



Understanding ionic Li diffusion in crystalline Li_3PS_4 and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ solid electrolytes, via *ab-initio* simulations

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Understanding Li^+ diffusion behavior in amorphous and crystalline Li_3PS_4 solid electrolytes, via *ab-initio* simulations

Prelude: Crystalline Comparisons

Outline

- I. Why solid state?
- II. Density Functional Theory (DFT) for predicting material properties
- III. Li_3PS_4 (LPS) and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) electrolytes
- IV. Diffusion mechanisms and results





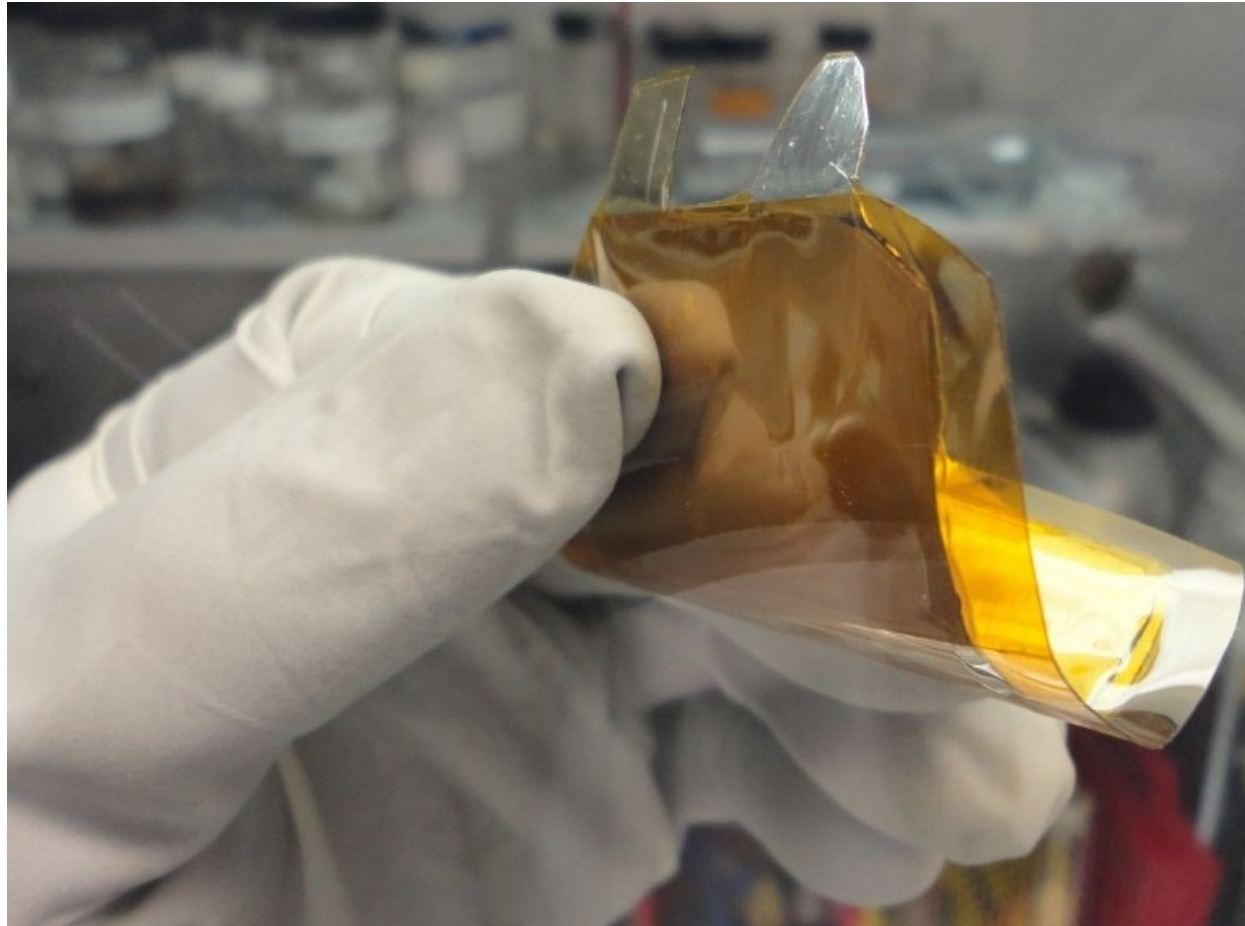
Tesla® all-electric vehicle .

Current Batteries – Too expensive, too big, and too unsafe.



Nima Leclerc, San Francisco State University

The Next Generation of Energy Storage



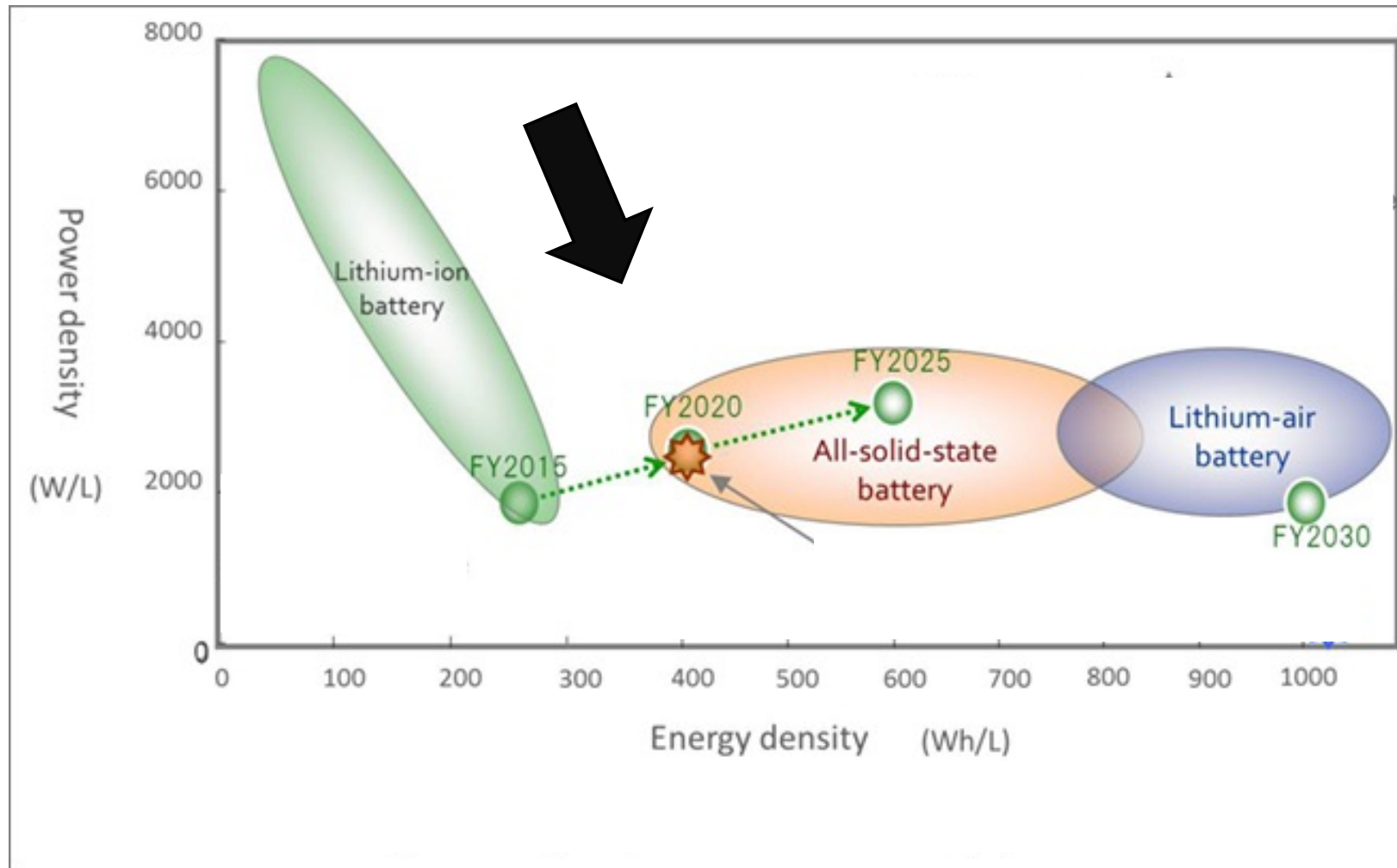
Future Batteries: ALL SOLID STATE

Applied Materials Inc.® thin-film Solid State Battery (LIPON electrolyte)

Nima Leclerc, San Francisco State University



Solid State Batteries can increase Power and Energy densities Simultaneously

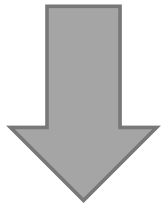


- Current Li-ion batteries cannot have both high power and energy densities
- Solid state batteries can achieve both!

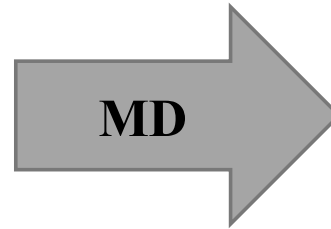


Large-scale predictive simulations require Density Functional Theory (DFT)

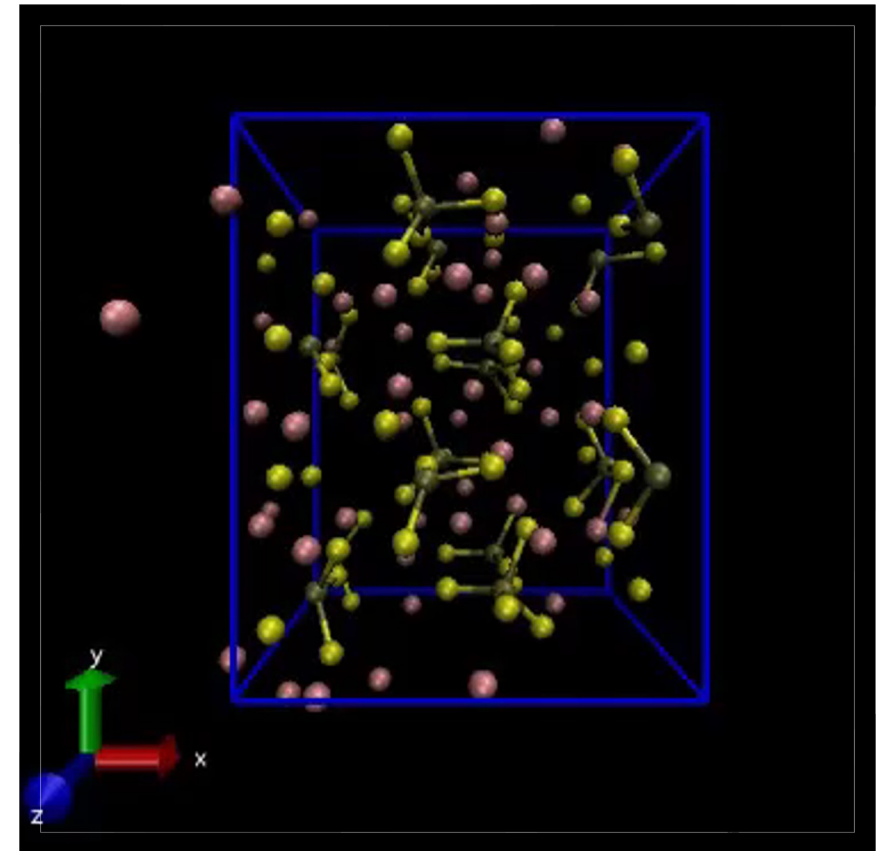
$$\left[\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] |\varphi\rangle = \varepsilon |\varphi\rangle$$



- No a-priori assumptions about bonding character between Li⁺ and lattice
- Molecular dynamics (MD) predicts diffusion mechanisms



LPS MD
system, 700 K



LLNL Computing Center

Nima Leclerc, San Francisco State University

I. Why solid state?

II. Density Functional Theory (DFT) for predicting material properties

III. Li_3PS_4 (LPS) and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) electrolytes

IV. Diffusion mechanisms and results



Why is $\sigma(\text{LGPS})$ greater than $\sigma(\text{LPS})$?

$\beta\text{-Li}_3\text{PS}_4$:

- Amorphous $\sigma \gg$ crystalline σ
- Amorphous electrolytes improve safety and manufacturing

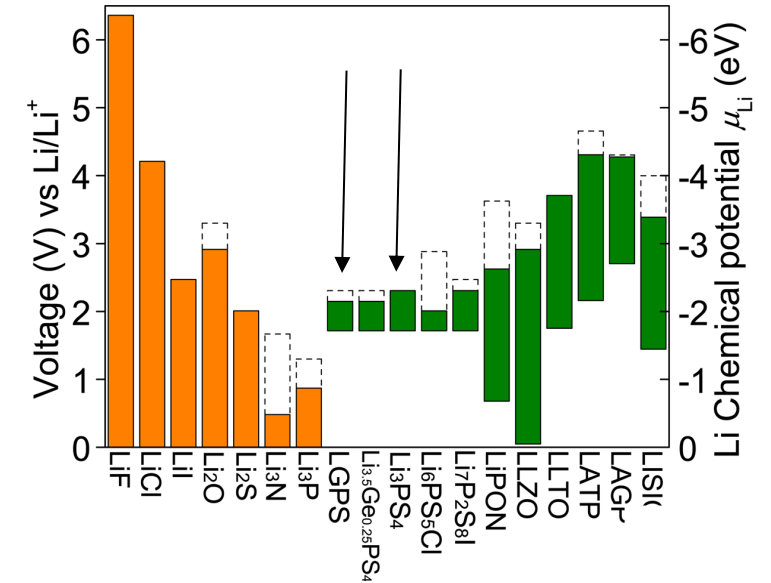
Conductivity at 300K	LPS (S/cm)	LGPS (S/cm)
Crystalline	5.56×10^{-5} [2]	1.2×10^{-2} [1]
Amorphous	1.24×10^{-4} [2]	1.5×10^{-5} [1]

$\text{Li}_{10}\text{GeP}_2\text{S}_{12}$:

- [1] Mori et al. Solid State Ionics (2017)
- [2] Hayamizu et al. Solid State Ionics (2015)
- [3] Zhu et al. Acs Applied Materials & interfaces (2015)

- Composition and structure is very similar to LPS
- One of the fastest Li^+ solid electrolytes
- Crystalline $\sigma \gg$ amorphous σ

Electrolyte electrochemical stability windows [3]



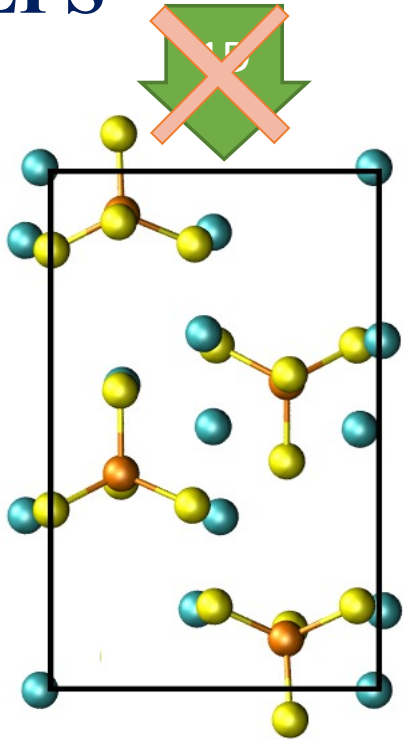
LGPS and LPS: both not very electrochemically stable. .

Is the LGPS structure better?



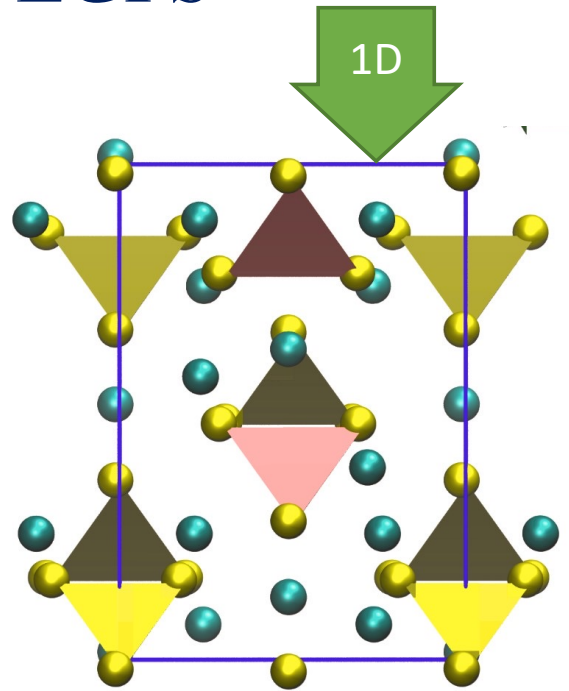
Do the 1D channels cause the higher diffusivity?

LPS



Predominantly
3D diffusion

LGPS



Fast 1D diffusion

Similarities and differences:

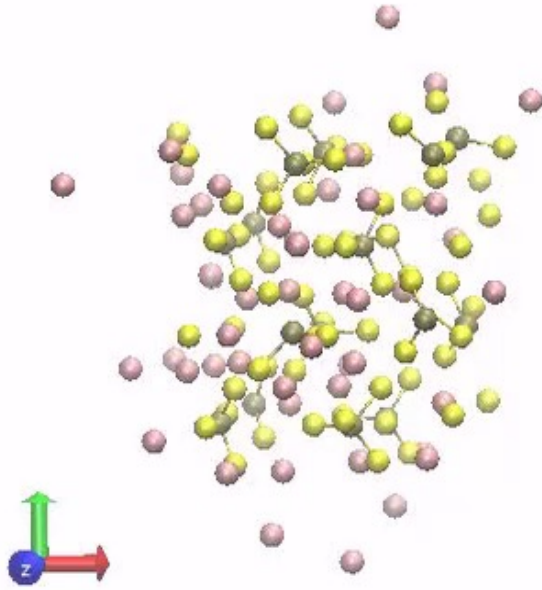
- Disconnected tetrahedra,
But in LGPS: substitute Ge^{4+} for P^{5+} ,
which improves Li^+ concentration
- Zig-zag chains of PS_4/GeS_4
 - LGPS: along two axes (creates 1 D channels)
 - LPS: 1 axis
- Orthorhombic
 - LGPS: $P4_2/nmc$
 - LPS: $Pnma$

Is the LGPS mechanism faster?

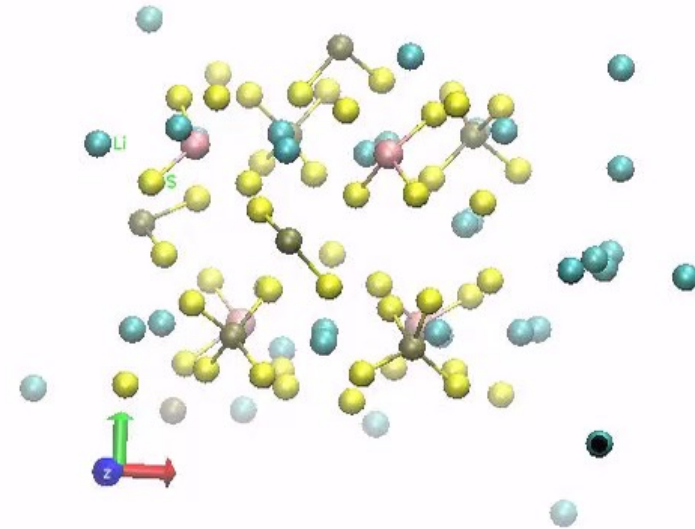


Do the 1D channels in LGPS cause the higher diffusivity?

VideoMach unregistered



VideoMach unregistered



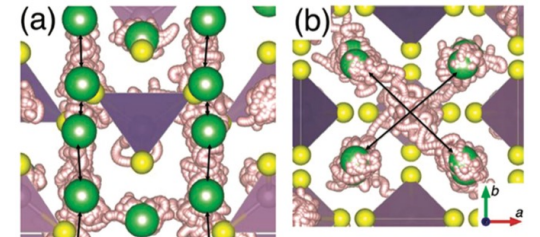
Simulations by Joel Varley (LLNL) and analysis by Alex Hall (SFSU).

Obviously there is faster diffusivity along the LGPS 1D channels, but it is enough?

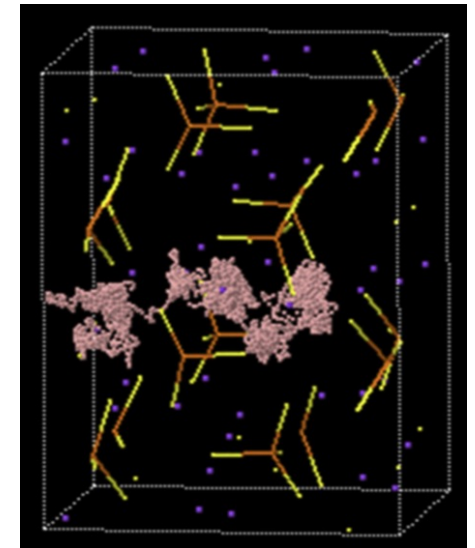
Do the 1D channels in LGPS cause the higher diffusivity? 1D channels are not enough for poly-crystalline materials.

LGPS: Many similar energy tetrahedral sites give low E_a in 1D (0.17 eV [0])
3D diffusion from a-b planes that connect the 1D channels

LPS: Many tetrahedral sites, but also square planar sites
3D diffusion is different than LGPS 1D channels



If LGPS mechanism is better = lower E_a
Else, significant correlated motion in LGPS may lead to high conductivity.



[0] Mo, Y. *et al.* Chemistry of Materials, 24, 15-17 (2012)

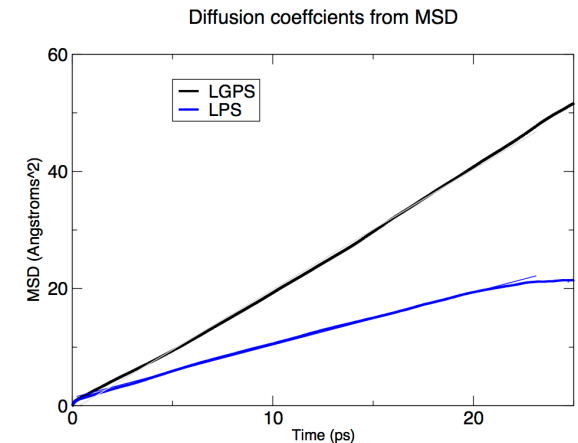
[1] Yang, J. and Tse, J. Computational Materials Science 107, 134-138 (2015).



Activation energies not very different for LSP and LGPS

Electrolyte	Experiment E_a	DFT E_a	σ (S/cm)
LGPS	0.22-0.25 eV [1]	0.28 eV (3D), 0.17 eV (1D) [0]	1.2×10^{-2}
β -LPS	0.3 eV [3]	0.4 eV (NEB) [2]	5.56×10^{-5}
γ -LPS	0.7 eV [3]	0.5 eV (NEB) [2]	2.61×10^{-7}
Amorphous LPS	0.187 eV [4]	N/A	1.24×10^{-4}

- $\Delta E_a \neq \Delta \sigma$ for LGPS vs. LPS
- Correlated motion PS_4 rotations (paddle wheel)?
 - Disorder: LGPS= GeS_4 , **LPS=amorphous** [5]
 - Ideal volume: LGPS= $Ge > P$, LPS=amorphous
 - Note, average volume/tetrahedra in **LGPS \leq LPS**



[0] Mo, Y. *et al.* Chemistry of Materials, 24, 15-17 (2012)

[1] Kamaya, N. *et al.* A lithium superionic conductor. *Nature Mater.* **10**, 682 (2011)

[2] Lepley, N. *et al.* *Physical Review B* **88**, 104103 (2013)

[3] Hommo, K. *et al.* *Solid State Ionics* **182**, 53 (2011)

[4] Mascaraque, N. *et al.* *Journal of Non-Crystalline Solids*, **405**, 159–162 (2014)

[5] Adams, S. and Rao, P. J. *Mater. Chem.*, 2012, **22**, 7687



Volumes Studies: Does the larger volume of the amorphous phase lead to greater conductivity?

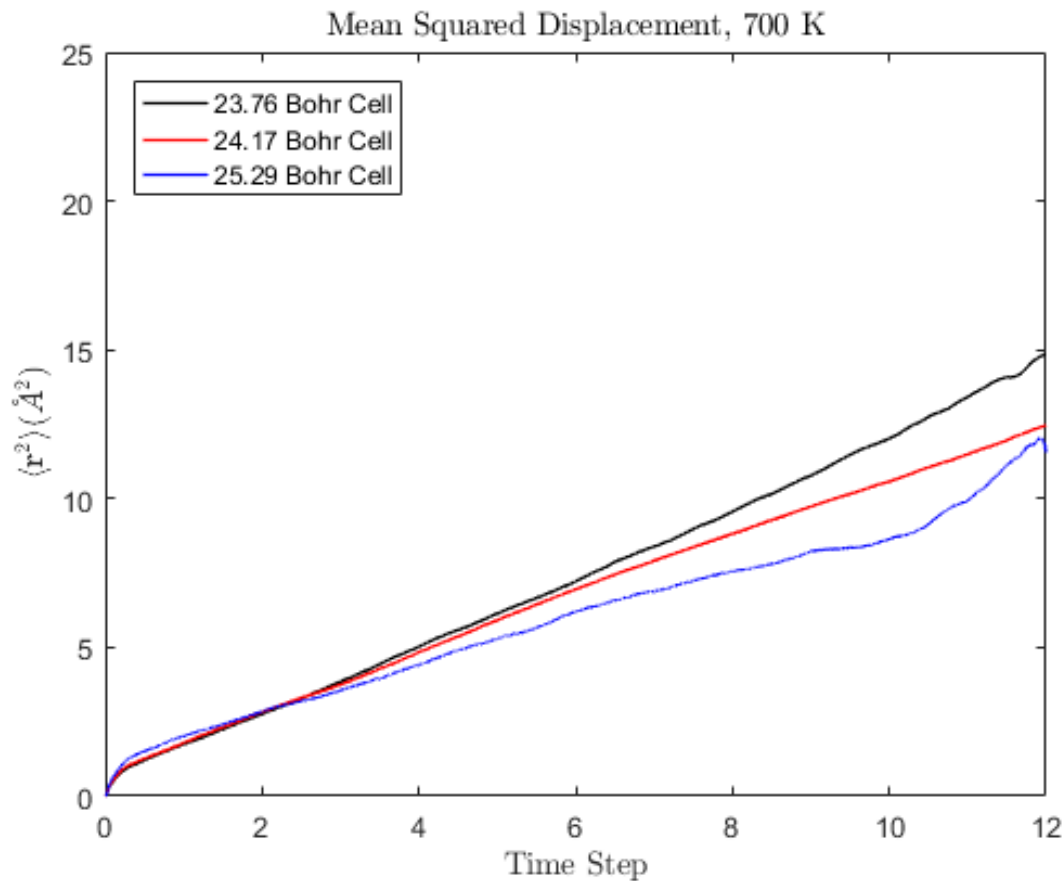
- LPS simulated at three sizes
- Minimum energy volume = 12.79 Å
- Look at the effect of smaller and larger volumes than minimum
- Larger volumes are a proxy for understanding the amorphous phase

LPS Lattice Vector a (Å)	Percent size difference
12.54 Å	-1.95 %
12.79 Å	Min. energy (a)
13.38 Å	+4.61%



Large volume the driver for high amorphous conductivity? No.

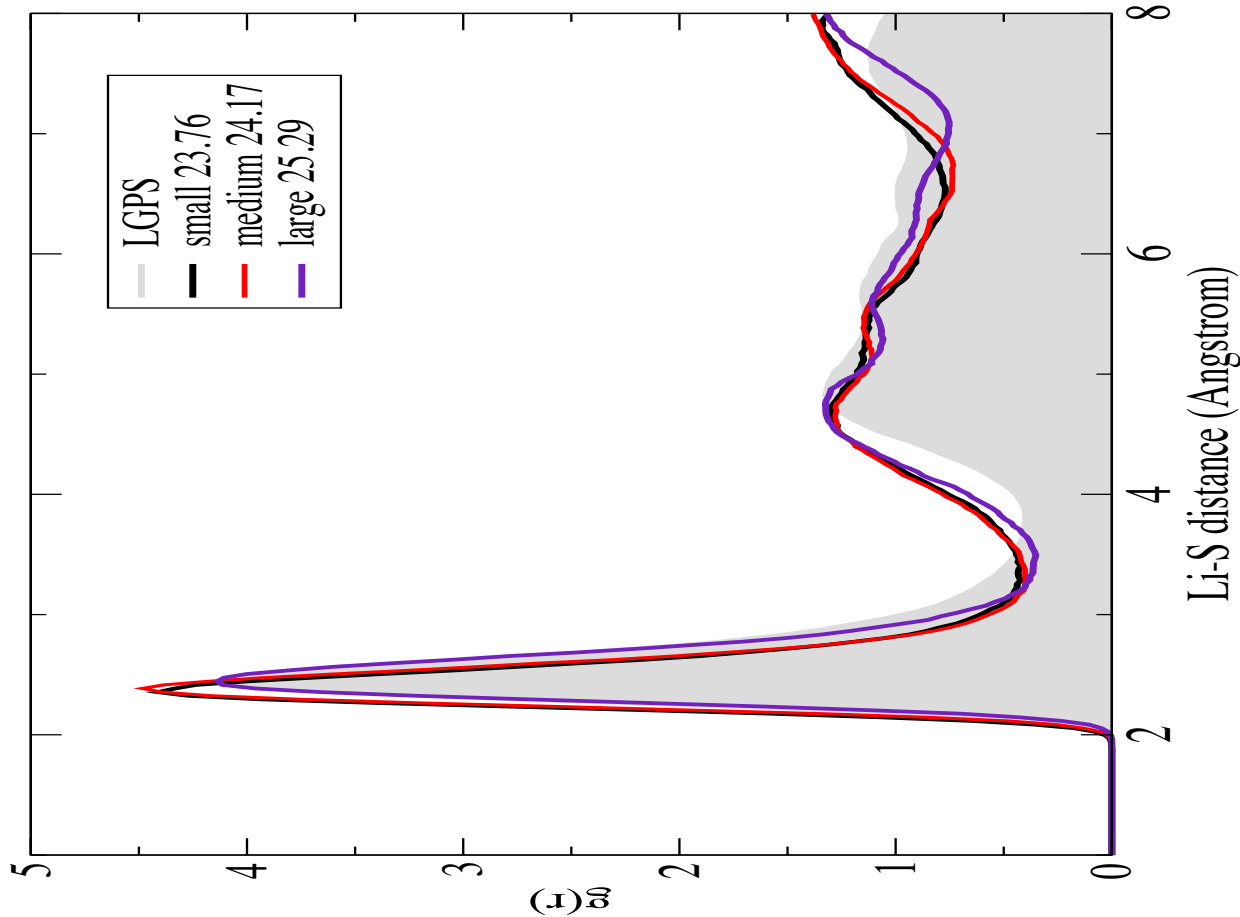
- Slope of MSD vs. t gives D
- Experiment: $0.69 \times 10^{-5} \frac{\text{cm}^2}{\text{s}}$ (500K)
- $4.03 \times 10^{-5} \frac{\text{cm}^2}{\text{s}}$ (800 K)



Cell Sizes	Computed (cm^2/s)
SMALL	4.36×10^{-5}
MIN. ENERGY	1.79×10^{-5}
LARGE	1.64×10^{-5}



Larger volume could give non-ideal Li-S bond distances



Cell Size a lattice vector	Percent Lattice Parameter Change	Percent Change in Peak Shift
23.76 Bohr	-1.3 %	0.0%
24.17 Bohr	Minimum energy size	Minimum energy size
15.29 Bohr	4.6 %	6.4%

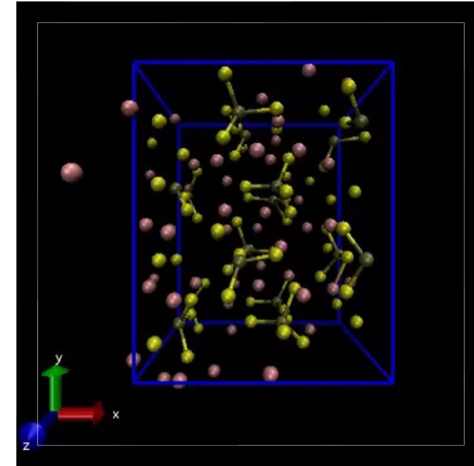
**Not the entire picture, but
its likely short Li-S bonds
lead to faster diffusion.**

Paddle-wheel mechanism?



Correlation, disorder, and amorphous LPS

- **The activation energy (low barriers between tetrahedral site) cannot solely explain the outstanding diffusivity in LGPS compared to LPS.**
- **Larger volumes do not improve diffusivity in LPS.**
- **Future work:**
 - **Compare diffusion mechanisms in the amorphous phase and crystalline phase at different volumes.**
 - **Compare correlated motion in LGPS and LPS, especially the effect of the lattice: polarization of sulfur ions and PS_4 , rotation of PS_4**



Thanks!

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