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ABSTRACT

We introduce a semi-classical approximation for calculating generalized multi-time correlation functions based on Matsubara dynamics, a classical dynamics approach that conserves the quantum Boltzmann distribution. This method is exact for the zero time and harmonic limits and reduces to classical dynamics when only one Matsubara mode is considered (i.e., the centroid). Generalized multi-time correlation functions can be expressed as canonical phase-space integrals, involving classically evolved observables coupled through Poisson brackets in a smooth Matsubara space. Numerical tests on a simple potential show that the Matsubara approximation exhibits better agreement with exact results than classical dynamics, providing a bridge between the purely quantum and classical descriptions of multi-time correlation functions. Despite the phase problem that prevents practical applications of Matsubara dynamics, the reported work provides a benchmark theory for the future development of quantum-Boltzmann-preserving semi-classical approximations for studies of chemical dynamics in condensed phase systems.

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I. INTRODUCTION

Thermal time correlation functions (TCFs) provide a powerful framework for studying chemical dynamical processes in the condensed phase. By expressing the dynamics of a system in terms of n -point quantum correlation functions involving time-evolved operators at different times, TCFs enable us to explore a wide range of phenomena, from linear and nonlinear (multidimensional) spectroscopy,^{1,2} to transport phenomena,^{3–5} and to quantum chaos.⁶ The classical descriptions of these TCFs can often yield a decent approximation; however, nuclear quantum effects, such as zero-point energy fluctuations and tunneling, can dramatically modify and regulate the structural and dynamical behavior of the system.^{7,8} Thus, there is currently significant interest in the development of semi-classical methods that incorporate quantum mechanical effects into condensed phase molecular dynamics simulations.

Several semi-classical methodologies have been introduced over the past decades, mainly focused on the simulation of two-point correlation functions. For example, methods based on the linearized semi-classical initial value representation (LSC-IVR)^{9–15} have successfully been used for simulations of quantum dynamics and infrared and Raman spectroscopy of condensed phase systems,^{16–24} despite the fact the method does not preserve the quantum statistics and neglects interference effects. Similarly, Boltzmann-preserving

methodologies derived from the path-integral formalism,^{7,25–29} such as Matsubara dynamics,^{30–33} Centroid Molecular Dynamics (CMD),^{34–39} Quasi-Centroid Molecular Dynamics (QCMD),⁴⁰ or Ring Polymer Molecular Dynamics (RPMD),^{41–44} where one follows the dynamics of a classical system in an extended phase-space, have been applied with incredible success for the calculation of one-time correlation functions.^{20,40,42,45–56} The path integral Liouville dynamics^{57–61} method has also shown promising results for the linear IR spectra of several gas-phase systems.^{62,63} However, despite the success of these methodologies, the application of these methods is mainly restricted to the calculation of two-point correlation functions. Understanding how these methods can be extended for the calculation of multidimensional response functions involving multi-point time correlation functions and what are the approximations of the exact quantum dynamics remains a non-trivial and outstanding challenge.^{64–67}

Recently, we have introduced an *exact* imaginary-time path-integral phase-space formulation of multi-time correlation functions.⁶⁸ This formalism provides an attractive platform for the development of approximate methods that incorporate nuclear quantum effects in chemical dynamics. The formalism is based on the discrete imaginary-time Feynman path integral representation of quantum mechanics.^{25,26,69} It enables us to describe various types

of n -point correlation functions as “sine/cosine” multi-time correlation functions that depend on imaginary-time-translation-invariant phase-space observables coupled through Poisson bracket operators evolving in an extended ring-polymer phase-space (Sec. II). This formulation is formally exact; however, due to the exact quantum Liouvillian governing the ring-polymer dynamical evolution (which is equivalent to solving the Schrödinger equation), the approach is computationally intractable for all but the simplest systems. Here, we extend the capabilities of the method by introducing semi-classical approximations in the evaluation of generalized multi-time correlation functions based on Matsubara dynamics.^{30,65}

The Matsubara dynamics formalism, originally implemented for calculations of Kubo transform (KT) single-time correlation functions³⁰ and recently extended to the evaluation of double-Kubo transform (DKT) correlation functions,⁶⁵ provides a semi-classical approximation that combines classical dynamics with exact quantum Boltzmann statistics while satisfying detailed balance.³⁰ This approximation is based on the realization that, in calculations of time-independent properties, only “smooth” Feynman paths in imaginary time (i.e., Matsubara modes) contribute to the Boltzmann factor and non-smooth, jagged paths can be discarded for calculations of static properties.³⁰ Classical dynamics emerges by assuming that the “smoothness” also applies to quantum dynamics, i.e., restricting the dynamics to the smooth Matsubara space.

Here, we extend and generalize the results of Refs. 30 and 65 to show that Matsubara dynamics can also be employed for the calculations of generalized “sine/cosine” n -point correlation functions. Specifically, we show that generalized multi-time correlation functions can be expressed within the Matsubara approximation in terms of classical-like correlation functions involving time-evolved observables coupled through Poisson brackets operators in a smooth Matsubara space. Matsubara dynamics offers a unique perspective into the correspondence between quantum and classical dynamics, being exact in the zero time and harmonic limit, and transitioning to classical dynamics when only one Matsubara mode (i.e., the centroid) is considered. This provides an effective bridge between a fully quantum and purely classical description of multi-time correlation functions. Moreover, the presence of the Poisson-bracket couplings between different observables is related to stability matrices that measure the sensitivity of dynamical variables to the initial conditions, providing an interpretation of quantum dynamics in terms of “interfering trajectories” of the ring-polymer in phase space. Unfortunately, the Matsubara quantum distribution presents a phase factor, rendering the methodology numerically challenging for applications to condensed phase systems (see, however, Ref. 70 for a recent application of Matsubara dynamics to a condensed phase model Hamiltonian). Despite this limitation, Matsubara dynamics can be used as a valuable benchmark for the development of quantum-Boltzmann-preserving semi-classical approximations for condensed phase systems.^{31,66} In effect, by performing a mean-field average of the dynamics over the fluctuation modes or further approximating the dynamics by discarding part of the Liouvillian, CMD and RPMD approximations to the multi-point TCFs presented in the present work can be developed (a detailed derivation and analysis will be provided elsewhere). While computationally challenging, due to the phase problem, Matsubara dynamics provides a solid foundation for the future development of quantum-Boltzmann-preserving semi-classical approximations for chemical dynamics in the condensed phase.

This paper is organized as follows: first, Sec. II reviews the exact ring-polymer phase-space formulation of multi-time correlation functions.⁶⁸ Section III presents the derivation of the Matsubara approximation for such multi-time correlation functions. Section IV then discusses the properties and limiting cases of the Matsubara dynamics, and Sec. V presents computational results, which test the accuracy of Matsubara dynamics on a model potential. Finally, Sec. VI provides final remarks and an outline of potential future applications.

II. EXACT RING-POLYMER PHASE-SPACE FORMULATION OF MULTI-TIME CORRELATION FUNCTIONS

In a recent paper, we derived an exact ring-polymer phase-space formulation of quantum mechanics for dynamical evolution taking place on single-surface (Born–Oppenheimer) potential energy surfaces.⁶⁸ Here, we summarize the main findings pertinent to the development of the Matsubara approximation. To make the presentation more accessible, we focus on a one-dimensional system with Hamiltonian $\hat{H} = \hat{p}^2/2m + V(\hat{q})$, although the results we derive apply to systems with any number of dimensions. Moreover, we restrict the analysis to equilibrium systems, namely systems in which the Hamiltonian controlling the dynamics and statistics is the same; generalizations for processes characterized by thermal non-equilibrium initial conditions are straightforward. For further information, we refer the reader to Ref. 68.

We begin by introducing the general “sine/cosine” n -point ring-polymer phase-space correlation functions defined as follows:⁶⁸

$$\begin{aligned} & \left\langle \hat{O}_n(t_n) \vec{f}_n \cdots \vec{f}_2 \hat{O}_1(t_1) \vec{f}_1 \hat{O}_0(t_0) \right\rangle_N \\ & \equiv \frac{Z_N^{-1}}{(2\pi\hbar)^N} \int d\mathbf{q} \int d\mathbf{p} \left[e^{-\beta\hat{H}} \right]_N(\mathbf{q}, \mathbf{p}) \\ & \quad \times \left\{ \left[\hat{O}_n(t_n) \right]_N \vec{f}_n \cdots \vec{f}_2 \left[\hat{O}_1(t_1) \right]_N \vec{f}_1 \left[\hat{O}_0(t_0) \right]_N \right\}, \quad (1) \end{aligned}$$

with partition function

$$Z_N = \frac{1}{(2\pi\hbar)^N} \int d\mathbf{q} \int d\mathbf{p} \left[e^{-\beta\hat{H}} \right]_N(\mathbf{q}, \mathbf{p}), \quad (2)$$

where $\int d\mathbf{q} = \int dq_1 \cdots \int dq_N$ represents a phase-space average over N ring-polymer position coordinates $\mathbf{q} = q_1, \dots, q_N$, with similar definitions for the momenta $\mathbf{p}$. The ring-polymer Boltzmann–Wigner operator, introduced by Eq. (1), is defined as follows:^{30,33,65,68}

$$\begin{aligned} \left[e^{-\beta\hat{H}} \right]_N(\mathbf{q}, \mathbf{p}) & \equiv \int d\Delta \prod_{l=1}^N e^{\frac{i}{\hbar} p_l \Delta_l} \left\langle q_{l-1} - \frac{\Delta_{l-1}}{2} \left| e^{-\beta_N \hat{H}} \right| q_l + \frac{\Delta_l}{2} \right\rangle \\ & = \left(\frac{m}{2\pi\beta_N \hbar^2} \right)^{N/2} \int d\Delta \left(\prod_{l=1}^N e^{\frac{i}{\hbar} p_l \Delta_l} \right) \\ & \quad \times \exp \left(-\frac{m}{2\beta_N \hbar^2} \sum_{l=1}^N \left[q_l + \frac{\Delta_l}{2} - q_{l-1} + \frac{\Delta_{l-1}}{2} \right]^2 \right) \\ & \quad \times \exp \left(-\frac{\beta_N}{2} \sum_{l=1}^N \left[V \left(q_l + \frac{\Delta_l}{2} \right) + V \left(q_l - \frac{\Delta_l}{2} \right) \right] \right), \quad (3) \end{aligned}$$

with $\beta_N = \beta/N$ defined by the inverse temperature $\beta = 1/k_B T$, with coordinates satisfying cyclic boundary conditions (i.e., $q_0 = q_N$). The time evolution of observables $[\hat{O}(t)]_N$, introduced by Eq. (1), is governed by the quantum Liouville equation,

$$[\hat{O}(t)]_N(\mathbf{q}, \mathbf{p}) = e^{\mathcal{L}_N^{\mathbf{q}, \mathbf{p}} t} [\hat{O}]_N(\mathbf{q}, \mathbf{p}), \quad (4)$$

where

$$\mathcal{L}_N^{\mathbf{q}, \mathbf{p}} = \left(\frac{2N}{\hbar} \right) \left[\frac{1}{N} \sum_{j=1}^N \left(\frac{p_j^2}{2m} + V(q_j) \right) \right] \sin \left(\frac{\hbar}{2} \overleftrightarrow{\Lambda}_N^{\mathbf{q}, \mathbf{p}} \right) \quad (5)$$

is the exact generalized quantum Liouvillian, in which

$$\overleftrightarrow{\Lambda}_N^{\mathbf{q}, \mathbf{p}} = \sum_{j=1}^N \frac{\overleftarrow{\partial}}{\partial p_j} \frac{\overrightarrow{\partial}}{\partial q_j} - \frac{\overleftarrow{\partial}}{\partial q_j} \frac{\overrightarrow{\partial}}{\partial p_j} \quad (6)$$

is the negative Poisson bracket in ring-polymer phase-space, with the arrows indicating the direction in which the derivative operator is applied. The generalized ring-polymer Wigner–Weyl transform of an operator $\hat{O}$ that depends only on position is given by the ring-polymer average (for general observables, refer to Ref. 68),^{30,33,65}

$$[\hat{O}(\hat{q})]_N(\mathbf{q}, \mathbf{p}) = \frac{1}{N} \sum_{j=1}^N O(q_j). \quad (7)$$

The analogous definition holds for operators that depend only on momenta.

To simplify the equations, we often suppress the $(\mathbf{q}, \mathbf{p})$ dependence and we use $\overleftrightarrow{\mathcal{T}}$ [as in Eq. (1)] to represent operators coupling ring-polymer Wigner–Weyl transforms, defined by either sine ($\overleftrightarrow{\mathcal{S}}$) or cosine ($\overleftrightarrow{\mathcal{C}}$) coupling operators as follows:

$$\overleftrightarrow{\mathcal{S}} = \left(\frac{2N}{\hbar} \right) \sin \left(\frac{\hbar}{2} \overleftrightarrow{\Lambda}_N^{\mathbf{q}, \mathbf{p}} \right) \quad (8)$$

and

$$\overleftrightarrow{\mathcal{C}} = \cos \left(\frac{\hbar}{2} \overleftrightarrow{\Lambda}_N^{\mathbf{q}, \mathbf{p}} \right). \quad (9)$$

Different n -point correlation functions emerge from Eq. (1) (see Appendix A for examples) by choosing a different number and combination of coupling operators $\overleftrightarrow{\mathcal{S}}$ and $\overleftrightarrow{\mathcal{C}}$.⁶⁸

The time correlation functions defined by Eq. (1) play an important role in providing an exact ring-polymer phase-space representation of correlations in Hilbert space in the limit of infinite N . This was demonstrated in Ref. 68, where it was shown that sine couplings in ring-polymer space are equivalent to commutators in Hilbert space as follows:

$$[\hat{O}_1]_N \overleftrightarrow{\mathcal{S}} [\hat{O}_2]_N \longleftrightarrow \left(\frac{i}{\hbar} \right) [\hat{O}_1, \hat{O}_2], \quad (10)$$

while the cosine couplings correspond to the (symmetrized) Kubo integrals as follows:

$$[\hat{O}_1]_N \overleftrightarrow{\mathcal{C}} [\hat{O}_2]_N \longleftrightarrow \frac{1}{\beta} \int_0^\beta d\lambda \hat{O}_1(-i\hbar\lambda) \hat{O}_2, \quad (11)$$

allowing us to map Hilbert space correlations into ring-polymer “sine/cosine” correlations (and vice versa). (See Appendix A for applications of the mapping.) Quite remarkably, correlation functions involving commutators and Kubo integrals are ubiquitous in quantum chemistry, appearing in the context of linear and nonlinear response theory, chaos theory, and chemical dynamics.^{1–6} As such, the “sine/cosine” correlation functions play the central dynamical role in quantum theory.

The expression for the sine/cosine correlation functions provided by Eq. (1) is general and involves no approximation. It is quantum-mechanically exact in the $N \rightarrow \infty$ limit. However, the evaluation of the quantum sine/cosine correlations is complicated, making it impractical to use in anything but the simplest of systems. Two factors contribute to this difficulty. First, the time evolution of ring-polymer phase-space observables [Eq. (4)] is equivalent to solving the Schrödinger equation. Second, by virtue of the Taylor expansion of the sine/cosine couplings [Eqs. (8) and (9)], the ring-polymer phase-space functions in Eq. (1) can be expressed in terms of an *infinite* series in powers of $\hbar$ of correlations involving the evaluation of $\overleftrightarrow{\Lambda}$ couplings between time-evolved ring-polymer observables (note that for operators that can be expressed as polynomials in ring-polymer phase-space coordinates, the expansion is exactly truncated at some order). Therefore, the development of semi-classical approximations for the practical evaluation of sine/cosine correlation functions is essential.

III. MATSUBARA APPROXIMATION

A. Normal modes

We introduce the ring-polymer normal mode transformation^{71,72} as follows:

$$X_k = \sum_{j=1}^N \frac{T_{jk}}{\sqrt{N}} x_j, \quad (12)$$

for $x_j = \{q_j, p_j, \Delta_j\}$ with corresponding associated normal-modes coordinates $X_j = \{Q_j, P_j, D_j\}$, with inverse

$$x_j = \sum_{k=-\tilde{N}}^{\tilde{N}} \sqrt{N} T_{jk} X_k \quad (13)$$

and matrix elements

$$T_{jk} = \begin{cases} \frac{1}{\sqrt{N}}, & k = 0, \\ \sqrt{\frac{2}{N}} \sin(2\pi jk/N), & 0 < k \leq \tilde{N}, \\ \sqrt{\frac{2}{N}} \cos(2\pi jk/N), & -\tilde{N} \leq k < 0, \end{cases} \quad (14)$$

with $\tilde{N} = (N - 1)/2$. The associated normal frequencies (i.e., square roots of the eigenvalues of the transformation matrix) are given by

$$\omega_n = \frac{2}{\beta_N \hbar} \sin \left(\frac{n\pi}{N} \right). \quad (15)$$

For convenience, N is chosen to be odd, although similar expressions can be derived for even N . Note that the transformation is not

unitary but defined such that the $k = 0$ normal mode converges to the centroid^{25,73} $X_0 = \frac{1}{N} \sum_j x_j$ of the ring-polymer distribution in the limit $N \rightarrow \infty$. The significance of the normal mode transformation is that it allows for a description of the ring-polymer coordinates in terms of the centroid X_0 as well as collective fluctuations $X_{|n|>0}$ of the free ring polymer distribution.

It is straightforward to apply the normal mode transformation to Eq. (1). In particular, note that the Janus and Liouvillian operators transform as follows:

$$\overleftrightarrow{\Lambda}_N^{\mathbf{Q},\mathbf{P}} \rightarrow \frac{1}{N} \overleftrightarrow{\Lambda}_N^{\mathbf{Q},\mathbf{P}} \quad (16)$$

and

$$\mathcal{L}_N^{\mathbf{Q},\mathbf{P}} \rightarrow \mathcal{L}_N^{\mathbf{Q},\mathbf{P}}, \quad (17)$$

where

$$\overleftrightarrow{\Lambda}_N^{\mathbf{Q},\mathbf{P}} = \sum_{j=-N}^N \frac{\overleftrightarrow{\partial}}{\partial P_j} \frac{\overleftrightarrow{\partial}}{\partial Q_j} - \frac{\overleftrightarrow{\partial}}{\partial Q_j} \frac{\overleftrightarrow{\partial}}{\partial P_j} \quad (18)$$

is the negative Poisson bracket in normal modes, while the Liouvillian in normal modes is given by

$$\mathcal{L}_N^{\mathbf{Q},\mathbf{P}} = \left(\frac{2N}{\hbar} \right) \left[\sum_{j=-N}^N \frac{P_j^2}{2m} + V(\mathbf{Q}) \right] \sin \left(\frac{\hbar}{2N} \overleftrightarrow{\Lambda}_N^{\mathbf{Q},\mathbf{P}} \right), \quad (19)$$

with

$$V(\mathbf{Q}) = \frac{1}{N} \sum_{j=1}^N V \left(\sum_{k=-N}^N \sqrt{N} T_{jk} Q_k \right). \quad (20)$$

Applying the normal mode transformation to Eq. (1), we obtain

$$\begin{aligned} & \left\langle \hat{O}_n(t_n) \overleftrightarrow{f}_n \cdots \overleftrightarrow{f}_2 \hat{O}_1(t_1) \overleftrightarrow{f}_1 \hat{O}_0(t_0) \right\rangle_N \\ &= \frac{Z_N^{-1} N^N}{(2\pi\hbar)^N} \int d\mathbf{Q} \int d\mathbf{P} \left[e^{-\beta\hat{H}} \right]_N(\mathbf{Q}, \mathbf{P}) \\ & \times \left\{ \left[\hat{O}_n(t_n) \right]_N \overleftrightarrow{f}_n \cdots \overleftrightarrow{f}_2 \left[\hat{O}_1(t_1) \right]_N \overleftrightarrow{f}_1 \left[\hat{O}_0(t_0) \right]_N \right\}, \end{aligned} \quad (21)$$

where $\left[e^{-\beta\hat{H}} \right]_N(\mathbf{Q}, \mathbf{P})$ is the ring-polymer Boltzmann-Wigner factor in normal mode coordinates [see Appendix B, Eq. (B1)]. The sine/cosine J -couplings are now given as follows:

$$\overleftrightarrow{s} = \left(\frac{2N}{\hbar} \right) \sin \left(\frac{\hbar}{2N} \overleftrightarrow{\Lambda}_N^{\mathbf{Q},\mathbf{P}} \right) \quad (22)$$

and

$$\overleftrightarrow{c} = \cos \left(\frac{\hbar}{2N} \overleftrightarrow{\Lambda}_N^{\mathbf{Q},\mathbf{P}} \right). \quad (23)$$

The time-evolved observables are given by

$$\left[\hat{O}(t) \right]_N(\mathbf{Q}, \mathbf{P}) = e^{\mathcal{L}_N^{\mathbf{Q},\mathbf{P}} t} O(\mathbf{Q}), \quad (24)$$

with $O(\mathbf{Q})$ defined similar to Eq. (20). Note that no approximation has been introduced so far, making Eq. (21) quantum mechanically exact.

B. Matsubara approximation

This section introduces the Matsubara approximation. The Matsubara modes^{28,30,74} are defined as the M lowest frequency ring-polymer normal modes in the limit $N \rightarrow \infty$ such that $M \ll N$, with frequencies defined as follows:

$$\omega_n = \lim_{\substack{N \rightarrow \infty \\ M \ll N}} \frac{2}{\beta_N \hbar} \sin \left(\frac{n\pi}{N} \right) = \frac{2\pi n}{\beta \hbar}. \quad (25)$$

They have the special property that any superposition of them produces a smooth ring-polymer distribution,^{28,75}

$$q(\tau) = Q_0 + \sqrt{2} \sum_{k=1}^{\tilde{M}} \sin(\omega_k \tau) Q_k + \cos(\omega_k \tau) Q_{-k}, \quad (26)$$

where $\tilde{M} = (M-1)/2$. We have identified $q(\tau) \equiv q_j$ with the imaginary time $\tau = \beta_N \hbar j$.

Note that the Matsubara modes represent the Fourier coefficients of $q(\tau)$.^{28,75-78} As such, the ring-polymer distribution $q(\tau)$ is guaranteed to be a smooth, continuous, and differentiable path in imaginary time (Fig. 1).^{30,79} This would not be true, in general, if $q(\tau)$ were built with both Matsubara and non-Matsubara modes, where the latter would give rise to jagged, discontinuous, non-smooth distributions. Thus, the ring-polymer distribution given by Eq. (26) can be interpreted as a Fourier filter of the original ring-polymer distribution.^{28,75}

The Matsubara approximation consists of assuming that one can describe the quantum dynamical evolution encoded in the TCFs using only Matsubara modes, so any initial smooth distribution in $\mathbf{q}$ and $\mathbf{p}$ remains smooth for all times.^{30,79} To effect this approximation in Eq. (21), we neglect the contribution of non-Matsubara modes to the exact Janus operator [Eq. (18)] to effectively decouple the Matsubara and non-Matsubara modes. The Janus operator is, thus, replaced by the Matsubara Janus operator defined as follows:⁶⁵

$$\overleftrightarrow{\Lambda}_M = \sum_{j=-M}^M \frac{\overleftrightarrow{\partial}}{\partial P_j} \frac{\overleftrightarrow{\partial}}{\partial Q_j} - \frac{\overleftrightarrow{\partial}}{\partial Q_j} \frac{\overleftrightarrow{\partial}}{\partial P_j}. \quad (27)$$

Note that the Matsubara Janus operator includes only Matsubara modes.

Considering that in the Matsubara approximation,

$$\frac{\hbar}{N} \overleftrightarrow{\Lambda}_M \sim \mathcal{O} \left(\frac{\hbar M}{N} \right), \quad (28)$$

it follows that in the limit $N \rightarrow \infty$, $M \ll N$, we obtain

$$\overleftrightarrow{s} \approx \lim_{\substack{N \rightarrow \infty \\ M \ll N}} \left(\frac{2N}{\hbar} \right) \sin \left(\frac{\hbar}{2N} \overleftrightarrow{\Lambda}_M \right) = \overleftrightarrow{\Lambda}_M, \quad (29)$$

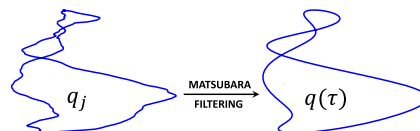


FIG. 1. Schematic representation of jagged ring-polymer imaginary-time paths q_j . When only a superposition of Matsubara modes is used, smooth imaginary-time paths $q(\tau)$ are obtained, which are differentiable in imaginary time τ .

$$\vec{c} \approx \lim_{\substack{N \rightarrow \infty \\ M \ll N}} \cos\left(\frac{\hbar}{2N} \vec{\Lambda}_M\right) = 1. \quad (30)$$

Therefore, the sine and cosine couplings become *linearized* in the subspace of Matsubara modes. Note that the presence of the $2N/\hbar$ factor in Eq. (29) guarantees the existence of this limit.

The linearization process that occurs under the Matsubara approximation has several interesting consequences. First, note that the Matsubara Liouvillian is obtained as follows:

$$\mathcal{L}_N^{\mathbf{Q},\mathbf{P}} \approx \mathcal{L}_M, \quad (31)$$

where

$$\mathcal{L}_M \equiv \sum_{j=-M}^M \left[\frac{p_j}{m} \frac{\partial}{\partial Q_j} - \frac{\partial V_M(\mathbf{Q})}{\partial Q_j} \frac{\partial}{\partial p_j} \right], \quad (32)$$

with

$$V_M(\mathbf{Q}) = \frac{1}{N} \sum_{j=1}^N V \left(\sum_{k=-M}^M \sqrt{N} T_{jk} Q_k \right) \quad (33)$$

representing the Matsubara potential (strictly speaking, the potential in Eq. (32) should be $V(\mathbf{Q})$ and this becomes $V_M(\mathbf{Q})$ after integrating out the non-Matsubara modes detailed below). Note that the Matsubara Liouvillian only contains first derivatives and is, therefore, a *classical* Liouvillian albeit in the Matsubara subspace.³⁰

Second, note that the elimination of the non-Matsubara modes from the Janus operator allows for the analytical integration and elimination of the non-Matsubara modes from Eq. (21). Indeed, following Refs. 30, in Appendix B, we show that in the Matsubara limit, Eq. (21) leads to the classical-like Matsubara correlation functions,

$$\begin{aligned} & \left\langle (O_n)_M(t_n) \vec{J}_n \cdots \vec{J}_2 (O_1)_M(t_1) \vec{J}_1 (O_0)_M(t_0) \right\rangle_M \\ &= \frac{Z_M^{-1}}{(2\pi\hbar)^M} \int d\mathbf{Q} \int d\mathbf{P} e^{-\beta(H_M(\mathbf{Q},\mathbf{P}) - i\theta_M(\mathbf{Q},\mathbf{P}))} \\ & \times \left\{ (O_n)_M(t_n) \vec{J}_n \cdots \vec{J}_2 (O_1)_M(t_1) \vec{J}_1 (O_0)_M(t_0) \right\}, \end{aligned} \quad (34)$$

where the phase-space integrals are now over Matsubara modes only, the Matsubara partition function is given by

$$Z_M = \frac{1}{(2\pi\hbar)^M} \int d\mathbf{Q} \int d\mathbf{P} e^{-\beta(H_M - i\theta_M)}, \quad (35)$$

and the Matsubara Hamiltonian and Matsubara phases are given, respectively, by

$$H_M(\mathbf{Q},\mathbf{P}) = \sum_{k=-M}^M \frac{p_k^2}{2m} + V_M(\mathbf{Q}) \quad (36)$$

and

$$\theta_M(\mathbf{Q},\mathbf{P}) = \sum_{k=-M}^M \omega_k Q_{-k} P_k. \quad (37)$$

The time-evolved observables in Eq. (34),

$$O_M(t) = e^{\mathcal{L}_M t} O_M(\mathbf{Q}) = O_M(\mathbf{Q}_t), \quad (38)$$

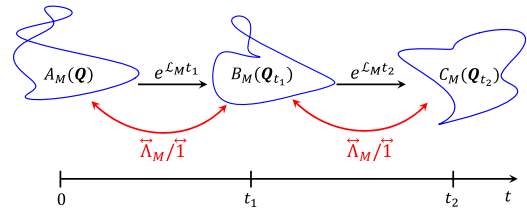


FIG. 2. Schematic representation of the generalized Matsubara correlation functions $\left\langle (O_n)_M(t_n) \vec{J}_n \cdots \vec{J}_2 (O_1)_M(t_1) \vec{J}_1 (O_0)_M(t_0) \right\rangle_M$ [Eq. (34)] for the case of three observables. An initial smooth ring-polymer distribution $\mathbf{Q}$ evolves in time by the classical Matsubara Liouvillian $\mathcal{L}_M$. Observables are computed along the trajectory. The coupling between observables at different times via $\vec{\Lambda}_M$ or $\vec{I}$ operators gives rise to different correlation functions.

are now classical-evolved functions of the smooth Matsubara observable $O_M(\mathbf{Q})$ [defined similar to Eq. (33)]. Finally, the Matsubara J -couplings correspond to the linearized versions of the sine and cosine couplings [Eqs. (29) and (30)], namely

$$\vec{J} = \begin{cases} \vec{\Lambda}_M, \\ \vec{I}. \end{cases} \quad (39)$$

Note that for simplicity, we will often omit the $\vec{I}$ coupling from the notation.

Equation (34) represents the main result of this paper, showing that general multi-time correlation functions can be expressed in terms of classical-like correlation functions involving time-evolved observables coupled through Poisson brackets in a smooth Matsubara space, e.g., $\left\{ \left\langle C_M(t_2) \vec{\Lambda}_M B_M(t_1) \right\rangle \vec{\Lambda}_M A_M(t_0) \right\}_M$ (see Fig. 2).

Note that when all $\vec{J} = \vec{I}$, Eq. (34) reduces to the Matsubara approximation of Kubo-like correlation functions, originally derived by Hele *et al.* in Ref. 30 for two-point KT correlations (namely, “cosine” TCFs) and extended for multi-point KT correlations (namely, all-“cosine” TCFs) by us in Ref. 65. The new insights provided in the current work are to show that Matsubara dynamics also holds for correlations involving $\vec{J} = \vec{\Lambda}_M$ couplings between observables. In other words, the novel result is to recognize that the Matsubara approximation can be applied to *generalized* correlation functions involving combinations of sine and cosine couplings, which while in Hilbert space translate to commutator and Kubo integrals between operators, in Matsubara space become $\vec{\Lambda}_M$ and $\vec{I}$ couplings between observables. We believe that this is a remarkable result that provides an interesting interpretation of quantum dynamics and a unique perspective into the correspondence between quantum and classical dynamics (see Sec. IV). To the best of our knowledge, Eq. (34) represents the first derivation of Matsubara dynamics for general multi-point time correlation functions.

IV. DISCUSSION

A. Classical-like correlation functions

The Matsubara approximation for general multi-point time correlation functions given by Eq. (34) produces a set of classical-like correlation functions. This is because the dynamics

generated by the Matsubara Liouvillian [Eq. (32)] is classical and emerges without having to explicitly assume that $\hbar \rightarrow 0$. It is worth noting that the exact Liouvillian [Eq. (19)] is an expansion in terms of the effective Planck constant $\hbar/N$ which, in the Matsubara space, vanishes as $N \rightarrow \infty$.³⁰ Thus, the classical-like correlation functions emerge naturally from linearization in the Matsubara subspace.

The decoupling of Matsubara and non-Matsubara modes not only produces a linearization of the dynamics in the Matsubara subspace but also allows for an exact truncation of the sine and cosine couplings to first order [i.e., Eqs. (29) and (30)]. We remark that this result naturally emerges from the presence of the effective Planck constant $\hbar/N$ and not for any $\hbar \rightarrow 0$ assumption. Quite remarkably, note that the presence of the $2N/\hbar$ factor in the definition of the sine coupling, which naturally emerges in the imaginary-time ring-polymer phase-space representation of quantum dynamics,⁶⁸ guarantees the existence of this limit. As a result, Eq. (34) involves multi-time correlation functions of classical-like time-evolved observables coupled through Poisson brackets in Matsubara space (Fig. 2). It is worth highlighting the remarkable similarity between the different Matsubara correlation functions that can be obtained from Eq. (34), which emerges from the similar structure of the original quantum expressions in terms of sine and cosine couplings.⁶⁸

The classical dynamics generated by $\mathcal{L}_M$ preserves both the Matsubara phase and the Matsubara Hamiltonian, namely $\mathcal{L}_M H_M = \mathcal{L}_M \theta_M = 0$,^{30,65,66} and consequently, conserves both the Matsubara phase factor $e^{i\theta_M}$ and classical Boltzmann distribution $e^{-\beta H_M}$. As such, Matsubara dynamics conserves the exact quantum Boltzmann distribution $e^{-\beta(H_M - i\theta_M)}$ during the classical evolution of the Matsubara modes. Additionally, since the dynamic is classical and Hamiltonian (cf. generated by H_M) albeit in the Matsubara subspace, Matsubara dynamics has several properties of Hamiltonian classical dynamics (see the supplementary material), such as the conservation of the phase-space volume element (namely, $d\mathbf{Q}d\mathbf{P} = d\mathbf{Q}_t d\mathbf{P}_t$) and the canonical invariance of the Poisson bracket to the change of variables $(\mathbf{Q}, \mathbf{P}) \rightarrow (\mathbf{Q}_t, \mathbf{P}_t)$. These properties provide interesting symmetries to the multi-time correlation functions in Eq. (34) that are shared with the exact quantum TCFs. For example, the TCFs are invariant to an overall shift in the time origin. Moreover, for time-independent observables, Matsubara dynamics reproduces the exact time-independent thermal expectation values.

B. Generalized fluctuation-dissipation relations in Matsubara space

It is worth remarking that sine/cosine TCFs share a remarkable connection in the Matsubara space. Specifically, using the fact that the Hamiltonian is the generator of the dynamics, namely

$$\frac{d}{dt} O_M(\mathbf{Q}_t) = \mathcal{L}_M O_M(\mathbf{Q}_t) = H_M \overleftrightarrow{\Lambda}_M O_M(\mathbf{Q}_t), \quad (40)$$

and the smoothness of the ring-polymer distribution to imaginary-time translations, namely³⁰

$$\frac{d}{d\tau} O_M(\mathbf{Q}_t) = \theta_M \overleftrightarrow{\Lambda}_M O_M(\mathbf{Q}_t) = 0, \quad (41)$$

it is straightforward to prove that

$$e^{-\beta(H_M - i\theta_M)} \overleftrightarrow{\Lambda}_M O_M(\mathbf{Q}_t) = -\beta e^{-\beta(H_M - i\theta_M)} \frac{d}{dt} O_M(\mathbf{Q}_t). \quad (42)$$

We remark that Eq. (42) resembles a Matsubara version of the Kubo identity.⁸⁰

The relation given by Eq. (42) has several implications for the connection between correlations in the Matsubara space. In particular, it is straightforward to show that the two-point Matsubara TCFs satisfy the following relation:

$$\langle B_M(t_1) \overleftrightarrow{\Lambda}_M A_M(t_0) \rangle_M = \beta \frac{d}{dt_1} \langle B_M(t_1) A_M(t_0) \rangle_M, \quad (43)$$

which corresponds to a Matsubara version of the well-known fluctuation-dissipation (FD) relation that relates the linear response of a system to Kubo two-point correlation functions.^{3,5,81} Furthermore, for three-point correlation functions, Eq. (42) allows us to establish the generalized FD relations,

$$\begin{aligned} \langle \{C_M(t_2) \overleftrightarrow{\Lambda}_M B_M(t_1)\} \overleftrightarrow{\Lambda}_M A_M(t_0) \rangle_M \\ = \beta \frac{d}{dt_0} \langle \{C_M(t_2) \overleftrightarrow{\Lambda}_M B_M(t_1)\} A_M(t_0) \rangle_M \end{aligned} \quad (44)$$

and

$$\begin{aligned} \langle \{C_M(t_2) \overleftrightarrow{\Lambda}_M B_M(t_1)\} A_M(t_0) \rangle_M \\ = \beta \frac{d}{dt_1} \langle C_M(t_2) B_M(t_1) A(t_0) \rangle_M \\ + \langle C_M(t_2) \{B_M(t_1) \overleftrightarrow{\Lambda}_M A_M(t_0)\} \rangle_M, \end{aligned} \quad (45)$$

highlighting the connection between different Matsubara TCFs. Similar relations can be derived for higher-order correlation functions.

The relations established by Eqs. (43)–(45) have implications for the calculation of linear and nonlinear response functions. Indeed, correlations involving commutators between operators at different times, which are equivalent to correlations involving sine couplings in ring-polymer space, are ubiquitous in the description of response theory.^{1,2,68} As such, the Matsubara correlation functions given by the left-hand side of Eqs. (43) and (44) provide approximations to linear and second-order response functions, respectively. The fluctuation relations established by Eqs. (43)–(45), however, allow us to express the response functions in terms of different Matsubara TCFs. We remark that this result is very encouraging since it guarantees the equivalence of response functions as computed with any TCF. Note, however, that, in practice, the calculation of the different TCFs can have different numerical convergences, since, for instance, the Matsubara approximation to sine-sine correlation functions involves the calculation of a double Poisson bracket, whereas the approximation to cosine-cosine TCF is a standard correlation function. As such, the equivalences given by Eqs. (44) and (45) provide a route that can be exploited as a numerical advantage.

The second significance of the generalized FD relations is that they provided a direct *time-domain* connection between response functions and multi-time correlation functions. To contrast, note

that in Ref. 66, we have derived relations between the second-order response functions and Kubo-like correlation functions in the Fourier domain that involve complicated correction factors. Similar considerations apply to the Fourier connection between third-order response functions and Kubo correlation functions derived recently by Jung and Markland.⁸² Additionally, the efficient semi-classical evaluation of the Fourier formulation in Refs. 66 and 82 required discarding “asymmetric” correlations that, at the time, were hypothesized to not have a semi-classical limit. The present formulation of Matsubara dynamics and FD relations Eqs. (43)–(45), along with similar relations that can be derived for the sine–sine–sine third-order response function, allows us to overcome these difficulties without the need to work in the Fourier domain or applied additional approximations. The drawback of the present formulation is that the direct computation of Poisson brackets can be challenging to converge for many-body molecular systems, although methods based on non-equilibrium and hybrid equilibrium/non-equilibrium molecular dynamics^{83,84} can be used to efficiently implement this for the condensed phase system.

C. Interference of trajectories in Matsubara space

The presence of the Poisson-bracket coupling in the Matsubara correlation functions [Eq. (34)] provides an interesting interpretation of the different time correlation functions in terms of “jumps” in phase-space⁸⁵ or classical “interfering trajectories” between closely lying trajectories⁸¹ albeit in the extended phase space. In particular, note that the evaluation of the Poisson bracket between two observables at different times, e.g., $B_M(t_1) \overleftrightarrow{\Lambda}_M A_M(t_0)$, requires the calculation of derivatives of $B_M(t_1)$ with respect to $X_j(t_0)$, with $X_j = (Q_j, P_j)$ denoting a Matsubara phase-space point. These derivatives involve the evaluation of stability matrices of the form (see Appendix D)

$$M_{jk}(t_1, t_0) = \frac{\partial X_j(t_1)}{\partial X_k(t_0)}, \quad (46)$$

which relates small deviations δX_j to δX_k at different times; namely, they measure the sensitivity of a trajectory at time t_1 to infinitesimal changes in the initial conditions at time t_0 . For example, considering for simplicity the correlation between linear operators that only involve the centroid modes Q_0 and P_0 (generalization to nonlinear operators is straightforward), the sine correlation function can be written in terms of stability matrices as

$$\left\langle Q_0(t_1) \overleftrightarrow{\Lambda}_M Q_0(t_0) \right\rangle_M = \left\langle \frac{\partial Q_0(t_1)}{\partial P_0(t_0)} \right\rangle_M, \quad (47)$$

which can be interpreted as follows: for each initial phase-space point $\mathbf{X}(t_0)$, two trajectories with infinitesimal close initial conditions δP_0 are launched. After time t_1 , the difference between the trajectories is computed. These trajectories interfere with one another in the sense that they make slightly different contributions to the correlation function. The final TCF is obtained by adding the contributions of all these trajectories (see Fig. 3). Alternatively, understanding derivatives in Eq. (46) as a response to an infinitesimal jump in phase-space variable, Eq. (47) can be computed in terms of deterministic trajectories that undergo an infinitesimal jump $P_0 \rightarrow P_0 + \delta P_0$ at time t_0 , opening the door to the development

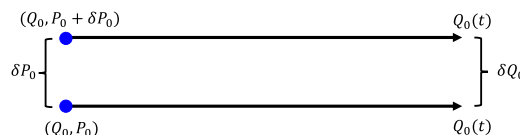


FIG. 3. Schematic representation of the interference of closely lying trajectories giving rise to the correlation involving Poisson bracket operators, for the case of linear operators. From the initial phase-space point (Q_0, P_0) , two trajectories with infinitesimal close initial conditions δP_0 are launched. The interference (i.e., difference) between these trajectories at a later time t determines the response of the system.

of methods based on non-equilibrium and hybrid equilibrium/non-equilibrium molecular dynamics.^{83,84} We remark that the concept of stability matrix is common in the context of classical response theory and classical chaos theory,^{81,86,87} providing an interpretation of classical response functions in terms of interfering trajectories and of chaos dynamics in terms of sensitivity of trajectories to initial conditions. The formulation of Matsubara dynamics presented in this work provides a natural extension of these concepts to the Matsubara ring-polymer phase space, providing a unique perspective into the correspondence between quantum and classical dynamics.

D. Limits

In this section, we analyze some limits of the Matsubara correlation functions.

1. Zero time limit

Noting that the Poisson bracket involves derivatives of momenta and position, it is easy to recognize that, for observables that are only functions of positions (or momenta), any correlation involving a $\overleftrightarrow{\Lambda}_M$ coupling vanishes at the zero time limit. More generally, since the Poisson bracket remains unchanged upon a canonical change of variables $(\mathbf{Q}, \mathbf{P}) \rightarrow (\mathbf{Q}, \mathbf{P}_t)$, it follows that $B_M(\mathbf{Q}_t) \overleftrightarrow{\Lambda}_M A_M(\mathbf{Q}_t) = 0$ as long as the observables are evaluated at any equal time t . Recalling that the $\overleftrightarrow{\Lambda}_M$ couplings arise from sine $\overleftrightarrow{s}$ couplings that map into commutators in Hilbert space, this zero $t = 0$ limit is, therefore, exact.

For the case of correlations not involving any $\overleftrightarrow{\Lambda}_M$ couplings, when $t = 0$, an alternative form of Eq. (34) can be obtained by performing an analytical continuation of the phase factor.^{30,31,66,88,89} In effect, making the change of variables $P_k \rightarrow P_k + im\omega_k Q_{-k}$ for each Matsubara mode, the quantum Boltzmann distribution can be transformed into the ring-polymer distribution in Matsubara modes,

$$e^{-\beta(H_M - i\theta_M)} \rightarrow e^{-\beta R_M}, \quad (48)$$

where the ring-polymer Hamiltonian is given by $R_M(\mathbf{Q}, \mathbf{P}) = H_M(\mathbf{Q}, \mathbf{P}) + S_M(\mathbf{Q})$, where the polymer spring potential is defined as

$$S_M(\mathbf{Q}) = \sum_{j=-\tilde{M}}^{\tilde{M}} \frac{m}{2} \omega_j^2 Q_j^2. \quad (49)$$

As such, the zero time limit of Eq. (34) when all $\vec{J} = \vec{1}$ is given by

$$\begin{aligned} \langle O_n \cdots O_1 O_0 \rangle_M \\ = \frac{Z_M^{-1}}{(2\pi\hbar)^M} \int d\mathbf{Q} \int d\mathbf{P} e^{-\beta R_M(\mathbf{Q}, \mathbf{P})} (O_n)_M \cdots (O_1)_M (O_0)_M, \end{aligned} \quad (50)$$

which represents an exact (smoothed) Fourier path-integral representation of the zero-time multi-Kubo correlation functions.^{39,64,65}

2. Harmonic limit

Matsubara dynamics is also exact in the harmonic limit for any observable $O_M(\mathbf{Q})$ due to the fact that for this particular potential, the non-Matsubara modes do not couple with the Matsubara modes.

In effect, the only approximation in the derivation of Matsubara dynamics is the removal of the coupling between the Matsubara modes and non-Matsubara modes in the dynamical evolution (via neglecting non-Matsubara modes in the Janus operator), which allows integrating, in the $N \rightarrow \infty$ limit, the non-Matsubara modes. For a harmonic potential with natural frequency Ω of the form $V(\hat{q}) = \frac{1}{2}m\Omega^2\hat{q}^2$, the Matsubara potential is given by

$$V_M(\mathbf{Q}) = \frac{1}{2}m\Omega^2 \sum_{k=-M}^M Q_k^2, \quad (51)$$

and it is straightforward to see that the decoupling between Matsubara and non-Matsubara modes naturally arises in the exact

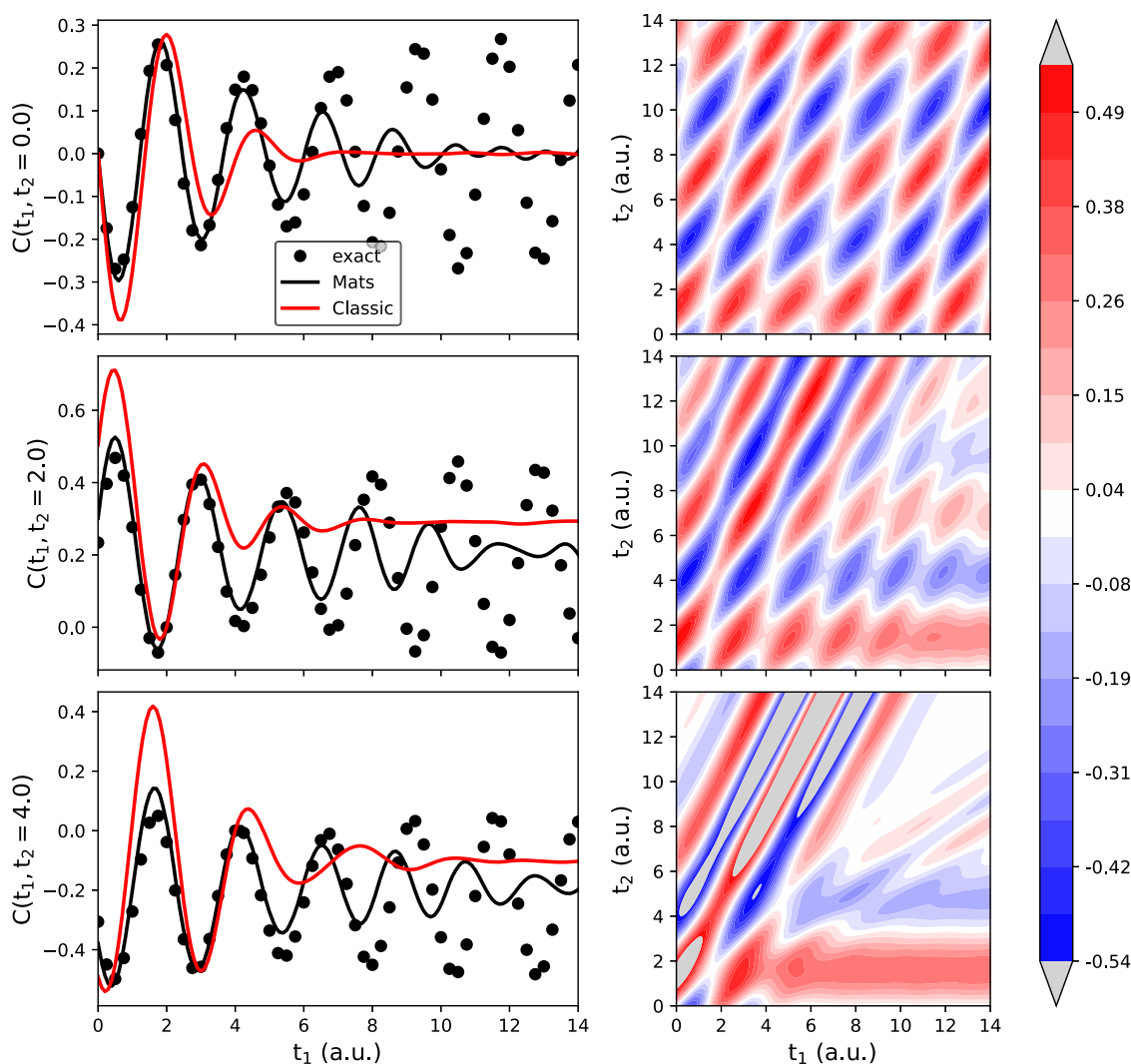


FIG. 4. Sine-cosine correlation function $\langle \{\hat{q}(t_2) \vec{s} \hat{q}^2(t_1)\} \vec{c} \hat{q} \rangle$ for the quartic potential at $\beta = 2$. (Right) 2D-contour plots of the exact (top panel), Matsubara (middle panel), and classical (bottom panel) correlation functions. (Left) Cuts along selected time slices.

Liouvillian [Eq. (18)], making Matsubara dynamics not an approximation in this limit. (See Appendix C for specific examples of simple TCFs.)

3. Classical limit

The classical limit is recovered as a special case of Matsubara dynamics if one considers only the centroid mode (i.e., $M = 1$). In effect, noting that the Matsubara phase does not depend on the centroid (since $\omega_0 = 0$) and that the Matsubara Hamiltonian and Matsubara Liouvillian reduce to the classical Hamiltonian and classical Liouvillian for $M = 0$, it follows that for the centroid mode alone, Eq. (34) reduces to classical versions of correlation functions involving Poisson bracket between observables. It is worth remarking that Matsubara dynamics recovers the classical description of response theory when $M = 1$.⁸¹ As such, Matsubara dynamics

provides a bridge between a purely quantum and purely classical description of response theory and dynamics.

4. The continuum limit

In Sec. III B, the imaginary-time path $q(\tau)$ was introduced to motivate the interpretation of the Matsubara modes as Fourier coefficients of the ring-polymer distribution. However, this continuum representation is not needed for the derivation of Matsubara dynamics [i.e., note the N dependence in Eq. (33)].^{30,79} Nevertheless, the interpretation of the Matsubara functions in terms of $q(\tau)$ and the associated smooth imaginary-time momenta $p(\tau)$ is advantageous for the derivation of symmetries and relations in Matsubara space.^{30,66,79} Here, for completeness, we discuss this limit.

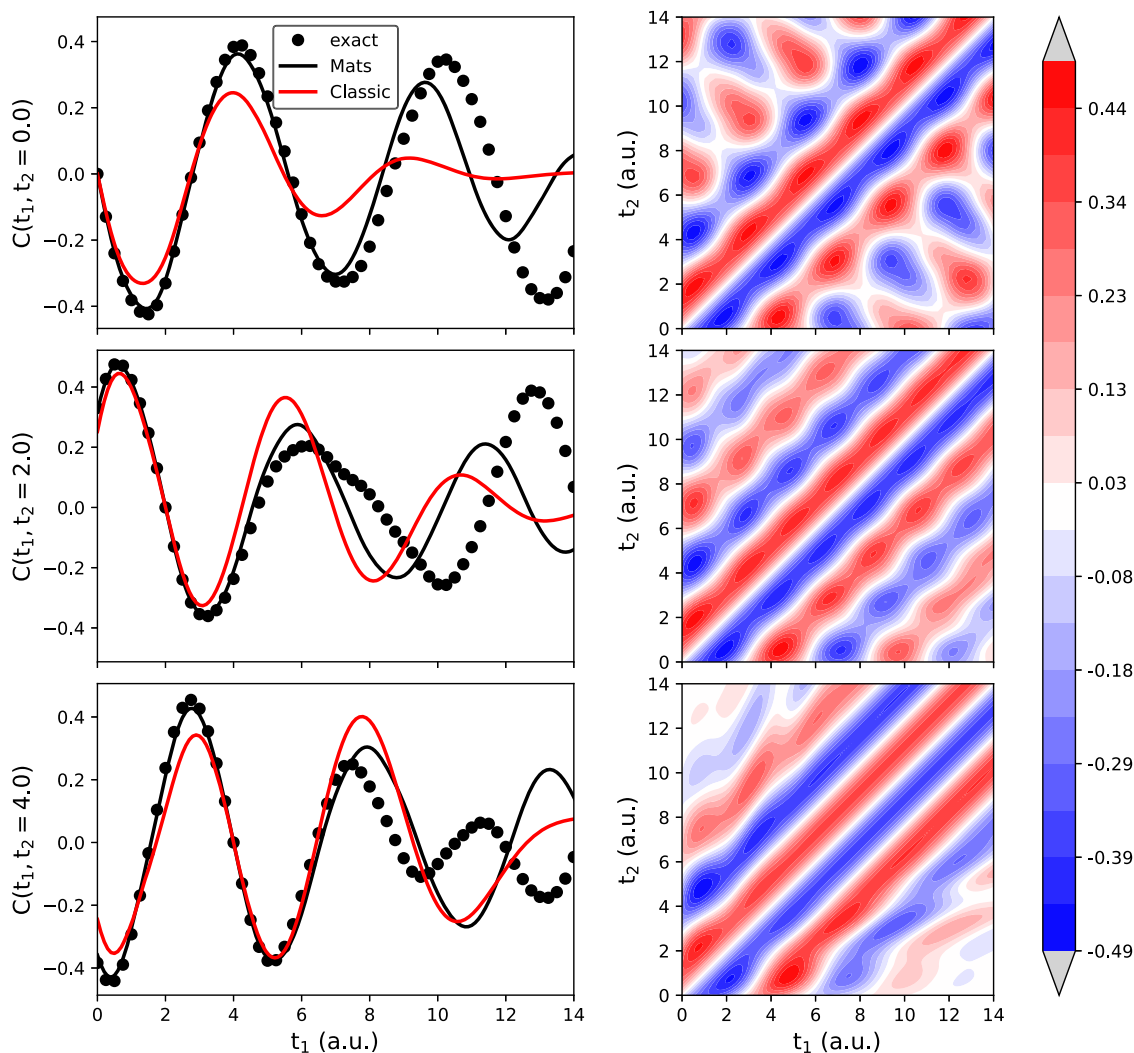


FIG. 5. Sine-cosine correlation function $\langle \{\hat{q}(t_2) \vec{s} \hat{q}(t_1)\} \vec{c} \hat{q}^2 \rangle$ for the quartic potential at $\beta = 2$. (Right) 2D-contour plots of the exact (top panel), Matsubara (middle panel), and classical (bottom panel) correlation functions. (Left) Cuts along selected time slices.

Specifically, in the continuum picture ($N \rightarrow \infty$), Matsubara's normal modes are given by

$$Q_k = \begin{cases} \frac{1}{\beta\hbar} \int_0^{\beta\hbar} d\tau q(\tau), & k = 0, \\ \frac{\sqrt{2}}{\beta\hbar} \int_0^{\beta\hbar} d\tau \sin(\omega_k \tau) q(\tau), & 0 < k \leq \tilde{M}, \\ \frac{\sqrt{2}}{\beta\hbar} \int_0^{\beta\hbar} d\tau \cos(\omega_k \tau) q(\tau), & -\tilde{M} \leq k < 0, \end{cases} \quad (52)$$

with a similar definition for the Matsubara momenta P_k in terms of $p(\tau)$. It is straightforward to verify that, in this continuum, all

Matsubara functions can be expressed as integrals over imaginary time; namely, the Matsubara kinetic energy is given by

$$\sum_{j=-\tilde{M}}^{\tilde{M}} \frac{P_j^2}{2m} = \frac{1}{\beta\hbar} \int_0^{\beta\hbar} d\tau \frac{p(\tau)^2}{2m}, \quad (53)$$

the Matsubara phase is given by

$$\theta(\mathbf{Q}, \mathbf{P}) = \frac{1}{\beta\hbar} \int_0^{\beta\hbar} d\tau p(\tau) \frac{\partial q(\tau)}{\partial \tau}, \quad (54)$$

the Matsubara ring-polymer spring potential is given by

$$S_M(\mathbf{Q}) = \frac{1}{\beta\hbar} \int_0^{\beta\hbar} d\tau \frac{m}{2} \left(\frac{\partial q(\tau)}{\partial \tau} \right)^2, \quad (55)$$

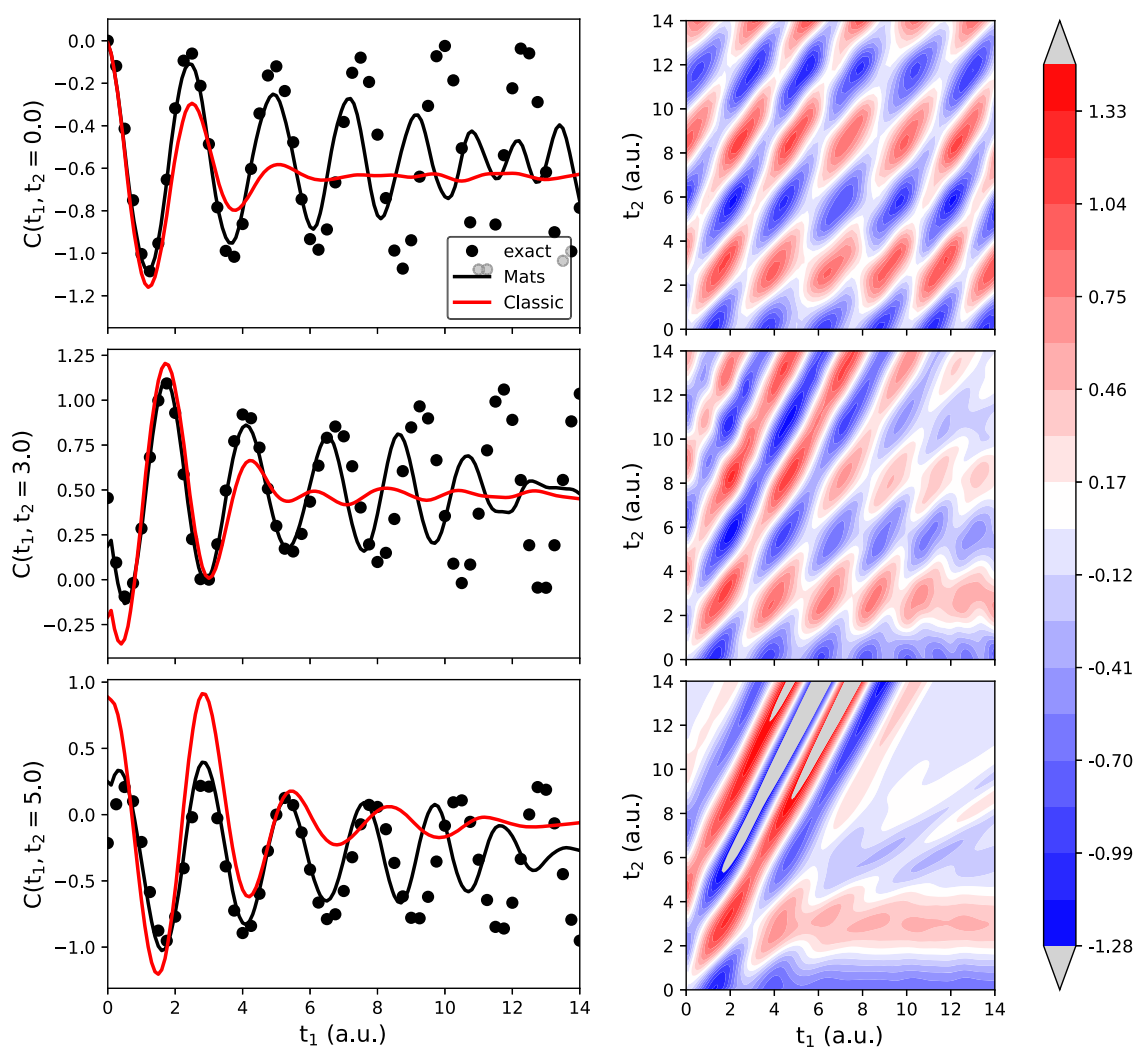


FIG. 6. Sine-sine correlation function $\langle \hat{q}(t_2) \overleftrightarrow{s} \hat{q}^2(t_1) \overleftrightarrow{s} \hat{q} \rangle$ for the quartic potential at $\beta = 2$. (Right) 2D-contour plots of the exact (top panel), Matsubara (middle panel), and classical (bottom panel) correlation functions. (Left) Cuts along selected time slices.

and the Matsubara potential is given by

$$V_M(\mathbf{Q}) = \frac{1}{\beta\hbar} \int_0^{\beta\hbar} d\tau V(q(\tau)), \quad (56)$$

with observable functions $O_M(\mathbf{Q})$ defined similar to $V_M(\mathbf{Q})$. We remark that this last expression is useful for obtaining analytical expressions in Matsubara modes for potentials and observables that are polynomial in q .³⁰

V. NUMERICAL RESULTS

To illustrate the performance of the Matsubara approximation to sine/cosine correlation functions beyond the harmonic, short-time, and classical limits, we present comparisons

between Matsubara dynamics and exact results for a simple one-dimensional model potential. We considered a particle with mass $m = 1$ in a quartic potential $V(q) = \frac{1}{4}q^4$ at an inverse temperature $\beta = 2$ (atomic units are used throughout). We focused on the calculation of three-point two-time correlation functions involving Poisson bracket couplings since these TCFs are novel to this study. We remark that the performance of Matsubara dynamics for one-time cosine (aka KT) correlation functions can be found in Refs. 30 and 31 and, for the two-time cosine-cosine (aka DKT), in Refs. 65 and 66. Additional computational details can be found in Appendix D.

We start by focusing on the sine-cosine correlation function $\langle \{ \hat{C}(t_2) \overleftrightarrow{S} \hat{B}(t_1) \} \overleftrightarrow{C} \hat{A} \rangle_{N'}$, which in Matsubara space is approximated by $\langle \{ C_M(t_2) \overleftrightarrow{\Lambda}_M B_M(t_1) \} A_M \rangle_M$. In Fig. 4, we present the

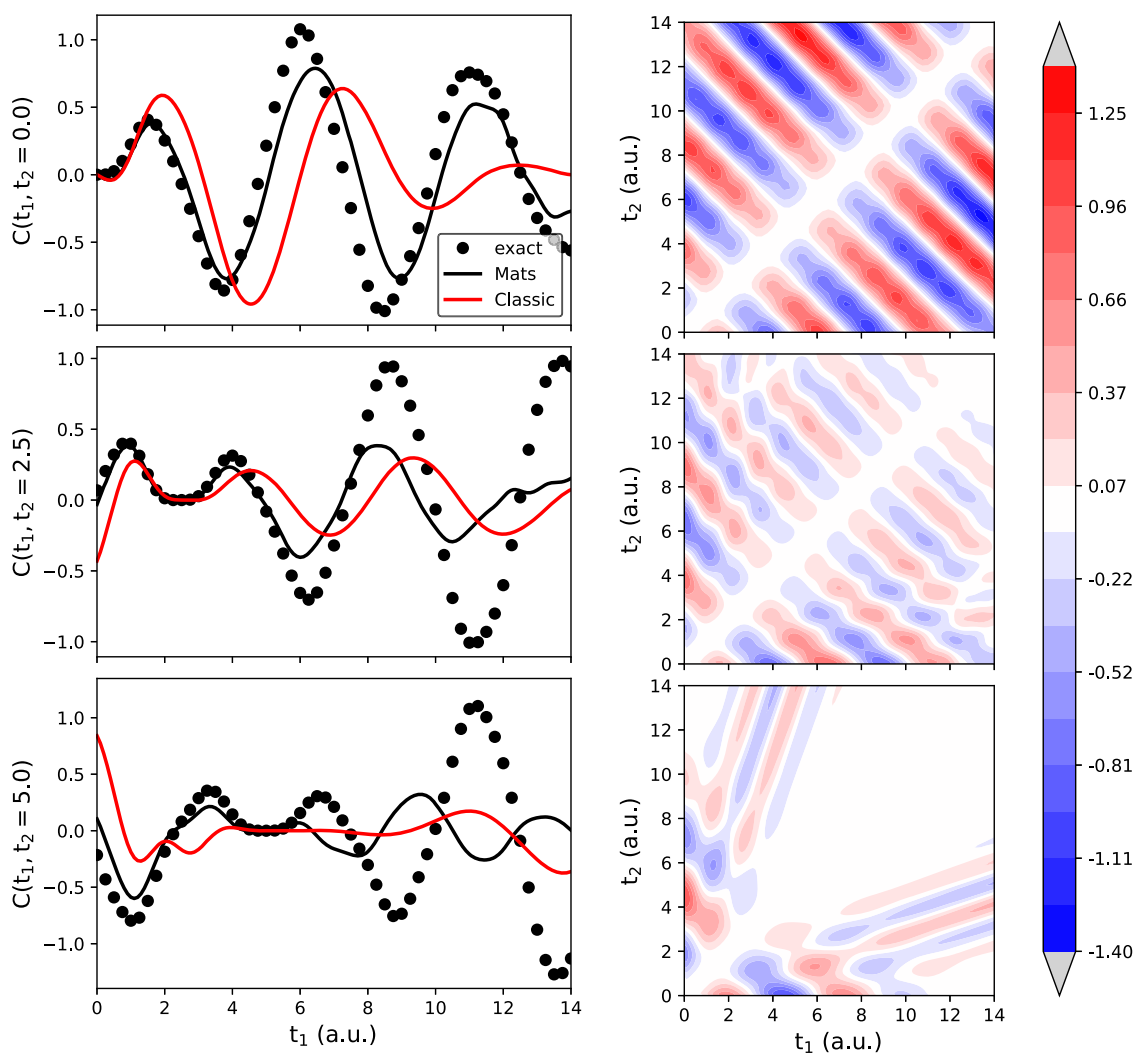


FIG. 7. Sine-sine correlation function $\langle \{ \hat{q}(t_2) \overleftrightarrow{S} \hat{q}(t_1) \} \overleftrightarrow{S} \hat{q}^2 \rangle$ for the quartic potential at $\beta = 2$. (Right) 2D-contour plots of the exact (top panel), Matsubara (middle panel), and classical (bottom panel) correlation functions. (Left) Cuts along selected time slices.

results for the case $\hat{A} = \hat{C} = \hat{q}$, $\hat{B} = \hat{q}^2$. For comparison, we also present the results for the classical correlation function (i.e., $M = 1$). At short times, Matsubara dynamics is seen to be an excellent approximation, reproducing almost perfectly the first recurrences of the TCF. As either t_1 or t_2 increases, the accuracy of Matsubara dynamics decreases. Note, however, that Matsubara dynamics gives a better treatment than classical dynamics in capturing the long-time oscillations of the TCF. The same trends are found for the sine-cosine correlation function with $\hat{A} = \hat{q}^2$ and $\hat{B} = \hat{C} = \hat{q}$ (see Fig. 5).

Figures 6 and 7 show the results of the Matsubara correlation $\left\langle \left\{ C_M(t_2) \tilde{\Lambda}_M B_M(t_1) \right\} \tilde{\Lambda}_M A_M \right\rangle_M$ and its corresponding exact sine-sine TCF. Note that this case provides a test for the performance of Matsubara dynamics in approximating the second-order response function. Comparisons of Matsubara and classical results show that the former reproduces the first oscillations of the exact response in terms of both intensity and frequency much better than the latter. Notice also the persistence of the oscillations and the slower damping of the signal in the Matsubara results.

The results shown in Figs. 4–7 mask an important aspect of Matsubara dynamics. In particular, note that since we are considering observables that are only functions of position, at zero time ($t_1 = t_2 = 0$), the Poisson bracket constrains the correlation to be zero, irrespective of the quantum or classical nature of the statistic. In other words, classical correlations are trivially exact at time zero. This would not be the case if one considers correlations involving position- and momenta-dependent observables (e.g., $\left\langle P_0(t_1) \tilde{\Lambda}_M Q_0(t_0) \right\rangle_M$), or correlation not involving Poisson bracket operators (namely, all-cosine TCFs). In these cases, the classical correlation would give an erroneous zero time value, which would become more apparent the lower the temperature. On the contrary, Matsubara dynamics would provide the exact zero time value, since it accounts for the exact quantum Boltzmann statistics.^{30,31,65,66}

The overall conclusion of the numerical results is that Matsubara dynamics performed better than classical dynamics in terms of both capturing the zero-time limit (by including the exact quantum Boltzmann statistics) and achieving a better agreement with the exact results at shorter times for multi-time correlation functions, providing a semi-classical bridge between classical and quantum response theory. Note, however, that the presence of the phase factor term renders Matsubara dynamics an impractical method for the simulation of condensed phase systems. Nevertheless, the present Matsubara dynamics formulation of second-order response theory represents a benchmark theory for the future development of Boltzmann preserving semi-classical approximations, such as CMD and RPMD.^{31–33,64,66,90}

VI. CONCLUSIONS

We have introduced a semi-classical approximation to calculate generalized n -point correlation functions based on Matsubara dynamics. The approach decouples a subspace of ring-polymer normal modes (Matsubara modes) from the rest of (non-Matsubara) modes, resulting in a linearization of the dynamics and the

coupling between quantum observables. We have demonstrated that when applied to the exact ring-polymer phase-space representation of quantum mechanics,⁶⁸ the Matsubara “filtering” produces classical dynamics that conserves the quantum Boltzmann distribution, resulting in classical-like multi-time correlation involving time-evolved observables coupled through Poisson brackets in a smooth Matsubara space. Matsubara dynamics is exact in the zero time and harmonic limit and recovers the classical limit of multi-time correlation functions when only one Matsubara mode (i.e., the centroid) is considered, offering a unique perspective into the correspondence between quantum and classical dynamics. Moreover, the presence of Poisson-bracket couplings in the formulation gives rise to stability matrices, providing an interesting interpretation of quantum dynamics in terms of “interfering trajectories” in an extended phase space. Our numerical tests have shown that Matsubara dynamics gives consistently better agreement with exact quantum TCFs than classical dynamics, making it a reliable way to incorporate quantum Boltzmann statistics in multi-time correlation functions.

TCFs obtained from Matsubara dynamics suffer from the well-known phase problem, making them impractical for simulations of condensed phase systems (see, however, Ref. 70). Nevertheless, they provide a solid foundation for the development of semi-classical approximations that preserve the quantum-Boltzmann distribution.^{31–33,89,90} In particular, by performing a mean-field average of the dynamics over the fluctuations modes or by discarding part of the Liouvillian, CMD and RPKT approximations for the evaluation of KT (aka cosine) and DKT (aka cosine-cosine) correlation functions can be obtained,^{31,66} two methodologies that do not suffer from the phase problem and can be applied to condensed phase systems. Similar approximations can be applied to the TCFs involving the Poisson bracket introduced in this work, resulting in practical methodologies for incorporating nuclear quantum effects in multi-time correlation functions (a detailed analysis will be provided elsewhere). Alternatively, Matsubara dynamics is also the starting point to develop approximations based on the planetary model³² or quasi-CMD⁴⁰ for the calculation of two-point TCFs; it remains to be seen if these approximations can be extended to calculate correlation functions involving Poisson brackets. On the other hand, the direct computation of Poisson brackets is highly challenging to converge for many-body molecular systems. Thus, classical mechanics approaches, such as non-equilibrium and hybrid equilibrium/non-equilibrium molecular dynamics, can be used to address this computational overhead. It would be interesting to explore if these methods can be adapted for calculating Poisson brackets in the extended Matsubara/ring-polymer subspace.^{83,84} The formalism developed in this work provides a benchmark theory for the future development of quantum-Boltzmann-preserving semi-classical approximations.

Finally, we would also like to remark that although the present work is focused on Matsubara dynamics, one can envision the derivation of alternative approximate methodologies from the exact path-integral phase-space representation of multi-time correlation functions (Sec. II). For example, by taking the $\hbar \rightarrow 0$ limit, one can also linearize the dynamics and sine/cosine couplings, giving rise to LSC-IVR-like correlation functions involving Poisson-bracket couplings between observables. We leave the

development and analysis of the performance of such approximations for future studies.

SUPPLEMENTARY MATERIAL

The supplementary material includes details of the derivation of the Matsubara approximation and the harmonic limit.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Pablo E. Videla: Conceptualization (equal); Investigation (lead); Writing – original draft (lead); Writing – review & editing (equal). **Victor S. Batista:** Conceptualization (equal); Funding acquisition (lead); Supervision (lead); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

APPENDIX A: MAPPING BETWEEN HILBERT SPACE AND IMAGINARY-TIME PHASE-SPACE CORRELATION FUNCTIONS

The general “sine/cosine” n -point ring-polymer phase-space correlation functions introduced by Eq. (1) are an exact representation of correlation functions in the Hilbert space.⁶⁸ The mapping given by Eqs. (10) and (11) provides a relation that allows mapping Hilbert space correlations into ring-polymer “sine/cosine” correlations, and vice versa. Here, we provide some examples.

For two-point correlation functions, the following identities hold in the $N \rightarrow \infty$ limit:⁶⁸

$$\langle \hat{B}(t_1) \overleftrightarrow{s} \hat{A}(t_0) \rangle_N = \left(\frac{i}{\hbar} \right) \text{Tr} \{ \hat{\rho} [\hat{B}(t_1), \hat{A}(t_0)] \}, \quad (\text{A1})$$

$$\langle \hat{B}(t_1) \overleftrightarrow{c} \hat{A}(t_0) \rangle_N = \frac{1}{\beta} \int_0^\beta d\lambda \text{Tr} \{ \hat{\rho} \hat{B}(t_1) \hat{A}_\lambda(t_0) \}, \quad (\text{A2})$$

where $\hat{O}(t) = e^{i\hat{H}t/\hbar} \hat{O} e^{-i\hat{H}t/\hbar}$ represents a Heisenberg-evolved operator, $\hat{O}_\lambda(t) = \hat{O}(t - i\hbar\lambda) = e^{+\lambda\hat{H}} \hat{O}(t) e^{-\lambda\hat{H}}$, and $\hat{\rho} = e^{-\beta\hat{H}}/Z$ is the density matrix of the system with partition function Z . Note that Eq. (A1) connects sine functions with correlations involving commutators in Hilbert space, whereas Eq. (A2) relates cosine functions

to Kubo transform correlation functions. We remark that sine and cosine correlation functions are relevant for linear response theory.⁶⁸

For three-point correlation functions, the mapping between ring-polymer phase-space and Hilbert space correlation functions is given by

$$\begin{aligned} & \langle \{ \hat{C}(t_2) \overleftrightarrow{s} \hat{B}(t_1) \} \overleftrightarrow{s} \hat{A}(t_0) \rangle_N \\ &= \left(\frac{i}{\hbar} \right)^2 \text{Tr} \{ \hat{\rho} [[\hat{C}(t_2), \hat{B}(t_1)], \hat{A}(t_0)] \}, \end{aligned} \quad (\text{A3})$$

$$\begin{aligned} & \langle \{ \hat{C}(t_2) \overleftrightarrow{s} \hat{B}(t_1) \} \overleftrightarrow{c} \hat{A}(t_0) \rangle_N \\ &= \frac{i}{\beta\hbar} \int_0^\beta d\lambda \text{Tr} \{ \hat{\rho} [\hat{C}(t_2), \hat{B}(t_1)] \hat{A}_\lambda(t_0) \}, \end{aligned} \quad (\text{A4})$$

$$\begin{aligned} & \langle \hat{C}(t_2) \overleftrightarrow{c} \hat{B}(t_1) \overleftrightarrow{c} \hat{A}(t_0) \rangle_N \\ &= \frac{1}{\beta^2} \int_0^\beta d\lambda_0 \int_0^\beta d\lambda_1 \text{Tr} \{ \hat{T}_\beta \hat{\rho} \hat{C}(t_2) \hat{B}_{\lambda_1}(t_1) \hat{A}_{\lambda_0}(t_0) \}, \end{aligned} \quad (\text{A5})$$

where $\hat{T}_\beta$ is an imaginary-time ordering operator that orders the product of operators so that their imaginary time arguments increase from right to left and ensure that there is no backward imaginary time propagation inside the integral. We remark that the three-point correlation functions defined by Eqs. (A3)–(A5) are relevant for second-order response theory.⁶⁸

APPENDIX B: NON-MATSUBARA MODES INTEGRATION

We start by recognizing that in normal mode coordinates, the generalized Boltzmann factor $[e^{-\beta\hat{H}}]_N$ is given by³⁰

$$\begin{aligned} [e^{-\beta\hat{H}}]_N(\mathbf{Q}, \mathbf{P}) &= \left(\frac{mN}{2\pi\beta_N\hbar^2} \right)^{N/2} \int d\mathbf{D} \prod_{l=-N}^N \left(e^{\frac{i}{\hbar} N P_l D_l} \right) \\ &\times \exp \left(-\frac{\beta_N}{2} \sum_{l=-N}^N [V(\eta_l^+(\mathbf{Q}, \mathbf{D})) + V(\eta_l^-(\mathbf{Q}, \mathbf{D}))] \right) \\ &\times \exp \left(-\beta \sum_{l=-N}^N \left[\frac{m}{2} \omega_l^2 Q_l^2 + \frac{m}{2} \Omega_l^2 D_l^2 + m\omega_l \Omega_l D_l Q_{-l} \right] \right), \end{aligned} \quad (\text{B1})$$

with

$$\eta_l^\pm(\mathbf{Q}, \mathbf{D}) = \sum_{k=-N}^N \sqrt{N} T_{lk} Q_k \pm \sum_{k=-N}^N \sqrt{N} T_{lk} \frac{D_k}{2}, \quad (\text{B2})$$

$\omega_l = \frac{2}{\beta_N\hbar} \sin(\pi l/N)$, and $\Omega_l = \frac{1}{\beta_N\hbar} \cos(\pi l/N)$.

To carry out the integration of the non-Matsubara modes in Eq. (21), we closely follow Ref. 30 and recognize that upon neglecting the non-Matsubara modes in the Janus operator, both the time-dependent observables $[\hat{O}(t)]_N$ and the sine/cosine $\overleftrightarrow{s}/\overleftrightarrow{c}$ couplings are independent of the non-Matsubara momenta $\mathbf{P}$. The only dependence on the non-Matsubara momenta comes, therefore, from the Boltzmann factor $[e^{-\beta\hat{H}}]_N$, which can be integrated out, giving rise

to a product of Dirac delta-functions in the non-Matsubara “stretch” $\mathbf{D}$ variables. This, then, allows us to integrate out the non-Matsubara $\mathbf{D}$ modes from the distribution. As a result, the Boltzmann factor $\left[e^{-\beta\hat{H}}\right]_{\bar{N}}$ in Eq. (B1) reduces to (we omit constant factors for simplicity; see the supplementary material for detailed derivation)

$$\begin{aligned} \left[e^{-\beta\hat{H}}\right]_{\bar{N}}(\mathbf{Q}, \mathbf{P}_M) &\propto \int d\mathbf{D}_M \left(\prod_{l=-\bar{M}}^{\bar{M}} e^{\frac{i}{\hbar} N P_l D_l} \right) \\ &\times \exp \left(-\frac{\beta_N}{2} \sum_{l=1}^N [V(\eta_l^+(\mathbf{Q}, \mathbf{D}_M)) \right. \\ &\quad \left. + V(\eta_l^-(\mathbf{Q}, \mathbf{D}_M))] \right) \\ &\times \exp \left(-\beta \sum_{l=-\bar{N}}^{\bar{N}} \frac{m}{2} \omega_l^2 Q_l^2 \right) \\ &\times \exp \left(-\beta \sum_{l=-\bar{M}}^{\bar{M}} \left[\frac{m}{2} \Omega_l^2 D_l^2 + m \omega_l \Omega_l D_l Q_{-l} \right] \right), \end{aligned} \quad (\text{B3})$$

where $\mathbf{P}_M$ and $\mathbf{D}_M$ include only Matsubara modes and

$$\eta_l^\pm(\mathbf{Q}, \mathbf{D}_M) = \sum_{k=-\bar{N}}^{\bar{N}} \sqrt{N} T_{lk} Q_k \pm \sum_{k=-\bar{M}}^{\bar{M}} \sqrt{N} T_{lk} \frac{D_k}{2}. \quad (\text{B4})$$

In the $N \rightarrow \infty$ limit, the Gaussian distributions over the Matsubara $\mathbf{D}_M$ modes in Eq. (B3) become nascent Dirac delta functions, namely

$$\exp \left(-\beta \frac{m}{2} \Omega_l^2 \left[D_l - i \frac{N}{\beta \hbar m \Omega_l^2} P_l + \frac{\omega_l}{\Omega_l} Q_{-l} \right]^2 \right) \xrightarrow{N \rightarrow \infty} \delta(D_l), \quad (\text{B5})$$

allowing us to integrate the $\mathbf{D}_M$ modes to obtain

$$\begin{aligned} \left[e^{-\beta\hat{H}}\right]_{\bar{N}}(\mathbf{Q}, \mathbf{P}_M) &\propto \exp \left(-\beta_N \sum_{l=1}^N V(q_l(\mathbf{Q})) \right) \\ &\times \exp \left(-\frac{\beta}{2m} \sum_{l=-\bar{M}}^{\bar{M}} P_l^2 - i\beta \sum_{l=-\bar{M}}^{\bar{M}} \omega_l P_l Q_{-l} \right) \\ &\times \exp \left(-\beta \frac{m}{2} \sum_{l=-\bar{M}+1}^{\bar{M}} \omega_l^2 (Q_l^2 + Q_{-l}^2) \right), \end{aligned} \quad (\text{B6})$$

where

$$q_l(\mathbf{Q}) = \sum_{k=-\bar{N}}^{\bar{N}} \sqrt{N} T_{lk} Q_k. \quad (\text{B7})$$

In the $N \rightarrow \infty$ limit, the Gaussian distributions over the non-Matsubara $\mathbf{Q}$ modes in Eq. (B6) become nascent Dirac delta functions, namely

$$\exp \left(-\beta \frac{m}{2} \omega_l^2 Q_l^2 \right) \xrightarrow{N \rightarrow \infty} \delta(Q_l). \quad (\text{B8})$$

Therefore, the non-Matsubara $\mathbf{Q}$ modes can be integrated out from the distribution $q_l(\mathbf{Q})$, giving rise to the smooth distribution

$$q_l(\mathbf{Q}_M) = \sum_{k=-\bar{M}}^{\bar{M}} \sqrt{N} T_{lk} Q_k \quad (\text{B9})$$

containing only Matsubara modes. Thus, upon integration of the non-Matsubara $\mathbf{Q}$ modes, the Boltzmann factor becomes

$$\begin{aligned} \left[e^{-\beta\hat{H}}\right]_{\bar{N}}(\mathbf{Q}_M, \mathbf{P}_M) &\propto \exp \left(-\beta \left[\sum_{l=-\bar{M}}^{\bar{M}} \frac{P_l^2}{2m} + V_M(\mathbf{Q}_M) \right] \right) \\ &\times \exp \left(-i\beta \sum_{l=-\bar{M}}^{\bar{M}} \omega_l P_l Q_{-l} \right), \end{aligned} \quad (\text{B10})$$

and position-dependent functions (including the potential in the Liouvillian and observables) effectively change as

$$O(\mathbf{Q}) = \frac{1}{N} \sum_{j=1}^N V(q_j(\mathbf{Q})) \rightarrow O_M(\mathbf{Q}_M) = \frac{1}{N} \sum_{j=1}^N V(q_j(\mathbf{Q}_M)). \quad (\text{B11})$$

The final result is Eq. (34), where we have dropped the M subscripts from the Matsubara positions and momenta since there is no longer a need to distinguish between the Matsubara and non-Matsubara modes. Only the Matsubara modes remain.

APPENDIX C: MATSUBARA DYNAMICS FOR HARMONIC POTENTIAL

For a harmonic potential with natural frequency Ω , it is straightforward to show (see the supplementary material) that the Matsubara dynamics approximation to the first nontrivial three-point correlation functions involving nonlinear operators is given by

$$\begin{aligned} &\left\langle \{q_M^2(t_2) \overleftrightarrow{\Lambda}_{MQM}(t_1)\} \overleftrightarrow{\Lambda}_{MQM}(t_0) \right\rangle_M \\ &= \frac{2}{m^2 \Omega^2} \sin(\Omega(t_2 - t_1)) \sin(\Omega(t_2 - t_0)), \end{aligned} \quad (\text{C1a})$$

$$\begin{aligned} &\left\langle \{q_M^2(t_2) \overleftrightarrow{\Lambda}_{MQM}(t_1)\} q_M(t_0) \right\rangle_M \\ &= \frac{2}{\beta m^2 \Omega^3} \sin(\Omega(t_2 - t_1)) \cos(\Omega(t_2 - t_0)), \end{aligned} \quad (\text{C1b})$$

$$\begin{aligned} &\left\langle \{q_M(t_2) \overleftrightarrow{\Lambda}_{MQM}(t_1)\} q_M^2(t_0) \right\rangle_M \\ &= \frac{1}{\beta m^2 \Omega} \left(\sum_k \frac{1}{\Omega^2 + \omega_k^2} \right) \sin(\Omega(t_2 - t_1)), \end{aligned} \quad (\text{C1c})$$

$$\begin{aligned} \left\langle q_M(t_2) q_M(t_1) q_M^2(t_0) \right\rangle_M &= \frac{1}{\beta^2 m^2 \Omega^4} [\cos(\Omega(t_2 + t_1 - 2t_0)) \\ &\quad + \cos(\Omega(t_2 - t_1))] + \frac{1}{\beta^2 m^2 \Omega^2} \\ &\quad \times \left(\sum_k \frac{1}{\Omega^2 + \omega_k^2} \right) \cos(\Omega(t_2 - t_1)). \end{aligned} \quad (\text{C1d})$$

Equations (C1a) and (C1b) are independent of M and agree with the exact quantum results (see the supplementary material). Using the identity⁹¹ (recall that $\omega_k = 2\pi k/\beta\hbar$)

$$\lim_{M \rightarrow \infty} \sum_{k=-M}^M \frac{1}{\Omega^2 + \omega_k^2} = \frac{\beta\hbar}{2\Omega} \coth(\beta\hbar\Omega/2), \quad (\text{C2})$$

Eqs. (C1c) and (C1d) also agree with the exact quantum results in the $M \rightarrow \infty$ limit (see the supplementary material).

APPENDIX D: COMPUTATIONAL DETAILS

To illustrate the performance of the Matsubara approximation to general multi-time correlation functions, we show comparisons between Matsubara dynamics and exact results for the calculation of two-time correlation functions in simple one-dimensional model potentials. We considered a particle with mass $m = 1$ in a quartic potential $V(q) = \frac{1}{4}q^4$ at an inverse temperature of $\beta = 2$ (atomic units are used throughout). Exact results were computed by the direct evaluation of the trace in a finite harmonic basis set.

The integration over the Matsubara phase was done by evaluating the ratio^{33,65,66}

$$\frac{\langle \cos(\beta\theta_M) \bullet \rangle_{H_M}}{\langle e^{-\beta S_M} \rangle_{H_M}}, \quad (\text{D1})$$

where $\langle \cdot \rangle_{H_M}$ denotes sampling from the Matsubara distribution $e^{-\beta H_M}$ and $\bullet$ is a placeholder for the time-dependent function of Matsubara modes (that depends on the observables and type of correlation computed). We remark that the presence of the phase θ_M in Eq. (34) means that Matsubara dynamics suffers from the sign problem, rendering the methodology unpractical for the simulation of condensed phase systems. A total of *circa* 10^9 configurations were necessary to converge the results for $M = 5$. Including additional modes or performing the simulations at a lower temperature makes the computation extremely challenging, highlighting the impracticality of Matsubara dynamics.

All simulations were performed in the (Matsubara) normal mode representation using an analytical form for polynomial potentials, as described in the supplementary material of Ref. 30. The dynamics were performed employing the velocity-Verlet algorithm with a time step of 0.01 a.u. Momenta were sampled from a classical Boltzmann distribution every 20 a.u. The evaluation of the Poisson bracket was performed using the following relation, valid for observables that are only dependent on position:

$$O_M(\mathbf{Q}_t) \vec{\Lambda}_M O'_M(\mathbf{Q}_{t'}) = \sum_{k,l,m} \frac{\partial O_M(\mathbf{Q}_t)}{\partial Q_m(t)} \frac{\partial O'_M(\mathbf{Q}_{t'})}{\partial Q_l(t')} \\ \times (M_{mk}^{QP}(t) M_{lk}^{QQ}(t') - M_{mk}^{QQ}(t) M_{lk}^{QP}(t')), \quad (\text{D2})$$

where $M_{jk}^{\alpha\beta}(t) = \frac{\partial \alpha_j(t)}{\partial \beta_k}$ represents an element of the stability matrix^{81,87,92} whose time evolution is given by

$$\frac{d}{dt} M_{jk}^{QP}(t) = \frac{1}{m_j} M_{jk}^{PP}(t), \quad (\text{D3a})$$

$$\frac{d}{dt} M_{jk}^{PP}(t) = \sum_l - \frac{\partial^2 U_M(t)}{\partial Q_j(t) \partial Q_l(t)} M_{lk}^{QP}(t), \quad (\text{D3b})$$

$$\frac{d}{dt} M_{jk}^{QQ}(t) = \frac{1}{m_j} M_{lk}^{PQ}(t), \quad (\text{D3c})$$

$$\frac{d}{dt} M_{jk}^{PQ}(t) = \sum_l - \frac{\partial^2 U_M(t)}{\partial Q_j(t) \partial Q_l(t)} M_{lk}^{QQ}(t), \quad (\text{D3d})$$

with the initial conditions

$$M_{jk}^{QP}(0) = M_{jk}^{PQ}(0) = 0, \quad (\text{D4a})$$

$$M_{jk}^{PP}(0) = M_{jk}^{QQ}(0) = \delta_{jk}. \quad (\text{D4b})$$

For the simple observables considered in the present paper, analytical expressions for O_M can be obtained and the derivatives in Eq. (D2) can be evaluated exactly.³⁰ The equations of motion Eq. (D3) were integrated along the dynamics with the same velocity-Verlet algorithm. To avoid the calculation of the second-order stability matrix involved in the double Poisson bracket, correlation functions involving two $\vec{\Lambda}_M$ couplings were computed using numerical differentiation based on relation Eq. (44).

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