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# Dimension-Free Ergodicity of Path Integral Molecular Dynamics

Xuda Ye[1,*] and Zhennan Zhou[2]

[1] *Beijing International Center for Mathematical Research, Peking University, Beijing 100871, China.*
[2] *Institute for Theoretical Sciences, Westlake University, Hangzhou, 310030, China.*

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**Abstract.** The quantum thermal average plays a central role in describing the thermodynamic properties of a quantum system. Path integral molecular dynamics (PIMD) is a prevailing approach for computing quantum thermal averages by approximating the quantum partition function as a classical isomorphism on an augmented space, enabling efficient classical sampling, but the theoretical knowledge of the ergodicity of the sampling is lacking. Parallel to the standard PIMD with $N$ ring polymer beads, we also study the Matsubara mode PIMD, where the ring polymer is replaced by a continuous loop composed of $N$ Matsubara modes. Utilizing the generalized $\Gamma$ calculus, we prove that both the Matsubara mode PIMD and the standard PIMD have uniform-in-$N$ ergodicity, i.e., the convergence rate towards the invariant distribution does not depend on the number of modes or beads $N$.

**AMS subject classifications**: 37A30, 82B31, 81S40

**Key words**: Quantum thermal average, path integral molecular dynamics, Matsubara modes, ergodicity, generalized $\Gamma$ calculus.

## 1 Introduction

Calculation of the quantum thermal average plays an important role in quantum physics and quantum chemistry, not only because it fully characterizes the canonical ensemble of the quantum system, but also because of its wide applications in describing the thermal properties of complex quantum systems, including the ideal quantum gases [1], chemical reaction rates [2,3], density of states of crystals [4], quantum phase transitions [5], etc. However, since the computational cost of direct discretization methods (finite difference,

*Corresponding author. *Email addresses:* abneryepku@pku.edu.cn (X. Ye), zhouzhennan@westlake.edu.cn (Z. Zhou)

 

pseudospectral methods, etc.) grows exponentially with the spatial dimension [6, 7], the exact calculation of the quantum thermal average is hardly affordable in high dimensions. In the past decades, there have been numerous methods committed to compute the quantum thermal average approximately, and the path integral molecular dynamics (PIMD) is among the most prevailing ones.

The PIMD is a computational framework to obtain accurate quantum thermal averages. Using the imaginary time-slicing approach in Feynman path integral [8], the PIMD maps the quantum system in $\mathbb{R}^d$ to a ring polymer of $N$ beads in $\mathbb{R}^{dN}$, where each bead represents a classical duplicate of the original quantum system, and adjacent beads are connected by a harmonic spring potential. When the number of beads $N$ is large enough, the classical Boltzmann distribution of the ring polymer in $\mathbb{R}^{dN}$ is expected to yield an accurate approximation of the quantum thermal average. Since the development of the PIMD in 1970s, this framework has been widely used in the calculations in the chemical reaction rates [9–11], transition state theory [12] and tunneling splittings [13, 14]. Several variants of the PIMD, the ring polymer molecular dynamics (RPMD) [15, 16], the centroid molecular dynamics (CMD) [17, 18] and the Matsubara dynamics [19, 20], have been employed to compute the quantum correlation function. Recently, there have been fruitful studies on designing efficient and accurate algorithms to enhance the numerical performance of the PIMD [21–24]. The PIMD can also be applied in multi-electronic-state quantum systems, see [25, 26] for instance. The general procedure to compute the quantum thermal average in the PIMD is demonstrated as follows:

1. **Ring polymer approximation**. Pick a positive integer $N$ and map the quantum system to a ring polymer system of $N$ beads, where each bead is a classical duplicate of the original system.

2. **Construction of sampling**. Equip the ring polymer system with a stochastic thermostat (e.g., Langevin, Andersen and Nosé–Hoover) so that the resulting stochastic process samples the Boltzmann distribution of the ring polymer.

3. **Stochastic simulation**. Evolve the stochastic process with a proper time discretization method, and approximate the quantum thermal average by the time average in the long-time simulation.

The PIMD framework based on the ring polymer beads is referred to as the standard PIMD in this paper.

Although the standard PIMD has become a mature framework to compute the quantum thermal average, a rigorous mathematical understanding of its convergence is still sorely lacking. A fundamental question is the dimension-free ergodicity, i.e., does the stochastic process sampling the Boltzmann distribution has a convergence rate which does not depend on the number of beads $N$? The property of uniform-in-$N$ ergodicity has been partially validated when the potential function is quadratic [27, 28], but a rigorous justification in the general case is still to be investigated.