Discontinuous methods for massively parallel quantum molecular dynamics: Lithium ion interface dynamics from first principles

John Pask (Lead), Vincenzo Lordi, Mitchell Ong
Condensed Matter and Materials Division, Lawrence Livermore National Laboratory

Chao Yang*, Mathias Jacquelin*, Gaigong Zhang, Wei Hu
Computational Research Division, Lawrence Berkeley National Laboratory
*SciDAC FASTMath Institute

Lin Lin
Department of Mathematics, University of California, Berkeley
Computational Research Division, Lawrence Berkeley National Laboratory

Erik Draeger, Timo Bremer**
Center for Applied Scientific Computing, Lawrence Livermore National Laboratory

Valerio Pascucci**, Attila Gyulassi
Scientific Computing and Imaging Institute, University of Utah
**SciDAC SDAV Institute
Overview

- Li-ion batteries have revolutionized consumer electronics and have the potential to do the same for transportation (e.g., plug-in hybrids, all-electrics, aircraft) and electrical distribution (e.g., load leveling)
- To do so, energy/power density, lifetime, safety must be increased
- Key issue: solid-electrolyte interphase (SEI) layer at electrolyte-anode interface, product of electrolyte decomposition
- Understanding has been hindered by need for both quantum mechanical description and sufficiently large length/time scales to capture necessary complexity
- In this work, we:
  - Develop new Discontinuous Galerkin (DG) based electronic structure method to accomplish quantum molecular dynamics (QMD) on an unprecedented scale
  - Apply new method to advance understanding of the chemistry & dynamics of electrolyte/SEI/anode systems
Simulations

- Initial phase of project, while new DG/PEXSI code is developed and optimized: **Qbox** [1] for systems of < 2,000 atoms
- Li⁺ solvation and diffusion: determine diffusion coefficients, effect of counter-ion, differences in bulk vs near interface

Molecular dynamics simulation of 50/50 ethylene carbonate/propylene carbonate electrolyte

**Ion solvation**

- Li$^+$ prefers tetrahedrally-coordinated first solvation shell
- Stronger solvation for Li$^+$ than PF$_6^-$
- Mixture shows preference for Li$^+$ to be solvated by EC over EMC
- PF$_6^-$ more mobile than Li$^+$ due to weaker solvation
### Ion diffusion

**Ethylene Carbonate (EC)**

<table>
<thead>
<tr>
<th></th>
<th>$D_{Li}$ ($10^{-6}$ cm$^2$/s)</th>
<th>$D_P$ ($10^{-6}$ cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>5.2 ± 0.8</td>
<td>7.1 ± 0.9</td>
</tr>
<tr>
<td>EMC</td>
<td>9.6 ± 1.6</td>
<td>30.8 ± 8.8</td>
</tr>
<tr>
<td>3:7 EC/EMC</td>
<td>2.6 ± 1.3</td>
<td>5.7 ± 2.4</td>
</tr>
</tbody>
</table>

**Ethyl Methyl Carbonate (EMC)**

- Motion of Li$^+$ and PF$_6^-$ in EMC less correlated than in EC
- Mixture shows correlated motion similar to EC
- Faster diffusion for Li$^+$ seen in EMC than EC
- PF$_6^-$ has larger diffusion coefficient than Li$^+$ since Li$^+$ is more strongly solvated than PF$_6^-$

**3:7 EC/EMC Mixture**

- Size of coefficient tied to solvation structure
Simulations

- As the new **DGDT/PEXSI** method and code ramp up, we transition to it for larger scale simulations, up to 10,000 atoms
- Full electrolyte-anode and electrolyte-SEI systems

**EC/PC mixture (+ LiPF₆) on graphite (left) and Li₂CO₃ (right)**, used to study chemical reactions on the anode surface (for initial SEI formation) and a representative SEI compound (for SEI growth/evolution)
How to reach the needed length and time scales?

Throw off the shackles of continuity.

Rethink the need for eigenfunctions.
Quantum molecular dynamics (QMD)

- Solve Kohn-Sham equations for electronic structure, compute quantum mechanical forces, move atoms, repeat – thousands to hundreds of thousand of times

Kohn-Sham equations

\[-\frac{1}{2} \nabla^2 \psi_i(x) + \hat{V}_{\text{eff}} \psi_i(x) = \varepsilon_i \psi_i(x),\]

\[\hat{V}_{\text{eff}} = V_I^e + V_{\text{nl}}^I + V_H + V_{xc}, \quad (\text{Schrödinger})\]

\[V_I^e = \sum_a V_{I,a}(x),\]

\[\hat{V}_{\text{nl}}^I \psi_i = \sum_a \int d\mathbf{x}' V_{I,a}^n(x, x') \psi_i(x'),\]

\[V_H = -\int d\mathbf{x}' \frac{\rho_e(x')}{|\mathbf{x} - \mathbf{x}'|}, \quad (\text{Poisson})\]

\[V_{xc} = V_{xc}(\mathbf{x}; \rho_e),\]

\[\rho_e = -\sum_i f_i \psi_i^*(x) \psi_i(x),\]

\[\sim 10^4 \text{ atoms, more eigenfunctions}\]

Self-consistent field (SCF) solution process

Start (guess): \(\rho_{in}\)

\[\hat{V}_{\text{eff}}[\rho_{in}]\]

Repeat:

\[\{\psi_i, \varepsilon_i\}_i\]

\[\text{new } \rho_{in} \xrightarrow{\text{mix}} \rho_{out}\]

\[\rho_{out} = \rho_{in}?\]

Yes

Done:

\[\{\psi_i, \varepsilon_i\}_i \Rightarrow \text{materials properties}\]
Pushing the current state of the art: Qbox application and development

- **Strong scaling to 65,536 cores** on BG/Q
  - Uses hardware threading & SIMD registers on BG/Q
  - Optimized BLAS/ScalAPACK kernels on BG/Q
  - Preconditioned steepest descent for occupied subspace
- → **1,700-atom anode-electrolyte system in 40 sec per QMD step**
- Up to **2,014-atom anode-electrolyte systems** presently: 79 sec per MD step on 64k cores
• Metallic calculations rely on diagonalization in the occupied subspace (Rayleigh-Ritz)

• Limits both efficiency ($N^3$) and parallel scaling

• In collaboration with **FASTMath**, we are investigating alternatives to minimize or eliminate Rayleigh-Ritz entirely
  
  – Trace penalty minimization: minimize trace of Rayleigh quotient and penalty term to enforce orthogonality [1]

  – Projected Preconditioned Conjugate Gradient (PPCG): Replace $3m \times 3m$ Rayleigh-Ritz with $m$ 3x3 ones [2]

  – PPCG now implemented in Quantum Espresso parallel planewave code

  – Initial tests indicate **factor of two speed up (already)** and **potentially superior parallel scalability** relative to current-state-of-the-art Davidson solver

• **Goal:** Metallic as fast as insulating, 2,000-atom metallic QMD

Moving beyond the current state of the art: DGDFT

- DG framework allows solving the Kohn-Sham equations in a discontinuous basis
- Because basis can be discontinuous, can possess number of desirable properties simultaneously:
  - Efficient (few tens of DOF/atom)
  - Systematically improvable
  - Strictly local: identically zero outside prescribed subdomain, zero overlap across subdomains
  - Orthonormal: standard eigenproblem, well-cond.
- How?
  - Partition domain into subdomains (elements)
  - Solve Kohn-Sham equations in each element
  - Basis is union of local Kohn-Sham solutions

Solve large $N$-atom problem in highly efficient basis of $O(N)$ local Kohn-Sham solutions
Discontinuity is accommodated by surface ("flux") terms [1 - 4]

Kohn-Sham Hamiltonian becomes

\[ H_{DG}(k', j'; k, j) = \frac{1}{2} \left( \langle \nabla u_{k', j'}, \nabla u_{k, j} \rangle_T + \alpha \langle [u_{k', j'}], [u_{k, j}] \rangle_S \right) - \frac{1}{2} \langle [u_{k', j'}], \{ \nabla u_{k, j} \} \rangle_S - \frac{1}{2} \langle \{ \nabla u_{k', j'} \}, [u_{k, j}] \rangle_S + \langle u_{k', j'}, V_{eff} u_{k, j} \rangle_T + \sum_{\ell} \gamma_{\ell} \langle u_{k', j'}, b_\ell \rangle_T \langle b_\ell, u_{k, j} \rangle_T \]

\( T = \) elements

\( S = \) element surfaces

\( u_{k, j} = \) jth basis function in kth element

\( \{ \cdot \} \) and \( [\cdot] \) = average and jump operators across surfaces

Kohn-Sham equations: \( H_{DG} c_i = \varepsilon_i c_i \)

Wavefunctions: \( \psi_i = \sum_{E_k \in T} \sum_{j=1}^{J_k} c_{i; k, j} u_{k, j} \)

Density: \( \rho = \sum_{E_k \in T} \sum_{i=1}^{N} \sum_{j=1}^{J_k} |\sum_{j=1}^{J_k} c_{i; k, j} u_{k, j}|^2 \)

Energy: \( E_{tot} = \sum_{i=1}^{N} \varepsilon_i - \frac{1}{2} \int \int \frac{\rho(x) \rho(y)}{|x - y|} \, dx \, dy + \int \varepsilon_{xc}[\rho(x)] \, dx - \int \varepsilon'_{xc}[\rho(x)] \rho(x) \, dx \)

Energies, forces, degrees of freedom

- Energies to < 1e-3 Ha/atom, forces to < 1e-3 Ha/au absolute error with ~10 basis funcs/atom
  
  Si 1x1x4: random displacements

  ~40 DOF/atom for 3D

- Hard atoms: Li-ion system – Li, P, F, C, H, O

- Forces to 1e-4 Ha/au absolute error with 15 basis funcs/atom

- Largest system so far: 4,392 atoms on 2,196 CPUs by direct diagonalization
Molecular dynamics

NVE MD simulation of liquid Si at 3000K using DGDT

Energy drift < 1.5 meV/atom/ps

Pair correlation for Si$_{0.12}$Al$_{0.88}$ alloy with 200 atoms

Agreement with previous literature and independent calculations
Current focus: local K-S solves

- Solution of the local \(\sim 50\)-atom Kohn-Sham problems in each element
- In collaboration with \textbf{FASTMath}, we are parallelizing the local K-S solutions to remove this bottleneck
- **OpenMP**: speedup by factor of 6
  - Time per SCF reduced from \textbf{180.2 s} (OMP=1) to \textbf{29.4 s} (OMP=12) for 24-atom Li-ion system
- **MPI**: PWDFM can use more than \textbf{160 cores} with \textbf{70-fold speedup} to generate DG basis
  - Time per SCF \(\sim 10\) s for 20-atom \(\text{Yb}_8\text{O}_{12}\) system
- More to come!
For the largest systems: PEXSI

• Solving for Kohn-Sham wavefunctions of $N$ atom system scales as $O(N^3)$

• Solve for density directly instead

$$\rho(x) = \text{diag} \left( f_\beta(\hat{H}[\rho(x)] - \mu \delta(x, x')) \right)$$

$\hat{H}$ = Hamiltonian, $\mu$ = chemical potential, $f_\beta(x) = 2/(1 + e^{\beta x})$

$\beta = 1/k_B T$, $k_B$ = Boltzmann constant, $T$ = temperature

• Need efficient approximation of Fermi function $\rightarrow$ Pole expansion [1]

$$f_\beta(\varepsilon - \mu) \approx \text{Im} \sum_{l=1}^{\mathcal{P}} \frac{\omega_l^0}{\varepsilon - (z_l + \mu)}$$

$z_l, \omega_l^0 \in \mathbb{C}$ are complex shifts and weights

• Need efficient inversion

• Need only diagonal $\rightarrow$ Selected Inversion [2]

$\rightarrow$ Pole Expansion and Selected Inversion (PEXSI)

• No need to compute eigenfunctions or eigenvalues

• Scaling $O(N)$ for quasi-1D systems; $O(N^2)$ for metallic 3D

Energies, forces, poles

- Metallic carbon nanotube, CNT (8,8), 512 atoms, atomic orbital basis [1]

- Accuracy of expansion at T = 300K

<table>
<thead>
<tr>
<th># Poles</th>
<th>$E_{PEPSI} - E_{ref}$ (eV)</th>
<th>MAE Force (eV/Angstrom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>5.868351108</td>
<td>0.400431</td>
</tr>
<tr>
<td>40</td>
<td>0.007370583</td>
<td>0.001142</td>
</tr>
<tr>
<td>60</td>
<td>0.000110382</td>
<td>0.000026</td>
</tr>
<tr>
<td>80</td>
<td>0.000000360</td>
<td>0.000002</td>
</tr>
</tbody>
</table>

- Largest 3D system so far: **24,000-atom** water using SIESTA DZP basis [2]
  - **314 sec** SCF iteration on 10,240 cores
  - **30-fold speedup** relative to diagonalization

PEXSI released

The PEXSI library is available online http://pexsi.org/, BSD license

• Integrated with SIESTA for accelerating atomic-orbital based calculations
• Being integrated into CP2K and other electronic structure packages
• Massively parallel to 10,000 – 100,000 processors on high performance computers

[M. Jacquelin, L. Lin and C. Yang, submitted]
• **2544-atom** Li-ion electrolyte

• 12x12x12 element partition, 68 basis functions per atom

• PESXI: ~250 sec per pole per $\mu$ iteration on 1024 cores

• High accuracy -> 40 poles, ~2 $\mu$ iterations -> ~500 sec/SCF on 40,960 cores
Current focus: factorization

• Parallel scaling of \textit{LU} factorization

• By pipelining and overlapping communication with computation, SelInv now faster and better scaling than SuperLU\_DIST

• SuperLU\_DIST scales to only $\sim$1000 CPU

• In collaboration with \textbf{FASTMath}, we are exploring alternatives for better scaling sparse direct factorization
  
  – More robust symbolic factorization

  – New symmetric factorization code under development: exploring block fan-out and fan-both methods for better parallel scaling

  – Leverage results of previous SCF iteration: previous $H, LU$?

• To get SCF step times down from minutes to seconds for 3D systems may require iterative methods to fully leverage information from previous SCF/MD steps
New collaboration: SDAV

• Valerio Pascucci, Attila Gyulassi (University of Utah), Timo Bremer (LLNL)

• Systematic topological analysis of quantum mechanical data: density, potential, wavefunctions

• Compute Morse-Smale complex: minima, maxima, saddle points $\rightarrow$ mountains, voids, ridges, valleys, connectivity

• Evolution in space and time

• Bond formation and breaking

• Voids/tunnels for Li$^+$ transport

• On the fly $\rightarrow$ inform/accelerate MD?

Valley lines connecting voids in QMD charge density

Saddle-max-saddle connections in distance field
Thanks for your attention!

Please visit us at http://www.dgdft-scidac.org