Thermodynamic modeling of multicomponent salt sytems for Generation IV nuclear reactors

Alexander Pisch

SIMAP-LTPCM
UMR 5614 (CNRS/INPG/UJF)

St Martin d'Heres – France

Now : Lafarge Centre de Recherche, St Quentin Fallavier, France

Molten salt nuclear reactors

- concept tested in the 60s (Oak Ridge)
- nuclear fuel dissolved in suited solvent (molten salt)
- U, Pu based fission reactor
- Th based breeding reactor

$^{232}Th + n \rightarrow {}^{233}Th \rightarrow {}^{233}Pa \rightarrow {}^{233}U$ (27d)

neutrons from adding small amounts of U and/or Pu

Fuel solvent conditions

- stable thermally
- resistant against radiation
- soluble for U, Pu, Th and higher actinides
- small neutron absorption cross section (breeder)
- low vapor pressure (safety)
- no reaction with the vessel material (Ni-based)
- cheap
- regeneration (gaseous and solid fission products, liquid solution)

^{7}LiF-BeF_2-ThF_4 + NaF, MgF_2, UF_4, PuF_3, LaF_3, CeF_3,...

Objectives

Establishment of a **Gibbs Energy database** of Th, Pu and U-based multicomponent salt systems in order to calculate

- Phase equilibria and phase diagrams
- Gibbs energy, enthalpy and heat capacity data
- Physical properties (density, viscosity, …)

as a function of composition, temperature and pressure

Methodology

Thermodynamic modeling using the phenomenological Calphad approach based on experimental data and ab-initio calculations.

Thermodynamic models

- gas : ideal mixture of stoechiometric species
- solids : stoechiometric or substitutional solutions (Bragg-Williams)
- liquid : modified quasichemical model in the quadruplet approximation [Chartrand and Pelton 2001]

Two sublattice model for the molten salt

Basic structure : (anions)(cations,vacancies)

→

- Definition of anions and cations : quadruplets
- Coordination numbers
- Interaction Gibbs energy

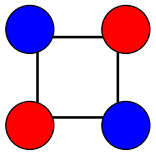
Electrostatic repulsion/attraction — First nearest neighbor

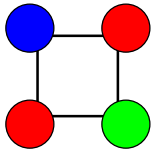
$$[Li\text{-}F]_{pair} + [Th\text{-}Cl]_{pair} \leftrightarrow [Li\text{-}Cl]_{pair} + [Th\text{-}F]_{pair} \qquad \Delta g_1 << 0$$

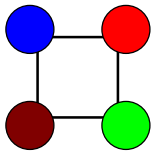
Polarisation: — Second nearest neighbor

$$[Li\text{-}F\text{-}Li]_{pair} + [Th\text{-}F\text{-}Th]_{pair} \leftrightarrow 2\,[Li\text{-}F\text{-}Th]_{pair} \qquad \Delta g_2 << 0$$

Li^+ Th^{4+} F^- Cl^-

Unary : LiF 

Binary: $LiF\text{-}ThF_4$ 

Reciprocal: $LiF\text{-}LiCl\text{-}ThF_4\text{-}ThCl_4$ 

$LiF - ThF_4$ and $MgF_2 - ThF_4$

- Influence of MgF_2 addition (melting point ?)
- only phase diagram information (DTA)
- RAMAN spectroscopy LiF - ThF_4 [1969Todt] :

  complex formation in the liquid ThF_8^{4-}, ThF_7^{3-} et $Th_2F_{10}^{2-}$

Model for the liquid phase $(Li^{+}, Th^{4+}[8], Th^{4+}[7], Th_2^{8+}[10])(F^{-},Va)$

→
- Three different Gibbs energies for ThF_4 (end members of solution)
- Six interaction Gibbs energies

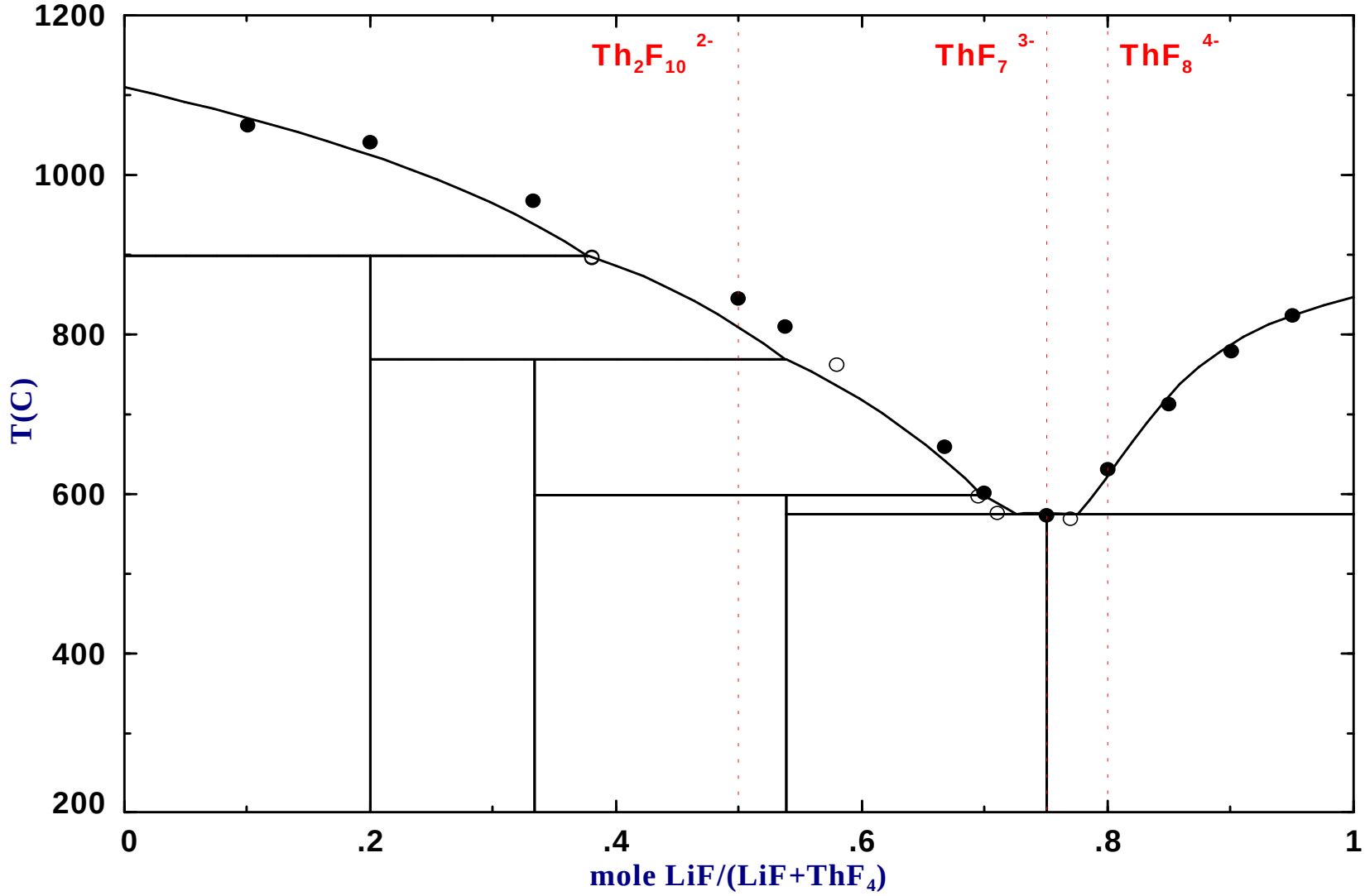
$Th_2F_8 = 2 * G(ThF_4)$ SGTE substance database

$ThF_4\,[7] = 12552+50.208*T + G(ThF_4)$

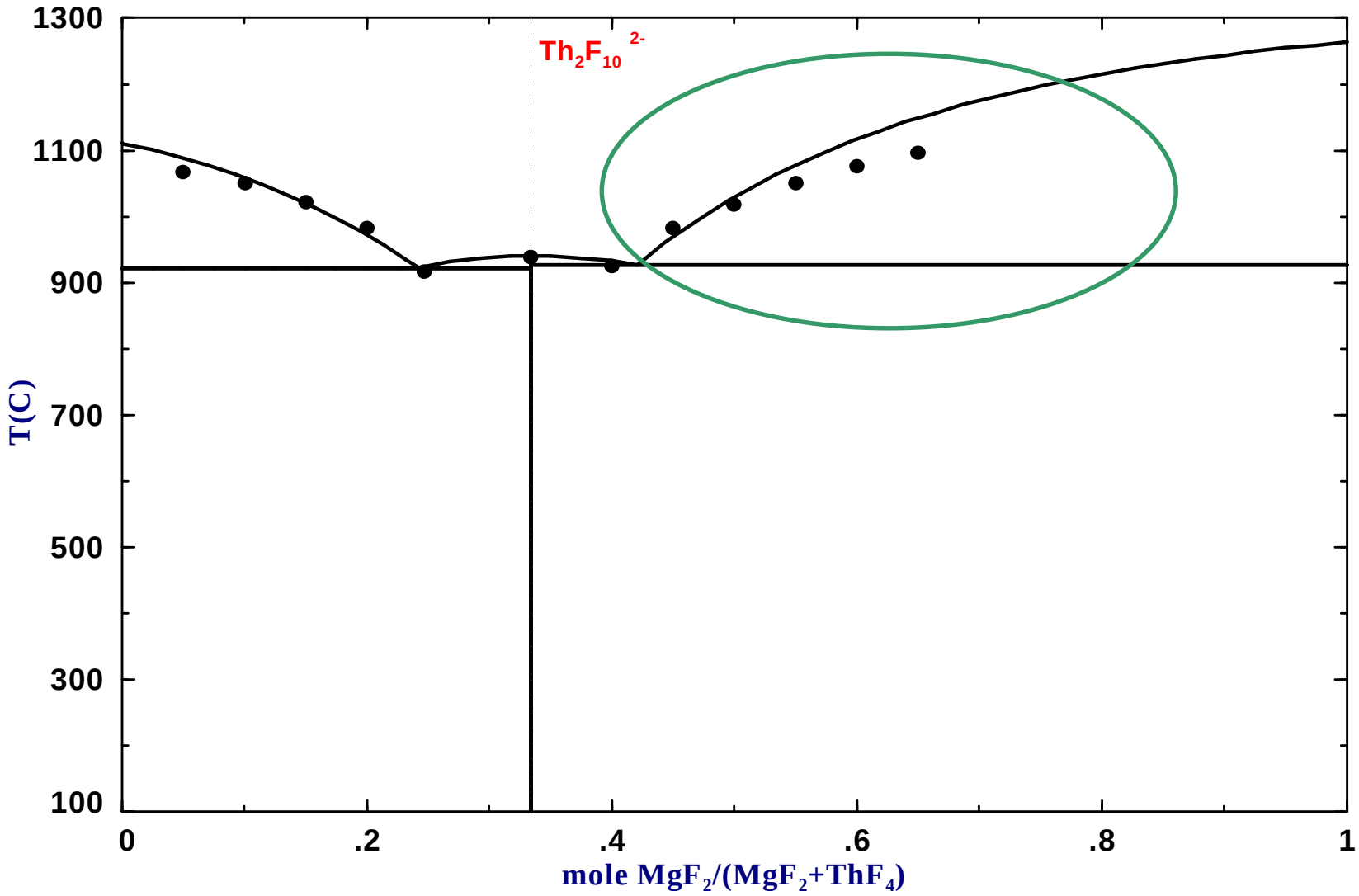
$ThF_4\,[8] = 25104+50.208*T + G(THF_4)$

Interaction : $Li,Th_2//F$, $Li,Th[7]//F$, $Li,Th[8]//F$, all others ideal

$LiF - ThF_4$

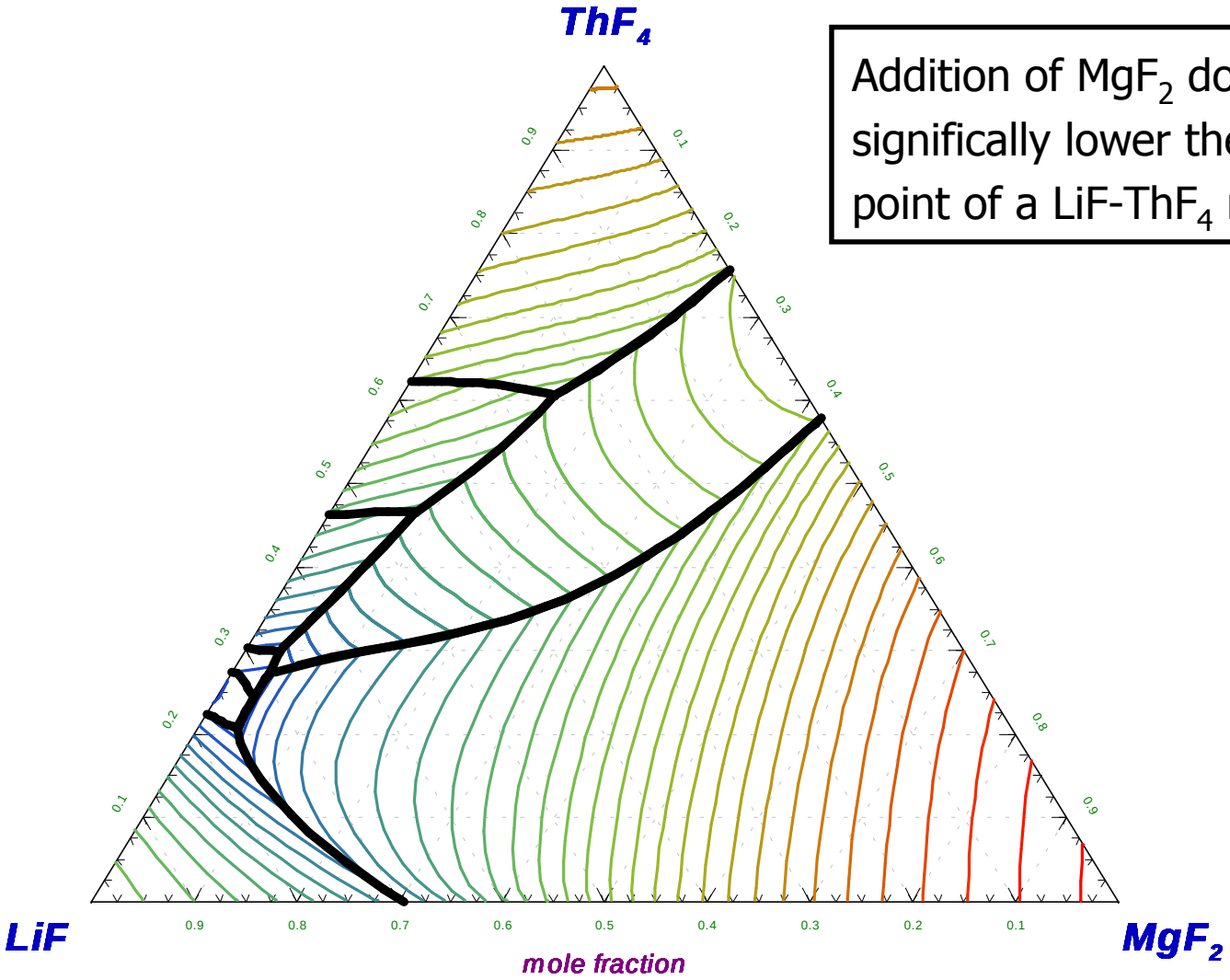

1200
1000
800
600
400
200
T(C)
0
.2
.4
.6
.8
1
mole LiF/(LiF+ThF4)
Th2F10 2-
ThF7 3-
ThF8 4-

MgF_2 - ThF_4


Th2F10 2-
1300
1100
900
700
500
300
100
T(C)
0
.2
.4
.6
.8
1
mole MgF2/(MgF2+ThF4)

$LiF - ThF_4 - MgF_2$

Surface de liquidus



Addition of MgF_2 does not significally lower the melting point of a LiF-ThF_4 mixture

$LiF-NaF-BeF_2$

- only limited experimental data available

- BeF_2 tends to form polymer species (equivalent SiO_2)

  -> high viscosity in the liquid state

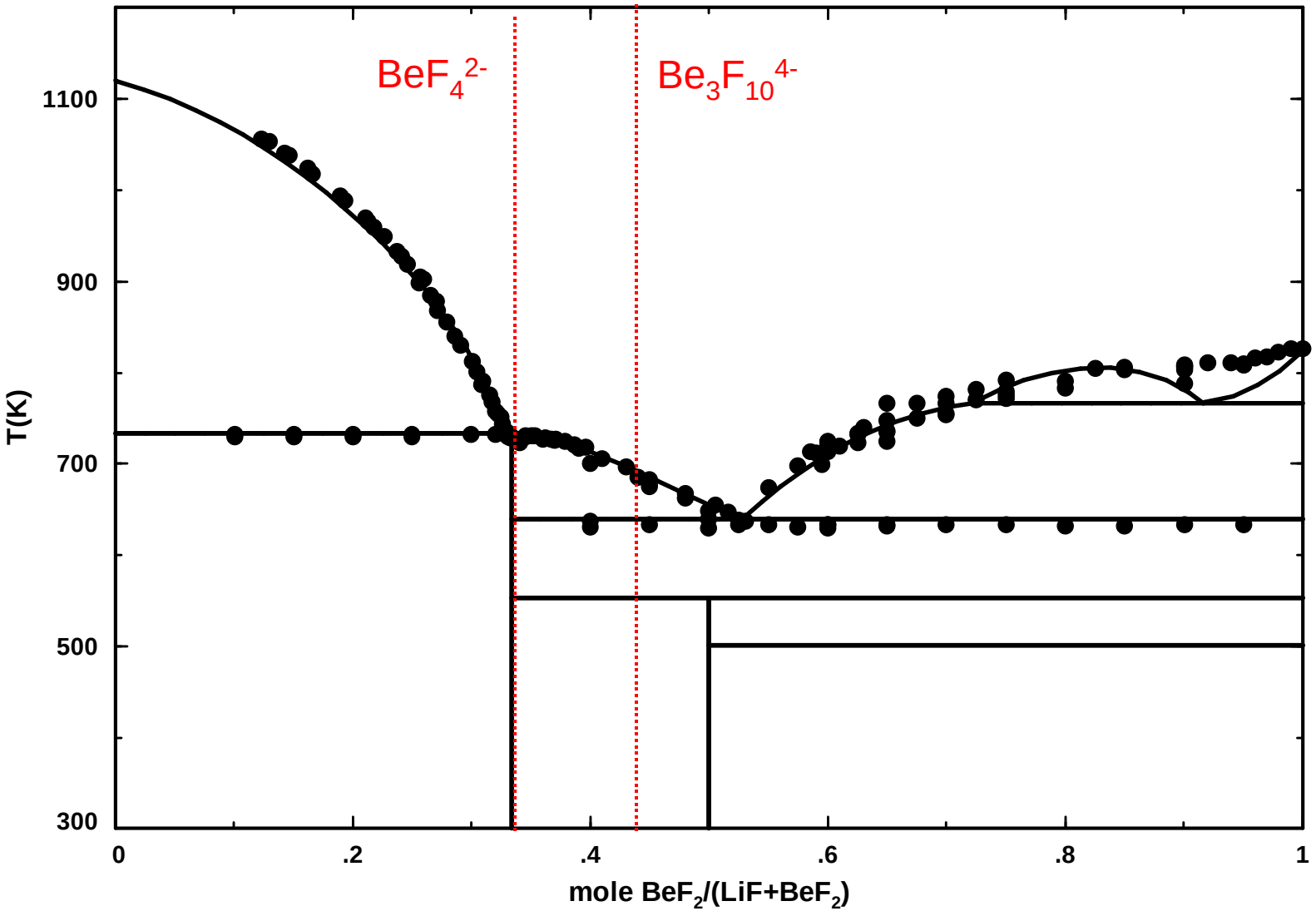
- MD calculations : dimer/trimer/polymer formation corner combination

  BeF_4^{2-}, $Be_2F_7^{3-}$, $Be_3F_{10}^{4-}$, polymers

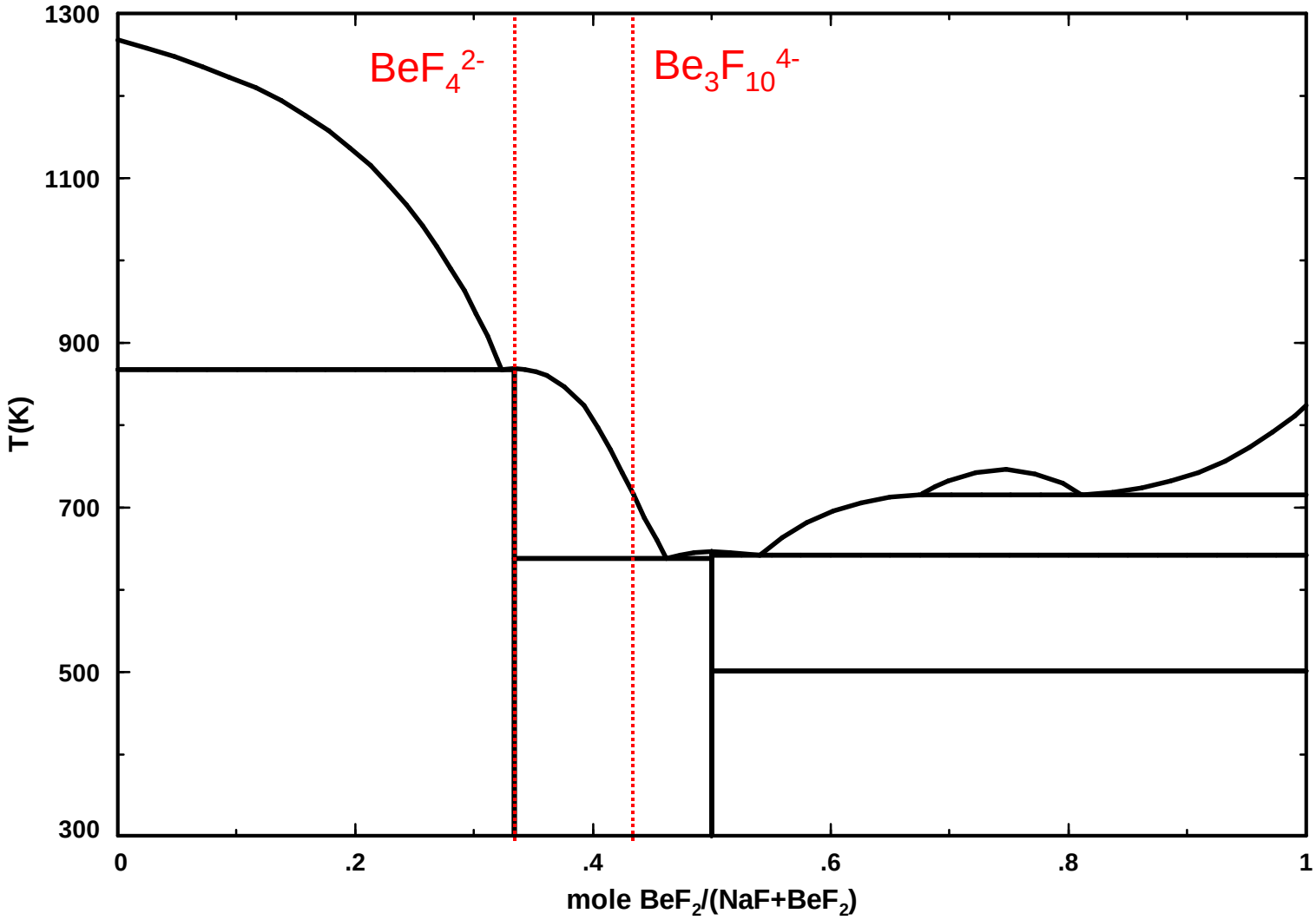
modified quasichemical model for the liquid phase

$(Li^+, Be^{2+}[4], Be_3^{6+}[10])(F^-,Va)$

$LiF - BeF_2$

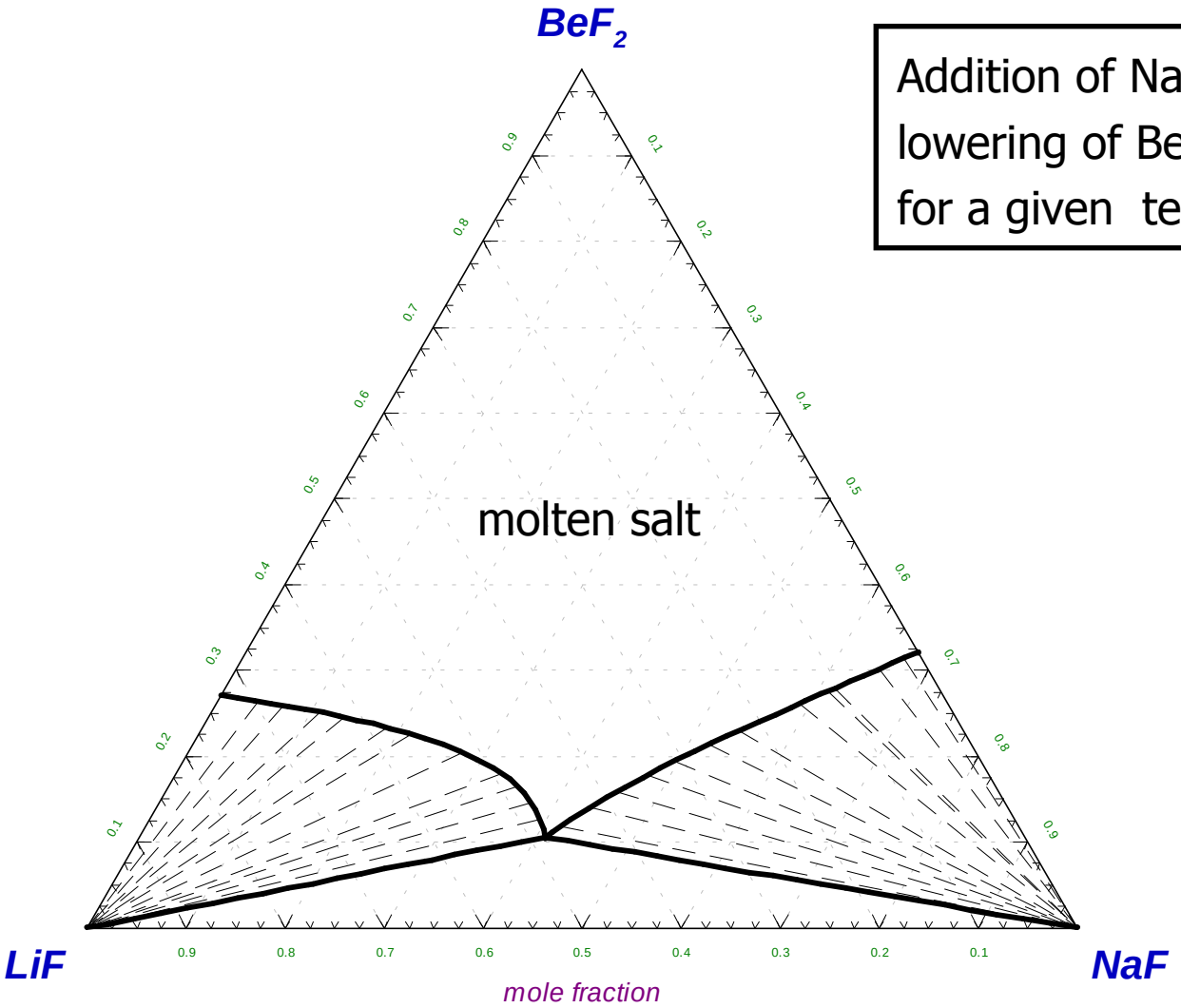

BeF_4^{2-}
$Be_3F_{10}^{4-}$
1100
900
700
500
300
T(K)
0
.2
.4
.6
.8
1
mole $BeF_2/(LiF+BeF_2)$

$NaF - BeF_2$


1300
1100
900
700
500
300
T(K)
0
.2
.4
.6
.8
1
mole BeF2/(NaF+BeF2)
BeF4 2-
Be3F10 4-

$NaF - BeF_2 - LiF$

873 K

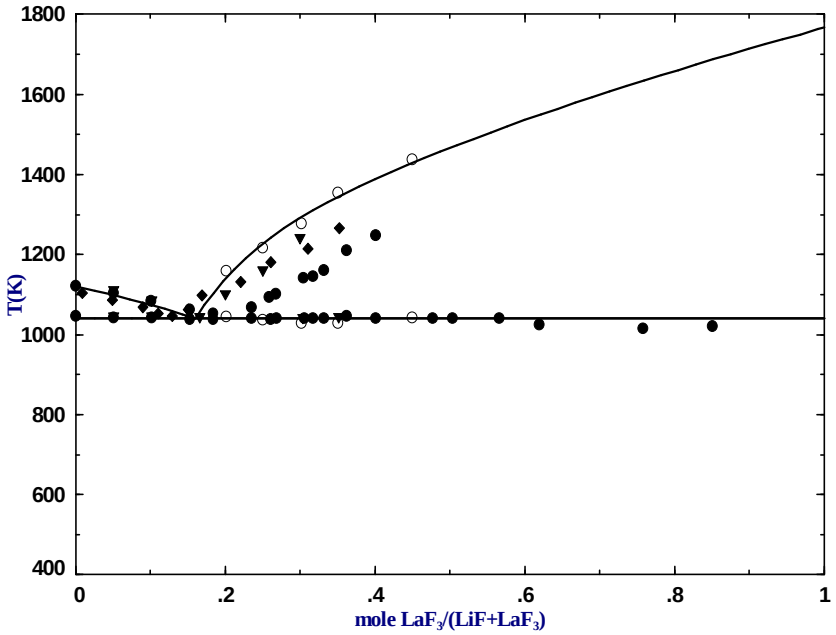


Addition of NaF:
lowering of BeF_2 content
for a given temperature

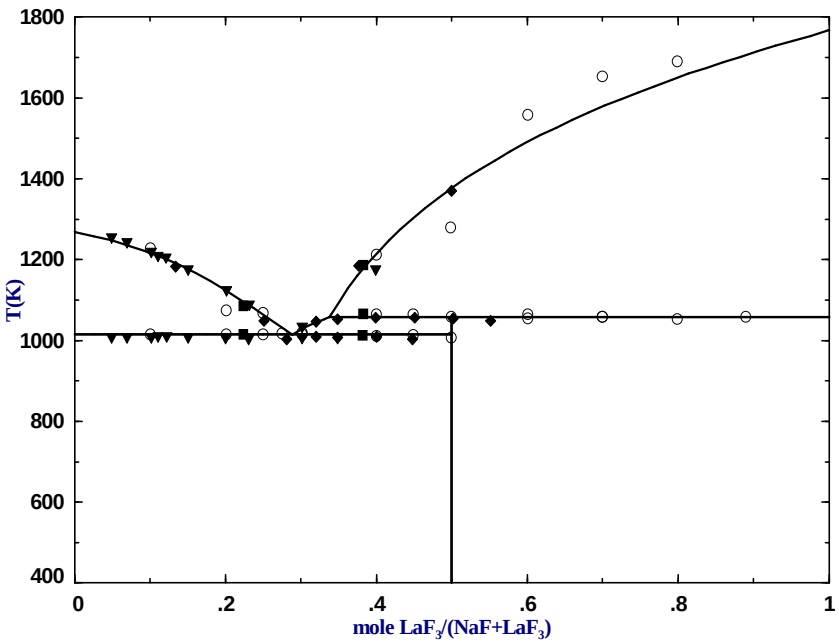
$LiF-NaF-XF_3$ (X=La, Ce et Pu)

- Limited amout of experimental information
  - phase diagram over the whole composition range
  - enthalpy of mixing LiF - LaF_3
- modeling of all binary systems
  - only excess enthalpy, no excess entropy
  - Neumann-Kopp+ constant for intermediate compounds
- ternary extrapolation (asymetrical)

LiF - LaF_3



NaF - LaF_3

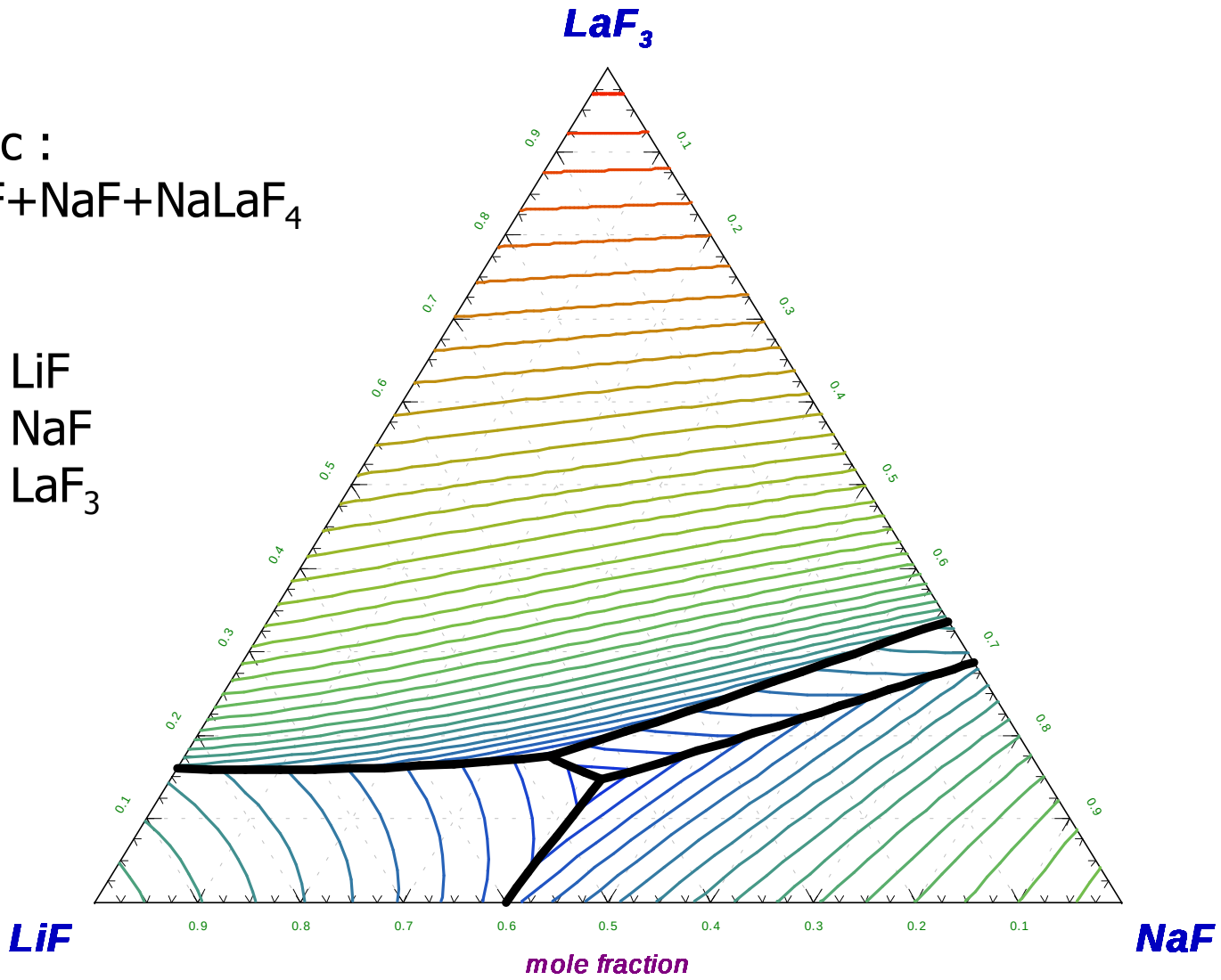


$NaF - LaF_3 - LiF$

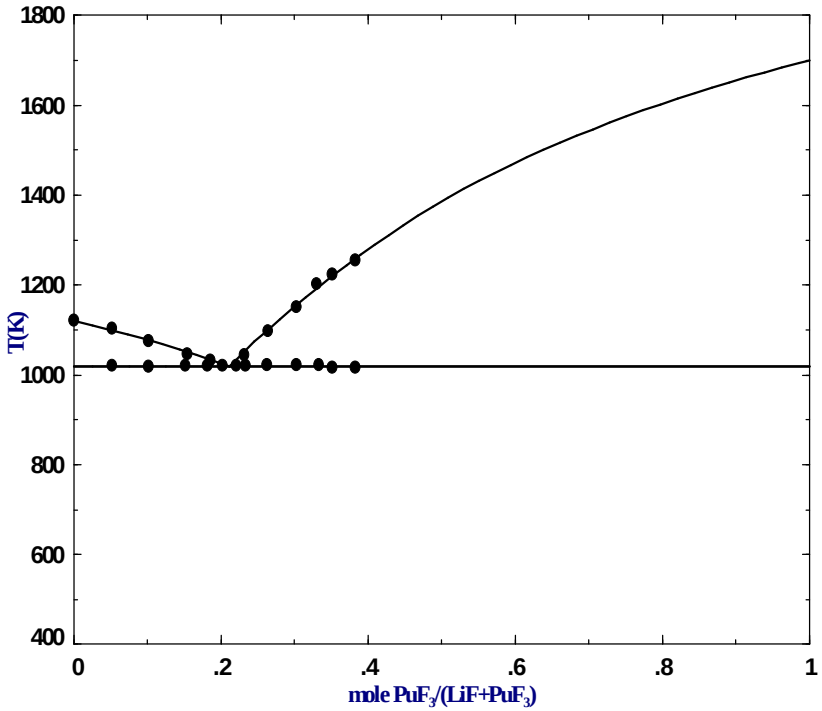
Surface de liquidus

Eutectic :
$L = LiF+NaF+NaLaF_4$

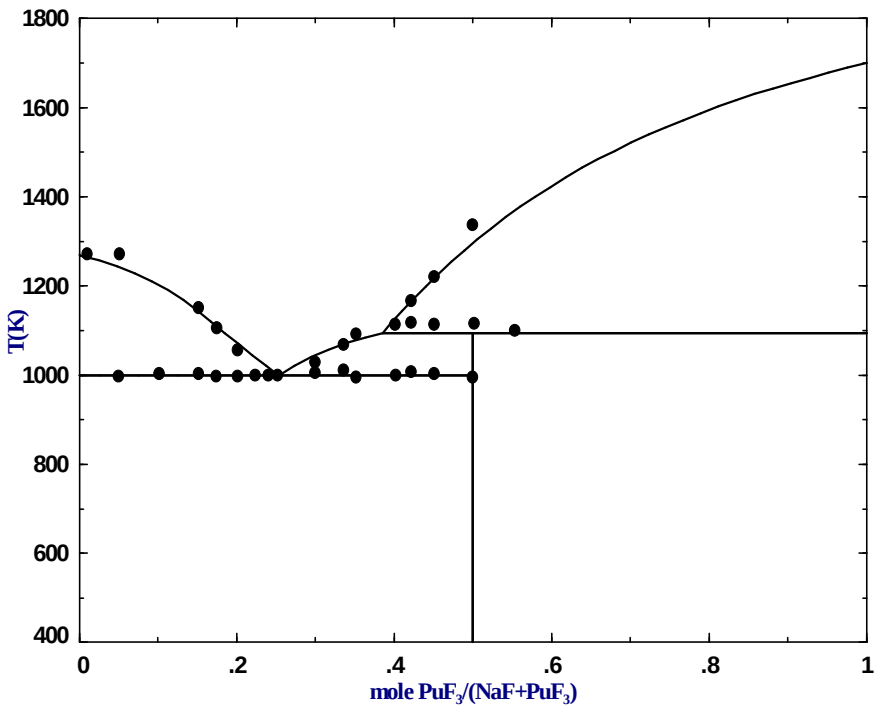
586 °C
43.2% LiF
42.0% NaF
14.8% LaF_3



LiF - PuF_3



NaF - PuF_3

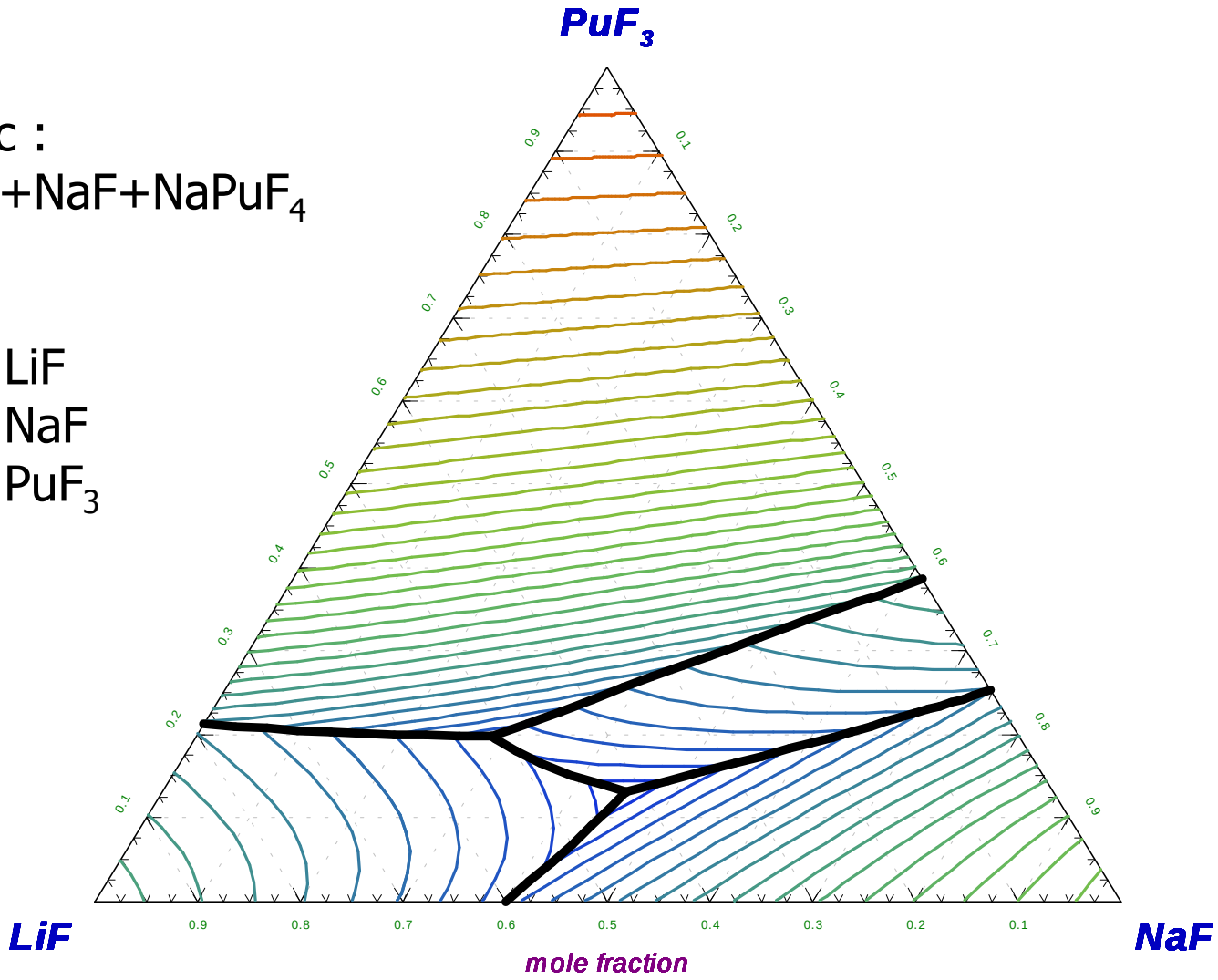


$LiF - NaF - PuF_3$

Surface de liquidus

Eutectic :
$L = LiF+NaF+NaPuF_4$

583 °C
41.7% LiF
45.2% NaF
13.1% PuF_3



Conclusions and Perpectives

Thermodynamic modeling of ThF_4 base salt systems for reactor applications

- LiF-ThF_4 : variation of Th coordination and SRO
- LiF-MgF_2-ThF_4 : addition of MgF_2 does not significantly lower the melting T
- LiF-BeF_2 and NaF-BeF_2 : polymerisation and SRO
- LiF-NaF-BeF_2 : NaF addition can lower BeF_2 content for given T
- LiF-NaF-XF_3 : identification of important ternary eutectics

Future work

- LiF-NaF-ThF_4 and LiF-BeF_2-ThF_4
- U-based binaries with LiF and NaF

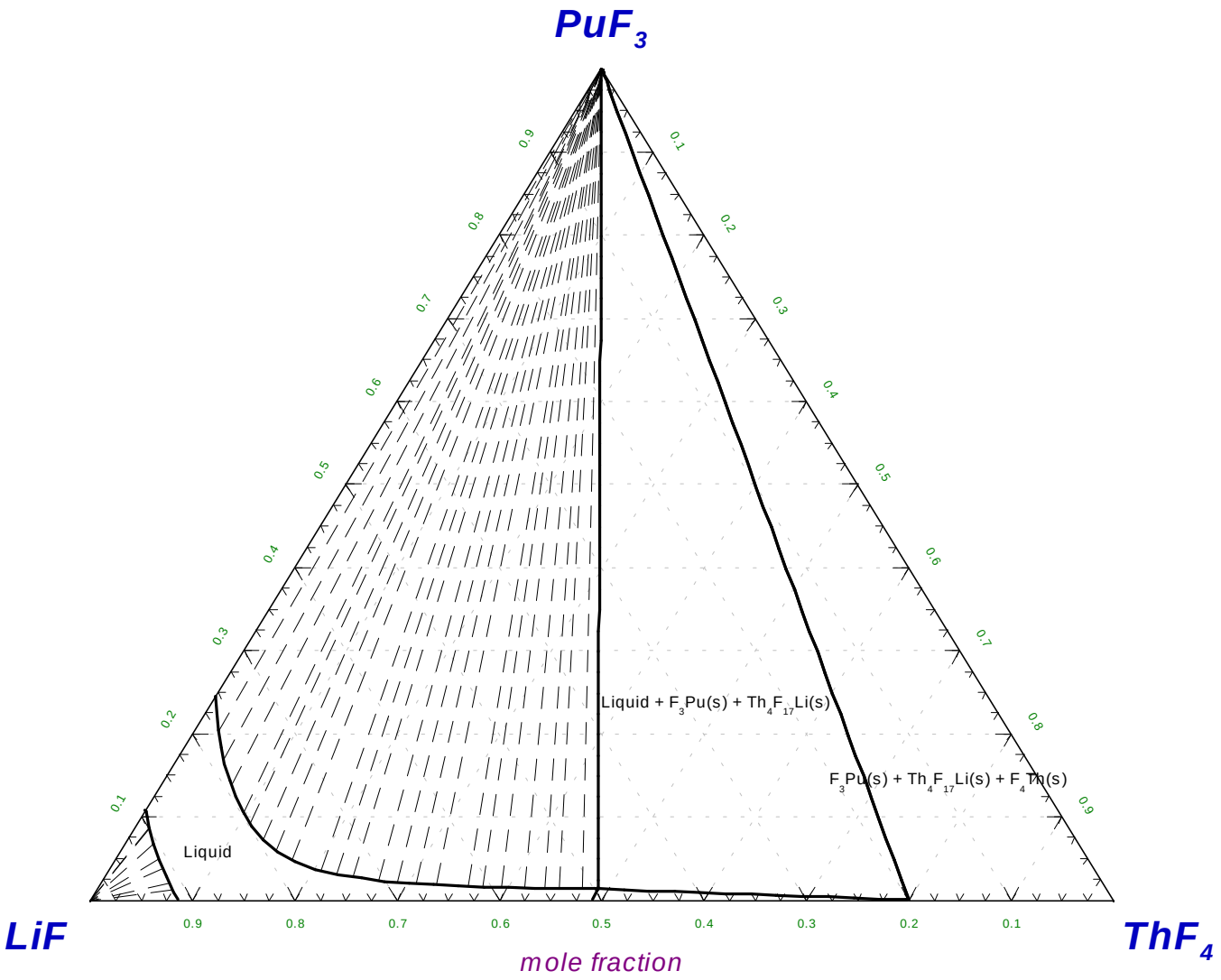
Database Application

Estimation of PuF_3 solubility in LiF-ThF_4 mixtures

- LiF-PuF_3 and LiF-ThF_4 from database
- PuF_3-ThF_4 no experimental information : assumed ideal
- Asymmetric (Toop) ternary extrapolation

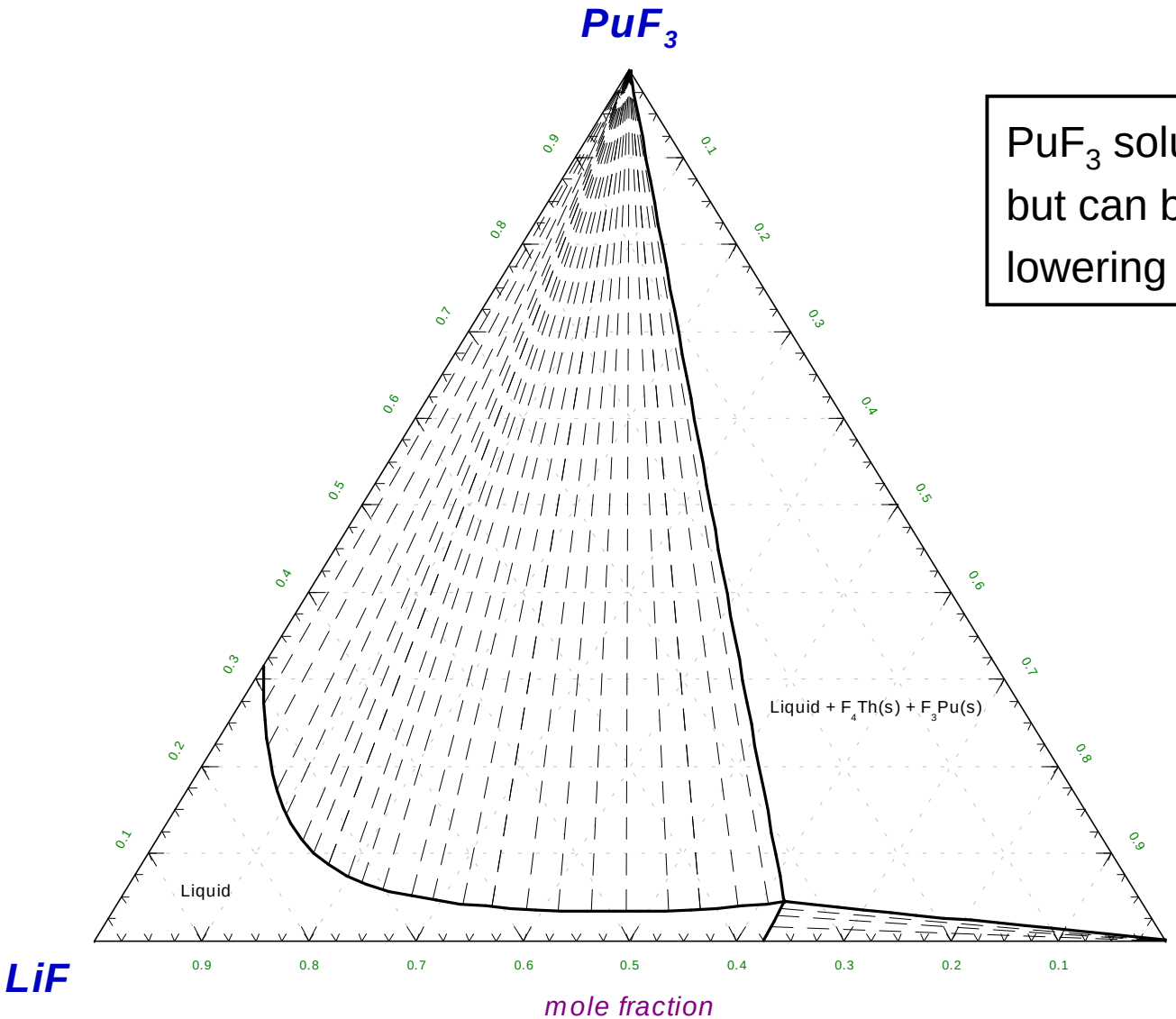
ThF_4 - PuF_3 - LiF

800C



ThF_4 - PuF_3 - LiF

900C



PuF_3 solubility small, but can be improved by lowering ThF_4 content

Acknowledgements

This work has been supported by the French National CNRS-PCR network on molten salt nuclear reactors.

Financial support of the EC is acknowledged for a research stay at ITU