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Path integral Liouville dynamics for thermal equilibrium systems

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We show a new imaginary time path integral based method—path integral Liouville dynamics (PILD), which can be derived from the equilibrium Liouville dynamics [J. Liu and W. H. Miller, J. Chem. Phys. 134, 104101 (2011)] in the Wigner phase space. Numerical tests of PILD with the simple (white noise) Langevin thermostat have been made for two strongly anharmonic model problems. Since implementation of PILD does not request any specific form of the potential energy surface, the results suggest that PILD offers a potentially useful approach for general condensed phase molecular systems to have the two important properties: conserves the quantum canonical distribution and recovers exact thermal correlation functions (of even nonlinear operators, i.e., nonlinear functions of position or momentum operators) in the classical, high temperature, and harmonic limits. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4881518]

I. INTRODUCTION

There is currently considerable effort focused on developing ways for including quantum mechanical effects in condensed phase molecular dynamics simulations. Several classes of trajectory-based dynamics methods have been proposed for simulating quantum correlation functions for large molecular systems in thermal equilibrium, since most dynamical quantities of interest can be expressed in terms of time correlation functions that are of the form

\[ C_{AB}(\tau) \equiv \langle \Delta A(t) \Delta B(t+\tau) \rangle = \frac{1}{Z} \text{Tr} \left( \hat{A} e^{i\hat{H}_1 t/\hbar} \hat{B} e^{-i\hat{H}_1 t/\hbar} \right), \]

where \( \hat{A} = e^{-\beta \hat{H}} \hat{A} \) is for the standard version of the correlation function, or \( \hat{A}_{\text{Kubo}}(\lambda) = \frac{1}{Z} \int_0^\lambda d\lambda e^{-\beta(\lambda-i\hbar)} \hat{A} e^{i\hat{H}_1 t/\hbar} \) for the Kubo-transformed version. Here, \( Z = \text{Tr}[e^{-\beta \hat{H}}] \) is the partition function, \( \hat{H} \) the (time-independent) Hamiltonian of the system with the total number of degrees of freedom \( N \), which we assume to be of standard Cartesian form

\[ \hat{H} = \frac{1}{2} \hat{p}^2 \hat{M}^{-1} \hat{p} + V(\hat{x}), \]

where \( \hat{M} \) is the diagonal “mass matrix,” and \( \hat{p} \) and \( \hat{x} \) are the momentum and coordinate operators, respectively; and \( \hat{A} \) and \( \hat{B} \) are operators relevant to the specific property of interest. These trajectory-based methods include the linearized semiclassical initial value representation (LSC-IVR)/classical Wigner, derivative forward-backward semiclassical dynamics (FBSD), centroid molecular dynamics (CMD), and ring polymer molecular dynamics (RPMD), etc.

More recently, we have proposed three families of approaches in phase space formulations of quantum mechanics [equilibrium Liouville dynamics (ELD), equilibrium continuity dynamics, and equilibrium Hamiltonian dynamics (EHD)] that are able to combine the important properties of LSC-IVR/FBSD and of CMD/RPMD. That is,

1. conserve the quantum canonical density distribution function for the thermal equilibrium system; and
2. treat both linear and nonlinear operators (i.e., linear and nonlinear functions of position or momentum operators) equally well and recover exact thermal correlation functions in the classical (\( \hbar \to 0 \)), high temperature (\( \beta \to 0 \)), and harmonic limits.

Several methodologies (such as the Feynman-Kleinert approximation and thermal Gaussian approximations in the position state or coherent state representation, etc.) have been presented for the applications of these three families of trajectory-based dynamics for describing quantum dynamic effects for thermal equilibrium systems. These methodologies are efficient when the potential of the system can be represented by polynomials, exponential, or Gaussian functions. However, Gaussian averages in these methodologies become computational demanding for complex molecular systems where angle and dihedral interactions (or induced dipole-dipole interactions) are important and accurate polynomial, exponential, or Gaussian fitting of potential surfaces is often intractable. It would thus be appealing to develop a methodology that does not require any specific form of the potential energy surface and is in principle feasible to be combined with ab initio calculations on the fly.

The purpose of this paper is to present a path integral representation of the ELD in the Wigner phase space and to test them with standard model problems. Section II briefly summarizes the ELD approach and discusses the expression of the effective force in the Wigner phase space. Section III proposes a path integral representation based on the staging transformation for evaluating the effective force, then shows how a molecular dynamics scheme can be constructed by introducing an adiabatic parameter. Section IV presents another point of view to derive this methodology from EHD in the spirit of the Hamilton equations of motion. Some numerical tests are demonstrated in Sec. V, including a strongly anharmonic oscillator, and a more challenging quartic well. Concluding remarks are given in Sec. VI.

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II. EQUILIBRIUM LIOUVILLE DYNAMICS

A. Theory

Following Refs. 29–31, one can express Liouville’s theorem in quantum mechanics in the Wigner or Husimi phase space as

\[
\frac{\partial \rho^{eq}(x, p; t)}{\partial t} = -p^T M^{-1} \frac{\partial \rho^{eq}}{\partial x} + \left( \frac{\partial \rho^{eq}(x, p; t)}{\partial p} \right)^T \cdot \frac{\partial V_{eff}(x, p)}{\partial x}.
\]

(3)

The following equality always holds:

\[
\frac{d \rho^{eq}(x, p; t)}{dt} = \frac{\partial \rho^{eq}(x, p; t)}{\partial t} + \frac{\partial \rho^{eq}(x, p; t)}{\partial x} \cdot \dot{x} + \frac{\partial \rho^{eq}(x, p; t)}{\partial p} \cdot \dot{p}.
\]

(4)

If the trajectory in the phase space is chosen to satisfy

\[
\frac{d \rho^{eq}(x, p; t)}{dt} = 0,
\]

(5)

then one reaches the equations of motion of ELD

\[
\dot{x} = M^{-1} p,
\]

\[
\dot{p} = -\frac{\partial V_{eff}(x, p)}{\partial x},
\]

(6)

(7)

with the effective force \(-\frac{\partial V_{eff}(x, p)}{\partial x}\) given by

\[
\frac{\partial \rho^{eq}(x, p; t)}{\partial p}, \quad \frac{\partial V_{eff}(x, p)}{\partial x} = p^T M^{-1} \frac{\partial \rho^{eq}(x, p; t)}{\partial x}.
\]

(8)

Here, \((x, p)\) is the phase point and \(\rho^{eq}(x, p)\) is the canonical distribution in the phase space. It is straightforward to show that the trajectory-based dynamics given by Eqs. (6) and (7) satisfies stationarity of the quantum canonical distribution function, i.e.,

\[
\frac{\partial \rho^{eq}(x, p; t)}{\partial t} = 0.
\]

(9)

Evaluation of the quantum correlation function Eq. (2) in the Wigner phase space with ELD\(^{20,31}\) takes the expression

\[
C_{AB}(t) = \frac{1}{Z} \int d x_0 \int d p_0 A_{W}^\beta(x_0, p_0) B_W(x_t, p_t)
\]

\[
\cdot \frac{d \rho^{eq}(x_0, p_0; t)}{dt} f_{W}^\beta(x, p_0) B_W(x_t, p_t).
\]

(10)

where \(A_{W}^\beta, B_W,\) and \(\rho^{eq}\) are the Wigner functions of the operators \(\hat{A}^\beta, \hat{B},\) and \(e^{-\beta H},\) respectively. One sees that it takes the same procedure to express the functions \(f_{W}^\beta\) and \(B_W\) as is often done in the Wigner phase space for the LSC-IVR/classical Wigner model.\(^{11}\) The only difference between ELD and the LSC-IVR/classical Wigner model is that the trajectory \((x_t, p_t)\) of the latter always follows classical dynamics rather than Eq. (6). Since Eqs. (5) and (8) hold in ELD, time-averaging Eq. (9) leads to

\[
C_{AB}(t) = \frac{1}{T_0} \int_0^{T_0} dt' \langle A(t') B(t' + t) \rangle
\]

\[
= \frac{1}{Z} \int d x_0 \int d p_0 \rho^{eq}(x_0, p_0)
\cdot \frac{1}{T_0} \int_0^{T_0} dt' \langle f_{W}^\beta(x_t, p_t) B_W(x_{t+t}, p_{t+t}) \rangle.
\]

(11)

If the dynamics of system is ergodic, the correlation function can be evaluated by a long time trajectory, i.e., Eq. (10) is simplified as

\[
C_{AB}(t) = \frac{1}{T_0} \int_0^{T_0} dt' \langle f_{W}^\beta(x_t, p_t) B_W(x_{t+t}, p_{t+t}) \rangle.
\]

(12)

B. Evaluation of the effective force

One can express \(\rho^{eq}(x, p)\) in the Wigner phase space with the local Gaussian approximation\(^{11,30,32}\) as

\[
\frac{1}{Z} \rho^{eq}_{W}(x, p) = \frac{1}{Z} \langle e^{-\beta H} \rangle \left( \frac{\beta}{2\pi} \right)^{N/2} |\det(M_{therm})|^{-1/2}
\times \exp \left[ -\frac{\beta}{2} p^T M_{therm}^{-1} p \right],
\]

(13)

where the thermal mass matrix \(M_{therm}\) is given by

\[
M_{therm}^{-1}(x) = M^{-1/2} T Q(u) T^T M^{-1/2}.
\]

(14)

Here, \(Q(u)\) is the (diagonal) quantum correction factor matrix with the LGA ansatz\(^{31}\) (also see the definition of \(u\) in Ref. 11), and \(T\) is an orthogonal matrix that transforms the mass-weighted Hessian matrix of the potential energy surface into a diagonal one. Using the relation (13) or

\[
\langle x - \frac{\Delta x}{2} \rangle \langle e^{-\beta H} | x + \frac{\Delta x}{2} \rangle \exp \left[ -\frac{\Delta x^T M_{therm}(x) \Delta x}{2\beta} \right],
\]

(15)

it is straightforward to follow the same procedure for the LSC-IVR/classical Wigner model as shown in Ref. 11 to express the correlation function in the Wigner phase space [i.e., obtain the function \(f_{W}^\beta(x, p)\) in Eq. (9)].

The ELD effective force defined by Eq. (7) with the density distribution Eq. (12) is

\[-\frac{\partial}{\partial x} V_{eff}(x, p) \]

\[
= \frac{1}{\beta} M_{therm}^{-1} \frac{\partial}{\partial x} \ln \rho_{W}^{eq}(x, p)
\]

\[
= M_{therm}^{-1} \left( \frac{1}{\beta} \frac{\partial}{\partial x} \ln \langle e^{-\beta H} | x \rangle - \frac{1}{2} p^T \frac{\partial M_{therm}^{-1}(x)}{\partial x} p \right)
\]

\[- \frac{1}{2\beta} \frac{\partial}{\partial x} \ln |\det(M_{therm})| \right).\]

While several methodologies\(^{29,31,32}\) have been proposed for evaluating Eq. (15), imaginary time path integral techniques\(^{33-40}\) can also be implemented for ELD. Below we show how such an efficient path integral presentation of ELD can be constructed.

If a system is harmonic, it is trivial to show

\[M_{therm}(x) \equiv M_{therm} = \beta \langle pp^T \rangle,
\]

(16)
where \((pp^T)\) is the canonical ensemble average of the covariance matrix of the momentum vector, which is independent of the position \(x\). If the thermal mass matrix \(M_{\text{therm}}\) of Eq. (12) is defined by Eq. (16) for general systems [i.e., replacing the local Gaussian momentum approximation by a global one], the ELD effective force [Eq. (15)] can be simplified as

\[
\frac{-\beta}{\partial x} V_{\text{eff}}(x, p) = \frac{1}{\beta} M_{\text{therm}}^{-1} \frac{\partial}{\partial x} \ln(x) e^{-\beta H(x)}.
\] (17)

Equation (17) provides a numerically more favorable form for evaluating the effective force of the equations of motion of Eq. (6). Note that the covariance matrix \((pp^T)\) of Eq. (16) can be always efficiently evaluated by path integral techniques\(^{33-41}\) before Eqs. (12) and (17) are employed in ELD. Evaluation of the thermal mass matrix \(M_{\text{therm}}\) as defined by Eq. (16) does not request any specific form of the potential energy surface and takes the similar procedure as we estimate thermodynamic properties such as the kinetic energy.

It is straightforward to see that ELD with the quantum canonical distribution \(\rho_{\text{eq}}(x, p)\) given by Eqs. (12) and (16) still rigorously satisfies the two important properties discussed in Sec. I. Note that the thermal mass matrix \(M_{\text{therm}}\) defined by the quantum canonical distribution \(\rho_{\text{eq}}(x, p)\) is often different from the (diagonal) physical mass matrix \(M\) except in the high temperature or classical limit.

### III. PATH INTEGRAL REPRESENTATION OF EQUILIBRIUM LIOUVILLE DYNAMICS

For simplicity, we choose the 1-dim case for demonstration below. Inserting path integral beads in Eq. (12) leads to

\[
\frac{1}{Z} \rho_{\text{eq}}^\text{eq}(x, p) \bigg|_{x_i=p_i=p} \lim_{P \to \infty} \frac{1}{Z} \left( \frac{MP}{2\pi\beta \hbar^2} \right)^{P/2} \int dx_2 \ldots \int dx_P \\
\times \exp \left\{ -\beta \sum_{j=1}^P \left[ \frac{1}{2} \bar{m}_j \omega_j^2 \xi_j^2 + \frac{1}{P} V(x_j, \xi_1, \ldots, \xi_P) \right] \right\} \\
\times \left( \frac{\beta}{2\pi} \right)^{1/2} \left| M_{\text{therm}} \right|^{-1/2} \exp \left\{ -\frac{\beta}{P} P_1^{-1} M_{\text{therm}}^{-1} P_1 \right\},
\] (18)

where \(P\) is the number of path integral beads. Here, one sees that the samplings of the path integral beads \((x_2, \ldots, x_P)\) have to be completed in order to implement ELD in Eq. (6) with the effective force given by Eq. (17).

Consider the staging transformation\(^{42,43}\)

\[
\xi_1 = x_1,
\]
\[
\xi_i = x_i - \frac{(i-1)x_{i+1} + x_i}{i} \quad (i = 2, P).
\] (19)

Its inverse transformation takes the following convenient recursive form:

\[
x_1 = \xi_1,
\]
\[
x_i = \xi_i + \frac{i-1}{i} x_{i+1} + \frac{1}{i} \xi_1 \quad (i = 2, P).
\] (20)

Here, \(x_{P+1} \equiv x_1\). If one defines

\[
\omega_P = \sqrt{\frac{\beta}{P \hbar^2}},
\] (21)

Eq. (18) becomes

\[
\frac{1}{Z} \rho_{\text{eq}}^\text{eq}(x, p) \bigg|_{x_i=p_i=p} \lim_{P \to \infty} \frac{1}{Z} \left( \frac{MP}{2\pi\beta \hbar^2} \right)^{P/2} \int dx_2 \ldots \int dx_P \\
\times \exp \left\{ -\beta \sum_{j=1}^P \left[ \frac{1}{2} \bar{m}_j \omega_j^2 \xi_j^2 + \frac{1}{P} V(x_j, \xi_1, \ldots, \xi_P) \right] \right\} \\
\times \left( \frac{\beta}{2\pi} \right)^{1/2} \left| M_{\text{therm}} \right|^{-1/2} \exp \left\{ -\frac{\beta}{P} P_1^{-1} M_{\text{therm}}^{-1} P_1 \right\},
\] (22)

with the masses given by

\[
\bar{m}_1 = 0,
\]
\[
\bar{m}_i = \frac{i}{i-1} \tilde{M} \quad (i = 2, P).
\] (23)

One sees that all the staging variables \((\xi_2, \ldots, \xi_P)\) have the same frequency and all the fictitious masses \((\bar{m}_2, \ldots, \bar{m}_P)\) are in the same scale. If one defines

\[
\phi(\xi_1, \ldots, \xi_P) = \frac{1}{P} \sum_{j=1}^P V(x_j, \xi_1, \ldots, \xi_P),
\] (24)

then one obtains the chain rule

\[
\frac{\partial \phi}{\partial \xi_1} = \sum_{j=1}^P \frac{\partial \phi}{\partial x_j} = \frac{1}{P} \sum_{j=1}^P V'(x_j),
\]
\[
\frac{\partial \phi}{\partial \xi_j} = \frac{\partial \phi}{\partial x_j} + \frac{j-2}{j-1} \frac{\partial \phi}{\partial \xi_{j-1}}, \quad (j = 2, P),
\] (25)

from Eqs. (19) and (20). Therefore, one can employ such as the staging Monte Carlo approach\(^{33,34,42}\) to efficiently evaluate the ELD effective force [Eq. (17)] from the following formula:

\[
\frac{-1}{\beta} \frac{\partial}{\partial x} \ln \rho_{\text{eq}}^\text{eq}(x, p) = \frac{-1}{\beta} \frac{\partial}{\partial x} \ln(x) e^{-\beta H(x)}
\]
\[
\lim_{P \to \infty} \frac{1}{Z} \left( \frac{MP}{2\pi\beta \hbar^2} \right)^{P/2} \int d\xi_2 \ldots \int d\xi_P \exp \left\{ -\beta \sum_{j=1}^P \left[ \frac{1}{2} \bar{m}_j \omega_j^2 \xi_j^2 + \phi(\xi_1, \ldots, \xi_P) \right] \right\} \frac{1}{P} \sum_{j=1}^P V'(x_j)
\]
\[
\lim_{P \to \infty} \frac{1}{Z} \left( \frac{MP}{2\pi\beta \hbar^2} \right)^{P/2} \int d\xi_2 \ldots \int d\xi_P \exp \left\{ -\beta \sum_{j=1}^P \left[ \frac{1}{2} \bar{m}_j \omega_j^2 \xi_j^2 + \phi(\xi_1, \ldots, \xi_P) \right] \right\}.
\] (26)
The real time propagation of the phase variables \((x, p) \equiv (\xi_1, p_1)\) [defined by the ELD equations of motions Eq. (6)] then involves an integral over \((\xi_2, \ldots, \xi_P)\) to evaluate at every time step. Below we introduce an efficient sampling of all variables in a molecular dynamics scheme.

Taking advantage of the isomorphism strategy proposed by Chandler and Wolynes,44 one can insert fictitious momenta \((p_2, \ldots, p_P)\) into Eq. (22) or Eq. (26). For instance, Eq. (22) becomes

\[
\frac{1}{Z} \rho^{eq}_P(x, p) \equiv \lim_{P \to \infty} \frac{1}{Z} \left( \frac{M P}{2 \pi \hbar^2} \right)^{P/2} \times \int d\xi_1 \ldots d\xi_P \int dp_2 \ldots \int dp_P 
\times \exp \left\{ -\beta \left[ \sum_{j=2}^{P} \frac{1}{2} \bar{m}_j \omega^2 \xi_j^2 + \phi(\xi_1, \ldots, \xi_P) \right] \right\} \times \left( \prod_{j=2}^{P} \frac{\beta}{2 \pi \bar{m}_j} \right)^{1/2} \exp \left\{ -\beta \sum_{j=2}^{P} \frac{p_j^2}{2 \bar{m}_j} \right\} \times \left( \frac{\beta}{2 \pi} \right)^{P/2} |M_{\text{therm}}|^{-1/2} \exp \left\{ -\beta \frac{1}{2} P_1 M_{\text{therm}}^{-1} P_1 \right\}. 
\]

(27)

If one chooses the corresponding fictitious masses \((\bar{m}_2, \ldots, \bar{m}_P)\) as

\[
\bar{m}_i = \gamma_{ad} \bar{m}_i \quad (i = 2, P)
\]

with \(\gamma_{ad} \in (0, 1)\) as an adiabatic parameter, and also defines the adiabatic frequencies \(\omega_{ad}\) as

\[
\omega_{ad} = \omega / \sqrt{\gamma_{ad}}.
\]

Eq. (27) then becomes

\[
\frac{1}{Z} \rho^{eq}_P(x, p) \equiv \lim_{P \to \infty} \frac{1}{Z} \left( \frac{M P}{2 \pi \hbar^2} \right)^{P/2} \times \int d\xi_1 \ldots d\xi_P \int dp_2 \ldots \int dp_P 
\times \exp \left\{ -\beta \left[ \sum_{j=2}^{P} \frac{1}{2} \bar{m}_j \omega^2 \xi_j^2 + \phi(\xi_1, \ldots, \xi_P) \right] \right\} \times \left( \prod_{j=2}^{P} \frac{\beta}{2 \pi \bar{m}_j} \right)^{1/2} \exp \left\{ -\beta \sum_{j=2}^{P} \frac{p_j^2}{2 \bar{m}_j} \right\} \times \left( \frac{\beta}{2 \pi} \right)^{P/2} |M_{\text{therm}}|^{-1/2} \exp \left\{ -\beta \frac{1}{2} P_1 M_{\text{therm}}^{-1} P_1 \right\}. 
\]

(30)

One sees that all the staging variables \((\xi_2, \ldots, \xi_P)\) share the same time scale that can be well separated from the time scale \(\xi_1 \equiv x\) with the choice of the adiabatic parameter \(\gamma_{ad}\). When the separation of time scales holds, one can define the following density distribution function:

\[
\frac{1}{Z} \rho^{eq}_P(\xi_1, \ldots, \xi_P, p_1, \ldots, p_P) \equiv \lim_{P \to \infty} \frac{1}{Z} \left( \frac{M P}{2 \pi \hbar^2} \right)^{P/2} \times \left( \prod_{j=2}^{P} \frac{\beta}{2 \pi \bar{m}_j} \right)^{1/2} \exp \left\{ -\beta \sum_{j=2}^{P} \frac{p_j^2}{2 \bar{m}_j} \right\} \times \left( \frac{\beta}{2 \pi} \right)^{1/2} |M_{\text{therm}}|^{-1/2} \exp \left\{ -\beta \frac{1}{2} P_1 M_{\text{therm}}^{-1} P_1 \right\}. 
\]

(31)

with the physical mass \(M\) for the physical phase space variables \((\xi_1, p_1) \equiv (x, p)\) and the fictional masses \(\bar{m}_j\) given in Eq. (28) for the other variables \((\xi_j, p_j)\), then the ELD equations of motion [Eqs. (6) and (7)] lead to

\[
\dot{\xi}_1 = \dot{x}_1 = \dot{x} = \frac{\gamma_{ad}}{\bar{m}_1} x, \\
\dot{p}_1 = \dot{\rho}_1 = -M_{\text{therm}} \frac{\partial \phi}{\partial \xi_1} = -M_{\text{therm}} \left( \frac{1}{P} \sum_{j=1}^{P} \frac{\partial V(x_j)}{\partial x_j} \right), \\
\dot{\xi}_j = \bar{m}_j^{-1} p_j, \\
\dot{p}_j = -\bar{m}_j \omega^2 \xi_j - \frac{\partial \phi}{\partial \xi_j} \quad (j = 2, P).
\]

(32)

In order to ensure a proper canonical distribution for \((\xi_2, \ldots, \xi_P, p_2, \ldots, p_P)\), the equations of motion for \((\xi_2, \ldots, \xi_P, p_2, \ldots, p_P)\) in Eq. (32) must be coupled to a thermostatting method, such as Anderson thermostat,45 Nosé-Hoover chain,46 generalized Gaussian moment,47 or Langevin dynamics,39, 48 etc. Note that the quantum phase space variables \((\xi_1, p_1) \equiv (x, p)\) should not be coupled to a thermostatting method. When the adiabatic parameter \(\gamma_{ad} \to 0\), Eq. (32) approaches the full adiabatic version of the path integral representation of ELD in the Wigner phase space, otherwise the partially adiabatic version of ELD is actually obtained, which could be more efficient. We note the path integral representation as path integral Liouville dynamics (PILD) in the paper. Fig. 1 provides a scheme representation of PILD.

One sees that PILD is reminiscent of the staging path integral molecular dynamics (PIMD) of Tuckerman et al.38, 43 when the following three conditions are satisfied:

(1) The variables \((\xi_1, p_1) \equiv (x, p)\) are also coupled to a thermostatting method.
(2) The thermal mass \(M_{\text{therm}}\) is reduced to the mass of the system.
(3) The adiabatic parameter \(\gamma_{ad}\) is chosen as 1.

It is trivial to further show that all thermodynamic properties can be exactly obtained in PILD in the same spirit as done in the staging PIMD, as long as the first condition
is satisfied. More importantly, PILD offers an approach for calculating dynamical properties and real time correlation functions.

As the relation between ELD and CMD has been discussed in Ref. 30, it is also interesting to compare PILD to the path integral version of CMD. 23, 49 While the former employs the staging transformation of the imaginary time path integral beads, the latter often uses the normal-mode transformation instead. CMD expresses the thermal correlation function with the position and momentum of the centroid of the path integral beads, and fails to give the correct result if both operators [ A and B in Eq. (1)] are nonlinear operators, even for a harmonic potential. 31, 32, 50–54 As comparison, PILD expresses the thermal correlation function with Eq. (9) in the Wigner phase space formulations of quantum mechanics,31, 32, 50–54 as we also show below. One can follow Ref. 32 to make a change of variables in Eq. (31)

\[ \rho_{\text{eff}} = \frac{M_{\text{eff}}}{M} \rho \]  

with the effective mass defined as

\[ M_{\text{eff}} = M M_{\text{therm}}^{-1} M. \]  

When the thermal mass $M_{\text{therm}}$ is given by Eq. (16), the effective mass $M_{\text{eff}}$ is independent of the position. In such a case, it is clear from Ref. 32 that ELD can be closely related to EHD in phase space formulations of quantum mechanics, as we also show below.

The transformation of Eq. (33) gives the determinant of the Jacobian matrix as

\[ \frac{\partial (\xi_1, \xi_2, \ldots, \xi_p, p_{\text{eff}}, p_2, \ldots, p_P)}{\partial (\xi_1, \xi_2, \ldots, \xi_p, p_1, p_2, \ldots, p_P)} = |M_{\text{eff}} M^{-1}| = |M M_{\text{therm}}^{-1}|. \]  

Here, $\xi$ is the position. The phase space distribution function with the new variables \((\xi_1, \xi_2, \ldots, \xi_p, p_{\text{eff}}, p_2, \ldots, p_P)\) thus takes the form

\[ \rho_{\text{eff}}^\text{eq} (\xi_1, \ldots, \xi_p, p_{\text{eff}}, p_2, \ldots, p_P) = |M_{\text{therm}} M^{-1}| \rho_{\text{eq}}^\text{eq} (\xi_1, \ldots, \xi_p, p_1, p_2, \ldots, p_P). \]  

Equations (31) and (36) lead to

\[ \frac{1}{Z} \rho_{\text{eff}}^\text{eq} (\xi_1, \ldots, \xi_p, p_{\text{eff}}, p_2, \ldots, p_P) = \frac{1}{Z} \left( \left( \frac{M P}{2 \pi \hbar} \right)^{P/2} \left( \prod_{j=2}^{P} \frac{\beta}{2 \pi m_j} \right)^{1/2} \left( \frac{\beta}{2 \pi} \right)^{1/2} |M_{\text{eff}}|^{-1/2} \times e^{-\beta H_{\text{staging}}^\text{move} (\xi_1, \ldots, \xi_p, p_{\text{eff}}, p_2, \ldots, p_P)} \right) \]  

with the effective staging Hamiltonian $H_{\text{staging}}^\text{eff}$ defined as

\[ H_{\text{staging}}^\text{eff} (\xi_1, \xi_2, \ldots, \xi_p, p_{\text{eff}}, p_2, \ldots, p_P) = \frac{1}{2} \sum_{j=2}^{P} \frac{p_j^2}{2 m_j} + \sum_{j=2}^{P} \frac{1}{2} m_j \omega_j^2 \xi_j^2 + \phi (\xi_1, \ldots, \xi_p). \]  

The Hamilton equations of motion generated from the effective staging Hamiltonian $H_{\text{staging}}^\text{eff}$ become

\[ \dot{\xi}_1 \equiv \dot{x}_1 \equiv \dot{x} = M_{\text{eff}}^{-1} p_{\text{eff}}, \]  

\[ \dot{p}_{\text{eff}} = - \frac{\partial \phi}{\partial \xi_1} \equiv - \frac{1}{P} \sum_{j=1}^{P} \frac{\partial V (x_j)}{\partial x_j}, \]  

\[ \dot{\xi}_j = \tilde{m}_j^{-1} p_j, \]  

\[ \dot{p}_j = - \tilde{m}_j \omega_j^2 \xi_j - \frac{\partial \phi}{\partial \xi_j} (j = 2, \ldots, P). \]  

Equation (39) is identical to Eq. (32) by virtue of the transformation of Eqs. (33) and (34). Thus, one sees that PILD can also be viewed as a path integral representation of EHD in the Wigner phase space.

Interestingly, the effective Hamiltonian Eq. (38) and the equations of motion (39) can be related to the adiabatic Wigner PIMD (AWPIMD) proposed by Martyna and Cao nearly 20 years ago. (We were not aware of their work when we were preparing the paper.) Nevertheless, the major differences between PILD and AWPIMD are

1. PILD employs Eq. (9)—an exact mapping of the thermal correlation function in the Wigner phase space, 20, 31 which leads to exact results in the harmonic limit for any time correlation functions even when nonlinear operators are involved. This is derived from Liouville’s theorem in quantum mechanics (i.e., the Von Neumann
equation) for the generalized density operator \( \hat{A}^\beta(t) = \frac{1}{(2\pi)^{D/2}} e^{-i\hat{H}t/\hbar} \hat{A} e^{i\hat{H}t/\hbar} \) as shown in Refs. 29 and 31. As comparison, the approach to evaluate the thermal correlation function in AWPIMD as explicitly discussed in Sec. II C of Ref. 56 does not guarantee exact results in the harmonic limit for correlation functions with any nonlinear operators.

(2) As pointed out by Martyna and Cao,55,56 the effective masses of AWPIMD “must be introduced in an appropriate set of normal modes,” which is not convenient to use for dynamics of molecular systems. The thermal mass matrix [Eq. (16)] or the effective mass matrix [Eq. (34)] introduced in PILD, however, is defined (and evaluated) in the Cartesian coordinates. As a result, PILD is much more convenient to use for general multi-dimensional systems.

V. NUMERICAL EXAMPLES

A. Algorithm for PILD with Langevin thermostat

In the paper, we employ a simple (white noise) Langevin dynamics39,48 to thermostat the staging path integral variables \((\xi_1, \ldots, \xi_P, p_1, \ldots, p_P)\) in PILD. Equation (32) becomes

\[
\begin{align*}
\dot{\xi}_1 &= \dot{x}_1 = M^{-1} p, \\
\dot{\rho}_1 &= \dot{\rho} = -M_{\text{therm}}^{-1} \frac{\partial \phi}{\partial \xi_1} \\
&= -M_{\text{therm}}^{-1} \left( \frac{1}{P} \sum_{j=1}^{P} \frac{\partial V(x_j)}{\partial x_j} \right), \\
\dot{\xi}_j &= \dot{m}^{-1}_j p_j, \\
\dot{p}_j &= -m_j \omega^2 \xi_j - \frac{\partial \phi}{\partial \xi_j} - \gamma_{\text{Lang}} p_j \\
&+ \sqrt{\frac{2m_j \gamma_{\text{Lang}}}{\beta}} \eta_j(t) \quad (j = 2, P),
\end{align*}
\]

where \(\eta_j(t)\) is an independent Gaussian-distributed random number with zero mean and unit variance \(\{\eta_j(t) = 0\text{ and } \langle \eta_j(t)\eta_j(t') \rangle = \delta(t - t')\}\), which is different for each physical degree of freedom, each staging mode \((j = \sum, P)\), and each time step. The Langevin friction coefficient \(\gamma_{\text{Lang}}\) is the same for all staging modes \((j = \sum, P)\) because they share the same frequency \(\omega_{\text{ad}}\).

When the system is a free particle, the Langevin dynamics of each staging mode \((j = \sum, P)\) reduces to that of a harmonic oscillator with the frequency \(\omega_{\text{ad}}\), i.e.,

\[
\begin{align*}
\dot{\xi}_j &= \dot{m}^{-1}_j p_j, \\
\dot{p}_j &= -m_j \omega^2 \xi_j - \gamma_{\text{Lang}} p_j \\
&+ \sqrt{\frac{2m_j \gamma_{\text{Lang}}}{\beta}} \eta_j(t) \quad (j = \sum, P).
\end{align*}
\]

Following Refs. 39 and 57, one can choose the Langevin friction coefficient \(\gamma_{\text{Lang}}\) as

\[
\gamma_{\text{Lang}}^{\text{opt}} = 2\omega_{\text{ad}}
\]

that gives the smallest relevant autocorrelation time of the harmonic oscillator Hamiltonian

\[
\tilde{H} = \frac{p^2_j}{2m_j} + \frac{1}{2} m_j \omega^2 \xi^2_j.
\]

Note that the autocorrelation time

\[
\tau_{\tilde{H}} = \frac{1}{\gamma_{\text{Lang}}} \frac{\gamma_{\text{Lang}}}{4\omega^2_{\text{ad}}}
\]

for the Langevin dynamics in Eq. (41). So Eq. (42) is suggested as the optimum value of Langevin friction coefficient \(\gamma_{\text{Lang}}\) in Eq. (4) for PILD because it is expected to offer the most efficient sampling for the staging path integral variables \((\tilde{\xi}_2, \ldots, \tilde{\xi}_P)\) [in the free particle limit]. We will further demonstrate that the PILD result is insensitive to the choice of the friction coefficient \(\gamma_{\text{Lang}}\) around the optimum regime.
The velocity Verlet algorithm can be constructed for integrating the equations of motion in Eq. (40) for PILD (as done for molecular dynamics by Bussi and Parrinello\textsuperscript{48} and for PIMD by Ceriotti \textit{et al.}\textsuperscript{39}). Such an algorithm for propagating the PILD trajectory through a time interval $\Delta t$ is as follows:

$$p_j \leftarrow c_1 p_j + c_2 \sqrt{\tilde{m}_j} \beta \eta_j \quad (j = 2, P),$$  

$$p_1 \leftarrow p_1 - M_{\text{therm}}^{-1} \frac{\partial \phi}{\partial \xi_1} \frac{\Delta t}{2},$$  

$$p_j \leftarrow p_j - \frac{\partial \phi}{\partial \xi_j} \frac{\Delta t}{2} \quad (j = 2, P),$$  

$$\xi_1 \leftarrow \xi_1 + M^{-1} p_1 \Delta t$$

$$\begin{pmatrix} \xi_j \\ p_j \end{pmatrix} \leftarrow \begin{pmatrix} \cos(\omega_{ad} \Delta t) & \sin(\omega_{ad} \Delta t) / \tilde{m}_j \omega_{ad} \\ -\tilde{m}_j \omega_{ad} \sin(\omega_{ad} \Delta t) & \cos(\omega_{ad} \Delta t) \end{pmatrix} \begin{pmatrix} \xi_j \\ p_j \end{pmatrix} \quad (j = 2, P),$$  

$$c_1 = \exp[-\gamma_{\text{Lang}} \Delta t / 2],$$  

$$c_2 = \sqrt{1 - (c_1)^2}.\quad (51)$$

Here, $\eta_j$ is the independent Gaussian-distributed random number as discussed for Eq. (40), which is different for each invocation of Eq. (46) or Eq. (50), and the coefficients $c_1$ and $c_2$ are\textsuperscript{39,48}

$$p_1 \leftarrow p_1 - M_{\text{therm}}^{-1} \frac{\partial \phi}{\partial \xi_1} \Delta t / 2,$$  

$$p_j \leftarrow p_j - \frac{\partial \phi}{\partial \xi_j} \Delta t / 2 \quad (j = 2, P),$$  

$$p_j \leftarrow c_1 p_j + c_2 \sqrt{\tilde{m}_j} \beta \eta_j \quad (j = 2, P).$$  

While the forces in Eq. (47) are obtained from the previous time step, those in Eq. (49) at the current time step can be efficiently evaluated by the chain rule Eq. (25). One sees that the inverse staging transformation Eq. (20) is invoked only once [for Eq. (49)] in the integrator [Eqs. (46)--(50)] and the staging transformation Eq. (19) is not involved at all.

We note that Leimkuhler and Matthews\textsuperscript{58,59} have recently investigated a few Langevin dynamics integrators, it will be
FIG. 5. (a) and (b) The PILD autocorrelation functions for the one-dimensional anharmonic oscillator for $\beta = 8$ with the choice of the friction coefficient $\gamma_{\text{Lang}}$ when the Langevin thermostat is employed. Black solid line: $\gamma_{\text{Lang}} = 0.01 \gamma_{\text{opt}}$. Red dotted line: $\gamma_{\text{Lang}} = 0.1 \gamma_{\text{opt}}$. Blue short-long-dashed line: $\gamma_{\text{Lang}} = \gamma_{\text{opt}}$. Green dotted-dashed line: $\gamma_{\text{Lang}} = 10 \gamma_{\text{opt}}$. (Here, the adiabatic parameter is $\gamma_{\text{ad}} = 10^{-6}$.)

interesting to employ and test some of them (such as the BAOAB method) for PILD in the future.

B. Model tests

We consider two correlation functions $\langle p(0)p(t) \rangle_{\text{Kubo}}$ and $\langle x^2(0)x^2(t) \rangle_{\text{std}}$, with $\hat{A}^\beta = \hat{p}^\beta_{\text{Kubo}}$ and $\hat{A}^\beta = e^{-\beta H} \hat{x}^2$ in Eq. (1), respectively. Expressing the correlation functions in the Wigner phase space [i.e., Eq. (9)] as is often done for the LSC-IVR/classical Wigner model leads to

$$f^W_{\hat{A}^\beta}(x, p) = M^{-1} \rho_{\text{therm}}$$

for $\hat{A}^\beta = \hat{p}^\beta_{\text{Kubo}}$ and

$$\text{Re}[f^W_{\hat{A}^\beta}(x, p)] = x^2 + \frac{\beta \hbar^2}{4} M_{\text{therm}}^{-1} - \frac{\beta^2 \hbar^2}{4} (M^{-1}_{\text{therm}} \rho)^2 M_{\text{therm}}^{-1}\rho$$

(53)

for the real part for $\hat{A}^\beta = e^{-\beta H} \hat{x}^2$. The Wigner function $B_W(x, p)$ is the classical function (of $\hat{B}$) itself in either correlation function.

The two models are the asymmetric anharmonic potential $V(x) = \frac{1}{2} M \omega^2 x^2 - 0.10 x^3 + 0.10 x^4$ (54) (with $M = 1$, $\omega = \sqrt{2}$, and $\hbar = 1$) and a more severe model – the pure quartic well

$V(x) = x^4/4$ (55)

(with $M = 1$ and $\hbar = 1$). Since PILD approaches LSC-IVR in the high temperature limit, we focus on a low temperature $\beta = 8$. The exact quantum correlation functions and the LSC-IVR results have been presented for comparison.

Figs. 2–5 show the PILD results for the first model [Eq. (54)]. As seen in Fig. 2, converged correlation functions are obtained with $\gamma_{\text{ad}} = 10^{-6}$ (with a time step $dt = 10^{-5} \sim 10^{-4}$). They match the exact quantum results almost perfectly, except a slight frequency shift and slight dephasing in the amplitude at long times as shown in Fig. 3. Both Figs. 2 and 3 demonstrate that the correlation function is in progressively better agreement with the quantum result at
longer times as the adiabatic parameter $\gamma_{ad}$ decreases. Interestingly, Fig. 4 shows that PILD with even a relatively larger adiabatic parameter $\gamma_{ad} = 10^{-3}$ or $10^{-4}$ (with a time step $dt \sim 10^{-3}$) is able to show systematical improvement over LSC-IVR at longer times. Fig. 5 shows how the PILD results change with the friction coefficient $\gamma_{\text{Lang}}$ when PILD is employed with the Langevin thermostat. When $\gamma_{\text{Lang}}$ is around the optimum value [Eq. (42)] or smaller, the PILD results are insensitive to the choice of the friction coefficient.

The PILD results for the pure quartic well [Eq. (55)] are demonstrated in Figs. 6–9. Figs. 6 and 7 show that the correlation function agrees increasingly better with the exact result at longer times as $\gamma_{ad}$ decreases. Converged data are obtained with $\gamma_{ad} = 10^{-6}$ (with a time step $dt = 10^{-5} \sim 10^{-4}$). The comparison with the exact results in Fig. 7 show that PILD describes the amplitude of oscillation reasonably well with a noticeable frequency shift after the first period, which significantly improves over LSC-IVR that shows too quick dephasing after one vibrational period. Fig. 8 further shows that systematical improvement over LSC-IVR at longer times can be achieved by PILD with even a relatively larger adiabatic parameter $\gamma_{ad} = 10^{-2}$ or $10^{-3}$ (with a time step $dt \sim 10^{-3}$). Similar to Fig. 5, Fig. 9 also shows that the PILD correlation function is insensitive to the choice of the friction coefficient $\gamma_{\text{Lang}}$ when it is around the suggested optimum value [Eq. (42)] or even smaller.

As comparison, it is well known that either CMD or RPMD works poorly for the correlation function of which both operators [â and b in Eq. (1)] are nonlinear operators.\cite{31,32,50–54,60,61} For instance, Fig. 1 of Ref. 50, Fig. 1 of Ref. 31, and Fig. 1 of Ref. 32 demonstrate that neither CMD nor RPMD leads to correct results for $\langle x^2(0)x^2(t) \rangle_{Kubo}$ even for a one-dimensional harmonic well. In addition to Fig. 5 of Ref. 60, Fig. 3 or Fig. 10 of Ref. 53 shows that CMD or RPMD produces poor results for $\langle x^2(0)x^2(t) \rangle_{Kubo}$ for a one-dimensional anharmonic potential or the pure quartic well [Eq. (55)]. Since these results have already been demonstrated and discussed in the literature, we do not include them in the paper.

C. Discussion

It is shown that ELD\cite{17,18} or EHD\cite{32} fails to describe quantum recurrence/rephrasing effects, so does the PILD approach. However, long-time quantum recurrence/rephrasing effects (often shown in one-dimensional bounded systems) are anticipated to be quenched by coupling among the various
degrees of freedom in condensed phase systems. As seen from the model tests (Figs. 2–9), PILD can accurately capture the most important short time dephasing behavior and extend the accuracy of correlation functions of both linear and nonlinear operators to longer time (comparing with LSC-IVR and other comparable methods). Because comparison of LSC-IVR to experiment has demonstrated that the physical decay often dominates in many condensed phase systems, it offers a potentially useful approach for general condensed phase molecular systems to have the two important properties listed in Sec. I.

Finally, we note that both LSC-IVR and PILD produce exact correlation functions (of both linear and nonlinear operators) in the harmonic limit (i.e., the second property listed in Sec. I). While PILD conserves the mapping canonical density distribution (the first property listed in Sec. I), LSC-IVR preserves the mapping Hamiltonian (in the Wigner phase space) that is equivalent to the classical energy. The former corresponds to the quantum commutation

$$\left[ e^{-\beta \hat{H}}, e^{-i \hat{H} t/\hbar} \right] = 0,$$

and the latter is the counterpart of the commutation

$$\left[ \hat{H}, e^{-i \hat{H} t/\hbar} \right] = 0.$$  

It will be interesting in future work to test PILD for various correlation functions in condensed phase molecular systems, for which LSC-IVR/classical Wigner already works rather well for short time dynamics. It would also certainly be of interest to compare PILD to other imaginary time path integral based methods such as CMD and RPMD for realistic molecular systems.

**Note added in proof:** In the reviewing process, we became aware of the work by Martyna and Cao on the adiabatic Wigner PIMD. We thank the 1st referee for pointing it out.

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