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Molten Salt Reactor PROGRAM

Ab initio molecular dynamics study of $MgCl_2$-KCl mixtures

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OBJECTIVE

We will generate missing thermophysical, structural, and transport data for $MgCl_2$–KCl mixtures at different temperatures and compositions using atomistic modeling and data science.

❑ Scope

- We propose to investigate the binary system of $MgCl_2$–KCl with different compositions and temperatures using ab initio molecular dynamics
- This research will be complementary to experimental studies by the team led by Kyle Makovsky at PNNL.

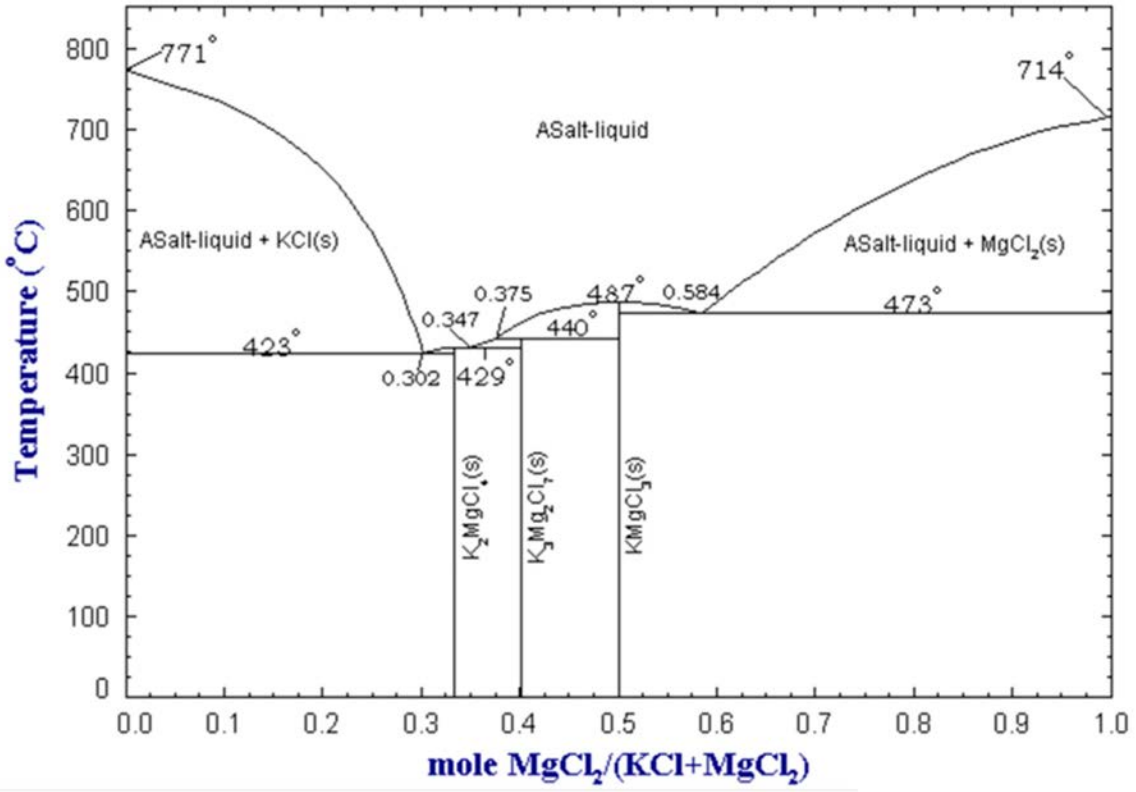
❑ Milestone

- Level 3 milestone, complete summary report on binary systems of $MgCl_2$-KCl using AIMD, due September 30, 2024.

Why $MgCl_2$-KCl?

- Important (and interesting)
- Abundant resource
- Relatively low melting point
- Can be used as coolant salts
- Not only for nuclear energy but also for solar energy.

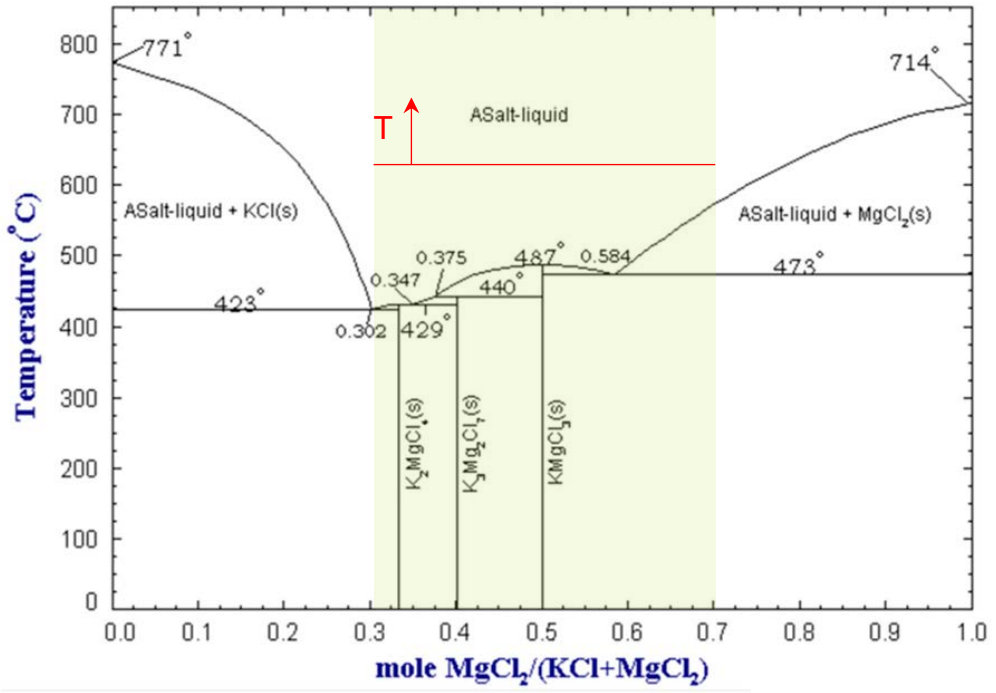
$MgCl_2$-KCl phase diagram



Milani et al. Metals **2023**, *13*(5), 832

Investigated systems

- Works in the literatures usually focus on the eutectic mixture (~ 0.32 $MgCl_2$ 0.68 KCl)
- Five $xMgCl_2(1-x)KCl$ compositions: x = 0.3, 0.4, 0.5, 0.6, and 0.7
- Four temperatures: 900, 1000, 1100, and 1200 K
- Totally, 20 systems.



Milani et al. Metals **2023**, *13*(5), 832

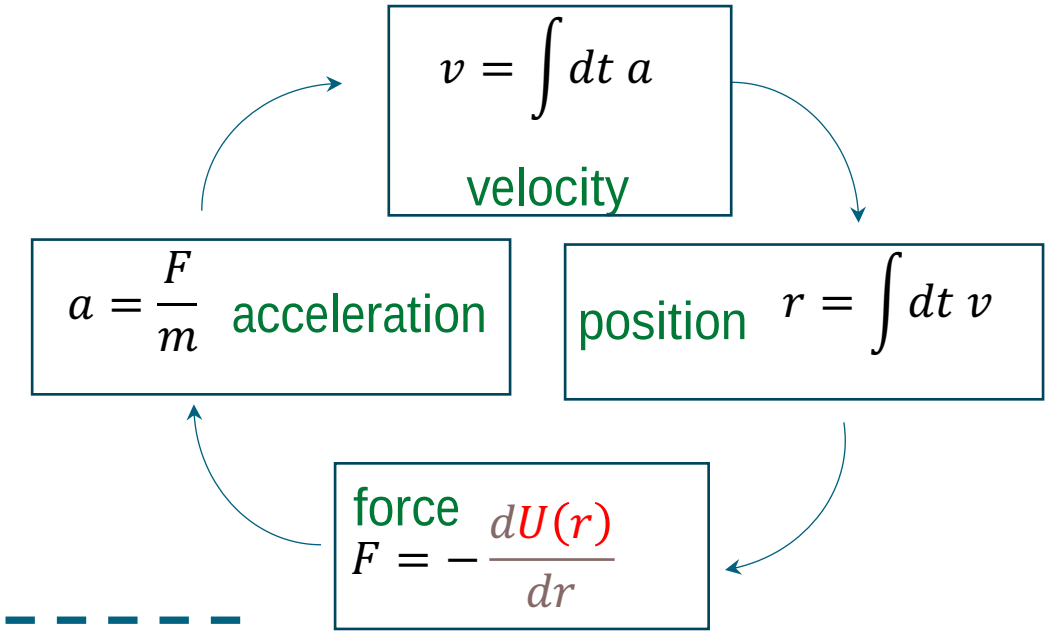
Molecular dynamics for molten salts

- Wide range of properties:
  - Density; Heat capacity
  - Mass transport; Charge transport
  - Heat transport; Viscosity
  - Enthalpy; Entropy
  - Structure.

AIMD (in use): **potential energy surface U(r)**

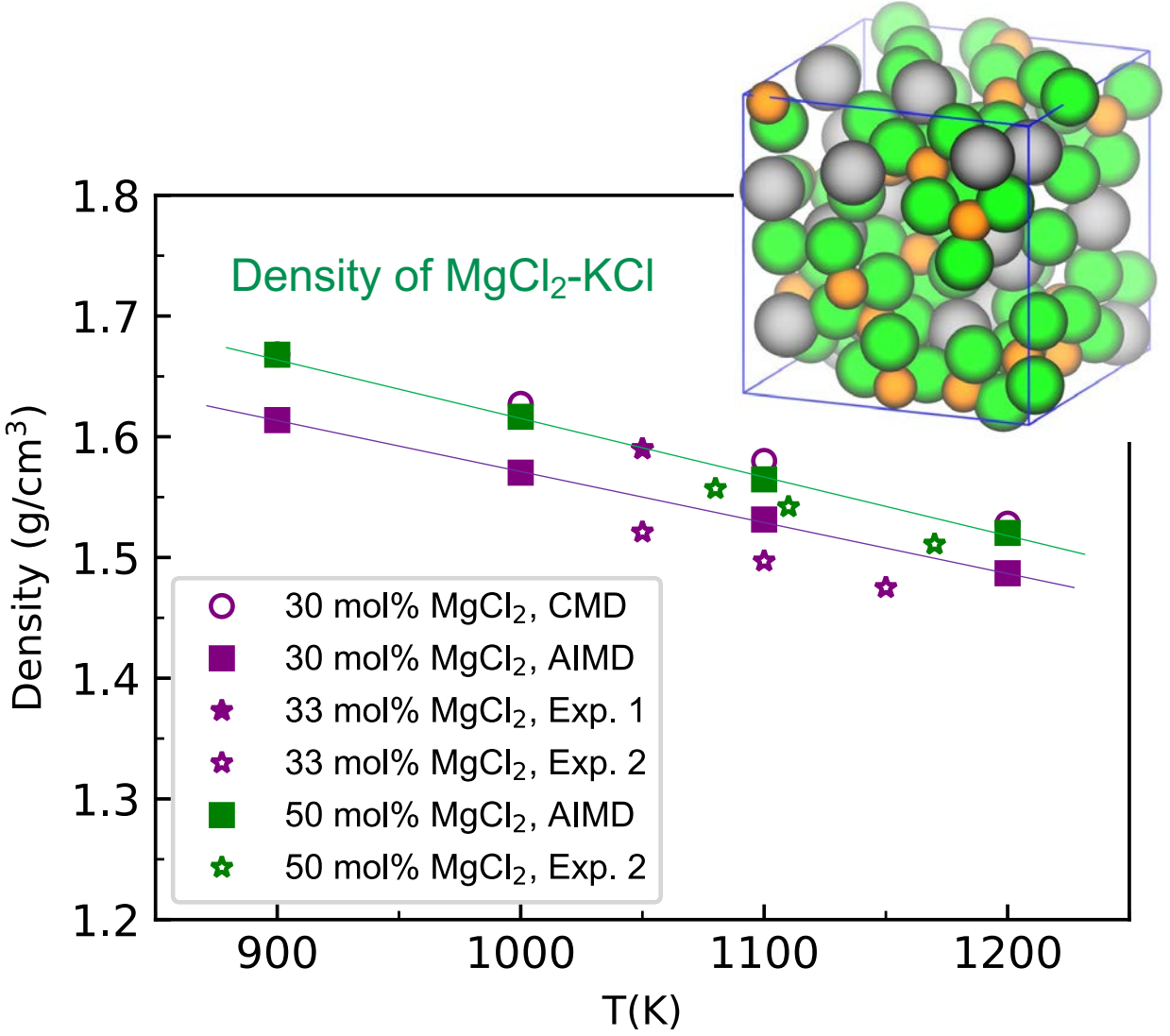
calculated with density functional theory (DFT)

Molecular dynamics in a nutshell



AIMD density validation

- Computational recipe:
  - CP2K code
  - Systems of ~ 110 atoms
  - First, classical molecular dynamics (CMD) using polarizable ion models: NPT ensemble.
  - Next, AIMD: NPT ensemble
  - Density = total mass / volume.
- Liquid density: linearly dependent on temperature.
- AIMD density is consistent with experimental data.

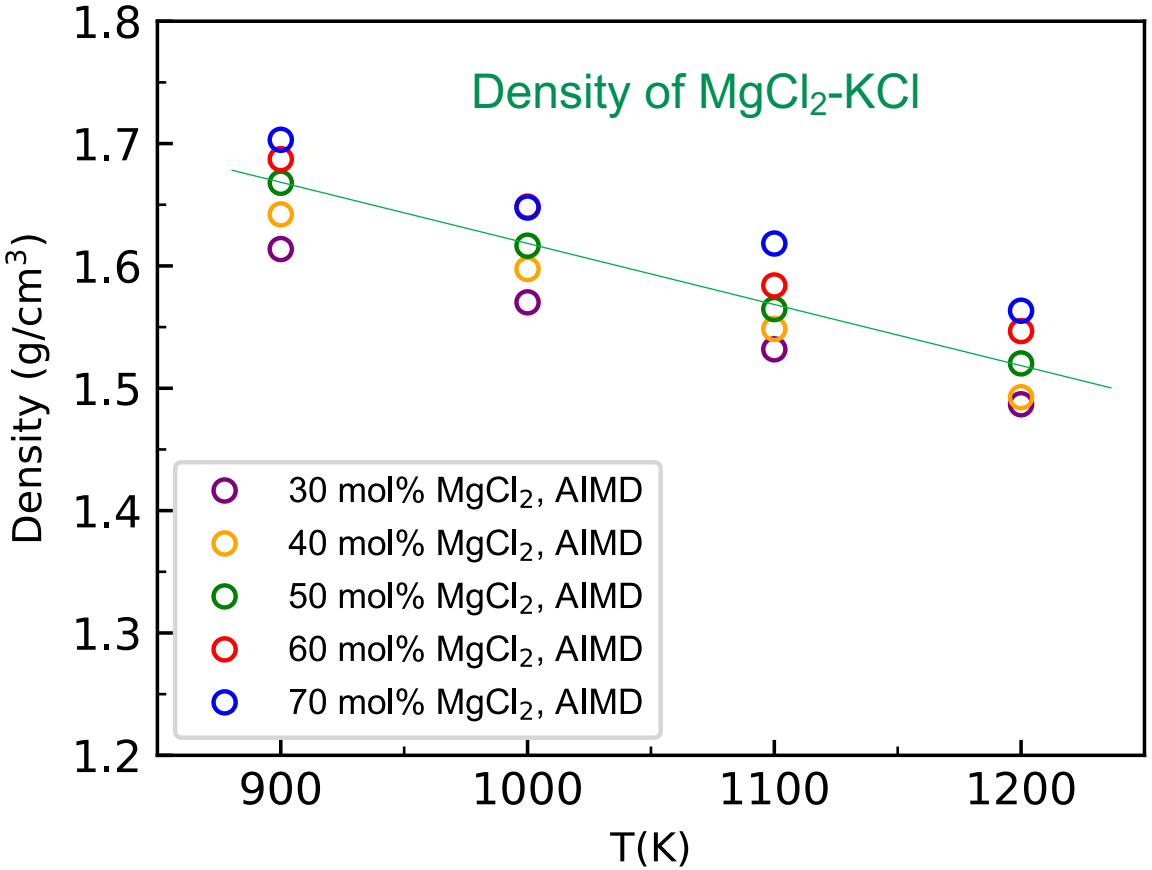


Exp 1: Kyle Makovsky (PNNL)
Exp 2: G. Janz et al. J. Phys. Chem. Reference Data 4, 871–1178. doi:10.1063/1.555527

Dependence of density on composition

- Higher $MgCl_2$ concentration leads to higher density
- Temperature-dependent equation
  - $\rho = B - A.T$

$MgCl_2$ mol%	B (g/cc)	A (10^{-4} g/cc / K)	T range (K)	Ref
30	1.99	4.19	900-1200	This work
32	1.93	4.48	770-863	AIMD, [1]
33	2.00	4.57	1030-1150	Exp., [2]
40	2.09	4.97	900-1200	This work
50	2.11	4.95	900-1200	This work
60	2.13	4.86	900-1200	This work
70	2.10	4.49	900-1200	This work



Ref 1: T. Xu et al. Journal of Molecular Liquids 347 (2022) 118275

Ref 2: G. Janz et al. J. Phys. Chem. Reference Data 4, 871–1178. doi:10.1063/1.555527

Diffusion coefficient from MD trajectories

- Mean square displacement (MSD)

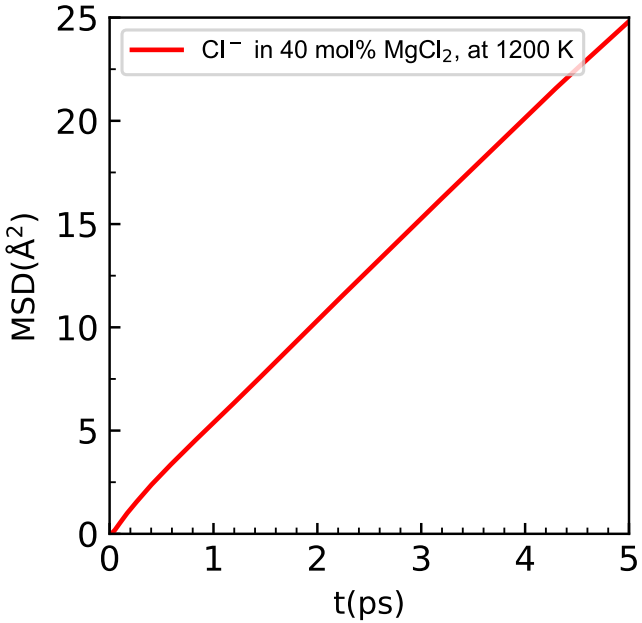
  of ion *i (e.g., Cl-)*:

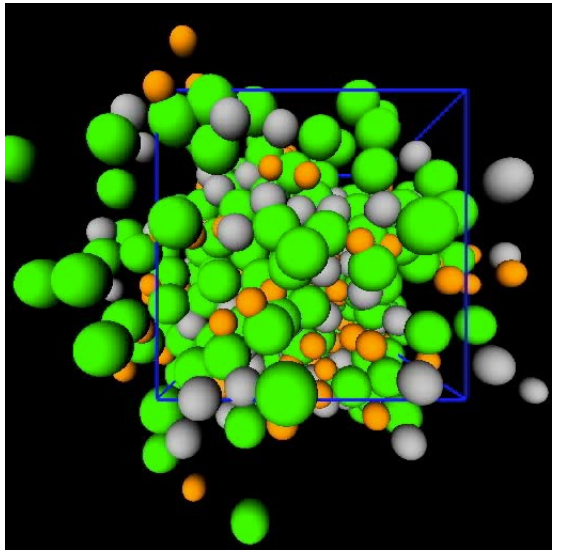
$$\mathrm{MSD_i} \equiv < |\mathrm{ri(t)} - \mathrm{ri(0)}|^2 >$$

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

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

- Consistent with literature.





Diffusion coefficient (10^{-5} cm^2/s)					
$MgCl_2$ mol%	T(K)	Mg^{2+}	K^+	Cl^-	Ref
30	900	2.20	3.66	3.56	This work
32	867	1.88	4.24	3.31	Ref [1]

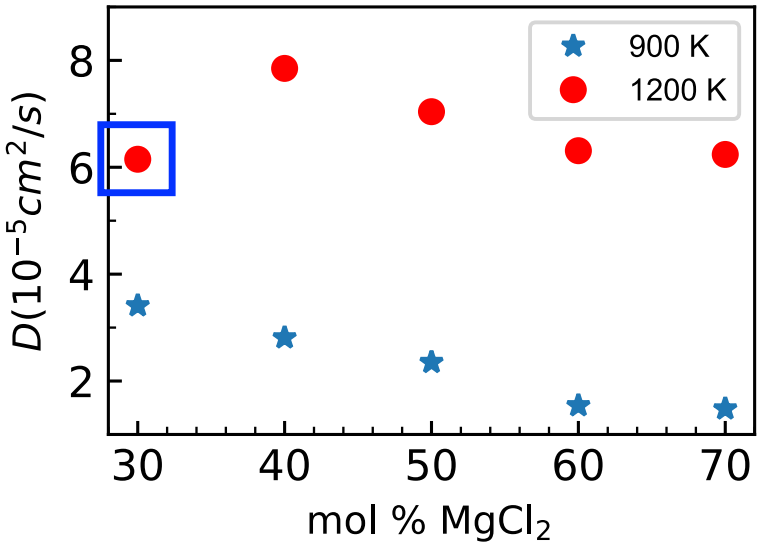
Ref [1]: T. Xu et al. Journal of Molecular Liquids 347 (2022) 118275

Dependence of diffusion coefficient on composition

- Trend 1: $D_{K+} > D_{Cl-} > D_{Mg2+}$

Atomic mass (au)		
Mg	Cl	K
24.305	35.453	39.0983

- Trend 2: D(low $MgCl_2$) > D(high $MgCl_2$)



Diffusion coefficient (10^{-5} cm^2/s)					
$MgCl_2$ mol%	T(K)	Mg^{2+}	K^+	Cl^-	All
30	900	2.20	3.66	3.56	3.41
	1200	3.86	7.04	6.20	6.15
40	900	1.87	3.27	2.88	2.81
	1200	6.21	8.25	8.15	7.85
50	900	1.59	2.47	2.56	2.35
	1200	5.42	8.32	7.15	7.04
60	900	1.08	1.76	1.65	1.54
	1200	5.03	7.39	6.52	6.31
70	900	1.14	2.17	1.49	1.48
	1200	5.42	8.33	6.21	6.24

Viscosity calculated using diffusion coefficient

- Stokes-Einstein relation $\eta = \frac{k_B T}{2\pi D r}$

- Combination rule for hydrodynamic radius

$$r = (d_{K-K} + d_{Mg-Mg} + d_{Cl-Cl} + 2d_{Cl-K} + 2d_{Cl-Mg})/7$$

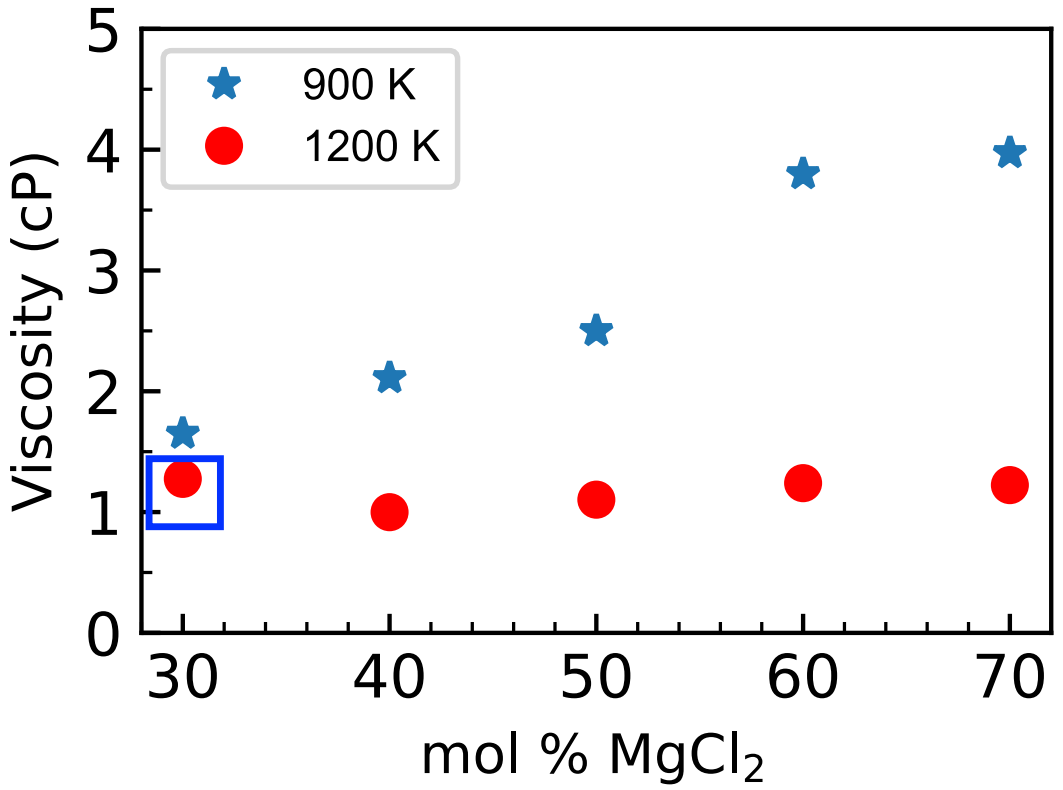
- Calculated data consistent with experimental data.

$MgCl_2$ mol%	T(K)	Viscosity (cP)	Note
30	900	1.65	This work
33	900	1.70	Experiment, Ref [1]

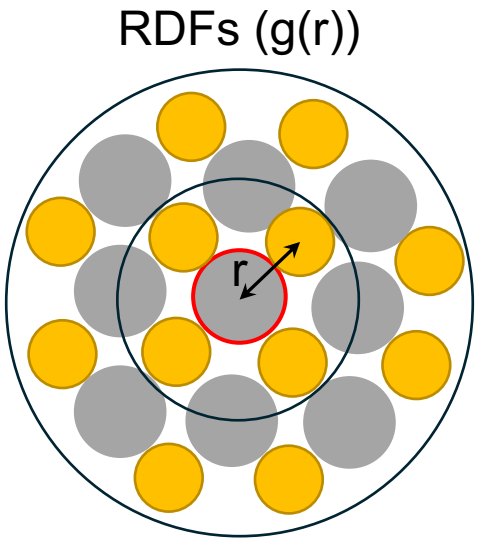
Ref [1]: G. Janz et al. J. Phys. Chem. Reference Data 4, 871–1178. doi:10.1063/1.555527

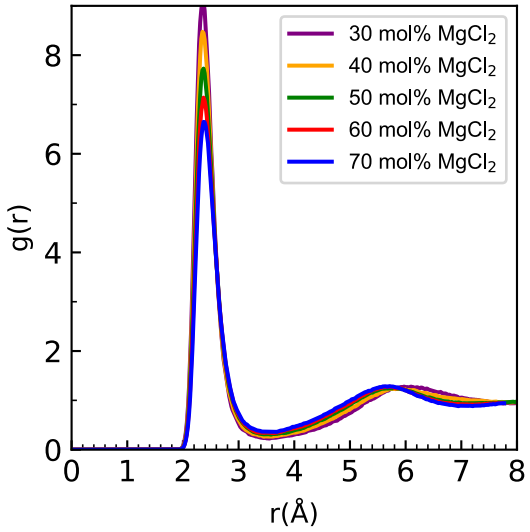
Dependence of viscosity on concentration

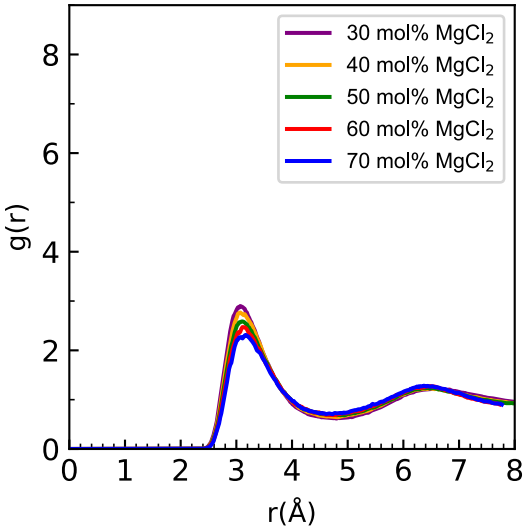
- High temperature, low viscosity
- The effect of $MgCl_2$ concentration on the viscosity is stronger at higher temperatures.



Radial distribution functions (RDFs)



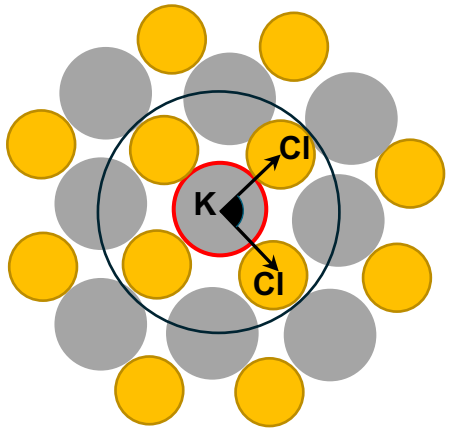


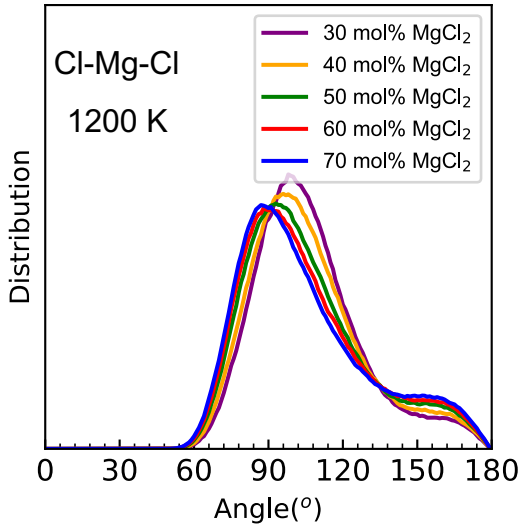


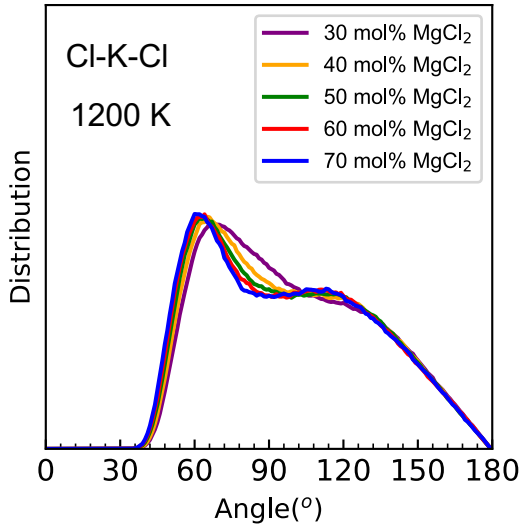
Ionic radii (pm)		
Mg^{2+}	K^{+}	Cl^{-}
86	152	167

- Mg-Cl interactions are stronger than K-Cl interactions
- Mg-Cl and K-Cl interactions are decreased with the $MgCl_2$ molar fraction.

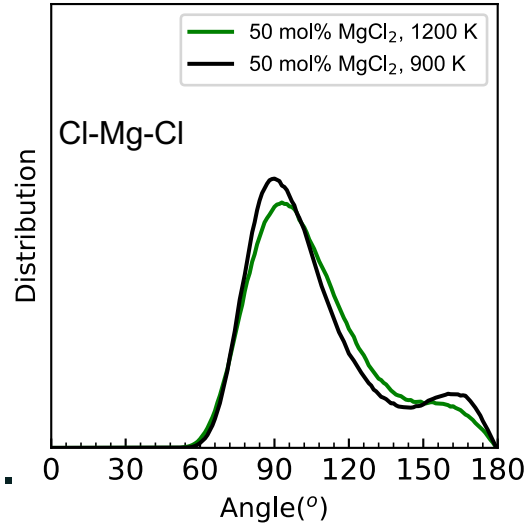
Angle distribution

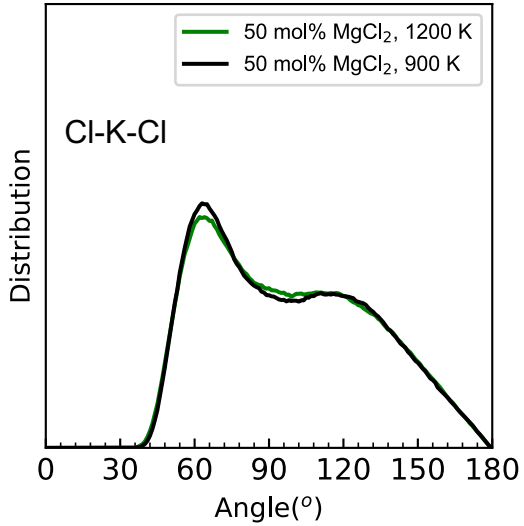




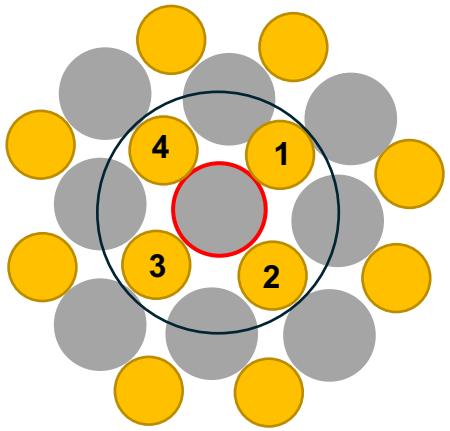


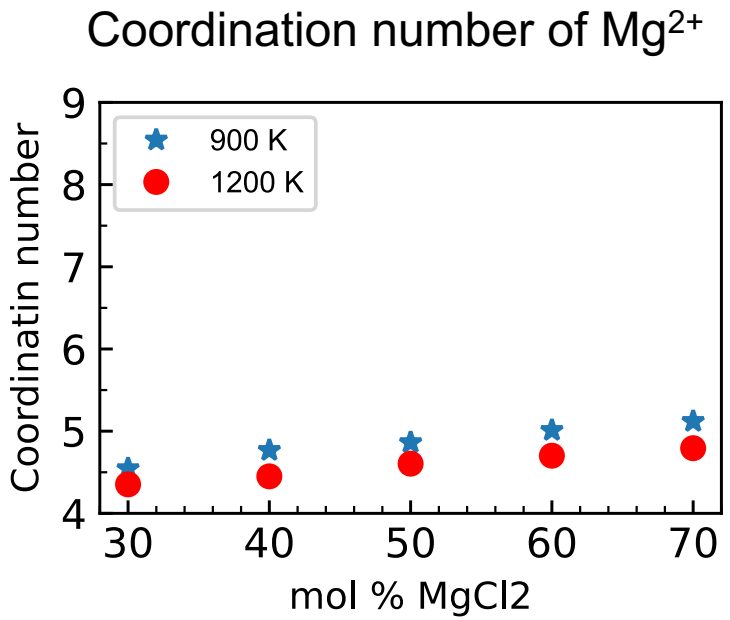
- The distribution of Cl-K-Cl is broader than that of Cl-Mg-Cl
- Cl-Mg-Cl peaks at ~90^{o} suggests octahedral structures
- Higher temperature leads to broader distribution.

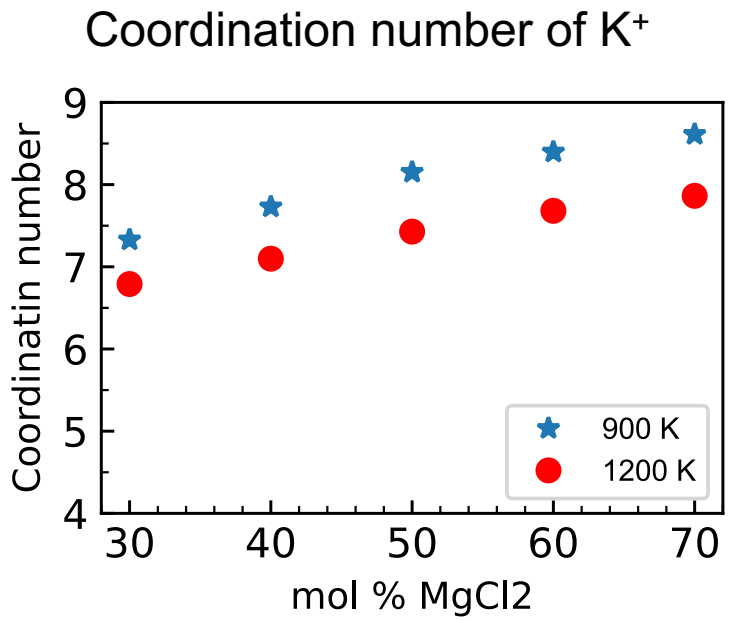




Coordination number







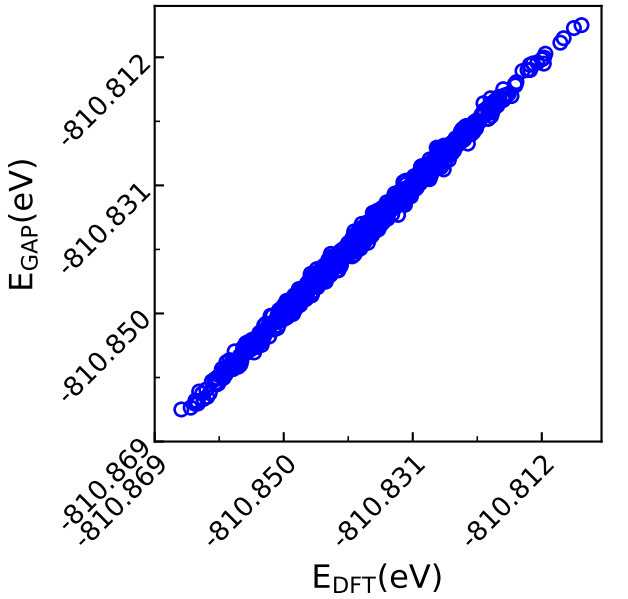
- Coordination number is increased with $MgCl_2$ concentration but decreased with the temperature
- Temperature shows a stronger effect on the coordination of K^+.

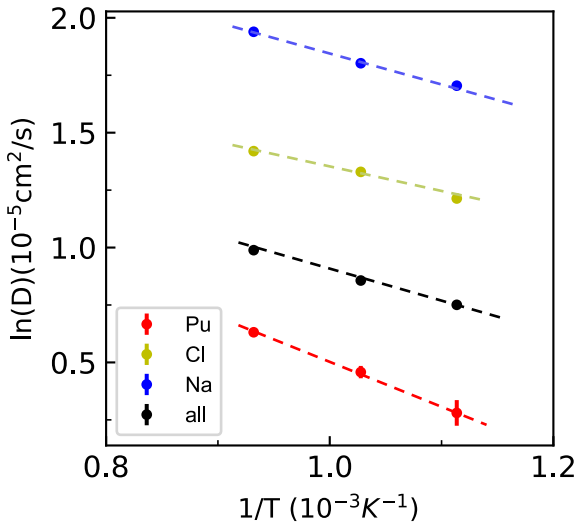
Summary and Next steps

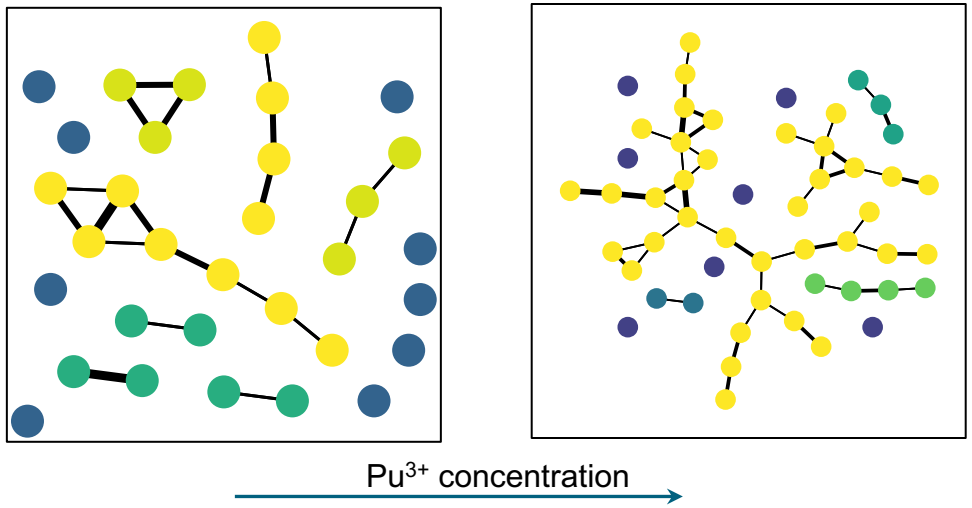
- The density of $MgCl_2$-KCl mixtures was determined for 5 compositions at 4 temperatures.
- Transport (diffusion coefficient and viscosity) properties are composition- (and temperature) dependent
- Coordination number is increased with temperature
- We will investigate specific heat and thermal conductivity.

Publications

- Manh-Thuong Nguyen *et al*. "Exploring NaCl-$PuCl_3$ molten salts with machine learning interatomic potentials and graph theory", Applied Materials Today 35, 101951 (2023).







AIMD and ML interatomic potentials

Transport

Clustering of Pu^{3+}

- Manh-Thuong Nguyen *et al*. "A combined computational and experimental study on NaCl-UCl_3-$PuCl_3$ molten salts" (in preparation).

Thank you

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