On ergodicity for multi-dimensional harmonic oscillator systems
with Nose-Hoover type thermostat

Ikuo Fukuda¹, Kei Moritsugu², and Yoshifumi Fukunishi³

¹Institute for Protein Research, Osaka University,
3-2 Yamadaoka, Suita, Osaka 565-0871,
Japan and Graduate School of Simulation Studies,
University of Hyogo, Kobe 650-0047, Japan
²Graduate School of Medical Life Science,
Yokohama City University, Yokohama 230-0045, Japan and
³Cellular and Molecular Biotechnology Research Institute, AIST

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Abstract

A simple proof and detailed analysis on the non-ergodicity for multidimensional harmonic oscillator systems with Nose-Hoover type thermostat are given. The origin of the nonergodicity is symmetries in the multidimensional target physical system, and is differ from that in the Nose-Hoover thermostat with the 1-dimensional harmonic oscillator. A new simple deterministic method to recover the ergodicity is also presented. An individual thermostat variable is attached to each degree of freedom, and all these variables act on a friction coefficient for each degree of freedom. This action is linear and controlled by a Nosé mass matrix \( Q \), which is a matrix analogue of the scalar Nosé’s mass. Matrix \( Q \) can break the symmetry and contribute to attain the ergodicity.
I. INTRODUCTION

The Nosé-Hoover (NH) [16, 29] equation has been utilized as basic equations of motion (EOM) in molecular dynamics (MD), which is now an important tool to perform a realistic simulation of a physical system [1, 17, 34]. The NH equation is an ordinary differential equation (ODE), based on the Newtonian EOM described by physical coordinates $x \in \mathbb{R}^n$ and momenta $p \in \mathbb{R}^n$. It is obtained by adding a friction force that is $-(\zeta/Q)p$ to the Newtonian EOM and by adding an EOM for $\zeta$, where $Q$ is a real parameter often called as the Nosé’s mass. The friction coefficient-like quantity $\zeta \in \mathbb{R}$ is thus a dynamical variable, and it is introduced to control the temperature of the target physical system described by $(x, p)$ and maintain the value around a desired value $T_{ex}$. It is shown that the physical system obeys the Boltzmann-Gibbs (BG), or canonical, distribution at temperature $T_{ex}$ if the total system described by $(x, p, \zeta)$ satisfies the ergodic condition.

1-dimensional harmonic oscillator (1HO) has been investigated, for theoretically studying the NH equation, as the most simple model system that describes near a physical equilibrium. In a viewpoint of dynamical system study, the NH equation with a 1HO has first been studied numerically [32] and revealed to include both regular and chaotic motions, implying that NH EOM with 1HO is nonergodic. The origin of the nonergodicity has been considered as a lack of “complexity”, that is, small degrees of freedom of the system (which is three) and a simple form of the ODE involving only two nonlinear terms $-\zeta p$ and $p^2$. Its non-ergodicity has been demonstrated theoretically in case of a sufficiently large $Q$ by using KAM theory to show the existence of invariant tori [23]. In contrast, the NH chain method, which is an extension of the original NH method via introducing multidimensional $\zeta \in \mathbb{R}^m$, has long been considered that it gives the ergodicity even in the case of the 1HO. However, recently, Patra and Bhattacharaya indicated in long-time numerical simulations that the NHC with 1HO is non ergodic [31].

However, 1HO is a special model in a viewpoint of the energy density of state $\Omega(e)$ for which $\Omega(e)=$constant, which is not increasing with respect to the energy $e$ of the physical system. In this respect, $n$-dimensional harmonic oscillator (nHO) with $n > 1$ is normal in that $\Omega(e) = ce^{n-1}$ ($c$ is irrelevant to $e$) shows the increasing. Despite the importance in this respect, NH with nHO has not been much investigated. One of a few examples is the study by Nosé [28], where recurrence phenomena strongly depending on initial conditions
were found and secular periodic modes can be captured by a simple Hamiltonian.

In the current study, we discuss the non-ergodicity of \( n \)HO with \( n > 1 \). We specifically show in a simple manner that the NH EOM with \( n \)HO with \( n > 1 \) is non-ergodic if the \( n \)HO is identical. This applies not only to the original NH system but also for NH type systems, which includes a number of kinds of EOM such as the NHC equation. The identical condition means that all masses and the spring constants are identical for all the degrees of freedom. With or without this condition, symmetry of the system may differ much and the dynamics of the system can differ quantitatively \[28\]. We also demonstrate the non-ergodicity of NH type with \( n \)HO with \( n > 1 \) under a condition that is slightly extended from the isotropic condition.

The origin of these non-ergodicities is underlying symmetries of multidimensional systems. Here, the original symmetry of the physical system is the mass spectrum and potential energy function, and they are reflected into the Newtonian EOM; for example, an interchange \((x_1, \ldots, x_i, \ldots, x_j, \ldots, x_n) \mapsto (x_1, \ldots, x_j, \ldots, x_i, \ldots, x_n)\) becomes one of the symmetries if the system is isotropic. Even if the EOM that is considered to be ergodic for 1HO, it should be non-ergodic for \( n \)HO with \( n > 1 \) (under an isotropic or isotropic-like condition) due to the existing symmetry, as long as the target EOM has a certain structure originated from the NH EOM. A number of the thermostat EOM share with this structure, and the NHC is not the exception, for example. Multidimensional thermostat EOM is faced with the symmetry and a number of EOM can not be free from the symmetry, which leads to the non-ergodicity in a certain condition. Hence, the origin of the non-ergodicity completely differ between the 1HO and \( n \)HO with \( n > 1 \). These issues will be clarified in the current study.

We further propose a method to recover the ergodicity even for the idealized model of \( n \)HO with \( n > 1 \). For this, we first modify the density dynamics (DD) scheme \[13\], which has been developed to produce an arbitrary phase-space density. The DD is described by \((x, p, \zeta)\) where \( \zeta \) is an additional scalar variable as in the NH EOM and plays a role to control the dynamics to yield the arbitrarily given phase-space density. We then obtain a new EOM (we call this splitting DD), which utilizes a vectorized \( \zeta \) and splits the role of the original additional variable to directly act on each degree of freedom. In general, the splitting DD can be free from the symmetry discussed above. Next, we apply the BG density, for the phase-space density, into the splitting DD to produce the BG distribution and have a new NH form EOM, which we call splitting NH EOM. This new EOM can also be free from the
symmetry through the splitting feature, even if $K(p)$ and $U(x)$, the source of the symmetry, are introduced.

One of the key issues to avoid the problem originated from the symmetry and to reach the ergodicity in the splitting NH is an extension of the original Nosé mass parameter $Q$. Nosé mass is not a scalar but a matrix. This extension can be viewed as natural in that the density of $\zeta$ is based on a quadratic form. Such a matrix approach would be simple, and only a few discussions have been done [33]. The simplicity of this idea might be the reason that it is has not paid much attention. However, we show that this idea gives a higher cost performance than supposed to avoid the nonergodicity.

The splitting NH should not be restricted in the applications to the $n$HO model system. As well as short-rage vibrational interactions, many part of long range interactions of particles in classical physical system can be approximated by harmonic interactions around their equilibriums, which can then be mimicked by $n$HO interactions. More directly, e.g., representations of the physical system as a set of harmonic oscillators in normal mode study well describe the feature of a biomolecular system. It is discussed that perturbations by a chemical reaction via enzyme or by a docking of a medicinal molecule excite normal modes [3, 36]. These excited normal modes allow an oscillator approximation such as elastic network model [35]. Conversely, intramolecular vibrational energy can be transferred from a given normal mode [27].

Thus, the ability to enhance the phase-space sampling and recover the ergodicity for the $n$HO with $n > 1$ is not limited to the theoretical interest but expected to work well in these realistic applications. To solve the intrinsic problem by breaking the symmetry should truly enhance the phase-space sampling and reach the equilibrium. We confirmed numerically the ergodic properties in $n$HO with $n = 2, 3$ for the splitting NH.

After briefly reviewing thermostat EOM in Section II we demonstrate the nonergodicity for the $n$HO model with $n > 1$ in Section III. The symmetries are explicitly discussed in Appendix. In Section IV we provide the splitting DD EOM for the basis of remedy against the nonergodicity. In Section V we apply this to obtain a new NH form EOM to generate the BG distribution and solve the problem. We present numerical studies in Section VI to illustrate the nonergodicity for the conventional EOM and the ergodicity for the new EOM.
II. EQUATIONS OF MOTION

Our target dynamical system can be represented as the following ODE:

\[
\begin{align*}
\dot{x} &= M^{-1}p \in \mathbb{R}^n, \\
\dot{p} &= F(x) + \lambda(\omega) p \in \mathbb{R}^n, \\
\dot{\zeta} &= \Lambda(\omega) \in \mathbb{R}^m,
\end{align*}
\]

(1)

where \( x \equiv (x_1, \ldots, x_n) \in D \subset \mathbb{R}^n \) and \( p \equiv (p_1, \ldots, p_n) \in \mathbb{R}^n \) are atomic coordinates and momenta of a physical system of \( n \) degrees of freedom; \( F \) represents a force, which is a \( C^1 \) function defined on a domain \( D \); \( M \) represents the mass parameters, which is a symmetric, positive-definite square matrix of size \( n \) over \( \mathbb{R} \). Along with these quantities associated with Newtonian EOM, \( \zeta \in \mathbb{R}^m \) is an additional dynamical variable, relating to a notion of frictional coefficient or thermostat. Thus the phase space is \( \Omega := D \times \mathbb{R}^n \times \mathbb{R}^m \subset \mathbb{R}^N \) with \( N \equiv 2n + m \), and the phase-space point is represented as \( \omega \equiv (x, p, \zeta) \in \Omega \). To the physical system, a \( C^1 \) function \( \lambda : \Omega \to \mathbb{R} \) provides \( -\lambda(\omega) \), which can be viewed as a dynamical frictional “coefficient” and essentially depends on the additional variable \( \zeta \in \mathbb{R}^m \). The time development of \( \zeta \) is described by \( \Lambda : \Omega \to \mathbb{R}^m \), which is of class \( C^1 \). The functions \( \lambda \) and \( \Lambda \) may contain potential energy \( U(x) \in \mathbb{R} \), wherein \( F = -\nabla U \), and kinetic energy \( K(p) \equiv \frac{1}{2} (p | M^{-1}p) - \frac{1}{2} \sum_{i,j=1}^n M_{ij}^{-1} p_i p_j \) of the physical system.

We give several examples that fall into the form of EOM (1).

**Example 1** \( \lambda(\omega) \equiv \zeta/Q \in \mathbb{R} \) and \( \Lambda(\omega) \equiv 2K(p) - nk_B T_{ex} \) with \( m \equiv 1 \), where \( Q > 0 \) is a parameter (often called as Nosé’s mass) give the the NH equation [16, 29]:

\[
\begin{align*}
\dot{x} &= M^{-1}p \in \mathbb{R}^n, \\
\dot{p} &= F(x) - (\zeta/Q) p \in \mathbb{R}^n, \\
\dot{\zeta} &= 2K(p) - nk_B T_{ex} \in \mathbb{R}^1.
\end{align*}
\]

(2)

This is introduced to control the physical system temperature \( 2K(p)/nk_B \) (\( k_B \) is Boltzmann’s constant) into a target temperature \( T_{ex} > 0 \) and can yield the canonical ensemble.

**Example 2** \( \lambda(\omega) \equiv \zeta_1/Q_1 \in \mathbb{R} \) and \( \Lambda(\omega) \equiv (G_1(\omega) - \zeta_1 \zeta_2/Q_2, \ldots, G_j(\omega) - \zeta_j \zeta_{j+1}/Q_{j+1}, \ldots, G_m(\omega)) \), with

\[
\begin{align*}
G_1(\omega) &\equiv 2K(p) - nk_B T_{ex} \in \mathbb{R}, \\
G_j(\omega) &\equiv \zeta_{j-1}^2/Q_{j-1} - k_B T_{ex} \in \mathbb{R}, \quad j = 2, \ldots, m,
\end{align*}
\]
where \( Q_1, \ldots, Q_m > 0 \) are parameters, give the NH chain (NHC) equation \([26]\):

\[
\begin{align*}
\dot{x} &= M^{-1}p \in \mathbb{R}^n, \\
\dot{p} &= F(x) - \left( \zeta_1/Q_1 \right) p \in \mathbb{R}^n, \\
\dot{\zeta}_j &= G_j(\omega) - \zeta_j \zeta_{j+1}/Q_{j+1} \in \mathbb{R}, \quad j = 1, \ldots, m-1, \\
\dot{\zeta}_m &= G_m(\omega) \in \mathbb{R}.
\end{align*}
\]

This can be viewed as an extended form of the NH EOM.

Example 3 The kinetic moments method \([15, 19]\), which can be represented by

\[
\begin{align*}
\dot{x} &= M^{-1}p \in \mathbb{R}^n, \\
\dot{p} &= F(x) - \left( \zeta_1/Q_1 + \hat{K}(p)\zeta_2/Q_2 \right) p \in \mathbb{R}^n, \\
\dot{\zeta}_1 &= \hat{K}(p) - 1 \in \mathbb{R}, \\
\dot{\zeta}_2 &= \hat{K}(p)(\hat{K}(p) - (n+2)/n) \in \mathbb{R},
\end{align*}
\]

where \( \hat{K}(p) \equiv 2K(p)/nk_BT_{ex} \), becomes an example of \((1)\).

Example 4 The generalized Gaussian moment thermostatting method \([25]\) represented by

\[
\begin{align*}
\dot{x} &= M^{-1}p \in \mathbb{R}^n, \\
\dot{p} &= F(x) - \left( \sum_{j=1}^{m} \sum_{k=1}^{j} a_{k-1}(2K(p))^{k-1}(k_BT_{ex})^{j-k} \zeta_j/Q_j \right) p \in \mathbb{R}^n, \\
\dot{\zeta}_j &= a_{j-1}(2K(p))^j - n(k_BT_{ex})^j \in \mathbb{R}, \quad j = 1, \ldots, m,
\end{align*}
\]

with \( a_j \equiv \prod_{k=1}^{j}(n+2k)^{-1} \), becomes also an example.

There can be found more examples in thermostat methods; see e.g., Refs. \([2, 4, 5, 7, 14, 18, 20, 22, 30, 33]\) for details on thermostat methods and their development. Other examples include e.g., the coupled NH equations of motion, which is introduced to fluctuate the temperature of the heat bath for the physical system \([9, 11]\).

### III. NON ERGODICITY FOR ISOTROPIC OSCILLATOR SYSTEM

The target ODE \((1)\) can be represented as

\[
\dot{\omega} = X(\omega),
\]

\[(4)\]
where $X$ becomes a $C^1$ vector field defined on a domain $\Omega$ of $\mathbb{R}^N$. Assuming the completeness of $X$, we let $\{T_t\} \equiv \{T_t : \Omega \to \Omega \mid t \in \mathbb{R}\}$ be the flow generated by the field $X$. Consider the case where we have an invariant measure $\mu$ of the flow $\{T_t\}$:

$$\forall t \in \mathbb{R}, \forall A \in \mathcal{L}_N^\Omega, \mu(T_t^{-1}A) = \mu(A),$$

where $\mathcal{L}_N^\Omega \equiv \mathcal{L}_N \cap \Omega$ with $\mathcal{L}_N$ being the Lebesgue measurable sets on $\mathbb{R}^N$. We assume that $0 < \mu(\Omega) < \infty$ and that

$$\mu \sim l_N,$$

i.e., $\mu$ and the Lebesgue measure $l_N$ of $\mathbb{R}^N$ are absolutely continuous each other. For example, on Examples 1 and 2 we have an invariant measure defined by

$$\mathcal{L}_N^\Omega \to [0, \infty), \ A \mapsto \mu(A) := \int_A \rho dl_N$$

with a (strictly positive and measurable) density $\rho : \Omega \to \mathbb{R}$, satisfying the Liouville equation

$$\text{div} \rho X = 0.$$

(7)

A subset $A \in \mathcal{L}_N^\Omega$ is said to be an invariant set if $T_t^{-1}(A) = A$ for all $t \in \mathbb{R}$. The ergodicity for the measure space $(\Omega, \mathcal{L}_N^\Omega, \mu)$ with the flow $\{T_t\}$ holds if any invariant set $A$ is trivial, i.e., $\mu(A) = 0$ or $\mu(\Omega \setminus A) = 0$. In other word, if we have an invariant set $A$ such that

$$\mu(A) > 0 \text{ and } \mu(\Omega \setminus A) > 0,$$

then the ergodicity does not hold.

We show $\{T_t\}$ is not ergodic for a harmonic oscillator system with $n > 1$. The condition for $n > 1$ is essential to the current discussion. The non ergodicity for a harmonic oscillator system with $n = 1$ is demonstrated in Ref. [23]. Here, an isotropic condition in a harmonic oscillator system in Eq. (1) is described by

$$M = m \mathbf{1}_n \text{ and } F(x) = -kx \in \mathbb{R}^n,$$

(9)

where $\mathbf{1}_n$ is the unit matrix of size $n$, and $m$ and $k$ are strictly positive parameters (representing a mass and spring constant, respectively); i.e., we have

$$\left\{ \begin{array}{l}
\dot{x} = m^{-1}p \in \mathbb{R}^n, \\
\dot{p} = -kx + \lambda(\omega) p \in \mathbb{R}^n, \\
\dot{\xi} = \Lambda(\omega) \in \mathbb{R}^m.
\end{array} \right.$$
Defining a map $\gamma : \Omega \to T^2(\mathbb{R}^n) \cong \mathbb{R}^{n^2}$ by

$$
\gamma(\omega) := x \wedge p
= \frac{1}{2}(x \otimes p - p \otimes x),
$$

(11)
we show

**Lemma 5** $\Upsilon^\pm_{ij} \equiv \{ \omega \in \Omega \mid \gamma_{ij}(\omega) \geq 0 \}$ is an invariant space for the flow of Eq. (10) for $i, j = 1, \ldots, n$.

**Proof.** For any solution of ODE (10), $\varphi : \mathbb{R} \supset J \to \Omega, t \mapsto \varphi(t) \equiv (x(t), p(t), \zeta(t))$, we have

$$
D(\gamma \circ \varphi)(t) = Dx(t) \wedge p(t) + x(t) \wedge Dp(t)
= m^{-1}p(t) \wedge p(t) + x(t) \wedge (-kx(t) + \lambda(\varphi(t))p(t))
= x(t) \wedge \lambda(\varphi(t))p(t)
= \lambda(\varphi(t))(\gamma \circ \varphi)(t)
$$

for all $t \in J$, which is an open interval (that may be $\mathbb{R}$) involving 0. Thus

$$
(\gamma \circ \varphi)(t) = \exp \left( \int_0^t \lambda(\varphi(s))ds \right) (\gamma \circ \varphi)(0) \in \mathbb{R}^{n^2}
$$

for any $t \in J$, implying that $(\gamma \circ \varphi)(0) = 0$ reads as $(\gamma \circ \varphi)(t) = 0$ for all $t$. Hence

$$
\Upsilon^0_{ij} \equiv \{ \omega \in \Omega | \gamma_{ij}(\omega) = 0 \}
$$

is an invariant space for $i, j = 1, \ldots, n$. For any $i$ and $j$, the continuity of $\gamma_{ij}$ indicates that $\Upsilon^+_{ij} = \{ \gamma_{ij} > 0 \}$ and $\Upsilon^-_{ij} = \{ \gamma_{ij} < 0 \}$ are also invariant. 

Thus, we get

**Proposition 6** The flow $\{ T_t \}$ of ODE (10) is not ergodic with respect to $(\Omega, \mathcal{L}_N^O, \mu)$.

**Proof.** Choose any $i, j \in \{1, \ldots, n\}$ such that $i \neq j$ (recall $n > 1$). We have $\Upsilon^\pm_{ij} \neq \emptyset$. From assumption (13) and the fact that $\Upsilon^\pm_{ij}$ becomes a nonempty open set of $\mathbb{R}^N$, we see $\mu(\Upsilon^+_{ij}) > 0$ and $\mu(\Omega \setminus \Upsilon^+_{ij}) \geq \mu(\Upsilon^-_{ij}) > 0$. 

The above discussion shows the non ergodicity for the harmonic oscillator system with $n > 1$, by showing the existence of an invariant set $\Upsilon^+_{ij}$ that has a desired property (for
this purpose, finding one such a set is relevant but the existence of many subsets such as
∪_{i,j} Y_{ij}^{±} and ∩_{i,j} Y_{ij}^{±} is less important). However, this discussion lacks explanations why and
how the invariant set Y_{ij}^{±} arises. In Appendix, we show that symmetry group O(N) acts on
ODE (10) and its invariant set splits the total phase space Ω producing invariant sets that
correspond to Y_{ij}^{±}. It should be noted that finding just one solution (or countably many
solutions) confined in a certain subset B does not necessarily indicate the non
ergodicity, since B may be a null set.

The above discussion on the isotropic harmonic oscillator case can be generalized to a
harmonic oscillator with F(x) = −Kx ∈ ℝ^n with K ∈ Endℝ^n under the condition that
M^{-1}K is symmetric, positive definite, and degenerate, i.e., there exist eigenvalues such
that λ_i = λ_j for i ≠ j. Proposition 3 in this case is proven by observing that ˜Υ_{ij}^{0} \equiv
\{ω ∈ Ω|γ_{ij}(ω) = 0\} becomes an invariant space, where ˜γ(ω) ≡ VGx ∧ GM^{-1}p with V ≡ GM^{-1}KG^{-1} being the diagonal matrix for a certain G ∈ GL(n), and by observing that
˜Υ_{ij}^{±} \equiv \{ω ∈ Ω|γ_{ij}(ω) ≥ 0\} becomes a nonempty open invariant set.

IV. SPLITTING DENSITY DYNAMICS

To attain the ergodicity for symmetric systems such as the nHO, we propose a generalized
version of the density dynamics (DD) [13]. The original version of the DD is defined by

\begin{align*}
\dot{x}_i &= D_{p_i}Θ(ω) ∈ ℝ, \quad i = 1, \ldots, n, \\
\dot{p}_i &= -D_{x_i}Θ(ω) - D_{ζ}Θ(ω) p_i ∈ ℝ, \quad i = 1, \ldots, n, \\
\dot{ζ} &= \sum_{i=1}^{n} D_{p_i}Θ(ω) p_i - nβ^{-1} ∈ ℝ,
\end{align*}

with Θ = −β^{-1} ln ρ, where ρ : Ω → ℝ is an arbitrarily given density function, i.e., ρ is a
function that is of class C^2, strictly positive, and integrable. ζ ∈ ℝ is a dynamical variable
and β > 0 is an arbitrary parameter. ODE (12) is designed so as to satisfy the Liouville
equation (7) for the density ρ, and it involves the NH EOM (2), viz., the NH is recovered if
we set ρ = ρ_{NH}, where

ρ_{NH}(ω) ≡ \exp \left[ -β \left( U(x) + K(p) + \frac{1}{2Q}ζ^2 \right) \right]

with β = 1/kBT_{ex}.

Our generalization for Eq. (12) is based on (i) an extension of the additional scalar
variable ζ ∈ ℝ to a vector variable ζ \equiv (ζ_1, \ldots, ζ_n) ∈ ℝ^n, and (ii) ζ_i ‘s EOM that is a
natural decomposition of the third equation of (12). Namely, a generalized DD, which we call splitting density dynamics, is

\[
\begin{align*}
\dot{x}_i &= D_{p_i} \Theta(\omega) \in \mathbb{R}, \quad i = 1, \ldots, n, \\
\dot{p}_i &= -D_{x_i} \Theta(\omega) - D_{\zeta_i} \Theta(\omega) \ p_i \in \mathbb{R}, \quad i = 1, \ldots, n, \\
\dot{\zeta}_i &= D_{p_i} \Theta(\omega) \ p_i - \beta^{-1} \in \mathbb{R}, \quad i = 1, \ldots, n.
\end{align*}
\tag{14}
\]

As is easily confirmed that the Liouville equation (7) holds for any density function \( \rho \), this new EOM can be replaced with Eq. (12). That is, for any \( P \)-integrable function \( g \) on phase space \( \Omega \),

\[
\bar{g} := \exists \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau g(T_t(\omega)) dt = \int_\Omega g \rho \ dl_N / \int_\Omega \rho dl_N =: \langle g \rangle \in \mathbb{R}
\tag{15}
\]

holds with respect to a \( P \)-almost every initial point \( \omega \), if the flow \( \{T_t\} \) is ergodic with respect to the measure \( P \equiv \rho dl_N \).

Some remarks are made [13]. First, fixed points for \( X \), which can be obstructions to the ergodicity, do not exist, as long as \( \beta > 0 \). Second, \( \text{div } X \neq 0 \), holds (otherwise \( \rho \) becomes an invariant function and should not be almost everywhere constant, so the system does not become ergodic), as long as

\[
\sum_{i=1}^n D_{\zeta_i} \rho \neq 0
\tag{16}
\]

(not identically zero). This is because \( \text{div } X = -\sum_{i=1}^n D_{\zeta_i} \Theta \). Condition (16) is valid in many cases (see the case later).

V. SPLITTING NOSÉ-HOOVER METHOD UTILIZING NOSÉ-MASS MATRIX

The meaning of the generalization of (i) and (ii) in Section IV will be clearer when we consider the NH limit. Here, the NH limit is obtained if we set \( \rho = \tilde{\rho}_{BG} \), where

\[
\tilde{\rho}_{BG}(\omega) \equiv \exp \left[ -\beta \left( U(x) + K(p) + K_z(\zeta) \right) \right]
\tag{17}
\]

with

\[
K_z(\zeta) \equiv \frac{1}{2} (\zeta | Q^{-1} \zeta) = \frac{1}{2} \sum_{i,j=1}^n Q_{ij}^{-1} \zeta_i \zeta_j
\tag{18}
\]
being a quantity corresponding to the kinetic energy for $\zeta$, and $\beta = 1/k_B T_{\text{ex}}$. The difference from Eq. \([13]\) is to utilize, as well as the vectorized $\zeta \in \mathbb{R}^n$, a matrix form of $Q$, which is a natural extension of the original scalar Nosé’s mass $Q$ (recovered when $n = 1$, of course). Specifically, $Q \equiv (Q_{ij}) \in \text{End}\mathbb{R}^n$ should be symmetric and positive definite: we should set it symmetric without loss of generality, considering that the kinetic energy is a quadratic form; and the positive-definite condition is a natural extension of $Q > 0$ and is actually required for ensuring the integrability condition of $\rho$. Now, applying Eq. \([17]\), the splitting DD \([14]\) turns out to be

\[
\dot{x}_i = (M^{-1}p)_i \in \mathbb{R}, \quad i = 1, \ldots, n, \quad (19a)
\]

\[
\dot{p}_i = F_i(x) - \tau_i(\zeta) \; p_i \in \mathbb{R}, \quad i = 1, \ldots, n, \quad (19b)
\]

\[
\dot{\zeta}_i = 2K_i(p) - k_B T_{\text{ex}} \in \mathbb{R}, \quad i = 1, \ldots, n, \quad (19c)
\]

where

\[
\tau_i(\zeta) \equiv -k_B T_{\text{ex}} D\dot{\zeta} \ln \hat{\rho}_{BG} (\omega) = D_i K_2(\zeta) = (Q^{-1}\zeta)_i = \sum_{j=1}^{n} Q^{-1}_{ij} \zeta_j
\]

\[
2K_i(p) \equiv (M^{-1}p)_i \; p_i. \quad (20)
\]

Thus, the dynamical frictional “coefficient” $\tau_i(\zeta)$ depends on not only one component for $\zeta$ (as in the NH and NHC) but also all components $\zeta_1, \ldots, \zeta_n$ or at least two components $\zeta_k, \zeta_l$ when we choose $Q$ as a non-diagonal matrix. This is a motivation of above \((i)\), and this “mixing” of $\zeta$ components will play a part for avoiding the nonergodicity, as detailed below.

Briefly speaking, the fact that the contribution of $\tau_i(\zeta)$ to $\dot{p}_i$ can be different for each $i$ is effective to break down the isotropic symmetry if it exists in the system. Equation \([19c]\) intends the law of equipartition, i.e., the expected equilibrium condition, $\dot{\zeta}_i \sim 0$, should contribute to the exact relationship of the law $2K_i = k_B T_{\text{ex}}$ for every degree of freedom $i$,.
which is validated by

\[ 2K_i = \langle 2K_i \rangle \]
\[ \equiv \int_\Omega (M^{-1}p_i \tilde{\rho}_{BG}(\omega) dl_N(\omega)) / \int_\Omega \tilde{\rho}_{BG} dl_N \]
\[ = k_B T_{ex} \] (22)

where the first equation is owing to (15) under the ergodic condition.

Some remarks are made. First note that the EOM (19) is still physically natural in the sense that the first equation is exactly same as that in the Newtonian EOM, and the \( i \)th component of the frictional force in Eq. (19b) is proportional to \( p_i \) and take a form \(-\tau_i(\zeta) p_i\) using a scalar quantity \( \tau_i(\zeta) \in \mathbb{R} \), which conforms to the conventional form for the classical dynamics treatment. Second, EOM (19) can be viewed as a generalization of the original NH. This is because, by setting

\[ Q^{-1} = Q^{-1} \mathbf{1} \equiv Q^{-1} \begin{bmatrix} 1 & \cdots & 1 \\ \vdots & \ddots & \vdots \\ 1 & \cdots & 1 \end{bmatrix} \in \text{End} \mathbb{R}^n \] (23)

with a scalar input \( Q^{-1} > 0 \) and a matrix \( \mathbf{1} \) whose every element is unity (not the unit matrix), we recover the original NH EOM via defining a redesigned scalar variable \( \zeta = \sum_{i=1}^n \zeta_i \in \mathbb{R} \), which plays the same role in the original NH variable. In this sense, we will call Eq. (19) splitting Nosé-Hoover EOM. Third, as can also be seen from Eq. (22), ODE (19) generates the BG distribution at temperature \( T_{ex} \) for physical quantities under the ergodic condition. This is clearly seen by separately rewriting \( \tilde{\rho}_{BG} \) such that

\[ \tilde{\rho}_{BG}(\omega) = \rho_{BG}(x, p) \rho_Z(\zeta), \]
\[ \rho_{BG}(x, p) \equiv \exp \left[ -\frac{1}{k_B T_{ex}} (U(x) + K(p)) \right], \]
\[ \rho_Z(\zeta) \equiv \exp \left[ -\frac{1}{k_B T_{ex}} K_z(\zeta) \right], \]

Eq. (15) implies the relation \( \bar{f} = \langle f \rangle_{BG} \) with respect to a physical quantity \( f : D \times \mathbb{R}^n \rightarrow \mathbb{R} \).
such that

\[
\bar{f} \equiv \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau f(x(t), p(t)) dt
\]

\[
= \int_{\Omega} f(x, p) \tilde{\rho}_{BG}(\omega) \, d\mathcal{L}_N \div \int_{\Omega} \tilde{\rho}_{BG} d\mathcal{L}_N \in \mathbb{R}
\]

\[
= \frac{\int_{D \times \mathbb{R}^n} f(x, p) \rho_{BG}(x, p) \, dx dp}{\int_{D \times \mathbb{R}^n} \rho_{BG}(x, p) \, dx dp} =: \langle f \rangle_{BG}.
\] (24)

Finally, note that Condition (16) is valid for \( \rho = \tilde{\rho}_{BG} \) since \( \sum_{i=1}^{\mathbb{n}} D_{\zeta_i} \Theta(\zeta) = \sum_{i,j=1}^{\mathbb{n}} Q_{ij}^{-1} \zeta_i \).

Note that matrix form of \( Q \) has been utilized before in literature. Samoletov et al. [33] have used it in their development of configurational thermostats, which are thermostat equations in configuration space. Their matrix \( Q \) is of size of 3, which corresponds to the additional 3-vector introduced for their purpose in order to control \( x \) instead of \( p \). They also utilized a diagonal form (uncoupled case) for \( Q \) in considering physical necessities, though admitted the possibility of coupled case. In these respects, their approach and ours are different. Leimkuhler et al. [24] has considered a NH type EOM with introducing random noise to improve ergodicity. The frictional term they treated is of form of \( \lambda(\omega) = \zeta \mathbf{1}_n + \mathbf{M} \mathbf{S}(t, \zeta) \in \text{End} \mathbb{R}^n \), where \( \zeta \) is a scalar as in the original NH, and \( \mathbf{S}(t, \zeta) \) is an anti-symmetric matrix depending on \( \zeta \). Thus, it is different from our term (20). They demonstrated the ergodicity for their stochastic dynamics with harmonic oscillators, relating as a counterpart to our statement of the nonergodicity for ODE.

A. On the choice of matrix \( Q \)

We describe how the matrix \( Q \) defines the the distribution of \( \zeta \) and how we should set \( Q \) for effectively realize the ergodicity.

1. \( Q \) determines \( \zeta \)'s distribution

In contrast to the (marginal) distribution of \((x, p)\) described by the RHS of Eq. (24), which is the BG distribution, the distribution of \( \zeta \) is characterized by the matrix \( Q \) and is
described by $P_\zeta \equiv P \pi^{-1}_\zeta : B^n \to \mathbb{R}$ such that
\[
B \mapsto P(\pi^{-1}_\zeta(B))
\]
\[
= \int_{D \times \mathbb{R}^n \times B} \tilde{\rho}_{BG} dl_N / \int_{\Omega} \tilde{\rho}_{BG} dl_N
\]
\[
= \int_B \rho_{\tilde{Z}}(\zeta) dl_n(\zeta) / \int_{\mathbb{R}^n} \rho_{\tilde{Z}} dl_n
\]
\[
= N_z \int_B \exp \left[ -\frac{1}{2k_B T_{ex}} (\zeta \mid Q^{-1} \zeta) \right] d\zeta,
\]
where $N_z \equiv [(2\pi k_B T_{ex})^n \det Q]^{-1/2}$. Namely, $\zeta \in \mathbb{R}^n$ is distributed ellipsoidally around the origin. Note that, instead of directly using $P_\zeta$, it is often convenient to use the distribution of principal component $y \equiv O^{-1} \zeta \in \mathbb{R}^n$ for which $Q^{-1}$ is diagonalized as $O^{-1}Q^{-1}O = \text{diag}(\lambda_1, \ldots, \lambda_n)$ with $\lambda_i$ being a strictly positive eigenvalue of $Q^{-1}$. The distribution of $y$ is given by $P_Y \equiv P(G^{-1} \circ \pi_\zeta^{-1} : B^n \to \mathbb{R}$ where
\[
B \mapsto P(\pi^{-1}_\zeta(G(B)))
\]
\[
= N_z \int_B \exp \left[ -\frac{1}{2k_B T_{ex}} \sum_{i=1}^{n} \lambda_i y_i^2 \right] dy,
\]
which is the joint distribution of 1-dimensional Gaussian distributions $\exp \left[ -\frac{1}{2k_B T_{ex}} \lambda_i y_i^2 \right] dy_i$, $i = 1, \ldots, n$. Note that the distribution of $\zeta$, or $y = O^{-1} \zeta$, is not used in obtaining physical information, such as the long-time average of physical variable in Eq. (24), but the explicit form of $P_Y$ can be utilized to monitor the convergence of the distribution generated by the flow and numerically judge the ergodicity.

2. We determine $Q$

Here we discuss how we determine $Q$ or $Q^{-1}$. Its overall amplitude can be set by a scale factor as in the case of the scalar $Q$, as in the original NH [30]. Thus we should determine the difference between the matrix elements it in a finer manner. Our criteria for setting the matrix $Q^{-1}$ are as follows:

(i) it is symmetric and positive definite;

(ii) its eigenvalues and eigen vectors are explicitly obtained;
(iii) it should not be diagonal;

(iv) its diagonal components are nevertheless sufficiently larger than off-diagonal components;

(v) randomness can be easily introduced in the elements.

The reason of these requirements is as follows: (i) has been already assumed and the necessity has also been discussed. (ii) is required to explicitly obtain the distribution of \( \zeta \) or \( y \equiv G^{-1}\zeta \). (iii) is needed to enhance the mixing of different components \( \zeta_1, \ldots, \zeta_n \) through the friction term

\[
-\tau_i(\zeta) p_i = -\left( Q_{i1}^{-1}\zeta_1 + \cdots + Q_{ii}^{-1}\zeta_i + \cdots Q_{in}^{-1}\zeta_n \right) p_i
\]

in Eq. (19b). Otherwise, Eq. (19b) turns out to be the same form as that of the original NH, leading to the nonergodicity in the case of the nHO as discussed in Section III. (iv) if \( Q_{ii}^{-1} \) is small, then the contribution of \( \zeta_i \) derived by Eq. (19c) will not be much assessed, so that the equipartition (22) will not be enhanced at least in a relatively short time scale. (v) is needed to break isotropy or symmetries in the target physical system. It is also useful to emphasize the difference between the splitting NH and the original NH, where the latter can be characterized as a uniform matrix \( Q^{-1} \) seen in (23).

Using the fact that a symmetric matrix \( W \in \text{End} \mathbb{R}^n \) is positive definite if and only if \( \exists O \in O(n) \), \( \exists d_1, \ldots, d_n > 0 \), \( W = O \text{ diag}(d_1, \ldots, d_n)^T O \), and using a representation of the group \( O(n) \), we propose the following procedures (1)–(4) for setting \( Q^{-1} \):

1. Choose values randomly for \( \theta_{k,j} \in ]0, \epsilon[ \) with \( 0 < \epsilon \ll \pi \) for \( 1 \leq j < k \leq n \),
2. define \( O := h_n h_{n-1} \cdots h_2 \) for which \( h_k := r_1(\theta_{k,1}) r_2(\theta_{k,2}) \cdots r_{k-1}(\theta_{k,k-1}) \), where

\[
r_i(\theta) \equiv \begin{bmatrix} 1_{i-1} & 0 & 0 \\ 0 & u_2(\theta) & 0 \\ 0 & 0 & 1_{n-i-1} \end{bmatrix} \in \text{End} \mathbb{R}^n
\]

with \( 1_i \) being the unit matrix of size \( i \) and \( u_2(\theta) \equiv \begin{bmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{bmatrix} \); for convenience, any \( q \in O(n) \), such as \( q \equiv \text{diag}(1, \ldots, 1, -1) \) or interchange matrices \( q \equiv J_{ij} \) can be inserted among the products of \( h_k \) in defining \( O \).
(3) set \( d_i = 1 + \delta_i \) with \(-\delta < \delta_i < \delta < 1\) for \( i = 1, \ldots, n\), where \( \delta_i \neq \delta_j \) for \( i \neq j \), and then, using a scale factor \( \lambda \), put \( D \equiv \lambda \text{diag}(d_1, \ldots, d_n) \equiv \text{diag}(\lambda_1, \ldots, \lambda_n) \), and finally,

(4) define

\[
Q^{-1} := O D^T O. \tag{27}
\]

Then, condition (i) holds, and (ii) is clear since the eigen values of \( Q^{-1} \) are \( \lambda_1, \ldots, \lambda_n \) and \( O_i \equiv (O_{1i}, \ldots, O_{ni}) \in \mathbb{R}^n \) is obtained to be the eigen vector corresponding to \( \lambda_i \) for \( i = 1, \ldots, n\). Condition (iii) will hold, or reset some values of \( \theta_{k,j} \) if needed. A small \( \epsilon \) that becomes the threshold of \( \theta_{k,j} \) is useful to contribute to the purpose (iv) in that each \( r_i(\theta) \) is near the identity matrix. Randomness can be introduced through the \( n(n - 1)/2 \) manifold parameters \( \theta_{k,j} \) for the sake of (v).

**Example 7** For \( n = 2 \), we have \( O = h_2 = r_1(\theta_{2,1}) = u_2(\theta_{2,1}) \). For \( n = 3 \), we have

\[
O = h_3 h_2 = r_1(\theta_{3,1}) r_2(\theta_{3,2}) r_1(\theta_{2,1})
\]

\[
= \begin{bmatrix}
\cos \theta_{3,1} & \sin \theta_{3,1} & 0 \\
-\sin \theta_{3,1} & \cos \theta_{3,1} & 0 \\
0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
1 & 0 & 0 \\
0 & \cos \theta_{3,2} & \sin \theta_{3,2} \\
0 & -\sin \theta_{3,2} & \cos \theta_{3,2}
\end{bmatrix}
\begin{bmatrix}
\cos \theta_{2,1} & \sin \theta_{2,1} & 0 \\
-\sin \theta_{2,1} & \cos \theta_{2,1} & 0 \\
0 & 0 & 1
\end{bmatrix}.
\]

Instead, we can use e.g., \( O = J_{12} r_1(\theta_{3,1}) J_{12} J_{12} r_2(\theta_{3,2}) J_{12} J_{13} r_1(\theta_{2,1}) J_{13} \), viz.,

\[
O = \begin{bmatrix}
\cos \theta_{3,1} & -\sin \theta_{3,1} & 0 \\
\sin \theta_{3,1} & \cos \theta_{3,1} & 0 \\
0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
\cos \theta_{3,2} & 0 & \sin \theta_{3,2} \\
0 & 1 & 0 \\
-\sin \theta_{3,2} & 0 & \cos \theta_{3,2}
\end{bmatrix}
\begin{bmatrix}
1 & 0 & 0 \\
0 & \cos \theta_{2,1} & -\sin \theta_{2,1} \\
0 & \sin \theta_{2,1} & \cos \theta_{2,1}
\end{bmatrix}, \tag{28}
\]

which indicates the composition of rotations in \( \mathbb{R}^3 \) around the \( x,y,z \)-axis with angles \( \theta_{2,1}, \theta_{3,2}, \) and \( \theta_{3,1} \), respectively.

**VI. NUMERICS**

We numerically tested our considerations, nonergodic property for the conventional schemes and the ergodic property for the current scheme, using the isotropic harmonic oscillator system defined by \( \Box \) with \( n > 1 \). We set both the mass \( m \) and spring constant \( k \) to be 1, and put \( k_B T_{ex} = 1 \) (all quantities were treated as dimensionless). Numerical integrations of ODEs were done by the explicit second order scheme described in Ref. \[8\] for
We show that conventional method employing an EOM of the form of Eq. (10) fail in the ergodic sampling, as stated in Proposition 6. As a conventional method, we have used the NHC method (Example 2) with the chain length \( m = 2 \) and masses \( Q_1 = Q_2 = 1 \). A first case we show is that with \( n = 2 \), where we used the initial value \( x(0) = (0, 0) \), \( p(0) = (1, 1) \), and \( \zeta(0) = (0, 0) \). Figure 1 shows that the trajectory of \((x_1, p_1)\) and their marginal distributions. The trajectory shows a hall in a vicinity of the origin, and this clearly affects the distribution of \( x_1 \). The distribution of \( p_1 \) is also weird. Due to the a special setting of the initial condition, \( x_1(t) = x_2(t) \) and \( p_1(t) = p_2(t) \) for all time \( t \), so that the trajectory of \((x_2, p_2)\) and the distributions are totally the same as that for \((x_1, p_1)\), respectively. In terms of the symmetry, this special initial condition obeys a symmetry of the interchange, \( S = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \in O(2) \), so that the initial value \( \omega_0 \equiv (x(0), p(0), \zeta(0)) \) falls in an invariant set \( A \subset A_{\mathbb{R}} = A_{O(2)_x} \), defined in Eq. (30) and utilized in the decomposition (29) (see Appendix). Thus, the solution always falls in the invariant set \( A \), indicating the fact that \( x_1(t) = x_2(t) \) and \( p_1(t) = p_2(t) \) for all \( t \). This initial condition, however, seems too special and very severe. Thus, we also treated another condition such that \( x_1(0) = x_2(0) = 0, p_1(0) = 1, p_2(0) = 2 \) (with \( \zeta(0) = (0, 0) \), which was the same in all the cases below). Nevertheless, this initial condition obeys a symmetry \( S = \frac{1}{5} \begin{bmatrix} -3 & 4 \\ 4 & 3 \end{bmatrix} \in O(2) \), so that this solution is also confined in the invariant space, \( \omega(t) \in A \) for all \( t \). Although it does not hold that \( x_1(t) = x_2(t) \) and \( p_1(t) = p_2(t) \) for all \( t \), this confinement severely effects the motion, and the trajectories of \( x, p \) and their distributions exhibited similar nonergodic behavior as that in Figure 1 (not shown).

In the second case, we changed the initial condition only and set as \( x_1(0) = 1, x_2(0) = 0, p_1(0) = 0, p_2(0) = 0.01 \), which does not have any symmetry in \( O(2)_x \). The initial value \( \omega_0 \) is in \( A_{\mathbb{R}} \) because \( \gamma_{12}(\omega_0) = \frac{1}{2}(x_1(0)p_2(0) - p_1(0)x_2(0)) > 0 \) (see Eq. (11) and Proposition 6). Thus the solution is not confined in the “small” subspace \( A \) but confined in \( A_{\mathbb{R}} \), which is “large”. However, as shown in Figure 2, the distributions are far from the theoretical Gaussian distributions and the trajectories are biased, suggesting a certain structure. The third case we studied is the case with \( x_1(0) = 1, x_2(0) = 0, p_1(0) = 0, p_2(0) = -2 \), which

10⁸ time steps with a unit time of \( h = 10^{-3} \), and the numerical errors were checked to be within a tolerance within the scheme of the extended system [12].
also has no symmetry in \( O(2) \times \omega_0 \in A^{[-1]} \) (because \( \gamma_{12}(\omega_0) < 0 \)). This yielded a relatively good results for trajectories and distributions (not shown). Although a hall (which is smaller compared with that in the above cases) was observed in the \((x, p)\) trajectories and unignorable errors were admitted in the distributions, it might be sufficient in practical simulations. However, a clear numerical evidence for nonergodicity is a definiteness of the signature of \( \gamma_{12}(\omega(t)) \). It should be a null occurrence that \( \gamma_{12}(\omega(t)) = 0 \) for all \( t \), if the flow is ergodic. Furthermore, there should not be the case where \( \gamma_{12}(\omega(t)) > 0 \) for all \( t \) or \( \gamma_{12}(\omega(t)) < 0 \) for all \( t \). Otherwise, it breaks the ergodicity and contradicts the BG distribution. In fact, its average should be zero under the BG distribution: \( \bar{\gamma}_{ij} = \langle \gamma_{ij} \rangle = \langle \gamma_{ij} \rangle_{\text{BG}} = 0 \) if the flow is ergodic with respect to \( \exp[-\beta U(x) + K(p)] \rho_Z(\zeta) \, d\omega \) for any smooth, positive, integrable \( \rho_Z \) (as long as \( \int_D x_k \exp[-\beta U(x)] \, dx \) are finite for \( k = i \) and \( j \)). Figure 3 shows \( \gamma_{12}(\omega(t)) \) for the three cases above. The first case (Fig. 3a) corresponds to the null case \( \gamma_{12}(\omega(t)) = 0 \) for all \( t \), and the second (Fig. 3b) and third (Fig. 3c) cases correspond to \( \gamma_{12}(\omega(t)) > 0 \) and \( \gamma_{12}(\omega(t)) < 0 \) for all \( t \), respectively. These results show that the conventional method sampled the phase space in a nonergodic manner. Note also that the magnitude of \( \gamma_{12}(\omega(t)) \) in the third case (Fig. 3c) is larger than the second case (Fig. 3b). This result may be the reason why the third case shows relatively good sampling; namely, trajectories staying near the invariant set \( A \) shows bad sampling, whereas trajectories that can be away from \( A \) relatively show good (but not exact) sampling. These staying features near \( A \) may suggest a kind of stability of the invariant set \( A \).

We tested the splitting NH EOM \cite{19}, currently provided scheme, using the same harmonic oscillator system as above. A first example is the case with \( n = 2 \), where the initial value is the same as the most stiff case used above, viz., \( x(0) = (0, 0), p(0) = (1, 1), \zeta(0) = (0, 0) \). We set \( Q^{-1} \) in the manner stated in Section \ref{VA2} where \( \delta_1 = 0, \delta_2 = 0.2, \lambda = 10, \) and \( \theta_{2,1} = 0.5 \) were used. The scatter plots of all variables \( x_1, x_2, p_1, p_2, \zeta_1, \) and \( \zeta_2 \) are shown in Figure 4. They are well sampled in the phase space. The distributions agreed the theoretical distribution, and the errors were sufficiently small, for which we have used variable \( y \), instead of \( \zeta \), as indicated in Eq. \ref{25}. We also observed that \( \gamma_{12}(\omega(t)) \) does not indicate the positive/negative definiteness, as in the conventional method, and rapidly converged to the theoretical value 0. We had similar results for other initial conditions. Next, we show the results for other setting of \( Q^{-1} \), where \( \delta_2 = 0.8 \) and \( \theta_{2,1} = 0.8 \), while the other conditions are the same as above. This is a setting where ellipsoid distributed feature for \( \zeta \)
is emphasized. We observe in Figure 5 that $\zeta$ were distributed ellipsoidally around the origin and sampled correctively, as indicated in the theoretical contours and the distributions for $y$.

The next example for the splitting NH EOM (19) is the case with $n = 3$. In the procedures for setting $Q^{-1}$, we put $\theta_{3,1} = \theta_{3,2} = \theta_{2,1} = 0.5$, $\delta_1 = -0.2$, $\delta_2 = 0$, $\delta_3 = 0.2$, and $\lambda = 10$, and utilized Eq. (28). Initial values were $x_i(0) = 0$, $p_i(0) = 1$, $\zeta_i(0) = 0$ for all $i = 1, 2, 3$ (same for the cases of $n = 2$). As shown in Figure 6, the scatter plots indicate the ergodic sampling, and the distribution for each variable $x_i$, $p_i$, $\zeta_i$ for $i = 1, 2, 3$ agree with the theoretical distribution, respectively, as indicated by the small errors. This also shows that the sampling were good even if $\theta_{k,j}$ were not set randomly. On the Basis of these results, we conclude that the current method accurately corresponds to the ergodicity.

Appendix

We say that a linear symmetry $S : \mathbb{R}^n \to \mathbb{R}^n$ acts on ODE (1) if it satisfies the following:

**Definition 8** $S \in \text{End} \mathbb{R}^n$ preserves the functions $\lambda$ and $\Lambda$ and the domain $D$ such that $\lambda(S(x), S(p), \zeta) = \lambda(x, p, \zeta)$ and $\Lambda(S(x), S(p), \zeta) = \Lambda(x, p, \zeta)$ hold for all $(x, p, \zeta) \in \Omega$ and $S(D) \subset D$. Commutativities also hold: $M^{-1} \circ S = S \circ M^{-1}$ and $F \circ S = S \circ F$.

We denote by $\mathcal{S}$ the set of all $S \in \text{End} \mathbb{R}^n$ that acts on ODE (1).

**Lemma 9** For any $S \in \mathcal{S}$, we have $S(x(t)) = x(t)$ and $S(p(t)) = p(t)$ for all $t$ in an interval $J \subset \mathbb{R}$, if $\varphi : J \to \Omega, t \mapsto (x(t), p(t), \zeta(t))$ is a solution of ODE (1) with an initial condition satisfying $S(x(0)) = x(0)$ and $S(p(0)) = p(0)$.

**Proof.** It follows from Definition 8 that $\varphi : \mathbb{R} \ni J \to \Omega, t \mapsto (S(x(t)), S(p(t)), \zeta(t))$ also becomes a solution of the $C^1$ ODE and $\varphi(0) = \varphi(0)$ holds. Thus, the uniqueness of the initial value problem ensures $\varphi = \varphi$, so that $S(x(t)) = x(t)$ and $S(p(t)) = p(t)$ for all $t \in J$.

We thus have for every $S \in \mathcal{S}$ an invariant set,

$$\Omega_S := \Gamma_s^D \times \Gamma_s \times \mathbb{R}^m,$$

with

$$\Gamma_s \equiv \{p \in \mathbb{R}^n | S(p) = p\}.$$
and $Γ_s^D ≡ Γ_s ∩ D ≡ \{x ∈ D \mid S(x) = x\}$, indicating that the symmetry $(S(x), S(p)) = (x, p)$ is kept in the dynamics or compatible with the ODE. To show the nonergodic condition [8], we take an approach that is to find an invariant set $A$ whether it meets condition [8] itself or it separates the total phase space into three invariant sets,

$$Ω = A ⊔ A^{[+] ⊔ A^{[-]},} \tag{29}$$

wherein $A^{[+]}$ meets condition [8]. For this, $A$ should be "large" (for otherwise situation in choosing $A = Ω_S$, there is the extremely small case $Γ_s = ∅$ or a case of a low dimensional subspace). Our target for $A$ is thus an invariant set that are summed up these $Ω_s$ in a certain manner:

$$A_R ≡ \bigcup_{s ∈ R} Ω_s = \bigcup_{s ∈ R}(Γ_s^D × Γ_s) × \mathbb{R}^m, \tag{30}$$

where $R$ is a certain subset of $S$ such that it is sufficiently large but not too large. For the latter condition, for example, we should remove the case where $S$ is the identity id$_{R^n}$, otherwise $A_S$ becomes "too large" ($S = \text{id}_{R^n}$ provides $Ω_{\text{id}_{R^n}} = Ω$ and so yields $Ω \setminus A_R = ∅$, which does not contribute to the nonergodic condition [8] for $A ≡ A_R$).

We will show that (29) holds with $A^{[±]} ≡ Υ^{±}_{ij}$ if $A ≡ A_R$, in a special case of the isotropic nHO. Here $Υ^{±}_{ij}$ are defined in Lemma 5 and this fact can explain the route why $Υ^{±}_{ij}$ arise. That is, they arise as a complementary set to a sum, in a certain range $R$, of the invariant set $Ω_S$ based on the symmetry $S$ that acts on the ODE. To show the issue, we restrict the condition such that the dependence of $x, p$ in the functions $λ$ and $Λ$ is only through the potential and kinetic energies; viz.,

**Condition 10** There exist $C^1$ functions $\tilde{λ}, \tilde{Λ} : \mathbb{R} × \mathbb{R} × \mathbb{R}^m → \mathbb{R}$ such that $λ(x, p, ζ) = \tilde{λ}(U(x), K(p), ζ) and Λ(x, p, ζ) = \tilde{Λ}(U(x), K(p), ζ)$ for all $(x, p, ζ) ∈ Ω$

This is not a special condition and are satisfied by Examples 1–4. For the harmonic oscillator system described by Eq. (9) under condition 10, orthogonal transforms of $\mathbb{R}^n$ actually act on ODE (11):

**Lemma 11** $S ⊃ O(n) ≡ \{S ∈ \text{End}\mathbb{R}^n \mid ^TS^S = \text{id}_{R^n}\}$ holds for the harmonic oscillator system.
Proof. Take any $S \in O(n)$. Since $U(S(x)) = U(x)$ and $K(S(p)) = K(p)$ hold for any $(x, p)$, and since $M^{-1}$ and $F$ become diagonal, the conditions in definition are valid, indicating $O(n) \subset S$. ■

We then put

$$\mathcal{R} \equiv O(n) \setminus \{\text{id}_{\mathbb{R}^n}\} =: O(n)_x,$$

viz., we sum up $\Omega_S$ to make $A_{\mathcal{R}}$ for all $S$ that is a non-identical orthogonal transform of $\mathbb{R}^n$. We also restrict our consideration for $n = 2$ for ease, wherein the discussion would be extended to a larger $n$. The following proposition shows how $\Upsilon_{12}^\pm$ arises from $\mathcal{R}$.

**Proposition 12** It holds that $A_{\mathcal{R}} = \Upsilon_{12}^0$, and the decomposition (29) holds with $A = A_{\mathcal{R}}$ and $A^{[\pm]} = \Upsilon_{12}^\pm$.

Proof. By using the fact that $O(2)$ is bijectively parametrized by $S^1$ and signature,

$$S^1 \times \{\pm 1\} \to O(2), \ (\theta, \sigma) \mapsto \begin{bmatrix} \cos \theta & -\sigma \sin \theta \\ \sin \theta & \sigma \cos \theta \end{bmatrix} =: s_{\theta}^\sigma,$$

and by solving an eigenvalue problem $s_{\theta}^\sigma(p) = p$, we see

$$\Gamma_{s_{\theta}^+} = \begin{cases} \mathbb{R}^2 & \text{if } \theta = 0 \\ \{0, 0\} & \text{otherwise} \end{cases},$$

$$\Gamma_{s_{\theta}^-} = \begin{cases} \mathbb{R} \times \{0\} & \text{if } \theta = 0 \\ \{0\} \times \mathbb{R} & \text{if } \theta = \pi \\ \{(p_1, p_2) \in \mathbb{R}^2 \mid p_2 = \frac{1 - \cos \theta}{\sin \theta} p_1 \} & \text{otherwise} \end{cases}.$$  

Note that $\Gamma_{s_{\theta}^\pm}$ is a line through origin of $\mathbb{R}^2$ with a gradient $k = k_{\theta}$ for $\theta \in S^1 \setminus \{0, \pi\}$, where $k_{\theta}$ can take any value in $\mathbb{R}_x$, and that $\Gamma_{s_{0}^-} = \mathbb{R} \times \{0\}$ and $\Gamma_{s_{\pi}^-} = \{0\} \times \mathbb{R}$ are also lines with gradients 0 and $\infty$, respectively. Thus $\Gamma_{s_{\theta}^\pm} = L_k$, a line through origin of $\mathbb{R}^2$ with a gradient $k \in (-\infty, \infty]$. Applying $\mathcal{R} = O(2)_x = \{s_{\theta}^+ \mid \theta \in S^1_x\} \cup \{s_{\theta}^- \mid \theta \in S^1\}$, we hence
get

\[
\bigcup_{S \in \mathcal{R}} (\Gamma_s^D \times \Gamma_s) = \bigcup_{\theta \in S_1} (\Gamma_{s_\theta^+} \times \Gamma_{s_\theta^+}) \cup \bigcup_{\theta \in S_1} (\Gamma_{s_\theta^-} \times \Gamma_{s_\theta^-}) = \bigcup_{\theta \in S_1} (\Gamma_{s_\theta^-} \times \Gamma_{s_\theta^-}) = \bigcup_{k \in (-\infty, \infty]} (L_k \times L_k) = \{(x_1, kx_1, p_1, kp_1) | x_1, p_1, k \in \mathbb{R}\} \cup \{0\} \times \mathbb{R} \times \{0\} \times \mathbb{R} = \{(x_1, x_2, p_1, p_2) \in \mathbb{R}^4 | x_1p_2 - x_2p_1 = 0\}.
\]

Thus \(A_{\mathcal{R}} = \bigcup_{S \in \mathcal{R}} (\Gamma_s^D \times \Gamma_s) \times \mathbb{R}^m = \{(x, p) \in \mathbb{R}^4 | x_1p_2 - x_2p_1 = 0\} \times \mathbb{R}^m = \{\omega \in \Omega | \gamma_{12}(\omega) = 0\} = \Upsilon_{12}^0\). Therefore, decomposition (29) holds as \(\Omega = \Upsilon_{12}^0 \cup \Upsilon_{12}^+ \cup \Upsilon_{12}^-\). □

Note that the explicit form of \(\Gamma_s\) in the proof directly indicates nontrivial examples to explain that \(\mathcal{R}\) should be sufficiently large. For example, if we take \(\mathcal{R}\) as a one point set, then \(A_{\mathcal{R}} = \bigcup_{S \in \mathcal{R}} (\Gamma_s^D \times \Gamma_s) \times \mathbb{R}^m\) does not separate the phase space into the three spaces as described in (29): if we set \(\mathcal{R} = \{s_\theta^+\}\) with \(\theta \neq 0\) or \(\mathcal{R} = \{s_\theta^-\}\), then \(\bigcup_{S \in \mathcal{R}} (\Gamma_s^D \times \Gamma_s) = \Gamma_{s_\theta^+} \times \Gamma_{s_\theta^+} = \{0, 0, 0, 0\} \subset \mathbb{R}^4\) or \(\bigcup_{S \in \mathcal{R}} (\Gamma_s^D \times \Gamma_s) = \Gamma_{s_\theta^-} \times \Gamma_{s_\theta^-} = \text{-line} \times \text{-line} \subset \mathbb{R}^4\), respectively, clearly induces no separation. So does for e.g. any finite set \(\mathcal{R} = \{s_\theta^+, \ldots, s_\theta^+\}\).

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Figure Captions

Fig. 1. Simulation results obtained by a conventional thermostat method (NHC with the chain length 2) for the 2HO using an initial condition $x_1(0) = x_2(0) = 0$, $p_1(0) = p_2(0) = 1$: (a) trajectory (scatter plot) of $(x_1, p_1)$ and marginal distributions for (b) $x_1$ and (c) $p_1$, where corresponding theoretical distributions and the discrepancies are also shown. The results for $x_2$ and $p_2$ are exactly the same as that for $x_1$ and $p_1$ (see text).

Fig. 2. Simulation results obtained by the NHC for the 2HO using $x_1(0) = 1$, $x_2(0) = 0$, $p_1(0) = 0$, $p_2(0) = 0.01$: (a) marginal distributions for (a) $x_1$ and (b) $p_1$, and trajectory of $(\zeta_1, \zeta_2)$.

Fig. 3. Trajectories of $\gamma_{12}(\omega)$ obtained by the NHC for the 2HO using initial conditions of (a) that in Fig. 1, (b) that in Fig. 2, and (c) $x_1(0) = 1, x_2(0) = 0$, $p_1(0) = 0$, $p_2(0) = -2$.

Fig. 4. Simulation results obtained by a current thermostat method (splitting NH) for the 2HO using $x_1(0) = x_2(0) = 0$, $p_1(0) = p_2(0) = 1$: (a) trajectories (scatter plot) of $(x_1, p_1)$ and (b) $(x_2, p_2)$, and the marginal distributions for (c) $x_1$ and $x_2$ and (d) $p_1$ and $p_2$ (theoretical distributions and the discrepancies are also shown); (e) trajectories of $(\zeta_1, \zeta_2)$ and (f) their marginal distributions represented in the principal components $y_1$ and $y_2$; (g) trajectories of $\gamma_{12}(\omega)$ and its time average.

Fig. 5. Simulation results obtained by the splitting NH for the 2HO, using the different setting of the Nosé mass matrix $Q$ than that in Fig. 4: (a) trajectory of $(\zeta_1, \zeta_2)$ and the contours of the theoretical distribution (rotated ellipsoids); the marginal distributions for principal components (b) $y_1$ and (c) $y_2$.

Fig. 6. Simulation results obtained by the splitting NH for the 3HO: trajectories and distributions for (a) $x_i$, (b) $p_i$, and (c) $y_i$ ($i = 1, 2, 3$).