BF-CMD: Centroid Molecular Dynamics Using Bead-Fourier Path-Integrals

VISTA Seminar 91

Nathan London

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Outline

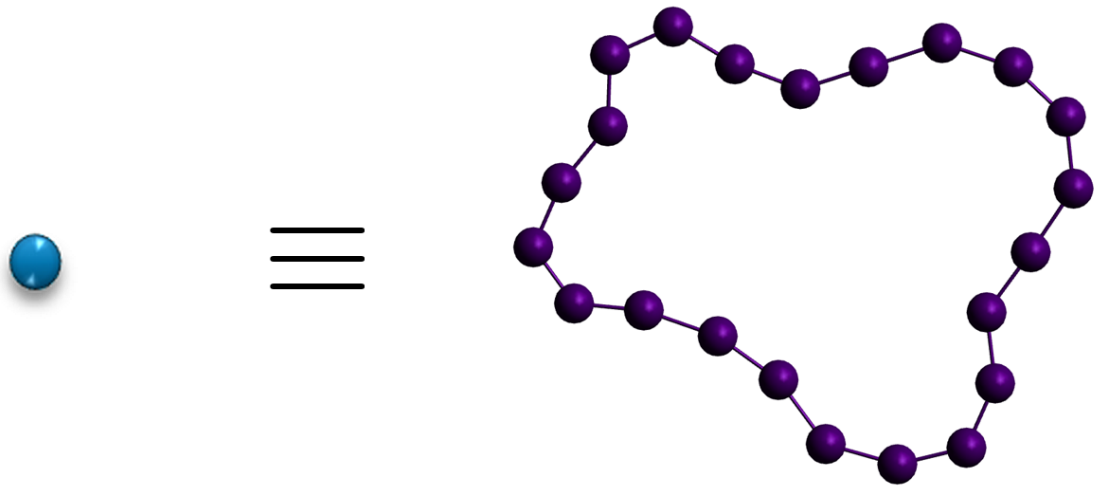
Introduction

- Path Integral (PI) based methods allow an efficient framework for incorporating nuclear quantum effects (NQEs) into classical simulations
- PI molecular dynamics (PIMD) can provide equilibrium properties and methods like ring polymer MD (RPMD) and centroid MD (CMD) approximate real-time dynamics
- Conventional PI methods can face issues in situations that require a large number of beads to converge NQEs
- Is there a rigorous method for representing PIs without needing as many beads?

Outline

Path-Integral Representations

- Conventional PIs represent a quantum particle using a series of classical particles connected by harmonic springs
- Represents discrete slices on an imaginary time path



- The continuous imaginary time path can also be considered
- Paths near classical trajectories contribute most
- Fourier PIs represent these paths using a Fourier sine series, but can require a very large number terms in the series
- Is there another way to represent these PIs?

Bead-Fourier Path Integrals

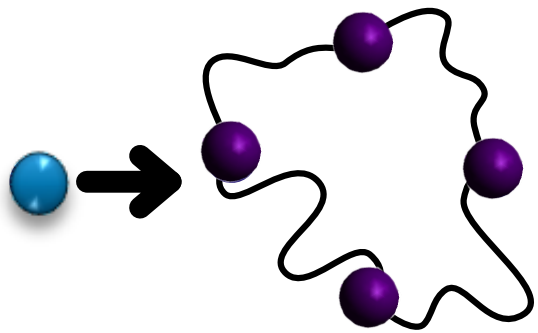
- BF-PIs discretize the continuous path, resulting in discrete beads with continuous path in between them

$$q_j(\xi) = q_j + (q_{j+1} - q_j)\xi + \sum_{k=1}^{k_{\max}} a_{jk} \sin(k\pi\xi)$$

- The external potential is evaluated along the path

$$H_{\mathrm{BF}} = \sum_{j=1}^{N} \left[\frac{1}{2}\omega_n^2 \left((q_{j-1} - q_j)^2 + \sum_{k=1}^{k_{\max}} \frac{(k\pi)^2}{2} a_{jk}^2 \right) + \frac{1}{n} \int_0^1 \mathrm{d}\xi \; V(q_j(\xi)) \right]$$

- BF-PIMD results show addition of a few Fourier components reduces the number of beads needed to converge equilibrium properties



Ivanov, S. D.; Lyubartsev, A. P.; Laaksonen, A. *Phys. Rev. E* **2003**, *67*, 066710

Centroid Molecular Dynamics

- Introduced by Voth and coworkers, where a particle is evolved under an effective potential defined by an imaginary time PI

$$H_{\mathrm{CMD}} = \frac{P^2}{2m} + F_{\mathrm{CMD}}(Q)$$

- The effective potential calculated as constrained ensemble average of external force

$$-\frac{\partial F_{\mathrm{CMD}}(Q)}{\partial Q} = -\left\langle \frac{\partial U(\mathbf{q})}{\partial Q} \right\rangle_Q$$

- The forces can be calculated on a grid before dynamics or "on-the-fly" as in adiabatic/partially adiabatic CMD

Cao, J.; Voth, G. A. *J. Chem. Phys.* **1994**, *100*, 5093–5105, Trenins, G.; Willatt, M. J.; Althorpe, S. C. *J. Chem. Phys* **2019**, *151*, 054109

Bead-Fourier CMD

- Create the effective potential using BF-PIs
- There are two ways to calculate estimators in BF-PI framework:
  - Pure bead: using just bead positions
  - Continuous: include path between beads
- In both cases, configuration sampling is done with the full BF-PI Hamiltonian
- For equilibrium properties, bead estimators converge faster
- Behavior for the effective potential will be explored
- Compute Kubo-transformed correlation function to study dynamical properties

$$\tilde{C}_{AB}(t) = \frac{1}{(2\pi\hbar)^2 Z} \int \mathrm{d}P \int \mathrm{d}Q \; \mathrm{e}^{-\beta H_{\mathrm{BF-CMD}}(P,Q)} A(Q) B(Q(t))$$

Outline

Simulation Details

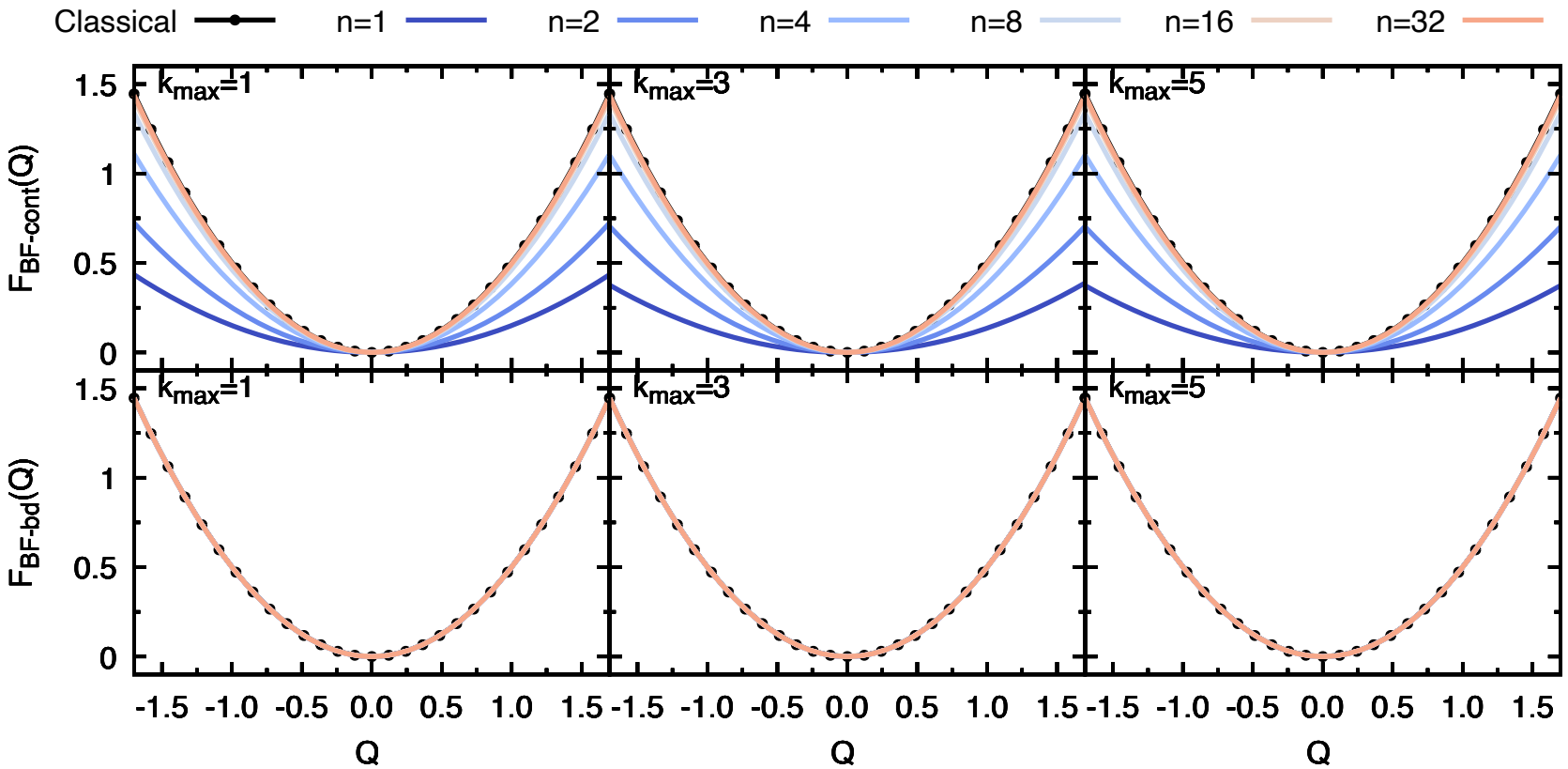
- Study a few one dimensional model systems where exact results can be compared against
- Effective potential calculations
  - Effective potential pre-calculated on grid
  - Monte Carlo (MC) sampling of BF-PI with centroid constrained at grid point
  - Two types of moves: bead moves and Fourier moves
  - Calculate ensemble average of force
  - Integrate to get effective potential
- Dynamical simulations
  - MC sampling of single particle on effective potential
  - 1×10^6 trajectories evolved using a time step of 0.001 a.u.
  - Calculate position autocorrelation function

London, N. and Momeni. M. R. arXiv:2505.13707

Outline

Harmonic Oscillator Effective Potential: $V(x) = \frac{1}{2}x^2$

- Classical dynamics gives exact Kubo-transformed CF
- Introducing Fourier components changes effective potential
- Flattening is significant using continuous estimator, especially with a few number of beads

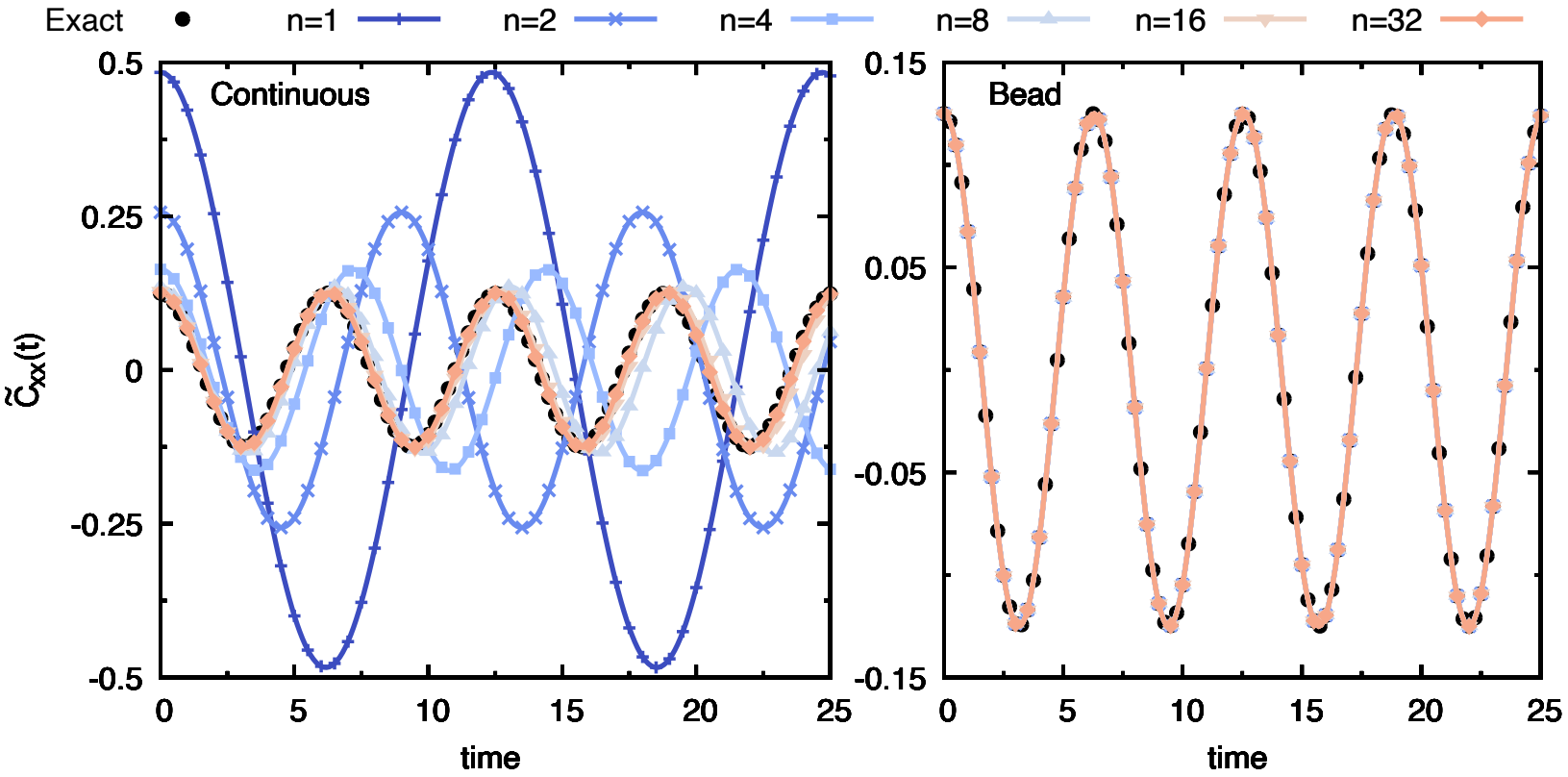


Effective potential of harmonic oscillator at $\beta = 8$

London, N. and Momeni. M. R. arXiv:2505.13707

Harmonic Oscillator Correlation Functions

- Flattening of potential results in larger oscillations at a lower frequency compared to exact results
- Bead estimated potential matches exact for all number of beads
- Effective potential calculated from bead estimator is clearly superior

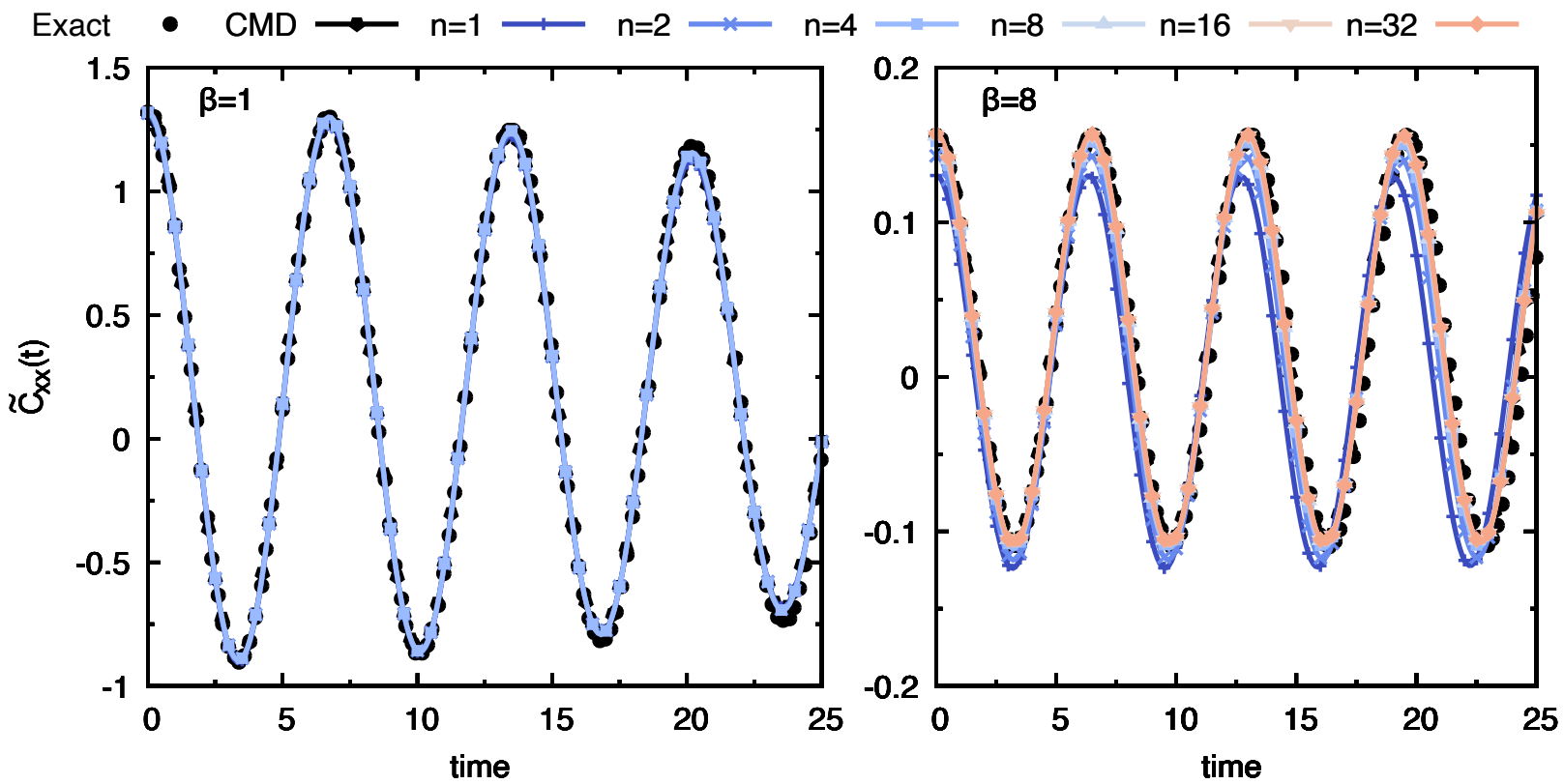


Kubo-transformed position autocorrelation function of harmonic oscillator at $\beta = 8$

London, N. and Momeni. M. R. arXiv:2505.13707

Mildly Anharmonic Oscillator: $V(x) = \frac{1}{2}x^2 + \frac{1}{10}x^3 + \frac{1}{100}x^4$

- Potentials with anharmonicity show power of the method
- At low temperatures, including just one Fourier component speeds up bead convergence 4-fold



Kubo-transformed position autocorrelation functions for mildly anharmonic oscillator

London, N. and Momeni. M. R. arXiv:2505.13707

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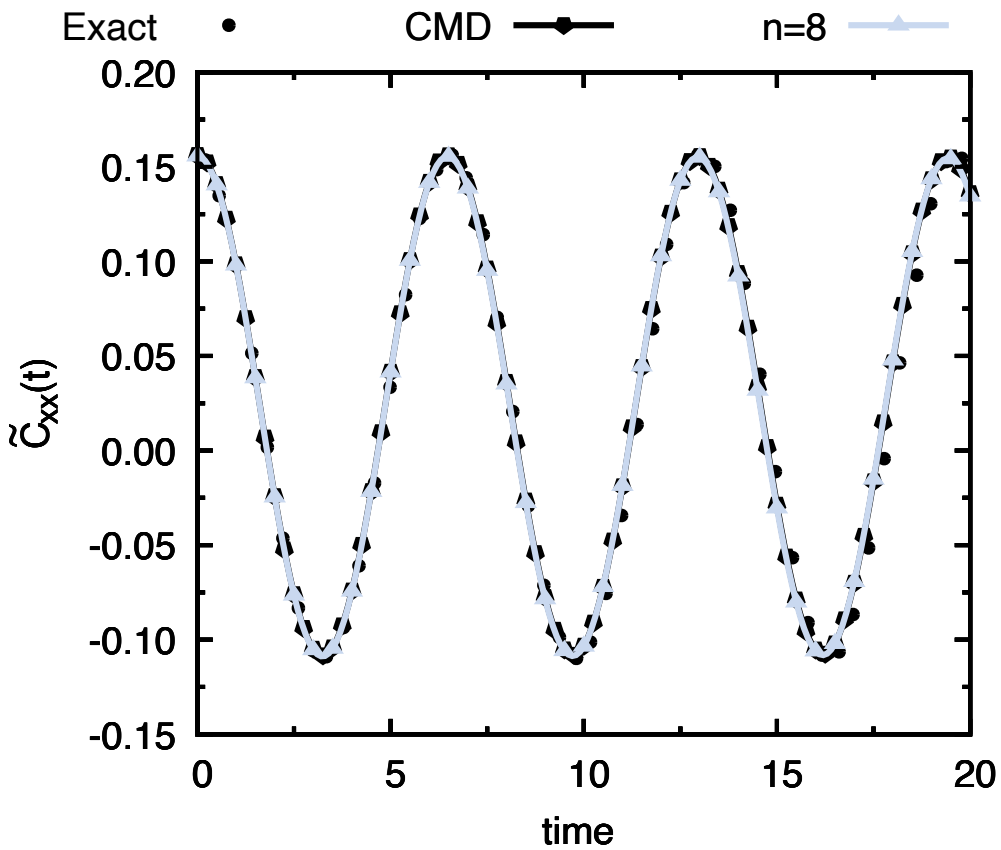
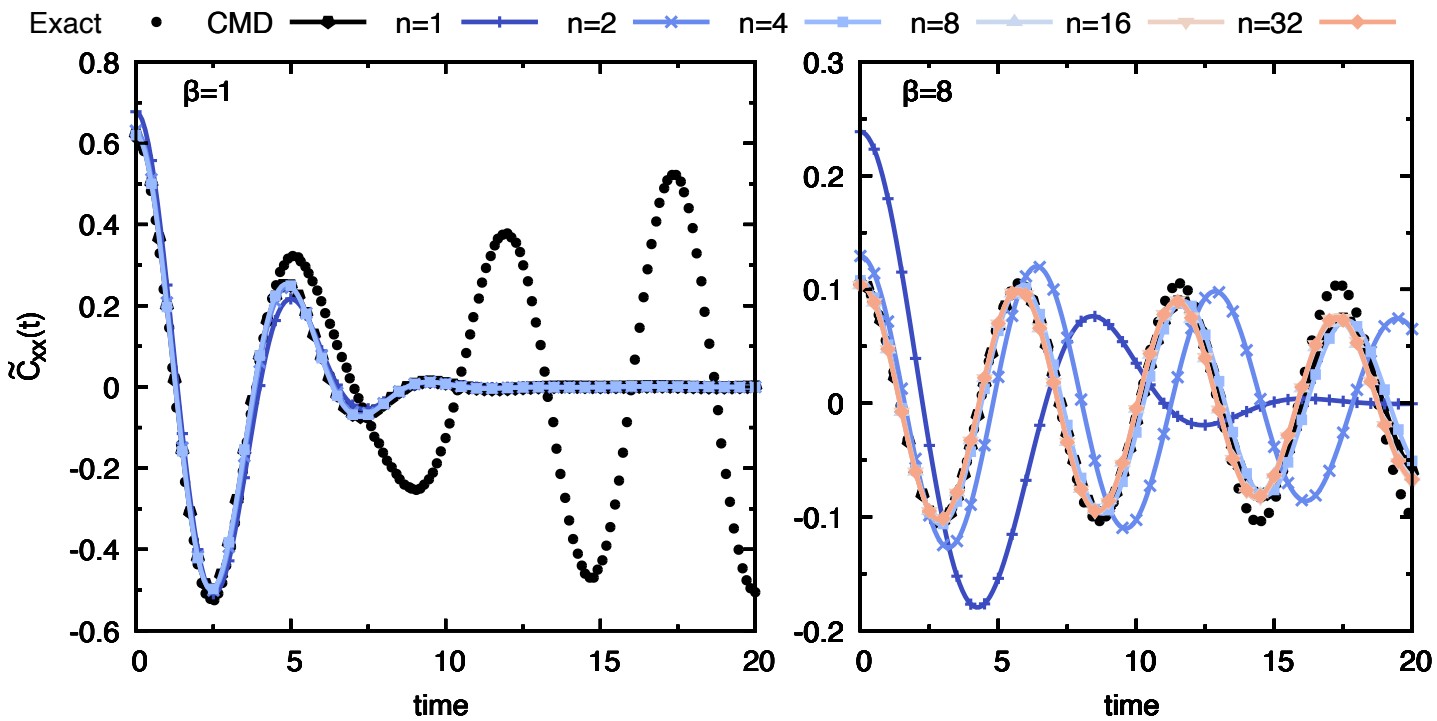


Comparison at $\beta = 8$ for $n = 8$ beads and 1 Fourier component

London, N. and Momeni. M. R. arXiv:2505.13707

Quartic Oscillator: $V(x) = \frac{1}{4}x^4$

- The quartic oscillator is a difficult system for PI methods
- Expected deviation from exact results at high temperature
- Low temperature simulations see same convergence increase as mildly anharmonic system



Kubo-transformed position autocorrelation functions for quartic anharmonic oscillator

London, N. and Momeni. M. R. arXiv:2505.13707

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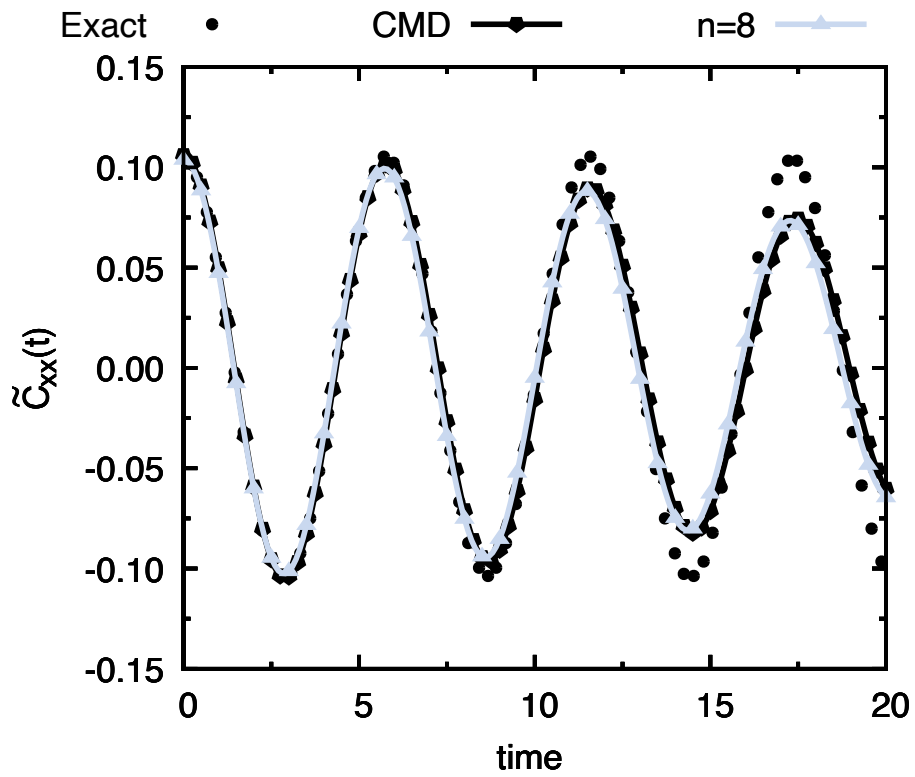

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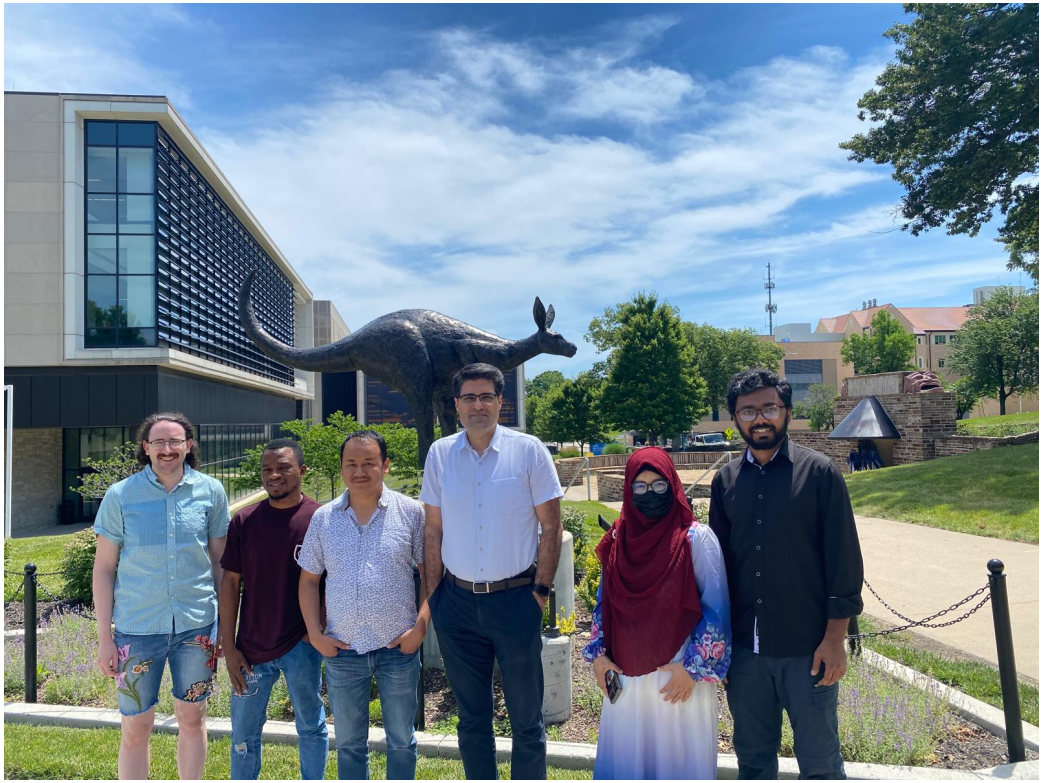

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