DOI: 10.1478/C1C1002002

AAPP | Atti della Accademia Peloritana dei Pericolanti
Classe di Scienze Fisiche, Matematiche e Naturali
ISSN 1825-1242

Vol. LXXXVIII, No. 2, C1C1002002 (2010)

ALGORITHMS FOR NON-HAMILTONIAN DYNAMICS

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ABSTRACT. Statistical averages in a variety of many-body problems can be efficiently calculated through deterministic dynamics. When thermodynamical constraints (such as constant-temperature and/or constant-pressure) must be enforced, energy-conserving non-Hamiltonian dynamics becomes the method of choice. Integration of the resulting associated equations of motion requires advanced algorithms. For a number of cases, we show in detail how to derive both time-reversible algorithms and time-reversible measure-preserving integration methods.

1. Introduction

In this contribution we review techniques for formulating non-Hamiltonian equations of motion in Molecular Dynamics (MD) computer simulation. Recently, it has been proven that the same mathematical structure that is used to write down energy-conserving non-Hamiltonian equations [1] leads to elegant numerical integration algorithms [2] which preserve the measure in phase space while at the same time being time-reversal invariant.

Non-Hamiltonian equations of motion that conserve a generalized energy were introduced into the practice of MD by Nosé [3, 4]. Time-reversible algorithms suited to a multiple time-step integration were given by Tuckerman *et al*. [5]. A general mathematical structure to formulate energy-conserving equations in non-Hamiltonian mechanics was given in [1]. Such a structure naturally led to a correct formulation of the equilibrium statistical mechanics of non-Hamiltonian systems [6, 7]. Non-Hamiltonian statistical theory has also been formulated through the mathematical language of differential forms [8, 9]. Exploiting the mathematical framework given in [1], it is possible to augment time-reversible integration algorithms with the property of conservation of phase space measure [2].

The organization of the paper is the following. In Sec. **2** a quite general conceptual introduction to MD simulation is presented. The intrinsic arbitrariness involved in the definition of dynamical mechanisms or laws, underlying computation of statistical averages, is discussed in Sec. **3**. The relative freedom in formulating evolution laws is exploited in the introduction of non-Hamiltonian dynamics. A brief sketch of Hamiltonian dynamics and statistical theory is given in Sec. **4**, then in Sec. **5** a formulation of energy-conserving non-Hamiltonian dynamics by means of almost-Poisson brackets is introduced. The concept of approximate theoretical complexity is used to justify/discuss the use of non-Hamiltonian

evolution laws *in silico*, i.e., on the computer. Exploiting the symmetric Trotter break-up of the propagator, time-reversible algorithms for the numerical integration of almost-Poissonian phase space flows are introduced in Sec. **6**. A generalization of this approach, which also enforces the conservation of the integration measure in phase space, is expounded in Sec. **7**. Finally, conclusions and perspectives are given in Sec. **9**.

2. Molecular Dynamics

Molecular Dynamics is a computer simulation method which can be applied to a wide variety of problems in condensed matter, high energy physics and astrophysics [10, 11, 12, 13, 14] From a technical point of view, these applications of MD are based on three main ingredients. One needs to have a problem where averages are to be calculated over some set of initial conditions (chosen randomly according to a desired thermodynamical ensemble or probability distribution). Some form of potential function must be defined on the system's configuration space so that forces can be calculated. As a consequence, the configuration space of the system can be explored by means of a deterministic dynamical evolution in time, using such forces.

This brief discussion should make clear that MD time evolution defines a process which has an inherently stochastic aspect, associated with the random selection of initial conditions. However, since the dynamical evolution law is deterministic, one can classify MD as a deterministic stochastic (Markov) process [15]. (The Markovian character arises from the fact that time evolution in phase space only requires knowledge of one time-slice of the entire process.)

MD is a very general simulation method, which is not at all limited to particle systems, or systems with a countable number of degrees of freedom. On the contrary, MD is routinely used to perform calculations with fields. In condensed matter physics, the Car-Parrinello method introduces the MD associated with the expansion coefficients of electronic orbitals [16]. In high energy and nuclear physics, Lattice Gauge Theories allow one to calculate hadronic masses from first principles by means of the MD of the gauge field coefficients at lattice points [17].

The previous discussion and examples make clear that the only preconditions for being able to use MD as a computational tool are that one must have both a function (Hamiltonian) specifying the energy of the system in terms of generalized coordinates and a probabilistic theory to make connection with observables. MD can be employed when these rather loose preconditions are met, and this flexibility explains the wide-spread use of the method.

Nevertheless, it cannot be denied that condensed matter physics is the main area of physics exploiting MD calculations. (We exclude from present consideration the many applications to problems of chemical and biological interest [10, 12, 14].) It is within condensed matter physics, and the ever-green problem of finding a bridge between the macroscopical, statistical properties of a many-body system and its microscopic dynamics, that MD was born. From such a perspective, MD simulation implements *in silico* Boltzmann's dream of directly deriving statistical properties from microscopical dynamical laws. As a

matter of fact, macroscopic observables are given as time averages by

$$\overline{A} = \lim_{t\to\infty} \frac{1}{t} \int_0^t dt' A(t') \ , \tag{1}$$

and the connection to Gibbsian phase space (or ensemble) averages is made under the assumption of ergodicity

$$\overline{A} = \langle A \rangle \ . \tag{2}$$

But which dynamical law is obeyed by $A(t)$ in Eq. (1)? Fundamental microscopic theories solemnly state that it is Hamiltonian dynamics. However, in the next section we will argue that things are a little more complicated than that and that there is some freedom in the dynamical mechanism underlying the time average (1). Such freedom can be exploited to devise generalized simulation schemes such as those employing non-Hamiltonian (or, more precisely, almost-Poissonian) dynamics.

3. The arbitrariness of dynamical laws

In this section we show that, despite the fundamental character of microscopic Hamiltonian dynamics, as far as statistical properties are concerned, there is a certain freedom in choosing the microscopical dynamical laws.

The goal of many-body theory is to describe the time evolution of average values and statistical correlations between events or sets of events. The necessity to compute averages follows from the fact that, until the advent of the era of single-molecule experiments [18, 19], bulk experiments could only register (or measure) average properties and correlations. Naturally, in the course of providing an explanation of statistical properties, theory usually also provides a conceptual picture of the phenomena treated. The other important aim of theory is to provide some predictive power to scientists. To this end, some dynamical mechanism on the microscopical level must be formulated. Hence, the theory provides equations of motion or dynamical laws. But are these uniquely determined by the measured statistics? The answer to this question is, perhaps surprisingly, no.

We illustrate this conclusion by treating, as a paradigmatic example, the connection between deterministic and stochastic laws of motion.

Under a set of specific conditions, the Feynman-Kac formula [20, 21] provides a very powerful and general connection between deterministic and stochastic processes. It is known that there is a general mathematical connection between ordinary differential equations (ODE) and partial differential equations (PDE). For example, such a connection lies behind the relation between Hamilton's equations of motion and the Hamilton-Jacobi theory [22]. Now, given a PDE with positive Green's function, the Feynman-Kac formula states that the solution of the PDE can be found in terms of averages over suitable defined stochastic trajectories. In this way a mapping from the ODE to random motion is established: an ODE can be represented in terms of a PDE for the evolution of a surface transverse to an ensemble of trajectories; if such a PDE has a positive Green function (which can be interpreted as a correlation function), then the Feynman-Kac formula allows one to solve the problem in terms of stochastic process.

The situation can also be described as follows: suppose that deterministic motion provides a certain correlation function which is positive definite or can be made so by means

of a suitable change of variables. This correlation function may then be interpreted as the Green function of a PDE, and this latter can be mapped, *via* the Feynman-kac formula, onto stochastic laws of motion. Hence, *unless* one has experimental access to the trajectories, as far the correlation is concerned one mechanism of motion is equivalent to the other: this is an example of the arbitrariness or freedom in choosing the dynamical mechanism behind the statistical properties. Loosely speaking, such freedom in choosing the dynamics is one of the ideas leading to the change from Hamiltonian to non-Hamiltonian dynamics *in silico*.

This point is elucidated further in the next section.

4. Statistics and Hamiltonian dynamics

Hamiltonian dynamics is widely believed to provide a fundamental description (in the classical limit) of the microscopic dynamics of many-body systems. In order to make connection with macroscopic observable, a statistical theory over phase space must also be defined. Within such a theory, macroscopic fields are given by averages such as

$$A(\boldsymbol{r},t) = \int dx f(x) a(x,t;\boldsymbol{r}) \ , \tag{3}$$

where $x = (q,p)$ is the multimensional point in phase space, comprising both the macroscopic configurational coordinates q and momenta p, while $\mathbf{r}$ is a point in ordinary space. The quantity $f(x)$, called the distribution function, weights each microscopic phase space point and it is interpreted as a probability density. The variable $a(x,t;\boldsymbol{r})$ is a microscopic property of the system while $A(\boldsymbol{r},t)$ is the observable macroscopic field. Equation (3) realizes the fundamental bridge between micro and macro scales in physics and it the core of statistical mechanics. Hamiltonian dynamics provides a prescription for calculating the time evolution of the microscopic variable $a(x,t;\boldsymbol{r})$ *via* the equation of motion:

$$\dot{a}(x,t;\boldsymbol{r}) = \mathcal{B}^{\mathrm{s}}_{ij} \left(\nabla_j H\right) \nabla_i a(x,t;\boldsymbol{r}) \tag{4}$$

where $\nabla_i = \partial/\partial x_i$ and

$$\boldsymbol{\mathcal{B}}^{\mathrm{s}} = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \tag{5}$$

is the standard symplectic matrix.

The right hand side of Eq. (4) introduces the Poisson bracket [23] in matrix form:

$$\{a,b\} = (\nabla_i a)\mathcal{B}_{ij}(\nabla_j b) \ . \tag{6}$$

The Poisson bracket obeys the properties [23]

$$\{a,b\} = -\{b,a\} \ , \tag{7a}$$

$$\{a+b,c\} = \{a,c\} + \{b,c\} \ , \tag{7b}$$

$$\{\mathrm{const} \times a, b\} = \mathrm{const} \times \{a,b\} \ , \tag{7c}$$

$$\{ab,c\} = a\{b,c\} + \{a,c\} \ . \tag{7d}$$

The Jacobi relation also holds [23]:

$$\{\{a,b\},c\} + \{\{c,a\},b\} + \{\{b,c\},a\} = 0 \ , \tag{8}$$

where a, b, c are arbitrary phase space functions. The validity of Eqs. (7a-7d) together with the Jacobi relation (8) means that the algebra of Poisson brackets is a Lie algebra [24, 23]. An important consequence of the Lie algebra property is that algebraic relations defined by Poisson brackets are left invariant under evolution in time. To express this result we introduce the Liouville operator L,

$$L = \mathcal{B}_{ij}(\nabla_j H)\nabla_i \ . \tag{9}$$

Hence, the time-translation invariance of the algebra of Poisson brackets can be expressed mathematically by

$$\exp[tL]\{a, b\} = \{a(t), b(t)\} \ . \tag{10}$$

The original formulation of MD was based on Hamiltonian dynamics. Assuming ergodicity, phase space averages are calculated as time averages over Hamiltonian trajectories. However, within a Hamiltonian theory, thermodynamical constraints, such as constant temperature and/or constant pressure, can be implemented only through the simulation of the system of interest coupled to a many-particle *bath*, and all the degrees of freedom, system plus bath, must be evolved in time. For such a reason, the Hamiltonian implementation of thermodynamical baths on the computer is highly inefficient, if indeed possible at all. One solution to this problem is provide by non-Hamiltonian dynamics [11, 25, 26, 27, 1, 6, 7, 8, 9, 2, 28].

5. Energy-conserving Non-Hamiltonian dynamics

Exploiting the unobservability of trajectories for bulk measurements, one can imagine changing the dynamical laws in order to obtain the statistics of the desired thermodynamical ensemble without the infinite bath. In practice, this can be achieved by means of a particular form of non-Hamiltonian dynamics, formulated in terms of an almost-Poisson bracket [29].

In place of the symplectic matrix $\boldsymbol{\mathcal{B}}^{\mathrm{s}}$, let us introduce a general antisymmetric tensor field

$$\boldsymbol{\mathcal{B}}(\xi) = -\boldsymbol{\mathcal{B}}^T(\xi) \ . \tag{11}$$

where $\xi = (x, \zeta)$ is a point in an enlarged phase space. Equipped with such an antisymmetric tensor field, we can also define a generalized bracket

$$\{a, b\}_{\boldsymbol{\mathcal{B}}} = (\nabla_i^{\xi} a)\mathcal{B}_{ij}(\nabla_j^{\xi} b) \ . \tag{12}$$

The generalized bracket defined in Eq. (12) can be classified as an "almost-Poisson" bracket since it satisfies all the properties (7a-7d) satisfied by the Poisson bracket with the exception of the Jacobi relation (8), which is no longer valid in general [30, 29]. In the cases in which the generalized bracket also satisfies the Jacobi relation, phase space is classified as a Poissonian manifold [23]. In such cases, the dynamics must be regarded as Hamiltonian since, because of the Darboux theorem, a non-canonical transformation of coordinates can (at least locally) put the tensor field $\boldsymbol{\mathcal{B}}$ in symplectic form $\boldsymbol{\mathcal{B}}^{\mathrm{s}}$ [31]. An almost-Poisson bracket defines a form of energy-conserving non-Hamiltonian dynamics since, because of its antisymmetry, the generalized Hamiltonian, $\tilde{H}$, is exactly conserved

$$\{\tilde{H}, \tilde{H}\}_{\boldsymbol{\mathcal{B}}} = 0 \ . \tag{13}$$

A non-Hamiltonian energy-conserving (or almost-Poisson) Liouville operator can be defined as [1, 6]

$$\tilde{L} = \mathcal{B}_{ij}(\nabla_j^\xi \tilde{H}(\xi))\nabla_i^\xi \ . \tag{14}$$

The failure of the Jacobi relation implies the absence of time-translation invariance in the algebra of almost-Poisson brackets

$$\exp[(t-t_0)\tilde{L}]\{\{a(t_0), b(t_0)\}_{\boldsymbol{\mathcal{B}}} \neq \{\{a(t), b(t)\}_{\boldsymbol{\mathcal{B}}} \ . \tag{15}$$

Statistical mechanics on an almost-Poisson manifold can be formulated exactly as for the Hamiltonian or Poisson manifold case [1, 6]. Now, however, there are cases (which are those of interest in MD) in which the phase space compressibility

$$\kappa = (\nabla_i^\xi)\mathcal{B}_{ij}(\nabla_j^\xi \tilde{H}) \tag{16}$$

is non-vanishing. At equilibrium, $\tilde{L}f(\xi) = 0$, and the invariant phase space measure is

$$d\mu = \exp[-w]d\xi \ , \tag{17}$$

where $dw/dt = \kappa$ [11, 26, 27, 1, 6].

The utility of almost-Poisson dynamics arises because it has been found that the tensor field $\boldsymbol{\mathcal{B}}(\xi)$ can be engineered so that integration over the additional variables ζ produces the desired thermodynamical ensemble for the physical system of interest. In this way, the use of few additional degrees of freedom, ζ, together with non-Hamiltonian dynamics is able to produce the desired average behaviour in a computable fashion [11, 12, 13, 14].

5.1. Approximate theoretical complexity. From a certain point of view, the substitution of non-Hamiltonian or almost-Poisson evolution for Hamiltonian dynamics transcends the mere idea of the arbitrariness of microscopic dynamical laws. There is something more. As discussed previously, by means of this substitution one renounces the time-invariance of the dynamical algebra. In statistical terms, such invariance breaking is mirrored in the properties of the correlation functions of an almost-Poissonian theory: some useful relations which are invoked in the Hamiltonian case, and are involved in the definitions of transport coefficients through Green-Kubo formulas, are no longer necessarily valid. How, then, can almost-Poissonian dynamics can be justified? In our view, a practical justification can be found by exploiting an analogy with *approximate computational complexity*, an approach used in numerical algebra (see [32] and references therein).

Within approximate computational complexity, a non-computable problem $\mathcal{P}$, characterized by a certain mathematical structure described by constraints $\sigma_1 = 0,\ \sigma_2 = 0,\ ...$, is mapped onto another problem $\mathcal{P}'$ with a modified structure. The structure of $\mathcal{P}'$ is characterized by the *relaxation* of at least one constraint of $\mathcal{P}$, for example $\sigma_1 \neq 0$. The augmented freedom in the structure of $\mathcal{P}'$ is accompanied by the appearance of some new numerical parameters, $k_1, k_2, ...$, effectively controlling the new degrees of freedom. For example, one can treat σ_1 as a dynamical variable, with a fictitious inertial parameter m_f and initial conditions $\sigma_1(t = t_0) = 0$. The mapping $\mathcal{P} \to \mathcal{P}'$ can be performed so that $\mathcal{P}'$ becomes computable. Moreover, for some specific choice of the ks (which effectively *restrain* the possible values taken by the relaxed constraints) the solution of problem $\mathcal{P}'$ approximates that of $\mathcal{P}$. This is so because one assumes (or proves) that the solution of $\mathcal{P}$ exists, although it is not readily calculable, and the calculations of $\mathcal{P}'$ are performed for

values of the ks chosen such that all the constraints of the original problem $\mathcal{P}$ are close to being satisfied.

By analogy, one can see that non-Hamiltonian theory implements the same idea as approximate computational complexity. However, in the case of non-Hamiltonian simulation schemes it is not simply the mathematical structure of the calculation which is changed: the relaxation of the Jacobi relation modifies the theory itself. It is as if, in this case, we have an instance of what might be called approximate *theoretical* complexity. The key point is that, while the dynamics of phase space points (x, ζ) in extended phase space has no immediate physical significance, the statistical average over the ζ degrees of freedom can provide an effective evolution of the physical degrees of freedom, x, with the desired statistical properties, without the need to simulate an infinite number of auxillary variables ζ. In this way, an original Hamiltonian problem which is not calculable is mapped to a non-Hamiltonian problem with a finite number of degrees of freedom. For suitable choices of the inertial parameter associated with the ζs, the calculated averaged dynamics of the x *is* physically meaningful.

6. Time-reversible algorithms

Having defined and justified non-Hamiltonian dynamics, one is then confronted with the practical issue of finding suitable integration algorithms for non-Hamiltonian equations of motion, which are usually more complicated than Hamiltonian ones. Since one is already renouncing some basic theoretical properties (such as time-invariance of the bracket algebra) it becomes even more desirable that the numerical algorithm does not break other symmetries of the problem. The main one is the time-reversal invariance of the phase space trajectory.

Actually, it turns out to be very easy to devise time-reversible algorithms: one simply has to use a symmetric Trotter decomposition of the propagator and the rest follows easily [13]. As a matter of fact, the Liouville operator can usually be split into a sum of terms

$$\tilde{L} = B_{ij} \frac{\partial \tilde{H}}{\partial \xi_j} \frac{\partial}{\partial \xi_i} = \sum_{k=1}^{n} \tilde{L}_k \ . \tag{18}$$

Hence, for a small time step, τ, one can introduce a time-reversible Trotter decomposition of the propagator:

$$e^{t\tilde{L}} = \left[\sum_{k=2}^{n} e^{(\tau/2) L_{2n-k-1}} \right] e^{\tau L_1} \left[\sum_{k=2}^{n} e^{(\tau/2) L_k} \right] + \mathcal{O}(\tau^3) \ . \tag{19}$$

The numerical algorithm is then found by unfolding the single time step action of the factorized propagator

$$x(t+\tau) \approx \left[\sum_{k=2}^{n} e^{(\tau/2) L_{2n-k-1}} \right] e^{\tau L_1} \left[\sum_{k=2}^{n} e^{(\tau/2) L_k} \right] x(t) \ . \tag{20}$$

To this end, the following fundamental operator identities can be used

$$\exp\left[c\frac{\partial}{\partial x}\right] f(x) = f(x+c)\ , \tag{21a}$$

$$\exp\left[cx\frac{\partial}{\partial x}\right] f(x) = f(x\exp(c)) \tag{21b}$$

$$\exp\left[\tau\Big(-\frac{p_\eta}{m_\eta}p + F(x)\Big)\frac{\partial}{\partial p}\right] p = p\exp\left[-\tau\frac{p_\eta}{m_\eta}\right] + \tau F(x)\exp\left[-\frac{\tau}{2}\frac{p_\eta}{m_\eta}\right]\sinh\left[-\frac{\tau}{2}\frac{p_\eta}{m_\eta}\right]\ . \tag{21c}$$

In order to illustrate how a time-reversible algorithm is built in practice, we tackle as an example the formulation of deterministic thermostats by means of non-Hamiltonian dynamics. In general, deterministic thermostats sample the canonical distribution function of a system S coupled to a deterministic bath B, represented by a few additional degrees of freedom. The use of such thermostats is really the culmination of a journey from Boltzmann to Gibbs and then back to Boltzmann. There are many such thermostats: Nosé-Hoover, Bulgac-Kusnezov, Nosé-Hoover Chains, and so on [12, 13, 14]. In the next section, we consider the dynamics of the Nosé-Hoover chain (NHC) [33] and illustrate the derivation of a time-reversible integration algorithm.

6.1. Time-reversible integration of NHC dynamics. In the interests of simplicity, we consider here a NHC with just one additional thermostat variable. In this case the phase space point is $\xi = (q, \eta_1, \eta_2, p, p_{\eta_1}, p_{\eta_2})$i, where q and p are the phase space coordinates of the physical system, η_1 and p_{η_1} the phase space coordinates of the first Nosé-Hoover thermostat, and η_2 and p_{η_2} those of the second Nosé-Hoover thermostat. The total NHC Hamiltonian is

$$H^{\mathrm{NHC}} = \frac{p^2}{2m} + \frac{p_{\eta_1}^2}{2m_{\eta_1}} + \frac{p_{\eta_2}^2}{2m_{\eta_2}} + \Phi(q) + Nk_BT(\eta_1+\eta_2)\ , \tag{22}$$

where N is the number of q coordinates, m_{η_1} and m_{η_2} are the inertial parameters of the thermostat coordinates, T the desired thermodynamical temperature, k_B is Boltzmann's constant, and $\Phi(q)$ is the physical potential energy. The NHC antisymmetric tensor is

$$\boldsymbol{\mathcal{B}}^{\mathrm{NHC}} = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 & -p & 0 \\ 0 & -1 & 0 & p & 0 & -p_{\eta_1} \\ 0 & 0 & -1 & 0 & p_{\eta_1} & 0 \end{bmatrix}\ . \tag{23}$$

Using the tensor (23) we can write the NHC equations of motion in matrix form

$$\dot{\xi}_i = \mathcal{B}_{ij}^{\mathrm{NHC}}\frac{\partial H^{\mathrm{NHC}}}{\partial \xi_j}\ . \tag{24}$$

Written explicitly they read

$$\dot{q} = \frac{p}{m} \,, \tag{25a}$$

$$\dot{p} = -\frac{\partial \Phi}{\partial q} - p\frac{p_{\eta_1}}{m_{\eta_1}} \,, \tag{25b}$$

$$\dot{\eta}_1 = \frac{p_{\eta_1}}{m_{\eta_1}} \,, \tag{25c}$$

$$\dot{p}_{\eta_1} = \frac{p^2}{m} - Nk_BT - p_{\eta_1}\frac{p_{\eta_2}}{m_{\eta_2}} \,, \tag{25d}$$

$$\dot{\eta}_2 = \frac{p_{\eta_2}}{m_{\eta_2}} \,, \tag{25e}$$

$$\dot{p}_{\eta_2} = \frac{p_{\eta_1}^2}{m_{\eta_1}} - Nk_BT \,, \tag{25f}$$

where we have used the forces

$$F(q) = -\frac{\partial \Phi}{\partial q} \,, \tag{26a}$$

$$F(p) = \frac{p^2}{m} - Nk_BT \,, \tag{26b}$$

$$F(p_{\eta_1}) = \frac{p_{\eta_1}^2}{m_{\eta_1}} - Nk_BT \,. \tag{26c}$$

We associate the Liouville operator L^{NHC} with the evolution equations Eqs. (25a)–(25f), and split it as $L^{\mathrm{NHC}} = \sum_{k=1}^{5} L_k^{\mathrm{NHC}}$, where the single terms are

$$L_1^{\mathrm{NHC}} = \tau \left(\frac{p}{m}\frac{\partial}{\partial q} + \frac{p_{\eta_1}}{m_{\eta_1}}\frac{\partial}{\partial \eta_1} + \frac{p_{\eta_2}}{m_{\eta_2}}\frac{\partial}{\partial \eta_2} \right) \,, \tag{27a}$$

$$L_2^{\mathrm{NHC}} = \frac{\tau}{2} F(x)\frac{\partial}{\partial p} \,, \tag{27b}$$

$$L_3^{\mathrm{NHC}} = -\frac{\tau}{2}\frac{p_{\eta_1}}{m_{\eta_1}}\frac{\partial}{\partial p} \,, \tag{27c}$$

$$L_4^{\mathrm{NHC}} = \frac{\tau}{2}\left(-\frac{p_{\eta_2}}{m_{\eta_2}} p_{\eta_1} + F(p) \right)\frac{\partial}{\partial p_{\eta_1}} \,, \tag{27d}$$

$$L_5^{\mathrm{NHC}} = \frac{\tau}{2} F(p_{\eta_1})\frac{\partial}{\partial p_{\eta_2}} \,. \tag{27e}$$

A propagator

$$U_i^{\mathrm{NHC}}(\tau) = \exp[\tau L_i^{\mathrm{NHC}}] \qquad i = 1, ..., 5 \tag{28}$$

is associated with each L_i^{NHC}. The NHC propagator

$$U^{\mathrm{NHC}}(\tau)\xi \quad = \quad \exp\left[\sum_{i=1}^{5} \tau L_i^{\mathrm{NHC}} \right] \xi = \xi(\tau) \tag{29}$$

can be decomposed using the symmetric Trotter formula as

$$U^{\mathrm{NHC}}(\tau) \approx U_5^{\mathrm{NHC}}\left(\frac{\tau}{2}\right) U_4^{\mathrm{NHC}}\left(\frac{\tau}{2}\right) U_3^{\mathrm{NHC}}\left(\frac{\tau}{2}\right) U_2^{\mathrm{NHC}}\left(\frac{\tau}{2}\right) \times U_1^{\mathrm{NHC}}(\tau) U_2^{\mathrm{NHC}}\left(\frac{\tau}{2}\right) U_3^{\mathrm{NHC}}\left(\frac{\tau}{2}\right) U_4^{\mathrm{NHC}}\left(\frac{\tau}{2}\right) U_5^{\mathrm{NHC}}\left(\frac{\tau}{2}\right) + \mathcal{O}(\tau^3) \,. \quad (30)$$

Because of the factorization, one is able to evaluate analytically the action of each U_i^{NHC} on the phase space point. The resulting time-reverisible algorithm can be written in a pseudo-code form:

$$U_5\left(\frac{\tau}{2}\right) : \left\{ p_{\eta_2} \to p_{\eta_2} + \frac{\tau}{2} F(p_{\eta_1}) \right. \quad (31a)$$

$$U_4\left(\frac{\tau}{2}\right) : \left\{ p_{\eta_1} \to p_{\eta_1} e^{\frac{\tau}{4}\frac{p_{\eta_2}}{m_{\eta_2}}} + \frac{\tau}{4} \frac{\sinh\left(\frac{\tau}{4}\frac{p_{\eta_2}}{m_{\eta_2}}\right)}{\frac{\tau}{4}\frac{p_{\eta_2}}{m_{\eta_2}}} \right. \quad (31b)$$

$$U_3\left(\frac{\tau}{2}\right) : \left\{ p \to p e^{\frac{\tau}{2}\frac{p_{\eta_1}}{m_{\eta_1}}} \right. \quad (31c)$$

$$U_2\left(\frac{\tau}{2}\right) : \left\{ p \to p + \frac{\tau}{2} F(q) \right. \quad (31d)$$

$$U_1(\tau) : \left\{ q \to q + \tau \frac{p}{m} \; \eta_1 \to \eta_1 + \tau \frac{p_{\eta_1}}{m_{\eta_1}} \; \eta_2 \to \eta_2 + \tau \frac{p_{\eta_2}}{m_{\eta_2}} \right. \quad (31e)$$

$$U_2\left(\frac{\tau}{2}\right) : \left\{ p \to p + \frac{\tau}{2} F(q) \right. \quad (31f)$$

$$U_3\left(\frac{\tau}{2}\right) : \left\{ p \to p e^{\frac{\tau}{2}\frac{p_{\eta_1}}{m_{\eta_1}}} \right. \quad (31g)$$

$$U_4\left(\frac{\tau}{2}\right) : \left\{ p_{\eta_1} \to p_{\eta_1} e^{\frac{\tau}{4}\frac{p_{\eta_2}}{m_{\eta_2}}} + \frac{\tau}{4} \frac{\sinh\left(\frac{\tau}{4}\frac{p_{\eta_2}}{m_{\eta_2}}\right)}{\frac{\tau}{4}\frac{p_{\eta_2}}{m_{\eta_2}}} \right. \quad (31h)$$

$$U_5\left(\frac{\tau}{2}\right) : \left\{ p_{\eta_2} \to p_{\eta_2} + \frac{\tau}{2} F(p_{\eta_1}) \right. \quad (31i)$$

which is readily implementable on the computer.

The stability of the algorithm can be tested by studying a simple one dimensional harmonic oscillator. We set $m = m_{\eta_1} = m_{\eta_2} = 1$ and use an integration time step $\tau = 0.0025$ in suitable units ($k_B = 1$). Figure 1 shows a comparison of the numerical fluctuations of the total NHC Hamiltonian (which should be rigorously conserved) with that of a simple Nosè-Hoover (NH) dynamics (obtained from the NHC by setting $\eta_1 = \eta_2 = p_{\eta_1} = p_{\eta_2} = 0$.

The NHC dynamics is more complicated than that of the simple Nosé-Hoover thermostat, mainly because of the coupling of p_{η_2} to the fast p_{η_1}. However, Fig. 1 proves that the integration is satisfactorily stable. To achieve the same level of accuracy as obtained for the Nosé-Hoover integration one should use higher order or multiple time step methods. Figure 2 shows the $q - p$ space sampled by NHC dynamics: the sampling is evidently ergodic. The ergodicity of NHC dynamics is main reason for using it in place of the simpler NH dynamics. The latter in fact is notoriously unable to sample ergodically the $q-p$ space of stiff oscillators.

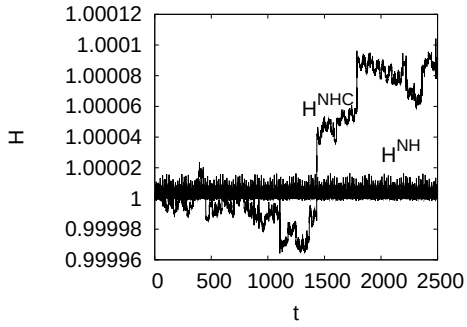

Figure 1. Comparison of Nosé-Hoover vs Nosé-Hoover Chain 1D Harmonic oscillator; $\tau = 0.0025$. Numerical stability of time-reversible integration.

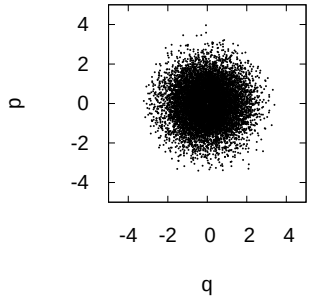

Figure 2. NHC Phase Space. $q - p$ Poincaré section

7. Measure-preserving algorithms

Time-reversible algorithms are easy to implement. They also usually conserve the total energy with high accuracy. However, the non-Hamiltonian invariant phase space measure

$$d\mu = e^{-w}\, dx_1 \wedge dx_2 \wedge ... \wedge dx_{2N} \tag{32}$$

is not necessarily conserved by the single propagation step, $U_i\mu \neq 0$, and so it is not always conserved by primitive time-reversible algorithms. Preservation of the phase space measure can be essential when using hybrid Monte Carlo/MD schemes or when reweighting trajectories.

A scheme for deriving integrators which are both time reversible and measure-preserving has recently been proposed [2]. Instead of implementing an arbitrary splitting of the Liouville operator, one starts with a splitting of the Hamiltonian

$$H = \sum_{\alpha=1}^{n_s} H_\alpha \ . \tag{33}$$

In turn, this determines a splitting of the Lioville operator according to

$$L = \sum_{\alpha=1}^{n_s} L_\alpha \ , \tag{34}$$

where

$$L_\alpha \equiv \mathcal{B}_{ij} \nabla_j \left(H_\alpha \right) \nabla_i \ . \tag{35}$$

One can see from Eq. (35) that each L_α is built in terms of the antusymmetric matrix $\mathcal{B}$. It has been proven [2] that if

$$\nabla_j \left[e^{-w} \mathcal{B}_{ij} \right] = 0 \ , \tag{36}$$

for $i = 1, ..., 2N$, then

$$L_\alpha d\mu = 0 \ , \tag{37}$$

for every α. This implies that upon defining propagators as

$$U_\alpha(\tau) = \exp[\tau L_\alpha] \ , \tag{38}$$

for $\alpha = 1, .../, n_s$ $\alpha = 1, .../, n_s$, one obtains single propagation steps that also preserve the phase space measure. Moreover, upon defining the complete propagator in terms of the symmetric Trotter formula,

$$U(\tau) = \left[\sum_{\alpha=2}^{n_s} U_{2\alpha-k-1}(\tau/2) \right] U_1(\tau) \left[\sum_{\beta=2}^{n} U_\beta(\tau/2) \right] + \mathcal{O}(\tau^3) \ , \tag{39}$$

one automatically obtains integration schemes that are both time-reversible and measure-preseving.

8. Bulgac-Kusnezov-Nosé-Hoover dynamics

In order to illustrate measure-preserving algorithms, we apply the theory of the previous section to the dynamics of the Bulgac-Kusnezov thermostat [34, 35]. The Bulgac-Kusnezov thermostat is more general than the standard Nosé-Hoover version; it can, for example, be applied to classical spin systems. Time-reversible measure-preserving algorithms for Bulgac-Kusnezov generalized thermostats have been recently proposed in [36].

Consider the following Hamiltonian [36]

$$\tilde{H}^{\rm BKNH} = H(q,p) + \frac{p_\zeta^2}{2m_\zeta} + \frac{p_\xi^2}{2m_\xi} + \frac{p_\eta^2}{2m_\eta} + k_B T(\zeta + \xi) + 2_B T \eta \ , \tag{40}$$

where the *demon* variables ξ and ζ appear together with the standard Nosé coordinate η. Corresponding momenta and masses also enter into the definition of $\tilde{H}^{\rm BKNH}$. Upon

defining the antisymmetric tensor field [36]

$$\tilde{\boldsymbol{\mathcal{B}}}^{\mathrm{BKNH}} = \begin{bmatrix} 0 & 0 & 0 & 0 & 1 & 0 & -q & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 & 0 & -p & 0 & 0 \\ 0 & -1 & 0 & 0 & p & 0 & 0 & -p_\zeta \\ q & 0 & -1 & 0 & 0 & 0 & 0 & -p_\xi \\ 0 & 0 & 0 & -1 & 0 & p_\zeta & p_\xi & 0 \end{bmatrix} , \tag{41}$$

one obtains the following Nos-Hoover-Bulgac-Kusnezov equations of motion

$$\dot{q} = \frac{p}{m} - q\frac{p_\xi}{m_\xi} , \tag{42a}$$

$$\dot{\zeta} = \frac{p_\zeta}{m_\zeta} , \tag{42b}$$

$$\dot{\xi} = \frac{p_\xi}{m_\xi} , \tag{42c}$$

$$\dot{\eta} = \frac{p_\eta}{m_\eta} , \tag{42d}$$

$$\dot{p} = F(q) - p\frac{p_\zeta}{m_\zeta} , \tag{42e}$$

$$\dot{p}_\zeta = \frac{p^2}{m} - k_B T - p_\zeta \frac{p_\eta}{m_\eta} , \tag{42f}$$

$$\dot{p}_\xi = -qF(q) - k_B T - p_\xi \frac{p_\eta}{m_\eta} , \tag{42g}$$

$$\dot{p}_\eta = \frac{p_\zeta^2}{m_\zeta} + \frac{p_\xi^2}{m_\xi} - 2k_B T , \tag{42h}$$

that display a coupling of the Nosé-Hoover variable to the Bulgac-Kusnezov demons in order to enhance the chaoticity of the dynamics of q and p.

Exploiting a suitable splitting of the Hamiltonian, one obtains the following measure preserving Liouville operators [36]:

$$L_A^{\mathrm{BKNH}} = F(q)\frac{\partial}{\partial p} + \frac{p_\eta}{m_\eta}\frac{\partial}{\partial \eta} - \frac{p_\eta}{m_\eta} p_\zeta \frac{\partial}{\partial p_\zeta} + \left(-\frac{p_\chi}{m_\chi} p_\xi + F_{p_\xi} \right) \frac{\partial}{\partial p_\xi} , \tag{43a}$$

$$L_B^{\mathrm{BKNH}} = \frac{p}{m}\frac{\partial}{\partial q} + F_{p_\zeta}\frac{\partial}{\partial p_\zeta} , \tag{43b}$$

$$L_C^{\mathrm{BKNH}} = -\frac{p_\zeta}{m_\zeta} p \frac{\partial}{\partial p} - \frac{p_\xi}{m_\xi} q \frac{\partial}{\partial q} + \frac{p_\zeta}{m_\zeta}\frac{\partial}{\partial \zeta} + \frac{p_\xi}{m_\xi}\frac{\partial}{\partial \xi} + F_{p_\eta}\frac{\partial}{\partial p_\eta} , \tag{43c}$$

where we define the forces

$$F_{p_\xi} = -qF(q) - k_BT \,, \tag{44a}$$

$$F_{p_\zeta} = \frac{p^2}{m} - k_BT \,, \tag{44b}$$

$$F_{p_\eta} = \frac{p_\zeta^2}{m_\zeta} + \frac{p_\xi^2}{m_\xi} - 2k_BT. \tag{44c}$$

The Trotter factorized propagator

$$\begin{aligned} U(\tau)^{\mathrm{BKNH}} &= U_B^{\mathrm{BKNH}}\left(\frac{\tau}{4}\right) U_C^{\mathrm{BKNH}}\left(\frac{\tau}{2}\right) U_B^{\mathrm{BKNH}}\left(\frac{\tau}{4}\right) \\ &\times U_A^{\mathrm{BKNH}}(\tau) \\ &\times U_B^{\mathrm{BKNH}}\left(\frac{\tau}{4}\right) U_C^{\mathrm{BKNH}}\left(\frac{\tau}{2}\right) U_B^{\mathrm{BKNH}}\left(\frac{\tau}{4}\right) \end{aligned} \tag{45}$$

leads to a time-reversible measure-preserving algorithms [36] that can be easily written in pseudo-code form as

$$U_B^{\mathrm{BKNH}}\left(\frac{\tau}{4}\right) : \begin{cases} q & \to & q + \frac{\tau}{4}\frac{p}{m} \\ p_\zeta & \to & p_\zeta + \frac{\tau}{4}F_{p_\zeta} \end{cases} \tag{46a}$$

$$U_C^{\mathrm{BKNH}}\left(\frac{\tau}{2}\right) : \begin{cases} p & \to & p\exp\left[-\frac{\tau}{2}\frac{p_\zeta}{m_\zeta}\right] \\ q & \to & q\exp\left[-\frac{\tau}{2}\frac{p_\xi}{m_\xi}\right] \\ \zeta & \to & \zeta + \frac{\tau}{2}\frac{p_\zeta}{m_\zeta} \\ \xi & \to & \xi + \frac{\tau}{2}\frac{p_\xi}{m_\xi} \\ p_\eta & \to & p_\eta + \frac{\tau}{2}F_{p_\zeta} \end{cases} \tag{46b}$$

$$U_B^{\mathrm{BKNH}}\left(\frac{\tau}{4}\right) : \begin{cases} q & \to & q + \frac{\tau}{4}\frac{p}{m} \\ p_\zeta & \to & p_\zeta + \frac{\tau}{4}F_{p_\zeta} \end{cases} \tag{46c}$$

$$U_A^{\mathrm{BKNH}}(\tau) : \begin{cases} p & \to & p + \tau F(q) \\ p_\xi & \to & p_\xi + \tau F_{p_\xi} \\ \eta & \to & \eta + \tau\frac{p_\eta}{m_\eta} \\ p_\zeta & \to & p_\zeta\exp\left[-\tau\frac{p_\eta}{m_\eta}\right] \end{cases} \tag{46d}$$

$$U_B^{\mathrm{BKNH}}\left(\frac{\tau}{4}\right) : \begin{cases} q & \to & q + \frac{\tau}{4}\frac{p}{m} \\ p_\zeta & \to & p_\zeta + \frac{\tau}{4}F_{p_\zeta} \end{cases} \tag{46e}$$

$$U_C^{\mathrm{BKNH}}\left(\frac{\tau}{2}\right) : \begin{cases} p & \to & p\exp\left[-\frac{\tau}{2}\frac{p_\zeta}{m_\zeta}\right] \\ q & \to & q\exp\left[-\frac{\tau}{2}\frac{p_\xi}{m_\xi}\right] \\ \zeta & \to & \zeta + \frac{\tau}{2}\frac{p_\zeta}{m_\zeta} \\ \xi & \to & \xi + \frac{\tau}{2}\frac{p_\xi}{m_\xi} \\ p_\eta & \to & p_\eta + \frac{\tau}{2}F_{p_\eta} \end{cases} \tag{46f}$$

$$U_B^{\mathrm{BKNH}}\left(\frac{\tau}{4}\right) : \begin{cases} q & \to & q + \frac{\tau}{4}\frac{p}{m} \\ p_\zeta & \to & p_\zeta + \frac{\tau}{4}F_{p_\zeta} \end{cases} \tag{46g}$$

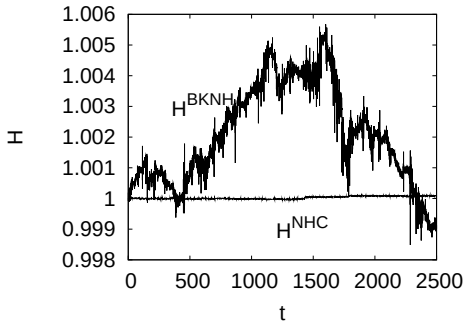

Figure 3. Numerical stability of the measure-preserving time-reversible integration. Comparison between the Nosé-Hoover chain (NHC) and the Nosé-Hoover-Bulgac-Kusnezov (BKNH) dynamics of a one-dimensional Harmonic oscillator; $\tau = 0.0025$.

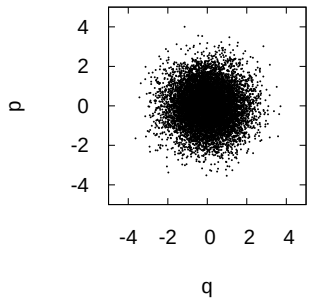

Figure 4. $q - p$ Poincaré section obtained from the Nosé-Hoover-Bulgac-Kusnezov dynamics of the one-dimensional harmonic oscillator.

Figure 3 shows a comparison between the numerical fluctuations of the total Hamiltonian between the measure-preserving time reversible integration of Nosé-Hoover chain and Nosé-Hoover-Bulgac-Kusnezov dynamics. Figure 4 shows the chaotic $q - p$ Poincaré section of the harmonic oscillator phase space. Figure 5 shows a comparison between the analytical and the numerically sampled radial probability of the one-dimensional harmonic oscillator, evolving under the Nosé-Hoover-Bulgac-Kusnezov dynamics. The Nosé-Hoover-Bulgac-Kusnezov dynamics displays a satisfactory numerical stability but is apparently "stiffer" than the simpler Nosé-Hoover chain flow. The advantage of the Nosé-Hoover-Bulgac-Kusnezov dynamics is that it can also be defined for classical spin systems, opening the way for the development of measure-preserving integration algorithms for thermostatted spin systems.

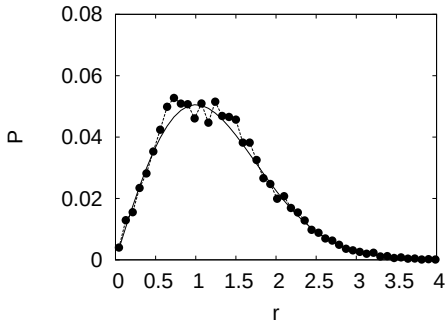

Figure 5. Comparison between the analytical and the numerically sampled radial probability of the one-dimensional harmonic oscillator, evolving under the Nosé-Hoover-Bulgac-Kusnezov dynamics.

9. Conclusions and perspectives

In this contribution, we have discussed some examples of non-Hamiltonian dynamics. The latter provides an approximate computational theory for systems with thermodynamic constraints. The formulation in terms of non-Hamiltonian (almost-Poisson) brackets leads to the design of very efficient and easily implementable time-reversible measure-preserving algorithms for integrating the equations of motion.

The theory and techniques presented here open up several interesting perspectives. Extensions to classical spin systems and phase space quantum dynamics of particles are currently under study.

Acknowledgments

A. S. is grateful to the *Accademia Peloritana dei Pericolanti* for the invitation. This work is based upon research supported by a Competitive Research Grant of the University of KwaZulu Natal and by the National Research Foundation of South Africa.

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Colloquium paper presented on 7 April 2010; published online 15 November 2010