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Jian Liu

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Two more approaches for generating trajectory-based dynamics which conserves the canonical distribution in the phase space formulation of quantum mechanics

Jian Liu[a)]
Department of Chemistry and K. S. Pitzer Center for Theoretical Chemistry, University of California, and Chemical Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720-1460, USA

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We show two more approaches for generating trajectory-based dynamics in the phase space formulation of quantum mechanics: "equilibrium continuity dynamics" (ECD) in the spirit of the phase space continuity equation in classical mechanics, and "equilibrium Hamiltonian dynamics" (EHD) in the spirit of the Hamilton equations of motion in classical mechanics. Both ECD and EHD can recover 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. Both ECD and EHD conserve the quasi-probability within the infinitesimal volume $dx_t dp_t$ around the phase point (x_t, p_t) along the trajectory. Numerical tests of both approaches in the Wigner phase space have been made for two strongly anharmonic model problems and a double well system, for each potential auto-correlation functions of both linear and nonlinear operators have been calculated. The results suggest EHD and ECD are two additional potential useful approaches for describing quantum effects for complex systems in condense phase. © *2011 American Institute of Physics*. [doi:10.1063/1.3589406]

I. INTRODUCTION

Phase space formulations of quantum mechanics[1–4] provide a natural framework for making the quantum-classical correspondence or analogy. By making an analogy to Liouville's theorem in classical mechanics, we proposed [in Paper I (Ref. 5)] an approach for generating trajectory-based dynamics which conserves the canonical distribution in the quantum phase space for the thermal equilibrium system. We referred to the approach as "equilibrium Liouville dynamics" (ELD). For thermal equilibrium systems, ELD satisfies stationarity of the quantum canonical distribution function P^{eq}, i.e.,

$$\frac{\partial P^{eq}(x, p; t)}{\partial t} = 0. \tag{1}$$

It is shown [in Paper II (Ref. 6)] how the quantum time correlation function can be exactly expressed in the unified classification scheme of Cohen[1] in the phase space formulation of quantum mechanics, as a generalization of our earlier work.[7] We implemented the "equilibrium distribution approximation" (EDA) to allow use of any trajectory-based dynamics satisfying Eq. (1) for evaluation of thermal correlation functions in the framework. ELD is such a family of trajectory-based dynamics that can give the exact quantum correlation function (of even nonlinear operators, i.e., nonlinear functions of position or momentum operators) in the classical ($\hbar \to 0$), high-temperature ($\beta \to 0$), and harmonic limits.

Besides Liouville's theorem, the phase space continuity equation and the Hamilton equations of motion are two other approaches to describe the evolution of the system in classical mechanics. (Quantum dynamics recovers these approaches in the classical limit.) By making analogies to both approaches in the phase space formulation of quantum mechanics, one can propose two more ways for generating trajectory-based dynamics which conserves the canonical distribution in the quantum phase space [i.e., Eq. (1)]. We refer to the one in the spirit of the phase space continuity equation as "equilibrium continuity dynamics" (ECD), and the other in the spirit of the Hamilton equations of motion as "equilibrium Hamiltonian dynamics" (EHD). As we will discuss in following sections, both ECD and EHD can give the exact quantum correlation function in the three important limits as ELD does.

The purpose of the paper is to present the ECD and EHD approaches and their applications to thermal correlation functions. The paper is organized as follows: Sec. II first reviews the phase space continuity equation in classical mechanics, then proposes the ECD approach in the quantum phase space, and finally applies ECD to thermal correlation functions. Section III presents EHD—another type of trajectory-based approach in the phase space formulation of quantum mechanics, by making the analogy to the Hamilton equations of motion in classical mechanics. Some numerical applications for standard, Kubo-transformed, and symmetrized auto-correlation functions are demonstrated in Sec. IV, including two anharmonic models and a double well potential. Conclusions are given in Sec. V.

a)Electronic mail: jianliu@berkeley.edu.

II. TRAJECTORY-BASED DYNAMICS GENERATED IN THE SPIRIT OF THE PHASE SPACE CONTINUITY EQUATION IN CLASSICAL MECHANICS

A. Phase space continuity equation in classical mechanics

For the system with the Hamiltonian

$$H(x, p) = \frac{p^2}{2m} + V(x) \tag{2}$$

in classical mechanics, the equations of motion of the classical trajectory are

$$\begin{aligned} \dot{x} &= \frac{p}{m}, \\ \dot{p} &= -V'(x). \end{aligned} \tag{3}$$

Here m is the mass. For the density distribution function P, Liouville's theorem of the first kind [Eq. (27) in Paper I] can be written as

$$\frac{\partial}{\partial t} P(x, p; t) = -\frac{\partial P}{\partial x}\dot{x} - \frac{\partial P}{\partial p}\dot{p}. \tag{4}$$

We define the vector $\boldsymbol{v} = (x, p)^T$ and $\nabla_{\boldsymbol{v}} = (\partial/\partial x, \partial/\partial p)^T$ for the phase space variables. According to Eq. (3), the phase space velocity field $\dot{\boldsymbol{v}} = (\dot{x}, \dot{p})^T$ of the classical trajectory is sourceless, i.e.,

$$\nabla_{\boldsymbol{v}} \cdot \dot{\boldsymbol{v}} \equiv \frac{\partial}{\partial \boldsymbol{v}} \cdot \dot{\boldsymbol{v}} \equiv \frac{\partial \dot{x}}{\partial x} + \frac{\partial \dot{p}}{\partial p} = 0. \tag{5}$$

So Eq. (4) leads to

$$\frac{\partial}{\partial t} P(x, p; t) = -\frac{\partial}{\partial x}(P\dot{x}) - \frac{\partial}{\partial p}(P\dot{p}). \tag{6}$$

With the mass flux density $\mathbf{j}$ defined as

$$\mathbf{j} = P\dot{\boldsymbol{v}}, \tag{7}$$

Eq. (6) can be written as

$$\frac{\partial P}{\partial t} = -\nabla_{\boldsymbol{v}} \cdot \mathbf{j}. \tag{8}$$

We refer to Eq. (6) or Eq. (8) as the phase space continuity equation of the first kind. By virtue of the classical equations of motion [i.e., Eq. (3)], an equivalent expression of Eq. (6) is

$$\frac{\partial}{\partial t} P(x, p; t) = -\frac{\partial}{\partial x}\left(P\frac{p}{m}\right) + \frac{\partial}{\partial p}\left(P\frac{\partial V(x)}{\partial x}\right), \tag{9}$$

which we refer to as the phase space continuity equation of the second kind.

Vice versa, one can derive the classical equations of motion [Eq. (3)] from the phase space continuity equation of the two kinds [Eq. (8) and Eq. (9)], by defining $\dot{x} = p/m$ to be the relation between the position and momentum in the phase space. Note that the phase space continuity equation of both kinds [Eq. (8) and Eq. (9)] are in the Eulerian picture (i.e., the coordinate system is fixed) since only partial time derivatives of the density distribution function are involved.

The physical meaning of $P(x, p)dxdp$ in classical mechanics[8] represents the number of systems dN_s in the infinitesimal region $dxdp$ around the phase space point (x, p). If we "flow with the fluid" (i.e., follow trajectories, in the Lagrangian picture), the phase space continuity equation [Eq. (8)] leads to the equality for the mass transport,

$$P(x_0, p_0; 0)\, dx_0 dp_0 = P(x_t, p_t; t)\, dx_t dp_t. \tag{10}$$

Equation (10) means that the number of systems is conserved locally along the trajectory in classical mechanics. Appendix A shows that Eq. (10) is in general an alternative statement of the phase space continuity equation of the first kind [Eq. (8)].

B. A heuristic viewpoint for deriving the force from the canonical distribution function for the thermal equilibrium system

For thermal equilibrium systems, the classical Boltzmann/canonical distribution $P^{eq}(x, p)$ is

$$P^{eq}(x, p) = \left(\frac{\beta}{2\pi m}\right)^{1/2} e^{-\beta\left(\frac{p^2}{2m} + V(x)\right)} = \left(\frac{\beta}{2\pi m}\right)^{1/2} e^{-\beta H(x,p)}, \tag{11}$$

with the classical partition function as the normalization factor

$$Z = \int dx\, e^{-\beta V(x)} = \int dx \int dp\, P^{eq}(x, p). \tag{12}$$

The canonical distribution function $P^{eq}(x, p)$ is stationary [i.e., Eq. (1)]. Substituting Eq. (1) into the phase space continuity equation of the second kind Eq. (9), one obtains

$$\frac{\partial}{\partial p}\left(P^{eq}(x, p)\frac{\partial V(x)}{\partial x}\right) = \frac{\partial}{\partial x}\left(P^{eq}(x, p)\frac{p}{m}\right). \tag{13}$$

The integration over the momentum in the above equation leads to

$$P^{eq}(x, p)\frac{\partial}{\partial x}V(x) = \int_{-\infty}^{p} dp' \frac{\partial P^{eq}(x, p')}{\partial x}\frac{p'}{m}. \tag{14}$$

(Note the boundary condition $\lim_{p\to-\infty} P^{eq}(x, p) = 0$.) One can verify that Eq. (14) gives an equivalent form to calculate the classical force $-V'(x)$ by using the canonical distribution function $P^{eq}(x, p)$ of the thermal equilibrium system. Since the classical canonical distribution function $P^{eq}(x, p)$ [Eq. (11)] is uniquely defined and continuous in the phase space, the classical force $-V'(x)$ given in Eq. (14) is thus well-defined.

For thermal equilibrium systems in classical mechanics, one can always define the classical equations of motion [i.e., Eq. (3)] based on the phase space continuity equation with the classical force given by Eq. (14). This insight provides a heuristic procedure for making the quantum-classical correspondence or analogy in the phase space formulation of quantum mechanics.

C. Equilibrium continuity dynamics

Similar to the phase space continuity equation of the second kind in classical mechanics [Eq. (9)], one can express the form of the quantum Liouville theorem [Eq. (35) of Paper I]

in the phase space formulation of quantum mechanics as

$$\frac{\partial}{\partial t}P(x,\,p;t) = -\frac{\partial}{\partial x}\left(P\frac{p}{m}\right) + \frac{\partial}{\partial p}\left(P\frac{\partial}{\partial x}V_{eff}(x,\,p)\right). \tag{15}$$

For example, the effective force $-\partial/\partial x V_{eff}(x,\,p)$ in Eq. (15) can be expressed as

$$P_W(x,\,p;t)\frac{\partial V_{eff}(x,\,p)}{\partial x} = P_W V'(x) - \frac{\hbar^2}{24}\frac{\partial^2 P_W}{\partial p^2}V^{(3)}(x) + \cdots \tag{16}$$

in the Wigner phase space representation according to Eq. (36) of Paper I (e.g., as Donoso and Martens suggested[9]), and

$$\begin{aligned} P_H(x,\,p;t)\frac{\partial V_{eff}(x,\,p)}{\partial x} = {} & P_H V'(x) - \frac{\hbar^2\Gamma}{2m}\frac{\partial P_H}{\partial x} \\ & + \hbar\frac{V^{(2)}(x)}{2!}\langle x,\,p|\left(-i\frac{\overleftarrow{\partial}}{\partial p}\right)\frac{\hat{\rho}}{2\pi\hbar} \\ & + \frac{\hat{\rho}}{2\pi\hbar}\left(-i\frac{\overrightarrow{\partial}}{\partial p}\right)|x,\,p\rangle \\ & + \hbar^2\frac{V^{(3)}(x)}{3!}\langle x,p|\left(-i\frac{\overleftarrow{\partial}}{\partial p}\right)^2\frac{\hat{\rho}}{2\pi\hbar} \\ & + \left(-i\frac{\overleftarrow{\partial}}{\partial p}\right)\frac{\hat{\rho}}{2\pi\hbar}\left(-i\frac{\overrightarrow{\partial}}{\partial p}\right) \\ & + \frac{\hat{\rho}}{2\pi\hbar}\left(-i\frac{\overrightarrow{\partial}}{\partial p}\right)^2|x,\,p\rangle + \cdots \end{aligned} \tag{17}$$

in the Husimi phase space representation by virtue of Eq. (37) of Paper I (e.g., similar to what Skodje *et al.* proposed[10]). [See Appendix B for more discussion.]

One sees the quantum-classical correspondence between Eq. (15) and its classical counterpart Eq. (9). Similar to the viewpoint that stationarity of the classical canonical distribution function enables one to obtain the classical force [Eq. (13)] according to the phase space continuity equation of the second kind [Eq. (9)], stationarity of the quantum canonical distribution function [i.e., Eq. (1)] provides a way to obtain the effective force $-\partial V_{eff}(x,\,p)/\partial x$,

$$\frac{\partial}{\partial p}\left(P^{eq}(x,\,p)\frac{\partial}{\partial x}V_{eff}(x,\,p)\right) = \frac{\partial P^{eq}(x,\,p)}{\partial x}\frac{p}{m}, \tag{18}$$

by virtue of Eq. (15). The integration over the momentum in the above equation leads to

$$P^{eq}(x,\,p)\frac{\partial}{\partial x}V_{eff}(x,\,p) = \int_{-\infty}^{p} dp\frac{\partial P^{eq}(x,\,p)}{\partial x}\frac{p}{m}. \tag{19}$$

Due to the *one-to-one* correspondence mapping, once a phase space is constructed based on a (real) distribution function in Sec. II of Paper I, the quantum canonical distribution function $P^{eq}(x,\,p)$ is then uniquely defined and continuous in the phase space. So Eq. (19) always gives a uniquely defined and continuous effective force $-\partial/\partial x V_{eff}(x,\,p)$ for any phase point $(x,\,p)$ (for one-dimensional systems). [See further discussion on multi-dimensional systems in Appendix D.]

If the trajectory-based dynamics is chosen to satisfy

$$\frac{\partial}{\partial t}P^{eq}(x,\,p;t) = -\frac{\partial}{\partial x}(P^{eq}\dot{x}) - \frac{\partial}{\partial p}(P^{eq}\dot{p}) \tag{20}$$

as an analogy to the phase space continuity equation of the first kind [Eq. (6) or Eq. (8)], one can use Eq. (20) and Eq. (15)—an alternative expression of the quantum Liouville theorem in the phase space formulation of quantum mechanics—to obtain

$$\begin{aligned} & \frac{\partial}{\partial x}\left[P^{eq}(x,\,p;t)\left(\dot{x} - \frac{p}{m}\right)\right] \\ & + \frac{\partial}{\partial p}\left[P^{eq}(x,\,p;t)\left(\dot{p} + \frac{\partial}{\partial x}V_{eff}(x,\,p)\right)\right] = 0. \end{aligned} \tag{21}$$

[Note that Eq. (21) can be derived from Eq. (15) and Eq. (20) even for non-equilibrium density distribution functions $P(x,\,p;t)$.] As before, we define $\dot{x} = p/m$ to be the relation between the position and momentum, which is independent of the density distribution function and independent of the system. According to Eq. (15) and Eq. (20), Eq. (21) holds for any phase point $(x,\,p)$ along the trajectory at any time for any density distribution function, then the solution to Eq. (21) consistent with all these conditions leads to the equations of motion for the trajectory,

$$\begin{aligned} \dot{x} &= \frac{p}{m}, \\ \dot{p} &= -\frac{\partial}{\partial x}V_{eff}(x,\,p). \end{aligned} \tag{22}$$

Due to Eq. (15), the equations of motion in Eq. (22) with the effective force given by the canonical distribution function $P^{eq}(x,\,p)$ [Eq. (19)] can generate a trajectory-based dynamics which conserves the canonical distribution function [Eq. (1)] in the quantum phase space based on any distribution function discussed in Sec. II of Paper I. We have *already* proposed the trajectory-based dynamics [i.e., Eq. (22) with Eq. (19)] in the Wigner phase space formulation in our earlier paper[7] (i.e., so called "full Donoso-Martens dynamics"). Here, we show the approach can be generalized for other distribution functions. We refer to the family of dynamics as "equilibrium continuity dynamics" (ECD).

We note that Eq. (20) can *not* be derived from the quantum Liouville theorem even though the phase space continuity equation of the first kind Eq. (6) is obtained from classical Liouville's theorem. The Heisenberg uncertainty principle prevents a unique definition for the equations of motion for trajectories in the phase space formulation of quantum mechanics. One sees the quantum-classical correspondence [between Eq. (9) and Eq. (15)] and non-correspondence [between Eq. (6) and Eq. (20)] in the phase space formulation of quantum mechanics. Equation (20) is a way to generate a family of trajectory-based dynamics (i.e., ECD) in the spirit of the phase space continuity equation of the first kind [Eq. (6)].

D. ECD trajectories and canonical ensemble averages

The ECD dynamics [i.e., Eq. (22) with Eq. (19)] has four important properties. First, the quasi-probability within the initial infinitesimal volume dx_0dp_0 around the initial phase point (x_0, p_0) is conserved as the ECD trajectory propagates, i.e.,

$$P^{eq}(x_0, p_0; 0)\, dx_0 dp_0 = P^{eq}(x_t, p_t; t)\, dx_t dp_t \tag{23}$$

Equation (23) follows from the proof in Appendix A because the ECD trajectory satisfies Eq. (20). Substituting Eq. (C11) in Appendix C of Paper I into Eq. (A2) in Appendix A, one obtains

$$P^{eq}(x_t, p_t; t) = P^{eq}(x_0, p_0; 0) \times \exp\left[\int_0^t \frac{\partial^2}{\partial p_{t'}\partial x_{t'}} V_{eff}(x_{t'}, p_{t'})\, dt'\right]. \tag{24}$$

One sees that $P^{eq}(x_t, p_t; t)$ is not constant as long as the ECD effective force $-\partial/\partial x_t V_{eff}(x_t, p_t)$ in Eq. (19) is a momentum dependent function. ECD preserves $P^{eq}(x_t, p_t)\, dx_t dp_t$, while ELD conserves $P^{eq}(x_t, p_t)$.

Similarly, one can show ECD shares with ELD all the other three properties listed in Sec. IV of Paper I. By virtue of these properties of ECD, it can provide a robust algorithm for describing quantum effects in complex systems in condensed phase. One can use Eq. (C1) or Eq. (C2) in Appendix C to evaluate a dynamic physical property for thermal equilibrium systems, i.e.,

$$\langle B(t)\rangle = \frac{1}{Z}\int dx_t \int dp_t\; P^{eq}(x_t(x_0, p_0), p_t(x_0, p_0); t) \times \tilde{B}(x_t(x_0, p_0), p_t(x_0, p_0)) = \frac{1}{Z}\int dx_0 \int dp_0 \times P^{eq}(x_0, p_0; 0)\tilde{B}(x_t(x_0, p_0), p_t(x_0, p_0)). \tag{25}$$

Because ECD conserves the quantum canonical distribution function by construction [i.e., Eq. (18)], one can show that thermodynamic properties $\langle B(t)\rangle$ and their fluctuations are invariant with time, i.e.,

$$\langle B(t)\rangle = \langle B(0)\rangle. \tag{26}$$

Implementing a time average in Eq. (25) for ECD, one can obtain Eqs. (52) and (53) of Paper I as well for ensemble averages for thermal equilibrium systems.

E. Choice of the phase space distribution function

Following the same arguments in Sec. IV C of Paper I, one can show that the ECD dynamics approaches classical dynamics in either the classical ($\hbar \to 0$) or high temperature ($\beta \to 0$) limit, regardless of which distribution function (discussed in Sec. II of Paper I) is employed to construct the phase space. So the harmonic limit is the criterion to choose the phase space distribution function for ECD.

When the Wigner distribution function is used, the canonical distribution function for the 1-dimensional harmonic potential $V(x) = \frac{1}{2}m\omega^2x^2$ is

$$P_W^{eq}(x, p) = \frac{1}{2\pi\hbar\cosh[u/2]} \times \exp\left[-\frac{\beta}{Q(u)}\left(\frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2\right)\right], \tag{27}$$

with the dimensionless parameter

$$u = \beta\hbar\omega, \tag{28}$$

and the quantum correction factor $Q(u)$ as

$$Q(u) = \frac{u/2}{\tanh[u/2]}. \tag{29}$$

It is trivial to show that the ECD effective force by Eq. (19) leads to the classical force in this case, i.e.,

$$-\frac{\partial V_{eff}^{ECD}(x, p)}{\partial x} = -m\omega^2 x. \tag{30}$$

The canonical distribution function in the Husimi phase space for the harmonic system is

$$P_H^{eq}(x, p) = \frac{1}{2\pi\hbar\sinh[u/2]} \times \left(\frac{\Gamma m u^2}{(\beta\hbar^2\Gamma + 2mQ(u))(2\Gamma Q(u) + \beta m\omega^2)}\right)^{1/2} \times \exp\left[-\frac{p^2}{(\hbar^2\Gamma + 2mQ(u)/\beta)} - \frac{\Gamma\beta m\omega^2}{2\Gamma Q(u) + \beta m\omega^2}x^2\right]. \tag{31}$$

Similarly, one can show that the ECD effective force by Eq. (19) reduces to the classical force, when the Husimi distribution function is used with the width parameter as

$$\Gamma = \frac{m\omega}{\hbar}, \tag{32}$$

i.e., when the Husimi distribution function goes to the Glauber Q function.[11] For the general anharmonic potential, one will have to find the optimal value (regime) for the width parameter Γ.

As one can verify, the Wigner function, the Husimi function, and the Glauber Q function are among those distribution functions that are able to make ECD approach classical dynamics in the harmonic limit. (Note that the Glauber Q function can be viewed as a special case of the Husimi function.) We refer to the ECD dynamics in the Wigner phase space as Wigner ECD (W-ECD). Similarly, we refer to ECD in the Husimi phase space as Husimi ECD (H-ECD). H-ECD has an adjustable parameter Γ while W-ECD has none.

With the same procedure in Sec. V of Paper I, one can show the centroid molecular dynamics (CMD) of Voth and coworkers[12,13] can be closely related to and even reformulated in the ECD approach.

F. Application to the thermal correlation function

In Paper II, we showed the exact expression of the quantum time correlation function in the phase space formulation

of quantum mechanics [i.e., Eq. (4) of Paper II]. The "equilibrium distribution approximation" (EDA) in Paper II allows use of any trajectory-based dynamics which conserves the canonical distribution in the quantum phase space for evaluation of the exact expression. That is,

$$\langle A(0)\,B(t)\rangle = \frac{1}{Z}\int dx_0 \int dp_0\; P^{eq}(x_0, p_0; 0) \times f_{A^\beta}(x_0, p_0; 0)\,\tilde{B}(x_t, p_t)\,, \tag{33}$$

where $Z = \mathrm{Tr}[e^{-\beta\hat{H}}]$ is the partition function, and $\tilde{B}$ and f_{A^β} are defined by Eqs. (6) and (21) of Paper II, respectively.

By virtue of EDA, ECD applies to Eq. (33) as well. One has

$$\begin{aligned}\langle A(t')B(t'+t)\rangle &= \frac{1}{Z}\int dx_{t'}\int dp_{t'}\; P^{eq}(x_{t'}, p_{t'}; t') \times f_{A^\beta}\left(x_{t'}, p_{t'}; t'\right)\tilde{B}\left(x_{t'+t}, p_{t'+t}\right)\\ &= \frac{1}{Z}\int dx_0\int dp_0\; P^{eq}(x_0, p_0; 0) \times f_{A^\beta}(x_{t'}, p_{t'}; t')\tilde{B}(x_{t'+t}, p_{t'+t})\end{aligned} \tag{34}$$

for ECD. It is straightforward to verify ECD gives the same results for Eq. (33) and for Eq. (34), according to Appendix C.

A time average of Eq. (34) leads to

$$\begin{aligned}C_{AB}(t) &= \frac{1}{T}\int_0^T dt'\langle A(t')B(t'+t)\rangle\\ &= \frac{1}{Z}\int dx_0\int dp_0\; P^{eq}(x_0, p_0; 0)\left[\frac{1}{T}\int_0^T dt' \times f_{A^\beta}(x_{t'}, p_{t'}; t')\tilde{B}(x_{t'+t}, p_{t'+t})\right].\end{aligned} \tag{35}$$

For ergodic systems, the above equation reduces to

$$C_{AB}(t) = \lim_{T\to\infty}\frac{1}{T}\int_0^T dt' f_{A^\beta}(x_{t'}, p_{t'}; t')\tilde{B}(x_{t'+t}, p_{t'+t})\,. \tag{36}$$

Note the difference between the first line of the RHS of Eq. (34) for ECD and that of Eq. (23) of Paper II for ELD. Except this point, ECD shares with ELD almost all the expressions for calculating thermal correlation functions. All the methods that we introduced for ELD in Paper II can be applied to ECD as well.

It is straightforward to show that ECD recovers exact thermal correlation functions in the classical ($\hbar \to 0$) and high temperature ($\beta \to 0$) limits. One can also prove that the W-ECD approach for the thermal correlation function reduces to the linearized semiclassical initial value representation (LSC-IVR)/classical Wigner model[7,14–24] and therefore gives correct quantum correlation functions (of even nonlinear operators) in the limit of a harmonic potential. Similarly, one can verify that this is also true for H-ECD with the width parameter given by Eq. (32).

III. TRAJECTORY-BASED DYNAMICS GENERATED IN THE SPIRIT OF THE HAMILTON EQUATIONS OF MOTION

A. Hamilton equations of motion in classical mechanics

For the system with the Hamiltonian as Eq. (2) in classical mechanics, another way to describe the dynamics is the Hamilton equations of motion, i.e.,

$$\begin{aligned}\dot{x}_t &= \frac{\partial H(x_t, p_t)}{\partial p_t},\\ \dot{p}_t &= -\frac{\partial H(x_t, p_t)}{\partial x_t},\end{aligned} \tag{37}$$

which give identical equations to Eq. (3).

For thermal equilibrium systems in classical mechanics, one can always use the canonical distribution function $P^{eq}(x, p)$ to define the Hamiltonian $H(x, p)$ from Eq. (11), and thus derive the classical equations of motion [i.e., Eq. (3)] based on the Hamilton equations of motion [i.e., Eq. (37)]. The insight provides another heuristic procedure for making the quantum-classical correspondence or analogy in the phase space formulation of quantum mechanics.

B. Equilibrium Hamiltonian dynamics

In principle, only the Husimi distribution function,[25] the Glauber Q function[11] and several others[26–28] for the Boltzmann operator are nonnegative, while other distribution functions lead to both positive and negative values. For many cases for which the local Gaussian approximations (LGAs) or the thermal Gaussian approximations (TGAs) are good enough (see more discussion in Paper II and Appendix E), such as the Wigner function for the Boltzmann operator with any of these approximations is also nonnegative. As discussed in our earlier work,[20] all the LGAs and TGAs lead to a (local) Gaussian approximation for the momentum distribution in the Wigner function for the Boltzmann operator. That is, the Wigner canonical distribution with any of these LGA approximations can be written in a general form as

$$P^{eq}(x, p) = \left(\frac{\beta}{2\pi}\right)^{1/2}|m_{therm}(x)|^{-1/2} \times \exp\left[-\beta\frac{p^2}{2m_{therm}(x)}\right]\langle x|\,e^{-\beta\hat{H}}\,|x\rangle\,, \tag{38}$$

where the (position-dependent) thermal mass $m_{therm}(x)$ is given by the approximation. (See further discussion in Appendix E.)

By making the analogy to Eq. (11), one can define the effective Hamiltonian $H_{eff}(x, p)$ from non-negative canonical distribution functions $P^{eq}(x, p)$. We first focus on the Wigner canonical distribution function. Consider first a 1-dim harmonic potential $V(x) = 1/2m\omega^2x^2$. The Wigner canonical distribution function for this system [i.e., Eq. (27)] can be written in the form as Eq. (38) with the "thermal mass" as

$$m_{therm} = mQ(u)\,. \tag{39}$$

One can verify that the effective Hamiltonian given by Eq. (11) does *not* generate the correct dynamics even for the harmonic case. This indicates that it is not useful to define the effective Hamiltonian in the original phase space (x, p). I.e., some transformation of the phase space variables is necessary.

We define the effective position x^{eff} and momentum p^{eff} as

$$x^{eff} = x, \tag{40}$$

and

$$p^{eff} = m_{eff} m^{-1} p, \tag{41}$$

respectively. Here the effective mass m_{eff} is given in such a way that the exponential term of the momentum distribution of the Wigner density [i.e., Eq. (38)] always satisfies

$$\beta \frac{(p^{eff})^2}{2m_{eff}} = \beta \frac{p^2}{2m_{therm}}. \tag{42}$$

The effective mass then becomes

$$m_{eff} = \frac{m^2}{m_{therm}}. \tag{43}$$

The module of the determinant of the Jacobian matrix for the transformation (Eqs. (40) and (41)) is

$$\left| \frac{\partial (x^{eff}, p^{eff})}{\partial (x, p)} \right| = \left| \frac{m_{eff}}{m} \right|. \tag{44}$$

For any transformation between (x, p) and (x', p') at any time t, the following equation for the density distribution function always holds,

$$P(x', p'; t) \left| \frac{\partial (x', p')}{\partial (x, p)} \right| = P(x, p; t). \tag{45}$$

From the transformation given by Eqs. (40) and (41) [i.e., $(x, p) \to (x^{eff}, p^{eff})$], one therefore obtains

$$P^{eq}_{eff}(x^{eff}, p^{eff}) = \left| \frac{m_{eff}}{m} \right|^{-1} P^{eq}(x, p). \tag{46}$$

[One sees from Eqs. (38)–(43) that the effective mass m_{eff} represents the associated scaled "mass" (in the local harmonic or Gaussian limit), while the position x of the phase space (x, p) corresponds to that of one path integral bead. Interestingly, one can show that the effective mass m_{eff} reduces to the physical mass m, while the position x is that of the centroid of the path integral beads [by virtue of Eqs. (62)–(70) in Sec. V of Paper I], which has been stated in the CMD model of Voth and co-workers[12,13].]

As an analogy to Eq. (11),

$$P^{eq}_{eff}(x^{eff}, p^{eff}) = \left(\frac{\beta}{2\pi m} \right)^{1/2} e^{-\beta H_{eff}\left(x^{eff}, p^{eff}\right)}. \tag{47}$$

defines the new effective Hamiltonian $H_{eff}(x^{eff}, p^{eff})$ from the "effective" canonical distribution function with the new variables (x^{eff}, p^{eff}). One can verify that Eq. (46) satisfies

$$\begin{aligned} Z &= \int dx \, \langle x | \, e^{-\beta \hat{H}} \, | x \rangle = \int dx \int dp P^{eq}(x, p) \\ &= \int dx^{eff} \int dp^{eff} P^{eq}_{eff}(x^{eff}, p^{eff}). \end{aligned} \tag{48}$$

By virtue of Eq. (38) and Eqs. (46) and (47), the new effective Hamiltonian becomes

$$\begin{aligned} H_{eff}(x^{eff}, p^{eff}) = \frac{(p^{eff})^2}{2m_{eff}(x)} - \frac{1}{\beta} \ln[\langle x | \, e^{-\beta \hat{H}} \, | x \rangle] \\ - \frac{1}{2\beta} \ln \left[\frac{m}{m_{eff}(x)} \right]. \end{aligned} \tag{49}$$

It is trivial to show the Hamilton equations of motion,

$$\begin{aligned} \dot{x}^{eff}_t &= \frac{\partial H_{eff}\left(x^{eff}_t, p^{eff}_t\right)}{\partial p^{eff}_t}, \\ \dot{p}^{eff}_t &= - \frac{\partial H_{eff}\left(x^{eff}_t, p^{eff}_t\right)}{\partial x^{eff}_t}, \end{aligned} \tag{50}$$

recover the exact equation of motion for x for the harmonic potential. From Eq. (41) and Eq. (50), one sees that the velocity keeps the same

$$\dot{x}_t \equiv \dot{x}^{eff}_t = m^{-1}_{eff} p^{eff}_t = m^{-1} p_t. \tag{51}$$

That is, $\dot{x}_t = m^{-1} p_t$ is still the relation between the position and momentum in the quantum phase space for the EHD approach. In the classical ($\hbar \to 0$) or the high temperature ($\beta \to 0$) limit, one has $u \to 0$, $Q(u) \to 1$, $m_{eff} \to m$, and $p^{eff} \to p$, so the trajectory-based dynamics also leads to classical dynamics.

It thus provides a way for generating a family of trajectory-based dynamics in the spirit of the Hamilton equations of motion, by defining the effective Hamiltonian from the quantum canonical distribution function. We refer to this family of dynamics as 'equilibrium Hamiltonian dynamics' (EHD). When the Wigner distribution function is employed, we refer to it as Wigner EHD (W-EHD). One can further generalize the procedure to other types of density distribution functions. For example, Eq. (38) can also be the general form for Husimi canonical distribution function $\langle x, p | \, e^{-\beta \hat{H}} \, | x, p \rangle$ for some types of approximations, as mentioned in Appendix E. Along similar lines, it is straightforward to derive the approach in the Husimi phase space. For instance, the effective mass is

$$m_{eff} = \frac{2m^2}{\beta \hbar^2 \Gamma + 2m Q(u)} \tag{52}$$

by virtue of Eq. (31) and Eqs. (42) and (43) in the Husimi phase space for the 1-dim harmonic potential $V(x) = 1/2 m\omega^2 x^2$. One can show that the approach recovers the exact equation of motion for x for the harmonic potential, when the Husimi distribution function is used with the width parameter as Eq. (32), i.e., when the Husimi distribution function goes to the Glauber Q function.[11] As before, one will have to find the optimal value (regime) for the width parameter Γ for the general anharmonic potential. We refer to this approach in the Husimi phase space as Husimi-EHD (H-EHD). H-EHD has an adjustable parameter Γ while W-EHD has none.

Following the same arguments in Section V of Paper I, one can show that CMD falls into the category of EHD trajectory-based dynamics in the phase space formulation of quantum mechanics.

As before, it is important to point out that the EHD trajectory-based dynamics [i.e., Eq. (50) with the effective Hamiltonian defined in Eqs. (46) and (47)] can *not* be derived from either the quantum Liouville theorem or Heisenberg's equation of motion in the phase space formulation of quantum mechanics. The phase space formulation of quantum mechanics provides us the framework for making the quantum-classical analogy from Eq. (11) and Eq. (37) of classical mechanics to Eqs. (46), (47) and Eq. (50) of EHD. EHD is a family of trajectory-based dynamics in the quantum phase space in the spirit of the Hamilton equations of motion in classical mechanics. In addition to ELD and ECD, EHD is another way for generating trajectory-based dynamics which conserves the quantum canonical distribution in the phase space formulation of quantum mechanics, and which reduces to classical dynamics in the classical, high temperature, and harmonic limits.

C. EHD trajectories

Once the effectively non-negative distribution function for the Boltzmann operator is chosen, the quantum canonical distribution function $P^{eq}(x, p)$ is uniquely defined and continuous in the phase space. The effective mass $m_{eff}(x)$ [such as Eq. (43)] and the effective Hamiltonian (Eqs. (46) and (47)) can therefore be uniquely well-defined from the quantum canonical distribution function $P^{eq}(x, p)$ for the thermal equilibrium system. [Note that (x^{eff}, p^{eff}) is a one-to-one correspondence mapping to the phase space point (x, p).]

One sees from Eq. (50) that EHD is a type of Hamiltonian dynamics. EHD trajectories behave much like classical trajectories. It is straightforward to show the EHD dynamics [i.e., Eq. (50) with the effective Hamiltonian defined in Eqs. (46) and (47)] conserves the effective Hamiltonian $H_{eff}(x^{eff}, p^{eff})$, the effective density distribution function $P^{eq}_{eff}(x^{eff}, p^{eff})$ [Eq. (47)], the value of the volume element, i.e.,

$$dx_t^{eff} dp_t^{eff} = dx_0^{eff} dp_0^{eff}, \tag{53}$$

(see Appendix D for further discussion), and the quasi-probability within the initial infinitesimal volume $dx_0^{eff} dp_0^{eff}$ around the initial variables (x_0^{eff}, p_0^{eff}), i.e.,

$$P^{eq}_{eff}\left(x_t^{eff}, p_t^{eff}; t\right) dx_t^{eff} dp_t^{eff} = P^{eq}_{eff}\left(x_0^{eff}, p_0^{eff}; 0\right) \times dx_0^{eff} dp_0^{eff}. \tag{54}$$

These properties suggest EHD can provide a robust algorithm for including quantum effects in (large) molecular systems.

Note that the phase space variables are rescaled in EHD. I.e., the effective momentum p^{eff} is rescaled in Eqs. (40) and (41). One sees that the effective momentum p^{eff} is not the conjugate variable to the position $x^{eff} \equiv x$ and thus not the *true* momentum of the *one-to-one* mapping in the phase space. Instead of the effective variables (x^{eff}, p^{eff}), one can use the true phase space variables (x, p) to express the EHD equations of motion as shown in the following subsection.

The central task for generating EHD is to obtain the effective mass $m_{eff}(x)$ (or the effective mass matrix $\mathbf{M}_{eff}(\mathbf{x})$ in the multi-dimensional system). When the partial distribution function for the momentum p at any fixed position x based on the canonical distribution function is not a *single* Gaussian function as in Eq. (38) (but a sum of Gaussian functions), the definition of the effective mass $m_{eff}(x)$ (or the effective mass matrix $\mathbf{M}_{eff}(\mathbf{x})$ in the multi-dimensional system) requires additional approximations. [E.g., when the Feynman-Kleinert approximation or the full thermal Gaussian approximation (full TGA) discussed in Paper II is employed.] Among the three approaches which conserve the canonical distribution in the phase space formulation of quantum mechanics, ELD and ECD can generally be well-defined with any approximations for the density distribution function for the Boltzmann operator, while EHD is more limited. [This was actually the reason why we did not publish W-EHD in our earlier paper,[7] although we thought of W-EHD (Ref. 29) before W-ELD and W-ECD.]

D. Relation between ECD and EHD

Note that Eq. (45) for the transformation between (x, p) and (x^{eff}, p^{eff}) at any time t leads to

$$P^{eq}(x, p; t) dx dp = P^{eq}_{eff}(x^{eff}, p^{eff}; t) dx^{eff} dp^{eff}. \tag{55}$$

By virtue of the property Eq. (54) of EHD, one can show EHD also satisfies Eq. (23). As discussed in Appendix A, Eq. (23) is an alternative statement of the phase space continuity equation of the first kind. So EHD satisfies Eq. (20). Either ECD or EHD conserves the quasi-probability within the infinitesimal volume $dx_t dp_t$ around the phase point (x_t, p_t) along the trajectory. As a contrast, ELD preserves the value of the density distribution function along the ELD trajectory, i.e.,

$$P^{eq}(x_0, p_0; 0) = P^{eq}(x_t, p_t; t). \tag{56}$$

According to Eq. (51), one obtains

$$\dot{p}_t^{eff} = m_{eff} m^{-1} \dot{p}_t + p_t m^{-1} \frac{\partial m_{eff}(x_t)}{\partial x_t} m^{-1} p_t. \tag{57}$$

The equations of motion of EHD can be expressed in the phase space (x, p) as

$$\begin{aligned} \dot{x}_t &= \frac{p_t}{m}, \\ \dot{p}_t &= -\frac{\partial}{\partial x_t} V^{EHD}_{eff}(x_t, p_t), \end{aligned} \tag{58}$$

with the EHD effective force given by

$$\begin{aligned} -\frac{\partial}{\partial x_t} V^{EHD}_{eff}(x_t, p_t) &= -m\, m^{-1}_{eff}(x_t) \left[\frac{\partial H_{eff}\left(x_t, p_t^{eff}\right)}{\partial x_t} \right. \\ &\left. + p_t m^{-1} \frac{\partial m_{eff}(x_t)}{\partial x_t} m^{-1} p_t \right] = m \\ &\times m^{-1}_{eff}(x_t) \left\{ \frac{1}{\beta} \frac{\partial \ln[P^{eq}(x_t, p_t)/|m_{eff}(x_t)|]}{\partial x_t} \right. \\ &\left. - p_t m^{-1} \frac{\partial m_{eff}(x_t)}{\partial x_t} m^{-1} p_t \right\}. \end{aligned} \tag{59}$$

We note that the EHD equations of motion Eqs. (58) and (59) are more convenient to use for calculating ensemble averages and thermal correlation functions because they are directly expressed in the phase space (x, p). For one-dimensional systems, it is straightforward to verify that the EHD effective force [Eq. (59)] satisfies Eq. (18) which defines the ECD effective force. That is, ECD is equivalent to EHD for the one-dimensional system for which the canonical distribution function in the phase space can be expressed as Eq. (38). For general multi-dimensional systems, however, the ECD effective force needs additional criteria to be uniquely defined, and EHD and ECD are often different approaches. [See further discussion in Appendixes F and G.] Nevertheless, it is easy to show that EHD shares with ECD all the properties (listed in Sec. II D).

E. Application to the canonical ensemble average and the thermal correlation function

By virtue of the properties of EHD [such as Eq. (23) and Eq. (55)], one can obtain Eq. (25) of this paper and Eqs. (52) and (53) of Paper I as well for ensemble averages for thermal equilibrium systems. The EDA in Paper II allows use of EHD for evaluation of thermal correlation functions as well. EHD shares with ECD all the expressions [i.e., Eqs. (33)–(36)] for calculating thermal correlation functions. Here one employs the EHD equations of motion [Eq. (58) and Eq. (59)] for propagating trajectories in the phase space.

It is trivial to show that EHD recovers exact thermal correlation functions in the classical ($\hbar \to 0$) and high temperature ($\beta \to 0$) limits. One can also verify that W-EHD reduces to LSC-IVR and therefore gives correct quantum correlation functions (of even nonlinear operators) in the harmonic limit.

IV. NUMERICAL IMPLEMENTATION AND EXAMPLES

We have presented in Paper II various methods (for obtaining the Wigner or Husimi functions for the Boltzmann operator) for the implementation of ELD. We note that all these methods can be applied to ECD as well. The only difference between ECD and ELD is evaluation of the effective force. [That is, Eq. (18) or Eq. (19) defines the ECD effective force, while Eq. (46) of Paper I gives the ELD effective force.]

The implementation of EHD requires the definition of the (position-dependent) effective mass $m_{eff}(x)$. As discussed in Appendix E, one can always obtain Eq. (38) with the LGA strategy for the Wigner canonical distribution function[20] or similar strategy for the Husimi canonical distribution function (introduced in Paper II).

Here, we use the LGA-TGA method introduced Paper II (Ref. 6) (and in our earlier work[20]) for demonstration for implementing both W-ECD and W-EHD. As discussed in Sec. III E, W-ECD with LGA-TGA can be shown to be equivalent to W-EHD with LGA-TGA for one-dimensional systems. We focus on how well W-ECD and W-EHD performs within the framework of Eq. (35), comparing the results to the exact quantum correlation functions, the LSC-IVR values, and the W-ELD results. [As in Paper II, the classical correlation functions are not shown because they work poorly in low temperature region as demonstrated in the literature[7,16].] We calculate the Kubo-transformed momentum autocorrelation function, the standard x^2 autocorrelation function, and the symmetrized force autocorrelation function (the latter two involving nonlinear local operators) for the two one-dimensional anharmonic models in Paper II. In addition, the first two autocorrelation functions are used for demonstration of the exactness in the harmonic limit and also tested for a demanding double-well potential.

A. Methods for ECD and EHD

1. W-ECD with LGA-TGA

By virtue of Eq. (43) in Paper II and Eq. (19), the LGA-TGA gives the W-ECD force as

$$-\frac{\partial}{\partial x}V_{eff}^{W-ECD}(x,p) = \mathrm{G}\left(\frac{\beta}{2};x\right)^{-1}\mathrm{M}^{-1}\left[\hbar^2\frac{\partial\gamma\left(\frac{\beta}{2};x\right)}{\partial x} - \frac{1}{2}p^T\frac{\partial \mathrm{G}\left(\frac{\beta}{2};x\right)}{\partial x}p - \frac{\hbar^2}{2}\mathrm{G}\left(\frac{\beta}{2};x\right)^{-1}\times\frac{\partial \mathrm{G}\left(\frac{\beta}{2};x\right)}{\partial x}\right]. \quad (60)$$

The ECD equations of motion [Eq. (22)] determine propagation of trajectories. Thermal correlation functions can then be evaluated along W-ECD trajectories as we show in Sec. II F. Here we use Eq. (35) with the time-averaging technique. Note that the functions f_{A^β} and $\tilde{B}$ for the correlation functions are the same as those discussed in Sec. IV of Paper II.

2. W-EHD with LGA-TGA

It is trivial to show the relation between the quantum correction factor $Q(u)$ [Eq. (29)] and the imaginary-time dependent matrix $G(\beta/2;x)$ [Eq. (41) of Paper II, which has also been suggested in our earlier work[20]] is

$$m_{therm} = mQ(u) = \frac{\beta\hbar^2}{2}G\left(\frac{\beta}{2};x\right)^{-1}. \quad (61)$$

The effective mass given by Eq. (43) becomes

$$m_{eff} = \frac{2m^2G\left(\frac{\beta}{2};x\right)}{\beta\hbar^2}. \quad (62)$$

For convenience, we can note (x^{eff}, p^{eff}) as (x, p^{eff}) for the transformation given by Eqs. (40) and (41). By virtue of Eq. (43) of Paper II, one obtains the effective canonical distribution function from Eq. (46) as

$$P_{eff,\ W}^{eq,\ LGA-TGA}(x,p^{eff}) = \frac{\beta\hbar}{4\pi m\left|G\left(\frac{\beta}{2};x\right)\right|}\exp\left[2\gamma\left(\frac{\beta}{2};x\right)\right]\times\exp\left[-\frac{(p^{eff})^2}{2m_{eff}(x)}\right]. \quad (63)$$

This leads to the effective Hamiltonian given by Eq. (49) as

$$H_{eff}(x,\,p^{eff}) = \frac{(p^{eff})^2}{2m_{eff}(x)} + \frac{1}{\beta}\ln\left|G\left(\frac{\beta}{2};x\right)\right| - \frac{2}{\beta}\gamma\left(\frac{\beta}{2};x\right) + \frac{1}{2\beta}\ln(4\pi) + \frac{1}{2\beta}\ln\left[\frac{2m}{\beta\hbar^2}\right]. \tag{64}$$

The equations of motion for W-EHD with LGA-TGA thus become

$$\dot{x}_t = \frac{p_t^{eff}}{m_{eff}(x_t)},$$

$$\dot{p}_t^{eff} = -\frac{\beta\hbar^2}{4m^2}\left(p_t^{eff}\right)^T\frac{\partial}{\partial x_t}G^{-1}\left(\frac{\beta}{2};x_t\right)p_t^{eff} - \frac{1}{\beta\left|G\left(\frac{\beta}{2};x_t\right)\right|}\frac{\partial}{\partial x_t}\left|G\left(\frac{\beta}{2};x_t\right)\right| + \frac{2}{\beta}\frac{\partial}{\partial x_t}\gamma\left(\frac{\beta}{2};x_t\right), \tag{65}$$

or equivalently

$$\dot{x}_t = \frac{p_t}{m},\ \dot{p}_t = \mathrm{G}\left(\frac{\beta}{2};x_t\right)^{-1}\mathrm{M}^{-1}\left[\hbar^2\frac{\partial\gamma\left(\frac{\beta}{2};x_t\right)}{\partial x_t} - \frac{1}{2}p_t^T\frac{\partial\mathrm{G}\left(\frac{\beta}{2};x_t\right)}{\partial x_t}p_t - \frac{\hbar^2}{2}\frac{1}{\left|G\left(\frac{\beta}{2};x_t\right)\right|}\frac{\partial\left|G\left(\frac{\beta}{2};x_t\right)\right|}{\partial x_t}\right], \tag{66}$$

in the phase space $(x,\,p)$. (EHD with LGA-TGA was already along the lines of our earlier work[7,20,29].) Note that the effective force given by EHD [Eq. (66)] is equivalent to that by ECD [Eq. (60)]. Here one verifies EHD and ECD are essentially the same for one-dimensional systems as long as the canonical distribution function can be expressed as Eq. (38).

3. Relation between W-EHD with LGA-TGA and Gaussian molecular dynamics

We noted that Georgescu and Mandelshtam independently proposed an effective Hamiltonian and an effective mass, which led to the Gaussian molecular dynamics (GMD) model for calculating symmetrized thermal correlation functions[30]. The GMD approach is constructed based on TGA in the position representation [see the discussion on TGAs in Paper II (Ref. 6)], which have also been implemented for calculating quantum time correlation functions in the LSC-IVR (Refs. 16–18, and 19) and in W-ELD/W-ECD (Ref. 7) much earlier. More recently, by following the CMD (Refs. 12 and 13) and ring polymer molecular dynamics (RPMD) (Ref. 31) ideas, Georgescu *et al.* further extended GMD for computing Kubo-transformed thermal correlation functions,[32] which gives correct results for such as linear operators (e.g., linear functions of the momentum operator) in the harmonic limit (not for nonlinear operators though).

Interestingly, though not specifically couched in the language of phase space distribution functions, the GMD model can be closely related to and even reformulated in a subcategory of W-EHD with LGA-TGA. It is easy to show that the equations of motion of GMD (Ref. 30) are equivalent to those of W-EHD with LGA-TGA [Eqs. (62)–(65)]. However, the way for calculating thermal correlation functions proposed in GMD is fairly different from that in W-EHD with LGA-TGA. We note that W-EHD with LGA-TGA can be applied to all versions of thermal correlation functions (i.e., both symmetrized and standard versions of any correlation functions, and Kubo-transformed version of such as momentum and force correlation functions, etc.) and can give correct results (even for nonlinear operators) in the harmonic limit, very much like LSC-IVR (as we showed in our earlier related work[7,20]). For some thermal correlation functions, the symmetrized version is not numerically favorable. For instance, the oscillation of $\langle\hat{x}^2(0)\hat{x}^2(t)\rangle_{mid}$ is located in a very narrow range in low temperature so that calculation of $\langle\hat{x}^2(0)\hat{x}^2(t)\rangle_{mid}$ is computationally demanding due to statistical errors. Another example is the kinetic energy flux ($\hat{F}_k = \frac{\hat{p}}{m}\frac{\hat{p}^2}{2m}$) autocorrelation function which the GMD model is not able to evaluate, it is straightforward to use W-EHD with LGA-TGA to calculate the standard version $\langle\hat{F}_k(0)\hat{F}_k(t)\rangle_{std}$ and the symmetrized one $\langle\hat{F}_k(0)\hat{F}_k(t)\rangle_{mid}$ (which recover correct results in the harmonic limit). W-EHD with LGA-TGA therefore offers a more widely useful approach.

B. Numerical examples

1. Harmonic potential

As discussed in Secs. I–IV A, all three approaches (ELD, ECD, and EHD) for the correlation function in the Wigner phase space representation reduces to LSC-IVR in the harmonic limit. [One sees that Eq. (2.8) of Ref. 7 recovers its classical form in the harmonic limit, irrespective of what the operator $\hat{A}$ is. Note that classical dynamics applies to this classical form. It is then straightforward to show that LSC-IVR gives exact quantum results by virtue of Eqs. (2.4) and (2.8) of Ref. 7. One can also prove this based on semiclassical theory or path integral formulation of the propagator ($e^{-i\hat{H}t/\hbar}$) (Refs. 14, 15, 24, 33, and 34, and 35).] Any of W-ELD, W-ECD, and W-EHD therefore recovers exact quantum correlation functions of even nonlinear operators. Similarly, one can verify that this is also true for the three approaches in the Husimi phase space representation when the width parameter is $\Gamma = m\omega/\hbar$.

Consider a harmonic potential $V(x) = 1/2m\omega^2x^2$ with $m = 1$, $\omega = 1$, and $\hbar = 1$. Figures 1(a) and 1(b) show the correlation functions $\langle p(0)p(t)\rangle_{Kubo}$ and $\langle x^2(0)x^2(t)\rangle_{std}$ for a low temperature $\beta = 8$. All three approaches (ELD, ECD, and EHD) are able to produce the exact results as LSC-IVR does. That is,

$$\langle p\,(0)\,p(t)\rangle_{Kubo}^{QM} = \frac{m}{\beta}\cos[\omega t] \tag{67}$$

and

$$\langle x^2\,(0)\,x^2(t)\rangle_{std}^{QM} = \frac{1}{2\,(1-s)^4}\left(\frac{\hbar}{m\omega}\right)^2\left[\frac{(1+s)^2}{2} + (1+s^2) \times \cos[2\omega t] + i(1-s^2)\sin[2\omega t]\right], \tag{68}$$

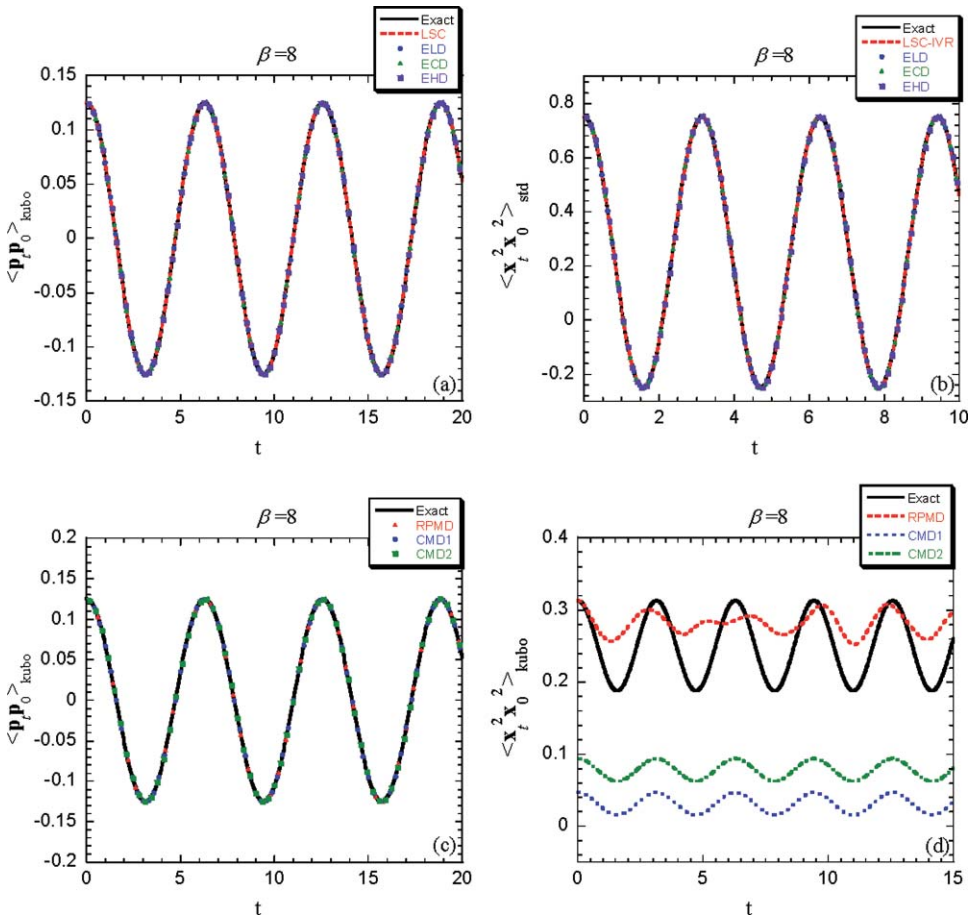

FIG. 1. The autocorrelation functions for the one-dimensional harmonic oscillator for $\beta = 8$. Panel (a) Kubo-transformed momentum autocorrelation function; (b) Real part of standard x^2 autocorrelation function. Solid line: Exact quantum result; dotted line: LSC-IVR; solid circles: ELD; solid triangles: ECD; solid squares: EHD. Panel (c) Kubo-transformed momentum autocorrelation function. Solid line: Exact quantum result; solid circles: RPMD; solid triangles: CMD with classical operator; solid squares: CMD with effective classical operator. (d) Kubo-transformed x^2 autocorrelation function. Solid line: Exact quantum result; dashed line: RPMD; dotted line: CMD with classical operator; dot-dashed line: CMD with effective classical operator.

with $s = e^{-\beta\hbar\omega}$. (It is straightforward to derive the exact results Eqs. (67)–(69) by using the basis of eigenstates of the Hamiltonian.)

In contrast, CMD (Refs. 12 and 13) and RPMD (Refs. 31 and 36) do not work well for correlation functions involving nonlinear operators even in the limit of a harmonic potential. For example, while the quantum result is

$$\langle x^2(0)\,x^2(t)\rangle_{Kubo}^{QM} = \left(\frac{\hbar}{2m\omega}\right)^2 \left[\frac{2}{u}\coth[u/2]\cos[2\omega t] + 2(\coth[u/2])^2 - 1\right], \tag{69}$$

CMD with the classical operator[12,13] gives

$$\langle x^2(0)\,x^2(t)\rangle_{Kubo}^{CMD1} = \left(\frac{1}{\beta m\omega^2}\right)^2 (\cos[2\omega t] + 2), \tag{70}$$

CMD with the effective classical operator[13] leads to

$$\langle x^2(0)\,x^2(t)\rangle_{Kubo}^{CMD2} = \left(\frac{1}{\beta m\omega^2}\right)^2 \left(\cos[2\omega t] + \frac{u}{2}\coth[u/2] + 1\right), \tag{71}$$

and RPMD[31] produces

$$\langle x^2(0)\,x^2(t)\rangle_{Kubo}^{RPMD} = \lim_{P\to\infty}\frac{1}{\beta^2 m^2}\left[\sum_{j=1}^{P}\frac{1}{\omega_j^4}(\cos[2\omega_j t]+1) + \sum_{j=1}^{P}\sum_{k=1}^{P}\frac{1}{\omega_j^2\omega_k^2}\right], \tag{72}$$

with $\omega_j = \sqrt{\omega^2 + (2P^2/\hbar^2\beta^2)[1-\cos(2j\pi/P)]}$. (We note that Eqs. (70)–(72) were shown earlier by Horikoshi and Kinugawa[37].) The results are demonstrated in Fig. 5(d).

For the same reasons discussed in Paper II, one sees that all three approaches (ELD, ECD, and EHD) combine the properties of LSC-IVR (Refs. 7, 14–23, and 24, and 38–45, and 46) /forward-backward semiclassical dynamics[47–50] (FBSD) and of CMD (Refs. 12 and 13)/RPMD (Ref. 31). That is, treat both linear and nonlinear operators equally well and recover exact results in the harmonic limit, while preserving the quantum canonical distribution.

2. Asymmetric anharmonic potential

Results for the asymmetric anharmonic oscillator

$$V(x) = \frac{1}{2}m\omega^2 x^2 - 0.10x^3 + 0.10x^4, \tag{73}$$

(with $m = 1$, $\omega = \sqrt{2}$, and $\hbar = 1$) at a high temperatures $\beta = 0.1$ are shown in Fig. 2. W-ECD/W-EHD gives correct results. This is not surprising since W-ECD/W-EHD correlation functions approach the LSC-IVR results in the high temperature regime where classical dynamics is a good approximation to the exact quantum correlation function. At a much lower temperature $\beta = 8$ (in Fig. 3), the correlation functions calculated by W-ECD/W-EHD with LGA-TGA match the exact quantum results almost perfectly, except a slight frequency shift and slight dephasing in the amplitude at long times. W-ECD/W-EHD shows systematical improvement over LSC-IVR at longer times.

3. Quartic potential

The third model is

$$V(x) = x^4/4, \tag{74}$$

with $m = 1$ and $\hbar = 1$. Note that the potential form contains no harmonic term, which represents a more severe test. Figure 4 shows that at the temperature $\beta = 0.1$ W-ECD/W-EHD with LGA-TGA can give correct results in the dephasing regime (up to three vibrational periods) but fails to describe the quantum rephasing at longer times. Figure 4 shows that the EDA (introduced in Paper II) is incapable of describing long-time quantum coherence effects. Results for the much lower temperature ($\beta = 8$) are shown in Fig. 5. W-ECD/W-EHD with LGA-TGA describes the amplitude of oscillation reasonably well (the small residual error and the dephasing originating in the LGA-TGA treatment) with a noticeable frequency shift after one vibrational period. Either approach significantly improves over LSC-IVR which shows too quick dephasing after the first period.

4. Double-well potential

The fourth model is a double-well potential

$$V(x) = -\frac{1}{2}x^2 + \frac{1}{10}x^4, \tag{75}$$

with $m = 1$, and $\hbar = 1$. The difference between the minimum and the top of the barrier is $\Delta E = 0.625$, and that between the ground state energy and the top of the barrier is $\Delta E_0 \approx 0.154$. The 1-dim double-well potential is a challenging model because of fast coherent interference (i.e., quantum recurrence) and coherent tunneling—purely quantum dynamical effects. We test all three approaches (ELD, ECD, and EHD) in the Wigner phase space with the LGA-TGA.

Figures 6(a) and 6(b) show that all three approaches (W-ELD, W-ECD, and W-EHD) reduce to LSC-IVR at high temperature ($\beta = 0.1$). All these methods can give correct results in the dephasing regime (up to three vibrational periods) but fails to describe the rephrasing at longer times. At low temperature $\beta = 8$, the thermal activation energy $k_B T$ is less than the

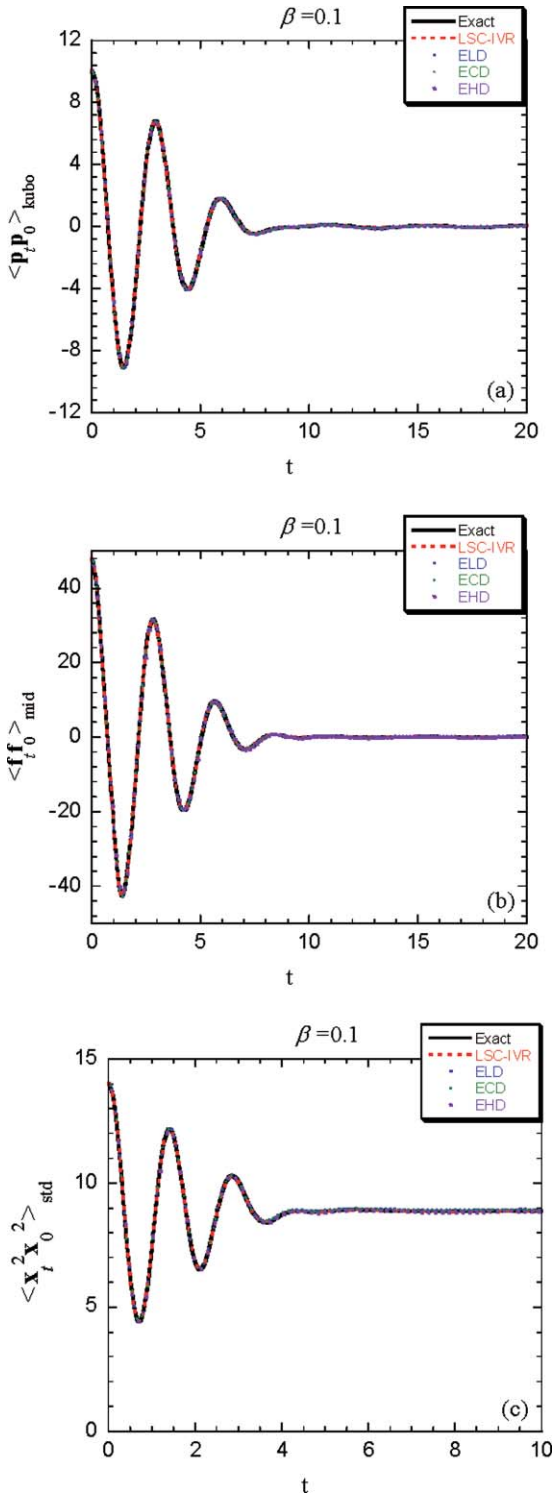

FIG. 2. The autocorrelation functions for the one-dimensional anharmonic oscillator for $\beta = 0.1$. Solid line: Exact quantum result. In the following results, the Boltzmann operator is treated by TGA. Dotted line: LSC-IVR with full TGA. Solid circles: W-ELD with LGA-TGA. Solid triangles: W-ECD with LGA-TGA. Solid squares: W-EHD with LGA-TGA. Panel (a) Kubo-transformed momentum autocorrelation function; (b) symmetrized force autocorrelation function; (c) real part of standard x^2 autocorrelation function.

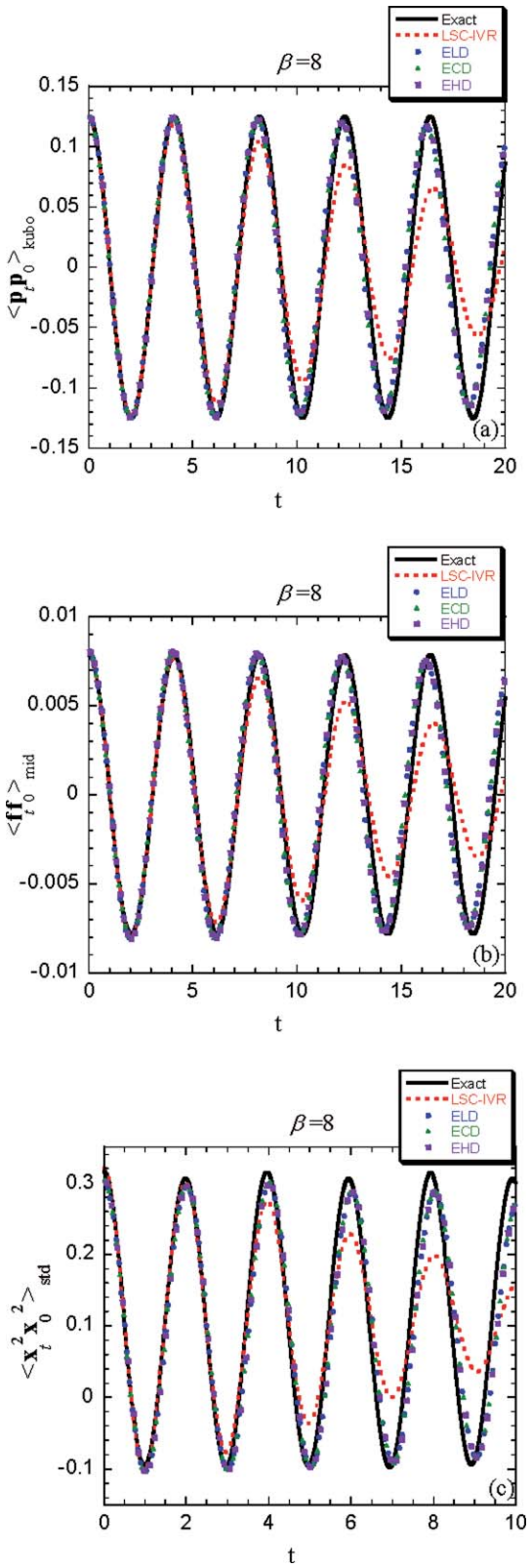

FIG. 3. As in Fig. 1, but for a much lower temperature $\beta = 8$.

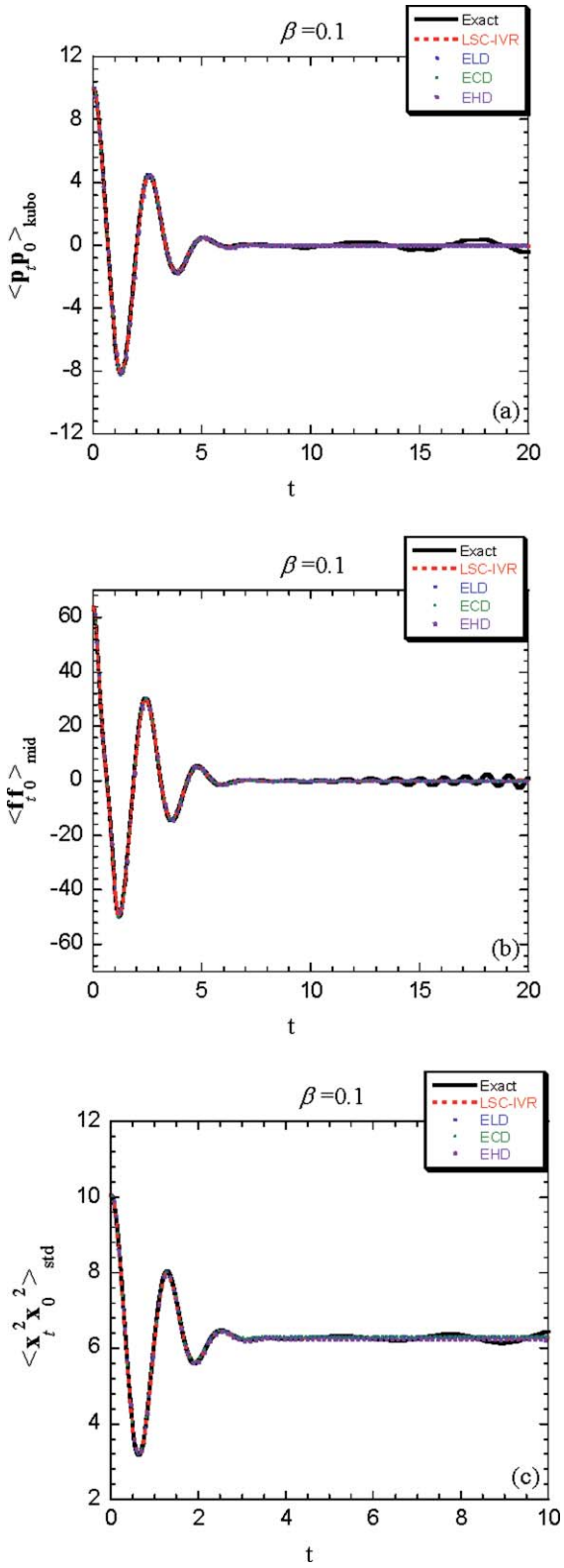

FIG. 4. The autocorrelation functions for the one-dimensional quartic oscillator for $\beta = 0.1$. Solid line: Exact quantum result. In the following results, the Boltzmann operator is treated by the TGA. Dotted line: LSC-IVR with full TGA. Solid circles: W-ELD with LGA-TGA. Solid triangles: W-ECD with LGA-TGA. Solid squares: W-EHD with LGA-TGA. Panel (a) Kubo-transformed momentum autocorrelation function; (b) symmetrized force autocorrelation function; (c) real part of standard x^2 autocorrelation function.

barrier height ΔE or even less than ΔE_0. Purely quantum coherence effects become even more significant at shorter times. Figures 6(c)–6(f) show that all three approaches with EDA still often extend the accuracy to longer time than LSC-IVR even for the difficult double-well model.

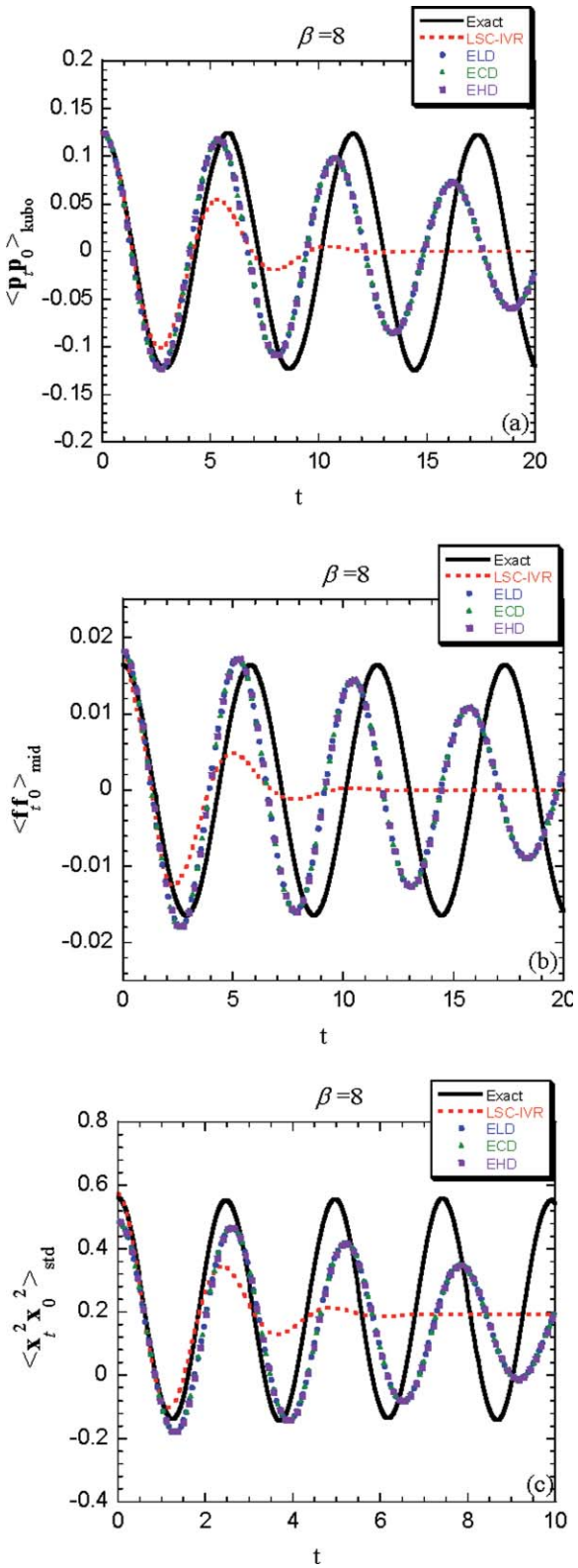

FIG. 5. As in Fig. 3, but for a much lower temperature $\beta = 8$.

It is straightforward to show that LGA-TGA (Refs. 6 and 20) can be viewed as a further approximation of full-TGA (Refs. 6 and 7) (i.e., approximate the width matrix $G(\beta/2; q_0)$ by $G(\beta/2; x)$ in the third line of RHS of Eq. (36) of Paper II[6] and then integrate over q_0). Because full-TGA is more accurate that LGA-TGA to obtain the Wigner function of the operator $\hat{A}^\beta$ or $e^{-\beta\hat{H}}$, full-TGA[6,7] often leads to better dynamics for any of the approaches than LGA-TGA does (when both work reasonably well). This has been demonstrated and discussed for ELD in Paper II. Comparison of Figs. 6(f) to 6(d) shows that this is also true for any of the approaches even for the 1-dim double-well model system for some correlation functions (with higher frequencies). [One also sees from Figs. 6(c) and 6(e) that full-TGA does nearly the same as LGA-TGA (only good for relatively short time) for other correlation functions for this challenging model and all three approaches (ELD, ECD, and EHD) fail as LSC-IVR does under this condition].

Based on Fig. 6 (and Fig. 4), it is fair to point out that none of the three approaches (ELD, ECD, and EHD) with the EDA are capable of accurately describing purely nondissipative quantum coherence effects, particularly in the regime of quantum recurrence (irrespective of high or low temperature). (Further work along these lines would be necessary.) However, such quantum recurrence effects are often quenched by coupling among the various degrees of freedom in condensed phase systems[33,51] [e.g., when a double well is coupled with a (dissipative) harmonic bath[14,51]]. The three approaches will extend the accuracy of correlation functions (of both linear and nonlinear operators) to longer time and provide the framework for the development of novel theoretical/computational tools for studying quantum dynamical effects in large/complex molecular systems.

Among all three approaches (ELD, ECD, and EHD) that conserve the canonical distribution in the phase space formulation of quantum mechanics, the equations of motion of ELD are different by construction from the other two, although one can show the effective forces share some terms. [For instance, when LGA-TGA is used, the W-ECD effective force [Eq. (60)] shares the first two terms with the ELD effective force [Eq. (44) of Paper II].] We note that the discussion and comparisons of other methodologies for ELD [either in Wigner or Husimi phase space representation] in Paper II also apply to ECD or EHD, although we do not show numerical results.

Finally we note that the calculation of different types of correlation functions for all three approaches (ELD, ECD and EHD) is in the same procedure as that for LSC-IVR as shown in Paper II (Ref. 6) [except that the trajectory-based dynamics is different]. For instance, by virtue of the identity

$$i\hbar\beta\hat{\dot{A}}^{\beta}_{Kubo} = [e^{-\beta\hat{H}}, \hat{A}], \tag{76}$$

and the strategy that we used in Appendix B of our earlier work,[16] one can often express (experiment-related) Kubo-transformed correlation functions[52,53] in the phase space based on their counterparts of the standard version.[6,16–18,20,21] The Kubo-transformed and standard versions are generally more convenient and numerically favorable to compute.[18,19] (The symmetrized version is useful while it is difficult to express the other two versions in the phase space. E.g., the flux-side correlation function.[20])

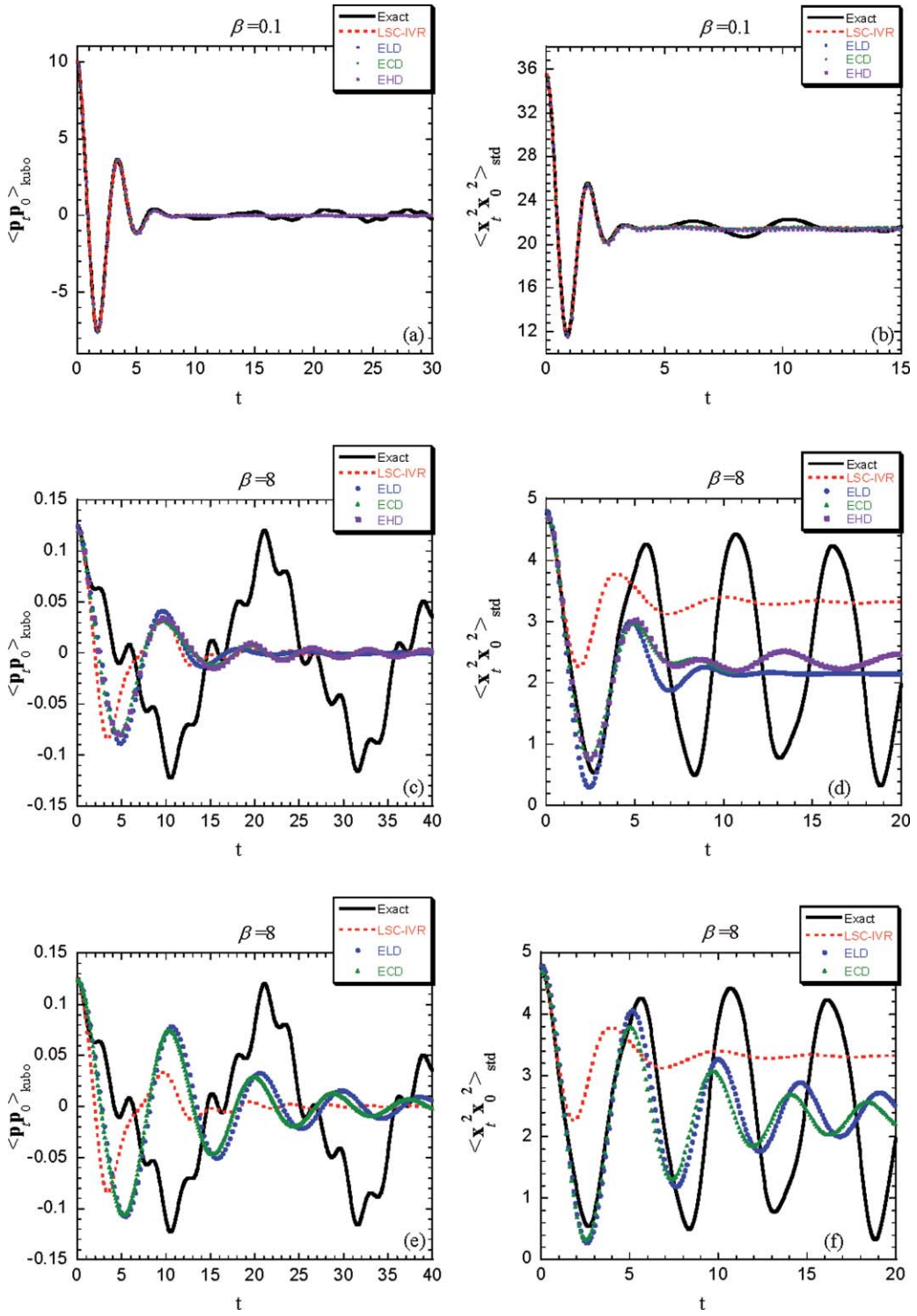

FIG. 6. The autocorrelation functions for the one-dimensional double well potential for $\beta = 0.1$ and for $\beta = 8$. Panels (a), (c), and (e): Kubo-transformed momentum autocorrelation function. Panels (b), (d), and (f): Real part of standard x^2 autocorrelation function. Panels (a)–(d)—Solid line: Exact quantum result; dotted line: LSC-IVR with LGA-TGA; solid circles: W-ELD with LGA-TGA; solid triangles: W-ECD with LGA-TGA; solid squares: W-EHD with LGA-TGA. Panels (e)–(f)—Solid line: Exact quantum result; Dotted line: LSC-IVR with LGA-TGA; Solid circles: W-ELD with full-TGA; Solid triangles: W-ECD with full-TGA.

V. CONCLUSION REMARKS

Following the two preceding papers (Papers I and II), in this paper we have presented two approaches in the spirit of the phase space continuity equation and of the Hamilton equations of motion in classical mechanics, for generating two families of trajectory-based dynamics (ECD and EHD, respectively) which also conserve the quantum canonical distribution in the phase space formulation of quantum mechanics for thermal equilibrium systems. By virtue of EDA that we implemented in Paper II, both ECD and EHD can be used for evaluation of quantum correlation functions for thermal equilibrium systems. Either ECD or EHD recovers exact quantum correlation functions (of even nonlinear operators) in the

classical ($\hbar \to 0$), high-temperature ($\beta \to 0$), and harmonic limits. In addition to ELD, ECD and EHD thus also provide appealing trajectory-based approximate quantum methods for thermal correlation functions which combine the properties of LSC-IVR (Refs. 7, 14–23, and 24, and 38–46) and other comparable approximate methods.[12,13,16,31,47–50,54–67] [Such as W-ELD, W-ECD, and W-EHD can also be viewed as improved versions of LSC-IVR (Ref. 7). More discussion on the relation between preserving the canonical ensemble and long time behavior can be found in Refs. 7, 18, 50, 68, and 69].

It is further shown that EHD and ECD are the same for one-dimensional systems as long as the canonical distribution function in the phase space can be expressed as Eq. (38), but not for general multi-dimensional systems. As discussed in Appendix F, EHD is always well defined for multi-dimensional systems as long as Eq. (E4) is a good approximation for the canonical distribution function, while one needs some additional criterion to uniquely define ECD for multi-dimensional systems. (See Appendixes F and G for more discussion.)

The three approaches (ELD, ECD, and EHD) consist of two types of trajectory-based dynamics which conserve canonical distribution in the phase space formulation of quantum mechanics: ECD and EHD preserve $P^{eq}(x_t, p_t)\,dx_t dp_t$, while ELD conserves $P^{eq}(x_t, p_t)$. These two types of trajectory-based dynamics offer the framework to unite and improve *all* trajectory-based approximate quantum methods in the past [such as W-ELD and W-ECD (Ref. 7), CMD (Refs. 12 and 13), and GMD (Ref. 30)] which are able to conserve the quantum canonical distribution in a single phase space for thermal equilibrium systems. One can even develop new trajectory-based dynamical methods in the framework of these approaches in phase space formulations of quantum mechanics. (Most discussions on ELD in the two preceding papers also apply to ECD and EHD.)

We note that all these approaches fail to describe long-time quantum rephasing (quantum recurrence) effects in thermal correlation functions. [More advanced SC-IVR methods[33,34,70,71] (than LSC-IVR) or real time path integral algorithms[72,73] (or other real time quantum approaches[81]) will be needed for capturing quantum recurrence effects.] For many cases in condensed phase systems, such long-time quantum coherence effects (often shown in one-dimensional bounded systems) are expected to be quenched by coupling among the various degrees of freedom.[33,74,75] Since these approaches 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), they can provide practical and promising tools for including quantum effects for large/complex molecular systems in condensed phase. In addition to the methods that we discussed in Paper II, an efficient path integral representation of these approaches will be proposed in a subsequent paper. It will be a subject of future interest to further test and compare these two types of trajectory-based dynamics for realistic (polyatomic) molecular systems in condensed phase.

Finally, we note that the strategies that we used to generate trajectory-based dynamics which conserves the canonical distribution in the phase space formulation of quantum mechanics in the series of papers (Papers I and II and the current manuscript) can be generalized for systems with multi-electronic potential surfaces. For example, one can extend our approaches (ELD, ECD, and EHD) to the Meyer-Miller-Stock-Thoss mapping model[76,77] for generating trajectory-based dynamics which satisfies detailed balance. All three approaches can also be used as models for systems with non-equilibrium initial conditions (i.e., pure states or mixed states) coupled with the bath with infinite modes, which defines the temperature of the whole system-bath system.

ACKNOWLEDGMENTS

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APPENDIX A: PHASE SPACE CONTINUITY EQUATION OF THE FIRST KIND AND ITS ALTERNATIVE STATEMENT

For convenience, we define the vector $\boldsymbol{v}_t = (x_t, p_t)^T$, $\nabla_t = (\partial/\partial x_t, \partial/\partial p_t)^T$, and the Jacobian matrix of the transformation (generated from the dynamics)

$$\mathbf{J}(t) = \frac{\partial(x_t, p_t)}{\partial(x_0, p_0)} \equiv \frac{\partial \boldsymbol{v}_t}{\partial \boldsymbol{v}_0}. \tag{A1}$$

Because the equality of Eq. (29) in Paper I always holds, one can obtain

$$\frac{dP}{dt} = \dot{\boldsymbol{v}}_t \cdot \nabla_t P + \frac{\partial P}{\partial t} = \dot{\boldsymbol{v}}_t \cdot \nabla_t P - \nabla_t \cdot (P\dot{\boldsymbol{v}}_t) = -P\nabla_t \cdot \dot{\boldsymbol{v}}_t, \tag{A2}$$

from the phase space continuity equation of the first kind [Eq. (8)].

If the dynamics is time-implicit (irrespective of whether it is Hamiltonian or non-Hamiltonian), one can show

$$\frac{d(P(\boldsymbol{v}_t;t)\det(\mathbf{J}(t)))}{dt} = \frac{dP(\boldsymbol{v}_t;t)}{dt}\det(\mathbf{J}(t)) + P(\boldsymbol{v}_t;t)\frac{d(\det(\mathbf{J}(t)))}{dt} = 0, \tag{A3}$$

with Eq. (C8) in Paper I and Eq. (A2). That is, $\rho(\boldsymbol{v}_t;t)\det(\mathbf{J}(t))$ is a constant during the dynamics, i.e.,

$$\rho(\boldsymbol{v}_t;t)\det(\mathbf{J}(t)) = \rho(\boldsymbol{v}_0;0)\det(\mathbf{J}(0)). \tag{A4}$$

The initial value of the Jacobian matrix is always an identity matrix, i.e.,

$$\mathbf{J}(0) = \mathbf{1}, \tag{A5}$$

which leads to

$$\det(\mathbf{J}(0)) = 1. \tag{A6}$$

The determinant of the Jacobian matrix $\mathbf{J}(t)$ by its definition in Eq. (A1) measures the change of the volume element during the dynamics, i.e.,

$$dx_t dp_t = \left|\frac{\partial(x_t, p_t)}{\partial(x_0, p_0)}\right| dx_0 dp_0 = \det(\mathbf{J}(t)) dx_0 dp_0. \tag{A7}$$

Substituting Eq. (A6) and Eq. (A7) into Eq. (A4), one obtains Eq. (10), or equivalently,

$$\frac{d(\rho(\boldsymbol{v}_t;t)d\boldsymbol{v}_t)}{dt} = 0. \tag{A8}$$

Eq. (10) or Eq. (A8) is an alternative statement of the phase space continuity equation of the first kind [Eq. (8)], as long as the dynamics is time-implicit.

APPENDIX B: MORE DISCUSSION ON THE EFFECTIVE FORCE AND THE CHOICE OF EQUATIONS OF MOTION IN ECD

It is important to point out that the effective force $-\partial/\partial x V_{eff}(x, p)$ is *not* guaranteed to be always well defined [in Eq. (16) or Eq. (17)] at any phase point (x, p), although the right-hand side (RHS) of Eq. (16) or Eq. (17) always exists. One should be careful with this particularly for nonstationary density distribution functions [while the phase points satisfy $P(x, p;t) = 0$]. For nonstationary systems, it is more convenient to work with nonnegative distribution functions, such as the Husimi distribution function,[25] the Glauber Q function[11] and several others.[26–28] Nevertheless, the effective force for the thermal equilibrium system is often well defined (even for such as the Wigner distribution function[2,78]), because those phase points for $P^{eq}(x, p) = 0$ do not change with time for the thermal equilibrium system and have no (or little) contribution to the integral over the phase space in such as Eq. (25) and Eq. (33) (that is those phase points can be effectively ignored).

Note that the definition of the ELD effective force (as discussed in Paper I) requires that the partial distribution function for the momentum p at any fixed position x based on the equilibrium density distribution $P^{eq}(x, p)$ be (effectively) a Gaussian function. The definition of the ECD effective force [given by Eq. (18) or Eq. (19)], however, does not particularly require that. So ECD can be more generally applied than ELD.

Rather than the effective potential $V_{eff}(x, p)$, it is more convenient to define the effective force $-\partial/\partial x V_{eff}(x, p)$ as we initially did in Ref. 7. Defining the effective force is adequate for the purpose of constructing trajectory-based dynamics in the phase space formulation of quantum mechanics, while defining the effective potential $V_{eff}(x, p)$ often involves much more redundant information.

For either ECD or EHD in the present paper, we always define $\dot{x} = p/m$ to be the relation between the position and momentum, which is independent of the density distribution function and independent of the system. Although this is perhaps the *most convenient and most useful* choice, there are still many other ways to define the equations of motion (from quantum Liouville's theorem) in the phase space formulation of quantum mechanics in the spirit of the phase space continuity equation of the first kind [Eq. (6) or Eq. (8)] or Hamilton equations of motion in classical mechanics. The discussion on ELD in Appendix B of Paper I can similarly apply to either ECD or EHD. For all these approaches (ELD, ECD, and EHD) which conserve the canonical distribution in the phase space formulation of quantum mechanics, one can define the equations of motion similar to those in the literature[10,79] and even propose some type of sourceless trajectory-based dynamics in the quantum phase space [i.e., Eq. (5) holds]. In addition, these approaches offer the framework for one to use the perturbation technique or the variational principle to define the equations of motion such that they lead to more accurate results. [Meanwhile one should also consider whether the choice of equations of motion is practical to obtain or not for general (complex) systems.] Further work along these lines would certainly be of interest.

We also note some other work[80] has been done since we first pointed out that a generalized density operator ($\hat{A}^{\beta}$ or $\hat{\rho}\hat{A}$) can be defined such that the quantum Liouville theorem can be applied for calculating quantum time correlation function.[7]

APPENDIX C: EXPECTATION VALUE OR ENSEMBLE AVERAGE IN ECD

Suppose $\boldsymbol{v} = (x, p)^T$ represents a point in a fixed framework of the coordinate system for the phase space. ρ is the density distribution function. Here, we focus on the trajectory-based dynamics that satisfies the phase space continuity equation of the first kind [i.e., Eq. (6) or Eq. (8)].

Note that the dynamics is already described in the Eulerian picture (i.e., the coordinate system is fixed), because only the partial time derivative is involved. This means one can exchange υ' with $\boldsymbol{v}_t$, so one has

$$\langle B(t)\rangle = \frac{1}{Z}\int \mathbf{d}\upsilon' \rho(\upsilon';t)\tilde{B}(\upsilon') = \frac{1}{Z}\int \mathbf{d}\upsilon_t \rho(\boldsymbol{v}_t;t)\tilde{B}(\boldsymbol{v}_t). \tag{C1}$$

By virtue of Eq. (10), which is an alternative statement of the phase space continuity equation of the first kind, Eq. (C1) becomes

$$\langle B(t)\rangle = \frac{1}{Z}\int \mathbf{d}\upsilon_0 \rho(\boldsymbol{v}_0;0)\tilde{B}(\boldsymbol{v}_t). \tag{C2}$$

Please note Eq. (C1) or Eq. (C2) applies to all kinds of time-implicit trajectory-based dynamics which satisfies Eq. (A8). Classical dynamics and ECD discussed in Sec. II are two examples.

Interestingly, one sees that Eq. (C2) is always the expression for evaluating the expectation value or ensemble

average, irrespective of whether the dynamics conserves $\rho(\boldsymbol{v}_t;t)$ or $\rho(\boldsymbol{v}_t;t)\,d\boldsymbol{v}_t$ along the trajectory, and regardless of whether the dynamics is Hamiltonian or non-Hamiltonian.

APPENDIX D: PROOF OF CONSERVATION OF THE VOLUME ELEMENT IN THE EQUILIBRIUM HAMILTON DYNAMICS

One can show the proof of Eq. (53) within the same procedure described in Appendix C of Paper I, by exchanging the phase space variables $\boldsymbol{v} = (x, p)^T$ with the new variables $\boldsymbol{v}^{eff} = (x^{eff}, p^{eff})^T$. For the dynamics [Eq. (50)] generated from the effective Hamiltonian $H_{eff}(x^{eff}, p^{eff})$ [such as Eq. (49)], it is straightforward to show the matrix $\partial \dot{\boldsymbol{v}}_t^{eff}/\partial \boldsymbol{v}_0^{eff}$ is given by

$$\frac{\partial \dot{\boldsymbol{v}}_t^{eff}}{\partial \boldsymbol{v}_0^{eff}} = \mathbf{T}_H(t)\frac{\partial \boldsymbol{v}_t^{eff}}{\partial \boldsymbol{v}_0^{eff}}, \tag{D1}$$

with the matrix $\mathbf{T}_H(t)$ given by

$$\mathbf{T}_H(t) = \begin{pmatrix} \dfrac{\partial^2 H_{eff}}{\partial x_t^{eff}\partial p_t^{eff}} & \dfrac{\partial^2 H_{eff}}{\left(\partial p_t^{eff}\right)^2} \\ -\dfrac{\partial^2 H_{eff}}{\left(\partial x_t^{eff}\right)^2} & -\dfrac{\partial^2 H_{eff}}{\partial x_t^{eff}\partial p_t^{eff}} \end{pmatrix}. \tag{D2}$$

One can verify that the RHS of Eq. (D1) is zero, which suggests that the velocity field $(\dot{x}^{eff}, \dot{p}^{eff})$ for EHD is sourceless. Followed from Eq. (C3) in Appendix C of Paper I, the determinant of the Jacobian matrix is invariant with time,

$$\frac{d}{dt}\det(\mathbf{J}(t)) = 0. \tag{D3}$$

Because the Jacobian matrix is an identity matrix at time $t = 0$ [Eq. (A5)], the determinant of the Jacobian matrix is always 1, i.e.,

$$\left|\frac{\partial\left(x_t^{eff}, p_t^{eff}\right)}{\partial\left(x_0^{eff}, p_0^{eff}\right)}\right| = 1. \tag{D4}$$

This proves conservation of the volume element during the dynamics [i.e., Eq. (53)].

As a special case, when $m_{eff} \to m$, $p_{eff} \to p$, and $x_{eff} \equiv x$, the above procedure also gives the proof for that classical dynamics conserves the volume element of the phase space (x, p).

APPENDIX E: LGA BASED ON LOCAL HARMONIC APPROXIMATION (LGA-LHA)

Preliminaries to this appendix are covered in Sec. II C of our earlier work.[20] Let $\mathbf{M}$ be the diagonal "mass matrix" and let $\mathbf{T}$ be an orthogonal matrix, which diagonalizes the mass-weighted Hessian matrix. By virtue of the fact that

$$\frac{\left\langle x - \frac{\Delta x}{2}\right| e^{-\beta\hat{H}} \left|x + \frac{\Delta x}{2}\right\rangle}{\langle x| e^{-\beta\hat{H}} |x\rangle} = \exp\left[-\frac{m\,Q(u)}{2\hbar^2\beta}(\Delta x)^2\right], \tag{E1}$$

for the 1-dim harmonic case which was first implemented in the local harmonic approximation (LHA) of Shi and Geva,[23] it is straightforward to show the Wigner function of the Boltzmann operator $e^{-\beta\hat{H}}$ is given by

$$P_W^{eq}(\mathbf{x}, \mathbf{P}) = \langle \mathbf{x}| e^{-\beta\hat{H}} |\mathbf{x}\rangle \prod_{k=1}^{N}\left[\left(\frac{\beta}{2\pi\,Q(u_k)}\right)^{1/2} \times \exp\left[-\beta\frac{(P_k)^2}{2Q(u_k)}\right]\right], \tag{E2}$$

where $u_k = \beta\hbar\omega_k$, P_k is the k-th component of the mass-weighted normal-mode momentum P and the quantum correction factor with the LGA ansatz proposed by Liu and Miller[20] for both real and imaginary frequencies is given by

$$Q(u) = \begin{cases} \dfrac{u/2}{\tanh(u/2)} & \text{for real } u, \\ = \dfrac{1}{Q(u_i)} = \dfrac{\tanh(u_i/2)}{u_i/2}, & \text{for imaginary } u(u = iu_i). \end{cases} \tag{E3}$$

We express Eq. (E2) in the phase space $(\mathbf{x}, \mathbf{p})$ as

$$P^{eq,\,LGA}(\mathbf{x}, \mathbf{p}) = \langle \mathbf{x}| e^{-\beta\hat{H}} |\mathbf{x}\rangle \left(\frac{\beta}{2\pi}\right)^{N/2} \left|\det\left(\mathbf{M}_{therm}^{-1}(\mathbf{x})\right)\right|^{1/2} \times \exp\left[-\frac{\beta}{2}\mathbf{p}^T\mathbf{M}_{therm}^{-1}\mathbf{p}\right], \tag{E4}$$

with the thermal mass matrix $\mathbf{M}_{therm}$ given by

$$\mathbf{M}_{therm}^{-1}(\mathbf{x}) = \mathbf{M}^{-1/2}\mathbf{T}\mathbf{Q}(\mathbf{u})^{-1}\,\mathbf{T}^T\mathbf{M}^{-1/2}, \tag{E5}$$

and the diagonal matrix $\mathbf{Q}(\mathbf{u}) = \{Q(u_k)\}$.

Note that the element $\langle \mathbf{x}| e^{-\beta\hat{H}} |\mathbf{x}\rangle$ in Eq. (E4) can be accurately evaluated by path integral techniques without any approximation on the Hamiltonian. In addition, the thermal mass matrix $\mathbf{M}_{therm}$ can be obtained from the Hesian of the bare potential [i.e., Eq. (2.15) of Ref. 20] or from that of the more sophisticated Gaussian averaged potential, by LGA-FKA or various TGAs (discussed in Paper II) when the potential can be fitted by polynomials or Gaussian functions.

It is straightforward to show Eq. (E4) is the general form for the Wigner canonical distribution function when any of the LGAs or TGAs with the LGA strategy mentioned in Paper II are used for the thermal mass matrix $\mathbf{M}_{therm}(\mathbf{x})$. (Note that the element $\langle \mathbf{x}| e^{-\beta\hat{H}} |\mathbf{x}\rangle$ can also approximately be evaluated by the TGAs.) For example, Eq. (43) of Paper II can be expressed as Eq. (E4) as well.

One can further show Eq. (E4) is also the general form for the Husimi canonical distribution function $\langle x, p| e^{-\beta\hat{H}} |x, p\rangle$ when it is evaluated with the strategy that we proposed in Appendix I-2 of Paper II. For instance, the Husimi canonical distribution function $\langle x, p| e^{-\beta\hat{H}} |x, p\rangle$ evaluated by a single imaginary time trajectory by the thermal Frozen Gaussian [Eqs. (A27) and (A28) of Paper II] or by the thermal Thawed Gaussian [Eqs. (A39) and (A40) of Paper II] can be written as Eq. (E4) too. (Note that Γ is a matrix in multi-dimensional systems.)

APPENDIX F: GENERALIZATION OF ECD FOR MULTI-DIMENSIONAL SYSTEMS

For multi-dimensional systems, the ECD equations of motion become

$$\begin{aligned}\dot{\mathbf{x}} &= \mathbf{M}^{-1}\mathbf{p},\\ \dot{\mathbf{p}} &= -\frac{\partial V_{eff}^{ECD}(\mathbf{x},\mathbf{p})}{\partial \mathbf{x}},\end{aligned} \tag{F1}$$

with the ECD effective force $-\partial V_{eff}^{ECD}(\mathbf{x},\mathbf{p})/\partial\mathbf{x}$ given by

$$\frac{\partial}{\partial \mathbf{p}}\cdot\left(P^{eq}(\mathbf{x},\mathbf{p})\frac{\partial V_{eff}^{ECD}(\mathbf{x},\mathbf{p})}{\partial \mathbf{x}}\right) = \frac{\partial P^{eq}(\mathbf{x},\mathbf{p})}{\partial \mathbf{x}}\mathbf{M}^{-1}\mathbf{p}. \tag{F2}$$

One sees that the ECD effective force $-\partial V_{eff}^{ECD}(\mathbf{x},\mathbf{p})/\partial\mathbf{x}$ is not uniquely defined by Eq. (F2) for multi-dimensional systems. There are infinitely many possible effective forces for Eq. (F2) in the multi-dimensional case, although one can choose one according to some additional criterion. (For example, one may request that each term of the dot product on the left-hand side equals to the counterpart of the other side of Eq. (F2), while it is expressed in mass-weighted normal mode coordinates.)

APPENDIX G: GENERALIZATION OF EHD FOR MULTI-DIMENSIONAL SYSTEMS

Similar to Sec. III, the generalization of EHD to multi-dimensional systems requires a transformation of phase space variables

$$\begin{aligned}\mathbf{x}^{eff} &= \mathbf{x},\\ \mathbf{p}^{eff} &= \mathbf{M}_{eff}(\mathbf{x})\,\mathbf{M}^{-1}\mathbf{p}.\end{aligned} \tag{G1}$$

The effective canonical distribution function with the new variables $(\mathbf{x}^{eff},\mathbf{p}^{eff})$ becomes

$$\begin{aligned}P_{eff}^{eq}(\mathbf{x}^{eff},\mathbf{p}^{eff}) &= \left|\frac{\partial(\mathbf{x},\mathbf{p})}{\partial(\mathbf{x}^{eff},\mathbf{p}^{eff})}\right| P^{eq}(\mathbf{x},\mathbf{p})\\ &= \left|\frac{\det(\mathbf{M})}{\det(\mathbf{M}_{eff}(\mathbf{x}))}\right| P^{eq}(\mathbf{x},\mathbf{p}).\end{aligned} \tag{G2}$$

The effective Hamiltonian $H_{eff}(\mathbf{x}^{eff},\mathbf{p}^{eff})$ is then defined by

$$P_{eff}^{eq}(\mathbf{x}^{eff},\mathbf{p}^{eff}) = \left(\frac{\beta}{2\pi}\right)^{N/2}|\det(\mathbf{M})|^{-1/2}\,e^{-\beta H_{eff}(\mathbf{x}^{eff},\mathbf{p}^{eff})}. \tag{G3}$$

Here, the effective mass matrix $\mathbf{M}_{eff}$ is defined in such a way that

$$\begin{aligned}&\exp\left[-\frac{\beta}{2}(\mathbf{p}^{eff})^T\mathbf{M}_{eff}^{-1}(\mathbf{x})\,\mathbf{p}^{eff}\right]\\ &\quad\equiv \exp\left[-\frac{\beta}{2}\mathbf{p}^T\mathbf{M}^{-1}\mathbf{M}_{eff}(\mathbf{x})\,\mathbf{M}^{-1}\mathbf{p}\right].\end{aligned} \tag{G4}$$

gives the same exponential term as that of the momentum distribution function based on the Wigner density function [i.e., $P_W^{eq}(\mathbf{x},\mathbf{p})$] with fixed $\mathbf{x}$. That is, Eq. (E4) leads to the effective mass matrix

$$\mathbf{M}_{eff}(\mathbf{x}) = \mathbf{M}\,\mathbf{M}_{thermal}^{-1}\mathbf{M}, \tag{G5}$$

as a generalization for Eq. (43). Note that the transformation in Eq. (G1) leads to

$$\dot{\mathbf{p}}^{eff} = \mathbf{M}_{eff}(\mathbf{x})\,\mathbf{M}^{-1}\dot{\mathbf{p}} + \mathbf{p}^T\mathbf{M}^{-1}\frac{\partial \mathbf{M}_{eff}(\mathbf{x})}{\partial \mathbf{x}}\mathbf{M}^{-1}\mathbf{p}. \tag{G6}$$

By virtue of Eq. (E4) and Eq. (G2), the EHD equations of motion can be expressed in the phase space $(\mathbf{x},\mathbf{p})$ as

$$\begin{aligned}\dot{\mathbf{x}} &= \mathbf{M}^{-1}\mathbf{p},\\ \dot{\mathbf{p}} &= -\frac{\partial}{\partial \mathbf{x}}V_{eff}^{EHD}(\mathbf{x}),\end{aligned} \tag{G7}$$

with the EHD effective force defined as

$$\begin{aligned}-\frac{\partial}{\partial \mathbf{x}}V_{eff}^{EHD}(\mathbf{x}) = \mathbf{M}\,\mathbf{M}_{eff}^{-1}\Bigg\{&-\frac{1}{2}\mathbf{p}^T\mathbf{M}^{-1}\frac{\partial \mathbf{M}_{eff}}{\partial \mathbf{x}}\mathbf{M}^{-1}\mathbf{p}\\ &+\frac{1}{\beta}\frac{\partial}{\partial \mathbf{x}}\ln[\langle\mathbf{x}|\,e^{-\beta\hat{H}}\,|\mathbf{x}\rangle]\\ &-\frac{1}{2\beta}\frac{\partial}{\partial \mathbf{x}}\ln[|\det(\mathbf{M}_{eff}(\mathbf{x}))|]\Bigg\}.\end{aligned} \tag{G8}$$

Equations (G7) and (G8) are the generalization of Eqs. (58) and (59) for the Wigner phase space for the multi-dimensional system.

Similarly, one can obtain the EHD equations of motion for the Husimi and other phase spaces based on Eqs. (G1)-(G5) and Eqs. (G6) and (G7).

APPENDIX H: THE W-ELD AND W-EHD APPROACHES WITH LGA-TGA FOR MULTI-DIMENSIONAL SYSTEMS

The Wigner canonical distribution function based on LGA-TGA is given by Eq. (43) of Paper II. It is straightforward to show the ELD effective force for multi-dimensional systems is

$$\begin{aligned}-\frac{\partial}{\partial \mathbf{x}}V_{eff}^{W-ELD}(\mathbf{x},\mathbf{p}) = \mathbf{G}\left(\frac{\beta}{2};\mathbf{x}\right)^{-1}\mathbf{M}^{-1}\Bigg[&\hbar^2\frac{\partial\gamma\left(\frac{\beta}{2};\mathbf{x}\right)}{\partial \mathbf{x}}\\ &-\frac{1}{2}\mathbf{p}^T\frac{\partial\mathbf{G}\left(\frac{\beta}{2};\mathbf{x}\right)}{\partial \mathbf{x}}\mathbf{p}\Bigg],\end{aligned} \tag{H1}$$

as a generalization from Eq. (44) of Paper II. The equations of motion for W-ELD with LGA-TGA then become

$$\begin{aligned}\dot{\mathbf{x}} &= \mathbf{M}^{-1}\mathbf{p}\\ \dot{\mathbf{p}} &= -\frac{\partial V_{eff}^{W-ELD}(\mathbf{x},\mathbf{p})}{\partial \mathbf{x}}.\end{aligned} \tag{H2}$$

Comparing the exponential term for the momenta distribution of Eq. (43) of Paper II to that of Eq. (E4), one obtains the relation

$$\mathbf{M}_{thermal}^{-1}(\mathbf{x}) = \frac{2}{\hbar^2\beta}\mathbf{G}\left(\frac{\beta}{2};\mathbf{x}\right). \tag{H3}$$

By virtue of Eq. (G5), the effective mass matrix becomes

$$\mathbf{M}_{eff}(\mathbf{x}) = \frac{2}{\hbar^2\beta}\mathbf{M}\,\mathbf{G}\left(\frac{\beta}{2};\mathbf{x}\right)\mathbf{M}, \tag{H4}$$

as a generalization for Eq. (62) or a special case for Eq. (G5).

According to Eqs. (58) and (59), one can express the equations of motion in the phase space $(\mathbf{x}, \mathbf{p})$ as Eq. (G7), with the EHD effective force given by

$$-\frac{\partial}{\partial \mathbf{x}} V_{eff}^{W-EHD}(\mathbf{x}) = \mathbf{G}\left(\frac{\beta}{2};\mathbf{x}\right)^{-1}\mathbf{M}^{-1} \times \left[\hbar^2 \frac{\partial \gamma\left(\frac{\beta}{2};\mathbf{x}\right)}{\partial \mathbf{x}} - \frac{1}{2}\mathbf{p}^T \frac{\partial \mathbf{G}\left(\frac{\beta}{2};\mathbf{x}\right)}{\partial \mathbf{x}}\mathbf{p} - \frac{\hbar^2}{2}\frac{\partial}{\partial \mathbf{x}} \ln\left|\mathbf{G}\left(\frac{\beta}{2};\mathbf{x}\right)\right|\right]. \tag{H5}$$

(Note the difference between Eq. (H1) for ELD and Eq. (H5) for EHD.) It is straightforward to show that Eq. (G8) of Appendix G directly lead to Eq. (H5) when the LGA-TGA is used for the Wigner density function. (Eqs. (G7) and (G8) of Appendix G are the general formula for any local Gaussian or thermal Gaussian approximations.)

As discussed in Appendix of Paper II, LGA-TGA requires that the potential surface be accurately fitted by polynomials, exponentials, or Gaussians such that the Gaussian integrals necessary to evaluate in the equations of motions could be evaluated analytically, otherwise performing these Gaussian integrals in multi-dimensional systems would be too computationally demanding. We also note that LGA-TGA does not work well in imaginary frequency regime at low temperature (e.g., for chemical reaction rates), while LGA-LHA (with imaginary time path integral) can still be applied. We will show an efficient path integral representation in a subsequent paper.

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