The time scale associated with Monte Carlo simulations

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Introduction

The time scale problem

- Molecular Dynamics (MD) simulations are a powerful tool to study static/dynamics properties at the atomistic level
- But many processes take place beyond the MD time scale (ns-μs range)
- Accelerated MD methods exist, but not generally applicable

Monte Carlo methods

- Stochastic, not deterministic displacements
- Average atomic displacement per step larger than in MD
- MC methods can take into account long time scale relaxation

Can we quantify this acceleration?

Methodology

Force-bias Monte Carlo (fbMC)[1]

Displacements are chosen according to

$$p(\xi_{i,j}) = \begin{cases} \dfrac{e^{\gamma_{i,j}(2\xi_{i,j}+1)} - e^{-\gamma_{i,j}}}{e^{\gamma_{i,j}} - e^{-\gamma_{i,j}}} & \text{if} \quad \xi_{i,j} \in [-1, 0[\\ \dfrac{e^{\gamma_{i,j}} - e^{\gamma_{i,j}(2\xi_{i,j}-1)}}{e^{\gamma_{i,j}} - e^{-\gamma_{i,j}}} & \text{if} \quad \xi_{i,j} \in]0, 1] \end{cases} \qquad \gamma_{i,j} = \frac{F_{i,j}\Delta_i}{2k_B T}$$

- Probability to displace along force > against force
- Maximal step size Δ
- Uniform acceptance: no acceptance/rejection criterion
- Implemented in LAMMPS[2]

Time scale quantification[3]

- Study various processes using both MD and fbMC
- Compare dynamic properties
- Effective MC "time scale"

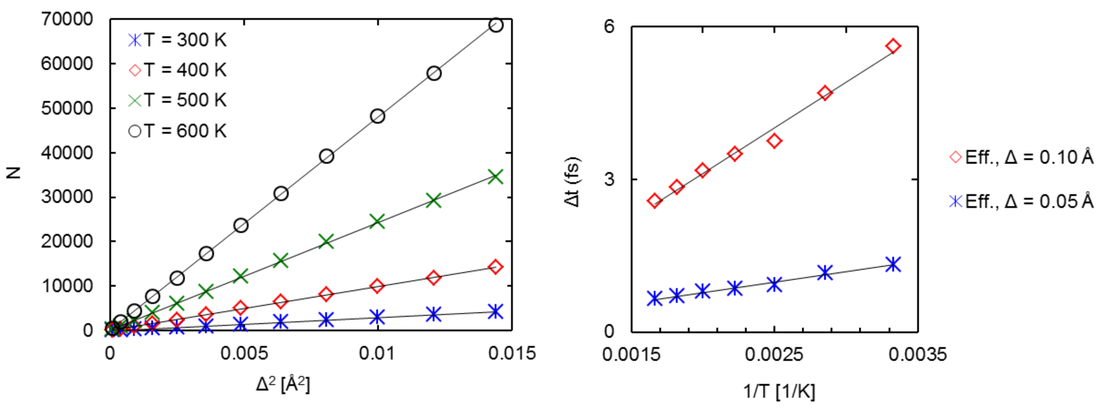
Results

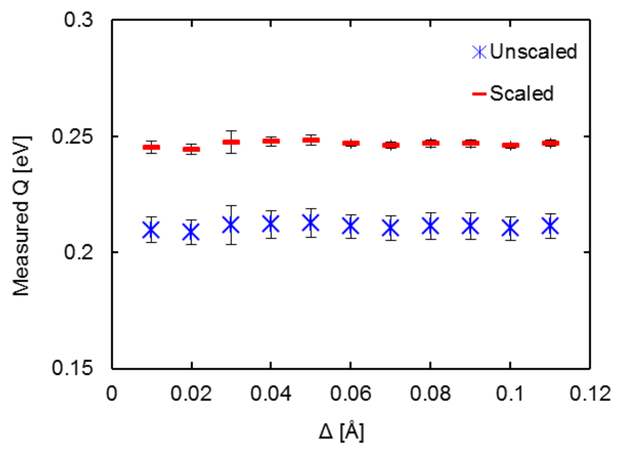
Simple 1D system

One particle, one dimension:

$$U(x) = \frac{Q}{2}\left[1 - \cos\left(\frac{2\pi x}{L}\right)\right]$$

- We find that
  - We can apply theory from random walk
  - $t \sim \Delta^2/T$

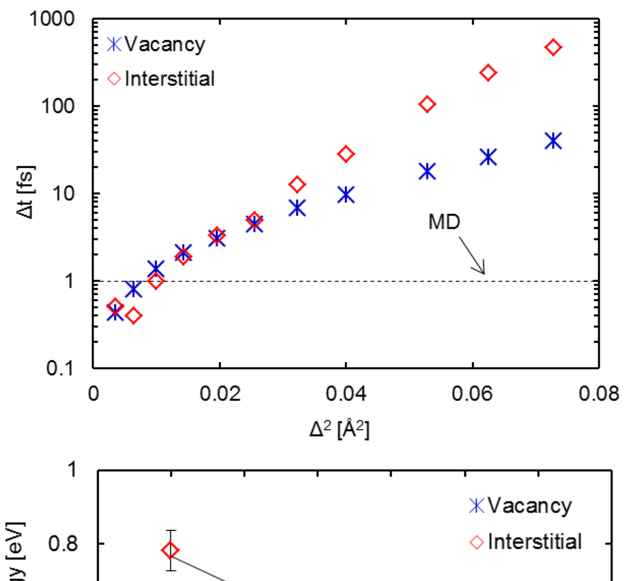




If we compensate for T-dependence of "time", correct relative dynamics is obtained

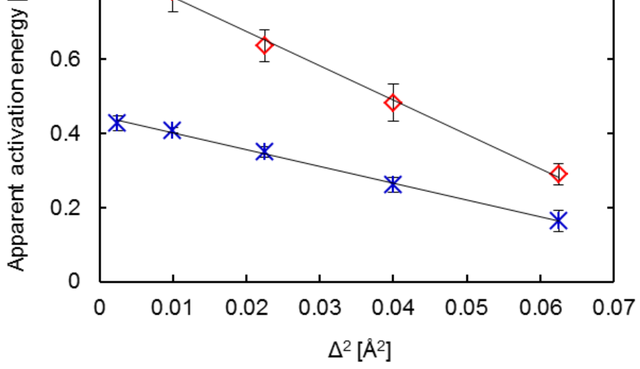
Realistic system: Point defects in Si

- Interactions described using a Stillinger-Weber potential
- Two mechanisms considered: vacancy and interstitial diffusion
- Calculate effective MC time step by comparing to MD



At 800K

- For Δ, relative dynamics is correct
- Time scales diverge for higher Δ: no correct relative dynamics!



Activation energies

- Dependent on Δ!
- Δ↑, E_A↓
- When $\Delta^2 \rightarrow 0$, E_A approaches MD result

Distortion of the lattice by large MC steps lower barriers, accelerating events but not preserving relative dynamics

Conclusion

fbMC simulations can accelerate atomistic simulations by orders of magnitude, at the cost of losing detailed correct relative dynamics.

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[1] M. J. Mees, G. Pourtois, E. C. Neyts, B. J. Thijsse, and A. Stesmans, Phys. Rev. B **85**, 134301 (2012).

[2] S. Plimpton, J. Comput. Phys. **117**, 1 (1995).

[3] K. M. Bal and E. C. Neyts, J. Chem. Phys. **141**, 204104 (2014).