Journal of Computational Physics 326 (2016) 773–779

Contents lists available at ScienceDirect

Journal of Computational Physics

www.elsevier.com/locate/jcp

Meaningful timescales from Monte Carlo simulations of particle systems with hard-core interactions

Liborio I. Costa

Etzbergstrasse 19c, 8405 Winterthur, Switzerland

ARTICLE INFO

Article history:
Received 21 March 2016
Received in revised form 5 September 2016
Accepted 9 September 2016
Available online 15 September 2016

Keywords:
Kinetic Monte Carlo
Rejection-free
Molecular dynamics
Timescale
Molecular simulations
Hard disks

ABSTRACT

A new Markov Chain Monte Carlo method for simulating the dynamics of particle systems characterized by hard-core interactions is introduced. In contrast to traditional Kinetic Monte Carlo approaches, where the state of the system is associated with minima in the energy landscape, in the proposed method, the state of the system is associated with the set of paths traveled by the atoms and the transition probabilities for an atom to be displaced are proportional to the corresponding velocities. In this way, the number of possible state-to-state transitions is reduced to a discrete set, and a direct link between the Monte Carlo time step and true physical time is naturally established. The resulting rejection-free algorithm is validated against event-driven molecular dynamics: the equilibrium and non-equilibrium dynamics of hard disks converge to the exact results with decreasing displacement size.

1. Introduction

Monte Carlo (MC) stochastic methods are currently well established as numerical tools for unraveling the complex behavior of a large variety of systems [1–11]. Most MC algorithms can be divided into two main groups: methods built on the importance sampling scheme of Metropolis et al. [12] (all denoted here as MMC [2,13–19]) and kinetic Monte Carlo (KMC) methods [20–22].

In MMC, the system evolves through randomly sampled configurations. Each new configuration is accepted or rejected according to specific rules to satisfy the Boltzmann equiprobability principle. The possibility of letting the system evolve through unphysical trajectories [14,15] makes MMC algorithms particularly efficient for calculating equilibrium properties. In fact, they are often preferred over molecular dynamics (MD) in those cases where relaxation times diverge. As representative examples, one can mention the melting transition of hard disks [2] and the conformations of the densely crowded molecular architectures [3] typical of dendronized polymers [23,24]. The price to pay in MMC is the lack of a physically meaningful timescale. In fact, although MMC can be used to obtain information about dynamics [1,5,6,9,10], often only in terms of scaling laws, it is at the same time recognized that the analogy between the MMC dynamics and actual time evolution is only superficial [1,6,16,19]. In the field of molecular simulations, notable exceptions are Brownian processes [7,25,26] and the bond-fluctuation model for polymer chains, which provides a good approximation of the Rouse model [1,16]. However, in both cases, the connection to physical time requires a priori knowledge, or at least an estimation, of the diffusion coefficient, which is not always easy to predict, especially in concentrated polymeric systems [27]. Additionally, these cases are the exceptions rather than the rule, and a general and definitive connection between physical time and the dynamic evolution

E-mail address: liborio78@gmail.com.

http://dx.doi.org/10.1016/j.jcp.2016.09.023
0021-9991/

of molecular systems determined through MMC simulations is still missing despite the many efforts in this direction [13,17,18,26].

The correct time evolution can be obtained, in principle, through KMC methods, which apply to systems that evolve dynamically from state to state, each state being identified with a minimum in the energy landscape [20,21,28]. Voter, for example [29], in one of his seminal works, used KMC to study the diffusion of rhodium clusters on Rh(100). In KMC, atomic vibrations are neglected, and, provided that one knows all possible states corresponding to the minima of the energy basins, a rate catalog for the transitions from one state to another can be build, where the rate constants are calculated using the transition state theory [30,31]. Once the rate catalogue is given, the trajectory of the system through such states can be obtained by means of a stochastic procedure [20,21,29]. On the other hand, if a system undergoes unexpected reaction pathways, the task to identify and quantify all possible states and to build the corresponding rate catalogue becomes extremely challenging. To this end, advanced KMC methods have been proposed, where the rate catalogue is built on the fly [22,32]. While promising, such methods add some complexity to the algorithm, and, in practice, one can never fully ensure that all states have been identified. As a consequence, to date, KMC methods can be used when the number of states is discrete and the transition probabilities for the state-to-state transitions are known or easy to identify, but they are not suitable or of difficult application for molecular systems evolving in a continuous space characterized by an infinite and unknown number of states. The reader can consult a very clear introduction on the topic by Voter for additional details on the pros and cons of KMC [21].

Therefore, in general terms, if the interest is in studying the dynamics of a molecular system with full atomistic detail (e.g. including the atomic vibrations) and without any a priori knowledge of the system behavior, one has to revert to MD. At the same time, it remains an open question whether the same type of information could be obtained by a generally valid MC. The aim of this contribution is to reduce the gap between MC and MD by proposing a new Markov Chain MC scheme that provides a reasonably accurate description of the dynamics of molecular systems without the above mentioned limitations of KMC methods. As a first step towards this goal, the case of systems characterized by hard-core interactions is considered here, and the corresponding algorithm is conveniently indicated as Monte Carlo Molecular Dynamics (MCMD). In what follows, I first introduce the concepts underlying MCMD and the resulting algorithm. Then, the method is validated against event-driven MD in terms of both static and dynamic properties for the case of hard disks in a box. Finally, an outlook for possible future generalizations and applications is given.

2. Analogy between motion and reaction network

Let us consider first the equations of motion for N non-interacting hard disks. In the absence of collisions, each disk i moves along a straight line parallel to its velocity v_i according to

$$dl_i/dt = v_i \tag{1}$$

where l_i is the distance traveled by disk i. The system of N equations (Eq. (1)) can be written in terms of the rescaled quantities $n_i = l_i/\delta$ and $a_i = v_i/\delta$ where the parameter δ is the "unit of displacement", such that n_i represents the number of steps δ traveled by disk i:

$$dn_i/dt = a_i \tag{2}$$

At the same time, we notice that solving Eq. (2) (and therefore Eq. (1)) is mathematically equivalent to solving a chemical reaction network where all reactions are of the external source type

$$\emptyset \xrightarrow{a_i} n_i \tag{3}$$

From this view point, n_i and a_i would represent the number of molecules of species i and the rate parameter of the i^{th} reaction generating the species i, respectively. By treating n_i as discrete variables, the probabilistic evolution of such a system is governed by the master equation

$$\frac{\partial P(t,\boldsymbol{n})}{\partial t} = \sum_{i=1}^{N} a_i [P(t, n_1, ..., n_i - 1, ..., n_N) - P(t,\boldsymbol{n})] \tag{4}$$

where $P(t,\boldsymbol{n})$ is the probability that the system is in state $\boldsymbol{n} = (n_1, ..., n_N)$ at time t. In turn, Eq. (4) can be solved using a KMC scheme, namely the stochastic simulation algorithm (SSA) [33]. SSA is an iterative algorithm where at each iteration, a reaction channel μ is sampled proportionally to the transition probability a_μ, named propensity in the terminology of the SSA, the state of the system is updated, $n_\mu \leftarrow n_\mu + 1$, and the time is advanced of the MC time step [34]

$$\tau = \frac{1}{A} = 1/\sum_{i=1}^{N} a_i \tag{5}$$

In other words, by restricting the infinite number of possible random displacements to the discrete set of N displacements parallel to the disks velocities, one can identify the state of the system at time t with the number of displacements δ