LDRD
innovation for our nation

Accelerated Quantum Molecular Dynamics

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Outline

- Quantum MD
  - Current approaches
  - Challenges
- Extended Lagrangian Born-Oppenheimer MD
- Accelerated MD
- Coupling XL-BOMD and AMD
  - Vacancies in graphene

Quantum based MD

Integrate the equations of motion of classical molecular trajectories

$$M_I \ddot{R}_I = -\frac{\partial U(\mathbf{R};\rho_{sc})}{\partial R_I}$$

with the forces calculated on the fly from a self-consistent quantum mechanical description of the electronic structure:

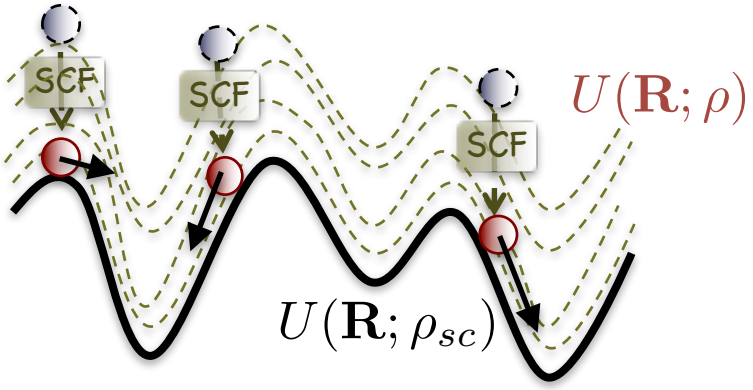
$$H[\rho]\Psi_i = \varepsilon_i \Psi_i$$

$$\text{SCF} \rightarrow \rho_{sc}$$

$$\rho = \sum_{\text{occ.}} |\Psi_i|^2$$

$$\#\text{SCF} \times \mathcal{O}(N^3)$$

Born-Oppenheimer MD



Goal: To develop a unique computational capability based on a new generation quantum based molecular dynamics that overcomes current limitations allowing design and prediction of materials and processes on time and length scales multiple orders of magnitude beyond current capacity.

Quantum based MD

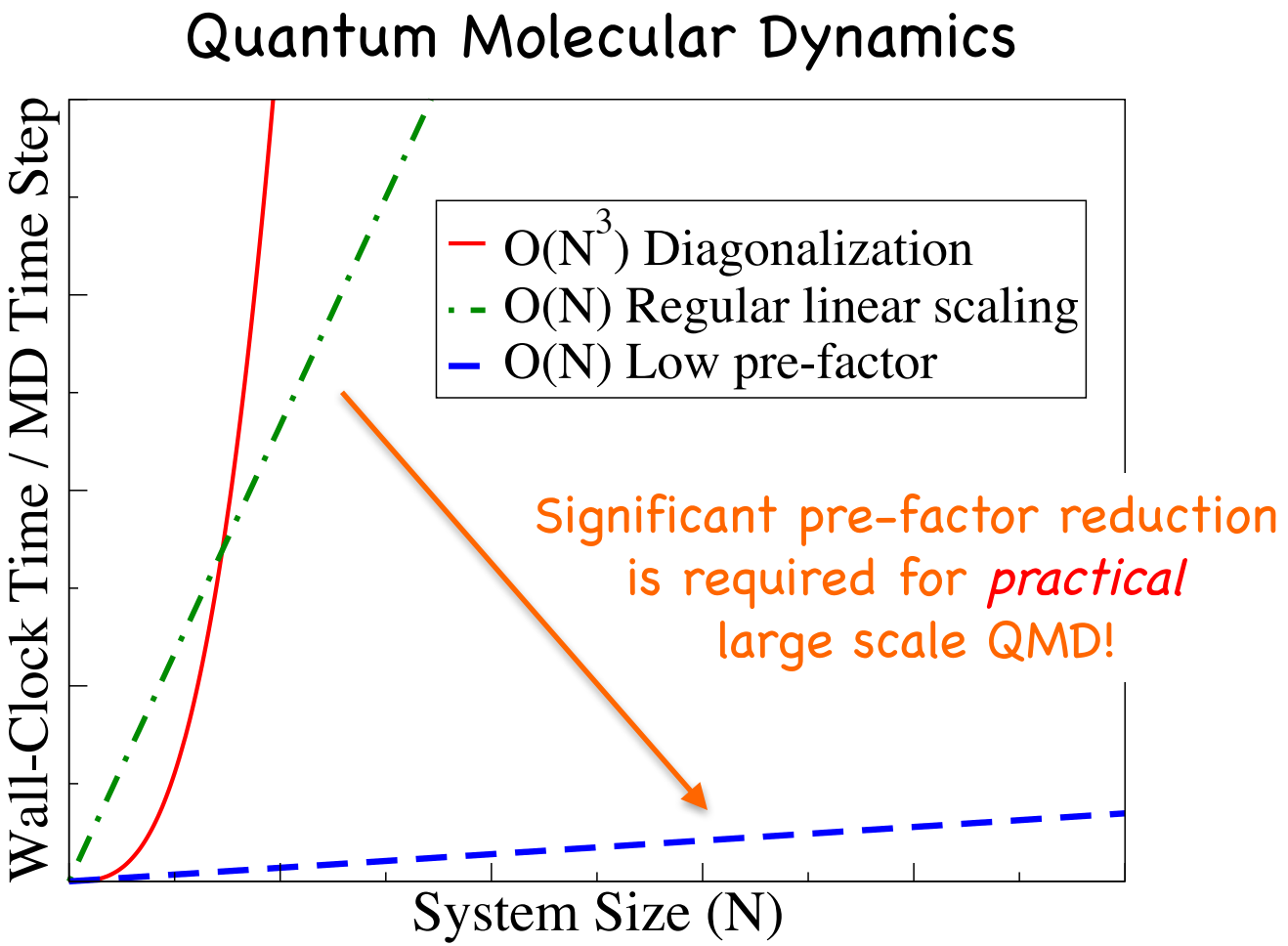
Born-Oppenheimer MD (1973)	Car-Parrinello MD (1985)
+ Accurate and reliable	- Parameter dependence
+ General, any material	- Material dependent
+ Long time steps	- Short time steps
- Energy drift	+ Small energy drift
- Expensive, SCF cost	+ Fast, no SCF required

The best of both worlds

New Generation Quantum Mechanical Molecular Dynamics

XL-BOMD

The Challenge



LATTE: Self-Consistent Charge Density Functional based Tight-Binding Theory

"Self-consistent-charge density-functional tight-binding method for simulations of complex materials properties"
M. Elstner et al. Phys. Rev. B 58, 7269 (1998) **+1,400 citations**

$$U_{\mathrm{DFTB}}(\mathbf{R};\rho) = 2Tr[\rho h] + \frac{1}{2}\sum_{i,j} q_i q_j \gamma_{ij} + E_{\mathrm{pair}}[\mathbf{R}]$$

$$H_{i\alpha,j\beta}[\mathbf{q}] = h_{i\alpha,j\beta} + \sum_{l} q_l \gamma_{il} \delta_{ij} \delta_{\alpha\beta}$$

$$q_i = 2\sum_{\alpha} \rho_{i\alpha,i\alpha} \qquad \rho = \theta\left(\mu I - H[\mathbf{q}]\right)$$

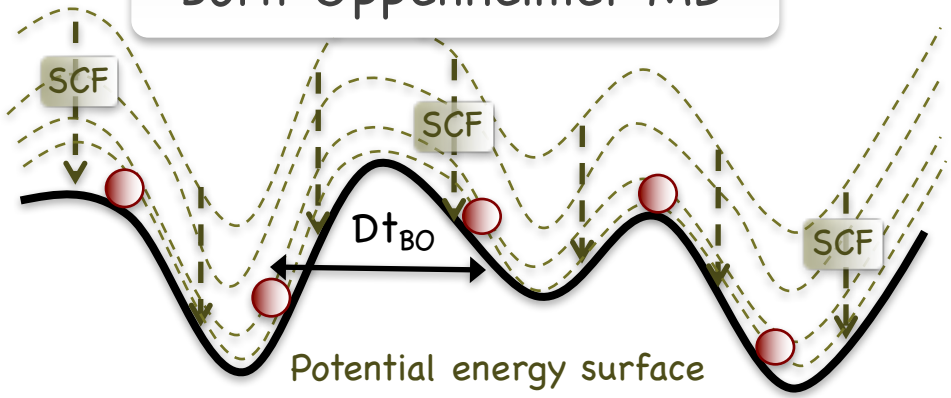
Maybe the simplest and most efficient approach to electronic structure theory that still covers the relevant features of "exact" ab initio Kohn-Sham DFT.

Typically two orders of magnitude in speed up (w.r.t. DFT)!

SCF-free Generalized XL-BOMD

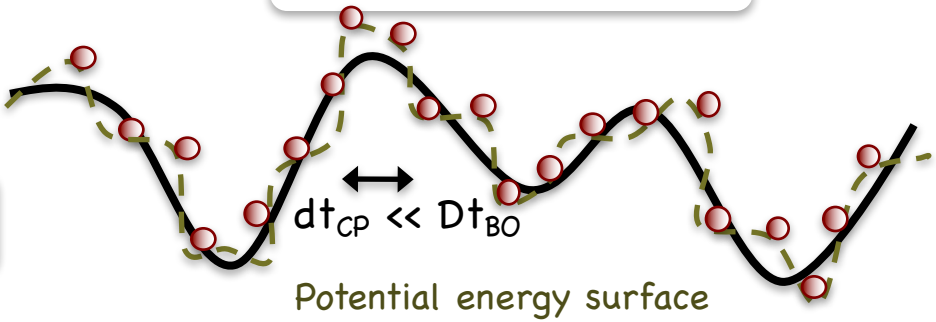
Niklasson & Cawkwell, JCP 141, 164123 (2014)

Born-Oppenheimer MD



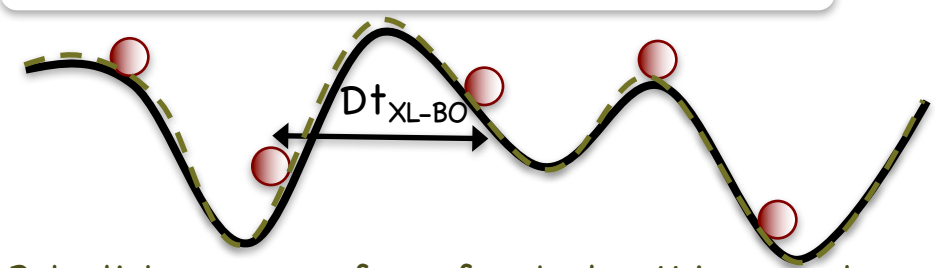
Potential energy surface
at the SCF optimized electronic ground state

Car-Parrinello MD



Potential energy surface
of a non-optimized electronic state

New Fast "SCF-free" GXL-BOMD



Potential energy surface of a shadow H is very close
to the exact SCF optimized electronic ground state

SCF-free Generalized XL-BOMD

Niklasson & Cawkwell, JCP 141, 164123 (2014)

$$\mathcal{L}^{\text{Shadow}}_{\text{XBO}} = \sum_I \frac{M_I \dot{R}_I^2}{2} - \mathcal{U}(\mathbf{R}, n) + \frac{\mu}{2}\int \dot{n}^2 d\mathbf{r} - \frac{\mu\omega^2}{2}\int (\rho - n)^\dagger K^\dagger K (\rho - n) d\mathbf{r}$$

$$\mathcal{L}^{\text{Shadow}}_{\text{XBO}} = \mathcal{L}^{\text{KS}}_{\text{BO}}, \quad \{\sim \text{BO approx. } \lim \omega \to \infty, \ \lim \mu \to 0, \ \lim \mu\omega \to \text{constant}\}$$

$$M_I \ddot{R}_I = -\left.\frac{\partial \mathcal{U}(\mathbf{R}, n)}{\partial R_I}\right|_n$$

$$\ddot{n}(\mathbf{r}) = -\omega^2 \int K(\mathbf{r}, \mathbf{r}') \left(\rho[n](\mathbf{r}') - n(\mathbf{r}')\right) d\mathbf{r}'$$

$$E_{\text{Tot}} = \frac{1}{2}\sum_I M_I \dot{R}_I^2 + \mathcal{U}(\mathbf{R}, n)$$

Shadow Hamiltonian

$$K(\mathbf{r}, \mathbf{r}') \sim \left(\frac{\delta\rho[n](\mathbf{r}}{\delta n(\mathbf{r}')} - \delta(\mathbf{r} - \mathbf{r}'\right)^{-1}$$

$$\mathcal{U}(\mathbf{R}, n) = \min_\rho \left\{ E^{(1)}_{\text{DFT}}(\mathbf{R}, \rho, n) \;\middle|\; \rho = \sum_{\text{occ}} |\Psi_i|^2, \langle \Psi_i | \Psi_j \rangle = \delta_{ij} \right\} + V_{\text{nn}}(\mathbf{R})$$

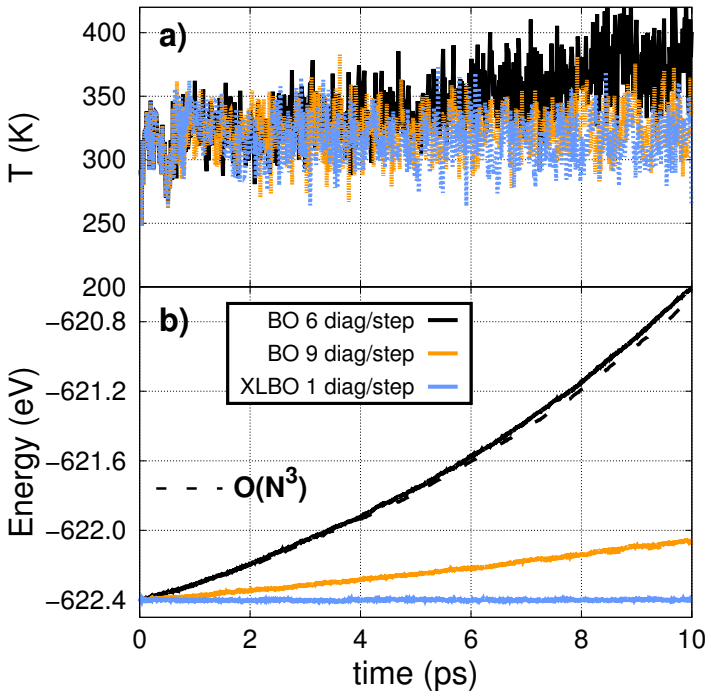
$$\rho[n] = \arg\min_\rho \left\{ E^{(1)}_{\text{DFT}}(\mathbf{R}, \rho, n) \;\middle|\; \rho = \sum_{\text{occ}} |\Psi_i|^2, \langle \Psi_i | \Psi_j \rangle = \delta_{ij} \right\}$$

$$E^{(1)}_{\text{DFT}}(\mathbf{R}, \rho, n) = E_{\text{DFT}}(\mathbf{R}, n) + \int \left.\frac{\delta E_{\text{DFT}}(\mathbf{R}, n)}{\delta\rho}\right|_{\rho=n} (\rho[n](\mathbf{r}) - n(\mathbf{r}))\, d\mathbf{r}$$

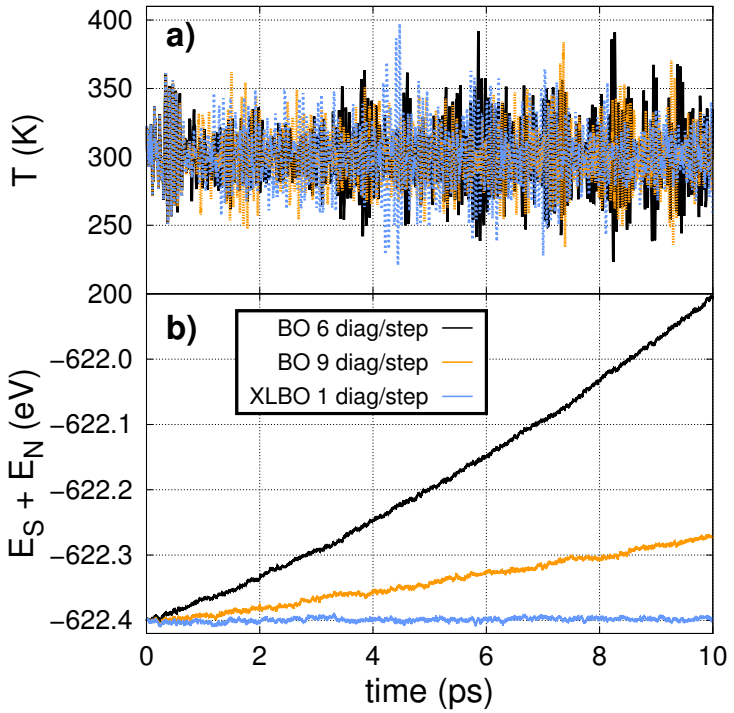
SCF-free Generalized XL-BOMD Canonical Ensemble

Isocyanic acid $(HNCO)_{24}$

NVE ensemble



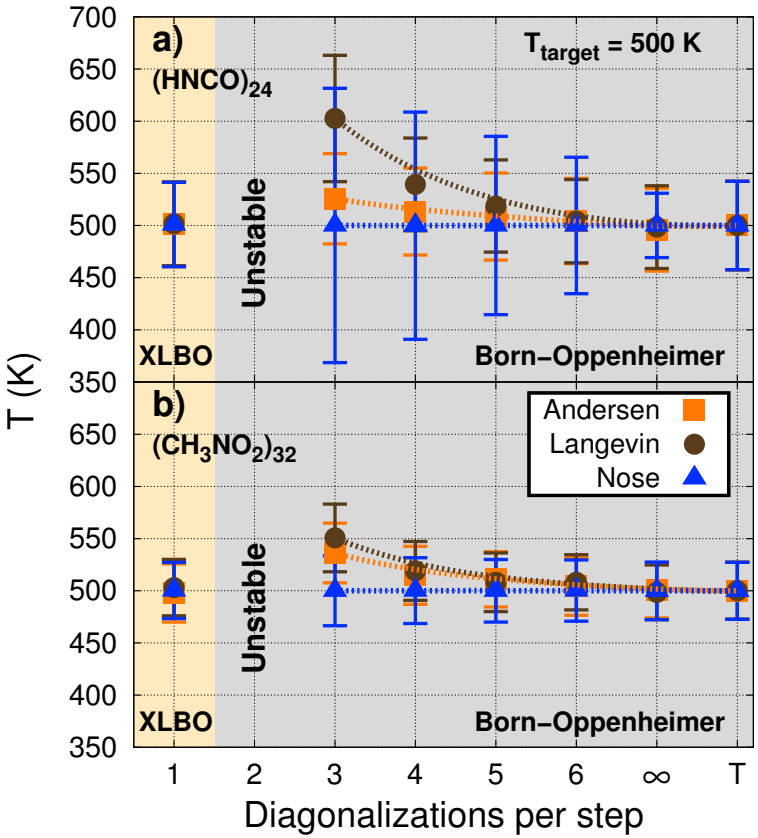
NVT ensemble
Nose thermostat

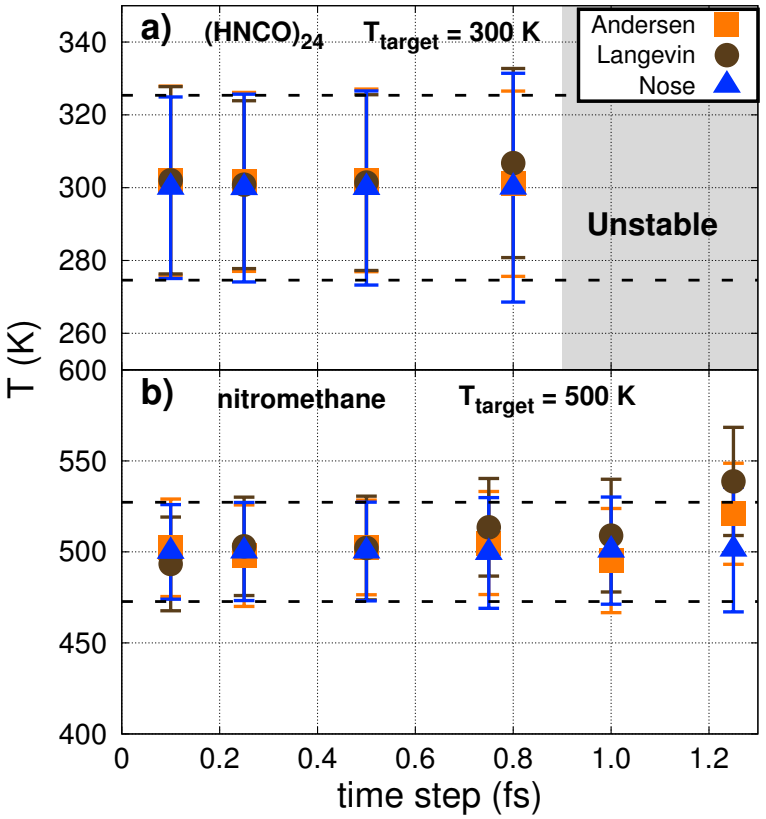


Is the XL-BOMD compatible with the thermostats? Does it help?

SCF-free Generalized XL-BOMD Canonical Ensemble

Average temperature and the square-root of its second moment

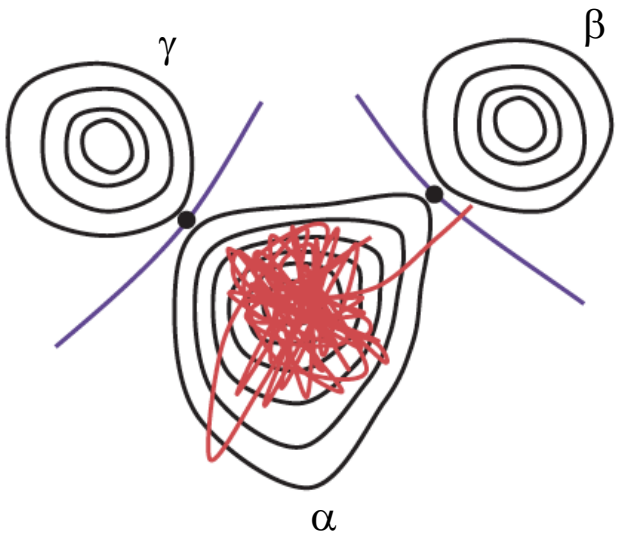




XL-BOMD converges faster with the right fluctuations

XL-BOMD + Accelerated Molecular Dynamics

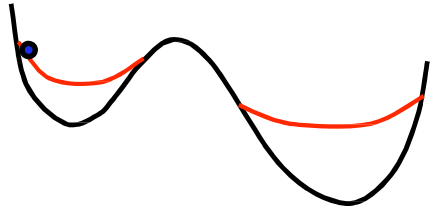
Infrequent Events



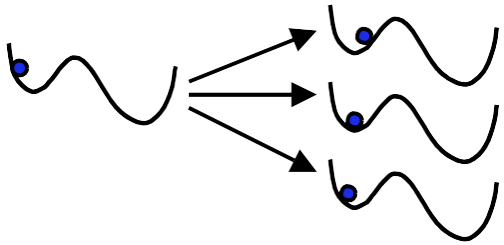
Can we accelerate the transition without perturbing the probabilities for the system to escape? ➡ **AMD**

Accelerated Molecular Dynamics

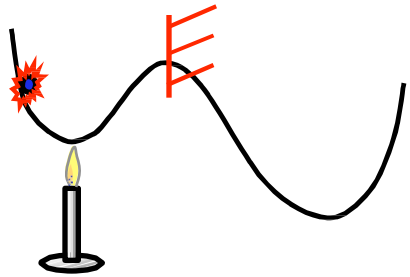
Hyperdynamics



Parallel Replica Dynamics

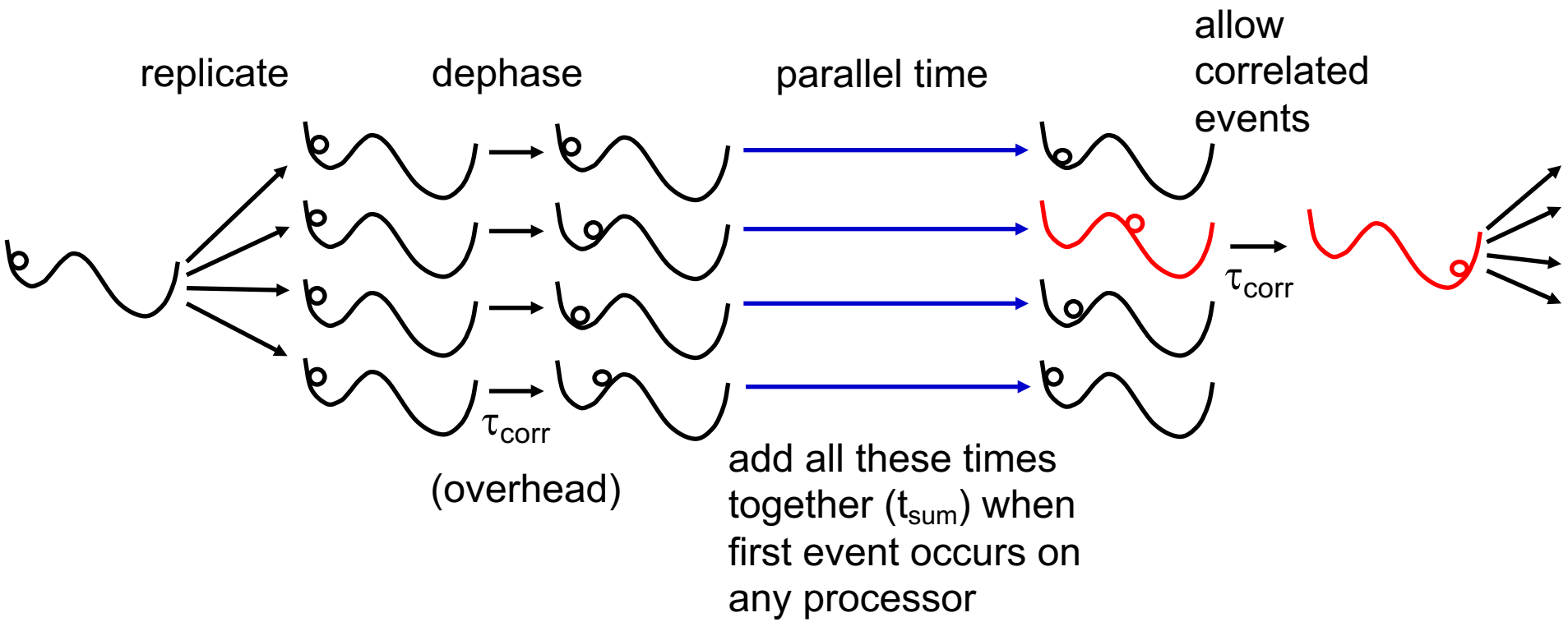


Temperature Accelerated Dynamics



Parallel Replica Dynamics

The properties of the exponential allow us to parallelize time, by having many processors seek the first escape event. The procedure:

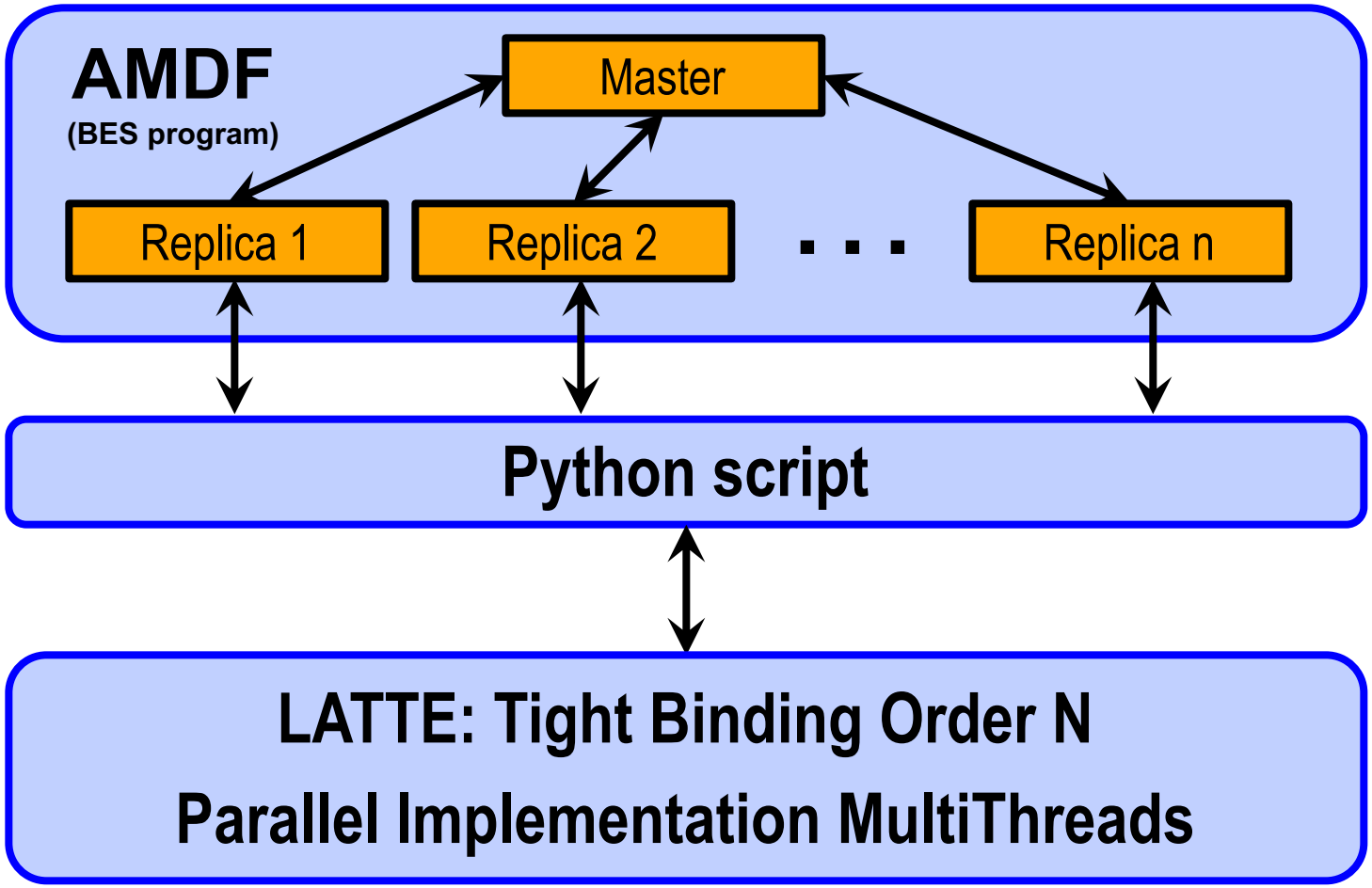


Must detect every transition.

Good parallel efficiency if $\tau_{rxn} / n_{proc} >> 2\tau_{corr}$

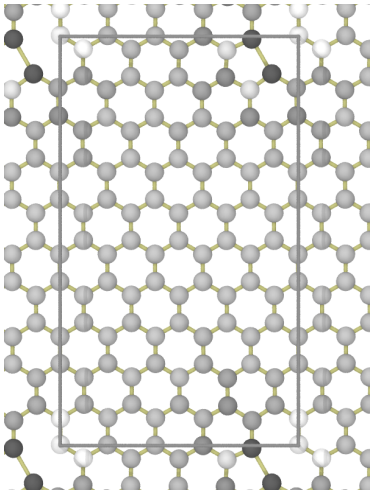
AFV, Phys. Rev. B 57, 13985 (1998).

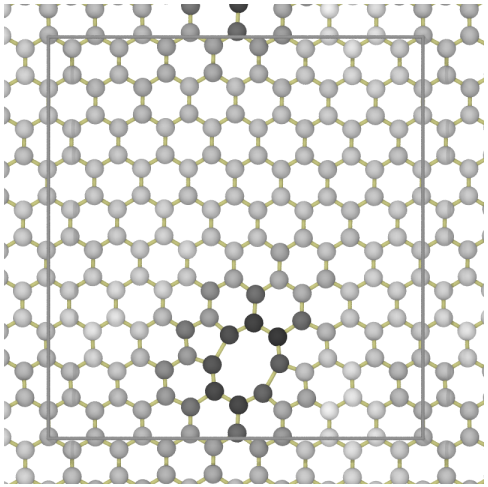
XL-BOMD + Accelerated Molecular Dynamics



Application: Vacancies in graphene

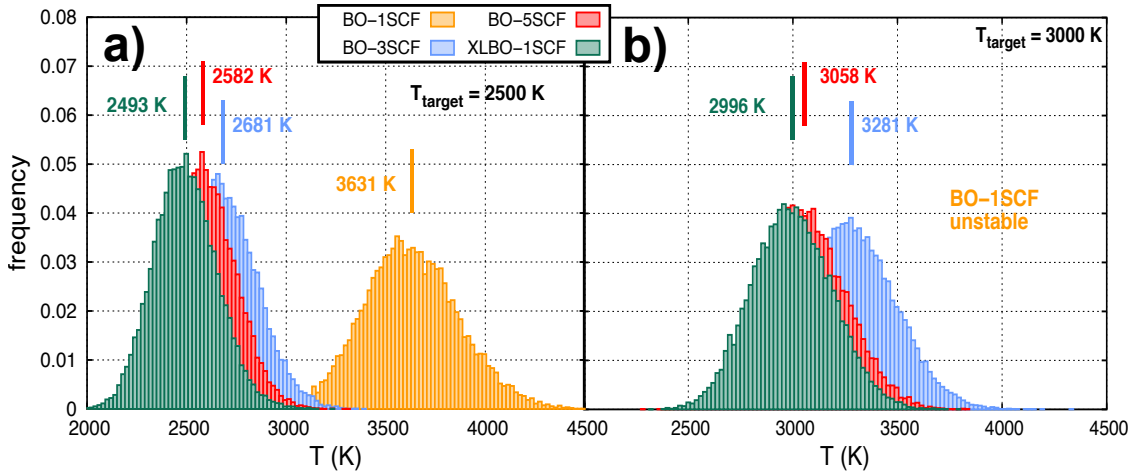
We have studied 1 and 2 vacancy diffusion





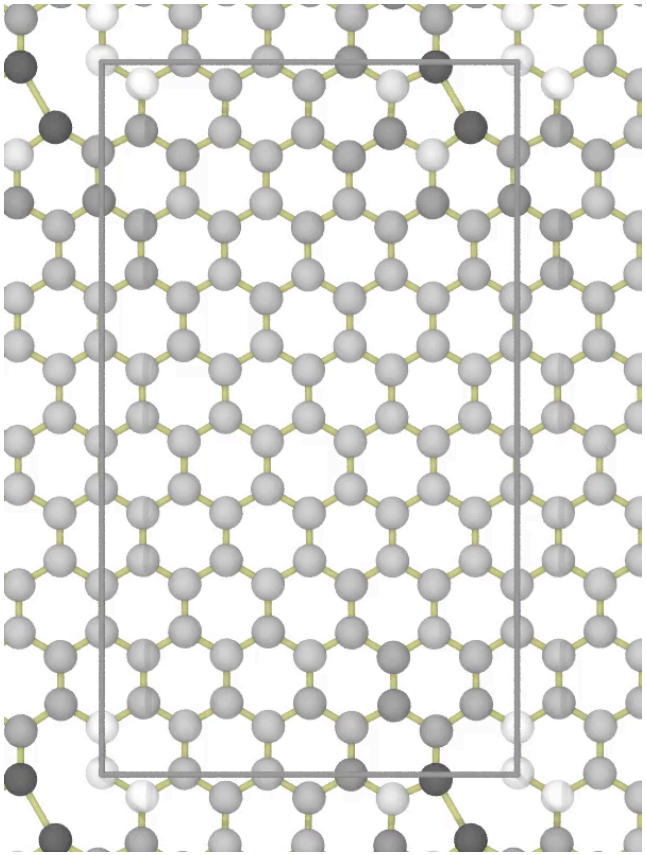
We have analyzed the normal modes to pick the dephasing time ~5ps. There are some slow modes perpendicular to the sheet plane

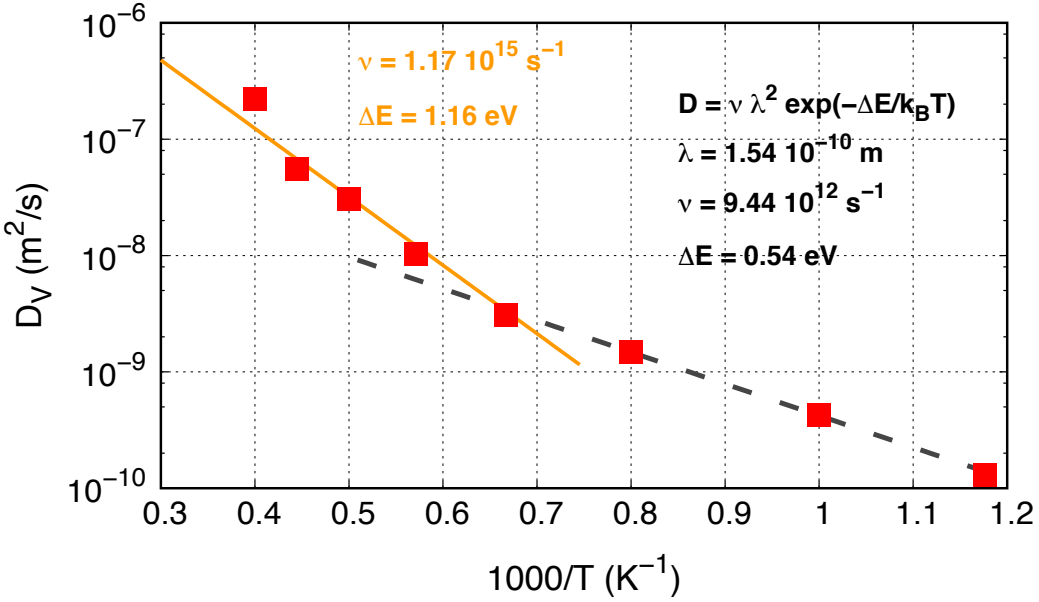
Temperature distribution of a graphene sheet containing 1V at 2500 and 3000 K in the NVT using Langevin Dynamics run for 100 ps



Application: Vacancies in graphene

1V diffusivities in NVT ensemble ParRep-LATTE, reaching on the order of hundreds of ns

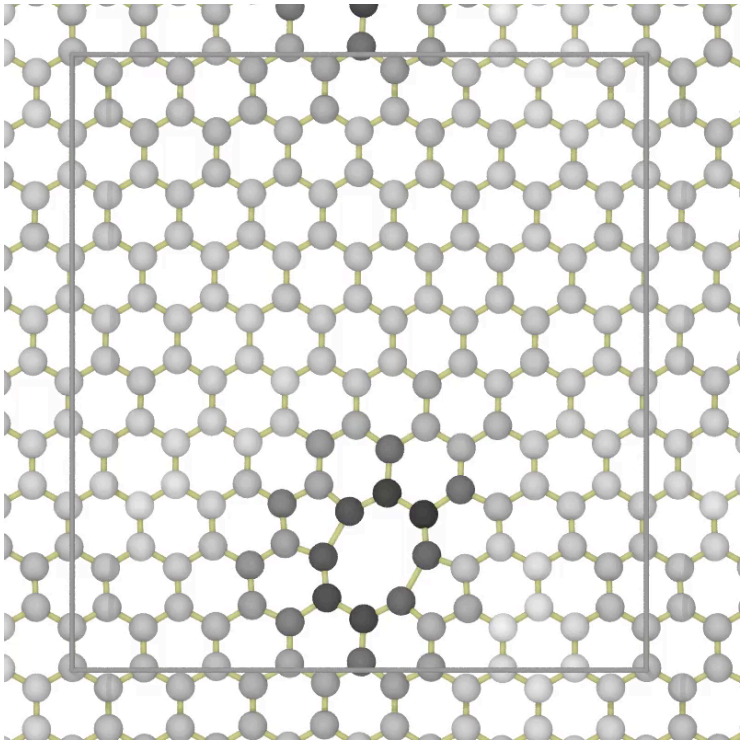


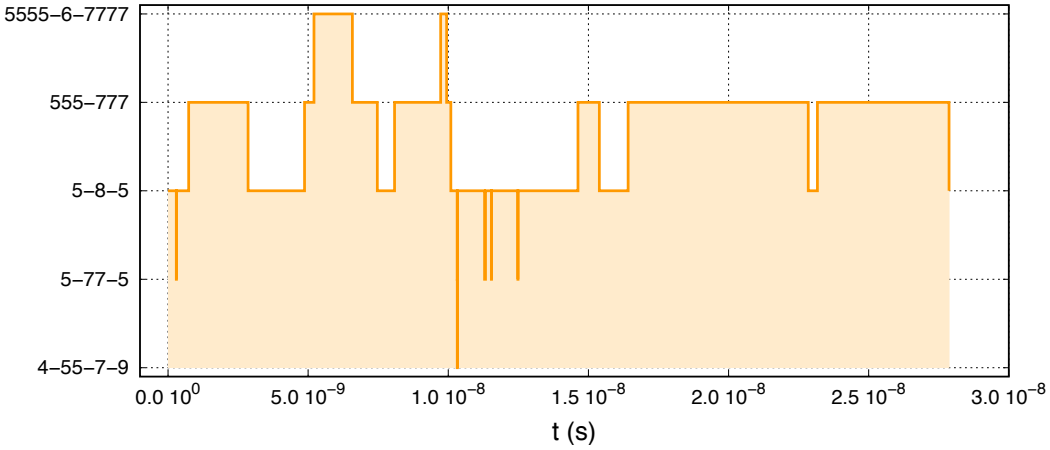


Migration barriers in agreement with recent DFT calculations
Competing events at higher temperatures

Application: Vacancies in graphene

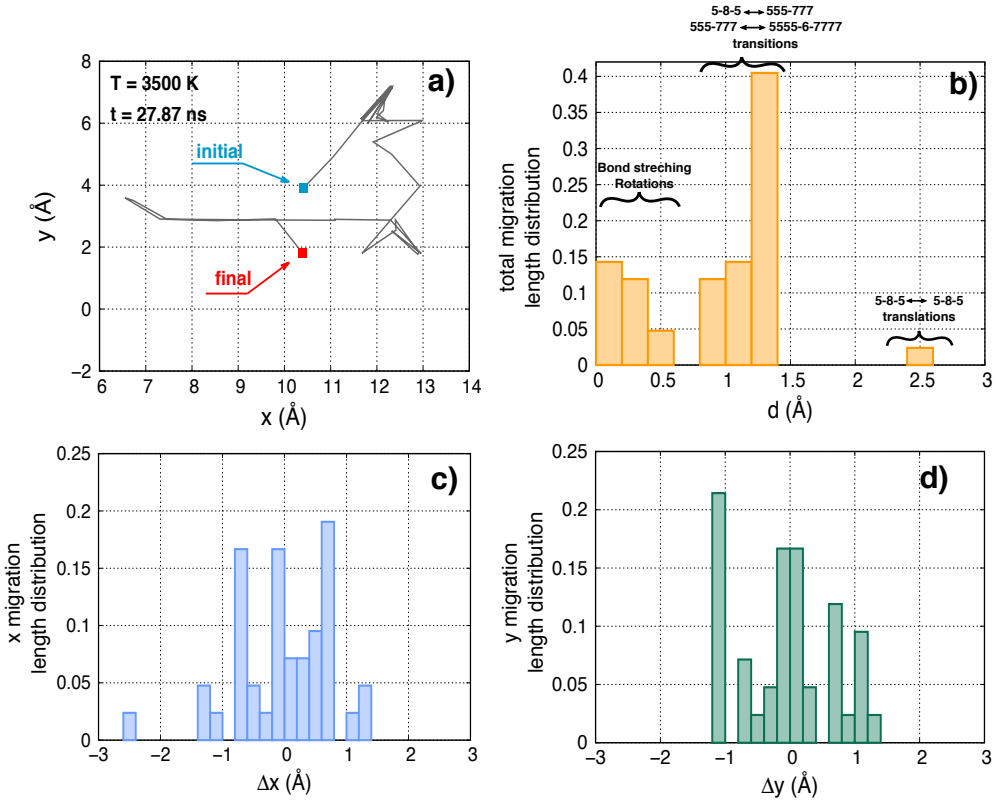
2V configurations at 3500 K in NVT ensemble ParRep-LATTE





Net translation of the center of mass

Application: Vacancies in graphene



Mobility and configurational distribution compatible with experiments

	5-8-5	555-777	5555-6-7777	2x(57)	4-55-7-9
Experiments	50.3%	14.1%	18.8%	1.8%	0%
Simulation	20.7%	65.2%	12.7%	0.6%	0.02%

Conclusions

- We have developed a tool coupling XL-BOMD and AMD that reaches ~2-3 orders of magnitude speedup with respect to traditional methods
- We have calculated single vacancy mobilities in graphene reaching hundreds of ns
- We have also studied the very stable 2V-complex migration