Reversible measure-preserving integrators for non-Hamiltonian systems

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We present a systematic method for deriving reversible measure-preserving integrators for non-Hamiltonian systems such as the Nosé-Hoover thermostat and generalized Gaussian moment thermostat (GGMT). Our approach exploits the (non-Poisson) bracket structure underlying the thermostat equations of motion. Numerical implementation for the GGMT system shows that our algorithm accurately conserves the thermostat energy function. We also study position and momentum distribution functions obtained using our integrator. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2215608]

I. INTRODUCTION

It is now widely recognized that numerical integration methods for ordinary differential equations preserving the geometrical structure of the underlying flow are likely to lead to more accurate long-term trajectory behavior than those more traditional methods that do not preserve geometric structure.[1]

Time evolution under Hamiltonian dynamics conserves the usual phase space volume element (Liouville's theorem for divergenceless vector fields[2,3]), and this conservation of phase volume is a cornerstone of conventional statistical mechanics.[4,5] More fundamentally, conservation of phase space volume is implied by (but does not imply) the existence of an invariant symplectic 2-form[6–10] in the phase space of Hamiltonian systems.[3,6,11–13] Numerical integration methods that preserve the symplectic structure of the Hamiltonian flow are referred to as symplectic integrators, and these methods have been applied to a broad array of Hamiltonian dynamical problems in both classical and quantum mechanics over the past two decades (for reviews and references to the extensive literature, see Refs. 1 and 14–16).

Non-Hamiltonian dynamics, characterized by nonvanishing divergence (phase space compressibility),[2,17–39] arises when treating the mechanics of thermostatted systems,[27,40–42] as in the simulation of ensembles other than microcanonical[29,43–46] and in the treatment of nonequilibrium steady states.[27,40,42,47] Various homogeneous thermostatting mechanisms have been introduced to remove heat supplied by nonequilibrium mechanical and thermal perturbations,[27,40,41,46] and the resulting equations of motion no longer necessarily conserve the standard phase space volume element. In the non-Hamiltonian form of the Nosé-Hoover thermostat, for example, the equations of motion have an associated invariant measure whose dependence on phase space coordinates is such that, when projected onto the phase space of the thermostatted subsystem, it reproduces the canonical phase space density for the subsystem.[44–46] Whether or not the numerically determined trajectory dynamics will actually sample the full phase space with probability determined by the invariant measure is then a separate question involving the degree of ergodicity of the thermostatted motion.

By the introduction of a coordinate-dependent reparametrization of time and working in extended phase space, it is possible to give a Hamiltonian formulation of Nosé-Hoover dynamics and so to employ symplectic integration algorithms for trajectory integration.[48–50] Rather than follow this symplectification route, in the present paper we address the problem of formulating structure-preserving integrators for non-Hamiltonian equations of motion of the type arising in the Nosé-Hoover thermostat. By "structure-preserving" we mean integration algorithms that exactly conserve the invariant measure (volume element) associated with the non-Hamiltonian flow (cf. the work of Legoll and Monneau, discussed further below[51]). Such algorithms should also be reversible, and will be constructed by the usual procedure of Trotter-type decomposition of the exponentiated Liouvillian operator.[1,16]

In contrast to the huge literature on symplectic integrators,[1,14,16] there has been relatively little work devoted to the study of integrators designed to explicitly conserve known invariants such as volume elements (Liouville integrators).[51–64] In the work of Legoll and Monneau,[51] a coordinate transformation is used to bring the original non-Hamiltonian equations of motion into a normal form that is manifestly divergence-free (see also the very recent work of Fukuda and Nakamura[39]); the invariant measure is then automatically conserved provided the integrator used is symplectic, for example.[51]

In the present paper we take a different approach, and instead build upon the observation of Sergi and Ferrario[30] and Sergi[33] that thermostatted equations of motion such as the Nosé-Hoover equations can be written in a form involving an antisymmetric cooordinate-dependent matrix such that conservation of the Hamiltonian-like quantity generating the equations of motion is obvious (see below). We show that this structure enables us to formulate integrators that conserve the relevant invariant volume elements by construc-

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tion. The importance of conservation of the invariant measure by numerical integration algorithms has been recognized previously.[51,65]

This paper is organized as follows: Section II describes general aspects of measure-preserving flows associated with non-Hamiltonian vector fields. We show how to formulate reversible and measure-preserving integrators using splitting methods. In Sec. III we give several examples of non-Hamiltonian measure-preserving vector fields, such as the Nosé-Hoover system, relevant to simulation of thermostatted systems. In Sec. IV we implement our general approach for the particular case of the generalized Gaussian moment thermostat (GGMT) discussed by Liu and Tuckerman.[66] Section V concludes with a brief discussion of error analysis for non-Hamiltonian integrators.

II. MEASURE-PRESERVING FLOWS AND REVERSIBLE INTEGRATORS: GENERAL ASPECTS

A. Volume-preserving flows with integral

We now consider some general aspects of volume-preserving (not necessarily Hamiltonian) flows. Let phase space coordinates be denoted as $\boldsymbol{x}=(x^1,x^2,\ldots,x^n)$. For the systems we consider, n is an even integer, and the coordinates partition naturally into two sets, coordinates $\boldsymbol{q}$ and momenta $\boldsymbol{p}$. This partitioning is by no means essential for our analysis.

Let the vector field $\bar{\boldsymbol{\xi}}$, with components $\dot{x}^i=\bar{\xi}^i$, be defined by

$$\bar{\xi}^i = A^{ij}(\boldsymbol{x})\frac{\partial H}{\partial x^j} \equiv A^{ij}(\boldsymbol{x})H_{,j}, \tag{2.1}$$

where $H=H(\boldsymbol{x})$ is an energy or Hamiltonian function of the phase space variables $\boldsymbol{x}$ and A^{ij} is an antisymmetric tensor ($n\times n$ matrix), $A^{ij}=-A^{ji}$. We adopt a summation convention for repeated indices i,j, etc.

From the antisymmetry of A, it follows that

$$\mathcal{L}_{\bar{\xi}}H \equiv \bar{\xi}^i\frac{\partial H}{\partial x^i} = A^{ij}H_{,i}H_{,j} = 0, \tag{2.2}$$

where $\mathcal{L}_{\bar{\xi}}$ is the Lie derivative along the flow induced by $\bar{\boldsymbol{\xi}}$. The energy function H is therefore conserved by any vector field $\bar{\boldsymbol{\xi}}$ of the form (2.1).[30,33]

Suppose that A also satisfies the condition

$$\frac{\partial A^{ij}}{\partial x^i} \equiv A^{ij}{}_{,i} = 0, \quad j=1,2,\ldots,n. \tag{2.3}$$

A tensor A with this property can be obtained from a completely antisymmetric third-rank tensor G^{ijk} as follows:[62]

$$A^{ij} = G^{ijk}{}_{,k} \tag{2.4}$$

since

$$A^{ij}{}_{,i} = G^{ijk}{}_{,ik} = 0 \tag{2.5}$$

by antisymmetry of G, and $F_{,ji}=F_{,ij}\equiv\partial^2F/\partial x^i\partial x^j$. Equation (2.3) implies that

$$\bar{\xi}^i_{,i} = A^{ij}{}_{,i}H_{,j} + A^{ij}H_{,ji} \tag{2.6a}$$

$$=0. \tag{2.6b}$$

The vector field $\bar{\boldsymbol{\xi}}$ is therefore divergenceless (with respect to the standard volume element), so that the volume element (volume form)

$$\omega = dx^1\wedge dx^2\wedge\cdots\wedge dx^n \tag{2.7}$$

is invariant under the flow associated with $\bar{\boldsymbol{\xi}}$. In the notation of differential forms,[7–9] the condition that the volume form ω be invariant under $\bar{\boldsymbol{\xi}}$ is

$$\mathcal{L}_{\bar{\xi}}\omega = (\mathrm{div}_\omega\,\bar{\boldsymbol{\xi}})\omega \tag{2.8a}$$

$$=\bar{\xi}^i_{,i}\omega \tag{2.8b}$$

$$=0, \tag{2.8c}$$

so that Eq. (2.6), in fact, shows that the so-called ω divergence of the vector field $\bar{\boldsymbol{\xi}}$ is zero.[7]

For a given antisymmetric tensor G^{ijk} we therefore obtain via Eqs. (2.1) and (2.4) a vector field conserving both the volume element ω and the energy function H. It is crucial to note that the volume element ω is conserved for *any* choice of H. Specific examples of tensors A and G are given in the next section.

A vector field of the form (2.1) is a special case of the general volume-preserving system discussed by McLachlan and Quispel,[62]

$$\bar{\xi}^i = S^{ik}{}_{,k}, \tag{2.9}$$

with the antisymmetric matrix S taken to be

$$S^{ik} = G^{ijk}H_{,j}. \tag{2.10}$$

At this point we have defined a vector field $\bar{\boldsymbol{\xi}}$ preserving both the volume element ω and the energy $H(\boldsymbol{x})$. The non-Hamiltonian flows of interest in the context of thermostatted systems do not, however, preserve the standard volume element (2.7); rather, they preserve a volume element $\bar{\omega}$ of the form

$$\bar{\omega} = \bar{\sigma}(\boldsymbol{x})\omega, \tag{2.11}$$

with $\bar{\sigma}(\boldsymbol{x})$ a strictly positive, smooth function of the phase space coordinates.[7] We therefore define the antisymmetric matrix

$$B^{ij} \equiv \bar{\sigma}(\boldsymbol{x})^{-1}A^{ij}. \tag{2.12}$$

Since the volume element ω is invariant under the flow associated with $\bar{\boldsymbol{\xi}}$, it follows immediately that the volume element $\bar{\omega}$ is invariant under the modified flow associated with the vector field $\boldsymbol{\xi}\equiv\bar{\boldsymbol{\xi}}/\bar{\sigma}$, where $\boldsymbol{\xi}$ has components

$$\xi^i = \frac{1}{\bar{\sigma}(\boldsymbol{x})}\bar{\xi}^i = B^{ij}H_{,j}. \tag{2.13}$$

In the notation of differential forms,[7] invariance of the volume form $\bar{\omega}$ under $\boldsymbol{\xi}$ is expressed by the condition

$$\mathcal{L}_{\xi}\bar{\omega} \equiv (\mathrm{div}_{\bar{\omega}}(\boldsymbol{\xi}))\bar{\omega} = 0, \tag{2.14}$$

or, as $\bar{\omega}$ is never zero, by the condition $\mathrm{div}_{\bar{\omega}}(\boldsymbol{\xi})=0$. The $\bar{\omega}$ divergence of $\boldsymbol{\xi}$ is[7]

$$\mathrm{div}_{\bar{\omega}}(\boldsymbol{\xi}) = \frac{1}{\bar{\sigma}(\boldsymbol{x})}\frac{\partial}{\partial x^i}[\bar{\sigma}(\boldsymbol{x})\xi^i]. \tag{2.15}$$

The ω and $\bar{\omega}$ divergence of a given vector field are not in general equal.

Using (2.14) and (2.15), it is straightforward to check whether the flow induced by a given vector field $\boldsymbol{\xi}'$, associated, for example, with a particular term in the decomposition of the Liouvillian, conserves a given volume form $\bar{\omega}=\bar{\sigma}(\boldsymbol{x})\omega$. Lengthy computations of Jacobians can thereby be avoided.[51,67]

Note that the requirement that $\bar{\sigma}$ be strictly positive means that the vector field $\boldsymbol{\xi}$ is everywhere well defined. Moreover, as B^{ij} is antisymmetric, it preserves any energy function $H(\boldsymbol{x})$. The system (2.13) is nevertheless *not* in general a Poisson system.[12] That is, the relation

$$B_{ij,k} + B_{jk,i} + B_{ki,j} = 0, \tag{2.16}$$

which is equivalent to the Jacobi identity, is not in general satisfied.[30,33] Here, B_{ij} is the matrix inverse to the matrix B^{ij} of (2.12) If (2.16) is not satisfied, then the equations of motion (2.13) are not simply Hamilton's equations expressed in terms of a noncanonical set of variables. We discuss the significance of this observation for the error analysis of measure-preserving integrators below.

B. Splitting and reversible measure-preserving integrators

We now show how the previous results can be used to define reversible integrators that automatically preserve the relevant volume form (invariant measure).

The energy function $H(\boldsymbol{x})$ can in general be decomposed into a sum of n_s terms,

$$H = \sum_{\alpha=1}^{n_s} H(\alpha), \tag{2.17}$$

where the decomposition (2.17) is of course not unique. The decomposition (2.17) induces a corresponding splitting of the vector field $\boldsymbol{\xi}$:

$$\boldsymbol{\xi} = \sum_{\alpha=1}^{n_s} \boldsymbol{\xi}(\alpha), \tag{2.18}$$

where

$$\xi(\alpha)^i = B^{ij}H(\alpha)_{,j} \tag{2.19}$$

and of the Lie derivative $\mathcal{L} \equiv \mathcal{L}_{\xi}$ $(=iL$, the usual Liouvillian[27]):

$$\mathcal{L} = \sum_{\alpha} \mathcal{L}_{\alpha}, \tag{2.20a}$$

$$\mathcal{L}_{\alpha} = \xi(\alpha)^i \frac{\partial}{\partial x^i}. \tag{2.20b}$$

It follows immediately from the results of the previous subsection that, for each term $\mathcal{L}_{\alpha}$ in the splitting of $\mathcal{L}$,

$$\mathcal{L}_{\alpha}\bar{\omega} = 0. \tag{2.21}$$

That is, the volume element $\bar{\omega}$ is invariant under *each* of the vector fields $\boldsymbol{\xi}(\alpha)$. [Each vector field $\boldsymbol{\xi}(\alpha)$ also preserves the corresponding energy term $H(\alpha)$.]

The splitting (2.20) can now be used in standard fashion[68–70] to define a reversible integrator for $\boldsymbol{\xi}$. For example, choosing some ordering for the n_s terms, the simplest (lowest-order) reversible integrator is obtained using a symmetric Trotter factorization,[1,16]

$$\exp[\mathcal{L}\Delta t] \simeq \exp\left[\mathcal{L}_1\frac{\Delta t}{2}\right]\cdots\exp\left[\mathcal{L}_{n_s-1}\frac{\Delta t}{2}\right]\exp[\mathcal{L}_{n_s}\Delta t] \times \exp\left[\mathcal{L}_{n_s-1}\frac{\Delta t}{2}\right]\cdots\exp\left[\mathcal{L}_1\frac{\Delta t}{2}\right] + \mathcal{O}(\tau^3). \tag{2.22}$$

As the volume element $\bar{\omega}$ is invariant under each of the vector fields $\boldsymbol{\xi}(\alpha)$, each factor in the product (2.22) preserves $\bar{\omega}$, so that the integrator (2.22), in addition to being reversible, also preserves the volume form $\bar{\omega}$. In all the cases that we shall consider below, it is possible to obtain an explicit expression for the action of each propagator $e^{\mathcal{L}_{\alpha}\Delta t}$ arising in our treatment. In the numerical studies reported below, a more accurate, higher-order Yoshida-Suzuki factorization is used.[71,72]

III. MEASURE-PRESERVING FLOWS: HAMILTONIAN AND NON-HAMILTONIAN EXAMPLES

We now discuss a number of examples of measure-preserving systems that can be written in the general form (2.13).

A. Hamiltonian system

Consider the case with $n=4$ phase space coordinates, $\boldsymbol{x}=\{x^1,x^2,x^3,x^4\}=\{q_1,p_1,q_2,p_2\}$, consisting of two coordinate-momentum pairs. Define the antisymmetric third-rank tensor G^{ijk} via

$$G^{ijk} = \tfrac{1}{2}x^{\lambda(i,j,k)}\mathrm{Sig}[i,j,k], \tag{3.1}$$

where $\mathrm{Sig}[i,j,k]$ is the signature of the triple (i,j,k) (equal to unity if i,j,k are distinct indices in lexical order, equal to the parity of the permutation required to bring the distinct indices into lexical order if they are not, and zero otherwise) and $\lambda(i,j,k)$ is the "unpaired" index when $i\neq j\neq k$. So, for example, $G^{133}=0$, $G^{123}=x^3=q_2$, $G^{132}=-x^3$, and so on. In this case, we have

$$A^{ij} = G^{ijk}{}_{,k} = B^{ij} = \begin{bmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{bmatrix}, \qquad (3.2)$$

the standard symplectic matrix.[3,11] The system (2.1) is then the usual Hamiltonian dynamics for Hamiltonian function $H(\boldsymbol{x})$.

Splitting the Hamiltonian function as in Eq. (2.17) then leads in the usual fashion to reversible symplectic integrators for the Hamiltonian flow.[16]

B. Nosé-Hoover system

For simplicity, we consider standard Nosé-Hoover dynamics for a single degree of freedom (q,p) coupled to thermostat variables (η,p_η),[44,45] $\boldsymbol{x}=(q,p,\eta,p_\eta)$. As noted by Sergi and Ferrario,[30] the Nosé-Hoover equations of motion,

$$\dot{q} = \frac{p}{m}, \qquad (3.3a)$$

$$\dot{p} = -\Phi_{,q} - \frac{pp_\eta}{Q}, \qquad (3.3b)$$

$$\dot{\eta} = \frac{p_\eta}{Q}, \qquad (3.3c)$$

$$\dot{p}_\eta = \frac{p^2}{m} - kT, \qquad (3.3d)$$

can be written in the form (2.13) with energy function

$$H(\boldsymbol{x}) = \frac{p^2}{2m} + \Phi(q) + kT\eta + \frac{p_\eta^2}{2Q} \qquad (3.4)$$

and antisymmetric matrix

$$B^{ij} = \begin{bmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & -p \\ 0 & 0 & 0 & 1 \\ 0 & p & -1 & 0 \end{bmatrix}. \qquad (3.5)$$

The Nosé-Hoover system (3.3) conserves the volume element

$$\bar{\omega} = e^{\eta} dq \wedge dp \wedge d\eta \wedge dp_\eta, \qquad (3.6)$$

so that

$$\mathrm{div}_{\bar{\omega}}\, \boldsymbol{\xi} = e^{-\eta} \frac{\partial}{\partial x^i}(e^{\eta}\xi^i) = 0, \qquad (3.7)$$

and the antisymmetric tensor $A^{ij}=e^{\eta}B^{ij}$ satisfies (2.3), that is, $A^{ij}{}_{,i}=0$. The associated antisymmetric third-rank tensor G^{ijk} is (listing nonzero independent elements only)

$$G^{123} = \frac{e^{\eta}}{2}, \quad G^{124} = p_\eta \frac{e^{\eta}}{2}, \quad G^{234} = pe^{\eta}. \qquad (3.8)$$

From (3.4), the invariant measure is

$$e^{\eta} = \exp\left[\frac{1}{kT}\left\{H - \frac{p^2}{2} - \Phi(q) - \frac{p_\eta^2}{2Q}\right\}\right]. \qquad (3.9)$$

It follows that conservation of both the invariant measure (3.6) and the energy function (3.4) is required to ensure that the phase space distribution function for the (p,q) variables is the appropriate canonical distribution characterized by temperature T.

The Lie derivative associated with the complete vector field (3.3) is

$$\mathcal{L} = \frac{p}{m}\partial_q - \left[\Phi_{,q} + \frac{pp_\eta}{Q}\right]\partial_p + \frac{p_\eta}{Q}\partial_\eta + \left[\frac{p^2}{m} - kT\right]\partial_{p_\eta}. \qquad (3.10)$$

Associated with the decomposition of the Hamiltonian, Eq. (2.17), where

$$H(1) = \Phi(q), \qquad (3.11a)$$

$$H(2) = \frac{p^2}{2m}, \qquad (3.11b)$$

$$H(3) = kT, \qquad (3.11c)$$

$$H(4) = \frac{p_\eta^2}{2Q}, \qquad (3.11d)$$

is a decomposition of the Lie derivative, Eq. (2.20), with

$$\mathcal{L}_1 = -\Phi_{,q}\partial_p, \qquad (3.12a)$$

$$\mathcal{L}_2 = \frac{p}{m}[\partial_q + p\partial_{p_\eta}], \qquad (3.12b)$$

$$\mathcal{L}_3 = -kT\partial_{p_\eta}, \qquad (3.12c)$$

$$\mathcal{L}_4 = \frac{p_\eta}{Q}[-p\partial_p + \partial_\eta]. \qquad (3.12d)$$

There are several important points to make concerning the splitting of the Lie derivative defined by Eq. (3.12). First, the splitting is a nontrivial decomposition of $\mathcal{L}$ and does not simply correspond to taking the four differential operators associated with each of the time derivatives in Eq. (3.3). Each Lie derivative in (3.12) preserves the volume element (3.6). That is, the $\bar{\omega}$ divergence of each vector field $\boldsymbol{\xi}(\alpha)$ is zero, $\mathrm{div}_{\bar{\omega}}\, \boldsymbol{\xi}(\alpha)=0$, $\alpha=1,2,3,4$. For example, the $\bar{\omega}$ divergence of the vector field $\boldsymbol{\xi}(4)$ is

$$\mathrm{div}_{\bar{\omega}}\, \boldsymbol{\xi}(4) = e^{-\eta}\left[\frac{\partial}{\partial p}\left(-\frac{e^{\eta}pp_\eta}{Q}\right) + \frac{\partial}{\partial\eta}\left(\frac{e^{\eta}p_\eta}{Q}\right)\right] = 0. \qquad (3.13)$$

Moreover, $\mathcal{L}_1$, $\mathcal{L}_2$, and $\mathcal{L}_3$ also conserve the standard volume element ω, so that $\mathrm{div}_\omega\, \boldsymbol{\xi}(\alpha)=0$, $\alpha=1,2,3$. For $\mathcal{L}_2$ and $\mathcal{L}_4$, each of which is the sum of more than one differential operator, the component operators commute with one another, so that the relevant factor (operator exponential) in Eq. (2.22) can be evaluated straightforwardly. Alternative splittings of $\mathcal{L}$ having the same property are

$$\mathcal{L}_1' = \frac{p}{m}\partial_q + \frac{p^2}{m}\partial_{p_\eta}, \tag{3.14a}$$

$$\mathcal{L}_2' = -\Phi_{,q}\partial_p - kT\partial_{p_\eta}, \tag{3.14b}$$

$$\mathcal{L}_4 = \frac{p_\eta}{Q}[-p\partial_p + \partial_\eta], \tag{3.14c}$$

or

$$\mathcal{L}_1'' = \frac{p}{m}\partial_q, \tag{3.15a}$$

$$\mathcal{L}_2'' = -\Phi_{,q}\partial_p, \tag{3.15b}$$

$$\mathcal{L}_3'' = \left[\frac{p^2}{2m} - kT\right]\partial_{p_\eta}, \tag{3.15c}$$

$$\mathcal{L}_4 = \frac{p_\eta}{Q}[-p\partial_p + \partial_\eta]. \tag{3.15d}$$

The decomposition (3.15) has already been used in a measure-preserving integrator for the Nosé-Hoover system by Ishida and Kidera.[67]

The above procedure is readily generalized to the case of N system coordinates coupled to a single Nosé-Hoover thermostat degree of freedom. In that case the invariant measure is $\bar{\omega}=e^{N\eta}\omega$ and the energy function is

$$H = \sum_{j=1}^{N}\frac{p_j^2}{2m_j} + \Phi(\boldsymbol{q}) + \frac{p_\eta^2}{2Q} + NkT\eta. \tag{3.16}$$

The energy function again naturally splits into four terms $H(\alpha)$, each associated with a measure-preserving generator $\mathcal{L}_\alpha$.

C. Nosé-Hoover chain

The considerations of Sec. III B can be generalized to treat the Nosé-Hoover chain thermostat.[73] We consider a single degree of freedom coupled to a "chain" of two thermostats, $\boldsymbol{x}=(q,p,\eta_1,p_{\eta_1},\eta_2,p_{\eta_2})$.

The equations of motion are

$$\dot{q} = \frac{p}{m}, \tag{3.17a}$$

$$\dot{p} = -\Phi_{,q} - \frac{pp_{\eta_1}}{Q_1}, \tag{3.17b}$$

$$\eta_1 = \frac{p_{\eta_1}}{Q_1}, \tag{3.17c}$$

$$\dot{p}_{\eta_1} = \frac{p^2}{m} - kT - \frac{p_{\eta_1}p_{\eta_2}}{Q_2}, \tag{3.17d}$$

$$\dot{\eta}_2 = \frac{p_{\eta_2}}{Q_2}, \tag{3.17e}$$

$$\dot{p}_{\eta_2} = \frac{p_{\eta_1}^2}{Q_1} - kT, \tag{3.17f}$$

with energy function

$$H(\boldsymbol{x}) = \frac{p^2}{2m} + \Phi(q) + \frac{p_{\eta_1}^2}{2Q_1} + kT\eta_1 + \frac{p_{\eta_2}^2}{2Q_2} + kT\eta_2 \tag{3.18}$$

and antisymmetric matrix

$$B^{ij} = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & -p & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & p & -1 & 0 & 0 & -p_{\eta_1} \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & p_{\eta_1} & -1 & 0 \end{bmatrix}. \tag{3.19}$$

The conserved volume element is

$$\bar{\omega} = e^{\eta_1+\eta_2}dq\wedge dp\wedge d\eta_1\wedge dp_{\eta_1}\wedge d\eta_2\wedge dp_{\eta_2} \tag{3.20}$$

and we have $A^{ij}{}_{,i}=0$, $A=e^{\eta_1+\eta_2}B$.

Decomposing Hamiltonian (3.18) into six terms results in the following measure-preserving splitting of the Lie derivative:

$$\mathcal{L}_1 = -\Phi_{,q}\partial_p, \tag{3.21a}$$

$$\mathcal{L}_2 = \frac{p}{m}[\partial_q + p\partial_{p_{\eta_1}}], \tag{3.21b}$$

$$\mathcal{L}_3 = -kT\partial_{p_{\eta_1}}, \tag{3.21c}$$

$$\mathcal{L}_4 = \frac{p_{\eta_1}}{Q_1}[-p\partial_p + \partial_{\eta_1} + p_{\eta_1}\partial_{p_{\eta_2}}], \tag{3.21d}$$

$$\mathcal{L}_5 = -kT\partial_{p_{\eta_2}}, \tag{3.21e}$$

$$\mathcal{L}_6 = \frac{p_{\eta_2}}{Q_2}[-p_{\eta_1}\partial_{p_{\eta_1}} + \partial_{\eta_2}]. \tag{3.21f}$$

D. Constant temperature and pressure dynamics

The constant T and P dynamics considered by Sergi and Ferrario is, for the simplest case of a single degree of freedom, of the form (2.13), with[30]

$$H = \frac{p^2}{2m} + \Phi(q,V) + \frac{p_\eta^2}{2M_\eta} + kT\eta + \frac{p_V^2}{2M_V} + P_{\text{ext}}V \tag{3.22}$$

and

$$B^{ij} = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & q/3V \\ -1 & 0 & 0 & -p & 0 & -p/3V \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & p & -1 & 0 & 0 & p_V \\ 0 & 0 & 0 & 0 & 0 & 1 \\ -q/3V & p/3V & 0 & -p_V & -1 & 0 \end{bmatrix}. \quad (3.23)$$

The system

$$\dot{q} = \frac{p}{m} + \frac{qp_V}{3VM_V}, \quad (3.24a)$$

$$\dot{p} = -\frac{pp_\eta}{M_\eta} - \frac{pp_V}{3VM_V} - \Phi_{,q}, \quad (3.24b)$$

$$\dot{\eta} = \frac{p_\eta}{M_\eta}, \quad (3.24c)$$

$$\dot{p}_\eta = \frac{p^2}{m} + \frac{p_V^2}{M_V} - kT, \quad (3.24d)$$

$$\dot{V} = \frac{p_V}{M_V}, \quad (3.24e)$$

$$\dot{p}_V = -\frac{p_\eta p_V}{M_\eta} - P_{\text{ext}} + \frac{p^2}{3mV} - \Phi_{,V} - \frac{q\Phi_{,q}}{3V} \quad (3.24f)$$

preserves the volume element

$$\bar{\omega} = e^{2\eta} dq \wedge dp \wedge d\eta \wedge dp_\eta \wedge dV \wedge dp_V, \quad (3.25)$$

and (2.3) is satisfied for $A = e^{2\eta}B$.

Decomposing the Hamiltonian (3.22) into six terms yields the associated splitting of the Lie derivative $\mathcal{L}$:

$$\mathcal{L}_1 = -\Phi_{,q}\left[\partial_p + \frac{q}{3V}\partial_{p_V}\right], \quad (3.26a)$$

$$\mathcal{L}_2 = \frac{p}{m}\left[\partial_q + p\partial_{p_\eta} + \frac{p}{3V}\partial_{p_V}\right], \quad (3.26b)$$

$$\mathcal{L}_3 = -kT\partial_{p_\eta}, \quad (3.26c)$$

$$\mathcal{L}_4 = \frac{p_\eta}{M_\eta}[-p\partial_p + \partial_\eta - p_V\partial_{p_V}], \quad (3.26d)$$

$$\mathcal{L}_5 = -(P_{\text{ext}} + \Phi_{,V})\partial_{p_V}, \quad (3.26e)$$

$$\mathcal{L}_6 = \frac{p_V}{M_V}\left[\frac{q}{3V}\partial_q - \frac{p}{3V}\partial_p + p_V\partial_{p_\eta} + \partial_V\right]. \quad (3.26f)$$

Each of the $\mathcal{L}_\alpha$ leaves $\bar{\omega}$ (3.25) invariant. Moreover, each $\mathcal{L}_\alpha$ except $\mathcal{L}_4$ also leaves the standard volume element ω unchanged. Each $\mathcal{L}_\alpha$ is a sum of commuting terms, except for $\mathcal{L}_6$. The Lie derivative $\mathcal{L}_6$ corresponds to the simultaneous differential equations

$$\dot{V} = \frac{p_V}{M_V}, \quad (3.27a)$$

$$\dot{p}_\eta = \frac{p_V^2}{M_V}, \quad (3.27b)$$

$$\dot{q} = \frac{p_V}{3M_V}\frac{q}{V}, \quad (3.27c)$$

$$\dot{p} = -\frac{p_V}{3M_V}\frac{p}{V}, \quad (3.27d)$$

which can be integrated directly to yield the propagation step

$$V(\Delta t) = V(0) + \Delta t\frac{p_V(0)}{M_V}, \quad (3.28a)$$

$$p_\eta(\Delta t) = p_\eta(0) + \Delta t\frac{p_V(0)^2}{M_V}, \quad (3.28b)$$

$$q(\Delta t) = q(0)\left[1 + \Delta t\frac{p_V(0)}{M_V V(0)}\right]^{+1/3}, \quad (3.28c)$$

$$p(\Delta t) = p(0)\left[1 + \Delta t\frac{p_V(0)}{M_V V(0)}\right]^{-1/3}. \quad (3.28d)$$

The set of six Lie operators (3.26) can then be used to formulate a reversible $\bar{\omega}$-preserving integrator for the constant T and P system (3.24).

E. GGMT dynamics

1. 1D particle, $M=2$ moments

The GGMT system[66] for a single degree of freedom with fourth moment controlled ($d=1$, $N=1$, $M=2$, in the notation of Ref. 66), with phase space coordinates $\boldsymbol{x} = (q, p, \eta_1, p_{\eta_1}, \eta_2, p_{\eta_2})$, has energy function identical to that for the Nosé-Hoover chain given previously, Eq. (3.18), and

$$B^{ij} = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & -p & 0 & -p^3/3m - pkT \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & p & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & p^2/m + kT \\ 0 & p^3/3m + pkT & 0 & 0 & -p^2/m - kT & 0 \end{bmatrix}. \quad (3.29)$$

The GGMT equations of motion are[66]

$$\dot{q} = \frac{p}{m}, \tag{3.30a}$$

$$\dot{p} = -\Phi_{,q} - \frac{pp_{\eta_1}}{Q_1} - \frac{p_{\eta_2}}{Q_2}\left[\frac{p^3}{3m} + pkT\right], \tag{3.30b}$$

$$\dot{\eta}_1 = \frac{p_{\eta_1}}{Q_1}, \tag{3.30c}$$

$$\dot{p}_{\eta_1} = \frac{p^2}{m} - kT, \tag{3.30d}$$

$$\dot{\eta}_2 = \frac{p_{\eta_2}}{Q_2}\left[\frac{p^2}{m} + kT\right], \tag{3.30e}$$

$$\dot{p}_{\eta_2} = \frac{p^4}{3m^2} - k^2T^2. \tag{3.30f}$$

The conserved volume element is

$$\bar{\omega} = e^{\eta_1+\eta_2} dq \wedge dp \wedge d\eta_1 \wedge dp_{\eta_1} \wedge d\eta_2 \wedge dp_{\eta_2}, \tag{3.31}$$

and again we verify that Eq. (2.3) is satisfied with $A = e^{\eta_1+\eta_2}B$.

Splitting the Hamiltonian (3.18) term by term yields the splitting of the Lie derivative,

$$\mathcal{L}_1 = -\Phi_{,q}\partial_p, \tag{3.32a}$$

$$\mathcal{L}_2 = \frac{p}{m}\left[\partial_q + p\partial_{p_{\eta_1}} + \left(\frac{p^3}{3m} + pkT\right)\partial_{p_{\eta_2}}\right], \tag{3.32b}$$

$$\mathcal{L}_3 = -kT\partial_{p_{\eta_1}}, \tag{3.32c}$$

$$\mathcal{L}_4 = \frac{p_{\eta_1}}{Q_1}[-p\partial_p + \partial_{\eta_1}], \tag{3.32d}$$

$$\mathcal{L}_5 = -kT\left(\frac{p^2}{m} + kT\right)\partial_{p_{\eta_2}}, \tag{3.32e}$$

$$\mathcal{L}_6 = \frac{p_{\eta_2}}{Q_2}\left[-\left(\frac{p^3}{3m} + pkT\right)\partial_p + \left(\frac{p^2}{m} + kT\right)\partial_{\eta_2}\right]. \tag{3.32f}$$

All operators in (3.32) preserve the volume element $\bar{\omega}$, while all operators except $\mathcal{L}_4$ and $\mathcal{L}_6$ conserve the standard volume element. All operators consist of mutually commuting terms except for $\mathcal{L}_6$, which requires further analysis.

The Lie derivative $\mathcal{L}_6$ corresponds to the simultaneous differential equations

$$\dot{p} = -\beta p(1 + \alpha p^2), \tag{3.33a}$$

$$\dot{\eta}_2 = +\beta(1 + 3\alpha p^2), \tag{3.33b}$$

with $\alpha \equiv 1/(3mkT)$ and $\beta \equiv p_{\eta_2}kT/Q_2$. These equations can be solved sequentially to yield the propagator

$$p(\Delta t) = p(0)[e^{2\beta\Delta t} - \alpha p(0)^2 + e^{2\beta\Delta t}\alpha p(0)^2]^{-1/2}, \tag{3.34a}$$

$$\eta_2(\Delta t) = \eta_2(0) - 2\beta\Delta t + \tfrac{3}{2}\ln[e^{2\beta\Delta t} - \alpha p(0)^2 + e^{2\beta\Delta t}\alpha p(0)^2]. \tag{3.34b}$$

It is straightforward to verify that the Jacobian for the propagation step (3.34) is

$$J = \frac{\partial(p(\Delta t), \eta_2(\Delta t))}{\partial(p(0), \eta_2(0))} = e^{-[\eta_2(\Delta t) - \eta_2(0)]} \tag{3.35}$$

so that the volume element $e^{\eta_2}dp \wedge d\eta_2$ is indeed conserved by the mapping $(p(0), \eta_2(0)) \mapsto (p(\Delta t), \eta_2(\Delta t))$ (all other coordinates remaining unchanged), as required by the invariance condition $\mathcal{L}_6\bar{\omega}=0$.

Finally, combining commuting operators from Eq. (3.32), we obtain a "minimal" splitting of $\mathcal{L}$ into four terms,

$$\mathcal{L}_A = -\Phi_{,q}\partial_p, \tag{3.36a}$$

$$\mathcal{L}_B = \frac{p}{m}\partial_q + G_1(p)\partial_{p_{\eta_1}} + G_2(p)\partial_{p_{\eta_2}}, \tag{3.36b}$$

$$\mathcal{L}_C = \frac{p_{\eta_1}}{Q_1}[-p\partial_p + \partial_{\eta_1}], \tag{3.36c}$$

$$\mathcal{L}_D = \frac{p_{\eta_2}}{Q_2}\left[-\left(\frac{p^3}{3m} + pkT\right)\partial_p + \left(\frac{p^2}{m} + kT\right)\partial_{\eta_2}\right], \tag{3.36d}$$

where $\mathcal{L}_A=\mathcal{L}_1$, $\mathcal{L}_B=\mathcal{L}_2+\mathcal{L}_3+\mathcal{L}_5$, $\mathcal{L}_C=\mathcal{L}_4$, and $\mathcal{L}_D=\mathcal{L}_6$, and

$$G_1(p) = \frac{p^2}{m} - kT, \tag{3.37a}$$

$$G_2(p) = \frac{p^4}{3m^2} - (kT)^2 \tag{3.37b}$$

in the notation of Liu and Tuckerman.[66] Each term in (3.36) has zero $\bar{\omega}$ divergence, with $\bar{\omega}$ given by Eq. (3.31), and can be exponentiated explicitly. [To exponentiate $\mathcal{L}_C$, we use the propagator (3.34) with $\alpha=0$.]

Note that $\mathcal{L}_A$ and $\mathcal{L}_B$ pertain to the system (plus extra terms), while $\mathcal{L}_C$ and $\mathcal{L}_D$ involve the thermostatting variables.

The splitting used by Liu and Tuckerman is defined in Eqs. C7 and C10 of Ref. [66]. By computing the $\bar{\omega}$ divergence, Eq. (2.15), it is easily verified that several of the individual Lie generators used in the factorization of Liu and Tuckerman do not conserve the invariant measure. For example, the $\bar{\omega}$ divergence of the vector field

$$\xi' = \frac{p_{\eta_1}}{Q_1}\partial_{\eta_1} + \left[\frac{p^2}{m} + kT\right]\frac{p_{\eta_2}}{Q_2}\partial_{\eta_2} \tag{3.38}$$

is

$$\mathrm{div}_{\bar{\omega}}(\xi') = \frac{p_{\eta_1}}{Q_1} + \left[\frac{p^2}{m} + kT\right]\frac{p_{\eta_2}}{Q_2}. \tag{3.39}$$

As individual terms in the reversible factorization used by Liu and Tuckerman do not conserve the appropriate volume element, we do not expect the overall propagator for one time step to preserve the invariant measure. In fact, lengthy calculations by Legoll and Monneau have shown analytically that the Liu-Tuckerman propagator does not conserve the invariant measure.[51]

2. 2 1D particles, M=2 *moments*

Now consider the more complicated case of two particles, mass m_1 and m_2, moving in one dimension (1D) with the fluctuations of the first two moments controlled ($d=1$, $N=2$ $M=2$). Phase space coordinates are $\boldsymbol{x}=(q_1,p_1,q_2,p_2,\eta_1,p_{\eta_1},\eta_2,p_{\eta_2})$. The conserved energy function is

$$H=\frac{p_1^2}{2m_1}+\frac{p_2^2}{2m_2}+\Phi(q_1,q_2)+\frac{p_{\eta_1}^2}{2Q_1}+\frac{p_{\eta_2}^2}{2Q_2}+2kT(\eta_2+\eta_2), \quad (3.40)$$

and the antisymmetric matrix B^{ij} is

$$B^{ij}=\begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & -p_1 & 0 & -p_1[kT+S/4] \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & -p_2 & 0 & -p_2[kT+S/4] \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & p_1 & 0 & p_2 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & [kT+S/2] \\ 0 & p_1[kT+S/4] & 0 & p_2[kT+S/4] & 0 & 0 & -[kT+S/2] & 0 \end{bmatrix}, \quad (3.41)$$

with

$$S=\frac{p_1^2}{m_1}+\frac{p_2^2}{m_2}, \quad (3.42)$$

leading to the following equations of motion (cf. Ref. [66]):

$$\dot{q}_1=\frac{p_1}{m_1}, \quad (3.43a)$$

$$\dot{p}_1=-\Phi_{,1}-p_1\frac{p_{\eta_1}}{Q_1}-\frac{p_{\eta_2}}{Q_2}p_1\left[kT+\frac{S}{4}\right], \quad (3.43b)$$

$$\dot{q}_2=\frac{p_2}{m_2}, \quad (3.43c)$$

$$\dot{p}_2=-\Phi_{,2}-p_2\frac{p_{\eta_1}}{Q_1}-\frac{p_{\eta_2}}{Q_2}p_2\left[kT+\frac{S}{4}\right], \quad (3.43d)$$

$$\dot{\eta}_1=\frac{p_{\eta_1}}{Q_1}, \quad (3.43e)$$

$$\dot{p}_{\eta_1}=S-2kT, \quad (3.43f)$$

$$\dot{\eta}_2=\frac{p_{\eta_2}}{Q_2}\left[kT+\frac{S}{2}\right], \quad (3.43g)$$

$$\dot{p}_{\eta_2}=\frac{S^2}{4}-2(kT)^2. \quad (3.43h)$$

The conserved volume element is

$$\bar{\omega}=e^{2(\eta_1+\eta_2)}dq_1\wedge dp_1\wedge dq_2\wedge dp_2\wedge d\eta_1\wedge dp_{\eta_1}\wedge d\eta_2\wedge dp_{\eta_2}, \quad (3.44)$$

and again we have $A^{ij}{}_{,i}=0$, with $A=e^{2(\eta_1+\eta_2)}B$.

IV. IMPLEMENTATION AND NUMERICAL RESULTS FOR THE GGMT SYSTEM

We now consider the numerical implementation of the general scheme for defining measure-preserving integrators in the case of the GGMT system. We shall treat the simplest case of a single particle in 1D with the first two even moments of p controlled ($d=1$, $N=1$, $M=2$).[66] This is the case examined by Legoll and Monneau.[51]

A. Reversible measure-preserving integrators by factorization

Reversible integrators accurate to a given order in time step τ are obtained by symmetric factorization of the exponential of the Lie derivative.[1,16] Each factor should correspond to a propagation step that can be implemented explicitly. As we have defined splittings of the Lie derivative wherein each term conserves the invariant measure, the resulting reversible integrators based on our splitting will automatically be measure preserving.

We define the basic second-order factorization

$$\tilde{\phi}_{JK}^{(2)}(\tau)\equiv\exp[(\tau/2)\mathcal{L}_J]\exp[\tau\mathcal{L}_K]\exp[(\tau/2)\mathcal{L}_J] \quad (4.1)$$

for a pair of Lie derivatives $\mathcal{L}_J$ and $\mathcal{L}_K$. A reversible measure-preserving second-order integrator for the splitting (3.36) is then

$$\tilde{\phi}^{(2)}_{ABCD}(\tau) = \tilde{\phi}^{(2)}_{CD}(\tau/2) * \tilde{\phi}^{(2)}_{AB}(\tau) * \tilde{\phi}^{(2)}_{CD}(\tau/2). \tag{4.2}$$

The step-by-step action of the propagator $\tilde{\phi}^{(2)}_{CD}(\tau)$ in (4.2) is

$$\eta_1 \to \eta_1 + \frac{p_{\eta_1}\tau}{2Q_1}, \tag{4.3a}$$

$$p \to p \exp\left[-\frac{\tau}{2}\frac{p_{\eta_1}}{Q_1}\right], \tag{4.3b}$$

$$\eta_2 \to \eta_2 - 2\beta\tau + \frac{3}{2}\ln[e^{2\beta\tau} - \alpha p^2 + e^{2\beta\tau}\alpha p^2], \tag{4.3c}$$

$$p \to p[e^{2\beta\tau} - \alpha p^2 + e^{2\beta\tau}\alpha p^2]^{-1/2}, \tag{4.3d}$$

$$\eta_1 \to \eta_1 + \frac{p_{\eta_1}\tau}{2Q_1}, \tag{4.3e}$$

$$p \to p \exp\left[-\frac{\tau}{2}\frac{p_{\eta_1}}{Q_1}\right], \tag{4.3f}$$

with $\beta = p_{\eta_2}kT/Q_2$ and $\alpha = 1/(3mkT)$, while that for $\tilde{\phi}^{(2)}_{AB}(\tau)$ is

$$p \to p - \Phi_{,q}(q)\frac{\tau}{2}, \tag{4.4a}$$

$$q \to q + \frac{\tau p}{m}, \tag{4.4b}$$

$$p_{\eta_1} \to p_{\eta_1} + \tau\left[\frac{p^2}{m} - kT\right], \tag{4.4c}$$

$$p_{\eta_2} \to p_{\eta_2} + \tau\left[\frac{p^4}{3m^2} - (kT)^2\right], \tag{4.4d}$$

$$p \to p - \Phi_{,q}(q)\frac{\tau}{2}. \tag{4.4e}$$

The fourth-order symmetric Yoshida-Suzuki[71,72] factorization is obtained by iteration of the second-order factorization,

$$\tilde{\phi}^{(4)}(\tau) = \tilde{\phi}^{(2)}(w_1\tau) * \tilde{\phi}^{(2)}(w_2\tau) * \tilde{\phi}^{(2)}(w_3\tau), \tag{4.5}$$

where the coefficients

$$w_1 = w_3 = \frac{1}{(2 - \sqrt[3]{2})}, \quad w_2 = 1 - 2w_1 \tag{4.6}$$

are determined by the requirement that the resulting integrator be accurate to the indicated order in τ. A fourth-order measure-preserving factorization for the GGMT system can then be written in terms of the second-order integrator (4.2) as

$$\tilde{\phi}^{(4)}_{ABCD}(\tau) = \tilde{\phi}^{(2)}_{ABCD}(w_1\tau) * \tilde{\phi}^{(2)}_{ABCD}(w_2\tau) * \tilde{\phi}^{(2)}_{ABCD}(w_3\tau). \tag{4.7}$$

Note that each complete propagation of the fourth-order iterated factorization (4.7) requires six evaluations of the system force associated with the Lie derivative $\mathcal{L}_A$. Alternative reversible factorizations can be given that require only two evaluations of the force per time step. An example similar in structure to the factorization of Liu and Tuckerman but based upon our splitting of the GGMT system (3.36) is

$$\tilde{\phi}_{\mu\text{-LT}}(\tau) = \tilde{\phi}^{(2)}_{CD}\left(w_1\frac{\tau}{2}\right) * \tilde{\phi}^{(2)}_{CD}\left(w_2\frac{\tau}{2}\right) * \tilde{\phi}^{(2)}_{CD}\left(w_1\frac{\tau}{2}\right) * \times \tilde{\phi}^{(2)}_{AB}(\tau) * \tilde{\phi}^{(2)}_{CD}\left(w_1\frac{\tau}{2}\right) * \times \tilde{\phi}^{(2)}_{CD}\left(w_2\frac{\tau}{2}\right) * \tilde{\phi}^{(2)}_{CD}\left(w_1\frac{\tau}{2}\right). \tag{4.8}$$

This factorization is by definition measure-preserving and necessitates only two force evaluations per time step. Nevertheless, comparison of reversible integrators (4.7) and (4.8) (unpublished) shows that the iterated factorization (4.7) gives superior performance (as judged by the conservation of the energy function) even when using a time step three times as long as that for (4.8) to make the number of force evaluations the same.

In Sec. IV B we discuss the numerical implementation of the factorization (4.7) and make a comparison with the results reported in Ref. [51].

B. Numerical results for symmetric measure-preserving integrator

The reversible measure-preserving propagator (4.7) for the GMMT system has been implemented for a single degree of freedom (q,p) coupled to two thermostat variables $(\eta_1, \eta_2, p_{\eta_1}, p_{\eta_2})$ ($d=1$, $N=1$, $M=2$). Following Legoll and Monneau, we take $\Phi(q)$ to be the double-well potential

$$\Phi(q) = D_0(a^2 - q^2)^2, \tag{4.9}$$

with parameter values $D_0=1$ and $a=1.5$, so that the barrier height is $D_0a^4=5.0625$. We take $kT=1$, $Q_1=1$, and $Q_2=8/3$.[66] Initial conditions are $q(0)=0$, $p(0)=1$, $\eta_1(0)=\eta_2(0)=0$, $p_{\eta_1}(0)=+1$, and $p_{\eta_2}(0)=-1$. The thermostatted particle is therefore initiated at the top of the barrier moving into the right well.

A very important indicator of the accuracy of an integrator for the type of non-Hamiltonian system considered here is the long-term behavior of the energy function $H(\mathbf{x})$ (initial value $H=6.25$) along the trajectory. (We note again that preservation of the invariant measure and conservation of the energy function are *both* necessary to generate the correct canonical phase space distribution for the thermostatted system.) In Fig. 1(a), we show the value of H along the trajectory with initial conditions given above calculated up to $t=2500$ with time step $h=0.003$. This value of the time step results in the same number of force evaluations per unit time as the two algorithms compared by Legoll and Monneau. Comparison of Fig. 1(a) with Fig. 7 of Ref. [51] (the axis scales are identical in both plots) shows that our integrator exhibits smaller fluctuations in the energy function H on short time scales than either of the algorithms of Ref. [51]. Several minor "shocks" of the type noted by Legoll and Monneau result in small changes in the value of H along the

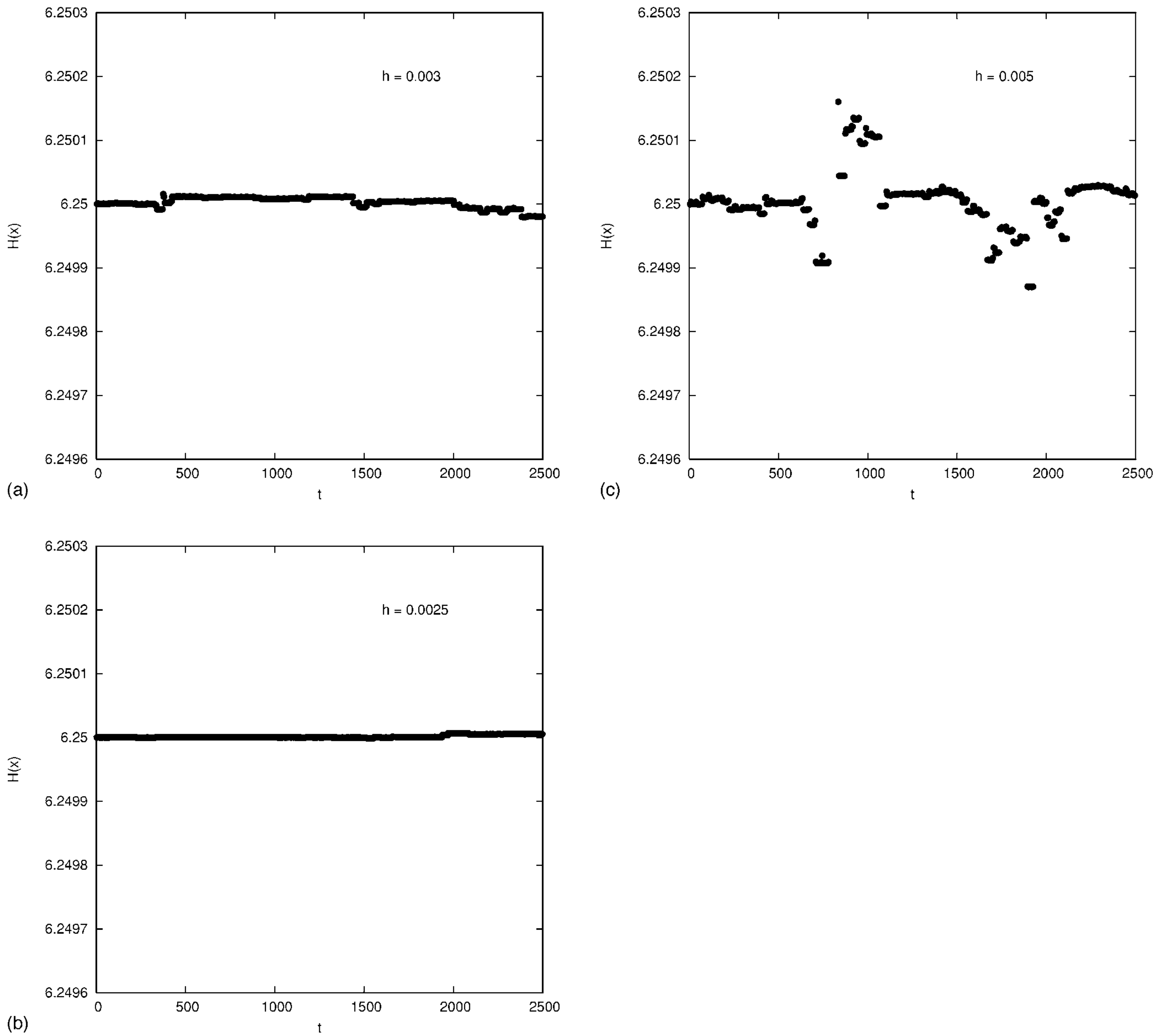

FIG. 1. Energy function H for the GGMT trajectory with initial conditions $q(0)=0$, $p(0)=1$, $\eta_1(0)=\eta_2(0)=0$, $p_{\eta_1}(0)=1$, and $p_{\eta_2}(0)=-1$, calculated using the reversible measure-preserving propagator, Eq. (4.7). (a) Time step $h=0.003$. (b) Time step $h=0.0025$. (c) Time step $h=0.005$.

trajectory. Reducing the integration time step slightly to $h=0.0025$ results in improved conservation of H up to $t=2500$ [Fig. 1(b)]. This value of the time step is to be compared with the smaller value $h=0.001$ used to obtain the results plotted in Fig. 7 of Ref. [51]. If the time step is increased to $h=0.005$ [Fig. 1(c)], we observe fluctuations in the energy of the same magnitude as those seen in Fig. 7 of Ref. 51; interestingly, although relatively large deviations of $H(\boldsymbol{x})$ from the initial value are seen at $t\simeq 800$ and $t\simeq 1800$, between these fluctuations the energy function returns to values close to the initial value.

At least for the trajectory considered, our integrator (4.7) is therefore found to yield, for comparable computational effort, considerably superior conservation of the energy function H. [The fact that a Yoshida-Suzuki factorization of the type (4.7) leads to improved energy conservation had, in fact, been anticipated by Legoll and Monneau[51]]. However, the dynamical origin of the shocks seen here and in previous work in the GGMT system and the time step dependence of the conservation of the energy function require further investigation.

One motivation for the use of explicitly measure-preserving integrators is the possibility that conservation of the invariant measure might assist in ergodic sampling of the thermostatted system phase space. Legoll and Monneau compared the distribution of the system coordinate obtained with their measure-preserving algorithm to that obtained with the Liu-Tuckerman integrator and found that the measure-preserving algorithm apparently led to more rapid convergence to a symmetric q distribution than the Liu-Tuckerman algorithm.[51]

In Fig. 2 we show the running time average $\langle q\rangle(t)$ of the system coordinate q over the time interval $0\leqslant t\leqslant 2500$ for the trajectory $[q(0)=0, p(0)=1, \eta_1(0)=0, p_{\eta_1}(0)=+1, \eta_2(0)=0, p_{\eta_2}(0)=-1]$, calculated using the integrator (4.7) with

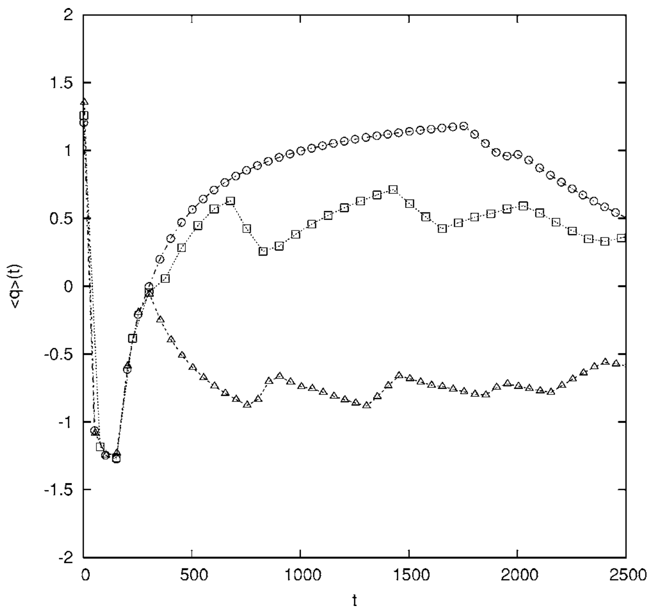

FIG. 2. Coordinate time average $\langle q\rangle(t)$ for the GGMT trajectory with initial conditions $q(0)=0$, $p(0)=1$, $\eta_1(0)=\eta_2(0)=0$, $p_{\eta_1}(0)=1$, and $p_{\eta_2}(0)=-1$, calculated using the reversible measure-preserving propagator, Eq. (4.7). Time step $h=0.0025$ (○), $h=0.003$ (□), and $h=0.005$ (△).

three different values of the time step, $h=0.0025$, 0.003, and 0.005, respectively. The converged value for an ergodic trajectory is $\langle q\rangle=0$. It is seen that the convergence of $\langle q\rangle$ to the equilibrium value has a somewhat erratic dependence on the value of the time step, and is overall less rapid than the convergence of the coordinate distribution function obtained by Legoll and Monneau.[51]

Figure 3 shows the convergence of the running time average of p^2 [Fig. 3(a)] and p^4 [Fig. 3(b)] to their canonical average values (1.0 and 3.0, respectively) for time step $h=0.0025$. For these functions of the momentum the convergence of the time averages to the canonical averages is comparable to that obtained by Legoll and Monneau.[51]

Additional insight into the phase space sampling properties of the measure-preserving integrator (4.7) is obtained by examining coordinate and momentum distribution functions associated with our trajectories. In Fig. 4(a) we show the cumulative coordinate probability distribution function $f(q)$ at $t=2500$ as a normalized histogram together with the exact canonical distribution (solid line) for the double-well potential (4.9). The time step used is $h=0.0025$. It can be seen that, even after 10^6 time steps, the cumulative coordinate distribution is by no means symmetric about $q=0$, exhibiting larger deviations from a symmetric distribution than the distribution obtained with the measure-preserving algorithm of Legoll and Monneau (Fig. 1 of Ref. 51). However, in Fig. 4(b), we show the cumulative coordinate distribution at $t=2500$ obtained using the larger time step $h=0.005$; this distribution is much more nearly symmetric than that obtained with the smaller time step $h=0.0025$. A similar result is found when examining the rate of approach of the cumulative distribution function to the canonical distribution. In Fig. 5 we plot $|f(q)-f_{\rm ex}(q)|$, the deviation of the cumulative coordinate probability distribution $f(q)$ at time t from the exact canonical distribution $f_{\rm ex}(q)$, as computed using a normalized histogram representation of each function with 22 bins. Comparison of Fig. 5(a) ($h=0.0025$) with Fig. 5(b) ($h=0.005$) shows that the trajectory with the larger time step exhibits more rapid convergence to the exact coordinate distribution.

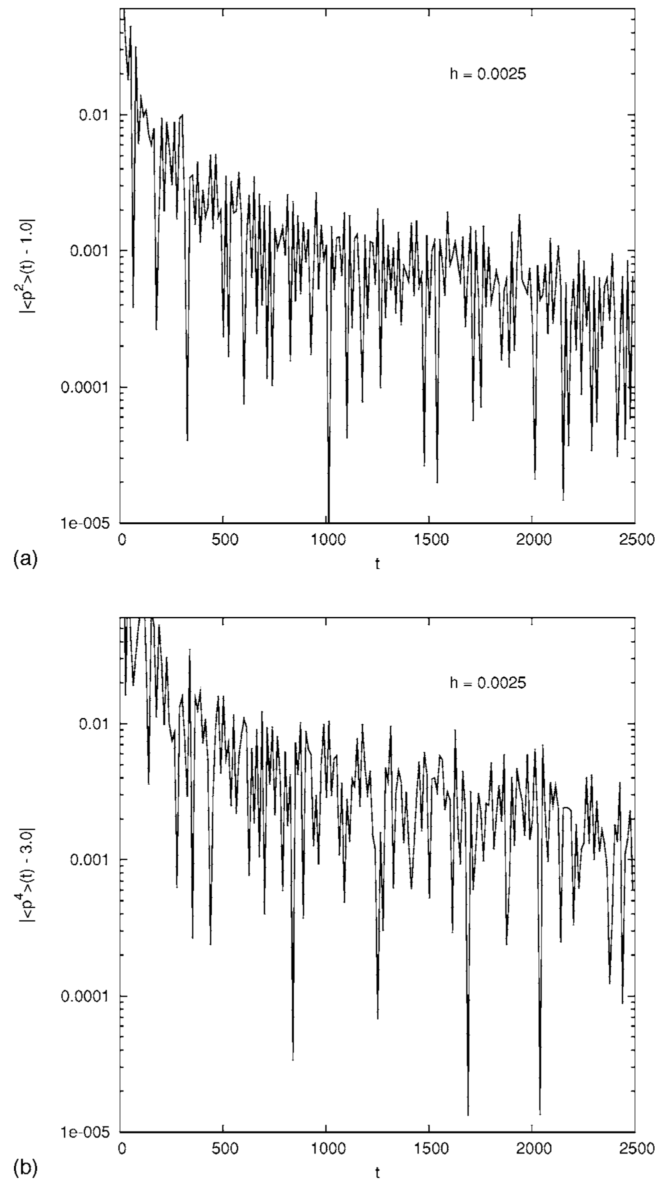

FIG. 3. (a) Difference $|\langle p^2\rangle(t)-1.0|$ between running time average of $\langle p^2\rangle(t)$ and canonical average value $\overline{p^2}=1.0$ for the GGMT trajectory with initial conditions $q(0)=0$, $p(0)=1$, $\eta_1(0)=\eta_2(0)=0$, $p_{\eta_1}(0)=1$, and $p_{\eta_2}(0)=-1$, calculated using the reversible measure-preserving propagator, Eq. (4.7), time step $h=0.0025$. (b) Difference $|\langle p^4\rangle(t)-3.0|$ between running time average $\langle p^4\rangle(t)$ and canonical average value $\overline{p^4}=3.0$.

As the trajectory with $h=0.0025$ exhibits better conservation of the energy function than either of the trajectories considered in Ref. 51, as well as conservation of invariant measure, we surmise that it is the most accurate. It therefore appears that the use of an accurate measure-preserving integrator does not necessarily lead to more ergodic trajectory behavior on the time scales considered here and in Ref. 51. It seems rather that the "noise" associated with relatively larger fluctuations in the energy function, as seen in the algorithm of Lagoll and Monneau or in the present case with a larger

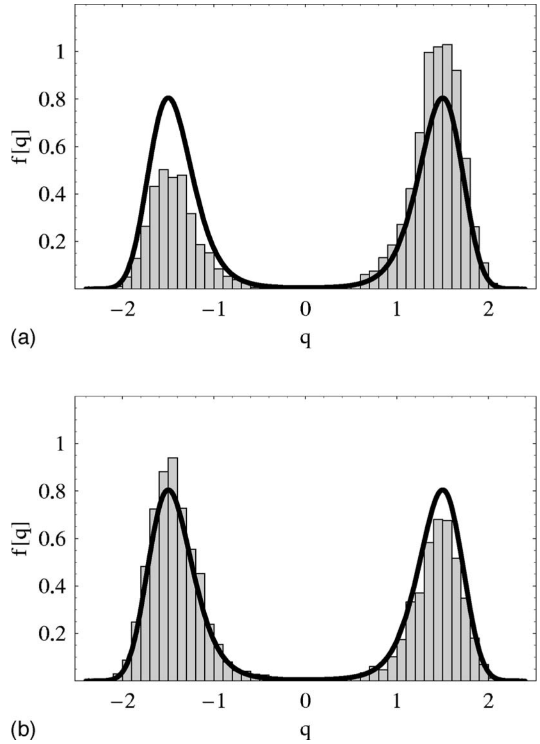

FIG. 4. Histogram of cumulative coordinate distribution function $f(q)$ at $t = 2500$ obtained from the GGMT trajectory with initial conditions $q(0)=0$, $p(0)=1$, $\eta_1(0)=\eta_2(0)=0$, $p_{\eta_1}(0)=1$, and $p_{\eta_2}(0)=-1$, calculated using the reversible measure-preserving propagator, Eq. (4.7). The solid line is the exact canonical distribution $f_{\rm ex}(q)$ for $kT=1$. (a) $h=0.0025$. (b) $h=0.005$.

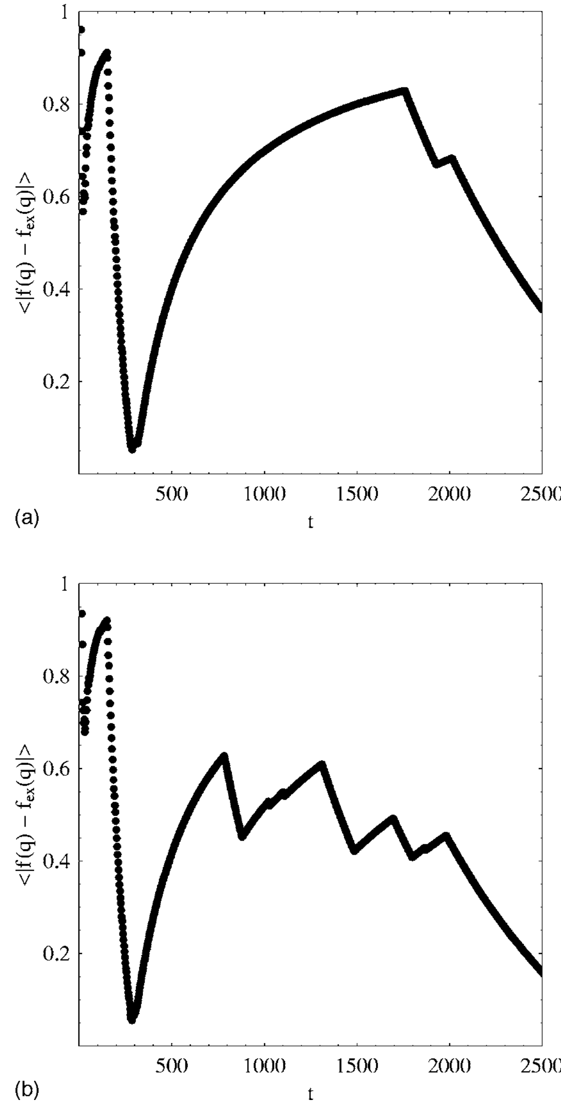

FIG. 5. Convergence of the cumulative coordinate distribution function $f(q)$ to the exact canonical distribution distribution $f_{\rm ex}(q)$ as a function of trajectory length. The quantity $|f(q)-f_{\rm ex}(q)|$ is plotted vs t for $0 \leq t \leq 2500$. (a) $h=0.0025$. (b) $h=0.005$.

time step, is instrumental in promoting more efficient exploration of the canonical coordinate distribution. This conclusion merits further investigation.

The cumulative momentum distribution is by contrast quite close to the appropriate canonical distribution (Fig. 6), and the rate of convergence to the exact result for our integrator (Fig. 7) is comparable to that obtained by Legoll and Monneau.

V. SUMMARY AND CONCLUSIONS

We have shown that the non-Poisson bracket structure noted by Sergi and Ferrario[30] and Sergi[33] for several common non-Hamiltonian thermostats and barostats can be exploited to obtain reversible integrators that conserve the relevant invariant measure automatically and exactly. We have implemented numerically a measure-preserving fourth-order Yoshida-Suzuki factorization algorithm for a symmetric double well coupled to the simplest generalized Gaussian moment thermostat[66] and have found that for comparable computational effort our integrator can conserve the energy function very accurately in comparison with other methods.[51] We have also investigated the convergence of the cumulative trajectory coordinate distribution to the exact (symmetric) distribution. The convergence obtained with our integrator is found to be time step dependent; in particular, more nearly ergodic behavior (symmetric average, distribution function) and more rapid convergence of the cumulative distribution to the exact result are obtained with integration time steps that

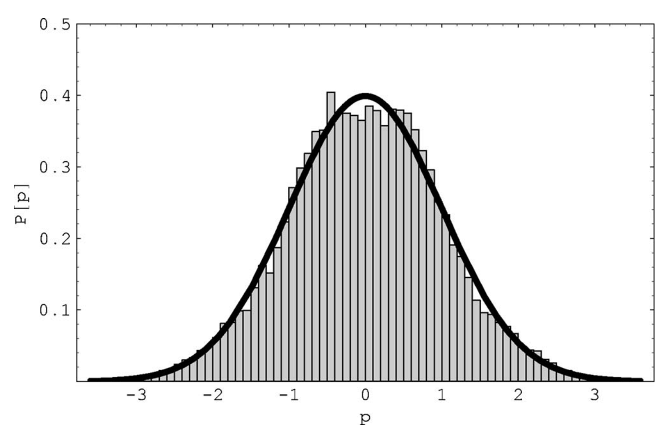

FIG. 6. Histogram of cumulative momentum distribution $f(p)$ at $t=2500$ obtained from the GGMT trajectory with initial conditions $q(0)=0$, $p(0)=1$, $\eta_1(0)=\eta_2(0)=0$, $p_{\eta_1}(0)=1$, and $p_{\eta_2}(0)=-1$, calculated using the reversible measure-preserving propagator, Eq. (4.7). The solid line is the exact canonical distribution for $kT=1$. Time step $h=0.0025$.

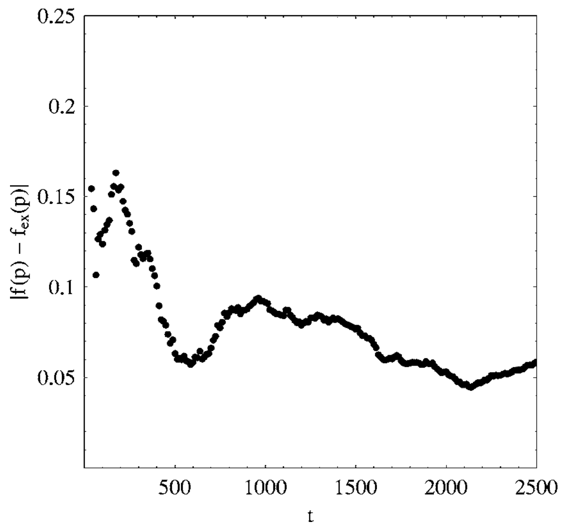

FIG. 7. Convergence of the cumulative momentum distribution function $f(p)$ to the exact canonical distribution distribution $f_{ex}(p)$ as a function of trajectory length. The quantity $|f(p)-f_{ex}(p)|$ is plotted vs t for $0 \leq t \leq 2500$. Time step $h=0.0025$.

lead to relatively larger fluctuations in the energy function. Further study of the properties of our measure-preserving integrators is certainly needed.

It is interesting to briefly consider the question of error analysis for measure-preserving integrators of the type considered here. In particular, why should the energy function $H(\boldsymbol{x})$ be so well conserved? An important general approach for symplectic integrators is the method of backward error analysis.[1] The error terms that arise when the exact propagator is factorized can be expressed in terms of vector fields obtained by taking repeated commutators of the vector fields characteristic of the particular splitting used. Since the commutator of two Hamiltonian vector fields is again a Hamiltonian vector field (as follows from the Jacobi identity), the net result is that the approximate propagation step can be interpreted as exact time evolution under a modified Hamiltonian that can, in principle, be calculated order by order.[1,14] Exact conservation of the modified Hamiltonian then restricts a given trajectory to the corresponding energy shell, and so limits the variation of the actual Hamiltonian over the trajectory.[1] (If an integrator conserves exactly both the symplectic form and the Hamiltonian, then it is exact up to a reparametrization of time.[74])

As already mentioned, the non-Hamiltonian systems considered here are not Poisson systems,[12] which means that the Jacobi identity is not satisfied [see Eq. (2.16)]. This in turn means that the commutator of two vector fields of the form (2.13) is *not* necessarily of the form (2.13) for some energy function H with the same matrix B, so that the usual backward error analysis apparently does not go through straightforwardly for these non-Hamiltonian systems. Note, however, that the commutator of two vector fields that conserve a given volume element $\bar{\omega}$ is a vector field that also conserves the volume element $\bar{\omega}$.

Okunbor has compared volume-preserving (Liouville) and symplectic versions of Runge-Kutta-Nyström integrators for two Hamiltonian systems, and has concluded that the both methods perform equally well.[60] Further work on the properties of measure-preserving but nonsymplectic integrators is clearly desirable.

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