U.S. DEPARTMENT OF ENERGY | Office of NUCLEAR ENERGY

Molten Salt Reactor PROGRAM

Experimental and AIMD Efforts for Molten Salt Thermophysical Property Characterization at ORNL– FY24

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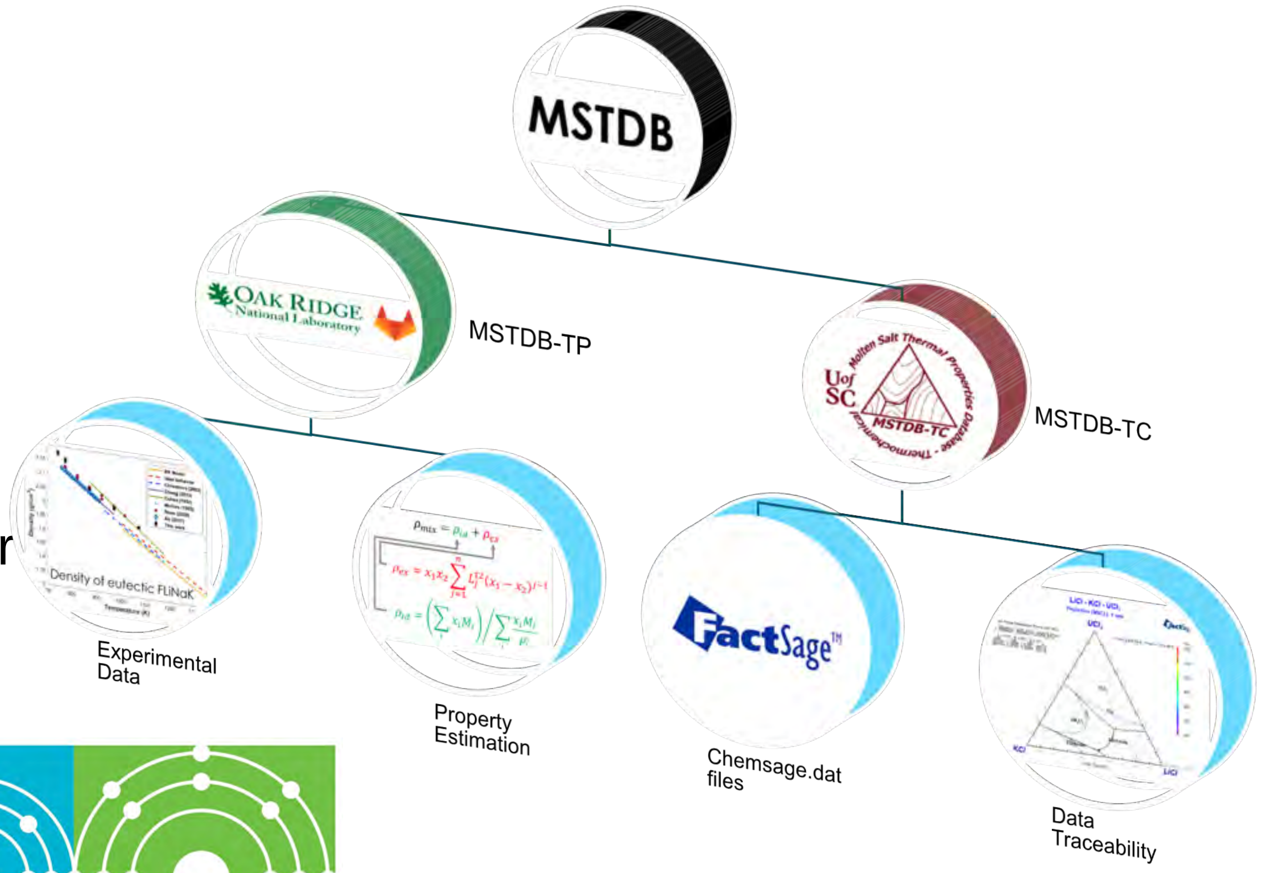
OAK RIDGE National Laboratory

Annual MSR Campaign Review Meeting 16-18 April 2024

Main Driver for Property Characterization: MSTDB

- The Molten Salt Thermal Property Database (MSTDB) is an effort funded by the DOE-NE funded Molten Salt Reactor (MSR) Campaign and the Nuclear Energy Advanced Modeling and Simulation (NEAMS) program.
- The goal of the MSTDB is to provide thermochemical and thermophysical characterizations of molten salt compounds and mixtures which are relevant to the nuclear industry
- MSTDB-TC is managed by UoSC, MSTDB-TP is managed by ORNL.

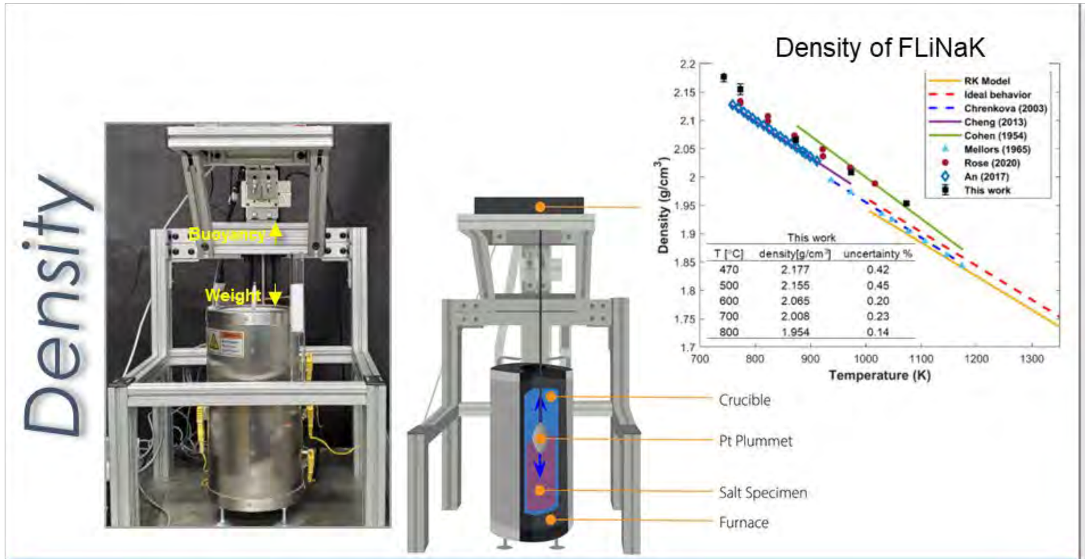


NEAMS
Nuclear Energy Advanced Modeling and Simulation

Molten Salt Reactor
PROGRAM

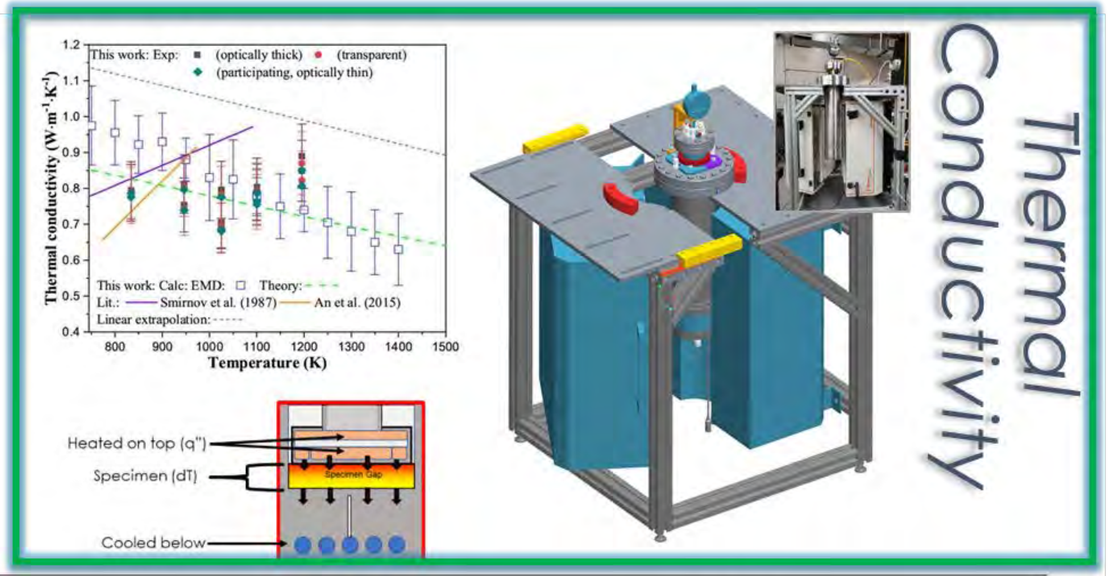
ORNL's Thermophysical Property Systems

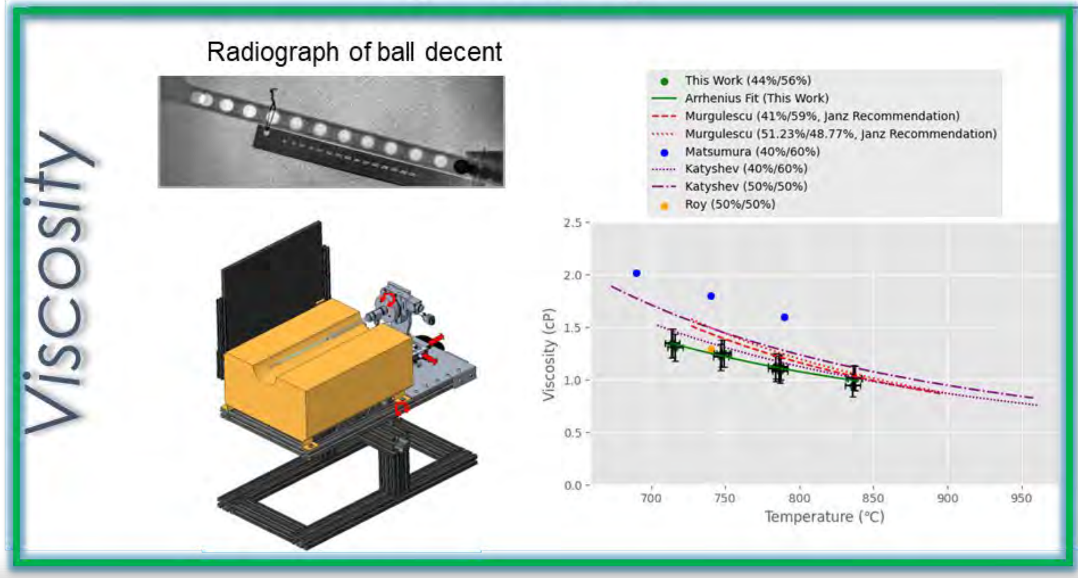
FY24 measurement focus – driven by MSTDB-TP

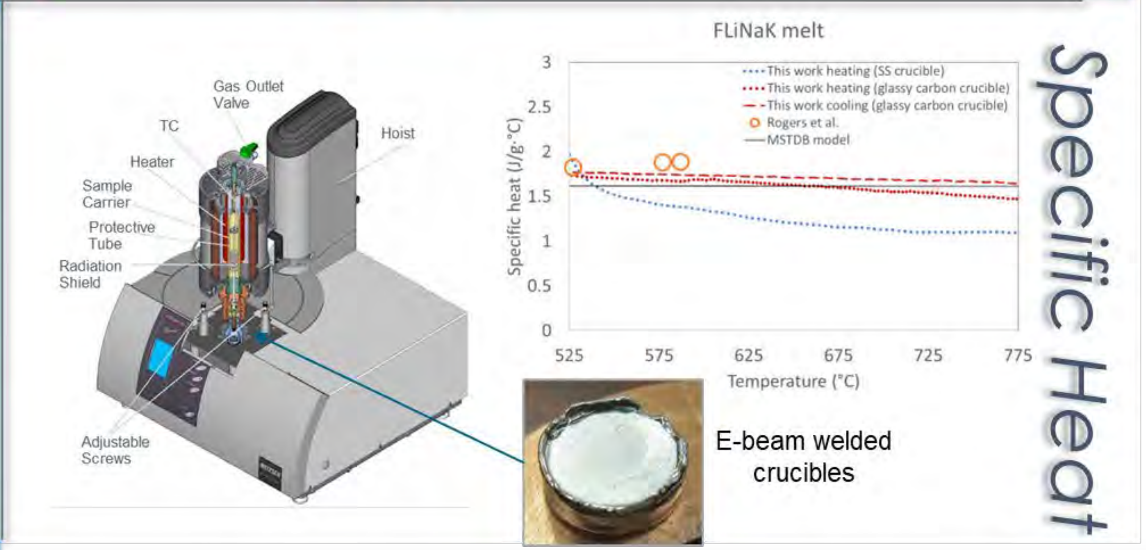


This work

T [°C]	density[g/cm³]	uncertainty %
470	2.177	0.42
500	2.155	0.45
600	2.065	0.20
700	2.008	0.23
800	1.954	0.14





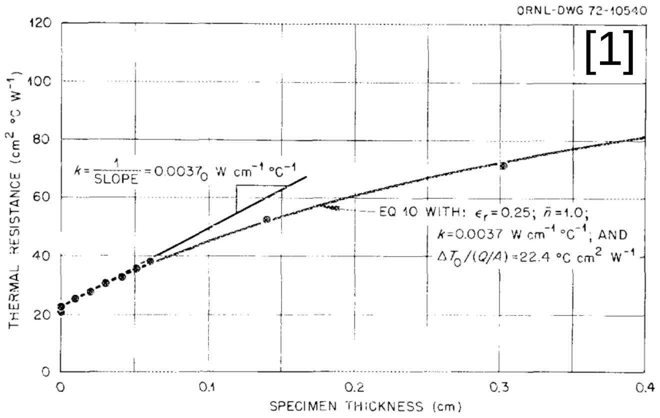


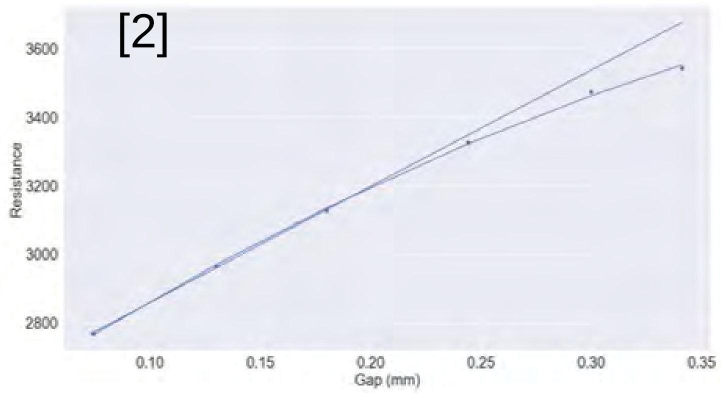
Thermal Conductivity System Functionality and Recent Improvements

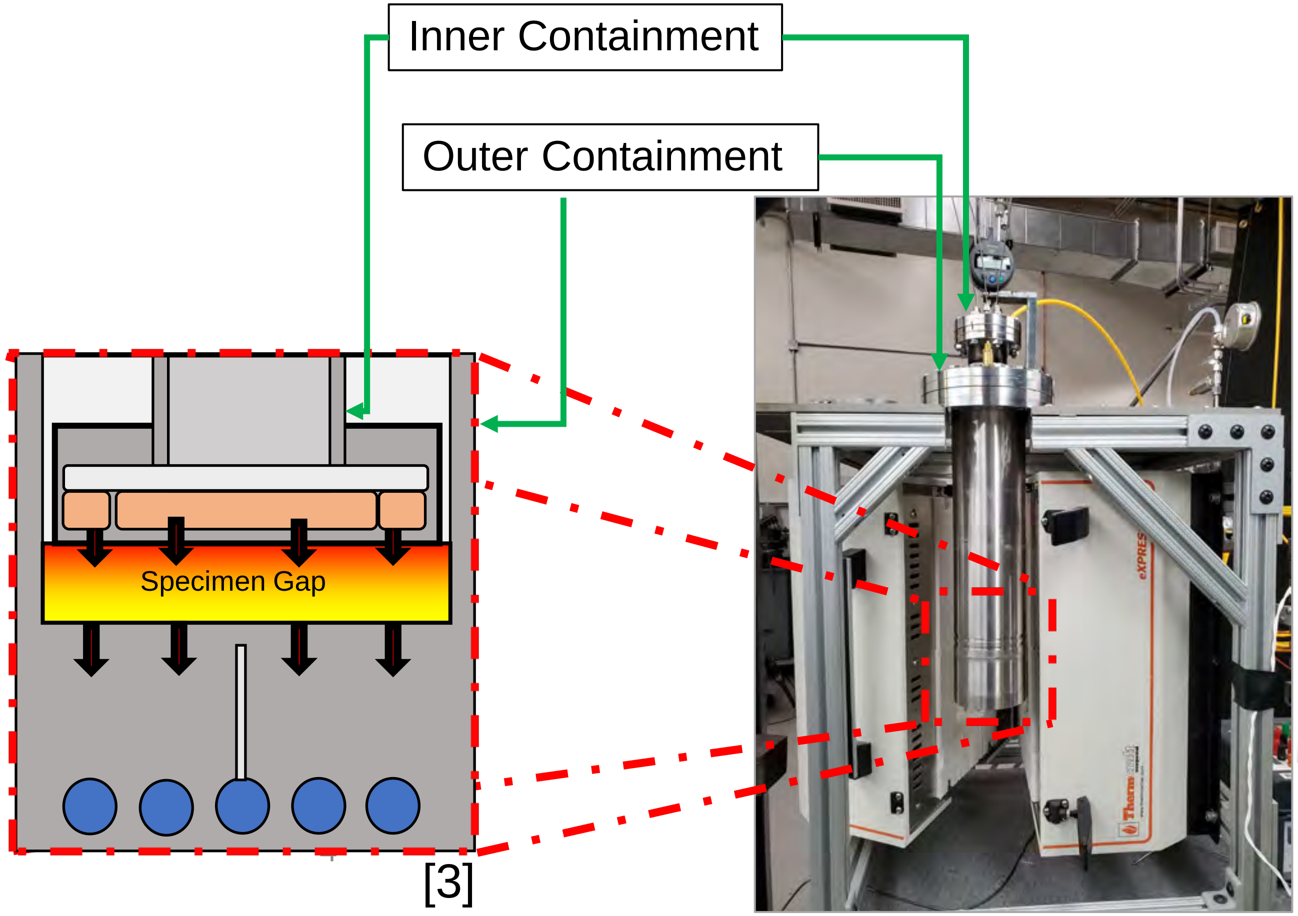
- Based on the variable gap technique
- New calibration scheme with He to isolate conductive heat transfer more carefully
  - Determination of heat flux correction factor
  - Determine limit as gap -> zero to remove radiant heat contribution
- Increased coolant pressure
- Oxygen filter integrated (~ppb levels)
- Designated CA zone and ventilation to enable actinide salt measurements

$$\frac{\Delta T_{spec}(x)}{(C_S)(q'')} = R_{th,fixed} + \frac{1}{\kappa_{cond} + \kappa_{rad}}x,$$

Helium Calibration Results (legacy versus current)



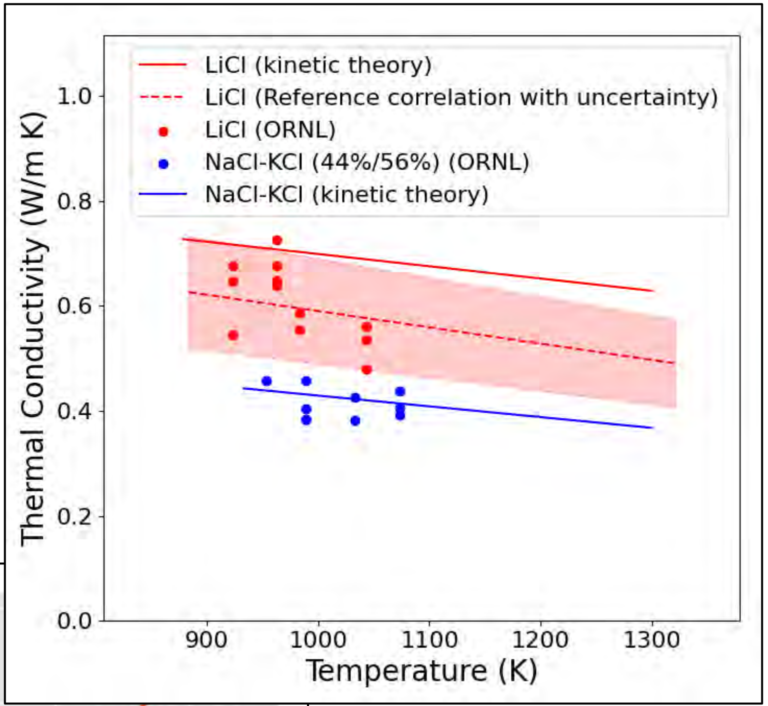


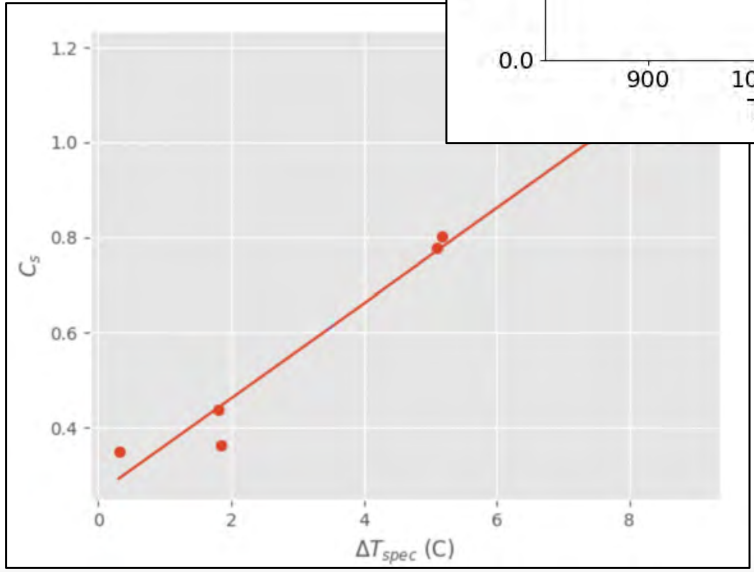


[1] ORNL-4831
[2] ORNL/TM-2023/3048
[3] Gallagher et al. (2022). *Int. J. Heat Mass Tran.*, *192*, 122763.

Recent Thermal Conductivity Measurements

- NaCl-KCl measurements (after detailed calibrations) documented in ORNL/TM-2023/3048
- LiCl Measurements taken and compared against reference correlation
  - Reference correlation from: Chliatzou et al. (2018). *JPCRD*, *47*(3).
- All data compared against kinetic theory model
  - Derived in: Gheribi, A. E., & Chartrand, P. (2016). *J. Chem. Phys.*, *144*(8).
  - Ultimately based on quantifying phonon mean free path
- These data give us confidence in moving forward with actinide bearing salts
- Both our chloride and fluoride salt containments are cleaned and ready for their next samples

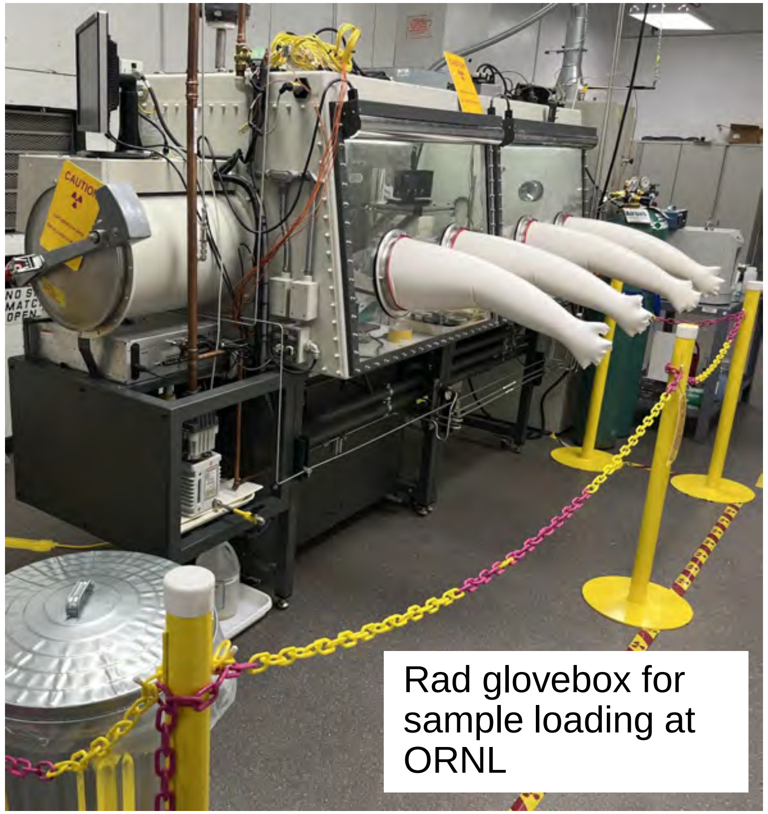




Upcoming Plans for Thermal Conductivity Measurements

- NaCl-KCl measurements (after detailed calibrations) documented in ORNL/TM-2023/3048
- Plans to measure:
  - NaCl-UCl3 eutectic
    - From INL
    - Synthesized by Bill Phillips
    - Onsite at ORNL
  - NaF-UF4 eutectic
    - From PNNL
    - Synthesized by Zach Huber and Bruce McNamara
    - Onsite at ORNL
  - NaF-KF-UF4 (57/16/27 mol %)
    - From VT
    - Synthesized by Amanda Leong
    - At VT, unlikely to measure this FY but possible

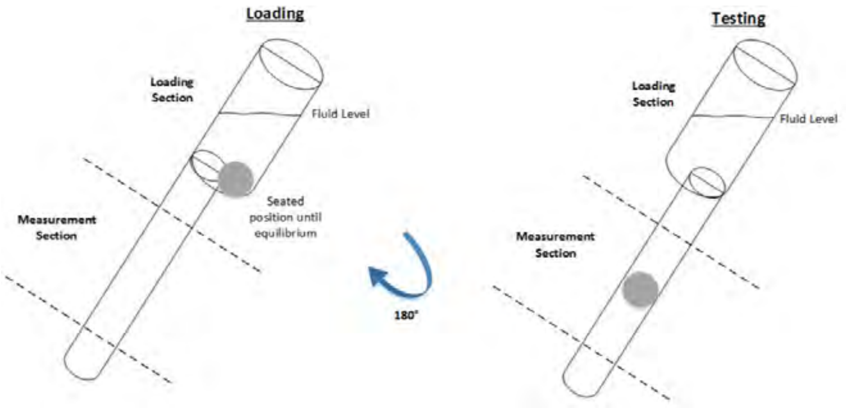
NaCl-UCl3 synthesized at INL (from INL/RPT-22-66727)

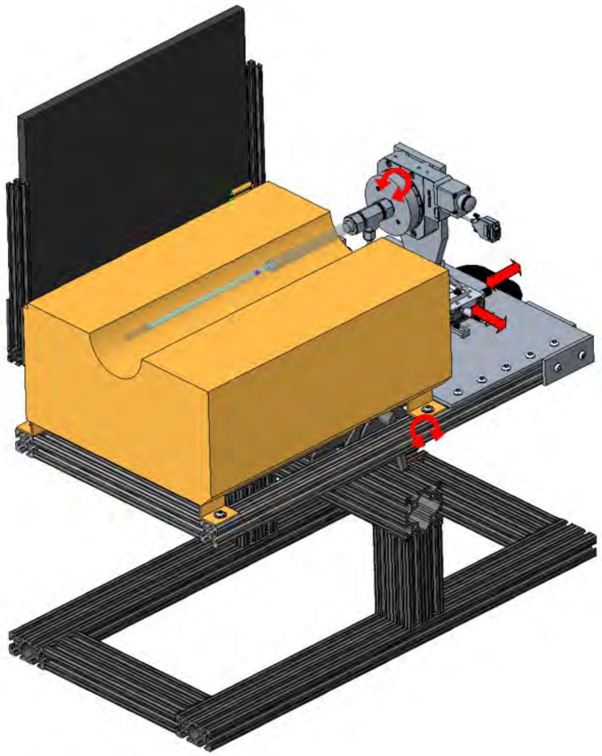


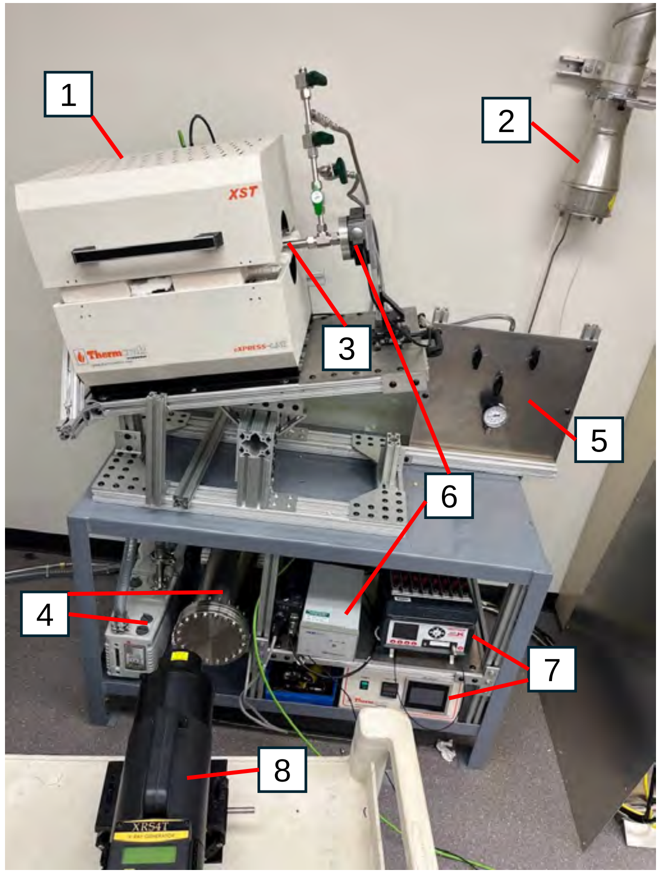
Rad glovebox for sample loading at ORNL

Viscosity System Functionality and Recent Improvements

- Based on Rolling Ball Technique
  - Terminal velocity of ball corresponds with viscosity of fluids
  - Correlation determined based on calibration with NIST standard oils
- Oxygen filter integrated (~ppb levels)
- Designated CA zone and ventilation to enable actinide salt measurements
- New x-ray system which requires minimal image processing
  - For fluoride and actinide bearing salts which can't be contained in fused quartz



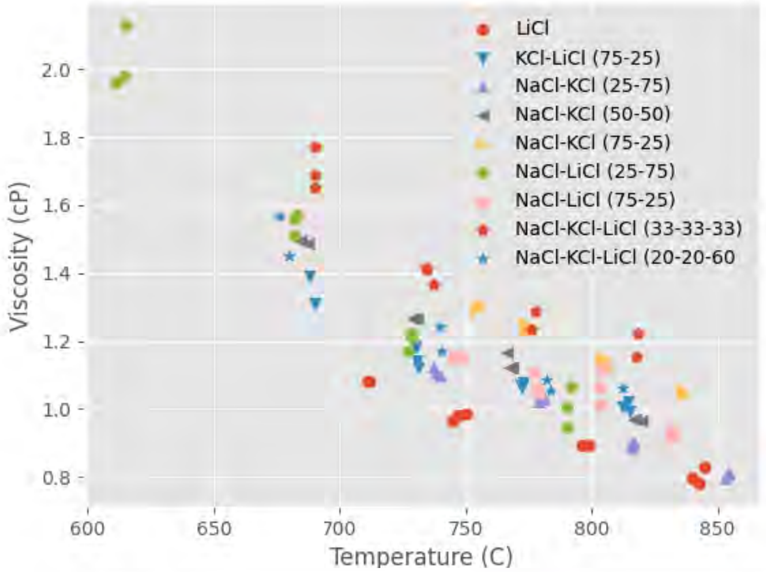


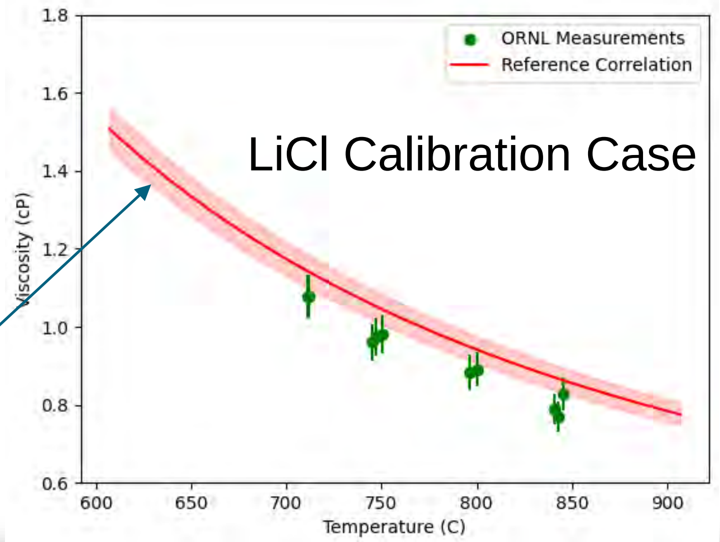


1. Furnace
2. Ventilation
3. Crucible
4. Backfill/ pressure maintenance system
5. Gas control
6. Rotation control
7. Heating/temperature control
8. X-ray system (detector behind furnace

Ongoing Viscosity Measurements

- Currently measuring various mixtures among the NaCl-KCl-LiCl compositional matrix
  - This is to demonstrate that the system is reasonably high throughput
  - Looking to unveil composition dependent trends
    - Does it match mixing models such as Grunburg-Nissan? Deviation from ideal mixing?
- Comparing this with AIMD generated data
  - Vanda Glezakou and Brett Smith leading this effort
- Great opportunity for students to get hands on lab experience
  - Relatively minimal hazards by focusing on alkali chlorides



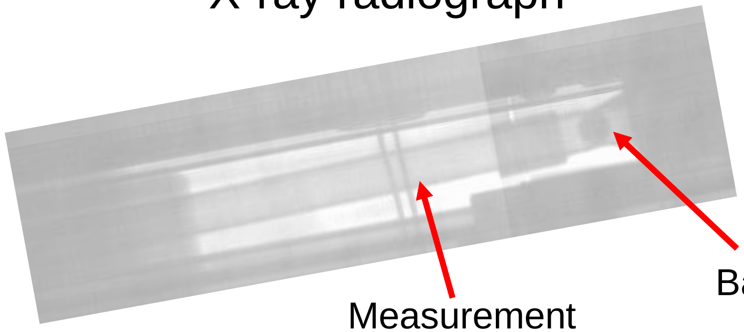


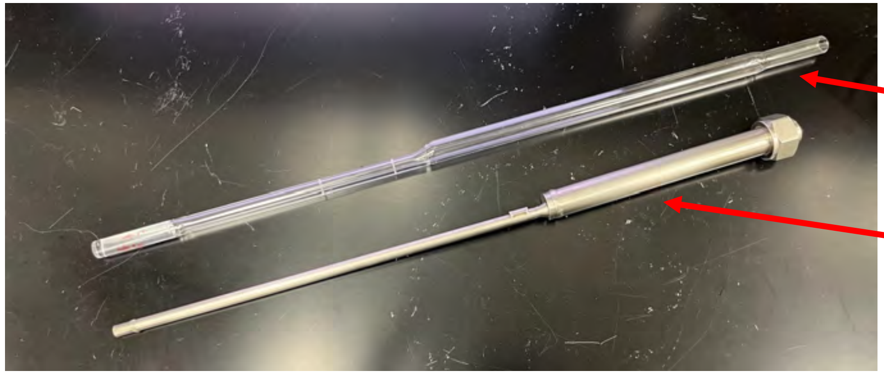
Reference correlation from:
Tasidou, et al. Reference correlations for the viscosity of 13 inorganic molten salts. *JPCRD*, *48*(1).

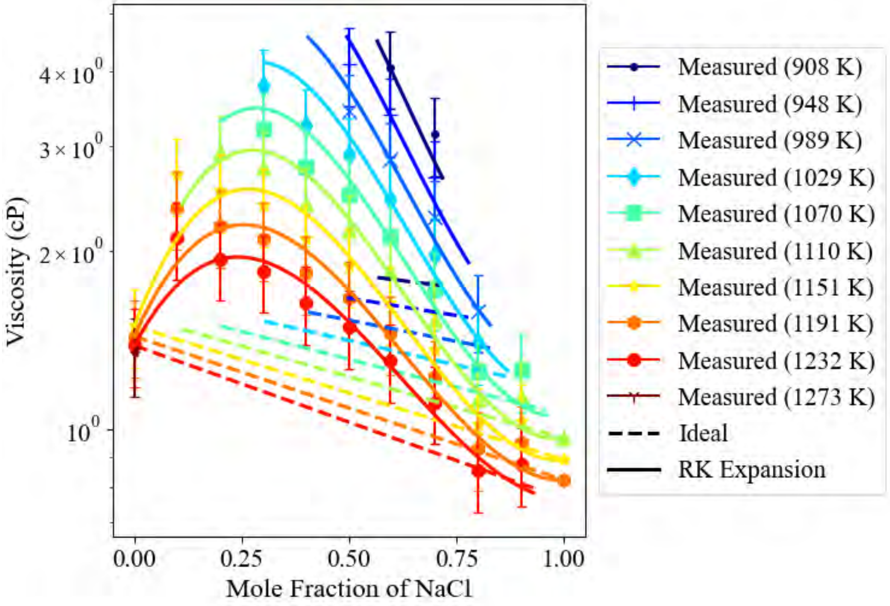
Upcoming Plans for Viscosity Measurements

- Optimize stainless steel crucibles for fluoride or actinide bearing salt experiments
  - Junction between loading section and measurement section causing issues
- Conduct measurement of a well-characterized salt (alkali halide) in the stainless-steel crucible
  - To ensure similar quality of data is generated as with fused quartz
- Measure NaCl-UCl3 viscosity before the end of the FY
  - Can compare against literature data by Katyshev
    - From: Katyshev, Sergey Filippovich. Properties of molten mixtures of alkali metal halides, zirconium, hafnium and uranium. Ural State Technical University, 2001.

X-ray radiograph

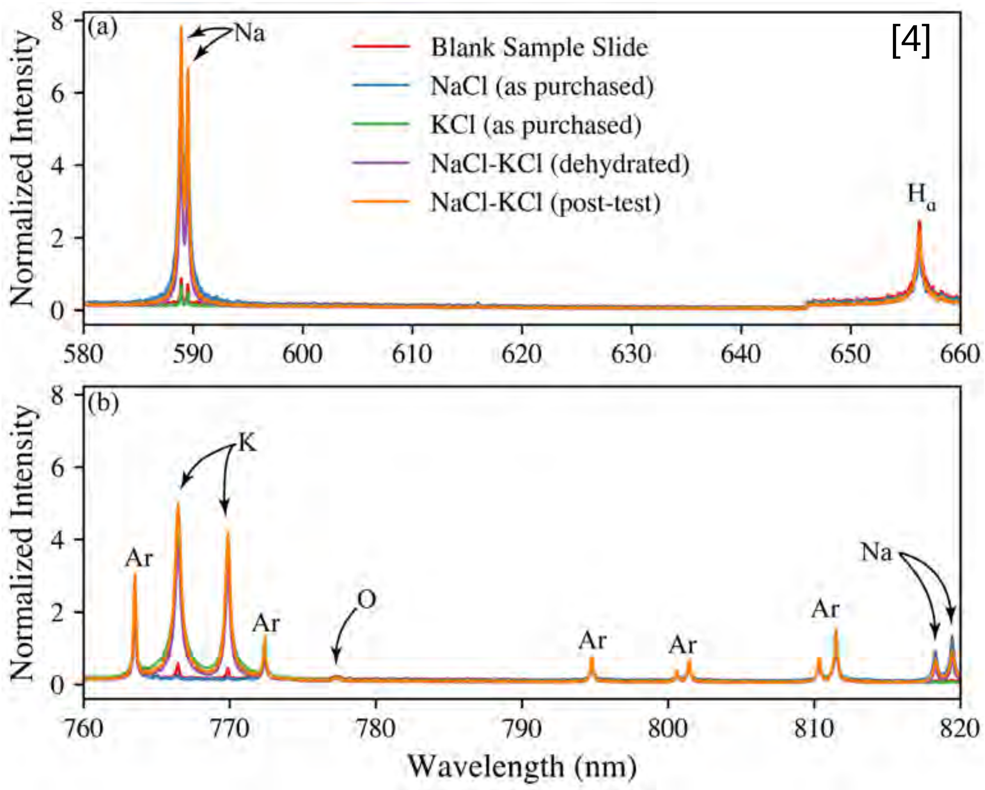


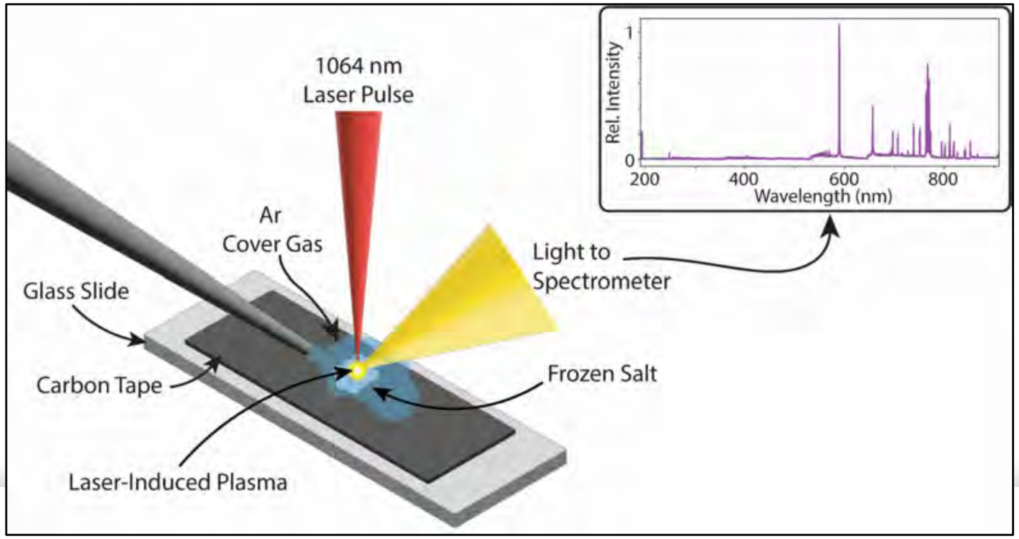




Moisture/Oxygen Content Analysis

- One challenge with these measurements is that salts tend to be hygroscopic
  - Some hydrolyze when heated, forming oxides
- While trace metal content can be determined with techniques such as XRD or ICP-MS/OES, low Z elements are hard to assess
- We are collaborating with Hunter Andrews to see H and O content of samples with LIBS
  - This will be crucial for compounds such as UCl3, whose hydrates form UO2 upon heating





Other References on LIBS salt characterization:

- Myhre, K. G., Andrews, H. B., Sulejmanovic, D., Contescu, C. I., Keiser, J. R., & Gallego, N. C. (2022). *Journal of Analytical Atomic Spectrometry*, *37*(8), 1629-1641.
- ORNL/TM-2023/3067

[4] Birri et al. (2023). *TSEP*, *44*, 102029.

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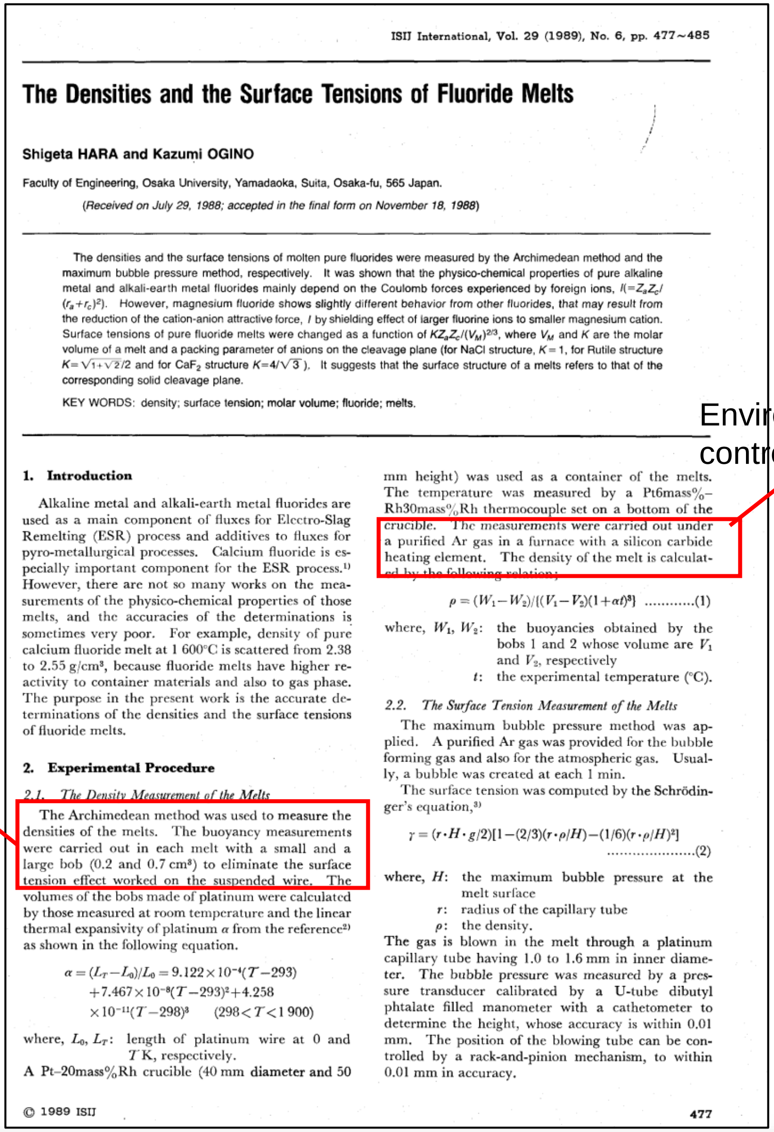
MSTDB-TP QA Effort Overview

Example Case from: Hara, S., & Ogino, K. (1989). *ISIJ Int.*, *29*(6), 477-485.

- Working in collaboration with ANL to apply quality rankings to data in MSTDB
  - Melissa Rose at ANL leading the effort
  - ORNL supporting data/reference needs for analysis
- The goal is to rank all duplicate data for each salt system based on:
  - Method used
  - Calibration
  - Composition analysis
  - Environmental Controls
  - Measurement Precision
- Note that MSTDB-TP is based on assessment of hundreds of documents
  - QA of the entire database would be a significant effort



ISIJ International, Vol. 29 (1989), No. 6, pp. 477–485

The Densities and the Surface Tensions of Fluoride Melts

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(*Received on July 29, 1988; accepted in the final form on November 18, 1988*)

The densities and the surface tensions of molten pure fluorides were measured by the Archimedean method and the maximum bubble pressure method, respectively. It was shown that the physico-chemical properties of pure alkaline metal and alkali-earth metal fluorides mainly depend on the Coulomb forces experienced by foreign ions, $I(=Z_aZ_c/(r_a+r_c)^2)$. However, magnesium fluoride shows slightly different behavior from other fluorides, that may result from the reduction of the cation-anion attractive force, I by shielding effect of larger fluorine ions to smaller magnesium cation. Surface tensions of pure fluoride melts were changed as a function of $KZ_aZ_c/(V_M)^{2/3}$, where V_M and K are the molar volume of a melt and a packing parameter of anions on the cleavage plane (for NaCl structure, $K=1$, for Rutile structure $K=\sqrt{1+\sqrt{2}}/2$ and for CaF_2 structure $K=4/\sqrt{3}$). It suggests that the surface structure of a melts refers to that of the corresponding solid cleavage plane.

KEY WORDS: density; surface tension; molar volume; fluoride; melts.

1. Introduction

Alkaline metal and alkali-earth metal fluorides are used as a main component of fluxes for Electro-Slag Remelting (ESR) process and additives to fluxes for pyro-metallurgical processes. Calcium fluoride is especially important component for the ESR process.[1] However, there are not so many works on the measurements of the physico-chemical properties of those melts, and the accuracies of the determinations is sometimes very poor. For example, density of pure calcium fluoride melt at 1 600°C is scattered from 2.38 to 2.55 g/cm³, because fluoride melts have higher reactivity to container materials and also to gas phase. The purpose in the present work is the accurate determinations of the densities and the surface tensions of fluoride melts.

2. Experimental Procedure

2.1. *The Density Measurement of the Melts*

The Archimedean method was used to measure the densities of the melts. The buoyancy measurements were carried out in each melt with a small and a large bob (0.2 and 0.7 cm³) to eliminate the surface tension effect worked on the suspended wire. The volumes of the bobs made of platinum were calculated by those measured at room temperature and the linear thermal expansivity of platinum α from the reference[2] as shown in the following equation.

$$\alpha=(L_T-L_0)/L_0=9.122\times10^{-4}(T-293)+7.467\times10^{-8}(T-293)^2+4.258\times10^{-11}(T-298)^3 \quad (298<T<1\,900)$$

where, L_0, L_T: length of platinum wire at 0 and T K, respectively.

A Pt–20mass%Rh crucible (40 mm diameter and 50 mm height) was used as a container of the melts. The temperature was measured by a Pt6mass%–Rh30mass%Rh thermocouple set on a bottom of the crucible. The measurements were carried out under a purified Ar gas in a furnace with a silicon carbide heating element. The density of the melt is calculated by the following relation;

$$\rho=(W_1-W_2)/\{(V_1-V_2)(1+\alpha t)^3\} \quad \text{............(1)}$$

where, W_1, W_2: the buoyancies obtained by the bobs 1 and 2 whose volume are V_1 and V_2, respectively

t: the experimental temperature (°C).

2.2. *The Surface Tension Measurement of the Melts*

The maximum bubble pressure method was applied. A purified Ar gas was provided for the bubble forming gas and also for the atmospheric gas. Usually, a bubble was created at each 1 min.

The surface tension was computed by the Schrödinger's equation,[3]

$$\gamma=(r\cdot H\cdot g/2)[1-(2/3)(r\cdot\rho/H)-(1/6)(r\cdot\rho/H)^2] \quad \text{............(2)}$$

where, H: the maximum bubble pressure at the melt surface

r: radius of the capillary tube

ρ: the density.

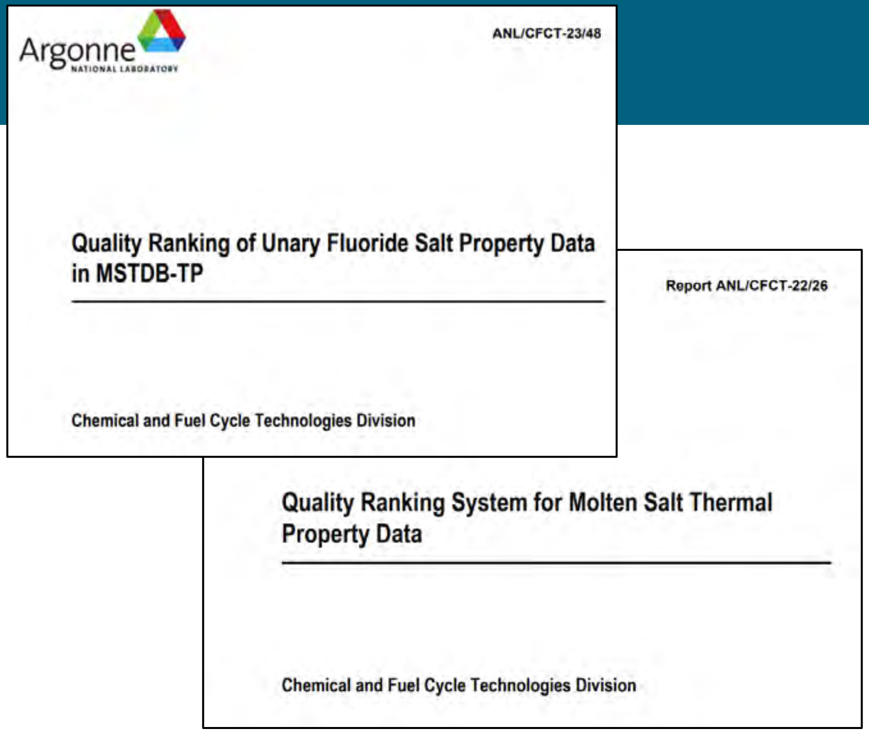
The gas is blown in the melt through a platinum capillary tube having 1.0 to 1.6 mm in inner diameter. The bubble pressure was measured by a pressure transducer calibrated by a U-tube dibutyl phtalate filled manometer with a cathetometer to determine the height, whose accuracy is within 0.01 mm. The position of the blowing tube can be controlled by a rack-and-pinion mechanism, to within 0.01 mm in accuracy.

Environmental controls

method details

Current and Ongoing Output MSTDB-TP QA Effort

- ANL has put out two reports on the QA process for MSTDB-TP
  - One detailing how the rankings work
  - Another on application to pure fluoride compounds for density and viscosity
- ORNL has organized all metadata to support this, including data visualization
  - Plots of all duplicate data, in conjunction with the quality rankings, allows a more careful honing on trustworthy data sets
- We plan to leverage this work for updated reference correlations of fluoride density and viscosity
  - The last known instance of this was in 1988 by Janz
    - Janz, G. J. (1988). *JPCRD*, 17.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ANL/CFCT-23/48

Quality Ranking of Unary Fluoride Salt Property Data in MSTDB-TP

Chemical and Fuel Cycle Technologies Division

Report ANL/CFCT-22/26

Quality Ranking System for Molten Salt Thermal Property Data

Chemical and Fuel Cycle Technologies Division

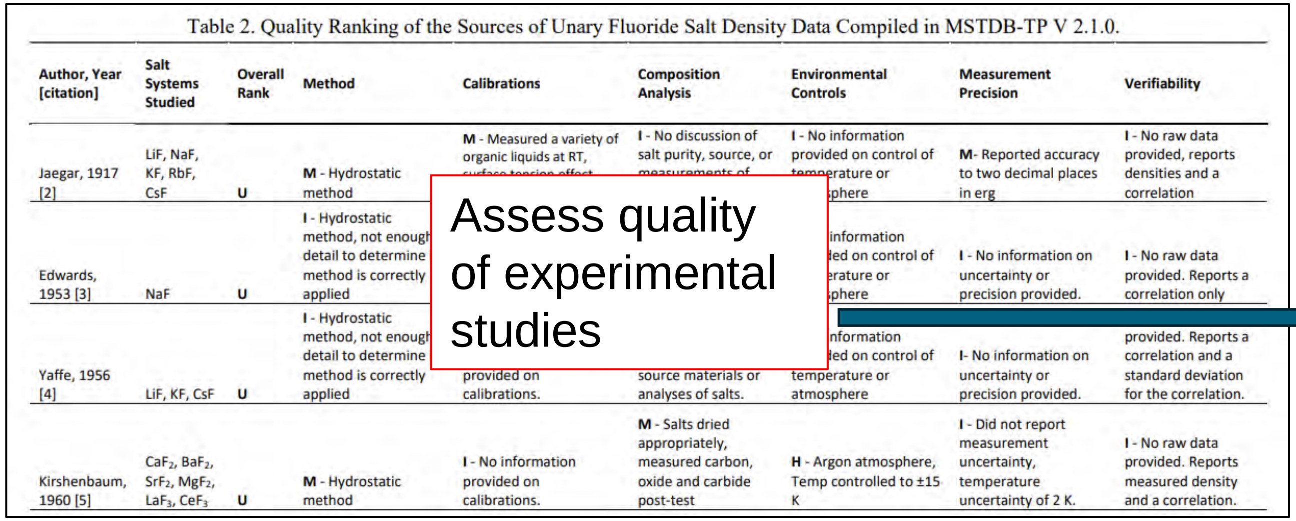
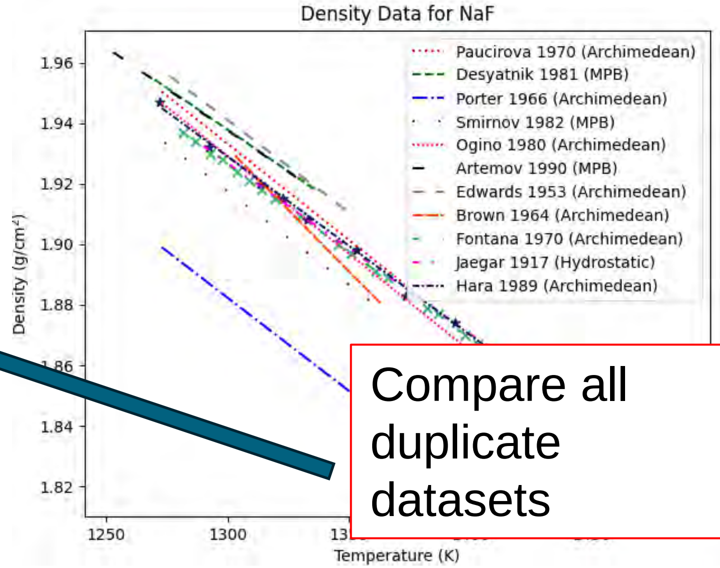


Table 2. Quality Ranking of the Sources of Unary Fluoride Salt Density Data Compiled in MSTDB-TP V 2.1.0.

Author, Year [citation]	Salt Systems Studied	Overall Rank	Method	Calibrations	Composition Analysis	Environmental Controls	Measurement Precision	Verifiability
Jaegar, 1917 [2]	LiF, NaF, KF, RbF, CsF	U	**M** - Hydrostatic method	**M** - Measured a variety of organic liquids at RT, surface tension effect	**I** - No discussion of salt purity, source, or measurements of	**I** - No information provided on control of temperature or …sphere	**M**- Reported accuracy to two decimal places in erg	**I** - No raw data provided, reports densities and a correlation
Edwards, 1953 [3]	NaF	U	**I** - Hydrostatic method, not enough detail to determine method is correctly applied			…information …ded on control of …erature or …sphere	**I** - No information on uncertainty or precision provided.	**I** - No raw data provided. Reports a correlation only
Yaffe, 1956 [4]	LiF, KF, CsF	U	**I** - Hydrostatic method, not enough detail to determine method is correctly applied	… provided on calibrations.	… source materials or analyses of salts.	…nformation …ded on control of temperature or atmosphere	**I**- No information on uncertainty or precision provided.	… provided. Reports a correlation and a standard deviation for the correlation.
Kirshenbaum, 1960 [5]	CaF_2, BaF_2, SrF_2, MgF_2, LaF_3, CeF_3	U	**M** - Hydrostatic method	**I** - No information provided on calibrations.	**M** - Salts dried appropriately, measured carbon, oxide and carbide post-test	**H** - Argon atmosphere, Temp controlled to ±15 K	**I** - Did not report measurement uncertainty, temperature uncertainty of 2 K.	**I** - No raw data provided. Reports measured density and a correlation.

Assess quality of experimental studies

Careful selection of trustworthy datasets



Compare all duplicate datasets

Ab-Initio Molecular Dynamic (AIMD)

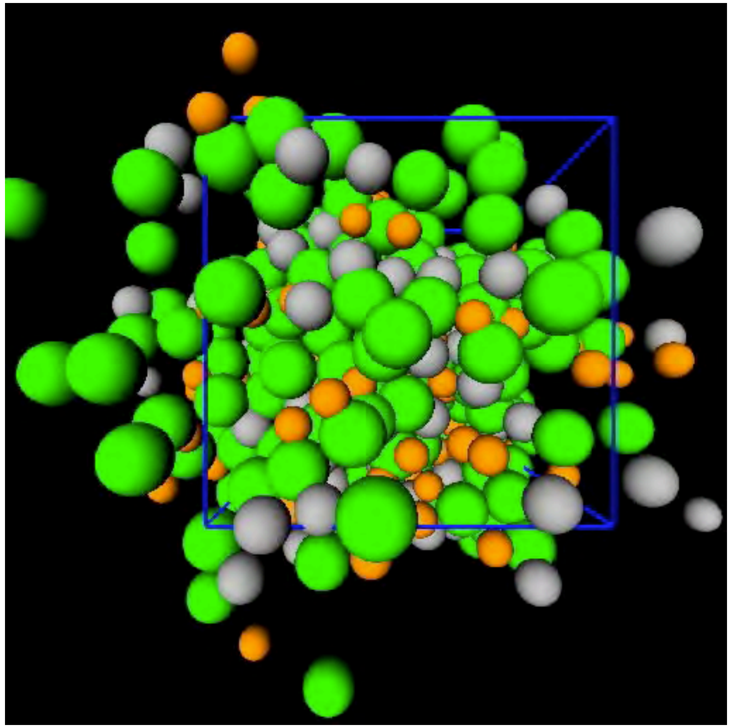
Molecular dynamics in a nutshell

$v = \int dt\, a$ velocity

position $r = \int dt\, v$

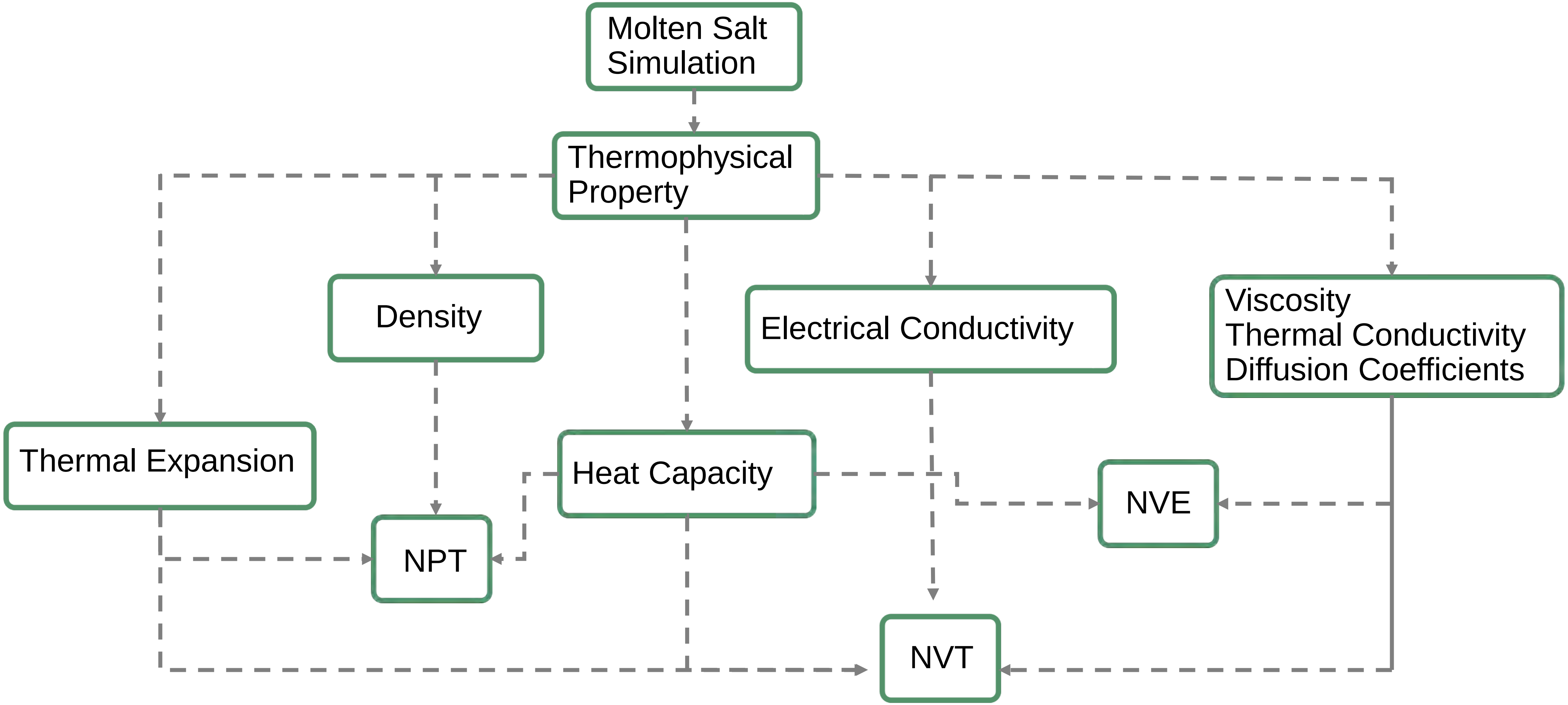
force $F = -\frac{dU(r)}{dr}$

$a = \frac{F}{m}$ acceleration



AIMD in use: potential energy surface U(r) calculated with density functional theory (**DFT**)

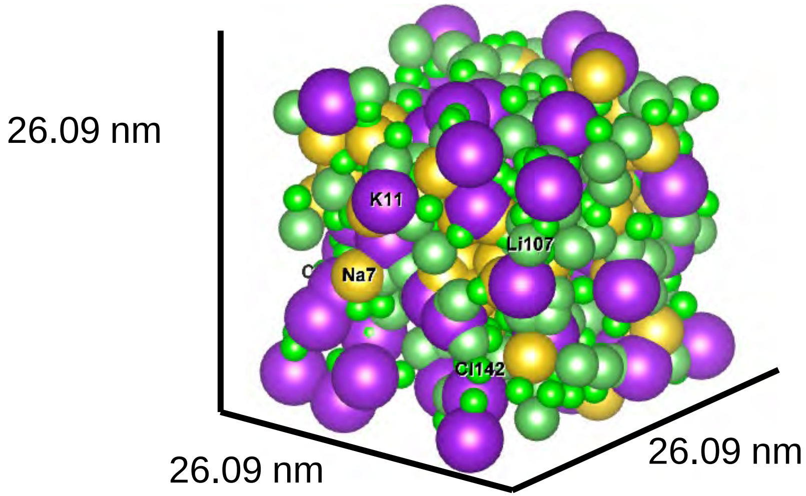
Thermophysical Properties from AIMD



Overview of Chloride Salt Systems

Mix #	System
1	NaCl-KCl (0.75-0.25)
2	NaCl-KCl (0.50-0.50)
3	NaCl-KCl (0.25-0.75)
4	NaCl-LiCl (0.75-0.25)
5	NaCl-LiCl (0.50-0.50)
6	NaCl-LiCl (0.25-0.75)
7	KCl-LiCl (0.75-0.25)
8	KCl-LiCl (0.50-0.50)
9	KCl-LiCl (0.25-0.75)
10	NaCl-KCl-LiCl (eutectic)
11	NaCl-KCl-LiCl (0.333-0.333-0.334)
12	NaCl-KCl-LiCl (0.20-0.40-0.40)
13	NaCl-KCl-LiCl (0.20-0.20-0.60)

Mix #	Density	Temperature	N_{NaCl}	N_{KCl}	N_{LiCl}	Dimensons (nm)
10	1.5249	695	21	105	154	25.697
11	1.4956	785	93	93	93	*26.092*
12	1.4930	785	56	112	112	26.125
13	1.4972	785	56	56	168	25.130



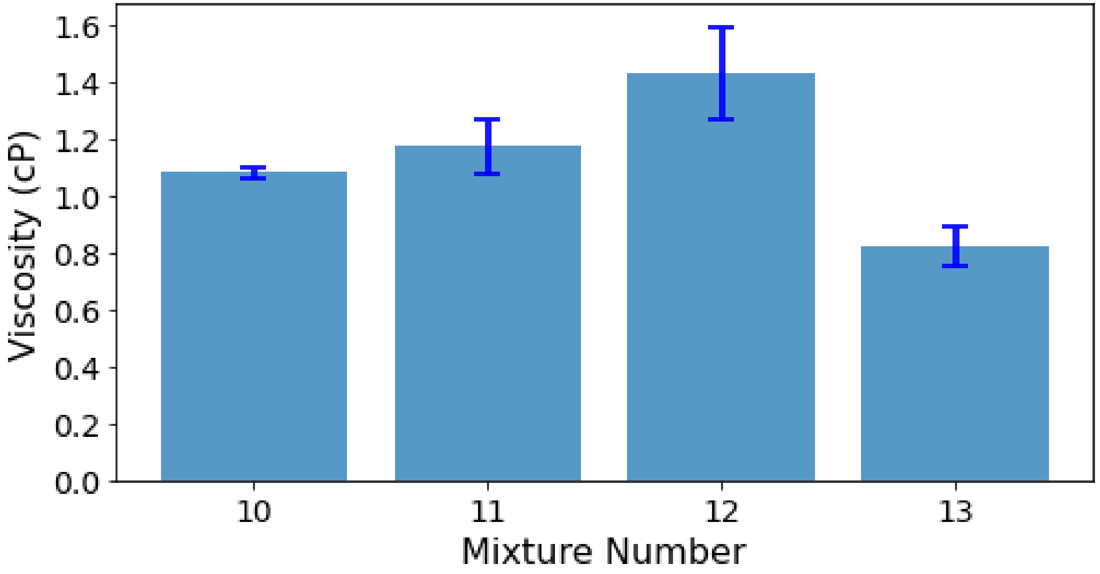
Status of the Chloride Mixtures

Completed

Running

Incomplete

Mix #	System	Computational Temp (K)	Computational Viscosity(cP)	Experimental Temp (K)	Experimental Viscoisty (cP)
10	NaCl-KCl-LiCl (0.075-0.375-0.55)	968	1.08±0.02 (50 ps)		
11	NaCl-KCl-LiCl (0.333-0.333-0.334)	1058	1.17±0.1 (34 ps)	1077K	1.28
12	NaCl-KCl-LiCl (0.20-0.40-0.40)	1058	1.42±0.16 (27 ps)		
13	NaCl-KCl-LiCl (0.20-0.20-0.60)	1058	0.82 ±0.07 (38 ps)	~1058K	1.06



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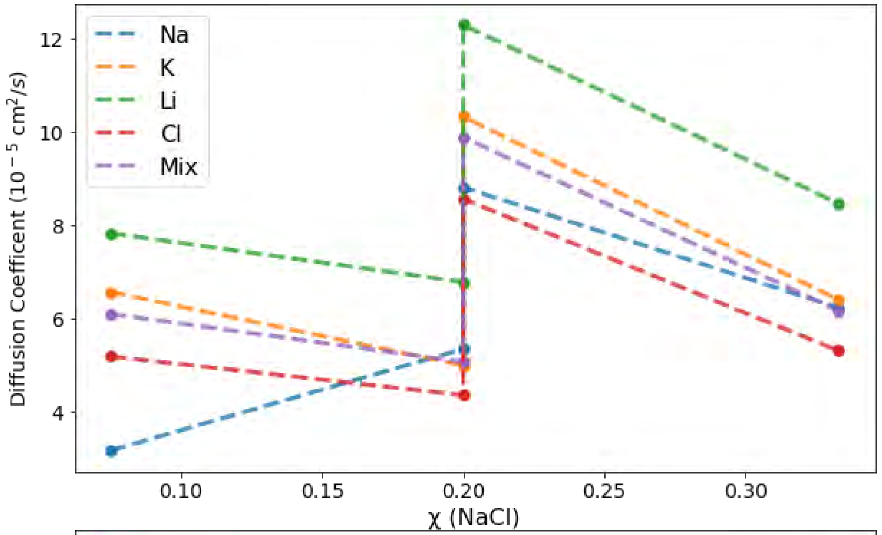
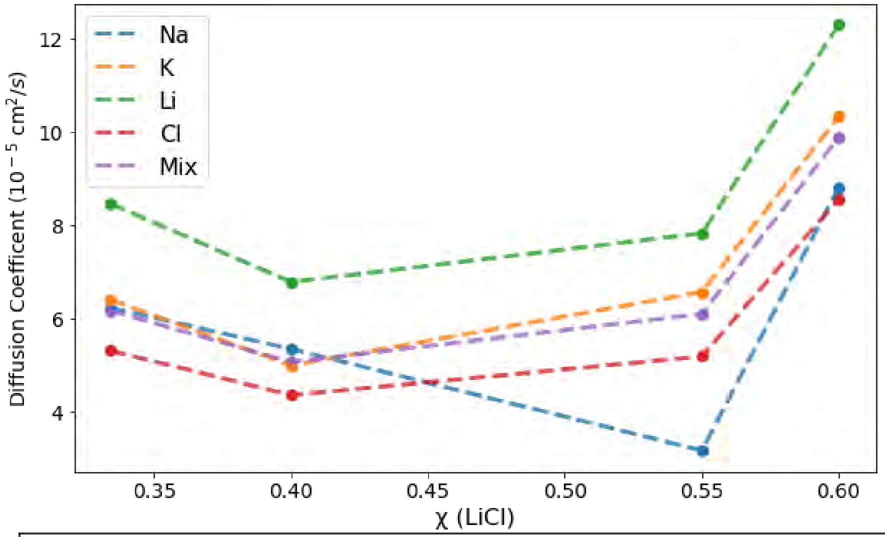
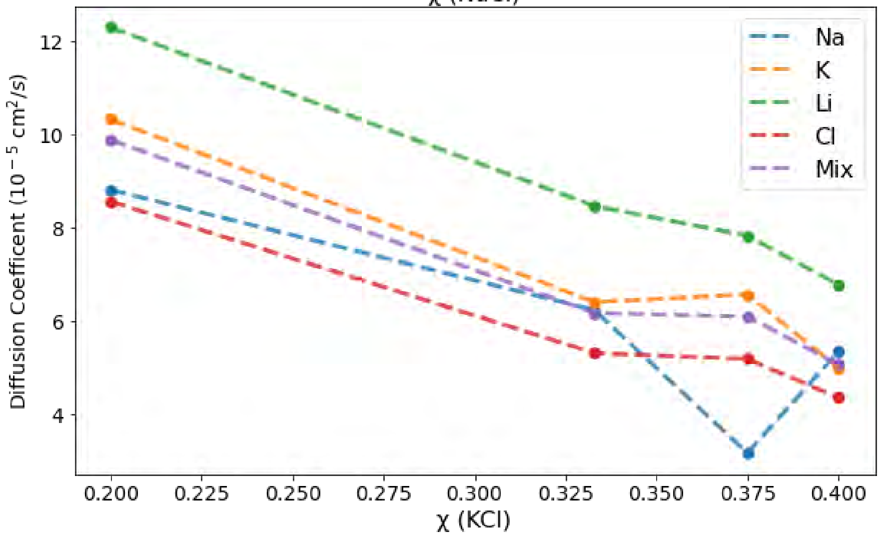
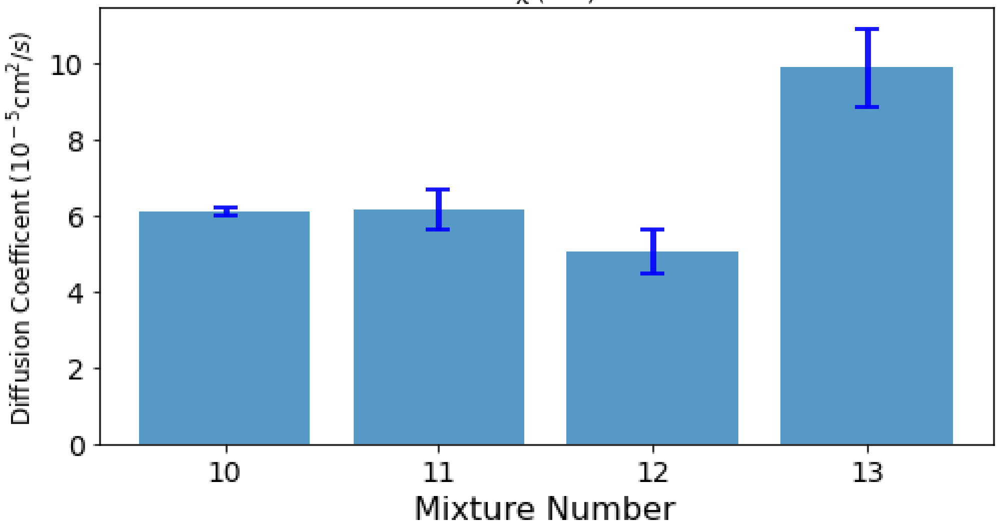
Diffusion Coefficients









Next Steps: Increased Scale of Simulation

Molecular dynamics in a nutshell

$$v = \int dt\, a$$

velocity

$$a = \frac{F}{m}$$

acceleration

position

$$r = \int dt\, v$$

force

$$F = -\frac{dU(r)}{dr}$$

AIMD in use: potential energy surface U(r) calculated with density functional theory (**DFT**)

Fit interatomic potentials using AIMD

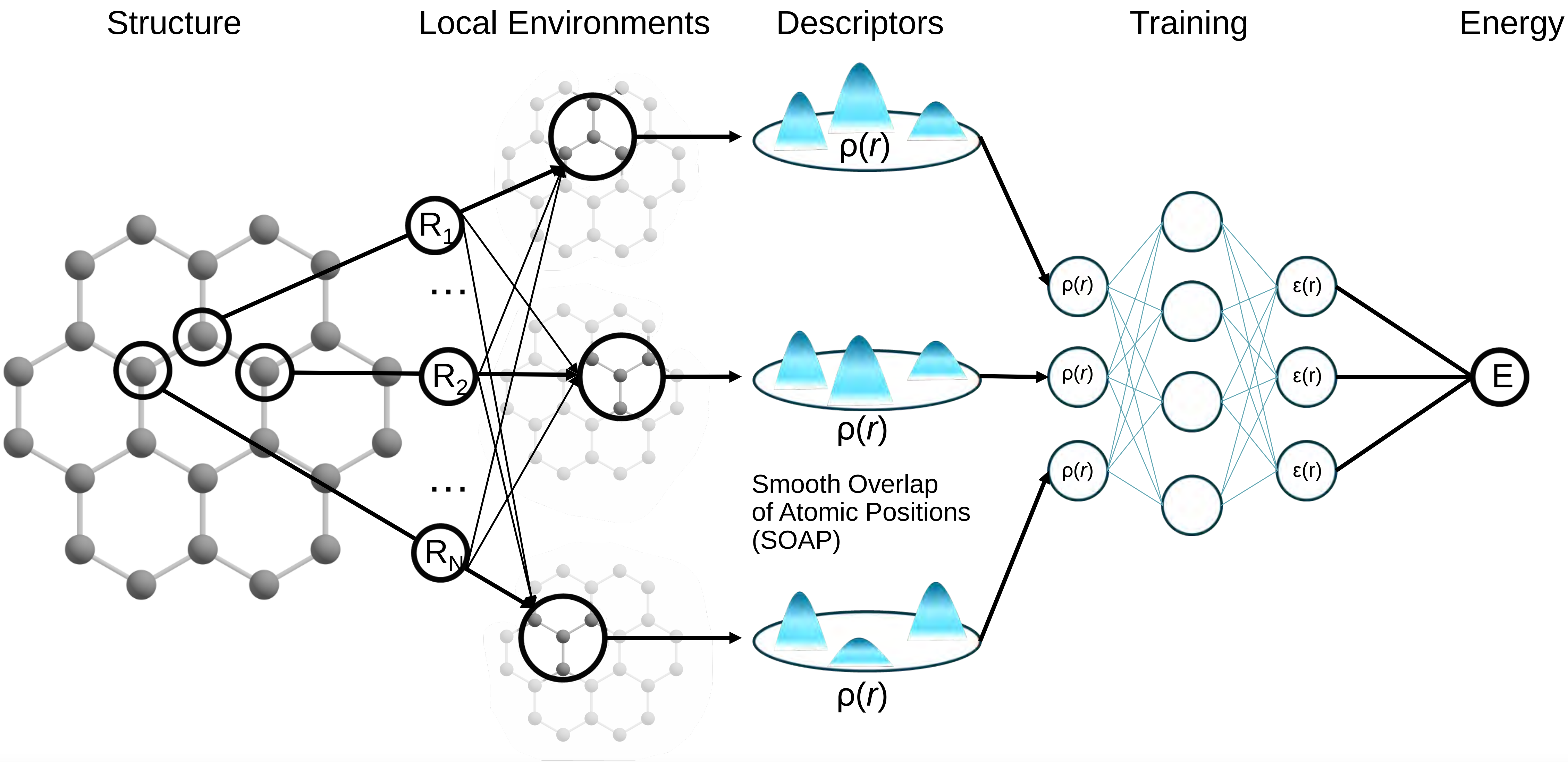
Simulations on a larger scale using classical force fields

Machine learning (ML) interatomic potentials

Simulations on a larger scale with near AIMD accuracy

Nguyen, M.T., Glezakou, V.A. MSR Campaign Review Meeting, April 2022

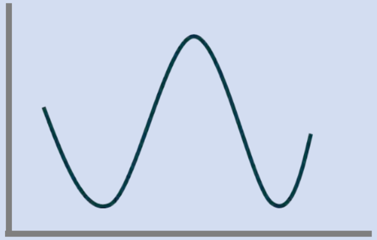
Machine Learned Interatomic Potentials



Active Learning Cycle

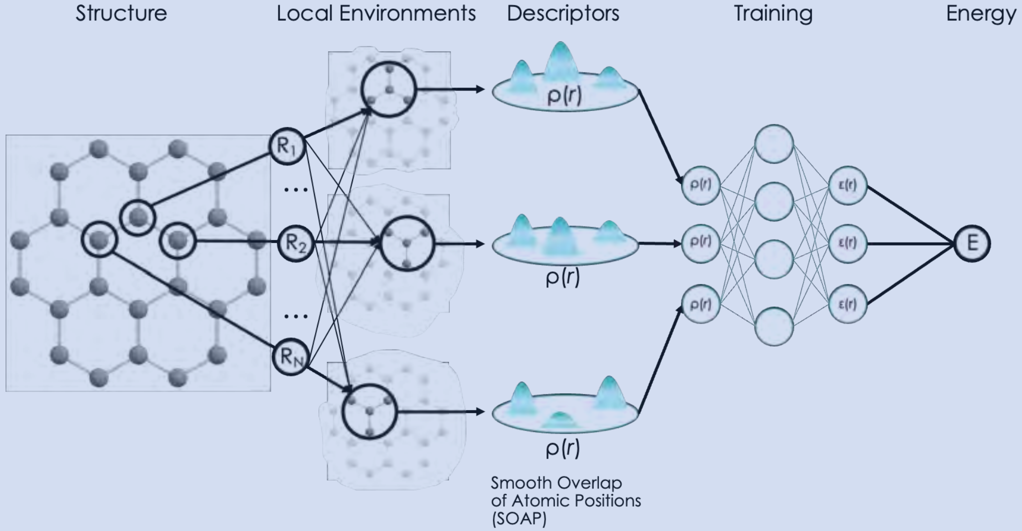
AIMD Simulations

- Molecular Trajectories
- Properties
  - Forces
  - Velocity
  - Acceleration

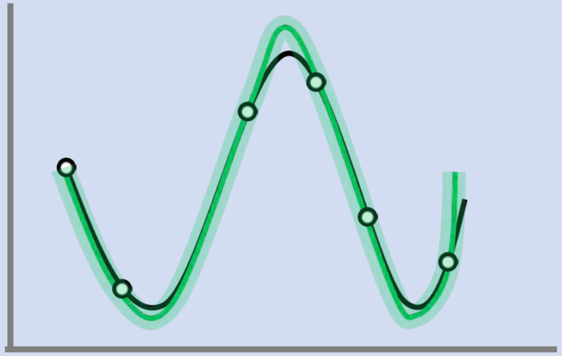


Potential Energy Surface

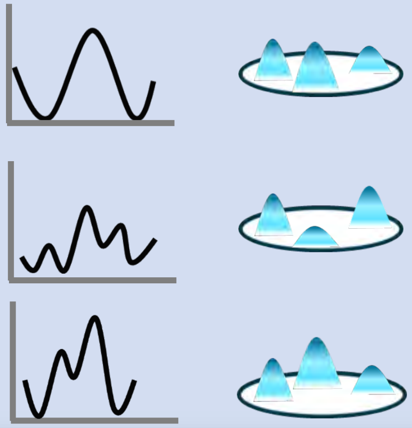
Machine Learning



Fitting Interatomic Potential



Potential Energy Surface



Active Learning

Iteratively introduce additional training data

Summary

- ORNL is working on thermophysical property characterization of molten salts through experiments and AIMD
- Our main focus is thermal conductivity and viscosity, because there are large gaps in MSTDB-TP for those properties
- We have carefully honed our experimental techniques to be more accurate, by improving our calibration methods and rigorously testing against well characterized salts
- We have established capabilities with alkali halides, and future work this FY will include actinide halides

Thank you

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