Discontinuous Methods for Accurate, Massively Parallel Quantum Molecular Dynamics:
Lithium Ion Interface Dynamics from First Principles

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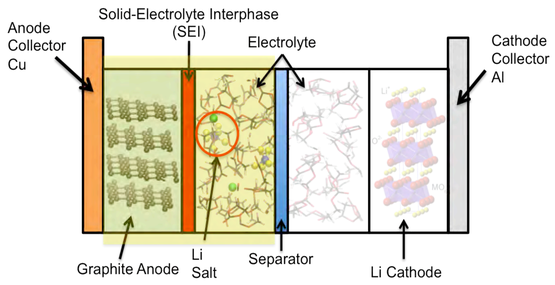
SciDAC Scientific Discovery through Advanced Computing

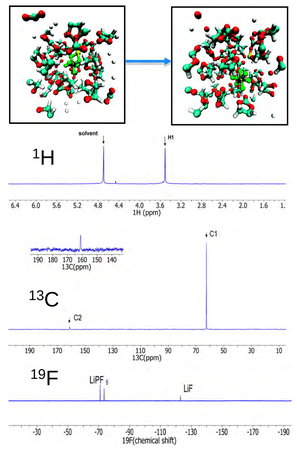
Introduction

Lithium Ion Batteries and SEI



- Li-ion batteries are key components of consumer electronics and electric/hybrid-electric transportation technologies
- Solid-electrolyte interphase (SEI) is a product of electrolyte decomposition; important for stability but limits ion transport
- Understanding formation and composition of SEI important to improve performance and safety of Li-ion batteries

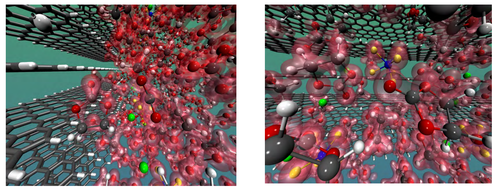
What's Known about SEI Formation?



- Spectroscopy reveals SEI composition for:
  - $LiPF_6$ + Ethylene Carbonate (EC)
  - $LiPF_6$ + Ethyl Methyl Carbonate (EMC)
  - $LiPF_6$ + EC/EMC (3:7)
- Experiments provide no mechanistic details of formation
- Simulations require quantum effects to treat chemical reactivity
- Solvation structures determined with quantum molecular dynamics, but using small system sizes (<600 atoms) and short time scales (<25 ps)

M. Nie, *et al., J. Phys. Chem. C.*, 2013, 117(3), 1257-1267
K. Leung and J. L. Budzien, *PCCP*, 2010, 12, 6583-6586
Ganesh *et al., J. Phys. Chem B.*, 2011, 115, 3085-3090
Ganesh *et al., J. Phys. Chem C.*, 2012, 116, 24476-24481

Project Goals



- Understand the reaction mechanisms and dynamics at the anode-electrolyte interface that lead to SEI formation and growth
- Examine the transport properties and solvation structures of Li ions in the bulk electrolyte and at the interface
- To achieve these goals, we perform massively parallel quantum molecular dynamics simulations at unprecedented time and length scales
- Enable design of new anode-electrolyte combinations for safe, reliable, high-capacity, high-charge rate batteries

Methods

- Quantum molecular dynamics (QMD) coupled with density functional theory (DFT) in **VASP** & **Qbox**
- PBE/GGA exchange–correlation functional
- Projector augmented wave (PAW) method used in **VASP**; norm-conserving pseudopotentials used in **Qbox**
- NVT (canonical ensemble) used for equilibration
  - **VASP**: Nose–Hoover thermostat
  - **Qbox**: Berendsen velocity scaling thermostat
- NVE (microcanonical ensemble) used to collect statistics
- Verlet algorithm using 0.5 fs time step
- Future QMD runs will use Discontinuous Galerkin density functional theory (**DGDFT**) code currently in development
  - Local, systematically improvable basis set
  - Enables scaling to system sizes of ~10,000+ atoms

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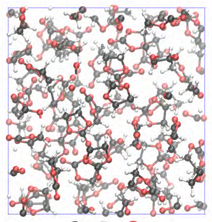
L. Lin, *et al., Phys. Rev. B*, 2012, 85(23): 235144

Computational Scaling & Code Improvements

Bulk Ethylene Carbonate (EC) Benchmark System



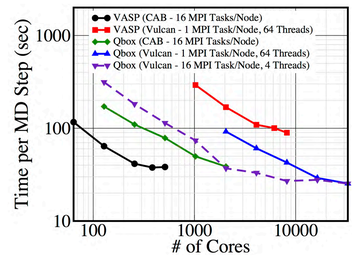
- $C_3H_4O_3$ (88.06 g/mol)
- 64 molecules
- 640 atoms
- 2176 electrons
- Box length: 19.039 Å
- Density: 1.36 g/cc

Qbox Improvements

# of Bands	VASP	Qbox (old)	Qbox (improved)
16 Bands	50	584	178
No Bands	42	112	107
Ratio	1.2	5.2	1.7

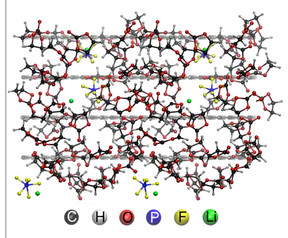
- Qbox modified to perform self consistent cycle faster using Harris-Foulkes estimate for energy convergence
- Enhanced performance when including empty states, important for metallic systems

VASP & Qbox Scaling Comparisons

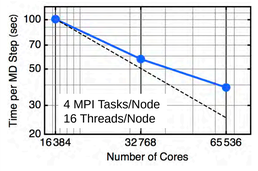


- VASP ideal for small systems
- Qbox scales better for larger systems
- Qbox utilizes hardware threading & SIMD registers on Vulcan (Blue Gene/Q) unlike VASP
- Qbox uses algorithms designed for massive scalability (*e.g.* preconditioned steepest descent)

Strong Scaling on Blue Gene/Q



- 98 EC + 6 $LiPF_6$ + 4L-Graphite (H-terminated)
- 1700 atoms
- 6020 electrons
- 38.5 x 14.8 x 40.8Å
- 0.83 M $LiPF_6$

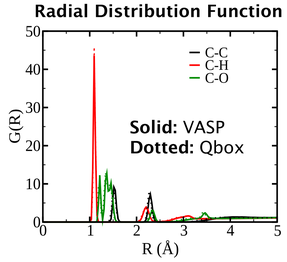


- Excellent scaling up to 65536 cores
- 1700 atoms in 40 sec/MD step
- Run 10-40 ps/month

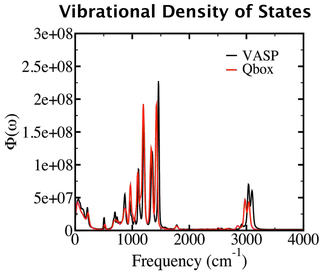
Initial Results

Bulk EC Macroscopic Properties

Radial Distribution Function

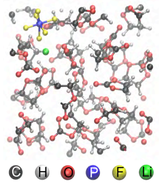


Vibrational Density of States



- Structural and vibrational properties in good agreement with experiment
- Small variations due to simulation parameters, including pseudopotential and thermostat
- Consistency between codes important if advantageous to use one code over another for different systems/properties

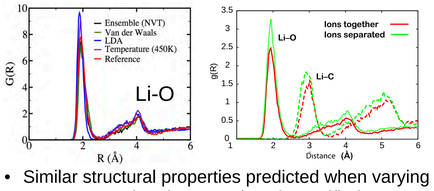
Smaller Bulk Electrolyte System



- 32 EC + $LiPF_6$
- $C_3H_4O_3$ (88.06 g/mol)
- $LiPF_6$ (151.91 g/mol)
- 318 atoms
- 1102 electrons
- Box length: 15.362 Å
- Density: 1.32 g/cc

Macroscopic Properties

Parameter Varied	C_v (J/g•K)	Viscosity (cP)
Reference (PBE, NVE, 450eV, 310K)	2.96	1.00
Ensemble (NVT)	2.81	1.04
Van der Waals	3.63	1.51
Exchange-Correlation (LDA)	2.86	1.69
Temperature (450K)	2.88	0.31
Experiment (EC)	1.52 (C_p)	1.86 (40°C)



- Similar structural properties predicted when varying parameters; chemistry needs to be verified
- If Li^+ and PF_6^- together, only 75% as many carbonyl oxygens around Li^+ compared to dissociated $LiPF_6$
- Li^+ diffusivity 2-3x faster when Li^+ and PF_6^- separate
- Heat capacity not affected by mixing solvents, but viscosity is nonlinear function of mixing

Next Steps

1) **Larger bulk electrolyte systems inspired by experiments**
   - Different electrolytes and salts
   - Effect of salt concentration and temperature
   - Finite size effects
2) **Anode + Electrolyte**
   - Important chemical reactions that lead to SEI formation
   - Examine the effect of different anode materials
   - Investigate the effect of liquid environment
   - Simulations of ~10,000+ atoms with new DGDFT code

Summary

- VASP faster for smaller systems, Qbox scales better for larger systems
- Qbox sped up by factor of three for metallic systems
- Excellent scaling of Qbox on Vulcan (BG/Q) system; timings show best performance for 1 MPI task/node using all OpenMP threads
- Consistency between VASP & Qbox in structural properties for bulk EC
- Separated $LiPF_6$ results in more carbonyl oxygen atoms around the Li^+ ion in the first solvation shell than when cation and anion are together
- Li^+ diffusivity 2-3x faster when $LiPF_6$ dissociates in solvent

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