Molten Salt Reactor Chemistry

Properties, database development, and modeling

Jake McMurray
Oak Ridge National Laboratory
N. Dianne Bull Ezell
Oak Ridge National Laboratory
David Andersson
Los Alamos National Laboratory
Chao Jiang
Idaho National Laboratory
Ted Besmann
University of South Carolina

U.S. DEPARTMENT OF ENERGY

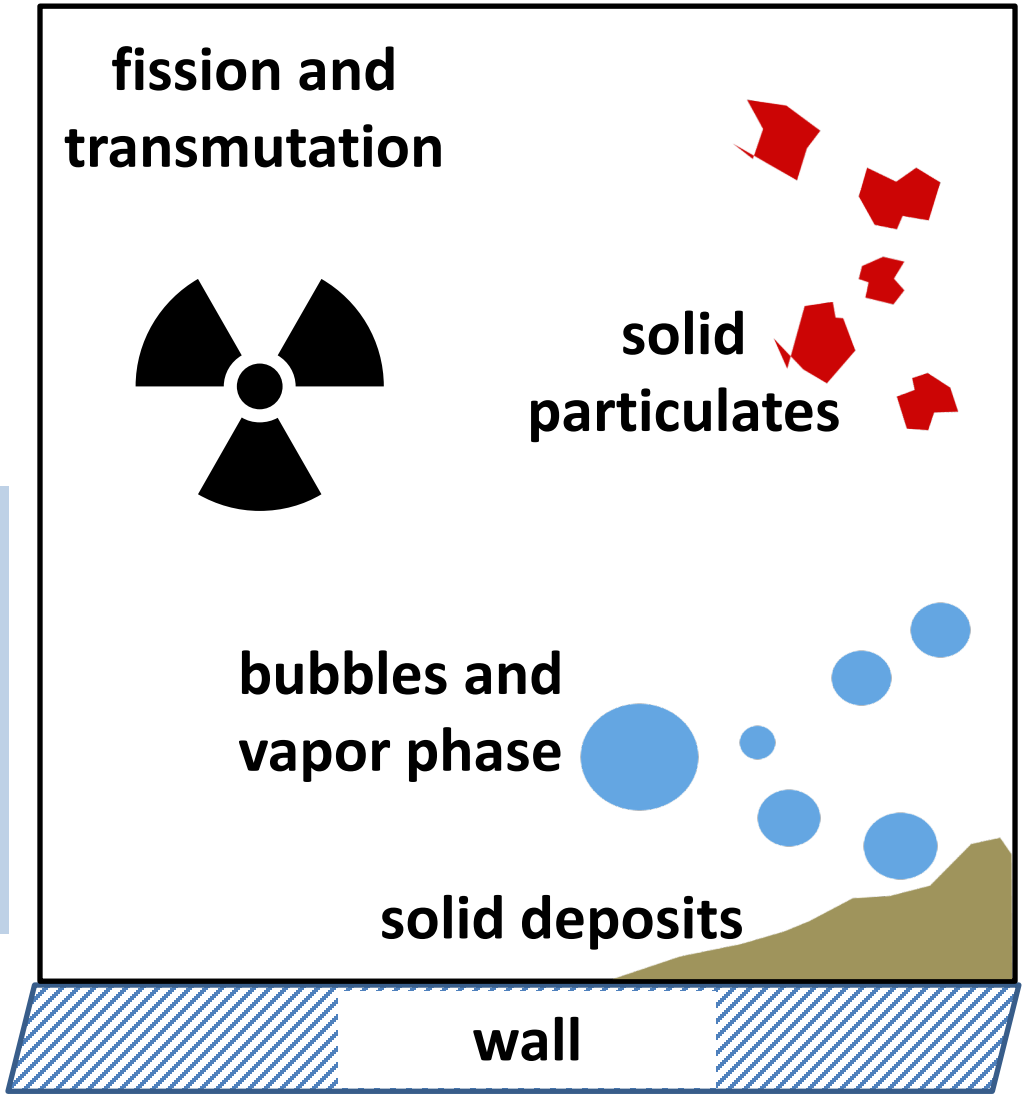
Molten Salt Reactor Workshop
October 2020

Mass accountancy modeling for MSRs is the objective

MSR Campaign

- Property measurements
  - Phase equilibria
  - Vapor pressures
  - Specific heat
  - Thermal conductivity
  - Viscosity
  - Density
- Physical models to describe
  - Nucleation of bubbles and particulates
  - Size distribution
  - Particle growth
  - Deposition
  - Vaporization
  - Leaching and erosion

Require thermodynamic inputs



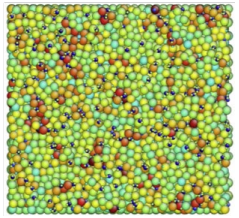
NEAMS

- Development of multi-physics, multi-scale tools for advanced modeling and simulation of these phenomena
- Computation of thermophysical properties
  - Thermal conductivity
  - Specific heat
  - Viscosity
  - Density
- Molten Salt Thermal Properties Database (MSTDB) development

NEAMS *Yellowjacket Corrosion Suite* multi-scale modeling tools

Length scale

Atomistic

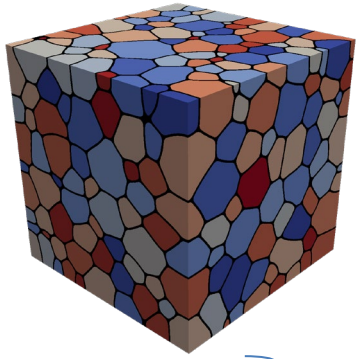


ab-initio and classical Molecular dynamics

Density
Viscosity
Thermal conductivity
Specific heat
Thermodynamic values

Meso – Yellowjacket

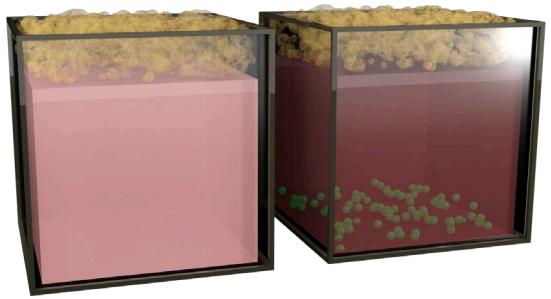
Phase Field Code



Diffusion kinetics
Reaction rates
Microstructure

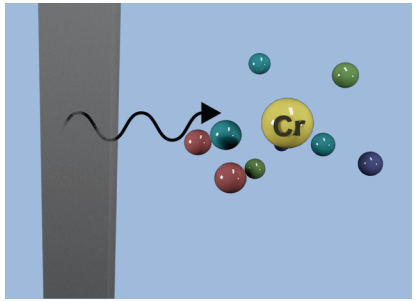
materials in contact with salt

Thermodynamic Gibbs Energy Minimizer and the Thermodynamic Database (MSTDB)

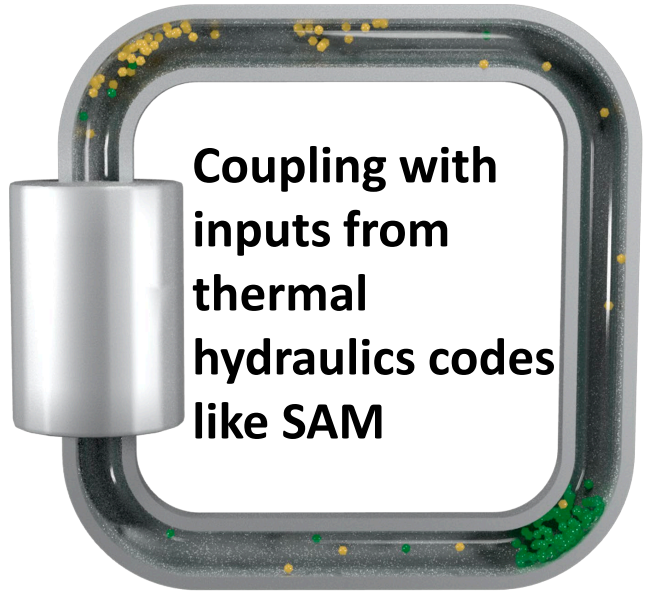


Chemical potentials/activities
Vapor pressures
Phase equilibria
Specific heat
Reaction energies

Engineering Mole



Finite element mass transport code for leaching and deposition



MOOSE

Multiphysics Object-Oriented Simulation Environment

Identification of systems to study based on industry input

System
FLiNaK
LiF-ThF4
FLiNaK - I2
FLiNak - Cs
UCl3 -UCl4
NaCl-MgCl2-ZrCl4
NaCl-KCl-ZrCl4
NaCl-MgCl2-AlCl3
NaCl-KCl-AlCl3
NaCl-ThCl4-6 mole% PuCl3
UF4 – UF3
LiF-BeF-UF4
LiF-BeF-ThF4
LiF-BeF-UF3
NaCl-MgCl2-PuCl3
NaCl-KCl-PuCl3
NaCl-KCl-UCl3
NaCl-MgCl2-UCl3
LiF-BeF2-iFP(FLiBe) (x 2)
LiF-BeF-PuF3
NaCl-MgCl2-sFPClx (x 8)
NaCl-MgCl2-iFP (x 2)
NaCl-KCl-sFPClx (x 8)
NaCl-KCl-iFP (x 2)
LiF-BeF-sFPFx (x 8)

0.25NaCl – 0.75MgCl2
0.50NaCl – 0.50MgCl2
0.75NaCl – 0.25MgCl2

0.25NaCl – 0.75ZrCl4
0.50NaCl – 0.50ZrCl4
0.75NaCl – 0.25ZrCl4

0.25MgCl2– 0.75ZrCl4
0.50MgCl2 – 0.50ZrCl4
0.75MgCl2 – 0.25ZrCl4

Formulated a loose framework for developing test matrices to generate property data

Goals

- Define a systematic approach
- Makes the problem more tractable
- Generic – to be sensitive to proprietary compositions
- Allows us to build property models based on fundamental pseudo-binary subsystems, combine, and extrapolate into multi-component space

Measurement roadmap report to be issue in FY21

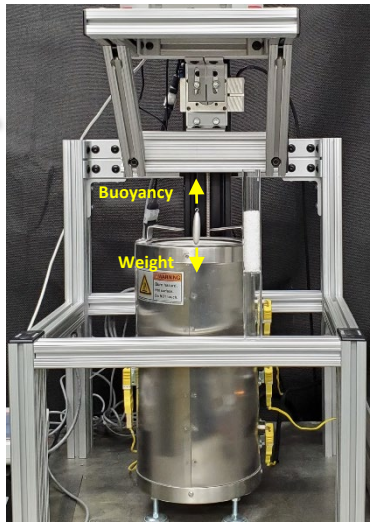
MSR and NEAMS effort with:

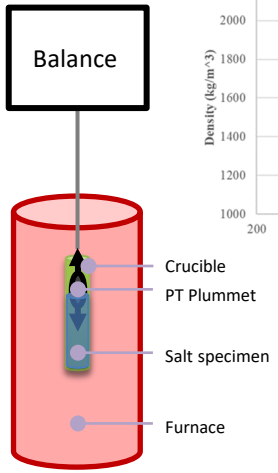
- ANL
- INL
- PNNL
- LANL
- University of S. Carolina (NEUP)
- Molten Salt Thermal Properties Working Group
  - Raluca Scarlat (UC-Berkeley) leading a Round Robin

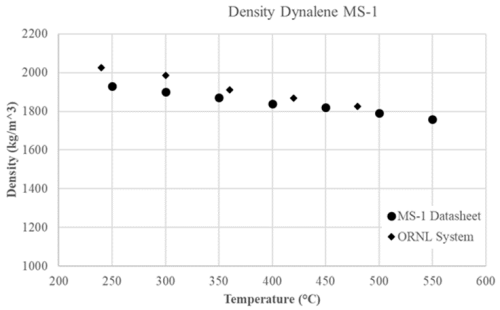
Thermophysical and thermochemical measurements

Density

Archimedes Bob Density Measurement Apparatus

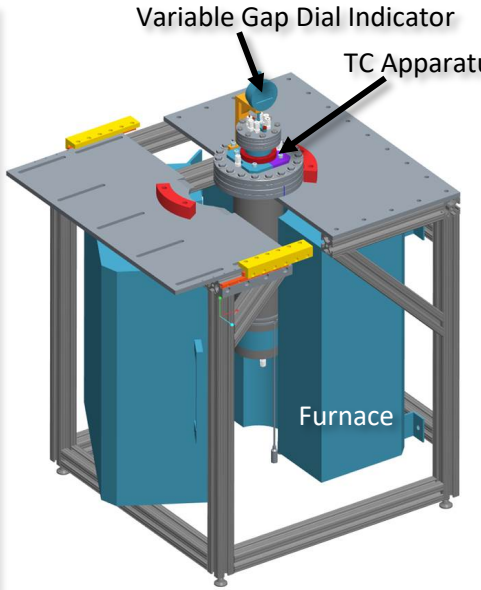


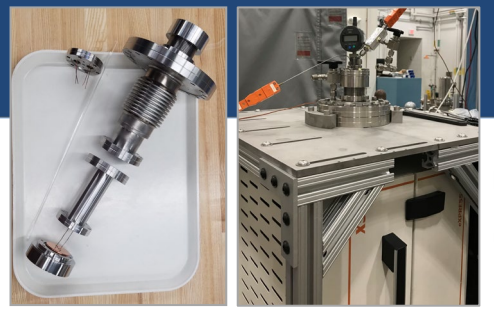




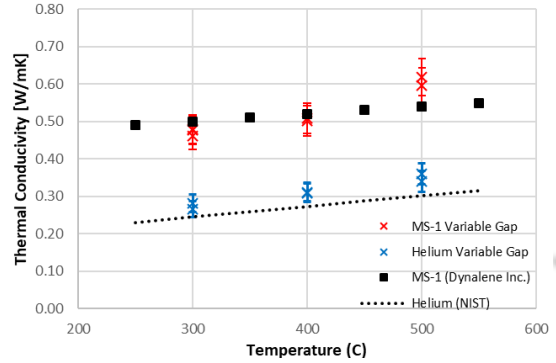
Alternate methods:
- Optical dilatometry
- X-ray dilatometry

Thermal Conductivity





$$\text{Thermal Resistance} = \frac{\text{Change in temperature across gap}}{\text{heat flux}}$$



Viscosity

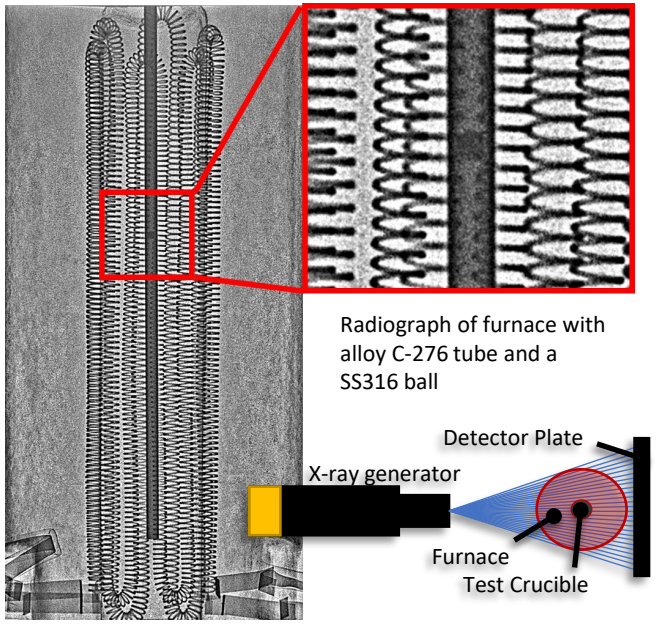
Equivalent to falling-ball optical measurements

Ratio of the differences between densities

$$\frac{\eta_{salt}}{\eta_{H_2O}} = \frac{\rho_{ball}-\rho_{salt}}{\rho_{ball}-\rho_{H_2O}} \frac{V_{salt}}{V_{H_2O}}$$

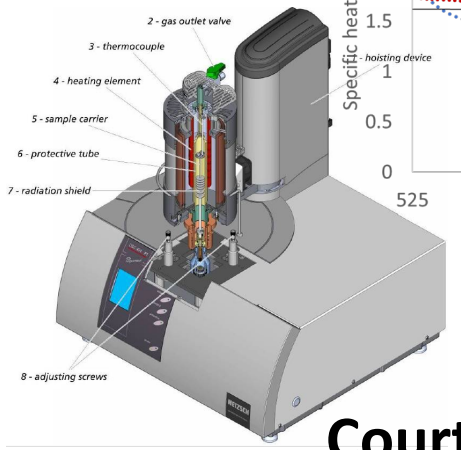
Ratio of viscosities

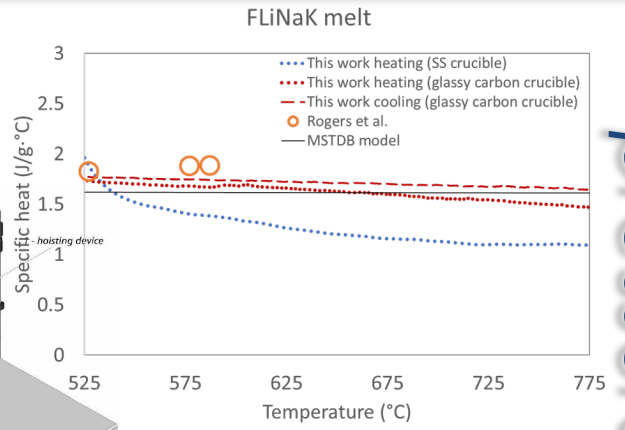
Ratio of terminal velocities



Radiograph of furnace with alloy C-276 tube and a SS316 ball

Calorimetry and vapor pressures



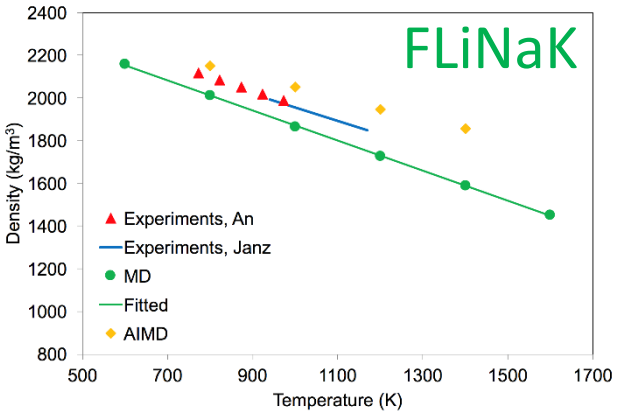


Courtesy of Dianne Ezell and team

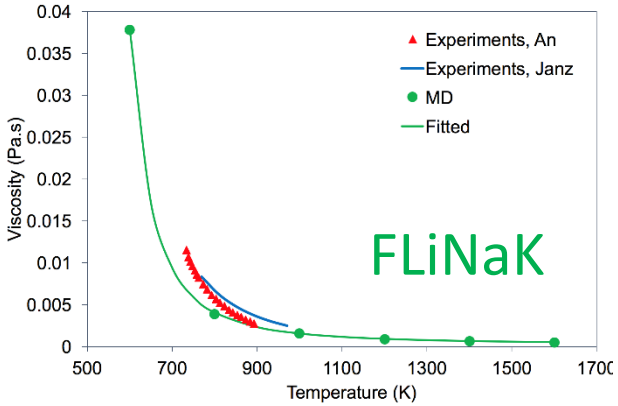
Computationally derived properties of non-actinide bearing molten salts

Molecular dynamics calculations complements of Chao Jiang, Idaho National Laboratory

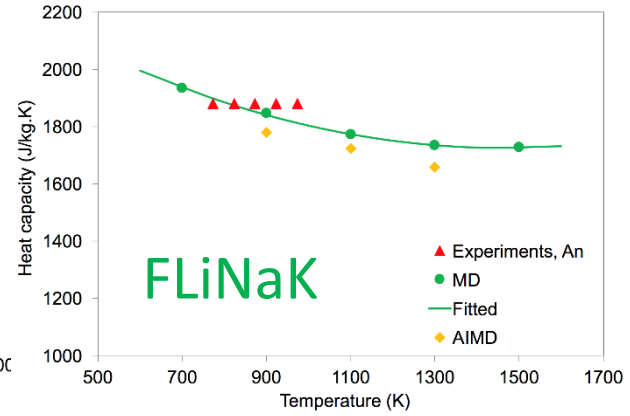
Density



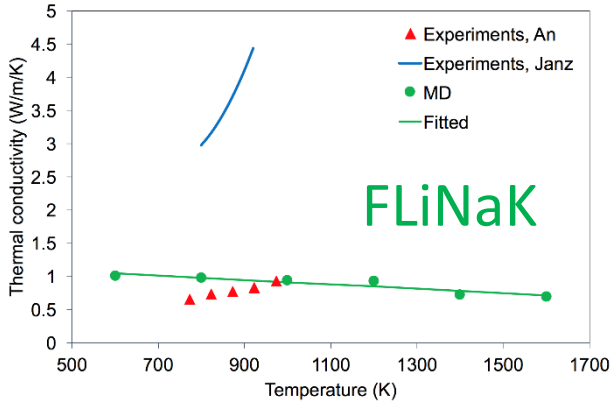
Viscosity

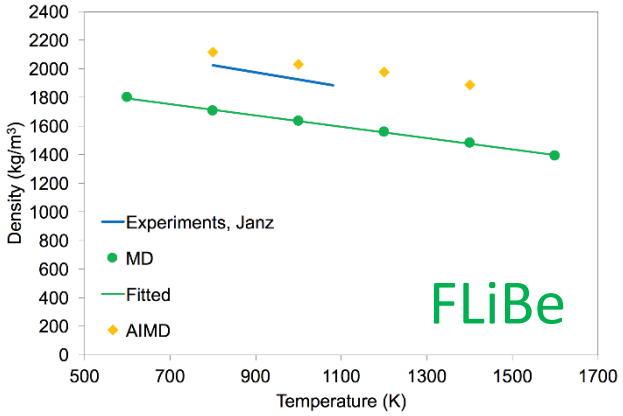


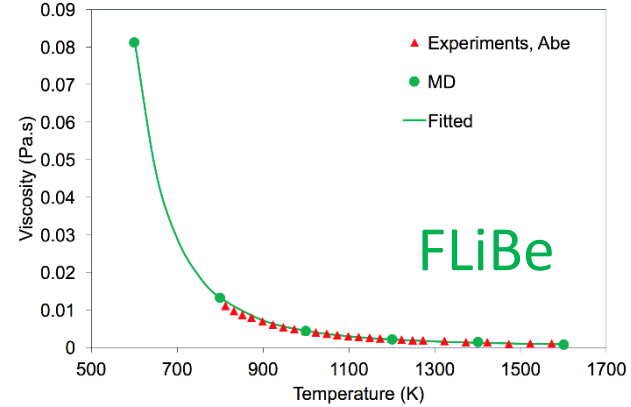
Cp

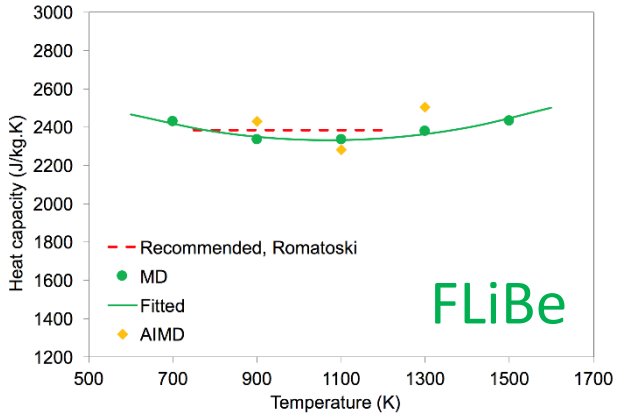


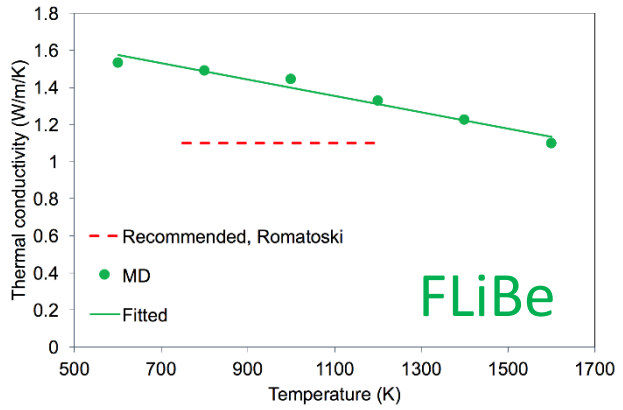
Thermal conductivity









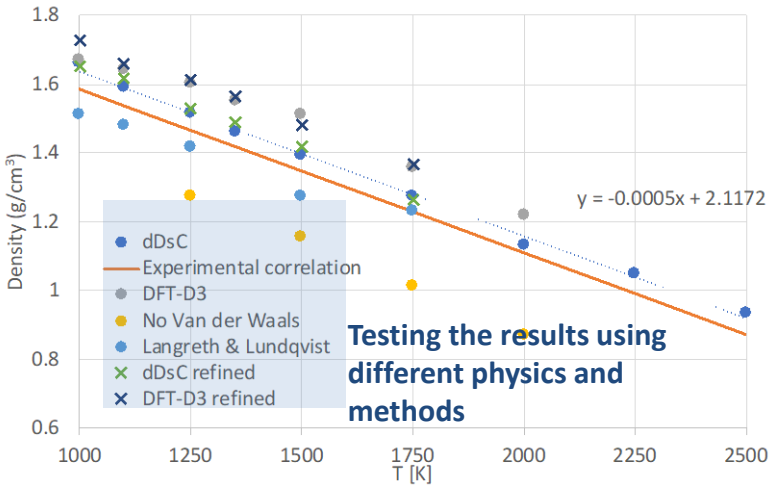


DFT simulations for actinide containing chloride salts

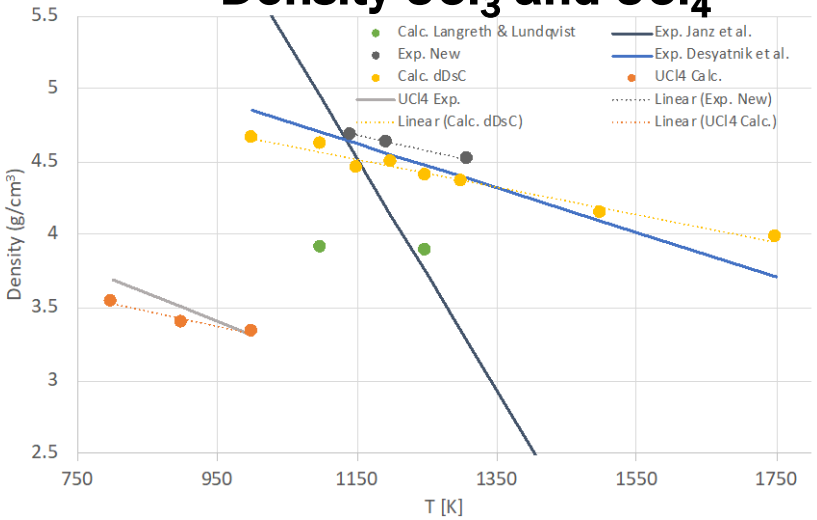
Calculations complements of David Andersson, Los Alamos National Laboratory

1. Initiated benchmarking and refinement of methodology to simulate chloride fuel salts from DFT based Ab Initio Molecular Dynamics (AIMD) simulations
2. AIMD preferred over classical potentials due to ability to treat complex chemistry, but some properties will be computationally too expensive to simulate (e.g. viscosity and thermal conductivity) and potentials can be used as a substitute for those cases.
3. Results for density indicate accurate predictions using the carefully selected methodology (van der Waals, DFT+U, spin-orbit, etc).

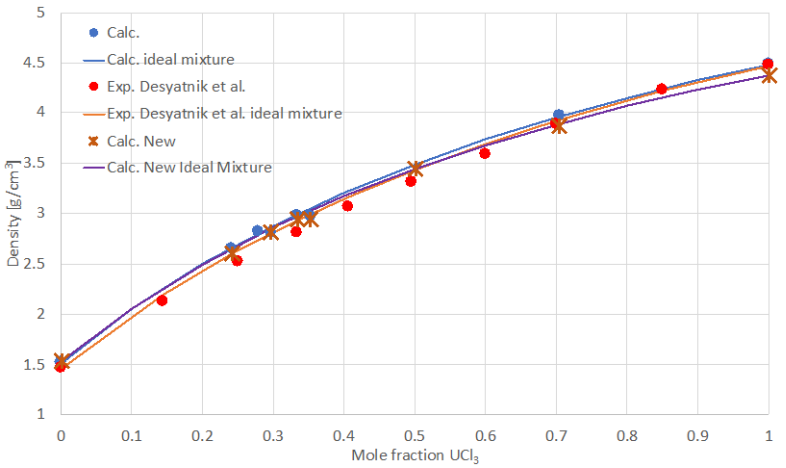
Density NaCl



Density UCl_3 and UCl_4



Density UCl_3-NaCl

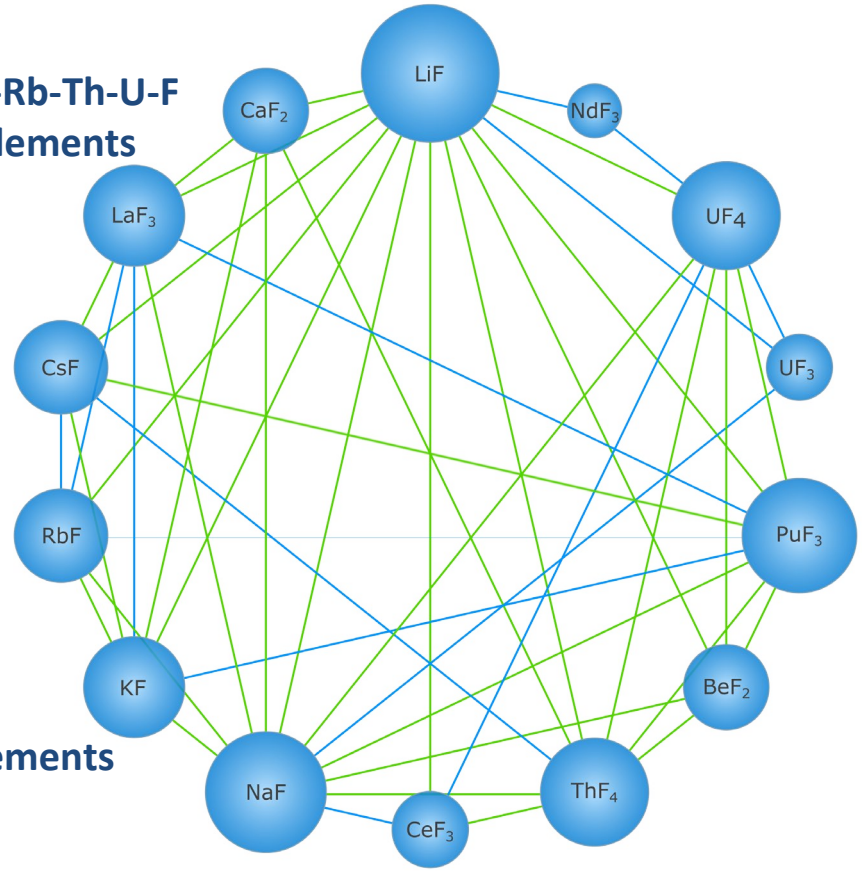


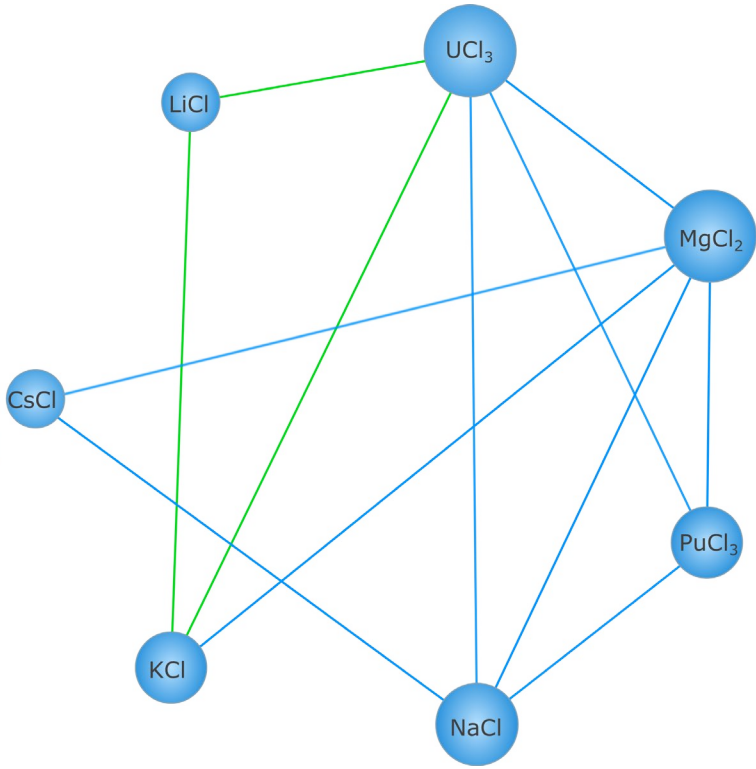
Thermodynamic database (MSTDB-tc) status

DOE is developing *Thermodynamic Database* (*MSTDB-tc*) with work led by ORNL (NEAMS and MSR campaign) and U*of*SC (NEUP)

Fluoride-based System

- Be-Ca-Ce-Cs-K-La-Li-Mg-Na-Ni-Nd-Pu-Rb-Th-U-F
- 108 stoichiometric compounds and elements
- 45 pseudo-binary subsystems
- 26 pseudo-ternary subsystems
- Higher order systems
  1. LiF-NaF-RbF-LaF_3
  2. LiF-NaF-CaF_2-LaF_3
  3. LiF-NaF-BeF_2-ThF_4-UF_4-PuF_3
  4. NaCl-$MgCl_2$-UCl_3-$PuCl_3$
- 22 solid solutions





Chloride-based System

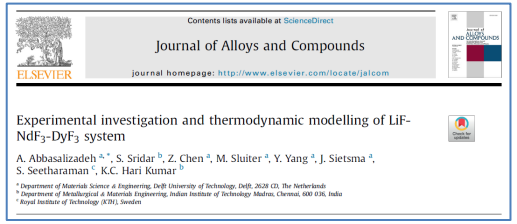
- Cs-K-Li-Mg-Na-Pu-U-Cl
- 37 stoichiometric compounds and elements
- 13 pseudo-binary subsystems
- 1 pseudo-ternary subsystem
- Higher order system: NaCl-$MgCl_2$-UCl_3-$PuCl_3$
- 3 solid solutions
- Models for excess K and Mg in solution

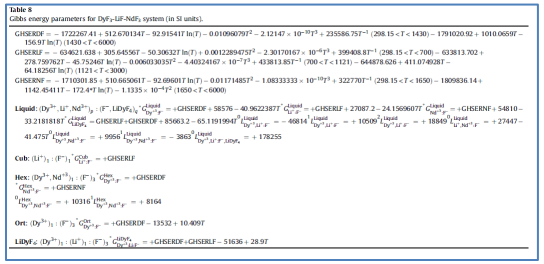
All MSTDB-tc values traceable to original sources

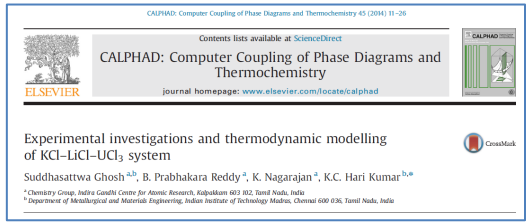
Courtesy of Ted Besmann and team

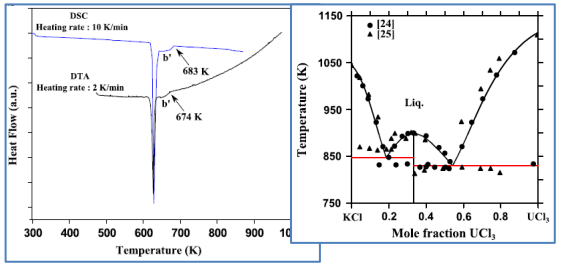
Information linked within the user database

- Pure substance, single cation phase values from tabulated sources, e.g., NIST, SGTE via FactSage™
- Melt, solid solution, or complex compound models and values/parameters are
  - Obtained as is from published papers/reports
  - Determined in assessments/reassessments using values from published papers/reports
  - Computed for compounds obtained using *ab initio* modeling & used in assessments
  - Obtained using measurements for assessments from original experimental efforts



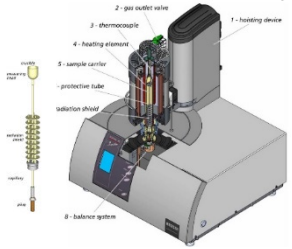


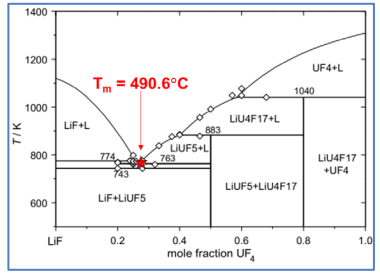


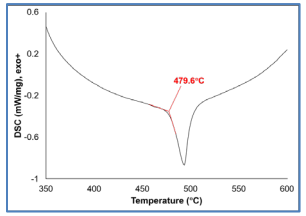


DFT

	H°0K (eV)	H°0K (J/mol)
K_2UF_6	-3.643	-3163464.3
K_3UF_7	-3.523	-3739095.7
$K_7U_6F_{31}$	-	
KU_2F_9	-3.858	-4466884.5







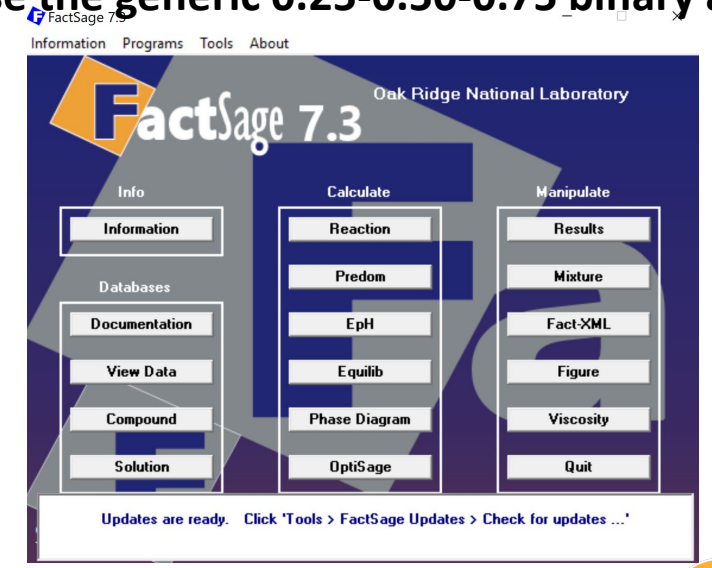
General Atomics SmartState Center for Transformational Nuclear Technologies

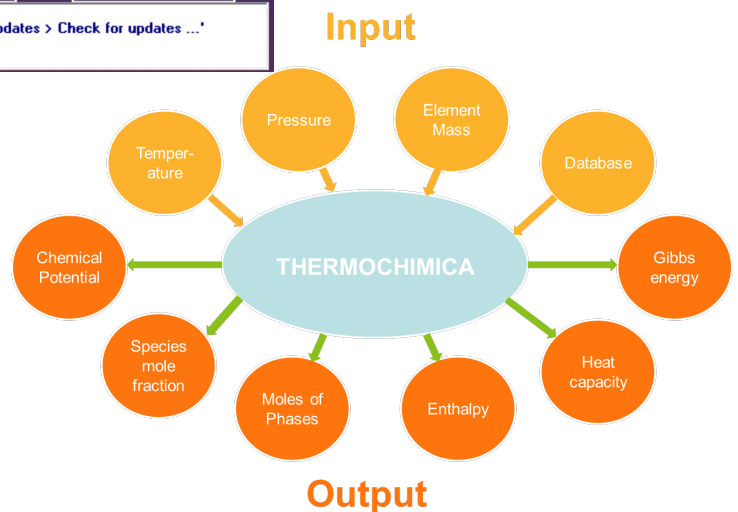
University of South Carolina

Point calculations for user defined compositions using MSTDB-tc

- This is not a database for specific salt compositions, e.g. a NIST thermophysical properties of fluid systems database
- Gibbs energy models for every phase in a system that represents the entire multi-dimensional temp.-comp. space
- Specific compositions were used as inputs for optimizing adjustable parameters of the models – all come from the open literature
- Moving forward to further develop the database, we plan to use the generic 0.25-0.50-0.75 binary approach

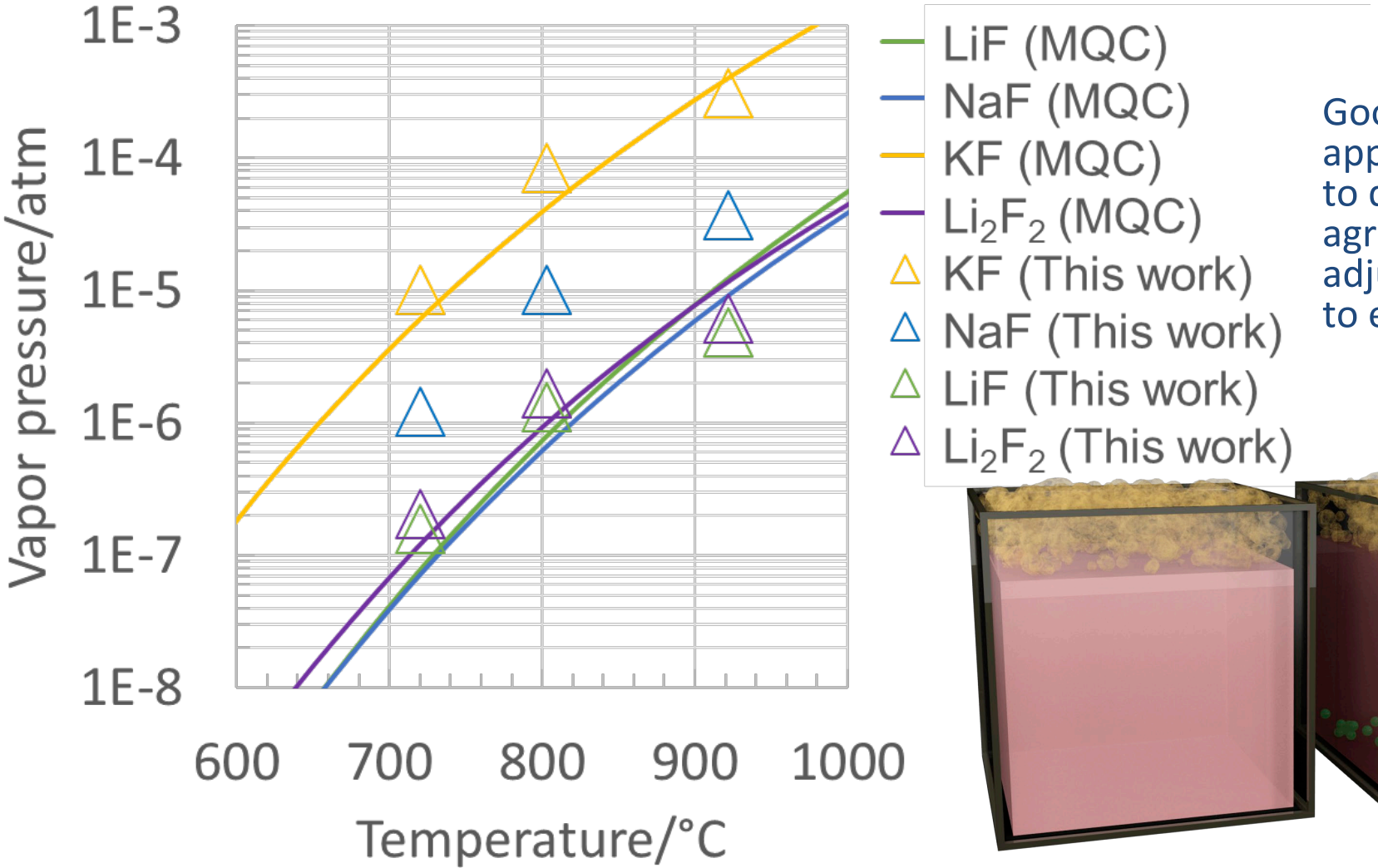
1. Requires a Gibbs Energy Minimizer a.k.a thermodynamic solver
2. Most are commercial – Thermocalc, Pandat, FactSage, etc.
3. FactSage is only commercial software that will handle the Modified Quasi-Chemical (MQC) model used to represent the molten salt
4. Thermochimica developed by Markus Piro at Ontario Tech is also handles the MQC, is open source, specifically developed for coupling to Multiphysics codes
5. PyCalphad is also open source, developed by Zi-Kui Liu at Penn State…working wit Markus Piro to implement the MQC
6. Continued solver (Yellowjacket GEM and Thermochimica) development funded through NEAMS





Output using MSTDB-tc compared to vapor pressures measured at ORNL

Measurements of vapor pressures over FLiNaK are in good agreement with the computed MSTDB Modified Quasi-chemical (MQC) values



Good illustration how the CALPHAD approach works. These data were not used to develop the models yet there is fair agreement. Minor optimization of adjustable parameters can improve the fit to experiments

Chemical potentials/activities
Vapor pressures
Phase equilibria
Specific heat
Reaction energies

Thermal properties database (MSTDB-tp) status

Salt	Density	Viscosity	Thermal conductivity	Specific heat	Salt	Density	Viscosity	Thermal conductivity	Specific heat
LiF	X	X	X	X	KCl	X	X	X	X
NaF	X	X	X	X	$MgCl_2$	X	X	X	X
KF	X	X	X	X	$CaCl_2$	X	X	X	X
MgF_2	X		X	X	$SrCl_2$	X	X	X	X
CaF_2	X		X	X	$BeCl_2$	X			X
SrF_2	X		X	X	UCl_3	X			X
BeF_2	X	X	X	X	$NpCl_3$				
UF_3				X	$PuCl_3$				X
UF_4	X	X		X	$LaCl_3$	X	X		X
NpF_3					$NdCl_3$	X			X
PuF_3				X	$GdCl_3$	X			X
LaF_3	X			X	LiCl-KCl	X	X		X
NdF_3				X	LiF-NaF-KF	X	X	X	X
GdF_3				X	$LiF-BeF_2$	X	X	X	X
LiCl	X	X	X	X	$KCl – MgCl_2$	X	X	X	
NaCl	X	X	X	X	$LiF-NaF-BeF_2$	X	X	X	X

Continued thermal properties database (MSTDB-tp) status

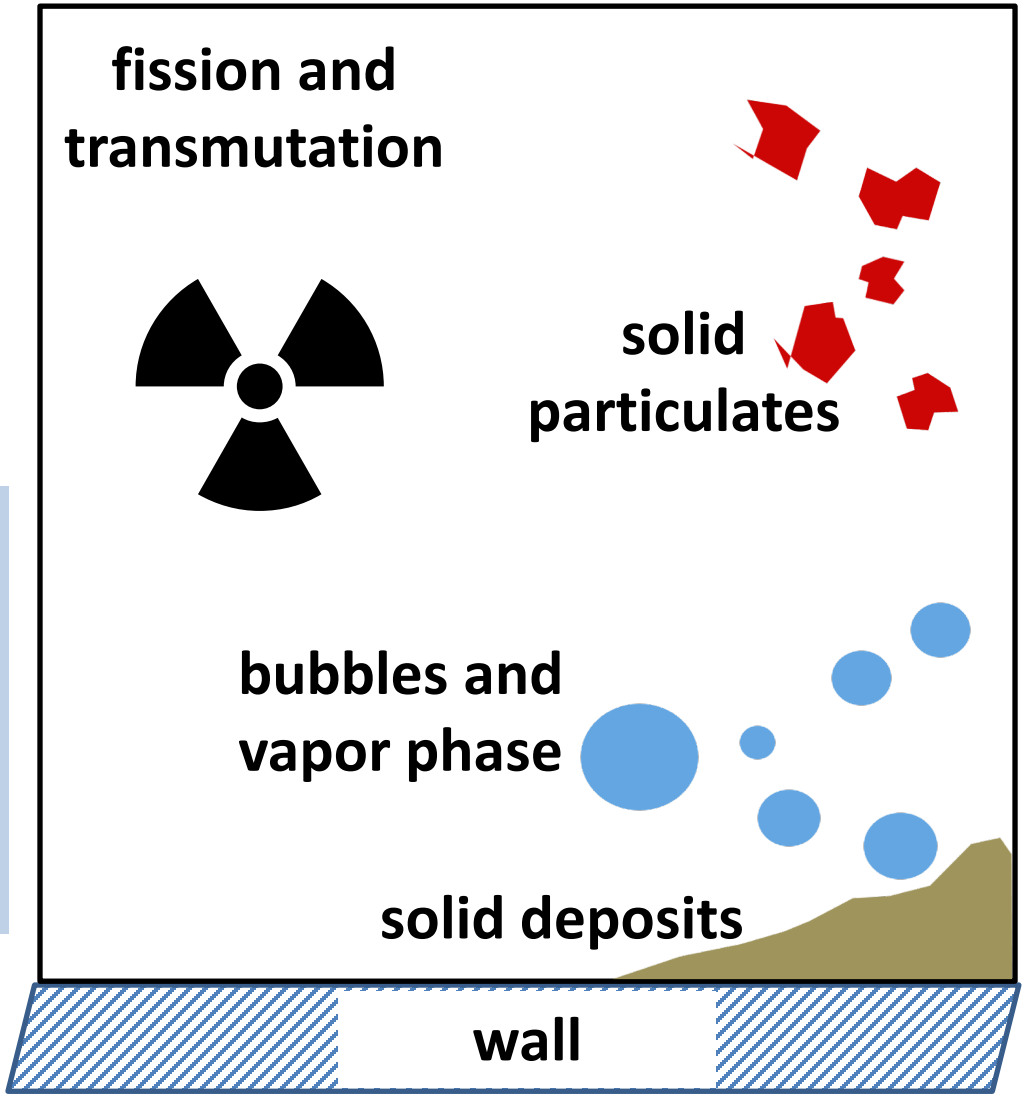
Salt	Density	Viscosity	Thermal conductivity	Specific heat	Salt	Density	Viscosity	Thermal conductivity	Specific heat
$NaF-KF-UF_4$		X			$NaF-KF-BeF_2$		X		
$NaF-LiF-KF-UF_4$		X			$RbF-ZrF_4-UF_4$		X		
$NaF-KF-ZrF_4$		X			$NaF-LiF-BeF_2$		X		
$NaF-ZrF_4-UF_4$		X			$NaF-LiF-BeF_2$		X		
$NaF-ZrF_4$		X			$NaF-LiF-BeF_2-UF_4$		X		
$NaF-BeF_2$		X			NaF-LiF		X		
$NaF-UF_4$		X			LiF-RbF		X		
$NaF-ZrF_4-UF_4$		X			$NaF-LiF-KF-UF_4$		X		
$NaF-ZrF_4-UF_4$		X			$LiF-BeF_2-UF_4-ThF_4$		X		
$LiF-BeF_2$		X			$LiF-BeF_2-ThF_4$	X	X		
$NaF-LiF-BeF_2$		X			$LiF-BeF_2-ThF_4$	X			
$NaF-LiF-ZrF_4$		X			$LiF-BeF_2-ThF_4$	X			
$NaF-LiF-ZrF_4-UF_4$		X			$LiF-BeF_2-ZrF_4$	X			
$RbF-ZrF_4-UF_4$		X			$LiF-BeF_2-ZrF_4-ThF_4$	X			
$NaF-LiF-BeF_2$		X			$LiF-BeF_2-ThF_4$		X		

Summary

MSR Campaign

- Property measurements
  - Phase equilibria
  - Vapor pressures
  - Specific heat
  - Thermal conductivity
  - Viscosity
  - Density
- Physical models to describe
  - Nucleation of bubbles and particulates
  - Size distribution
  - Particle growth
  - Deposition
  - Vaporization
  - Leaching and erosion

Require thermodynamic inputs



NEAMS

- Development of multi-physics, multi-scale tools for advanced modeling and simulation of these phenomena
- Computation of thermophysical properties
  - Thermal conductivity
  - Specific heat
  - Viscosity
  - Density
- Molten Salt Thermal Properties Database (MSTDB) development