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An approach for generating trajectory-based dynamics which conserves the canonical distribution in the phase space formulation of quantum mechanics. I. Theories

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We have reformulated and generalized our recent work [J. Liu and W. H. Miller, J. Chem. Phys. **126**, 234110 (2007)] into an approach for generating a family of trajectory-based dynamics methods in the phase space formulation of quantum mechanics. The approach (equilibrium Liouville dynamics) is in the spirit of Liouville's theorem in classical mechanics. The trajectory-based dynamics is able to conserve the quantum canonical distribution for the thermal equilibrium system and approaches classical dynamics in the classical ($\hbar \to 0$), high temperature ($\beta \to 0$), and harmonic limits. Equilibrium Liouville dynamics provides the framework for the development of novel theoretical/computational tools for studying quantum dynamical effects in large/complex molecular systems. © *2011 American Institute of Physics*. [doi:10.1063/1.3555273]

I. INTRODUCTION

Quantum mechanics has several equivalent representations, e.g., the Schrödinger wavefunction formulation, the Heisenberg operator picture, and Feynman's path integral interpretation.[1] There also exist phase space formulations of quantum mechanics since Wigner's work in 1932.[2] Because phase space formulations provide a natural framework for using concepts of classical mechanics to describe quantum phenomena and can offer useful insight about the quantum-classical correspondence, they have been widely used in many areas of physics and chemical physics, such as statistical physics,[2,3] quantum optics and electronics,[4,5] dynamics of nonlinear or nonintegrable systems,[6,7] molecular collisions,[8–11] and quantum transport.[12,13] Recently they have also been used to provide an approximate description of quantum effects in the dynamics of condensed phase systems: for example, the Wigner distribution function[2,14] arises naturally when a linearized approximation[15–26] to the initial value representation of semiclassical theory[27–29] [i.e., linearized semiclassical initial value representation (LSC-IVR)] is used for time correlation functions, and the forward–backward semiclassical dynamics approach of Makri and co-workers[30–36] employs the Husimi distribution function[37] when treating these same quantities.

The LSC-IVR/classical Wigner model, for example, gives the following classical-like expression for generalized time correlation functions:

$$\mathrm{Tr}[\hat{A}e^{i\hat{H}t/\hbar}\hat{B}e^{-i\hat{H}t/\hbar}] = \int dx_0 \int dp_0 A_W(x_0, p_0; 0) B_W(x_t, p_t), \tag{1}$$

where $\hat{H}$ is the Hamiltonian of the system; A_w and B_w are the Wigner functions[2,14] [cf. Eqs. (18) and (23) below, respectively] corresponding to operators $\hat{A}$ and $\hat{B}$. Here (x_0, p_0) is the set of initial conditions (i.e., coordinates and momenta) for a classical trajectory, $(x_t(x_0, p_0), p_t(x_0, p_0))$ being the phase point at time t along this trajectory. As discussed in the literature,[19–23] the LSC-IVR/classical Wigner model gives the correct quantum result in the short-time, classical, and harmonic limits for generalized time correlation functions, and also in the high temperature limits for thermal equilibrium correlation functions. In spite of these merits, however, the LSC-IVR/classical Wigner approximation does not give a time-invariant result for thermodynamic properties of thermal equilibrium systems: i.e., while the following quantum expression:

$$\begin{aligned}\langle B(t)\rangle &= \frac{1}{Z}\mathrm{Tr}[e^{-\beta\hat{H}}e^{i\hat{H}t/\hbar}\hat{B}e^{-i\hat{H}t/\hbar}] \\ &= \frac{1}{Z}\mathrm{Tr}[e^{-\beta\hat{H}}\hat{B}] = \langle B(0)\rangle,\end{aligned} \tag{2}$$

is clearly time independent, the corresponding LSC-IVR/classical Wigner result [with $\hat{A} = e^{-\beta\hat{H}}$ in Eq. (1)] is not

$$\langle B(t)\rangle^{\mathrm{LSC-IVR}} \neq \langle B(0)\rangle^{\mathrm{LSC-IVR}}, \tag{3}$$

because classical dynamics in general does not conserve the Wigner distribution function,

$$A_W(x_t, p_t; 0) \neq A_W(x_t, p_t; t). \tag{4}$$

In order to remedy this inconsistency of LSC-IVR/classical Wigner approximation, Liu and Miller proposed several years ago[19] two kinds of trajectory-based dynamics in the Wigner phase space to replace the classical dynamics in Eq. (1); the Wigner density distribution function is conserved for thermal equilibrium systems with either of them.

However, the phase space density distribution function[14,38–40]—the primary object of a phase space formulation of quantum mechanics—is not limited to the Wigner distribution function:[2,14] due to the noncommutivity of quantum mechanical operators, it is not possible to define

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a unique probability at a phase-space point (x, p), leading to a variety of different distribution functions[2,4,5,14,37,41–50] that have been proposed and found useful application for different problems. The purpose of this paper is to *reformulate and generalize* the approach that Liu and Miller proposed[19] to *any* kind of distribution function for quantum thermal equilibrium systems. For the distribution function of choice, we wish to define a generalized trajectory-based dynamics that satisfies at least the following desirable properties:

(1) It should be constructed based on the phase space formulation of quantum mechanics [i.e., Eqs. (5)–(8)] so that it is able to describe correctly all thermal fluctuations of (large) molecular systems at equilibrium.
(2) Its dynamical evolution should conserve the equilibrium phase space distribution function (i.e., the quantum canonical phase space distribution function of choice).
(3) It reduces naturally to classical dynamics in the classical ($\hbar \to 0$) and high-temperature ($\beta \to 0$) limits and also gives correct quantum results in the limit of a harmonic system with an ensemble of classical trajectories.

The paper is organized as follows: Sec. II gives a brief introduction to the phase space density distribution function and the phase space formulation of quantum mechanics. Section III first reviews Liouville's theorem in classical mechanics, then presents a heuristic viewpoint to derive the force from the canonical density distribution function for the thermal equilibrium system, and finally introduces Liouville's theorem in the phase space formulation of quantum mechanics. Section IV proposes a family of trajectory-based dynamics in the spirit of Liouville's theorem in classical mechanics, which conserves the quantum canonical density distribution function in the phase space formulation of quantum mechanics. Section V further demonstrates that the centroid molecular dynamics (CMD) model of Voth and co-workers[51,52] can be reformulated to fall into the family of dynamics. Section VI summaries and concludes.

II. PHASE SPACE DENSITY DISTRIBUTION FUNCTION AND PHASE SPACE FORMULATION OF QUANTUM MECHANICS

In quantum mechanics, the density distribution function in the phase space is not uniquely defined. Quite a few representations[2,4,5,14,37,41–50] of the distribution function have been proposed, which are able to generate a *one-to-one* correspondence mapping from the density operator $\hat{\rho}$ (either a pure state or a mixed state) to the phase space. Thus, the expectation value of an *arbitrary* operator $\hat{B}(\hat{x}, \hat{p})$ corresponding to an experimental observable for the system at time t in quantum mechanics can be calculated by using the distribution function $\mathsf{P}(x, p; t)$ as

$$\begin{aligned}\langle B(t)\rangle &= \mathrm{Tr}[\hat{\rho}(t)\hat{B}]/\mathrm{Tr}[\hat{\rho}(t)] \\ &= \frac{1}{N_c(t)}\int dx \int dp\, \mathsf{P}(x, p; t)\,\tilde{B}(x, p),\end{aligned} \tag{5}$$

where the function $\tilde{B}(x, p)$ can be obtained from the operator $\hat{B}(\hat{x}, \hat{p})$ by a well-defined correspondence rule based on the representation. Here the normalization factor,

$$N_c(t) = \mathrm{Tr}[\hat{\rho}(t)] = \int dx \int dp\, \mathsf{P}(x, p; t), \tag{6}$$

is usually time independent, i.e., a constant $N_c(t) = N_c(0) \equiv N_c$.

Most of these phase-space representations can be expressed in the unified classification scheme of Cohen[38] given by the following equations:

$$\begin{aligned}\mathsf{P}(x, p; t) = \frac{1}{4\pi^2}\int d\zeta \int d\eta\, \mathrm{Tr}[\hat{\rho}(t)\, e^{i\zeta\hat{x}+i\eta\hat{p}} f(\zeta, \eta)] \\ \times e^{-i\zeta x - i\eta p}\end{aligned} \tag{7}$$

and

$$\begin{aligned}\tilde{B}(x, p) = \frac{2\pi\hbar}{4\pi^2}\int d\zeta \int d\eta\, \mathrm{Tr}[f(-\zeta, -\eta)^{-1} e^{i\zeta\hat{x}+i\eta\hat{p}}\hat{B}] \\ \times e^{-i\zeta x - i\eta p}.\end{aligned} \tag{8}$$

For example, the Wigner function[2,14] has

$$f(\zeta, \eta) = 1, \tag{9}$$

the Husimi function[37]

$$f(\zeta, \eta) = e^{-(\zeta^2/4\Gamma)-(\hbar^2\Gamma/4)\eta^2}, \tag{10}$$

the Kirkwood antistandard-ordered function,[42,43]

$$f(\zeta, \eta) = e^{i\hbar\zeta\eta/2}, \tag{11}$$

the Mehta standard-ordered function[44]

$$f(\zeta, \eta) = e^{-i\hbar\zeta\eta/2}, \tag{12}$$

the Rivier function,[45,46]

$$f(\zeta, \eta) = \cos\left[\frac{1}{2}\hbar\zeta\eta\right], \tag{13}$$

the Glauber–Sudarshan P function,[4,5,41]

$$f(\zeta, \eta) = e^{\hbar\zeta^2/4m\omega + \hbar m\omega\eta^2/4}, \tag{14}$$

and its generalized versions,[50,53] the Glauber Q function[5]

$$f(\zeta, \eta) = e^{-\hbar\zeta^2/4m\omega - \hbar m\omega\eta^2/4}, \tag{15}$$

the normal-antinormal ordered function[40]

$$f(\zeta, \eta) = \cosh\left[\frac{\hbar}{4m\omega}\zeta^2 + \frac{\hbar m\omega}{4}\eta^2\right], \tag{16}$$

and the distribution function of Born and Jordan[47]

$$f(\zeta, \eta) = \frac{\sin\left[\frac{1}{2}\hbar\zeta\eta\right]}{\frac{1}{2}\hbar\zeta\eta}, \tag{17}$$

etc. All these distribution functions are actually equivalent in the sense that they contain *all the physically meaningful information* and can be connected with one another.[38–40] For example, the Wigner function

$$\begin{aligned}\mathsf{P}_W(x, p) &= \frac{1}{4\pi^2}\int_{-\infty}^{\infty} d\zeta \int_{-\infty}^{\infty} d\eta \mathrm{Tr}[e^{i\zeta(\hat{x}-x)+i\eta(\hat{p}-p)}\hat{\rho}] \\ &= \frac{1}{2\pi\hbar}\int dy \left\langle x - \frac{y}{2}\right| \hat{\rho} \left| x + \frac{y}{2}\right\rangle e^{iyp/\hbar}\end{aligned} \tag{18}$$

and the Husimi function

$$\mathsf{P}_H(x,p) = \frac{1}{4\pi^2}\int_{-\infty}^{\infty}d\zeta\int_{-\infty}^{\infty}d\eta \times \mathrm{Tr}[e^{-(\zeta^2/4\Gamma)-(\hbar^2\Gamma/4)\eta^2}e^{i\zeta(\hat{x}-x)+i\eta(\hat{p}-p)}\hat{\rho}] = \frac{1}{2\pi\hbar}\langle x,p|\,\hat{\rho}\,|x,p\rangle \quad (19)$$

are related by

$$\mathsf{P}_H(x,p) = \frac{1}{\pi\hbar}\int dx'\int dp'\mathsf{P}_W(x',p')e^{-\Gamma(x-x')^2-(p-p')^2/\hbar^2\Gamma}, \quad (20)$$

or equivalently

$$\mathsf{P}_W(x,p) = \exp\left[-\frac{\Gamma}{4}\frac{\partial^2}{\partial x^2}-\frac{1}{4\Gamma}\frac{\partial^2}{\partial p^2}\right]\mathsf{P}_H(x,p). \quad (21)$$

Here the coherent state $|x,p\rangle$ can be expressed in coordinate space as

$$\langle y\,|x,p\rangle = \left(\frac{\Gamma}{\pi}\right)^{1/4}e^{-(\Gamma/2)(y-x)^2+(i/\hbar)p(y-x)}. \quad (22)$$

For the function $\tilde{B}(x,p)$ of Eq. (5), one has

$$\tilde{B}_W(x,p) = \frac{2\pi\hbar}{4\pi^2}\int_{-\infty}^{\infty}d\zeta\int_{-\infty}^{\infty}d\eta\mathrm{Tr}[e^{i\zeta(\hat{x}-x)+i\eta(\hat{p}-p)}\hat{B}] = \int dy\left\langle x-\frac{y}{2}\middle|\hat{B}\middle|x+\frac{y}{2}\right\rangle e^{iyp/\hbar} \quad (23)$$

in the Wigner representation, and

$$\tilde{B}_H(x,p) = \frac{2\pi\hbar}{4\pi^2}\int_{-\infty}^{\infty}d\zeta\int_{-\infty}^{\infty}d\eta \times \mathrm{Tr}[e^{(\zeta^2/4\Gamma)+(\hbar^2\Gamma/4)\eta^2}e^{i\zeta(\hat{x}-x)+i\eta(\hat{p}-p)}\hat{B}] \quad (24)$$

in the Husimi representation. [Note $\tilde{B}_H(x,p) \neq \langle x,p|\,\hat{B}\,|x,p\rangle$ in most cases.] The Wigner function,[2,14] the Husimi function,[37] the Glauber–Sudarshan P function,[4,5,41] the Glauber Q function,[5] the Rivier function,[45,46] and some others[48–50] are all real valued, which are the distribution functions that we discuss in this paper. Obviously, *all* these distribution functions are able to correctly describe thermal fluctuations of the (molecular) system at equilibrium since they contain all the physically meaningful information. The phase space formulation of quantum mechanics provides a solid basis for making the quantum-classical correspondence or analogy, as we will discuss further in Secs. IV and VI and two subsequent papers.

III. LIOUVILLE'S THEOREM IN CLASSICAL MECHANICS AND QUANTUM MECHANICS

A. Liouville's theorem in classical mechanics

1. Liouville's theorem

For the density distribution function P of the system with the Hamiltonian,

$$H(x,p) = \frac{p^2}{2m}+V(x), \quad (25)$$

in classical mechanics, Liouville's theorem in the Eulerian viewpoint[54] states

$$\frac{\partial\mathsf{P}(x,p;t)}{\partial t} = -\{P,H\}_{\mathrm{Poisson}} = -\left(\frac{\partial\mathsf{P}(x,p;t)}{\partial x}\frac{\partial H(x,p)}{\partial p}-\frac{\partial\mathsf{P}(x,p;t)}{\partial p}\frac{\partial H(x,p)}{\partial x}\right), \quad (26)$$

which for the Hamiltonian [Eq. (25)] is

$$\frac{\partial\mathsf{P}(x,p;t)}{\partial t} = -\frac{\partial\mathsf{P}(x,p;t)}{\partial x}\frac{p}{m}+\frac{\partial\mathsf{P}(x,p;t)}{\partial p}V'(x). \quad (27)$$

In this paper, we refer to Eqs. (26) or (27) as Liouville's theorem of the first kind in classical mechanics. In classical mechanics, an alternative statement of the theorem[54] [in the Lagrangian picture, i.e., following the classical trajectory (x_t,p_t)] is

$$\frac{d\mathsf{P}(x_t,p_t;t)}{dt} = 0, \quad (28)$$

i.e., the value of the density distribution function is invariant along the classical trajectory. We refer to Eq. (28) as Liouville's theorem of the second kind in classical mechanics.

The following equality *always* holds:

$$\frac{d\mathsf{P}(x_t,p_t;t)}{dt} = \frac{\partial\mathsf{P}(x_t,p_t;t)}{\partial x_t}\dot{x}_t+\frac{\partial\mathsf{P}(x_t,p_t;t)}{\partial p_t}\dot{p}_t+\frac{\partial\mathsf{P}(x_t,p_t;t)}{\partial t}, \quad (29)$$

where the first two terms on the right-hand side (RHS) arise from the implicit dependence, and the last term on the RHS from the explicit dependence. Since Eqs. (27)–(29) hold for *any phase point at any time for any arbitrary density distribution function* $\mathsf{P}(x_t,p_t;t)$, if one selects $\dot{x}_t = p_t/m$ to be the relation between the position and momentum which is independent of the density distribution function and of the system, then one obtains the classical equations of motion from Liouville's theorem,

$$\begin{aligned}\dot{x}_t &= \frac{p_t}{m}\\ \dot{p}_t &= -V'(x_t).\end{aligned} \quad (30)$$

Since the classical force $-V'(x_t)$ is uniquely defined, the classical equations of motion above are deterministic and thus time reversible.

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

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

$$\mathsf{P}^{\mathrm{eq}}(x,p) = \left(\frac{\beta}{2\pi m}\right)^{1/2}e^{-\beta((p^2/2m)+V(x))} = \left(\frac{\beta}{2\pi m}\right)^{1/2}e^{-\beta H(x,p)}, \quad (31)$$

with the classical partition function as the normalization factor

$$Z = \int dx\, e^{-\beta V(x)} = \int dx \int dp\, \mathsf{P}^{\rm eq}(x, p). \tag{32}$$

It is easy to see that the classical equations of motion [Eq. (30)] conserve the classical canonical distribution [Eq. (31)], i.e., the canonical distribution function $\mathsf{P}^{\rm eq}(x, p)$ is stationary,

$$\frac{\partial \mathsf{P}^{\rm eq}(x, p; t)}{\partial t} = 0. \tag{33}$$

Equation (33) provides alternative ways to derive the classical force from the canonical density distribution function for the thermal equilibrium system, as we show below.

By virtue of Liouville's theorem of the first kind in classical mechanics, substituting Eq. (33) into Eq. (27), one has

$$\frac{\partial \mathsf{P}^{\rm eq}(x, p)}{\partial p} V'(x) = \frac{\partial \mathsf{P}^{\rm eq}(x, p)}{\partial x} \frac{p}{m}, \tag{34}$$

which gives an equivalent form to calculate the classical force $-V'(x)$ by using its canonical density distribution function $\mathsf{P}^{\rm eq}(x, p)$ for the thermal equilibrium system. Since the partial distribution function for the momentum p at any fixed position x is a Gaussian function according to Eq. (31), the classical force $-V'(x)$ given in Eq. (34) is always *uniquely* defined by the classical Boltzmann/canonical density distribution function $\mathsf{P}^{\rm eq}(x, p)$ [Eq. (31)].

For thermal equilibrium systems in classical mechanics, one can always define the classical equations of motion [i.e., Eq. (30)] based on Liouville's theorem with the classical force given by Eq. (34). The insight provides a heuristic procedure for making the quantum-classical correspondence or analogy in the phase space formulation of quantum mechanics.

B. Liouville's theorem in the phase space formulation of quantum mechanics

Liouville's theorem in quantum mechanics (the von Neumann equation) states that

$$\frac{\partial \hat{\rho}(t)}{\partial t} = -\frac{1}{i\hbar}[\hat{\rho}(t), \hat{H}]. \tag{35}$$

As shown in Appendix A, Eq. (35) can be written in the Wigner phase space representation as

$$\frac{\partial \mathsf{P}_W(x, p; t)}{\partial t} = -\frac{\partial \mathsf{P}_W}{\partial x}\frac{p}{m} + \frac{\partial \mathsf{P}_W}{\partial p} V'(x) - \frac{\hbar^2}{24}\frac{\partial^3 \mathsf{P}_W}{\partial p^3} V^{(3)}(x) + \cdots, \tag{36}$$

which is known as the Wigner–Moyal equation;[2,3] and in the Husimi phase space representation as

$$\begin{aligned}\frac{\partial \mathsf{P}_H(x, p; t)}{\partial t} = &-\frac{\partial \mathsf{P}_H}{\partial x}\frac{p}{m} + \frac{\partial \mathsf{P}_H}{\partial p} V'(x) - \frac{\hbar^2\Gamma}{2m}\frac{\partial^2 \mathsf{P}_H}{\partial p \partial x} \\ &+ \hbar \frac{V^{(2)}(x)}{2!}\frac{\partial}{\partial p}\langle x, p| \left(-i\frac{\overleftarrow{\partial}}{\partial p}\right)\frac{\hat{\rho}}{2\pi\hbar} \\ &+ \frac{\hat{\rho}}{2\pi\hbar}\left(-i\frac{\overrightarrow{\partial}}{\partial p}\right)|x, p\rangle + \hbar^2 \frac{V^{(3)}(x)}{3!}\frac{\partial}{\partial p} \\ &\times \langle x, p|\left(-i\frac{\overleftarrow{\partial}}{\partial p}\right)^2 \frac{\hat{\rho}}{2\pi\hbar} + \left(-i\frac{\overleftarrow{\partial}}{\partial p}\right)\frac{\hat{\rho}}{2\pi\hbar} \\ &\times \left(-i\frac{\overrightarrow{\partial}}{\partial p}\right) + \frac{\hat{\rho}}{2\pi\hbar}\left(-i\frac{\overrightarrow{\partial}}{\partial p}\right)^2 |x, p\rangle \\ &+ \cdots\end{aligned} \tag{37}$$

with the notation for half operators (acting on either the coherent state ket or bra) defined as

$$\begin{aligned}\hbar\langle x, p|\left(-i\frac{\overleftarrow{\partial}}{\partial p}\right)\hat{\rho} &= \langle x, p|(\hat{x} - x)\hat{\rho} \\ \hbar\hat{\rho}\left(-i\frac{\overrightarrow{\partial}}{\partial p}\right)|x, p\rangle &= \hat{\rho}(\hat{x} - x)|x, p\rangle.\end{aligned} \tag{38}$$

Similarly, one can also express quantum Liouville's theorem in the phase space based on any of the other distribution functions discussed in Sec. II. A general form of the phase space formulation of Liouville's theorem can be obtained as shown by Cohen[38] and Lee.[40]

For thermal equilibrium systems, the canonical distribution function $\mathsf{P}^{\rm eq}(x, p)$, i.e., the density distribution function for the Boltzmann operator $e^{-\beta\hat{H}(\hat{x},\hat{p})} \equiv e^{-\beta((\hat{p}^2/2m)+V(\hat{x}))}$ in the phase space, can be rigorously generated from the distribution functions in Sec. II. For instance, the Wigner density distribution function for the Boltzmann operator gives

$$\begin{aligned}\mathsf{P}_W^{\rm eq}(x, p) &= \frac{1}{4\pi^2}\int_{-\infty}^{\infty} d\zeta \int_{-\infty}^{\infty} d\eta {\rm Tr}[e^{i\zeta(\hat{x}-x)+i\eta(\hat{p}-p)}e^{-\beta\hat{H}}] \\ &= \frac{1}{2\pi\hbar}\int dy \left\langle x - \frac{y}{2}\right| e^{-\beta\hat{H}} \left|x + \frac{y}{2}\right\rangle e^{iyp/\hbar}\end{aligned} \tag{39}$$

and the Husimi distribution function

$$\begin{aligned}\mathsf{P}_H^{\rm eq}(x, p) &= \frac{1}{4\pi^2}\int_{-\infty}^{\infty} d\zeta \int_{-\infty}^{\infty} d\eta \\ &\quad \times {\rm Tr}[e^{-(\zeta^2/4\Gamma)-(\hbar^2\Gamma/4)\eta^2} e^{i\zeta(\hat{x}-x)+i\eta(\hat{p}-p)} e^{-\beta\hat{H}}] \\ &= \frac{1}{2\pi\hbar}\langle x, p| e^{-\beta\hat{H}} |x, p\rangle,\end{aligned} \tag{40}$$

with the quantum partition function as the normalization factor

$$Z = {\rm Tr}[e^{-\beta\hat{H}}] = \int dx \int dp\, \mathsf{P}^{\rm eq}(x, p). \tag{41}$$

Because the system is at thermal equilibrium, the canonical distribution function $\mathsf{P}^{\rm eq}(x, p)$ is stationary no matter which phase space representation of the distribution function is used, i.e.,

$$\frac{\partial \mathsf{P}^{\rm eq}(x, p; t)}{\partial t} = 0. \tag{42}$$

There are various ways to rewrite the phase space formulation of quantum Liouville's theorem [e.g., Eq. (36) or Eq. (37)] for making analogies to classical mechanics (i.e., to

show the quantum-classical correspondence), as we will discuss in Sec. IV, Appendix B, and a subsequent paper.

IV. TRAJECTORY-BASED DYNAMICS IN THE SPIRIT OF LIOUVILLE'S THEOREM IN CLASSICAL MECHANICS

A. Equilibrium Liouville dynamics

If one can define an effective force $-(\partial/\partial x)V_{\rm eff}(x,p)$ in Eq. (36) as

$$\left(\frac{\partial \mathsf{P}_W}{\partial p}\right)\frac{\partial V_{\rm eff}(x,p)}{\partial x}=\left(\frac{\partial \mathsf{P}_W}{\partial p}\right)V'(x)-\frac{\hbar^2}{24}\frac{\partial^3 \mathsf{P}_W}{\partial p^3}V^{(3)}(x)+\cdots \quad (43)$$

[e.g., as in Lee and Scully's "Wigner trajectories" in 1980s[55]], or in Eq. (37) as

$$\begin{aligned}\left(\frac{\partial \mathsf{P}_H}{\partial p}\right)\frac{\partial V_{\rm eff}(x,p)}{\partial x}&=\left(\frac{\partial \mathsf{P}_H}{\partial p}\right)V'(x)-\frac{\hbar^2\Gamma}{2m}\frac{\partial^2 \mathsf{P}_H}{\partial p\partial q}\\&+\hbar\frac{V^{(2)}(x)}{2!}\frac{\partial}{\partial p}\langle x,p|\left(-i\frac{\overleftarrow{\partial}}{\partial p}\right)\frac{\hat\rho}{2\pi\hbar}+\frac{\hat\rho}{2\pi\hbar}\left(-i\frac{\overrightarrow{\partial}}{\partial p}\right)|x,p\rangle\\&+\hbar^2\frac{V^{(3)}(x)}{3!}\frac{\partial}{\partial p}\langle x,p|\left(-i\frac{\overleftarrow{\partial}}{\partial p}\right)^2\frac{\hat\rho}{2\pi\hbar}\\&+\left(-i\frac{\overleftarrow{\partial}}{\partial p}\right)\frac{\hat\rho}{2\pi\hbar}\left(-i\frac{\overrightarrow{\partial}}{\partial p}\right)+\frac{\hat\rho}{2\pi\hbar}\left(-i\frac{\overrightarrow{\partial}}{\partial p}\right)^2|x,p\rangle\\&+\cdots,\end{aligned} \quad (44)$$

then Eq. (36) or Eq. (37) becomes

$$\frac{\partial \mathsf{P}(x,p;t)}{\partial t}=-\frac{\partial \mathsf{P}}{\partial x}\frac{p}{m}+\frac{\partial \mathsf{P}}{\partial p}\frac{\partial V_{\rm eff}(x,p)}{\partial x}. \quad (45)$$

Equation (45) is another expression of Liouville's theorem in the phase space formulation of quantum mechanics. One sees the quantum-classical correspondence between Eq. (45) and its classical counterpart Eq. (27). [However, it is important to point out that the effective force $-(\partial/\partial x)V_{\rm eff}(x,p)$ is *not* guaranteed to be always well defined [in Eq. (43) or Eq. (44)] at any phase point (x,p), although the RHS of Eq. (43) or Eq. (44) always exists and is equal to $(\partial \mathsf{P}(x,p;t)/\partial t)+(\partial \mathsf{P}/\partial x)(p/m)$. One should be careful with this particularly for nonstationary density distribution functions [while the phase points satisfy $(\partial \mathsf{P}(x,p;t)/\partial p)=0$]. Nevertheless, the effective force for the thermal equilibrium system is often well defined as we will discuss below.]

Similar to the viewpoint that stationarity of the classical canonical distribution function enables one to obtain the classical force [i.e., Eq. (34)], stationarity of the quantum canonical distribution function [i.e., Eq. (42)] provides a way to obtain the effective force $-(\partial V_{\rm eff}(x,p)/\partial x)$,

$$\frac{\partial \mathsf{P}^{\rm eq}(x,p)}{\partial p}\frac{\partial V_{\rm eff}(x,p)}{\partial x}=\frac{\partial \mathsf{P}^{\rm eq}(x,p)}{\partial x}\frac{p}{m}. \quad (46)$$

Once a phase space is constructed based on a (real) distribution function in Sec. II, the quantum canonical distribution function $\rho^{\rm eq}(x,p)$ is uniquely defined and continuous in the phase space. If the partial distribution function for the momentum p at any fixed position x based on the equilibrium density distribution $\mathsf{P}^{\rm eq}(x,p)$ is (effectively) a Gaussian function, then Eq. (46) always gives a *uniquely* defined and continuous effective force $-(\partial V_{\rm eff}(x,p)/\partial x)$ for any phase point (x,p). [See more discussion in Appendix E.]

If the trajectory in the phase space is chosen to satisfy

$$\frac{d\mathsf{P}^{\rm eq}(x_t,p_t;t)}{dt}=0 \quad (47)$$

as an analogy to Liouville's theorem of the second kind in classical mechanics [Eq. (28)], one can use the equality Eq. (29) and the phase space formulation of Liouville's theorem in quantum mechanics Eq. (45) to obtain

$$\frac{d\mathsf{P}^{\rm eq}(x_t,p_t;t)}{\partial t}=\frac{\partial \mathsf{P}^{\rm eq}(x_t,p_t;t)}{\partial x_t}\left(\dot x_t-\frac{p_t}{m}\right)+\frac{\partial \mathsf{P}^{\rm eq}(x_t,p_t;t)}{\partial p_t}\left(\dot p_t+\frac{\partial V_{\rm eff}(x_t,p_t)}{\partial x_t}\right). \quad (48)$$

[Note that one can derive Eq. (48) from Eqs. (29) and (45) for not only equilibrium density distribution functions $\mathsf{P}^{\rm eq}(x_t,p_t;t)$ but also nonequilibrium density distribution functions $\mathsf{P}(x_t,p_t;t)$.] As before, we define $\dot x_t=p_t/m$ to be the relation between the position and momentum, which is independent of the density distribution function and independent of the system. Equation (47) requires that the RHS of the above equation always be zero for any phase point (x_t,p_t) along the trajectory at any time for any density distribution function in Eq. (47). The solution to Eq. (48) consistent with all these conditions leads to the equations of motion for the trajectory

$$\begin{aligned}\dot x_t&=\frac{p_t}{m}\\ \dot p_t&=-\frac{\partial V_{\rm eff}(x_t,p_t)}{\partial x_t}.\end{aligned} \quad (49)$$

By virtue of Eq. (45), the equations of motion [Eq. (49)] with the effective force given by its equilibrium density distribution function $\mathsf{P}^{\rm eq}(x,p)$ [Eq. (46)] are able to generate a trajectory-based dynamics that conserves the equilibrium density distribution [Eq. (42)] based on *any* distribution function discussed in Sec. II. We have already proposed the trajectory-based dynamics [i.e., Eq. (49) with Eq. (46)] in the Wigner phase space formulation as one of the key results of our recent paper[19] (i.e., so-called "full Wigner dynamics"). Here we show that the approach can be generalized to other distribution functions in Sec. II. We refer to this family of dynamics as "equilibrium Liouville dynamics" (ELD).

It is important to point out that Eq. (47) cannot be derived from quantum Liouville's theorem even though Eq. (28) is Liouville's theorem of the second kind in classical mechanics. This is not surprising. Due to the Heisenberg uncertainty principle, there is no *unique* way to define the equations of motion for trajectories in the phase space formulation of quantum mechanics. The phase space formulation of quantum mechanics naturally gives insights into the quantum-classical

correspondence [e.g., between Eqs. (27) and (45)] and noncorrespondence [e.g., Eq. (28) always holds in classical mechanics but Eq. (47) is not required in quantum mechanics] for Liouville's theorem. Equation (47) is a way to generate a family of trajectory-based dynamics (i.e., ELD) in the spirit of the classical Liouville's theorem of second kind [Eq. (28)]. One can define other types of trajectory-based dynamics in other ways. More discussions are available in Appendix B and a subsequent paper.

B. ELD trajectories and canonical ensemble averages

We now show four important properties of the ELD dynamics [i.e., Eq. (49) with Eq. (46)]. First, the value of the density distribution function that the ELD trajectory carries is invariant as the trajectory propagates due to Eq. (47), i.e.,

$$\mathsf{P}^{\mathrm{eq}}\left(x_t\left(x_0,\, p_0\right),\, p_t\left(x_0,\, p_0\right);t\right) = \mathsf{P}^{\mathrm{eq}}\left(x_0,\, p_0;0\right). \tag{50}$$

The ELD trajectory evolves on a shell with a constant value of the density distribution function $\mathsf{P}^{\mathrm{eq}}(x,\, p)$ (i.e., the equiquasidensity hypersurface).

Second, any two trajectories from different initial phase points in the phase space governed by the dynamics do *not* cross each other. Due to the *one-to-one* correspondence mapping of the density distribution function described in Sec. II, the canonical distribution function and the effective force $-(\partial V_{\mathrm{eff}}(x,\, p)/\partial x)$ given by Eq. (46) are uniquely defined at any phase point $(x,\, p)$ for the thermal equilibrium system. So any two trajectories from different initial phase points do not cross each other in the phase space, similar to classical dynamics.

Third, the ELD trajectory is time reversible. This follows for the same reasons as above —the density distribution function and the effective force $-(\partial V_{\mathrm{eff}}(x,\, p)/\partial x)$ given by Eq. (46) are uniquely defined at any phase point $(x,\, p)$ for the thermal equilibrium system, such that the ELD equations of motion in Eq. (49) are deterministic.

Fourth, the phase space represented by the variables $(x_t,\, p_t)$ at time t is a *one-to-one* correspondence mapping of the phase space represented by the variables $(x_0,\, p_0)$ at time 0. The mapping rule is governed by the equations of motion Eq. (49) with the effective force defined in Eq. (46). Because of the noncrossing and time-reversibility properties outlined above, $(x_0,\, p_0)$ and $(x_t,\, p_t)$ are in one-to-one correspondence. As long as the ensemble of initial points $(x_0,\, p_0)$ is able to represent the whole phase space $(x,\, p)$ in the Eulerian picture, its counterpart ensemble of points $(x_t,\, p_t)$ at time t is able to do the same as well, i.e., no area of the phase space in the Eulerian picture will not be visited by the ensemble of trajectories.

These properties suggest ELD can provide a robust algorithm for including quantum effects in (large) molecular systems. One can use Eq. (D5) or Eq. (D6) in Appendix D to evaluate a dynamical physical property [i.e., Eq. (5)] for systems at thermal equilibrium, i.e.,

$$\langle B\left(t\right)\rangle = \frac{1}{Z}\int dx_0 \int dp_0\, \mathsf{P}^{\mathrm{eq}}\left(x_0,\, p_0;0\right)\tilde{B}(x_t(x_0,\, p_0),\, p_t(x_0,\, p_0)). \tag{51}$$

Because ELD conserves the (thermal) equilibrium density distribution by construction [i.e., Eq. (42) or Eq. (46)] and satisfies Eq. (50), one can switch Eq. (51) to the Eulerian viewpoint [i.e., Eq. (5)] based on Eq. (D5) to show that canonical ensemble averages or thermodynamic properties (such as the average kinetic energy) and their thermal fluctuations for systems at equilibrium are invariant with time as the exact case is [i.e., Eq. (2)].

One can implement the time average in Eq. (51) to obtain the ensemble average of the thermal equilibrium system, i.e.,

$$\begin{aligned}\langle B\rangle &= \frac{1}{T}\int_0^T dt\, \langle B\left(t\right)\rangle \\ &= \frac{1}{Z}\int dx_0 \int dp_0\, \mathsf{P}^{\mathrm{eq}}\left(x_0,\, p_0;0\right) \\ &\quad\times\left[\frac{1}{T}\int_0^T dt\, \tilde{B}\left(x_t\left(x_0,\, p_0\right),\, p_t\left(x_0,\, p_0\right)\right)\right].\end{aligned} \tag{52}$$

For ergodic systems, Eq. (52) can be given by

$$\langle B\rangle = \lim_{T\to\infty}\frac{1}{T}\int_0^T dt\, \tilde{B}\left(x_t\left(x_0,\, p_0\right),\, p_t\left(x_0,\, p_0\right)\right). \tag{53}$$

C. Choice of the phase space distribution function

Since the ELD approach can generate trajectory-based dynamics that conserves the quantum canonical distribution in any phase space formulation of quantum mechanics, one might conclude that it is a matter of taste to choose the distribution function for ELD. However, this is often not the case. Whether a reasonable description on quantum dynamics is obtained or not actually depends on the choice of phase space distribution function. This is because Eq. (47) or Eq. (49) is a *sufficient but not necessary* condition for conserving the quantum canonical distribution function. Although Liouville's theorem in classical mechanics can be expressed in either Eq. (27) or Eq. (28), its correspondence in the phase space formulation of quantum mechanics only requires Eq. (45) but not Eq. (47). Due to the Heisenberg uncertainty principle, it is impossible to uniquely define the distribution function and trajectory-based dynamics in the phase space formulation of quantum mechanics. Criterion 3 suggested in Sec. I helps choose a particular phase space distribution function that is able to get quantum dynamics results in the following three important limits.

1. Classical limit

In the classical limit $\hbar \to 0$, quantum Liouville's theorem in any phase space representation (i.e., with any distribution function in Sec. I) naturally reduces to classical Liouville's theorem. For example, in the limit of $\hbar \to 0$, Eq. (36) or Eq. (37) [with $\Gamma \to \infty$, i.e., coherent state goes to position state] leads to the classical form [Eq. (34)], the effective force $-V'_{\mathrm{eff}}(x,\, p)$ in Eq. (46) approaches the classical force $-V'(x)$, and dynamics in Eq. (49) becomes classical dynamics.

2. High temperature limit

In the high temperature limit $\beta \to 0$, one has $e^{-\beta\hat{H}} \to e^{-\beta(\hat{p}^2/2m)}e^{-\beta\hat{V}(\hat{x})}$. It is straightforward to show the canonical distribution in any representation (i.e., for any distribution function in Sec. I) becomes the classical density distribution. For example, the Wigner or Husimi representation [Eq. (39) or Eq. (40)] naturally reduces to the classical form [Eq. (31)], the effective force $-V'_{\rm eff}(x,\,p)$ in Eq. (46) approaches the classical force $-V'(x)$, and dynamics in Eq. (49) becomes classical dynamics.

3. Harmonic limit

For a 1-dim harmonic potential $V(x) = (1/2)m\omega^2x^2$, one has

$$\langle x|\, e^{-\beta\hat{H}}\, |y\rangle = \left(\frac{m\omega}{2\pi\hbar\sinh[u]}\right)^{1/2} \times \exp\left[-\frac{m\omega}{2\hbar\sinh[u]}\,(\cosh[u](x^2+y^2)-2xy)\right] \tag{54}$$

with the dimensionless parameter

$$u = \beta\hbar\omega. \tag{55}$$

Defining the quantum correction factor $Q\,(u)$ as

$$Q(u) = \frac{u/2}{\tanh[u/2]}, \tag{56}$$

it is then trivial to show that the Wigner density distribution function is

$$\mathsf{P}_W^{\rm eq}(x,\,p) = \frac{1}{2\pi\hbar\cosh\left[u/2\right]} \times \exp\left[-\frac{\beta}{Q\,(u)}\left(\frac{p^2}{2m}+\frac{1}{2}m\omega^2x^2\right)\right] \tag{57}$$

and the effective force defined in Eq. (46) is

$$-\frac{\partial V_{\rm eff}(x,\,p)}{\partial x} = -m\omega^2x. \tag{58}$$

The equations of motion in ELD [Eq. (49)] then reduces to the classical case.

One can also show that the Husimi density distribution function is

$$\mathsf{P}_H^{\rm eq}(x,\,p) = \frac{1}{2\pi\hbar\sinh[u/2]}\left(\frac{\Gamma mu^2}{(\beta\hbar^2\Gamma+2mQ(u))(2\Gamma Q(u)+\beta m\omega^2)}\right)^{1/2} \times \exp\left[-\frac{p^2}{(\hbar^2\Gamma+2mQ\,(u)/\beta)}-\frac{\Gamma\beta m\omega^2}{2\Gamma Q\,(u)+\beta m\omega^2}x^2\right]. \tag{59}$$

The effective force is

$$-\frac{\partial V_{\rm eff}(x,\,p)}{\partial x} = -m\omega^2x\left(\frac{2\Gamma Q\,(u)+\beta\hbar^2\Gamma^2/m}{2\Gamma Q\,(u)+\beta m\omega^2}\right). \tag{60}$$

It becomes the classical force if and only if

$$\Gamma = \frac{m\omega}{\hbar}, \tag{61}$$

i.e., when the Husimi distribution function is the same as the Glauber Q function[5] listed in Eq. (15). For the general anharmonic potential, one will have to find the optimal value (regime) for the width parameter Γ. (See Paper II for more discussions.)

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 ELD approach classical dynamics in the harmonic limit. Note that the Glauber Q function can be viewed as a special case of the Husimi function. When the Wigner distribution function Eq. (39) is used for the dynamics Eq. (49), we refer to it as Wigner ELD (W-ELD) for convenience. Similarly, we refer to the ELD dynamics Eq. (49) with the Husimi function Eq. (40) as Husimi ELD (H-ELD). One sees that H-ELD has an adjustable parameter Γ while W-ELD has none.

V. THE RELATION BETWEEN THE ELD TRAJECTORY-BASED DYNAMICS AND CENTROID MOLECULAR DYNAMICS

The Baker–Campbell–Hausdorff formula

$$e^{\hat{A}}e^{\hat{B}} = e^{\hat{A}+\hat{B}+(1/2)[\hat{A},\hat{B}]+(1/12)[\hat{A}-\hat{B},\,[\hat{A},\hat{B}]]+\cdots}, \tag{62}$$

leads to the inequality

$$e^{i\zeta\hat{x}+i\eta\hat{p}}e^{-\beta\hat{H}} \neq e^{i\zeta\hat{x}+i\eta\hat{p}-\beta\hat{H}}. \tag{63}$$

If one ignores the noncommutivity of quantum mechanical operators, then one can show the following formula with the Trotter product formula and with the path integral representation:

$$\begin{aligned} e^{i\zeta\hat{x}+i\eta\hat{p}}e^{-\beta\hat{H}} &\approx e^{i\zeta\hat{x}+i\eta\hat{p}-\beta\hat{H}} \\ &= \lim_{P\to\infty}(e^{i(\zeta/P)\hat{x}+i(\eta/P)\hat{p}-(\beta/P)\hat{H}})^P \\ &= \lim_{P\to\infty}(e^{i(\zeta/2P)\hat{x}-(\beta/2P)\hat{V}(\hat{x})}e^{-(\beta/P)(\hat{p}^2/2m)+i(\eta/P)\hat{p}}e^{i(\zeta/2P)\hat{x}-(\beta/2P)\hat{V}(\hat{x})})^P \\ &= \lim_{P\to\infty}\int dx_1\cdots\int dx_{P+1}\,|x_1\rangle\, e^{-(\beta/2P)V(x_1)+i\zeta(x_1/2P)}\,\langle x_1|\, e^{-(\beta/P)(\hat{p}^2/2m)+i\eta(\hat{p}/P)}\,|x_2\rangle\cdots \\ &\quad\times e^{-(\beta/P)V(x_P)+i\zeta(x_P/P)}\,\langle x_P|\, e^{-(\beta/P)(\hat{p}^2/2m)+i\eta(\hat{p}/P)}\,|x_{P+1}\rangle\, e^{-(\beta/2P)V(x_P)+i\zeta(x_P/2P)}\,\langle x_{P+1}|\,. \end{aligned} \tag{64}$$

With the equality

$$\langle x|\, e^{-(\beta/P)(\hat{p}^2/2m)+i\eta(\hat{p}/P)}\,|y\rangle = \int dp_1\, \langle x|\ p_1\rangle\, e^{-(\beta/P)(p_1^2/2m)+i\eta(p_1/P)}\, \langle p_1\ |y\rangle$$
$$= \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{1/2} e^{-(Pm/2\beta\hbar^2)(x-y)^2-(m/\beta\hbar)(x-y)\eta-(m/2\beta P)\eta^2}, \tag{65}$$

Equation (64) becomes

$$e^{i\zeta\hat{x}+i\eta\hat{p}}e^{-\beta\hat{H}} \approx e^{i\zeta\hat{x}+i\eta\hat{p}-\beta\hat{H}}$$
$$= \lim_{P\to\infty}\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2}\int dx_1\cdots\int dx_{P+1}\,|x_1\rangle\, e^{-(Pm/2\beta\hbar^2)\sum_{j=1}^{P}(x_j-x_{j+1})^2-(\beta/P)\left((1/2)V(x_1)+\sum_{j=2}^{P}V(x_j)+(1/2)V(x_{P+1})\right)}$$
$$\times\, e^{i\zeta\left[(1/P)\left((1/2)x_1+\sum_{j=2}^{P}x_j+(1/2)x_{P+1}\right)\right]}e^{-(m/2\beta)\eta^2-(m/\beta\hbar)(x_1-x_{P+1})\eta}\,\langle x_{P+1}|\,. \tag{66}$$

One can then show that the Wigner density distribution function Eq. (39) can be approximated by

$$\mathsf{P}_W^{\mathrm{eq}}(x,p) = \frac{1}{Z}\frac{1}{4\pi^2}\int_{-\infty}^{\infty}d\zeta\int_{-\infty}^{\infty}d\eta\,\mathrm{Tr}[e^{i\zeta(\hat{x}-x)+i\eta(\hat{p}-p)}e^{-\beta\hat{H}}]$$
$$= \frac{1}{Z}\frac{1}{4\pi^2}\mathrm{Tr}\left[\int_{-\infty}^{\infty}d\zeta\int_{-\infty}^{\infty}d\eta\; e^{i\zeta(\hat{x}-x)+i\eta(\hat{p}-p)}e^{-\beta\hat{H}}\right]$$
$$\approx \frac{1}{Z}\frac{1}{4\pi^2}\mathrm{Tr}\left[\int_{-\infty}^{\infty}d\zeta\int_{-\infty}^{\infty}d\eta\; e^{i\zeta(\hat{x}-x)+i\eta(\hat{p}-p)-\beta\hat{H}}\right]$$
$$= \frac{1}{Z}\left(\frac{\beta}{2m\pi}\right)^{1/2}e^{-\beta(p^2/2m)}\rho_c(x) \tag{67}$$

with the definition of the centroid variable

$$x_c = \frac{1}{P}(x_1 + x_2 + \cdots + x_P) \tag{68}$$

and the centroid density

$$\rho_c(x) = \lim_{P\to\infty}\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2}\int dx_1\cdots\int dx_P\,\delta(x-x_c)$$
$$\times\exp\left\{-\frac{Pm}{2\beta\hbar^2}[(x_1-x_2)^2+\cdots+(x_P-x_1)^2]\right\}$$
$$\times\exp\left\{-\frac{\beta}{P}[V(x_1)+\cdots+V(x_P)]\right\}, \tag{69}$$

which gives the partition function

$$Z = \int dx\ \rho_c(x). \tag{70}$$

By virtue of Eq. (46) in the ELD approach, one obtains the effective force for the thermal equilibrium system as

$$-\frac{\partial V_{\mathrm{eff}}^{\mathrm{ELD}}(x,p)}{\partial x} = \frac{\frac{1}{\beta}\frac{\partial\rho_c(x)}{\partial x}}{\rho_c(x)} = \frac{1}{\beta}\frac{\partial}{\partial x}\ln[\rho_c(x)]\,. \tag{71}$$

With the choice of the equations of motion Eq. (49) of ELD, one then obtains the CMD initially proposed by Cao and Voth[51] and rederived by Jang and Voth[52] [We note that Eqs. (64)–(70) can be closely related to the work of Jang and Voth in Refs. 52 and 56 while neglecting the inequality Eq. (63).]

Comparing Eq. (67) to Eq. (39), one sees that the position x of the phase space (x, p) of W-ELD corresponds to that of one path integral bead, while the position x in CMD is that of the centroid of the path integral beads. Similar to ELD, CMD conserves the quantum canonical distribution Eq. (67). To evaluate a dynamical variable (observable) $B(t)$, Eq. (5) or its equivalent version for the thermal equilibrium system

$$\langle B(t)\rangle = \frac{1}{Z}\int dx\int dp\ \mathsf{P}_W^{\mathrm{eq}}(x,p)B_W(x_t(x,p),p_t(x,p)) \tag{72}$$

can be used by following the trajectories in either "CMD with the classical operator" [i.e., substituting Eq. (67) into Eq. (72)], or W-ELD (as described in Sec. IV). [Note that the Wigner function of the operator $\hat{B}$ is the classical function itself when it is a function only of coordinate or only of momentum, i.e., $\tilde{B}(x) = B_W(x) = B_{\mathrm{cl}}(x)$ or $\tilde{B}(p) = B_W(p) = B_{\mathrm{cl}}(p)$.] However, due to the inequality [Eq. (63)], CMD with the classical operator is not a one-to-one correspondence mapping required in the phase space formulation of quantum mechanics as Eq. (5) is—it fails to give exact values for general operators $\hat{B}$ (even in the harmonic limit) and thus cannot correctly describe all thermal fluctuations of the large (molecular) system at equilibrium. [Jang and Voth[52] has further proposed "CMD with the effective classical operator" to give the correct result for $\langle B(t)\rangle$, although it still fails to work for correlation functions involving nonlinear operators.] CMD with the classical operator can be viewed as an approximation to W-ELD due to Eq. (67).

From another point of view, in order to make the mapping with the density distribution function in Eq. (67) rigorously

correct in the phase space formulation of quantum mechanics, one needs to employ a system-dependent function $f(\zeta, \eta)$ in Eq. (7), i.e.,

$$f(\zeta, \eta) = e^{-i\zeta\hat{x}-i\eta\hat{p}} e^{\beta\hat{H}} e^{i\zeta\hat{x}+i\eta\hat{p}-\beta\hat{H}}. \tag{73}$$

[Note that the function $f(\zeta, \eta)$ in Eq. (7) is usually independent of the system for most distribution functions in Sec. II and can also be applied to the system in a pure state.] That is, Eq. (7) with the function $f(\zeta, \eta)$ defined by Eq. (73) leads to the density distribution function as

$$\begin{aligned} \mathrm{P}^{\mathrm{eq}}_{\mathrm{CMD}}(x, p) &= \frac{1}{Z}\frac{1}{4\pi^2}\int_{-\infty}^{\infty} d\zeta \int_{-\infty}^{\infty} d\eta \, \mathrm{Tr}[e^{i\zeta\hat{x}+i\eta\hat{p}-\beta\hat{H}}]\, e^{-i\zeta x-i\eta p} \\ &= \frac{1}{Z}\left(\frac{\beta}{2m\pi}\right)^{1/2} e^{-\beta(p^2/2m)}\rho_c(x). \end{aligned} \tag{74}$$

[While Eq. (74) has already been stated in Refs. 52 and 56, Eq. (73) suggests that it can be included in the unified classification scheme of Cohen[38] and its extension.] However, since the function $f(\zeta, \eta)$ in Eq. (73) is system dependent, this gives rise to ambiguity in using Eq. (8) to obtain the function $\tilde{B}_{\mathrm{CMD}}(x_t(x, p), p_t(x, p))$ for general nonlinear operators $\hat{B}$ along the CMD trajectory. Further work along this line will be of interest to see whether one can give a unique definition of $\tilde{B}_{\mathrm{CMD}}$ so that CMD can give exact autocorrelation functions of nonlinear operators in the harmonic limit.

Nevertheless, from either point of view, CMD falls into the category of ELD trajectory-based dynamics, which conserves the quantum canonical distribution in the phase space formulation of quantum mechanics.

VI. CONCLUDING REMARKS

In this paper, we have presented an approach based on our previous work,[19] and in the spirit of Liouville's theorem in classical mechanics, for generating a family of trajectory-based dynamics (ELD) which conserves the quantum canonical distribution in the phase space formulation of quantum mechanics for thermal equilibrium systems. Requiring the generated dynamics to approach classical dynamics in three limits—the classical $(\hbar \to 0)$, high temperature $(\beta \to 0)$, and harmonic limits—provides guidance in choosing the phase space distribution function. Although we derive most equations for one-dimensional systems in the present paper, the generalization to the multidimensional case is straightforward (see Appendix E).

Though not specifically couched in the language of phase space distribution functions, the CMD model by Voth and coworkers[51,52] can be closely related to and even reformulated in our proposed trajectory-based approach (ELD). Our approach offers the framework to unite and improve the dynamical methods in a single phase space proposed in the past [such as W-ELD (Ref. 19) and CMD (Refs. 51 and 52)] which are able to conserve the quantum canonical distribution for systems at thermal equilibrium. Although we only demonstrate two examples, the Wigner function and the Husimi function, the framework will also be useful in exploring all other possible distribution functions and studying their associated trajectory-based dynamics. One can even propose new (either system dependent or system independent) functions for $f(\zeta, \eta)$ in Eqs. (5)–(8) (or the extension of the scheme of Cohen) and then use the ELD approach to generate trajectory-based dynamics for equilibrium systems in a given field of interest. [As we point out at the end of Sec. IV A, the ELD approach is still an approximate one because Eq. (47) is not required in quantum mechanics for Liouville's theorem.]

As an analog to classical dynamics, the ELD family of dynamics satisfies the three criteria in Sec. I, providing a powerful tool to study physical and chemical properties of large molecular systems at thermal equilibrium. For instance, one can use several long-time trajectories with a time average to study macroscopic transport properties[57] (such as the self-diffusion constant, shear and bulk viscosity coefficients, thermal conductivity, etc.) either by the mean-squared displacement

$$\gamma = \lim_{t\to\infty} \frac{\partial\langle|B(t) - B(0)|^2\rangle}{\partial t} \tag{75}$$

or by the thermal correlation function approach

$$\gamma = \int_0^{\infty} dt \langle \dot{B}(0)\, \dot{B}(t)\rangle. \tag{76}$$

Another application is to canonical chemical reaction rates. One either follows the trajectory to count the times that it goes across the dividing surface or uses the flux–flux or flux–side correlation functions.[58]

Although we focus on the real phase space with the position and momentum (x, p) in the paper, we note that our mapping approach can also be applied or generalized to the real phase space with other conjugate variables that are canonical transformations of (x, p) and also to the complex space (α, α^*) or (β, β^*), which are popular in quantum optics and electronics,[4,5] etc. Here α and α^* are the complex conjugate variables corresponding to the two operators $\hat{\alpha} = \sqrt{(m\omega/2\hbar)}\hat{x} + (i/\sqrt{2\hbar m\omega})\hat{p}$ and $\hat{\alpha}^+ = \sqrt{(m\omega/2\hbar)}\hat{x} - (i/\sqrt{2\hbar m\omega})\hat{p}$, respectively, and (β, β^*) for $\hat{\beta} = \sqrt{(\Gamma/2)}\hat{x} + (i/\sqrt{2\hbar^2\Gamma})\hat{p}$ and $\hat{\beta}^+ = \sqrt{(\Gamma/2)}\hat{x} - (i/\sqrt{2\hbar^2\Gamma})\hat{p}$, respectively.

The strategy that we use in the present paper is not limited to thermal equilibrium systems. It would also be useful for studying systems under other stationary conditions, e.g., systems at other types of equilibrium or stationary nonequilibrium systems. Further work along these lines would certainly be of interest.

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APPENDIX A: QUANTUM LIOUVILLE'S THEOREM IN THE WIGNER OR HUSIMI PHASE SPACE REPRESENTATION

For any operator $\hat{A}$, it is trivial to show that

$$\langle x-\Delta x/2|\hat{p}\hat{A}|y\rangle = -i\hbar\frac{\partial}{\partial x}\langle x-\Delta x/2|\hat{A}|y\rangle = 2i\hbar\frac{\partial}{\partial \Delta x}\langle x-\Delta x/2|\hat{A}|y\rangle \quad \text{(A1)}$$

and

$$\langle y|\hat{A}\hat{p}|x+\Delta x/2\rangle = i\hbar\partial/\partial x\langle y|\hat{A}|x+\Delta x/2\rangle = 2i\hbar\partial/\partial\Delta x\langle y|\hat{A}|x+\Delta x/2\rangle. \quad \text{(A2)}$$

Based on Eqs. (A1) and (A2), one can show

$$\langle x-\Delta x/2|\hat{p}\hat{A}+\hat{A}\hat{p}|x+\Delta x/2\rangle = 2i\hbar\partial/\partial\Delta x\langle x-\Delta x/2|\hat{A}|x+\Delta x/2\rangle \quad \text{(A3)}$$

and

$$\langle x-\Delta x/2|\,\hat{A}\hat{p}-\hat{p}\hat{A}\,|x+\Delta x/2\rangle = i\hbar\partial/\partial x\,\langle x-\Delta x/2|\,\hat{A}\,|x+\Delta x/2\rangle\,. \quad \text{(A4)}$$

Note

$$[\hat{\rho},\frac{\hat{p}^2}{2m}] = \frac{\hat{p}}{2m}[\hat{\rho},\hat{p}]+[\hat{\rho},\hat{p}]\frac{\hat{p}}{2m}. \quad \text{(A5)}$$

One can derive the following equation from Eqs. (A3)–(A5),

$$\left\langle x-\frac{\Delta x}{2}\right|-\frac{1}{i\hbar}\left[\hat{\rho},\frac{\hat{p}^2}{2m}\right]\left|x+\frac{\Delta x}{2}\right\rangle = -\frac{i\hbar}{m}\frac{\partial}{\partial\Delta x}\frac{\partial}{\partial x}\left\langle x-\frac{\Delta x}{2}\right|\hat{\rho}\left|x+\frac{\Delta x}{2}\right\rangle. \quad \text{(A6)}$$

Integrating by parts over Δx for the above equation leads to

$$\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}d\Delta x\left[\left\langle x-\frac{\Delta x}{2}\right|-\frac{1}{i\hbar}\left[\hat{\rho},\frac{\hat{p}^2}{2m}\right]\left|x+\frac{\Delta x}{2}\right\rangle e^{ip\Delta x/\hbar}\right] = -\frac{p}{m}\frac{\partial}{\partial x}\mathsf{P}_W(x,p). \quad \text{(A7)}$$

Expanding the potential $V(x)$ into a Tyler series, one can show

$$\left\langle x-\frac{\Delta x}{2}\right|\left[\hat{\rho},\hat{V}(\hat{x})\right]\left|x+\frac{\Delta x}{2}\right\rangle = \left\langle x-\frac{\Delta x}{2}\right|\hat{\rho}\left|x+\frac{\Delta x}{2}\right\rangle\left[V\left(x+\frac{\Delta x}{2}\right)-V\left(x-\frac{\Delta x}{2}\right)\right] = \left\langle x-\frac{\Delta x}{2}\right|\hat{\rho}\left|x+\frac{\Delta x}{2}\right\rangle\left[V'(x)\Delta x+\frac{2}{3!}V^{(3)}(x)\left(\frac{\Delta x}{2}\right)^3+\cdots\right]. \quad \text{(A8)}$$

Integrating by parts over Δx again, one has

$$\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}d\Delta x\left[\left\langle x-\frac{\Delta x}{2}\right|-\frac{1}{i\hbar}\left[\hat{\rho},\hat{V}(\hat{x})\right]\left|x+\frac{\Delta x}{2}\right\rangle e^{ip\Delta x/\hbar}\right] = \frac{\partial\mathsf{P}_W}{\partial p}V'(x)-\frac{\hbar^2}{24}\frac{\partial^3\mathsf{P}_W}{\partial p^3}V^{(3)}(x)+\cdots. \quad \text{(A9)}$$

Finally, Eqs. (A7) and (A8) demonstrate that the Wigner phase space representation of quantum Liouville's theorem [Eq. (35)] can be expressed as Eq. (36), which is known as the Wigner–Moyal equation.[2,3]

With the coherent state defined in Eq. (22), one can show

$$\langle y|\,\hat{p}\,|x,p\rangle = i\hbar\frac{\partial}{\partial x}\langle y\,|x,p\rangle = -i\hbar\frac{\partial}{\partial y}\langle y\,|x,p\rangle = -i\hbar\left[-\Gamma(y-x)+\frac{i}{\hbar}p\right]\langle y\,|x,p\rangle \quad \text{(A10)}$$

and

$$\langle x,p|\,\hat{p}\,|y\rangle = -i\hbar\frac{\partial}{\partial x}\langle x,p\,|y\rangle = i\hbar\frac{\partial}{\partial y}\langle x,p\,|y\rangle = i\hbar\left[-\Gamma(y-x)-\frac{i}{\hbar}p\right]\langle x,p\,|y\rangle\,, \quad \text{(A11)}$$

and then

$$\langle x,p|\left[\hat{A},\hat{p}\right]|x,p\rangle = i\hbar\frac{\partial}{\partial x}\langle x,p|\,\hat{A}\,|x,p\rangle\,. \quad \text{(A12)}$$

One can also show

$$\frac{\partial}{\partial p}\langle x,p|\hat{A}|x,p\rangle = \int dy\int dy'\langle x,p|y\rangle\langle y|\hat{A}|y'\rangle\langle y'|x,p\rangle\frac{i}{\hbar}(y'-y). \quad \text{(A13)}$$

and then

$$\langle x,p|\,\hat{p}\hat{A}+\hat{A}\hat{p}\,|x,p\rangle = \int dy\int dy'\langle x,p|y\rangle\langle y|\hat{A}|y'\rangle\langle y'|x,p\rangle(2p+i\hbar\Gamma(y'-y)) = \left(2p+\hbar^2\Gamma\frac{\partial}{\partial p}\right)\langle x,p|\,\hat{A}\,|x,p\rangle\,. \quad \text{(A14)}$$

By virtue of the equality Eq. (A5), one can further show

$$\frac{1}{2\pi\hbar}\langle x,p|-\frac{1}{i\hbar}\left[\hat{\rho},\frac{\hat{p}^2}{2m}\right]|x,p\rangle = -\frac{p}{m}\frac{\partial}{\partial x}\mathsf{P}_H(x,p)-\frac{\hbar^2\Gamma}{2m}\frac{\partial^2}{\partial p\partial x}\mathsf{P}_H(x,p). \quad \text{(A15)}$$

Expanding the potential $V(x)$ as a Tyler series around the position x, one can show

$$\begin{aligned}
&\langle x, p|[\hat{\rho}, \hat{V}(\hat{x})]|x, p\rangle \\
&= \int dy \int dy' \langle x, p|y\rangle\langle y|\hat{\rho}|y'\rangle\langle y'|x, p\rangle[V(y')-V(y)] \\
&= \int dy \int dy' \langle x, p|y\rangle\langle y|\hat{\rho}|y'\rangle\langle y'|x, p\rangle \\
&\quad\times\left\{V'(x)(y'-y)+\frac{V''(x)}{2!}(y'-y)[(y-x)+(y'-x)]\right. \\
&+\frac{V^{(3)}(x)}{3!}(y'-y)[(y-x)^2+(y-x)(y'-x)+(y'-x)^2] \\
&\quad\left.+\cdots\right\}. \qquad \text{(A16)}
\end{aligned}$$

With Eq. (A13), one has

$$\begin{aligned}
&\frac{1}{2\pi\hbar}\left\langle x, p\left|\frac{1}{i\hbar}\left[\hat{\rho}, \hat{V}(\hat{x})\right]\right| x, p\right\rangle \\
&\quad= V'(x)\frac{\partial}{\partial p}\mathsf{P}_H(x, p)+\frac{V''(x)}{2!}\frac{\partial}{\partial p} \\
&\quad\times\left\langle x, p\left|(\hat{x}-x)\frac{\hat{\rho}}{2\pi\hbar}+\frac{\hat{\rho}}{2\pi\hbar}(\hat{x}-x)\right|x, p\right\rangle+\frac{V^{(3)}(x)}{3!}\frac{\partial}{\partial p} \\
&\quad\times\left\langle x, p\left|(\hat{x}-x)^2\frac{\hat{\rho}}{2\pi\hbar}+(\hat{x}-x)\frac{\hat{\rho}}{2\pi\hbar}(\hat{x}-x)\right.\right. \\
&\quad\left.\left.+\frac{\hat{\rho}}{2\pi\hbar}(\hat{x}-x)^2\right|x, p\right\rangle+\cdots. \qquad \text{(A17)}
\end{aligned}$$

With Eqs. (A15) and (A17), one can prove that the Husimi phase space representation of the quantum Liouville theorem (Eq. (35)) leads to Eq. (37). It is trivial to show that Eq. (37) has another expression[59] as

$$\begin{aligned}
\frac{\partial \mathsf{P}_H(x, p; t)}{\partial t} &= -\frac{\partial \mathsf{P}_H}{\partial x}\frac{p}{m}-\frac{\hbar^2\Gamma}{2m}\frac{\partial^2\mathsf{P}_H}{\partial p\partial x} \\
&\quad+\sum_{l=1}^{\infty}\sum_{j=0}^{\infty}\sum_{k=0}^{\mathrm{int}[j/2]}C_{ljk}\frac{\partial^{j+2l+1}V}{\partial x^{j+2l+1}}\frac{\partial^{2l+1}\partial^{j-2k}\mathsf{P}_H}{\partial p^{2l+1}\partial x^{j-2k}}, \qquad \text{(A18)}
\end{aligned}$$

where $C_{ljk}=(-1)^l\hbar^{2l}/\Gamma^{j-k}[2^{2l+j}(2l+1)!k!(j-2k)!]$ and $\mathrm{int}[j/2]$ as the integer part of $j/2$.

Although we show the proofs above for the one-dimensional case, the generalization to the multidimensional case is straightforward.

APPENDIX B: MORE DISCUSSION ON THE CHOICE OF EQUATIONS OF MOTION IN THE PHASE SPACE FORMULATION OF QUANTUM MECHANICS

Due to the Heisenberg uncertainty principle, it is not possible to define a unique probability at a phase space point (x, p), nor is it possible to uniquely define trajectory-based dynamics in the phase space formulation of quantum mechanics. There are various ways to define trajectory-based dynamics that conserves the quantum canonical distribution in the phase space formulation of quantum mechanics. Criterion 3 proposed in Sec. I is important for determining whether they are physically meaningful.

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 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 Liouville's theorem of the second kind in classical mechanics. They can also satisfy all three criteria listed in Sec. I.

For instance, one can rewrite quantum Liouville's theorem as

$$\frac{\partial \mathsf{P}(x, p; t)}{\partial t}=-\frac{\partial \mathsf{P}}{\partial x}\frac{p^{\mathrm{eff}}}{m}+\frac{\partial \mathsf{P}}{\partial p}V'(x) \qquad \text{(B1)}$$

with the effective momentum p^{eff} in the Wigner phase space [i.e., Eq. (36)] defined as

$$-\frac{\partial \mathsf{P}_W}{\partial x}\frac{p^{\mathrm{eff}}}{m}=-\frac{\partial \mathsf{P}_W}{\partial x}\frac{p}{m}-\frac{\hbar^2}{24}\frac{\partial^3\mathsf{P}_W}{\partial p^3}V^{(3)}(x)+\cdots \qquad \text{(B2)}$$

or that in the Husimi phase space [i.e., Eq. (37)] defined as

$$\begin{aligned}
-\frac{\partial \mathsf{P}_H}{\partial x}\frac{p^{\mathrm{eff}}}{m} &= -\frac{\partial \mathsf{P}_H}{\partial x}\frac{p}{m}-\frac{\hbar^2\Gamma}{2m}\frac{\partial^2\mathsf{P}_H}{\partial p\partial x} \\
&\quad+\hbar\frac{V^{(2)}(x)}{2!}\frac{\partial}{\partial p}\langle x, p|\left(-i\overleftarrow{\frac{\partial}{\partial p}}\right)\frac{\hat{\rho}}{2\pi\hbar} \\
&\quad+\frac{\hat{\rho}}{2\pi\hbar}\left(-i\overrightarrow{\frac{\partial}{\partial p}}\right)|x, p\rangle+\hbar\frac{V^{(3)}(x)}{3!}\frac{\partial}{\partial p}\langle x, p| \\
&\quad\times\left(-i\overleftarrow{\frac{\partial}{\partial p}}\right)^2\frac{\hat{\rho}}{2\pi\hbar}+\left(-i\overleftarrow{\frac{\partial}{\partial p}}\right)\frac{\hat{\rho}}{2\pi\hbar}\left(-i\overrightarrow{\frac{\partial}{\partial p}}\right) \\
&\quad+\frac{\hat{\rho}}{2\pi\hbar}\left(-i\overrightarrow{\frac{\partial}{\partial p}}\right)^2|x, p\rangle+\cdots. \qquad \text{(B3)}
\end{aligned}$$

Using Eq. (B1) rather than Eq. (45), the equality Eq. (29) leads to

$$\begin{aligned}
\frac{d\mathsf{P}^{\mathrm{eq}}(x_t, p_t; t)}{dt} &= \frac{\partial \mathsf{P}^{\mathrm{eq}}(x_t, p_t; t)}{\partial x_t}\left(\dot{x}_t-\frac{p_t^{\mathrm{eff}}}{m}\right) \\
&\quad+\frac{\partial \mathsf{P}^{\mathrm{eq}}(x_t, p_t; t)}{\partial p_t}\left(\dot{p}_t+\frac{\partial V(x_t)}{\partial x_t}\right). \qquad \text{(B4)}
\end{aligned}$$

[One can compare Eq. (48) to Eq. (B4).] If we define $\dot{p}=-V'(x)$ to be the relation between the position and momentum which is independent of the density distribution function but dependent of the system, then the equations of motion from Eq. (B4) are

$$\begin{aligned}
\dot{x}_t &= \frac{p_t^{\mathrm{eff}}(x_t, p_t)}{m} \\
\dot{p}_t &= -\frac{\partial V(x_t)}{\partial x_t}.
\end{aligned} \qquad \text{(B5)}$$

For the thermal equilibrium system, the density distribution function is stationary, i.e., Eq. (42), which presents a way to calculate the effective momentum p^{eff}, i.e.,

$$\frac{\partial \mathsf{P}^{\text{eq}}}{\partial x}\frac{p^{\text{eff}}(x,\,p)}{m} = \frac{\partial \mathsf{P}^{\text{eq}}}{\partial p}V'(x). \tag{B6}$$

One can verify that the trajectory-based dynamics governed by the equations of motion Eq. (B5) with the effective momentum given by Eq. (B6) (e.g., in the Wigner phase space) approaches classical dynamics in the classical, high temperature, and harmonic limits. These dynamics, therefore, comprise another category in ELD. However, Eq. (B6) is not as convenient as Eq. (46) for use in the multidimensional system due to the following reason: the effective force in Eq. (46) is always uniquely defined in the multidimensional system as long as the partial distribution function $[\mathsf{P}^{\text{eq}}(x_t,\,p_t)$ with the fixed position $x_t]$ is a Gaussian, but the effective momentum $p^{\text{eff}}(x_t,\,p_t)$ in Eq. (B6) is not. There are infinitely many possible effective momenta for Eq. (B6) in the multidimensional case, although one might choose one according to some additional criterion.

The ELD trajectory-based dynamics in the phase space formulation of quantum mechanics is generated in the spirit of Liouville's theorem in classical mechanics. Following the procedure in Sec. IV, it is straightforward to construct other families of trajectory-based dynamics in the phase space formulation of quantum mechanics in the spirit of the phase space continuity equation or Hamilton's equations of motion in classical mechanics as we will discuss in a subsequent paper. [For example, we will reformulate and generalize our recent work[19] related to Refs. 60–62 into another approach for generating a family of trajectory-based dynamics, which can conserve the canonical distribution in the phase space formulation of quantum mechanics.]

APPENDIX C: DETERMINANT OF THE JACOBIAN MATRIX IN THE TRAJECTORY-BASED DYNAMICS

It can be shown that the trajectory-based dynamics [i.e., Eq. (49)] proposed in Sec. IV does not, in general, conserve the volume element of the phase space. Note the Jacobian matrix of the transformation [generated from the dynamics (Eq. (49)] as

$$\mathbf{J}(t) = \frac{\partial(x_t,\,p_t)}{\partial(x_0,\,p_0)} \equiv \frac{\partial \boldsymbol{\upsilon}_t}{\partial \boldsymbol{\upsilon}_0} \tag{C1}$$

and its inverse as

$$\mathbf{J}(t)^{-1} = \frac{\partial(x_0,\,p_0)}{\partial(x_t,\,p_t)} \equiv \frac{\partial \boldsymbol{\upsilon}_0}{\partial \boldsymbol{\upsilon}_t}. \tag{C2}$$

The equations of motion in the non-Hamiltonian dynamics [i.e., Eq. (49)] are not time explicit, so the time derivative of the Jacobian matrix is

$$\frac{d}{dt}\mathbf{J}(t) \equiv \frac{\partial \dot{\boldsymbol{\upsilon}}_t}{\partial \boldsymbol{\upsilon}_0}. \tag{C3}$$

The determinant of a matrix satisfies

$$\det(\mathbf{J}(t)) = \exp[\mathrm{Tr}[\ln \mathbf{J}(t)]]. \tag{C4}$$

Its time derivative is then given by

$$\frac{d}{dt}\det(\mathbf{J}(t)) = \det(\mathbf{J}(t))\,\mathrm{Tr}\left[\mathbf{J}(t)^{-1}\frac{d}{dt}\mathbf{J}(t)\right]. \tag{C5}$$

In the second term of the RHS of Eq. (C5), we use the chain rule to obtain

$$\mathrm{Tr}\left[\mathbf{J}(t)^{-1}\frac{d}{dt}\mathbf{J}(t)\right] = \sum_{i,j}\frac{\partial \upsilon_0^i}{\partial \upsilon_t^j}\frac{\partial \dot{\upsilon}_t^j}{\partial \upsilon_0^i} = \sum_{i,j,k}\frac{\partial \upsilon_0^i}{\partial \upsilon_t^j}\frac{\partial \dot{\upsilon}_t^j}{\partial \upsilon_t^k}\frac{\partial \upsilon_t^k}{\partial \upsilon_0^i}. \tag{C6}$$

The summation over i in Eq. (C6) leads to

$$\mathrm{Tr}\left[\mathbf{J}(t)^{-1}\frac{d}{dt}\mathbf{J}(t)\right] = \sum_{j,k}\delta_{jk}\frac{\partial \dot{\upsilon}_t^j}{\partial \upsilon_t^k} = \nabla_t \cdot \dot{\boldsymbol{\upsilon}}_t. \tag{C7}$$

Equation (C5) then becomes

$$\frac{d}{dt}\det(\mathbf{J}(t)) = (\nabla_t \cdot \dot{\boldsymbol{\upsilon}}_t)\det(\mathbf{J}(t)). \tag{C8}$$

The integration over time for Eq. (C8) gives

$$\det(\mathbf{J}(t)) = \exp\left[\int_0^t \nabla_t \cdot \dot{\boldsymbol{\upsilon}}_t dt\right], \tag{C9}$$

for which we use the initial condition that the Jacobian matrix is an identity matrix at time $t = 0$, i.e.,

$$\mathbf{J}(0) = \mathbf{1}. \tag{C10}$$

We note that Eqs. (C1)–(C10) apply to any trajectory-based dynamics in the phase space.

For the trajectory-based dynamics [i.e., Eq. (49)], one has

$$\nabla_t \cdot \dot{\boldsymbol{\upsilon}}_t = -\frac{\partial^2}{\partial p_t \partial x_t}V_{\text{eff}}(x_t,\,p_t). \tag{C11}$$

Equation (C9) shows that the determinant of the Jacobian matrix is always positive and in general variant with time. That is, the volume element of the phase space is usually not conserved along the trajectories.

If the effective force $-(\partial V_{\text{eff}}(x_t,\,p_t)/\partial x_t) \equiv -(\partial V_{\text{eff}}(x_t)/\partial x_t)$ is independent of the momentum p_t (i.e., only a function of the position x_t) and well defined in the phase space, Eq. (C9) leads to

$$\det(\mathbf{J}(t)) = 1, \tag{C12}$$

i.e., the volume element of the phase space is conserved during the dynamics. Classical mechanics can be viewed as a special case. The classical force $-V'(x)$ does not depend on the momentum, so classical dynamics satisfies Eq. (C12). The harmonic oscillator is another example.

APPENDIX D: EXPECTATION VALUE OR ENSEMBLE AVERAGE IN THE TRAJECTORY-BASED DYNAMICS

Consider the kind of trajectory-based dynamics that satisfies $d\rho/dt = 0$ in the Lagrangian picture. As discussed in Appendix C, the size of the volume element of the phase space can change as the trajectory propagates. It might be complicated to obtain the form for the expectation value of a dynamic property in the Lagrangian picture when non-Hamiltonian dynamics is involved. We provide a simple approach in the Eulerian viewpoint to accomplish the task.

Suppose $\boldsymbol{v} = (x, p)^T$ represents a point in a fixed framework of the coordinate system for the phase space. Define a density distribution function ρ with the two conditions:

(1) The function ρ at the phase point $\boldsymbol{v}$ at time $t = 0$ has the value $\rho(\boldsymbol{v}; 0)$.
(2) Some trajectory-based dynamics governs the evolution of the function ρ. The function ρ along the trajectory starting from the initial phase point $\boldsymbol{v}$ is invariant with time, i.e., $d\rho/dt = 0$ or

$$\rho(\boldsymbol{v}_t(\boldsymbol{v}; t); t) = \rho(\boldsymbol{v}; 0). \tag{D1}$$

Suppose $\boldsymbol{v}' = (x', p')^T$ represents another point in the same fixed framework of the coordinate system for the phase space (i.e., Eulerian viewpoint). Then the value of the function ρ at the phase point $\boldsymbol{v}'$ at time t is given by

$$\begin{aligned}\rho(\boldsymbol{v}'; t) &= \int d\boldsymbol{v}\rho(\boldsymbol{v}_t(\boldsymbol{v}; t); t)\delta(\boldsymbol{v}' - \boldsymbol{v}_t(\boldsymbol{v}; t)) \\ &= \int d\boldsymbol{v}\rho(\boldsymbol{v}; 0)\delta(\boldsymbol{v}' - \boldsymbol{v}_t(\boldsymbol{v}; t)).\end{aligned} \tag{D2}$$

Note that Eq. (D2) holds for any trajectory-based dynamics with $d\rho/dt = 0$, irrespective of whether it is Hamiltonian or non-Hamiltonian dynamics. If the equations of motion in the trajectory-based dynamics are not time explicit, then one has

$$\rho(\boldsymbol{v}'; t) = \int d\boldsymbol{v}\rho(\boldsymbol{v}; 0)\delta(\boldsymbol{v}' - \boldsymbol{v}_t(\boldsymbol{v})) \tag{D3}$$

according to Eq. (D2). By virtue of Eq. (5) and the fact that

$$\begin{aligned}\int \mathbf{d}\boldsymbol{v}'\rho(\boldsymbol{v}'; t) &= \int \mathbf{d}\boldsymbol{v}' \int d\boldsymbol{v}\rho(\boldsymbol{v}; 0)\delta(\boldsymbol{v}' - \boldsymbol{v}_t(\boldsymbol{v})) \\ &= \int d\boldsymbol{v}\rho(\boldsymbol{v}; 0) \equiv Z\end{aligned} \tag{D4}$$

is a constant, the expectation value or the ensemble average for physical property B at time t is given by

$$\begin{aligned}\langle B(t)\rangle &= \frac{1}{Z}\int \mathbf{d}\boldsymbol{v}'\rho(\boldsymbol{v}'; t)\tilde{B}(\boldsymbol{v}') \\ &= \frac{1}{Z}\int \mathbf{d}\boldsymbol{v}' \int d\boldsymbol{v}\rho(\boldsymbol{v}; 0)\delta(\boldsymbol{v}' - \boldsymbol{v}_t(\boldsymbol{v}))\tilde{B}(\boldsymbol{v}') \\ &= \frac{1}{Z}\int d\boldsymbol{v}\rho(\boldsymbol{v}; 0)\tilde{B}(\boldsymbol{v}_t(\boldsymbol{v})).\end{aligned} \tag{D5}$$

If one also defines $\boldsymbol{v}_0 = (x_0, p_0)^T$ to represent any point in the same coordinate system for the phase space, one can exchange $\boldsymbol{v}$ with $\boldsymbol{v}_0$ in Eq. (D5) to obtain

$$\langle B(t)\rangle = \frac{1}{Z}\int d\boldsymbol{v}_0\rho(\boldsymbol{v}_0; 0)\tilde{B}(\boldsymbol{v}_t(\boldsymbol{v}_0)). \tag{D6}$$

According to Eq. (D1), the above equation can also be expressed as

$$\begin{aligned}\langle B(t)\rangle &= \frac{1}{Z}\int d\boldsymbol{v}_0\rho(\boldsymbol{v}_t(\boldsymbol{v}_0); t)\tilde{B}(\boldsymbol{v}_t(\boldsymbol{v}_0)) \\ &= \frac{1}{Z}\int d\boldsymbol{v}_t\left|\frac{\partial\boldsymbol{v}_0}{\partial\boldsymbol{v}_t}\right|\rho(\boldsymbol{v}_t(\boldsymbol{v}_0); t)\tilde{B}(\boldsymbol{v}_t(\boldsymbol{v}_0)).\end{aligned} \tag{D7}$$

Note that Eqs. (D5)–(D7) apply to all kinds of *time-implicit* trajectory-based dynamics with $d\rho/dt = 0$, which include classical dynamics and ELD discussed in the paper.

APPENDIX E: GENERALIZATION OF ELD TO MULTIDIMENSIONAL SYSTEMS

Equations (46) and (49) give the ELD effective force and the ELD equations of motion, respectively, for one-dimensional systems. For multidimensional systems, the equations of motion of ELD become

$$\begin{aligned}\dot{\mathbf{x}}_t &= \mathbf{M}^{-1}\mathbf{p}_t \\ \dot{\mathbf{p}}_t &= -\frac{\partial V_{\text{eff}}^{\text{ELD}}(\mathbf{x}_t, \mathbf{p}_t)}{\partial\mathbf{x}_t}\end{aligned} \tag{E1}$$

with the ELD effective force $-\frac{\partial V_{\text{eff}}^{\text{ELD}}(\mathbf{x}_t, \mathbf{p}_t)}{\partial\mathbf{x}_t}$ given by

$$\frac{\partial \mathsf{P}^{\text{eq}}(\mathbf{x}_t, \mathbf{p}_t)}{\partial\mathbf{p}_t}\cdot\frac{\partial V_{\text{eff}}^{\text{ELD}}(\mathbf{x}_t, \mathbf{p}_t)}{\partial\mathbf{x}_t} = \frac{\partial \mathsf{P}^{\text{eq}}(\mathbf{x}_t, \mathbf{p}_t)}{\partial\mathbf{x}_t}\mathbf{M}^{-1}\mathbf{p}_t. \tag{E2}$$

Here $(\mathbf{x}_t, \mathbf{p}_t)$ is the phase point and $\mathbf{M}$ is the diagonal "mass matrix." According to the various approximations for the canonical distribution $\mathsf{P}^{\text{eq}}(\mathbf{x}_t, \mathbf{p}_t)$ in the Wigner or Husimi phase space mentioned in Ref. 22 and Paper II, $\mathsf{P}^{\text{eq}}(\mathbf{x}_t, \mathbf{p}_t)$ with any fixed position vector $\mathbf{x}_t$ can often be (effectively) approximated as a (local) Gaussian function of the momenta $\mathbf{p}_t$ for large molecular systems as shown in various examples in the literature[15,17–23,63,64] (which include multiwell and imaginary frequency situations). The ELD effective force $-(\partial V_{\text{eff}}^{\text{ELD}}(\mathbf{x}_t, \mathbf{p}_t)/\partial\mathbf{x}_t)$ is thus always uniquely defined (and can practically be evaluated) by Eq. (E2) even for large molecular systems. [That is, the vector $\mathbf{p}_t$ can be cancelled out on both sides of Eq. (E2).] This guarantees the robustness of the ELD dynamics regardless of the momentum dependence of the ELD effective force, as we discussed in Sec. IV B. More discussion and numerical examples for multidimensional systems will be shown in a subsequent paper.

When the canonical distribution $\mathsf{P}^{\text{eq}}(\mathbf{x}_t, \mathbf{p}_t)$ cannot be (effectively) approximated as a (local) Gaussian function of the momenta $\mathbf{p}_t$ [e.g., the effective force may be ill-defined at the phase points with $(\partial \mathsf{P}^{\text{eq}}(\mathbf{x}_t, \mathbf{p}_t)/\partial\mathbf{p}_t) = 0$], further development to extend the strategy in the current paper will be necessary. We will discuss more about this point in the subsequent paper mentioned at the end of Appendix B.

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