



# Acceleration of diffusive molecular dynamics simulations through mean field approximation and subcycling time integration



X. Sun<sup>a</sup>, M.P. Ariza<sup>b</sup>, M. Ortiz<sup>c</sup>, K.G. Wang<sup>a,\*</sup>

<sup>a</sup> Department of Aerospace and Ocean Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, United States

<sup>b</sup> Escuela Técnica Superior de Ingeniería, Universidad de Sevilla, Sevilla 41092, Spain

<sup>c</sup> Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA 91125, United States

## ARTICLE INFO

### Article history:

Received 8 June 2017

Received in revised form 10 August 2017

Accepted 31 August 2017

Available online xxxx

### Keywords:

Diffusive molecular dynamics

Mean field approximation

Subcycling time integration

Long-term processes

Hydrogen diffusion

Phase transformation

## ABSTRACT

Diffusive Molecular Dynamics (DMD) is a class of recently developed computational models for the simulation of long-term diffusive mass transport at atomistic length scales. Compared to previous atomistic models, e.g., transition state theory based accelerated molecular dynamics, DMD allows the use of larger time-step sizes, but has a higher computational complexity at each time-step due to the need to solve a nonlinear optimization problem at every time-step. This paper presents two numerical methods to accelerate DMD based simulations. First, we show that when a many-body potential function, e.g., embedded atom method (EAM), is employed, the cost of DMD is dominated by the computation of the mean of the potential function and its derivatives, which are high-dimensional random variables. To reduce the cost, we explore both first- and second-order mean field approximations. Specifically, we show that the first-order approximation, which uses a point estimate to calculate the mean, can reduce the cost by two to three orders of magnitude, but may introduce relatively large error in the solution. We show that adding an approximate second-order correction term can significantly reduce the error without much increase in computational cost. Second, we show that DMD can be significantly accelerated through subcycling time integration, as the cost of integrating the empirical diffusion equation is much lower than that of the optimization solver. To assess the DMD model and the numerical approximation methods, we present two groups of numerical experiments that simulate the diffusion of hydrogen in palladium nanoparticles. In particular, we show that the computational framework is capable of capturing the propagation of an atomically sharp phase boundary over a time window of more than 30 seconds. The effects of the proposed numerical methods on solution accuracy and computation time are also assessed quantitatively.

© 2017 Elsevier Inc. All rights reserved.

## 1. Introduction

In a number of areas of application, the behavior of materials depends sensitively on processes that pertain to dissimilar time scales, ranging from atomic vibrations on the order of femtoseconds (fs), to diffusive transport of mass on the order

\* Corresponding author.

E-mail address: kevinwgy@vt.edu (K.G. Wang).

of seconds or even longer time scales [1–4]. This disparity of scales poses a significant challenge to atomistic modeling and simulation and has motivated long-standing extensive research. Classical Molecular Dynamics (MD) constitutes a powerful computational tool as it explicitly models the atoms of the material and their interactions. However, its time-step size is limited to the order of femtosecond by the frequency of atomic vibrations, resulting in total simulation time that is typically less than one microsecond [5]. Extensive research has been devoted to expanding the simulation time window while maintaining an atomistic description of the material [6]. For instance, transition state theory based (TST-based), accelerated MD (AMD) methods [7,8] and kinetic Monte Carlo (KMC) methods [9] track the transitions between microscopic states without explicitly resolving atomic vibrations. However, for mass transport problems the total time window accessible to these methods is limited by the frequency of individual atom/vacancy hops within the material sample and is typically less than one second [10].

Diffusive Molecular Dynamics (DMD) is a relatively new class of methods that has demonstrated potential for simulating diffusion processes in crystalline solids beyond seconds while maintaining the atomistic resolution. The basic assumption underlying DMD is that the time scale of diffusion is much larger than that of microscopic state transitions. Therefore, at an intermediate time scale, the microscopic state variables – such as the instantaneous position and occupancy of a lattice site – can be considered as random variables. Elements of DMD can be traced back to the generalized TDDFT (time-dependent density functional theory) method proposed by Perez and Lewis [11]. More recently, Li et al. [12] have extended DMD to handle diffusive mass transport by vacancy exchange and have applied it to study nanoindentation and sintering processes [12] and dislocation reaction mechanisms [13]. Venturini et al. [14–16] have developed a general framework for diffusive molecular processes, including heat and mass transport. Farmer et al. [17] have formulated a spin-diffusion stochastic process to interpret the DMD model. A recent theoretical review of DMD can be found in [18].

Following [14], in the present work we couple an empirical diffusion model, or *master equation*, driving the evolution of the mean value of atomic site occupancies, with a non-equilibrium statistical thermodynamics model that determines the mean value of atomic positions by minimizing a grand-canonical free entropy. In terms of numerical implementation, our approach involves the numerical integration of the *master equation*, and the numerical solution of a highly nonlinear optimization problem at every time-step. By working with atomic fractions, the characteristic time-step size of our DMD simulations can be much larger than those based on either AMD or KMC methods, since we do not explicitly track the individual atom/vacancy hops. As a consequence, the time-step size in our calculations is not restricted by the frequency of those events. Instead, it is only limited by the diffusive time scale, e.g., by the speed of the propagation of a phase boundary, which can be as slow as 1 nm/s [19].

However, this time-wise acceleration takes place at some computational expense, since the computational cost of a DMD step, which is dominated by the optimizer, can be significant. Thus, we show that when a many-body embedded atom method (EAM) potential is employed, the computational complexity of our DMD scheme is  $\mathcal{O}(Q^2N)$  per time-step, where  $N$  and  $Q$  denote the number of atomic sites in the material sample and the average number of neighbors of an atomic site within the cut-off distance of the EAM potential, respectively. For many EAM potentials  $Q$  can be as large as 100, which makes the  $\mathcal{O}(Q^2)$  scaling problematic. By contrast, the one-step cost of classical MD, TST-based AMD, and KMC is typically of the order of  $\mathcal{O}(QN)$  [20],  $\mathcal{O}(QN)$  [6] and  $\mathcal{O}(N \log N)$  [9], respectively. It is therefore of interest to investigate ways of reducing the computational cost of DMD by means of additional numerical approximations.

To this end, we begin by noting that the cost of numerical optimization in calculations employing EAM potentials is dominated by the computation of the mean value of the embedding energy  $F(\omega)$  with respect to a trial Gauss distribution, i.e.,  $\langle F(\omega_i) \rangle_0$ , where  $\omega_i$  denotes the electron density on site  $i$ . For many EAM potentials, e.g., [21,22],  $F(\omega)$  is convex over a broad range of  $\omega$ , which suggests the use of Jensen's lower bound as an approximation [14], i.e.,

$$\langle F(\omega_i) \rangle_0 \approx F(\langle \omega_i \rangle_0). \quad (1)$$

This approximation is the result of estimating the random variable  $\omega_i$  by its mean value. We show that the direct implementation of this approximation suffers from low accuracy in certain cases. In order to overcome this limitation, we introduce a second-order approximation of the form

$$\langle F(\omega_i) \rangle_0 \approx F(\langle \omega_i \rangle_0) + \frac{1}{2} F''(\langle \omega_i \rangle_0) \langle (\omega_i - \langle \omega_i \rangle_0)^2 \rangle_0. \quad (2)$$

Finally, we show that, by a further appeal to mean field approximation, the computational complexity of DMD reduces from  $\mathcal{O}(Q^2N)$  to  $\mathcal{O}(QN)$  per time-step, which results in a considerable acceleration of the calculations, especially where complex potentials are concerned. The second idea explored in this study concerns the use of subcycling on the numerical integration of the empirical diffusion model. Subcycling naturally suggests itself because the cost of explicit integration of the diffusion equations is significantly lower than that of the optimizer. Subcycling has been widely used in the simulation of multiphysics problems when the time-step limit or computational cost of different physical fields differ significantly [23–25].

In order to verify the proposed numerical algorithms and assess their performance, we simulate the diffusion of hydrogen (H) in palladium (Pd) nanoparticles. This problem is relevant to several energy-related areas of application such as electrical batteries [4] and hydrogen storage systems [1]. In this system, the fundamental event is the hopping of H atoms among the interstitial sites of the primary metal lattice. However, the overall diffusion process often takes minutes to hours to reach equilibrium and occurs simultaneously with a number of phenomena of interest such as lattice distortion [1], slow

Download English Version:

<https://daneshyari.com/en/article/4967087>

Download Persian Version:

<https://daneshyari.com/article/4967087>

[Daneshyari.com](https://daneshyari.com)