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Multi-Model Simulations of Li-Ion Dynamics

in Battery Materials with Applied Electric Field

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Abstract

The possibility of combining multiple atomistic models within one single simulation allows one to achieve elaborate computational workflows. Here, we demonstrate the use of a multi-model approach, as implemented in the atomistic simulation platform QuantumATK[1], to investigate Li-ion diffusion in cathode materials. Such multi-model approach is used to study diffusion processes including temperature effects by performing classical molecular dynamics (MD) simulations - in the presence of an external electric field, in which the time-dependent fluctuation of the atomic charges is described by density functional theory (DFT) calculations. The combination of Brownian motion and displacement field resulting from the voltage difference applied between the anode and the cathode has seldom been considered in atomistic simulations[2] and normally such atomistic simulations consider only one of the two components in the diffusivity of ionic species.

Results

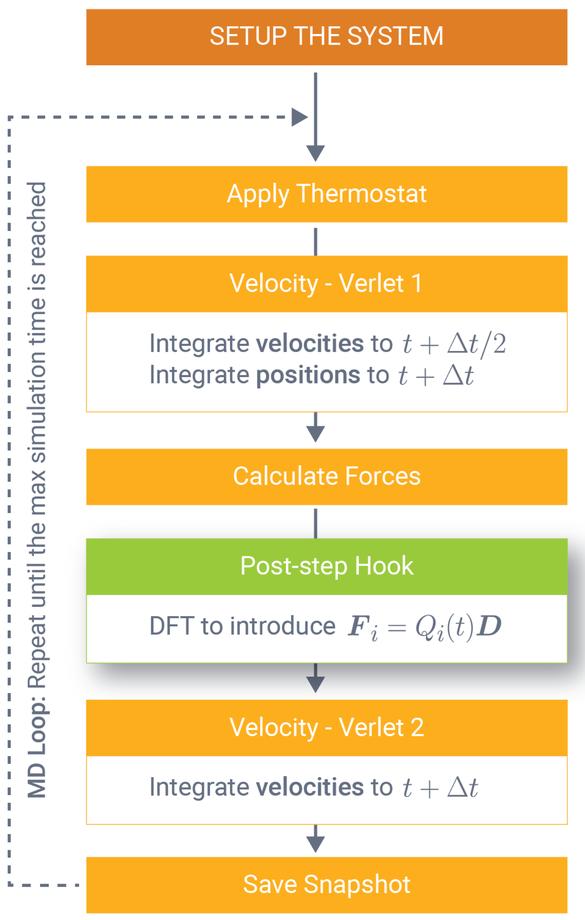
- Displacement field accounted for by an extra force: $\boldsymbol{F}_i = Q_i(t)\boldsymbol{D}$
- Time-dependent charge fluctuation described as:

$$Q_i(t) = Q_i^{FF}(t) + \Delta Q_i(t)$$

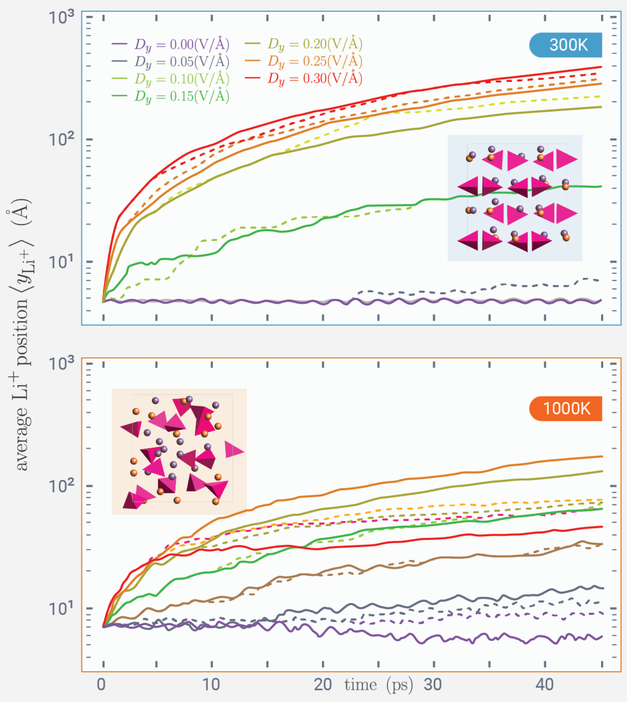
$$\Delta Q_i(t) = \Delta Q_i^{DFT}(t) - Q_i^{DFT,ref}$$

FINDINGS

- No field ($\boldsymbol{D} = 0$). Li^+ hopping is a rare event (Brownian motion) at both 300K and 1000K.
- Finite field along [010] channels ($\boldsymbol{D} \neq 0$). Li^+ hopping primarily due to field-induced drift.
- Collision events due to vibration of the $FePO_4$ lattice limit Li^+ effective velocity.
- Li^+ diffusion is strongly dependent not only on the applied field and the temperature itself, but also on the probability of collision events between the diffusing Li^+ ions and the $FePO_4$ lattice.



- **System investigated:** Li^+ hopping in $LiFePO_4$

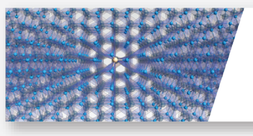


Plots: Average displacement $\langle y_{Li^+} \rangle$ of the Li^+ ions along the y cartesian direction, i.e., along the [010] channels of the $FePO_4$ scaffold.

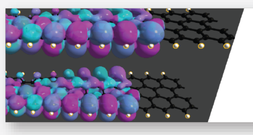
QuantumATK Platform

QuantumATK is an integrated software suite for atomic-scale modeling. It combines the power of a (Python) scripting engine, with the ease-of-use provided by an intuitive GUI.

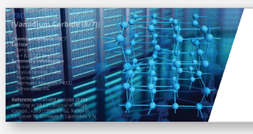
- NanoLab GUI:



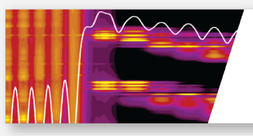
Atomic 3D Builder — Set Up Structures and Devices



View Results — Visualize 2D and 3D Data



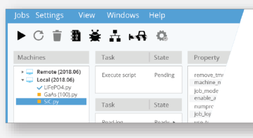
Databases — Import Ready-to-Use Structures



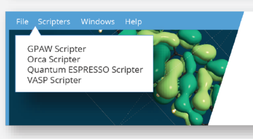
Advanced Analysis — Use Flexible Tools for Complex Studies

Set Up Calculations — Prepare Input Files with Script Generator

Python Scripts — Write Your Own Custom Scripts

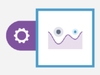


Job Manager — Execute and Manage Local & Remote Jobs



NanoLab Links — Link to External Simulation Engines

- Simulation Engines:



Semi-Empirical → 10^5 atoms

DFT-LCAO → 10^3-10^4 atoms

ForceField → 10^5-10^7 atoms

DFT-PlaneWave → 10^2-10^3 atoms

NEGF, SGF device & surface simulations

Computational Details

- **System:** $LiFePO_4$ (112 atoms)
- **QuantumATK DFT-LCAO:**
  - Spin-Polarized GGA-PBE Exchange-Correlation functional
  - Basis set: Double-Zeta Polarized for all atoms
  - FHI Pseudopotentials 3x3x2 Monkhorst Pack Grid k-point sampling
- **QuantumATK ForceField[3]:** Pedone parameters potential set[4].
- **MD Simulations:**
  - 5ps NPT equilibration run
  - NVT Nose Hoover thermostat
  - 1 fs time-step

References

[1] QuantumATK version O-2018.06-SP1-1, Synopsys QuantumATK (https://www.synopsys.com/silicon/quantumatk.html)
[2] N. J. English and C. J. Waldron, Phys. Chem. Chem. Phys. **17**, 12407 (2015).
[3] J. Schneider, J. Hamaekers, S. T. Chill, S. Smidstrup, J. Bulin, R. Thesen, A. Blom, and K. Stokbro, ATK-ForceField: A New Generation Molecular Dynamics Software Package, IOP Publishing, Modelling Simul. Mater. Sci. Eng. **25**, 085007 (2017)
[4] Pedone, G. Malavasi, M. Menziani, A. Cormack, and U. Segre, A New Self-Consistent Empirical Interatomic Potential Model for Oxides, Silicates and Silica-Based Glasses, J. Phys. Chem. B, **110**, 11780 (2006)