Extending the Time and Length Scale of \textit{Ab-initio} 
Molecular Dynamics Simulations

M. Krack\textsuperscript{1} \quad S. Caravati\textsuperscript{2} \quad T. D. Kühne\textsuperscript{2} \quad M. Parrinello\textsuperscript{2} \quad M. Bernasconi\textsuperscript{3}

\textsuperscript{1}Paul Scherrer Institut
\textsuperscript{2}ETH Zurich
\textsuperscript{3}University of Milano-Bicocca

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Motivation

Goal:
- \textit{Ab-initio} simulations for extended time and length scales
- Elucidate structure and dynamical behaviour of complex materials

Prerequisites:
- Efficient energy and force evaluation for an atomic configuration
- Accelerated molecular dynamics scheme for time propagation
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What is \textit{ab-initio}?

- First-principle or \textit{ab-initio} methods:
  - Directly derived from established laws of physics
    \[\Rightarrow\] from \textit{first principles} of physics
  - No ad-hoc assumptions
  - No fitting of model parameters to experimental data

- Example: (related to the discussed case)
  - Electronic structure methods based on the Schrödinger equation that do not include any fitting to experimental data
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## Ab-initio, why bother?

Just an indicative comparison

<table>
<thead>
<tr>
<th>Electronic structure</th>
<th>Empirical potential</th>
</tr>
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<tbody>
<tr>
<td>Motion of nuclei and electrons</td>
<td>Motion of atoms</td>
</tr>
<tr>
<td>No a priori knowledge of the interatomic interactions</td>
<td>Pre-defined fitted interaction potentials</td>
</tr>
<tr>
<td>Dynamic bonding processes</td>
<td>Bonding pre-defined (topology)</td>
</tr>
<tr>
<td>Predictive</td>
<td>Only limited predictive</td>
</tr>
<tr>
<td>Computationally very costly</td>
<td>Computationally rather cheap</td>
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</table>
Ab-initio methods

- Hartree-Fock based methods (e.g. MP2, CCSD)
  → accurate, but often expensive

- Kohn-Sham density functional theory (KS-DFT)
  → efficient and most of the times sufficiently accurate
The open source project CP2K

- Program package to perform molecular dynamics simulations

- Methods implemented in CP2K (Fortran 90/95):
  - *Ab-initio* density functional methods (QUICKSTEP)
  - Semiempirical methods (AM1, MNDO, PM3, PM6)
  - Density functional tight-binding methods (DFTB)
  - Empirical potential methods (FIST)

- More informations:

  http://cp2k.berlios.de
CP2K/QUICKSTEP

- Based on Kohn-Sham density functional theory (KS-DFT)
- Hybrid basis set (Gaussian Plane Waves method):
  - Linear combination of Gaussian-type orbitals (LC-GTO) for the Kohn-Sham orbitals
  - Auxiliary plane waves basis set for the electronic charge density
- *Ab-initio* DFT calculations for atomic, molecular, liquid or crystalline systems are feasible
- Kohn-Sham matrix construction scales linearly
  → fast energy and force calculation
Ab-initio molecular dynamics (AIMD)

Basic types

- Born-Oppenheimer molecular dynamics (BOMD):
  - Optimize electronic structure in each time step tightly

- Car-Parrinello molecular dynamics (CPMD):
  - *Fictitious* dynamics for the wavefunctions (orbitals)
  - Nuclear and electronic degrees of freedom are propagated together
### Ab-initio molecular dynamics

**Pros and Cons: BOMD versus CPMD**

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- **Goal:** Combine the best of both methods
  - Stable: CPMD-like propagation scheme
  - Accurate: adaptively approaching BOMD
  - Efficient: large (BOMD-like) integration time steps, but no SCF
  - Robust: small band gap systems can be handled
Ab-initio molecular dynamics
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New method for accelerated ab-initio MD

- Stable predictor-corrector method for the propagation of the electronic degrees of freedom
- Efficient preconditioned minimizer method (corrector step)
- Langevin-type dynamics to propagate the nuclear degrees of freedom
Validation of the method
Is the kinetic energy distribution Maxwell distributed?

Test system: Molten silicon
Simulation cell: 64 Si atoms
Temperature: $T = 3000$ K
Simulation time: $t > 1$ ns
Simulation method: DFT MD
Code: CP2K/QUICKSTEP

A correct canonical sampling of the Boltzmann distribution is performed.
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Validation of the method
Deviation from the Born-Oppenheimer surface

- Test system: Molten silica
- Simulation cell: 24 SiO₂ units
- Temperature: T = 3500 K
- Bonds are swiftly broken and formed
- Worst case scenario as the electronic density is rapidly varying
Validation of the method
Deviation from the Born-Oppenheimer surface

![Graph showing energy deviation over time](image-url)
Validation of the method
Deviation from the Born-Oppenheimer surface

-865.4
-865.2
-865
-864.8
Energy [Hartree]

BOMD reference
1 corrector step

0 200 400 600 800 1000
Time [fs]

Instantaneous mean force deviation
Average mean force deviation

Mean force deviation [a.u.]
Validation of the method
Deviation from the Born-Oppenheimer surface

![Graph showing energy and mean force deviation over time](image_url)
Validation of the method
Deviation from the Born-Oppenheimer surface

![Graph showing energy and mean force deviation over time](image)
Validation of the method
Deviation from the Born-Oppenheimer surface

- Small and almost constant energy shift
- Energy differences are very well reproduced
- No tight wavefunction optimization
- Deviation from the BO surface is systematically controllable
Validation of the method
Structural properties

For these systems a speed-up of two orders of magnitude is observed
Validation of the method
Structural properties

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Modeling of phase change materials (PCMs)

- Phase change material (PCM) for non-volatile memory (NVM):
  - Ge$_2$Sb$_2$Te$_5$ (GST), e.g. for DVD-RAM
  - Fast and reversible crystal-amorphous transition

- Not much is known:
  - about the amorphous phase structure
  - about the transition mechanism
  - why does GST work so well?

- AIMD is effective, as no force fields are available (ternary system)
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Crystalline phase of Ge$_2$Sb$_2$Te$_5$ (GST)

- Rocksalt (NaCl-type) structure
- Fully occupied Te sublattice
- Local distortion: mainly for Ge and Sb

Amorphous phase of Ge$_2$Sb$_2$Te$_5$ (GST)
Ge$_2$Sb$_2$Te$_5$: Simulation vs. Experiment

Structure factors $S(Q)$ and pair correlation functions $T(r)$
Dynamical properties

- Diffusion coefficient $D$ of the liquid:
  - $D = 4.88 \cdot 10^{-5}$ cm$^2$/s (accelerated AIMD, this work)
  - $D = 4.55 \cdot 10^{-5}$ cm$^2$/s (conventional BOMD, this work)
  - $D = 4.67 \cdot 10^{-5}$ cm$^2$/s (CPMD, J. Akola and R. O. Jones)
Pressure-induced amorphization of GST

![Graph showing pressure-induced amorphization of GST]

(normalized intensity vs. Pressure (GPa))

Te — Te — Te
Ge — Te — Sb
Te — Ge — Te
Te — Ge — Te
Te — Te — Sb
Pressure-induced amorphization of GST

12 GPa

14 GPa
Summary

- Development and validation of a new accelerated AIMD method
- First successful application to a real-world problem (PCMs)
- Amorphous GST samples could be simulated and structural and dynamical properties could be analyzed
- Simulation of pressure-induced amorphization yields transition pressure close to experiment
- Possible mechanism of amorphization elucidated
- Results may guide future materials design
- Computers help to understand their own components
Acknowledgment

- DEISA (RZ Garching and FZ Jülich)
- Swiss National Supercomputing Centre (CSCS)
- ETH Zurich (IT Services: Scientific Computing)
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Thank you for attention!