Designing Molten Salt Eutectics

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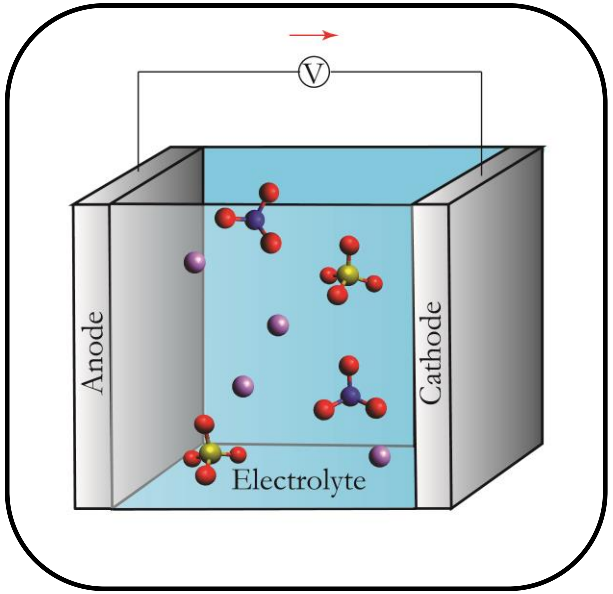
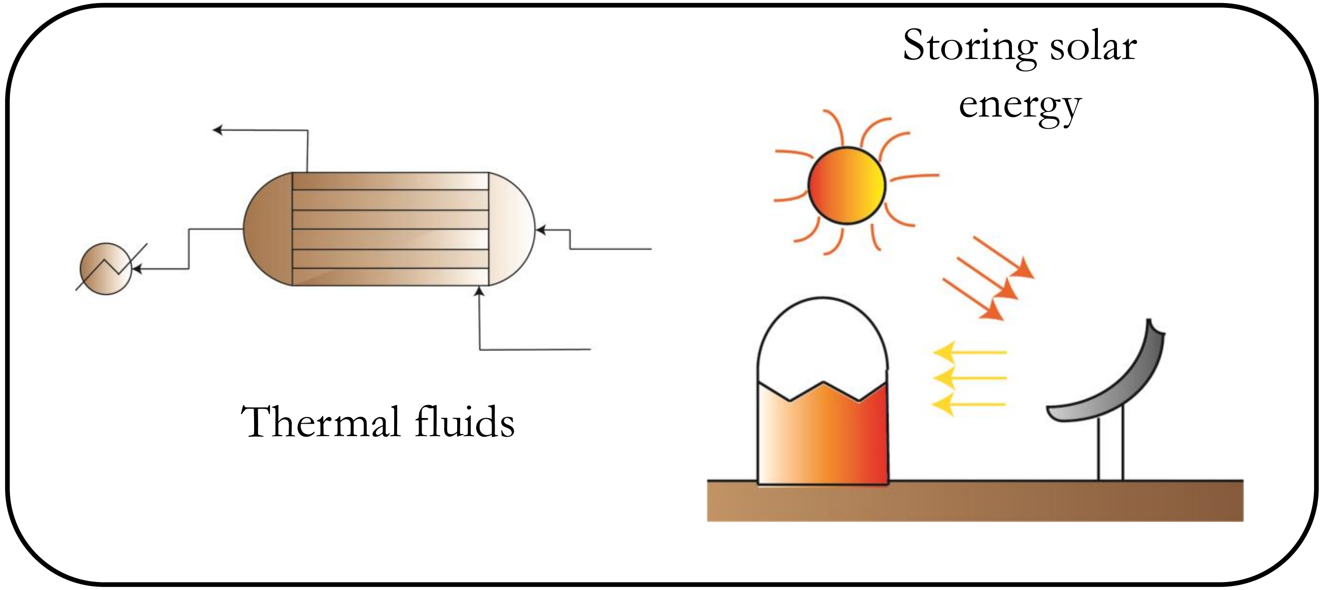
Molten Salts and its Applications

Battery electrolytes



Solar thermal storage and heat transfer fluids



Stability

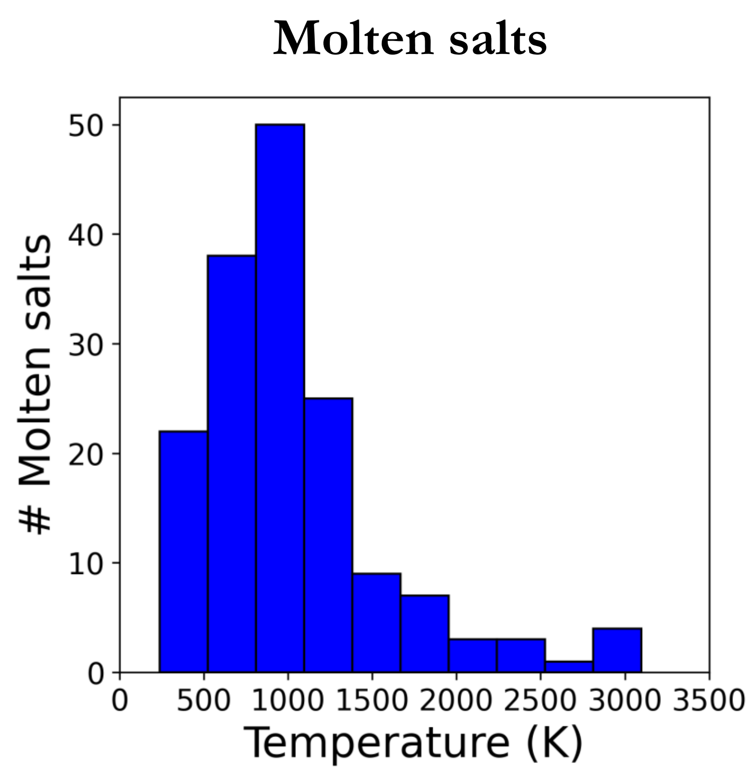
Minimal parasitic reactions

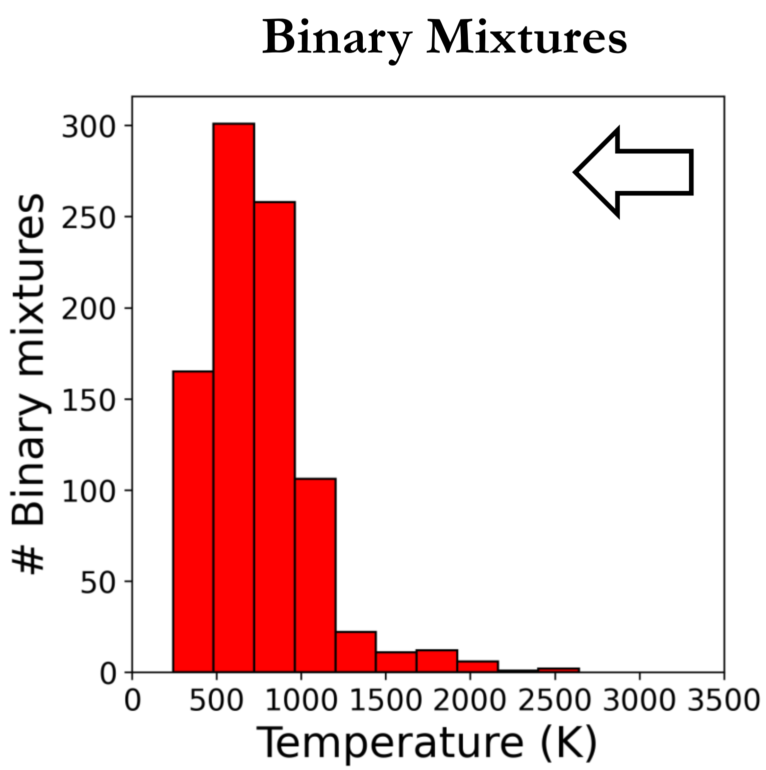
High heat capacity

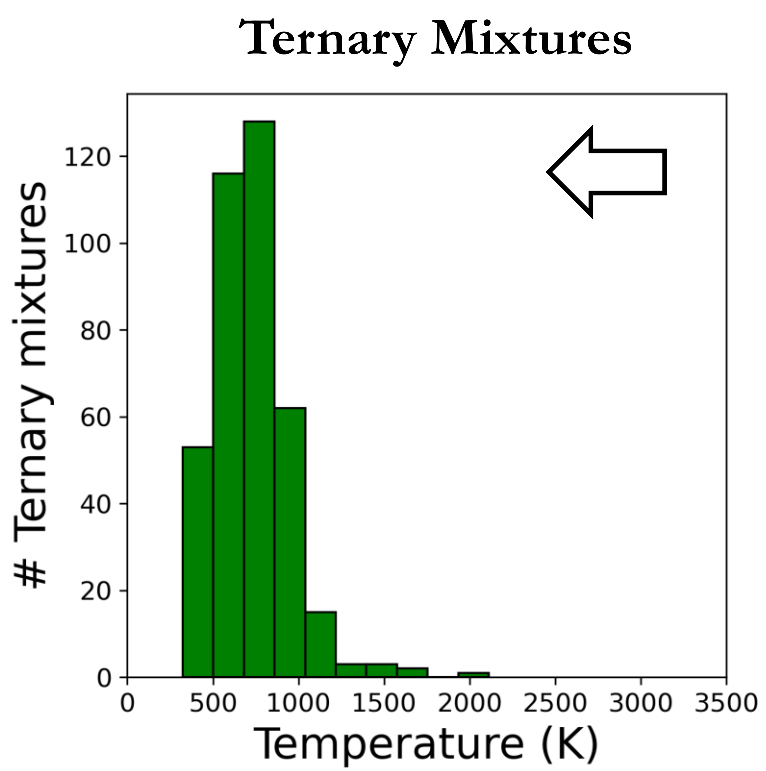
High thermal conductivity

Operating temperature – Low temperature molten salts are challenging to design

Necessity to Design Higher Order Eutectic Mixtures

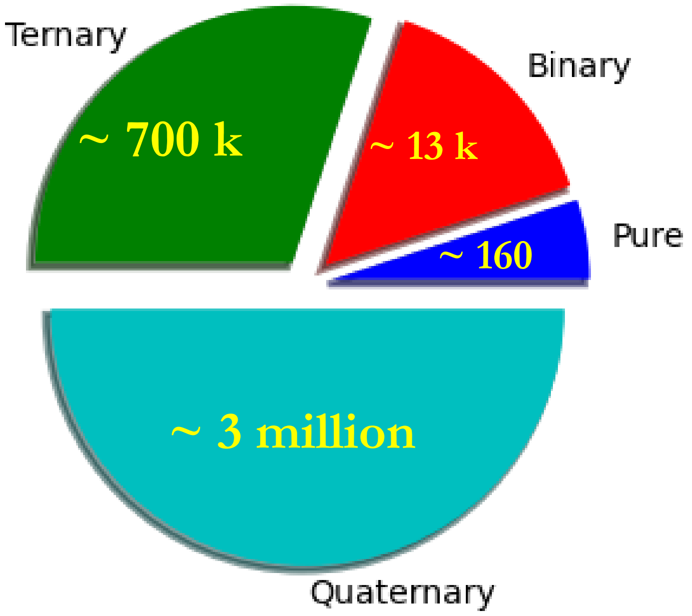






Multicomponent eutectic mixtures needed to bring down the operating temperature

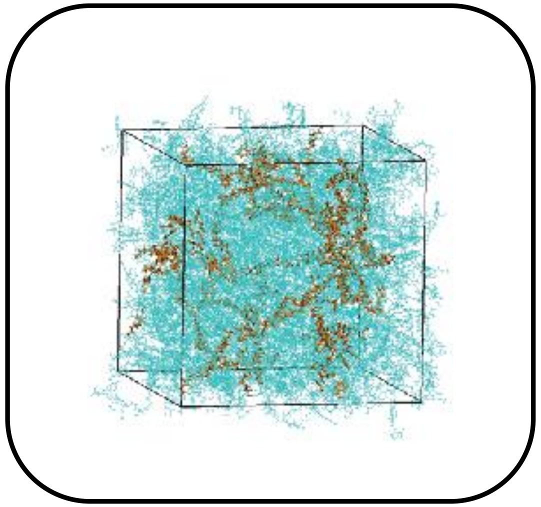
Dimensionality of the Design Space



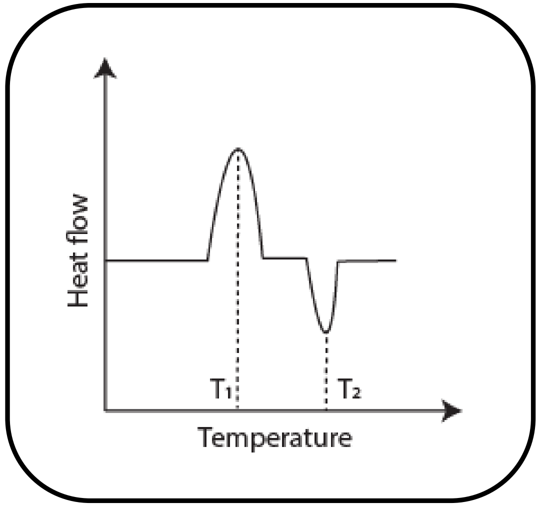
Millions of mixtures to screen

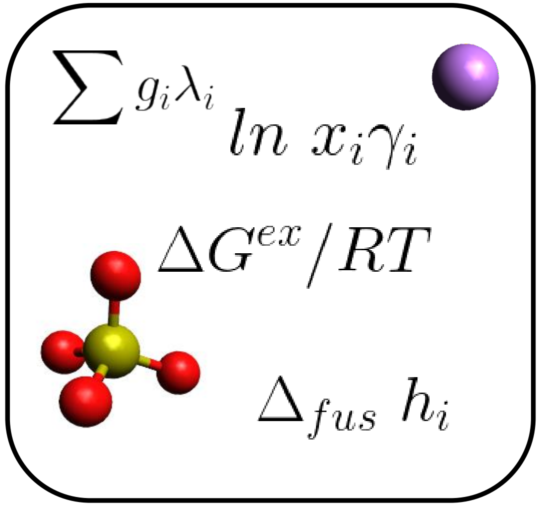
Eutectic temperature prediction

Molecular simulations

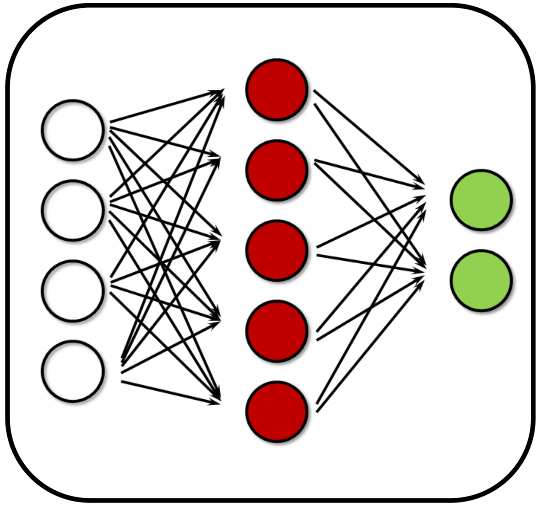


Experiments





Thermodynamic models



Machine learning

Combination of thermodynamic modeling and machine learning for property prediction

Methods and Experimental Data

Computational Methods

Phase equilibria

Fusion enthalpy

Melting point

$$\ln \frac{1}{\gamma_i x_i} = \frac{\Delta_{\mathrm{fus}} h_i}{R T_{\mathrm{m}}} \left(\frac{T_{\mathrm{m}}}{T} - 1 \right)$$

Activity Coefficient

Mole fraction

Machine Learning

KNN

Linear regression

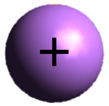
Gradient boosting

Radius neighbors

ANN

Data Source

Cations and anions



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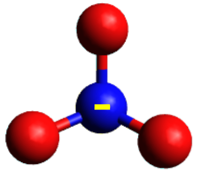

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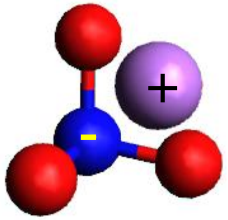
Pure salts



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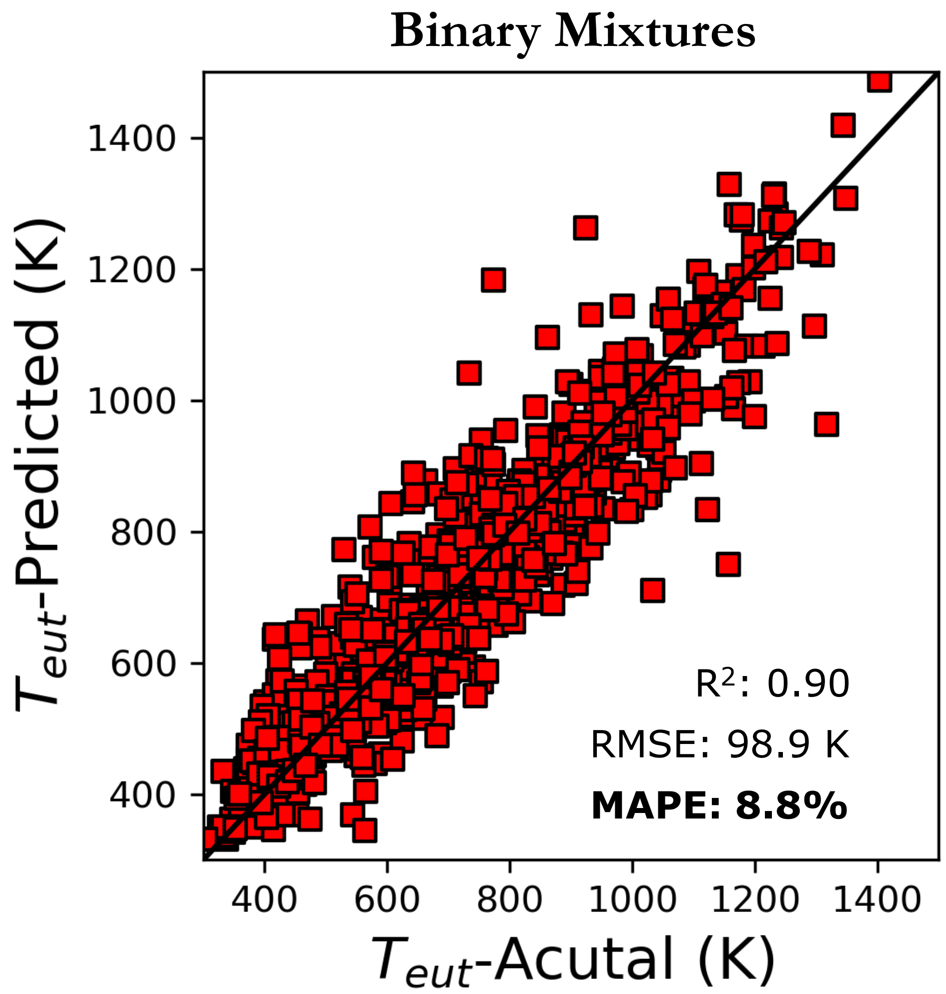
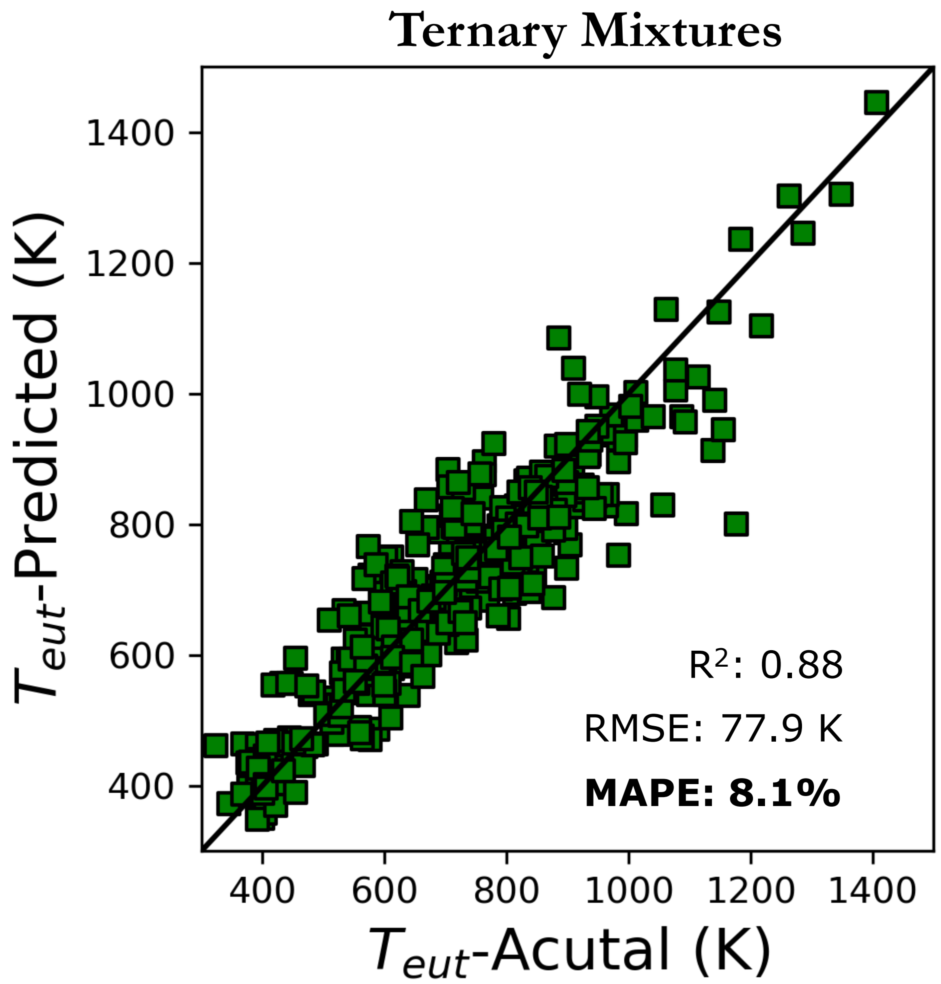
Mixture	Relevant eutectic data
Binary	884
Ternary	383
Quaternary	28
Quinary	1

Janz, George J., et al. "Physical properties data compilations relevant to energy storage. 1. Molten salts: Eutectic data." *Recon Technical Report N* 78 (1978): 31589.

Baseline Thermodynamic Model – Ideal Behavior

$$ln\ \gamma_i^{ideal} = 0$$

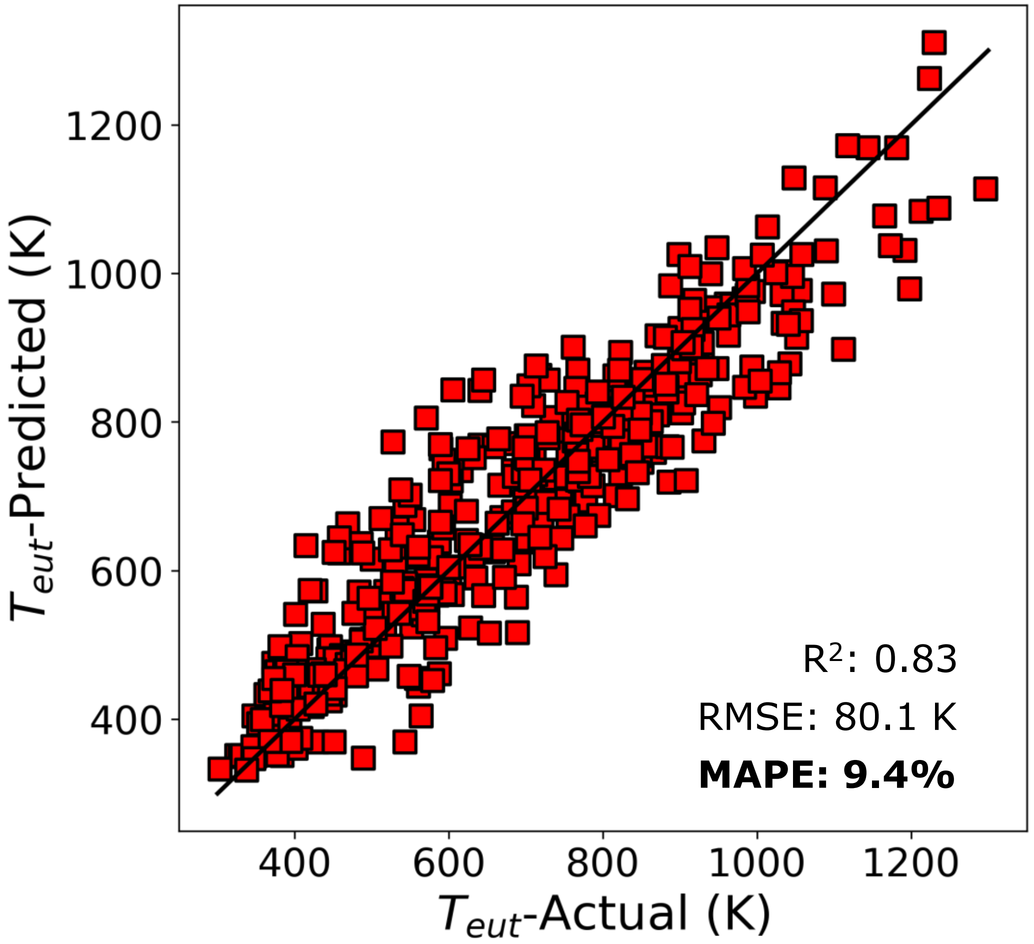




Ideal model predicts the eutectic temperature for a wide range of mixtures with reasonable accuracy

Combinatorial Thermodynamic Model

Binary Mixtures



Coordination number

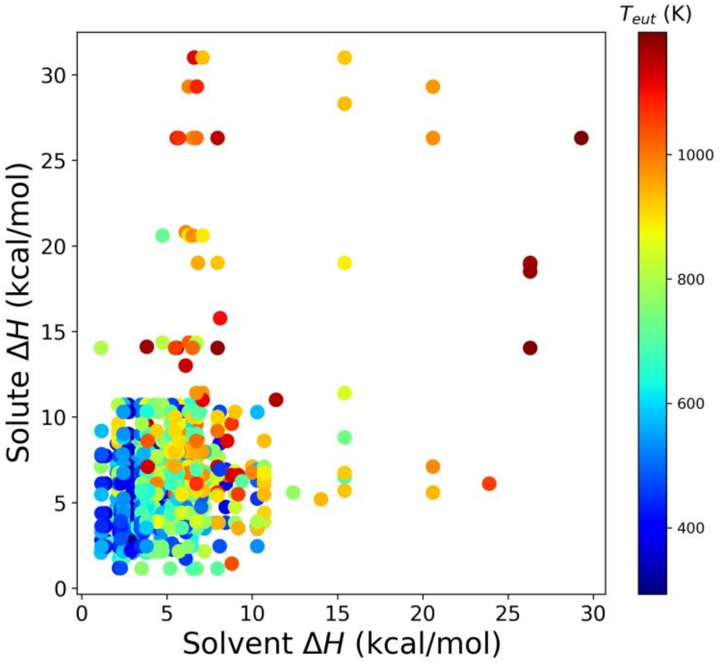
Surface fraction

$$\ln \gamma_i^{comb} = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum x_j l_j$$

Volume fraction

Marginal improvement over the ideal thermodynamic model

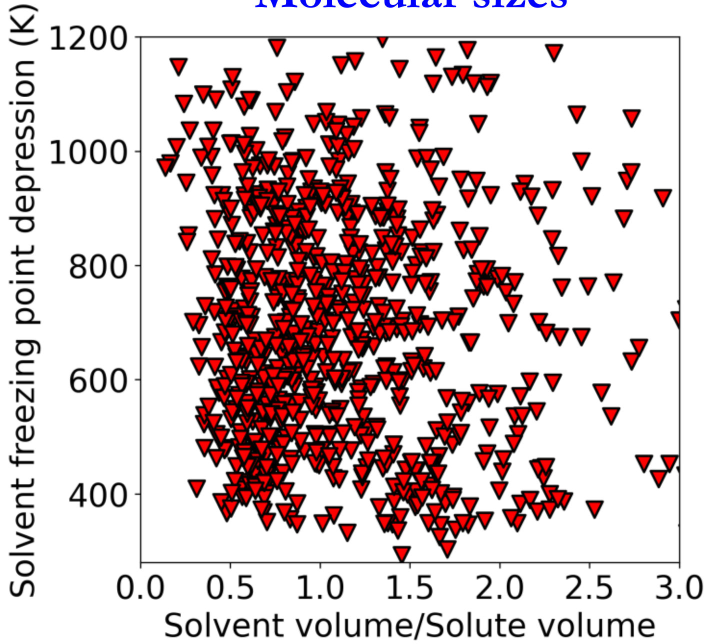
Feature Selection

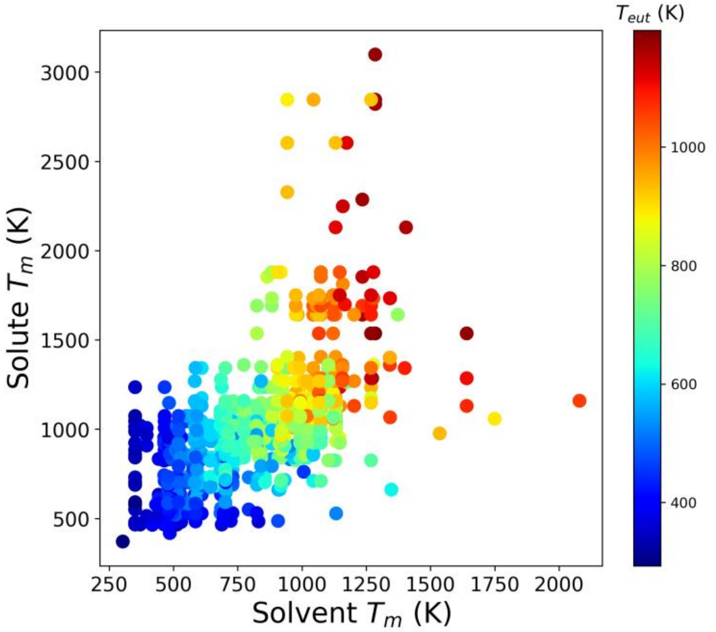


ΔH^{fus}

Relevant features	Correlation coefficient
Melting temperature	0.73 to 0.87
Fusion enthalpy	0.42 to 0.5
Molecular weight	-0.17
Molecular sizes	0.10

Molecular sizes





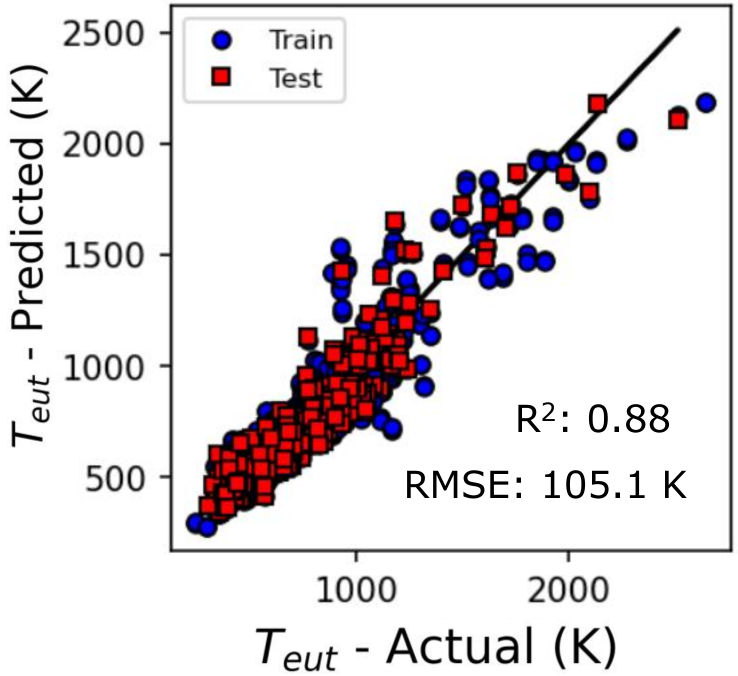
Melting temperature

Melting temperature and enthalpy of fusion most correlated to the eutectic temperature

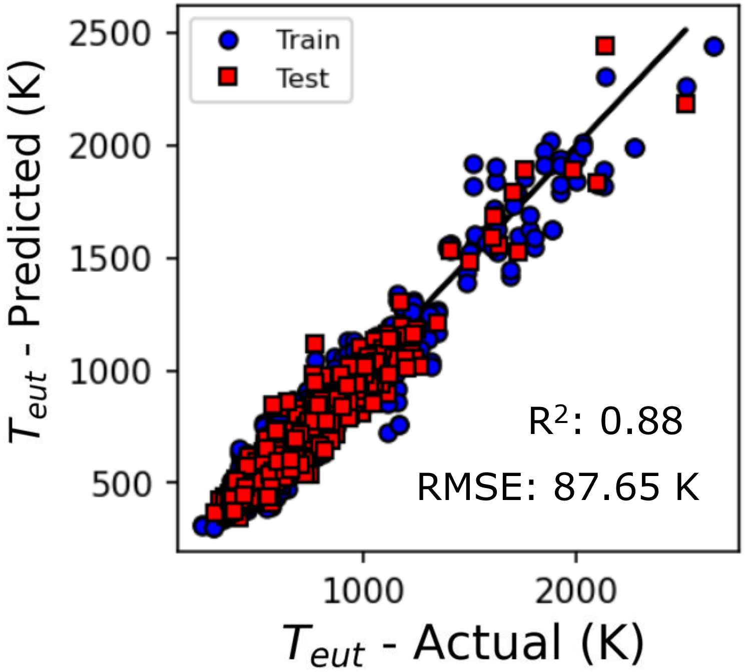
Machine Learning Models

Binary Mixtures

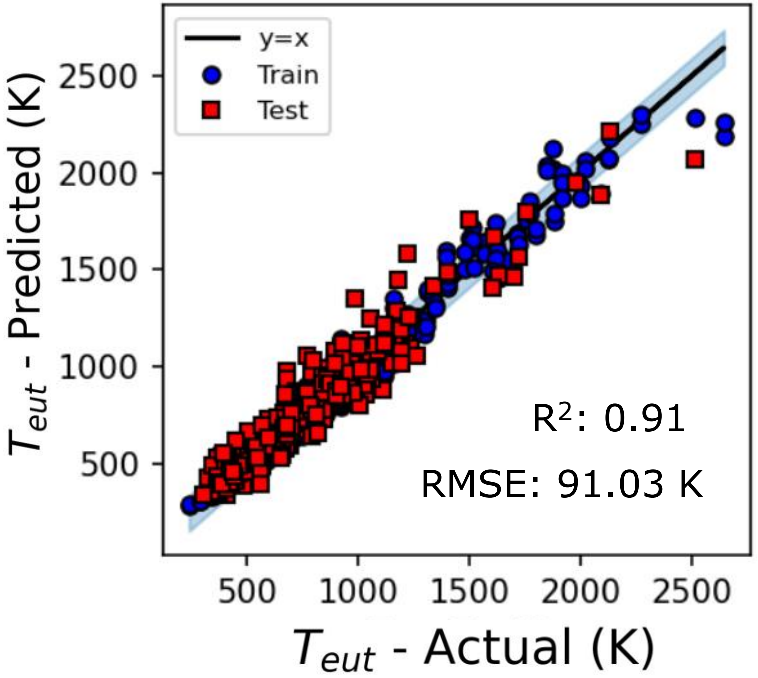
Linear regression



K-Nearest Neighbors



Neural Networks

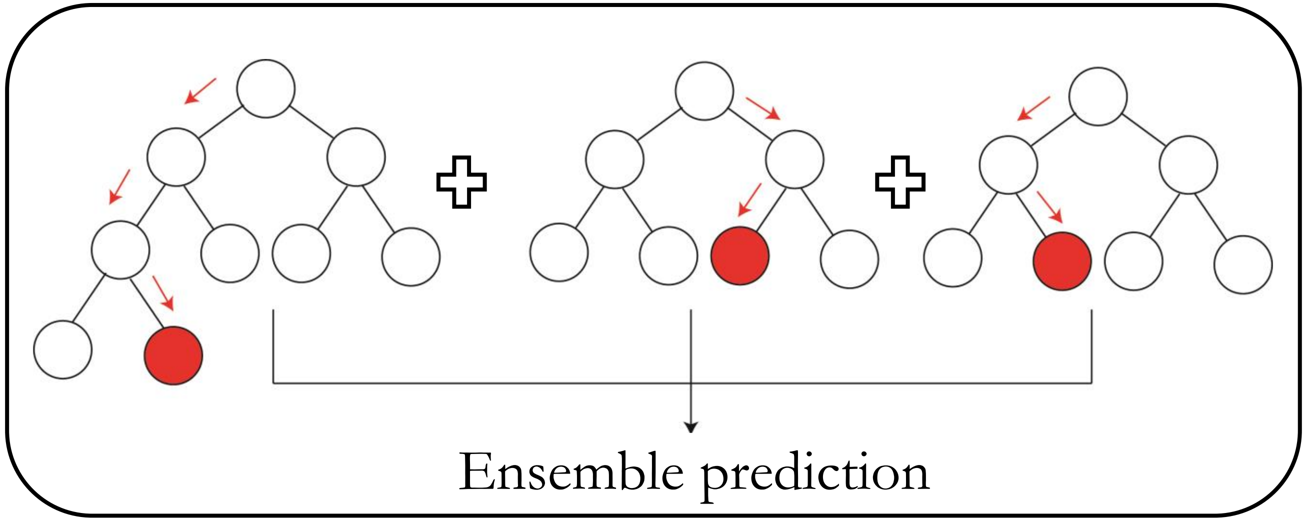


Increasing model complexity

High RMSE for all models with different complexity

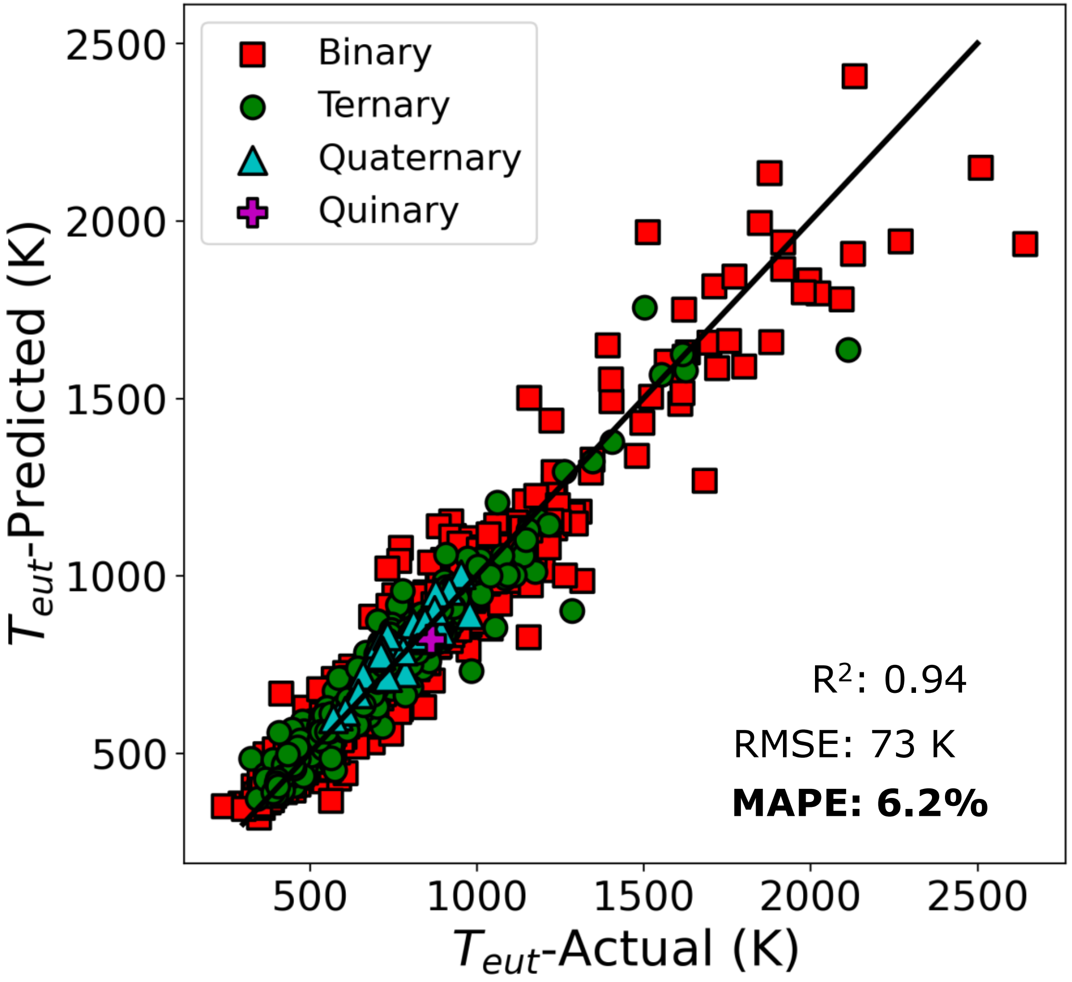
Machine Learning Models - Gradient Boosting

One model for all order mixtures



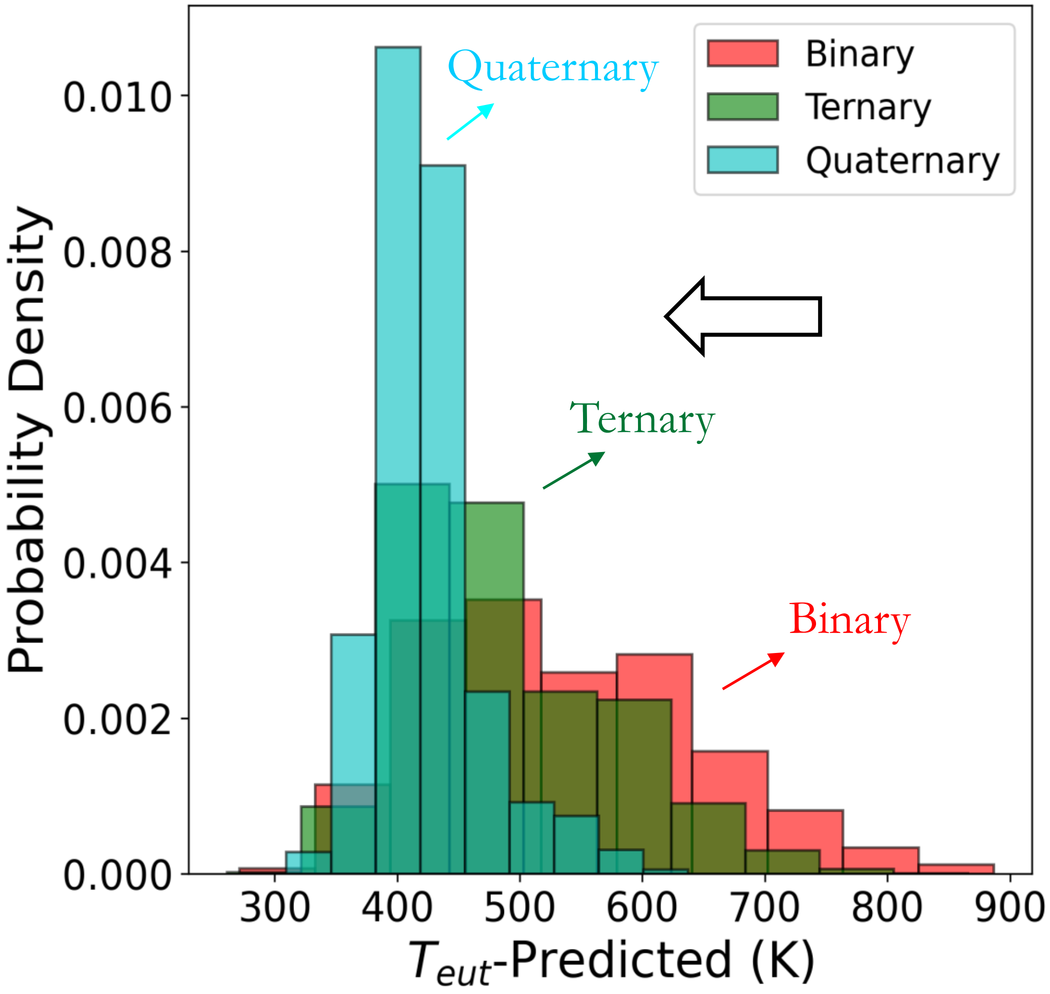
Model details	
Features	MAGPIE + T_m + # Components
# Estimators	800
Learning rate	0.01
Cross-validation	10-fold

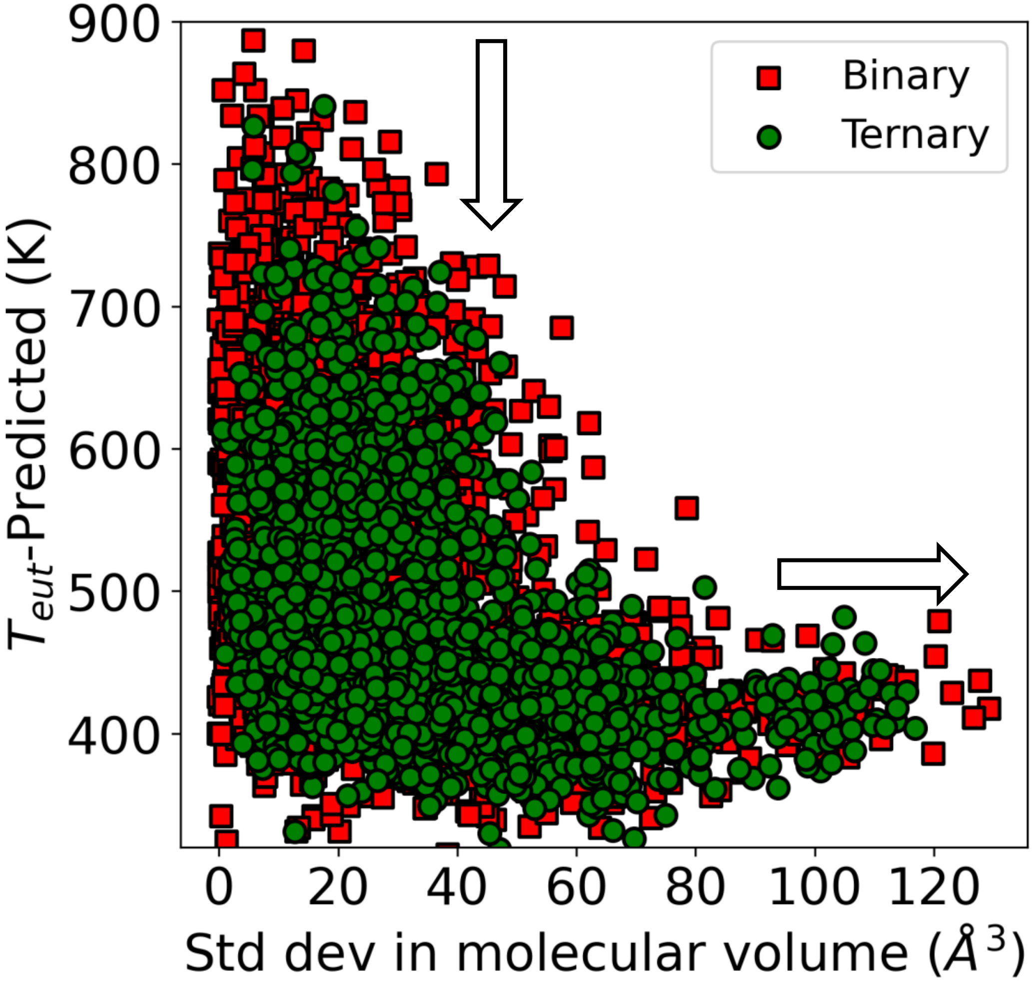
~1300 mixtures



Best performing model – GB

Designing New Mixtures – Overall Distribution

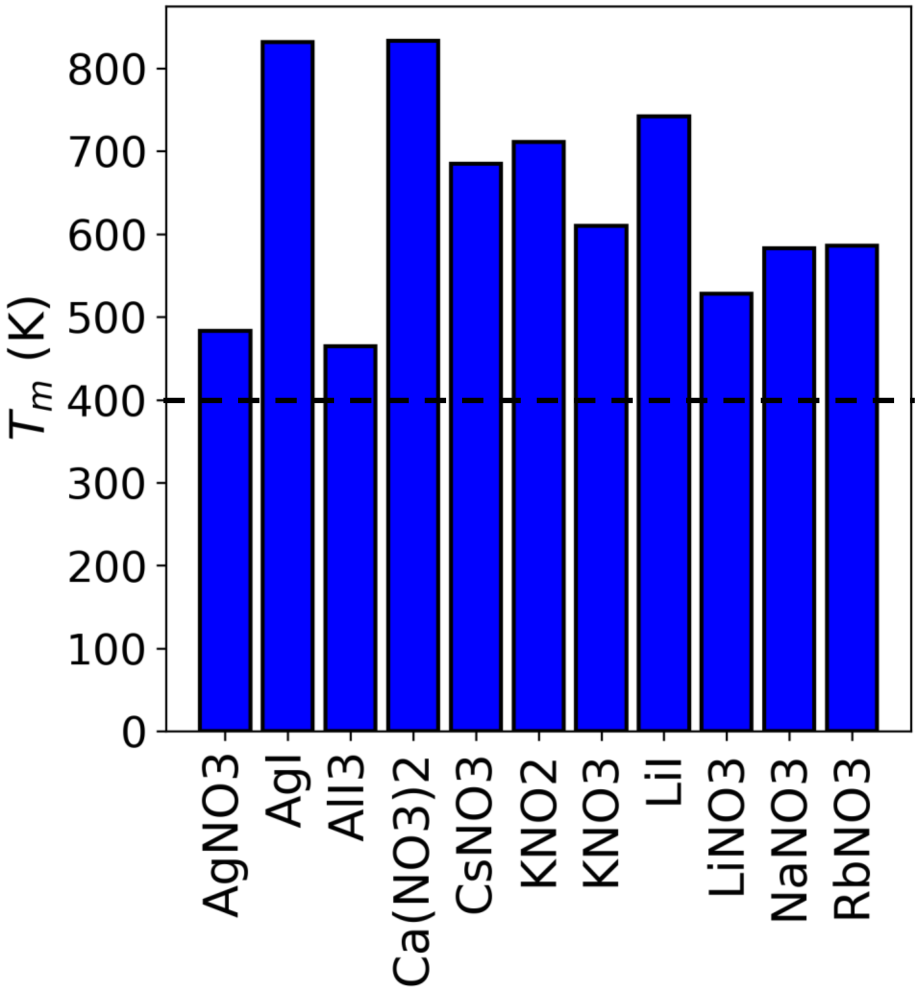




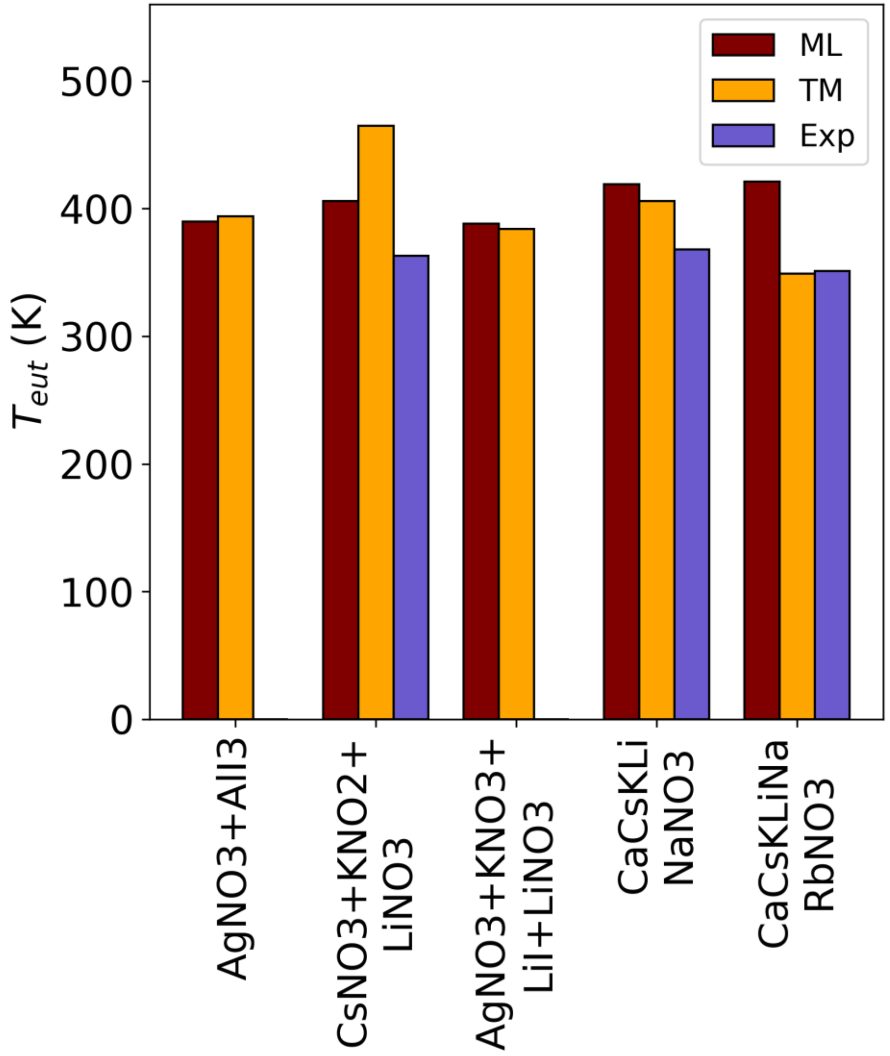
Configurational entropy and molecular sizes are important in designing low temperature eutectics

Designing New Mixtures – Specific Mixtures

Pure component T_m



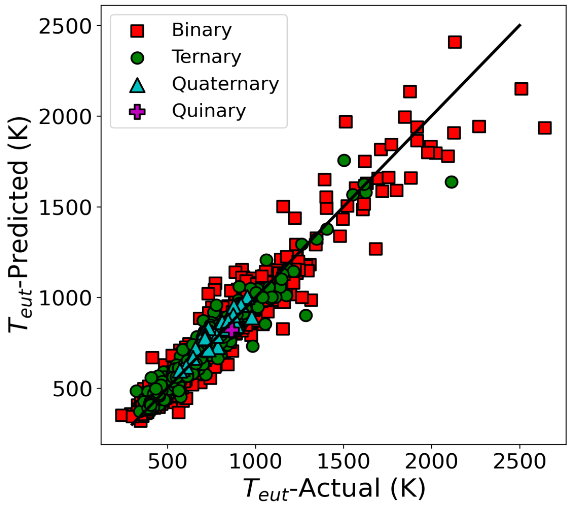
Selected novel eutectics



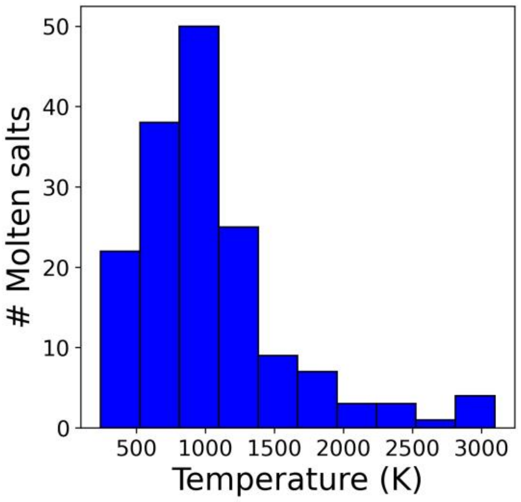
High throughput screening identifies novel molten salt mixtures

Summary

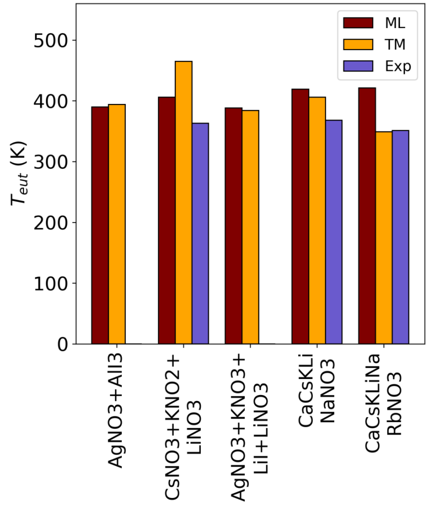
Combination of ML and thermodynamic modeling provides independent validation



Correlation to molecular features provides design insight



Pure component properties → ML ✚ Thermodynamic modeling → **High throughput screening**



Acknowledgments

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Backup

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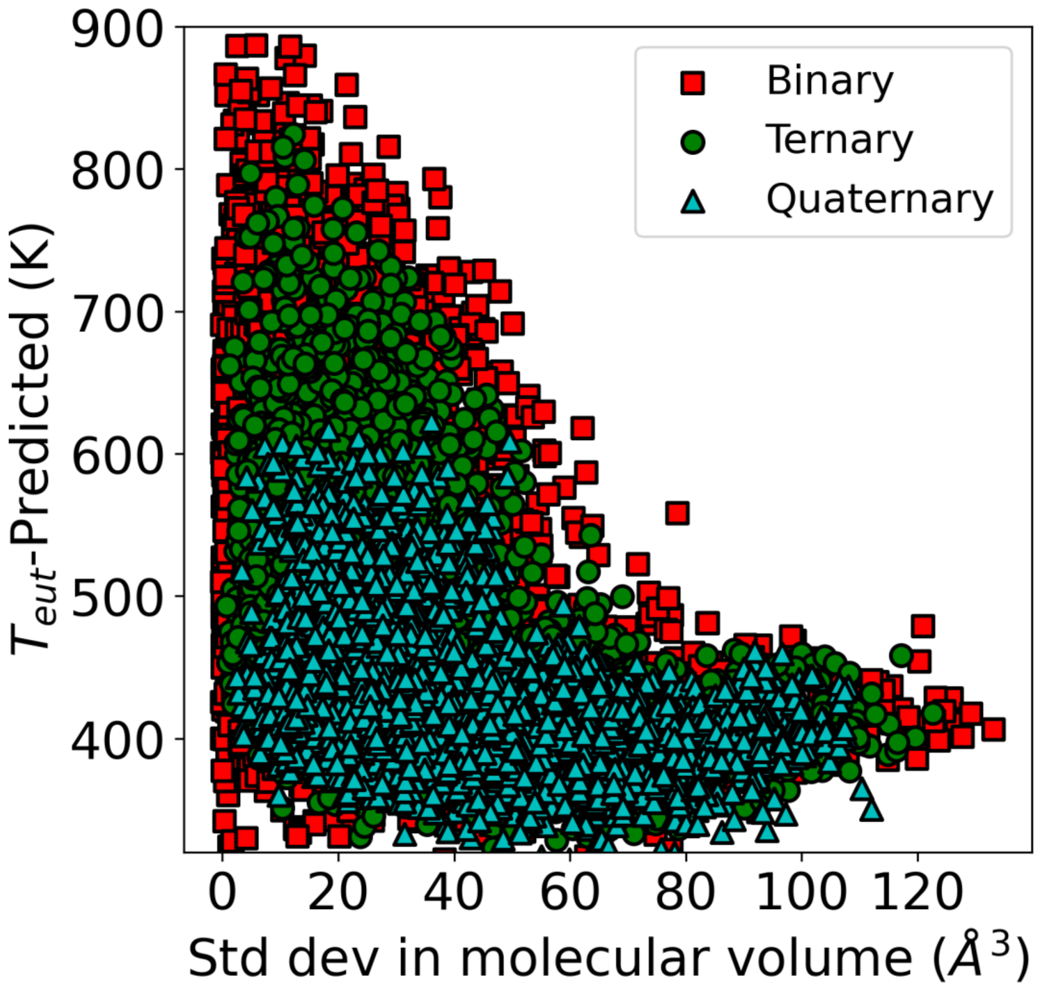
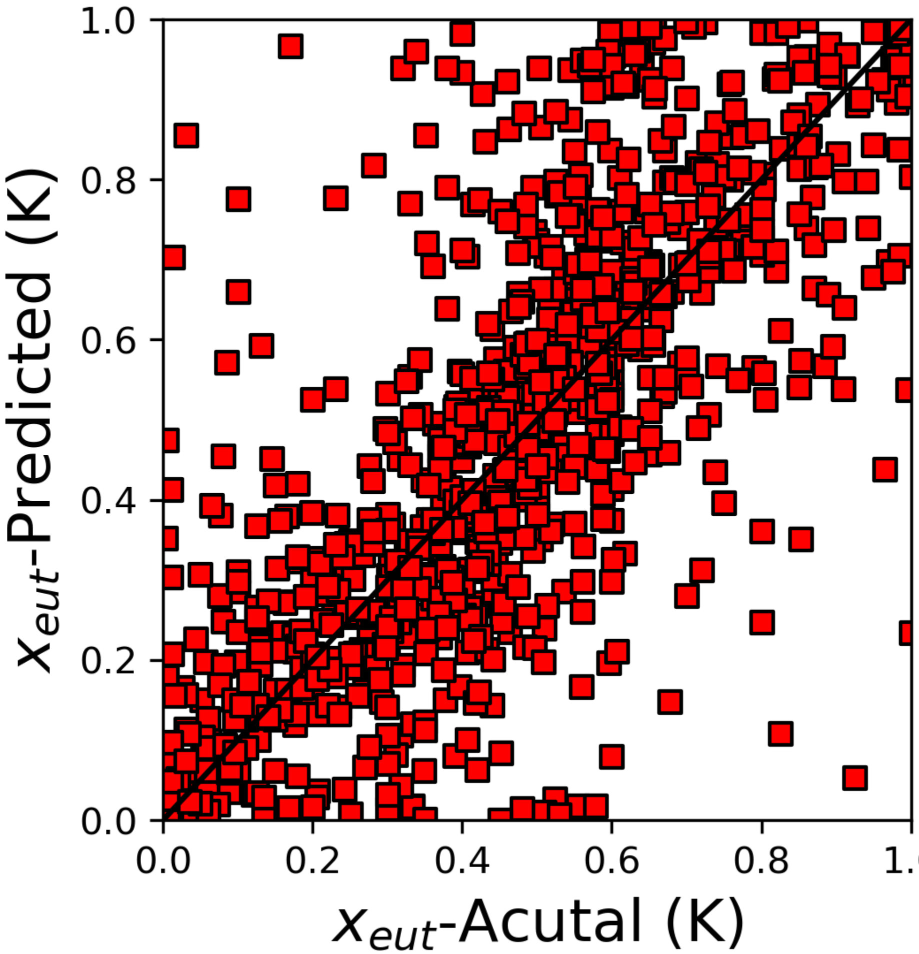
Correlation to molecular volume



Composition prediction – Ideal Thermodynamic Model



Designing New Mixtures

Binary mixture

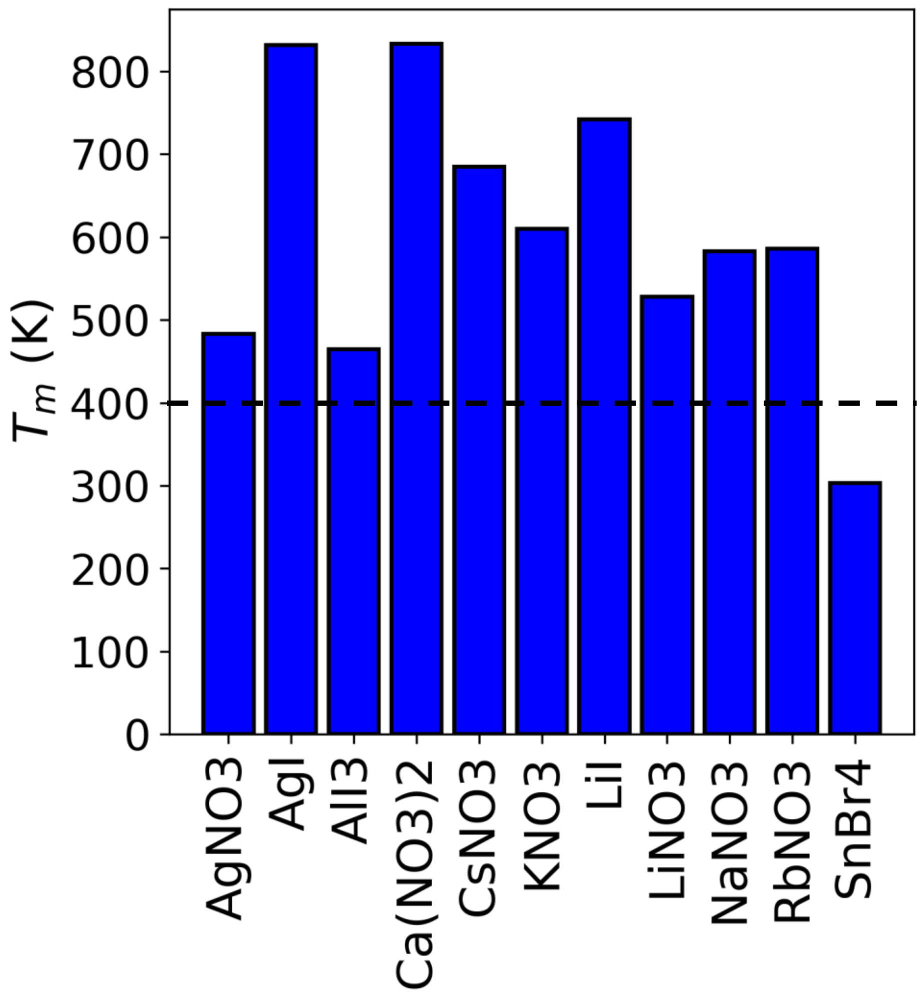
Mixture	Predicted (K)	
	ML	TM
AgNO3+AlI3	390	394

Ternary mixture

Mixture	Predicted (K)	
	ML	TM
AgI+AgNO3+ LiNO3	380	407

Quaternary mixture

Mixture	Predicted (K)	
	ML	TM
AgNO3+KNO3 +LiI+LiNO3	388	384



Quinary mixture

Mixture	Predicted (K)		Expt (K)
	ML	TM	
CaCsKLiNaNO3	419	406	368

Six component mixture

Mixture	Predicted (K)		Expt (K)
	ML	TM	
CaCsKLiNaRb NO3	421	349	351