Molten Salt Reactor PROGRAM

Thermophysical Properties of $AmCl_3$ - $CaCl_2$ Systems Determined via Molecular Dynamics

Manh-Thuong Nguyen

Physical and Computational Sciences Directorate

Pacific Northwest National Laboratory

Richland, Washington 99354, USA

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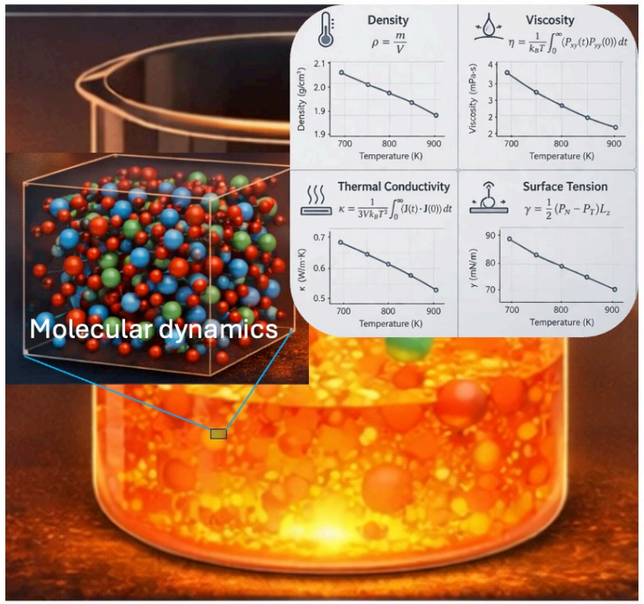
$AmCl_3$-$CaCl_2$: Computational

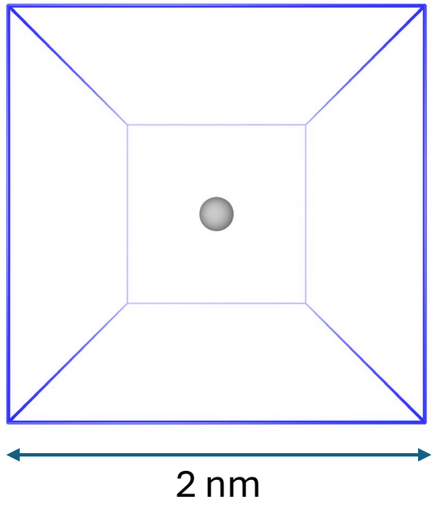
Milestone Number	Milestone title	Due Date	Status
M3AT-26PN070407	Complete computational determination of the thermophysical properties of $AmCl_3$-$CaCl_2$ system using molecular dynamics	09/30/2026	On schedule

Content

- Computational approach.
- Density for 0, 50, and 100 mol% $AmCl_3$ systems.
- Heat capacity.
- Thermal conductivity & thermal diffusivity.
- Publications & presentations.

General approach: Machine learning interatomic potentials, trained on ab initio data, are used to accelerate molecular dynamics simulations

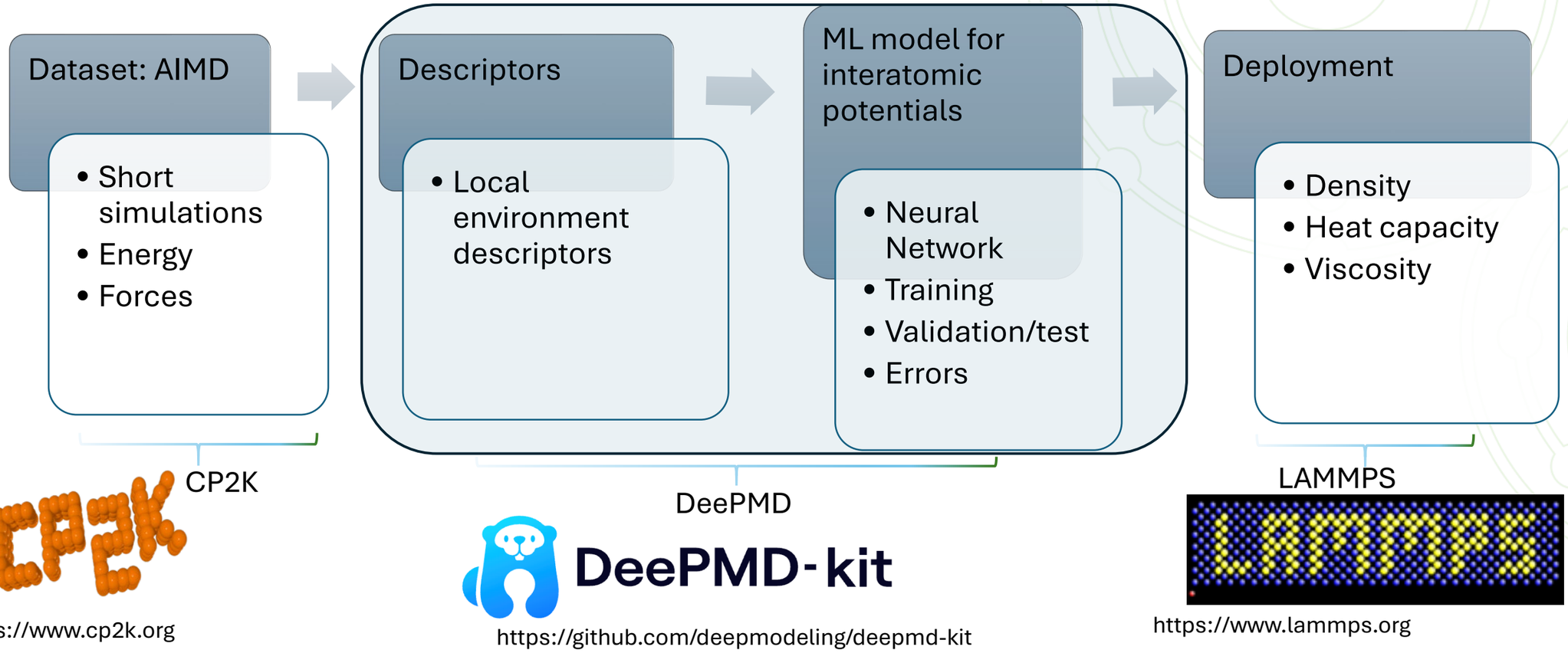




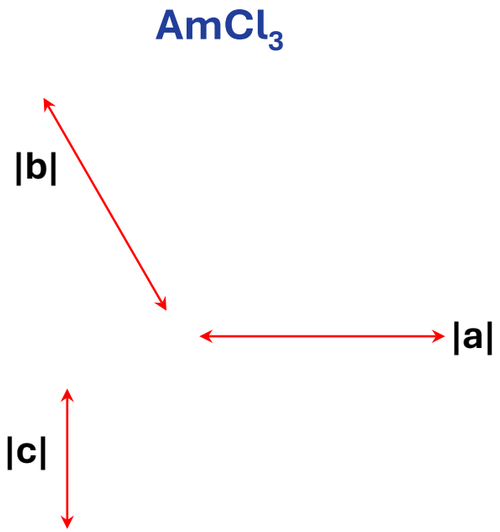
Ab initio (DFT) calculation for 1 atom using 1CPU of Apple M2 Ultra, 64 GB		
Atom	Ca	Am
Valance electrons	$3s^2\ 3p^6\ 4s^2$	$5f^7\ 6s^2\ 6p^6\ 7s^2$
CPU time	~6 mins	~ 30 mins

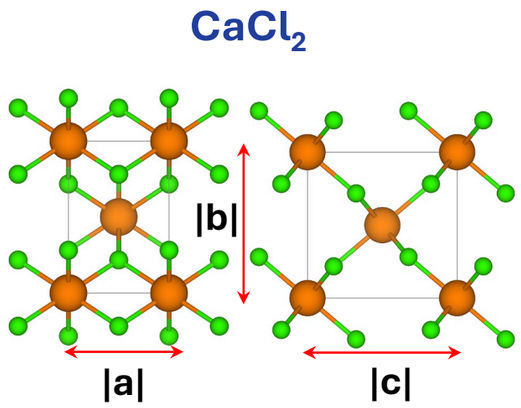
- Ab initio molecular dynamics (AIMD): accurate but computationally demanding.
- Machine learning interatomic potentials, trained on AIMD data, provide a viable approach.

General approach: Machine learning interatomic potentials, trained on ab initio data, are used to accelerate molecular dynamics simulations



Step1: Solid-state calculations serve as a benchmark for validating the used methodology





	$AmCl_3$			$CaCl_2$		
	Theory	Exp.	Error(%)	Theory	Exp.	Error(%)
|a| (Å)	7.337	7.390	0.7	4.16	4.20	0.9
|b|(Å)	7.337	7.390	0.7	6.12	6.24	1.2
|c| (Å)	4.234	4.234	~0.0	6.43	6.43	~0.0

Ab initio calculations

- revPBE-vdW density functional.
- GPW approach: DZVP basis sets, 600 Ry cutoff.
- GTH pseudopotentials.
- CP2K code.
- Small errors with respect to experimental data.

Exp.: Asprey et al., Inorg. Chem. 1965, 4, 7, 985–986
Bever et al. Kristallgeometrie, Kristallphysik, Kristallchemie 1935, 90, 374– 376

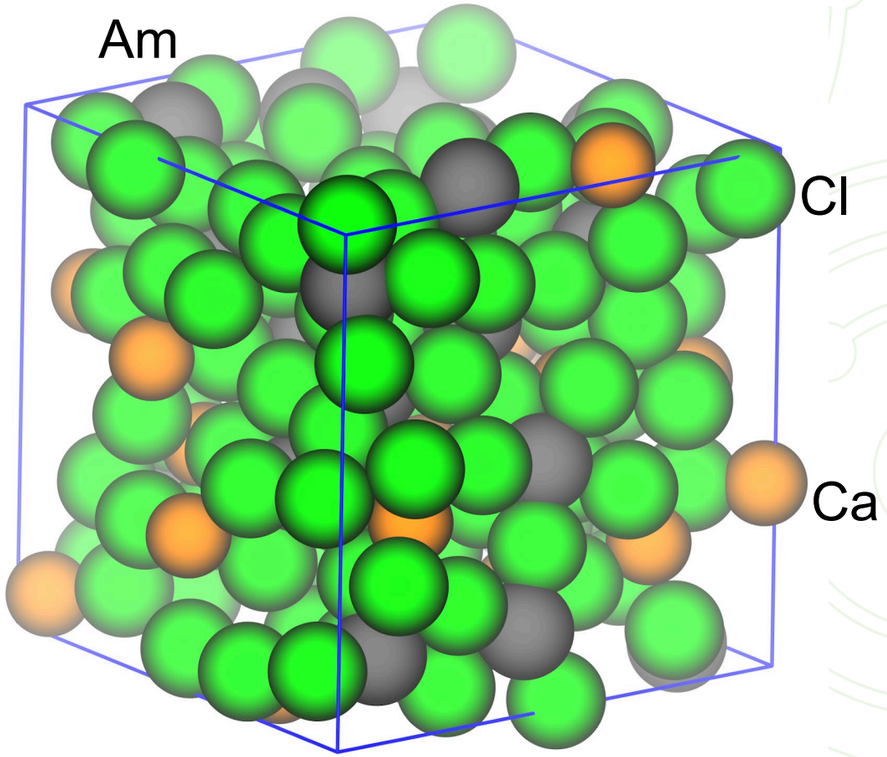
We constructed a database for each liquid system using AIMD

$AmCl_3$ –$CaCl_2$ systems:

- Compositions: 0, 50, and 100 mol% $AmCl_3$.
- Over 170 atoms per simulation cell.

Molecular dynamics recipe:

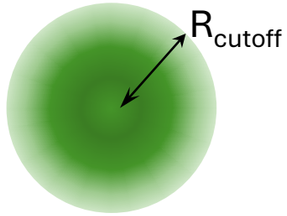
- Classical molecular dynamics – equilibrated systems as starting points.
- NPT ensemble, dt=2.5 fs.
- CP2K code.
- 100 ps trajectories.



Step 2: Error metrics show that machine learning interatomic potentials (MLIP) are accurate

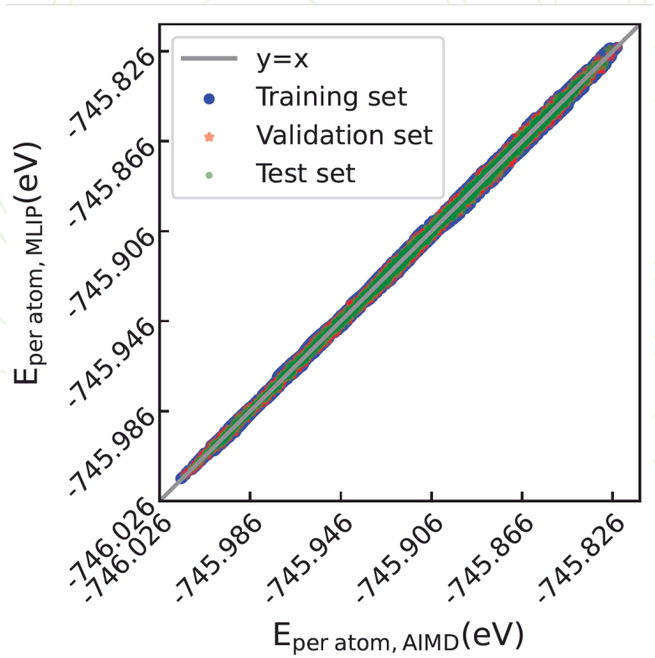
DeePMD method

- 32K frames for training set (coordinates, energies, forces).
- 4K frames for validation set.
- 4K frames for test set.
- Loss function for energy and force.
- 6.5 Å cutoff.
- {250,250,250} fitting network.
- Small energy and force errors.



$$\boldsymbol{R}_i = \{\boldsymbol{r}_{ij} \equiv \boldsymbol{r}_i - \boldsymbol{r}_j\}$$

$$\mathcal{L} = p_E|\Delta E|^2 + \frac{p_f}{3N}\sum_i |\Delta F_i|^2$$



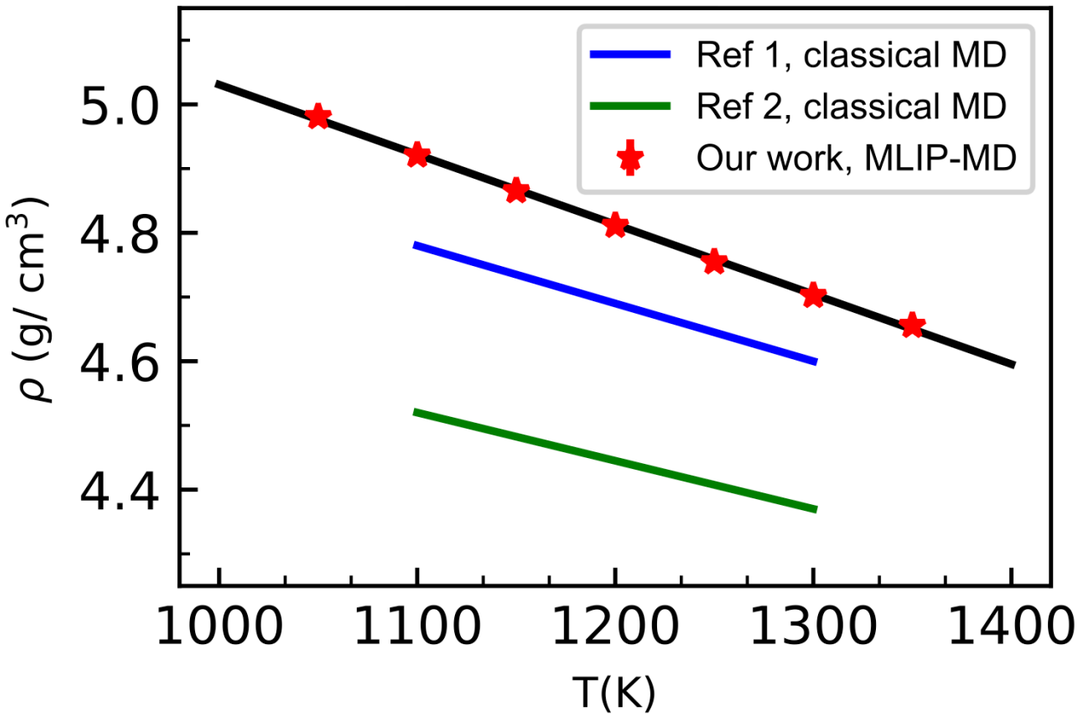
50 mol% $AmCl_3$ system	Training set	Validation set	Test set
Energy MAE/atom (meV)	1.03	1.02	1.04
Energy RMSE/atom (meV)	1.31	1.29	1.32
Force MAE (meV/Å)	56	56	57
Force RMSE (meV/Å)	75	75	75

Step 3: The liquid density was calculated over a range of temperatures

$$\rho = \frac{m}{V}$$

- MLIP molecular dynamics.
- NPT ensemble.
- P = 1 atm, T= ~1050-1400 K.
- Barostat and thermostat.
- LAMMPS code.
- Exhibits deviation from classical molecular dynamics results reported in the literature for $AmCl_3$.

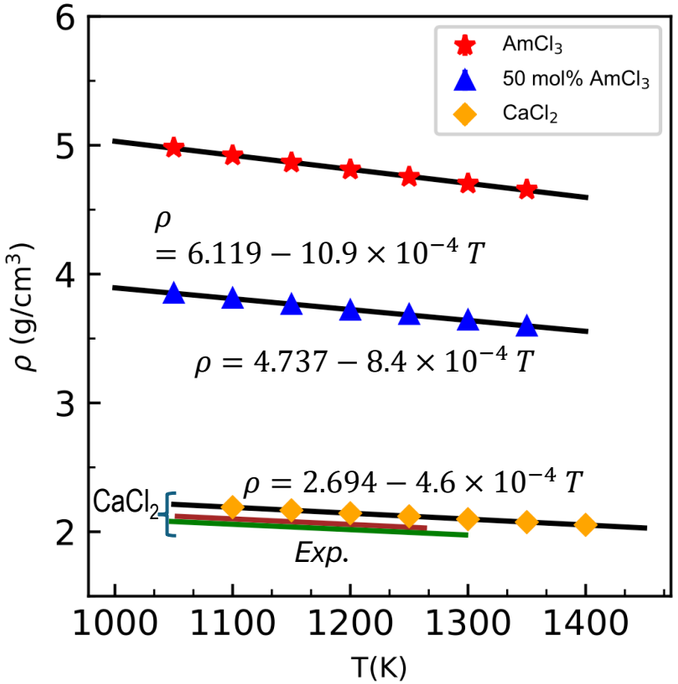
$AmCl_3$ density



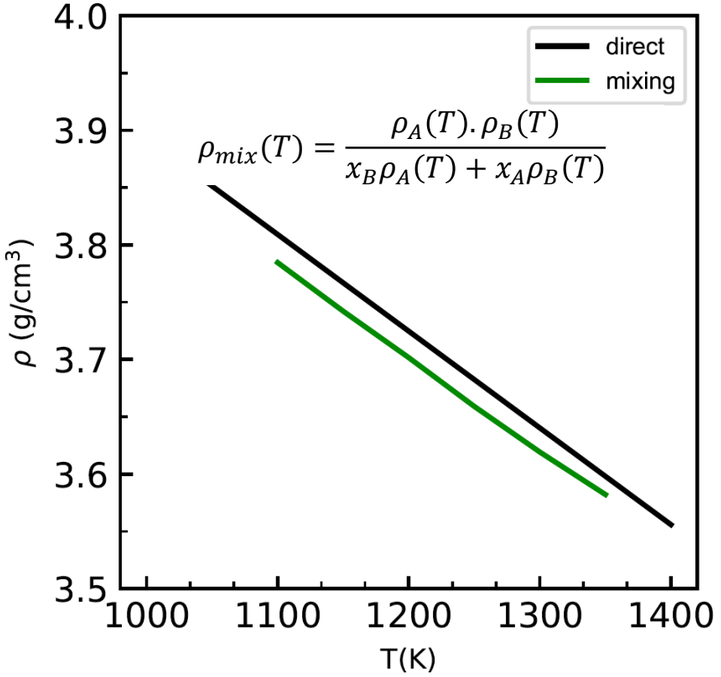
Ref 1: Notarangelo et al. J. Phys. Chem. B **2026**, 130, 2, 814–828
Ref 2: Pireddu et al. J. Nucl. Mater. 612 (**2025**) 155822

Calculated density strongly depends on the composition

$AmCl_3 – CaCl_2$ density



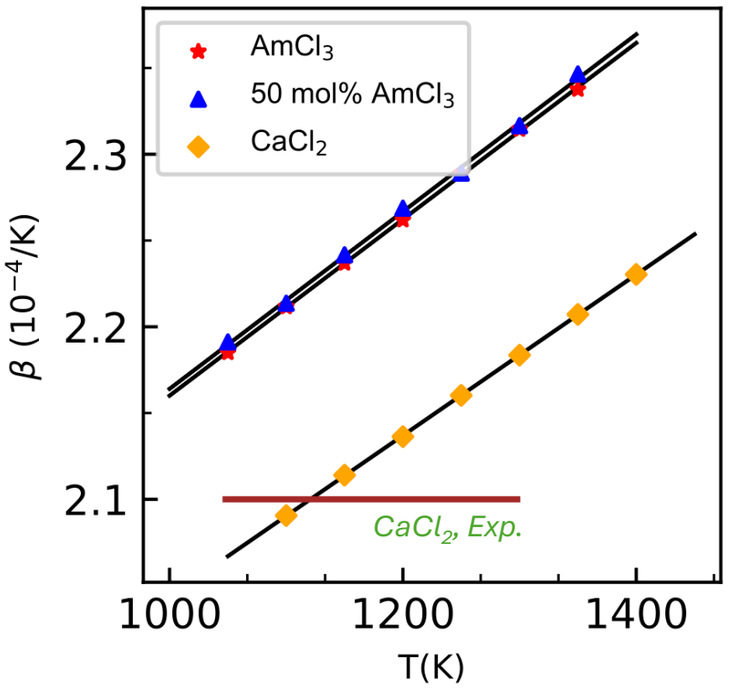
50 mol% $AmCl_3$ density

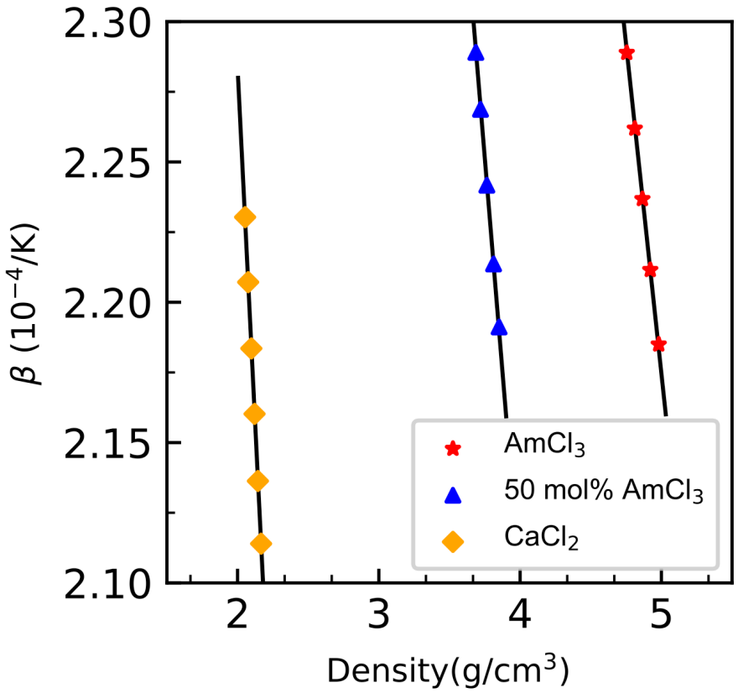


- The calculated density of $CaCl_2$ is consistent with experiment.
- The density of $AmCl_3$ varies most strongly with temperature.
- The density of the $AmCl_3$-$CaCl_2$ system slightly deviates from the mixing rules, indicating small excess molar volume.

*Exp.: Katyshev and Desyatnik. Soviet Atomic Energy 51.6 (**1981**): 810-812*
Parker et al., Journal of Molecular Liquids 346 (**2022**): 118147.

The stronger temperature dependence of density in the $AmCl_3$ system reflects its larger volumetric thermal expansion coefficient



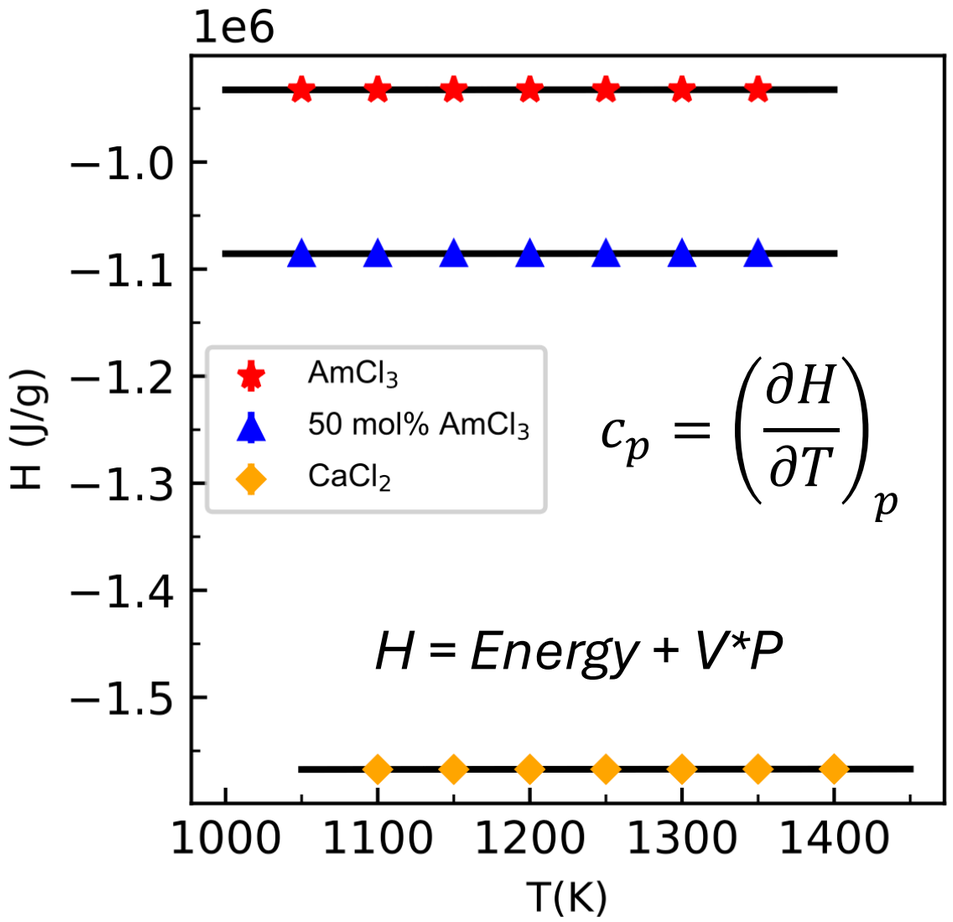


$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p$$

- Salts expand with temperature.
- Small, but linearly increased with temperature.
- $AmCl_3 \approx AmCl_3\text{-}CaCl_2 \gg CaCl_2$.

Exp.: Parker et al., Journal of Molecular Liquids 346 (**2022**): 118147.

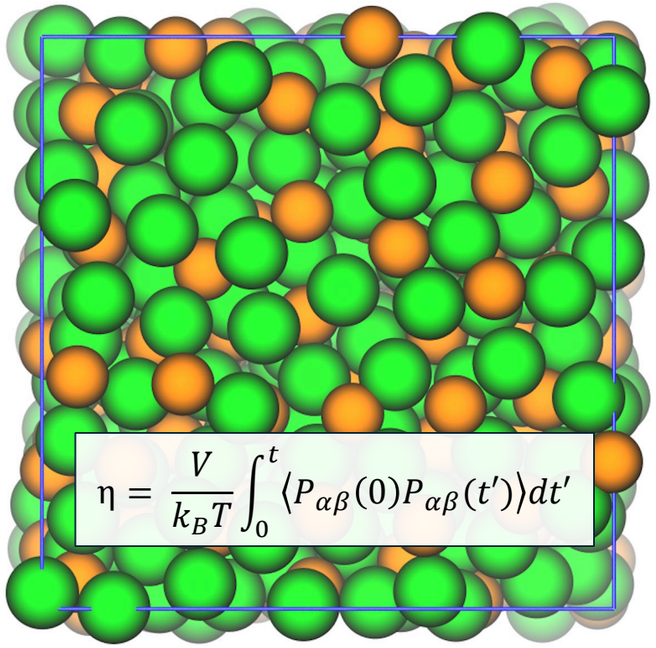
Calculated specific heat capacity c_p for $AmCl_3$ agrees with experimental data



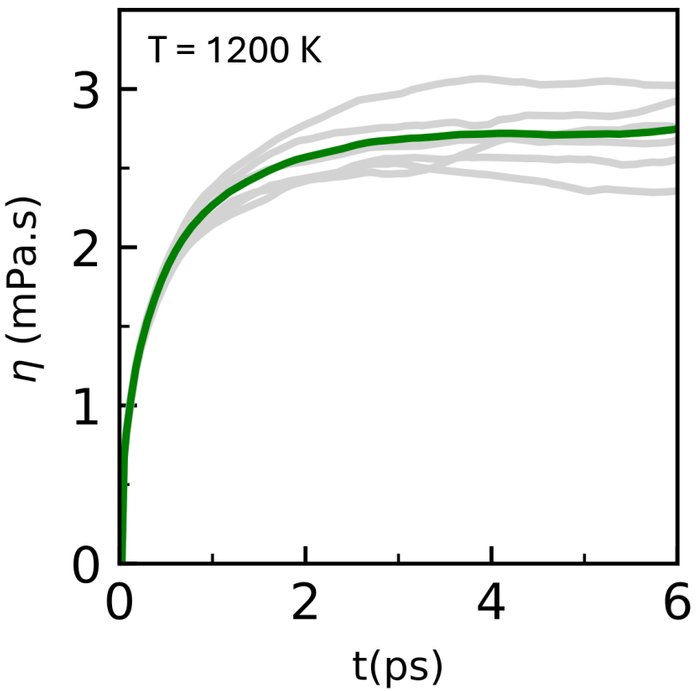
	c_p(J /g K)		
	This work	Exp.	Classical MD
$AmCl_3$	0.41	0.41[1] 0.41[2]	0.38[3] 0.39[4]
50mol% $AmCl_3$	0.56		
$CaCl_2$	0.98		

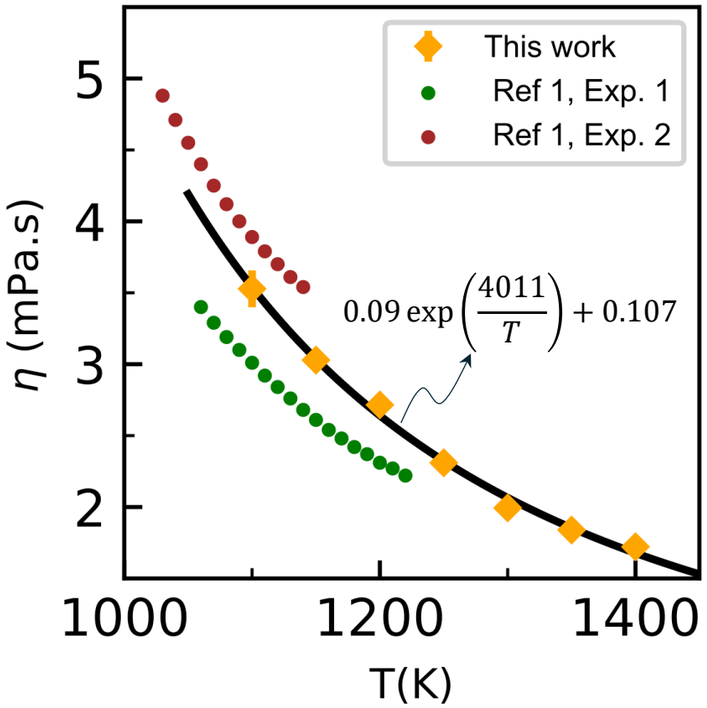
Ref 1: Masset et al., *J. Nucl. Mater.* **2005**, *344*, 173– 179
Ref 2: Sero et al., Electrochimica acta 51.19 (**2006**): 4024-4032
Ref 3: Notarangelo et al. J. Phys. Chem. B **2026**, 130, 2, 814–828
Ref 4: Ref 2: Pireddu et al. J. Nucl. Mater. 612 (**2025**) 155822

The viscosity of $CaCl_2$ shows a strong decrease with increasing temperature



540 atoms; ~2.5 nm each dimension

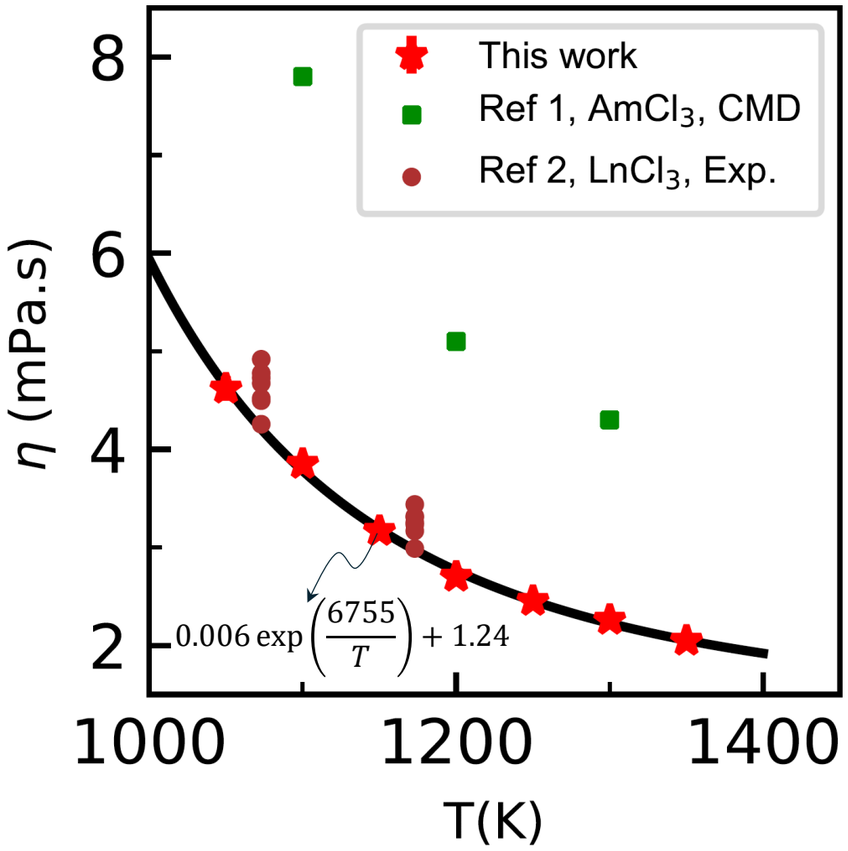




- Large simulation systems; Green-Kubo approach; multiple simulations for 1 data point.
- Calculated viscosity ”consistent” with experimental data.

Ref 1: Janz et al. J. Phys. Chem. Ref. Data. 4, 871 (**1975**)

Calculated viscosity of $AmCl_3$ significantly differs from literature data



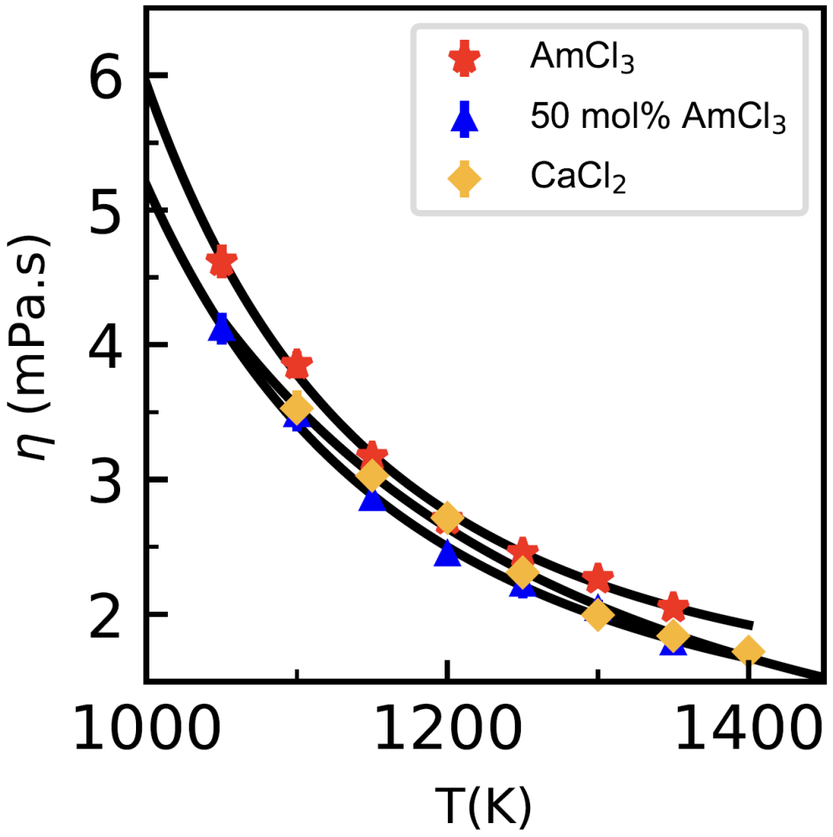
- No available experimental data.
- Consistent with measured data for lanthanide chloride ($LnCl_3$) surrogates.
- About 2 times lower than reported classical molecular dynamics (CMD) data.

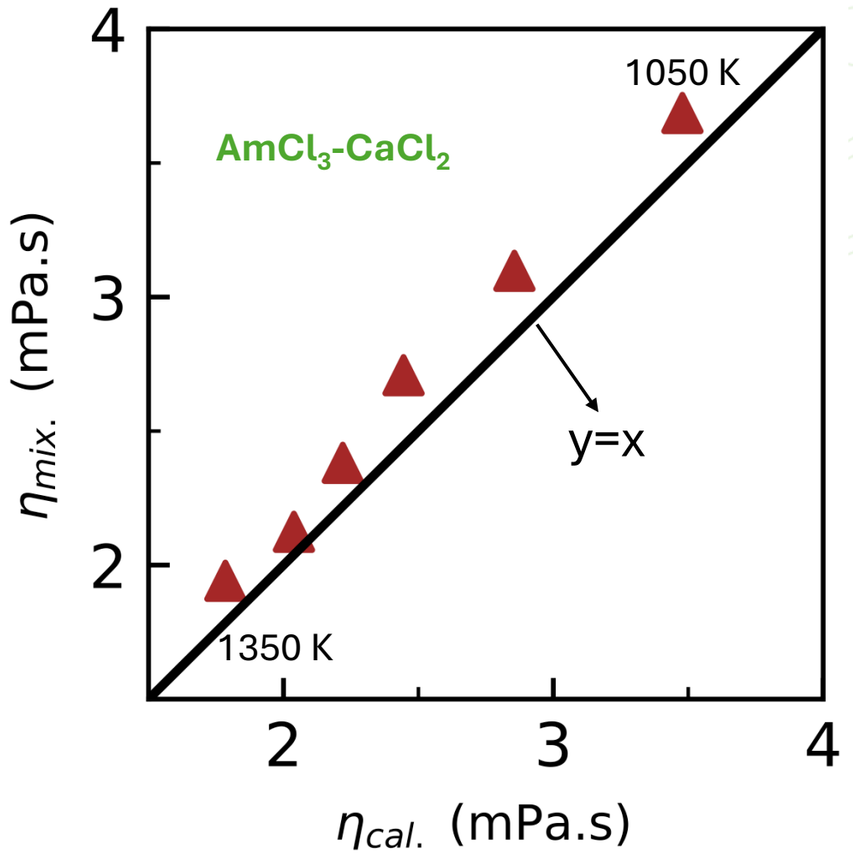
Ref 1: Notarangelo et al. J. Phys. Chem. B **2026**, 130, 2, 814–828
Ref 2: Potapov and Sato. Zeitschrift für Naturforschung A 66.10-11 (**2011**): 649-655.

Viscosity exhibits a slight dependence on composition

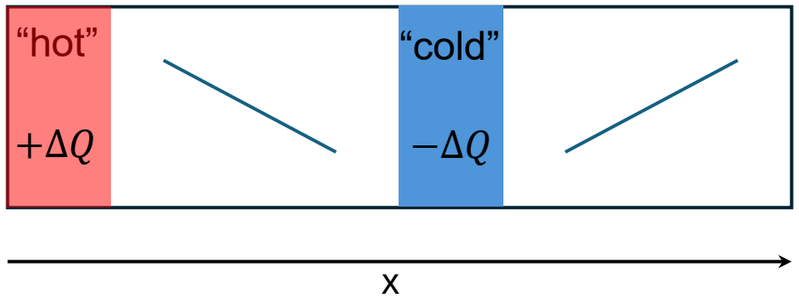
Logarithmic (Arrhenius-type) mixing rule

$$\ln \eta_{mixing} = x_A \ln \eta_A + x_B \ln \eta_B$$



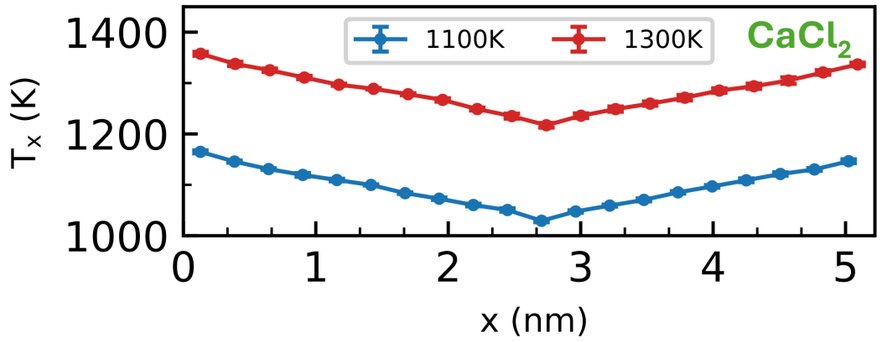


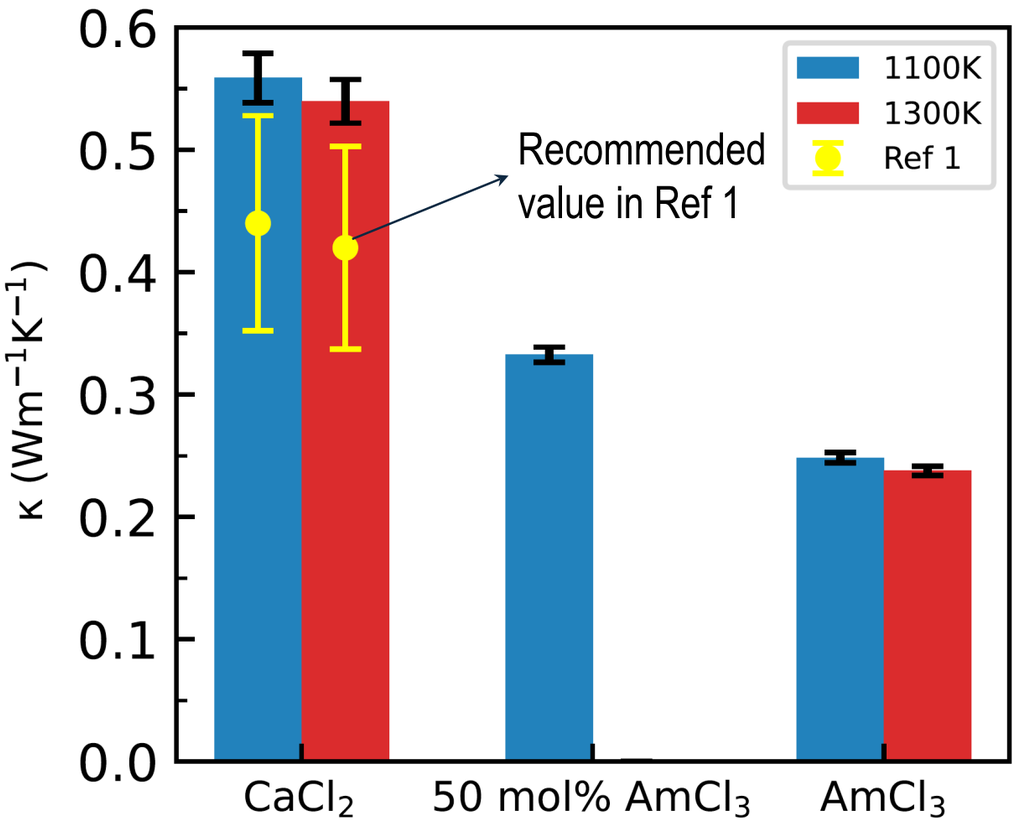
The thermal conductivity of molten $AmCl_3$ is low



- Non-equilibrium molecular dynamics.
- Fourier's Law

$$\kappa = \frac{\Delta Q}{2S_{yz}\Delta t \frac{\Delta T}{\Delta x}}$$

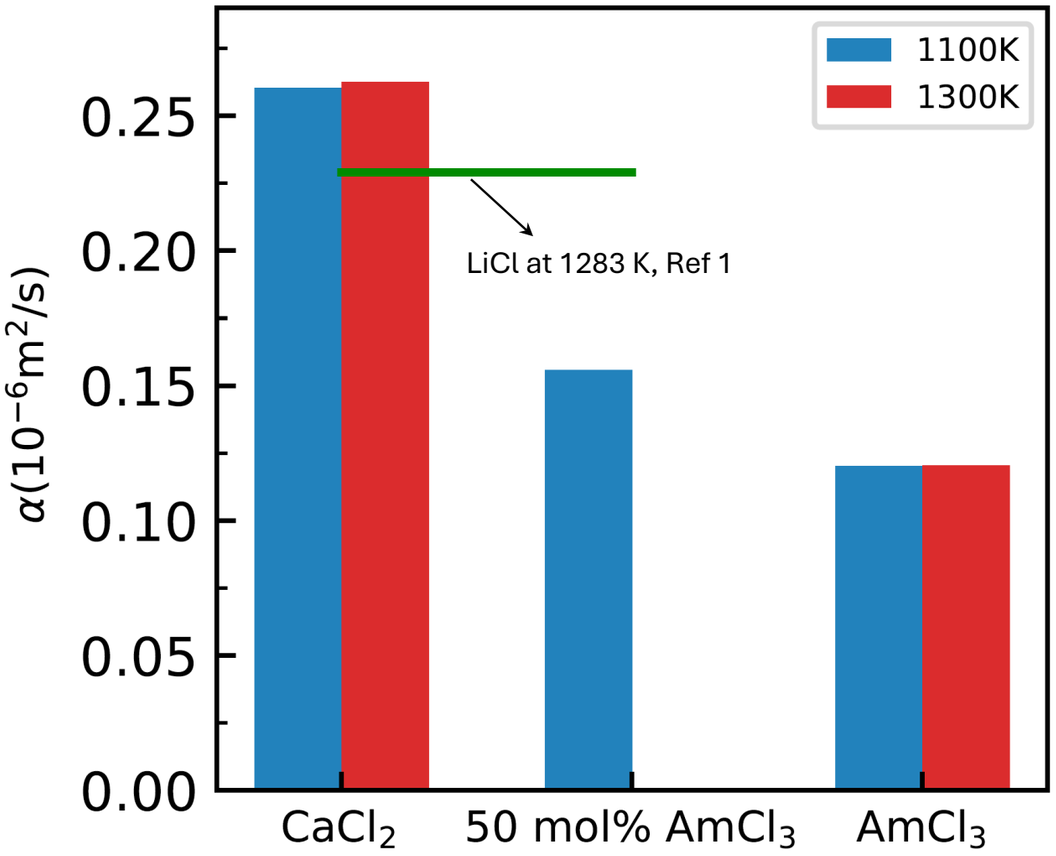




- Higher with $CaCl_2$.
- Slightly decreased with temperature.

*Ref 1: Gheribi et al. Solar Energy Materials & Solar Cells 126 (**2014**) 11–25*

$CaCl_2$ improves thermal diffusivity



$$\alpha = \frac{\kappa}{\rho c_p}$$

- No experimental data.
- Faster heat transport with $CaCl_2$.

Ref 1: Nagasaka et al., *Int. J. Thermophys.*13.4 (**1992**): 555-574

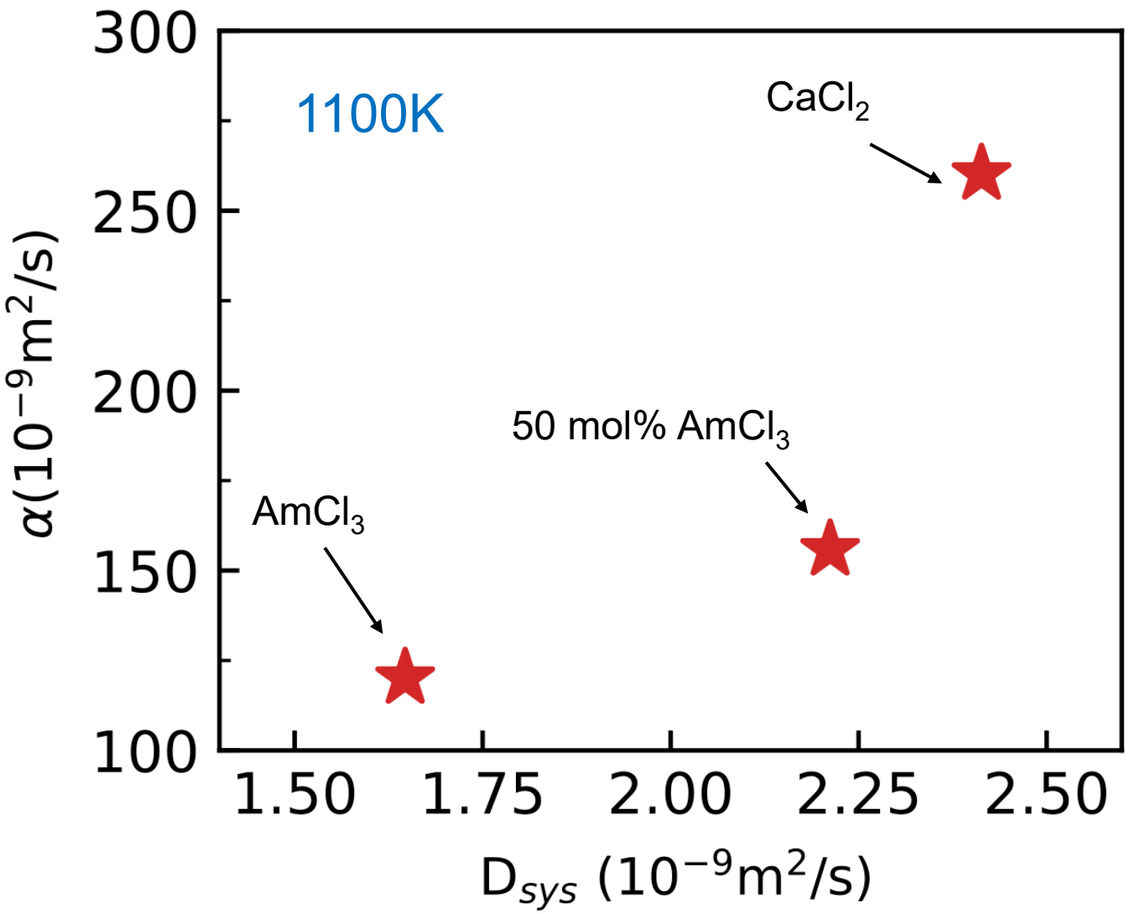
As expected, heat transport is faster than mass transport

$$MSD_i \equiv < |ri(t) - ri(0)|^2 >$$

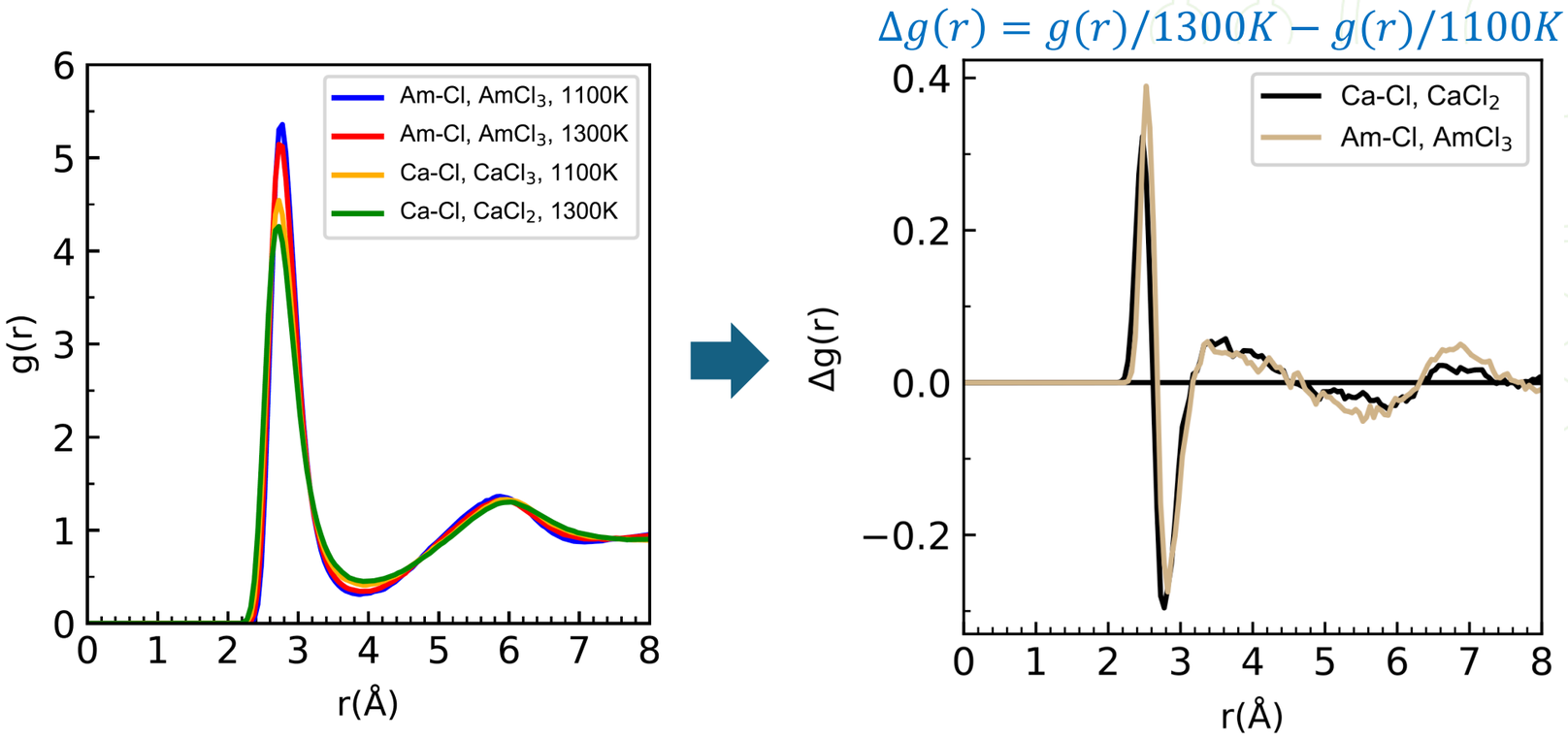
$$D_i = \frac{1}{6}\frac{d(MSDi)}{dt}$$

$$D_{sys} = \sum_i a_i D_i$$

- Diffusion coefficients calculated using mean square displacement (MSD).
- Thermal diffusivity correlated with diffusivity.



Why do some properties of $AmCl_3$ exhibit a stronger temperature dependence than those of $CaCl_2$?– An interpretation



- The radial distribution function of metal-Cl pairs is changed by the temperature.
- Reorganization of Am^{3+} coordination environments shows greater temperature effects.

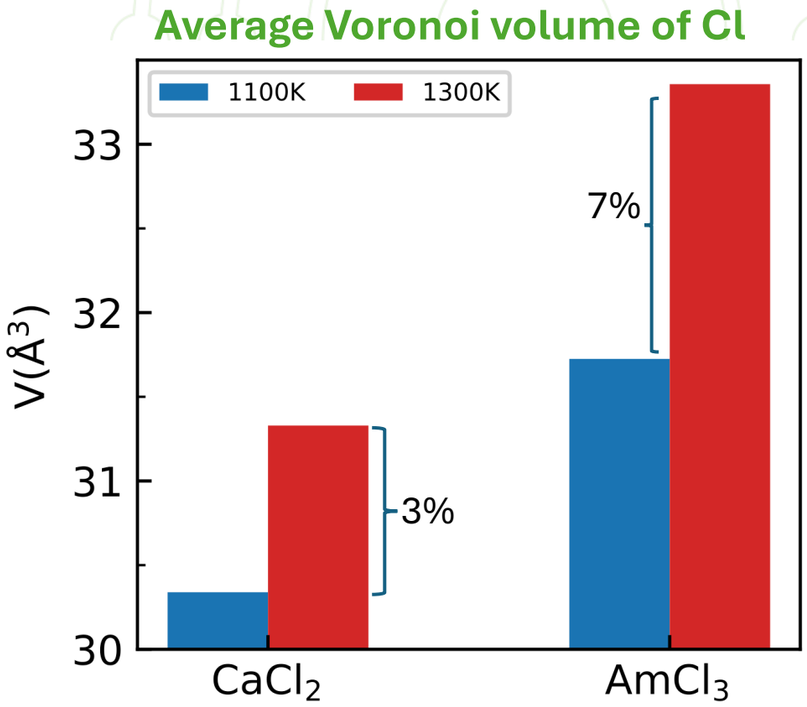
Voronoi volume changes with temperature are consistent with corresponding density variations

Density

$$\rho_{AmCl_3} = 6.119 - 10.9 \times 10^{-4}\, T$$

$$\rho_{CaCl_2} = 2.694 - 4.6 \times 10^{-4}\, T$$

Voronoi diagram
(credit: wikipedia)



- The density of $AmCl_3$ changes more rapidly with temperature than that of $CaCl_2$.
- The salts expand with temperature through an increase in local free space and local packing volume.
- Voronoi volume can be used as a microscopic proxy for density.

Summary

- Thermophysical properties of $AmCl_3$, $AmCl_3$-$CaCl_2$, and $CaCl_2$ are calculated by using accurate machine learning interatomic potentials.
- The dependence of density and thermal expansion coefficients on the temperature is more significant in $AmCl_3$ than in $CaCl_2$.
- The viscosity of the mixture approximately following the logarithmic mixing rule.
- Calculated heat capacity of $AmCl_3$ is consistent with experimental data.
- Thermal conductivity decreases with increasing $AmCl_3$ content.
- Temperature-dependent changes in some thermophysical properties can be linked to microscopic features such as radial distribution functions and Voronoi volumes.

Next steps

- Investigate 25 (and 75) mol % $AmCl_3$ system.
- Develop structure-property relationship.

Publications and Presentations

***Peer-reviewed journals*:**

- Michaella S. Harris, Kyle A. Makovsky, Manh-Thuong Nguyen, Ji-Hye Seo, and Kent Detrick, "A Combined Experimental and Computation Study of KCl-$MgCl_2$ for Molten Salt Applications", *Nuclear Engineering and Design* (*under review*).
- Manh-Thuong Nguyen, "Toward Rapid Prediction of Molten Salt Properties: A Machine Learning Study of Liquid Density" (*in preparation*).

***Presentations*:**

- "Modeling Molten Salts Using Electronic Structure, Statistical Mechanics, and Data Science", Seminar at the University of Alabama, Tuscaloosa, AL 35487, United States; March 10, 2026.

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Thank you

manhthuong.nguyen@pnnl.gov