Performing density-functional tight-binding calculations with LAMMPS and the LATTE library

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Los Alamos National Laboratory

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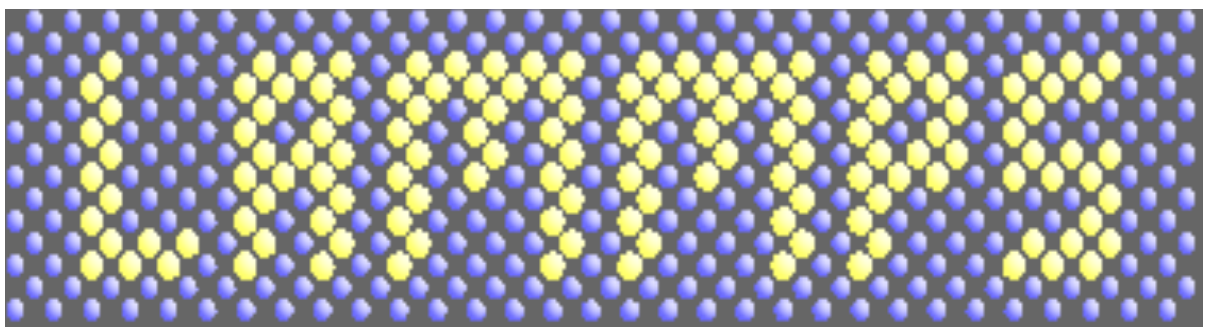
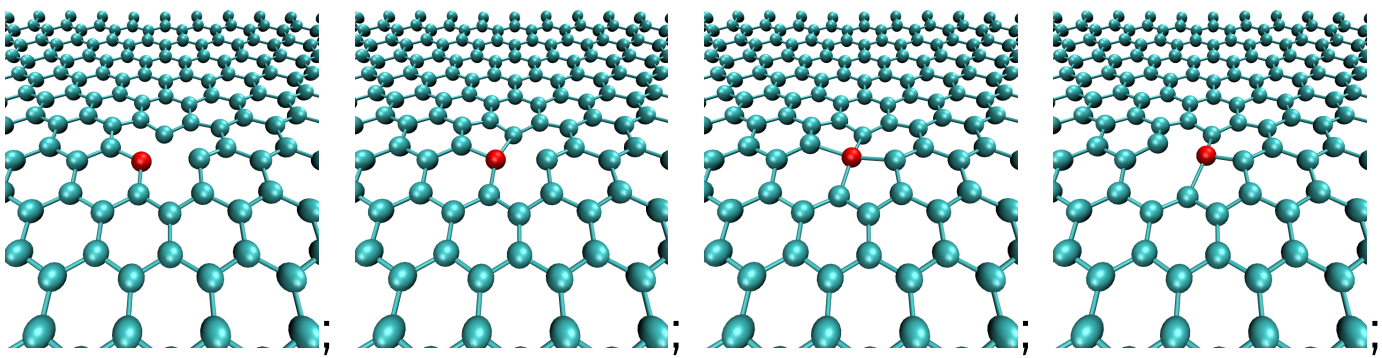


Outline

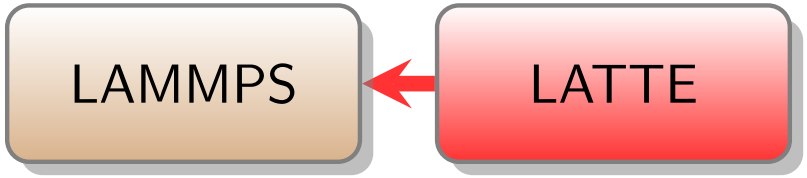
Quantum based MD

- Takes the quantum nature of the chemical bond explicitly into account.
- Free from the arbitrariness of choosing a particular force field.
- Allows for formation and rupture of bonds (chemical reactions).
- Electronic properties can be monitored along the simulation.
- Computationally more demanding than classical MD.



- Modeling the Long-Term Behavior of Vacancy Complexes in Graphene E. Martínez et al.

Extending LAMMPS to DFTB-based QMD



- LAMMPS: We benefit from most of the LAMMPS functionalities.
  - Integration of the nuclear degrees of freedom (Verlet)
  - Provides thermostats and barostasts to perform NVT and NVP simulations.
  - Provides all the infrastructure to do geometry optimization using different algorithms.
  - We can compute transition barriers with the NEB method.
- LATTE (**M. Cawkwell**): Forces computed at the SCC-DFTB level.
  - Provides forces and the potential component of the total energy.
  - Integrates the electronic degrees of freedom (XL) (provides charges)
  - Solves the electronic structure of the system.
  - Several solvers such as SP2, Truncated SP2, Chebyshev polynomial expansion, etc.

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Our computational framework:

Capabilities in the format of a library.

- LATTE: A molecular dynamics package based around self-consistent-charge density functional tight binding theory (DFTB. We have also used this libraries in DFTB+.
- PROGRESS: This is a set of new capabilities offered as modules that rely entirely on BML. Several $\mathcal{O}(N)$ solvers for ρ are available.
- BML: Only linear algebra or mathematically related operations are performed. We have a fast sparse matrix-matrix multiplication.

- https://github.com/qmmd/bml
- https://github.com/lanl/qmd-progress
- https://github.com/lanl/LATTE

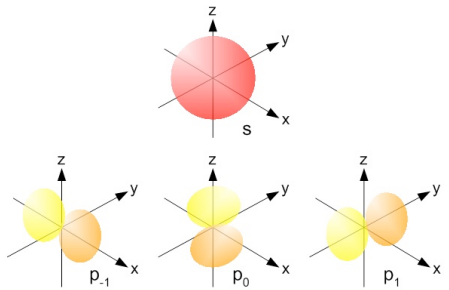
LATTE scf-dftb physical model

$$H^0_{i\alpha,j\beta}(r_{ij}) = A_0 \exp(A_1 r_{ij} + A_2 (r_{ij})^2 + A_3 (r_{ij})^3 + A_4 (r_{ij})^4)$$

$$S_{i\alpha,j\beta}(r_{ij}) = B_0 \exp(B_1 r_{ij} + B_2 (r_{ij})^2 + B_3 (r_{ij})^3 + B_4 (r_{ij})^4)$$

$$H_{i\alpha,j\beta} = H^0_{i\alpha,j\beta} + \tfrac{1}{2} S_{i\alpha,j\beta}(V_i + V_j)$$

$$\mathbf{P} = [f(\mathbf{H})]_{\mathrm{SCF}}$$



$$q_i = \tfrac{1}{2} \sum_{\alpha \in i} (P_{j\beta,i\alpha} S_{i\alpha,j\beta} + P_{i\alpha,j\beta} S_{j\beta,i\alpha}) - n_i^e$$

$$E = 2\mathrm{Tr}(\mathbf{PH}) + \tfrac{1}{2} \sum_{i,j \neq i} \gamma_{ij} q_i q_j + E_{\mathrm{pair}}$$

$$F_{ij} = -\mathrm{Tr}\left[\mathbf{P} \frac{\partial \mathbf{H}}{\partial r_{ij}}\right] - \tfrac{1}{2} \sum_i \sum_{j \neq i} q_i q_j \frac{\partial \gamma_{ij}}{\partial r_k} - \frac{\partial E_{\mathrm{pair}}}{\partial r_{ij}}$$

- https://github.com/lanl/LATTE

Why LATTE?

- Fast analytical physical model based on product of exponentials.
- Improves transferability.
- Provides linear scaling solvers for the density matrix.
- Provides linear scaling solvers for the inverse overlap.
- Provides the Extended Lagrangian method.
- Efforts in obtaining highly accurate parametrizations are ongoing (EPO code developed by **N. Aguirre**)
- Solvers will be ported to Exascale computing through ongoing projects.

Compiling latte as a library

- The standalone LATTE code can be easily compiled as a library (`lattelib.a`).

```
$ cd; git clone git@github.com:lanl/LATTE.git
$ cd ~/LATTE; make
```

- Both ifort (Intel) and gfortan (GNU) fortran compilers have been tested.
- LATTE can be easily linked to LAMMPS.

```
$ cd ~/lammps/src
$ make yes-latte
$ make yes-molecule
$ make serial
```

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What do we need to run?

- LAMMPS usual input files (`data.system` and `in.system`)
- Add a "fix latte" to the input file:

```
fix     2 all latte NULL
```

- LATTE control file (`latte.in`) and parameters folder (`TBparams`)
- Everything should be inside the same folder we are running.
- And we will run as:

```
$ ~/lammps/src/lmp_serial < in.system
```

That's all!

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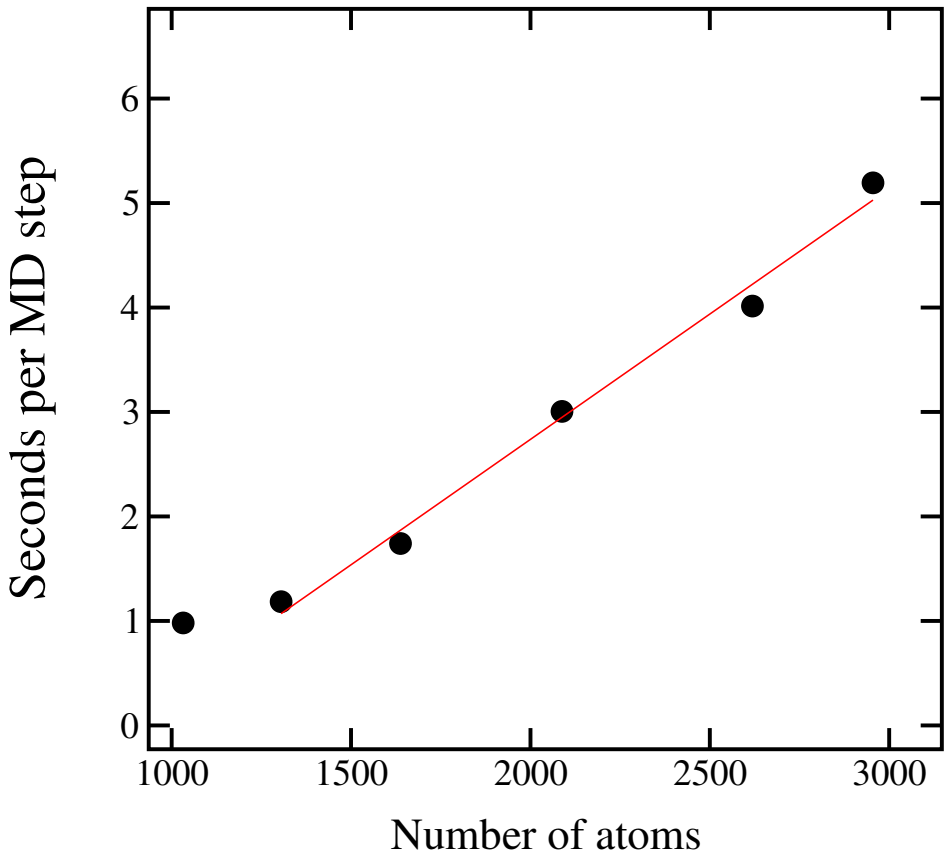
Linear scaling using SP2 and XL methods



Linear scaling up to 3000 atoms system. Water boxes of different sizes. Calculations were performed on a 18-core 2.10 GHz Intel Xeon E5-2695 v4 processors.

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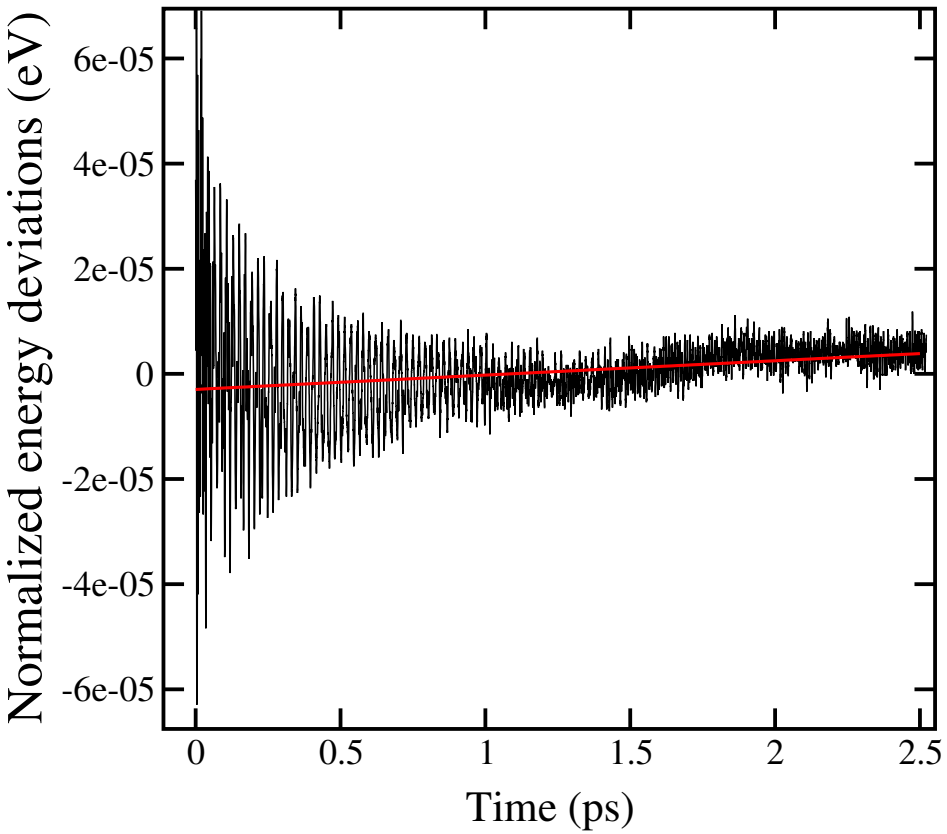
Energy stability



Energy deviations for a 2955 atoms water box showing small energy fluctuations and energy drift. For this case the average fluctuation is no larger than 5 μeV/atom and the drift is about 3 μeV/ps-atom

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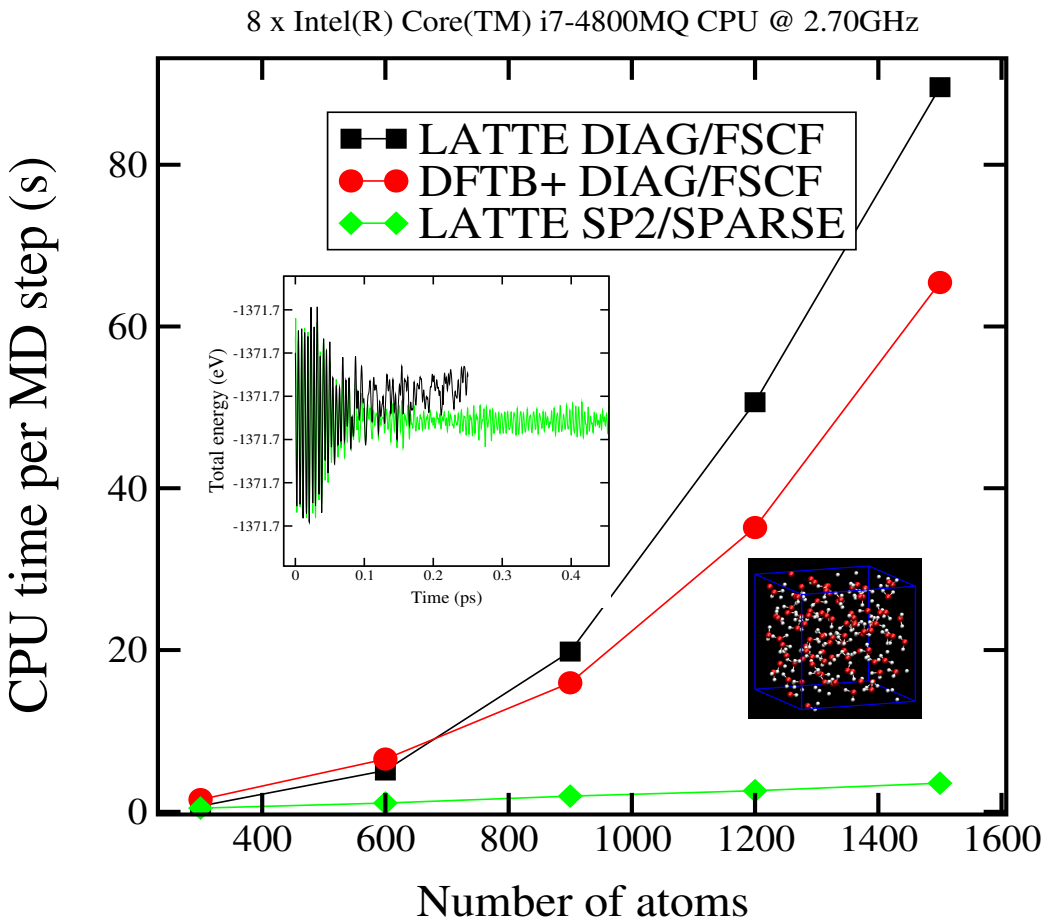
Linear scaling XLBO MD



- Linear scaling with low prefactor (green curve in graph)
- Full accuracy control.
- Perfect energy stability (green curve in the inset)

- B. Aradi, A. M. N. Niklasson and Th. Frauenheim, *JCTC*, **2015**

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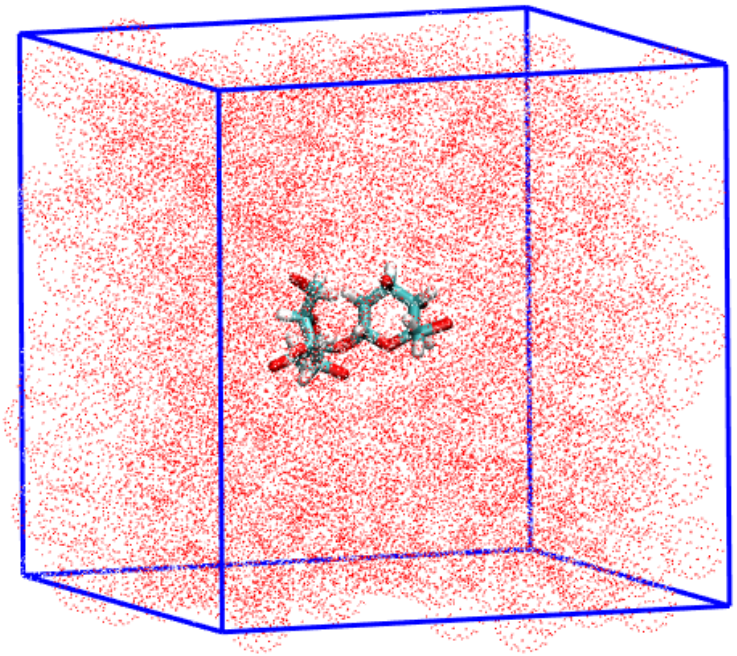
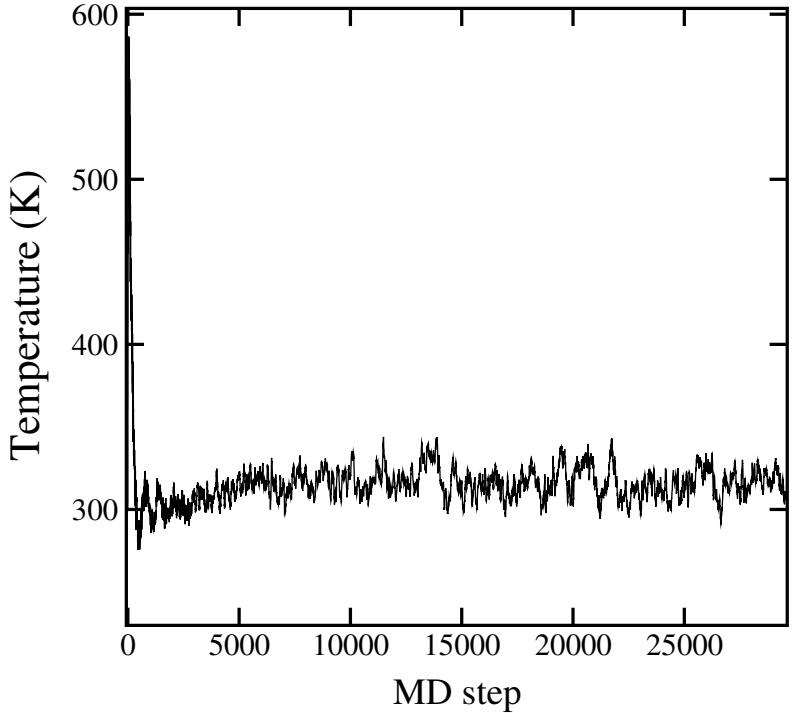
Sucrose conformers in water (A. Redondo)

Linear scaling XLBO NVT QMD.





Left: Sucrose molecule solvated in 535 water molecules. Rigth: Temperature as a function of the molecular dynamics time step for an simulation with constant number of particles, temperature and pressure (NTP).

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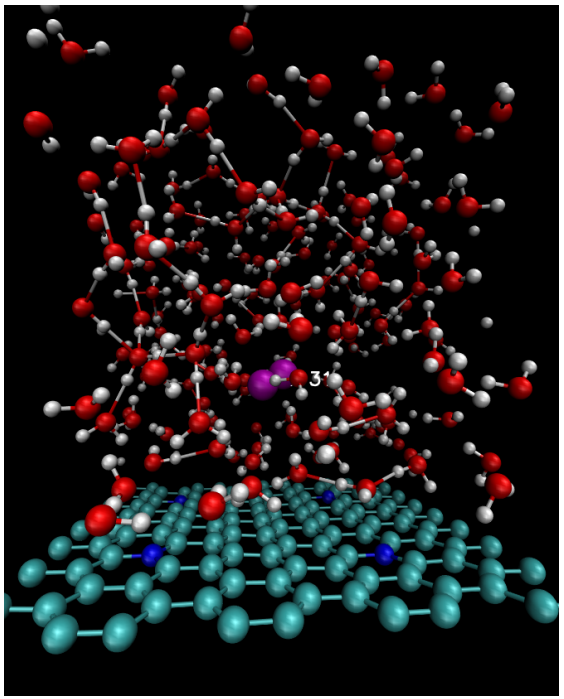
Next generation fuel cells (I. Matanovic)

Full SCF NVT QMD with low electronic temperature.

$$O_2 + 2\,H_2O + 4\,e^- \longrightarrow 4\,OH^- \quad \text{(Reduction)} \qquad [R_b1]$$

$$\text{Surf} \longrightarrow \text{Surf}^{(4+)} + 4\,e^- \quad \text{(Oxidation)} \qquad [R_b2]$$

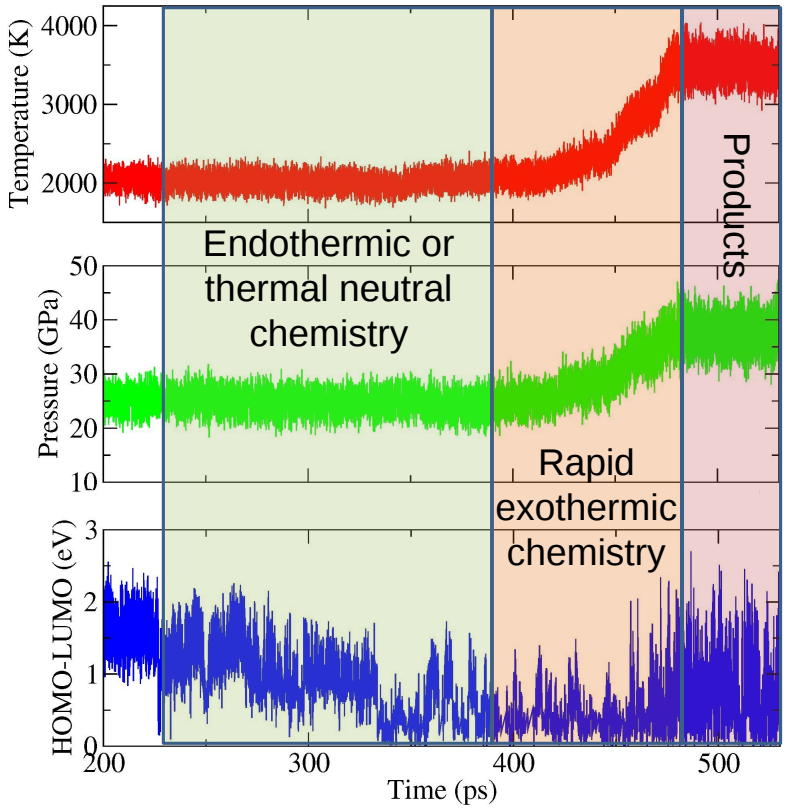


- K. Artyushkova, I. Matanovic, H. Barr, and P. Atanassova *J. Phys. Chem. C*, **2017**.

Hugoniot schock compression (R. Perriot)

XL with limited SCF NVP QMD with high electronic and ionic temperature.

- 30 nitromethane molecules
- P=24 GPa, T$\sim$ 2000K
- NVE for 500 + ps
- Monitor T, P, HOMO-LUMO
- Reaction starts at $\sim$230 ps
- $\sim$ 15 ps/day on 16 threads



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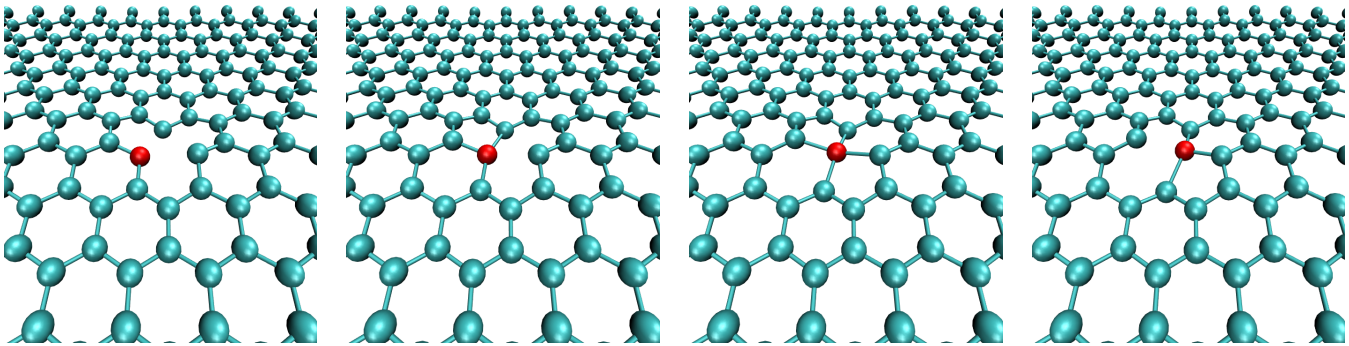
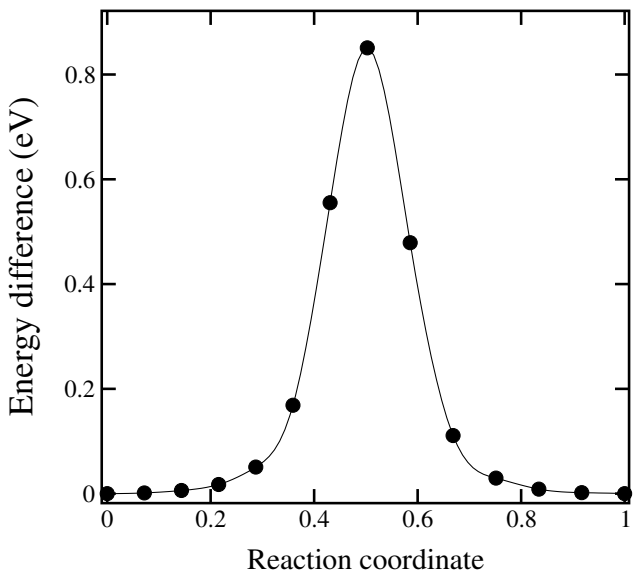
C vacancy movements in graphene (E. Martinez)

NEB (CG geometry optimization) with high-accuracy SCF convergence and moderate electronic temperature.





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Conclusions

. . . We have extended the capabilities of LAMMPS to do fast quantum-based molecular dynamics simulations. The interface to LATTE will be available in the next LAMMPS release.

Thanks!

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