

Simulating with Path Integrals: PIMD

The path integral formulation provides a powerful theoretical tool by mapping a quantum system onto an equivalent classical system of ring polymers. This classical system has a standard Boltzmann probability distribution, which means we can use well-established simulation techniques to sample it. The two main approaches are Monte Carlo (MC) and Molecular Dynamics (MD).

Path Integral Molecular Dynamics (PIMD) 🏃

To use molecular dynamics, we need to define a kinetic energy to generate motion. In PIMD, we introduce **fictitious masses and velocities** for each bead of the ring polymers. This allows us to write a Lagrangian for the entire classical system:

$$L_{PIMD} = \sum_{s=1}^P \sum_{I=1}^N \frac{1}{2} \tilde{m}_I (\dot{R}_I^{(s)})^2 - V_{eff}(\{R_I^{(s)}\})$$

From this Lagrangian, we can derive the equations of motion for each bead:

$$\tilde{m}_I \ddot{R}_I^{(s)} = -m_I \omega_P^2 (2R_I^{(s)} - R_I^{(s-1)} - R_I^{(s+1)}) - \frac{1}{P} \nabla_{R_I^{(s)}} V$$

This equation describes the motion of bead s of particle I . The forces come from two sources: the harmonic springs connecting it to its neighbors (beads $s-1$ and $s+1$) and the scaled physical potential V .

It is crucial to remember that this is a **fictitious dynamic** created solely for the purpose of sampling the configuration space correctly. It **does not represent the real quantum dynamics** of the system.

The Ergodicity Problem in PIMD 🧩

A significant challenge in PIMD is **ergodicity breaking**. The problem arises from the weak coupling between different vibrational modes of the ring polymer. The intramolecular forces (the harmonic springs) are very strong, while the intermolecular forces (the physical potential) are scaled down by $1/P$.

This mismatch means that energy does not flow efficiently between the different modes. Some modes get "hot" while others remain "cold," and the system fails to explore the entire phase space correctly. This issue is similar to the famous Fermi-Pasta-Ulam problem.

To solve this, several **ergodic PIMD** methods have been developed:

- **Hybrid PIMD/PIMC:** Combines MD propagation with stochastic Monte Carlo moves to ensure proper energy distribution.
- **Langevin (PI)MD:** Introduces friction and stochastic forces that satisfy the fluctuation-dissipation theorem, effectively coupling the system to a heat bath. A modern variant is the Generalized Langevin Equation (GLE).
- **Nose-Hoover Chains:** Couples a chain of thermostats to each degree of freedom to rigorously enforce the canonical temperature distribution.

Practical Considerations 💡

Calculating Observables

For an operator that depends only on position, $\hat{A}(\hat{R})$, its quantum expectation value is calculated as a simple average over all the beads of the ring polymer and over the entire simulation trajectory:

$$\langle \hat{A} \rangle = \left\langle \frac{1}{P} \sum_{s=1}^P A(\underline{R}^{(s)}) \right\rangle_{PIMD}$$

Number of Beads (P)

In a real simulation, the number of beads P cannot be infinite. One must perform **convergence tests** by running simulations with an increasing number of beads (e.g., P = 2, 4, 8, 16...) until the calculated properties no longer change. More beads are required for lower temperatures and lighter masses.

The Potential V({R})

The physical potential can be obtained from several sources:

- **Classical Force Fields:** One must be careful, as these are often fitted to experimental data and may already implicitly include some quantum effects.
- **Ab initio PIMD:** The forces are calculated "on-the-fly" using electronic structure methods for each replica at every step, which is extremely expensive.
- **Machine Learning Potentials:** Potentials fitted to high-level ab initio data offer a balance of accuracy and efficiency.

Outlook: Approximate Quantum Dynamics

While PIMD is a method for static equilibrium properties, the time evolution of certain path integral quantities can be used to approximate real quantum dynamics. Two prominent methods based on this idea are **Centroid Molecular Dynamics (CMD)** and **Ring Polymer Molecular Dynamics (RPMD)**.