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Pairwise adaptive thermostats for improved accuracy and stability in dissipative particle dynamics

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ABSTRACT

We examine the formulation and numerical treatment of dissipative particle dynamics (DPD) and momentum-conserving molecular dynamics. We show that it is possible to improve both the accuracy and the stability of DPD by employing a pairwise adaptive Langevin thermostat that precisely matches the dynamical characteristics of DPD simulations (e.g., autocorrelation functions) while automatically correcting thermodynamic averages using a negative feedback loop. In the low friction regime, it is possible to replace DPD by a simpler momentum-conserving variant of the Nosé–Hoover–Langevin method based on thermostatting only pairwise interactions; we show that this method has an extra order of accuracy for an important class of observables (a superconvergence result), while also allowing larger timesteps than alternatives. All the methods mentioned in the article are easily implemented. Numerical experiments are performed in both equilibrium and nonequilibrium settings; using Lees–Edwards boundary conditions to induce shear flow.

1. Introduction

Classical molecular dynamics (MD), where the motion of individual atoms is governed by Newton's law in the microcanonical ensemble (where energy, i.e., the Hamiltonian of the system, is conserved), has been widely used in molecular simulations [1,2]. However, the constant energy setting is not relevant to a real-world laboratory environment since energy, as an extensive variable, depends on system size. In typical cases, one replaces the microcanonical ensemble by the canonical one, where temperature is conserved using suitable "thermostat" techniques.

One popular thermostat is Langevin dynamics, whereby each particle is subject to dissipative and collisional interactions with the particles of an artificial "heat bath" and modeled by supplementing the conservative Newtonian equations of motion with balanced damping and stochastic terms in such a way that the desired target system temperature is maintained. However, as pointed in [3], in order to be consistent with hydrodynamics, a particle model should respect Galilean invariance, and, in particular, should conserve momentum, something that Langevin dynamics fails to do. Fundamentally, Langevin dynamics and its overdamped Brownian dynamics limit, are appropriate for modeling systems in or near thermodynamic equilibrium and therefore do not take into account the possibility of an underlying fluid flow, thereby precluding their use in situations where the flow of the soft matter system cannot be predicted beforehand (e.g., when dealing with interfaces or nonuniform flow). Moreover, it has been reported in [4] that, due to the violation of global momentum conservation,

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Langevin dynamics can lead to nonphysical screening of hydrodynamic interactions with a screening length proportional to the inverse square root of the friction coefficient of the algorithm. In order to control simulation artifacts, one is led to use a very small friction coefficient, effectively reducing Langevin dynamics to Hamiltonian dynamics in the microcanonical ensemble. Therefore, when hydrodynamics is of interest, standard thermostats should be replaced by momentum-conserving thermostats, in particular the so-called dissipative particle dynamics (DPD) method of Hoogerbrugge and Koelman [3].

DPD was first proposed in order to recover the properties of isotropy (and Galilean invariance) that were broken in the so-called lattice-gas automata method [5]. In DPD, each body is regarded as a coarse-grained particle. These particles interact in a soft (and short-ranged) potential, allowing larger integration timesteps than would be possible in MD, while simultaneously decreasing the number of degrees of freedom required. As in Langevin dynamics, a thermostat consisting of well-balanced damping and stochastic terms is applied to each particle. However, unlike in Langevin dynamics, both terms are pairwise and the damping term is based on relative velocities, leading to the conservation of both the angular momentum and the linear momentum. The property of Galilean invariance (i.e., the dependence on the relative velocity) makes DPD a profile-unbiased thermostat (PUT) [6,7] by construction and thus it is an ideal thermostat for nonequilibrium molecular dynamics (NEMD) [8]. The momentum is expected to propagate locally (while global momentum is conserved) and thus the correct hydrodynamics is expected in DPD [8], as demonstrated previously in [9]. Due to the aforementioned properties, DPD has been widely used to recover thermodynamic, dynamical, and rheological properties of complex fluids, with applications in polymer solutions [10], colloidal suspensions [11], multiphase flows [12], and biological systems [13]. DPD has been compared with Langevin dynamics for out-of-equilibrium simulations of polymeric systems in [14], where as expected the correct dynamic fluctuations of the polymers were obtained with the former but not with the latter.

Given its promising prospects from the applications perspective, and its widespread use in large scale simulations, the optimal design of numerical methods for DPD becomes crucially important, in particular the numerical efficiency in practice [15–18]. Numerous numerical schemes [15,19–24] have been proposed in the last two decades following the introduction of DPD, which are intended to reduce nonphysical artifacts (especially in the large stepsize regime) induced by the discretization error. Recently, we have systematically examined the performance (in terms of accuracy, efficiency, and robustness) of a number of the most popular methods in the literature [25].

In addition, we have proposed in [25] an alternative stochastic momentum-conserving thermostat, the pairwise Nosé–Hoover–Langevin (PNHL) thermostat. This method mimics the DPD system in the regime of low friction, however achieving much higher accuracy and computational efficiency. One contribution of the current article is a perturbation analysis showing that averages of observables of a certain (common) form performed using a nonsymmetric splitting of the PNHL system (i.e., the PNHL-N method [25]) have unexpected second order accuracy (as a power of the stepsize), justifying the enhanced performance of PNHL observed in simulations.

The second important contribution of this article is a new pairwise adaptive Langevin (PAdL) thermostat to replace DPD in the regime of moderate or high friction. This method draws on work on adaptive thermostats [26–28], by supplementing a DPD type pairwise stochastic perturbation by an auxiliary control law (also pairwise) to maintain the thermodynamic state. The new method fully captures the dynamics of DPD (for example, autocorrelation functions in DPD are precisely reproduced) and thus can be directly applied in the setting of momentum-conserving simulations as a replacement for DPD. We describe a simple splitting-based numerical method for PAdL. While PAdL has similar per-timestep computational cost, the method is shown to generate substantially more accurate approximations to thermodynamic averages at the same stepsize as DPD (as much as an order of magnitude). Moreover, and perhaps more significantly, the stepsize can be increased by around 50% using PAdL, for similar accuracy, resulting in a much more efficient overall simulation method.

Furthermore, we discuss the proper treatment of Lees–Edwards boundary conditions in the DPD setting, an essential part of modeling shear flow.

The rest of the article is organized as follows. In Section 2, we review the formulation of DPD and the momentum-conserving PNHL method, and introduce the newly proposed PAdL thermostat that mimics the dynamics of DPD. We investigate in Section 3 numerical methods for PNHL and PAdL and give results on the order of accuracy of various schemes, in particular showing that the PNHL-N method is second order in its approximation of ergodic (long time) averages of a certain class of observables. Section 4 presents numerical experiments in both equilibrium and nonequilibrium cases, comparing the performance of numerous popular numerical methods in practice. The proper treatment of Lees–Edwards boundary conditions in the context of momentum-conserving thermostats is also discussed in Section 4. Our findings are summarized in Section 5.

2. Dissipative particle dynamics and pairwise thermostats

In this section, we review the formulation of DPD and the momentum-conserving PNHL thermostat, followed by the introduction of the PAdL thermostat.

2.1. Dissipative particle dynamics (DPD)

The original DPD system was updated in discrete time steps and was later reformulated by Español and Warren [29] as a system of Itō stochastic differential equations (SDEs).