UNIFORM-ACCEPTANCE FORCE-BIAS MONTE CARLO METHOD WITH TIME SCALE TO STUDY SOLID-STATE DIFFUSION

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Abstract

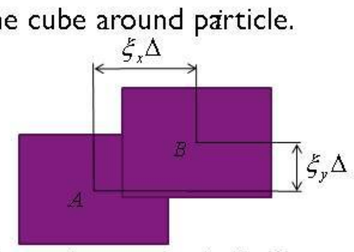
Monte Carlo (MC) methods have a long-standing history as partners of molecular dynamics (MD) to simulate the evolution of materials at the atomic scale. Among these techniques, the uniform-acceptance force-bias Monte Carlo (UFMC)method [G. Dereli, Mol. Simul. **8**, 351 (1992)] has recently attracted attention [M. Timonova et al., Phys. Rev. B **81**, 144107 (2010)] thanks to its apparent capacity of being able to simulate physical processes in a reduced number of iterations compared to classical MD methods. The origin of this efficiency remains, however, unclear. In this work, we derive a UFMC method starting from basic thermodynamic principles, which lead to an intuitive and unambiguous formalism. The approach includes a statistically relevant time step per Monte Carlo iteration, showing a significant speed-up compared to MD simulations. This time-stamped force-bias Monte Carlo (tfMC) formalism is tested on both simple one-dimensional and three-dimensional systems. Both test-cases give excellent results in agreement with analytical solutions and literature reports. The inclusion of a time scale, the simplicity of the method, and the enhancement of the time window compared to classical MD methods make this method very appealing for studying the dynamics of many-particle systems.

The tfMC algorithm

- Dynamics of a N-particles system is described by the motion of N cubic volumes, in each of which, a particle is located. Motion of the volumes is determined by Monte Carlo method with the probability function:

$$p_{i,j}=\begin{cases}\dfrac{\exp\left(\beta(2\xi_{i,j}+1)F_{i,j}\Delta_i/2\right)-\exp\left(-\beta F_{i,j}\Delta_i/2\right)}{\exp\left(\beta F_{i,j}\Delta_i/2\right)-\exp\left(-\beta F_{i,j}\Delta_i/2\right)}, & \xi_{i,j}\in[-1,0]\\ \dfrac{\exp\left(\beta F_{i,j}\Delta_i/2\right)-\exp\left(\beta(2\xi_{i,j}-1)F_{i,j}\Delta_i/2\right)}{\exp\left(\beta F_{i,j}\Delta_i/2\right)-\exp\left(-\beta F_{i,j}\Delta_i/2\right)}, & \xi_{i,j}\in[0,1]\end{cases} \quad (1)$$

In this, β is equal to $(k_BT)^{-1}$ and $F_{i,j}$ is the force acting on particle i in the j direction. Further, Δ_i is a fixed number which together with $\xi_{i,j}$, determines the next location of the cube. It also defines the length of the sides of the cube around particle.



Notice that Δ_i determines the maximal displacement of particle i. The link between different Δ_i is given by:

$$\Delta_i=\Delta\sqrt{\frac{m_{\min}}{m_i}} \quad (2)$$

- With classical Monte Carlo methods, the time evolution got lost. In our method, a time-step per calculation is proposed to be:

$$\langle\Delta t\rangle=\frac{\Delta}{3}\sqrt{\frac{\pi m_{\min}}{2k_BT}} \quad (3)$$

For a realistic choice of $\Delta=0.12\,\text{Å}$, the time-step is given by

	$T=200$ K	$T=300$ K	$T=400$ K	$T=500$ K	$T=600$ K	$T=700$ K
$m_{\min}=1$ u	$\langle\Delta t\rangle=3.89$ fs	$\langle\Delta t\rangle=3.17$ fs	$\langle\Delta t\rangle=2.75$ fs	$\langle\Delta t\rangle=2.46$ fs	$\langle\Delta t\rangle=2.24$ fs	$\langle\Delta t\rangle=2.08$ fs
$m_{\min}=50$ u	$\langle\Delta t\rangle=27.5$ fs	$\langle\Delta t\rangle=22.4$ fs	$\langle\Delta t\rangle=19.4$ fs	$\langle\Delta t\rangle=17.4$ fs	$\langle\Delta t\rangle=15.9$ fs	$\langle\Delta t\rangle=14.7$ fs
$m_{\min}=100$ u	$\langle\Delta t\rangle=38.9$ fs	$\langle\Delta t\rangle=31.7$ fs	$\langle\Delta t\rangle=27.5$ fs	$\langle\Delta t\rangle=24.6$ fs	$\langle\Delta t\rangle=22.4$ fs	$\langle\Delta t\rangle=20.8$ fs
$m_{\min}=150$ u	$\langle\Delta t\rangle=47.6$ fs	$\langle\Delta t\rangle=38.9$ fs	$\langle\Delta t\rangle=33.7$ fs	$\langle\Delta t\rangle=30.1$ fs	$\langle\Delta t\rangle=27.5$ fs	$\langle\Delta t\rangle=25.4$ fs
$m_{\min}=200$ u	$\langle\Delta t\rangle=55.0$ fs	$\langle\Delta t\rangle=44.9$ fs	$\langle\Delta t\rangle=38.9$ fs	$\langle\Delta t\rangle=34.8$ fs	$\langle\Delta t\rangle=31.7$ fs	$\langle\Delta t\rangle=29.4$ fs

Derivation of tfMC

- The probability density function and the Hamiltonian of the N-particles system are the basic equations for the canonical ensemble:

$$\rho(\vec{x},\vec{p})=\frac{\exp[-\beta H(\vec{x},\vec{p})]}{\int\exp[-\beta H(\vec{x},\vec{p})]d\vec{x}d\vec{p}}, \qquad H(\vec{x},\vec{p})=\sum_i\frac{p_i^2}{2m_i}+U(\vec{x}) \quad (4)$$

The probability density function can be rewritten in a "small" volume of coordination space as:

$$\tilde{\rho}(\vec{x})=\frac{\exp\left[-\beta\left(U(\vec{x}^*)-\sum_i\vec{F}_i\cdot(\vec{x}_i-\vec{x}_i^*)\right)\right]}{\int\exp[-\beta U(\vec{x})]d\vec{x}} \quad (5)$$

- If we consider the initial volume V_i defined as:

$$V_i=\bigcup_i\left[x_{i,j}^*-\Delta_i,x_{i,j}^*+\Delta_i\right] \quad (6)$$

in which, all particles are located, then the probability that the particles move from V_i to a volume V_f identical to V_i, but shifted to

$$\vec{x}_f=\vec{x}_i+\vec{\xi}\cdot\vec{\Delta} \quad (7)$$

is given by:

$$P(V_f\,|\,V_i)=\frac{P\left[(\vec{x}\in V_i)\cap(\vec{x}\in V_f)\right]}{P(\vec{x}\in V_i)}=\frac{\int_{V_i\cap V_f}\rho(\vec{x})d\vec{x}}{\int_{V_i}\rho(\vec{x})d\vec{x}}=\frac{\int_{V_i\cap V_f}\tilde{\rho}(\vec{x})d\vec{x}}{\int_{V_i}\tilde{\rho}(\vec{x})d\vec{x}}=\frac{\int_{V_i\cap V_f}e^{-\beta\sum_i\vec{F}_i\cdot(\vec{x}_i-\vec{x}_i^*)}d\vec{x}}{\int_{V_i}e^{-\beta\sum_i\vec{F}_i\cdot(\vec{x}_i-\vec{x}_i^*)}d\vec{x}}$$

Working out the last term gives you equation (1).

- When the particles go from the volume V_i to the volume V_f, they feel a constant force (first-order Taylor expansion), which inspired us to define a time step as

$$\langle\Delta t_{i,j}\rangle=\langle|\Delta x_{i,j}|\rangle/\langle|v_{i,j}|\rangle=\frac{\frac{\Delta_i}{2}\left[1-\frac{\gamma_{i,j}\cosh(\gamma_{i,j})-\sinh(\gamma_{i,j})}{\gamma_{i,j}^2\sinh(\gamma_{i,j})}\right]}{\sqrt{2k_BT/\pi m_i}}, \qquad \gamma_{i,j}=\frac{F_{i,j}\Delta_i}{2k_BT} \quad (8)$$

$$\approx\frac{\Delta}{3}\sqrt{\frac{\pi m_{\min}}{2k_BT}}$$

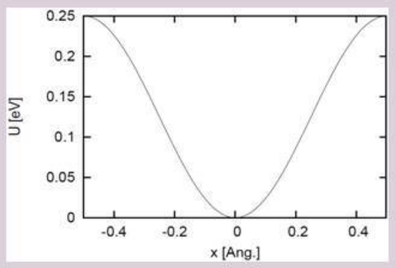
Notice that equation (2) makes sure that all particle have the same time step.

Results obtained with tfMC

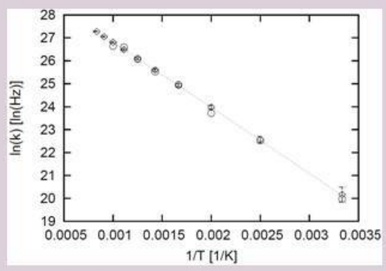
- Test performed on a simple 1D and a more complex 3D system

1D system

- Particle moving in 1D sinusoidal potential surface:

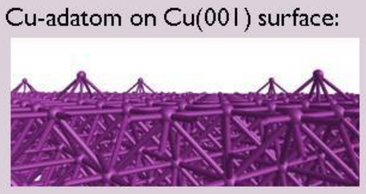


- Simulated Arrhenius plot in excellent agreement with theoretical TST plot if $\Delta\leq 0{,}10$ Ang.

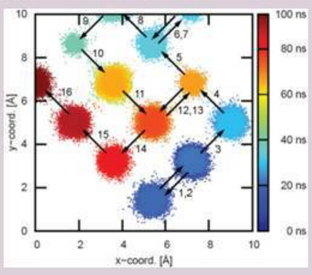


3D system

- Cu-adatom on Cu(001) surface:



- tfMC-simulated path of adatom:



- Literature[1-5] activation energies and frequency factors fall inside calculated uncertainty interval

$$E_A=0{,}48\pm0{,}04\ \text{eV}$$
$$\nu_0=14{,}7\pm e^{1{,}95}\ \text{THz}$$

- Tests in 1D system show that $\Delta=0{,}10$ Ang. is a rather robust choice.

Conclusion

A new uniform-acceptance force-bias Monte Carlo method (tfMC) is developed based on the fundamental principles of a canonical ensemble. We report that the time step taken per tfMC iteration is, in many cases, larger than the "standard" 1fs used for classical MD simulations. The method has been successfully tested in a simple one-dimensional sinusoidal potential and in one a more complex system of Cu-adatom diffusion. The inclusion of a time-scale together with the appealing simplicity of the method and the enhancement of the time step compared to classical MD approach, make this method very promising for material science simulations.

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