Non-Hamiltonian equations of motion with a conserved energy

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In 1980 Andersen introduced the use of ''extended system'' as a means of exploring by molecular dynamics simulation the phase space of a physical model according to a desired ensemble distribution different from the standard microcanonical function. Following his original work on constant pressure-constant enthalpy a large number of different equations of motion, not directly derivable from a Hamiltonian, have been proposed in recent years, the most notable of which is the so-called Nosé-Hoover formulation for ''canonical'' molecular dynamics simulation. Using a generalization of the symplectic form of the Hamilton equations of motion we show here that there is a unique general structure that underlies most, if not all the equations of motion for ''extended systems.'' We establish a unifying formalism that allows one to identify and separately control the conserved quantity, usually known as the ''total energy'' of the system, and the phase-space compressibility. Moreover, we define a standard procedure to construct conservative non-Hamiltonian flows that sample the phase space according to a chosen distribution function [Tuckerman *et al.*, Europhys. Lett. **45**, 149 (1999)]. To illustrate the formalism we derive new equations of motion for two example cases. First we modify the equations of motion of the Nosé-Hoover thermostat applied to a one-dimensional harmonic oscillator, and we show how to overcome the ergodicity problem and obtain a canonical sampling of phase space without making recourse to additional degrees of freedom. Finally we recast an idea recently put forward by Marchi and Ballone [J. Chem. Phys. **110**, 3697 (1999)] and derive a dynamical scheme for sampling phase space with arbitrary statistical biases, showing as an explicit application a demixing transition in a simple Lennard-Jones binary mixture.

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I. INTRODUCTION

A major impulse to the molecular dynamics computational approach has certainly come from the 1980 introduction by Andersen of constant pressure molecular dynamics (MD) simulation using the ''extended system'' dynamics [1]. The ability of controlling the choice of the ensemble by a modification of the way the MD trajectory samples dynamically the phase space, with the addition of *ad hoc* dynamical variables opportunely coupled to the system of interest, has allowed the gain of a great insight into the behavior of condensed matter systems under various thermodynamical conditions [1–3]. Extended systems are characterized by a non-Hamiltonian dynamics [4] that, however, maintains a well defined conserved energy, taking the place of the Hamiltonian, in the extended phase space. Dynamically the system explores a constant energy hypersurface that corresponds to a microcanonical-like distribution function in the extended phase space. This becomes, when contracted by averaging on the extended variables, the desired ensemble distribution in the phase space of the physical system of interest.

There is not a unique method to derive extended systems dynamics. As a matter of fact there are two principal routes. One is to start with the equations of motion in canonical form of a suitable Hamiltonian system and then to apply a noncanonical transformation to phase space coordinates [1] and on the time [2]; the other one is just to postulate from scratch equations of motion, largely on intuitive grounds [3]. Moreover, different equations of motion can lead to the same distribution function in the phase space [6,7]. An effective theoretical approach to non-Hamiltonian extended systems should allow both to formulate new equations of motion and to control the statistical weight in phase space. This would give the flexibility needed to control the thermodynamics conditions and might open new routes to overcome the limitations inherent within dynamical sampling of the phase space in the presence of well separated length or time scales in the physical problem.

In this work we introduce a general mathematical structure for non-Hamiltonian conservative equations of motion. As it will be shown, the conserved dynamical quantity, the ''extended energy,'' is involved in the specification of the phase space flow and from now on it will be referred to simply as the Hamiltonian, to distinguish it from the energy of the physically meaningful system of interest, even if this term is not, mathematically, precise.

It turns out from the general structure of the equations of motion that for a given fixed expression of the (conserved) Hamiltonian one has still much freedom left to select the compressibility of the phase space and with it the corresponding ensemble distribution for the physical system of interest. As it has been recently shown [8], the compressibility is the key ingredient to build the invariant measure of phase space in the case of non-Hamiltonian dynamics. In the present work we try to clarify the relation between the con-

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served Hamiltonian, the equations of motion, and the compressibility. In particular, we exploit the features of the general formalism to devise some dynamical flows having special statistical weights on the phase space. Furthermore, it should be mentioned that the possibility to derive general phase space dynamics with a conserved Hamiltonian has a technical interest by itself. As a matter of fact the conservation law for the Hamiltonian is the first, if not most important, check that is applied to assess the accuracy of the numerical integration.

In Sec. II we introduce the mathematical formalism for non-Hamiltonian conservative equations of motion. The theory is a simple generalization of Hamiltonian equations of motion written in symplectic form [9–11]. In Sec. III we show that some well-known extended systems phase space flows, such as the Nosé-Andersen constant pressure-constant temperature dynamics and the constant temperature Nosé-Hoover chain, share the general structure given in Sec. II. In Sec. IV we present a set of original equations of motion for constant temperature simulations, that are a simple generalization of the ones for the Nosé-Hoover thermostat, and we outline for the one-dimensional harmonic oscillator the conditions that numerically lead to an ergodic sampling of phase space without having to recourse to the addition of extra dynamical variables. In Sec. V we illustrate an extended system that produces a biased sampling of phase space. The biased dynamics is dynamically achieved by means of *ad hoc* accelerations that steer the system to special regions of phase space. We apply the scheme to a binary Lennard-Jones mixture and by means of a selective term we obtain a phase separation while keeping constant the Hamiltonian of the system. We show that also in this case an explicit phase space distribution function can be formulated that, if desired, can be unbiased to collect standard averages over the canonical ensemble. The last section is devoted to our comments and conclusions.

II. NON-HAMILTONIAN DYNAMICS

In this section we introduce a general formalism to write equations of motion in phase space that conserve a chosen time-independent Hamiltonian $\mathcal{H}$. In order to keep notation simple the point in phase space, including both generalized coordinates and momenta, will be written as $\mathbf{x}=(\mathbf{q},\mathbf{p})$. Introducing the antisymmetric matrix

$$B_{ij}^T=-B_{ji}, \quad i,j=1,2N, \tag{1}$$

which has the same dimensions $2N$ as the phase space, a general form of the equations of motion is readily established as [9]

$$\dot{x}_i=\sum_{j=1}^{2N} B_{ij}\frac{\partial \mathcal{H}}{\partial x_j}, \quad i=1,2N. \tag{2}$$

For the particular definition of the matrix of Eq. (2), in block form

$$\mathbf{B}^{(c)}=\begin{pmatrix} \mathbf{0} & \mathbf{1} \\ -\mathbf{1} & \mathbf{0} \end{pmatrix}$$

one has simply obtained a rewriting of the canonical equations of motion for a Hamiltonian system [9]. The canonical matrix $\mathbf{B}^{(c)}$ is invariant under canonical transformations of phase space [9]. When one applies a noncanonical transformation of the phase space coordinates, the form of Eq. (2) is conserved, the matrix **B** remains antisymmetric but loses its canonical form [10]. Now the elements **B** can be complicated functions of the phase space point **x**. Flux in the phase space remains Hamiltonian [10] if **B** satisfies for any given choice of the index i,j,k the equation

$$\sum_{n=1}^{2N} B_{in}\frac{\partial B_{jk}}{\partial x_n}+B_{kn}\frac{\partial B_{ij}}{\partial x_n}+B_{jn}\frac{\partial B_{ki}}{\partial x_n}=0. \tag{3}$$

If Eqs. (1) and (3) hold then Eq. (2) determines what is known as a noncanonical Hamiltonian flow in phase space [10,11]. An example of noncanonical Hamiltonian dynamics is given by the well-known Andersen constant pressure equations of motion [1].

We suggest that it is possible to generally define conservative non-Hamiltonian flows in phase space by using the structure of Eq. (2). In practice the definition of a non-Hamiltonian flow can be done by independently choosing an antisymmetric matrix **B**, with elements that are functions of the phase space point **x**, and a conserved Hamiltonian $\mathcal{H}$. In this respect it is no longer necessary to derive the form **B** by means of coordinate transformations on the symplectic form $\mathbf{B}^{(c)}$. It is to be noted that with an arbitrary **B**, not derived from a noncanonical transformation of phase space, the property of Eq. (3) will not hold in general. For example, it can be easily verified that in the case of the Nosé-Hoover equations of motion Eq. (3) is not satisfied. This is not surprising at all because the Nosé-Hoover equations of motion, written in real time, involve a scaling of the proper time variable along the phase space trajectory. The final result is that the real time variable is no longer integrable and depends on the trajectory in phase space. It can be checked that the relations (3) hold if the Nosé-Hoover equations are expressed in virtual time, i.e., without performing the time scaling along the trajectory. Thus according to Refs. [10,11] the Nosé-Hoover thermostat equations in virtual time describe a noncanonical Hamiltonian flow. In the general case, when the property of Eq. (3) does not hold, the phase space flow is non-Hamiltonian.

The important fact to be noted is that, by definition, due to the antisymmetry of **B**, Eq. (2) conserves the Hamiltonian function $\mathcal{H}$ regardless of relations (3) being satisfied or not. This is easily verified by taking the total time derivative of $\mathcal{H}$

$$\frac{d\mathcal{H}}{dt}=\sum_{i=1}^{2N}\frac{\partial \mathcal{H}}{\partial x_i}\dot{x}_i=\sum_{i=1}^{2N}\sum_{j=1}^{2N}\frac{\partial \mathcal{H}}{\partial x_i}B_{ij}\frac{\partial \mathcal{H}}{\partial x_j}=0. \tag{4}$$

The total time derivative of $\mathcal{H}$ vanishes because, in the end, we take the trace of the product of the antisymmetric matrix B_{ij} with the symmetric one $\partial\mathcal{H}/\partial x_i \partial\mathcal{H}/\partial x_j$. Equation (4)

establishes that in order to define a non-Hamiltonian flow with a conserved energy, one needs only the antisymmetry of an otherwise completely general matrix **B**. It is interesting to note that a time-independent Hamiltonian $\mathcal{H}$ will always be conserved, even when **B** is an explicitly time-dependent antisymmetric matrix as long as Eq. (4) remains valid for flows described by Eq. (2). This could suggest how to generalize conservative phase space flows to the case of nonequilibrium systems, as it was the case for some equations of motion for nonequilibrium molecular dynamics proposed in Ref. [12], which had a conserved quantity if time-dependent boundary conditions were not used. In fact, it can be easily shown that the equations of Ref. [13] share the general structure given by Eq. (2). In the following, we restrict our discussion to time-independent **B** and thus to the dynamics of system at equilibrium.

As we already noted $\mathcal{H}$ and **B** can be chosen independently but together they determine the equations of motion for the system. In general the equations of motion will lead to a nonzero compressibility

$$\kappa(\mathbf{x}) = \sum_{i=1}^{2N} \frac{\partial \dot{x}_i}{\partial x_i} = \sum_{i=1}^{2N} \sum_{j=1}^{2N} \frac{\partial B_{ij}}{\partial x_i} \frac{\partial \mathcal{H}}{\partial x_j}, \tag{5}$$

which means that the phase space will not be sampled uniformly by the dynamics. Under the hypothesis of ergodicity, the corresponding weight in the phase space can be explicitly determined, for example, by means of the approach to statistical mechanics of non-Hamiltonian systems proposed in Ref. [8]. The structure of Eq. (2) is useful, because it allows us to choose the form of the conserved Hamiltonian $\mathcal{H}$; then a particular phase space compressibility κ can be obtained by exploiting the freedom in choosing the the matrix elements B_{ij}. This amounts to the possibility of designing conservative non-Hamiltonian equations of motion with a controlled statistical weight of the phase space. We expect that this approach will open the route to the formulation of novel non-Hamiltonian dynamics with statistical constraints. However, it must be recognized that an arbitrary non-Hamiltonian flow could modify the dynamical properties of the system [13]. Thus, care is required in the calculation of correlation functions as their physical meaning must be assessed in each case. To address general features of non-Hamiltonian dynamics we will restrict the following discussion to static equilibrium properties. Within these bounds one could design equations of motion to force the system to explore regions in phase space that would be otherwise visited very infrequently or not at all. In the present work, Sec. V, we will show a simple example of a demixing transition in a binary fluid.

III. EXTENDED SYSTEM DYNAMICS

It is remarkable that the structure of Eq. (2) underlies most, if not all the equations of motion of extended systems used up to now in molecular dynamics simulations. In this section we give two explicit examples: the equations for Nosé-Hoover chain [5] thermostat and those for constant pressure constant-temperature dynamics [14].

In order to keep the tensorial notation to a minimum we limit the chain to only two thermostat variables. This allows us both to write fully the matrix **B** with all elements explicitly shown and to delay a block matrix notation to later on. For a one-dimensional system coupled to a Nosé-Hoover chain thermostat the phase space is six-dimensional and its points are denoted by $\mathbf{x}=(q,\eta_1,\eta_2,p,p_{\eta_1},p_{\eta_2})$. The Hamiltonian is

$$\mathcal{H}' = \frac{p^2}{2m} + \frac{p_{\eta_1}^2}{2M_{\eta_1}} + \frac{p_{\eta_2}^2}{2M_{\eta_2}} + \Phi(q) + gk_BT(\eta_1+\eta_2), \tag{6}$$

where η_1 and η_2 are the two thermostat variables with conjugated momenta p_{η_1} and p_{η_2}; the number of degrees of freedom $g=1$ is fixed to get the canonical distribution function, k_B is the Boltzmann constant, and T is the thermostat temperature. The equations of motion are given by [5]

$$\dot{q} = \frac{p}{m}, \tag{7}$$

$$\dot{\eta}_1 = \frac{p_{\eta_1}}{M_{\eta_1}}, \tag{8}$$

$$\dot{\eta}_2 = \frac{p_{\eta_2}}{M_{\eta_2}}, \tag{9}$$

$$\dot{p} = -\frac{\partial \Phi}{\partial q} - \frac{p_{\eta_1}}{M_{\eta_1}} p, \tag{10}$$

$$\dot{p}_{\eta_1} = \frac{p^2}{m} - gk_BT - p_{\eta_1}\frac{p_{\eta_2}}{M_{\eta_2}}, \tag{11}$$

$$\dot{p}_{\eta_2} = \frac{p_{\eta_1}^2}{M_{\eta_1}} - gk_BT. \tag{12}$$

By exploiting Eq. (2) and computing explicitly $\partial\mathcal{H}'/\partial\mathbf{x}$, it is possible to find the matrix $\mathbf{B}_{NHC}$ that allows us to rewrite Eqs. (7)–(12) in tensorial form

$$\begin{pmatrix} \dot{q} \\ \dot{\eta}_1 \\ \dot{\eta}_2 \\ \dot{p} \\ \dot{p}_{\eta_1} \\ \dot{p}_{\eta_2} \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 & -p & 0 \\ 0 & -1 & 0 & p & 0 & -p_{\eta_1} \\ 0 & 0 & -1 & 0 & p_{\eta_1} & 0 \end{pmatrix} \times \begin{pmatrix} \frac{\partial \Phi}{\partial q} \\ g k_B T \\ g k_B T \\ \frac{p}{m} \\ \frac{p_{\eta_1}}{M_{\eta_1}} \\ \frac{p_{\eta_2}}{M_{\eta_2}} \end{pmatrix}. \tag{13}$$

Equation (13) shows how the Nosé-Hoover chain equations of motion satisfy the structure of non-Hamiltonian conservative phase space flow given in Eq. (2).

For the other case of constant pressure and temperature dynamics we choose the one [14] out of many possible sets of equations of motion, which is more familiar to us having recently derived for it a time reversible integration algorithm [16], following the lines of the RESPA approach [15]. In this case the phase-space point is denoted by $\mathbf{x} = (\mathbf{q}, V, \eta, \mathbf{p}, P_V, p_\eta)$ and the Hamiltonian is

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + \Phi(\{\mathbf{q}\}^N, V) + \frac{p_\eta^2}{2M_\eta} + g k_B T \eta + \frac{P_V^2}{2M_V} + P_{ext} V, \tag{14}$$

where the thermostat variables are η and p_η, V is the volume of the MD box and P_V the barostat momentum with P_{ext} the external pressure; N is the number of particles in the system and the number of degrees of freedom is set as $g = 3(N-1)+1$ to take into account also the other conserved quantity, which is related to the total momentum of the particles:

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m} + \mathbf{q}_i \frac{P_V}{3VM_V}, \tag{15}$$

$$\dot{\eta} = \frac{p_\eta}{M_\eta}, \tag{16}$$

$$\dot{V} = \frac{P_V}{M_V}, \tag{17}$$

$$\dot{\mathbf{p}}_i = -\frac{\partial \Phi}{\partial \mathbf{q}_i} - \mathbf{p}_i \frac{P_V}{3VM_V} - \mathbf{p}_i \frac{p_\eta}{M_\eta}, \tag{18}$$

$$\dot{p}_\eta = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m} + \frac{P_V^2}{M_V} - g k_B T, \tag{19}$$

$$\dot{P}_V = \frac{1}{3V}\left[\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m_i} - \frac{\partial \Phi}{\partial \mathbf{q}_i}\mathbf{q}_i\right] - \frac{\partial M}{\partial V} - P_V \frac{p_\eta}{M_\eta}. \tag{20}$$

Again from the computation of the gradient of the conserved Hamiltonian in Eq. (14) we can easily find the matrix $\mathbf{B}_{NPT}$ that recasts Eqs. (15)–(20) in the form of Eq. (2). Using block matrix notation

$$\begin{pmatrix} \dot{\mathbf{q}}_i \\ \dot{V} \\ \dot{\eta} \\ \dot{\mathbf{p}}_i \\ \dot{P}_V \\ \dot{p}_\eta \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 1 & 0 & \frac{\mathbf{q}_i}{3V} \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 & -\mathbf{p}_i & -\frac{\mathbf{p}_i}{3V} \\ 0 & -1 & 0 & \mathbf{p}_i & 0 & P_V \\ -\frac{\mathbf{q}_i}{3V} & 0 & -1 & \frac{\mathbf{p}_i}{3V} & -P_V & 0 \end{pmatrix} \times \begin{pmatrix} \frac{\partial \Phi}{\partial \mathbf{q}_i} \\ \frac{\partial M}{\partial V} \\ g k_B T \\ \mathbf{p}_i / m \\ P_V / M_V \\ p_\eta / M_\eta \end{pmatrix}. \tag{21}$$

Equations (13) and (21) show in two particular cases (but the check can easily be done along the lines shown for all the other cases) that the generalized structure given in Eq. (2) is hidden in extended system equations of motion already known and commonly used in practical applications.

IV. MODIFIED NOSÉ THERMOSTAT

In this section we introduce yet another set of non-Hamiltonian equations of motion for constant temperature dynamics. By using Eq. (2) we modify the original equations of the Nosé-Hoover (NH) thermostat [2,3] in order to achieve the canonical sampling of the phase space, also in those cases where they have been showed to fail. In fact it is now well known that for stiff harmonic systems the sampling obtained by means of the Nosé-Hoover thermostat [2,3] appears not to be ergodic [5]. A solution to this problem has been given and it is the so called Nosé-Hoover chain (NHC) thermostat [5] we have introduced in the the preceding section. We believe this is a good case to show the capabilities of the present approach with a relatively simple system. Let us remind also that a more complex continuous dynamical

method to generate the canonical ensemble has been recently proposed [17].

The smart idea behind the Nosé-Hoover chain method is to obtain a canonical sampling of phase space by augmenting the dimensionality of the extended system using additional, chained thermostat variables. This has the effect of enhancing the fluctuations of the Nosé variable that realizes the thermostat of the physical degrees of freedom. We exploit the structure of Eq. (2) to show how a similar effect on the fluctuations of the Nosé variable can be obtained following a different route, without augmenting the dimensionality of phase space. By inspection of Eq. (13) one realizes that at disposal there are many null elements in the antisymmetric matrix **B** that can be modified without changing the compressibility of the phase space and thus the statistical distribution.

Following Ref. [5] we consider the one-dimensional harmonic oscillator choosing, as a conserved energy, the Hamiltonian of the Nosé-Hoover thermostat

$$\mathcal{H}=\frac{p^2}{2m}+\frac{p_\eta^2}{2M_\eta}+\Phi(q)+k_BT\eta. \tag{22}$$

The coordinate and the momentum of the particle to be thermostatted are q and p, respectively, m is the particle mass, and $\Phi(q)=\frac{1}{2}kq^2$ is, in this case, the quadratic harmonic potential energy; η is the Nosé variable with its momentum p_η and inertial factor M_η. The phase space point is (q,η,p,p_η). With this definition it is very easy to write a matrix **B** leading to equations of motion that generalize the Nosé-Hoover ones. Let

$$\mathbf{B}=\begin{pmatrix} 0 & 0 & 1 & \tau p/m \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & -p \\ -\tau p/m & -1 & p & 0 \end{pmatrix}, \tag{23}$$

where we introduced the (time) dimensional parameter τ. In particular, when τ is set to zero the standard Nosé-Hoover equations of motion are recovered. The compressibility is still given by $\kappa=-p_\eta/M_\eta$. Thus one can straightforwardly build the invariant measure of phase space [8] and check that the canonical phase-space distribution function is obtained. With $\tau\neq 0$ we obtain the new equations

$$\dot{q}=\frac{p}{m}\left(1+\tau\frac{p_\eta}{M_\eta}\right), \tag{24}$$

$$\dot{\eta}=\frac{p_\eta}{M_\eta}, \tag{25}$$

$$\dot{p}=-\frac{\partial\Phi}{\partial q}-p\frac{p_\eta}{M_\eta}, \tag{26}$$

$$\dot{p}_\eta=\frac{p^2}{m}-k_BT-\tau\frac{p}{m}\frac{\partial\Phi}{\partial q}. \tag{27}$$

Two new nonzero elements $B_{41}=-B_{14}$ contribute to driving the dynamics of the Nosé variable η. By inspection of Eq (27) it is recognized that the fluctuations of p_η is influenced, through the coupling parameter τ, by the term $\tau p/m\partial\Phi/\partial q$. If Eq. (24) were canonical the driving term could be considered as the power $d\Phi/dt$ dissipated by the particle along its trajectory, and we will refer to them as the Nosé-Hoover power (NHP) thermostat. Above a threshold value $\tau=0.5$, in scaled units, the system becomes chaotic and Eqs. (24)–(27) sample ergodically the phase space (q,p) of the oscillator. Also the NHC equation (13) reduces to the standard Nosé-Hoover ones for large values of the coupling inertia M_{η_2}. When M_{η_2} becomes large, the driving term in the equation for p_{η_1} becomes negligible and the sampling is no longer canonical. Anyway, a glance at Eq. (24) reveals that the NHP thermostat couples the thermostat momentum p_η directly to the physical velocities of the particles. This modifies significantly the dynamical properties of the system and as a result NHP thermostat can be used only to study static equilibrium properties in the canonical ensemble.

Both NHC and NHP equations of motion require some care in the numerical integration compared to the Nosé-Hoover equations. If the same accuracy as the NH case is desired, a higher order algorithm should be used. Our experience is that Eq. (13) appears to be slightly simpler to integrate than Eqs. (24)–(27), using a reversible reference system propagator algorithm (RESPA) [15,18] in so far as it is enough to apply a multiple time step (MTS) approach with a smaller time step to the propagators involving velocities [18] while we found more satisfactory in the NHP case to apply a global higher order scheme treating on the same level both q and p that are coupled to the fast variable p_η. In particular in the tests we report below we desired a very high accuracy (energy is conserved within 1 part over 10^9) and we obtained that using the lowest Δt^4 Yoshida approach [19] (of order three), which is after all very simple to apply and, when applied globally, gives results that are, to our experience, far superior than an MTS approach with comparable computer time cost.

Following our previous work [16] we have used a simplified decomposition of the propagator deriving from Eqs. (24)–(27):

$$\hat{L}_1=\left(\frac{p}{m}+\tau\frac{p}{m}\frac{p_\eta}{M_\eta}\right)\frac{\partial}{\partial q}, \tag{28}$$

$$\hat{L}_2=\left(-\frac{\partial\Phi}{\partial q}\right)\frac{\partial}{\partial p}, \tag{29}$$

$$\hat{L}_3=\left(-p\frac{p_\eta}{M_\eta}\right)\frac{\partial}{\partial p}, \tag{30}$$

$$\hat{L}_4=\left(\frac{p_\eta}{M_\eta}\right)\frac{\partial}{\partial\eta}, \tag{31}$$

$$\hat{L}_5=\left(-\tau\frac{p}{m}\frac{\partial\Phi}{\partial q}+\frac{p^2}{m}-k_BT_{ext}\right)\frac{\partial}{\partial p_\eta}. \tag{32}$$

We use Yoshida's prescription with $n_y=3$ and weights

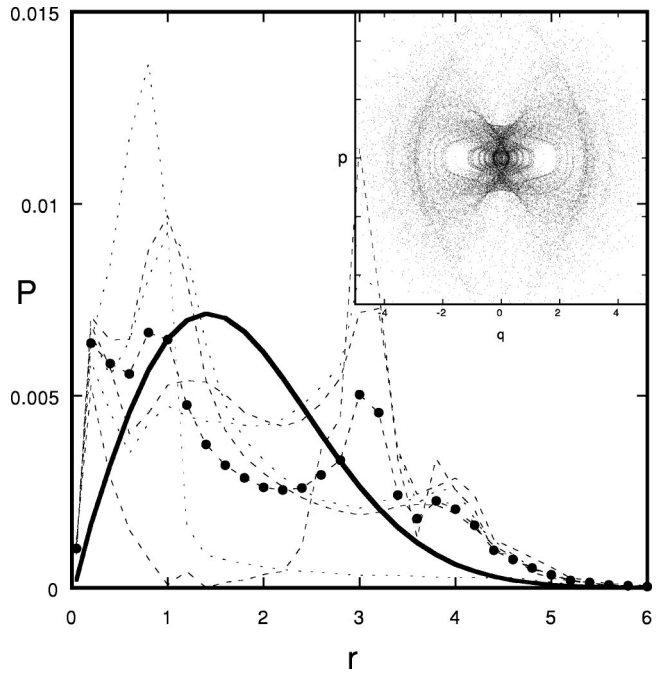

FIG. 1. Normalized probability distribution P in the q-p plane for the harmonic oscillator with the NH thermostat. The integrated value along the radial coordinate r is reported. Full thick line, theoretical prediction; circles, histogram average over all 30° sectors; dashed lines, individual histogram over each of the 12 30° sectors. In the inset the trajectory in the q-p plane is a shown as a collection of points. q, p, and r are in scaled units.

$$w_1=\frac{1}{4-4^{1/3}}, \quad w_2=1-2w_1, \quad w_3=w_1. \tag{33}$$

The following higher order propagator is obtained:

$$\hat{G}(\delta t)=\prod_{y=1}^{n_y}\exp\left(\frac{\delta t}{2}\frac{w_y}{n_y}\hat{L}_5\right)\exp\left(\frac{\delta t}{2}\frac{w_y}{n_y}\hat{L}_4\right)\exp\left(\frac{\delta t}{2}\frac{w_y}{n_y}\hat{L}_3\right)\times\exp\left(\frac{\delta t}{2}\frac{w_y}{n_y}\hat{L}_2\right)\exp\left(\delta t\frac{w_y}{n_y}\hat{L}_1\right)\exp\left(\frac{\delta t}{2}\frac{w_y}{n_y}\hat{L}_2\right)\times\exp\left(\frac{\delta t}{2}\frac{w_y}{n_y}\hat{L}_3\right)\exp\left(\frac{\delta t}{2}\frac{w_y}{n_y}\hat{L}_4\right)\exp\left(\frac{\delta t}{2}\frac{w_y}{n_y}\hat{L}_5\right). \tag{34}$$

The use of the higher order propagator (34) allows a very stable numerical integration in conjunction with a canonical sampling of the q-p space of the oscillator. In Figs. 1–3 we show on the q-p plane the sampling of phase space obtained with a trajectory of $M=50$ millions steps with $\Delta t=0.0025$ for three different cases: a standard Nosé-Hoover thermostat (Fig. 1), NHC thermostat (Fig. 2), NHP thermostat (Fig. 3).

The kind of phase-space sampling is shown by computing the histogram of the probability distribution as a function of both q and p by dividing the q-p plane in 12 sectors with an angular width of 30° using polar coordinates. In fact for $m=k=1$

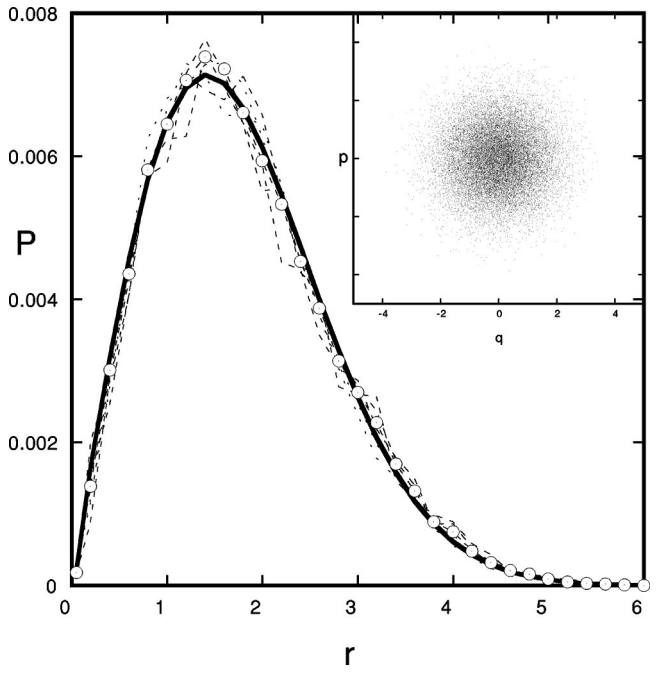

FIG. 2. Same as Fig. 1 for the harmonic oscillator with the NHC thermostat.

$$e^{-\beta H}=\exp\left[-\left(\frac{p^2}{2}+\frac{q^2}{2}\right)\Big/(k_BT)\right]=e^{-r^2/(2k_BT)}, \tag{35}$$

where $r^2=q^2+p^2$. The theoretical value over each sector does not depend on the angle and is given, in general, by the integral

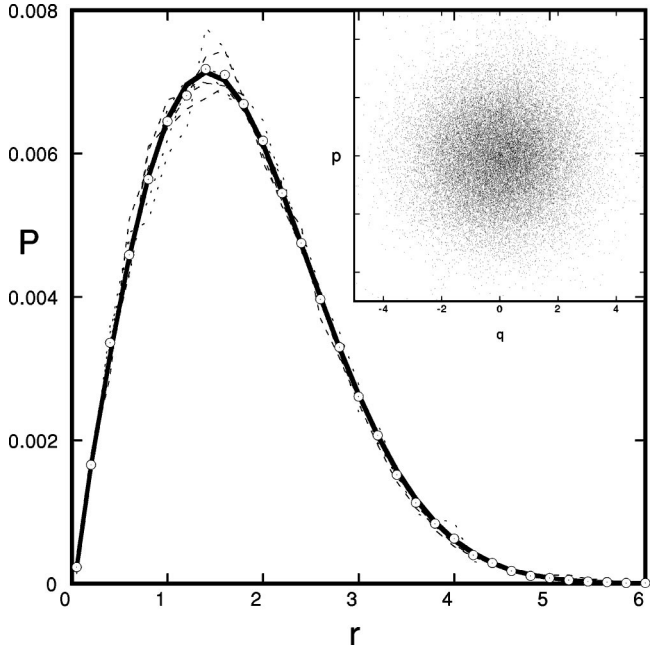

FIG. 3. Same as Fig. 1 for the harmonic oscillator with the NHP thermostat.

$$\int_{\alpha_1}^{\alpha_2} d\phi \int_{r_1}^{r_2} dr r e^{-r^2/(2k_BT)} = (\alpha_2-\alpha_1)(e^{-r_1^2/(2k_BT)}-e^{-r_2^2/(2k_BT)}). \quad (36)$$

The full thick line on the graphs shows the theoretical value compared to the histogram values averaged over all sectors, represented by the points. To give an idea of the behavior in each sector the results for all 12 sectors are individually plotted as dashed lines. There is a striking evidence of no difference between the NHC and the NHP thermostat, within both cases a very small fluctuation of the individual curves around the average. The NH thermostat samples the phase space in an irregular way, strongly dependent upon the initial conditions. There are clearly different results in the various sectors as it is also made evident in the inset where the trajectory on the q-p plane is shown. The trajectories in the NHC and NHP cases, also shown as insets in Figs. 2 and 3, on the contrary sample isotropically the two-dimensional phase space.

V. BIASED MOLECULAR DYNAMICS

Recently a method has been proposed to move into special regions of the phase space by means of molecular dynamics techniques. In particular the authors of Ref. [20] have used a dynamical scheme where the Hamiltonian is augmented with a time-dependent potential Φ_b. The potential is chosen in order to obtain a bias on the sampling of the system configurations so that infrequent regions of phase space can be explored. If the biasing potential can be made a small perturbation slowly evolving in time it is possible to move on a constant-energy surface. In other words the sum of the kinetic energy and of the interaction potential between particles is approximately a constant of motion. A drawback of the method presented in Ref. [20] is that the statistical distribution in phase space cannot be determined.

In the present work we formulate a scheme for statistical biased molecular dynamics within the framework of non-Hamiltonian extended systems with conservative non-Hamiltonian equations of motion. By exploiting again the matrix **B** in Eq. (2) a bias that is not explicitly dependent on time can be introduced. To this end we define an extended system that for zero bias reduces to the standard Nosé-Hoover equations of motion. For checking the statistical properties of the scheme it is useful to derive the bias from a potential-like $\Phi_b(\{\mathbf{r}\}^N)$ function of the particle coordinates in the system. As it will be shown here below, this feature allows to determine easily the statistical weight associated with the dynamical trajectory in phase space. The conserved Hamiltonian is the same as in the Nosé-Hoover case

$$\mathcal{H}=\sum_i^N \frac{\mathbf{p}_i^2}{m}+\sum_{i<j}\Phi(\mathbf{r}_{ij})+\frac{p_\eta^2}{M_\eta}+gk_BT\eta=\mathcal{H}_T+gk_BT\eta \quad (37)$$

and it is not modified by the presence of the bias in the equations of motion. N is the number of particles in the systems and accordingly $g=dN$, where d is the dimensionality of the geometrical space. At variance with Ref. [20] in our case the Hamiltonian of Eq. (37) is an exact constant of motion even if the perturbation is nonadiabatic. In practical terms, depending on the nature of the biasing potential the numerical integration of the equations of motion could become a delicate issue.

The statistical weight of the biased dynamics can once more be established by employing the formalism of Ref. [8]. It can be shown that the constant surface in phase space upon which the system moves is determined by the Hamiltonian of Eq. (37). Each point of this surface is visited with a statistical weight depending from the compressibility of phase space.

To define the proper extended system we calculate the phase-space gradient of the Hamiltonian

$$\frac{\partial H}{\partial x_i}=\left[\frac{\partial\Phi}{\partial\mathbf{r}_i},gk_BT,\frac{\mathbf{p}_i}{m},\frac{p_\eta}{M_\eta}\right], \quad (38)$$

we define the biasing force

$$\mathbf{F}_i^b=-\frac{1}{gk_BT}\frac{\partial\Phi_b}{\partial\mathbf{r}_i}, \quad i=1,3N, \quad (39)$$

where $\Phi_b(\mathbf{r})$ is an arbitrary function of the particle coordinates $\mathbf{r}$ that does not explicitly depend on time, and finally we choose the matrix **B** and write the equations of motion in block matrix form

$$\begin{bmatrix}\dot{\mathbf{r}}_i\\ \dot{\eta}\\ \dot{\mathbf{p}}_i\\ \dot{p}_\eta\end{bmatrix}=\begin{bmatrix}0&0&1&0\\0&0&-\mathbf{F}_i^b&1\\-1&\mathbf{F}_i^b&0&-\mathbf{p}_i\\0&-1&\mathbf{p}_i&0\end{bmatrix}\begin{bmatrix}\frac{\partial\Phi}{\partial\mathbf{r}_i}\\ gk_BT\\ \frac{\mathbf{p}_i}{m}\\ \frac{p_\eta}{M_\eta}\end{bmatrix}. \quad (40)$$

In the more usual form, with the explicit expression of the biasing force, the equations of motion are

$$\dot{\mathbf{r}}_i=\frac{\mathbf{p}_i}{m}, \quad (41)$$

$$\dot{\eta}=\frac{p_\eta}{M_\eta}+\frac{1}{gk_BT}\sum_i\frac{\mathbf{p}_i}{m}\frac{\partial\Phi_b}{\partial\mathbf{r}_i}, \quad (42)$$

$$\dot{\mathbf{p}}_i=-\frac{\partial\Phi}{\partial\mathbf{r}_i}-\mathbf{p}\frac{p_\eta}{M_\eta}-\frac{\partial\Phi_b}{\partial\mathbf{r}_i}, \quad (43)$$

$$\dot{p}_\eta=\sum_i\frac{\mathbf{p}_i^2}{m}-gk_BT. \quad (44)$$

Equations (41)–(44) conserve the Hamiltonian of Eq. (37). The biasing potential $\Phi_b(r)$ appears in the equation of motion for particle momenta, as proposed in Ref. [20].

The statistical weight can be expressed in terms of the function $\mathcal{H}_T$ by using the formalism of Ref. [8]. It can be easily shown that the distribution function is given by

$$\rho = \delta(H-E)\exp[-\beta(H_T+\Phi_b)]. \tag{45}$$

This can be proved by computing the compressibility from Eqs. (41)–(44)

$$\kappa(t) = \sum_{ij} \frac{\partial B_{ij}}{\partial x_i}\frac{\partial H}{\partial x_j} = -dN\frac{p_\eta}{M_\eta}. \tag{46}$$

[A more careful derivation should take into account the conservation law associated with the total impulse that will give $g=d(n-1)$.] Then

$$\frac{dH_T}{dt} = -\sum_i \frac{p_i}{m}\frac{\partial \Phi_b}{\partial r_i} - gk_BT\frac{p_\eta}{M_\eta}. \tag{47}$$

We thus obtain for the compressibility

$$\kappa(t) = \beta\frac{dH_T}{dt} + \beta\frac{d\Phi_b}{dt}. \tag{48}$$

The compressibility can be integrated in time

$$\int \kappa(t')dt' = H_T + \Phi_b. \tag{49}$$

This result allows one to easily find the distribution function given in Eq. (45).

The distribution function of Eq. (45) ensures that the statistical mechanics of the bias is under control. The bias appears just as an extra weight in the distribution function. By integrating only the equations of motion for **r** and **p** and neglecting the extra variables η and p_η the conserved Hamiltonian would have been $H' = H + \Phi_b$. The Hamiltonian dynamics would have given the distribution $\delta(H'-H'(0))$ that cannot be easily unbiased. Instead the complete set of Eqs. (41)–(44) gives the distribution of Eq. (45) that can be unbiased to give a canonical ensemble average. For example, a standard canonical average of an arbitrary observable $O(\{\mathbf{r}\}^N,\{\mathbf{p}\}^N)$ can be obtained from the integration by considering the average of $\exp[\beta\Phi_b(\mathbf{r})]O(\mathbf{r},\mathbf{p})$.

As a numerical example we have applied Eqs. (41)–(44) to a simple two-dimensional Lennard-Jones binary mixture composed of $N=216$ particles. With regard to the interaction potential the two components of the mixture are exactly the same. The particles are just tagged in the program in order to belong to one component or to the other one. The system is simulated in a square box using scaled units so that the mass of all the particles is 1, and the same holds for the parameters specifying the Lennard-Jones potential. The initial condition has been set up in order to realize a homogenous mixture of the two components. The configuration is equilibrated with a constant temperature dynamics. In Fig. 4(a) we show the configuration obtained at the end of the equilibration.

Then we have used Eqs. (41)–(44) to force a demixing transition. The potential Φ_b has been chosen to be repulsive between particles belonging to different components according to a simple inverse power law

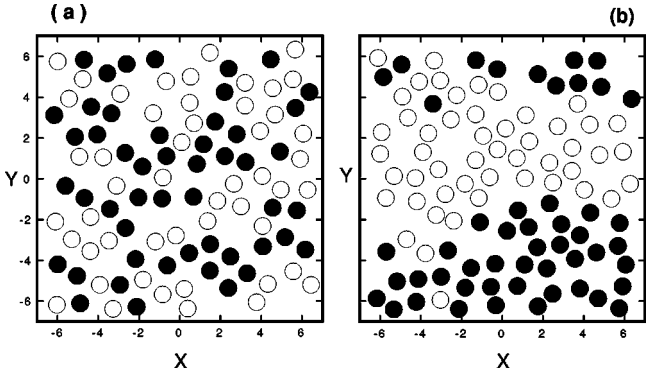

FIG. 4. Initial (a) and final (b) configurations for the LJ mixture in XY (coordinates in scaled units). The two species are distinguished using filled and empty circles. The size of the circles has no physical meaning.

$$\Phi_b(r) = +\frac{\alpha}{(r)^\gamma}. \tag{50}$$

The potential of Eq. (50) is set to zero when the particles belong to the same component; α is a numerical parameter that has been put equal to 2 while different values of γ have been tried. The results we show have been obtained with $\gamma=3$ (the smaller the value of γ the faster is the phase separation). The demixing is showed by the final configuration in Fig. 4(b). The numerical integration of the equations of motion has been done with a time step of 0.0025 (in scaled units) using once more a simple decomposition of the Liouville operator along the lines given in [16]. At variance with what was found in the case of the NHP thermostat in Sec. IV it is not necessary to use a higher order integration scheme. In Fig. 5 we show the behavior of the Hamiltonian when the law of evolution in time is given by Eqs. (41)–(44), com-

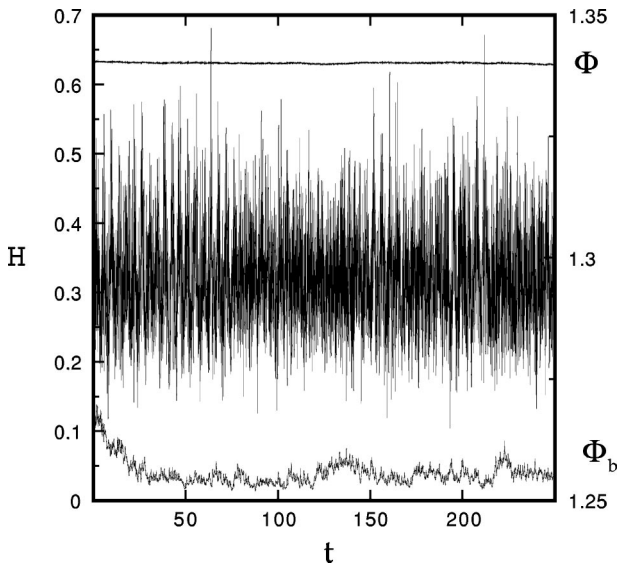

FIG. 5. Dynamical behavior of the Hamiltonian H, potential energy Φ, and biasing potential Φ_b. The scale on the right refers to the Hamiltonian while the one on the left to Φ and Φ_b. H, Φ, and Φ_b are in scaled units.

pared with the behavior of the potential energy in the system and with the biasing potential (note that a different *y* scale is used for the conserved energy).

VI. CONCLUSION

In this work a general structure for non-Hamiltonian conservative equations of motion suitable for application in equilibrium molecular dynamics simulations has been presented. Extended system equations of motion have been shown to be a particular case of this more general structure. The formalism has been applied with success to make the Nosé dynamics chaotic in phase space. The equations of motion derived with the aid of the antisymmetric matrix **B** are well suited to be integrated with standard reversible algorithm based on the Trotter factorization of the propagator. Nevertheless it can be expected that a much more complex matrix **B** would require the use of higher order algorithms to get accurate numerical conservation of the Hamiltonian. The recognition of the matrix structure of the equations of motion is of great help when it is necessary to devise new equations of motion having a specified statistical weight in phase space. To this end we have introduced a general scheme to obtain a biased sampling of phase space by means of a properly extended system. We have consistently used the statistical mechanics of non-Hamiltonian system to check the weight in phase space of the dynamics proposed. We believe that the ease gained in devising general conservative non-Hamiltonian flow gives interesting perspectives. We plan further studies on more realistic applications.

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