Generating Phase Diagrams via HLD-NAC

Andrew Nyland, Jack Heller, Nick Furth, Dr. Adam Imel, Dr. Thomas Zawodzinski

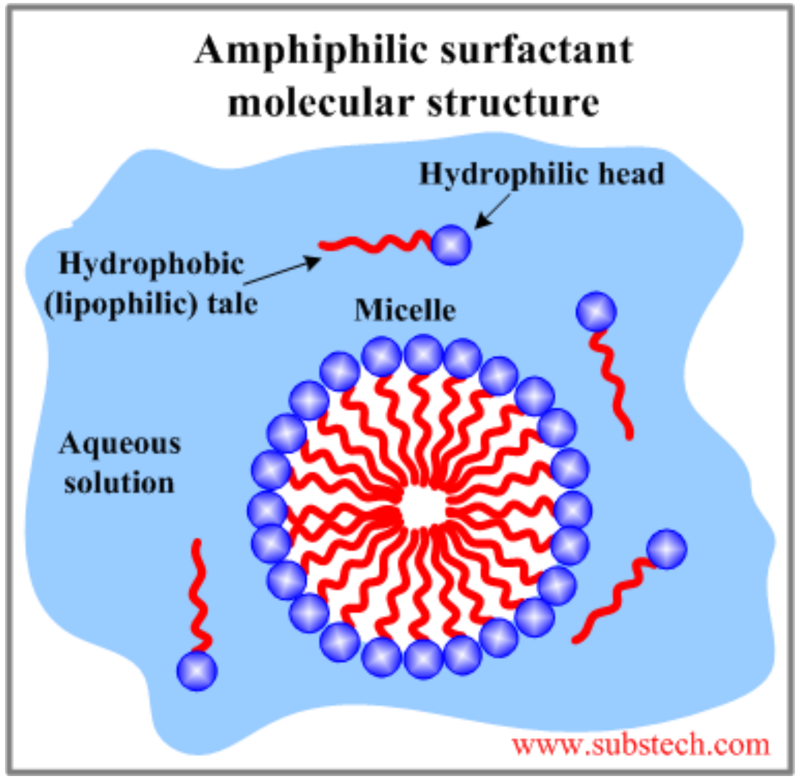
THE UNIVERSITY OF TENNESSEE
KNOXVILLE

Introduction and Goal

- Advancing investigations into microemulsions as breakthrough electrolytes for redox flow batteries and supercapacitors
  - Find the balance between oil, water, and surfactant that produces the highest energy density and conductivity while minimizing surfactant concentration
  - More oil = greater energy density

Goal: Simulate phase diagrams among various conditions allowing for comparison – simpler and faster

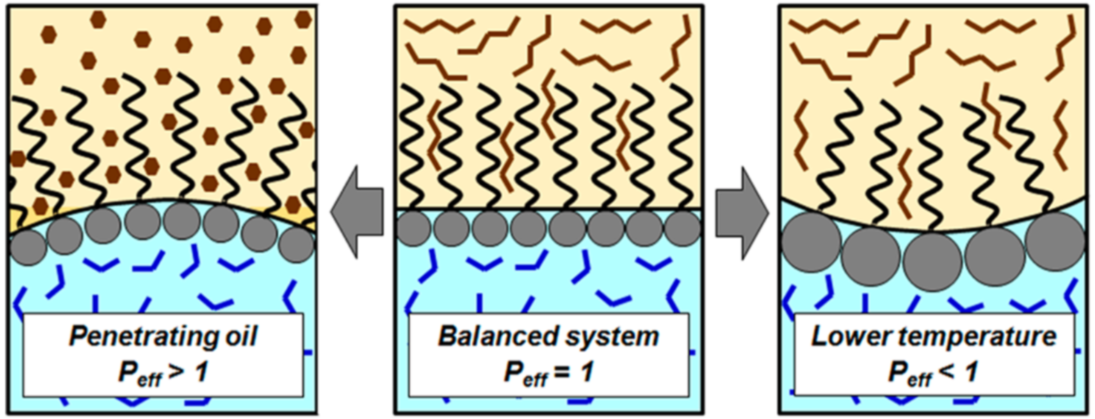
The Hydrophillic-Lipophillic Difference

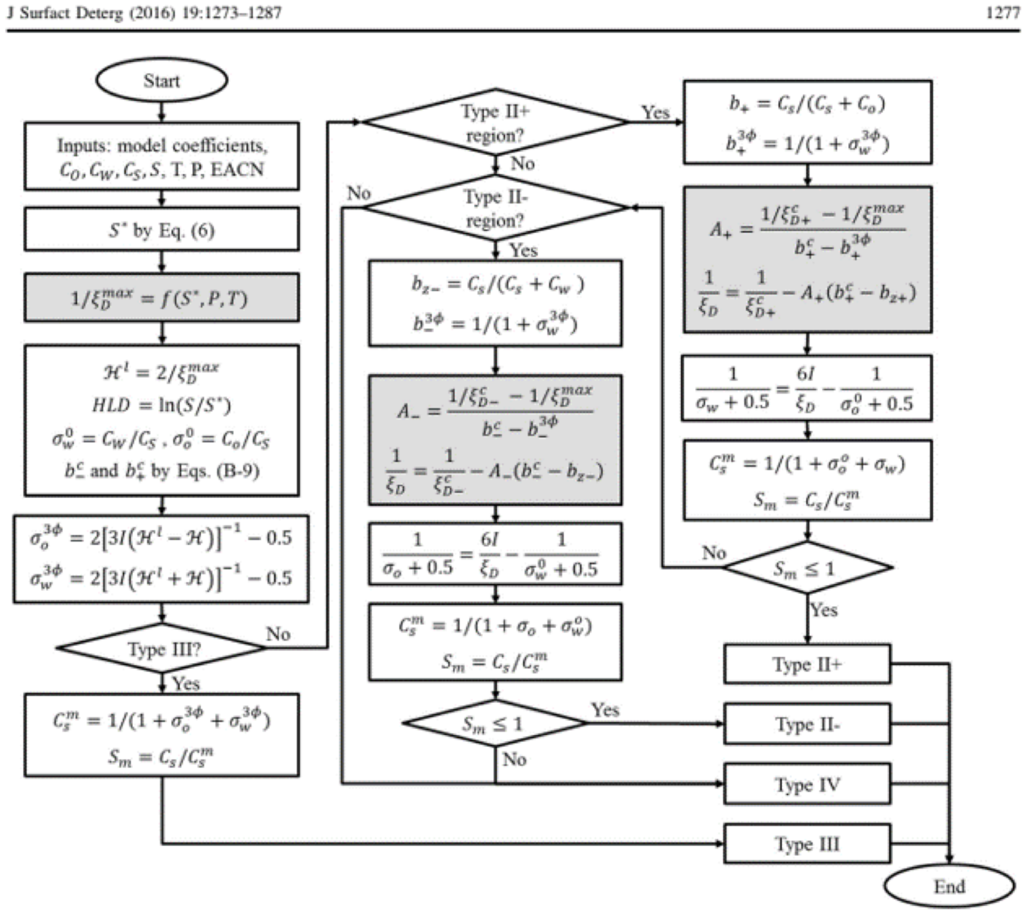


- *HLD = ln(S) - K x EACN - αT (T - T*) + Cc + f(A)*
- Where:
  - S = salinity (electrolyte concentration, g/100ml)
  - EACN = equivalent alkane carbon number - comparable oils
  - K = slope of the logarithm of optimum salinity
  - f(A) = function of alcohol type and concentration
  - Cc = characteristic parameter of the surfactant
  - T, T* = current and optimum temperature
  - αT = temperature coefficient

The Flash Algorithm - NAC (Net Average Curvature) improved

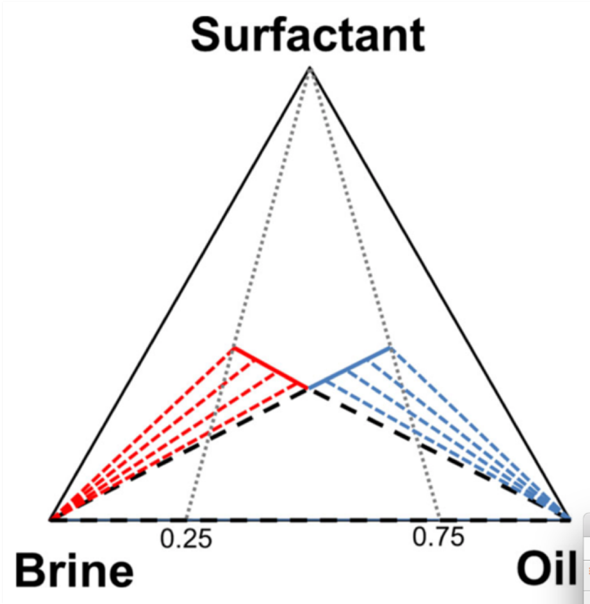
- Net curvature:
  - $H_n = \left|\frac{1}{R_{oil}}\right| - \left|\frac{1}{R_{water}}\right| = \frac{-HLD}{L}$
- Average curvature:
  - $H_a = 0.5 * \left(\left|\frac{1}{R_{oil}}\right| + \left|\frac{1}{R_{water}}\right|\right) \geq \frac{1}{\xi}$

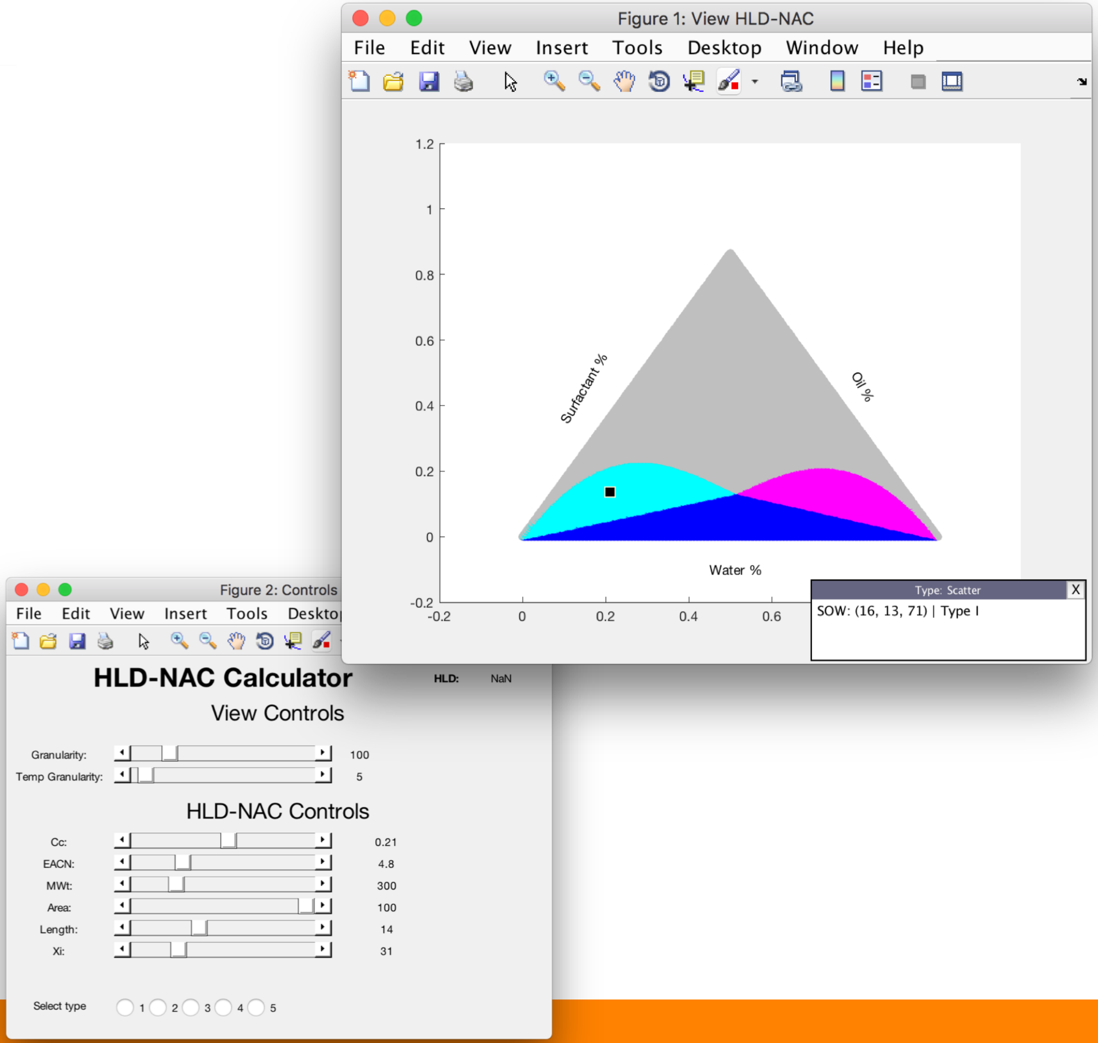




Khorsandi, S., Johns, R.T. Robust Flash Calculation Algorithm for Microemulsion Phase Behavior. *J Surfact Deterg* **19,** 1273–1287 (2016). https://doi.org/10.1007/s11743-016-1877-9
Lukowicz, T., Benazzouz, et al. (2015). Rationalization and Prediction of the Equivalent Alkane Carbon Number (EACN) of Polar Hydrocarbon Oils with COSMO-RS σ-Moments. *Langmuir : the ACS journal of surfaces and colloids*, *31*(41), 11220–11226. https://doi.org/10.1021/acs.langmuir.5b02545

Generating a ternary diagram





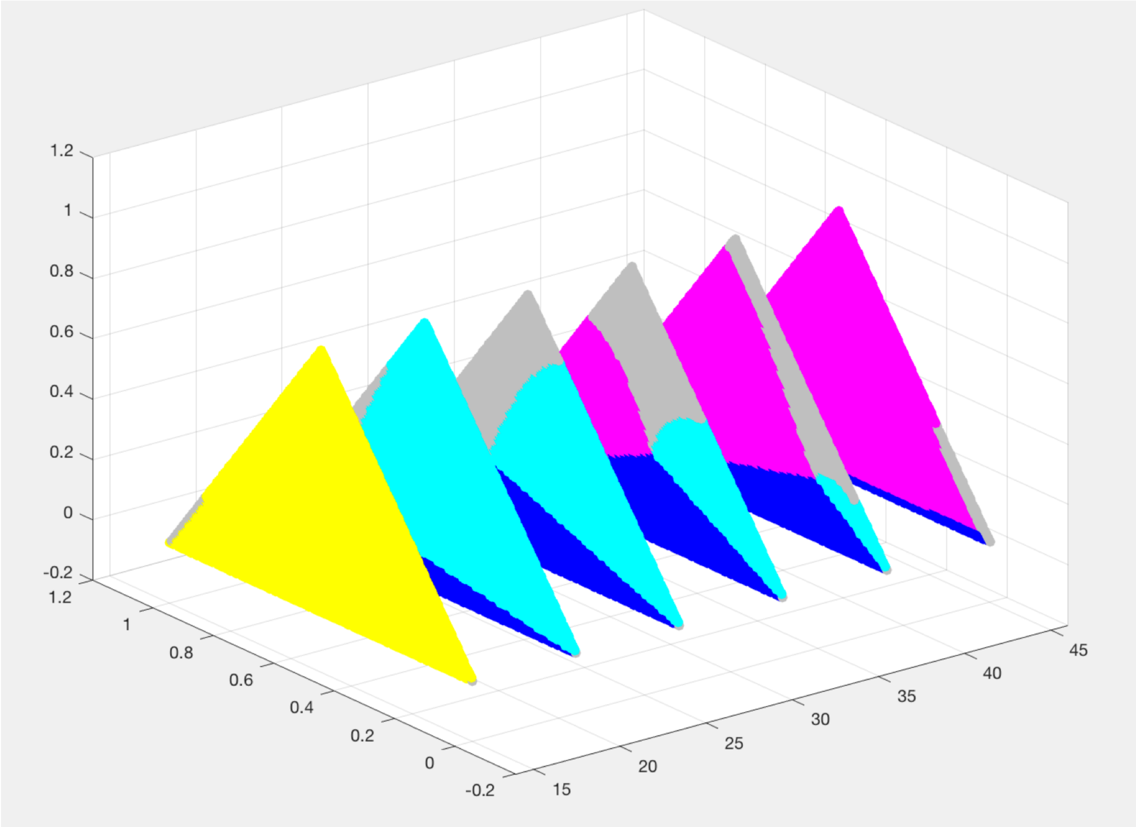
Viewer + Controls:

- Updates live as sliders are updated
- Ternary diagram can be inspected in detail at each point

Phase types:
Gray = single phase
Cyan = Type 1
Purple = Type 2
Blue = Type 3

Khorsandi, S., Johns, R.T. Robust Flash Calculation Algorithm for Microemulsion Phase Behavior. *J Surfact Deterg* **19,** 1273–1287 (2016). https://doi.org/10.1007/s11743-016-1877-9

Generating a tent/prism diagram

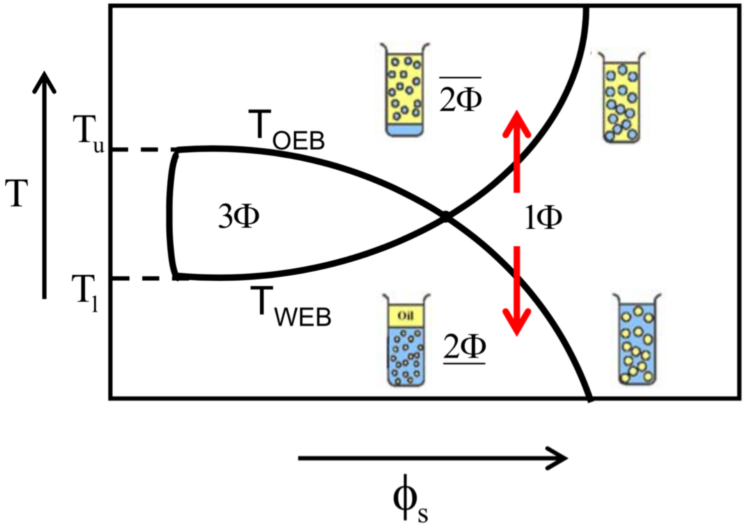


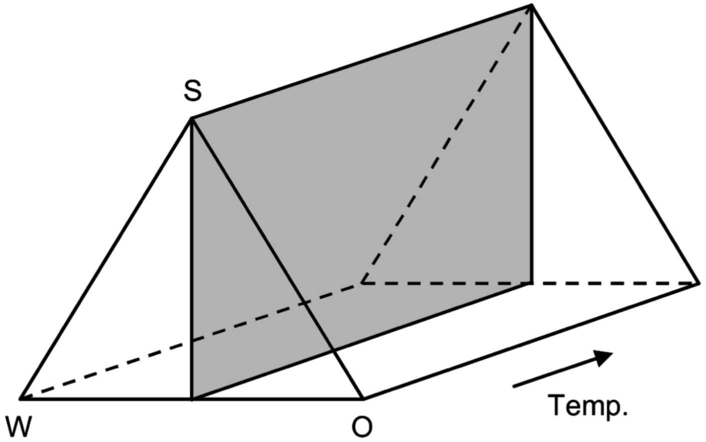
- 2D ternary diagram expanded on a 3rd dimension
  - Usually temperature or salinity
- Used to generate other diagrams
  - Fish cut diagram
  - Schinoda diagram
  - Volumes

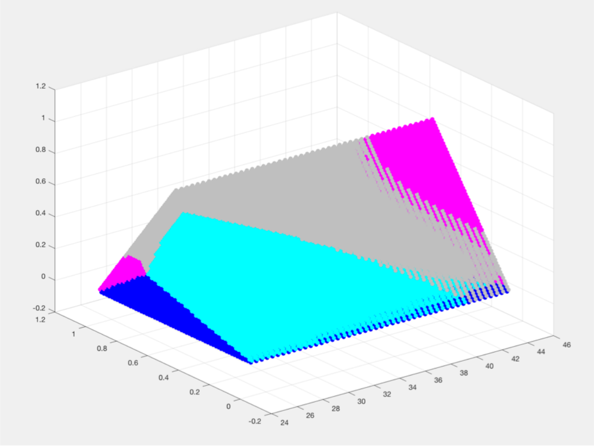
This view contains ~30,000 data points.

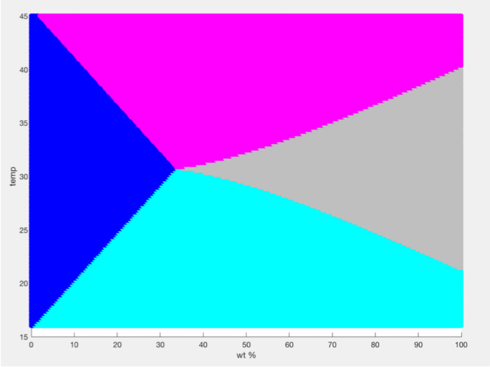
Generating a fish cut diagram

- Typically temperature/salinity plotted against surfactant concentration
- Useful for determining the conditions of when and which types of microemulsion form







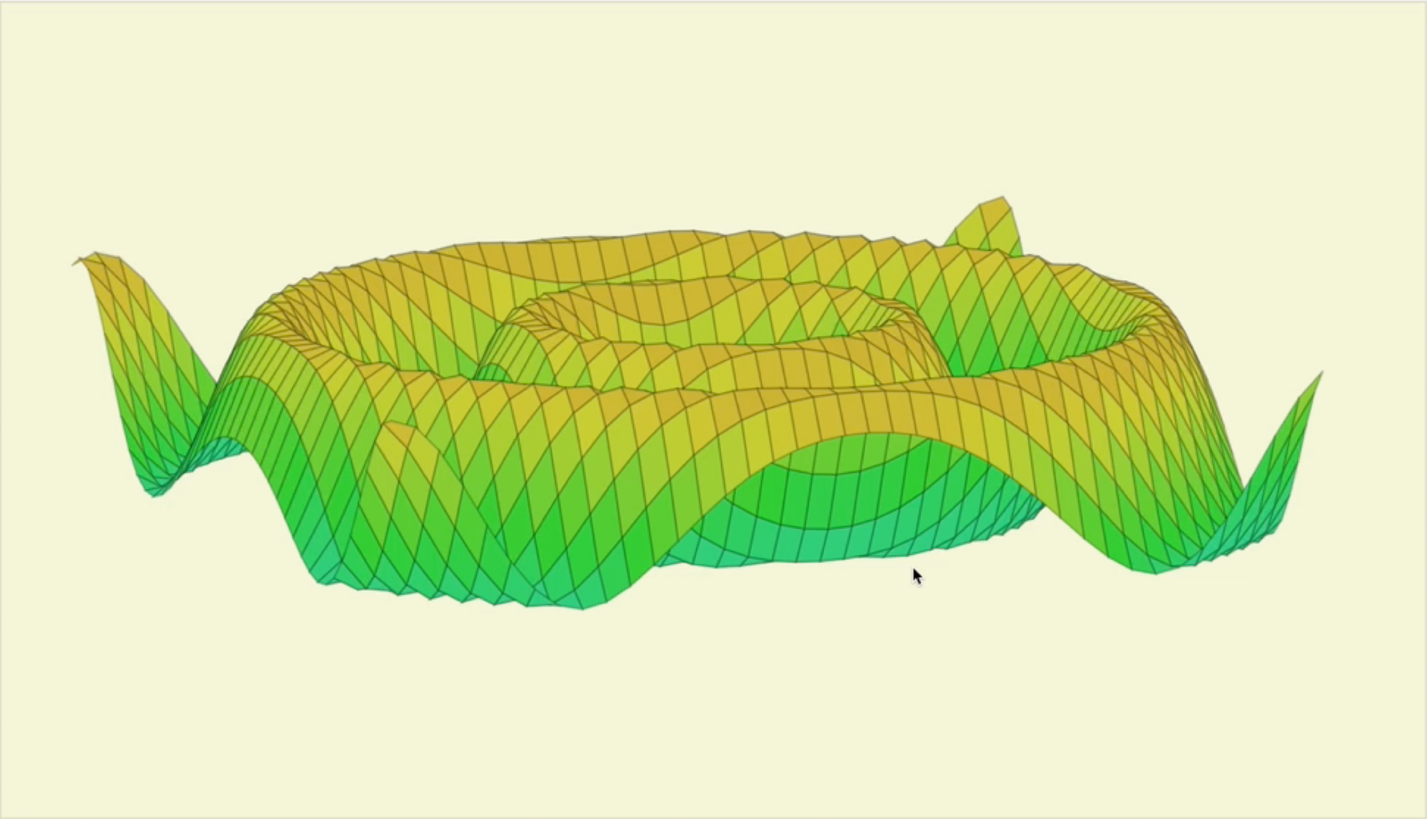


Alternate languages or viewing tools

Dataset 1

Dataset 2

Dataset 3



Problem: out of scope of MATLAB

Typical graphing in 3D assumes an equation such as:

$\boldsymbol{z = f(x, y)}$ or in our case

$$type = f(surfactant\%, oil\%, water\%)$$

However, our equation is:

$\boldsymbol{type = f(x, y, z)}$ or

$$type = f(surf\%, oil\%, water\%, temp)$$

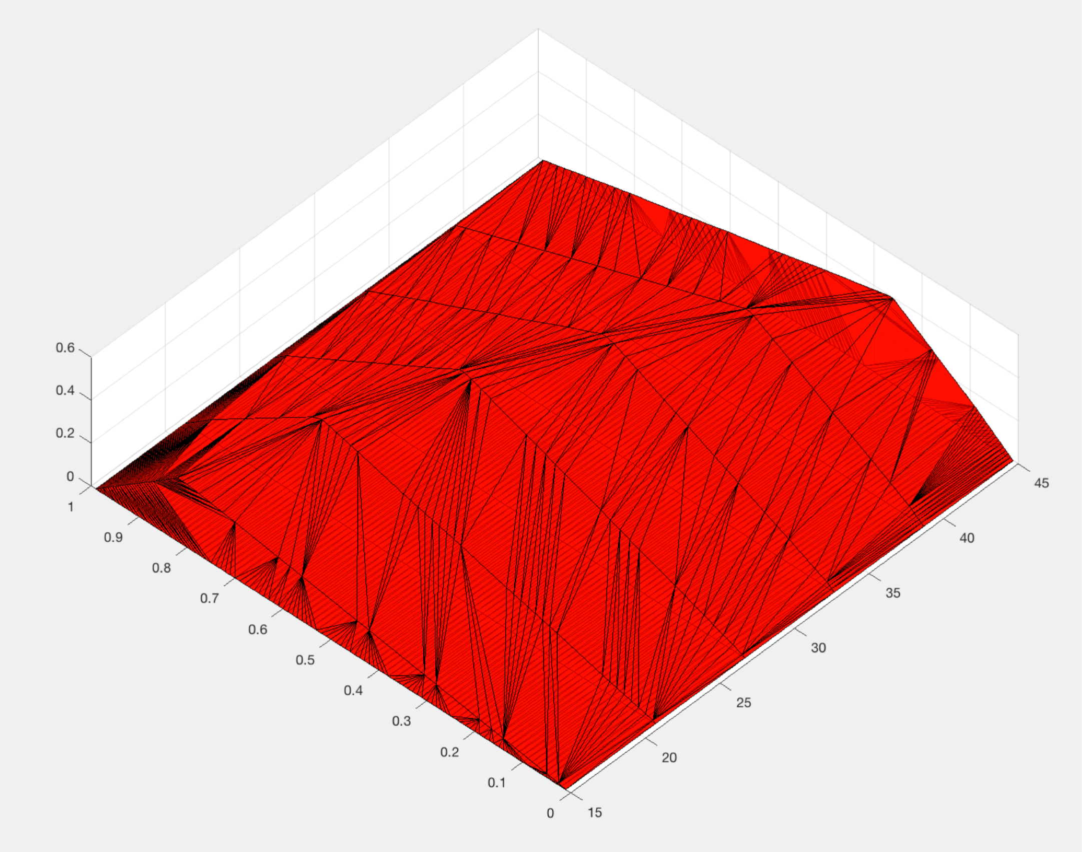
(when z is our added dimension of temperature, salinity, etc)

Generating volumes

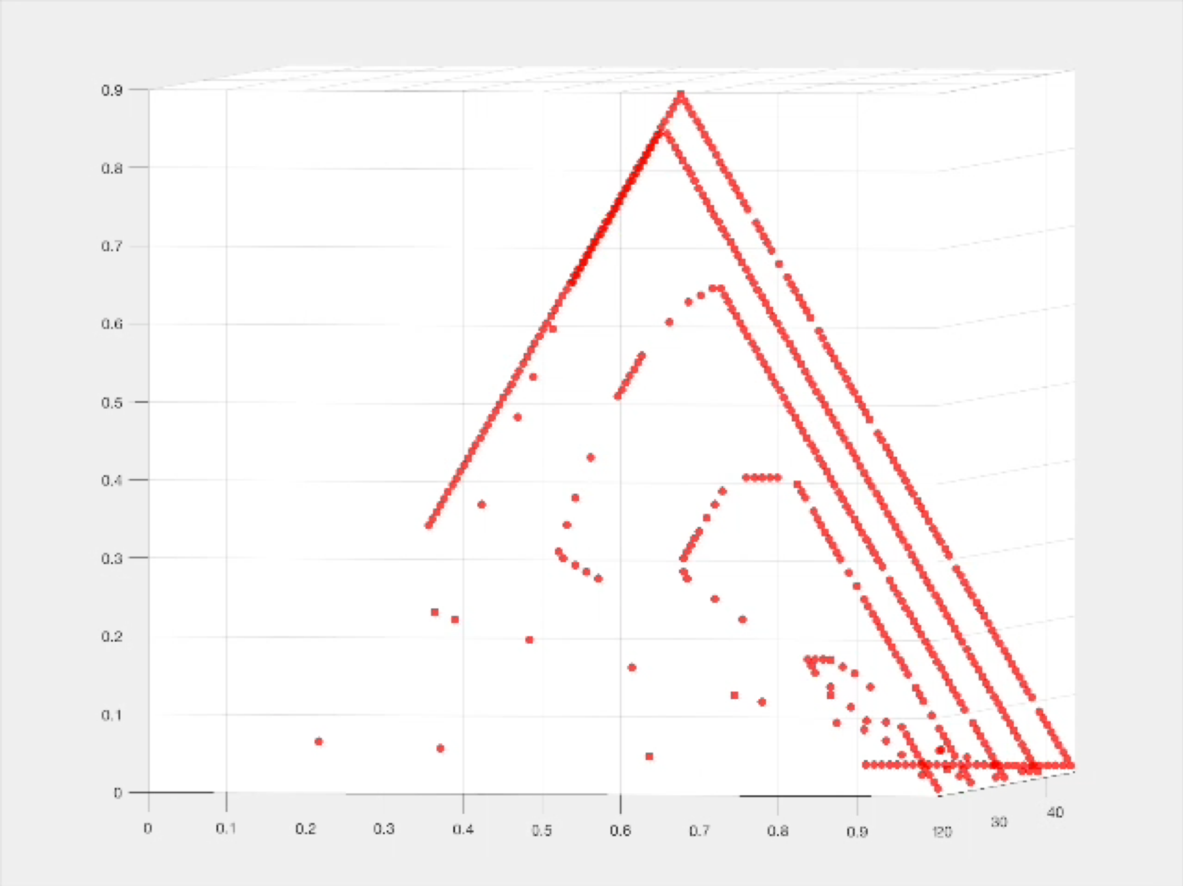
- Steps required:

1. Generate prism
2. Select all points of a certain type
3. Find edge points of that region
4. Triangulate the remaining points
5. Render as volume

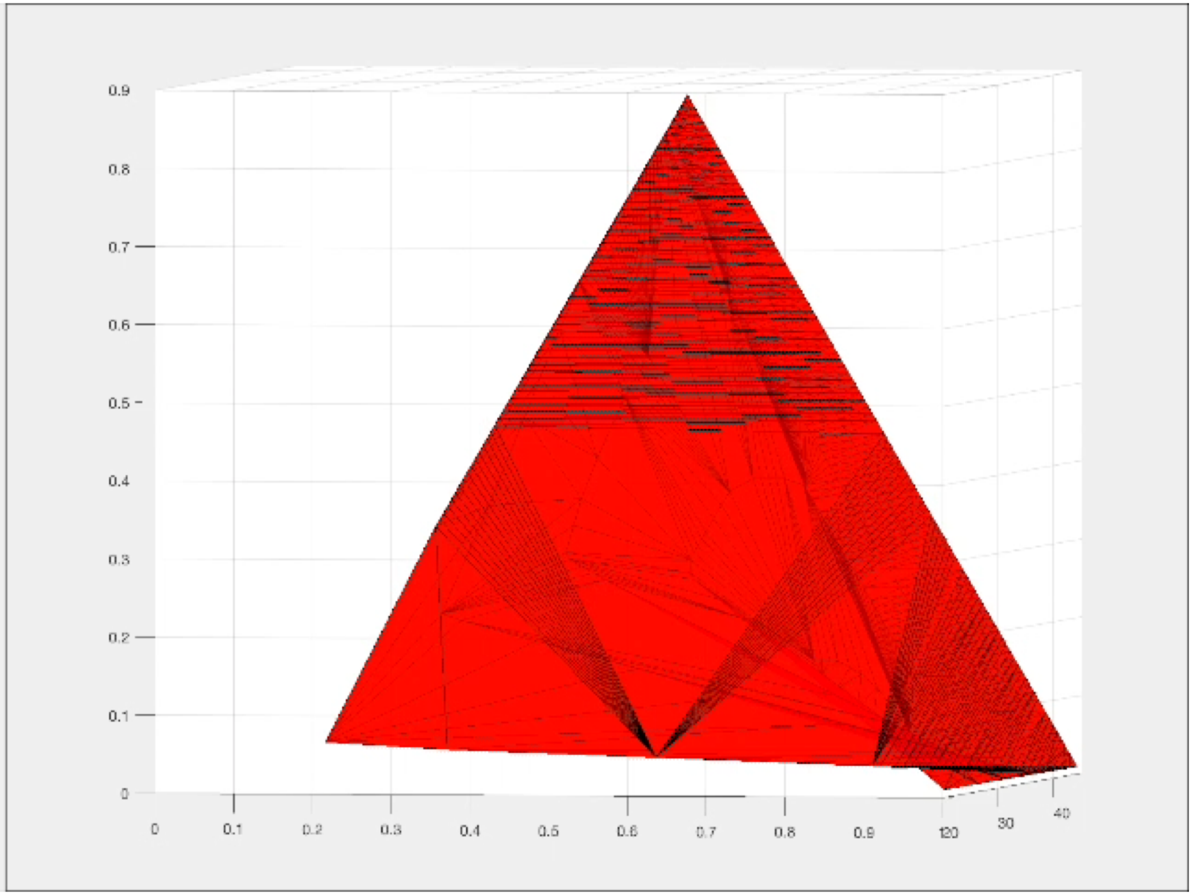
Useful for interpreting contiguous data, determining important conditions of single phase regions, and comparison of different scenarios.



Prism slices to volumes (rotates to right)



Scattered points from slices, reduced to edges



Triangulated volume view

Next Steps

- Add feature: comparing generated data to lab determined data
  - Allows for tuning of constants or certain equations
  - Validation of current HLD-NAC equations
- Improved User Interface
  - Finer control of input variable values, control of selected types
  - May require a different programming environment
- Automated bulk analysis
  - Allowing for many preconfigured situations to be simulated and analyzed with limited human interaction, as needed

Questions / Comments?

- People involved:
  - Andrew Nyland – Western Colorado University
  - Jack Heller – Lehigh University
  - Nicholas Furth – New Jersey Institute of Technology
  - Adam Imel, Ph.D. – University of Tennessee, Knoxville
  - Brian Barth – University of Tennessee, Knoxville
  - Thomas Zawodzinski, Ph.D. – University of Tennessee, Knoxville

- This work was performed during the 2021 Student Mentoring and Research Training (SMaRT) program that was jointly supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) through award number DE-EE0009177 provided to the University of Tennessee Oak Ridge Innovation Institute (UT-ORII) and the UT Science Alliance program.