This project has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 661891

SAMOFAR Final Meeting

4 July 2019

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PAUL SCHERRER INSTITUT

PSI

PSI contribution

PSI contribution to SAMOFAR Project 2.1 Thermodynamic data of salts

by Sergii Nichenko

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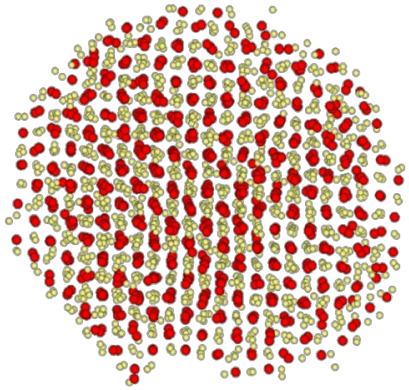
Goal

Application of Molecular Dynamic for:

- Calculation of viscosity
- Thermal conductivity calculation
- Excess properties calculations



Path

- **Difficulty**

  The idea was not working

- **Development**

  Force Field Model, Genetic algorithm

- **Optimization**

  fit FF for: LiF, KF, NaF,

  UF_4 , ThF_4 , PuF_3 almost there

- **Calculate**

  Thermal conductivity

  Viscosity

  Excess properties

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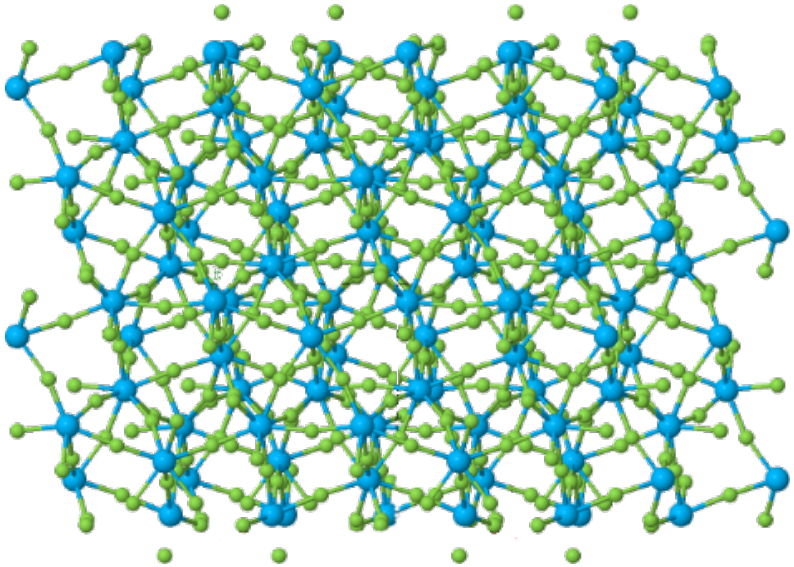
Difficulties

Initially selected Force Field model

Morse Potential $V_{ij} = D_i D_j \left(e^{-2(a_i+a_j)(r_i+r_j-r_{ij})} - 2e^{-(a_i+a_j)(r_i+r_j-r_{ij})} \right)$



Solid ThF_4 structure

Problem (BIG)

Initially selected Force Field model was not able to reproduce structural properties of complex tetrafluoride systems (ThF_4 and UF_4) – very **complex**

That's why

No molecular dynamic modelling of solid ThF_4 and UF_4 systems are **published**

Goal

Develop Force Field model capable of reproducing solid structures of complex systems

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Developed Force Field model

Total energy

$$E = \sum_i \left(F_i(\rho_i) + \frac{1}{2} \sum_{j \neq i} V_{ij}(R_{ij}) \right)$$

Idea

Include **MEAM** potential as a part of the Force Field Model to account for **multibody interactions** in the systems

Morse Potential

Pairwise interactions $V_{ij} = D_i D_j \left(e^{-2(a_i+a_j)(r_i+r_j-r_{ij})} - 2e^{-(a_i+a_j)(r_i+r_j-r_{ij})} \right)$

MEAM

Multibody contribution to the total energy

$$\rho_i^0 = \sum_{j \neq i} \rho_j^{a(0)}(R_{ij}) \qquad (\rho_i^1)^2 = \sum_\alpha \left(\sum_{j \neq i} x_{ij}^\alpha \rho_j^{a(1)}(R_{ij}) \right)^2$$

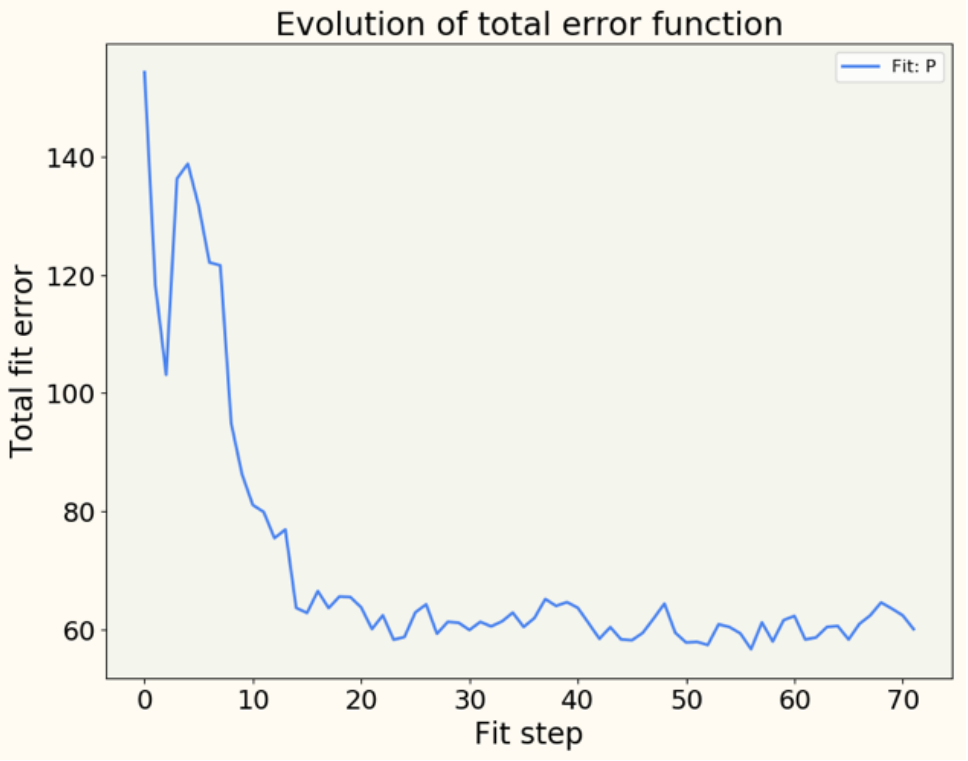
$$(\rho_i^2)^2 = \sum_{\alpha\beta} \left(\sum_{j \neq i} x_{ij}^\alpha x_{ij}^\beta \rho_j^{a(2)}(R_{ij}) \right)^2 - \frac{1}{3} \left(\sum_{j \neq i} \rho_j^{a(2)}(R_{ij}) \right)^2$$

$$(\rho_i^3)^2 = \sum_{\alpha\beta\gamma} \left(\sum_{j \neq i} x_{ij}^\alpha x_{ij}^\beta x_{ij}^\gamma \rho_j^{a(3)}(R_{ij}) \right)^2$$

Optimization task

Difficulty, another one

Have to optimize up to 15 parameters per ion, hardly doable task to be performed manually



Solution

Develop Genetic Algorithm, implement in AMoDy code, and optimize

Result

1. crystal structure and
2. density of the solid and liquid phase at various temperatures.

The fit of the parameters to different structures and densities at different temperatures implies also a fit of the parameters to the thermal expansion and melting temperatures of compounds.

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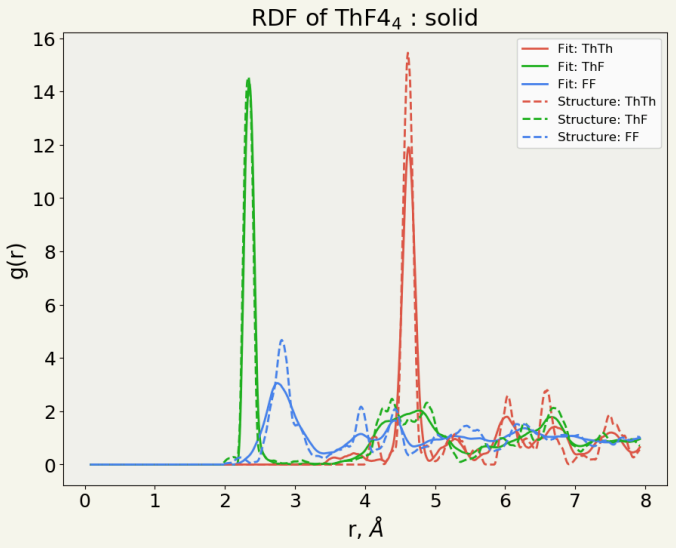
Results: RDF and density profiles

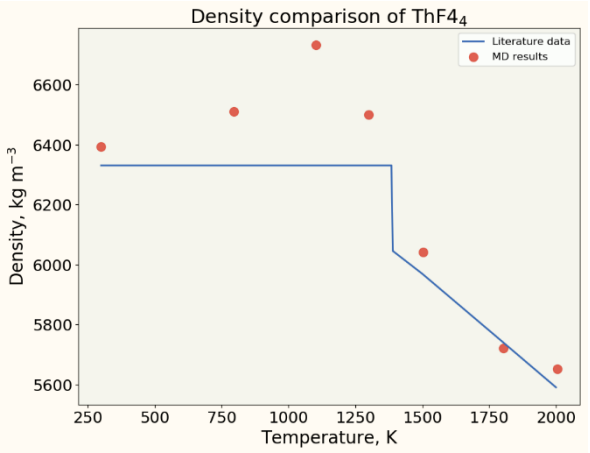
Result

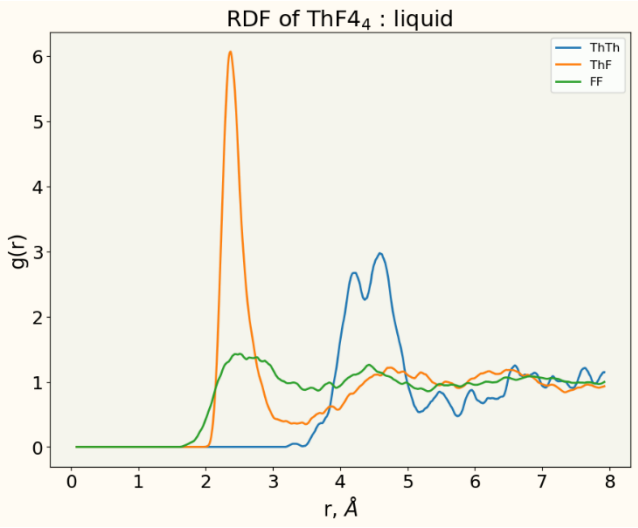
Developed algorithm allowed allows for both an accurate description of **Radian Distribution Function** (RDF) and **density profiles** for solid and liquid phases



RDF of solid ThF_4

Density (peculiar) of solid ThF_4





RDF of liquid ThF_4

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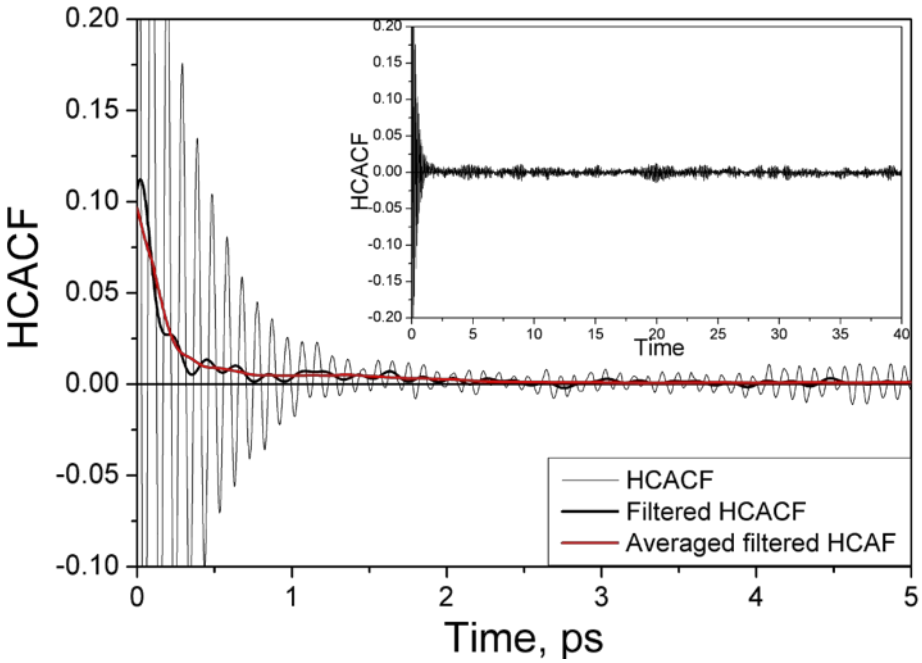
Approach

Thermal Conductivity and Viscosity Calculations

The Green-Kubo approach is used for the thermal conductivity and viscosity calculations.

The viscosity calculation routine was developed and tested



Thermal conductivity

$$\lambda = \frac{1}{3Vk_bT^2}\int \langle J(t)\cdot J(0)\rangle dt$$

Viscosity

$$\eta = \frac{V}{k_bT}\int \langle P_{xy}(t)\cdot P_{xy}(0)\rangle dt$$

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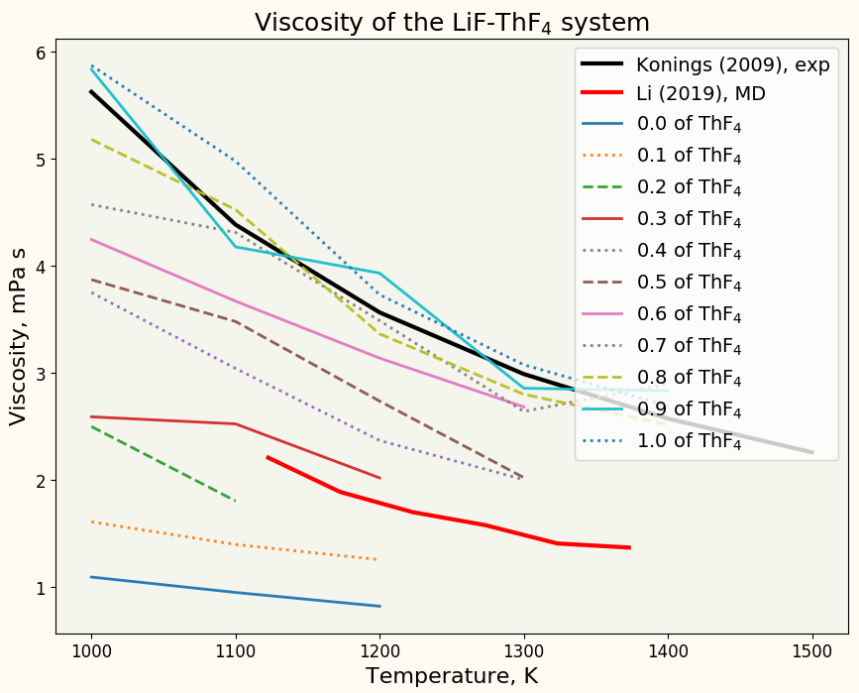
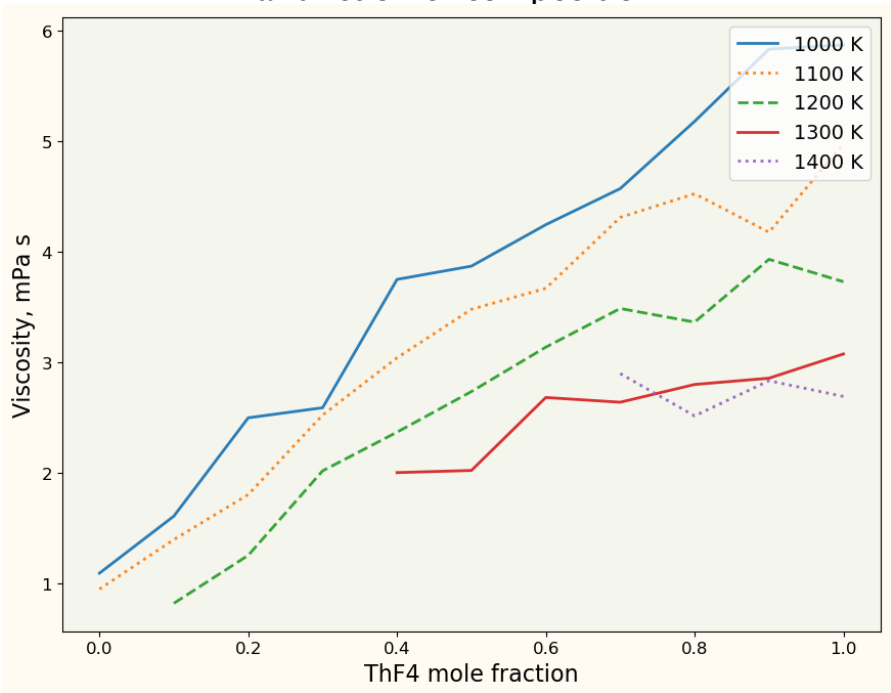
Results: Viscosity Calculations

The Green-Kubo approach was used to calculate viscosity of LiF-ThF_4

Calculated viscosity of LiF-ThF_4 system as a function of temperature



Calculated viscosity of LiF-ThF_4 system as a function of composition



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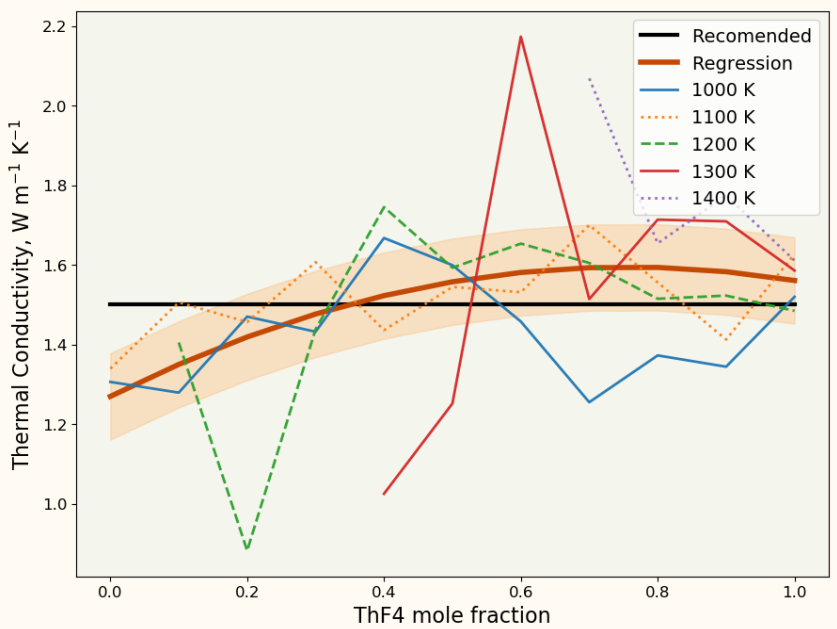
Results: Thermal conductivity calculations

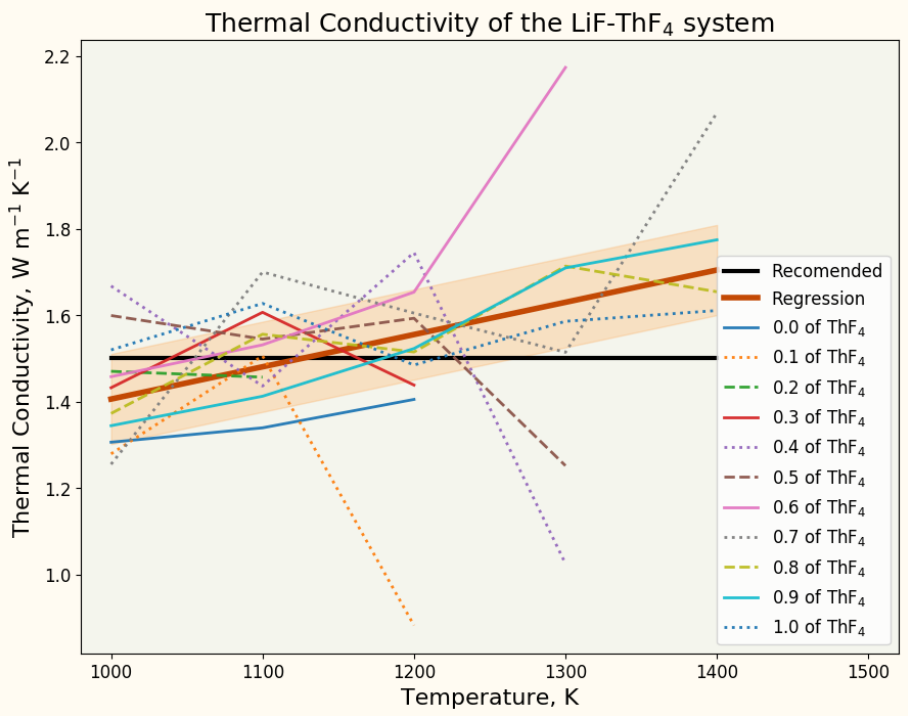
The Green-Kubo approach was used as well to calculate thermal conductivity of LiF-ThF_4

Thermal conductivity of LiF-ThF_4 system as a function of composition



$$\lambda = 1.2694 + 0.8606 \cdot x_{ThF_4} - 0.5694 \cdot {x_{ThF_4}}^2$$

Thermal conductivity of LiF-ThF_4 system as a function of temperature



$$\lambda = 0.6591 + 0.0007466 \cdot T$$

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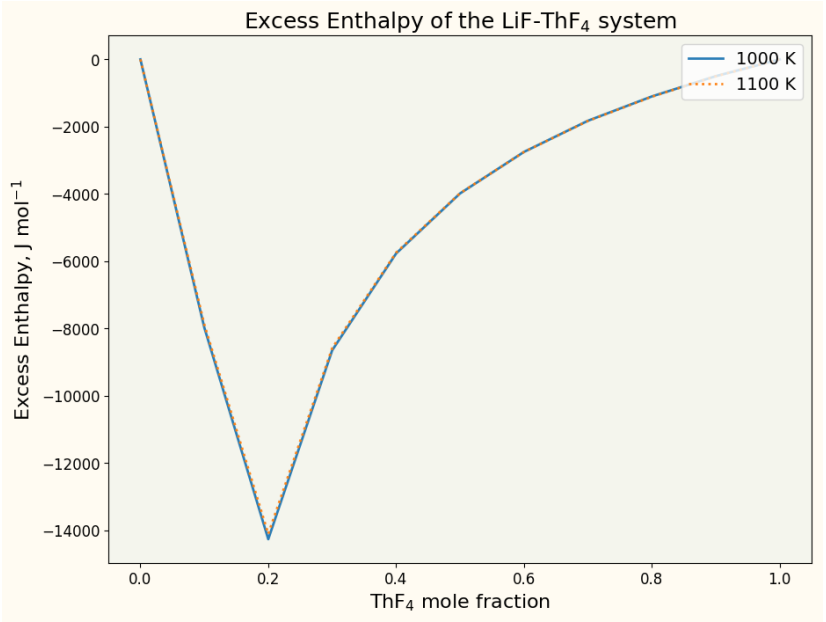
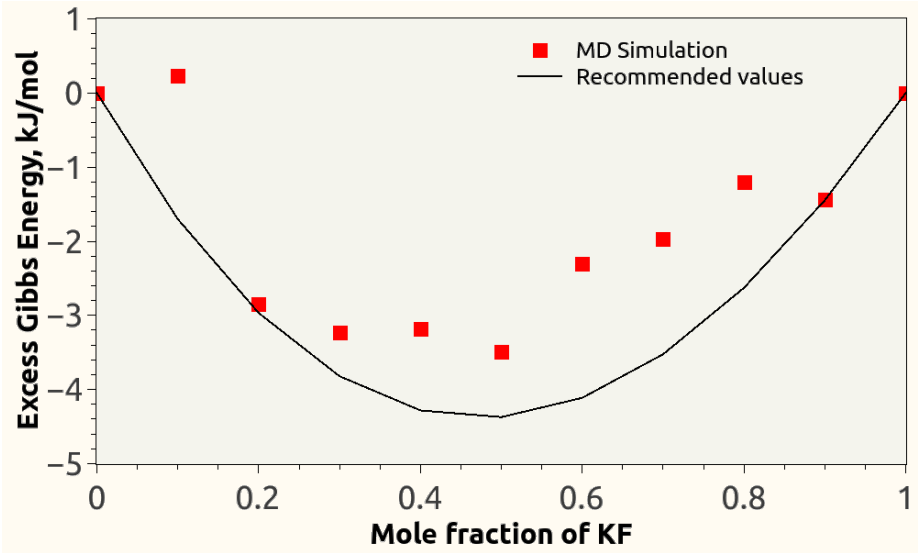
Results: Excess Properties

Excess properties have been calculated using the developed Force Field model

Excess Enthalpy of $LiF-ThF_4$ system as a function of composition



Excess Enthalpy of LiF-KF system as a function of composition



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Recap and Outlook

Recap

- Advanced Force Field model has been developed with a capability to reproduce complex tetrafluoride structures together with the Genetic Algorithm routine to fit the parameters
- Viscosity calculation routine has been developed
- Force Field model parameters fit has been done for LiF, ThF_4, UF_4, PuF_3. KF and NaF are still being refined
- Viscosity and thermal conductivity calculation for the LiF–ThF_4 system were obtained
- Excess properties (as a ”by–product”) for LiF–ThF_4 and KF–LiF systems have been calculated

Outlook

- Extend viscosity calculations to the Li–Th–U–F system
- As well as thermal conductivity calculations for the Li–Th–U–F system

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