DFT simulations of Li-ion conductor Li2(OH)Cl

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NSF grant DMR-1507942

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UNIVERSITY

Outline

- Motivation
- Background of material
- Low temperature phase structure search
- Molecular dynamics simulations of high temperature phase

Motivation

- Solid state , fast lithium ion conductor

- Finding structure for low temperature phase is stepping stone for understanding the phase transition.

  related materials $Li_{2+x}OH_{1-x}Cl$, $Li_2(OH)_{1-x}F_xCl$, $Li_2(OH)Br$

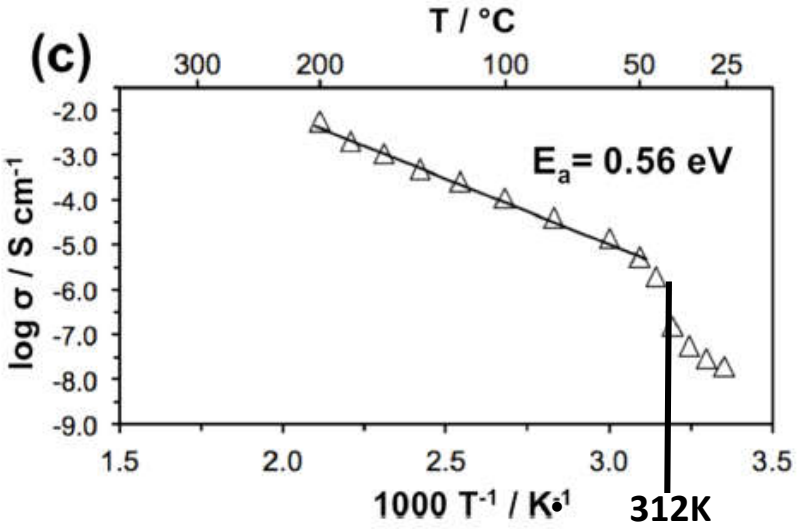
- Understanding the structure of the low temperature phase can help to understand the differences in the phase transitions or lack there of for the related materials

- Understanding the properties of diffusion on a disordered lattice is of general interest

- In principle the combination of calculated tracer diffusion coefficients and experimentally measured conductivity can allow for a calculation of the Haven ratio.

Background of Li2OHCl

- Two phases orthorhombic -> cubic(disordered) at 312K
- Low temperature phase poor Li-ion conductor
- Disordered cubic phase is a good Li-ion conductor



Hood, Zach et al. , Li2OHCl "*Crystalline Electrolyte for Stable Metallic Lithium Anodes*". J. Am. Chem. Soc. 2016, 138, 1768−1771

- Has been cycled with a lithium anode with the apparent creation of stabilizing SEI layer

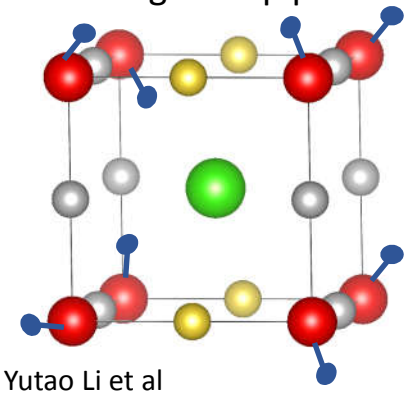
Methods

- Quantum Espresso ***QUANTUM ESPRESSO*** **.** (Giannozzi et al. *JPCM* **21,** 394402 (2009)

- PAW formalism with LDA, data sets generated with ***ATOMPAW***
(Holzwarth et al. *CPC* **135**, 329 (2001)) http://pwpaw.wfu.edu

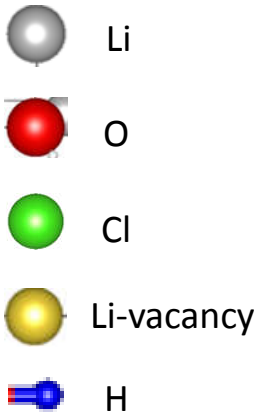
Low Temperature structure

Cubic high temp phase



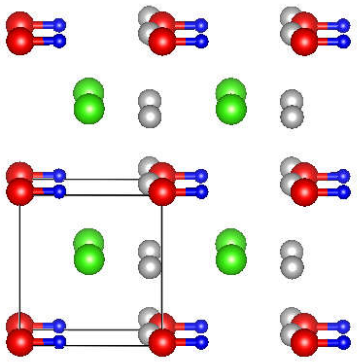
Yutao Li et al
International Edition: DOI:
10.1002/anie.201604554

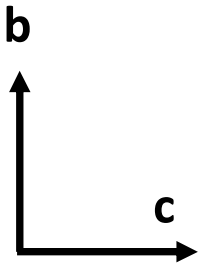
- Orthorhombic, diffraction peaks available but no cif file as of yet
- Rapid change in conductivity orthorhombic -> cubic indicates order-> disorder transition of lithium sites
- Schwering et. al. has experimentally predicted lattice parameters
  Schwering, Georg CHEMPHYSCHEM 2003, 4, 343 - 348
- My DFT studies predict a tetragonal ground state , a Orthorhombic structure slightly higher in energy is also predicted



Eo

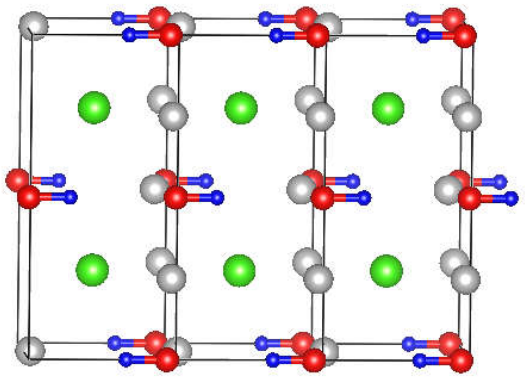
Tetragonal





0.02 eV + Eo

Orthorhombic



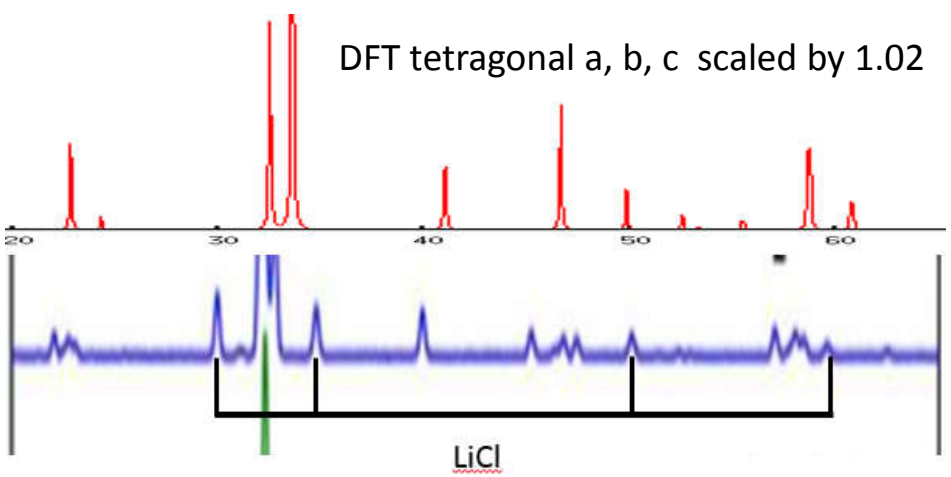
Lattice parameters and XRD

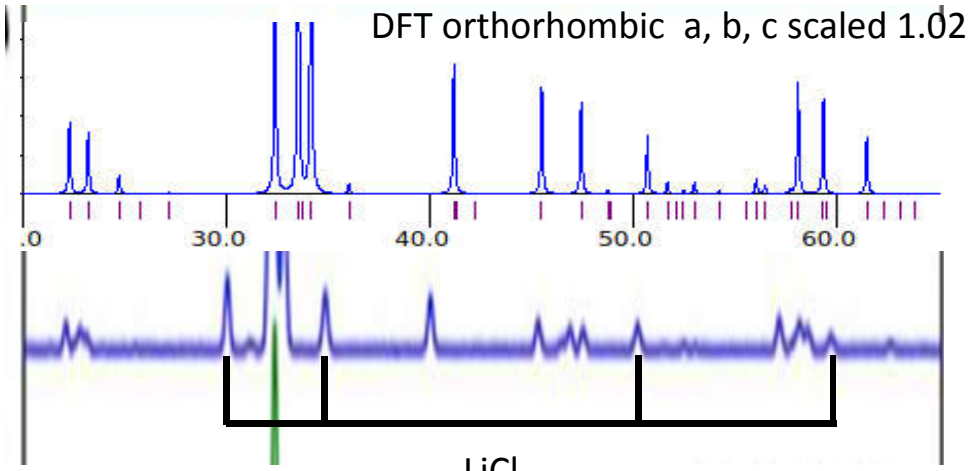
- Orthorhombic phase lattice parameters reported by Schwering et al. In angstrom

  a – 3.82 b – 7.998 c – 7.74, (b/2 = 3.999, c/2 = 3.87) Schwering, Georg CHEMPHYSCHEM 2003, 4, 343 - 348

- Tetragonal lattice parameters (DFT) Orthorhombic lattice parameters (DFT)

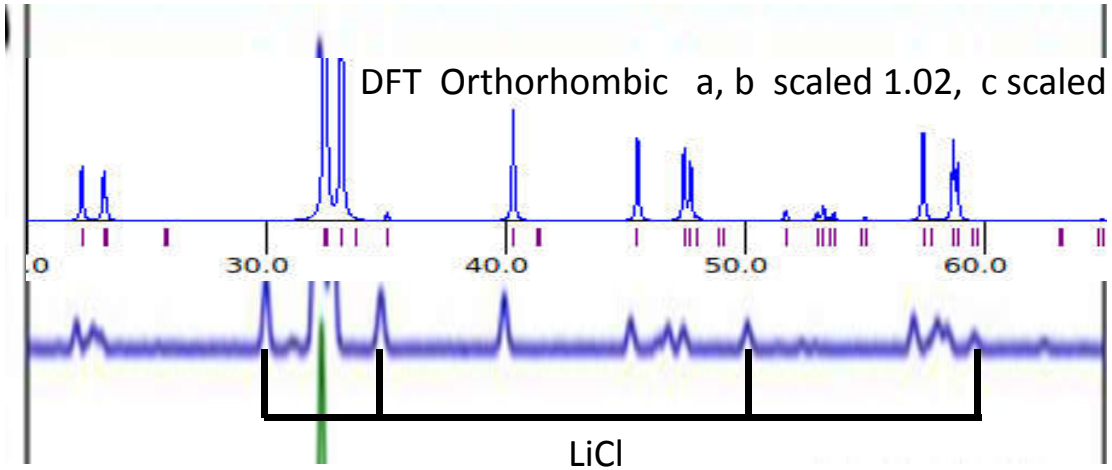
  a – 3.89 b – 3.89 c – 3.66 a – 3.83 b – 7.97 c – 3.6 (if scaled by 1.08 c = 3.81)





Hood, Zach et al. ,. J. Am. Chem. Soc. 2016, 138, 1768−1771

Candidate DFT orthorhombic with a-axis and b-axis scaled by 1.02 and c-axis scaled by 1.08



Hood, Zach et al. ,. J. Am. Chem. Soc. 2016, 138, 1768−1771

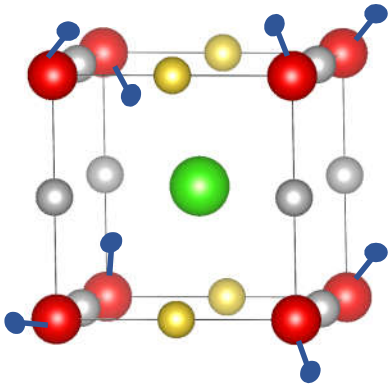
Azuma et al report and underestimation of up to 8% in the axis along the OH bond in

$$Mg(OH)_2\,, \qquad Ca(OH)_2, \qquad LiOH, \qquad and\ NaOH$$

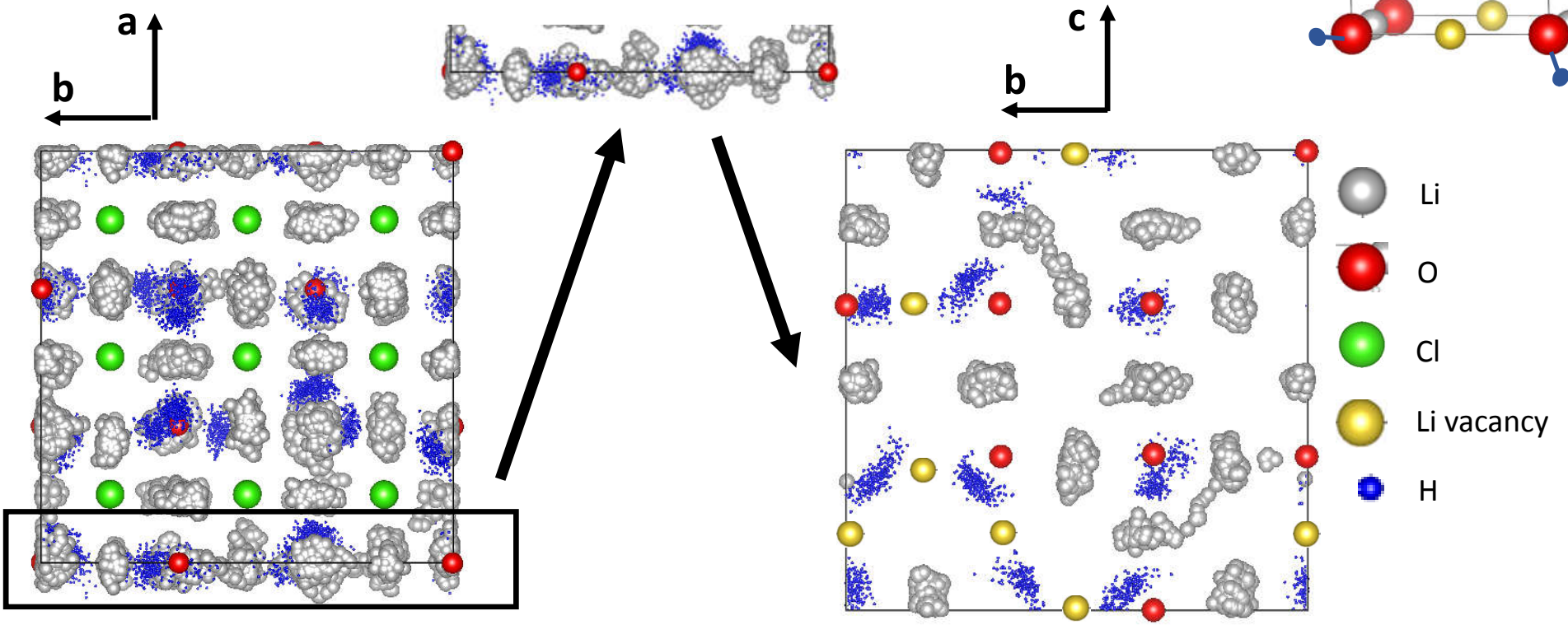
Azuma et al , *Computational and Theoretical Chemistry* 963 (2011) 215–220

Molecular Dynamics of disordered cubic phase

- Started from randomly placing lithium on available sites
- Used the micro-canonical ensemble , 1 shifted Kpoint, Ecut 45ryd, 1fm second t-step



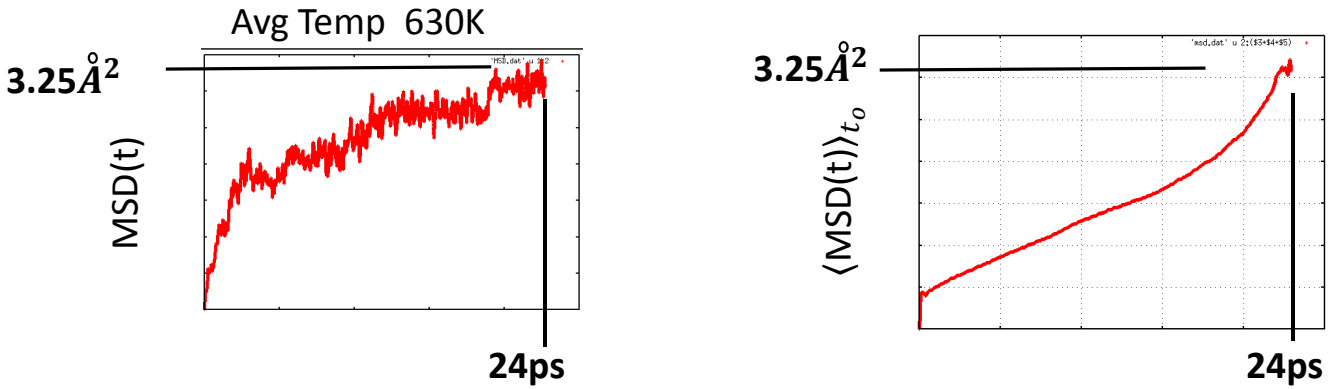
"Scatter" plots of Lithium and hydrogen positions



Goals of MD simulations

- Calculate tracer diffusion coefficients from slopes of mean square displacement vs time plots

MSD(t) = $\frac{1}{\#Li} * (R(Li)_t - R(Li)_{t_o})^2$ $\langle MSD(t) \rangle_{t_o}$ vs t



- Tracer diffusion coefficients are related to the ionic conductivity by the equation

$$\sigma(T) = \frac{D^*(T)\rho e^2}{kTH_r}$$ where $D^*(T)$ - tracer diffusion coefficient

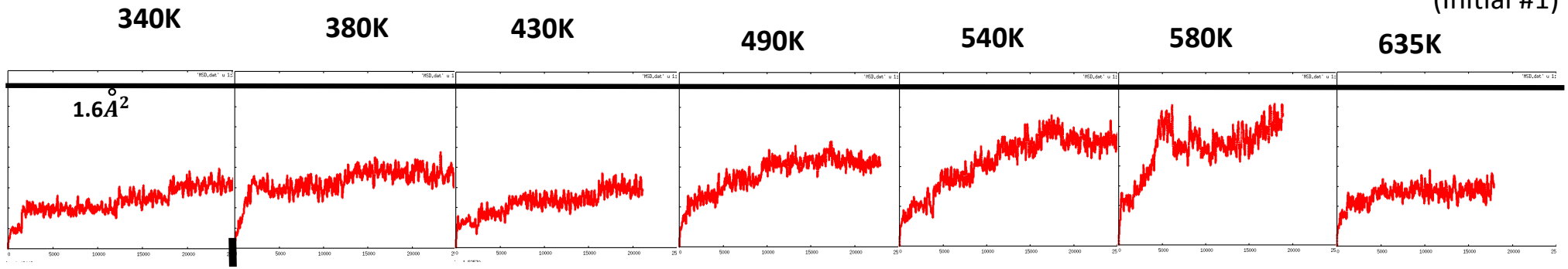
G.E. Murch Solid State Ionics 7 (1982) 177-198

ρ - density of mobile ions per unit volume , e - fundamental charge, k – Boltzmann constant

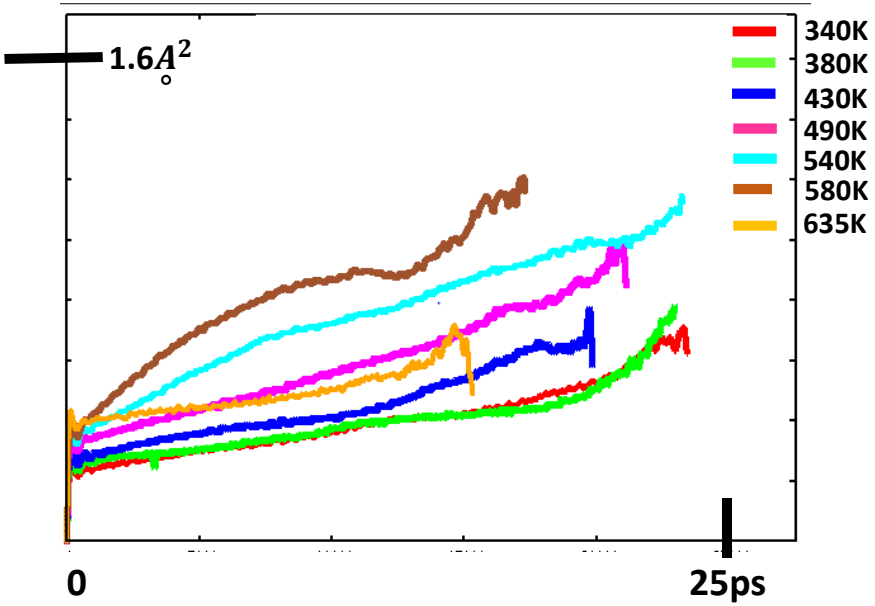
T – temperature , H_r- the Haven ratio

MSD continued

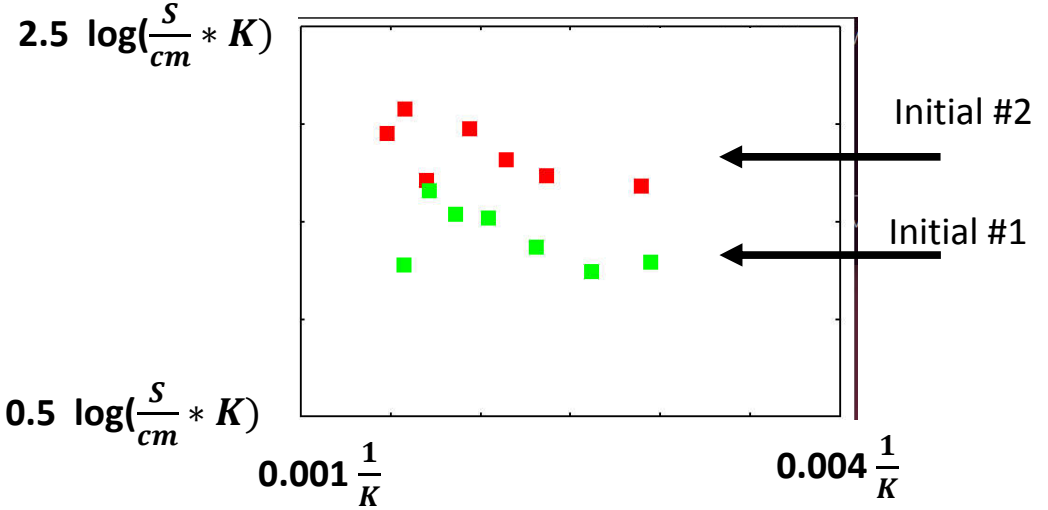
(Initial #1)



$$\frac{1}{6}\langle \text{MSD(t)}\rangle_{t_o,Li} = D^*(t - to) - c \qquad \sigma(T) = \frac{D^*(T)\rho e^2}{kTH_r}$$



$\log(\sigma^*T)$ vs $\frac{1}{T}$

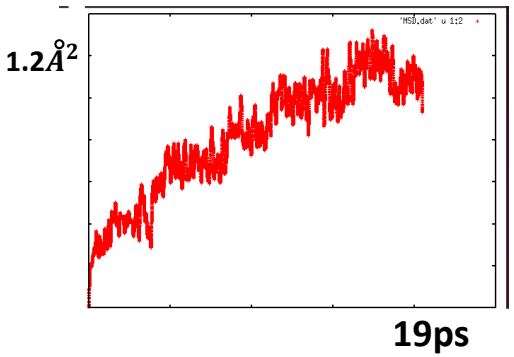


Conclusions

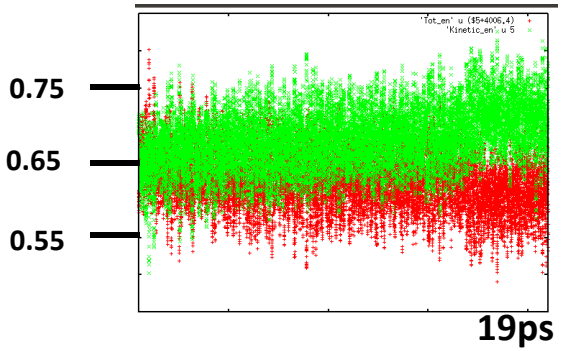
- T = 0K ground state predicated to be tetragonal
- A candidate structure is found for the low temperature Orthorhombic structure
- MD simulations show Lithium hopping that corresponds to the proposed model for lithium jumps
- Hydrogen positions qualitatively correlated with Li vacancies
- Measurable diffusion occurring ~350K-650K but results are not converged enough to produce accurate Arrhenius plots

Internal energy, kinetic energy, total energy and temperature In Micro Canonical Ensemble

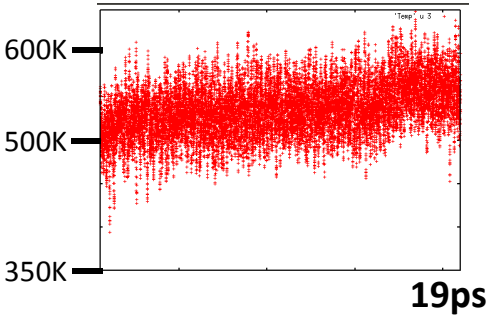
MSD(t) = $\frac{1}{\#Li} * (R(Li)_t - R(Li)_{t_o})^2$



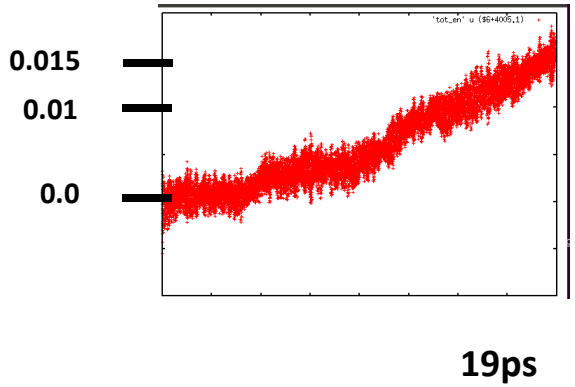
Kinetic ( ) and internal ( )



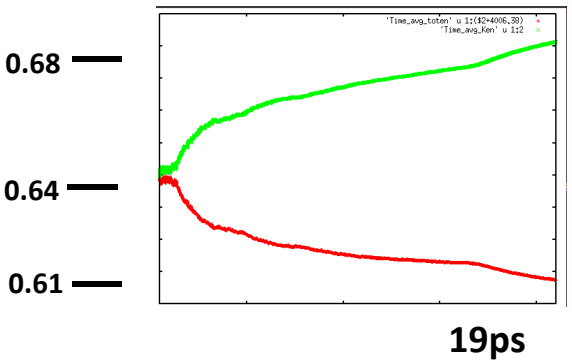
Temperature



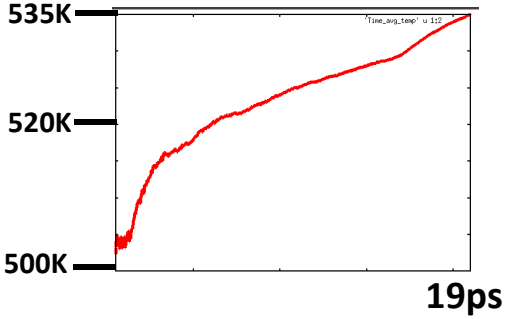
kinetic + internal

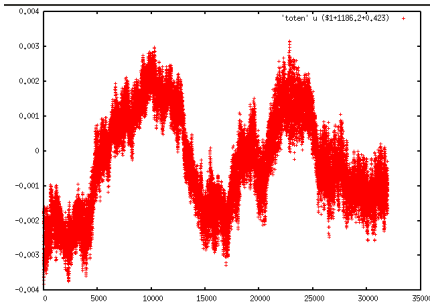


time avg kinetic and internal



time avg temperature





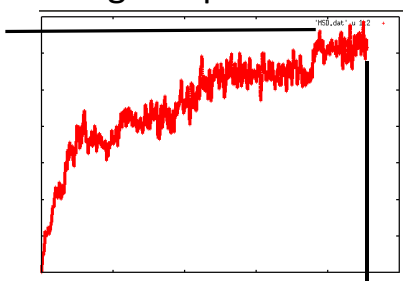
Order parameter analysis

- Need a parameter that can gauge if the simulation is long enough
- Define $\langle SO_i \rangle_t = \frac{1}{t}\int_0^t SO_i(t)dt$ where $SO_i(t) = 1$ if a lithium is occupying the site i at time t
  $SO_i(t) = 0$ if a lithium is not occupying the site i at time t
- Because each site should be equally occupied and there are 3 sites for every 2 lithium's
  $\langle SO_i \rangle_t \rightarrow \frac{2}{3}$ at long t
- For a supercell this leads to $\left\langle \left| \frac{2}{3} - \langle SO_i \rangle_t \right| \right\rangle_i \rightarrow 0$ for long t. The index i is for the possible Li sites in simulation cell

$$\text{MSD(t)} = \frac{1}{\#Li} * (R(Li)_t - R(Li)_{t_o})^2$$

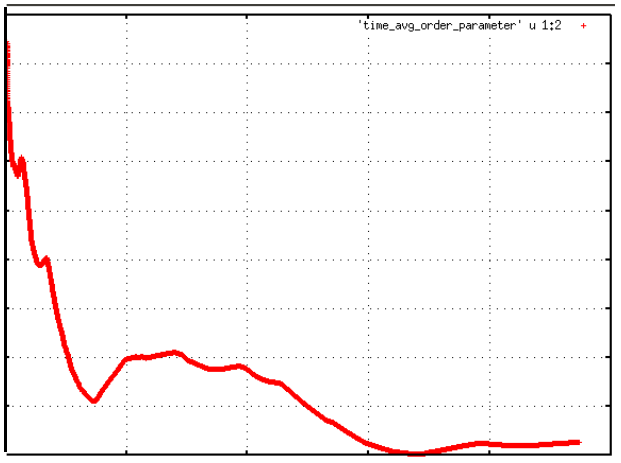
Avg Temp 630K

3.25A^2



24ps

$$\left\langle \left| \frac{2}{3} - \langle SO_i \rangle_t \right| \right\rangle_i (t)$$



0.44

0.36

24ps

Effective temperature in the Micro canonical ensemble

- Tempurature flucates in MD simulation in small(not in Thermodynamic limit) supercell

- Calculated diffusion constants are an average over a range of temperatures

$$\langle D(T)\rangle_T = \int_{T_{min}}^{T_{max}} \rho(T) D_o e^{-\frac{Ea}{kT}} dT = D_o e^{-\frac{Ea}{kT_{eff}}} = D(T_{eff})$$

Where $\rho(T)$ probability of the Temperature T during the run.

T_{eff} is an effective temperature for the run