Commun. Comput. Phys.
doi: 10.4208/cicp.OA-2024-0303

Vol. **38**, No. 3, pp. 630-660
September 2025

A Second-Order Langevin Sampler Preserving Positive Volume for Isothermal–Isobaric Ensemble

Lei Li[1,2,3,*] and Yuzhou Peng[1]

[1] *School of Mathematical Sciences, Shanghai Jiao Tong University, Shanghai 200240, China*
[2] *Institute of Natural Sciences and MOE-LSC, Shanghai Jiao Tong University, Shanghai 200240, China*
[3] *Shanghai Artificial Intelligence Laboratory, Shanghai, China*

Received 11 December 2024; Accepted (in revised version) 27 May 2025

Abstract. We propose in this work a second-order Langevin sampler for the isothermal-isobaric ensemble (the NPT ensemble), preserving a positive volume for the simulation box. We first derive the suitable equations of motion for particles to be coupled with the overdamped Langevin equation of volume by sending the artificial mass of the periodic box to zero in the work of Liang et al., [J. Chem. Phys., 157(14)]. We prove the well-posedness of the new system of equations and show that its invariant measure is the desired ensemble. The new continuous time equations not only justify the previous cell rescaling methods, but also allow us to choose a suitable friction coefficient so that one has additive noise after a change of variable by taking logarithm of the volume. This observation allows us to propose a second-order weak scheme that guarantees the positivity of the volume. Various numerical experiments have been performed to demonstrate the efficacy of our method.

AMS subject classifications: 65C05, 92E10, 37M25

Key words: Molecular dynamics, NPT ensemble, zero-mass limit, operator splitting, weak convergence.

1 Introduction

Molecular dynamics (MD) simulation has made a great contribution to the study of the thermodynamic properties of complex multi-particle systems across various disciplines, including physics, chemistry, biology and pharmaceuticals [1,7,17,21,38]. Given the large or infinite number of particles in these macro-scale systems, periodic boxes are typically utilized to approximate the entire system, dividing the whole space into infinitely many adjacent simulation boxes, with one being the original simulation box and others being

*Corresponding author. *Email addresses:* leili2010@sjtu.edu.cn (L. Li), pengyz@sjtu.edu.cn (Y. Peng)

copies called images. Periodic boundary conditions enable particles leaving one side of the simulation box to re-enter from the opposite side with the same momenta, ensuring that all the particles within the box experience a similar environment. The application of periodic boxes facilitates the study of larger systems with fewer particles, reducing computational costs while still providing accurate insights into the behavior of the system as a whole [14]. In practice, these systems are often subjected to constant temperature and/or constant pressure conditions. This work focuses on the isothermal–isobaric ensemble, where the monatomic particle system interacts with an external bath that maintains constant temperature and pressure throughout the simulation. This ensemble, commonly known as the NPT ensemble because the number of particles, pressure and temperature are all kept constant, reflects laboratory conditions typical in simulations of solvated proteins, membranes and viruses [37].

Various thermostats and barostats have been developed to modeled constant temperature and pressure in the external baths. The first barostat for maintaining pressure during the MD simulation was proposed in the pioneering work of Andersen [2], where the volume of the simulation box fluctuates based on the difference between external and internal pressure. The thermostat for preserving temperature works through stochastic collisions modeled by momenta resampling. Subsequently, Parrinello and Rahman extended Andersen's barostat to accommodate periodic boxes of arbitrary symmetry in the isoenthalpic-isobaric ensemble [34,35]. Later, Andersen's technique was extended to deal with rigid molecule systems, where the intermolecular potential is based on atom–atom interactions [36] and the periodic box could be trigonal [31, 32]. However, Andersen's method lacks effectiveness in preserving the dynamical properties of the systems.

An alternative approach to controlling temperature and pressure was proposed by Berendsen et al., where the momenta of the particles and the volume of the simulation box fluctuate according to the difference between the instantaneous value of temperature and pressure and their desired counterparts [4]. Although efficient in equilibrating the system, Berendsen's barostat inaccurately samples the target ensemble and is typically employed as a burn-in technique [6]. Motivated by the stochastic version of the Berendsen thermostat [8, 10], a carefully chosen stochastic term was incorporated into the Berendsen barostat, leading to the development of the stochastic cell rescaling method [5]. However, concerns remain regarding its algorithmic specifics and fidelity to the invariant measure under typical discretizations such as the commonly used Euler-Maruyama scheme.

The Nosé–Hoover thermostat [18, 29, 30, 33] replaces the stochastic collisions in Andersen's thermostat with an auxiliary variable to simulate the effects of the bath, ensuring smooth, deterministic and time-reversible trajectories and performing better in preserving the dynamical properties of the system. However, it is inefficient in equilibrating the system due to the lack of ergodicity [14]. The Nosé–Hoover chain method was then proposed to solve this problem by introducing additional parameters [26]. Later, the Martyna-Tobias-Klein (MTK) algorithm, combining Nosé-Hoover thermostats with suitable barostats, and its subsequent extensions have found widespread use in NPT ensem-