Computational Materials Science 128 (2017) 1–7

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Quantum molecular dynamics: Accelerating diffusion via parallel replica method.

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ARTICLE INFO

Article history:
Received 6 July 2016
Received in revised form 4 October 2016
Accepted 30 October 2016

Keywords:
Parallel replica dynamics
Quantum molecular dynamics
Point defects
Self-diffusion
Aluminum

ABSTRACT

Parallel replica dynamics (PRD) is known to be a robust algorithm for accelerated modeling of infrequent-event processes. In this paper we apply PRD to speed up quantum molecular dynamics on the example of vacancy diffusion in aluminum. At first, in order to decrease uncertainties introduced by the acceleration technique, we investigate the effect of PRD internal parameters on its outcome and propose a method of eliminating the errors. Subsequently, the latter is used to refine the values of vacancy jump rates obtained from quantum molecular dynamics simulations. Corresponding self-diffusion coefficients nicely agree with experimental data up to the melting point including slight deviations from the Arrhenius dependence.

1. Introduction

Nowadays, computer simulations have reached the level when they are able to provide not only qualitative, but quantitative results. That makes the modeling especially interesting for technological applications since it can partially replace expensive experimental studies. However, computational materials science still experience some difficulties meeting demands of technology. For example, simulations of diffusion remains a challenging task for computational methods, yet important for applications [1–3].

The main challenge of diffusion is its rate, which rapidly decreases with temperature. Thus, even classical molecular dynamics (CMD) simulations of diffusion often becomes computationally too expensive already at somewhat about 700 K [4–7].

An advantage of diffusion process is that it could be separated into two stages: long waiting periods, while atoms oscillate around their equilibrium positions, and fast diffusive jumps, when one or more atoms change their cites. Regarding this specificity, parallel replica method (PRD) can be used to effectively speedup simulation [8]. In fact, CMD + PRD approach was successfully applied to a huge variety of problems: from diffusion-controlled processes [9–11] to chemical reactions [12–14] and even protein folding [15].

However, this approach inherits all limitations of classical MD. Firstly, it has relatively low accuracy compared to quantum MD (QMD). Secondly, the one would need existing interatomic potentials for all types of interactions in the system. This would be especially difficult for complicated systems such as multicomponent alloys [16–18] or near-surface regions [19,1]. Probably the most straightforward way of surmounting this difficulties is to use quantum molecular dynamics (QMD) directly.

In this work we show that QMD can be effectively coupled with PRD to produce fast, accurate and efficient computation technique. The paper is organized as follows. In the "Methodology" section we give a brief outline of parallel replica method and specify appropriate technical details. The "Results and Discussion" is divided into two parts. In the first one PRD algorithm itself is investigated. Noteworthy, here we do not intend to give a formal mathematical description of the algorithm, which is done nicely in [20,21]. Instead, PRD is considered from the users side: If I choose inappropriate parameters, how it will affect the result? Finally, in the second part of the "Results and Discussion" we apply QMD + PRD to calculation of self-diffusion in aluminum and highlight the main points in the "Conclusion".

2. Methods

Parallel replica method was designed to accelerate a first-order process, which obeys the infrequent event kinetics [8]. Without

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http://dx.doi.org/10.1016/j.commatsci.2016.10.043
0927-0256/

loss of generality, let us further consider the problem of self-diffusion - a good example of such processes.

At low temperatures diffusion is very slow, and if we have only one diffusing defect in the simulation cell, it takes too much time to gain reliable statistics of atomic jumps. Probably the most intuitive way of increasing total diffusive jumps rate is to include several defects in the cell. But in this case to prevent defect-defect interaction we have to accordingly increase the size of the simulation box. However, this might be not efficient for DFT, since the amount of interprocess communication is a steep function of the number of atoms in the cell.

For such cases parallel replica method provides an efficient way of parallelization. The main idea of the method is to run several statistically independent copies of the initial system in parallel [8]. The copies are obtained by replication of initial system and decorrelation of corresponding atomic positions and velocities, this procedure is called dephasing. During dephasing each atom's velocity is changed to a new random vector, while the "new" velocities are generated in order to reproduce distribution of the "old" ones. After re-assignment of velocities, system equilibrates for t_{deph} steps. The whole re-assignment - equilibration loop is performed n_{deph} times to guarantee statistical independence of generated configurations. Importantly, after dephasing replicas should remain in the same potential basin as the initial state. To verify this condition event search is performed.

For this purpose each replica creates a copy of its current configuration and perform energy minimization. The latter is done in order to eliminate atomic thermal vibrations. Accuracy of the minimization is controlled by E_{diff} parameter, which is the maximum energy tolerance allowed for convergence. Subsequently, minimized copy of the system is compared with the reference state. If no atom has moved by a distance larger than some predetermined value (hereafter Δ), the replica is believed to be in the same potential well as the reference state. Otherwise, an event is detected. In both cases replica restores its unminimized state and reports whether event was detected or not.

If a transition occurred during dephasing, replicas copy initial system once again and repeat the whole dephasing loop. If no events were detected, simulation proceeds to the next stage.

After dephasing, diverged configurations start to run in parallel. Each replica interrupts dynamics every t_c steps and searches for events as described above. If there were no events across all replicas, simulation continues to run for another t_c steps and the search is performed again. Otherwise the parallel stage terminates, simulation time is incremented by the times spent over all replicas since the last dephasing, and event is logged.

Normally, one would expect only one replica to detect a transition. If events were detected on several replicas, the algorithm randomly chooses one of them. Transitions that were reported on this check by other replicas are called coincident. If we often register coincident events, it means that t_c or the number of replicas is too big. Then the chosen replica updates reference state and starts to search for correlated transitions. As in the parallel stage, it runs dynamics and periodically checks for events. If an event during the last t_{corr} steps was detected, it is considered to be correlated. Simulation time is incremented by t_{corr}, the transition is logged, replica updates reference configuration and continues dynamics. If no jump during the last t_{corr} steps was detected, final state of the system is copied to other replicas, they dephase and the parallel stage is started again.

Thus, PRD accelerates total jump frequency by effectively inducing the number of diffusing particles, yet keeping all systems small and parallelization - highly efficient. This makes the idea of coupling PRD with QMD very tempting.

However, as any acceleration technique, PRD introduces additional uncertainties to simulation results. Therefore, to take full advantage of QMD accuracy, all of the PRD errors should be controlled. After this is done, the whole PRD + QMD approach is to be tested on realistic problem. Consequently, our work consists of two parts:

- Firstly, we investigate the influence of PRD internal parameters on its outcome. Since we examine the PRD algorithm itself, there is no need to employ computationally expensive QMD, hence PRD + CMD is used in this part.
- Subsequently, we employ the set of optimized parameters to demonstrate applicability of the QMD + PRD approach. As an example, we calculate self-diffusion coefficient in aluminum. The metal was chosen for two reasons: firstly, there are a lot of reference data available in literature; secondly, QMD of aluminum is relatively easy task from computational point of view.

Let us specify some technical details for both of the parts below.

2.1. Classical MD

To perform classical molecular dynamics we employed the LAMMPS package [22]. Interatomic interactions were described via embedded atom method potential for aluminum parametrized by Mishin [23].

Initially, atoms were placed in simulation box in order to form face-centered cubic lattice. System size is $3 \times 3 \times 3$ unit cells with one vacancy inside (107 atoms in total). The system was equilibrated to desired temperature (800 K) and zero stresses via standard routines. Afterwards, thermostat and barostat were disabled and simulations were continued in microcanonical ensemble. Typical run lasts for 10 ns with timestep of 1 fs, which is normally sufficient to obtain statistics of more than thousand diffusive jumps.

There are two major types of simulations employed in this work. The first one is intended to investigate the influence of event checking options separately from dephasing and correlation check parameters. For such simulations conventional MD runs were performed. During each of the runs we recorded snapshots of the system every 0.1 ps. Afterwards the snapshots were analyzed using different values of t_c, E_{diff} and Δ. Further we will refer to this type of simulations as single trajectory processing or STP. Remarkably, STP allows to examine exactly the same MD trajectory with different set of options, thus eliminating undesirable random errors.

To examine the impact of dephasing and correlation check, simulations of the second type were carried out. These are essentially identical to the ones discussed above, but instead of conventional MD parallel replica dynamics was employed. PRD runs were conducted using four replicas, E_{diff} was taken to be 10^{-6} and $\Delta = 2$ Å.

2.2. Quantum MD

To perform QMD simulations, we employed projector augmented wave pseudopotentials [24,25] generated with generalized gradient approximation in the from of *Perdew, Burke* and *Ernzerhof* [26]. The calculations were carried out for aluminum with 3 out-of-core electrons using the VASP code [27]. The plain wave basis cutoff was set to 300 eV, Brillouin zone sampling was performed using 1 gamma-centered k-point.

As in the case of classical MD, simulation cell included 107 atoms and one vacancy. To suppress thermal drift Nóse thermostat with $SMASS = 2.7$ was employed. This *SMASS* value sets the frequency of induced temperature fluctuations to 5 THz which conforms with the typical phonon frequency in aluminum [28].