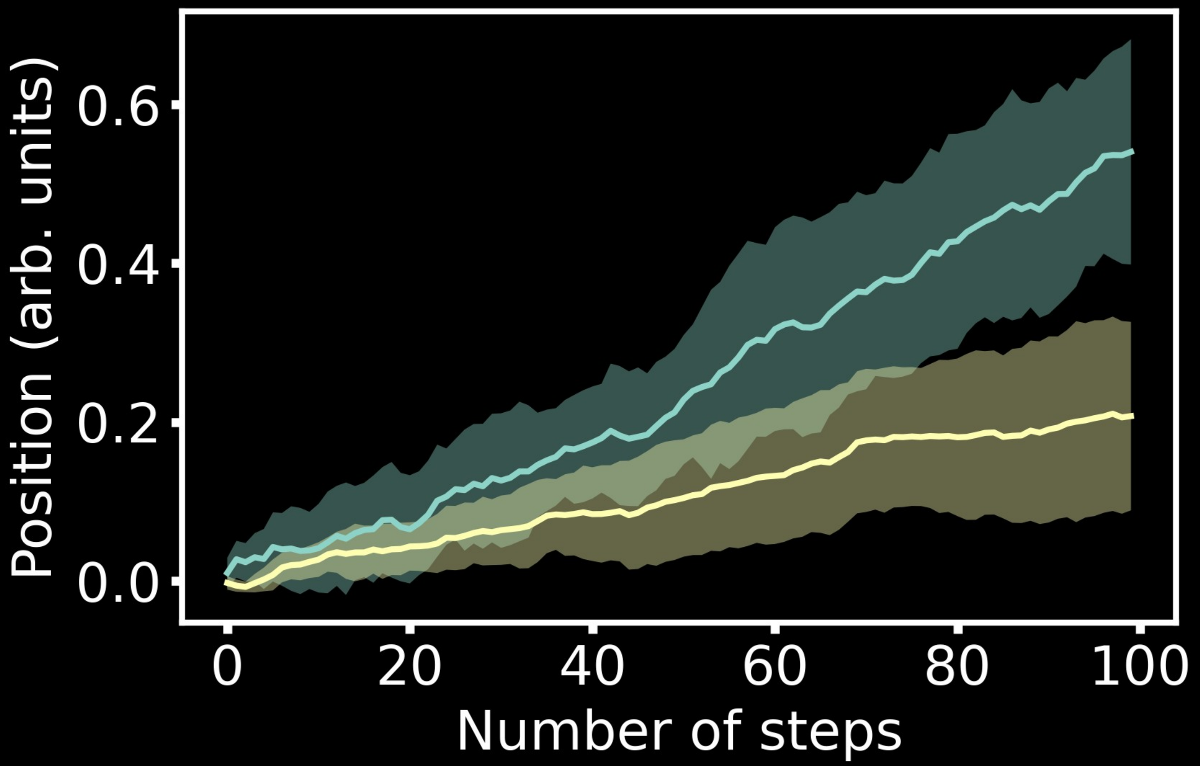
Square ratio!



Grid lines as guide to eye
(WW is meh)

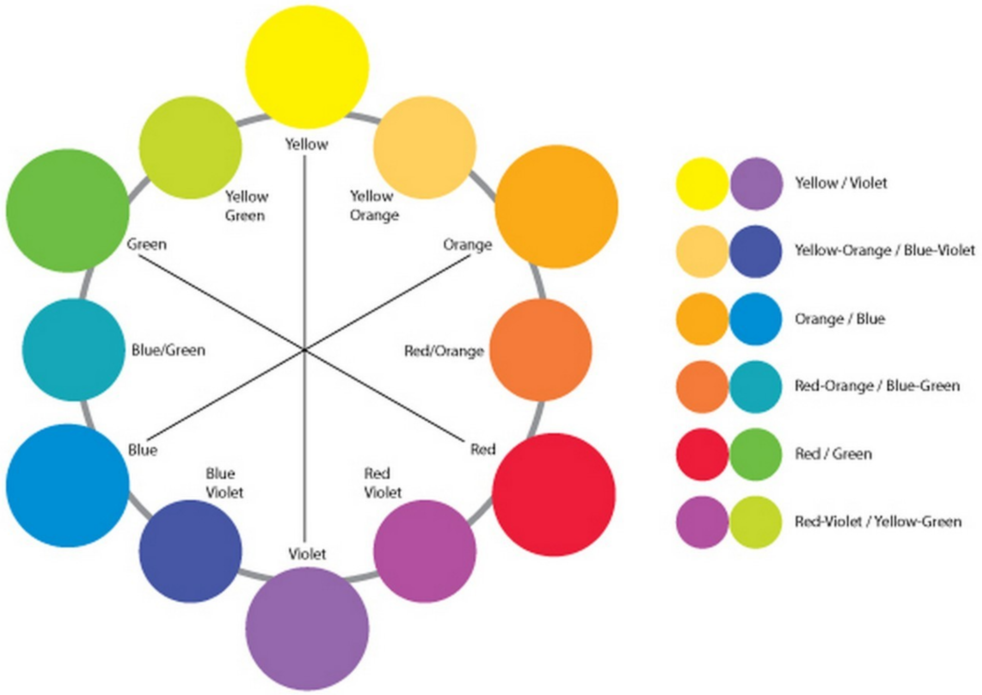
Dark Background?

It can work,
but you need to be
careful of visibility

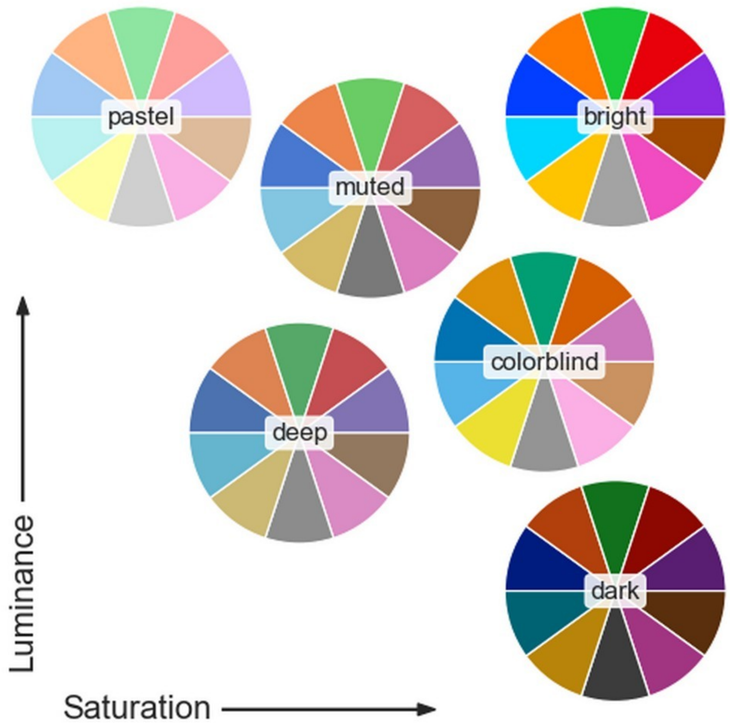


Color is important

Complementary colors

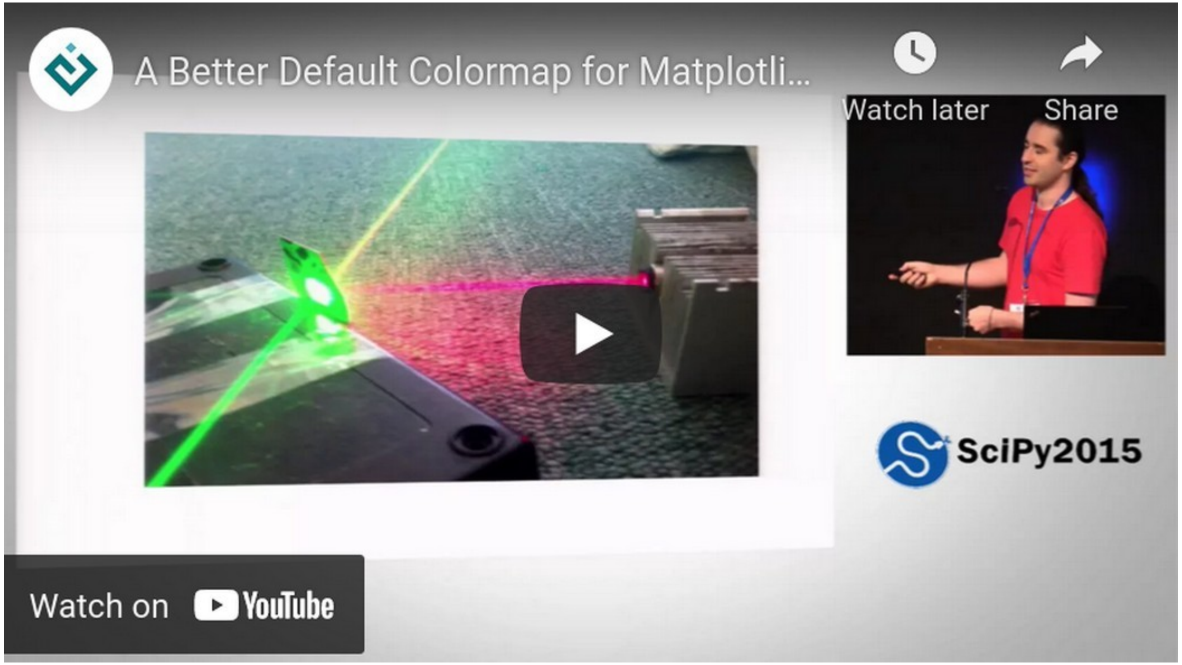


seaborn color palettes



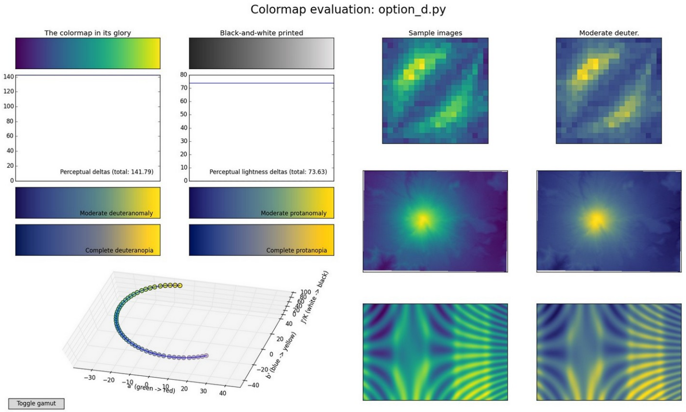
Color Maps

Avoid default jet (rainbow) setting... not great



https://youtu.be/xAoljeRJ3lU

Viridis, Parula are better!



https://bids.github.io/colormap/

Perceptually uniform,
Translates well to greyscale,
Better for the colorblind,...

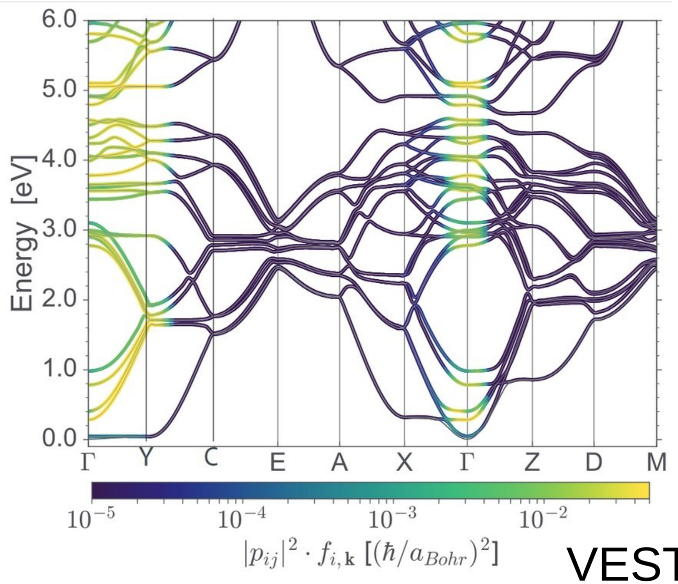
Example Tools (open source!)

- GIMP (bitmap images)
- Inkscape (vector image)
- Xmgrace, gnuplot (plotting from terminal or script)
- Python, matplotlib, seaborn
- VESTA, Xcrysden, ASE (visualize structure); Ovito (animations)
- Blender (3D rendering and animation)
- TikZ, Asymptote (vector graphics for textbook-like schematics, scriptable)
- ...many, many more

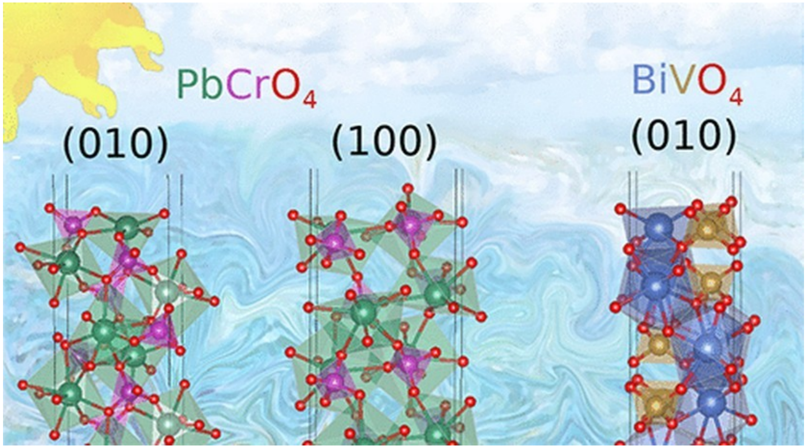
R. Schmied. Using Mathematica for Quantum Mechanics: A Student’s Manual.
https://arxiv.org/pdf/1403.7050.pdf

Example Figures

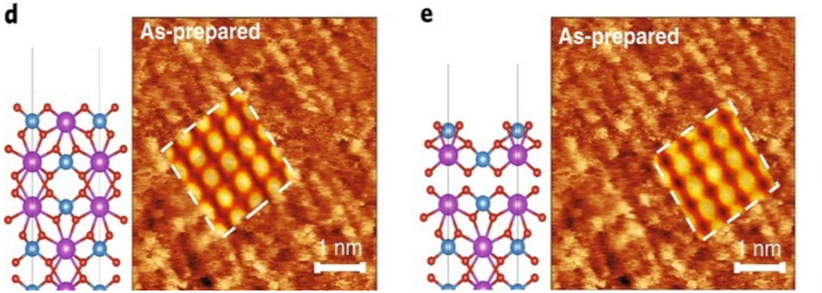
Python matplotlib



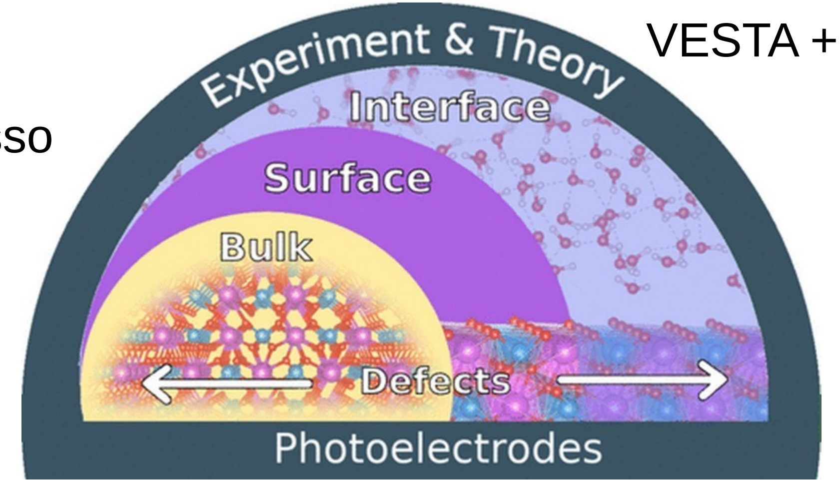
VESTA + Pixabay + GIMP



VESTA + GIMP + Quantum Espresso



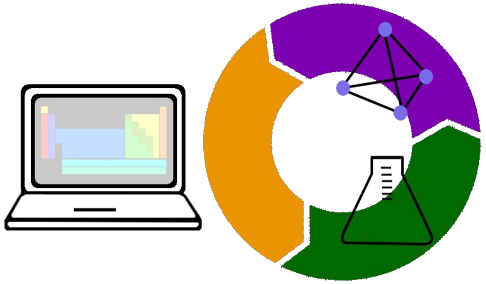
VESTA + GIMP



Example Figures

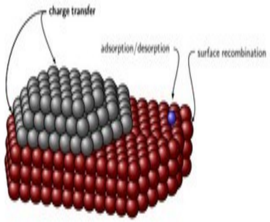
Example scripts and presentation:
https://github.com/wangmatgroup/tutorials

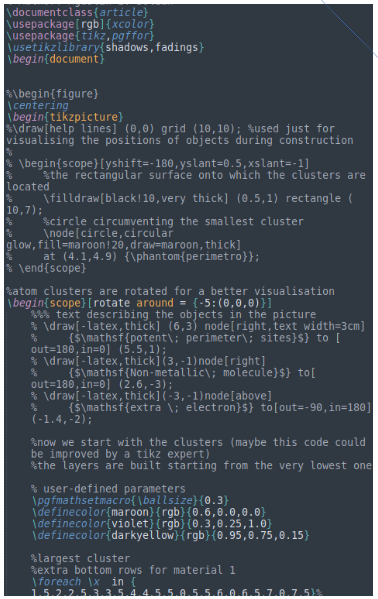
GIMP



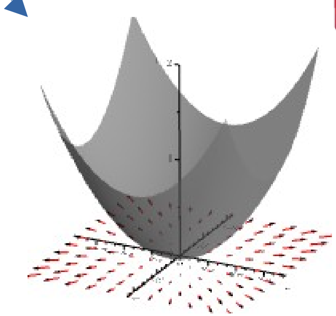
Vector graphics

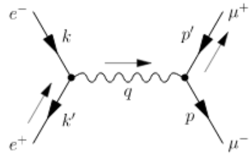
Tikz (TeX)





```
\documentclass{article}
\usepackage[rgb]{xcolor}
\usepackage{tikz,pgffor}
\usetikzlibrary{shadows,fadings}
\begin{document}


%\begin{figure}
\centering
\begin{tikzpicture}
%\draw[help lines] (0,0) grid (10,10); %used just for
visualising the positions of objects during construction
%
% \begin{scope}[yshift=-180,yslant=0.5,xslant=-1]
%     %the rectangular surface onto which the clusters are
located
%     \filldraw[black!10,very thick] (0.5,1) rectangle (
10,7);
%     %circle circumventing the smallest cluster
%     \node[circle,circular
glow,fill=maroon!20,draw=maroon,thick]
%     at (4.1,4.9) {\phantom{perimetro}};
% \end{scope}

%atom clusters are rotated for a better visualisation
\begin{scope}[rotate around = {-5:(0,0,0)}]
    %%% text describing the objects in the picture
    % \draw[-latex,thick] (6,3) node[right,text width=3cm]
    %     {$\mathsf{potent\; perimeter\; sites}$} to [
    out=180,in=0] (5.5,1);
    % \draw[-latex,thick](3,-1)node[right]
    %     {$\mathsf{Non-metallic\; molecule}$} to[
    out=180,in=0] (2.6,-3);
    % \draw[-latex,thick](-3,-1)node[above]
    %     {$\mathsf{extra \; electron}$} to[out=-90,in=180]
    (-1.4,-2);

    %now we start with the clusters (maybe this code could
    be improved by a tikz expert)
    %the layers are built starting from the very lowest one

    % user-defined parameters
    \pgfmathsetmacro{\ballsize}{0.3}
    \definecolor{maroon}{rgb}{0.6,0.0,0.0}
    \definecolor{violet}{rgb}{0.3,0.25,1.0}
    \definecolor{darkyellow}{rgb}{0.95,0.75,0.15}

    %largest cluster
    %extra bottom rows for material 1
    \foreach \x  in {
```

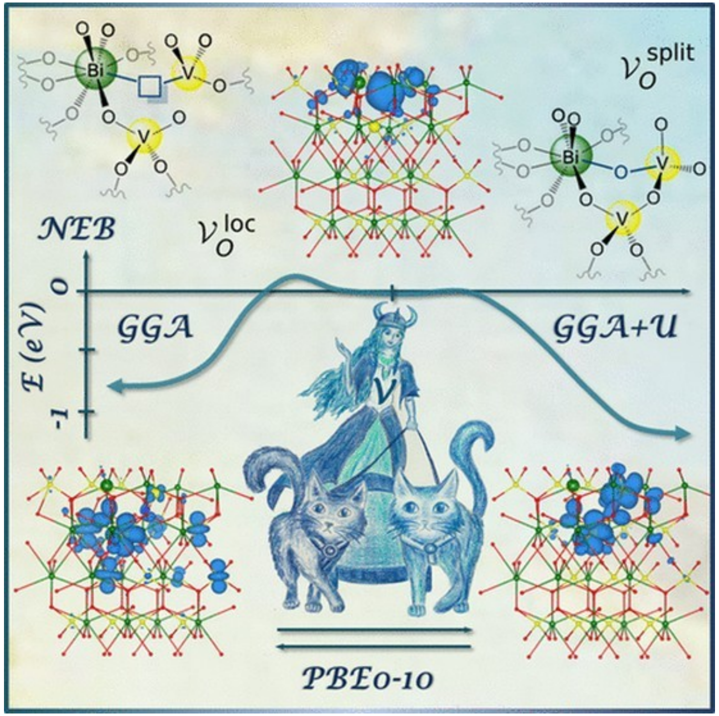




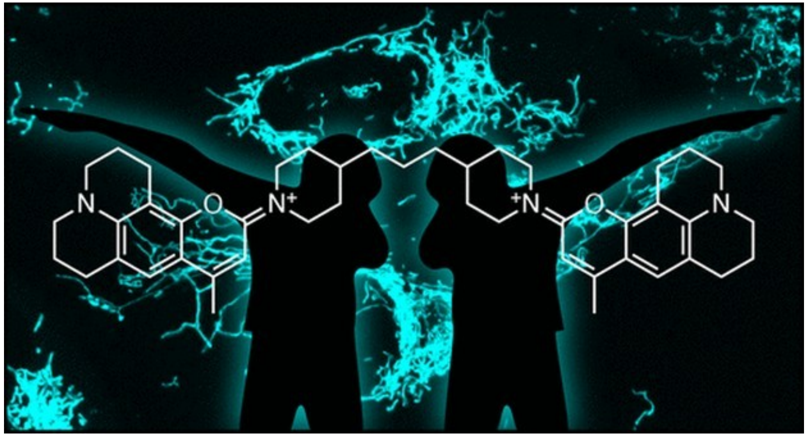
https://asymptote.sourceforge.io/gallery/

https://tocrofl.tumblr.com/

TOC graphics



https://pubs.acs.org/doi/10.1021/acs.jpclett.9b02552



https://href.li/?https://pubs.acs.org/doi/10.1021/acsbiomedchemau.1c00068

https://href.li/?https://www.sciencedirect.com/science/
article/pii/S0022328X21004721?dgcid=rss_sd_all

Random tips

- Save in the native file format of the editing program
- Save several intermediate files- there will be times you need to slightly modify a figure
- Save a final high-resolution version that can be converted to other file formats
- Ask for feedback on your plots

Other resources on visual design

- Jean-Luc Doumont, Felice Frankel
- MRS Science as art
- Ram Seshadri's Preparing Figures

OPEN ACCESS | Science Applications Forum

Fundamentals of graphic design—essential tools for effective visual science communication

Authors: Karen J. Murchie and Dylan Diomede | AUTHORS INFO & AFFILIATIONS

Publication:FACETS • 11 June 2020 • https://doi.org/10.1139/facets-2018-0049